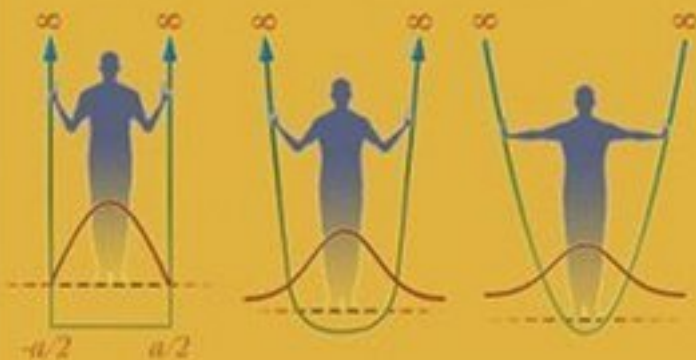


Charles E. Burkhardt
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Foundations of Quantum Physics



Springer

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*Helen, Charlie, Sarah, and Michelle
Bette, Andy, Bradley, Dan, and Tina
In loving memory of Steve Leventhal*

Preface

This book is meant to be a text for a first course in quantum physics. It is assumed that the student has had courses in Modern Physics and in mathematics through differential equations. The book is otherwise self-contained and does not rely on outside resources such as the internet to supplement the material. SI units are used throughout except for those topics for which atomic units are especially convenient.

It is our belief that for a physics major a quantum physics textbook should be more than a one- or two-semester acquaintance. Consequently, this book contains material that, while germane to the subject, the instructor might choose to omit because of time limitations. There are topics and examples included that are not normally covered in introductory textbooks. These topics are not necessarily too advanced, they are simply not usually covered. We have not, however, presumed to tell the instructor which topics must be included and which may be omitted. It is our intention that omitted subjects are available for future reference in a book that is already familiar to its owner. In short, it is our hope that the student will use the book as a reference after having completed the course.

We have included at the end of most chapters a “Retrospective” of the chapter. This is not meant to be merely a summary, but, rather, an overview of the importance of the material and its place in the context of previous and forthcoming chapters. For example, the Retrospective in Chapter 3 we feel is particularly important because, in our experience, students spend so much time learning about eigenstates that they get the impression that physical systems “live” in eigenstates.

We believe that students should, after a very brief review of salient experiments and concepts that led to contemporary quantum physics (Chapter 1), begin solving problems. That is, the formal aspects of quantum physics, operator formalism, should be introduced only after the student has seen quantum mechanics in action. This is certainly not a new approach, but we prefer it to the alternative of the formal mathematical introduction followed by problem solving. More importantly, we believe that the students benefit from this approach. To this end we begin with a derivation (read: rationalization) of the Schrödinger equation in Chapter 2. This chapter continues with a discussion of the nature of the solutions of the Schrödinger equation, particularly the wave function. We discuss at length both the utility of the wave function and its characteristics. It is our observation that the art of sketching wave functions has been neglected. We are led to this conclusion from discussions

with graduate students who have had the undergraduate course, but are unable to sketch wave functions for an arbitrarily drawn potential energy function. We think that such a skill is crucial for understanding quantum mechanics at the introductory level and, thus, we spend a good deal of Chapter 2 discussing qualitative aspects of the wave function.

In Chapter 3 we solve the Schrödinger equation for two of the most important potential energy functions, the infinite square well and the harmonic oscillator. A point of contrast between these potentials is penetration of oscillator wave functions into the classically forbidden region. We discuss this penetration at length because, in our experience, students have a great deal of difficulty with this concept. We then elaborate upon this concept by presenting the details of a problem not often seen in elementary texts, an infinite square well with a barrier in the middle. This affords the opportunity to see that, for energies less than the barrier height, the particle can be found on either side of the classically impenetrable barrier, thus making the particle's presence inside the barrier undeniable. This problem also sets the stage for solution of the more conventional barrier penetration problems in Chapter 5.

In Chapter 4 we discuss time-dependent states. We choose to do this at this point to contrast these states with those studied in the previous chapter. While we discuss the free particle wave packet (as does virtually every other text), we also present wave packets under the influence of a constant force and of a harmonic force. This discussion will, we believe, relate nicely to a later presentation of harmonic oscillator coherent states (Chapter 7).

Chapter 5 is an extension of Chapter 3 in that we solve the time-independent Schrödinger equation for several different one-dimensional potential energies. Included is one of the most successful analytic potential energy functions for characterizing diatomic molecular vibrations, the Morse potential. The chapter concludes with the WKB method for approximating solutions.

Chapter 6 presents the formalism of quantum physics, the mechanics of quantum mechanics, including a set of postulates. For completeness we also discuss the Schrödinger and Heisenberg pictures. Chapter 7 is devoted to the operator solution of the Schrödinger equation for the harmonic oscillator with emphasis on the properties of the ladder operators. Harmonic oscillator coherent states are also discussed. Chapter 8 introduces three-dimensional problems and is devoted to angular momentum. It is emphasized in this chapter that the concept of angular momentum in quantum mechanics transcends three-dimensional rotations (orbital angular momentum).

Chapters 9 and 10 are devoted to solving the radial Schrödinger equation for several different central potentials. In addition to the common central potentials, Chapter 9 includes a thorough discussion of the isotropic harmonic oscillator using the shell model of the nucleus as an example. The isotropic oscillator also permits introduction of the concept of accidental degeneracy. Because they are constituents of oscillator eigenfunctions, an attempt is made to decrypt the different conventions that are used for Laguerre polynomials and associated Laguerre polynomials. In our experience, this is a source of confusion to many students. Also contained in this chapter is an elaboration on the Morse potential in which three-dimensional

molecular motion is considered through rotation–vibration coupling. The discussion of the hydrogen atom, the sole content of Chapter 10, is standard, but, as for the isotropic oscillator, accidental degeneracy is stressed. Chapter 11 is included to demonstrate to the student that there are angular momenta in quantum mechanics other than orbital and spin angular momenta. It includes the introduction of the Lenz vector, its consequences and ramifications. This subject is not usually covered at the introductory level, but it is certainly not beyond the beginning student.

The material in the remaining four chapters depends heavily upon approximation methods. Chapter 12 presents time-independent approximation methods, while Chapter 13 illustrates the use of these methods to solve problems of physical interest. One problem that is included in Chapter 13, albeit superficially, is the effect of fine structure on the shell model of the nucleus. Chapter 14 treats the Stark and Zeeman effects. Particular attention is paid to the consequences of breaking the spherical symmetry of central potentials by application of an external field. Chapter 15 presents time-dependent approximation methods, followed by a discussion of atomic radiation including the Einstein coefficients.

There are more than two hundred problems. A detailed solutions manual is available. There are a number of appendixes to the book, including the answers to all problems for which one is required. Among the other appendixes is one listing the Greek alphabet with notations on common usage of these symbols in the book. There is also a short table of acronyms used in the book. The remaining appendixes contain material that is intended to be quick reference material and helpful with the core material in the book. A list of (the inevitable) corrections can be found at: <http://users.stlcc.edu/cburkhardt/> and <http://www.umsl.edu/~jjl/homepage/>.

We are indebted to several people, without whose help this manuscript would not have been completed. Helen and Charles Burkhardt, parents, read the manuscript critically. Discussions with Dr. J. D. Kelley were invaluable, as was his critical reading of the manuscript. Professor. S. T. Manson also read the manuscript and made many useful suggestions. Discussions with Dr. M. J. Kernan were very helpful, as were her suggestions. To all of these people we offer our sincere thanks.

Charles E. Burkhardt
Jacob J. Leventhal

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Chapter 1

Introduction

As students begin their study of quantum physics they are usually bombarded with descriptions of experiments and theoretical innovations from the early part of the twentieth century that demonstrated and attempted to clarify the inadequacy of the physics at that time. We will describe only a few of the experiments and some of the concepts that are particularly pertinent to the material to be presented in this book. We take some liberties with chronology to dramatize the details.

1.1 Early Experiments

1.1.1 The Photoelectric Effect

The photoelectric effect was discovered in 1887 by Gustav Ludwig Hertz while performing experiments directed toward confirming Maxwell's theory of electromagnetic waves. He observed that charged particles (electrons) were ejected from metal surfaces when the surface was illuminated by light. The electron flux was strongly dependent upon the wavelength of the light. Although Hertz did not follow up on his discovery, one of his students, Philipp Eduard Anton von Lenard, reported quantitative measurements of the effect in 1902. For this work Lenard received the Nobel Prize in 1905. The citation reads: "for his work on cathode rays." Subsequently, in 1925, Hertz shared the Nobel Prize for a different body of work, a subject that will be discussed later in this chapter.

The origin of the photoelectric effect remained a mystery until, in one of his three remarkable papers published in 1905, Albert Einstein, using Max Planck's treatment of blackbody spectra, explained the effect. Subsequently, in 1916, Robert Andrews Milliken performed detailed experiments that confirmed Einstein's explanation. Einstein received the Nobel Prize in 1921 for this work, although many think that his work on relativity also deserves a prize. The citation for Einstein's prize reads: "for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect." Milliken was also awarded a Nobel Prize, his in 1923, the citation for which reads: "for his work on the elementary charge of electricity and on the photoelectric effect."

In 1901 Max Karl Ernst Ludwig Planck published his revolutionary hypothesis. In equation form, it is

$$E = nh\nu \quad (1.1)$$

where E and ν are the energy and frequency of an oscillator in the solid; n is a positive integer. The constant $h = 6.626 \times 10^{-34}$ J·s is Planck's constant. For this innovation Planck was awarded the Nobel Prize in 1918, the citation for which reads “in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta”.

Equation 1.1, the Planck relation, is often written in terms of the angular frequency $\omega = 2\pi\nu$ and $\hbar = h/2\pi$. The symbol \hbar is read “h-bar” and

$$E = n\hbar\omega \quad (1.2)$$

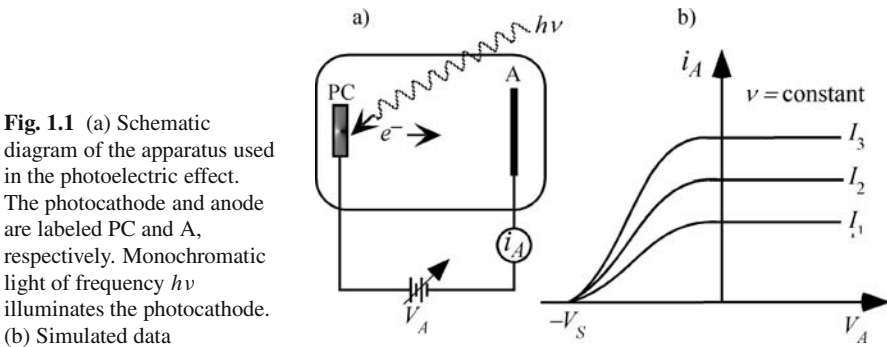
Einstein's explanation of the photoelectric effect rested on Planck's assumption that Equation 1.1 also applied to light emitted by the oscillators. As a consequence, it was inferred that light (electromagnetic radiation) could be considered to be made up of bundles or “quanta” called photons, each having energy E and frequency ν . Thus was born the concept of wave particle duality. That is, light exhibits both particle properties, quanta having energy E , and wave properties as represented by the frequency ν . It is common to speak of light in terms of the wavelength λ rather than the frequency, in which case Equation 1.1 takes the form

$$E = \frac{hc}{\lambda} \quad (1.3)$$

where c is the speed of light.

Now, what are the details of the photoelectric effect? The observations are best understood in terms of the experiments. A schematic diagram of the apparatus used by Lenard, and later Milliken, is shown in Fig. 1.1a.

Light of a fixed frequency (monochromatic light) illuminates an elemental metal, the photocathode. Electrons are emitted from the photocathode, collected on the



anode, and measured using an ammeter as shown in Fig. 1.1. The photocathode and the anode are encased in a glass envelope from which the air has been evacuated. The potential difference between the photocathode and the anode is variable as shown and may be either positive or negative. Because the ejected electrons acquire kinetic energy, the anode voltage V_A , if sufficiently negative, can repel them and prevent them from being collected and detected.

Several modes of data acquisition are employed, but one of the most striking is a plot of V_A versus I_A at fixed intensity of the light I . As seen in the hypothetical data in Fig. 1.1b for three different intensities, the anode current saturates at sufficiently high values of V_A , but the value of the stopping voltage $V_A = -V_S$ at which the electrons are turned around is independent of the intensity. This shows unequivocally that the electron kinetic energy is not determined by the intensity of the light. Moreover, experiments performed with different frequencies show that the value of V_S changes with both the frequency of the light and the material out of which the photocathode is constructed.

Einstein explained these data in terms of quanta of light called photons. These photons each carry an amount of energy in accord with Equation 1.1. Thus, the kinetic energy imparted to each electron (having charge of magnitude e) depends upon the energy per photon, not I , the number of photons per second falling upon the photocathode. Einstein wrote a simple relation between the photon energy $h\nu$, the electron kinetic energy KE , and the stopping voltage V_S

$$KE = h\nu - eV_S \quad (1.4)$$

Equation 1.4 tells us that the kinetic energy of the ejected electron is equal the photon energy $h\nu$ minus the energy required to liberate the electron from the photocathode. This amount of energy, called the work function $W = eV_S$, differs for each different photocathode material. Equation 1.4 is usually written in the form

$$KE = h\nu - W \quad (1.5)$$

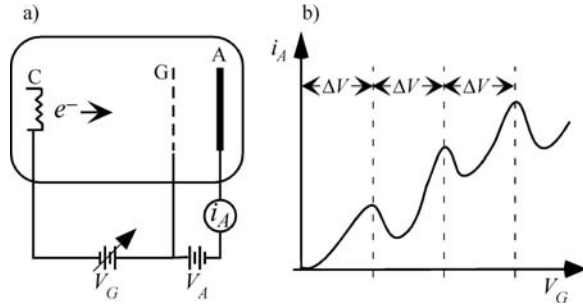
and is known as the Einstein relation.

It is not our goal here to study the photoelectric effect in detail. We wish to note that Einstein's explanation clearly showed that light exhibited particle characteristics. While the wave properties of light had been known for centuries before the photoelectric effect, its explanation in terms of particles was revolutionary.

1.1.2 The Franck–Hertz Experiment

The Franck–Hertz experiments provided early evidence of the quantization of atomic energy levels. They demonstrated that the amount of energy that could be stored in an atom was not arbitrary. Rather, these energies come in discrete increments. Moreover, the increments were different for different atoms. For their work, first reported in 1914, James Franck and Gustav Ludwig Hertz shared the 1925

Fig. 1.2 (a) Schematic diagram of the apparatus used in the Franck–Hertz experiment. The cathode, grid and anode are labeled C, G, and A, respectively. (b) Simulated data



Nobel Prize in Physics. The citation for the 1925 prize reads: “for their discovery of the laws governing the impact of an electron upon an atom.” Notice that this is the same Hertz who discovered the photoelectric effect and whose student, Lenard, won the Nobel Prize for elucidating it.

Figure 1.2a shows a schematic diagram of the apparatus used for this experiment. It consists of a cathode C from which electrons are emitted by heating with a high current (not shown in the diagram), an anode A to collect the electrons, and a grid G between the cathode and anode. The entire apparatus is contained within a glass envelope from which the air has been evacuated and atoms of a given species introduced. In the original experiments, mercury atoms were used, but any atom will suffice. Electrons emitted from the cathode are accelerated by the grid voltage V_G , pass through the grid and are collected at the anode. The anode is kept at a slightly lower potential than the grid to prevent the electrons from acquiring additional kinetic energy. Electrons arriving at the anode are collected and the current i_A measured.

Data are in the form of graphs of V_G versus i_A . As expected, the current increases as V_G increases, but it decreases at regular intervals as shown in the hypothetical data plotted in Fig. 1.2b. These data clearly suggest quantized atomic energy levels. For any setting of the grid voltage the maximum electronic kinetic energy in the apparatus is eV_G . When eV_G is lower than energy separation between the lowest atomic level, referred to as the “ground state”, and the next highest level, the “first excited state,” none of the electronic kinetic energy can be converted to atomic internal energy. This is because there simply isn’t any level to excite between the ground state and the first excited state. The only thing that can occur is elastic scattering between the electrons and the atoms. When, however, eV_G reaches the energy separation between the ground state and the first excited state some of the atoms “become excited.” In these inelastic collisions the exciting electrons lose kinetic energy (by an amount equal to the excitation energy) and are thus not collected at the anode. The result is that the current decreases. As V_G is further increased, the electrons that have already excited the atom once can be reaccelerated and collected. The current thus increases again. When these electrons are accelerated to a kinetic energy sufficient to excite the atom again, the anode current again decreases. (For simplicity we are assuming that only the ground and first excited states are important in this experiment.) Thus, the peaks in the curve of V_G versus i_A will be equally

spaced. From the hypothetical data we would conclude that the energy separation between the ground state and the first excited state is $e\Delta V$. This experiment clearly demonstrates that the atomic energy levels are quantized, for if they weren't the current would simply rise continuously and then level off (saturate) when all the electrons were collected.

While energies in the SI system are measured in joules, this is a rather large unit for measurement and discussion of atomic energies. It is frequently more convenient to use the electron-volt, abbreviated eV. One electron-volt is the kinetic energy acquired by a particle of charge e when it is accelerated through a potential difference of one volt. Thus,

$$\begin{aligned} 1\text{eV} &= (1.602 \times 10^{-19}\text{C})(1\text{V}) \\ &= 1.602 \times 10^{-19}\text{J} \end{aligned} \quad (1.6)$$

It is often convenient to write Planck's constant in terms of eV rather than J in which case $\hbar = 6.58 \times 10^{-16} \text{ eV} \cdot \text{s}$. In the original Franck-Hertz experiment the separation between peaks along the abscissa was roughly 4.9 V.

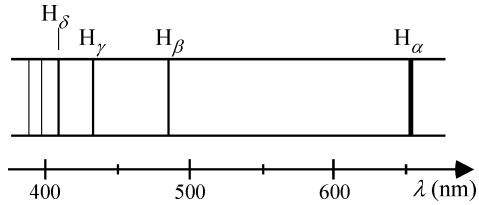
1.1.3 Atomic Spectroscopy

Emission Spectroscopy

Perhaps the most important experiments for the development of quantum theory were those using atomic spectroscopy. There are two general types of atomic spectroscopy, absorption and emission spectroscopy. In emission spectroscopy a sample of atoms is "excited," usually with an electrical discharge such as a spark. This has the effect of exciting the atoms, not just to the first excited state, but to a variety of excited states. In general, however, these states have finite lifetimes. When they decay to lower states, not just the ground state, they do so by emitting light. (Whether visible or not, physicists generally refer to electromagnetic radiation as "light.") Because the energy levels are uniquely quantized for each atom, the energy of the emitted light is quantized and hence, in accord with Equation 1.3, the wavelengths that are emitted are unique. Emission spectroscopy is routinely used for identification and trace analysis. In the early days of spectroscopy, the latter part of the nineteenth century and the beginning of the twentieth century, the detector in common use (aside from the human eye) was a photographic plate. Using prisms or diffraction gratings, the light in an emission spectroscopy experiment was dispersed into its constituent wavelengths and focused on a photographic plate. Because only certain discrete wavelengths were emitted most of the plate was dark, that is, not exposed. The portion that was exposed exhibited lines at the discrete wavelengths emitted by the atoms. These atomic spectra were thus known as "line spectra" and the transitions are known, even today, as lines.

Figure 1.3 shows a schematic diagram of a photographic plate of an emission spectrum of atomic hydrogen. Never mind that hydrogen occurs naturally as

Fig. 1.3 Schematic diagram of a photographic plate of the emission spectrum of atomic hydrogen in the visible region of the electromagnetic spectrum. Shown are the lines of the Balmer series



diatomic molecules. When an electrical discharge occurs, most of the molecules dissociate and become atoms, so the observed spectrum is predominantly that of atomic hydrogen. The first lines of atomic hydrogen to be discovered were those of the Balmer series, so named because in 1885 a Swiss school teacher, J. J. Balmer, without any physical explanation, set forth a formula that accurately predicted the observed wavelengths of the known lines of atomic hydrogen.

The wavelengths of these Balmer lines had been known for many years, but it was Balmer who first related them through his now-famous formula. There are many other lines in the spectrum of atomic hydrogen, but the lines of the Balmer series were discovered first because the strongest of these lines lie in the visible region of the spectrum. The Balmer series actually terminates in the near-ultraviolet region of the spectrum at a wavelength of about 365 nm (see Problem 3). Because Balmer was unaware of the origination of these lines he designated them H_α , H_β and so on, meaning the first hydrogen line, the second line, and so on. The lines of series that were discovered later employ a similar designation, but using the first letter of the discoverer's name. For example, the first line of the Lyman series is L_α .

The wavelengths of the Balmer lines λ_B are given by the relation

$$\lambda_B = 364.56 \frac{n^2}{n^2 - 2^2} \text{ nm} \quad (1.7)$$

where n is an integer that is greater than 2. Thus, for example, the wavelength of H_α is 656.2 nm. Equation 1.7 can, however, be put in a more convenient form for later use by writing the inverse of the wavelength:

$$\frac{1}{\lambda_B} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad (1.8)$$

where R_H is called the Rydberg constant because Johannes Rydberg was instrumental in developing a generalized version of Equation 1.8 that predicted the wavelength λ_{nm} between any two states, m and n , of hydrogen. In this generalized formula the 2^2 was replaced by the square of another integer. Thus,

$$\frac{1}{\lambda_{nm}} = R_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right) \quad (1.9)$$

From Equation 1.7 and the known Balmer wavelengths, $R_H \approx 1.097 \text{ m}^{-1}$. While the Balmer formula was deduced on purely empirical grounds it was, as we shall see, crucial to the development of the Bohr theory of hydrogen.

There is a very useful relation between the wavelength of light λ and the energy E of a photon of that wavelength. This relation is easily obtained from Equation 1.3 using convenient units, nm and eV. We have

$$\begin{aligned}\lambda(\text{in nm})E(\text{in eV}) &= hc \\ &= 1240\end{aligned}\tag{1.10}$$

For example, according to this simple formula, the energy per photon of red light of wavelength 620 nm is 2eV. On the other hand, photons having energy of 5eV correspond to a wavelength of 248 nm.

Absorption Spectroscopy

In absorption spectroscopy a continuous source of light such as light from an incandescent bulb (blackbody radiation) irradiates an atomic sample. The light passing through the sample is detected. Again a photographic plate may be used as the detector. In this case the background is the continuous bright incident light, but there are “holes” in the continuum due to absorption at specific wavelengths by the atomic sample. This might be thought of as a Frank–Hertz experiment with photons. One of the earliest such experiments was performed in 1824 by Fraunhofer. He dispersed the light from the sun. His continuous source was the solar interior and the atomic sample was the solar atmosphere. There are also molecules in the solar atmosphere, but let us concentrate on the atomic constituents. Fraunhofer observed an abundance of lines which he labeled alphabetically from the red end of the spectrum. Because the solar atmosphere contains hydrogen it would be surprising if lines of the Balmer series were not present. Indeed, C and F are H_α and H_β , respectively. Interestingly, the fourth line from the red end, a strong “hole” in the yellow portion of the spectrum, was, of course, labeled D. We now know this line (actually a pair of lines) to be the result of absorptions by atomic sodium. Observation of the “D-line” is a favorite test for the presence of sodium in elementary chemistry. In that test, the heat from the flame from the Bunsen burner excites sodium atoms to the first excited state from which they decay, emitting yellow light, the D-line.

1.1.4 Electron Diffraction Experiments

Two seminal experiments were reported in 1925. One of these, commonly referred to as the Davisson–Germer experiment, was performed in the United States. The other was performed by G. P. Thomson and his coworkers in Great Britain. These experiments are complementary to the photoelectric effect because, while the explanation of the photoelectric effect relied on the particle nature of light, the

explanation of these results relied on the wave nature of particles (electrons). This made clear that the same wave–particle duality associated with photons exists for material particles. Just how particles behave as waves is the subject of this book and, indeed, quantum physics. More about that later in this chapter.

Davisson and Germer were studying electron scattering from metallic surfaces when an experimental accident forced them to subject a nickel surface to a high temperature. The effect was to crystallize the nickel and make it, in effect, a diffraction grating for electrons. The data were explainable as a diffraction pattern. That is, the electrons were interfering with each other in the same way that light waves were known to interfere to produce familiar diffraction patterns. This experiment was performed *after* Louis de Broglie’s hypothesis (see below) that ascribed wave properties to matter. The explanation of the data was consistent with de Broglie’s hypothesis. Thomson’s experiments were also consistent with de Broglie’s hypothesis. They were similar in nature to the Davisson–Germer experiment, but Thomson used thin metal foils as the “diffraction grating.”

In 1937 Clinton Joseph Davisson and George Paget Thomson shared the Nobel Prize in Physics “for their experimental discovery of the diffraction of electrons by crystals.” Interestingly, George Thomson was the son of yet another Nobel laureate, Joseph John Thomson, who was awarded the Nobel Prize in 1906 “in recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases”.

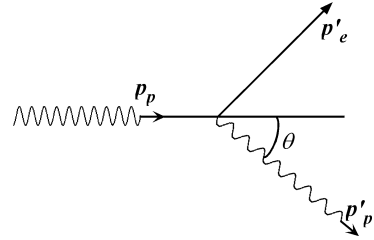
In summary, while the wave–particle duality was hard to understand for photons, it was virtually incomprehensible for material particles. The question to be answered was: what is it that is doing the waving? This is the subject of this book.

1.1.5 The Compton Effect

The Compton effect was studied in 1922 and was additional evidence of the wave particle duality of photons. It was performed using x-rays, high-frequency electromagnetic radiation, scattered from electrons that are bound in atoms. For this work Arthur Holly Compton was awarded the Nobel Prize in Physics in 1927 the citation for which read “for his discovery of the effect named after him.” Because the Compton effect is of considerable importance we will derive the result.

Figure 1.4 shows a schematic diagram of the scattering process. A photon of frequency ν is incident on an electron at rest. The electron is not actually at rest, but its kinetic energy is small compared with the energy of the x-rays. The initial momentum of the photon is $p_p = h\nu/c$ where c is the speed of light. The photon is assumed scattered at an angle θ with momentum $p'_p = h\nu'/c$ where ν' is the frequency of the scattered photon. The momentum of the scattered electron is \mathbf{p}'_e , a vector. We wish to find the wavelength $\lambda' = c/\nu'$ of the scattered photon.

Fig. 1.4 The kinematics of Compton scattering



Conservation of energy dictates that

$$h\nu + m_e c^2 = h\nu' + \sqrt{p_e'^2 c^2 + m_e^2 c^4} \quad (1.11)$$

where m_e is the mass of the electron. We (necessarily) used the relativistic formula for the energy of the electron. We can isolate $p_e'^2$ in Equation 1.11 by squaring:

$$p_e'^2 = \left[\left(\frac{h\nu}{c} - \frac{h\nu'}{c} \right) + m_e c \right]^2 - m_e^2 c^2 \quad (1.12)$$

To eliminate $p_e'^2$ we note from Fig. 1.4 that

$$\begin{aligned} p_e'^2 &= (\mathbf{p}_p - \mathbf{p}'_p)^2 \\ &= p_p^2 + p_p'^2 - 2p_p p_p' \cos \theta \\ &= \left(\frac{h\nu}{c} \right)^2 + \left(\frac{h\nu'}{c} \right)^2 - 2 \left(\frac{h\nu}{c} \right) \left(\frac{h\nu'}{c} \right) \cos \theta \end{aligned} \quad (1.13)$$

Substituting Equation 1.13 into Equation 1.12 and writing the resulting equation in terms of the difference in wavelengths between the incident and scattered photons $\Delta\lambda$ we have

$$\begin{aligned} \Delta\lambda &= \lambda' - \lambda \\ &= \lambda_c (1 - \cos \theta) \end{aligned} \quad (1.14)$$

where λ_c is known as the Compton wavelength of the electron:

$$\lambda_c = \frac{h}{m_e c} \approx 2.43 \times 10^{-3} \text{ nm} \quad (1.15)$$

Equation 1.15 can be put in another form by multiplying the numerator and denominator by c , the speed of light. The denominator is thus the rest mass of the electron, 0.51×10^6 MeV, while the numerator is 1240 (see Equation 1.10).

Equation 1.14 is known as the Compton equation. One of the remarkable features of it is that the change in wavelength of the photon does not depend upon its

incident wavelength. The maximum difference in wavelength that can be detected is twice (when $\theta = \pi$) the Compton wavelength, $\sim 5 \times 10^{-3}\text{nm}$. For this reason it is very difficult to perform Compton scattering experiments using visible light ($\lambda \approx 400 - 700\text{nm}$) because the $\Delta\lambda$ would be only a tiny fraction of the wavelength of the incident photon wavelength. For much shorter wavelengths, as short as $\sim \lambda_c$, however, $\Delta\lambda/\lambda$ can be large enough to measure. Thus, an incident photon of energy comparable with the rest energy of the electron, $\sim 500\text{keV}$, is required. Compton used x-rays having wavelength 0.071nm , roughly 17keV in his experiments. While 17keV is more than an order of magnitude lower than the rest mass of the electron, the effect was indeed detectable.

The Compton wavelength is often seen written as

$$\lambda_c = \frac{h}{m_e c} \approx 0.39 \times 10^{-3}\text{nm} \quad (1.16)$$

The reason for this is that the actual value of the Compton wavelength is not really important. It is the order of magnitude of it that is significant. This will be discussed later in this chapter.

Equation 1.14 shows that the wavelength of the scattered photon is always longer than the wavelength of the incident photon because $\cos \theta$ is always less than unity. Thus, $\Delta\lambda > 0$. The process can thus be envisioned as one in which the photon is elastically scattered by the electron, imparting momentum and kinetic energy to the electron. Because conservation of energy dictates that the photon loses energy, it must, in accord with Equations 1.2, have lower frequency and longer wavelength.

1.2 Early Theory

1.2.1 The Bohr Atom and the Correspondence Principle

Confronted with overwhelming evidence that the amounts of internal energy that could be stored in an atom were not arbitrary, but were, instead, quantized, physicists attempted to explain the origin of these quantum levels. The experiments performed in Great Britain by Lord Rutherford clearly established that the atom consisted of a tiny massive positively charged nucleus surrounded by very light negatively charged electrons that orbited this nucleus. A major problem was that, according to classical electromagnetic theory, accelerating charges emit electromagnetic energy (light). Thus, an orbiting electron should lose energy as it revolves about the nucleus, thus spiraling into the nucleus. If that spiraling process were to take a very long time, say 10^{50} years, then there would be no problem because that is longer than the age of the universe. On the other hand, if the “lifetime” of these atoms is short, then the planetary model of the atom had to be reconciled with classical electromagnetic theory. Because it is important to understand the problem that presented itself to these pioneers of quantum physics it is worthwhile to do a simple calculation to

estimate τ , the classical lifetime for a hydrogen atom, that is, the decay time due to radiation of an electron in orbit around a proton.

From electromagnetic theory the famous Larmor formula gives the instantaneous power P radiated by an electron undergoing acceleration a . In SI units, which we will use throughout this book unless otherwise stated,

$$P = -\frac{e^2 a^2}{6\pi\epsilon_0 c^3} \quad (1.17)$$

where the minus sign indicates that power is being radiated away. If we assume that each successive loop of the spiral toward the nucleus is a circle of radius r , then we may compute the acceleration a using Coulomb's law:

$$a = \frac{1}{m_e} \left(\frac{1}{4\pi\epsilon_0} \right) \frac{e^2}{r^2} \quad (1.18)$$

The total mechanical energy (TME) E of the electron in the orbit is the sum of kinetic energy and the Coulomb potential energy:

$$E = \frac{1}{2} m_e v^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{e^2}{r} \quad (1.19)$$

The motion is assumed to be circular so we can eliminate the velocity by equating the centripetal force to the Coulomb force between the electron and proton. This results in

$$E = -\frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \frac{e^2}{r} \quad (1.20)$$

Now, P is the rate of loss of energy dE/dt so we may differentiate Equation 1.20 with respect to time and equate it to Equation 1.17. We obtain

$$\frac{dr}{dt} = -\frac{4}{3} \frac{e^4}{m_e^2 c^3 r^2} \quad (1.21)$$

which, when integrated from the initial radius R to the nucleus, yields τ :

$$\tau = \frac{m_e^2 c^3 R^3}{4e^4} \quad (1.22)$$

From Rutherford's experiments it was known that $R \sim 0.1\text{nm}$. The other parameters in this equation for τ were reasonably well known. When inserted in Equation 1.22 the result is $\tau \sim 10^{-11}\text{s}$, hardly comparable with the age of the universe. There was clearly a problem.

Niels Bohr attempted to explain the quantized levels using a combination of classical ideas, quantal hypotheses, and postulates of his own [1]. This pioneering work was published in 1913 and Bohr was awarded the Nobel Prize in Physics in 1922 “for his services in the investigation of the structure of atoms and of the radiation emanating from them.”

To deal with the problem of radiation by an accelerating charge Bohr simply avoided it by postulating his way out of it. Paraphrasing the first of his postulates:

I. An atom exists in a series of energy states such that the accelerating electron does not radiate energy when in these states. These states are designated as stationary states.

The designation as “stationary states” has survived time and is used today. Why the accelerating electron ignored the classical laws of electromagnetic theory by not radiating was simply finessed, that is, ignored. Bohr’s second postulate accounted for the emitted and absorbed radiation in terms of the stationary states.

II. Radiation is absorbed or emitted during a transition between two stationary states. The frequency of the absorbed or emitted radiation is given by Planck’s theory.

Bohr’s reference here to “Planck’s theory” is the relationship between the energy and the frequency, Equation 1.1, that was used by Planck to explain blackbody radiation. The energy was taken to be the difference in the energies of the two states involved in the transition. Thus, the frequency, ν , of this radiation is given by

$$h\nu = E' - E'' \quad (1.23)$$

where h is Planck’s constant and E' and E'' are the energies of the two states involved in the emission or absorption.

Bohr had a third postulate, although he did not state it as such. It is the famous and ingenious correspondence principle. Loosely stated, the correspondence principle states that when quantum systems become large they behave in a manner that is consistent with classical physics. Bohr essentially used this as his third postulate, although many derivations of the consequences of the Bohr model of the atom often ignore the correspondence principle. Instead, these treatments postulate that the angular momentum must be quantized in units of \hbar . Bohr made no such postulate, although it does lead to the correct answers without appealing to the correspondence principle. These derivations usually then present the correspondence principle as a consequence of this erroneous postulate.

It is a simple matter to obtain the relationship between the TME of the electron E and the circular orbital radius r using elementary classical mechanics and electromagnetic theory. Equating the centripetal force to the Coulomb force we have

$$\frac{m_e v^2}{r} = \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{r^2} \quad (1.24)$$

where v is the speed of the electron in the orbit of radius r . For simplicity and convenience we are assuming that the reduced mass of the electron–proton system

is the same as m_e . From Equation 1.24 we can solve for the kinetic energy of the electron so the TME is

$$\begin{aligned} E &= \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{r} - \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{r} \\ &= -\frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{r} \end{aligned} \quad (1.25)$$

If we now apply Postulate II assuming a transition from state n to state m , we note that the only variable in the expression for the energy, Equation 1.25, is the orbital radius r . We must therefore attach a subscript to r to designate to which state it belongs. For definiteness we assume that $n > m$ and, applying Postulate II, we write

$$h\nu_{nm} = \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{1}{r_m} - \frac{1}{r_n} \right) \quad (1.26)$$

where ν_{nm} is the frequency of the photon emitted in the transition from the higher state n to the lower state m .

At this point there were two ingenious steps taken by Bohr. The first was to note the similarity between Equation 1.26 and the generalized Balmer formula, Equation 1.9 (recall the reciprocal relationship between ν and λ). The orbital radius is the only variable in Equation 1.26 so it is clear that it is r_n that is quantized. That is, each of the stationary states must have a unique orbital radius. Moreover, to be consistent with Equation 1.9 these orbital radii must be such that

$$r_n = n^2 a_0 \quad (1.27)$$

where a_0 has units of length. It is called the Bohr radius. To find it Bohr imposed the correspondence principle.

We had noted that accelerating charges radiate electromagnetic energy. But that is not the whole story. If these accelerating charges are being accelerated periodically, for example, a harmonically oscillating charge or a circularly moving charge, then the frequency of the emitted radiation is the same as the frequency of the motion. Bohr therefore stated that as n and m become very large, the frequency ν_{nm} in Equation 1.26 must approach the frequency ν_{orbit} of the circular motion of the electron at the n th Bohr radius. The orbital frequency is

$$\nu_{\text{orbit}} = \frac{v_n}{2\pi r_n} \quad (1.28)$$

where v_n is the orbital speed in the n th Bohr orbit, Equation 1.24. Working with the square of ν_{orbit} for convenience and using Equation 1.28 we have

$$v_{\text{orbit}}^2 = \frac{1}{4\pi^2 n^4 a_0^2} \left[\frac{1}{m_e} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{n^2 a_0} \right] \quad (1.29)$$

We can calculate $v_{(n+1)n}^2$ for high values of n from Equation 1.26 by substituting Equation 1.27 for the orbital radii. We obtain

$$\begin{aligned} \lim_{n \rightarrow \infty} v_{(n+1)n}^2 &= \lim_{n \rightarrow \infty} \left\{ \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{ha_0} \left[\frac{1}{n^2} - \frac{1}{(n+1)^2} \right] \right\}^2 \\ &= \lim_{n \rightarrow \infty} \left\{ \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{ha_0} \left[\frac{(2n+1)}{n^2(n+1)^2} \right] \right\} \\ &= \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{ha_0} \frac{1}{n^3} \end{aligned} \quad (1.30)$$

To apply the correspondence principle we equate v_{orbit}^2 and $v_{(n+1)n}^2$ for high n and obtain

$$a_0 = (4\pi\epsilon_0) \frac{\hbar^2}{m_e e^2} \quad (1.31)$$

Examination of Equation 1.25 shows that, because the orbital radii are quantized in accord with Equation 1.27, the total internal energy of the atom must also be quantized. We may thus write Equation 1.25, replacing r with $n^2 a_0$ and E with E_n to indicate the n th energy level. We obtain

$$E_n = - \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{2n^2 a_0} \quad (1.32)$$

where n is called the principal quantum number. Substituting for a_0 we have

$$E_n = - \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left(\frac{m_e}{\hbar^2} \right) \cdot \frac{1}{n^2} \quad (1.33)$$

Note that the minus sign is required since the electron is bound to the proton. The TME must therefore be negative. $E = 0$ corresponds to infinitely separated proton and electron each having zero kinetic energy.

Equation 1.33 is called the Bohr energy. Although the Bohr model is not entirely correct, the Bohr energy *is* correct. It applies to any quantum level of the hydrogen atom as designated by the quantum number n . In fact, it applies to *any* one-electron atom, for example helium with one electron removed, when the number of protons in the nucleus is included. When compared with Equation 1.9, the Bohr energy yields the value of the Rydberg constant, which is found to be

$$\begin{aligned}
 R_H &= \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m_e}{4\pi c \hbar^3} \\
 &= 1.0973731568525 \times 10^7 \text{ m}^{-1}
 \end{aligned}
 \tag{1.34}$$

where the numerical value given is the accepted value today. The agreement between this theoretically obtained value and that empirically determined using atomic spectroscopy was astonishing. While we know today that some of the concepts of the Bohr model are incorrect, it remains a paradigm of clear and creative thinking. Bohr's use of known empirical facts together with his statement of the correspondence principle led to a breakthrough in physics that gave birth to quantum physics as we know it today. Although physicists know that the wave nature of matter, as exemplified by, for example, the Davisson–Germer experiment, makes precise location of particles problematic, most nevertheless envision a Bohr-like atom when thinking about atoms (even if they don't admit it in public). Besides permitting visualization, the Bohr model also gives the correct order of magnitude and scaling with principal quantum number of parameters, such as orbital distances and electronic velocities. Most importantly, it also gives the correct quantized energies.

It also follows from the above analysis that the electronic angular momentum must be quantized in units of \hbar , the postulate that is incorrectly attributed to Bohr. Indeed, this postulate follows as a consequence of his two stated postulates and the correspondence principle. Note, however, that \hbar has units of angular momentum (as does h).

Before leaving the Bohr energy it is useful to cast this important quantity in terms of other, more revealing, parameters. One of the most convenient ways of writing it is in terms of the fine structure constant, which is a combination of fundamental constants that results in a pure number that is very nearly 1/137. This number is of fundamental importance in quantum physics. It is given by

$$\begin{aligned}
 \alpha &= \left[\frac{e^2}{(4\pi\epsilon_0) \hbar c} \right] \\
 &\simeq \frac{1}{137}
 \end{aligned}
 \tag{1.35}$$

The Greek letter α is universally used for the fine structure constant. Regrettably, it is also universally used for a number of other important quantities. In terms of the fine structure constant the Bohr energy is

$$E_n = -\frac{1}{2} \alpha^2 \frac{(m_e c^2)}{n^2}
 \tag{1.36}$$

The reason Equation 1.36 is convenient is that most physics students know that the rest mass of the electron is 0.51 MeV (1 MeV = 10^6 eV). A simple calculation shows that the lowest energy state of the Bohr atom, and, consequently, hydrogen, is -13.6 eV. This energy is also called the ionization potential since it is the *minimum*

energy required to liberate the electron from the hydrogen atom, leaving behind a “hydrogen ion.” A hydrogen ion is simply a proton, but the term “ionization potential” is applied to all atoms and molecules. It is also convenient to remember the Bohr energy in electron-volts. For this purpose we may rewrite Equation 1.33 as

$$E_n = -\frac{13.6056923 \text{ eV}}{n^2} \quad (1.37)$$

from which it is clear that the ionization potential of hydrogen is 13.6 eV.

From the Bohr energy as given in Equation 1.37 it is a simple matter to calculate energy differences between any pair of levels. We have

$$\Delta E_{nn'} = 13.6056923 \text{ eV} \left(\frac{1}{n^2} - \frac{1}{n'^2} \right) \quad (1.38)$$

where it is assumed that $n < n'$. If we let $n = 2$ and use the relation $E = hc/\lambda$ we immediately recover the Balmer formula, Equation 1.9, the formula that predicts the wavelengths of emitted radiation for which the lower state is $n = 2$, the Balmer series. There are, however, other series that are observed. For example, if we let $n = 1$ we obtain a formula that predicts the wavelengths of the Lyman series. Because the ground state lies much lower than $n = 2$ these energy differences are considerably greater than those of the Balmer series. Consequently, transitions in the Lyman series yield radiation in the ultraviolet region of the spectrum.

Let us now investigate the relationship between the quantum number n and the angular momentum. From Equations 1.24, 1.31, and 1.27 the electronic velocity in the n th orbit is

$$\begin{aligned} v_n &= \sqrt{\frac{1}{m_e} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{n^2 a_0}} \\ &= \frac{1}{m_e} \frac{\hbar}{n^2 a_0} \end{aligned} \quad (1.39)$$

so the angular momentum of the electron in the n th orbit is

$$\begin{aligned} L_n &= m_e v_n r_n \\ &= n\hbar \end{aligned} \quad (1.40)$$

We have therefore resurrected the “postulate” that the orbital angular momentum is quantized in units of \hbar . Interestingly, this result is incorrect because, as we will learn later, the states of hydrogen can have any integer multiple of \hbar or zero as long as it is less than the principal quantum number n . This means that the electronic angular momentum in the ground state is zero, not unity as predicted by Equation 1.40. Nonetheless, the Bohr model of the atom provides us with quantities that give the correct order of magnitude of actual atomic parameters. For this reason it is

extremely useful. For example, a bit of algebra permits us to write v_n in the form (see Problem 5)

$$v_n = \frac{\alpha}{n}c \quad (1.41)$$

Notice that Equation 1.41 tell us that the highest orbital velocity for an electron occurs in the ground state, but, even then, this velocity is more than two orders of magnitude smaller than the speed of light, thus justifying the nonrelativistic treatment. It is often convenient to express Bohr parameters in terms of the fine structure constant, so we present in Table 1.1 a partial listing.

Before leaving the subject of the Bohr atom we discuss another of the conveniences afforded by it. Since the model is that of an electron circling a proton, the electric current that is the result of the electronic motion is the source of a magnetic field. Therefore, a Bohr atom has a magnetic dipole moment associated with the orbital motion of the electron about the proton and the atom generates a magnetic field identical to that of a bar magnet. The magnitude of this magnetic moment for the ground state of the Bohr atom is referred to as the Bohr magneton, and is designated by the symbol μ_B . Magnetic moments are often measured in terms of the Bohr magneton so we calculate its value. Figure 1.5 is a schematic diagram of the Bohr atom with the magnetic field lines due to the orbital motion of the electron. Also indicated in this figure are the relevant parameters.

The magnetic moment of a current-carrying loop is given by the product of the area of the loop and the current. The current is the electronic charge divided by the period of the motion, $T = 2\pi a_0/v$. Therefore, the magnetic moment is

Table 1.1 Quantities from the Bohr model of the atom in terms of the fine structure constant α

$$\begin{aligned} \alpha &= \frac{e^2}{(4\pi\epsilon_0)\hbar c} \\ E_n &= -\frac{1}{2}\alpha^2 \frac{m_e c^2}{n^2} \\ a_0 &= \frac{\hbar}{m_e c \alpha} \\ v_n &= \frac{\alpha}{n}c \end{aligned}$$

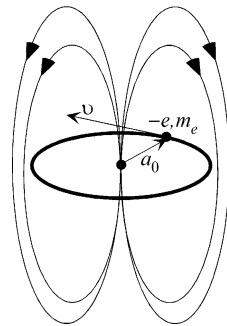


Fig. 1.5 The Bohr model of the atom shown with the magnetic field lines generated by the orbiting electron

$$\begin{aligned}\mu &= e \left(\frac{v}{2\pi a_0} \right) (\pi a_0^2) \\ &= \frac{ev a_0}{2}\end{aligned}\tag{1.42}$$

which may be written in terms of the orbital angular momentum $L = m_e v a_0$ as

$$\mu = -\frac{e}{2m_e} L\tag{1.43}$$

where the vector nature of the angular momentum has been taken into account. Because the electronic charge is negative, the angular momentum and the magnetic moment are in opposite directions. From Equation 1.43 it is clear that there is a direct relationship between the magnetic moment and the angular momentum. Because the angular momentum is quantized in units of \hbar (see Equation 1.40), the magnitude of the magnetic moment in the first Bohr orbit, the Bohr magneton, is

$$\mu_B = \frac{e\hbar}{2m_e}\tag{1.44}$$

1.2.2 The de Broglie Wavelength

In 1923 Louis de Broglie, in his doctoral thesis at the Sorbonne in Paris, proposed that material particles, that is, particles having nonzero mass such as electrons, exhibit a wave-particle duality as had been established for light. At first this notion was met with skepticism, but after some encouragement from notable scientists, particularly Einstein, it gained credibility. A few years later, the experiments of Davisson and Germer validated the idea as did other experiments performed in other laboratories. In 1929 de Broglie was awarded the Nobel Prize in Physics “for his discovery of the wave nature of electrons.”

de Broglie set forth a relationship between the momentum of a particle and the “wavelength” of matter waves, as they were called. Today we simply refer to the de Broglie wavelength. He deduced a relation between photons and their momentum and proposed the same relation for particles. The relativistic relation between energy and momentum for a particle of rest mass, m_0 , is given by

$$E = \sqrt{p^2 c^2 + m_0^2 c^4}\tag{1.45}$$

which, for the massless photon, reduces to

$$E = pc\tag{1.46}$$

de Broglie inserted the Planck relation, Equation 1.3, for the energy and arrived at a relation between the wavelength and momentum of a photon:

$$p = \frac{h}{\lambda} \quad (1.47)$$

He then postulated that this relation also applied to material particles and that the wavelength of the matter wave is

$$\lambda = \frac{h}{p} \quad (1.48)$$

What is it that is doing the waving in the case of matter waves is, at this point, still not clear, but, for now let us simply note that this was indeed a brilliant step. Experiments of the type described in Section 1.1.4 verified the validity of Equation 1.48.

It is interesting that the Bohr energy can be easily derived by simply requiring that a half-integral number of de Broglie wavelengths fit in each allowed Bohr orbital circumference (see Problem 8). Why a half-integral number of wavelengths? Because that is what is required to establish a standing wave which, in this context, may be correlated with Bohr's *stationary* states. This is important because the de Broglie hypothesis is consistent with the Bohr model of the atom.

1.2.3 The Uncertainty Principle

Among his many scientific accomplishments, one of Heisenberg's most important is his formulation of the uncertainty principle. For this, and other contributions, Werner Karl Heisenberg was awarded the Nobel Prize in Physics in 1932 "for the creation of quantum mechanics, the application of which has, inter alia (among other things), led to the discovery of the allotropic forms of hydrogen."

In his 1927 paper Heisenberg introduced the concept that position and momentum could not be measured with unlimited precision. The principle may be stated mathematically as

$$\Delta x \Delta p_x \geq \hbar/2 \quad (1.49)$$

where Δx and Δp_x are the uncertainties in the measurements of position and momentum, respectively. For simplicity we confine the discussion to one-dimension and specify the x -component of the momentum to emphasize that the principle holds only when the coordinate and the component of the linear momentum are the same. It is important to understand that the uncertainties, Δx and Δp_x , are not the result of any flaw in our measurement technique or apparatus. They are consequences of the wave-particle duality that, as we have seen above, is inherent in nature.

The principle can be illustrated by examining the familiar single-slit diffraction experiment from physical optics as is illustrated in Fig. 1.6. If the monochromatic waves of wavelength λ that are incident on the single slit of width a are light waves, the diffraction pattern observed on the screen will be proportional to $\sin^2 \beta / \beta^2$ where $\beta = \pi a \sin \theta / \lambda$. From physical optics, the position of the first minimum is

$$\sin \theta = \frac{\lambda}{a} \quad (1.50)$$

which we take to be the angular spread.

We can also imagine the incident “waves” to be monoenergetic electrons, that is, electrons that all have the same kinetic energy $p^2/2m_e$. Therefore, all of the electrons will have the same de Broglie wavelength $\lambda = h/p$ and the same pattern will be observed. (Recall we have not yet specified what it is that is doing the waving.) What causes the diffraction pattern in either case, photons or electrons, is an uncertainty in the x -component of momentum. This uncertainty is given by

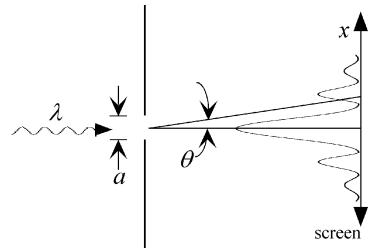
$$\begin{aligned} \Delta p_x &= p \sin \theta \\ &= \left(\frac{h}{\lambda} \right) \left(\frac{\lambda}{a} \right) \end{aligned} \quad (1.51)$$

Note that, from relativity and from the de Broglie relation, Equation 1.48, the momentum is (h/λ) for either photons or electrons. Now, the uncertainty in x , Δx , is the width of the slit a , so we have recovered the uncertainty principle. The important point to be made here is that the wave properties of light and matter and the uncertainty principle are inextricably linked.

There is another experiment that can be carried out using electrons and slits that demonstrates the wave nature of matter. It is analogous to the two-slit experiment first performed by Young in 1801. We will not go into detail about this experiment here other than to note that it also demonstrates the interference properties of matter waves.

Equation 1.49 is not the only uncertainty relationship. Because \hbar has units of angular momentum it is, at least dimensionally, correct (always a good start). There are, however, other combinations of variables, the products of which have the correct units, that could provide suitable uncertainty relations. An important such relation is

Fig. 1.6 Schematic diagram of a single-slit diffraction experiment showing the intensity of the diffraction pattern. The secondary maxima have been exaggerated for clarity



the energy–time uncertainty relation. We can rationalize the relationship by imagining a particle having kinetic energy $E = p^2/2m$. The uncertainty in energy is then

$$\Delta E = \frac{p\Delta p}{m} \geq v \left(\frac{\hbar/2}{\Delta x} \right) = \left(\frac{\hbar/2}{\Delta x/v} \right) \quad (1.52)$$

But $\Delta x/v = \Delta t$, the uncertainty in time which leads to the relation

$$\Delta E \Delta t \geq \hbar/2 \quad (1.53)$$

This energy–time uncertainty relation has many consequences. For example, even if the resolution of the photographic plates were perfect and there were no other mechanism for broadening the lines observed in atomic spectroscopy, some lines would be broader than others. This is because the lifetimes of the initial states involved in the transitions can differ by orders of magnitudes. These finite lifetimes, which may be regarded as Δt in the uncertainty relation, are accompanied by an uncertainty in the energy. Thus, the photon energies are not truly monoenergetic and a broadened line is observed on the photographic plate. In practice there are other mechanisms that serve to broaden the lines, but modern spectroscopic techniques can eliminate these so the “natural” linewidth, that associated with the uncertainty in the energy of the state, can be observed.

1.2.4 The Compton Wavelength Revisited

It was noted in our discussion of the Bohr atom that, although not strictly correct, it provides a good model for visualization and it leads to correct orders of magnitudes and scaling for atomic parameters. In view of the uncertainty principle, we wish to examine the question of whether it is reasonable to consider the electron (with its wavelike properties) to really be “pointlike” as compared with the size of an atom, $\sim a_0$. To this end we ask the question: when are the nonrelativistic treatment offered by the Bohr theory and the (nonrelativistic) quantum mechanics in this book valid?

Evidently, relativity will become important when the kinetic energy T of any of the particles (including massless particles) is sufficient to cause creation of particle pairs, that is, when $T \sim m_e c^2$. Let us imagine performing a Compton scattering experiment in which we try to confine an electron within a small distance δ (we will use one-dimension for simplicity). The more precisely we try to confine the electron, that is, the smaller we wish to make δ (which is essentially the uncertainty in position), the greater is the uncertainty in momentum Δp of the photon. As Δp

increases, so does the energy of the incident photon. In terms of the uncertainty principle this means that

$$\delta = \frac{\hbar/2}{\Delta p} \quad (1.54)$$

Multiplying numerator and denominator by c makes the denominator the energy of the (massless) photon in accord with the relativistic formula given in Equation 1.45. If we now require that this energy be less than the amount of energy required to create an electron–positron pair, namely, $\sim m_e c^2$, we have

$$\begin{aligned} \delta &= \frac{\hbar c}{2c\Delta p} \\ &= \frac{\hbar c}{2m_e c^2} \\ &\sim \lambda_c \end{aligned} \quad (1.55)$$

Thus, the minimum dimension for δ in which the electron may be localized before relativistic considerations are required is the *order of* the Compton wavelength. We may, therefore, regard the Compton wavelength as the intrinsic quantum mechanical “size” of an electron. The Compton wavelength is, very roughly, the minimum length in which a particle may be localized according to quantum mechanics. To localize it further would require such a high momentum that the energy would be sufficient for pair production.

Returning to the Bohr model, we may compare the size of the electron λ_c with the size of the atom $\sim a_0$. According to Equation 1.31,

$$\begin{aligned} a_0 &= (4\pi\epsilon_0) \frac{\hbar^2}{m_e e^2} \\ &= \left[\frac{(4\pi\epsilon_0) \hbar c}{e^2} \right] \left(\frac{\hbar}{m_e c} \right) \\ &= \frac{1}{\alpha} \lambda_c \end{aligned} \quad (1.56)$$

where α is the fine structure constant, Equation 1.35. Therefore, in terms of the Bohr radius the size of the electron, the Compton wavelength, is

$$\begin{aligned} \lambda_c &= \alpha a_0 \\ &\sim \frac{1}{137} a_0 \end{aligned} \quad (1.57)$$

which means that the electron’s intrinsic quantum mechanical size is roughly two orders of magnitude smaller than the diameter of the atom. We conclude, therefore,

that the Bohr model of the atom is viable in the sense that it can, indeed, be viewed as a point electron orbiting a stationary nucleus.

1.2.5 The Classical Radius of the Electron

While the fact that the Compton wavelength is much smaller than the Bohr radius validates the assumption of nonrelativistic quantum mechanics, there is another quantity of interest, the classical radius of the electron. The assumptions that go into the calculation of the classical radius are of dubious validity, but comparison of it with the Compton wavelength of the electron is interesting.

The calculation is simple. We imagine that the charge e of the electron is distributed uniformly over the surface of a sphere of radius R_e , the classical radius of the electron. We now assume that the energy required to assemble this charge, W , is equal to the rest energy of the electron. There are several ways to calculate the energy of the charge distribution. One way is to use the fact that the energy to assemble the charges is the sum of charge multiplied by the electric potential. Adapted to the current problem this means that we must integrate the product of the surface charge density and the potential at $r = R_e$ over the surface of the sphere and multiply by one-half. Thus,

$$\begin{aligned} W &= \frac{1}{2} \left(\frac{e}{4\pi R_e^2} \right) \left(\frac{e}{4\pi\epsilon_0 R_e} \right) \int_S dS \\ &= \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0 R_e} \right) \end{aligned} \quad (1.58)$$

Equating W to the rest energy of the electron $m_e c^2$ leads to

$$\begin{aligned} R_e &= \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{1}{m_e c^2} \right) \\ &= \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right) \left(\frac{\hbar}{m_e c} \right) \\ &\sim \alpha \tilde{\lambda}_c \\ &\sim \alpha^2 a_0 \end{aligned} \quad (1.59)$$

which shows that the classical radius of the electron is roughly two orders of magnitude smaller than the Compton wavelength of the electron and four orders of magnitude smaller than an atom. Thus, although the concept upon which the calculation of the classical radius of the electron is suspect, it is consistent with the visualization of the electron as a “probability cloud,” the radius of which is the Compton wavelength. Moreover, physicists love it when quantities can be expressed in terms of previously known parameters multiplied by the fine structure constant.

1.3 Units

In this book we will usually use SI units, although eV will frequently be used. In addition to these units, it is often convenient to devise units of energy that are tailored to a particular problem. For example, the eV, while convenient for the Bohr atom, is so much smaller than nuclear quantum levels that the MeV, one million eV, is usually used. Another commonly used unit of “energy” is the MHz. Technically, this is a unit of frequency, but, in accord with Equation 1.1, it may be regarded as a unit of energy if it is understood that it is actually the energy divided by Planck’s constant. Table C.1 contains a listing of some of these contrived, but nonetheless, very useful, units and their relationships to the eV.

Problems involving atomic or molecular calculations can be facilitated using yet another system of units, atomic units, abbreviated a.u. These units can lessen the calculational burden because many of the common atomic parameters are set equal to unity. After obtaining answers in a.u. it is a relatively simple matter to convert back to more familiar units.

In atomic units, by definition, the electronic charge e , the mass of the electron m_e , and \hbar are all set equal to unity. The unit of length is chosen to be the Bohr radius $a_0 = [(4\pi\epsilon_0)\hbar^2] / (m_e e^2)$. Thus, in atomic units

$$e = 1 = \hbar = m_e = \frac{1}{4\pi\epsilon_0} = 1 \quad (1.60)$$

The conversion between a.u. and SI units can be effected with the aid of Table 1.2.

Notice that the unit of velocity is simply the velocity of the electron in the first Bohr orbit while the unit of time is the period of the electron in the first Bohr orbit divided by 2π . The unit of energy is twice the ground-state Bohr energy, or 27.2 eV. The extra factor of 2 is merely a convenience. Interestingly, from the definition of the fine structure constant, Equation 1.35, the speed of light is simply $c = \alpha^{-1}$. That is, in a.u. the speed of light is 137 a.u. of length/a.u. of time (see Problem 6).

Table 1.2 Atomic units (a.u.)

Quantity	a.u.	Value (SI)
Mass	$m_e = 1$	9.10×10^{-31} kg
Charge	$e = 1$	1.60×10^{-19} C
Angular momentum	$\hbar = 1$	1.06×10^{-34} Js
Length	$a_0 = 1$	5.29×10^{-11} m
Velocity	$v_0 = \alpha c$	2.20×10^6 m/s
Time	$a_0/v_0 = 1/\alpha c$	2.42×10^{-17} s
Energy	$e^2 / (4\pi\epsilon_0 a_0) = 1$	4.36×10^{-18} J
Electric field	$e / (4\pi\epsilon_0 a_0^2) = 1$	5.14×10^{11} V/m
Bohr magneton	$e\hbar / (2m_e) = 1/2$	9.274×10^{-24} J/T

In practice two of these quantities are used more than the others, length and energy. Both have names in a.u. although they are seldom used. The unit of length in a.u. is the bohr and the unit of energy is the hartree, so named for D. R. Hartree who proposed the unit in 1926. Usually, however, most physicists simply say “one a.u. of length” or “one a.u. of energy.”

1.4 Retrospective

A variety of experimental observations during the late nineteenth and early twentieth centuries showed that classical physics was inadequate for describing many phenomena. These observations led to the formulation of quantum physics as we know it today, the subject of this book. Only a few of these early studies that led to the development of contemporary quantum physics have been discussed in this chapter because the chapter is intended primarily as background for the remainder of the book. Emphasis was placed on key points that required resolution in the new quantum physics including the particlelike behavior of light and the wavelike behavior of particles. This wave–particle duality, which Bohr elaborated upon in his principle of complementarity, is dealt with in quantum mechanics by incorporating both the Planck relation $E = h\nu$ and the de Broglie wavelength $\lambda = h/p$ in the mathematical formulation. It is the inclusion of these quantities that accounts for the quantized nature of subatomic energy levels. It remains “merely” to deduce an equation of motion that adequately describes quantum mechanical systems. After that we are done—except for the calculational details. In essence, this is all of quantum physics, at least in a first formulation which we now embark upon.

1.5 References

1. N. Bohr, “On the quantum theory of line-spectra,” in “Sources of Quantum Mechanics,” edited by B. L. van der Waerden (Dover, New York, 1967).

Problems

1. Light of wavelength λ illuminates a metal surface and photoelectrons having maximum kinetic energy of 1 eV are ejected. The light source is replaced by a one which emits light of wavelength $\lambda/2$ and the photoelectrons are observed to have a maximum kinetic energy of 4.28 eV. What is the work function of the metal? Find a table of work functions and decide which metal it is.
2. If the state of mercury atoms that is excited by electrons in the Franck–Hertz experiment decays back to the state from which it was excited by emitting light, what will be the wavelength of that light?

3. Calculate the following:
 - (a) The wavelengths in nm of the first three lines of the Lyman series and the Balmer series.
 - (b) The series limit of the Lyman and Balmer series. The series limit is defined as the shortest possible wavelength.
4. It is possible to form a hydrogenlike atom with a proton and a negative μ -meson having mass $m_\mu \approx 200m_e$. Find the radius of the first Bohr orbit in terms of a_0 , the velocity of the μ -meson in the first Bohr orbit in terms of the same quantity for hydrogen, and the ionization energy from the ground state in electron-volts.
5. Show that $a_0 = \hbar / (m_e c \alpha)$ and that the speed of the electron in the n th Bohr orbit is $v_n = \alpha c / n$.
6. Using the definition of the fine structure constant α , (Equation 1.35), and its known value, show that, in atomic units, the speed of light is 137 a.u. of length per a.u. of time.
7. Compton scattering experiments can be performed using protons rather than electrons.
 - (a) Find the Compton wavelength of the proton in terms of the Compton wavelength of the electron.
 - (b) If the apparatus is such that $\Delta\lambda/\lambda$ must be ~ 0.03 , what must be the wavelength of the incident photon? In what region of the electromagnetic spectrum are photons of this energy?
8. Show that fitting de Broglie waves to the circumference of the Bohr orbits leads to the postulate that Bohr never made, that is, angular momentum is quantized in units of \hbar .

Chapter 2

Elementary Wave Mechanics

2.1 What is Doing the Waving?

In nonrelativistic quantum physics, particles are treated as points. That is, they have no finite dimensions (zero volume) so they cannot, for example, spin. We are therefore justified in asking “what is doing the waving?” The answer is that it is the probability of finding the particle in a particular region of space. Actually, it is the probability of finding the particle within a particular range of some physically measurable parameters such as linear momentum or angular momentum, but let us confine our attention to coordinates for now. The application of quantum physics to solve problems thus becomes one of solving the appropriate equation of motion for the function that represents this probability. The mechanics of doing this is called quantum mechanics or, archaically, wave mechanics. The intention of this chapter is to introduce this equation of motion and, using it, to better understand the answer to the question what is doing the waving.

2.2 A Gedanken Experiment—Electron Diffraction Revisited

It is reasonable to ask if we can imagine an experiment that will demonstrate the wave nature of the probability and, simultaneously, the pointlike “structure” of the particles. Gedanken is the German word for thought, so a Gedanken experiment is not one that can actually be performed, but one that can be imagined and used to understand a particular phenomenon. Modern technology has, however, made it possible to perform experiments that were envisioned as Gedanken experiments during the development of quantum mechanics. Because of the counterintuitive nature of quantum physics, many Gedanken experiments were imagined, especially in the early development of quantum physics. For the present purpose, we return to the electron diffraction experiment described in Section 1.2.3 and use it to perform a Gedanken experiment.

Imagine the screen to be constructed of a material that phosphoresces when struck by an electron. Phosphorescent materials continue to emit light after being energized and we assume, for the purpose of this experiment, that our screen

phosphoresces indefinitely. Now, let us lower the intensity of the electron beam so we can easily see each electron as it strikes the screen, lights it up, and leaves a signature of its presence in the form of a persistent pinpoint of light. The first electron strikes somewhere, we cannot predict where with certainty. From the known diffraction pattern we know where it is most likely to strike. Perhaps it is a contrary electron and strikes in a region in which the diffraction pattern has low intensity, perhaps not. Bear in mind that it is a single event. Wherever it strikes, it leaves its signature. A second electron arrives. It too leaves its signature. Again, we do not know where it will land, only where it is most likely to land. After perhaps 100 electrons have struck the screen we have a pattern, but it may not look like the known diffraction pattern because 100 is not, statistically speaking, a very large number. When, however, a large number of electrons have struck the screen it is lit up with the known diffraction pattern. This pattern is composed of many points of light representing the point electrons, but the pattern represents the diffraction pattern characteristic of wave motion.

The important point to remember is that the particles are not magically turning into slithering sausages as they make their way through the narrow slit. They maintain their identity as point particles. It is, perhaps, Avogadro's number of them that are required to demonstrate the wavelike properties of matter.

2.3 The Wave Function

Paramount to obtaining the probability distribution is the wave function, $\Psi(x, t)$. We use the capital Greek letter to designate the wave function when the time is included and, for now, we work with only one-dimension, x . We point out that the wave function need not be written in terms of any coordinates. It could be in terms of another variable (called an observable in quantum mechanics), but we will consider only coordinates and time for now. Now, by postulate, $\Psi(x, t)$ contains all the information that the uncertainty principle permits us to know about the particle. Using an asterisk to signify the complex conjugate, the probability that the particle will be found in the interval dx at time t is given by

$$\Psi^*(x, t) \Psi(x, t) dx = |\Psi(x, t)|^2 dx \quad (2.1)$$

provided $\Psi(x, t)$ has been normalized so that

$$\int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx = 1 \quad (2.2)$$

Normalization assures that the total probability cannot exceed unity. The complex conjugate is required because $\Psi(x, t)$ may very well be a complex function. On the other hand, the probability must be real so the absolute value in Equation 2.1 assures us that the probability will be real. We see then that, while $\Psi(x, t)$ does not give physical information, its absolute square does. The quantity $|\Psi(x, t)|^2$ is

the probability *density* so that, in one-dimension, it has units of probability per unit length.

If we wish to calculate the average value of some quantity that is a function of x , say $f(x)$, we multiply this function by the normalized probability distribution $\Psi^*(x, t) \Psi(x, t) dx$, which weights the values of $f(x)$. We then integrate over all possible values of x to obtain $\langle f(x) \rangle$, the average value of $f(x)$. This procedure is analogous to calculating the class average on an examination by multiplying each possible score by the number of students achieving that score, adding these quantities, and then dividing by the total number of students. Division by the total number has already been accounted for if the wave function is normalized. If not, the integral in Equation 2.2 must be computed, which amounts to normalizing the wave function. In the case of the class average the number of students is a discrete number as are the possible test scores. Clearly the computation of $\langle f(x) \rangle$ requires integration so we define

$$\langle f(x) \rangle \equiv \int_{-\infty}^{\infty} \Psi^*(x, t) f(x) \Psi(x, t) dx = 1 \quad (2.3)$$

Notice that $\langle f(x) \rangle$ need not be one of the possible values $f(x)$ just as the class average of an examination need not be a score that any particular student actually achieved. In quantum physics the average value as defined in Equation 2.3 is often referred to as the expectation value, a fancy term for average value.

2.4 Finding the Wave Function—the Schrödinger Equation

Just as there are equations of motion in classical physics, there are equations of motion of the wave function in quantum physics. Such equations are called wave equations. In this book we deal with nonrelativistic quantum physics so we will use the Schrödinger wave equation, an equation that cannot be *derived*. It can be rationalized, but it cannot be derived. This is not the first time you have encountered such an equation. Newton's second law, $F = ma$, cannot be derived. It works though, so we accept it as being a law (at least nonrelativistically). It was deduced by Newton. We can presume that he tried others, but settled on $F = ma$ as the correct law of motion because it worked. This is the same approach taken by Erwin Schrödinger who shared the 1933 Nobel Prize in Physics with Paul Adrien Maurice Dirac. The citation for their prize reads: "for the discovery of new productive forms of atomic theory."

The validity of the Schrödinger equation lies in the fact that it satisfactorily explains nonrelativistic quantal phenomena. It is, however, worthwhile to see how this equation can be rationalized because we can see what is built into the Schrödinger equation. The (nonrelativistic) TME E of a particle of mass m in terms of the potential energy $U(x)$, the particle's momentum p is

$$E = \frac{p^2}{2m} + U(x) \quad (2.4)$$

If we incorporate both of the important quantal relations, the Planck relation, Equation 1.2, and the de Broglie wavelength, Equation 1.48, into Equation 2.4, we have

$$\hbar\omega = \frac{(\hbar k)^2}{2m} + U(x) \quad (2.5)$$

where we have replaced the de Broglie wavelength with the wave number k defined as

$$k = 2\pi/\lambda \quad \Rightarrow \quad p = \hbar k \quad (2.6)$$

The term in Equation 2.5 that makes it particularly difficult to write a wave equation for a particle is the potential energy, so we will temporarily ignore it. (We are, after all, only rationalizing, not deriving.) If the particle were massless, for example a photon, then the electromagnetic wave equation would pertain. That is, the equation of motion is

$$\frac{\partial^2 A(x, t)}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 A(x, t)}{\partial t^2} \quad (2.7)$$

where $A(x, t)$ is the space- and time-dependent amplitude (electric or magnetic field) of the wave, and c is, as usual, the speed of light. Partial derivatives are required because the wave function is a function of two variables. A solution to Equation 2.7 is a plane wave

$$A(x, t) = K e^{i(kx - \omega t)} \quad (2.8)$$

where K is a constant and $i = \sqrt{-1}$. Before proceeding let us recall that wave motion is always described by a function of $(x - vt)$ where v is the velocity of the wave. Equation 2.8 is such a function with $v = \omega/k$. For electromagnetic waves $v = c$, the speed of light.

Suppose we try to apply Equation 2.7 to the case of a material particle (nonzero mass), but, for simplicity, continue to let $U(x) = 0$. When $U(x) = 0$ we have a “free particle.” We then replace the amplitude $A(x, t)$ with the wave function $\Psi(x, t)$, let $c \rightarrow v$ and assume a plane wave solution analogous to Equation 2.8 and insert this solution into Equation 2.7. After dividing by the $\Psi(x, t)$ on both sides of the equation we obtain

$$(ik)^2 = \frac{1}{v^2} (-i\omega)^2 \quad (2.9)$$

Equation 2.9 is, however, inconsistent with Equation 2.5 because, with $U(x) = 0$, $k^2 \propto \omega$, not ω^2 . We can see that in order to get only the first power of ω we must

differentiate $\Psi(x, t)$ only once with respect to time. This results in a modification of Equation 2.7 with $A(x, t) \rightarrow \Psi(x, t)$ and $\partial^2 A(x, t) / \partial t^2 \rightarrow \partial \Psi(x, t) / \partial t$ to yield

$$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = K \frac{\partial \Psi(x, t)}{\partial t} \quad (2.10)$$

where K is a constant. Inserting Equation 2.8 into Equation 2.10 and solving for K we have

$$K = \frac{k^2}{i\omega} \quad (2.11)$$

But, from Equation 2.5 we see, with $U(x) = 0$,

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \implies \frac{k^2}{\omega} = \frac{2m}{\hbar} \quad (2.12)$$

Therefore,

$$K = -i \frac{2m}{\hbar} \quad (2.13)$$

and we have

$$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = -i \frac{2m}{\hbar} \frac{\partial \Psi(x, t)}{\partial t} \quad (2.14)$$

This equation can be put in its usual form by multiplying both sides by $-\hbar^2/2m$, the advantage of which is that both sides have units of energy. We have

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} = -\frac{\hbar}{i} \frac{\partial \Psi(x, t)}{\partial t} \quad (2.15)$$

This wave equation is applicable only to a free particle, that is, a particle for which the de Broglie wavelength is constant throughout. The de Broglie wavelength is constant because the total energy is presumed constant, so the kinetic energy and therefore the momentum is constant. How do we account for a nonzero potential energy? A constant potential energy is easy because the de Broglie wavelength is constant; $U(x) = 0$ is a special case of $U(x) = U_0 = \text{a constant}$. Thus, we can, without any guilt, write

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U_0 \right] \Psi(x, t) = -\frac{\hbar}{i} \frac{\partial \Psi(x, t)}{\partial t} \quad (2.16)$$

which is consistent with Equation 2.5 with $U(x)$ replaced by U_0 . Notice that we have factored the $\Psi(x, t)$ to the right of the bracket on the left-hand side of Equation 2.16. The significance of this is that the quantity in brackets is an operator and

it operates to the right. The first term is a differential operator and must be kept to the left of the function $\Psi(x, t)$. The second term is, however, merely a multiplicative operator, but an operator nonetheless. We will see that, in quantum mechanics, observable quantities such as energy, momentum, and position are represented by operators. We will deal with this in depth in a later chapter touching on it only superficially here. It is not a great leap of faith to replace U_0 in Equation 2.16 with the function $U(x)$ thus obtaining the time-dependent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right] \Psi(x, t) = -\frac{\hbar}{i} \frac{\partial \Psi(x, t)}{\partial t} \quad (2.17)$$

which, for brevity, we will refer to as the TDSE.

You may be wondering why we went through all this sleight of hand to arrive at Equation 2.17, after having stated at the outset that it couldn't be derived. After all, you probably never had anyone rationalize $F = ma$. Why then go to all the trouble to rationalize the TDSE? Why not just state it and get down to business solving quantum mechanics problems? The reason lies in Equation 2.5. This equation for the total energy of the particle comprises the two fundamental relations of quantum physics, the de Broglie wavelength and the Planck relation. Thus, these manifestly quantal quantities are incorporated in the TDSE.

There are a few mathematical consequences of using the TDSE as our equation of motion that we should recognize. First, it is a homogeneous linear differential equation. This means that linear combinations of solutions are also solutions, a characteristic that has profound physical consequences. Second, the TDSE is merely a differential equation. As such, it does not quantize anything. It could very well appear at the end of a chapter in a book on differential equations as an exercise asking the student to solve it for a given function $U(x)$. It is the physics of a particular system that imposes quantization on a system, if indeed quantization occurs. In other words, we as physicists must specify the conditions on the wave function that are dictated by the system under consideration. These conditions may or may not quantize the energy levels, as well as other physical parameters.

2.5 The Equation of Continuity

The TDSE, together with the probability interpretation of $|\Psi(x, t)|^2$ leads to a continuity equation for probability. This means that there is a flux of probability that must be conserved. To take a concrete example, if an electron is moving from, say, left to right, the probability is leaving one region of space and occupying another. Let us be quantitative and examine the time dependence of the normalization of the wave function:

$$\frac{\partial}{\partial t} |\Psi(x, t)|^2 = \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial t} + \Psi(x, t) \frac{\partial \Psi^*(x, t)}{\partial t} \quad (2.18)$$

We may, however, replace the partial derivatives with respect to time on the right-hand side of Equation 2.18 using the TDSE Equation 2.17 and its complex conjugate. The potential energy function, being a real function, drops out and we have

$$\begin{aligned}\frac{\partial}{\partial t} |\Psi(x, t)|^2 &= \frac{\hbar}{2im} \left[\Psi(x, t) \frac{\partial^2 \Psi^*(x, t)}{\partial x^2} - \Psi^*(x, t) \frac{\partial^2 \Psi(x, t)}{\partial x^2} \right] \\ \frac{\partial}{\partial t} |\Psi(x, t)|^2 &= \frac{\partial}{\partial x} \left\{ \frac{\hbar}{2im} \left[\Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial x} - \Psi(x, t) \frac{\partial \Psi^*(x, t)}{\partial x} \right] \right\} \quad (2.19)\end{aligned}$$

Now, define the quantity in curly brackets as the probability current $j(x, t)$:

$$j(x, t) = \frac{\hbar}{2im} \left[\Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial x} - \Psi(x, t) \frac{\partial \Psi^*(x, t)}{\partial x} \right] \quad (2.20)$$

which leads to

$$\frac{\partial |\Psi(x, t)|^2}{\partial t} + \frac{\partial}{\partial x} j(x, t) = 0 \quad (2.21)$$

which is the desired continuity equation. The analogy with the equation of continuity in electricity is often made. This analogy is more concrete if we imagine the wave function to represent a beam of electrons so that the electronic charge e multiplied by $|\Psi(x, t)|^2$ is, in a very real sense, the charge density. Thus, if we multiply Equation 2.21 by e we recover the continuity equation from electricity inasmuch as we now identify the quantity $ej(x, t)$ with the current density.

2.6 Separation of the Schrödinger Equation—Eigenfunctions

The potential energy term in Equation 2.17 does not contain the time. This will almost always be the case (certainly in this book). We attempt to solve the TDSE equation by the time-honored technique of separation of variables assuming a solution of the form

$$\Psi(x, t) = \psi(x) T(t) \quad (2.22)$$

Notice that the Greek psi on the right-hand side is lower-case which we reserve for a function of coordinates only. Inserting Equation 2.22 into Equation 2.17 and dividing by $\psi(x) T(t)$ we have

$$\frac{1}{\psi(x)} \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi(x) = -\frac{\hbar}{i} \frac{dT(t)}{dt} \quad (2.23)$$

Note that, on the left-hand side of Equation 2.23, the $\psi(x)$ in the denominator and the $\psi(x)$ in the numerator do not cancel because the one in the numerator must be operated upon by the quantity in square brackets.

Now, the left-hand side of Equation 2.23 contains only coordinates while the right-hand side only time. The only way these quantities, each containing a variable, can be equal is if they are each equal to a constant which we choose to be E (because we know the answer). Now, the equation in x cannot be solved unless we know $U(x)$, but the equation for time can be easily solved. The general solution is

$$T(t) = e^{-i(E/\hbar)t} \quad (2.24)$$

which is the universal time part of the wave function *as long as the potential energy is independent of time*. We need not bother with a normalization constant in Equation 2.24 because that will be absorbed in the normalization for $\psi(x)$.

Setting the left-hand side of Equation 2.23 equal to the separation constant E we have

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi(x) = E \psi(x) \quad (2.25)$$

This is the time-independent Schrödinger equation, the TISE. We will devote much of the remainder of this book to the solution of Equation 2.25. It should be noted that, as discussed above, the quantity in square brackets is an operator. This operator represents the total energy of the system and is called the Hamiltonian, the same Hamiltonian as in classical mechanics. If the potential energy does not contain the time, the Hamiltonian, designated by the symbol \hat{H} , is the TME. Moreover, since the TME is the sum of kinetic plus potential energies it is clear the the first term is the kinetic energy operator which can be written in terms of the momentum, $\hat{p}_x^2/2m$. The “hat” over the momentum signifies that it is an operator. We will also use a hat to designate a unit vector in any coordinate system, for example, \hat{i} , \hat{j} , \hat{k} in Cartesian coordinates or \hat{a}_r , \hat{a}_θ , \hat{a}_ϕ in spherical coordinates. This should cause no confusion with the hat designation of operators. Now, the momentum is a vector quantity (operator), so we use the subscript to denote the component even though we are dealing with only one-dimension in this chapter. In terms of the Hamiltonian, the (one-dimensional) TISE may be written as

$$\begin{aligned} \hat{H} \psi(x) &= E \psi(x) \\ &= \left[\frac{\hat{p}_x^2}{2m} + U(x) \right] \psi(x) \end{aligned} \quad (2.26)$$

and the time-dependent Schrödinger wave equation, the TDSE, is

$$\hat{H} \Psi(x, t) = -\frac{\hbar}{i} \frac{\partial \Psi(x, t)}{\partial t} \quad (2.27)$$

In general, there will be many solutions of the TISE, each corresponding to a different value of $\psi(x)$ and its corresponding eigenvalue, E . We therefore attach subscripts to distinguish the different $\psi_n(x)$ and to correlate them with their corresponding eigenvalues, E_n . Equations that have the form of Equation 2.26 are called eigenvalue equations. The different values of E_n are the eigenvalues and the corresponding values of $\psi_n(x)$ are called eigenfunctions. It is also possible that some eigenfunctions can share the same eigenvalue, in which case the eigenfunctions are said to be degenerate. We will ignore degeneracy for now because, for bound states in one-dimension, the eigenfunctions are nondegenerate. It will, however, be an important consideration when we attack three-dimensional problems.

We can actually find the form of the x -component of the momentum operator by noting that the square of an operator simply means that we should apply it twice in succession. Thus, comparing the first terms in the brackets of Equations 2.25 and 2.26 we see that

$$\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} \quad (2.28)$$

The appearance of the imaginary number i is not a cause of concern because the wave functions themselves can be complex functions. Recall that it is the absolute squares of the wave functions that must be real. It will, however, be a requirement that the eigenfunctions of any operator that represents an observable quantity, such as momentum or energy, must be real, for it would be absurd to imagine measuring an imaginary momentum.

2.7 The General Solution to the Schrödinger Equation

As noted above, an important property of the TISE is that it is a linear differential equation. This means that linear combinations of solutions are also solutions. Moreover, as will be shown later, the eigenfunctions constitute a *complete* set of functions. That is, the eigenfunctions are complete in the sense that any function can be represented as a linear combination of them, much as any vector in three-dimensional space can be represented as a linear combination of the unit vectors \hat{i} , \hat{j} , and \hat{k} . Indeed, the eigenfunctions span a vector space, the “vectors” being any function that can be constructed as a linear combination of the $\psi_n(x)$. Thus, a *general* solution to the TISE, call it $\psi(x)$, the absence of a subscript signifying that it is not an eigenfunction, may be written

$$\psi(x) = \sum_{n=1}^{\infty} a_n \psi_n(x) \quad (2.29)$$

where, because $\psi(x)$ may be complex, as may be the expansion coefficients, the a_n . An additional property that will be proven in a later chapter is that the $\psi_n(x)$ are

orthogonal in the same sense that the unit vectors are orthogonal. To designate this orthogonality, the notation can be condensed to

$$\int_{-\infty}^{\infty} \psi_n(x) \psi_m(x) dx = 0 \quad m \neq n \quad (2.30)$$

The integral in Equation 2.30 is the equivalent of the dot product for real vectors.

Suppose that $\psi(x)$, as given by Equation 2.29, represents the total wave function at $t = 0$, that is,

$$\begin{aligned} \Psi(x, 0) &= \psi(x) \\ &= \sum_{n=1}^{\infty} a_n \psi_n(x) \end{aligned} \quad (2.31)$$

then, using the universal time dependence, Equation 2.24, it is a simple matter to write the wave function for all time. We have

$$\Psi(x, t) = \sum_{n=1}^{\infty} a_n \psi_n(x) e^{-i(E_n/\hbar)t} \quad (2.32)$$

Equations 2.29 and 2.32 represent one of the most important theorems in quantum mechanics, the superposition theorem. At this stage in our discussion these two equations are merely mathematical constructions, but we will see that they have profound implications for the behavior of physical systems and the states that they occupy.

Because $\Psi(x, t)$, as given in Equation 2.32, is a solution of the TDSE, it is said that the system is in a superposition of states. Moreover, the expansion represented by Equation 2.32 is a *coherent* superposition of states in the sense the “components” of the expansion have definite phase with respect to each other as contained in the expansion coefficients and the time dependence. Suppose we have a large number of identical systems and a measurement of some physical quantity, say the energy, is made on a single one of these systems. The only possible result of this measurement is one of the energy eigenvalues. If an identical measurement is made on another of these systems, again, only one of the eigenvalues could result, but, possibly, a different one than the other measurement. If measurements are made on many of these identical systems (by many we mean *many*, say Avogadro’s number), then the absolute squares of the expansion coefficients, the a_n , give the probabilities of measuring the corresponding E_n ’s.

The measurement process described above alters the system and changes the wave function by forcing the system into the particular eigenstate, the eigenstate that corresponds to the measured eigenvalue. In particular, if the energy measurement yielded the i th eigenvalue E_i , then the wave function of the system becomes the eigenfunction $\psi_i(x)$. The language that goes with this is that the wave function has been “collapsed” into the i th state.

Consider a simple example. Suppose we have only two states in the expansion and that the normalized wave function $\Psi(x, t)$ is given by

$$\Psi(x, t) = \frac{1}{\sqrt{3}}\psi_1(x)e^{-i\omega_1 t} + \sqrt{\frac{2}{3}}\psi_2(x)e^{-i\omega_2 t} \quad (2.33)$$

where $\omega_i = E_i/\hbar$. For simplicity, let $\psi_1(x)$ and $\psi_2(x)$ be real functions. The probability density is

$$|\Psi(x, t)|^2 = \frac{1}{3} \left\{ |\psi_1(x)|^2 + 2|\psi_2(x)|^2 + 2\sqrt{2}\psi_1(x)\psi_2(x)\cos[(\omega_1 - \omega_2)t] \right\} \quad (2.34)$$

which is oscillatory, the frequency depending upon the difference in the energy and the amplitude depending upon the expansion coefficients. Incidentally, it is clear from Equation 2.34 that if there is only one component of $\Psi(x, t)$ then $|\Psi(x, t)|^2$ does not contain the time, thus justifying its designation as a “stationary state”.

Let us assume that we have a large number of identical systems, each described by the wave function of Equation 2.33. Now, what can we expect if we measure the energy of each of these identical systems? We have already stated that the only possible result of such a measurement is one of the eigenvalues. In the present case the measurement can yield only E_1 or E_2 because the system is in a superposition of only $\psi_1(x)$ and $\psi_2(x)$. What is the probability of measuring each of these eigenvalues? Without resorting to mathematical formalism to which we have not yet been exposed, it is relatively easy to deduce the answer. Suppose, rather than the expansion coefficients used in Equation 2.33, $\Psi(x, t)$ is an equal admixture of only $\psi_1(x)$ and $\psi_2(x)$. (For an unknown reason it is customary to use the word admixture here rather than mixture.) For this equal admixture only E_1 or E_2 could be measured, but with equal probabilities, $\frac{1}{2}$. The normalized wave function must therefore be

$$\Psi(x, t) = \frac{1}{\sqrt{2}}\psi_1(x)e^{-i\omega_1 t} + \frac{1}{\sqrt{2}}\psi_2(x)e^{-i\omega_2 t} \quad (2.35)$$

Consequently, we conclude that it is the square of the expansion coefficient that gives the probability of measuring the corresponding eigenvalue. If the system is described by the wave function of Equation 2.33, we would therefore measure E_2 twice as often as we would measure E_1 .

The consequence of the above discussion is that the system is indeed in more than one eigenstate—as long as we are not “looking,” that is “making a measurement.” When we make the measurement (and look), we necessarily perturb the system, immediately collapsing the wave function into one of the eigenstates.

2.8 Stationary States and Bound States

Bohr's characterization of the states of hydrogen as stationary states has been broadened and retained in modern quantum physics. It refers to any state $\Psi(x, t)$ for which the expansion, Equation 2.32, consists of a single term. Thus, the probability density $|\Psi(x, t)|^2$ reduces to

$$\begin{aligned} |\Psi(x, t)|^2 &= \psi_n(x) e^{-i(E_n/\hbar)t} \psi_n^*(x) e^{+i(E_n/\hbar)t} \\ &= \psi_n(x) \psi_n^*(x) \\ &= \text{function of } x \text{ only} \end{aligned} \quad (2.36)$$

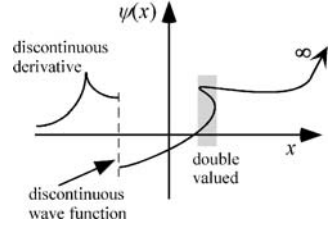
Because this probability density is independent of time, it is defined as a “stationary state.” On the other hand, if the wave function, $\Psi(x, t)$, contains two or more terms in Equation 2.32, the probability density will be time-dependent and the state does not qualify as a stationary state (see for example Equation 2.34).

If a particle is confined to a region of space by a potential energy function, then the resulting quantum states are referred to as “bound states.” Incidentally, physicists often get sloppy and refer to the potential energy function as, simply, the potential. We will follow this custom and use the two interchangeably. Obviously Bohr's stationary states are examples of bound states, but there are many other examples of bound states. The wave function representing a particle confined by such a potential energy function may be a stationary state or it may be a linear combination of them as in Equation 2.32. If there is more than one term in the expansion of the wave function that represents the quantum system, then the system is said to be in “a superposition of states.” More will be said about this designation when we discuss the formalism of quantum mechanics. In this chapter we will concentrate on the characteristics of stationary bound states of some simple systems. A great simplification exists for bound states in one-dimensional problems. They are always nondegenerate (see Problem 3).

2.9 Characteristics of the Eigenfunctions $\psi_n(x)$

What must be the character of an eigenfunction $\psi_m(x)$? First, it may be a real, imaginary, or complex function because it is the absolute square of $\psi_n(x)$ that gives the probability density. It must, however, be single valued and it must be continuous. Even in the mysterious world of quantum mechanics a particle cannot be in two places at once. If $\psi_n(x)$ had, say, two different values at a given value of x , then $|\psi_n(x)|^2$ would be similarly double valued and there would be two *different* probabilities of finding the particle at a given value of x . Accepting that this is absurd, even in quantum physics, we require that $\psi_n(x)$ is single valued. A similar incongruity would occur if the wave function were discontinuous. These are, in fact, characteristics of any general solution to the TISE $\psi(x)$, not just eigenfunctions. Figure 2.1 illustrates three hypothetical wave functions $\psi(x)$ that are unacceptable.

Fig. 2.1 Hypothetical wave functions $\psi(x)$ that, for the indicated reasons, would be unacceptable bound state wave functions



In addition to these general conditions on $\psi(x)$, we are also interested in the important case in which $U(x)$ supports bound states. This means that the particle motion is restricted to a particular region of space by the potential energy function, similar to the way the planets are bound by the potential energy of the sun. In such cases the particle is confined by the potential energy function and, as a consequence, the probability density and therefore the wave function must approach zero as $|x| \rightarrow \infty$. The language that goes with this is to say that the wave function is “normalizable” or “square integrable.” This means that the wave function can be multiplied by a constant such that

$$\int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx = 1 \quad (2.37)$$

Equation 2.37 is called the normalization integral and it signifies that the probability of finding the particle somewhere is unity. Moreover, for bound states it cannot be found at infinity because the nature of the potential localizes it in space. Notice that multiplication of the eigenfunction by a constant does not change the magnitude of the corresponding eigenvalue because the eigenfunction $\psi(x)$ occurs in each term of the TISE, Equation 2.25. Combining the orthogonality property with normalization, we may write for eigenfunctions

$$\int_{-\infty}^{\infty} \psi_n^*(x) \psi_m(x) dx = \delta_{mn} \quad (2.38)$$

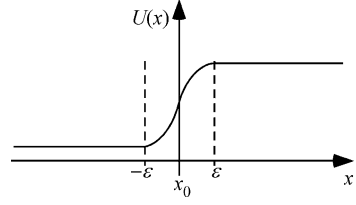
where δ_{mn} is the Kronecker delta defined as

$$\begin{aligned} \delta_{mn} &= 0 & \text{if } m \neq n \\ &= 1 & \text{if } m = n \end{aligned} \quad (2.39)$$

Eigenfunctions that obey Equation 2.38 are said to be orthonormal.

Now we must ask about the derivative of $\psi(x)$. The TISE contains the second derivative, so that if $U(x)$ is a continuous function, both $\psi(x)$ and $d\psi(x)/dx$ must be continuous. Even if $U(x)$ has a finite discontinuity, both $\psi(x)$ and $d\psi(x)/dx$ must be continuous. This is so because, from the TISE, $d^2\psi(x)/dx^2$ will then have a finite discontinuity (imagine solving Equation 2.23 for $d^2\psi(x)/dx^2$) from which it follows that $d\psi(x)/dx$ must be continuous and that $\psi(x)$ is continuous. An

Fig. 2.2 Sketch of a hypothetical potential energy with a discontinuity that occurs as $\varepsilon \rightarrow 0$



unacceptable discontinuity of the derivative is illustrated in Fig. 2.1. To place this on a more mathematical foundation we may imagine a potential energy function that has a finite discontinuity at some value of x , say $x = x_0$ as illustrated in Fig. 2.2.

We simply integrate the TISE across the discontinuity from $x_0 - \varepsilon$ to $x_0 + \varepsilon$:

$$\int_{-\varepsilon}^{\varepsilon} \frac{d}{dx} \left[\frac{d\psi_n(x)}{dx} \right] dx = \left(-\frac{2m}{\hbar^2} \right) \int_{-\varepsilon}^{\varepsilon} [E - U(x)] \psi_n(x) dx \quad (2.40)$$

and take the limit as $\varepsilon \rightarrow 0$:

$$\begin{aligned} & \lim_{\varepsilon \rightarrow 0} \left. \frac{d\psi_n(x)}{dx} \right|_{x=\varepsilon} - \lim_{\varepsilon \rightarrow 0} \left. \frac{d\psi_n(x)}{dx} \right|_{x=-\varepsilon} \\ &= \left(-\frac{2m}{\hbar^2} \right) \lim_{\varepsilon \rightarrow 0} \int_{-\varepsilon}^{\varepsilon} [E - U(x)] \psi_n(x) dx \end{aligned} \quad (2.41)$$

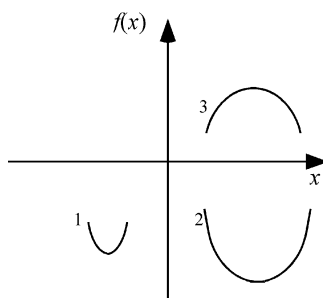
As long as the discontinuity in $U(x)$ that occurs when $\varepsilon \rightarrow 0$ is finite, the integral on the right-hand side of Equation 2.41 vanishes in the limit and $d\psi/dx$ must be continuous at $x = x_0$. If, on the other hand, the discontinuity is infinite, as would occur if $U \rightarrow \infty$, then the integral on the right-hand side does not necessarily vanish in the limit and the derivative need not be continuous.

There is a great deal that we can learn about the nature of the eigenfunctions, the $\psi_n(x)$, without ever actually solving the TISE. Let us solve Equation 2.25 for the second derivative and, again, for simplicity, imagine $\psi_n(x)$ to be a real function:

$$\frac{d^2\psi_n(x)}{dx^2} = \left(-\frac{2m}{\hbar^2} \right) [E - U(x)] \psi_n(x) \quad (2.42)$$

Now, recall that the second derivative of a function is a measure of the curvature of the function. A high value of the second derivative means a “tight” curve, while a low value means a gentle curve. Moreover, the sign of the second derivative indicates the direction of curvature. (Recall that this is the basis for determining whether a zero of the first derivative is a maximum or a minimum.) A negative second derivative means that the function is concave down while a positive second derivative is concave up. These features of the second derivative are summarized in Fig. 2.3 for an arbitrary function $f(x)$.

Fig. 2.3 Illustrations of various possible second derivatives of the function $f(x)$. The curves labeled 1 and 2 have positive values of $d^2 f(x)/dx^2$ and are therefore concave up. Curve 3 is concave down. The second derivative of curve 1 is greater than that of curve 2



If the curvature of a wave function $\psi(x)$ is high as, for example, the curve labeled number 1 in Fig. 2.3, then the de Broglie wavelength of the particle that it represents is short and the momentum and kinetic energy are high. This is characteristic of a high-energy state. Thus, we expect the lowest energy states to have the longest de Broglie wavelengths and their eigenfunctions to have the gentlest curvatures. In such a case the wave function will not go through zero (a node) except at $\pm\infty$ so the lowest state, the ground state, will have no nodes. The first excited state, having slightly higher energy, has one node, and so on. In essence, we are fitting de Broglie waves into the region of space that is dictated by the potential energy function. In this sense the ground state is the fundamental and the first excited state the first overtone.

There is still more that we can learn from Equation 2.42. Figure 2.4 shows a sketch of a fictitious potential energy curve.

The horizontal line represents E , the TME of a particle. Let us temporarily assume classical motion so that E can take on any value as determined by the initial conditions. Because $U(x)$ (in the illustration) extends to values higher than E , the motion will be bound. The limits of this motion will be x_{c1} and x_{c2} . These points are known as classical turning points. At these points the particle has zero kinetic energy and it turns around. Classically, the particle cannot move beyond the classical turning points because this would require a negative kinetic energy and, thus, an imaginary speed. Nevertheless, quantum mechanics, being the contrary branch of physics that it is, permits motion into this “classically forbidden region.” Let us

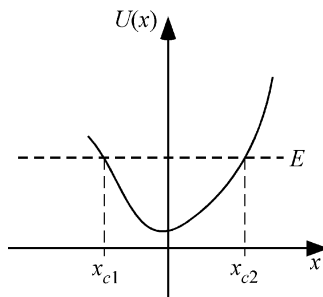


Fig. 2.4 A hypothetical potential energy curve with a presumed total mechanical energy (TME) showing the classical turning points x_{c1} and x_{c2}

examine the nature of $\psi(x)$ in both the classically allowed and forbidden regions of space.

In the classically allowed region E is always greater than $U(x)$ so the quantity in square brackets in Equation 2.42 is necessarily positive. Thus, if $\psi(x)$ is positive, the second derivative is negative. On the other hand, if $\psi(x)$ is negative, then $d^2\psi(x)/dx^2 > 0$. The consequence of this is that, in the classically allowed region, the wave function always curves toward the x -axis as illustrated in Fig. 2.5 where we have superposed a presumed wave function on the potential function of Fig. 2.4 using the line representing the TME as the zero of $\psi(x)$. Thus, the second derivative is shown to be positive on the left-hand side where $\psi(x)$ is negative and negative on the right-hand side where it is positive. At the x_{c2} , where the wave function crosses into the classically forbidden region, the wave function undergoes an inflection point and the second derivative changes from negative to positive.

These characteristics of the second derivative are typical of sinusoidal functions for the classically allowed region and exponentially decaying functions for the forbidden regions. Indeed, the wave functions in the forbidden regions must decrease as $x \rightarrow \pm\infty$ in order for the wave function to be normalizable, as it must be to correctly describe a bound state.

There is yet another bit of general information that can be obtained in certain cases from the TISE equation. Let us make the assumption that the potential function is an even function so that $U(x) = U(-x)$. Recall that functions *may* have definite parity. That is, they may be even or they may be odd. They may also be neither. To check the parity of a function $f(x)$ simply let $x \rightarrow -x$. If $f(x)$ has definite parity, then one of the conditions

$$\begin{aligned} f(x) &= f(-x) && \text{even} \\ f(x) &= -f(-x) && \text{odd} \end{aligned} \quad (2.43)$$

will prevail. An easy way to think of these functions is that even functions are symmetric with respect to the ordinate, while odd functions are symmetric with respect to the origin as illustrated in Fig. 2.6.

We let $x \rightarrow -x$ in the TISE, Equation 2.25 with the condition that $U(x) = U(-x)$ and obtain

Fig. 2.5 A hypothetical wave function sketched on the potential curve shown in Fig. 2.4. The signs of the second derivative of the wave function, the curvature, in different regions are displayed; inflection points are indicated by solid circles

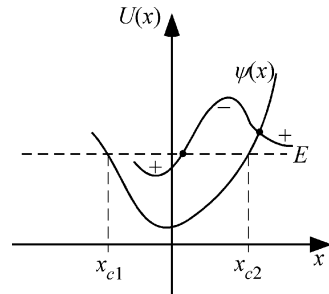
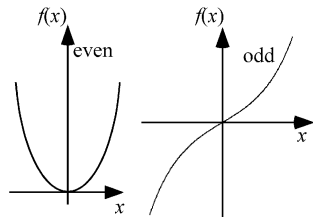


Fig. 2.6 Even and odd functions of x , $f(x)$



$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi_n(-x) = E \psi_n(-x) \quad (2.44)$$

where we have used the subscripts on the wave function to emphasize that they are eigenfunctions. Clearly $\psi_n(-x)$ and $\psi_n(x)$ are solutions of the same TISE, and, importantly, have the same eigenvalue E_n . Because $\psi_n(-x)$ and $\psi_n(x)$ have the same eigenvalue, they can differ only by a constant. That is,

$$\psi_n(-x) = \beta \psi_n(x) \quad (2.45)$$

We can, however, change the sign of x again so that

$$\begin{aligned} \psi_n(x) &= \beta \psi_n(-x) \\ &= \beta [\beta \psi_n(x)] \\ &= \beta^2 \psi_n(x) \end{aligned} \quad (2.46)$$

from which it is clear that $\beta = \pm 1$. The conclusion is, therefore, that in the not so special case in which the potential energy is an even function, the eigenfunctions of the TISE have definite parity. That is, if $U(x) = U(-x)$, then the eigenfunctions $\psi_n(x)$ are such that they have definite parity, $\psi_n(x) = \pm \psi_n(-x)$. We note that the ground state must have no nodes so it must have even parity.

2.10 Retrospective

The statistical nature of the quantum description of matter is the most important distinction between quantum physics and classical physics. The concept of a wave function from which all allowable information can be extracted is new to most students and the idea that probabilities, averages, and other statistical quantities must be employed to describe a physical system is novel. The Schrödinger equation, which is the equation of motion for the wave function, incorporates the Planck relation and the de Broglie wavelength, neither of which have classical analogs. Thus, one

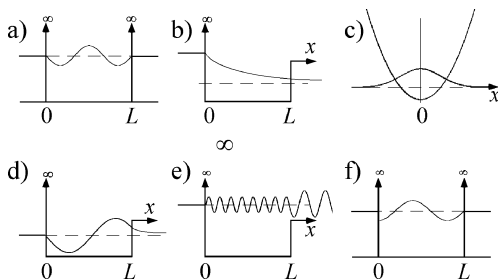
can, in principle, find the wave function for a given set of conditions. But, what is this wave function? It isn't something that we can measure. Obviously though, it is important. From our current perspective, the perspective that the wave function is a solution to the TDSE and is a function of position and time, we must regard it as a function, such that when its absolute square is taken, it yields the probability of finding the particle between x and $x + dx$ during the time interval between t and $t + dt$. We can say no more. This is, however, a great deal—quantum mechanically speaking. It should thus be borne in mind when going through the mathematical gymnastics required to solve the TDSE that we ultimately seek these probabilities.

Problems

1. A particle of mass m that is confined in a potential well is known to be in an eigenstate having eigenfunction $\psi(x) = Ae^{-\alpha^2 x^2/2}$ and energy $(\alpha\hbar)^2/(2m)$.
 - (a) Find the potential energy function $U(x)$ that confines the particle.
 - (b) What is the force that confines the particle?
 - (c) Find the value of the constant A that is required to normalize this eigenfunction.
2. The normalized wave function of a particle of mass m is given by

$$\Psi(x, t) = \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-\alpha^2 x^2/2} e^{i(kx - \omega t)}$$

- (a) What is the probability of finding the particle between x and $x + dx$ at time t ?
 - (b) What is the probability of finding the particle in the range $-\infty < x < \infty$?
3. Prove that for bound states in one-dimension the energy eigenfunctions are non-degenerate. Note that it is crucial that this proof applies only to one-dimension and to bound states.
4. A particle is represented by the wave function $\psi(x) = Ae^{i(kx - \omega t)}$ where $k = p/\hbar = 2\pi/\lambda$ where λ is the de Broglie wavelength and p is the momentum.
 - (a) Calculate the probability current density $j(x, t)$.
 - (b) The particle encounters a rise in potential energy that causes p to decrease by a factor of 2. Find the resulting change in amplitude of the wave after the encounter.
5. Six potential wells with possible wave functions $\psi(x)$ sketched on the wells are shown. The dashed lines are located at the energy of the state that $\psi(x)$ is intended to represent. The dashed lines also represent $\psi(x) = 0$. Which $\psi(x)$ are acceptable wave functions and which are unacceptable? Give reasons.



Potential wells and possible wave functions for Problem 5

6. Assume that the TISE has been solved for a potential energy function that supports bound states and the orthonormal energy eigenfunctions are denoted by $\psi_n(x)$ with corresponding energy eigenvalues E_n . A large number of energy measurements are made, but only three different values of the energy are actually observed, E_1 , E_2 , and E_3 . The ratio of occurrences of these values is (in order) 3 : 4 : 5.
 - (a) What is the normalized wave function $\Psi(x, 0)$ at $t = 0$?
 - (b) What is the normalized wave function $\Psi(x, t)$?
 - (c) What is the expectation value of the energy at $t = 0$?
 - (d) What is the expectation value of the energy for $t > 0$?
7. A free particle having wave number k_1 is traveling in the $+x$ direction when it encounters a sudden change in the potential energy to some constant lower value. After a finite distance the potential energy increases to its original value. Sketch the wave function that represents this particle in all three regions of space. Pay particular attention to the de Broglie wavelengths in each region. Note the properties of this wave function such as amplitude, continuity, and derivatives.
8. A particle of mass m is subjected to a potential energy such that at $t = 0$ the wave function that describes the particle is given by

$$\Psi(x, 0) = \left[\frac{\sqrt{2}}{3} \psi_1(x) + \frac{\sqrt{6}}{3} \psi_2(x) + \frac{1}{3} \psi_3(x) \right]$$

where the $\psi_n(x)$ are eigenfunctions of the Hamiltonian \hat{H} , each of which has energy eigenvalue $-(1/n^2) E_0$ where E_0 is a positive constant.

- (a) If an energy measurement is made, what are the possible results of the measurement?
- (b) What is the probability of measuring each of these energies?
- (c) What is the expectation value of the energy?
- (d) Suppose there is another physical quantity that may be measured, a quantity that is represented mathematically by Q . Assume that the $\psi_n(x)$ are also eigenfunctions of the operator that represents this quantity, \hat{Q} , with

eigenvalues nQ_0 . If the energy is measured first and found to be $-(1/9)E_0$ and then a measurement of Q is made, what will be the value of Q that is measured?

9. A one-dimensional potential energy function is given in a.u. by

$$U(x) = \begin{cases} \infty & x \leq 0 \\ -\frac{1}{x} & x > 0 \end{cases}$$

- (a) Sketch the potential energy. Is it possible that this potential will support bound states?
 (b) Only one of the wave functions listed below is the eigenfunction that represents the ground state. Which one?

$$\begin{aligned} \psi_1(x) &= Ae^{-\alpha x}; \quad \psi_2(x) = Axe^{-\alpha x} \\ \psi_3(x) &= Ae^{-\alpha^2 x^2}; \quad \psi_4(x) = A(x - 2x^2)e^{-\alpha^2 x^2} \end{aligned}$$

- (c) What is the ground state energy in a.u.?
 (d) What is $\langle x \rangle$ for the ground state?

Chapter 3

Quantum Mechanics in One Dimension—Bound States I

3.1 Simple Solutions of the Schrödinger Equation

3.1.1 The Infinite Square Well—the “Particle-in-a-Box”

Eigenfunctions and Eigenvalues

The L -box

One of the most important problems in the study of quantum mechanics is the infinite square well often referred to as the particle-in-a-box. It is important because it is simple and easily solvable, so the mathematical details do not obscure the physics. The particle-in-a-box is also often used as a basis for tractable problems in more advanced aspects of quantum mechanics. We begin by specifying the potential energy function $U(x)$ for this problem. It is

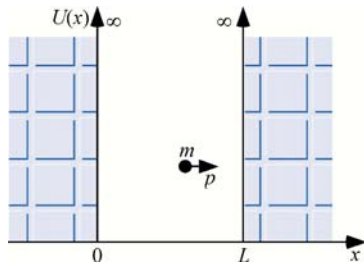
$$\begin{aligned} U(x) &= 0 & 0 \leq x \leq L \\ &= \infty & \text{otherwise} \end{aligned} \quad (3.1)$$

For convenience, we refer to this potential energy function as the L -box. We remind the reader again (see Section 2.8) that physicists often refer to potential energy functions as potentials. All physics students know that there is a monumental difference between the electric potential and the potential energy, but that is the way physicists converse. We will adhere to this longstanding tradition of casual (read “sloppy”) jargon and often use the term potential when we really mean potential energy.

Graphically $U(x)$ has the form shown in Fig. 3.1. Despite the simplicity of this potential, we will be compelled to employ the exception to the rule about continuity of the derivative of the wave function. Recall that this continuity was emphasized in Section 2.9, but with the caveat that it would not be continuous at an infinite discontinuity in the potential energy. This is such a case so we should be prepared for it at $x = 0$ and $x = L$. The rule about continuity of $\psi(x)$ itself is, however, inviolable.

The potential energy in the box is zero so the particle moves freely between the walls. All of the mechanical energy in this region is kinetic energy. The walls

Fig. 3.1 Potential energy function for an infinite square well, an L -box



are, however, “rigid” as signified by the infinity of the potential energy. This means that they are impenetrable, classically and quantum mechanically. When the particle encounters infinite potentials, it encounters a brick wall. Quantum mechanically this means that the probability of finding the particle in the walls is zero! We therefore must force the wave function to vanish in the classically forbidden region, a considerable simplification. Thus, the wave function must vanish at the walls so that

$$\begin{aligned}\psi_1(x) &= 0 & x &\leq 0 \\ \psi_3(x) &\equiv 0 & x &\geq L\end{aligned}\tag{3.2}$$

The TISE inside the box is simply

$$\frac{d^2\psi_2(x)}{dx^2} + k^2\psi_2(x) = 0\tag{3.3}$$

where $k^2 = 2mE/\hbar^2$. The choice of the letter k was not capriciously made. As substitution of Equation 2.6 shows, it is indeed the wave number, so its designation as k is justified. Equation 3.3 is perhaps the most ubiquitous equation in all of physics. It describes simple harmonic motion and has sinusoidal solutions (which, incidentally, curve toward the abscissa). A convenient form in which to write these sinusoidal solutions for this problem is

$$\psi(x) = A \sin kx + B \cos kx\tag{3.4}$$

It is customary to designate the solution inside the well by $\psi(x)$, without any reference being made to it being inside the well because the remaining portion of the wave function (outside the well) is zero. We adopt this convention, but it should be borne in mind that the region in which $\psi(x) = 0$ is should not be ignored.

The boundary condition at $x = 0$ clearly shows that $B = 0$ for if it were not the cosine term would prevent $\psi(x)$ from vanishing at $x = 0$. Inserting the boundary condition at $x = L$ imposes the restriction that

$$k_n = \frac{n\pi}{L}\tag{3.5}$$

where n is an integer. A subscript n has been attached to the wave number in Equation 3.5 because it is obviously quantized since n is an integer. The eigenfunction is thus

$$\begin{aligned}\psi_n(x) &= A \sin\left(\frac{n\pi x}{L}\right) & 0 \leq x \leq L \\ &= 0 & \text{otherwise}\end{aligned}\quad (3.6)$$

Evidently any sine wave having an argument that is an integral multiple of $(\pi x/L)$ is acceptable. Thus, there are an infinite number of solutions. This is not surprising inasmuch as the well is infinitely deep. It is important to include the portions of the eigenfunction that are zero, $\psi_1(x)$ and $\psi_3(x)$. This portion of the wave function is just as important as the sinusoidal part. (Zero is a perfectly good constant.) To complete the job of obtaining the eigenfunction we must normalize it, a simple task that will be left as an exercise (see Problem 2). Normalization requires that $|A|^2 = 2/L$.

The energy eigenvalues that are associated with each of the energy eigenfunctions, Equation 3.6, are easily obtained by squaring k_n in Equation 3.5, inserting the value of the constant k , and solving for the energy E . We have

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (3.7)$$

where we have attached a subscript n to the energy as required by the condition imposed on k_n by the boundary condition. Notice that the quantum numbers n begin with $n = 1$, not $n = 0$. This is consistent with the uncertainty principle for, in view of Equation 3.7, if n were zero, then the (kinetic) energy and hence the momentum would be zero. This would make the uncertainty in position infinite although we know that, at maximum, $\Delta x = L$.

There is a great deal of physics still to be learned from the L -box. First, let us not forget the de Broglie wavelength. Because, for a given energy state, the kinetic energy in the box is constant, the momentum p is also constant. We should designate it p_n because $p_n = \hbar k_n$. Thus, the de Broglie wavelength for each state, $\lambda_n = h/p_n$, is constant. The lowest energy state will (always) have the longest de Broglie wavelength. Moreover, the impenetrability of the walls means that the de Broglie waves must have nodes at the walls. In short, de Broglie waves must fit in the well. Actually, it is half de Broglie waves that must fit in the well because a full wave has a node in the middle and we know that the ground state has no nodes. (In this problem the nodes at $x = \pm\infty$ are the same as the nodes at the walls.) The longest de Broglie wave that will fit in the box is therefore one having wavelength twice the length of the box. Thus, for the ground state of the box $\lambda_1 = 2L$. The de Broglie wavelength of the first excited state will be L , the second excited state $(2/3)L$, etc. In general,

$$\lambda_n = 2\frac{L}{n} = \frac{h}{p_n} \quad (3.8)$$

which is identical with Equation 3.7 (see Problem 4). This shows that the energy is quantized merely by fitting de Broglie waves in the box. This is only possible because in this particularly simple case the de Broglie wavelength is constant within the well. Thus, de Broglie could have solved for the energy eigenvalues of the particle-in-a-box. The derivation of the energy eigenvalues of the particle-in-a-box using Equation 3.8 emphasizes, however, that the TISE is indeed a wave equation. As such, it could appear as an exercise at the end of a chapter in a course on differential equations with a variety of different potential energy functions $U(x)$. It is, however, the imposition of the boundary conditions that fit de Broglie waves in the box that causes the quantization.

The a -box

The a -box is also an infinite square well, but with the x -axis translated so the potential energy function is given by

$$\begin{aligned} U(x) &= 0 & -a/2 \leq x \leq a/2 \\ &= \infty & \text{otherwise} \end{aligned} \quad (3.9)$$

While this may not seem to be a very significant change, it often makes some aspects of the problem more apparent. First, this potential energy function is symmetric about the $U(x)$ axis, that is, it is an even function. As was seen in Section 2.9, when the potential energy function is even, the eigenfunctions must have definite parity, they must be even or odd. Parity is very important in quantum mechanics. Parity considerations can save a great deal of labor. Of course, the eigenfunctions for the L -box obviously have definite parity with respect to the line $x = L/2$, but there can be advantages to using the a -box. One disadvantage, however, is that the eigenfunctions cannot be written as simply as they can for the L -box for which they are all sine waves, see Equation 3.6. In this case the eigenfunctions alternate between cosines and sines and are easily found to be

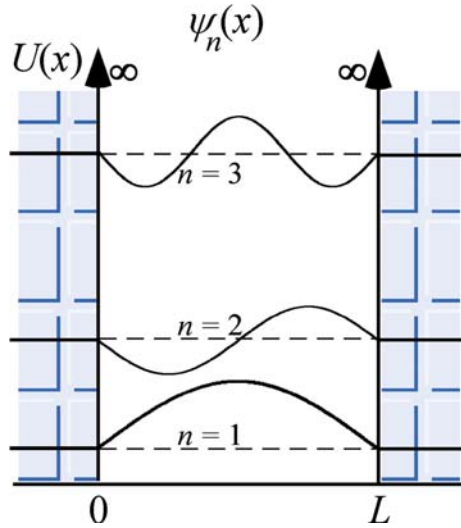
$$\begin{aligned} \psi_n(x) &= \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi x}{a}\right) & -\frac{a}{2} \leq x \leq \frac{a}{2} & \quad n \text{ odd (even parity)} \\ \psi_n(x) &= \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) & -\frac{a}{2} \leq x \leq \frac{a}{2} & \quad n \text{ even (odd parity)} \\ &= 0 & \text{otherwise for all values of } n \end{aligned} \quad (3.10)$$

Of course the energy is the same as Equation 3.7, with L replaced with a .

Information Obtained from the Eigenfunctions

Figure 3.2 shows the first three eigenfunctions for the particle-in-a-box. For this discussion we will use the L -box, but the conclusions pertain to both boxes. A common way of displaying the eigenfunctions is to graph them directly on the potentials from

Fig. 3.2 Eigenfunctions for the first three states of an L -box. The zeros of these wave functions are taken to be the corresponding energy eigenvalues. Notice that the eigenfunctions continue outside the box where they vanish

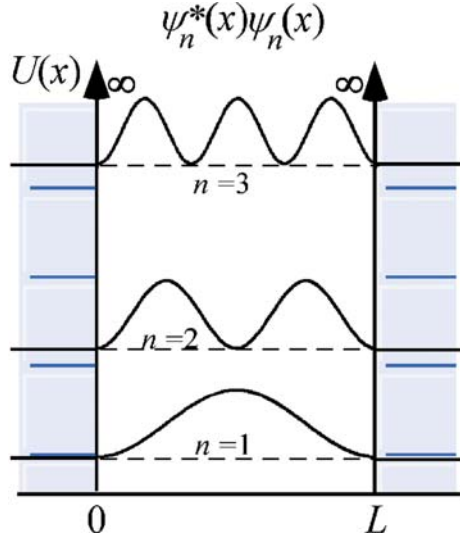


which they arise, and vertically at the energy eigenvalue to which they correspond. The amplitudes have been adjusted to fit on the figure. As noted above, it is important to remember that the eigenfunctions continue into the brick wall region. They happen to be zero in there, but they are there. Recall that it is the continuity of the wave function that forced us to match the wave function inside the wall (zero) to the wave function in the box that produced the actual wave function in the box.

Clearly the sinusoidal eigenfunctions fit the criterion that the wave function in the classically allowed region must curve toward the axis. It was noted that the condition on the second derivative in the classically forbidden region was typical of exponential decay. In this extreme case (extreme because of the infinite walls) we can imagine the exponential to be $e^{-\kappa|x|}$ where κ is a real number (and a Greek kappa) in the limit $\kappa \rightarrow \infty$. We have already discussed the discontinuity of the derivative at the walls as being due to the infinite discontinuity in the potential energy. Incidentally, if this were a finite box, that is, a box with infinite slope, but finite depth, the derivative would indeed have to be continuous.

We do not expect the eigenfunctions for the L -box to have definite parity because the potential energy is not even, at least with respect to $x = 0$. We do, however, expect the eigenfunctions of the a -box to have definite parity because the a -box potential energy is even. Indeed, the pure cosines and sines that are the eigenfunctions alternate between even and odd for the a -box. When making a choice between the two boxes for working a given problem, the L -box offers the advantage that the wave functions all have the same form, sines. On the other hand, the a -box offers the advantage that the wave functions have definite parity and this may be helpful if there are many integrals to compute. Incidentally, it is easy to remember that the ground state of the a -box is the cosine because, despite the fact the $n = 1$ (an odd number), the eigenfunction must be even to keep it nodeless.

Fig. 3.3 Probability distributions for the first three states of an infinite square well



Once we have the eigenfunctions, the most obvious physical quantity that we can find is the probability density (probability per unit length) which will be different in different states. For the n th eigenstate, this density will simply be

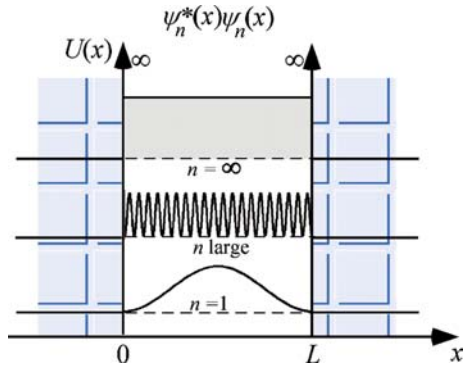
$$P_n(x) = \psi_n^*(x) \psi_n(x) \quad (3.11)$$

Graphs of $P_n(x)$ for the lowest three eigenstates are shown in Fig. 3.3.

Clearly the probability of finding the particle at the walls is zero. In the ground state we see that the maximum probability occurs in the middle. That is, if many measurements of the location of the particle were made, most of these measurements would yield values near $x = L/2$. On the other hand, if the particle were in the first excited state, we would almost never find it to be near $x = L/2$ because there is a node there. Indeed, if the particle is in any excited state having an even quantum number, it could never be found in the middle because there must be a node there. This is more obvious using an a -box because of the definite parity of the wave functions. Recall that states with odd quantum numbers have even parity.

If we were to examine the problem classically, the probability distribution would be a straight line because the speed is constant throughout the box. Therefore, the particle spends an equal amount of time in any given interval dx . Figure 3.4 shows this uniform probability distribution characteristic of a classical particle-in-a-box at the top of the figure, together with the probability distribution for $n = 20$, which was chosen to be characteristic of a “high quantum number”. While $n = 20$ is “high,” the oscillations in the probability density are still apparent. Also shown for comparison is the probability density for the ground state. The important point here is that as the quantum number becomes large, the peculiar behavior that was deduced at low quantum numbers such as the particle being prohibited from being found at certain

Fig. 3.4 Probability distributions for the ground state of an L -box for a state of high quantum number ($n = 20$) and for the classical limit, the horizontal line at the top



locations disappears. This is a manifestation of the correspondence principle. As the system approaches classical dimensions and the quantum number becomes large, the behavior tends toward familiar classical behavior.

It is of interest to concentrate on the low quantum states, and consider the peculiar probability distribution as compared with the classical expectation. We may focus on the ground state to be definite and, without loss of generality, consider symmetric potentials (an a -box may be more comfortable here). From our discussion of the general features of wave functions it is clear that the ground state probability will always have a maximum in the middle (or near the middle, if the potential isn't symmetric). This is because the ground state wave function cannot have any nodes—it must be even. It is a matter of semantics, but, here, we are not designating the zeros of $\psi_n(x)$ at $x = 0$ and $x = L$ to be nodes.

There is more. Because $|\psi(x)|^2$ gives the distribution over x we may calculate the average value (expectation value) of any function of x say $f(x)$ as discussed in Section 2.3. We illustrate by calculating $\langle x^2 \rangle$, the average value of the square of the position. We could calculate $\langle x \rangle$ instead of $\langle x^2 \rangle$, but that would be too easy. It is obviously $L/2$ for the L -box and zero for the a -box. Notice that this is true for any of the eigenstates, including the odd states for which the probability of finding the particle at $L/2$ is zero because $|\psi(x)|^2$. In general, an average value is not one of the averaged numbers. For example, the average of 7 and 9 is 8.

To evaluate $\langle x^2 \rangle$ we simply sum (integrate) x^2 over the distribution function. We don't have to worry about dividing by anything (analogous to the number of students in the class) as long as the wave functions are normalized. If they were not, we would simply divide by

$$\int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx$$

which is equivalent to having normalized the wave function in the first place. Using the L -box, evaluation of our expectation value is accomplished by performing a single simple integral:

$$\begin{aligned}
\langle x^2 \rangle_n &= \int_{-\infty}^{\infty} \psi_n^*(x) x^2 \psi_n(x) dx \\
&= \frac{2}{L} \int_{-\infty}^{\infty} x^2 \sin^2\left(\frac{n\pi x}{L}\right) dx \\
&= \frac{L^2}{3} \left[1 - \frac{3}{2(n\pi)^2} \right]
\end{aligned} \tag{3.12}$$

In Equation 3.12 we have attached a subscript n to $\langle x^2 \rangle$ because it is clear that the average value depends upon which state (as designated by the quantum number n) is chosen. Obviously as $n \rightarrow \infty$ the value approaches $L^2/3$. Notice that if we evaluate $\langle x^2 \rangle$ for an a -box, the physics would, of course, be the same. The calculation would be a bit more laborious because we would have to do it twice, once for the odd eigenfunctions and once for the even.

Clearly the average value of any function of x can be evaluated in this way. This, however, leaves a gap in our knowledge. How about the kinetic energy, $p^2/2m$? How can we evaluate the expectation value of the square of the momentum if we have only the probability distribution for x ? We will consider this question later.

Consider now the relationship between the quantities Δx and Δp as introduced in the Heisenberg uncertainty principle (see Equation 1.49) and the average values as discussed above. The uncertainty of a quantity Q , call it ΔQ , is defined in quantum physics to be the root mean square of a quantity, also known as the standard deviation:

$$\Delta Q = \sqrt{\langle (\hat{Q} - \langle \hat{Q} \rangle)^2 \rangle} \tag{3.13}$$

Squaring and carrying out the operations, we have

$$\begin{aligned}
(\Delta Q)^2 &= \langle \hat{Q}^2 \rangle - 2 \langle \hat{Q} \rangle \langle \hat{Q} \rangle + \langle \hat{Q} \rangle^2 \\
&= \langle \hat{Q}^2 \rangle - \langle Q \rangle^2
\end{aligned} \tag{3.14}$$

We may as well use Equation 3.14 to check our assertion that the nonzero ground state energy is consistent with the uncertainty principle. Inside the well the TME is all kinetic energy. In an eigenstate the expectation value of the energy is simply the energy eigenvalue (see Problem 1). Therefore, according to Equation 3.7

$$\begin{aligned}
\langle E_1 \rangle &= \frac{\langle \hat{p}_1^2 \rangle}{2m} \\
&= \frac{\pi^2 \hbar^2}{2mL^2}
\end{aligned} \tag{3.15}$$

Because, however, $\langle \hat{p}_1 \rangle = 0$, $\langle \hat{p}_1^2 \rangle = (\Delta \hat{p})^2$. That $\langle \hat{p}_1 \rangle = 0$ is because neither the $+x$ nor the $-x$ direction is favored. A more mathematical proof can be obtained by

inserting the operator equivalent for \hat{p}_x , Equation 2.28, in the computation of $\langle \hat{p}_1 \rangle$. That is,

$$\begin{aligned}
 \langle \hat{p}_x \rangle &= \frac{2}{L} \int_0^L \sin\left(\frac{\pi x}{L}\right) \hat{p}_x \sin\left(\frac{\pi x}{L}\right) dx \\
 &= \frac{2}{L} \int_0^L \sin\left(\frac{\pi x}{L}\right) \left(\frac{\hbar}{i} \frac{d}{dx}\right) \sin\left(\frac{\pi x}{L}\right) dx \\
 &= \frac{2\pi\hbar}{iL^2} \int_0^L \sin\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right) dx \\
 &= \frac{2\hbar}{iL} \int_0^\pi \sin y \cos y dy \\
 &\equiv 0
 \end{aligned} \tag{3.16}$$

Returning to Equation 3.15 we may write for $n = 1$

$$(\Delta \hat{p})^2 = \frac{\pi^2 \hbar^2}{L^2} \tag{3.17}$$

Using Equation 3.12 with $n = 1$ we calculate $(\Delta x)^2$

$$\begin{aligned}
 (\Delta x)^2 &= \langle x^2 \rangle_1 - \langle x \rangle^2 \\
 &= \frac{L^2}{3} \left[1 - \frac{3}{2\pi^2} \right] - \left(\frac{L}{2} \right)^2 \\
 &\approx 0.324 L^2
 \end{aligned} \tag{3.18}$$

Solving Equation 3.18 for L^2 and inserting it in Equation 3.17 we find the uncertainty product to be

$$\Delta \hat{p} \Delta x = 0.18\pi \hbar > \hbar/2 \tag{3.19}$$

Thus, the lowest energy state, the zero-point energy of the infinite square well, is consistent with the uncertainty principle.

Energy Estimates Using the Particle-in-a-Box

Let us examine the expression for the values of the quantized energy, Equation 3.7, more closely because it exhibits features that are characteristic of quantum mechanical energies. The quantity of interest is ΔE , the spacing between adjacent levels. It is

$$\begin{aligned}
 \Delta E &= E_{n+1} - E_n \\
 &= \frac{\pi^2 \hbar^2}{2mL^2} (2n + 1)
 \end{aligned} \tag{3.20}$$

Now, the exact dependence of ΔE on n is unimportant. Rather, we are interested in the dependence of ΔE on the parameters of the well and the particle, in particular, the mass m and dimension of the well L . The $(2n + 1)$ that appears in Equation 3.20 is peculiar to the infinite square well and is not important here. We see that the energy is inversely proportional to both m and the L^2 . Thus, the lighter the particle, the greater will be the spacing between the levels. Additionally, the narrower the box, the greater will be the spacing between levels. The box can be used as a crude model for an atom or a nucleus. We can easily estimate these energies using atomic units. To simulate an atom and estimate the energy difference between the $n = 2$ and $n = 1$ states using a.u. we choose $m = 1$ and $L = 8$ (the atomic *diameter* of the $n = 2$ state) and obtain for $n = 1$

$$\Delta E = \frac{\pi^2}{2 \cdot 64} (5) \approx 0.39 \approx 10.5 \text{ eV} \quad (3.21)$$

The actual difference between the $n = 2$ and $n = 1$ states of the hydrogen atom is 10.4 eV, but this close agreement should not be taken seriously. This correlation is actually too good to be true and, given the crudeness of the estimate involved, must be considered a coincidence (although Mother Nature abhors coincidence). The important point here is not the actual value obtained, but the fact that the energy difference has the correct order of magnitude. That is, our estimate of ΔE yielded $\sim \text{eV}$, which is the correct order of magnitude for the difference between atomic energy levels. On the other hand, if the mass of the confined particle is increased by a factor of 2000 making it comparable with that of a nucleon, but the dimension of the box shrunk by a factor of $\sim 10^5$ making it roughly the size of a nucleus, then the energy level spacing increases by a factor of about 10^7 . In this case $\Delta E \approx 10 \text{ MeV}$ comparable with the energy level spacing of typical nuclei.

3.1.2 The Harmonic Oscillator

While there is a great deal of quantum physics to be learned in the simple particle-in-a-box problem, there are some features of it that can be misleading. This is because the rigid walls, together with the zero potential energy within the box, cause the de Broglie wavelengths of the eigenfunctions within the box to be constant. This constant de Broglie wavelength manifests itself as a purely sinusoidal eigenfunction within the well. Equally important, however, is that we, by virtue of the rigid walls, have forced the eigenfunctions to vanish in the classically forbidden region. It was thus a simple matter to find the boundary condition, that is, to match the wave function at the boundary between the classically forbidden region and the classically allowed region. If, however, the potential energy function is not impenetrable, then the boundary conditions are more challenging.

When the potential energy varies with x we may think of the de Broglie wavelength in the classically allowed region as being variable across the well, changing as the kinetic energy (and therefore the momentum) changes. Because of its

importance in a wide variety of applications we will study the harmonic oscillator in detail. This potential is the basis for all problems in which vibrations occur ranging from molecular and nuclear vibrations as well as vibrations of electromagnetic fields. For now, however, we concentrate on the details of the solution. In this chapter we will solve the problem by brute force. That is, we will solve the TISE equation by a conventional method for solving differential equations. In truth, the labor of solving the differential equation isn't very interesting, but there is some interesting physics near the end of it so it is worthwhile (a bit like medicine). Later we will learn a more elegant and more useful method of solving the TISE with the harmonic oscillator potential energy function. Again, we should bear in mind as we solve the TISE that most of the effort is rather mechanical. The fun begins when we impose the physical conditions that lead to quantization and the curious phenomena predicted by quantum physics.

We begin by writing the potential as

$$\begin{aligned} U(x) &= \frac{1}{2}kx^2 \\ &= \frac{1}{2}m\omega^2x^2 \end{aligned} \quad (3.22)$$

where k is the usual spring constant and m is the mass of the particle that is trapped in this potential well. The usual substitution, $\omega^2 = k/m$, has also been made. Classically, the particle executes simple harmonic motion with the amplitude depending upon the TME of the system. The TME is a characteristic of the system and may be regarded as an initial condition. Thus, we may imagine the TME to be imparted to the oscillator either by an initial displacement (potential energy), an initial velocity (kinetic energy), or a combination of the two. The TME is assumed to remain constant because there are no dissipative forces acting. Figure 3.5 shows a graph of the simple harmonic oscillator potential with a given TME of value E drawn as a horizontal line. For any given value of E there are two limits of the classical motion, the amplitudes. They are here designated $\pm x_c$, and are referred to in this context as the classical turning points. One can imagine the motion of an imaginary particle sliding on the inside of the well that is defined by the potential energy curve. At the

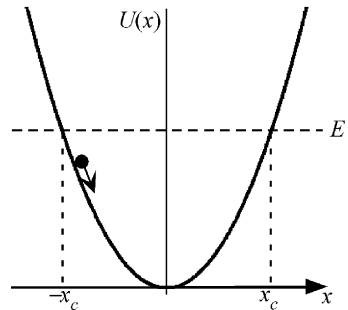


Fig. 3.5 Potential energy function for a harmonic oscillator showing the classical turning points $x = \pm x_c$ for total mechanical energy E of the particle

intersection of the horizontal line E and the potential energy curve this particle has zero kinetic energy and maximum potential energy, $(1/2)m\omega^2x_c^2$. At $x = 0$ the particle has zero potential energy and maximum kinetic energy, also $(1/2)m\omega^2x_c^2$. At values of x between the classical turning points and not at the origin the particle has both potential energy and kinetic energy. The total is always E . Classically E can take on any value as determined by the initial conditions and this value determines the value of x_c .

Before actually solving the TISE with the harmonic oscillator potential let us try to visualize the eigenfunctions based on the considerations of Section 2.9 and our experience with the particle-in-a-box. Although it is always dangerous to project a special case such as the infinite square well to a more general case such as a harmonic oscillator, we risk it because the exercise provides insight. Imagine yourself in the middle of an a -box standing with your palms on each of the rigid walls. You now push the walls so they slant out (symmetrically) and simultaneously cause the bottom of the well to bulge as illustrated in Fig. 3.6. Thus, the derivative of the potential energy curve is no longer infinite at $x = \pm a/2$ and the corners on the infinite well are rounded. The right-hand wall has positive slope and the left-hand wall negative slope. Because the walls no longer have infinite slope, the wave function need not, indeed, *cannot* vanish at the classical turning point. The walls are “soft”! Notice that Fig. 3.6 also illustrates the transition of the ground state eigenfunction from that for an infinite square well to that of a harmonic oscillator.

All three of the potential energy curves in Fig. 3.6 are infinitely deep. It is the infinite slope together with the infinite potential energy of the rigid walls of the infinite square well that causes the wave function to vanish in the classically forbidden region. In view of the Gedanken experiment illustrated in Fig. 3.6, we expect the wave function to be finite at the classical turning points and to penetrate the classically forbidden region. We fully expect the ground state to have the appearance shown in the figure. Of course, it will have no nodes, but it will penetrate the classically forbidden region. In accord with the correspondence principle, we expect the extent of penetration into the forbidden region to decrease with increasing quantum state.

We must now solve the TISE with the harmonic oscillator potential. We have

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2 \right] \psi(x) = E\psi(x) \quad (3.23)$$

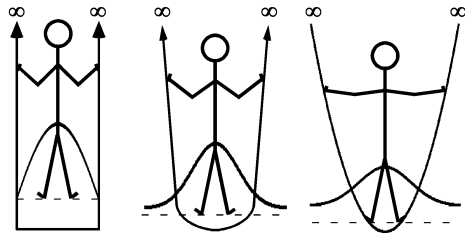


Fig. 3.6 Illustration of the transition of an infinite square well distorted to become a harmonic oscillator potential and the resulting effect on the ground state eigenfunction

which we write in the form

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2}m\omega^2 x^2 \right) \psi(x) = 0 \quad (3.24)$$

It is useful to rescale x and the energy E to eliminate constants. To rescale x we use the Greek letter ξ (xi), and for the energy we use the Greek letter ϵ and write

$$\xi = \alpha x \quad \text{where} \quad \alpha = \sqrt{\frac{m\omega}{\hbar}} \quad (3.25)$$

$$\epsilon = \frac{2E}{\hbar\omega} \quad (3.26)$$

Clearly ϵ is dimensionless, and, because α has dimensions inverse length, ξ is also dimensionless. Making these substitutions we have

$$\frac{d^2\psi(\xi)}{d\xi^2} + (\epsilon - \xi^2) \psi(\xi) = 0 \quad (3.27)$$

and it is now our task to solve this deceptively simple equation.

A tried-and-true method of solving such a differential equation is to attempt a series solution, sometimes referred to as the method of Frobenius. Before using this method we examine the asymptotic solution. At large ξ , the ϵ term in Equation 3.27 is insignificant so, asymptotically, the equation to be solved is

$$\frac{d^2\psi_a(\xi)}{d\xi^2} - \xi^2\psi_a(\xi) = 0 \quad (3.28)$$

where we use the subscript a to designate the asymptotic solution. This equation is very nearly satisfied if we take

$$\psi_a(\xi) = e^{-\xi^2/2} \quad (3.29)$$

since

$$\frac{d\psi_a(\xi)}{d\xi} = -\xi e^{-\xi^2/2} \quad (3.30)$$

and

$$\frac{d^2\psi_a(\xi)}{d\xi^2} = \xi^2 e^{-\xi^2/2} - e^{-\xi^2/2} \quad (3.31)$$

Inserting this into Equation 3.28 we must have $e^{-\xi^2/2} = 0$ which is in keeping with our quest for the asymptotic solution. Therefore, Equation 3.29 is indeed the asymptotic solution.

We can write the most general solution of the TISE, Equation 3.27, as a product of the asymptotic solution, Equation 3.29, and an infinite power series in ξ , call it $H(\xi)$:

$$\psi(\xi) = H(\xi) e^{-\xi^2/2} \quad (3.32)$$

Inserting Equation 3.32 into Equation 3.27, and dividing by $e^{-\xi^2/2}$ (which can never be zero) we have a differential equation for $H(\xi)$:

$$\frac{d^2 H(\xi)}{d\xi^2} - 2\xi \frac{dH(\xi)}{d\xi} + (\epsilon - 1) H(\xi) = 0 \quad (3.33)$$

It is important to remember that, because $\psi(\xi)$ as written in Equation 3.32 must be normalizable. Therefore, the function $H(\xi)$ cannot violate the condition

$$\lim_{\xi \rightarrow \infty} H(\xi) < e^{\xi^2/2} \quad (3.34)$$

Indeed, if this condition is violated the wave function will diverge as $\xi \rightarrow \infty$.

Now we must replace $H(\xi)$ by an infinite series and attempt to solve for that infinite series. It is worth reiterating that, because the harmonic oscillator potential is an even function, the eigenfunctions will have definite parity. Therefore, because $e^{-\xi^2/2}$ is even, the series part of the eigenfunctions, the $H(\xi)$, will alternate between even and odd in successive eigenstates. Of course, the ground state will be even. Nonetheless, we will maintain generality, at least temporarily. Writing $H(\xi)$ as

$$H(\xi) = \sum_{n=0}^{\infty} a_n \xi^n \quad (3.35)$$

substituting this expansion into Equation 3.33 and collecting coefficients of like powers of ξ we have

$$\begin{aligned} \sum_{n=2}^{\infty} n(n-1) a_n \xi^{n-2} + \sum_{n=0}^{\infty} (\epsilon - 1 - 2n) a_n \xi^n &= 0 \\ \sum_{k=0}^{\infty} (k+2)(k+1) a_{k+2} \xi^k + \sum_{n=0}^{\infty} (\epsilon - 1 - 2n) a_n \xi^n &= 0 \end{aligned} \quad (3.36)$$

where we have let $n = k + 2$ in the first summation in Equation 3.36. The indices are dummy indices so we may factor all coefficients of like powers of ξ and change back to a summation over n to obtain

$$\sum_{n=0}^{\infty} [(n+2)(n+1) a_{n+2} + (\epsilon - 1 - 2n) a_n] \xi^n = 0 \quad (3.37)$$

The powers of ξ are linearly independent, so the only way Equation 3.37 can be valid is if the coefficient of each power of ξ vanishes. We thus obtain a relation between a_{n+2} and a_n . Such a relation is called a recursion relation. Notice that, in accord with our knowledge of parity of the eigenfunctions, the recursion relation is not between successive terms. Rather, it skips a term thus assuring definite parity for the solution which it must have because $U(x) = \frac{1}{2}kx^2$ is an even function.

The recursion relation is

$$a_{n+2} = -\frac{(\epsilon - 1 - 2n)}{(n+2)(n+1)}a_n \quad (3.38)$$

According to Equation 3.38, if we know a_n , we may find a_{n+2} from which we may find a_{n+4} and so on. In principle, the problem has been solved. We must provide both a_0 and a_1 to start us off, but that is not surprising since the TISE is, after all, a second-order differential equation and, thus, there will be two constants of integration. Of course, we know from parity considerations that one of these two constants must be zero.

So far our solution has been purely mathematical. Now, here comes the physics. The particle must be bounded by the potential energy. Therefore, we must make sure that our solution is bounded. That is, we must make sure that the eigenfunction as given by Equation 3.32 is normalizable with $H(\xi)$ defined by Equations 3.35 and 3.38. Therefore, we must demand that $H(\xi)$ does not overpower $e^{-\xi^2/2}$ as $\xi \rightarrow \pm\infty$. If it does, then our solution, Equation 3.32, while a solution of the TISE, will not be acceptable on physical grounds. We must therefore investigate the convergence of $H(\xi)$. As discussed in connection with the restriction placed on $H(\xi)$ by Equation 3.34, even if it does converge, it must converge in accord with this relation. From Equation 3.38 the ratio of successive coefficients is

$$\lim_{n \rightarrow \infty} \frac{a_{n+2}}{a_n} = \frac{2}{n} \quad (3.39)$$

we know that $H(\xi)$ does indeed converge. Our concern is *how* it converges.

We must compare the behavior of $H(\xi)$ for large ξ with that of $e^{-\xi^2/2}$ for large ξ . We choose to speculate that $H(\xi) \propto e^{+\beta\xi^2}$ with $\beta > 0$. If this is indeed the case, then the eigenfunction in Equation 3.32 will diverge for $\beta > \frac{1}{2}$. Beginning with the series expansion for e^x (see Equation I.2) we obtain the series expansion for $e^{+\beta\xi^2}$ by letting $x \rightarrow \beta\xi^2$:

$$\begin{aligned} e^{+\beta\xi^2} &= 1 + \frac{(\beta\xi^2)}{1!} + \frac{(\beta\xi^2)^2}{2!} + \frac{(\beta\xi^2)^3}{3!} + \dots \\ &= \sum_{k=0}^{\infty} \frac{\beta^k \xi^{2k}}{k!} \\ &= \sum_{n=0}^{\infty} b_n \xi^n \implies b_n = \frac{\beta^{n/2}}{(n/2)!} \end{aligned} \quad (3.40)$$

The ratio of successive powers of ξ is

$$\begin{aligned}\frac{b_{n+2}}{b_n} &= \frac{\beta^{(n/2)+1}}{[(n/2) + 1]!} \cdot \frac{(n/2)!}{\beta^{n/2}} \\ &= \frac{\beta}{[(n/2) + 1]} = \frac{2\beta}{n + 2}\end{aligned}\quad (3.41)$$

Now we compare the ratio of successive terms in Equation 3.41 with that in Equation 3.39. We have

$$\lim_{n \rightarrow \infty} \frac{b_{n+2}}{b_n} = \frac{2\beta}{n} \quad (3.42)$$

Thus, the asymptotic behavior of the series solution for $H(\xi)$ is identical with the series expansion for $e^{\beta\xi^2}$ with $\beta = 1$ so, in the limit of large ξ , the series that represents $H(\xi)$ behaves as e^{ξ^2} . As it stands $H(\xi)$ will overpower $e^{-\xi^2/2}$ as $\xi \rightarrow \infty$ in Equation 3.32, making it impossible to normalize the eigenfunction. The infinite series that represents $H(\xi)$ is therefore unacceptable! What can we do? The only way to salvage our solution is to force this series to terminate. If $H(\xi)$ is a *finite* series, there is no convergence problem. We impose physics on the solution! That is, we force the eigenfunctions to be normalizable, so that they conform to the known physical situation. These are boundary conditions.

To terminate the series we must force a_n to vanish for some value of n . This, in turn, forces every subsequent term of the same parity to vanish because the recursion relation is between powers of the same parity. We have already deduced that *either* a_0 or a_1 vanishes. To force termination of the infinite series, we set the numerator of Equation 3.38 equal to zero and, substituting for ϵ , Equation 3.26, we have

$$\left(\frac{2E}{\hbar\omega} - 1 - 2n\right) = 0 \quad (3.43)$$

Solving for the energy and attaching a subscript n we have

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega \quad (3.44)$$

This expression for the energy eigenvalues of the simple harmonic oscillator is unusual in the sense that it is one of the few systems in quantum mechanics in which the energy quantum number begins with zero. Notice, however, that there is a built-in “zero point” energy of $\frac{1}{2}\hbar\omega$. That is, even in the lowest state, the total energy is not zero. This means that, even in the lowest energy state the momentum is nonzero and there is an uncertainty associated with it as was the case for the particle-in-a-box. This is characteristic of quantum mechanical systems, for if the TME were zero, the kinetic energy would be zero, the momentum would be zero, and the position would be completely uncertain. This is inconsistent with the system

being in a bound state. If it is bound, we must know *something* about its position because it is localized in space. Therefore, all bound quantum mechanical systems must have a “zero point” energy. In the case of the harmonic oscillator that energy is $\frac{1}{2}\hbar\omega$.

Returning to the eigenfunctions, we can write Equation 3.32 in terms of the quantum number n and a yet-to-be-determined normalization constant N_n . Note the subscript on the normalization constant, indicating that, in general, we expect it to depend upon the quantum state. Our single experience with such constants was for the particle-in-a-box, which is unusual in that the normalization constant is independent of the quantum state.

The harmonic oscillator eigenfunctions are

$$\psi_n(\xi) = N_n H_n(\xi) e^{-\xi^2/2} \quad (3.45)$$

The $H(\xi)$ are finite polynomials that are well known special functions, Hermite polynomials, which are listed in any handbook of mathematical functions. They are solutions to Hermite’s differential equation which need not concern us here. They may be generated by a Rodrigues formula [1]:

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n e^{-\xi^2}}{d\xi^n} \quad (3.46)$$

While Equation 3.46 can be used to generate any of the polynomials, symbolic mathematics computer programs already contain these special functions so it is not necessary to actually generate them. As expected, the index n signifies the parity of the polynomial; it is also the highest power of ξ that occurs in the polynomial. Hermite polynomials are defined in a way such that the coefficient of the highest power of ξ is 2^n . This is illustrated in Table 3.1 which is a listing of the first six Hermite polynomials, more than will be needed for any problem in this book.

Fortunately, there is a great deal known about the Hermite polynomials and their properties. One important property is the integral formula

$$\int_{-\infty}^{\infty} H_n(\xi) H_m(\xi) e^{-\xi^2} d\xi = \sqrt{\pi} 2^n n! \delta_{mn} \quad (3.47)$$

Table 3.1 The first six
Hermite polynomials

$H_0(\xi) = 1$
$H_1(\xi) = 2\xi$
$H_2(\xi) = 4\xi^2 - 2$
$H_3(\xi) = 8\xi^3 - 12\xi$
$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$
$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$

which is an orthogonality relation with the weighting factor $e^{-\xi^2}$. We may take advantage of Equation 3.47 to find the normalization constant N_n for the eigenfunctions as follows:

$$\begin{aligned}
 \int_{-\infty}^{\infty} dx \psi_n^*(x) \psi_n(x) &= 1 \\
 &= \int_{-\infty}^{\infty} (\alpha d\xi) \psi_n^*(\xi) \psi_n(\xi) \\
 &= |N_n|^2 \alpha \int_{-\infty}^{\infty} d\xi H_n(\xi) H_m(\xi) e^{-\xi^2} \\
 &= |N_n|^2 \alpha (\sqrt{\pi} 2^n n!) \quad (3.48)
 \end{aligned}$$

Solving for $|N_n|^2$ and replacing ξ with αx , the normalized harmonic oscillator eigenfunctions are

$$\psi_n(x) = \sqrt{\frac{\alpha}{2^n n!}} \left(\frac{1}{\pi} \right)^{1/4} H_n(\alpha x) e^{-\alpha^2 x^2 / 2} \quad (3.49)$$

From Equation 3.49, it is clear that the harmonic oscillator eigenfunctions are simple Gaussian functions, multiplied by the appropriate Hermite polynomial. Because $H_0(\xi) = 1$, the ground state eigenfunction and probability density are simple Gaussian functions.

There are a number of other relations involving the Hermite polynomials that are helpful for determining the properties of the harmonic oscillator. Some of the most useful of these relations are compiled in Table 3.2 together with the few that were listed above.

Table 3.2 Some properties of the Hermite polynomials

Generating function	$e^{2\mu\xi - \mu^2} = \sum_{n=0}^{\infty} \frac{H_n(\xi) \mu^n}{n!}$
Rodrigues formula	$H(\xi) = (-)^n e^{\xi^2} \frac{d^n e^{-\xi^2}}{d\xi^n}$
Orthogonality	$\int_{-\infty}^{\infty} d\xi H_n(\xi) H_m(\xi) e^{-\xi^2} = \sqrt{\pi} 2^n n! \delta_{mn}$
Parity	$H_n(\xi) = (-)^n H_n(-\xi)$ $H_{2n-1}(0) = 0$
Special result	$H_{2n}(0) = (-)^n 2^n \cdot 1 \cdot 3 \cdot 5 \cdots (2n-1)$
Recurrence relation	$2\xi H_n(\xi) = H_{n+1}(\xi) + 2n H_{n-1}(\xi)$
Recurrence relation	$\frac{dH_n(\xi)}{dx} = 2n H_{n-1}(\xi)$

Table 3.3 The first four complete harmonic oscillator eigenfunctions

$\psi_0(x) = \sqrt{\frac{\alpha}{\sqrt{\pi}}} e^{-\alpha^2 x^2/2}$
$\psi_1(x) = \sqrt{\frac{\alpha}{2\sqrt{\pi}}} 2(\alpha x) e^{-\alpha^2 x^2/2}$
$\psi_2(x) = \sqrt{\frac{\alpha}{2\sqrt{\pi}}} [2(\alpha x)^2 - 1] e^{-\alpha^2 x^2/2}$
$\psi_3(x) = \sqrt{\frac{\alpha}{3\sqrt{\pi}}} [2(\alpha x)^3 - 3(\alpha x)] e^{-\alpha^2 x^2/2}$

For convenience, the first four normalized eigenfunctions are listed in Table 3.3 in terms of x .

It is worthwhile to examine these eigenfunctions in some detail. Figure 3.7 is a graph of the first five of the wave functions superimposed on the harmonic oscillator potential energy.

The zero of these functions is taken to be the energy eigenvalue corresponding to the eigenfunction as was done for the particle-in-a-box in Fig. 3.2. The first, almost startling characteristic of these wave functions is that they actually penetrate the classically forbidden region. This means that the probability density $|\psi(x)|^2$ also penetrates the classically forbidden region, a region in which the particle will have a negative kinetic energy. True! It can happen. Why? The uncertainty principle. yBecause of the uncertainty in position and momentum, the particle can indeed find itself in the classically forbidden region where it will have a negative kinetic energy. It cannot be observed to be there because a measurement of its position would alter the momentum (kinetic energy) and force the particle into the classically allowed region. Recall that the wave functions for the particle-in-a-box do not penetrate the classically forbidden region because, in that case, it was really classically forbidden because of the infinite potential walls.

Although it is not obvious from the five eigenfunctions plotted in Fig. 3.7, as expected from the correspondence principle, penetration of the classically forbidden region decreases as n increases. This can be clarified by examining the probability

Fig. 3.7 The first five eigenfunctions for the harmonic oscillator superimposed on the harmonic oscillator potential energy plotted with their zeros at the corresponding eigenvalues

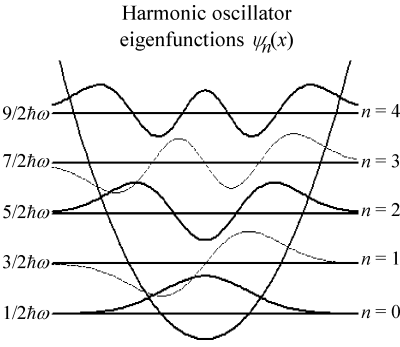
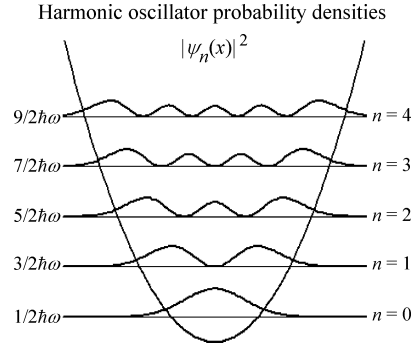


Fig. 3.8 Probability densities of the first five eigenstates of the harmonic oscillator superimposed on the harmonic oscillator potential energy plotted with their zeros at the corresponding eigenvalues



densities for the same states shown in Fig. 3.7. These probability densities are shown in Fig. 3.8. Although it is difficult to see at these low quantum numbers, it is indeed true that the fraction of probability density that occupies the classically forbidden region decreases with increasing n as required by the uncertainty principle.

It is instructive to compare the probability density with that expected for a classical oscillator. Calculation of the classical probability density, $P_{cl}(x)$, is based on time spent in an interval Δx . It is the fraction of a period T that the particle spends in the interval. The time spent in the interval is just Δx divided by the velocity which is a function of x . The classical equation of motion is

$$x = x_0 \sin \omega t \quad (3.50)$$

where x_0 is the amplitude of the motion. Differentiating to find the velocity $dx/dt = \dot{x} = \omega x_0 \cos \omega t$ and eliminating the time we find that

$$\dot{x} = \omega \sqrt{x_0^2 - x^2}$$

Classically, the probability that the particle will be found in the interval Δx is the probability density $P_{cl}(x)$ times Δx . We have then

$$P_{cl}(x) \Delta x = \left(\frac{2\Delta x}{\dot{x}} \right) \cdot \left(\frac{1}{T} \right) \quad (3.51)$$

$$= \frac{\Delta x}{\pi \sqrt{x_0^2 - x^2}} \quad (3.52)$$

where we have used the relation between frequency and period, $T = 2\pi/\omega$. The factor of 2 in Equation 3.51 arises because the particle occupies Δx “coming” and

“going.” Solving for P_{cl} and using the relation between the TME energy E and the amplitude $x_0 = \sqrt{2E/m\omega^2}$ we have

$$P_{cl}(x) = \frac{1}{\pi \sqrt{\frac{2E}{m\omega^2} - x^2}} \quad (3.53)$$

Equation 3.53 gives the probability density for a classical oscillator of energy E . It has the expected form because the particle spends most of its time at the turning points where it is instantaneously stopped. It spends the least time in the center where the kinetic energy, and hence the speed, is the greatest. Notice that while the probability *density* $P_{cl}(x)$ is infinite at the turning points, the probability of finding the particle in a region dx is $P_{cl}(x)dx$ and is always less than unity.

Figure 3.9 is a graph of the quantal and classical probability densities for the ground state of the harmonic oscillator. $P_{cl}(x)$ is the curve marked classical with $E = (1/2)\hbar\omega$. The Gaussian curve labeled quantum is $|\psi_0(x)|^2$ for the harmonic oscillator. It is clear that the quantum mechanical and classical results are antithetical. Moreover, the quantum mechanical result is counterintuitive because the particle is expected to spend the least time where it is moving the fastest, at $x = 0$.

Disturbing as the discrepancy between the two curves in Fig. 3.9 is, the comparison is a bit of a ruse because, while the Gaussian curve does indeed represent the ground state of the *quantum mechanical* oscillator, the classical curve does not represent the ground state of the *classical* oscillator. The two curves in Fig. 3.9 represent the probability distributions for the same oscillator *energies*, but not the same oscillator *states*. Indeed, the ground state of the classical oscillator is patently uninteresting, $E = 0$, $x = 0$, and $v = 0$. In short, in the classical ground state, the particle is at rest at the origin. Nothing is going on. There is no quantum mechanical analog to this state because the classical probability density is a spike at $x = 0$ and zero otherwise. (We will discuss this very useful function in more detail in Chapter 4.) It is clear that such a probability distribution is a violation of the uncertainty principle because both $\Delta x = 0$ and $\Delta p = 0$. As discussed above, such a situation is quantum mechanically forbidden. Thus, although comparison of the probability

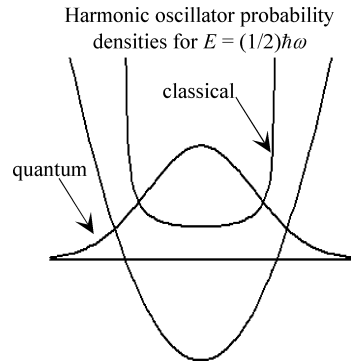
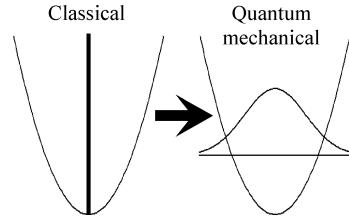


Fig. 3.9 Quantum mechanical and classical probability densities for a harmonic oscillator having energy $\frac{1}{2}\hbar\omega$ superimposed on the $U(x) = (1/2)kx^2$ potential energy curve

Fig. 3.10 Illustration of the transition of the probability distribution of the ground state of the classical harmonic oscillator into the ground state of the quantum mechanical harmonic oscillator



densities in Fig. 3.9 is often used to illustrate the differences between the quantum mechanical and classical solutions, a more appropriate comparison would be that of the Gaussian curve with a spike at the origin representing the probability density of the classical ground state.

Figure 3.10 is an illustration of the evolution of the classical ground state into the quantum mechanical ground state. The solid line at the center of the left-hand potential energy curve with its base at the minimum of the curve is meant to illustrate the parameters of the classical ground state, $E = 0$ and $x = 0$. If one imagines the conversion of this classical system into its quantum mechanical analog, the energy must be raised because Δp cannot be zero. Note that Δp cannot be zero because this is a *bound* state. This means that the particle is confined to some region of space and thus Δx cannot be infinity, implying that $\Delta p \neq 0$. This produces the zero point energy discussed above and the concomitant Δx which, in the case of the oscillator ground state, manifests itself as a Gaussian distribution.

While a proper comparison of probability distributions may indeed be that shown in Fig. 3.10, the probability distributions in Fig. 3.9 are nonetheless conflicting. In particular, the quantum mechanical probability distribution remains counterintuitive. As with many aspects of quantum physics, the best way to rationalize such instances is to appeal to the correspondence principle. As the quantum number increases, we expect the quantum and classical results to coincide. Figure 3.11 is a graph of the quantal and classical probability densities as in Fig. 3.9, but in this case for $n = 10$.

Fig. 3.11 Quantum mechanical and classical probability densities for the $n = 10$ state of the harmonic oscillator superimposed on the harmonic oscillator potential energy curve, $U(x) = (1/2)kx^2$. Because the potential energy curve is so steep in this region it essentially defines the classically allowed and forbidden regions of space

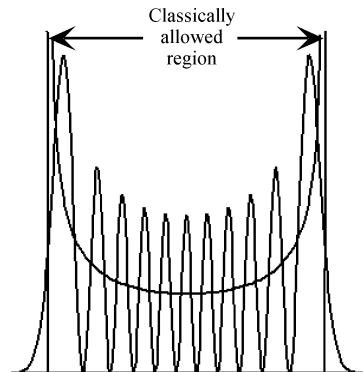
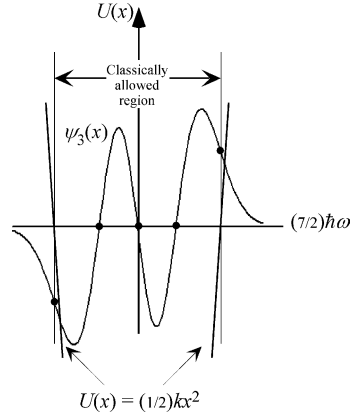


Fig. 3.12 Harmonic oscillator eigenfunction for the $n = 3$ state on an expanded scale to show the penetration of the particle into the classically forbidden region



Even though the state displayed in Fig. 3.11 is not a truly high quantum number, it can be seen that, except for the oscillations in the quantum mechanical probability density, they are beginning to approach each other. In accord with the correspondence principle, as $n \rightarrow \infty$ we fully expect the two to match.

Before leaving the discussion of the nature of the harmonic oscillator eigenfunctions, let us examine one of them, $\psi_3(x)$, in more detail. In particular, we wish to see how the harmonic oscillator eigenfunctions conform with the general characteristics of eigenfunctions laid out at the beginning of this chapter. The eigenfunctions for the particle-in-a-box do indeed conform, but, as noted previously, the infinite step in the potential energy and zero potential energy in the box introduced features and peculiarities in the wave function that are not present when the potential energy is a smooth (more realistic) function. Figure 3.12 is a graph of $\psi_3(x)$ on an expanded scale compared with that of the previous figures.

Several of the aforementioned characteristics of wave functions are apparent. First, it is clear that in the classically allowed region, the region between the portions of the potential energy curve, the wave function curves *toward* the abscissa. For example, if $\psi_3(x) > 0$, then $d^2\psi_3(x)/dx^2 < 0$. Whether positive or negative $\psi_3(x)$ always curves toward the axis. On the other hand, in the classically forbidden region the wave function curves away from the abscissa, characteristic of an exponentially decaying probability density. We also see that the $\psi_3(x)$ has three nodes, exactly what we expect since, because of the quantum numbering peculiar to the harmonic oscillator, the quantum number also signifies the number of nodes.

3.2 Penetration of the Classically Forbidden Region

Let us consider in more detail the question of the nonzero probability density for a bound state in the classically forbidden region. To do this we examine the ground state of the harmonic oscillator. In the classically forbidden region, the kinetic

energy is negative so the momentum (speed) is imaginary. This is absurd, so a measurement of the momentum cannot be made. Therefore, a measurement of the position while the particle is in the classically forbidden region cannot be made either. Why not? Of course, the answer is the uncertainty principle. What happens is that the measurement of x adds so much energy to the particle that it makes the kinetic energy positive again. That is, the measurement drives the particle back into the classically allowed region. Another way of saying this is to say that the uncertainty in position, Δx , is large compared with the penetration distance into the classically forbidden region. Therefore, the measurement of x causes the particle to go back where it belongs into the classically allowed region.

The ground state eigenfunction of the harmonic oscillator is given by

$$\psi_0(x) = \sqrt{\frac{\alpha}{\sqrt{\pi}}} e^{-\alpha^2 x^2/2} \quad (3.54)$$

so the probability density is

$$\begin{aligned} P_0(x) &= \psi^*(x) \psi_0(x) \\ &= \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 x^2} \end{aligned} \quad (3.55)$$

We wish to compare the degree of penetration with the uncertainty in position of the ground state Δx_0 which is (see Problem 9)

$$\begin{aligned} (\Delta x_0)^2 &\equiv \langle x^2 \rangle - \langle x \rangle^2 \\ &= \frac{1}{2\alpha^2} \end{aligned} \quad (3.56)$$

To make the penetration definite, we arbitrarily define the penetration depth δ as that depth into the forbidden region when $P_0(x)$ has decreased by one e -fold of the value it had when it entered the forbidden region at one of the classical turning points. For the ground state, these turning points occur at

$$x_{c_0} = x_c = \pm \frac{1}{\alpha} \quad (3.57)$$

so that

$$\begin{aligned} P_0(x_c + \delta) &= \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2(x_c + \delta)^2} \\ &= \frac{\alpha}{\sqrt{\pi}} \exp[-(1 + \alpha\delta)^2] \end{aligned} \quad (3.58)$$

We may, however, compute $P_0(x_c + \delta)$ from the definition of δ :

$$\begin{aligned}
 P_0(x_c + \delta) &= \frac{1}{e} P_0(x_c) \\
 &= \frac{1}{e} \left(\frac{\alpha}{\sqrt{\pi}} e^{-1} \right) \\
 &= \frac{\alpha}{\sqrt{\pi}} e^{-2}
 \end{aligned} \tag{3.59}$$

Comparing Equation 3.59 with Equation 3.58 we see that

$$(1 + \alpha\delta) = \sqrt{2} \tag{3.60}$$

from which we find that

$$\begin{aligned}
 \delta &= \frac{1}{\alpha} (\sqrt{2} - 1) \\
 &\approx \frac{0.414}{\alpha}
 \end{aligned} \tag{3.61}$$

We may express α in terms of Δx_0 from Equation 3.56:

$$\frac{1}{\alpha} = \sqrt{2} \Delta x_0 \tag{3.62}$$

which permits us to express δ in terms of Δx_0 . We have

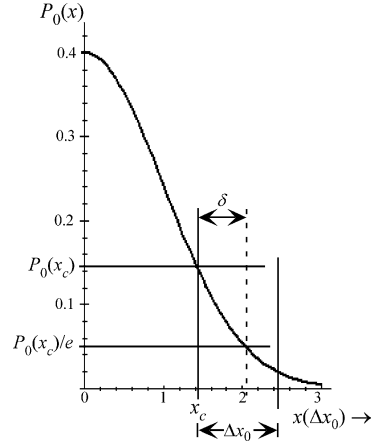
$$\begin{aligned}
 \delta &= \sqrt{2} \Delta x_0 (\sqrt{2} - 1) \\
 &\approx 0.59 \Delta x_0
 \end{aligned} \tag{3.63}$$

which shows that, indeed, $\delta < \Delta x_0$.

Figure 3.13 shows a plot of $P_0(x)$ for positive values of x . The units on the abscissa are Δx_0 . Note that the uncertainty in x extends well into that portion of the classically forbidden region for which there is appreciable probability of finding the particle. This suggests that a measurement of the position in this region will force the momentum (and thus the energy) uncertainty beyond the negative value of the kinetic energy that must accompany the particle's incursion into the forbidden region.

To make a measurement that detects the particle to be in the forbidden region we must make it to within an uncertainty of less than $\sim \delta$ (or some other arbitrary, but reasonable penetration depth). According to Equation 3.63, δ is about 3/5 of the uncertainty in position. This is verified graphically in Fig. 3.13. We can argue that to successfully make such a measurement we must have an uncertainty smaller

Fig. 3.13 The probability density for the ground state of the harmonic oscillator (positive x). The units of the abscissa are Δx_0 , the uncertainty in position of the ground state as calculated from $(\Delta x_0)^2 = \langle x^2 \rangle - \langle x \rangle^2$. Also shown are the classical turning point x_c , $P(x_c)$, and $e^{-1}P(x_c)$



than the penetration depth, but, since this is smaller than the inherent uncertainty in a measurement of position, such a measurement is quite impossible. We may use the uncertainty principle to see this mathematically. For the ground state of the harmonic oscillator

$$\Delta x_0 \Delta p_0 = \frac{\hbar}{2} \quad (3.64)$$

so we have

$$\Delta p_0 = \frac{\hbar}{2} \cdot \frac{1}{\Delta x_0} = \frac{\hbar}{2} \cdot \sqrt{2}\alpha = \frac{1}{\sqrt{2}} \sqrt{\frac{m\omega}{\hbar}} \cdot \hbar = \sqrt{2m\hbar\omega} \quad (3.65)$$

The uncertainty in the kinetic energy ΔT that is introduced by the measurement of position is thus given by

$$\begin{aligned} \Delta T &= \frac{(\Delta p)^2}{2m} \\ &= \frac{1}{2m} (2m\hbar\omega) \\ &= \hbar\omega \end{aligned} \quad (3.66)$$

But, this uncertainty in the kinetic energy is twice the maximum kinetic energy that the particle can ever have in the ground state, again showing that you just can't beat the uncertainty principle.

3.2.1 The Infinite Square Well with a Rectangular Barrier Inside

Consider an infinite square well, an a -box. We choose an a -box to take advantage of the symmetry. Inside the well, symmetrically placed, is a finite rectangular barrier of height U_0 , as shown in Fig. 3.14. The width of the barrier is αa where $0 < \alpha < 1$.

We wish to analyze a bound state eigenfunction corresponding to an eigenvalue $E < U_0$. This restriction on the eigenvalue assures us that if the particle's position is measured and found to be on one side of the barrier and later found to be on the other side of it, penetration of the forbidden region must have occurred. The algebra required to solve this problem is a bit more tedious than that in our previous problems, but it is straightforward. It simplifies matters somewhat that we are only interested in the form of the eigenfunction, not the precise analytic function. Moreover, we are not even interested in the exact eigenvalue, but we may as well see how these eigenvalues can be obtained because similar techniques will be employed later.

Because there are discontinuities, we must solve the TISE in each region of space and then match the boundary conditions. There are five such regions, but the ones to the left and right of $x = -(a/2)$ and $x = +(a/2)$ are trivial because the wave function vanishes due to the infinite potential energy. We therefore label the three regions with Roman numerals as shown in Fig. 3.14. The TISE inside the box is then

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2 \psi_I(x)}{dx^2} &= E \psi_I(x) \\ -\frac{\hbar^2}{2m} \frac{d^2 \psi_{II}(x)}{dx^2} + U_0 \psi_{II}(x) &= E \psi_{II}(x) \\ -\frac{\hbar^2}{2m} \frac{d^2 \psi_{III}(x)}{dx^2} &= E \psi_{III}(x) \end{aligned} \quad (3.67)$$

The solutions to these differential equations may be written as

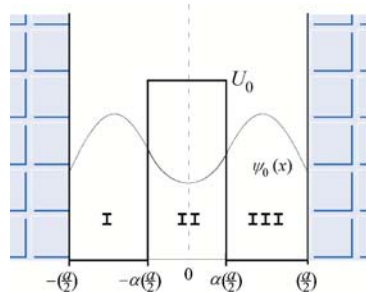


Fig. 3.14 An infinite square well, an a -box, with a rectangular bump of height U_0 in the middle as shown. Also shown is a sketch of the ground state eigenfunction for this well

$$\begin{aligned}
\psi_I(x) &= A \sin(kx + B) \quad \text{where} \quad k^2 = \frac{2mE}{\hbar^2} \\
\psi_{II}(x) &= C'e^{\kappa x} + D'e^{-\kappa x} \quad \text{where} \quad \kappa^2 = \frac{2m(U_0 - E)}{\hbar^2} \\
\psi_{III}(x) &= F \sin(kx + G)
\end{aligned} \tag{3.68}$$

where all of the capital letters, except the energy eigenvalue E , are constants of integration. The primes are inserted for later convenience. Now $U(x)$ is an even function so $C' = \pm D'$. Therefore, we may write $\psi_{II}(x)$ as an even function $\psi_{II}^e(x)$ or an odd function $\psi_{II}^o(x)$. That is,

$$\begin{aligned}
\psi_{II}^e(x) &= C \cosh(\kappa x) \\
\psi_{II}^o(x) &= C \sinh(\kappa x)
\end{aligned} \tag{3.69}$$

Applying the boundary conditions at $x = -a/2$ we have

$$\begin{aligned}
\psi^e &: A \sin \left[-k\alpha \left(\frac{a}{2} \right) + B \right] \\
&= C \cosh \left[-\kappa\alpha \left(\frac{a}{2} \right) \right] = C \cosh \left[\kappa\alpha \left(\frac{a}{2} \right) \right] \\
\psi^o &: A \sin \left[-k\alpha \left(\frac{a}{2} \right) + B \right] \\
&= D \sinh \left[-\kappa\alpha \left(\frac{a}{2} \right) \right] = -C \sinh \left[\kappa\alpha \left(\frac{a}{2} \right) \right] \\
\frac{d\psi^e}{dx} &: Ak \cos \left[-k\alpha \left(\frac{a}{2} \right) + B \right] \\
&= C\kappa \sinh \left[-\kappa\alpha \left(\frac{a}{2} \right) \right] = -C\kappa \sinh \left[\kappa\alpha \left(\frac{a}{2} \right) \right] \\
\frac{d\psi^o}{dx} &: Ak \cos \left[-k\alpha \left(\frac{a}{2} \right) + B \right] \\
&= D\kappa \cosh \left[-\kappa\alpha \left(\frac{a}{2} \right) \right] = D\kappa \cosh \kappa\alpha \left(\frac{a}{2} \right)
\end{aligned} \tag{3.70}$$

The derivatives of the wave function must be continuous at $x = \pm a/2$ despite the discontinuity in the potential because the discontinuity is finite. The wave function itself must be continuous everywhere. We can eliminate the constants that are not part of the arguments of the trigonometric and hyperbolic functions by dividing these boundary conditions, even and odd, to obtain:

$$k \cot \left(-k\alpha \frac{a}{2} + B \right) = -\kappa \tanh \left(\kappa\alpha \frac{a}{2} \right) \quad \text{even} \tag{3.71}$$

and

$$k \cot \left(-k\alpha \frac{a}{2} + B \right) = -\kappa \coth \left(\kappa\alpha \frac{a}{2} \right) \quad \text{odd} \tag{3.72}$$

Employing the same procedure at the other finite discontinuity, $x = \alpha (a/2)$ we have

$$k \cot \left(k\alpha \frac{a}{2} + F \right) = -\kappa \tanh \left(\kappa \alpha \frac{a}{2} \right) \quad \text{even} \quad (3.73)$$

and

$$k \cot \left(k\alpha \frac{a}{2} + F \right) = -\kappa \coth \left(\kappa \alpha \frac{a}{2} \right) \quad \text{odd} \quad (3.74)$$

Now, the equations at $x = +\alpha (a/2)$ must be consistent with those at $x = -\alpha (a/2)$. For example, the even function, Equation 3.71, can be rewritten as

$$\begin{aligned} -k \cot \left[- \left(k\alpha \frac{a}{2} - B \right) \right] &= -\kappa \tanh \left(\kappa \alpha \frac{a}{2} \right) \\ k \cot \left(k\alpha \frac{a}{2} - B \right) &= -\kappa \tanh \left(\kappa \alpha \frac{a}{2} \right) \end{aligned} \quad (3.75)$$

Comparing the two expressions for $-\kappa \tanh \left(\kappa \alpha \frac{a}{2} \right)$ in Equations 3.75 and 3.73 it is clear that $F = -B$. Applying the same treatment to the odd transcendental equations verifies this relation.

We may eliminate the remaining constants by applying the boundary conditions at $x = \pm a/2$. We have

$$\psi_I \left(-\frac{a}{2} \right) = 0 \quad \Rightarrow \quad k \left(-\frac{a}{2} \right) + B = 2n\pi \quad (3.76)$$

and

$$\psi_I \left(\frac{a}{2} \right) = 0 \quad \Rightarrow \quad k \left(\frac{a}{2} \right) - B = 2m\pi \quad (3.77)$$

Subtracting leads to

$$-ka + 2B = 2(n - m)\pi \quad \Rightarrow \quad B = k\frac{a}{2} + \frac{(n - m)}{2}\pi \quad (3.78)$$

We can, however, drop the term in π because the cotangent is periodic in π , so we have for the transcendental equations that will determine the energy eigenvalues:

$$\text{even:} \quad -k \cot \left[k \left(\frac{a}{2} \right) (1 - \alpha) \right] = \kappa \tanh \left[\kappa \alpha \left(\frac{a}{2} \right) \right] \quad (3.79)$$

$$\text{odd:} \quad -k \cot \left[k \left(\frac{a}{2} \right) (1 - \alpha) \right] = \kappa \coth \left[\kappa \alpha \left(\frac{a}{2} \right) \right] \quad (3.80)$$

At this point it is worthwhile to examine our solution to see if it has a chance of being correct. That is, does it reduce to a known result if we simplify? An obvious limit is that for which $\alpha \rightarrow 0$, in which case we should retrieve the result for an a -box. For the even eigenvalues (which correspond to odd quantum numbers) we have

$$\alpha = 0: \quad -k \cot \left[k \left(\frac{a}{2} \right) \right] = 0 \quad \Rightarrow \quad k \left(\frac{a}{2} \right) = n \frac{\pi}{2} \quad (3.81)$$

Substituting for k yields the correct result for the particle-in-a-box. While this limit does not *prove* that our results are correct, it does provide us some comfort.

Now, let us briefly review. Our goal here is to verify that the wave function sketched in Fig. 3.14 does indeed represent a possible eigenstate of this particular $U(x)$. If it does, then the probability density $|\psi(x)|^2$ will have significant values on each side of the barrier and there will be substantial probability inside the barrier. As discussed previously, a measurement of position cannot reveal the particle's presence inside the barrier (classically forbidden region), but if measurements of position yield values on each side of the barrier we have no choice than to believe that the particle was actually inside the classically forbidden region. The mathematics used in the solution above assumed that the energy eigenvalue was lower than U_0 , the height of the barrier. That is how the real exponential and the subsequent hyperbolic functions were obtained. Indeed, Fig. 3.14 was sketched under this assumption. It is, however, to be determined if such a solution can exist. We therefore wish to determine whether there is some combination of values of α and U_0 that will yield an energy eigenvalue $E < U_0$. If so, then the particle had to have traversed the classically forbidden region. We are only interested in one value, so we examine the ground state for which the even transcendental equation, Equation 3.71, is appropriate.

We begin by defining two new variables

$$\eta = ka \quad ; \quad \varsigma = \kappa a \quad (3.82)$$

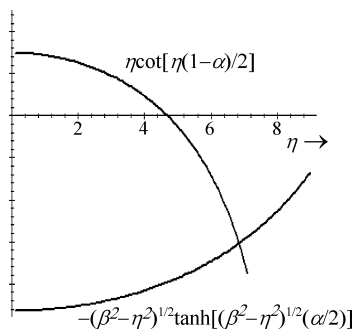
In view of the definitions of k and κ we find that

$$\begin{aligned} \eta^2 + \varsigma^2 &= \frac{2mU_0}{\hbar^2} a^2 \\ &\equiv \beta^2 \end{aligned} \quad (3.83)$$

where $\beta^2 = 2mU_0a^2/\hbar^2$ and is a manifestly positive number. Notice that β^2 is an intrinsic property of this system [mass of the particle m and the potential energy function $U(x)$] in that it contains no variables. We multiply both sides of Equation 3.71 by a and insert η and ς . We then eliminate ς using Equation 3.83 and obtain a new transcendental equation

$$\eta \cot \left[\eta \frac{(1 - \alpha)}{2} \right] = -\sqrt{\beta^2 - \eta^2} \tanh \left[\sqrt{\beta^2 - \eta^2} \left(\frac{\alpha}{2} \right) \right] \quad (3.84)$$

Fig. 3.15 Graph of the two functions that make up the left- and right-hand sides of Equation 3.84 showing an intersection at approximately $\eta = 6.8$



Although this is a formidable-looking equation, we only require a single solution subject to the restriction $\eta^2 < \beta^2$. This restriction is necessary to keep the expression under the radical real. It also assures an eigenvalue $E < U_0$. The method of solution is to pick values of α and β and then plot the left- and the right-hand sides of Equation 3.84 as separate functions on the same graph. Their intersection determines the common value of η and, thus, the solutions. Choosing $\alpha = 1/3$, which is roughly the width of the barrier shown in Fig. 3.14, and $\beta = 10$, the graph is as shown in Fig. 3.15. Examination of this graph reveals an intersection at roughly $\eta = 6.8$ which meets the condition for an eigenvalue to be lower in value than the height of the barrier. Therefore, we conclude that, indeed, the particle must have penetrated the classically forbidden region and tunneled through the barrier.

3.3 Retrospective

By virtue of their simplicity, two of the most important problems in quantum physics are the particle-in-a-box and the harmonic oscillator. They are of pedagogical importance, but their value transcends pedagogy. They are often used as a basis for estimating the properties of more complicated systems.

The emphasis placed on obtaining the eigenstates in this chapter might lead the student to infer that quantum mechanical systems “live” in eigenstates. This is not true! In general they do not. Rather, quantum mechanical systems may be described as existing in a superposition of these states since, as will be seen in a later chapter, the eigenstates constitute a complete set, a basis set, upon which any arbitrary wave function may be expanded. These superpositions are possible only because the Schrödinger equation is a linear differential equation, so that linear combinations of solutions are also solutions.

3.4 References

1. G. B. Arfken and H. J. Weber, *Mathematical Methods for Physicists* (Harcourt, New York, 2001).

Problems

1. Show that in the n th eigenstate of any potential energy function that supports bound states, the expectation value of the energy is the eigenvalue E_n .
2. Normalize the eigenfunctions for a particle in an L -box. That is, find A in Equation 3.6.
3. The zero point energy of a particle-in-a-box is the ground state energy. If an electron is confined to the box, what must be the length of the box such that the zero point energy equals the rest energy of the electron? Express your answer in terms of the Compton wavelength of the electron $\lambda_c = 2\pi\hbar/m_e c \approx 2.43 \times 10^{-12}\text{m}$.
4. Show that the expression for the energy eigenvalues for an L -box, Equation 3.7, can be obtained by fitting de Broglie waves into the box.
5. Show that $\langle \hat{p}_x^2 \rangle$ for any state of a particle-in-a-box is $(n^2\pi^2\hbar^2/L^2)$, consistent with Equation 3.17.
6. The normalized wave function for a particle in an L -box at $t = 0$ is given by

$$\Psi(x, 0) = \frac{1}{\sqrt{3}}\psi_1(x) + \sqrt{\frac{2}{3}}\psi_2(x)$$

where $\psi_1(x)$ and $\psi_2(x)$ represent the ground and first excited state eigenfunctions.

- (a) What is the expectation value of the energy at $t = 0$?
 - (b) What is the wave function $\Psi(x, t)$ for any time $t > 0$?
7. The normalized wave function for a particle in an L -box at $t = 0$ is given by

$$\Psi(x, 0) = \sqrt{\frac{8}{L}} \sin\left(\frac{2\pi x}{L}\right) \cos\left(\frac{2\pi x}{L}\right)$$

What is the expectation value of the energy at $t = 0$?

8. For an L -box:
 - (a) Calculate the classical probability density
 - (b) Find the classical values of $\langle x \rangle_{\text{classical}}$ and $\langle x^2 \rangle_{\text{classical}}$ and show that the quantum mechanical values of $\langle x \rangle$ and $\langle x^2 \rangle$ approach the classical values as the quantum number $n \rightarrow \infty$.
9. Calculate Δx_0 , the uncertainty in position for the ground state of the harmonic oscillator.
10. For an L -box:
 - (a) Use symmetry considerations to determine the expectation value of the momentum \hat{p} .
 - (b) Calculate the expectation value of the square of the momentum \hat{p}^2 using two methods. First, use the form of the momentum operator in coordinate

space given in Equation 2.28 as in Problem 5. Second, notice that the square of the momentum is proportional to the kinetic energy operator.

11. Find Δx , the uncertainty in x for an arbitrary eigenstate of an L -box, and show that it is always less than the dimension of the box.
12. A particle is in the ground state of an L -box. At $t = 0$ the wall at $x = L$ is suddenly moved to $2L$.
 - (a) If an energy measurement is made after the wall is moved, what is the probability of measuring the energy to be that of the ground state of the new box?
 - (b) What is the probability of measuring the energy to be that of the first excited state of the new box?
13. The wave function at $t = 0$ for a particle of mass m trapped in an a -box is given by

$$\Psi(x, 0) = Kx \left(1 - \frac{2x}{a}\right) \left(1 + \frac{2x}{a}\right) \quad -\frac{a}{2} < x < \frac{a}{2}$$

$$= 0 \quad \text{otherwise}$$

- (a) Normalize $\Psi(x, 0)$.
 - (b) Find the probability that a measurement of the energy $t = 0$ will produce the n th energy eigenfunction. Rather than work out the required integrals, it is suggested that a mathematical handbook be consulted to obtain the Fourier series for $\Psi(x, 0)$. What is the probability that the energy of the ground state will be measured? The first excited state? Can you rationalize the result?
 - (c) Check your answer to part b by summing over all states.
 - (d) Find the expectation value of the energy $\langle E \rangle$ by direct integration and by using the probabilities found in part b. Put the answer in terms of E_2 the energy eigenvalue of the first excited state and discuss the answer. Verify that the value of $\langle E \rangle$ is the same using both methods.
14. A particle is in the ground state of an a -box. At $t = 0$ both walls are suddenly moved symmetrically to $-a$ and a .
 - (a) If an energy measurement is made after the walls are moved, what is the probability of measuring the energy to be that of the ground state of the new box?
 - (b) What is the probability of measuring the energy to be that of the first excited state of the new box?
 - (c) Why are the answers different from those in Problem 12?
15. Show that for the harmonic oscillator $\alpha = \sqrt{m\omega/\hbar}$ has dimensions inverse length.

16. Find the uncertainties Δx and Δp , and therefore the uncertainty product, for the ground state of the harmonic oscillator.
17. Calculate the probability that a particle under the influence of a harmonic oscillator potential will be found in the classically forbidden region for the lowest two states to see the trend toward the correspondence principle. You will need to use the error function defined as:

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$$

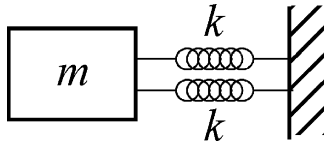
Two values that will be essential are: $\operatorname{erf}(1) = 0.843$ and $\operatorname{erf}(\sqrt{3}) = 0.986$.

18. Verify the uncertainty relation in the classically allowed region of a harmonic oscillator in a way that is similar to that employed for the classically forbidden region. Take the Δx to be one-half of the allowed region.
19. Find the eigenvalues and eigenfunctions for the “half-harmonic oscillator,” that is, a potential energy function.

$$\begin{aligned} U(x) &= \frac{1}{2} m \omega^2 x^2 & x > 0 \\ &= \infty & x \leq 0 \end{aligned}$$

No calculations are required.

20. Consider a particle in one-dimension that is initially coupled to two identical springs, each with constant k , in parallel as shown.



Spring configuration for Problem 20

- (a) What are the energy eigenvalues of the particle when it is connected to both springs? What is the ground state energy eigenfunction?
 - (b) One spring is cut so the particle is bound to a single spring. If the particle was in the ground state of the two-spring system before the cut, what is the probability that it will be in the ground state of the one-spring system after the cut?
 - (c) What will be the probability that the particle will be in the first excited state of the one-spring system after the cut?
21. Starting with an a -box, let $a/2 = L$ so the width of the box is $2L$. Write the energy eigenfunctions and the energy eigenvalues. Now apply the same technique as that used in Problems 19 to recover the correct eigenfunctions and energy eigenvalues for an L -box.

22. At $t = 0$ the normalized wave function of a particle of mass m subject to a harmonic oscillator potential $U(x) = \frac{1}{2}m\omega^2 x^2$ is

$$\Psi(x, 0) = \sqrt{\frac{\beta}{\pi^{1/2}}} e^{-\beta^2 x^2 / 2}$$

where $\beta \neq \alpha = \sqrt{m\omega/\hbar}$, but β is real and positive.

- (a) If a measurement of the energy E is made, what is the probability P of measuring $E = \frac{1}{2}\hbar\omega$?
 - (b) Show that if $\beta = \alpha$, then $P = 1$, but if $\beta \neq \alpha$, then $P < 1$.
23. An electron is subject to a harmonic oscillator potential with natural frequency ω . At $t = 0$ a constant electric field $\mathbf{F} = F\hat{\mathbf{i}}$ is applied.
- (a) Find the energy eigenfunctions and eigenvalues after the field has been switched on.
 - (b) Assuming that the electron was in the ground state of the field-free oscillator potential what is the probability of finding it in the ground state of the oscillator plus field?

Chapter 4

Time-Dependent States in One Dimension

Thus far our detailed studies have been of the stationary states of quantum mechanical systems. It was remarked in Section 3.3, however, that, in general, quantum mechanical systems exist in a superposition of states. In such states the probability density is necessarily time-dependent (see Section 2.7). These states are usually referred to as “wave packets” because it is a superposition of waves of differing de Broglie wavelengths that constitute the wave function. Indeed, wave packets provide the mechanism by which a quantum mechanical particle “moves” and this movement provides the connection between quantal and classical particles. We will first examine the connection between the expectation values of position and momentum and the classical concepts of these quantities. Following this we will examine a few specific wave packets in detail.

4.1 The Ehrenfest Equations

In 1927 P. Ehrenfest demonstrated the relationship between the motion of a wave packet and the motion of a classical particle, yet another manifestation of the correspondence principle. Let us first examine the expectation value of position:

$$\langle x \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) x \Psi(x, t) dx \quad (4.1)$$

where it is assumed that the wave function is normalized so they vanish at $x = \pm\infty$. Differentiating $\langle x \rangle$ with respect to time and substituting from the TDSE, Equation 2.17, we have

$$\begin{aligned} \frac{d}{dt} \langle x \rangle &= \int_{-\infty}^{\infty} \frac{\partial \Psi^*(x, t)}{\partial t} x \Psi(x, t) dx + \int_{-\infty}^{\infty} \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial t} x \frac{\partial \Psi(x, t)}{\partial t} dx \\ &= \frac{i}{\hbar} \int_{-\infty}^{\infty} x \left(-\frac{\hbar^2}{2m} \right) \left[\Psi(x, t) \frac{\partial^2}{\partial x^2} \Psi^*(x, t) - \Psi^*(x, t) \frac{\partial^2}{\partial x^2} \Psi(x, t) \right] dx \\ &= \left(-\frac{i\hbar}{2m} \right) \int_{-\infty}^{\infty} x \frac{\partial}{\partial x} \left[\Psi(x, t) \frac{\partial}{\partial x} \Psi^*(x, t) - \Psi^*(x, t) \frac{\partial}{\partial x} \Psi(x, t) \right] dx \end{aligned} \quad (4.2)$$

Notice that the terms involving the potential energy cancel so the potential energy (assumed to be real) does not appear. Integrating by parts with

$$u = x$$

$$dv = \frac{\partial}{\partial x} \left[\Psi(x, t) \frac{\partial}{\partial x} \Psi^*(x, t) - \Psi^*(x, t) \frac{\partial}{\partial x} \Psi(x, t) \right] dx \quad (4.3)$$

and recalling that the wave functions vanish at $\pm\infty$ we have

$$\frac{d}{dt} \langle x \rangle = \left(\frac{i\hbar}{2m} \right) \int_{-\infty}^{\infty} \left[\Psi(x, t) \frac{\partial}{\partial x} \Psi^*(x, t) - \Psi^*(x, t) \frac{\partial}{\partial x} \Psi(x, t) \right] dx \quad (4.4)$$

Now integrating the first integral by parts with

$$u = \Psi(x, t)$$

$$dv = \frac{\partial}{\partial x} \Psi^*(x, t) dx \quad (4.5)$$

we arrive at

$$\frac{d}{dt} \langle x \rangle = \left(\frac{1}{m} \right) \int_{-\infty}^{\infty} \Psi^*(x, t) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi(x, t) dx \quad (4.6)$$

From Equation 2.28 we recognize the quantity in parentheses in the integrand as the momentum operator. Therefore,

$$\frac{d}{dt} \langle x \rangle = \frac{\langle p \rangle}{m} \quad (4.7)$$

which is the classical relationship between position and momentum applied to the expectation values of these quantities. Thus, it is the average values of these variables that correspond to their classical counterparts. Equation 4.7 is often referred to as the first Ehrenfest equation.

The second Ehrenfest equation may be obtained by differentiating the first in the form of Equation 4.6. We have

$$\frac{d^2}{dt^2} \langle x \rangle = \left(\frac{\hbar}{im} \right) \int_{-\infty}^{\infty} \left[\frac{\partial \Psi^*(x, t)}{\partial t} \frac{\partial \Psi(x, t)}{\partial x} + \Psi^*(x, t) \frac{\partial^2 \Psi(x, t)}{\partial t \partial x} \right] dx \quad (4.8)$$

After interchanging the order of differentiation in the second derivative we replace the partial derivatives with respect to time using the TDSE, Equation 2.17. In this case the potential energy does not cancel and, after integrating by parts twice, we obtain

$$\frac{d^2}{dt^2} \langle x \rangle = \left(\frac{1}{m} \right) \int_{-\infty}^{\infty} \Psi^*(x, t) \left(-\frac{dU(x)}{dx} \right) \Psi(x, t) dx \quad (4.9)$$

or, noting that the negative gradient ($-d/dx$ in one-dimension) is the force, we have a relationship between the average force and the acceleration, Newton's second law:

$$\left\langle -\frac{dU(x)}{dx} \right\rangle = m \frac{d^2}{dt^2} \langle x \rangle \quad (4.10)$$

Equation 4.10 is the second Ehrenfest equation. We will see in Section 6.3.3 that these results can be generalized to obtain the time derivative of the expectation value of any quantum mechanical operator.

4.2 The Free Particle

As the name implies, the free particle is one that is not subjected to any potential energy function so $U(x) = 0$. This condition leads to a deceptively simple wave function. The solution to the TISE is

$$\begin{aligned} \Psi(x, t) &= (Ae^{ikx} + Be^{-ikx}) e^{-i\omega t} \\ &= Ae^{i(kx - \omega t)} + Be^{-i(kx + \omega t)} \\ &= Ae^{ik(x - \omega t/k)} + Be^{-ik(x + \omega t/k)} \end{aligned} \quad (4.11)$$

where A and B are constants and, as usual,

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad \omega = \frac{E}{\hbar} = \frac{\hbar k^2}{2m} \quad (4.12)$$

Of course, Equations 4.11 can also be written in terms of sines and cosines using the Euler relations, but, for now, the exponentials are more convenient. Because $U(x) = 0$, the TME is $E = p^2/2m$ and we may write

$$k = \frac{p}{\hbar} \quad \text{and} \quad \omega = \frac{p^2}{2m\hbar} \quad (4.13)$$

Recalling that wave motion in one-dimension is characterized by a function of $x \pm vt$ where v is the velocity of propagation (minus represents motion to the right and plus to the left), we see the terms in Equations 4.11 represent waves propagating in opposite directions. It is clear that ω is the angular frequency of the motion; k is referred to as the wave number and is, in essence, the momentum.

Suppose we have a free particle propagating to the right so that $B = 0$. We see immediately that the wave function for such a particle cannot be normalized. This

state represents a stationary state, but $\Psi(x, t) \Psi^*(x, t) = |\Psi(x, t)|^2 = |A|^2$ which, because

$$\int_{-\infty}^{\infty} \Psi(x, t) \Psi^*(x, t) dx = \infty \quad (4.14)$$

cannot be normalized. This is consistent with the uncertainty principle because the free particle, by its very nature, has definite momentum so $\Delta p = 0$ and, commensurately, $\Delta x = \infty$. The fact that the wave function cannot be normalized should not be a cause for concern. All this means is that the wave function does not represent a bound state which, by definition, is confined by some potential energy function to a specific region of space. Only bound state wave functions must be normalizable, square integrable.

Now, how about the speed of the “particle”? Because

$$kx \pm \omega t = k \left(x \pm \frac{\omega}{k} t \right) \quad (4.15)$$

it is clear that the speed of the wave that represents the particle is

$$\begin{aligned} v_{wave} &= \frac{\omega}{k} \\ &= \frac{p}{2m} \end{aligned} \quad (4.16)$$

This is in contrast to the (classical) speed of the particle, p/m . Therefore, ω/k cannot correspond to the speed of the particle. More will be said about this later. Notice that the free particle has a fixed de Broglie wavelength, which in terms of k is

$$\begin{aligned} \lambda &= \frac{h}{p} \\ &= \frac{2\pi}{k} \end{aligned} \quad (4.17)$$

A free particle propagating in either direction, $A = 0$ or $B = 0$ in Equation 4.11, is usually referred to as a plane wave because $\Psi(x, t)$ does not depend upon either y or z .

4.3 Quantum Representation of Particles—Wave Packets

In Chapter 2 we noted that, because the TISE is a linear differential equation, it was possible to write the wave function for any *bound* state as a linear combination of eigenstates with the appropriate exponential time dependences. Such an expansion is

not limited to bound states. Indeed, particles need not be bound by a potential energy function. They may be free as discussed above or they may be subject to a potential energy function that does not confine them to a region of space, for example, a step function. For such a situation we may use the free particle as a starting point to construct a quantum mechanical representation for a particle, but the formalism is not limited to unbound particles. We merely wish to localize the particle and seek a wave representation for such a particle. To do this we may imagine a superposition of free particle wave functions each of a different de Broglie wavelength. These free particle wave functions can interfere constructively and destructively to form a localized packet of probability that will adequately represent a quantum mechanical particle. Because there are available to us a continuously variable supply of de Broglie wavelengths, it will be necessary to form the sum over wave numbers as an integral rather than a summation.

The framework for this superposition of k -states already exists, namely, the Fourier integrals (see Appendix J). If we include the time in the wave function, we can construct a wave packet as

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k, t) e^{ikx} dk \quad (4.18)$$

where $A(k)$ is the amplitude of the k th component of the wave packet. The factor $1/\sqrt{2\pi}$ is inserted for convenience (see below). Equation 4.18 is nothing more than an expansion of a function $\Psi(x, t)$ on the complete set of coordinate space eigenfunctions of the free particle Hamiltonian e^{ikx} where the time dependence is contained in $A(k, t)$. Because, however, we know that the time dependence of the free particle eigenfunctions is simply $e^{-iEt/\hbar}$, we may write

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) \left[e^{ikx} e^{-i\hbar k^2 t/2m} \right] dk \quad (4.19)$$

where we have replaced the free particle energy with

$$\begin{aligned} E &= \frac{p^2}{2m} \\ &= \frac{\hbar^2 k^2}{2m} \end{aligned} \quad (4.20)$$

The Fourier integral is a generalization of the Fourier series in which the $\sin n\theta$ and $\cos n\theta$ are used in exactly the same way that the unit vectors \hat{i} , \hat{j} , and \hat{k} are used to form any arbitrary vector. The unit vectors are basis vectors upon which any vector may be expanded. Similarly, the sines and cosines are basis “vectors” or functions upon which any periodic function may be expanded. The fact that there are an infinite number of sines and cosines while there are only three unit vectors is a mere technicality. Of course, the sines and cosines can be written in exponential form so the step from Fourier *series* to Fourier *integral* is not too steep. We see that

the function $A(k)$ simply weights the free particle wave numbers, presumably in a way that will cause them to constructively and destructively interfere to represent a localized particle.

Before proceeding, we return to the question of the actual speed of the particle that our packet is to represent. Let us write Equation 4.18 by substituting the Planck relation $E = \hbar\omega$ in the exponent:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(kx - \omega t)} dk \quad (4.21)$$

The wave frequency ω is, in general, a function of the wave number k . If it is assumed that ω is slowly varying and expand it in a Taylor series about some arbitrary value of $k = k_0$ for which $\omega = \omega_0$ we have

$$\omega(k) \approx \omega_0 + \left(\frac{d\omega}{dk} \right)_{k=k_0} (k - k_0) + \dots \quad (4.22)$$

which, when inserted in Equation 4.21, gives

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} e^{ik_0(x - \omega_0 t/k_0)} \int_{-\infty}^{\infty} A(k) \exp \left\{ i \left[x - \left(\frac{d\omega}{dk} \right)_{k=k_0} t \right] (k - k_0) \right\} dk \quad (4.23)$$

From Equation 4.23 it can be seen that the wave function $\Psi(x, t)$ represents a plane wave (see Equation 4.11) propagating with velocity $v_p = \omega_0/k_0 = p_0/m$ that is reshaped by the integral that multiplies it. As was noted previously, v_p , called the phase velocity, is not the particle velocity. It is the velocity of the plane wave under the condition that the exponential in the integral is equal to unity, the so-called stationary phase condition. The velocity of the centroid of the packet, called the group velocity, moves with constant velocity and, for a free particle of wave number k_0 , is given by

$$\begin{aligned} v_g &= \left(\frac{d\omega}{dk} \right)_{k=k_0} \\ &= \left[\frac{d}{dk} \left(\frac{\hbar k^2}{2m} \right) \right]_{k=k_0} \end{aligned} \quad (4.24)$$

$$\begin{aligned} &= \frac{\hbar k_0}{m} \\ &= \frac{p_0}{m} \end{aligned} \quad (4.25)$$

which is, indeed, the classical particle velocity.

Because the expansion of $\Psi(x, t)$ in Equation 4.18 is an expansion on free particle wave functions, the energy is simply the free particle energy, the kinetic energy

of a particle of momentum $p = \hbar k$, that is, $p^2/2m$. We may therefore replace ω in Equation 4.18 using

$$\begin{aligned} E &= \hbar\omega \\ &= p^2/2m \\ &= \hbar^2 k^2/2m \end{aligned} \quad (4.26)$$

so that

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{ikx} e^{-ik^2 \hbar t/(2m)} dk \quad (4.27)$$

Before considering the movement of wave packets we examine the relationship between the two functions, $\Psi(x, t = 0)$ and $A(k)$. The Fourier integral at $t = 0$ is [using the notation $\Psi(x, 0) = \psi(x)$]

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{ikx} dk \quad (4.28)$$

The function $\psi(x)$ in Equation 4.28 is the Fourier transform of $A(k)$ while $A(k)$ is the Fourier transform of $\psi(x)$:

$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} dx \quad (4.29)$$

We may also write an expression for $A(k, t)$. It is

$$\begin{aligned} A(k, t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, t) e^{-ikx} dx \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} e^{-ik^2 \hbar t/(2m)} dx \end{aligned} \quad (4.30)$$

where $e^{-ikx} e^{-ik^2 \hbar t/(2m)}$ are the momentum space eigenfunctions.

Notice the symmetry between Equations 4.27 and 4.30. While $\psi(x)$ is the familiar wave function in what we will now refer to as coordinate space, $A(k)$ has all the earmarks of a wave function, but rather than being a function of x it is a function of $k = p/\hbar$, the momentum. Recall that x and p are the variables that appear in the Heisenberg uncertainty relation. Thus, while $A(k)$ plays the role of the expansion coefficients in the infinite sum (that is actually an integral) in Equation 4.28 to produce $\psi(x)$, we see that $\psi(x)$ plays exactly the same role if we regard $A(k)$ as a wave function that is a function of momentum. What then is the usefulness of this $A(k)$? We might (correctly) presume, by analogy, that the quantity $|A(k)|^2 dk$ represents the probability that the particle can be found with wave number between k and $k+dk$

just as $|\psi(x)|^2 dx$ represents the probability that the particle can be found between x and $x + dx$. The function $A(k)$ is referred to as the wave function in momentum space (even though k is only *proportional* to the momentum). We note that the relations between $\psi(x)$ and $A(k)$ in their Fourier transforms are not restricted to unbound particles. These relations hold for any wave functions including the bound stationary states that we have already studied in Chapter 3.

Rather than writing the Fourier transform of $\psi(x)$ in terms of wave number k and $A(k)$ it is often useful to write it in terms of the momentum p and the momentum wave function $\phi(p)$ defined as

$$\begin{aligned}\phi(p) &\equiv \frac{1}{\sqrt{\hbar}} A(k) \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x) e^{-ipx/\hbar} dx\end{aligned}\quad (4.31)$$

and

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} e^{-ip^2t/(2m\hbar)} dx \quad (4.32)$$

Clearly $\phi(p)$ is also a wave function in momentum space. Inserting the $A(k) \equiv \sqrt{\hbar}\phi(p)$ into Equation 4.28 we obtain $\psi(x)$ in terms of $\phi(p)$:

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p) e^{ipx/\hbar} dp \quad (4.33)$$

The symmetry between Equations 4.31 and 4.33 makes clear the reason for the factor of $1/\sqrt{\hbar}$ in the defining relation between $A(k)$ and $\phi(p)$. We may also rewrite Equation 4.27 in terms of the momentum. We have

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p) e^{ipx/\hbar} e^{-ip^2t/(2m\hbar)} dp \quad (4.34)$$

4.3.1 Momentum Representation of the Operator x

Previously, Equation 2.28, we deduced a representation for the momentum operator \hat{p}_x in terms of the coordinate x . That is, we found that

$$\hat{p} = \frac{\hbar}{i} \frac{d}{dx} \quad (4.35)$$

where we have dropped the subscript on the momentum operator because we are working in one-dimension. Let us examine the effect of this operator on $\psi(x)$ by operating on Equation 4.33 (ignoring the relation in Equation 4.35):

$$\begin{aligned}
\hat{p}\psi(x) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} p\phi(p) e^{ipx/\hbar} dp \\
&= \left[\frac{\hbar}{i} \frac{d}{dx} \right] \left\{ \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p) e^{ipx/\hbar} dp \right\} \\
&= \left[\frac{\hbar}{i} \frac{d}{dx} \right] \psi(x)
\end{aligned} \tag{4.36}$$

which confirms the result in Equation 4.35.

The derivation of the expression for \hat{p} , Equation 4.35, suggests that it may be possible to obtain an analogous expression for the coordinate “operator” x . After all, if x and \hat{p} are on an equal footing, they should both be considered to be operators in the quantum mechanical sense. Indeed they are, although the “hat” is frequently suppressed for coordinate operators. We will follow this tradition except where noted. Proceeding as we did with \hat{p}_x we investigate the effect of operating on $\phi(p)$ with x . We have

$$\begin{aligned}
x\phi(p) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} x\psi(x) e^{-ipx/\hbar} dx \\
&= \left[-\frac{\hbar}{i} \frac{d}{dp} \right] \left\{ \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x) e^{-ipx/\hbar} dx \right\} \\
&= \left[-\frac{\hbar}{i} \frac{d}{dp} \right] \phi(p)
\end{aligned} \tag{4.37}$$

Thus, we see that the coordinate operator is given by

$$x = -\frac{\hbar}{i} \frac{d}{dp} \tag{4.38}$$

4.3.2 The Dirac δ -function

At this point it is worthwhile to digress from the main subject of this chapter to introduce an extremely useful function that pervades quantum physics, the Dirac δ -function, or simply the δ -function. To do this we replace $\phi(k)$ in Equation 4.28 with Equation 4.29, interchange the order of integration, and obtain

$$\begin{aligned}
\psi(x) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x') e^{-ikx'} dx' \right] e^{ikx} dk \\
&= \int_{-\infty}^{\infty} \psi(x') dx' \left[\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x')} dk \right]
\end{aligned} \tag{4.39}$$

where we have used x' as a dummy variable to distinguish it from x which is on the left-hand side of the equation. The quantity in square brackets is defined to be the

δ -function. Note that it depends only on $(x - x')$ because the k integrates out. By definition then

$$\delta(x - x') \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x')} dk \quad (4.40)$$

Now, the integral in Equation 4.40 is undefined as can be seen by converting the exponential to sines and cosines. What then is its meaning? In fact, the name δ -“function” is not proper. Mathematicians refer to such an entity as a distribution. No matter! We must use it in the context of its properties and its usage in quantum mechanics. In terms of the δ -function Equation 4.39 is

$$\psi(x) = \int_{-\infty}^{\infty} \delta(x - x') \psi(x') dx' \quad (4.41)$$

This equation illustrates one of the most important properties of the δ -function, the sifting property. According to Equation 4.41 $\delta(x - x')$ sifts out the value of $\psi(x')$ at $x' = x$ and replaces the entire integral with $\psi(x' = x)$.

The properties of the δ -function are usually listed in terms of some arbitrary function $f(x)$ and a constant. Three of the most important properties of the δ -function are listed in Table 4.1.

The fact that the δ -function is an even function can be proved by making the substitution $y = -x$ in the first line of Table 4.1 with $x_0 = 0$.

$$\begin{aligned} \int_{-\infty}^{\infty} \delta(-x) f(x) dx &= \int_{\infty}^{-\infty} \delta(y) f(-y) (-dy) \\ &= \int_{-\infty}^{\infty} \delta(y) f(-y) dy \\ &= f(0) \\ &= \int_{-\infty}^{\infty} \delta(x) f(x) dx \end{aligned} \quad (4.42)$$

Thus, $\delta(-x)$ and $\delta(x)$ have the same effect on the integral so they must be equal. Examination of the sifting property of the δ -function as described in Table 4.1 clearly shows that it is nonzero only at x_0 . The picture that emerges is one of an infinitely high spike of zero width at $x = x_0$, but, because of the normalization integral,

Table 4.1 Some properties of the Dirac delta-functions

Mathematical operation	Name
$f(x_0) = \int_{-\infty}^{\infty} \delta(x - x_0) f(x) dx$	Sifting property
$\delta(-x) = \delta(x)$	Parity: even (if $x_0 = 0$)
$\int_{-\infty}^{\infty} \delta(x - x_0) = 1$	Normalization
$\delta(ax) = (1/ a) \delta(x)$	None

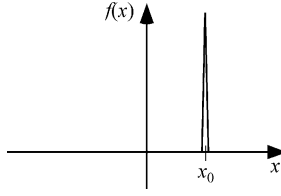


Fig. 4.1 Schematic illustration of the function $\delta(x - x_0)$. It is zero everywhere except at $x = x_0$ at which point it is infinitely high, but has zero width. Nonetheless, (believe it or not) the area under this spike is unity

the “area” under this spike is unity. This is precisely the function we alluded to in Chapter 3 when discussing the probability density of the ground state of the classical harmonic oscillator (with $x_0 = 0$). This abstraction is extremely useful. A highly schematic conception of a δ -function is illustrated in Fig. 4.1. Note that $\delta(x - x_0)$ has even parity with respect to $x = x_0$.

4.3.3 Parseval's Theorem

We may use the δ -function to prove an important theorem, Parseval's theorem. We begin with the integral over all momenta of the absolute square of $\phi(k)$ and insert the Fourier transforms:

$$\begin{aligned}
 \int_{-\infty}^{\infty} \phi(k) \phi^*(k) dk &= \int_{-\infty}^{\infty} \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} dx \right] \\
 &\quad \times \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi^*(x') e^{ikx'} dx' \right] dk \\
 &= \int_{-\infty}^{\infty} \psi(x) dx \left\{ \int_{-\infty}^{\infty} \psi^*(x') \left[\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x'-x)} dk \right] dx' \right\} \\
 &= \int_{-\infty}^{\infty} \psi(x) dx \left\{ \int_{-\infty}^{\infty} \psi^*(x') [\delta(x' - x)] dx' \right\} \\
 &= \int_{-\infty}^{\infty} \psi(x) dx \{ \psi^*(x) \} \\
 &= \int_{-\infty}^{\infty} \psi(x) \psi^*(x) dx
 \end{aligned} \tag{4.43}$$

Written in the more usual form we have

$$\int_{-\infty}^{\infty} |\phi(k)|^2 dk = \int_{-\infty}^{\infty} |\psi(x)|^2 dx \tag{4.44}$$

which makes it clear that the normalization is preserved in going from coordinate space to momentum space.

4.4 The Harmonic Oscillator Revisited—Momentum Eigenfunctions

In Chapter 3 we solved the TISE for the bound state eigenfunctions and energy eigenvalues for the harmonic oscillator potential $U(x) = \frac{1}{2}m\omega^2x^2$. In view of our discussion in this chapter, however, we should clarify the nature of wave functions that we obtained by noting that they are coordinate space wave functions. That is, in the context of this chapter, the wave functions that we obtained in Chapter 3 were $\psi(x)$'s rather than $\phi(p)$'s.

The harmonic oscillator is a very special problem in quantum physics. One reason for its uniqueness is that the coordinate x occurs in the TISE to exactly the same power as does the momentum p . Inserting the potential energy function into Equation 2.26 the TISE may be written

$$\left[\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2x^2 \right] \psi(x) = E\psi(x) \quad (4.45)$$

Because we are working in one-dimension we have again dropped the subscript x that denotes the component of the momentum. Examination of Equation 4.45 together with the (near) symmetric operator relations

$$\hat{p} \rightarrow \frac{\hbar}{i} \frac{d}{dx} \quad \text{and} \quad x \rightarrow -\frac{\hbar}{i} \frac{d}{dp} \quad (4.46)$$

makes it clear that the momentum and coordinate energy eigenfunctions must have the same general form. It is not necessary to actually solve the TISE in momentum space to obtain the set of $\phi_n(p)$ since we have already done the work. All we must do is replace x by its operator equivalent in p -space and put the resulting equation in the form of the differential equation that led us to the coordinate space eigenfunctions:

$$\psi_n(x) = \sqrt{\frac{1}{2^n n!}} \left(\frac{m\omega}{\pi \hbar} \right)^{1/4} H_n \left(\sqrt{\frac{m\omega}{\hbar}} x \right) e^{-m\omega x^2 / (2\hbar)} \quad (4.47)$$

We then find the analogous constants and simply write the solutions (see Problem 11). The harmonic oscillator momentum eigenfunctions are found to be

$$\phi_n(p) = \sqrt{\frac{1}{2^n n!}} \left(\frac{1}{\pi m\omega \hbar} \right)^{1/4} H_n \left(\frac{1}{\sqrt{m\omega \hbar}} p \right) e^{-p^2 / (2m\omega \hbar)} \quad (4.48)$$

It may seem peculiar that in the midst of this chapter we have seemingly digressed to reexamine an already solved problem. If, however, the relationship between $\psi(x)$ and $\phi(p)$ that is contained in their Fourier transforms is valid, we should be able to check it with the easily derived oscillator eigenfunctions. We examine the ground state for which both the coordinate and momentum space

eigenfunctions are simple Gaussian functions. Including normalization constants we have (recalling that $\alpha = \sqrt{m\omega/\hbar}$)

$$\begin{aligned}\psi_0(x) &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/(2\hbar)} \\ &= \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-\alpha^2 x^2/2}\end{aligned}\quad (4.49)$$

and

$$\begin{aligned}\phi_0(p) &= \left(\frac{1}{\pi m\omega\hbar}\right)^{1/4} e^{-p^2/(2m\omega\hbar)} \\ &= \frac{1}{\pi^{1/4}\sqrt{\alpha\hbar}} e^{-p^2/(2\alpha^2\hbar^2)}\end{aligned}\quad (4.50)$$

Inserting Equation 4.49 in the Fourier transform, Equation 4.31, we have

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \int_{-\infty}^{\infty} e^{-m\omega x^2/(2\hbar)} e^{-ipx/\hbar} dx \quad (4.51)$$

Completing the square and using the integral given in Equation H.4 we do indeed recover $\phi(p)$ as given by Equation 4.50.

There is more! Let us examine the uncertainty principle for the ground state of the harmonic oscillator, that is, for a Gaussian wave function. (Note that we need not specify whether we mean a Gaussian wave function in coordinate space or momentum space because the Fourier transform of a Gaussian is a Gaussian.) By symmetry, it is clear that both $\langle x \rangle$ and $\langle p \rangle$ vanish. We need calculate only $(\Delta x)^2 = \langle x^2 \rangle$ and $(\Delta p)^2 = \langle p^2 \rangle$. Using the definite integral, Equation H.5, we find (see Problem 6) that

$$\Delta x = \frac{1}{\sqrt{2}\alpha} = \sqrt{\frac{\hbar}{2m\omega}} \quad \text{and} \quad \Delta p = \frac{1}{\sqrt{2}}\alpha\hbar = \sqrt{\frac{m\omega\hbar}{2}} \quad (4.52)$$

so that

$$\Delta x \Delta p \equiv \frac{1}{2}\hbar \quad (4.53)$$

Thus, for the ground state of the harmonic oscillator the uncertainty relation is an equality. That is, the Gaussian wave function has the minimum uncertainty possible. From Equation 4.52 it is clear that as Δp increases (decreases), Δx decreases (increases).

Finally, we note that in terms of the wave number k the ground state wave function is

$$A_0(k) = \frac{1}{\pi^{1/4} \sqrt{\alpha}} e^{-k^2/(2\alpha^2)} \quad (4.54)$$

and the uncertainty in the wave number Δk is

$$\Delta k = \frac{1}{\sqrt{2}} \alpha \quad (4.55)$$

so, in terms of x and k , the uncertainty relation is

$$\Delta x \Delta k = \left(\frac{1}{\sqrt{2}\alpha} \right) \left(\frac{1}{\sqrt{2}} \alpha \right) \quad (4.56)$$

$$= \frac{1}{2} \quad (4.57)$$

4.5 Motion of a Wave Packet

We wish to investigate the fate of a wave packet with increasing time. To do this we must specify either $\Psi(x, 0)$ or $\Phi(p, 0)$ and find the time-dependent wave functions. To be definite we will assume that the initial wave functions are Gaussians. Our reasoning is that we already know that if the momentum wave function is Gaussian, the coordinate wave function is also Gaussian. Moreover, the values of the definite integrals involving Gaussian functions are known. Now, let us be clear that because we are starting with a Gaussian does *not* mean that we are starting with the ground state of the harmonic oscillator, an eigenstate (see Problem 22 of Chapter 3). How can we imagine the creation of such a packet? There is more than one way. Suppose that we have a bound system, for example a particle subjected to a harmonic oscillator potential. Suppose further that the particle is not in an eigenstate, but that the wave function is a Gaussian. This means that the constant $\alpha = \sqrt{m\omega/\hbar}$ is not present in the exponent in the wave function. If the constant analogous to α is designated β with the stipulation that $\beta \neq \alpha$, then the initial Gaussian wave packet cannot be an eigenfunction of the harmonic oscillator. There is another method of creating an initial Gaussian wave packet that is not the ground state wave function, in this case even if the system is initially in the ground state. This will be explained below. Our initial wave functions can be represented as linear combinations of the eigenstates of the harmonic oscillator. (Indeed, it can be represented as a linear combination of the eigenstates of *any* Hamiltonian provided the potential energy has the same boundary conditions as the harmonic oscillator potential.)

To create the initial conditions, we imagine a particle that is initially subjected to a harmonic oscillator potential and at $t = 0$ is described by a momentum wave function $\Phi(p, 0)$ and a coordinate wave function $\Psi(x, 0)$ that are Fourier

transforms of each other. We specify, however, that they are each some form of Gaussian, but not the ground state of a harmonic oscillator. Physically, we may imagine the particle is attached to a spring and oscillating, but not in any eigenstate of the harmonic oscillator Hamiltonian. Thus, our Gaussian wave packet has been *created* while under the influence of a harmonic oscillator potential. At $t = 0$ we investigate the fate of the packet under three different circumstances.

- Case I. The spring is cut and nothing is done thereafter (it is a free packet/particle).
- Case II. The spring is cut and a constant field is turned on at $t = 0$.
- Case III. Nothing is done. That is, the packet remains under the influence of the spring.

In our treatment of these three cases we will tailor our initial Gaussian packet for computational convenience of the particular case. Before doing this we write the wave functions in coordinate space and momentum space for a general Gaussian packet. That is, suppose we imagine a Gaussian wave packet that is displaced from the origin by an amount x_0 and given initial momentum p_0 . The wave functions are Fourier transforms of each other and are given by

$$\Psi(x, 0) = \frac{\sqrt{\beta}}{\pi^{1/4}} e^{-\beta^2(x-x_0)^2/2} \cdot e^{ip_0x/\hbar} \quad (4.58)$$

and

$$\Phi(p, 0) = \frac{1}{\pi^{1/4} \sqrt{\beta \hbar}} e^{-(p-p_0)^2/2\beta^2 \hbar^2} \cdot e^{-ipx_0/\hbar} \quad (4.59)$$

where we have used the constant β (rather than α as defined in Equation 3.25) to emphasize that, even though it has the appearance of the ground state eigenfunction of the harmonic oscillator, the system is *not* in an eigenstate. It is easily shown that for these wave packets $\Delta x_0 = 1/(\sqrt{2}\beta)$ and $\Delta p_0 = \beta\hbar/\sqrt{2}$ (see Problem 6). We may therefore write Equations 4.58 and 4.59 in terms of the uncertainties Δx_0 and Δp_0 :

$$\Psi(x, 0) = \frac{1}{\pi^{1/4}} \left(\frac{1}{2^{1/4} \sqrt{\Delta x_0}} \right) e^{-(x-x_0)^2/4\Delta x_0^2} \cdot e^{ip_0x/\hbar} \quad (4.60)$$

$$\Phi(p, 0) = \frac{1}{\pi^{1/4}} \left(\frac{1}{2^{1/4} \sqrt{\Delta p_0}} \right) e^{-(p-p_0)^2/4\Delta p_0^2} \cdot e^{-ipx_0/\hbar} \quad (4.61)$$

Equations 4.60 and 4.61 illustrate an important property of Fourier transforms of Gaussian wave packets. Their uncertainties are equal in the sense that they occur in precisely the same form in each $\Psi(x, 0)$ and $\Phi(p, 0)$. An alternative way of saying this is that if $(x - x_0)$ and $(p - p_0)$ are measured in units of their respective uncertainties, then the functions have decreased by the same amount. For example,

if $(x - x_0) = 2\Delta x$, then $\Psi(x, 0)$ has decreased by one e -fold. In order for $\Phi(p, 0)$ to decrease by one e -fold requires $(p - p_0) = 2\Delta p$.

It is actually more useful to have the absolute squares of $\Psi(x, 0)$ and $\Phi(p, 0)$ in terms of Δx_0 and Δp_0 at our disposal. They are

$$|\Psi(x, 0)|^2 = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{\Delta x_0} \right) e^{-(x-x_0)^2/2\Delta x_0^2} \quad (4.62)$$

$$|\Phi(p, 0)|^2 = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{\Delta p_0} \right) e^{-(p-p_0)^2/2\Delta p_0^2} \quad (4.63)$$

In what follows we will be interested in finding the time dependence of the uncertainties. It is a simple matter to include the time in the last two equations. We have

$$|\Psi(x, t)|^2 = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{\Delta x(t)} \right) e^{-(x-x_0)^2/2[\Delta x(t)]^2} \quad (4.64)$$

$$|\Phi(p, t)|^2 = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{\Delta p(t)} \right) e^{-(p-p_0)^2/2[\Delta p(t)]^2} \quad (4.65)$$

4.5.1 Case I. The Free Packet/Particle

We choose to cut the spring at a time such that $x_0 = 0$. The packet will then have nonzero average momentum p_0 . The Gaussian packet in momentum space at $t = 0$ is therefore (see Equation 4.59)

$$\Phi(p, 0) = \frac{1}{\pi^{1/4} \sqrt{\beta \hbar}} e^{-(p-p_0)^2/2\beta^2 \hbar^2} \quad (4.66)$$

Let us first ask what we expect. Certainly we expect the packet to propagate in the direction of p_0 , $+x$ or $-x$. We also expect the packet to change shape. The mathematics will tell us exactly how the packet propagates and how it reshapes after it is free. On the other hand, being a free particle we expect no change in the momentum so that the initial spread in momentum Δp cannot change in time.

First we will find the wave function in coordinate space $\Psi(x, t)$. Inserting $\Phi(p, 0) = \phi(p)$ in Equation 4.34 we have

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi \hbar}} \frac{1}{\pi^{1/4} \sqrt{\beta \hbar}} \int_{-\infty}^{\infty} e^{-(p-p_0)^2/(2\beta^2 \hbar^2)} e^{ipx/\hbar} e^{-ip^2 t/(2m\hbar)} dp \quad (4.67)$$

Now, there is some unpleasant algebra in the exponent, but it is straightforward to complete the square and integrate. The result is

$$\begin{aligned}
 \Psi(x, t) = & \frac{\beta^{1/2}}{\pi^{1/4}} \frac{1}{\sqrt{1 + \frac{i\beta^2 \hbar t}{m}}} \\
 & \times \exp \left[-\frac{\beta^2 (x - p_0 t/m)^2}{2 \left(1 + i\beta^2 \hbar t/m\right)} \right] \\
 & \times \exp \left[\frac{i}{\hbar} p_0 \left(x - \frac{p_0}{2m} t \right) \right]
 \end{aligned} \tag{4.68}$$

The absolute square of the wave function, the probability density, tells us how the packet spreads. Squaring Equation 4.68 we obtain

$$|\Psi(x, t)|^2 = \frac{1}{\sqrt{\pi}} \frac{\beta}{\sqrt{1 + \frac{\beta^4 \hbar^2 t^2}{m^2}}} \exp \left\{ -\beta^2 \left[\frac{(x - p_0 t/m)^2}{\left(1 + \frac{\beta^4 \hbar^2 t^2}{m^2}\right)} \right] \right\} \tag{4.69}$$

or in terms of $\Delta x_0 = 1/(\sqrt{2}\beta)$

$$|\Psi(x, t)|^2 = \frac{1}{\sqrt{2\pi}} \frac{1}{\Delta x_0 \sqrt{1 + \frac{\hbar^2 t^2}{4m^2 \Delta x_0^4}}} \exp \left\{ - \left[\frac{(x - p_0 t/m)^2}{2\Delta x_0^2 \left(1 + \frac{\hbar^2 t^2}{4m^2 \Delta x_0^4}\right)} \right] \right\} \tag{4.70}$$

From Equation 4.69 we see that, because x and t occur in the combination $x - vt$, the probability packet travels with group velocity $v_g = p_0/m = \langle p \rangle / m$ which corresponds to the classical particle velocity. Moreover, $\langle x(t) \rangle = (p_0/m)t$ which corresponds to the particle position. Additionally, the phase factor in Equation 4.68 shows that the phase velocity $v_p = p_0/(2m)$.

Comparing Equation 4.69 with Equation 4.64, we see that the uncertainty as a function of time is given by

$$\Delta x(t) = \Delta x_0 \sqrt{1 + \left(\frac{\hbar t}{2\Delta x_0^2 m} \right)^2} \tag{4.71}$$

so that, in terms of $\Delta x(t)$, Equation 4.70 may be written more compactly as

$$|\Psi(x, t)|^2 = \frac{1}{\sqrt{2\pi}} \frac{1}{\Delta x(t)} \exp \left\{ - \left[\frac{(x - p_0 t/m)^2}{2\Delta x(t)^2} \right] \right\} \tag{4.72}$$

Notice that comparison with Equation 4.64 provides a double check because $\Delta x(t)$ occurs in both the exponent and the preexponential factor. From Equation 4.71

it is seen that, in coordinate space, the packet spreads as it moves along. On the other hand, this is a free particle so Δp must be independent of time. This may be seen quantitatively by examining the appropriate integrals. Because the only time dependence in the momentum wave function is in the imaginary exponent, the time will not appear in the integrand of either $\langle p^2 \rangle$ or $\langle p \rangle$. The time appears in Δx because x and x^2 must be changed to their momentum notation, derivatives, which operate on the time-dependent part of the imaginary exponent. Thus, the uncertainty product $\Delta x \Delta p$, while initially its minimum value, grows with time. Figure 4.2 illustrates the motion in time of the packet.

Another feature of this packet is that the amplitude of the probability density decreases as indicated by the preexponential factor. This decrease in amplitude is compensated by the spreading with time of $\Delta x(t)$. The normalization of $\Psi(x, t)$ is preserved in time as may be seen by evaluating the integral of $|\Psi(x, t)|^2$ (see Problem 8). Thus, while the Gaussian wave packet propagates and spreads with increasing time, the area under it remains constant. Note that if we imagine the packet to have originated from cutting the spring when the particle was in an eigenstate of the harmonic oscillator so that $\langle p \rangle = 0$, the packet would not propagate because $v_g = 0$. The packet would, however, spread just as described by Equation 4.71 because the momentum does not enter into this result. In other words, the concave up parabola that is $U(x)$ disintegrates and the Gaussian ground state in coordinate space would spread symmetrically forever.

The probability density represented in Equation 4.69 may be more revealing if it is cast in terms of the initial uncertainty in position $\Delta x(t=0) = \Delta x_0 = 1/(\sqrt{2}\beta)$, which is identical with Equation 4.52 with $\alpha \rightarrow \beta$. Rewriting Equation 4.71 and letting

$$t_0 = \frac{2m}{\hbar} \Delta x_0^2 \quad (4.73)$$

we have

$$\Delta x(t) = \Delta x_0 \sqrt{1 + \frac{t^2}{t_0^2}} \quad (4.74)$$

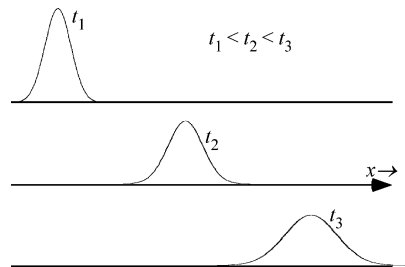


Fig. 4.2 A free Gaussian wave packet shown at three different times. Note that the width of the packet increases in time, but the area under the curve remains constant

We see from Equation 4.74 that $\Delta x(t) > \Delta x_0$ for $t > 0$. Naturally, we expect this effect to be evident only at the microscopic level. For a free electron we can assume the initial uncertainty to be the order of the Compton wavelength $\hbar/(m_e c)$ so that

$$\begin{aligned} t_0 &= \frac{2\hbar}{m_e c^2} \\ &= \frac{2(6.58 \times 10^{-16} \text{eV} \cdot \text{s})}{0.51 \times 10^6 \text{eV}} \\ &= 2.6 \times 10^{-21} \text{s} \end{aligned} \quad (4.75)$$

Thus, the probability density representing a *free* electron initially confined to a region of space comparable with its own Compton wavelength spreads very rapidly. On the other hand, if it is a macroscopic particle of mass say 10^{-4}kg having diameter 10^{-3}m , appreciable spreading takes more than 10^{17}s , roughly the age of the universe.

4.5.2 Case II. The Packet/Particle Subjected to a Constant Field

At $t = 0$ the Gaussian packet is subjected to a constant force φ . How could such a situation arise? If the particle of mass m carries an electrical charge and if it is in a region of constant electric field, then the force is the product of the charge and the electric field. It would also occur if a particle oscillating on a hanging spring were suddenly set free by cutting the spring. After cutting the spring the particle is subjected to the constant gravitational force.

Without specifying the origin of the force we may write the potential as

$$U(x) = -\varphi x; \quad -\infty < x < \infty \quad (4.76)$$

To simplify the mathematics we take the Gaussian packet to be one for which the average momentum and average displacement are zero. In momentum space the initial packet is described by

$$\Phi(p, 0) = \frac{1}{\pi^{1/4} \sqrt{\beta \hbar}} e^{-p^2/2\beta^2 \hbar^2} \quad (4.77)$$

The TDSE with the potential energy of Equation 4.76 can be solved exactly in coordinate space (see Section 5.5), but for the present purpose it is convenient to write the TDSE in momentum space. Using Equation 4.38 to replace $x \rightarrow (i\hbar) \partial/\partial p$ in the TDSE with a linear potential, we have

$$\frac{p^2}{2m} \Phi(p, t) - i\hbar \varphi \frac{\partial \Phi(p, t)}{\partial p} = i\hbar \frac{\partial \Phi(p, t)}{\partial t} \quad (4.78)$$

This partial differential equation may be solved by making the substitution

$$\Phi(p, t) = \Theta(p') f(p) \quad \text{where } p' = p - \varphi t \quad (4.79)$$

which leads to a differential equation for the function $f(p)$

$$\varphi \frac{df(p)}{dp} = \frac{p^2}{2m(i\hbar)} f(p) \quad (4.80)$$

the solution to which is

$$f(p) = \exp\left(-\frac{ip^3}{6m\hbar\varphi}\right) \quad (4.81)$$

so that

$$\Phi(p, t) = \Theta(p - \varphi t) \exp\left(-\frac{ip^3}{6m\hbar\varphi}\right) \quad (4.82)$$

where $\Theta(p - \varphi t)$ is *any* function of $(p - \varphi t)$ (see Problem 12). Initial conditions fix $\Theta(p - \varphi t)$.

To determine the $\Theta(p - \varphi t)$ that corresponds to the wave packet in Equation 4.77 we set $t = 0$ in Equation 4.82 and equate the result to the wave function representing the initial Gaussian wave packet, Equation 4.77. This permits determination of $\Theta(p)$ which can immediately be converted to $\Theta(p - \varphi t)$ because this function can contain p and t in only the combination $(p - \varphi t)$ (see Problem 13). We obtain

$$\Theta(p - \varphi t) = \left(\frac{1}{\pi^{1/4}\sqrt{\beta\hbar}}\right) \exp\left(-\frac{(p - \varphi t)^2}{2\beta^2\hbar^2} + \frac{i(p - \varphi t)^3}{6m\hbar\varphi}\right) \quad (4.83)$$

Substituting Equation 4.83 into Equation 4.82 we obtain the time-dependent wave function in momentum space for a Gaussian wave packet:

$$\Phi(p, t) = \left(\frac{1}{\pi^{1/4}\sqrt{\beta\hbar}}\right) \exp\left(-\frac{(p - \varphi t)^2}{2\beta^2\hbar^2}\right) \exp\left[i\left(\frac{(p - \varphi t)^3 - p^3}{6m\hbar\varphi}\right)\right] \quad (4.84)$$

and the probability density in momentum space is

$$|\Phi(p, t)|^2 = \left(\frac{1}{\sqrt{\pi}\beta\hbar}\right) \exp\left[-\frac{(p - \varphi t)^2}{\beta^2\hbar^2}\right] \quad (4.85)$$

or in terms of $\Delta p_0 = \beta \hbar / \sqrt{2}$

$$|\Phi(p, t)|^2 = \left(\frac{1}{\sqrt{2\pi} \Delta p_0} \right) \exp \left[-\frac{(p - \varphi t)^2}{2\Delta p_0^2} \right] \quad (4.86)$$

Comparing Equation 4.85 with Equation 4.65 reveals that

$$\Delta p(t) = \Delta p_0 \quad (4.87)$$

which contains no time dependence. Thus, as for the free particle Gaussian wave packet, this packet does not spread in momentum. Why is this? After all, there is a force applied. The force is, however, constant so all momentum components are affected equally. The packet moves as a unit in momentum space, but it does not spread.

It is straightforward to extract the time-dependent expectation values $\langle x(t) \rangle$ and $\langle p(t) \rangle$ (see Problem 15). We obtain

$$\langle x(t) \rangle = \frac{\varphi t^2}{2m} \quad \text{and} \quad \langle p(t) \rangle = \varphi t \quad (4.88)$$

both of which are consistent with the Ehrenfest equations. Note that $\langle x(t) \rangle$ has the familiar t^2 dependence of any particle under the influence of a constant force because, by Newton's second law, the acceleration is φ/m . The expectation value of the momentum is indeed Newton's second law because the force is the time rate of change of the (average) momentum.

Consider now the uncertainty in position $\Delta x(t)$. We already know $\langle x(t) \rangle$ so one method of obtaining $\Delta x(t)$ is to compute $\langle x(t)^2 \rangle$ using the momentum space wave function, Equation 4.84, and replacing x^2 in the integral with $\hbar^2 d^2/dp^2$. Alternatively, we could obtain $\Psi(x, t)$ by performing a Fourier transform on the momentum wave function, squaring, and identifying $\Delta x(t)$ by comparing with Equation 4.64. The Fourier transform yields

$$\Psi(x, t) = \frac{1}{\pi^{1/4}} \sqrt{\frac{\beta}{\gamma}} \exp \left[\frac{i\varphi t}{\hbar} \left(x - \frac{\varphi t^2}{6m} \right) \right] \cdot \exp \left\{ -\frac{[x - \varphi t^2/(2m)]^2}{(2\gamma/\beta^2)} \right\} \quad (4.89)$$

where, defining $t_0 = m/(\hbar\beta^2)$ as in Equation 4.73,

$$\gamma = 1 + \frac{it}{t_0} \quad \text{and} \quad t_0 = \frac{m}{\hbar\beta^2} = \frac{2m}{\hbar} \Delta x_0^2 \quad (4.90)$$

The probability density in coordinate space is then

$$|\Psi(x, t)|^2 = \frac{1}{\sqrt{\pi}} \left(\frac{1}{\sqrt{|\gamma|^2/\beta^2}} \right) \exp \left\{ -\frac{[x - \varphi t^2/(2m)]^2}{(|\gamma|^2/\beta^2)} \right\} \quad (4.91)$$

Comparing Equation 4.91 with Equation 4.64 we see that

$$2\Delta x(t)^2 = \frac{|\gamma|^2}{\beta^2} \quad (4.92)$$

so that in terms of $\Delta x(t)$ we have

$$|\Psi(x, t)|^2 = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{\Delta x(t)} \right) \exp \left\{ -\frac{[x - \varphi t^2/(2m)]^2}{2\Delta x(t)^2} \right\} \quad (4.93)$$

where, recalling that $\Delta x_0 = 1/(\sqrt{2}\beta)$

$$\Delta x(t) = \Delta x_0 \left(1 + \frac{t^2}{t_0^2} \right)^{1/2} \quad (4.94)$$

which is identical to Equation 4.71, again a consequence of the constant force being applied.

4.5.3 Case III. The Packet/Particle Subjected to a Harmonic Oscillator Potential

In this case we assume that we have a Gaussian wave packet that is a linear superposition of harmonic oscillator eigenstates and that we know the wave function in coordinate space $\Psi(x, 0)$. To be specific we choose an initial wave function of the form

$$\Psi(x, 0) = \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-\alpha^2(x-x_0)^2/2} \quad (4.95)$$

where, in this case, $\alpha = \sqrt{m\omega/\hbar}$, the same constant that appears in the eigenfunctions of the harmonic oscillator. The inclusion of a nonzero average displacement, however, assures us that Equation 4.95 is not an eigenfunction of the harmonic oscillator Hamiltonian. Of course, it may be expanded upon the complete set of harmonic oscillator eigenfunctions. Despite not being an eigenfunction, Equation 4.95 is nonetheless a Gaussian distribution with average displacement x_0 and zero initial momentum which (classically) is equivalent to pulling the particle to $x = x_0$

and releasing it with no initial momentum. Such a state is sometimes referred to as a displaced ground state. In the case studied here, the particle remains under the influence of the potential energy $U(x) = \frac{1}{2}kx^2$.

We wish to find the function $\Psi(x, t)$ so that we may determine the time dependence of the probability distribution $|\Psi(x, t)|^2$. There is no need to determine the momentum space wave function so we do not require any Fourier transforms. Using the superposition theorem we write

$$\Psi(x, t) = \sum_{n=1}^{\infty} a_n \psi_n(x) e^{-i(E_n/\hbar)t} \quad (4.96)$$

Of course, it makes sense to choose as our complete set, the $\psi_n(x)$, the harmonic oscillator eigenfunctions; the E_n in the exponents are then the corresponding harmonic oscillator energy eigenvalues. To complete the task we would have to multiply both sides by $\Psi(x, 0)$ and integrate, taking advantage of the orthogonality of the eigenfunctions. In this particular case, however, there is an easier way. It involves using the generating function for the Hermite polynomials. Although generating functions may seem intimidating, this exercise will illustrate the friendliness of such functions. Recall that for the Hermite polynomials the generating function is (see Table 3.2)

$$e^{2\mu\xi - \mu^2} = \sum_{n=0}^{\infty} \frac{H_n(\xi) \mu^n}{n!} \quad (4.97)$$

For simplicity of notation let us temporarily use the scaled distance $\xi = \alpha x$. The initial packet is

$$\Psi(\xi, 0) = \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-(\xi - \xi_0)^2/2} \quad (4.98)$$

which, with a prescient eye toward using the generating function we let $\xi_0 = 2\mu$ so that

$$\begin{aligned} \Psi(\xi, 0) &= \frac{\sqrt{\alpha}}{\pi^{1/4}} \exp\left[-\frac{\xi^2}{2} + 2\mu\xi - \mu^2\right] \\ &= \frac{\sqrt{\alpha}}{\pi^{1/4}} \exp\left[-\frac{\xi^2}{2} - \mu^2 + 2\mu\xi - \mu^2\right] \\ &= \frac{\sqrt{\alpha}}{\pi^{1/4}} \exp\left[-\left(\frac{\xi^2}{2} + \mu^2\right)\right] \cdot \exp(2\mu\xi - \mu^2) \end{aligned} \quad (4.99)$$

In this form, the last term is recognized as the generating function of the Hermite polynomials. We may therefore replace it using Equation 4.97:

$$\begin{aligned}
\Psi(\xi, 0) &= \frac{\sqrt{\alpha}}{\pi^{1/4}} \exp\left[-\left(\frac{\xi^2}{2} + \mu^2\right)\right] \sum_{n=0}^{\infty} \frac{H_n(\xi) \mu^n}{n!} \\
&= \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-\mu^2} \sum_{n=0}^{\infty} \frac{\mu^n}{n!} \left\{ e^{-\xi^2/2} H_n(\xi) \right\}
\end{aligned} \tag{4.100}$$

Notice, however, that the terms in the brackets in Equation 4.100 are precisely the harmonic oscillator eigenfunctions. Comparing Equation 4.100 with Equation 4.96 we see that we have “accidentally” calculated the expansion coefficients, the a_n .

To include the time in the wave function we multiply each harmonic oscillator eigenfunction in the summation by an exponential that contains the corresponding energy eigenvalue. Inserting the time dependence into Equation 4.100 we have

$$\begin{aligned}
\Psi(\xi, t) &= \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-\mu^2} \sum_{n=0}^{\infty} \frac{\mu^n}{n!} \left\{ e^{-\xi^2/2} H_n(\xi) \right\} \exp\left[-i\left(n + \frac{1}{2}\right)\omega t\right] \\
&= \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-\mu^2} e^{-i\omega t/2} \sum_{n=0}^{\infty} \frac{\mu^n}{n!} \left\{ e^{-\xi^2/2} H_n(\xi) \right\} e^{-in\omega t}
\end{aligned} \tag{4.101}$$

Removing $e^{-\xi^2/2}$ from the summation and regrouping the terms we have

$$\Psi(\xi, t) = \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-\mu^2} e^{-i\omega t/2} e^{-\xi^2/2} \sum_{n=0}^{\infty} \left[\frac{(\mu e^{-i\omega t})^n}{n!} H_n(\xi) \right] \tag{4.102}$$

Incredibly, the summation is the generating function for the Hermite polynomials with $\mu \rightarrow \mu e^{-i\omega t}$ as is easily seen from Equation 4.97. That is,

$$\sum_{n=0}^{\infty} \frac{H_n(\xi) (\mu e^{-i\omega t})^n}{n!} = \exp\left[2\xi \mu e^{-i\omega t} - (\mu e^{-i\omega t})^2\right] \tag{4.103}$$

so that, after substituting $\mu = \xi_0/2$, Equation 4.102 becomes

$$\Psi(\xi, t) = \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-i\omega t/2} \exp\left[-\left(\frac{\xi^2}{2} + \frac{\xi_0^2}{4}\right)\right] \cdot \exp\left[\xi_0 \xi e^{-i\omega t} - \frac{\xi_0^2}{4} e^{-2i\omega t}\right] \tag{4.104}$$

Converting to sines and cosines, we have

$$\begin{aligned}
\Psi(\xi, t) &= \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-i\omega t/2} \exp\left[-\frac{1}{2}\left(\xi^2 + \frac{\xi_0^2}{2}(1 + \cos 2\omega t) - 2\xi_0 \xi \cos \omega t\right)\right] \\
&\quad \times \exp\left[\frac{i}{2}\left(\frac{\xi_0^2}{2} \sin 2\omega t - 2\xi_0 \xi \sin \omega t\right)\right]
\end{aligned} \tag{4.105}$$

Finally, the time-dependent probability density is

$$\begin{aligned} |\Psi(\xi, t)|^2 &= \frac{\alpha}{\sqrt{\pi}} \exp \left\{ - \left[\xi^2 + \frac{\xi_0^2}{2} (1 + \cos 2\omega t) - 2\xi_0 \xi \cos \omega t \right] \right\} \\ &= \frac{\alpha}{\sqrt{\pi}} \exp \left[-(\xi - \xi_0 \cos \omega t)^2 \right] \end{aligned} \quad (4.106)$$

or, in terms of the coordinate x ,

$$|\Psi(x, t)|^2 = \frac{\alpha}{\sqrt{\pi}} \exp \left[-\alpha^2 (x - x_0 \cos \omega t)^2 \right] \quad (4.107)$$

Equation 4.107 shows that the wave packet oscillates about $x = 0$ so the expectation value of position as a function of time is (see Problem 18)

$$\langle x(t) \rangle = x_0 \cos \omega t \quad (4.108)$$

Comparison with Equation 4.64 shows that the uncertainty in position is

$$\Delta x(t) = \frac{1}{\sqrt{2}\alpha} = \Delta x_0 \quad (4.109)$$

which is time-independent. The packet oscillates without any change in shape! (Remember, the harmonic oscillator is special.) This was first pointed out by Schrödinger in 1926 and is often referred to as *the* coherent state, but, in truth, it is really *a* coherent state. We will return to this state in a future chapter. The reason for this special behavior is that the energy levels are equally spaced. There are few other systems that exhibit such a feature. The behavior is illustrated in Fig. 4.3 at three different values of the time.

There are some other interesting features of this wave packet. Rewriting $\Psi(\xi, 0)$ from Equation 4.100 we have

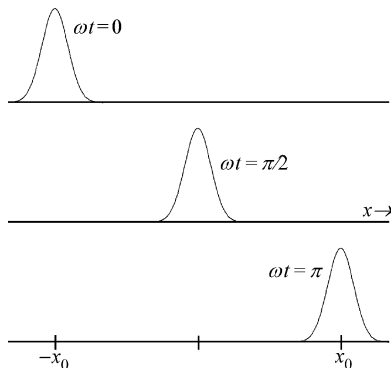


Fig. 4.3 A Gaussian wave packet under the influence of a harmonic oscillator potential shown at three different times. Note that the shape of the packet does not change

$$\begin{aligned}
\Psi(\xi, 0) &= \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-\xi_0^2/4} \sum_{n=0}^{\infty} \frac{(\xi_0/2)^n}{n!} e^{-\xi^2/2} H_n(\xi) \\
&= \sum_{n=0}^{\infty} \left(\frac{\xi_0^n e^{-\xi_0^2/4}}{\sqrt{2^n n!}} \right) \left[\sqrt{\frac{\alpha}{2^n n!}} \frac{1}{\pi^{1/4}} e^{-\xi^2/2} H_n(\xi) \right] \quad (4.110)
\end{aligned}$$

The form of this last equation isolates the expansion coefficients a_n in Equation 4.96 because the expression in the square brackets represents the normalized harmonic oscillator eigenfunctions (see Equation 3.49). Thus,

$$\begin{aligned}
a_n &= \frac{\xi_0^n e^{-\xi_0^2/4}}{\sqrt{2^n n!}} \\
&= \frac{\alpha^n x_0^n e^{-\alpha^2 x_0^2/4}}{\sqrt{2^n n!}} \quad (4.111)
\end{aligned}$$

As $x_0 \rightarrow 0$ it is clear from the form of the initial wave packet that it approaches the ground state of the harmonic oscillator, a stationary state. It might be said that the packet oscillates about $x = 0$ with zero amplitude. Thus, we expect that $a_0 = 1$ and all other expansion coefficients vanish. Note that in Equation 4.111 the limit as $x_0 \rightarrow 0$ for $n = 0$ is indeterminate because zero to the zero power is indeterminate. On the other hand,

$$\lim_{x_0 \rightarrow 0} a_n \equiv 0 \text{ for all } n \geq 1 \quad (4.112)$$

so we conclude that, in this case, indeed, the mathematics yield $a_0 = 1$.

In the opposite extreme the correspondence principle tells us that the motion should emulate that of a classical oscillator. In that case it can be shown that for large x_0 high harmonic oscillator eigenstates make significant contributions. Moreover, for high n the maximum contribution to the admixture comes from the state that has the same energy as the classical oscillator having amplitude x_0 (see Problem 19).

4.6 Retrospective

Wave packets provide the crucial link between classical and quantum physics. Understanding of this concept should not be obscured by the morass of Fourier transforms attendant to the mathematical description of wave packets. While quantum mechanics permits particles to retain their pointlike properties, the probabilistic nature of quantum physics manifests itself via constructive and destructive interference of probability waves that produce localized probability distributions, thus emulating the characteristics of a classical particle. As we have seen, however, the

price that Mr. Heisenberg exacts from us for having precise knowledge of position is that we must ante up by relinquishing knowledge of the particle's momentum. On the other hand, a pure de Broglie wave is the antithesis of such a particle. Here we have precise knowledge of the momentum so we must pay by having no idea of the particle's position. Such is the life of a quantum mechanic. Mathematically, Fourier transforms account for the Heisenberg uncertainty principle, but physical comprehension should trump mathematical quagmires.

Problems

1. Derive the Ehrenfest equation that is the relationship between the expectation values of the time rate of change of momentum and the force.
2. To see how the superposition of waves can cause the probability density to cluster, add two waves of differing frequencies and make a plot of their sum as a function of time at a fixed value of x . For ease of computation use $\Psi_1(x, t) = 15x \cos t$ and $\Psi_2(x, t) = -3x \cos(17t)$. The trigonometric identity $\cos A - \cos B = 2 \sin \left[\frac{1}{2}(A + B) \right] \sin \left[\frac{1}{2}(B - A) \right]$ will be helpful.
3. Find $(\Delta x)^2 = \langle x^2 \rangle$ and $(\Delta p)^2 = \langle p^2 \rangle$ for the ground state of the harmonic oscillator to show that, indeed, $\Delta x \Delta p \equiv \frac{1}{2} \hbar$ for a Gaussian wave function.
4. For the wave functions

$$\Psi(x, 0) = \frac{\sqrt{\beta}}{\pi^{1/4}} e^{-\beta^2(x-x_0)^2/2} e^{ip_0x/\hbar}$$

and

$$\Phi(p, 0) = \frac{1}{\pi^{1/4} \sqrt{\beta \hbar}} e^{-(p-p_0)^2/2\beta^2 \hbar^2} \cdot e^{-ipx_0/\hbar}$$

show that $\langle x \rangle = x_0$ and $\langle p \rangle = p_0$. Do the calculations in both coordinate and momentum space.

5. (a) Show that for $\phi(p) = \frac{1}{\pi^{1/4} \sqrt{\hbar \beta}} e^{-(p-p_0)^2/(2\beta^2 \hbar^2)}$, $\langle p \rangle = p_0$ and $\langle p^2 \rangle = \frac{\beta^2 \hbar^2}{2} + p_0^2$ so that $(\Delta p)^2 = \langle p^2 \rangle - \langle p \rangle^2 = \frac{\beta^2 \hbar^2}{2}$.
 (b) Show that both of these average values are independent of time.
6. Show that for the Gaussian wave packet

$$\Psi(x, 0) = \frac{\sqrt{\beta}}{\pi^{1/4}} e^{-\beta^2(x-x_0)^2/2}$$

the uncertainty in position and momentum at $t = 0$ are $\Delta x = 1/(\sqrt{2}\beta)$ and $\Delta p = (\beta \hbar / \sqrt{2})$.

7. For a free particle Gaussian wave packet for which

$$\Psi(x, 0) = \frac{\sqrt{\beta}}{\pi^{1/4}} e^{-\beta^2(x-x_0)^2/2} \cdot e^{ip_0x/\hbar}$$

and

$$\Phi(p, 0) = \frac{1}{\pi^{1/4} \sqrt{\beta \hbar}} e^{-(p-p_0)^2/2\beta^2 \hbar^2} \cdot e^{-ipx_0/\hbar}$$

show that

- (a) the time-dependent expectation value of the position $\langle x(t) \rangle$ is consistent with the first of Ehrenfest equations, Equation 4.7.
- (b) the uncertainty in position as a function of time is given by

$$\Delta x(t) = \frac{1}{\sqrt{2}\beta} \sqrt{1 + \left(\frac{\beta^2 \hbar}{m} \right)^2 t^2}$$

8. Show that the normalization is preserved in time for the free Gaussian wave packet for which the probability density is given by Equation 4.69.
9. Prove the property of δ -functions: $\delta(ax) = (1/|a|) \delta(x)$.
10. At $t = 0$ a position measurement of a particle of mass m in an a -box reveals it to be in the middle of the box.
 - (a) What is the wave function in coordinate space at $t = 0$? Do not attempt to normalize!
 - (b) Find the probabilities that a measurement of the energy of the particle at $t = 0$ will yield each of the energy eigenvalues. Why was normalization not recommended?
 - (c) Could you have guessed at least part of the answer to Part b?
 - (d) Find the wave function for $t > 0$.
11. Use Equation 2.28 to write the TISE in momentum representation for the harmonic oscillator and find the normalized momentum energy eigenfunctions.
12. Show that Equation 4.78 can be solved using the substitutions given in Equation 4.79 and that the result is

$$\Phi(p, t) = \Theta(p - \varphi t) \exp\left(-\frac{ip^3}{6m\hbar}\right)$$

13. Derive Equation 4.83 if the initial wave packet is given by Equation 4.77 and it is under the influence of a constant force φ .
14. Use Equation 2.28 to write the TISE in momentum representation for the potential

$$\begin{aligned}
 U(x) &= eFx & x > 0 \\
 &= \infty & x \leq 0
 \end{aligned}$$

where the product eF is a constant and find the unnormalized momentum energy eigenfunctions.

15. Show that for an initial Gaussian wave packet having expectation values $\langle x(t=0) \rangle = x_0 = 0$ and $\langle p(t=0) \rangle = p_0 = 0$, Equation 4.77, the expectation values as a function of time are given by

$$\langle x(t) \rangle = \frac{\varphi t^2}{2m} \quad \text{and} \quad \langle p(t) \rangle = \varphi t$$

16. Supply the missing steps in the derivation of the time-dependent Gaussian wave function, Equation 4.106, under the influence of a harmonic oscillator potential.
17. Perform the integration in which the Fourier transform of the ground state wave function of the harmonic oscillator in coordinate space

$$\psi_0(x) = \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-\alpha^2 x^2/2}$$

is shown to be the ground state wave function of the harmonic oscillator in momentum space (see Problem 11):

$$\phi_0(p) = \frac{1}{\pi^{1/4} \sqrt{\alpha \hbar}} e^{-p^2/(2\alpha^2 \hbar^2)}$$

18. Show that for Case III in Section 4.5 the expectation value of x is given by Equation 4.108 thus confirming that the wave packet oscillates about $x = 0$.
19. Show that for the Gaussian wave packet subjected to a harmonic oscillator potential and having large average displacement from the origin x_0 , the energy of the eigenstate giving maximum contribution to the admixture is equal to that of the classical oscillator having average displacement of the packet. Ignore the zero-point energy. Apply Stirling's approximation to the logarithm of the expansion coefficient for large n and then maximize n . Stirling's approximation is: $\ln n! \approx n \ln n - n$.

Chapter 5

Stationary States in One Dimension II

In this chapter we continue the work begun in Chapter 3 on solutions of the TISE for one-dimensional potentials. The two potentials that were studied in detail in that chapter, the infinite potential well (particle-in-a-box) and the harmonic oscillator, are perhaps the most important of these potentials from a pedagogical point of view, but other potentials offer additional insight into quantum physics. We emphasize that stationary states are not necessarily bound states as we will see in the first example.

5.1 The Potential Barrier

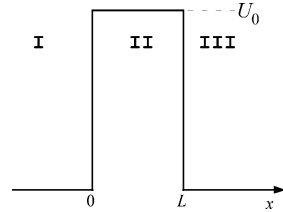
In Section 3.2 we discussed penetration of the classically forbidden region by a particle. This concept was elaborated upon in Section 3.2.1 where the TISE was solved for an infinite square well with a barrier inside the well. It was found that penetration of the barrier inside the well could lead to the appearance of the particle on either side of the barrier, even though the particle did not have sufficient energy to surmount the barrier in the middle of the well. In this section we will examine further the effects of a barrier on a (previously) free particle. Indeed, we can imagine that if the particle penetrates far enough into the barrier it could well materialize on the classically forbidden side of the barrier. This is referred to as the tunnel effect.

It might be supposed that the solution already obtained for bound state problem for the barrier inside the square well might be extended by taking the limit as the walls of the square well approach infinity. This approach, while aesthetically appealing, actually offers no simplification over beginning the problem anew. We therefore consider a potential energy function

$$\begin{aligned} U(x) &= 0 & x < 0 \\ &= U_0 & 0 < x < L \\ &= 0 & x > 0 \end{aligned} \tag{5.1}$$

which is a rectangular barrier as shown in Fig. 5.1. The notation is intended to be consistent with that used for the L -box.

Fig. 5.1 The potential barrier as described in the text. The three regions of space in which the TISE must be solved are designated by Roman numerals



The most interesting case to consider is that in which a free particle of kinetic energy $E < U_0$ is incident from the left of the barrier (moving in the $+x$ direction). The momentum of this particle is k so the kinetic energy $E = \hbar^2 k^2 / 2m$. Classically, the particle would simply bounce off the barrier and move in the $-x$ direction and that would be that. Nothing interesting would happen. Perhaps the barrier would heat up due to an inelastic collision, but that is not our concern here. We are interested in more esoteric quantum effects.

To investigate the effect of the barrier on the moving particle we solve the TISE in each of the three regions of space indicated in Fig. 5.1. We assume that a particle is incident from the left of the barrier traveling in the $+x$ direction and seek the probability that the particle will be reflected upon encountering the barrier. This will provide the probability of transmission through the barrier inasmuch as there are only two possibilities, reflection or transmission. The probability of transmission is simple to comprehend. It is the absolute square of any portion of the wave function that we find that is nonzero in region III. Because quantum mechanics permits the incoming beam to penetrate the classically forbidden region, the barrier, this penetration could be sufficiently deep to allow it to seep through the barrier and emerge into region III. In other words, if a particle makes it a distance L through the barrier it has indeed tunneled its way through. Classically this is nonsense. Quantum mechanically it is perfectly reasonable.

Before solving the TISE let us discuss the physical situation from another point of view. Suppose instead of a single particle incident on the barrier, we have a beam of particles, all of the same energy, a monoenergetic beam. In this case the formulation of the problem is identical to that for the single particle except that for a beam the probabilities give the fraction of particles reflected and transmitted. Frequently the discussion involves the “flux” of incident, reflected, and transmitted particles, but often the term flux is applied to the probability current. In this sense the word is similar to its application in electricity and magnetism. Nonetheless, incident beams of particles are used in many experiments in physics. These are referred to as scattering experiments. Either point of view is satisfactory.

From our experience with the barrier in the square well we can immediately write the wave function in the three regions of space. For completeness we will include the time dependence.

$$\begin{aligned}
\Psi_I(x, t) &= (Ae^{ikx} + Be^{-ikx})e^{-i\omega t} \\
\Psi_{II}(x, t) &= (Ce^{\kappa x} + De^{-\kappa x})e^{-i\omega t} ; \quad \kappa^2 = 2m(U_0 - E)/\hbar \\
\Psi_{III}(x, t) &= (Fe^{ikx} + Ge^{-ikx})e^{-i\omega t}
\end{aligned} \tag{5.2}$$

(Note that we did not use E as one of the constants of integration to avoid confusion with the energy.) We evaluate the constants of integration by matching the boundary conditions. That is, we must match the wave functions and their derivatives at $x = 0$ and at $x = a$. Before doing so, however, let us understand the form of the wave functions in Equations 5.2. We see that the time dependences all have the same value ω . What is ω ? As usual, it is the energy corresponding to the spatial part of the wave function. In regions I and III the energy is all in the form of kinetic energy E . In region II the energy is divided between kinetic and potential energy, but the total energy is, nonetheless, E . Therefore, the ω 's in Equation 5.2 are all the same and, for the purpose of determining the constants, we can ignore them. It is possible to eliminate one of the constants in Equation 5.2 before we begin matching the boundary conditions. The first terms in regions I and III, $e^{i(kx - \omega t)}$, represent plane waves traveling in the $+x$ direction while the second, $e^{-i(kx + \omega t)}$, describes a plane wave traveling in the $-x$ direction. We are prepared to entertain the possibility that the particle will be reflected as would a classical particle. Therefore, there is a plane wave traveling in the $-x$ direction in region I so that $B \neq 0$. On the other hand, initially there was no beam moving in that direction in region III so it is absurd to imagine that one would appear, even in quantum mechanics. Therefore, the constant $G = 0$. Finally, as in the barrier in the square well, we cannot discard the positive real exponential in region II because this region does not extend to infinity. Both exponentials must be retained.

Ignoring the time dependence because this is a state we have

$$\begin{aligned}
\psi_I(x) &= Ae^{ikx} + Be^{-ikx} & x < 0 \\
\psi_{II}(x) &= Ce^{\kappa x} + De^{-\kappa x} & 0 < x < L \\
\psi_{III}(x) &= Fe^{ikx} & L < x
\end{aligned} \tag{5.3}$$

Before applying the boundary conditions and solving for the constants let us examine their meanings. This will lead to some simplification in the calculations. If we apply the equation of continuity, Equation 2.21, to $\psi_I(x)$ and $\psi_{III}(x)$, we find that the probability currents (see Problem 4, Chapter 2) in the two regions are

$$j_I(x) = \frac{\hbar k}{m} (|A|^2 - |B|^2) \tag{5.4}$$

and

$$j_{III}(x) = \frac{\hbar k}{m} |F|^2 \tag{5.5}$$

Now, the two terms in $j_I(x)$ represent the incident and reflected probability currents, respectively. Note that $\hbar k/m$ is simply the particle velocity and the amplitudes represent the probabilities associated with the incoming and reflected probabilities, respectively. It is now clear that we should measure the transmission and reflection in terms of the probability currents. An obvious definition is that the transmission coefficient T should be defined as the ratio of the transmitted probability current to the incident current so that

$$\begin{aligned} T &= \frac{\frac{\hbar k}{m} |F|^2}{\frac{\hbar k}{m} |A|^2} \\ &= \frac{|F|^2}{|A|^2} \end{aligned} \quad (5.6)$$

Similarly, the reflection coefficient is

$$R = \frac{|B|^2}{|A|^2} \quad (5.7)$$

and we must have

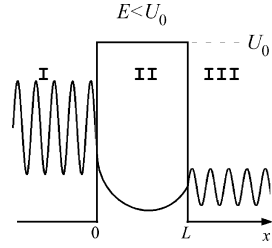
$$R + T = 1 \quad (5.8)$$

Note that the particle velocity does not appear in the expression for T . This is because the particle velocity in region III is the same as it is in region I *in this problem*. If, for example, the potential energy on the right-hand side of the barrier were, say, $(1/2)U_0$, but zero to the left of the barrier, then the velocities would enter into the equation for T . Of course, this is not a consideration for R because the incident and reflected waves occupy the same region of space. Incidentally, a more judicious choice for the constants would have been to choose $A = 1$ since we can normalize the incident probability to any number we please, unity being particularly convenient. We will, however, keep the constants we have chosen for the time being.

As discussed at length in Chapter 2, we can sketch the wave functions before we evaluate the constants. The nature of these wave functions is shown in Fig. 5.2. While these are merely sketches, they do contain the essential features including continuity of the wave functions and their derivatives at the boundaries. Notice that the de Broglie wavelength in regions I and III are the same although the amplitude in region III has been reduced on the presumption that there will be some reflection at the barrier. The curvature of the wave function inside the classically forbidden barrier is away from the x -axis.

Applying continuity of the wave function and its derivative at $x = 0$ and $x = L$ we have

Fig. 5.2 Sketch of the wave functions for a particle incident on a rectangular barrier from the left traveling with energy $E < U_0$



$$\begin{aligned}
 A + B &= C + D \\
 ik(A - B) &= \kappa(C - D) \\
 Ce^{\kappa L} + De^{-\kappa L} &= Fe^{ikL} \\
 \kappa(Ce^{\kappa L} - De^{-\kappa L}) &= ikFe^{ikL}
 \end{aligned} \tag{5.9}$$

These are four simultaneous equations with five unknowns. Because we are free to choose any one of them we elect to set $A = 1$. Moreover, the constants C and D are patently uninteresting. It is only B and F that give the information that we desire. One way to solve these equations for only the constants that we desire is to use the method of determinants. While the algebra is uninspiring, the result is of interest. We obtain

$$T_{E < U_0} = \left[1 + \frac{1}{4} \left(\frac{k^2 + \kappa^2}{k\kappa} \right)^2 \sinh^2(\kappa L) \right]^{-1} \tag{5.10}$$

After substituting the original parameters back into the equations we obtain

$$T_{E < U_0} = \frac{1}{\left[1 + \frac{U_0^2}{4E(U_0 - E)} \sinh^2 \left(\frac{L}{\hbar} \sqrt{2m(U_0 - E)} \right) \right]} \tag{5.11}$$

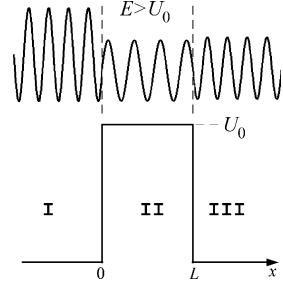
and, using Equation 5.8, we have

$$R_{E < U_0} = \left[1 + \frac{4E(U_0 - E)}{U_0^2 \sinh^2 \left(\frac{L}{\hbar} \sqrt{2m(U_0 - E)} \right)} \right]^{-1} \tag{5.12}$$

Equation 5.11 shows that, as we predicted, there is transmission through the barrier even when $E < U_0$. Because the transmission coefficient depends upon the hyperbolic sine there are, however, no interference effects.

There are some interesting effects even when $E > U_0$. In this case the wave function inside the barrier is sinusoidal rather than exponential, but the de Broglie wavelength is longer than it is outside the barrier because the kinetic energy inside

Fig. 5.3 Sketch of the wave functions for a particle incident on a rectangular barrier from the left travelling with energy $E > U_0$



the barrier is reduced. Fig. 5.3 shows the barrier together with a sketch of the wave function in each of the three regions of space.

Because the only difference between this case and the case for which $E < U_0$ is the sinusoidal wave function in the barrier, the only changes that must be made are in the third and fourth of Equations 5.9. We do not have to solve the problem again. We merely make the substitution $\kappa \rightarrow ik'$ where $k' = \sqrt{2m(E - U_0)}$ in Equation 5.10 noting that $\sinh ix = i \sin x$. The transmission coefficient is therefore

$$\begin{aligned}
 T_{E>U_0} &= \left[1 + \frac{1}{4} \left(\frac{k^2 - k'^2}{kk'} \right)^2 \sin^2(k'L) \right]^{-1} \\
 &= \left[1 + \frac{U_0^2}{4E(E - U_0)} \sin^2 \left(\frac{L}{\hbar} \sqrt{2m(E - U_0)} \right) \right]^{-1} \\
 &= \frac{4E(E - U_0)}{4E(E - U_0) + U_0^2 \sin^2 \left(\frac{L}{\hbar} \sqrt{2m(E - U_0)} \right)} \quad (5.13)
 \end{aligned}$$

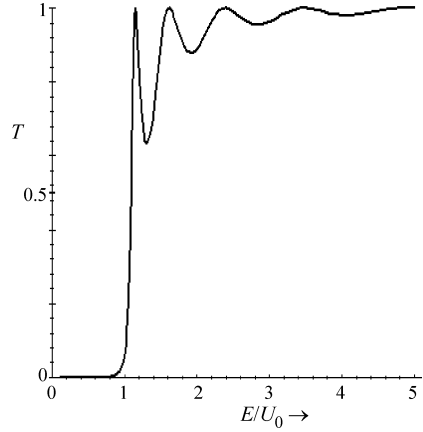
The reflection coefficient is, according to Equation 5.8,

$$R_{E>U_0} = \left[1 + \frac{4E(E - U_0)}{U_0^2 \sin^2 \left(\frac{L}{\hbar} \sqrt{2m(E - U_0)} \right)} \right]^{-1} \quad (5.14)$$

While we found the counterintuitive result that transmission occurs for $E < U_0$, it is equally surprising that reflection occurs for $E > U_0$. That is, there is not total transmission for all values of $E > U_0$. There is total transmission only when the sine function in Equation 5.13 vanishes which occurs when the argument of the sine is equal to integral values of π . Fig. 5.4 is a plot of the transmission as a function of E/U_0 for this ratio greater than and less than unity, that is, the figure contains both Equations 5.11 and 5.13 in a single graph.

It is clear that there are resonances in the transmission (and reflection) for $E/U_0 > 1$. One way to view these resonances is that the classically illogical

Fig. 5.4 The transmission coefficient T as a function of the ratio E/U_0



reflections occur when de Broglie waves fail to “fit” in the barrier. This can be seen by writing the last of Equations 5.13 in terms of the de Broglie wavelength *in the barrier* $\lambda_d = \sqrt{2m(E - U_0)}/h$.

$$T_{E>U_0} = \frac{4E(E - U_0)}{4E(E - U_0) + U_0^2 \sin^2 \left[2\pi \left(\frac{L}{\lambda_d} \right) \right]} \quad (5.15)$$

Now imagine keeping the ratio of the incident particle energy E to the barrier height U_0 fixed and plot $T_{E>U_0}$ versus the ratio L/λ_d as shown in Fig. 5.5.

From this figure it is seen that perfect transmission occurs when the barrier width is an integral multiple of half de Broglie wavelengths. This phenomenon is identical to that which occurs in optics and is the basis for the operation of the Fabry-Perot interferometer.

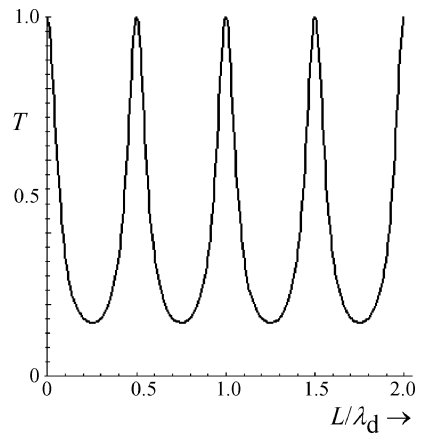


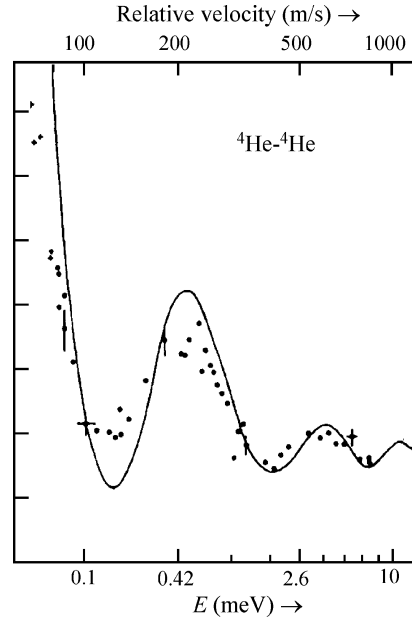
Fig. 5.5 The transmission coefficient for a rectangular barrier as a function of the ratio of the barrier width to the deBroglie wavelength of the particles inside the barrier. The ratio E/U_0 is fixed at a value greater than unity

Although the one-dimensional barrier might seem to be a contrived example, it does exhibit features encountered in nature. Physicists often make rather audacious approximations merely to get an answer, any answer, just to get an idea of what is going on. There is a famous story about the multinational company that took over an unsuccessful racetrack. To rehabilitate their finances the company brought in experts including nutritionists, veterinarians, and a lone physicist. On the appointed day all gave their reports, the last being by the physicist who began with “ladies and gentlemen, consider the horse as a sphere.” Well, the rectangular barrier is such an approximation to, say, an atom. Certainly it doesn’t look like an atom, but it does have some features that, believe it or not, can simulate an atom. We must, however, be careful with our expectations. For example, we cannot compare the resonances in the transmission to those that Franck and Hertz observed in their experiments. Why? Because their experiments were inelastic scattering experiments. They observed transfer of kinetic energy to internal energy of the mercury atoms. The fact that the energy transferred had to be quantized was a manifestation of the quantum nature of the bound states of atoms, analogous to the bound states that we have already studied. Notwithstanding, the type of resonances encountered in the barrier problem have indeed been observed in atomic scattering experiments. In the 1920s C. Ramsauer and J. Townsend, independently, discovered that when electrons were scattered from inert gas atoms there were certain electron energies at which the gas seemed to be transparent to the electrons. This is elastic scattering because there is no internal energy change in the inert gas atoms as there was in the mercury atoms in the Franck–Hertz experiments. In other words, there was nearly total transmission of the electrons through the gas at energies corresponding to resonant de Broglie wavelengths. This is almost the problem we have been discussing, but not quite because the electron inert gas interaction is an attractive one so, rather than a barrier, the analogy with a one-dimensional problem would be to scattering from a (finite) square *well* (see Problem 7, Chapter 2). In fact, the mathematics is identical. All that is required is to make the substitution $U_0 \rightarrow -U_0$. The result is that instead of the de Broglie wavelength inside the barrier being longer than outside, the de Broglie wavelength inside the well is shorter than outside because the kinetic energy, and hence the momentum, is greater.

Since the original electron–rare gas experiments were performed, a great deal of effort has been devoted to investigating other collision systems searching for similar effects. One such experiment that is analogous to the barrier potential is helium–helium scattering [3]. Helium atoms do not form diatomic molecules because the interatomic potential for helium atoms in their ground states is repulsive. Likening these atoms to the spherical horse, we approximate the interatomic potential as a rectangular barrier. Figure 5.6 shows the actual data from the helium–helium scattering experiment [3] in which the Ramsauer–Townsend effect was observed.

The lower abscissa in this figure is the relative energy E while the upper abscissa is the relative velocity which is the form in which the original data were presented. The ordinate is the “scattering cross section” which is a measure of the degree to which the incoming He atoms are scattered. In the context of our discussion, the scattering cross section may be considered to be analogous to the *reflection*

Fig. 5.6 Data showing elastic scattering of helium atoms on helium atoms excerpted with permission from Reference [3]. Copyrighted by the American Physical Society. The ordinate represents the probability that a He atom is scattered. The minimum near $E = 0.1$ meV is the Ramsauer minimum and represents a *maximum* in the transmission



coefficient. Thus, the dip in the data just above $E = 0.1$ eV, which is known as a Ramsauer minimum, corresponds to a maximum in transmission. This represents a matching of the de Broglie wavelengths of the barrier that is presented by one helium atom to another. (It is not known as to why the minimum is not referred to as a Ramsauer–Townsend minimum.)

5.2 The Potential Step

The potential step, as depicted in Fig. 5.7, might, at first, seem to be a special case of the barrier. That is, we should be able to obtain the reflection and transmission coefficients by simply taking the appropriate limits as $L \rightarrow \infty$. Indeed, this can be done, but there are some interesting aspects of this problem that are not apparent from the solution of the potential barrier.

If $E < U_0$, it is a simple matter to take the limit as $L \rightarrow \infty$ because $\lim_{x \rightarrow \infty} \sinh^2 x = \infty$. Thus, from Equations 5.11 and 5.12 we see immediately that the reflection coefficient is unity while the transmission coefficient vanishes. This is

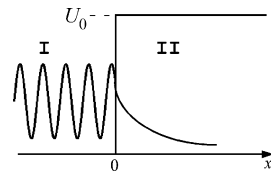


Fig. 5.7 Potential step and a sketch of the wave function for incident energy $E < U_0$, the height of the step

sensible because, no matter how far the particle penetrates the semi-infinite barrier it must eventually be squirted back into region I as indicated by the sketched wave function in Fig. 5.7.

The case for which $E > U_0$ presents a bit of a mathematical dilemma since one cannot take the limit of a sine function as the argument approaches infinity. Moreover, we must consider the fact that the particle velocities in the two regions of space are different. Recall that in regions I and III in the case of the finite barrier the particle velocities were the same. Using the same notation as that in Section 5.1 we write the wave function for this step as

$$\begin{aligned}\psi_I(x) &= Ae^{ikx} + Be^{-ikx} & x < 0 \\ \psi_{II}(x) &= Fe^{ik'x} & 0 < x\end{aligned}\quad (5.16)$$

Because the wave numbers are real in both regions of space we designate them by $k = \sqrt{2mE}/\hbar$ and $k' = \sqrt{2m(E - U_0)}/\hbar$ for regions I and II, respectively. The probability currents are then

$$\begin{aligned}j_I(x) &= \frac{\hbar k}{m} (|A|^2 - |B|^2) \\ j_{II}(x) &= \frac{\hbar k'}{m} |F|^2\end{aligned}\quad (5.17)$$

and, as before,

$$R = \frac{|B|^2}{|A|^2}\quad (5.18)$$

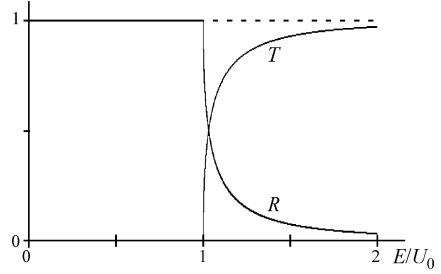
In this case, however, T must be the ratio of the intensity of the transmitted probability current to the incident probability current (see Problem 4, Chapter 2) which is given by the ratio

$$T = \frac{\frac{\hbar k'}{m} |F|^2}{\frac{\hbar k}{m} |A|^2}\quad (5.19)$$

Solving for the coefficients A , B , and F yields R and T (see Problem 4) and, including the results for $E < U_0$, we have

$$\begin{aligned}R &= \frac{(1 - \sqrt{1 - U_0/E})^2}{(1 + \sqrt{1 - U_0/E})^2} & E > U_0 \\ &= 1 & E < U_0\end{aligned}\quad (5.20)$$

Fig. 5.8 The transmission and reflection coefficients R and T for a step function potential as a function of E/U_0



and

$$T = \frac{4\sqrt{1 - U_0/E}}{(1 + \sqrt{1 - U_0/E})^2} \quad E > U_0$$

$$= 0 \quad E < U_0 \quad (5.21)$$

From Equations 5.20 and 5.21 it can be seen that there is perfect reflection and zero transmission when $E = U_0$, but that the reflection decreases monotonically for higher values of the incident energy. As expected, the transmission approaches unity for high values of the incident energy. Figure 5.8 shows graphs of the reflection and transmission coefficients. The feature of the potential step that is not present in the case of the potential barrier is the necessity of accounting for the different speeds of the particle in the two regions of space.

5.3 The Finite Square Well—Bound States

The potential energy function for a finite square well may be written as

$$U(x) = 0 \quad x < -a$$

$$= -U_0 \quad -a < x < a$$

$$= 0 \quad x > a \quad (5.22)$$

where U_0 is a positive number. This well is shown in Fig. 5.9.

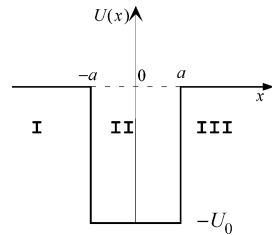


Fig. 5.9 Finite square well potential having $-U_0 \leq U(x) \leq 0$

As was noted in Section 5.1, the positive energy states of such a well form a continuum. These are the scattering solutions. Suppose, however, that a particle is bound in the well so that the TME of the particle is in the range $-U_0 < E < 0$. We expect that the solution of the TISE will yield quantized bound states. The study of a well of finite depth provides the opportunity to examine a condition that we have not yet encountered. Previously we solved the TISE for the bound states of potential energy functions that extended to infinity, the infinite square well and the harmonic oscillator. Such wells support an infinite number of bound states because the particle will always be confined. For a well of *finite* depth, however, we expect, in general, a limited number of bound states, if indeed the well can support any bound states at all. It may be that the parameters of the well are such that even a single bound state cannot fit in the well. The finite square well provides the opportunity to examine the conditions under which a limited number of bound states can exist and to determine the number of such bound states that a given well will support.

We have chosen $U(x)$ to be centered on the ordinate to take advantage of the parity of the eigenfunctions. The zero of potential energy is at the top of the well so bound states can only occur for values of the energy $E < 0$. Notice that, in contrast to the (infinite) a -box, the width of this well is $2a$, not a . This dimension was chosen for mathematical convenience. Because the eigenfunctions must have definite parity, we need only work with two of the three regions of space. The TISE in regions II and III are

$$\begin{aligned} \frac{d^2\psi_{II}(x)}{dx^2} + k^2\psi_{II}(x) &= 0; \quad k = \sqrt{2m(E + U_0)}/\hbar^2 \\ \frac{d^2\psi_{III}(x)}{dx^2} - \kappa^2\psi_{III}(x) &= 0; \quad \kappa = \sqrt{2m(-E)}/\hbar^2 \end{aligned} \quad (5.23)$$

Before discussing the solutions of these equations let us discuss the signs of k and κ . For bound states $E < 0$ so κ is real and the $\psi_{III}(x)$ will curve away from the abscissa as a decreasing exponential. The depth of the well U_0 is, by our definition, a positive number (see Fig. 5.9) so $|E| < U_0$. Therefore, k is real and $k^2 > 0$. This assures us that the wave functions inside the well will curve toward the abscissa. Because the TME E must be less than zero, κ is also real.

We proceed as we did when we solved the problem of the barrier within the infinite square well. We can use our knowledge that the wave functions have definite parity to shorten the task. First, we know that the solutions to the TISE in region II will be linear combinations of sines and cosines. That is,

$$\psi_{II}(x) = C \sin kx + D \cos kx \quad (5.24)$$

where C and D are constants. Because the wave function must be odd or even, *either* C or D must vanish. The solutions in regions I and III are

$$\psi_I(x) = Ae^{\kappa x} + Be^{-\kappa x} \quad (5.25)$$

and

$$\psi_{III}(x) = Fe^{\kappa x} + Ge^{-\kappa x} \quad (5.26)$$

As usual, the increasing exponential cannot be present in the classically forbidden regions I and III because these regions extend to $x = \pm\infty$ so we must set $B = F = 0$. Moreover, again from parity considerations, we know that $A = \pm G$, where the sign will be chosen to conform with the known parity of the eigenfunction. We have then two sets of solutions, one even and one odd. We list the even ones first because we know that they will include the nodeless ground state.

even

$$\begin{aligned} \psi_I(x) &= Ae^{\kappa x} \\ \psi_{II}(x) &= D \cos kx \\ \psi_{III}(x) &= Ae^{-\kappa x} \end{aligned} \quad (5.27)$$

odd

$$\begin{aligned} \psi_I(x) &= Ae^{\kappa x} \\ \psi_{II}(x) &= D \sin kx \\ \psi_{III}(x) &= -Ae^{-\kappa x} \end{aligned} \quad (5.28)$$

To solve for the energies of the bound states it is not necessary to evaluate the constants. To eliminate them we apply the boundary conditions to the wave functions and their derivatives. At this point it is useful to introduce the logarithmic derivative. Rather than apply the boundary conditions to the wave function and its derivative separately we demand continuity of the logarithmic derivative of the wave function. Why the logarithmic derivative? Because it is the same as applying the boundary conditions on the wave function and its derivative and then dividing each side to eliminate the constants. It is some fancy, but universally used semantics, but, because the constants fall out immediately, it is a convenient mathematical construction.

The logarithmic derivative is defined as

$$\text{logarithmic derivative} = \frac{1}{\psi(x)} \frac{d\psi(x)}{dx} \quad (5.29)$$

Requiring continuity of the logarithmic derivative at $x = a$ for the even eigenfunctions we have

$$\frac{1}{D \cos ka} (-Dk \sin ka) = \frac{1}{Ge^{-\kappa a}} - \kappa Ge^{-\kappa a} \quad (5.30)$$

or

$$k \tan ka = \kappa \quad (5.31)$$

Similarly, for the odd eigenfunctions

$$k \cot ka = -\kappa \quad (5.32)$$

Equations 5.31 and 5.32 are deceptively simple. They cannot yield the wave functions because the constants have been eliminated, but the quantized energies are contained in these equations, buried in k and κ . Unfortunately, these equations are transcendental, meaning that they cannot be solved in closed form for E . This is not a problem today with modern computers, but our goal here is an understanding of the physics, not necessarily to crank out solution after solution for various parameters. Actually, solving the transcendental equations the old-fashioned way, graphically, does indeed provide insight into the nature of the energy levels for the finite square well.

We begin by making the same substitutions that were made in the case of the barrier in the infinite square well, Section 3.2.1. Let

$$\eta = ka; \quad \varsigma = \kappa a \quad (5.33)$$

which leads to

$$\begin{aligned} \eta^2 + \varsigma^2 &= \frac{2m(U_0 a^2)}{\hbar^2} \\ &= \rho^2 \end{aligned} \quad (5.34)$$

Plotting η and ς as Cartesian coordinates, Equation 5.34 is the equation of a circle of radius $\rho = \sqrt{2m(U_0 a^2)/\hbar^2}$. Notice that for a given well the “strength” of the well, the quantity $(U_0 a^2)$ and the mass m of the confined particle determine the radius of this circle. Therefore, ρ is peculiar to a given problem. It depends only upon the parameters of the well and the mass of the confined particle. The allowed energies are contained in the values of η and ς that are common to the circle defined by Equation 5.34 and the equations

$$\varsigma = \eta \tan \eta \quad \text{even eigenfunctions} \quad (5.35)$$

and

$$\varsigma = -\eta \cot \eta \quad \text{odd eigenfunctions} \quad (5.36)$$

which are simply Equations 5.31 and 5.32, respectively, after having multiplied each by a .

To obtain the energies corresponding to the even wave functions, that is, the ground state, the second excited state, etc., we must find the values of k that are

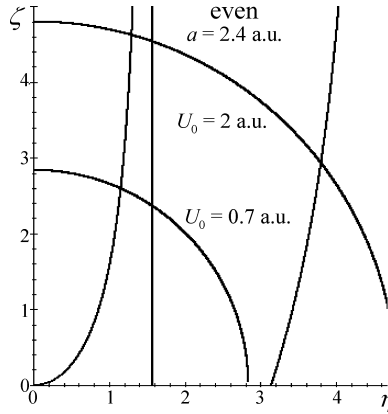


Fig. 5.10 Graphical solution of Equations 5.34 and 5.35 for two different well depths. The points of intersection lead to the allowed quantized energies. For $U_0 = 2$ a.u. there are two such intersections. Thus, there are either three or four bound quantum levels for this particular well, depending upon the number of energy eigenvalues corresponding to odd eigenfunctions. For $U_0 = 0.7$ a.u. there are either one or two bound quantum levels

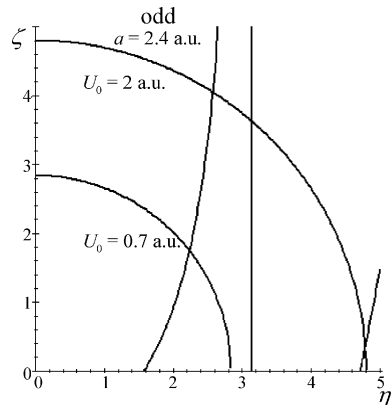
common to Equations 5.34 and 5.35. This is conveniently done by plotting each equation on Cartesian axes as shown in Fig. 5.10.

The points of intersection represent those values of η and, therefore the energies, that are solutions to Equation 5.35 subject to the condition of Equation 5.34. Both η and ζ must be positive so we are interested only in the first quadrant of the graph. It is clear that, because the branch of Equation 5.35 that lies in the range $0 < \eta < \pi/2$ intersects the origin (because $\tan 0 = 0$) no matter what the well parameters, there will always be at least one bound state. Figure 5.10 shows the solutions of the even transcendental equations for two different sets of well parameters. In both cases the half-width of the well is taken to be $a = 1$ a.u. and the mass is that of an electron (1 a.u.), but two different values of U_0 are used. The circle of larger radius for which there are two solutions has $U_0 = 2$ a.u. while the smaller circle for which there is only one energy level has $U_0 = 0.7$ a.u. Notice that in the case in which there are two solutions there must be at least three solutions because there will be at least one odd solution in between these two even ones.

To examine the odd solutions we must solve the transcendental equation for the odd solutions, Equation 5.36. Figure 5.11 shows the solutions for the same well parameters employed in Fig. 5.10. We see that for $U_0 = 0.7$ a.u. and $a = 2.4$ a.u. there are exactly two energy levels, one even and the other odd. Indeed, for any combination of parameters such that $\rho < 4.032$ a.u. there will be exactly two energy levels as given by the solutions shown in Figs. 5.10 and 5.11.

Because the smallest positive value of $-\eta \cot \eta$ occurs when $\cot \eta = 0$, ($\eta = \pi/2$) it is possible to have well parameters that will yield a circle of radius ρ that is too small to intersect $-\eta \cot \eta$. Thus, it is possible that there will not be an odd eigenstate, but there must be at least one even state. Therefore, for the symmetric

Fig. 5.11 Graphical solution of Equations 5.34 and 5.36. The well parameters are identical with those of Fig. 5.10. As in that figure, the points of intersection lead to the allowed quantized energies



finite square well of Equation 5.22 there must be at least one bound state, but not necessarily more.

Concentrating on the case for which $U_0 = 2 \text{ a.u.}$ and $a = 2.4 \text{ a.u.}$ or, more generally for which $U_0 a^2 = 11.52$, we see from Figs. 5.10 and 5.11 that there will be four bound states. Moreover, the highest of these levels is expected to be only barely bound as evidenced by the intersection of the circle and the curve near $\eta = 5$ in Fig. 5.11. These energies as obtained from the solutions of the transcendental equations for $U_0 a^2 = 11.52$ are listed in Table 5.1.

As anticipated, the highest energy level, the $n = 4$ state, is only barely bound. To illustrate the magnitudes of these energies, Fig. 5.12 is a plot of these levels superposed on this finite square well. The difference between $E = 0$ at which point the continuum of energies begins and the highest energy bound state E_4 has been exaggerated by a factor of 25 to make it obvious. Otherwise E_4 would have coincided with $E = 0$ on the scale of the drawing.

The probability densities, the absolute squares of the wave functions, for each of the four bound states are shown in Fig. 5.13. Notice that the penetration of the classically forbidden region is minimal for the deepest state, the ground state, but for the highest state there is considerable penetration. Of course, the next state up is a continuum state that is, in essence, a pure sinusoid extending from minus to positive infinity.

One final point is worth making before leaving the finite square well. The probabilities shown in Fig. 5.13 were based on eigenfunctions that were, necessarily, calculated using their correct energy eigenvalues. The correct energies are those

Table 5.1 Energies for a finite square well of half-width 2.4 a.u. and depth 2 a.u

n	Energy (a.u.)
1	-1.85
2	-1.42
3	-0.75
4	-0.011

Fig. 5.12 Energy levels for a finite square well having $U_0 = 2$ a.u. and $a = 2.4$ a.u. ($U_0 a^2 = 11.52$) plotted on the well. Note that the highest energy bound state is very close to the continuum states. The dashed levels correspond to odd eigenfunctions and the solid levels to even eigenfunctions

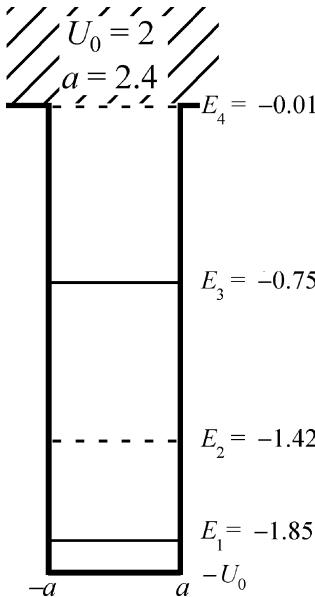


Fig. 5.13 Squares of the eigenfunctions corresponding to the four bound states that are supported by the finite square well having $U_0 = 2$ a.u. and $a = 2.4$ a.u. ($U_0 a^2 = 11.52$). The vertical scales are the same

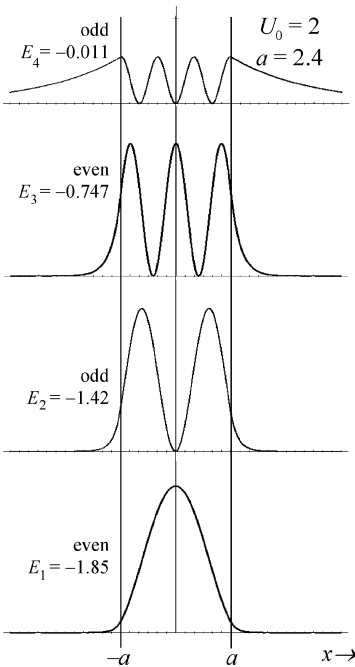
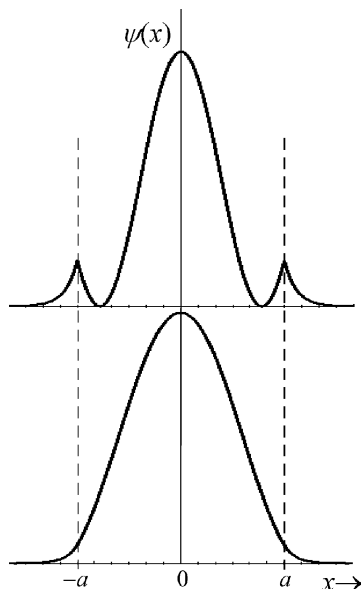


Fig. 5.14 Comparison of the correct ground state wave function (bottom) used in computing the probability density shown in Fig. 5.13 with one obtained by using a slightly incorrect eigenenergy illustrating the dramatic discontinuity that is introduced in the derivative of the wave function



that have been forced on us by continuity of the logarithmic derivative. This means that the de Broglie wavelengths fit into the well as described in Section 2.9. To emphasize the sensitivity of the eigenfunctions to the continuity conditions, we show in Fig. 5.14 the correct ground state wave function together with a function obtained using only a *nearly* correct energy eigenvalue for the computation. The dramatic consequences on the discontinuity in the derivative of the wave function at $x = \pm a$ are clear and illustrate the importance of fitting de Broglie wave in the well by the boundary conditions as discussed at length in Section 2.9.

5.4 The Morse Potential

Although the potential well problems we have studied might seem somewhat contrived (another example of the spherical horse), they do provide a basis for understanding more realistic potentials. One potential function that is indeed a realistic one has been employed to describe the interaction of the two atoms that constitute a diatomic molecule. Molecules can have vibrational and rotational energy states as well as the electronic states that are characteristic of atoms. Electronic states are states that depend upon the motion of the electron in an atom or molecule. In this section we will concentrate on vibration of the nuclei.

Let us understand exactly what particle it is that is bound. For molecular vibrations the “particle” of mass equal to the reduced mass μ of the two nuclei is bound by the potential energy between the nuclei. We can imagine two positively charged nuclei being glued together by sharing the negatively charged electrons between them. The electrons, in effect, shield the nuclei from each other, thus negating

(to a degree) the Coulomb repulsion between the nuclei. This electron glue is not rigid so it acts as a spring and the atoms vibrate. Because they are subject to the laws of quantum physics, the vibrational energy levels must be quantized, reminiscent of a harmonic oscillator.

Because we are ignoring rotation, we may treat the problem as a one-dimensional problem. At large internuclear separations there is virtually no bonding of the atoms and the potential energy is nonexistent. At small internuclear separations the Coulomb repulsion between the nuclei wins over the bonding of the electrons so the potential energy must become very large. In between these two extremes, there is a minimum in the potential energy if the molecule is bound. Therefore, there is a potential well that supports the bound states that comprise the vibrational states of the molecule. The minimum in the well occurs at an internuclear separation r_e which is called the equilibrium internuclear separation.

There have been a number of proposals for analytic forms of potentials that would accurately simulate potential energy functions for diatomic molecules. Perhaps the most successful of these in the sense that it is relatively easy to solve the TISE and the results give a reasonable approximation to reality is that proposed by Philip M. Morse in 1929 [1]. It is given by

$$U(r) = D_e [e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}] \quad (5.37)$$

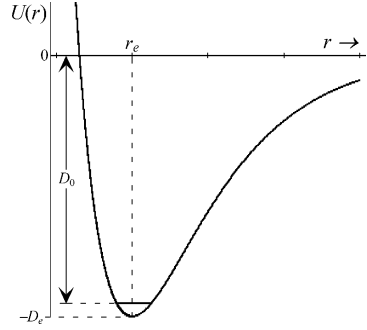
where the variable r is the internuclear separation; D_e and α are constants that are peculiar to each diatomic molecule as is r_e the equilibrium internuclear separation, also peculiar to a given molecule. It is easy to show that r_e is the position of the minimum in $U(r)$ (see Problem 10). Figure 5.15 shows a graph of Equation 5.37 and illustrates the significance of the parameters D_e and r_e .

From Equation 5.37 it is seen that for $r = 0$ the potential energy is finite. In a real molecule when the nuclei are on top of each other the potential energy must be infinite. The (incorrect) finite value of the Morse potential at $r = 0$ is not a significant deficiency of this potential because the region near $r = 0$ is never sampled by the nuclei. The ground vibrational level has been sketched at the bottom of the well in Fig. 5.15 to show the parameter D_0 which is known as the dissociation energy of the molecule. This is the amount of energy required to break the bond and separate the constituent atoms (with zero kinetic energy). Notice that, at this time, we are using the coordinate r as is customary in molecular spectroscopy. We are, however, considering only one-dimensional rotationless levels in this section so we will change to x shortly. Before doing so it is instructive to estimate the spacing between the vibrational levels and compare this spacing to typical atomic energy level spacing as epitomized by the Bohr atom.

We write a general potential energy function that can support bound states as a Taylor expansion about the internuclear separation r_e :

$$U(r) = U(r_e) + \frac{1}{2} \left. \frac{d^2U(r)}{dr^2} \right|_{r=r_e} (r - r_e)^2 + \dots \quad (5.38)$$

Fig. 5.15 Morse curve showing the lowest vibrational level of the diatomic molecule that it represents



The first derivative is not present because it vanishes at $r = r_e$. Equation 5.38 shows that, except for the constant term $U(r_e)$, the leading term is quadratic in $(r - r_e)$ so the first approximation to the vibrational levels is that of a harmonic oscillator with

$$\frac{1}{2} \left. \frac{d^2 U(r)}{dr^2} \right|_{r=r_e} = \frac{1}{2} \mu \omega^2 \quad (5.39)$$

Of course, as $(r - r_e)$ increases, the higher order terms must be included. Nonetheless, we can use the harmonic approximation to estimate the order of magnitude of the spacing between vibrational levels. Incidentally, this estimate is independent of the specific potential energy function.

The Coulomb potential between the two nuclei is the dominant contributor to the potential energy. It is $\sim ZZ'e^2/(4\pi\epsilon_0 r)$ where Z and Z' are the atomic numbers of each of the nuclei. Therefore, we set

$$\frac{1}{2} \left. \frac{d^2 U(r)}{dr^2} \right|_{r=r_e} = ZZ' \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_e} \right)^3 \quad (5.40)$$

Typically, however, internuclear separations are the order of Bohr radii so we let $r_e = a_0$ in Equation 5.40 and, in the harmonic approximation, we have

$$\frac{1}{2} \mu \omega^2 = ZZ' \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{a_0} \right)^3 \quad (5.41)$$

With the aid of Equation 1.32 we write Equation 5.41 as

$$\begin{aligned} \frac{1}{2} \mu \omega^2 &= 2ZZ' \left[\left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{1}{2a_0} \right) \right] \left(\frac{1}{a_0} \right)^2 \\ &= 2ZZ' [E_1] \left(\frac{4\pi\epsilon_0}{e^2} \right)^2 4E_1^2 \end{aligned} \quad (5.42)$$

where E_1 is the ground state energy of the hydrogen atom. Solving for the vibrational spacing which is $\sim \hbar\omega$ we have, using Equation 1.33 to eliminate $4\pi\epsilon_0/e^2$,

$$\hbar\omega = 2\sqrt{\frac{2ZZ'm_e}{\mu}}E_1 \quad (5.43)$$

Equation 5.43 gives the approximate vibrational spacing in terms of the Bohr energy, 13.6 eV. We see that this spacing is determined largely by the square root of the ratio of the electronic mass to the reduced mass of the nucleus the smallest value of which is one-half the mass of the proton (for the hydrogen molecule). Therefore, in general, the radical in Equation 5.43 will almost always be a fraction that is considerably smaller than unity so the vibrational energy level spacing is ~ 0.1 eV as compared with typical energy level spacings which are \sim eV. For typical molecules $D_e \sim 5 - 10$ eV so it is expected that a potential energy curve can support many vibrational levels.

Now we return to the solution of the TISE with the Morse potential without rotational motion, a one-dimensional problem. When we deal with three dimensions we will deal with rotation of the diatomic molecule. To simplify the calculation we make the substitution $x = r - r_e$ which merely shifts the zero of the abscissa. This substitution also permits easier comparison with the solutions of the harmonic oscillator potential (see Section 3.1.2). To facilitate this comparison we write the constituent terms, the exponentials, of the Morse function, Equation 5.37, in a Taylor series about $x = 0$ ($r = r_e$) and obtain

$$\begin{aligned} U(x) &= D_e [e^{-2\alpha x} - 2e^{-\alpha x}] \\ &= D_e [-1 + \alpha^2 x^2 \dots] \end{aligned} \quad (5.44)$$

Notice that the linear term in x is not present because $[dU(x)/dx]_{x=0} = 0$. Thus, the leading term in the expansion (aside from the constant) is the quadratic term. Comparing with the harmonic oscillator we find that

$$D_e \alpha^2 = \frac{1}{2} \mu \omega_0^2 \quad (5.45)$$

where μ is the reduced mass of the two-nucleus system and ω_0 is the frequency of vibration of an equivalent simple harmonic oscillator. Both D_e and ω_0 , which determine α , can be determined experimentally. For the purpose of the graph shown in Fig. 5.15 and subsequent graphs in this section we have selected the parameters in arbitrary units. These parameters are listed in Table 5.2. The numbers have been chosen merely for convenience and do not represent any particular molecule.

The TISE can be solved exactly for the Morse potential. That is, it is possible to obtain both the eigenfunctions and the eigenvalues. Inserting the Morse potential in the form of Equation 5.44 we have

Table 5.2 Parameters used in constructing the graphs of the Morse functions in this section

Parameter	Value
\hbar	1
D_e	10
α	1
μ	10
ω_0	$\sqrt{2}$

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi(x)}{dx^2} + D_e [e^{-2\alpha x} - 2e^{-\alpha x}] \psi(x) = E \psi(x) \quad (5.46)$$

The method of solution is reminiscent of that employed to solve the TISE with the harmonic oscillator potential. We first make the substitution

$$y = K e^{-\alpha x} \quad (5.47)$$

which, together with the chain rule for differentiation, leads to

$$\frac{d^2\psi(x)}{dx^2} = \alpha^2 y^2 \frac{d^2\psi(y)}{dy^2} + \alpha^2 y \frac{d\psi(y)}{dy} \quad (5.48)$$

Making these substitutions in the TISE we have

$$\frac{d^2\psi(y)}{dy^2} + \frac{1}{y} \frac{d\psi(y)}{dy} + \frac{2\mu}{\alpha^2 \hbar^2} \left(\frac{E}{y^2} - \frac{D_e}{K^2} + \frac{2D_e}{Ky} \right) \psi(y) = 0 \quad (5.49)$$

This equation can be simplified by judicious choice of K , in particular

$$K^2 = \frac{8\mu D_e}{\alpha^2 \hbar^2} \quad (5.50)$$

which converts Equation 5.49 into

$$\frac{d^2\psi(y)}{dy^2} + \frac{1}{y} \frac{d\psi(y)}{dy} + \left(-\frac{\beta^2}{y^2} - \frac{1}{4} + \frac{K}{2y} \right) \psi(y) = 0 \quad (5.51)$$

where

$$\beta^2 = -\frac{K^2 E}{4D_e} \quad (5.52)$$

Recall that $E < 0$ so $\beta^2 > 0$. It is much more convenient to write the constant K in terms of the equivalent harmonic oscillator potential, that is, the harmonic oscillator approximation to the Morse potential as embodied in Equation 5.45. Making the substitutions we obtain

$$K^2 = \frac{16D_e^2}{\hbar^2\omega_0^2} \quad (5.53)$$

Now, to solve for the eigenfunction $\psi(y)$, as was done for the harmonic oscillator, we examine the asymptotic solution and make it part of our test solution. As $r \rightarrow \infty$, $x \rightarrow \infty$, and $y \rightarrow 0$ so the $1/y^2$ dominates. Therefore, as $y \rightarrow 0$ we have

$$\frac{d^2\psi(y)}{dy^2} + \frac{1}{y} \frac{d\psi(y)}{dy} - \frac{\beta^2}{y^2} \psi(y) = 0 \quad (5.54)$$

a solution of which is $\psi(y) = y^\beta$. Because the Morse potential is not an even function, as is the harmonic oscillator potential, we must also consider the case of $x \rightarrow -\infty$ for which $t \rightarrow \infty$. In this case Equation 5.49 reduces to

$$\frac{d^2\psi(y)}{dy^2} - \frac{1}{4}\psi(y) = 0 \quad (5.55)$$

The solution of this asymptotic equation that we will keep is $\psi(y) = e^{-y/2}$.

Before solving the differential equation, let us scrutinize these limits. The $r \rightarrow \infty$, $x \rightarrow \infty$, $y \rightarrow 0$ limit is no problem because there is no restriction on $r \rightarrow \infty$. This simply means that dissociation occurs and the atoms are free of each other. On the other hand, the limit $x \rightarrow -\infty$, $y \rightarrow \infty$ implies that $r \rightarrow -\infty$. This is clearly impossible since $r = 0$ is the minimum value. One of the inadequacies of the Morse potential that was mentioned above is that it is finite at $r = 0$. The true interatomic potential energy should become infinite (like the Coulomb potential) at $r = 0$. As noted above, however, in practice this is not a serious limitation. Nonetheless, because we are solving the problem in one-dimension the necessity of letting $x \rightarrow -\infty$ deserves some attention. We permit this artifact merely so the problem can be solved. It is of no consequence since the limitation on the bound states that can be supported by the Morse function is determined by its behavior for positive r .

We may now write the wave function $\psi(y)$ as a product of these two asymptotic forms and a function that can be expanded as a power series which we designate $F(y)$ (F is the Greek letter digamma which we use because we are running out of symbols that do not traditionally designate other functions). Our wave function takes the form

$$\psi(y) = e^{-y/2} y^\beta F(y) \quad (5.56)$$

subject to the condition that

$$\lim_{y \rightarrow \infty} y^\beta F(y) < e^{y/2} \quad (5.57)$$

Inserting this into Equation 5.49 and performing the operations we obtain a differential equation for $F(y)$.

$$y \frac{d^2 F(y)}{dy^2} + (2\beta + 1 - y) \frac{dF(y)}{dy} + \left(-\beta - \frac{1}{2} + \frac{K}{2} \right) F(y) = 0 \quad (5.58)$$

Expanding $F(y)$ in a power series as was done for the harmonic oscillator we have

$$F(y) = \sum_{n=0}^{\infty} a_n y^n \quad (5.59)$$

which, when inserted into Equation 5.58, yields

$$\sum_{n=1}^{\infty} [(n-1) + (2\beta + 1)] n a_n y^{n-1} + \sum_{n=0}^{\infty} \left(\frac{K}{2} - \beta - \frac{1}{2} - n \right) a_n y^n = 0 \quad (5.60)$$

Letting $n \rightarrow n+1$ in the first summation in order to make both summations cover the same range yields

$$\sum_{k=0}^{\infty} [k + (2\beta + 1)] (k+1) a_{k+1} y^k + \sum_{n=0}^{\infty} \left(\frac{K}{2} - \beta - \frac{1}{2} - n \right) a_n y^n = 0 \quad (5.61)$$

Factoring all coefficients of like powers of y in Equation 5.61 we have

$$\sum_{n=0}^{\infty} \left[(n+1)(n+2\beta+1) a_{n+1} + \left(\frac{K}{2} - \beta - \frac{1}{2} - n \right) a_n \right] y^n = 0 \quad (5.62)$$

Because the powers of y are linearly independent the coefficient of each power of y must vanish. This leads to a recursion relation between a_{n+1} and a_n given by

$$a_{n+1} = - \frac{(K/2 - \beta - 1/2 - n)}{(n+1)(n+2\beta+1)} a_n \quad (5.63)$$

In principle, we have solved the differential equation. As in the case of the harmonic oscillator, however, we must make sure that the eigenfunctions that we have obtained are physically acceptable. Because we are dealing with a potential well that will confine the particle to a specific region of space, the particle must be bounded and the wave function must be normalizable in accord with the condition set forth in Equation 5.57 which assures that the wave function in Equation 5.56 is normalizable. From the recursion relation Equation 5.63 it is seen that

$$\lim_{n \rightarrow \infty} \frac{a_{n+1}}{a_n} = \frac{1}{n} \quad (5.64)$$

It is a relatively simple matter to show that, in the limit as $x \rightarrow \infty$, the coefficients of the Taylor series for e^x behave in the same way (see Problem 9). Therefore, for large values of y , $F(y)$ behaves as e^y which overpowers $e^{-y/2}$ in Equation 5.56. Note that the y^β term in Equation 5.56 is of no consequence in this regard because Equation 5.64 is still valid as $n \rightarrow \infty$. As was necessary in the case of the harmonic oscillator, we must terminate the series that represents $F(y)$. To accomplish this we set the numerator equal to zero thus terminating the recursion relation after some n th term. The constant β contains the energy so we expect to obtain the quantized energies. We have

$$\left(\frac{K}{2} - \beta_n - \frac{1}{2} - n\right) = 0 \quad (5.65)$$

where we have attached a subscript to β to signify that they will be functions of the index n . Substituting for β_n and solving for the energy we obtain

$$E_n = -D_e + \left(n + \frac{1}{2}\right) \frac{4D_e}{K} - \left(n + \frac{1}{2}\right)^2 \frac{4D_e}{K^2} \quad (5.66)$$

Equation 5.66 can be put into a much more revealing form by substituting for K in terms of the first approximation to the Morse potential, the harmonic oscillator parameters, Equation 5.53. We obtain

$$E_n = -D_e + \left(n + \frac{1}{2}\right) \hbar\omega - \left(\frac{1}{4D_e}\right) \left[\left(n + \frac{1}{2}\right) \hbar\omega\right]^2 \quad (5.67)$$

which casts the Morse levels in terms of the equivalent harmonic oscillator levels. The first term D_e merely shifts the scale to the bottom of the well while the second term is the harmonic oscillator energy levels. As the Morse oscillator is excited, oscillator levels are excited, but the third term in Equation 5.67 causes the separation between adjacent levels to decrease. This decrease clearly becomes more important as n increases. The fact that the depth of the well appears in the denominator of the third term reflects the fact that near the bottom of the well the harmonic oscillator is a good approximation to the Morse function (as well as most other functions of similar shape). As the energy increases and the well deviates from a parabola the levels become more closely spaced. Figure 5.16 shows a graph of both the Morse potential and the harmonic oscillator potential. As can be seen, on the side of the potential at which the molecule is stretched, $r > r_e$, the Morse potential is “soft.” That is, the force, the derivative of the potential energy, is lower than that of an equivalent harmonic oscillator. In compression, however, the Morse potential is “hard.” The softness of the potential for $r > r_e$ causes the levels to become more closely spaced as the state of excitation of the molecule approaches dissociation of the molecule into isolated atoms.

Figure 5.17 is a plot of a Morse potential with the levels for that well superposed on the well. As may be seen, the levels appear to be those of a harmonic oscillator

Fig. 5.16 Morse potential and harmonic oscillator potential plotted on the same axis showing the close correlation between the two near their respective minima, but the subsequent divergence

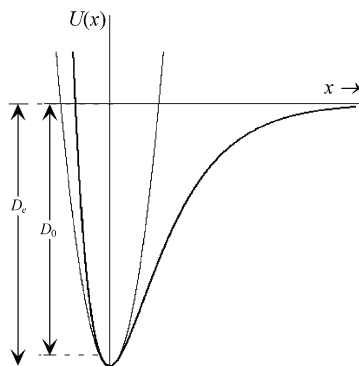
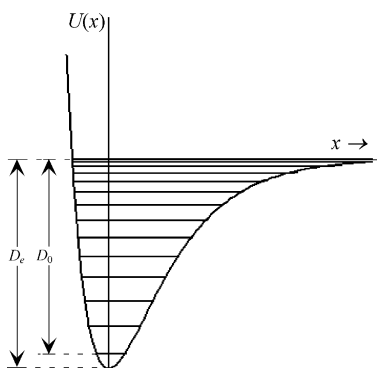


Fig. 5.17 Morse potential plotted with the energy levels for this particular well

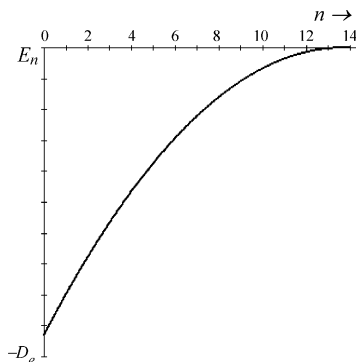


near the bottom of the well, but get closer together as the top of the well is approached, consistent with the formula in Equation 5.67.

Because the well has a finite depth there may be only a finite number of levels that can be supported. We can deduce the number of levels that will fit in the well by noting that a plot of E_n versus n in Equation 5.67 is a concave-downward parabola. The value of n at which the maximum of this parabola occurs is the maximum number of levels that fit in a given Morse potential well. For the parameters used in this section the significant portion of the parabola is shown in Fig. 5.18. From this figure it is seen that this maximum occurs near $n = 14$. Indeed, if we find the maximum of Equation 5.67 it is at roughly $n = 14$ (see Problem 11) so there are 15 levels.

Before leaving the subject of molecular vibrations it is worthwhile to discuss briefly molecular excited states and units. Molecules, like atoms, have excited states that are formed when electrons are “promoted.” In molecules these states are referred to as electronic states. The designation as electronic states is unnecessary in atoms because there are no other types of excited states. In molecules, however, there are also excited rotational states and vibrational states. The eigenstates of the Morse potential are vibrational states of a particular electronic state, the electronic state being that associated with the Morse potential. When an electron is excited, a new electronic state is formed. To this new state corresponds a new potential

Fig. 5.18 Graph of E_n versus n in Equation 5.67 for the parameters used in this section showing that for these parameters the Morse potential supports only 14 levels



energy curve which supports a different set of vibrational levels. This curve too may be represented by a Morse potential. Electromagnetic transitions occur with the absorption or emission of photons between these states. Transitions between electronic states (which are complicated by transitions between different vibrational and rotational levels of each of the electronic states involved) usually involve energies of the order of eV, just as for atoms. Transitions between vibrational levels of the same electronic state occur at lower energies so these transitions are in the infrared region of the spectrum. Of course, these vibrational transitions are complicated by having different rotational levels superposed. Transitions between rotational levels of the same vibrational level occur at still lower energies and are characteristic of the far-infrared region of the spectrum.

The arbitrary units used in Table 5.2 were chosen for convenience of illustration. Typical dissociation energies are the order of eV. If the value $D_e = 10$ that was used in the illustrations were actually 10 eV, the molecule would be a rather strongly bound one, perhaps nitrogen, N_2 which has three electron pairs to glue the two atoms together. Some important molecules (important to physicists because they are simple) such as once ionized hydrogen H_2^+ have much lower dissociation energies, ~ 2.7 eV, because H_2^+ doesn't have as much glue as, for example, N_2 .

5.5 The Linear Potential

The list of potential energy functions for which the TISE can be solved exactly is not very long. One deceptively simple function is linear in x for $x > 0$, but infinite for $x \leq 0$. Such a situation might exist for a particle falling in a uniform gravitational field and reflected elastically at the surface. Another such situation is that of a charged particle, say an electron, forced against an infinite potential wall by a constant electric field of magnitude F (we choose F for the electric field rather than E to avoid confusion with the energy). The potential may thus be written

$$\begin{aligned} U(x) &= eFx & x > 0 \\ &= \infty & x \leq 0 \end{aligned} \quad (5.68)$$

In Section 4.5.2 we examined the fate of a Gaussian wave packet under the influence of a linear potential without the infinite wall. In that case the potential extended from $-\infty$ to $+\infty$ so it could not support bound states. In the present case the force for $x > 0$ is given by

$$\begin{aligned} \mathbf{F}(x) &= -\frac{dU(x)}{dx} \hat{\mathbf{i}} \\ &= -eF \hat{\mathbf{i}} \end{aligned} \quad (5.69)$$

so the electron is confined in a potential well as illustrated in Fig. 5.19 and bound states are expected.

The TISE for $x > 0$ is

$$\left[-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} + eFx \right] \psi(x) = E \psi(x) \quad (5.70)$$

subject to the boundary conditions $\psi(0) = 0$ and $\psi(\infty) \rightarrow 0$. Our goal is to find the energy eigenvalues $E_n > 0$ and the eigenfunctions in coordinate space. Of course the energy eigenvalues are independent of the space in which the eigenfunctions are viewed, but there are two ways of solving for the eigenfunctions. One is to simply attempt to solve the TISE in coordinate space, an approach we have taken several times. Another is to convert this equation to momentum space and solve for the $\phi_n(p)$ as was done in Problem 11 of Chapter 4 for the harmonic oscillator. The coordinate space eigenfunctions can always be recovered by taking the Fourier transforms of the $\phi_n(p)$. We elect to first convert to momentum space.

In momentum space the TISE, Equation 5.70, is

$$\left[\frac{p^2}{2m_e} - eF \frac{\hbar}{i} \frac{d}{dp} \right] \phi(p) = E \phi(p) \quad (5.71)$$

In contrast to the TISE in coordinate space, this equation is separable! We have

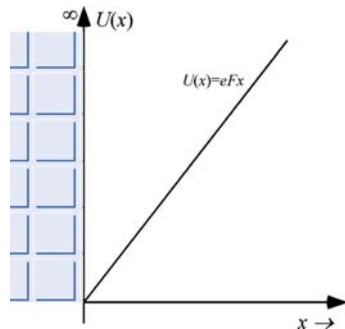


Fig. 5.19 Graph of potential energy function in Equation 5.68

$$\frac{d\phi(p)}{\phi(p)} = \frac{i}{eF\hbar} \left(\frac{p^2}{2m_e} - E \right) dp \quad (5.72)$$

Integrating both sides we have

$$\ln \phi(p) = \frac{i}{eF\hbar} \left(\frac{p^3}{6m_e} - Ep \right) + \ln K \quad (5.73)$$

where the constant of integration has been written as $\ln K$ for convenience. Solving for $\phi(p)$ we have

$$\phi_n(p) = K \exp \left[\frac{i}{eF\hbar} \left(\frac{p^3}{6m_e} - E_n p \right) \right] \quad (5.74)$$

where we have attached the subscript to $\phi(p)$ and E to indicate that we are presuming quantization. We may now evaluate the constant K by normalizing $\phi_n(p)$. The orthogonality and normalization condition is

$$\int_{-\infty}^{\infty} \phi_{n'}^*(p) \phi_n(p) dp = \delta(E_n - E_{n'}) \quad (5.75)$$

which, after substituting Equation 5.74, becomes

$$|K|^2 \int_{-\infty}^{\infty} \exp \left[\frac{i}{eF\hbar} (E_n - E_{n'}) p \right] dp = \delta(E_n - E_{n'}) \quad (5.76)$$

Now, from the definition of the δ -function, Equation 4.40, we see that the integral is $2\pi\delta[(E_n - E_{n'})/(eF\hbar)]$ so, applying the last of the relations in Table 4.1, that is, $\delta(ax) = (1/|a|)\delta(x)$, we obtain

$$|K|^2 = \frac{1}{2\pi\hbar eF} \quad (5.77)$$

thus giving the complete eigenfunction in momentum space. We have not, however, found the eigenvalues because we have not applied the boundary conditions that will force quantization on the system. The boundary conditions are, however, in coordinate space, not momentum space. We must therefore find the coordinate eigenfunctions $\psi_n(x)$ from the momentum eigenfunctions $\phi_n(p)$ using the Fourier transform. Using the Fourier transform in Equation 4.33 we have

$$\psi(x) = \frac{1}{2\pi\hbar\sqrt{eF}} \int_{-\infty}^{\infty} \exp \left[\frac{i}{eF\hbar} \left(\frac{p^3}{6m_e} - E_n p \right) \right] \cdot e^{ipx/\hbar} dp \quad (5.78)$$

Applying the condition $\psi(0) = 0$ means that the integrand vanishes. This may not seem like much of a simplification until we recall that the remaining exponential

can be written as the sum of a sine and a cosine. Because the sine is an odd function, the integral over symmetric limits vanishes. We are left with

$$\int_0^\infty \cos \left[\frac{1}{eF\hbar} \left(\frac{p^3}{6m_e} - E_n p \right) \right] dp = 0 \quad (5.79)$$

where we have replaced the lower limit of integration by zero because the cosine is even. Equation 5.79 still doesn't look familiar, but the integral is a well known function, the Airy function. Not only is it well-known and well-tabulated, but most symbolic mathematics computer programs have it in their libraries. To put Equation 5.79 in standard form we make the substitution $y = p / (2m_e e F \hbar)^{1/3}$ which leads to

$$\frac{1}{\pi} \int_0^\infty \cos \left[\frac{y^3}{3} - E_n \left(\frac{2m_e}{e^2 F^2 \hbar^2} \right)^{1/3} y \right] dy = \text{Ai} \left[-E_n \left(\frac{2m_e}{e^2 F^2 \hbar^2} \right)^{1/3} \right] \quad (5.80)$$

Thus, the condition specified by Equation 5.79 determines the quantized energies. We see that for given values of F , m_e , and e the quantized energies are determined by the zeros of the Airy function

$$\text{Ai} \left[-E_n \left(\frac{2m_e}{e^2 F^2 \hbar^2} \right)^{1/3} \right] = 0 \quad (5.81)$$

Moreover, as seen from Equation 5.78, the eigenfunctions in coordinate space are merely the Airy functions. It is left as an exercise to show that the argument of the Airy function is indeed dimensionless (see Problem 12). To understand how to compute the energy eigenvalues we carefully examine the Airy function $\text{Ai}(\xi)$ which is plotted in Fig. 5.20 to include the first ten of its zeros.

The zeros that are shown in Fig. 5.20 are also listed in Table 5.3 where ξ_n represents the coordinate of a zero of the function and n the order of the zero.

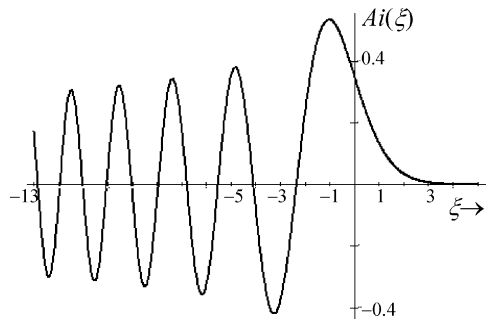


Fig. 5.20 The Airy function $\text{Ai}(\xi)$ showing the first ten zeros

Table 5.3 The first ten zeros of the Airy function

n	ξ_n
1	-2.338
2	-4.088
3	-5.521
4	-6.787
5	-7.944
6	-9.023
7	-10.040
8	-11.009
9	-11.936
10	-12.829

The energies are computed by setting

$$-E_n \left(\frac{2m_e}{e^2 F^2 \hbar^2} \right)^{1/3} = \xi_n \quad (5.82)$$

from which we find

$$E_n = -\xi_n \left(\frac{e^2 F^2 \hbar^2}{2m_e} \right)^{1/3} \quad (5.83)$$

Notice that the energies are positive as they must be for the potential of Equation 5.68.

We now return to the TISE for the linear potential in coordinate space, Equation 5.70, which we rewrite as

$$\left[-\frac{d^2}{dx^2} + \left(\frac{2m_e e F}{\hbar^2} x - \frac{2m_e E}{\hbar^2} \right) \right] \psi(x) = 0 \quad (5.84)$$

To simplify further we make the substitution

$$\begin{aligned} \left(\frac{2m_e e F}{\hbar^2} x - \frac{2m_e E}{\hbar^2} \right) &= \alpha x - \beta \\ &= \gamma \xi \end{aligned} \quad (5.85)$$

where

$$\alpha = 2m_e e F / \hbar^2 \quad \text{and} \quad \beta = 2m_e E / \hbar^2 \quad (5.86)$$

and γ is a constant to be determined; ξ is a variable. Equation 5.84 becomes

$$\left[-\frac{d^2}{dx^2} + \gamma \xi \right] \psi(x) = 0 \quad (5.87)$$

We must now convert all quantities to the variable ξ in Equation 5.87. Using the chain rule

$$\begin{aligned}\frac{d\psi}{dx} &= \frac{d\psi}{d\xi} \frac{d\xi}{dx} \\ &= \frac{d\psi}{d\xi} \frac{\alpha}{\gamma}\end{aligned}\quad (5.88)$$

and

$$\frac{d^2\psi}{dx^2} = \frac{d^2\psi}{d\xi^2} \left(\frac{\alpha}{\gamma}\right)^2 \quad (5.89)$$

so that Equation 5.84 becomes

$$\frac{d^2\psi(\xi)}{d\xi^2} - \left(\frac{\gamma^3}{\alpha^2}\right) \xi \psi(\xi) = 0 \quad (5.90)$$

The form of this equation suggests that a propitious choice of γ would be $\gamma^3 = \alpha^2 = (2m_e e F / \hbar^2)^2$ thus making Equation 5.90

$$\frac{d^2\psi(\xi)}{d\xi^2} - \xi \psi(\xi) = 0 \quad (5.91)$$

This is precisely Airy's equation, the solutions to which are Airy functions. Being a second-order differential equation, there are two Airy functions, but only one

$$\begin{aligned}\psi(\xi) &= Ai(\xi) \\ &= \frac{1}{\pi} \int_0^\infty \cos\left(\frac{y^3}{3} + \xi y\right) dy\end{aligned}\quad (5.92)$$

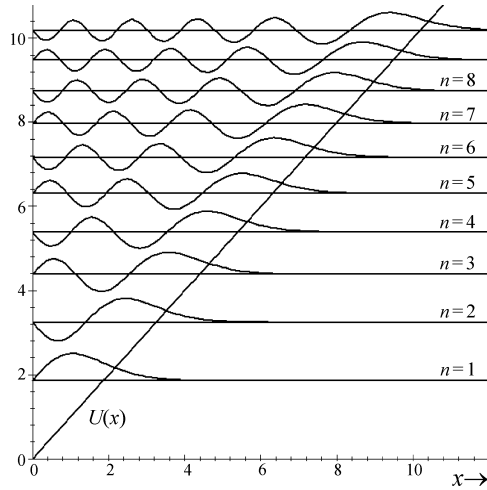
will be of interest here because the other one diverges at infinity. The other Airy function $Bi(\xi)$ will be useful later. To plot the eigenfunctions in coordinate space we must replace ξ with x in Equation 5.92. We obtain

$$\psi_n(x) = Ai\left[\left(\frac{2m_e e F}{\hbar^2}\right)^{1/3} x - E_n \left(\frac{2m_e}{e^2 F^2 \hbar^2}\right)^{1/3}\right] \quad (5.93)$$

which can be shown to be identical to Equation 5.78 that was obtained as the Fourier transform of the momentum space wave function.

We have already seen how to compute the energy eigenvalues. Using Equation 5.93 (or a suitably modified Equation 5.78) we can compute the wave functions. To simplify the calculation we set all the parameters equal to unity, that is, $e = F = m_e = \hbar$. Then, in these reduced units the energy eigenvalues are simply

Fig. 5.21 Normalized eigenfunctions for the linear potential using the reduced units discussed in the text. The ordinate is the energy E



the ξ_n divided by $2^{1/3} \approx 1.26$. Figure 5.21 is a plot of the normalized eigenfunctions superposed on the potential energy function and located at the values of their respective energy eigenvalues. These eigenfunctions clearly have the characteristics that are expected. They have increasing numbers of nodes starting with zero nodes for the ground state. There is an inflection point at the classical turning point and the wave function in the classically forbidden region curves away from the x -axis.

5.6 The WKB Approximation

5.6.1 The Nature of the Approximation

The potential energy functions we have encountered to this point have all been such that the TISE was exactly solvable. The Wentzel, Kramers, Brillouin (WKB) approximation provides a method for approximating the energy levels of bound states and their wave functions when an exact solution of the TISE is not possible. It also makes it possible to estimate the rate at which particles penetrate and emerge through a potential barrier of arbitrary shape, called tunneling, thus permitting calculations of important physical constants such as rates of alpha decay.

The WKB approximation is applicable in cases in which the potential energy is a slowly varying function over several de Broglie wavelengths. To make this statement more concrete we write the TISE in the form

$$\left[\frac{p(x)^2}{2m} + U(x) \right] \psi(x) = E \psi(x) \quad (5.94)$$

where $p(x)$ is the momentum which is given by

$$p(x) = \sqrt{2m[E - U(x)]} \quad (5.95)$$

Because the momentum and the de Broglie wavelength λ_d are inextricably entwined, we may regard the de Broglie wavelength in a region in which $U(x)$ is not constant, that is, anything but a square well, to be a function of position. If, however, the momentum, and therefore λ_d , are constant, the solutions to Equation 5.94 are sinusoidal in the classically allowed region and decaying exponential in the classically forbidden regions. Concentrating our attention on the classically allowed region, we can imagine a zeroth approximation to the wave function to be

$$\psi(x) = e^{\pm i(p/\hbar)x} \quad (5.96)$$

where p is a constant. If we generalize to a situation in which the momentum is a function of position, we may, following the derivation of Rapp [2], make the substitution

$$\psi(x) = F(x)e^{iS(x)} \quad (5.97)$$

This form of the wave function merely permits us to keep track of which part of it represents the momentum and therefore the inverse of the de Broglie wavelength. This can be seen by noting that when $U(x)$ is constant $S(x) = \pm(p/\hbar)x$ where p is a constant. We see also that $dS(x)/dx \doteq p(x)$. (The symbol \doteq stands for “corresponds to.”)

Substituting Equation 5.97 into the TISE yields

$$\left\{ \frac{d^2 F(x)}{dx^2} - F(x) \left[\frac{dS(x)}{dx} \right]^2 + k(x)^2 F(x) \right\} + i \left\{ 2 \frac{dF(x)}{dx} \frac{dS(x)}{dx} + F(x) \frac{d^2 S(x)}{dx^2} \right\} = 0 \quad (5.98)$$

Notice that the wave number $k(x)$ has been explicitly designated as a function of x .

Now, if a complex number vanishes, its real and imaginary parts must each vanish. Therefore,

$$\frac{d^2 F(x)}{dx^2} - F(x) \left[\frac{dS(x)}{dx} \right]^2 + k(x)^2 F(x) = 0 \quad (5.99)$$

and

$$2 \frac{dF(x)}{dx} \frac{dS(x)}{dx} + F(x)^2 \frac{d^2 S(x)}{dx^2} = 0 \quad (5.100)$$

So far, there is no approximation involved. We have merely assumed a form of $\psi(x)$, Equation 5.97, and inserted it into the TISE. The resulting equations, Equations 5.99 and 5.100, are equivalent. Equation 5.100 is recognizable as an exact differential of $F(x)^2 dS(x)/dx$ so that

$$d \left[F(x)^2 \frac{dS(x)}{dx} \right] = 0 \quad (5.101)$$

and

$$F = \frac{C}{\sqrt{dS/dx}} \quad (5.102)$$

where C is a constant. This permits us to eliminate $F(x)$ from our assumed form of $\psi(x)$, Equation 5.97. This is not too surprising since we wrote the single function $\psi(x)$ in terms of two unknown functions $F(x)$ and $S(x)$. Nevertheless, our assumed $\psi(x)$, which, incidentally, is still exact, is written in a form in which there is a physically significant quantity, the momentum (de Broglie wavelength). We have

$$\psi(x) = \frac{C}{\sqrt{dS/dx}} e^{iS(x)} \quad (5.103)$$

An interesting feature of Equation 5.103 is that the probability density $|\psi(x)|^2 \propto 1/p(x)$. For this reason (and others) the WKB approximation is often referred to as the semiclassical approximation because, classically, the probability of the finding the particle in a particular region of space should indeed be inversely proportional to its speed in that region.

Now for the approximation. Wentzel, Kramers, and Brillouin cleverly arranged it so the derivative of $S(x)$ represents the momentum (give or take an \hbar). To see this, note that any exponent must be unitless. If $U(x)$ were constant, then $S(x) = kx$ ($k = p/\hbar = \text{constant}$). If $U(x)$ is slowly varying, then $S(x)$ and its derivative (slope) will also be slowly varying. Equation 5.102 assures us that $F(x)$ is also slowly varying and we may take the second derivative term in Equation 5.99 to be negligible with respect to the others. The resulting differential equation is

$$\left(\frac{dS}{dx} \right)^2 - [k(x)]^2 = 0 \quad (5.104)$$

so that

$$\frac{dS}{dx} = \pm k(x) \quad (5.105)$$

This gives us the denominator of Equation 5.103. Integrating once gives the exponent

$$S(x) = \pm \int k(x) dx \quad (5.106)$$

which leads immediately to a general solution to the TISE. Therefore, in the classically allowed region a linear combination of

$$\psi_{\text{allowed}}(x) = \frac{C_{\pm}}{\sqrt{k(x)}} \exp \left[\pm i \int k(x) dx \right] \quad (5.107)$$

is an approximate solution to the TISE under the condition of a slowly varying potential energy function.

To convert Equation 5.107 to make it valid in the classically forbidden region for which $U(x) > E$ we let

$$\kappa(x) = \sqrt{\frac{2m[U(x) - E]}{\hbar^2}} \quad (5.108)$$

and replace $ik(x)$ in the integral of Equation 5.107 with $\kappa(x)$ and obtain the WKB approximation wave function for the classically forbidden region

$$\psi_{\text{forbidden}}(x) = \frac{C'_{\pm}}{\sqrt{\kappa(x)}} \exp \left[\pm \int \kappa(x) dx \right] \quad (5.109)$$

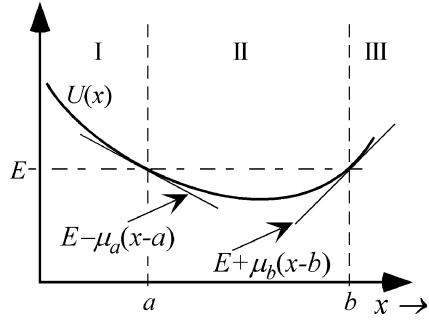
One of our goals is to find an expression for the quantized energy levels. We are not quite ready to do this though because there is some trouble with the approximate wave functions that we have derived. The trouble is that they are inversely proportional to the square root of the momentum and the momentum vanishes at the classical turning points. Thus, the approximate wave functions blow up at the turning points. This is not good! To correct the problem we must connect the wave function that is valid in the classically allowed region to the one that is valid in the classically forbidden region. This is done by assuming a form of the potential in the region of the turning points and deriving formulas that connect these two wave functions across the turning points.

5.6.2 The Connection Formulas for Bound States

We assume the potential has the form shown in Fig. 5.22. If the energy is E , as shown in the figure, the turning points are at $x = a$ and $x = b$ and, as usual, we have designated the three regions of space by Roman numerals.

From our knowledge of the characteristics of wave functions and from Equations 5.107 and 5.109 the approximate wave functions in the three regions of space, according to the WKB approximation, are

Fig. 5.22 Potential energy curve $U(x)$ with classical turning points at $x = a$ and $x = b$ for a particle energy E . Also shown is the linear potential used to connect the approximate wave functions at the right-hand classical turning point



$$\psi_I(x) = \frac{A}{\sqrt{\kappa(x)}} \exp \left[\int_x^a \kappa(x) dx \right] \quad (5.110)$$

$$\begin{aligned} \psi_{II}(x) = & \frac{B}{\sqrt{k(x)}} \exp \left[i \int_a^x k(x) dx \right] \\ & + \frac{C}{\sqrt{k(x)}} \exp \left[-i \int_a^x k(x) dx \right] \end{aligned} \quad (5.111)$$

$$\psi_{III}(x) = \frac{D}{\sqrt{\kappa(x)}} \exp \left[- \int_b^x \kappa(x) dx \right] \quad (5.112)$$

The wave function $\psi_{II}(x)$ could have been written in terms of the turning point at $x = b$ in which case, for consistency, the limits of integration would have been from x to b , maintaining our convention of going from left to right.

To connect these wave functions at the turning points we assume a form of the potential energy in the vicinity of the turning points. The simplest function that is not a constant is a linear potential. For convenience we will first work with the right-hand turning point at $x = b$. This permits us to consider $x \rightarrow +\infty$ first and avoids a pesky minus sign. We will deal with the left-hand turning point at $x = a$ after we are seasoned veterans of connection formula mathematics.

We assume a potential energy function near this turning point of the form

$$U(x) = E + \mu_b(x - b) \quad (5.113)$$

The Greek letter μ , which is not otherwise used in this section, has been chosen to indicate the slope of the straight line because the traditional choice of m might be confused with mass. The assumed connecting potential $U(x)$ is shown in Fig. 5.22 which makes clear that μ_b is a positive number. The TISE in the vicinity of this turning point may be written in the form

$$\frac{d^2\psi(x)}{dx^2} - \left(\frac{2m\mu_b}{\hbar^2}\right)^{2/3} \left[\left(\frac{2m\mu_b}{\hbar^2}\right)^{1/3} (x-b)\right] \psi(x) = 0 \quad (5.114)$$

which can be translated and rescaled with the substitution

$$\xi = \left(\frac{2m\mu_b}{\hbar^2}\right)^{1/3} (x-b) \quad (5.115)$$

This transforms Equation 5.114 into

$$\frac{d^2\psi(\xi)}{d\xi^2} - \xi\psi(\xi) = 0 \quad (5.116)$$

Note that the translation defined by Equation 5.115 means that the turning point occurs at $\xi = 0$.

To those who have read Section 5.5 Equation 5.116 will be recognized as being identical to Equation 5.91, the solutions to which are Airy functions $Ai(\xi)$ and $Bi(\xi)$. In that section we knew that we were dealing with bound states so we immediately discarded the Airy function $Bi(\xi)$ on physical grounds because it diverges at infinity. Here, however, we must include it. The general solution to Equation 5.116 is

$$\psi(\xi) = \eta Ai(\xi) + \zeta Bi(\xi) \quad (5.117)$$

where η and ζ are constants. Thus, Equation 5.117 is the general form of the wave function for the linearized potential.

The approach will be to find an approximate wave function that is a solution to Equation 5.116, which is essentially the TISE for a linear potential in the region of the turning point. We will then compare this wave function with the wave function obtained from the WKB approximation. Recall that the WKB wave function is not good, indeed it is invalid at the turning points, so we must compare it to the linearized potential solution far away. How can we do this since we are linearizing the potential in the region of the turning point? The answer lies in the nature of the approximation. We are assuming that the potential is “slowly varying”. Therefore, the linear potential is assumed good over a wide range of x (or ξ), see Equation 5.115. The consequence of all this is that we will require asymptotic forms of the Airy functions for comparison with the WKB wave functions. These asymptotic forms of $Ai(\xi)$ are

$$Ai(\xi) \sim \frac{1}{2\sqrt{\pi}\xi^{1/4}} \exp\left(-\frac{2}{3}\xi^{3/2}\right) \quad \xi > 0 \quad (5.118)$$

$$Ai(\xi) \sim \frac{1}{\sqrt{\pi}(-\xi)^{1/4}} \sin \left[\frac{2}{3}(-\xi^{3/2}) + \frac{\pi}{4} \right] \quad \xi < 0 \quad (5.119)$$

and the asymptotic forms of $Bi(\xi)$ are

$$Bi(\xi) \sim \frac{1}{\sqrt{\pi}\xi^{1/4}} \exp \left(\frac{2}{3}\xi^{3/2} \right) \quad \xi > 0 \quad (5.120)$$

$$Bi(\xi) \sim \frac{1}{\sqrt{\pi}(-\xi)^{1/4}} \cos \left[\frac{2}{3}(-\xi^{3/2}) + \frac{\pi}{4} \right] \quad \xi < 0 \quad (5.121)$$

A graph of $Ai(\xi)$ is shown in Fig. 5.20 while that of $Bi(\xi)$ is shown in Fig. 5.23.

To the right of the turning point at $\xi = 0$ the wave function based on the linearized potential must have the asymptotic form (see Equations 5.117, 5.118, and 5.120)

$$\psi(\xi) = \eta \frac{1}{2\sqrt{\pi}\xi^{1/4}} \exp \left(-\frac{2}{3}\xi^{3/2} \right) + \zeta \frac{1}{\sqrt{\pi}\xi^{1/4}} \exp \left(\frac{2}{3}\xi^{3/2} \right) \quad (5.122)$$

We must now find the WKB form of the wave function for the linearized potential. In the vicinity of $x = b$ we write the TME E as the sum of the kinetic energy and the potential energy

$$E = \frac{(\hbar k)^2}{2m} + E + \mu_b(x - b) \quad (5.123)$$

or, substituting from Equation 5.115, we have

$$k^2 = - \left(\frac{2m\mu_b}{\hbar^2} \right)^{2/3} \xi \quad (5.124)$$

so that

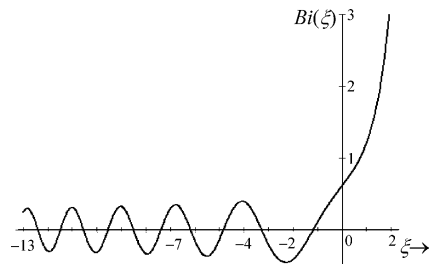


Fig. 5.23 The Airy function $Bi(\xi)$ showing the divergence for $\xi \rightarrow \infty$

$$k(\xi) = \left(\frac{2m\mu_b}{\hbar^2} \right)^{1/3} (-\xi)^{1/2} \quad (5.125)$$

in the classically allowed region. In the classically forbidden region we have

$$\kappa(\xi) = \left(\frac{2m\mu_b}{\hbar^2} \right)^{1/3} (\xi)^{1/2} \quad (5.126)$$

The WKB wave function in Region III is therefore

$$\begin{aligned} \psi_{III}(\xi) &= \frac{D}{\xi^{1/4}} \exp \left[- \int_0^\xi \left(\frac{2m\mu_b}{\hbar^2} \right)^{1/3} \xi^{1/2} \frac{\hbar^{2/3} d\xi}{(2m\mu_b)^{1/3}} \right] \\ &= \frac{D}{\xi^{1/4}} \exp \left[- \int_0^\xi \xi^{1/2} d\xi \right] \\ &= \frac{D}{\xi^{1/4}} \exp \left[- \frac{2}{3} \xi^{3/2} \right] \end{aligned} \quad (5.127)$$

where the constants associated with $\xi^{1/4}$ have been embedded in D . Lo and behold this matches the asymptotic form of the wave function deduced from the exact solution for the linear potential, Equation 5.122, provided

$$\eta = 2\sqrt{\pi}D \quad \text{and} \quad \zeta = 0 \quad (5.128)$$

We must now force matching for Region II in which the WKB wave function for the linearized potential is

$$\psi_{II}(\xi) = \frac{1}{(-\xi)^{1/4}} \left\{ B \exp \left[i \frac{2}{3} (-\xi)^{3/2} \right] + C \exp \left[-i \frac{2}{3} (-\xi)^{3/2} \right] \right\} \quad (5.129)$$

Before we compare the WKB wave function in Equation 5.129 with the wave function from the exact solution for the linear potential, Equation 5.122, it is important to point out that our deduction that $\zeta = 0$ in Equation 5.128 is still valid in Region II. The reason for this is that the Airy functions are continuous across the turning point and are therefore the solutions of the differential equation, Equation 5.116, over all space. This is in contrast to, for example, the case of the finite square well where the discontinuous potential requires separate solutions to the TISE in each of the three regions of space. Thus, the comparison of the wave function in Equation 5.129 is facilitated by knowledge that $Bi(\xi)$ has already been excluded from the comparison. In fact, $Bi(\xi)$ will be excluded from any region of space that includes $x = \pm\infty$ for a bound state problem because it diverges.

The solution to the linear potential to which Equation 5.129 must be compared is (see Equation 5.119)

$$\psi(\xi) = \frac{\eta}{\sqrt{\pi}(-\xi)^{1/4}} \sin \left[\frac{2}{3}(-\xi^{3/2}) + \frac{\pi}{4} \right] \quad \xi < 0 \quad (5.130)$$

We therefore make the substitution $C = -ie^{i\pi/2}B$ in Equation 5.129 and obtain

$$\begin{aligned} \psi_{II}(\xi) &= \frac{B}{(-\xi)^{1/4}} \left\{ e^{i\pi/4} \exp \left[i \frac{2}{3}(-\xi)^{3/2} \right] \right. \\ &\quad \left. - e^{-i\pi/4} \exp \left[-i \frac{2}{3}(-\xi)^{3/2} \right] \right\} \\ &= \frac{2B}{(-\xi)^{1/4}} \sin \left[\frac{2}{3}(-\xi^{3/2}) + \frac{\pi}{4} \right] \end{aligned} \quad (5.131)$$

which shows that

$$\eta = 2\sqrt{\pi}B \quad (5.132)$$

We can, however, eliminate η (for the same reason that $\zeta = 0$ over the whole range of x using Equation 5.128). We obtain

$$B = D \quad (5.133)$$

Thus, the wave functions on each side of $x = b$ are given by

$$\psi_{II}^b(x) = \frac{2D}{\sqrt{k(x)}} \sin \left[\int_b^x k(x) dx + \frac{\pi}{4} \right] \quad (5.134)$$

$$\psi_{III}(x) = \frac{D}{\sqrt{\kappa(x)}} \exp \left[- \int_b^x \kappa(x) dx \right] \quad (5.135)$$

where a superscript b has been associated with the $\psi_{II}(x)$ in Equation 5.134 to designate the fact that it was derived from the turning point at $x = b$. Note the change of the limits of integration in Equation 5.134 since $\xi = 0 \rightarrow x = b$ (see Equation 5.115).

To find an expression for the bound state energy we must obtain another expression for $\psi_{II}(x)$, an expression derived from consideration of the other turning point. It is, after all, the existence of the *two* turning points that confines the particle and makes this a bound state problem. We follow the same procedure as above for the turning point at $x = a$. The potential at the left-hand turning point is written

$$U(x) = E - \mu_a(x - a) \quad (5.136)$$

where μ_a is the slope and taken to be a positive number at $x = a$ (see Fig. 5.22). The TISE is

$$\frac{d^2\psi(x)}{dx^2} + \left(\frac{2m\mu_a}{\hbar^2}\right)^{2/3} \left[\left(\frac{2m\mu_a}{\hbar^2}\right)^{1/3} (x - a)\right] \psi(x) = 0 \quad (5.137)$$

and we make the substitution

$$\xi = -\left(\frac{2m\mu_a}{\hbar^2}\right)^{1/3} (x - a) \quad (5.138)$$

so, again, $\xi = 0$ corresponds to the turning point. With this substitution we arrive at exactly the same equation, Equation 5.116, for which the solutions are the Airy functions. The difference of the minus sign in Equations 5.115 and 5.138 makes the arguments of the Airy functions negative so the graphs in Figs. 5.20 and 5.23 should be mirror images. That is, as $x \rightarrow \infty$, $\xi \rightarrow -\infty$. The procedure is identical to that above and we obtain analogous formulas

$$\psi_I(x) = \frac{A}{\sqrt{\kappa(x)}} \exp\left[\int_x^a \kappa(x) dx\right] \quad (5.139)$$

$$\psi_{II}^a(x) = \frac{2A}{\sqrt{k(x)}} \sin\left[\int_a^x k(x) dx + \frac{\pi}{4}\right] \quad (5.140)$$

where a superscript a has been associated with the $\psi_{II}(x)$ in Equation 5.140 to designate that it originated from the turning point at $x = a$.

Now, the two expressions for $\psi_{II}^a(x)$ and $\psi_{II}^b(x)$ in Equations 5.134 and 5.140 represent the same wave function. They must therefore be identical except perhaps for a multiplicative constant K . Note that these two expressions do indeed differ because they have different limits of integration. Equating the two expressions and rewriting the left-hand side we have

$$\begin{aligned} \sin\left[\int_a^x k(x) dx + \frac{\pi}{4}\right] &= K \sin\left[\int_b^x k(x) dx + \frac{\pi}{4}\right] \\ \sin\left[\int_a^b k(x) dx + \int_b^x k(x) dx + \frac{\pi}{4}\right] &= K \sin\left[\int_b^x k(x) dx + \frac{\pi}{4}\right] \end{aligned} \quad (5.141)$$

Equation 5.141 is valid only if the first integral on the left-hand side is equal to a half-integral multiple of π and if $K = (-1)^n$. This leads to the quantization of energy in the form

$$\int_a^b k(x) dx = \left(n + \frac{1}{2}\right) \pi \quad (5.142)$$

which is more customarily seen in terms of the momentum

$$\int_a^b p(x) dx = \left(n + \frac{1}{2}\right) \pi \hbar \quad (5.143)$$

We note that, classically, the particle would oscillate between the turning points so a cycle of the particle plotted in the $p - x$ plane, referred to as phase space, would be

$$\oint p(x) dx = \left(n + \frac{1}{2}\right) h \quad (5.144)$$

In this form the integral represents the Bohr–Sommerfeld quantization rule, a rule that we have not discussed, but which bridged the gap between the Bohr theory of the atom and the development of the TDSE. For our purpose we write Equation 5.144 in terms of the de Broglie wavelength

$$\oint \frac{dx}{\lambda(x)} = \left(n + \frac{1}{2}\right) \quad (5.145)$$

which is equivalent to requiring a half-integral number of wavelengths in a complete “orbit” in the $p - x$ plane. Moreover, in the spirit of the WKB approximation, these expressions are truly valid only for large n . For example, if we consider an infinite square well, an L -box, $\lambda(x) = \text{constant}$ and the integral is equal to $2L$. Thus,

$$\frac{2L}{\lambda_n} = \left(n + \frac{1}{2}\right) \implies E_n = \frac{p^2}{2m} = \frac{(2n+1)^2 \hbar^2}{32L^2m} \quad (5.146)$$

These are not the correct energy eigenvalues, but they *are* correct in the limit as $n \rightarrow \infty$ (see Problem 13). Another point of view is to consider Equation 5.142 to be the accumulated phase shift of a one-way trip from a to b , $k(x) = 2\pi/\lambda(x)$.

5.6.3 A Bound State Example—the Linear Potential

In Section 5.5 we found the exact solution to the problem of an electron bound in a linear potential. We may therefore use these exact results to assess the validity of the WKB approximation to this same problem. The potential energy is given by Equation 5.68.

$$\begin{aligned} U(x) &= eFx & x > 0 \\ &= \infty & x \leq 0 \end{aligned} \quad (5.147)$$

Before embarking on the calculation, however, we must modify the quantization condition, Equation 5.142, to account for the necessity of having $\psi(0) = 0$ due to the infinite wall at $x = 0$. This is easily done by examining the first of Equations 5.141 with $a = 0$ and with b the turning point corresponding to a given TME E_n where we have attached a subscript to the energy because we know the values will be quantized. To fulfill this boundary condition we must have

$$\sin \left[\int_0^0 k(x) dx + \frac{\pi}{4} \right] = K \sin \left[\int_0^b k(x) dx + \frac{\pi}{4} \right] \quad (5.148)$$

where the left-hand side is zero. Equation 5.148 requires that

$$\int_0^b k(x) dx + \frac{\pi}{4} = n\pi \quad (5.149)$$

or

$$\int_0^b p(x) dx = \left(n - \frac{1}{4} \right) \pi \hbar \quad (5.150)$$

Now

$$b_n = \frac{E_n}{eF} \quad (5.151)$$

so

$$\begin{aligned} p(x) &= \sqrt{2m_e(E - eFx)} \\ &= (2m_e eF)^{1/2} \sqrt{b_n - x} \end{aligned} \quad (5.152)$$

Using the notation from Section 5.5, Equation 5.86, let

$$\alpha = \frac{2m_e eF}{\hbar^2} \quad (5.153)$$

so that

$$\begin{aligned} p(x) &= \left(\frac{2m_e eF}{\hbar^2} \right)^{1/2} \hbar \sqrt{b_n - x} \\ &= \alpha^{1/2} \hbar \sqrt{b_n - x} \end{aligned} \quad (5.154)$$

The integral in Equation 5.150 is then

$$\begin{aligned}
 \int_0^{b_n} p(x) dx &= \alpha^{1/2} \hbar \int_0^{b_n} \sqrt{b_n - x} dx \\
 &= \frac{2}{3} b_n^{3/2} \hbar \alpha^{1/2}
 \end{aligned} \tag{5.155}$$

Equating the values of the integrals found in Equations 5.150 and 5.155 we have

$$\frac{2}{3} b_n^{3/2} \hbar \alpha^{1/2} = \left(n - \frac{1}{4} \right) \pi \hbar \tag{5.156}$$

Substituting for b_n using Equation 5.151 and solving for the energy we obtain (see Problem 14)

$$E_n = \left(\frac{e^2 F^2 \hbar^2}{2m_e} \right)^{1/3} \left[\frac{3\pi}{8} (4n - 1) \right]^{2/3} \tag{5.157}$$

Now let us rearrange the equation that yielded the exact energies, Equation 5.83, to facilitate comparison with the WKB result. We have

$$E_n = \left(\frac{e^2 F^2 \hbar^2}{2m_e} \right)^{1/3} (-\xi_n) \tag{5.158}$$

where the ξ_n are the zeros of the Airy function. It is seen that the factors that depend upon the parameters of the problem in the approximation, Equation 5.157, and the exact energy, Equation 5.158, are identical. Thus, to compare the approximation with the exact answer we need only compare the numerical factor in square brackets in Equation 5.157 with the (negatives of the) positions of the zeros of the Airy function. This comparison is shown in Table 5.4. It is clear that the approximation produces remarkably close results, even at low quantum numbers.

Table 5.4 The negatives of the first ten zeros of the Airy function $-\xi_n$ compared with the numerical factor $F(n) = [(3\pi/8)(4n - 1)]^{2/3}$ in the approximate expression for the energy as derived from the WKB approximation for the linear potential

n	$-\xi_n$	$F(n)$
1	2.338	2.320
2	4.088	4.082
3	5.521	5.517
4	6.787	6.785
5	7.944	7.943
6	9.023	9.021
7	10.040	10.039
8	11.009	11.008
9	11.936	11.935
10	12.829	12.828

5.6.4 Tunneling

The penetration of a rectangular barrier and subsequent emergence from this barrier, the tunnel effect, was discussed in Section 5.1. If, however, a barrier has some arbitrary shape, then an approximation is often required. The method most often employed is the WKB approximation. A sketch of a barrier of arbitrary shape is shown in Fig. 5.24 as well as the three regions of interest. We assume a beam incident from left to right on the barrier.

The wave functions may be written in an analogous manner to the bound state case, only, in a manner of speaking, inside out. That is, the real exponentials and the imaginary exponentials are exchanged. Using the same constants that were used in the treatment of the rectangular barrier in Equation 5.3 of Section 5.1 we have

$$\begin{aligned}
 \psi_I(x) &= \frac{A}{\sqrt{k(x)}} \exp \left[i \int_a^x k(x) dx + \frac{\pi}{4} \right] \\
 &\quad + \frac{B}{\sqrt{k(x)}} \exp \left[-i \int_a^x k(x) dx + \frac{\pi}{4} \right] \\
 \psi_{II}(x) &= \frac{C}{\sqrt{\kappa(x)}} \exp \left[- \int_a^x \kappa(x) dx \right] \\
 &\quad + \frac{D}{\sqrt{\kappa(x)}} \exp \left[\int_a^x \kappa(x) dx \right] \\
 \psi_{III}(x) &= \frac{F}{\sqrt{k(x)}} \exp \left[i \int_b^x k(x) dx + \frac{\pi}{4} \right]
 \end{aligned} \tag{5.159}$$

where we have added the $\pi/4$ phase in the oscillatory terms taking advantage of our now veteran status and knowledge of the asymptotic forms of the Airy functions with which we will be comparing the WKB wave functions, Equations 5.119 and 5.121. This phase factor is merely a constituent of the constants in $\psi_I(x)$ and $\psi_{III}(x)$. Additionally, as for the rectangular barrier, we have not included the term in $\psi_{III}(x)$ that represents a wave traveling from right to left. We seek $T = |F|^2 / |A|^2$ and $R = |B|^2 / |A|^2 = 1 - T$ and this is the aim of the WKB approximation for transmission through a barrier.

To establish the relations between the coefficients we must use the connection formulas, but we must now include the Airy function $Bi(x)$ in the wave functions because its divergence at infinity is not forbidden. Figure 5.23 shows a graph of a

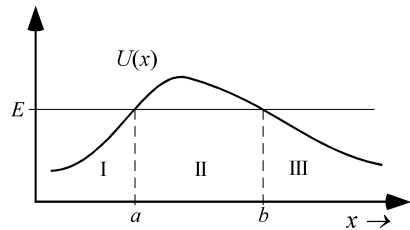


Fig. 5.24 Potential energy curve $U(x)$ with classical turning point at $x = a$ for a particle energy E incident from the left

portion of $Bi(\xi)$ that illustrates the divergence for positive ξ . Our goal is to find the coefficients in Region I in terms of F the coefficient of the outgoing wave in Region III. The constants C and D are of no consequence except that they link the constants of interest.

Again we begin with the right-hand turning point. We will connect the wave functions in precisely the same way as was done for the case of bound states taking advantage of the algebra that we have already performed. We write the general form of the wave function for the linearized potential in Region III as before:

$$\psi_{III}(\xi) = \eta Ai(\xi) + \zeta Bi(\xi) \quad (5.160)$$

The WKB form of the wave function in Region III is a wave traveling from left to right as indicated in Equation 5.159. Because of Equations 5.129 and 5.159 we know that $\psi_{III}(\xi)$ must have the form

$$\psi_{III}(\xi) = \frac{F}{(-\xi)^{1/4}} \exp \left\{ i \left[\frac{2}{3} (-\xi)^{3/2} + \frac{\pi}{4} \right] \right\} \quad (5.161)$$

To compare the form of the wave function in Equation 5.161 with the asymptotic forms of the Airy functions, Equations 5.119 and 5.121, we must convert the exponential in Equation 5.161 to trigonometric functions. The comparison yields

$$\frac{\eta}{\sqrt{\pi}} = iF; \quad \frac{\zeta}{\sqrt{\pi}} = F \implies \alpha = i\beta \quad (5.162)$$

The linear combination of Airy functions for $\psi_{II}(\xi)$, to be used for comparison with the WKB wave function in that region, can now be written in terms of a single constant because the constants η and ζ are valid in Regions II and III in the vicinity of $x = b$. We have

$$\psi_{II}(\xi) = i\zeta Ai(\xi) + \zeta Bi(\xi) \quad (5.163)$$

and, from Equations 5.159 and 5.127 this is to be compared to

$$\psi_{II}^b(\xi) = \frac{C}{\xi^{1/4}} \exp \left(-\frac{2}{3} \xi^{3/2} \right) + \frac{D}{\xi^{1/4}} \exp \left(\frac{2}{3} \xi^{3/2} \right) \quad (5.164)$$

where, necessarily, the increasing exponential term has been included in Equation 5.164. Using Equations 5.118 and 5.120 we compare Equations 5.163 and 5.164 and find that

$$\begin{aligned} C &= \frac{i\zeta}{2\sqrt{\pi}} = \frac{i}{2} F \\ D &= \frac{\zeta}{\sqrt{\pi}} = F \end{aligned} \quad (5.165)$$

so that

$$\psi_{II}^b(x) = \left(\frac{i}{2}F\right) \frac{1}{\sqrt{\kappa(x)}} \left\{ \exp\left[-\int_x^b \kappa(x) dx\right] - 2i \exp\left[\int_x^b \kappa(x) dx\right] \right\} \quad (5.166)$$

We must now perform the same connection mathematics at $x = a$ in order to find the constant A that represents the initial particle flux. While $\psi_{II}^b(x)$ as given in Equation 5.166 is the wave function that was obtained by matching to the wave function in Region III, it can be used at the turning point at $x = a$ by rewriting the integrals

$$\begin{aligned} \int_x^b \kappa(x) dx &= \int_x^a \kappa(x) dx + \int_a^b \kappa(x) dx \\ &= -\int_a^x \kappa(x) dx + \int_a^b \kappa(x) dx \end{aligned} \quad (5.167)$$

The last integral in Equation 5.167 is a definite integral so we may designate it by a symbol. Let

$$\Gamma = \exp\left[-\int_a^b \kappa(x) dx\right] \quad (5.168)$$

The wave function $\psi_{II}^a(x)$, as derived from $\psi_{II}^b(x)$, is

$$\begin{aligned} \psi_{II}^a(x) &= \left(\frac{i}{2}F\right) \frac{1}{\sqrt{\kappa(x)}} \left\{ \Gamma \exp\left[\int_a^x \kappa(x) dx\right] - 2i\Gamma^{-1} \exp\left[-\int_a^x \kappa(x) dx\right] \right\} \\ &= \frac{F}{\sqrt{\kappa(x)}} \left\{ \frac{i}{2}\Gamma \exp\left[\int_a^x \kappa(x) dx\right] + \Gamma^{-1} \exp\left[-\int_a^x \kappa(x) dx\right] \right\} \end{aligned} \quad (5.169)$$

Converting Equation 5.169 to $\psi(\xi)$ for the linearized potential in the vicinity of $x = a$ we have

$$\psi_{II}(\xi) = \frac{1}{\xi^{1/4}} \left[\frac{i}{2}F\Gamma \exp\left(\frac{2}{3}\xi^{3/2}\right) + F\Gamma^{-1} \exp\left(-\frac{2}{3}\xi^{3/2}\right) \right] \quad (5.170)$$

which is to be compared to the general form of the wave function for the linearized potential in Region II which we write

$$\psi_{II}(\xi) = \gamma Ai(\xi) + \delta Bi(\xi) \quad (5.171)$$

The constants γ and δ were used in Equation 5.171 to emphasize that they are different from the constants in Equation 5.160. Using the asymptotic forms Equations 5.118 and 5.120 the comparison between Equations 5.170 and 5.171 yields

$$\frac{\gamma}{2\sqrt{\pi}} = F\Gamma^{-1}; \quad \frac{\delta}{\sqrt{\pi}} = \frac{i}{2}F\Gamma \quad (5.172)$$

Now we must turn our attention to Region I. From Equations 5.159 and 5.129 we can write

$$\begin{aligned} \psi_I(\xi) &= \frac{1}{(-\xi)^{1/4}} [A \exp(i\vartheta) + B \exp(-i\vartheta)] \\ &= \frac{1}{(-\xi)^{1/4}} [(A+B) \cos \vartheta + i(A-B) \sin \vartheta] \end{aligned} \quad (5.173)$$

where

$$\vartheta = \frac{2}{3}(-\xi)^{3/2} + \frac{\pi}{4} \quad (5.174)$$

Since the relation between the constants γ and δ is valid in Region I we may write

$$\psi_I(\xi) = 2\sqrt{\pi}F\Gamma^{-1}Ai(\xi) + \frac{i}{2}\sqrt{\pi}F\Gamma Bi(\xi) \quad (5.175)$$

Comparison of Equations 5.173 and 5.175 leads to

$$A+B = 2F\Gamma^{-1}; \quad A-B = \frac{F\Gamma}{2} \quad (5.176)$$

from which we can solve for F in terms of A , thus permitting calculation of the transmission coefficient T . We find

$$\begin{aligned} \frac{F}{A} &= \frac{1}{\left(\frac{1}{\Gamma} + \frac{\Gamma}{4}\right)} \\ &= \left(\frac{\Gamma}{1 + \Gamma^2/4}\right) \end{aligned} \quad (5.177)$$

Typically, the WKB approximation for penetration of a barrier is applied to a high, broad barrier. Thus, the definite integral Γ is small which is tantamount to saying that the probability of transmission through the barrier is small. In this approximation $F/A \approx \Gamma$ and the transmission coefficient T is given by

$$\begin{aligned}
T &= \Gamma^2 \\
&= \exp \left[-2 \int_a^b \kappa(x) dx \right] \\
&= \exp \left[-\frac{2}{\hbar} \int_a^b \sqrt{2m[U(x) - E]} dx \right]
\end{aligned} \tag{5.178}$$

5.6.5 Comparison with a Rectangular Barrier

It is important to clarify the meaning of the terms “high” and “broad.” Because we are discussing physics and not poetry, it is incumbent upon us to specify these terms. High with respect to what? Broad with respect to what? To do this we compare the WKB result, Equation 5.178, with the exact result for a rectangular barrier obtained in Section 5.1. This will give us a sense of the approximation made and the meaning of these terms.

For a rectangular barrier of height U_0 and length L , see Fig. 5.3, the WKB approximation predicts a transmission probability

$$\begin{aligned}
T_{WKB} &= \exp \left[-2 \int_0^L \kappa(x) dx \right] \\
&= \exp \left[-\frac{2}{\hbar} \int_0^L \sqrt{2m(U_0 - E)} dx \right] \\
&= \exp \left[-\frac{2L}{\hbar} \sqrt{2m(U_0 - E)} \right]
\end{aligned} \tag{5.179}$$

The exact result for T for the energy $E < U_0$ the transmission probability is given by Equation 5.11:

$$T_{E < U_0} = \frac{1}{\left[1 + \frac{U_0^2}{4E(U_0 - E)} \sinh^2 \left(\frac{L}{\hbar} \sqrt{2m(U_0 - E)} \right) \right]} \tag{5.180}$$

where L is the length of the barrier. For a broad, high barrier the argument of the hyperbolic sine is large so that $\sinh x \rightarrow (\frac{1}{2}) e^x$ and $\sinh^2 x \rightarrow (\frac{1}{4}) e^{2x}$ and the second term in the denominator is a large number which we may write in the form

$$\begin{aligned}
T_{E < U_0} &= \frac{1}{[1 + X]} \approx \frac{1}{X} \\
&\approx \left[\frac{16E(U_0 - E)}{U_0^2} \right] \exp \left[-\frac{2L}{\hbar} \sqrt{2m(U_0 - E)} \right]
\end{aligned} \tag{5.181}$$

Thus, in order for the WKB result and the exact result to match, $E \approx (1/16) U_0$ which we may consider to be a definition of the term high.

5.6.6 A Tunneling Example—Predissociation

There are numerous examples of applications of the WKB tunneling formula, Equation 5.178, to physical phenomena. Among the first was the satisfactory explanation of α -decay, a process in which a bare helium nucleus (no electrons), an α particle, is emitted from a more massive nucleus. Although the potential energy that confines the α particle within the nucleus is greater than the kinetic energy of the α particle inside the nucleus, it nonetheless escapes. This is α -decay. In 1928 George Gamow and, independently, R. W. Gurney and E. U. Condon explained the phenomenon using tunneling and the WKB approximation. Since this α -decay is described in numerous texts we will resist the temptation to do so here. Instead, we will present an example from molecular physics.

Consider, for example, the Morse potential discussed in Section 5.4. It is conceivable that this potential energy curve might be modified by any of several different mechanisms. For example, we ignored molecular rotation in Section 5.4 because we were concentrating on one-dimensional problems. If, however, the molecule is rotating, there is the usual centrifugal term proportional to $1/r^2$ that must be added to the potential energy. This term will, as in classical mechanics, cause a modification of the potential energy curve as illustrated in Fig. 5.25.

The hump in the potential energy above $U(x) = 0$ is caused by addition of a centrifugal term to a Morse potential. The exact mechanism that causes the hump is of no consequence in the present discussion. It can have causes other than molecular rotation. What *is* significant is that the hump can support bound states, vibrational states with positive energy. Because positive energy implies that the constituent molecules are separated, that is, dissociated, for large x , we see why tunneling through this barrier is termed *predissociation*. These states are then not really bound because they will ultimately decay by leaking through the barrier. Such states are usually referred to as quasibound states.

Can we calculate the decay rate using the WKB approximation? Of course we can if we know the shape of the barrier. That is not to say the decay rate that we calculate will be accurate, but we can certainly go through the mechanics of the computation.

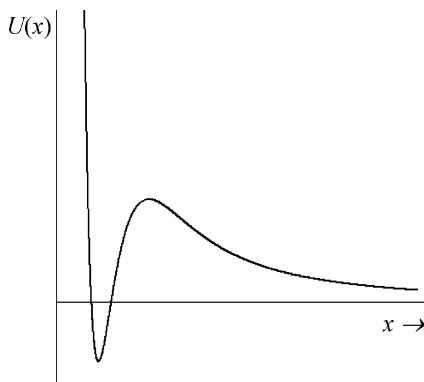


Fig. 5.25 Modified Morse curve showing the effects of centrifugal distortion

(There is that spherical horse again.) We simply take the digitized form of the curve that represents the barrier, put it in an appropriate computer program and crank out the answer. This is not very pedagogically interesting so, for our purpose we assume a curve that looks like the barrier, but one that is judiciously chosen to make the integral in Equation 5.178 analytically viable. We choose a parabola such as that illustrated in Fig. 5.26. While the actual barrier width is considerably wider than the parabola, our purpose will be met with the added benefit of analytic tractability.

We may as well choose the center of the parabola at the origin to facilitate the calculation so we write the potential for the barrier as

$$U(x) = U_0 \left(1 - \frac{x^2}{L^2} \right) \quad (5.182)$$

where $x = \pm L$ are the zeros of $U(x)$. The parabola is shown in Fig. 5.27. It is assumed that the energy of the tunneling particle is E .

By symmetry, the limits of integration in Equation 5.178 go from $-a$ to $+a$ where a is given by

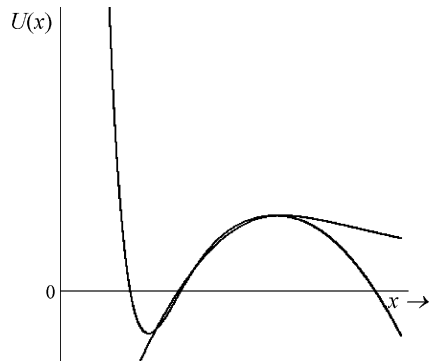


Fig. 5.26 Morse curve with rotational barrier and a parabola approximating the barrier

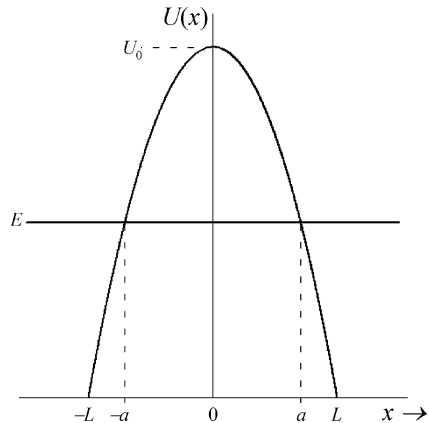


Fig. 5.27 Parabola used to simulate the barrier in Figure 5.26

$$a^2 = L^2 \left(1 - \frac{E}{U_0} \right) \quad (5.183)$$

Solving Equation 5.183 for E and inserting it and $U(x)$ into the integrand in Equation 5.178 we have

$$T = \exp \left[-2 \frac{\sqrt{2mU_0}}{\hbar L} \int_{-a}^a \sqrt{a^2 - x^2} dx \right] \quad (5.184)$$

Using the integral given in Equation H.7 we have

$$T = \exp \left[-2 \frac{\sqrt{2mU_0}}{\hbar L} \frac{1}{2} \pi L^2 \left(1 - \frac{E}{U_0} \right) \right] \quad (5.185)$$

$$= \exp \left[-\frac{\sqrt{2mU_0}}{\hbar} \pi L \left(1 - \frac{E}{U_0} \right) \right] \quad (5.186)$$

where we have substituted for a^2 using Equation 5.183.

This result shows that, as usual, the WKB approximation should be valid if the barrier is broad (large L) and high (large U_0). Notice also that if the tunneling particle is massive, the tunneling rate is low, something we already knew from our experience with the rectangular barrier. For diatomic molecules the mass is actually the reduced mass. For this reason, predissociation has often been studied using hydrides, molecules containing one hydrogen atom for which the reduced mass is essentially the mass of the hydrogen atom.

5.7 References

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2. D. Rapp, Quantum Mechanics (Holt, Rinehart and Winston, New York, 1971).
3. R. S. Grace, W. M. Pope, D. L. Johnson, and J. G. Skofronick, "Ramsauer-Townsend effect in the total cross section of $^4\text{He} + ^4\text{He}$ and $^3\text{He} + ^3\text{He}$," Phys. Rev., **A14**, 1006–1008 (1976).

Problems

1. Assume that a monoenergetic beam of particles of mass m is incident on a potential barrier at $x = 0$ in the form of a δ -function so that

$$U(x) = U_0 \delta(x) \quad \text{where} \quad U_0 > 0$$

Find the reflection and transmission coefficients. To handle the discontinuity in the potential integrate the TISE across $x = 0$ from $-\epsilon \rightarrow +\epsilon$ as described in Section 2.9.

2. Suppose the potential energy function is a δ -function such that

$$U(x) = -U_0\delta(x) \quad \text{where } U_0 > 0$$

Assuming that U_0 is a positive constant so this potential might support bound states of a particle of mass m , show that there will be one and only one bound state (state of negative energy). Find the energy of this bound state and its eigenfunction.

3. For a potential well

$$\begin{aligned} U(x) &= \infty & x < 0 \\ &= -U_0 & 0 < x < a \\ &= 0 & x > a \end{aligned}$$

where U_0 is a real positive number

- sketch the wave function for particles of positive energy E incident on the potential well.
 - find the expression for the transmission coefficient for incident particles of kinetic energy E .
 - show that perfect transmission occurs when the kinetic energy of the particles while “over the well” is exactly equal to one of the quantized energies of an L -box of the same dimensions.
4. Solve for the coefficients A , B , and F and hence R and T in the case of $E > U_0$ for the potential step and convince yourself that, indeed, $R + T = 1$.
5. Find the eigenfunctions for the problem for which the potential energy is given by

$$\begin{aligned} U(x) &= \infty & x < 0 \\ &= -U_0 & 0 < x < a \\ &= 0 & x > a \end{aligned}$$

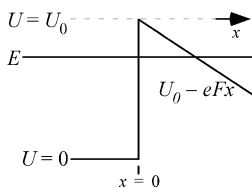
No calculations are required. You may state the answer.

- If the strength of a finite well is $U_0 a^2 < \pi^2 \hbar^2 / (8m)$, show that there can be only a single bound state.
- Assuming that $U_0 a^2 \ll \pi^2 \hbar^2 / (8m)$ for a finite square well, see Problem 6, find the approximate energy eigenvalue of the lone energy level. In the spirit of this approximation take $\pi^2/8 \approx 1$.
- Consider the odd solutions to a finite square well.
 - Find the ratio of the probabilities that the particle is inside the well to outside the well for an arbitrary odd bound state.
 - Under what conditions on the strength of the well ($U_0 a^2$) can the probability of finding the particle inside the well go to zero?

9. Show that in the limit as $x \rightarrow \infty$ the ratio of successive coefficients of the Taylor series for e^x behave as $1/n$.
10. Show that the minimum in the Morse potential, Equation 5.37, occurs at $r = r_e$ and that $U(r_e) = -D_e$.
11. Find the maximum value of the quantity $(n + 1/2)$ in the equation for the energy for the Morse oscillator, Equation 5.67, and show that for the Morse parameters used to produce the graphs in Section 5.4 (see Table 5.2) the maximum number of levels is 15.
12. Show that the argument of the Airy function that leads to quantization of the energy for the linear potential is indeed unitless as it should be.
13. Show that the WKB result for the expression for the energy levels of an infinite square well, an L -box, Equation 5.146, reduces to the exact result, Equation 3.7, in the limit of large n .
14. Verify Equation 5.157.
15. Use the WKB approximation to find the energy levels of the harmonic oscillator.
16. Use the WKB approximation to find the energy levels of a one-dimensional hydrogen atom for which the potential is

$$U(x) = -\frac{K}{x} \quad \text{where} \quad K = \frac{e^2}{4\pi\epsilon_0}$$

17. One of the first successes of the WKB approximation was the correct description of α -decay. As noted in the text, this problem is treated in most books on this subject. The inverse process, capture of an α -particle (as well as other atomic nuclei), occurs in nature when stars burn. This is called nuclear fusion. In this case an incoming charged particle must surmount the Coulomb repulsive barrier between the capturing nucleus and the incoming nucleus. Compute the transmission probability for such a capture process. Comment on the dependence of the transmission coefficient on the kinetic energy E of the incoming nucleus to see why the temperature must be very high for fusion to occur.
18. The electrons in a metal having work function W (see Section 1.1.1) may be considered to be trapped in a finite square well. If a constant electric field is applied, the wall on one side of the well can be lowered forming a triangular barrier as shown in the figure below.



Potential energy diagram for Problem 18

Assuming that the potential representing the barrier can be represented as

$$\begin{aligned}
 U(x) &= 0 \quad x < 0 \\
 &= U_0 - eFx
 \end{aligned}$$

where F is the magnitude of the field, calculate the probability that an electron having the highest energy of any electron in the well E will tunnel through the barrier. Assume the work function is $W = U_0 - E$. Transmission through this barrier is referred to as field emission.

Chapter 6

The Mechanics of Quantum Mechanics

The quantum mechanics of Schrödinger relies on the solution of a differential equation to describe the physical properties of a system. This is a convenient way to introduce the mysterious properties of quantum physics. As we shall see in subsequent chapters, however, there are quantities that do not lend themselves to description through differential equations. It is therefore necessary to have alternative methods of describing quantal phenomena in our mathematical toolbox. In fact, Heisenberg, simultaneous with Schrödinger, developed a mathematical formalism based on matrix algebra, a formalism that is equivalent to the Schrödinger description. Later, Dirac used linear vector spaces to unify the two approaches and provide a concise method of treating quantum mechanical problems. In this chapter we will describe the formalism of quantum mechanics using both the matrix algebra of Heisenberg and the vector space notation of Dirac. This formalism constitutes the mechanics of quantum physics and thus accounts for the title of this chapter. At the end of the chapter we will correlate this new formalism to a problem that we have already encountered.

6.1 Abstract Vector Spaces

The three-dimensional Cartesian Euclidean space is a special case of an abstract vector space. Because it is a familiar vector space it is convenient to relate abstract spaces to the Euclidean vector space. In Euclidean space any three-dimensional vector α may be written as the sum of its components

$$\alpha = \alpha_x \hat{i} + \alpha_y \hat{j} + \alpha_z \hat{k} \quad (6.1)$$

where the unit vectors \hat{i} , \hat{j} , \hat{k} point in the x , y , and z directions, respectively. Thus, \hat{i} , \hat{j} , \hat{k} constitute an orthonormal basis set (although not a unique one) because $\mathbf{e}_n \cdot \mathbf{e}_m = \delta_{nm}$ where \mathbf{e}_n and \mathbf{e}_m represent any of the \hat{i} , \hat{j} , and \hat{k} . These vectors are said to span the space because any vector in the space may be written as a linear combination of them. The components of α are simply

$$\alpha_x = \boldsymbol{\alpha} \cdot \hat{\mathbf{i}} \quad \alpha_y = \boldsymbol{\alpha} \cdot \hat{\mathbf{j}} \quad \alpha_z = \boldsymbol{\alpha} \cdot \hat{\mathbf{k}} \quad (6.2)$$

where the dot or scalar product has the usual meaning. The dot product is, however, a special case of the inner product, a term that applies to any vector space. Note that if two vectors, Euclidean or otherwise, are orthogonal, their inner product vanishes.

Before continuing, let us clarify the statement that $\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}$ do not constitute a unique orthonormal basis set. This is easily done by noting that, for example, the three unit vectors

$$\frac{1}{\sqrt{2}}(\hat{\mathbf{i}} + \hat{\mathbf{j}}) ; \frac{1}{\sqrt{2}}(\hat{\mathbf{i}} - \hat{\mathbf{j}}) ; \hat{\mathbf{k}} \quad (6.3)$$

constitute an orthonormal basis set (see Problem 1). Clearly other linear combinations will also span the space. Thus, generalizing to the case in which the vectors are functions, linear combinations of the basis functions can also form a basis set.

Let us return to one of the problems for which we solved the TISE for the energy eigenfunctions and their eigenvalues, the L -box. Because the TISE is a linear differential equation, linear combinations of the eigenfunctions $\sqrt{2/L} \sin(n\pi x/L)$ having different values of n are also solutions. In this case the linear combinations are Fourier series. If an energy measurement is made, the probability of measuring the energy eigenvalue associated with a particular energy eigenfunction is the square of the expansion coefficient of that eigenfunction in the linear combination. This is reminiscent of the components of $\boldsymbol{\alpha}$ discussed above. The eigenfunctions do indeed constitute an orthonormal basis set upon which any wave function may be expanded. In the case of an L -box the basis consists of the all functions $\sqrt{2/L} \sin(n\pi x/L)$ where n goes from $1 \rightarrow \infty$. Thus, there are an infinite number of basis functions so the space is of infinite dimension. Although the infinity of functions seems to be much more complicated than the case for which $\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}$ span the Euclidean space, the concept of spanning the space is the same. Never mind if there are a few more basis vectors (functions)! Any vector/function can be expressed as a linear combination of the basis vectors/functions. Note that, in general, the set of functions $\sin(n\pi x/L)$ and $\cos(n\pi x/L)$ are required to span the space, but the limits imposed by the potential energy function for the L -box make the inclusion of the cosines unnecessary. They are, however, required if one uses an a -box. The analog of the dot product, the inner product, in the case of the Fourier series is the integral

$$\int_0^L \left(\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{m\pi x}{L} \right) dx = \delta_{nm} \quad (6.4)$$

A knowledge of abstract vector spaces is crucial in quantum physics because the state of a system is represented by a vector called a “state vector.” The state vector is a more general description of the state of a system than is a wave function because it contains *all* the information that can be known about the system, not just coordinate or momentum information. We will derive the relationship between state

vectors and wave functions later in this chapter. Given that the state vector contains all the available information about the system, we may use the formalism of abstract vector spaces to extract that information.

To summarize, we must expand our conception of a vector. Vector spaces do not necessarily consist of arrows that represent three-dimensional quantities such as displacement and velocity. Vectors may be functions such as sines and cosines or, indeed, any of a number of other entities.

6.1.1 Matrix Representation of a Vector

We can represent vectors by matrices after specifying the basis set with which we are working. For example, the vector α in Equation 6.1 may be represented as a three-component matrix in which the components are simply α_x , α_y , and α_z so the basis set is \hat{i} , \hat{j} , \hat{k} . The matrix can be either a column matrix or a row matrix depending upon its function. For example, because of the rules for matrix multiplication, the inner product $\alpha \cdot \beta$ must be written

$$\begin{aligned}\alpha \cdot \beta &= (\alpha_x \ \alpha_y \ \alpha_z) \begin{pmatrix} \beta_x \\ \beta_y \\ \beta_z \end{pmatrix} \\ &= \alpha_x \beta_x + \alpha_y \beta_y + \alpha_z \beta_z\end{aligned}\tag{6.5}$$

To write the column matrix first would make it impossible to perform the multiplication. As we have seen in the problems that we have solved, there may be many bound states, in some cases an infinite number, so the vectors in our spaces are not restricted to being composed of only three components. Moreover, there is no *a priori* restriction that the components are real. Thus, our row and column matrices may have any number of elements and these elements can be real, imaginary, or complex. So, while Equation 6.5 is quite satisfactory for a three-dimensional space in which the components are real numbers, we must generalize the relationship of a row matrix to its corresponding column matrix in the case in which the components may be complex. This is done by defining the Hermitian (pronounced hermishun) conjugate matrix, a definition that applies to matrices in general, not just column and row matrices. For now let us define the Hermitian conjugate for the column and row matrices. The dagger symbol (\dagger) is commonly used to designate the Hermitian conjugate so we will apply it to a three-element matrix:

$$\begin{pmatrix} \alpha_x \\ \alpha_y \\ \alpha_z \end{pmatrix}^\dagger \equiv (\alpha_x^* \ \alpha_y^* \ \alpha_z^*)\tag{6.6}$$

where the asterisk denotes the complex conjugate. Obviously, $\alpha^{\dagger\dagger} = \alpha$ and the Hermitian conjugate of a scalar is the complex conjugate of the scalar. The Hermitian

conjugate of a matrix is also referred to as the conjugate transpose because the rows and columns are transposed (exchanged) and complex conjugated.

6.1.2 Dirac Notation for a Vector

Dirac used the term “ket” to designate a vector. A ket is equivalent to a column matrix so we write

$$|\alpha\rangle \hat{=} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ . \\ . \\ \alpha_N \end{pmatrix} \quad (6.7)$$

where we have now allowed for the possibility that the vector space is N -dimensional. (Recall that the symbol $\hat{=}$ means “corresponds to.”) The equivalent of a row vector, the Hermitian conjugate of the ket $|\alpha\rangle$ is written $\langle\alpha|$ and is called a “bra.” The inner product $\alpha \cdot \beta$ in the multi-dimensional space is the $\langle\text{bra}|\text{ket}\rangle$

$$\langle\alpha|\beta\rangle = (\alpha_1^* \alpha_2^* \dots \alpha_N^*) \begin{pmatrix} \beta_1 \\ \beta_2 \\ . \\ . \\ \beta_N \end{pmatrix} \quad (6.8)$$

The complex conjugate of an inner product is obtained by simply reversing the bra and ket as is easily seen from Equation 6.8. Thus,

$$\langle\alpha|\beta\rangle^* = \langle\beta|\alpha\rangle \quad (6.9)$$

In terms of components we may write $|\alpha\rangle$ as a linear combination on some basis set. The vector space is, however, of infinite dimension so we will require a more generalizable notation than \hat{i} , \hat{j} , \hat{k} . We choose to represent each of the orthonormal basis vectors by the ket $|e_i\rangle$. Because they are orthonormal we have

$$\langle e_i | e_j \rangle = \delta_{ij} \quad (6.10)$$

An arbitrary ket may then be written

$$|\alpha\rangle = \sum_{i=1}^N \alpha_i |e_i\rangle \quad (6.11)$$

and its Hermitian conjugate

$$\langle \alpha | = \sum_{i=1}^N \langle \mathbf{e}_i | \alpha_i^* \quad (6.12)$$

The inner product of a vector with itself is called the norm. More usually it is referred to as the square of the absolute value by analogy with the length of a three-dimensional vector being the square root of its dot product with itself. Thus,

$$\begin{aligned} \langle \alpha | \alpha \rangle &= \sum_{j=1}^N \sum_{i=1}^N \alpha_i \alpha_j^* \langle \mathbf{e}_j | \mathbf{e}_i \rangle \\ &= \sum_{i=1}^N |\alpha_i|^2 \\ &\geq 0 \end{aligned} \quad (6.13)$$

The norm of a vector/ket is often written $||\alpha||$, but it may also be written with only a single vertical line on each side. We will use the single vertical line, $|\alpha|$. As in three dimensions, if the inner product of a vector with itself is unity, the vector is said to be normalized.

6.1.3 Operators in Quantum Mechanics

It should be clear from the discussion above that the wave functions that we have discussed in the preceding chapters will now, in a formal sense, correspond to vectors (kets), that is, state vectors. This does not mean that the state vectors are necessarily eigenvectors. In general, a wave function can be represented as a linear combination of the eigenfunctions. In the language of the current discussion we say that a state vector may be represented as a linear combination of eigenvectors. It is only the act of measurement that forces the system into one of the eigenstates, the state vector of which is an eigenvector. Thus, the state vector is collapsed by the act of measurement. This is identical to the collapse of the wave function discussed in Section 2.7. Mathematically, the act of measuring is a projection of the state vector onto one of the eigenstates of the observable being measured.

To make a geometrical analogy, suppose we wish to project an arbitrary vector in a plane $\mathbf{A} = A_x \hat{\mathbf{i}} + A_y \hat{\mathbf{j}}$ onto the x -axis. This projection can be accomplished using matrix multiplication:

$$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} A_x \\ 0 \end{pmatrix} \triangleq A_x \hat{\mathbf{i}} \quad (6.14)$$

The 2×2 matrix in Equation 6.14 is a “projection operator”. This is a trivial example, but in quantum mechanics, projection operators select a component of a state vector in an analogous manner.

Operators in quantum mechanics transform vectors into other vectors. In terms of kets we may represent such an operation by the equation

$$\hat{A} |\alpha\rangle = |\beta\rangle \quad (6.15)$$

where \hat{A} is an operator. In quantum mechanics the vast majority of the operators that we will deal with are *linear* operators. That is, they have the property

$$\hat{A} (a |\alpha\rangle + b |\beta\rangle) = a \hat{A} |\alpha\rangle + b \hat{A} |\beta\rangle \quad (6.16)$$

where a and b are complex constants.

The inner product of $\langle\beta|$ with $\hat{A} |\alpha\rangle$ is written

$$\langle\beta| (\hat{A} |\alpha\rangle) = \langle\beta| \hat{A} |\alpha\rangle \quad (6.17)$$

Inner products such as the one in Equation 6.17 are often referred to as matrix elements.

Successive operations with operators

Different operators may be applied in succession and are represented as products of operators which obey the distributive and associative laws, but not necessarily the commutative law. That is,

$$\hat{A} \hat{B} \neq \hat{B} \hat{A} \quad (6.18)$$

Thus, in general, \hat{A} and \hat{B} do not commute.

Functions of operators

A power series of operators is defined by the series that has the same coefficients as the analogous power series in a common variable. That is, if a series of operations, not necessarily an infinite series, is represented by

$$f(\hat{A}) = \sum_{n=0}^{\infty} a_n \hat{A}^n \quad (6.19)$$

then $f(\hat{A})$ is the same function as the power series that it represents. This has important ramifications. For example, suppose an infinite series of successive operations by an operator \hat{A} is given by

$$f(\hat{A}) = 1 + \frac{\hat{A}}{1!} + \frac{\hat{A}^2}{2!} + \frac{\hat{A}^3}{3!} \cdots \quad (6.20)$$

Then

$$f(\hat{A}) = e^{\hat{A}} \quad (6.21)$$

Such a representation pertains to any exponentiated operator \hat{A} .

The identity operator

The definition of the identity operator \hat{I} , also known as the unit operator, may seem trivial, but it is vital to subsequent operations. It is defined such that

$$\hat{I} |\alpha\rangle = |\alpha\rangle \quad (6.22)$$

If $|\alpha\rangle$ is represented by a column matrix having N components, the matrix representation of \hat{I} is an $N \times N$ matrix consisting of zeros except for ones along the diagonal.

The matrix representation of an operator is a diagonal matrix if the basis set consists of the eigenvectors of the operator

If a matrix is diagonal, then the diagonal elements are the eigenvalues. Unless the basis set used to construct the matrix that represents an operator consists of the eigenkets of the operator, the matrix is *not* diagonal. If \hat{A} is an operator having eigenvalues A_{ii} , then the eigenvectors $|\alpha_i\rangle$ are represented as column matrices with only a single nonzero entry. For example, if $i = 1 \rightarrow 4$, then the eigenvalue equation for the eigenvector $|\alpha_2\rangle$ is, in matrix notation

$$\begin{pmatrix} A_{11} & 0 & 0 & 0 \\ 0 & A_{22} & 0 & 0 \\ 0 & 0 & A_{33} & 0 \\ 0 & 0 & 0 & A_{44} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = A_{22} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \quad (6.23)$$

If the operator is not diagonal, the process of solving the eigenvalue equation and then representing the operator in terms of the eigenvectors is called “diagonalizing the matrix”.

The inverse of an operator

The inverse of an operator \hat{A} , designated \hat{A}^{-1} , is defined such that

$$\hat{A}\hat{A}^{-1} = \hat{I} \quad (6.24)$$

It is conceivable that the inverse may not exist, but we will not concern ourselves with this technicality at this point.

The Hermitian conjugate of an operator

In Section 6.1.1 we defined the Hermitian conjugate of a column/row matrix as the conjugate transpose. This definition persists beyond column/row matrices. More illuminating, however, are the properties of the Hermitian conjugate of an operator in Dirac notation. It is easiest to begin with the an operational definition of the Hermitian conjugate of a ket, which, from our definition of the conjugate of a column/row matrix, is

$$(|\alpha\rangle)^\dagger = \langle\alpha| \quad (6.25)$$

so that

$$(\hat{A} |\alpha\rangle)^\dagger = \langle\alpha| \hat{A}^\dagger \quad (6.26)$$

In view of Equation 6.26 we may take the Hermitian conjugate of the inner product in Equation 6.17:

$$(\langle\beta| \hat{A} |\alpha\rangle)^\dagger = \langle\alpha| \hat{A}^\dagger |\beta\rangle \quad (6.27)$$

We can also examine the Hermitian conjugate of a product of operators $\hat{A}\hat{B}$ using Equation 6.26 and the identifications $|\alpha\rangle \rightarrow \hat{B} |\alpha\rangle$ and $\langle\beta| \hat{A} \rightarrow \langle\beta| \hat{A}$:

$$\begin{aligned} (\langle\beta| \hat{A}\hat{B} |\alpha\rangle)^\dagger &= \langle\beta| \hat{A} \hat{B} |\alpha\rangle^\dagger \\ &= \langle\alpha| \hat{B}^\dagger \hat{A}^\dagger |\beta\rangle \end{aligned} \quad (6.28)$$

The inner product in Equation 6.28 may also be written

$$(\langle\beta| \hat{A}\hat{B} |\alpha\rangle)^\dagger = \langle\alpha| (\hat{A}\hat{B})^\dagger |\beta\rangle \quad (6.29)$$

Comparing the right-hand sides of Equations 6.28 and 6.29 shows that

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger \quad (6.30)$$

Unitary operators

If the inverse of an operator \hat{U} is equal to its Hermitian conjugate \hat{U}^\dagger , then the operator is said to be unitary. Thus, \hat{U} is unitary if

$$\hat{U}^{-1} = \hat{U}^\dagger \quad (6.31)$$

and

$$\begin{aligned}\hat{U}\hat{U}^{-1} &= \hat{U}\hat{U}^\dagger \\ &= \hat{I}\end{aligned}\tag{6.32}$$

Hermitian operators

The most important of all linear operators in quantum physics is the Hermitian operator. Quite simply, an operator is Hermitian if it is equal to its Hermitian conjugate. That is, \hat{A} is Hermitian if

$$\hat{A} = \hat{A}^\dagger\tag{6.33}$$

In quantum mechanics, the observable quantities, quantities that can be measured, are represented by Hermitian operators for reasons that we shall see very shortly.

The commutator

It was seen above, that, in general

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}\tag{6.34}$$

This property of quantum mechanical operators has extremely important consequences, so important that the difference $\hat{A}\hat{B} - \hat{B}\hat{A}$ is given a special symbol and a special name. It is written as

$$\begin{aligned}[\hat{A}, \hat{B}] &\equiv \hat{A}\hat{B} - \hat{B}\hat{A} \\ &= -[\hat{B}, \hat{A}]\end{aligned}\tag{6.35}$$

and called the commutator of \hat{A} and \hat{B} . If two operators commute, their commutator vanishes.

It is often useful to employ commutator identities such as those listed in Appendix K. These are frequently proved by adding and subtracting the necessary terms to the expansion of the left-hand side. For example,

$$\begin{aligned}[\hat{A}, \hat{B}\hat{C}] &= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} + (\hat{B}\hat{A}\hat{C} - \hat{B}\hat{A}\hat{C}) \\ &= (\hat{A}\hat{B}\hat{C} - \hat{B}\hat{A}\hat{C}) + (\hat{B}\hat{A}\hat{C} - \hat{B}\hat{C}\hat{A}) \\ &= (\hat{A}\hat{B} - \hat{B}\hat{A})\hat{C} + \hat{B}(\hat{A}\hat{C} - \hat{C}\hat{A}) \\ &= [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]\end{aligned}\tag{6.36}$$

A specific example of a noncommuting operator is in order here. In this chapter we have, so far, been very abstract. The payoff for this abstract formalism is that it will simplify computations later (you have heard that before). Nonetheless, let us

consider the operators that we discussed in Section 4.3.1. Recall that the momentum operator in coordinate representation is given by (see Equation 2.28)

$$\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} \quad (6.37)$$

Let us examine the commutator $[x, \hat{p}_x]$. When an operator is a differential operator the method that must be employed to determine its action is to examine its operation on a function, in this case some arbitrary function of x , call it $f(x)$. Thus, performing the indicated operations

$$\begin{aligned} [x, \hat{p}_x] f(x) &= \frac{\hbar}{i} \left\{ x \frac{df(x)}{dx} - \frac{d[xf(x)]}{dx} \right\} \\ &= -\frac{\hbar}{i} f(x) \end{aligned} \quad (6.38)$$

We conclude therefore that $[x, \hat{p}_x]$ is an example of a commutation relation that does not vanish. Moreover, we have evaluated it and found that

$$[x, \hat{p}_x] = i\hbar \hat{I} \quad (6.39)$$

Often the \hat{I} is understood, but in Equation 6.39 it has been displayed for clarity.

While Equation 6.39 pertains specifically to the coordinate x and the x -component of linear momentum, it can be generalized to reflect the fact that the coordinates are independent as are the components of momentum. Therefore, we may write

$$\begin{aligned} [x_i, \hat{p}_j] &= i\hbar \delta_{ij} \\ [x_i, x_j] &= 0 \\ [\hat{p}_i, \hat{p}_j] &= 0 \end{aligned} \quad (6.40)$$

where the subscripts i and j refer to any of the x , y , or z -components. For example, $x_2 = y$ and $p_2 = p_y$. These commutation rules are sometimes referred to as the canonical commutation rules because they are often taken to be postulates of quantum physics.

From the first of Equations 6.40 we can derive a commutation rule involving the powers of x_i or \hat{p}_j . Using the identity given in Equation K.3, the canonical commutation rules, and mathematical induction, we may derive the relation (see Problem 10)

$$[x, \hat{p}_x^n] = i\hbar n \hat{p}_x^{n-1} \quad (6.41)$$

Moreover, if a function of \hat{p}_x , $f(\hat{p}_x)$ is assumed to be expandable in a power series we may write

$$[x, f(\hat{p}_x)] = i\hbar \frac{\partial f(\hat{p}_x)}{\partial x} \quad (6.42)$$

In an analogous fashion the companion commutation rule for \hat{p}_x and $g(x)$, a function of x that can be expressed as a power series,

$$[\hat{p}_x, g(x)] = -i\hbar \frac{\partial g(x)}{\partial x} \quad (6.43)$$

can also be derived. Of course, Equations 6.42 and 6.43 can be generalized to the other coordinates as well.

6.2 The Eigenvalue Equation

To continue with our three-dimensional analogy, suppose an operator merely changes the length of the vector. In Dirac notation this simple operation is represented by

$$\hat{A}|\alpha\rangle = a|\alpha\rangle \quad (6.44)$$

where, in this case, a is the factor by which \hat{A} stretches or compresses the vector $|\alpha\rangle$. This is a trivial example of an eigenvalue equation, almost too trivial to make the point that an operator operating on an (unknown) eigenvector reproduces that eigenvector multiplied by an eigenvalue. In the general case, the eigenvalue, which is a number, might be a complex number. Additionally, there will be a set of eigenvectors, each having its own eigenvalue.

We have already encountered the eigenvalue equation in disguise, the TISE. Written in Dirac notation to be consistent with Equation 6.44 the TISE is

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \quad (6.45)$$

where \hat{H} is the Hamiltonian operator, the $|\psi_n\rangle$ are the eigenvectors, or eigenkets, and the E_n are the corresponding eigenvalues. As previously, we attach a subscript to signify that the solution of the eigenvalue equation consists of an array of eigenvectors and eigenvalues, possibly even an infinite array. The particle-in-a-box and the harmonic oscillator are examples of potentials that cause their Hamiltonian operators to have an infinite array of eigenvectors and eigenvalues.

To complicate matters, there are cases in which the same eigenvalue corresponds to two or more distinctly different eigenvectors. In such cases the eigenstates represented by the eigenvector are said to be degenerate. The number of eigenstates having the same eigenvalue is called the degree of degeneracy or simply the degeneracy of the states. For one-dimensional potentials, however, there is no degeneracy of the energy eigenstates (see Problem 3, Chapter 2).

When the operator in an eigenvalue equation is Hermitian, the eigenvectors and eigenvalues possess special properties that are particularly important for quantum

mechanical applications. We therefore present some of the most important of these properties.

6.2.1 Properties of Hermitian Operators and the Eigenvalue Equation

The eigenvalues of Hermitian operators are real.

For a Hermitian operator the eigenvalues are real. This is important because it is Hermitian operators that are used to represent physical observables, for example, $\hat{H} \hat{=}$ energy. Surely the eigenvalues, the possible results of a measurement, cannot be imaginary if they are to represent observable quantities! The proof is straightforward.

Proof

Let \hat{A} represent an arbitrary Hermitian operator such that

$$\hat{A}|\alpha_i\rangle = \alpha_i|\alpha_i\rangle \quad i = 1, 2, \dots, N \quad (6.46)$$

That is, the set of numbers α_i are the eigenvalues associated with the eigenkets $|\alpha_i\rangle$. Taking the complex conjugate of Equation 6.46 we have

$$\langle\alpha_j|\hat{A}^\dagger = \langle\alpha_j|\alpha_j^* \quad j = 1, 2, \dots, N \quad (6.47)$$

Now take the inner product of Equation 6.46 with the bra $\langle\alpha_j|$. This is commonly referred to as “multiplying on the left” by $\langle\alpha_j|$. Similarly, multiply Equation 6.47 on the right by $|\alpha_i\rangle$. The resulting inner products on the left-hand sides are identical because \hat{A} is Hermitian. We may therefore equate the right-hand sides and obtain

$$\alpha_i \langle\alpha_j|\alpha_i\rangle = \alpha_j^* \langle\alpha_j|\alpha_i\rangle \quad (6.48)$$

or

$$(\alpha_j^* - \alpha_i) \langle\alpha_j|\alpha_i\rangle = 0 \quad (6.49)$$

Now set $i = j$. The inner product of a vector with itself cannot vanish so we must have

$$\alpha_i^* = \alpha_i \quad (6.50)$$

thus proving that the eigenvalues of a Hermitian operator are real.

The eigenvectors of a nondegenerate Hermitian operator are mutually orthogonal.

Proof

Using Equation 6.49 from the proof above with $i \neq j$ we have

$$\langle \alpha_j | \alpha_i \rangle = \delta_{ij} \quad (6.51)$$

because we have already proved that the eigenvalues are real. Also, in Equation 6.51 we have assumed that the eigenvectors are normalized. Note that Equation 6.51 is only true if the operator is nondegenerate for if $\alpha_j = \alpha_i$ the inner product in Equation 6.49 can take on any value.

Degeneracy is an important property of quantum mechanical operators. We therefore discuss this property before returning to the properties of Hermitian operators.

The eigenvectors corresponding to the same eigenvalue are not unique. Any linear combination of degenerate eigenvectors is also an eigenvector with the same eigenvalue.

Proof

Assume a twofold degeneracy such that

$$\hat{B} |\beta_1\rangle = \beta |\beta_1\rangle \quad \text{and} \quad \hat{A} |\beta_2\rangle = \beta |\beta_2\rangle \quad (6.52)$$

We form two arbitrary linear combinations of $|\beta_1\rangle$ and $|\beta_2\rangle$ as follows:

$$|\alpha_1\rangle = a |\beta_1\rangle + b |\beta_2\rangle \quad \text{and} \quad |\alpha_2\rangle = c |\beta_1\rangle + d |\beta_2\rangle \quad (6.53)$$

where a , b , c , and d are arbitrary constants. Clearly $|\alpha_1\rangle$ and $|\alpha_2\rangle$ are eigenvectors of \hat{B} with eigenvalue β as may be seen by simply operating on them. As an example we choose $|\alpha_1\rangle$.

$$\begin{aligned} \hat{B} |\alpha_1\rangle &= a \hat{B} |\beta_1\rangle + b \hat{B} |\beta_2\rangle \\ &= a\beta |\beta_1\rangle + b\beta |\beta_2\rangle \\ &= \beta (a |\beta_1\rangle + b |\beta_2\rangle) \\ &= \beta |\alpha_1\rangle \end{aligned} \quad (6.54)$$

Thus, the eigenvectors $|\beta_1\rangle$ and $|\beta_2\rangle$ are not unique since we may choose any values of the constants a , b , c , and d and still obtain an eigenvector with the same eigenvalue.

The operator $|\alpha_i\rangle \langle \alpha_i|$ is called a projection operator and picks out the α_i th “component” of an arbitrary vector $|\psi\rangle$ that is given by

$$|\psi\rangle = \sum_{i=1}^N \alpha_i |\alpha_i\rangle \quad (6.55)$$

Proof

Assume that $|\psi\rangle$ in Equation 6.55 is normalized and take the inner product with $\langle \alpha_j |$ to get

$$\langle \alpha_j | \psi \rangle = \alpha_j \quad (6.56)$$

Now replace a_j in Equation 6.55 using Equation 6.56 with $j = i$. We have

$$\begin{aligned} |\psi\rangle &= \sum_{i=1}^N |\alpha_i\rangle (\langle \alpha_i | \psi \rangle) \\ &= \left(\sum_{i=1}^N |\alpha_i\rangle \langle \alpha_i| \right) |\psi\rangle \end{aligned} \quad (6.57)$$

Now, $|\psi\rangle$ is an arbitrary vector so the quantity in parentheses must be the identity operator, that is,

$$\left(\sum_{i=1}^N |\alpha_i\rangle \langle \alpha_i| \right) = \hat{I} \quad (6.58)$$

Equation 6.58 is known as the completeness relation. Because the quantity in parentheses in Equation 6.58 is the identity it may be inserted virtually anywhere in a string of bras and kets in order to facilitate a proof.

Let us assume that $|\psi\rangle$ is normalized and take the inner product $\langle \psi | \psi \rangle$. Bearing in mind that the $|\alpha_i\rangle$ are orthonormal $\langle \psi | \psi \rangle$ may be written

$$\begin{aligned} \langle \psi | \psi \rangle &= 1 \\ &= \langle \psi | \hat{I} | \psi \rangle \\ &= \langle \psi | \left(\sum_{i=1}^N |\alpha_i\rangle \langle \alpha_i| \right) | \psi \rangle \\ &= \sum_{i=1}^N \langle \psi | \alpha_i \rangle \langle \alpha_i | \psi \rangle \end{aligned}$$

$$\begin{aligned}
&= \sum_{i=1}^N |\langle \alpha_i | \psi \rangle|^2 \\
&= \sum_{i=1}^N |\alpha_i|^2
\end{aligned} \tag{6.59}$$

This shows that, as long as $|\psi\rangle$ is normalized, the sum of the absolute squares of the expansion coefficients is equal to unity.

The inside out inner product that is part of the completeness relation, Equation 6.58, must be an operator. Clearly it is not a vector, but, when operating on a vector it produces another vector. This fits the definition of an operator. Let us see what operation it performs by having it operate on an arbitrary vector, say $|\psi\rangle$ as expressed as the linear combination of the basis set $|\alpha_i\rangle$ in Equation 6.55.

$$\begin{aligned}
(|\alpha_i\rangle \langle \alpha_i|) |\psi\rangle &= (|\alpha_i\rangle \langle \alpha_i|) \sum_{j=1}^N \alpha_j |\alpha_j\rangle \\
&= |\alpha_i\rangle \left(\langle \alpha_i | \sum_{j=1}^N \alpha_j |\alpha_j\rangle \right) \\
&= \langle \alpha_i | \left(\sum_{j=1}^N \alpha_j \langle \alpha_i | \alpha_j \rangle \right) \\
&= \langle \alpha_i | (\alpha_j \delta_{ij} \langle \alpha_i | \alpha_j \rangle) \\
&= \alpha_i |\alpha_i\rangle
\end{aligned} \tag{6.60}$$

The operator $|\alpha_i\rangle \langle \alpha_i|$, which is sometimes referred to as an outer product, picks out the α_i th “component” of the vector $|\psi\rangle$. It therefore *projects* $|\psi\rangle$ onto the $|\alpha_i\rangle$ state and is called a projection operator.

We may apply this formalism to the two-dimensional vector \mathbf{A} as in Section 6.1.3. We identify $|\psi\rangle \triangleq \mathbf{A}$ and, for example, $|\alpha_i\rangle \triangleq \hat{\mathbf{i}}$. We have

$$\begin{aligned}
(\hat{\mathbf{i}}\hat{\mathbf{i}}) \cdot \mathbf{A} &= \hat{\mathbf{i}} (\hat{\mathbf{i}} \cdot \mathbf{A}) \\
&= \hat{\mathbf{i}} (\hat{\mathbf{i}} \cdot A_x \hat{\mathbf{i}} + \hat{\mathbf{i}} \cdot A_y \hat{\mathbf{j}}) \\
&= A_x \hat{\mathbf{i}}
\end{aligned} \tag{6.61a}$$

from which it is clear that the “operator” $\hat{\mathbf{i}}\hat{\mathbf{i}}$ “projects” the vector \mathbf{A} onto the x -axis. It is understood that the operator on the right-hand side of the projection operator $\hat{\mathbf{i}}\hat{\mathbf{i}}$ must act first. In quantum mechanical terms, they project a vector onto the “axis” corresponding to a particular eigenvector. To simplify the notation we designate a projection operator as

$$\hat{P}_i = |\alpha_i\rangle \langle \alpha_i| \tag{6.62}$$

so that

$$\hat{P}_i |\psi\rangle = \alpha_i |\alpha_i\rangle \quad (6.63)$$

Clearly the eigenvectors of the projection operator are the basis vectors themselves so that

$$\hat{P}_j |\alpha_i\rangle = \delta_{ij} |\alpha_i\rangle \quad (6.64)$$

It is seen then that the matrix representation of the $|\alpha_i\rangle$ consists of column vectors with N entries, all of which are zero except for unity in the i th position. This means that the matrix representation of the projection operator \hat{P}_i is an $N \times N$ matrix with all entries zero except for unity in the i th location along the diagonal (see Equation 6.14). This shows us how to represent the outer product $|\alpha_i\rangle \langle\alpha_i|$ by a matrix.

The eigenvectors corresponding to the same eigenvalue are not (necessarily) orthogonal, but an orthogonal set can always be constructed.

Proof

From the proof in Section 6.2.1 it is clear that we may choose a , b , c , and d such that the inner product

$$\langle\alpha_1|\alpha_2\rangle \neq 0 \quad (6.65)$$

which means that there is no requirement that any set of linearly independent degenerate eigenvectors need be mutually orthogonal. On the other hand, proper choice of a , b , c , and d would guarantee that an orthonormal set can be constructed. The process by which an orthogonal set is constructed is known as the Gram–Schmidt orthogonalization procedure.

To demonstrate, we construct a set of orthogonal eigenvectors by judiciously choosing linear combinations of the eigenvectors associated with the degenerate eigenvalue, the degenerate eigenvectors. Assume that the set of N linearly independent normalized kets $|\beta_1\rangle, |\beta_2\rangle, |\beta_3\rangle \dots |\beta_N\rangle$ all have the same eigenvalue β . We wish to use these eigenvectors to construct a set of orthonormal eigenvectors $|\alpha_1\rangle, |\alpha_2\rangle, |\alpha_3\rangle, \dots, |\alpha_N\rangle$, all of which have the eigenvalue β . We begin by letting

$$|\alpha_1\rangle = |\beta_1\rangle \quad (6.66)$$

and use terminology borrowed from Euclidean vector spaces in an effort to clarify the procedure by analogy.

To guarantee that $|\alpha_2\rangle$ has no component parallel to $|\alpha_1\rangle$, thus guaranteeing that they are orthogonal, we simply subtract the component of $|\beta_2\rangle$ along the $|\alpha_1\rangle$ (and $|\beta_1\rangle$) axis from the eigenvector $|\beta_2\rangle$. This is easily done using the projection operator

$|\alpha_1\rangle \langle \alpha_1|$ which, when operating on $|\beta_2\rangle$, produces the component of $|\beta_2\rangle$ along the $|\alpha_1\rangle$ axis. We therefore construct $|\alpha_2\rangle$ as

$$c_2 |\alpha_2\rangle = |\beta_2\rangle - |\alpha_1\rangle \langle \alpha_1 | \beta_2 \rangle \quad (6.67)$$

where the constant c_2 is to be adjusted to insure that $|\alpha_2\rangle$ is normalized. Note that $|\alpha_1\rangle$ is automatically normalized because the $|\beta_i\rangle$ are assumed to be normalized.

We can verify that $|\alpha_2\rangle$ as given in Equation 6.67 is orthogonal to $|\alpha_1\rangle$ by taking the inner product $\langle \alpha_1 | \alpha_2 \rangle = \langle \beta_1 | \alpha_2 \rangle$.

$$c_2 \langle \alpha_1 | \alpha_2 \rangle = \langle \alpha_1 | \beta_2 \rangle - \langle \alpha_1 | \alpha_1 \rangle \langle \alpha_1 | \beta_2 \rangle \quad (6.68)$$

Because $\langle \alpha_1 | \alpha_1 \rangle = \langle \beta_1 | \beta_1 \rangle = 1$, it is clear that $\langle \alpha_1 | \alpha_2 \rangle = 0$.

The constant c_2 is evaluated by demanding normality of the $|\alpha_2\rangle$. Therefore,

$$\begin{aligned} |c_2|^2 \langle \alpha_2 | \alpha_2 \rangle &= |c_2|^2 \\ &= \langle \beta_2 | \beta_2 \rangle - 2 |\langle \beta_2 | \alpha_1 \rangle|^2 \\ &\quad + \langle \beta_2 | \alpha_1 \rangle \langle \alpha_1 | \alpha_1 \rangle \langle \alpha_1 | \beta_2 \rangle \\ &= 1 - |\langle \beta_2 | \alpha_1 \rangle|^2 \end{aligned} \quad (6.69)$$

and the normalization constant c_2 is given by

$$c_2 = \sqrt{1 - |\langle \beta_2 | \alpha_1 \rangle|^2} \quad (6.70)$$

Of course, the procedure can be continued N times until all of the $|\alpha_i\rangle$ have been constructed. For example, $|\alpha_3\rangle$ will be

$$c_3 |\alpha_3\rangle = |\beta_3\rangle - |\alpha_1\rangle \langle \alpha_1 | \beta_3 \rangle - |\alpha_2\rangle \langle \alpha_2 | \beta_3 \rangle \quad (6.71)$$

where now both the components along the $|\alpha_1\rangle$ and $|\alpha_2\rangle$ axes have been subtracted from $|\alpha_3\rangle$ and c_3 must be adjusted for normality.

Because an orthonormal set can always be constructed from the degenerate eigenvectors there will always be a complete set of eigenvectors upon which any arbitrary vector may be expanded. This set would be composed of the orthonormal sets of degenerate eigenvectors plus any nondegenerate eigenvectors. The nondegenerate eigenvectors are orthogonal to the degenerate orthogonal eigenvectors by virtue of having different eigenvalues.

The number of eigenvectors may be finite or, indeed, it may be infinite, but the set of mutually orthogonal $|\alpha_i\rangle$ do indeed constitute a basis set. Here the set $|\alpha_i\rangle$ is taken to represent the *complete* set of eigenvectors, degenerate and nondegenerate. This is analogous to the paradigm three-dimensional geometrical case represented by Equation 6.1 in which an arbitrary vector is expanded on the $\hat{i}, \hat{j}, \hat{k}$ basis set. Thus, we may still expand an arbitrary ket as given in Equation 6.55. In quantum

physics it is assumed that the set of $|\alpha_i\rangle$ span the space so that any suitable state vector may be written as a linear combination of the $|\alpha_i\rangle$.

6.2.2 Properties of Commutators

It will be seen later that the vanishing of the commutator has important consequences. We will therefore consider the properties of commuting operators in some detail.

If two operators have common eigenvectors, then they commute.

Proof

Suppose

$$\hat{A} |\alpha\rangle = \alpha |\alpha\rangle \quad \text{and} \quad \hat{B} |\alpha\rangle = \beta |\alpha\rangle \quad (6.72)$$

Operating on the left side of the first equation with \hat{B} and the left side of the second equation with \hat{A} and subtracting we have

$$\begin{aligned} (\hat{B}\hat{A} - \hat{A}\hat{B}) |\alpha\rangle &= \hat{B}\alpha |\alpha\rangle - \hat{A}\beta |\alpha\rangle \\ &= (\alpha\beta - \beta\alpha) |\alpha\rangle \\ &= 0 \end{aligned} \quad (6.73)$$

Therefore,

$$[\hat{A}, \hat{B}] = 0 \quad (6.74)$$

Moreover, the converse is also true.

If two nondegenerate operators commute, they have a common set of eigenvectors.

Proof

Let

$$\hat{A} |\alpha_i\rangle = \alpha_i |\alpha_i\rangle \quad (6.75)$$

and assume that the nondegenerate operators \hat{A} and \hat{B} commute. Now operate on Equation 6.75 with \hat{B} and interchange the order of operation because \hat{A} and \hat{B} commute

$$\hat{A} \{ \hat{B} |\alpha_i\rangle \} = \alpha_i \{ \hat{B} |\alpha_i\rangle \} \quad (6.76)$$

which shows that $\{\hat{B} |\alpha_i\rangle\}$ is an eigenvector of the operator \hat{A} with eigenvalue α_i . But, it has been assumed that \hat{A} is nondegenerate. Therefore, $\{\hat{B} |\alpha_i\rangle\}$ cannot be different from $|\alpha_i\rangle$ except by a multiplicative constant.

Having proved that nondegenerate commuting operators have common eigenvectors we now undertake the much more formidable task of proving it for degenerate operators.

If any two operators commute, they have a common set of eigenvectors

Proof

Let

$$\hat{G} |\gamma_i\rangle = \gamma |\gamma_i\rangle \quad (6.77)$$

where γ is an n -fold degenerate eigenvalue of \hat{G} . Assume that the operators \hat{G} and \hat{F} commute. Operate on Equation 6.77 with \hat{F} and taking advantage of the commutation with \hat{G} we have

$$\hat{G} \{\hat{F} |\gamma_i\rangle\} = \gamma \{\hat{F} |\gamma_i\rangle\} \quad (6.78)$$

where γ is the same eigenvalue for all of the $|\gamma_i\rangle$. As above, it is clear that $\{\hat{F} |\gamma_i\rangle\}$ is an eigenvector of \hat{G} , although we must deal with the degeneracy now which we do by expanding $\{\hat{F} |\gamma_i\rangle\}$ on the complete set $|\gamma_i\rangle$.

$$\{\hat{F} |\gamma_i\rangle\} = \sum_{j=1}^n g_{ij} |\gamma_j\rangle \quad (6.79)$$

Now multiply by a constant c_i and sum over all i and obtain

$$\begin{aligned} \hat{F} \sum_{j=1}^n c_j |\gamma_j\rangle &= \sum_{i,j=1}^n g_{ij} c_i |\gamma_j\rangle \\ &= \sum_{j=1}^n |\gamma_j\rangle \left(\sum_{i=1}^n c_i g_{ij} \right) \\ &= \sum_{j=1}^n \varphi g_j |\gamma_j\rangle \end{aligned} \quad (6.80)$$

where we have made the substitution

$$\sum_{i=1}^n c_i g_{ij} = \varphi c_j \quad (6.81)$$

in the last line of Equation 6.80.

To understand Equation 6.81 it is best to write out the first few terms. We have

$$g_{1j}c_1 + g_{2j}c_2 + \dots + (g_{jj} - \varphi)c_j + \dots + g_{nj}c_n = 0 \quad (6.82)$$

Several things are apparent. First, there are n such equations, one for each value of j . Second, the term for which $i = j$ has φ in the coefficient of c_j . Finally, the set of n simultaneous equations are homogeneous equations. That is, the right-hand sides are all equal to zero. Such equations have a nontrivial solution only if the determinant of the coefficients vanishes. The equation that results from setting this determinant equal to zero is called the secular equation. This procedure occurs quite often in quantum mechanics so it is worth noting the reason that the only nontrivial solutions are the roots of the secular equation.

Recall Cramer's rule for solving simultaneous equations. For simplicity use two equations and two unknowns. Suppose we wish to solve

$$\begin{aligned} a_1x + b_1y &= c_1 \\ a_2x + b_2y &= c_2 \end{aligned} \quad (6.83)$$

To apply Cramer's rule we form the determinant of the coefficients

$$D = \begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix} \quad (6.84)$$

Now, to solve for x , form D_x by inserting the right-hand sides into the x -positions in D . That is,

$$D_x = \begin{vmatrix} c_1 & b_1 \\ c_2 & b_2 \end{vmatrix} \quad (6.85)$$

According to the rule, x is given by

$$x = \frac{D_x}{D} \quad (6.86)$$

If, however, both c_1 and c_2 are zero, then $D_x \equiv 0$ because one column of a determinant consists of all zeros. Therefore, x must vanish *unless* D is also zero in which case the quotient D_x/D is indeterminate and a nonzero solution for x (and y) is possible. Of course, the extension to multi-dimensions is obvious. Nonetheless, the secular equation is used countless times in quantum mechanics and, indeed, in all branches of physics.

While the array of equations represented by Equation 6.82 has the c 's as the unknowns, it is actually the n roots of φ that the secular equation will yield. Each root, φ_j , will have associated with it a solution $c_i^{(j)}$. We may write a new vector using these expansion coefficients:

$$|\varphi_j\rangle = \sum_{i=1}^n c_i^{(j)} |\chi_i\rangle \quad (6.87)$$

Thus, the $|\varphi_j\rangle$ are eigenvectors of both \hat{G} and \hat{F} and constitute a complete set of simultaneous eigenvectors of these two operators.

6.3 The Postulates of Quantum Mechanics

6.3.1 Listing of the Postulates

Now that we have the mathematical tools to apply to an abstract formulation of quantum physics we state six postulates to guide our study. We emphasize that virtually every textbook contains a listing of postulates numbering about five, give or take a few, depending upon author's inclination for consolidation. We present them in an order that is considered logical and conducive to understanding. For convenience, we first list them and then discuss them separately.

Postulate I—The measurement postulate

All observable quantities such as position, momentum, and energy are represented by linear operators. The only possible result of a measurement of an observable A is one of the eigenvalues of the operator \hat{A} .

Postulate II—The Hermitian postulate

The operator that represents any observable quantity in quantum mechanics must be a Hermitian operator. Thus, the observable quantity A corresponds to the operator $\hat{A} = \hat{A}^\dagger$. A may be a scalar or vector quantity in which case the corresponding operators are scalar or vector operators, respectively. \hat{A} may also contain the time.

Postulate III—The state vector postulate

The state of any physical system is specified by a state vector which we designate by the ket $|\Psi\rangle$. We use the capital Greek letter to conform with our previous notation where the capital represented the time-dependent wave function; $|\Psi\rangle$ also contains variables other than time. This ket contains all the information that it is possible to extract about the system. For convenience we assume, because it is always possible to do so for bound states, that $|\Psi\rangle$ is normalized. If $|\Psi\rangle$ does not contain the time, it is designated $|\psi\rangle$.

Postulate IV—The expansion postulate

It is assumed that the state vector $|\psi\rangle$ at a given time may be expressed as a linear combination of the eigenvectors of \hat{A} ; this expansion is referred to as a coherent

superposition of (eigen)states. This postulate implies that the set of eigenvectors of \hat{A} form a basis set for the vector space of interest. The term “vector space of interest” refers to the vector space that is spanned by the set of eigenvectors since the only possible results of a measurement are their eigenvalues (Postulate I). Note that this circumvents any detailed discussion of the completeness of the eigenvectors since Postulate I defines the vector space of interest. Therefore, no further discussion of completeness is required.

If $|\psi\rangle$ is normalized so that $\langle\psi|\psi\rangle = 1$, then the absolute squares of the expansion coefficients represent the probabilities of measuring the eigenvalues associated with each particular eigenvector or component of the state vector. This is often referred to as the Born interpretation in honor of Max Born who was awarded the Nobel Prize in Physics 1954 “for his fundamental research in quantum mechanics, especially for his statistical interpretation of the wavefunction.”

Postulate V—The uncertainty postulate

If two different observables A and B are measured, the results will, in general, depend upon the order in which the measurements are made. This interference between successive measurements manifests itself mathematically as the noncommutativity of the operators \hat{A} and \hat{B} . This is another statement of the Heisenberg uncertainty principle which was discussed qualitatively in Section 1.2.3. The quantitative statement of the restrictions on the uncertainties in \hat{A} and \hat{B} is given below.

Postulate VI—The time evolution postulate

The time evolution of a system is dictated by the TDSE which we may write in terms of the state vector as

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle \quad (6.88)$$

where \hat{H} is the Hamiltonian operator first introduced in Equations 2.17 and 2.25 for one-dimensional problems. As noted there, it represents the TME in the usual case for which the potential energy is independent of time. Even if \hat{H} contains the time, Equation 6.88 still determines the time evolution of the system. (In this textbook \hat{H} will rarely contain the time.)

6.3.2 Discussion of the Postulates

Postulate I—The measurement postulate

The significance of this postulate belies its brevity. This significance will also be considered in the discussion of Postulate IV—the expansion postulate. For now it is sufficient to note that we have already encountered an example of an eigenvalue

equation that leads to the possible energies of a system, the TISE. Because the Hamiltonian is the energy operator, the TISE is the energy eigenvalue equation.

Postulate II—The Hermitian postulate

It is absurd to imagine that a measurement of a legitimate observable quantity would yield anything but a real number. Therefore, because of Postulate I and because Hermitian operators must have only real eigenvalues (see Section 6.2.1), it is natural that observables are represented by Hermitian operators.

Postulate III—The state vector postulate

Clearly the state vector concept is a generalization of the wave function that was encountered earlier in this book. The reason that the concept must be generalized is that there are some observables for which it is impossible to write a function as was done in the problems solved previously. The most often encountered observable for which a function cannot be written is the “spin” which represents the magnetic moment of a particle.

Postulate IV—The expansion postulate

If $\langle \psi | \psi \rangle = 1$ and if $|\psi\rangle$ is expressed as a linear combination of the eigenvectors $|\alpha_i\rangle$ of the operator \hat{A} so that

$$|\psi\rangle = \sum_{i=1}^N \alpha_i |\alpha_i\rangle \quad (6.89)$$

where the α_i are, in general, complex numbers, then the probability of measuring the j th eigenvalue of \hat{A} (as set forth in Postulate I) is the absolute square of the expansion coefficient α_j which may be determined by application of the appropriate projection operator

$$\begin{aligned} \alpha_j |\alpha_j\rangle &= \hat{P}_j |\psi\rangle \\ &= (|\alpha_j\rangle \langle \alpha_j|) |\psi\rangle \end{aligned} \quad (6.90)$$

Therefore,

$$\alpha_j = \langle \alpha_j | \psi \rangle \quad (6.91)$$

and the expansion of the state vector $|\psi\rangle$ in Equation 6.89 may be written as in Equation 6.57 as

$$|\psi\rangle = \sum_{i=1}^N |\alpha_i\rangle \langle \alpha_i | \psi \rangle \quad (6.92)$$

Now, the probability of measuring the j th eigenvalue \wp_j is simply the square of the expansion coefficient

$$\wp_j = |\alpha_j|^2 \quad (6.93)$$

which is also the probability of finding the system in the j th state unless a degeneracy exists in which case the probability of measuring the degenerate eigenvalue is simply the sum of the probabilities of finding the system in each of the degenerate eigenstates. Note that the measurement actually changes the quantum mechanical system by forcing it into one of the eigenstates of \hat{A} . This is referred to as “collapsing” the state vector since the act of measurement has converted the superposition of states in Equation 6.89 into a single state, one of the complete set of $|\alpha_i\rangle$.

Notice that it is necessary to take the absolute value of the expansion coefficient α_j because α_j is a complex number and probabilities must be real fractions. Moreover, because any complex number may be written

$$\alpha_{jj} = e^{i\varphi} |\alpha_{jj}| \quad (6.94)$$

where φ is the phase that $|\psi\rangle$, as given in Equation 6.89, is said to represent a *coherent* state.

Introductory quantum physics courses such as the one to which this book is directed concentrate on solutions of the eigenvalue problem, in particular the TISE. This postulate makes it clear, however, that quantum mechanical systems need not reside in an eigenstate. Indeed, it is rare that they are in an eigenstate. Rather, such systems are generally in a superposition of states, a superposition that is represented mathematically by Equation 6.89. What does this mean physically? Does it mean that the atoms “flit” between the different states $|\alpha_i\rangle$ and the result of a measurement depends upon which state the atom occupied at the instant the measurement was made? This is one point of view. Another point of view is to imagine that rather than a single system, there are a large number of systems (atoms in the present example). Each atom is in an eigenstate, but not all atoms are in the same eigenstate. The result of a large number of measurements divided by the square of the number of measurements leads to precisely the square of the coefficients as given in Equation 6.89. Thus, given this ensemble of systems, the probability of measuring a particular state is given by Equation 6.93. Both of these points of view are useful to conceptualize a superposition of states, but, in reality, neither makes obvious the interference effects that can occur.

This postulate is the heart and soul of modern quantum physics. It provides a prescription by which the quantum mechanical probabilities may be determined. In addition, it implies that the set of eigenvectors of any operator corresponding to an observable quantity is a complete set upon which any acceptable state vector may be expanded.

We can revisit the concept of expectation value that was introduced in Section 3.1.1. If we wish to find the expectation value of the observable A , we merely sum

the products of the probabilities of measuring a given eigenvalue and the eigenvalue. Thus,

$$\begin{aligned}
 \langle A \rangle &= \sum_{i=1}^N \alpha_i \wp_i \\
 &= \sum_{i=1}^N \alpha_i |\langle \alpha_i | \psi \rangle|^2 \\
 &= \sum_{i=1}^N \langle \psi | \alpha_i \rangle \langle \alpha_i | \hat{A} | \psi \rangle \\
 &= \langle \psi | \left(\sum_{i=1}^N |\alpha_i \rangle \langle \alpha_i| \right) \hat{A} | \psi \rangle \\
 &= \langle \psi | \hat{A} | \psi \rangle
 \end{aligned} \tag{6.95}$$

Equation 6.95 is the Dirac notation equivalent to the expectation value in Equation 3.12. Of course, Equation 6.95 is much more general inasmuch as it pertains to any observable quantity. Notice that in Equation 3.12 the operator, x^2 , was “sandwiched” between $\psi^*(x)$ and $\psi(x)$. These integrals are frequently written this way by analogy with Equation 6.95. Such integrals are often referred to as sandwich integrals.

Because there are as many “components” of $|\psi\rangle$ as there are eigenvectors of \hat{A} , a column matrix that represents $|\psi\rangle$ must have as many rows as there are eigenvectors. This could be an infinite number. For example, both the infinite square well and the harmonic oscillator have an infinite number of eigenstates. Therefore, a general expansion of the wave vector (wave function) in terms of either of these complete sets would require provision to include an infinite number of basis states. This would require $N \rightarrow \infty$ in the summation in Equation 6.89. This is certainly not a new concept since any such expansion on the eigenstates of the infinite square well is simply a Fourier series.

Postulate V—The uncertainty postulate

Although this postulate follows formally from Postulate II, it has been elevated to postulate status because it is crucial to the physical interpretation of quantum mechanics and, in particular, the differences between quantum and classical physics. The Gedanken experiment that was employed in Section 1.2.3 to derive the inequality

$$\Delta x \Delta p_x \geq \hbar/2 \tag{6.96}$$

can, with the aid of the mathematical formalism introduced in this chapter, be generalized to apply to any two observable quantities that are represented by noncommuting Hermitian operators. The uncertainty of an observable quantity A is denoted by ΔA and is defined as

$$\Delta A = \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2} \quad (6.97)$$

Note that the first term on the right-hand side $\langle \hat{A}^2 \rangle = \langle \Psi | \hat{A} \hat{A} | \Psi \rangle$. Using this definition, the general statement of the uncertainty principle will now be proved.

The general uncertainty principle:

Given two observables A and B that are represented by Hermitian operators \hat{A} and \hat{B} , then the product of the uncertainties in measurements of A and B is subject to the inequality

$$(\Delta A)^2 (\Delta B)^2 \geq -\frac{1}{4} \langle [\hat{A}, \hat{B}] \rangle^2 \quad (6.98)$$

Proof:

Define the operators

$$\begin{aligned} \hat{Q} &= \hat{A} - \langle \hat{A} \rangle \\ \hat{R} &= \hat{B} - \langle \hat{B} \rangle \end{aligned} \quad (6.99)$$

Now define yet another new operator \hat{Z} as

$$\hat{Z} = \hat{Q} + i\lambda \hat{R} \quad (6.100)$$

where λ is a real number. Note that while \hat{Q} and \hat{R} are Hermitian, \hat{Z} is not.

Now examine the function

$$\begin{aligned} f(\lambda) &= \langle \Psi | \hat{Z}^\dagger \hat{Z} | \Psi \rangle \\ &\geq 0 \end{aligned} \quad (6.101)$$

This function has been chosen because it is manifestly positive and permits introduction of an inequality.

Our goal now is to write $f(\lambda)$ in terms of the original operators \hat{A} and \hat{B} and find the value of λ that makes it a minimum. Thus,

$$\begin{aligned} \hat{Z}^\dagger \hat{Z} &= (\hat{Q} + i\lambda \hat{R}) (\hat{Q} - i\lambda \hat{R}) \\ &= \hat{Q}^2 + \lambda^2 \hat{R}^2 + i\lambda [\hat{Q}, \hat{R}] \end{aligned} \quad (6.102)$$

so that

$$f(\lambda) = \langle \Psi | \hat{Q}^2 | \Psi \rangle + \lambda^2 \langle \Psi | \hat{R}^2 | \Psi \rangle + i\lambda \langle \Psi | [\hat{Q}, \hat{R}] | \Psi \rangle \quad (6.103)$$

Also

$$\begin{aligned} \langle \Psi | \hat{Q}^2 | \Psi \rangle &= \langle \Psi | (\hat{A} - \langle \hat{A} \rangle) (\hat{A} - \langle \hat{A} \rangle) | \Psi \rangle \\ &= \langle \Psi | \hat{A}^2 | \Psi \rangle - 2\langle \hat{A} \rangle \langle \Psi | \hat{A} | \Psi \rangle + \langle \hat{A} \rangle^2 \langle \Psi | \Psi \rangle \\ &= \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2 \\ &= (\Delta A)^2 \end{aligned} \quad (6.104)$$

Of course, we also have $\langle \Psi | \hat{R}^2 | \Psi \rangle = (\Delta B)^2$.

We must also evaluate the commutator in $f(\lambda)$. We have

$$\begin{aligned} [\hat{Q}, \hat{R}] &= [(\hat{A} - \langle \hat{A} \rangle), (\hat{B} - \langle \hat{B} \rangle)] \\ &= [\hat{A}, \hat{B}] \end{aligned} \quad (6.105)$$

Note that the last three terms in Equation 6.105 vanish because the expectation values are merely numbers.

We may now write $f(\lambda)$ in terms of the original operators \hat{A} and \hat{B} . We have

$$f(\lambda) = (\Delta A)^2 + \lambda^2 (\Delta B)^2 + i\lambda \langle \Psi | [\hat{A}, \hat{B}] | \Psi \rangle \quad (6.106)$$

To minimize $f(\lambda)$ we set $df/d\lambda$ equal to zero and obtain λ_0 , the value of λ that minimizes $f(\lambda)$:

$$\begin{aligned} \lambda_0 &= -\frac{i}{2} \frac{\langle \Psi | [\hat{A}, \hat{B}] | \Psi \rangle}{(\Delta B)^2} \\ &= -\frac{i}{2} \frac{\langle [\hat{A}, \hat{B}] \rangle}{(\Delta B)^2} \end{aligned} \quad (6.107)$$

Inserting this value into Equation 6.106 and taking note of the inequality we obtain

$$\begin{aligned} (\Delta A)^2 - \frac{1}{4} \frac{\langle [\hat{A}, \hat{B}] \rangle^2}{(\Delta B)^4} (\Delta B)^2 + i \left(-\frac{i}{2} \frac{\langle [\hat{A}, \hat{B}] \rangle}{(\Delta B)^2} \right) \langle [\hat{A}, \hat{B}] \rangle &\geq 0 \\ (\Delta A)^2 + \frac{1}{4} \frac{\langle [\hat{A}, \hat{B}] \rangle^2}{(\Delta B)^2} &\geq 0 \end{aligned} \quad (6.108)$$

or

$$(\Delta A)^2 (\Delta B)^2 \geq -\frac{1}{4} \langle [\hat{A}, \hat{B}] \rangle^2 \quad (6.109)$$

which is the generalized uncertainty relation, Equation 6.98.

It is a simple matter to retrieve the uncertainty relation between Δx and Δp_x , Equation 1.49, from Equations 6.98 and 6.39. We have

$$\begin{aligned} (\Delta x)^2 (\Delta p_x)^2 &\geq -\frac{1}{4} \langle [x, \hat{p}_x] \rangle^2 \\ &\geq -\frac{1}{4} (i\hbar)^2 \\ &\geq \frac{\hbar^2}{4} \end{aligned} \tag{6.110}$$

which leads directly to Equation 1.49.

Postulate VI—The time evolution postulate

Equation 6.88 is the TDSE in Dirac notation. We have already seen in Section 2.6 how, using separation of variables, the solution of the TDSE reduces to an exponential time factor multiplied by the solutions of the TISE provided the Hamiltonian operator does not contain the time. This is the usual case, so we limit our discussion to time-independent-Hamiltonians. In the notation of this chapter the TISE is

$$\hat{H} |\psi\rangle = E |\psi\rangle \tag{6.111}$$

where, as above, $|\psi\rangle$ is the state vector at a particular time so it is time-independent.

Now, how about the rest of the TDSE? To examine this we introduce the time evolution operator $\hat{U}(t, t_0)$, an operator that is defined such that when it operates on the state vector as it exists at a given time t_0 it converts it into the state vector at the time t . Thus, the action of the time evolution operator is given by

$$|\Psi(t)\rangle = \hat{U}(t, t_0) |\Psi(t_0)\rangle \tag{6.112}$$

where, for emphasis, we have noted that $|\Psi\rangle \equiv |\Psi(t)\rangle$. The almost universal symbol for the time evolution operator is $\hat{U}(t, t_0)$ because (as will be shown below) it is a unitary operator. In our notation, $|\Psi(t_0)\rangle$ could appear as $|\psi\rangle$, but we would have to, in some way, specify the time at which $|\psi\rangle$ is evaluated. This could be done with a following subscript such as $|\psi\rangle_{t_0}$, but we choose the notation shown in Equation 6.112 for (it is hoped) clarity.

If we now insert $|\Psi(t)\rangle$ as given by Equation 6.112 into the TDSE, Equation 6.88, we obtain

$$i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) |\Psi(t_0)\rangle = \hat{H} \hat{U}(t, t_0) |\Psi(t_0)\rangle \tag{6.113}$$

where we have used the fact that \hat{H} and $\hat{U}(t, t_0)$ obviously commute when, as we are assuming, \hat{H} is time-independent. Using Equation 6.112, Equation 6.113 may be written

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \quad (6.114)$$

which is readily solved for $|\Psi(t)\rangle$:

$$|\Psi(t)\rangle = e^{-i\hat{H}(t-t_0)/\hbar} |\Psi(t_0)\rangle \quad (6.115)$$

Comparing this result with Equation 6.112 we make the identification

$$\hat{U}(t, t_0) = e^{-i\hat{H}(t-t_0)/\hbar} \quad (6.116)$$

where the operation of the exponential operator is given by the series representation as described in Section 6.1.3. Thus,

$$e^{-i\hat{H}(t-t_0)/\hbar} = 1 + \frac{[i\hat{H}(t-t_0)/\hbar]}{1!} + \frac{[i\hat{H}(t-t_0)/\hbar]^2}{2!} + \dots \quad (6.117)$$

From Equation 6.117 it is clear that, because \hat{H} is Hermitian, $e^{-i\hat{H}(t-t_0)/\hbar}$ is also Hermitian. Moreover, it is indeed unitary because $\hat{U}(t, t_0)^\dagger = \hat{U}(t, t_0)^{-1}$ as seen from

$$\begin{aligned} \hat{U}(t, t_0) \hat{U}(t, t_0)^\dagger &= e^{-i\hat{H}(t-t_0)/\hbar} e^{i\hat{H}(t-t_0)/\hbar} \\ &= \hat{I} \end{aligned} \quad (6.118)$$

The operator $\hat{U}(t, t_0)$ given in Equation 6.116 is called the time evolution operator, the time development operator, or the propagator. To show why it is so named we operate on the expansion of $|\Psi(t_0)\rangle$ as given by Equation 6.89 with the time evolution operator recalling that the $|\alpha_i(t_0)\rangle$ are eigenvectors of \hat{H} with eigenvalues E_i . We obtain

$$\begin{aligned} \hat{U}(t, t_0) |\Psi(t_0)\rangle &= \sum_{i=1}^N a_i \hat{U}(t, t_0) |\alpha_i(t_0)\rangle \\ &= \sum_{i=1}^N a_i \left\{ \hat{I} + \frac{[-i\hat{H}(t-t_0)/\hbar]}{1!} + \dots \right\} |\alpha_i(t_0)\rangle \\ &= \sum_{i=1}^N a_i \left\{ 1 + \frac{[-iE_i(t-t_0)/\hbar]}{1!} + \dots \right\} |\alpha_i(t_0)\rangle \\ &= \sum_{i=1}^N a_i e^{-iE_i(t-t_0)/\hbar} |\alpha_i(t_0)\rangle \end{aligned} \quad (6.119)$$

where we have explicitly shown that the basis vectors are evaluated at $t = t_0$. The correspondence between Equation 6.119 and Equation 2.32 is obvious.

6.3.3 Further Consequences of the Postulates

The Ehrenfest Theorem

In Section 4.1 we derived two equations of motion for the expectation values of the position and momentum and referred to them as the Ehrenfest equations. These equations permitted a connection to be made between classical and quantum mechanical variables. These Ehrenfest equations are special cases of what is usually referred to as Ehrenfest's *theorem* which applies to the time derivative of the expectation of any observable A . As in Section 4.1 we use the TDSE and its complex conjugate to eliminate partial derivatives of $|\Psi\rangle$ and $\langle\Psi|$ with respect to time from the total time derivative of the expectation value of an arbitrary Hermitian operator \hat{A} :

$$\begin{aligned}
 \frac{d\langle\hat{A}\rangle}{dt} &= \frac{d\langle\Psi|\hat{A}|\Psi\rangle}{dt} \\
 &= \langle\Psi|\hat{A}\frac{\partial|\Psi\rangle}{\partial t} + \frac{\partial\langle\Psi|}{\partial t}\hat{A}|\Psi\rangle + \langle\Psi|\frac{\partial\hat{A}}{\partial t}|\Psi\rangle \\
 &= \frac{1}{i\hbar}\langle\Psi|\hat{A}\hat{H}|\Psi\rangle - \frac{1}{i\hbar}\langle\Psi|\hat{H}\hat{A}|\Psi\rangle + \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle \\
 &= \frac{i}{\hbar}\langle\Psi|[\hat{H}, \hat{A}]|\Psi\rangle + \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle
 \end{aligned} \tag{6.120}$$

Equation 6.120 is Ehrenfest's theorem, although when $\hat{A} = \hat{x}$ and $\hat{A} = \hat{p}$ the resulting relations are often referred to as Ehrenfest's theorems. Usually the operator \hat{A} does not contain the time explicitly so the last term in Equation 6.120 vanishes, a condition we assume. Therefore, the Ehrenfest theorem takes the form

$$\frac{d\langle\hat{A}\rangle}{dt} = \frac{i}{\hbar}\langle\Psi|[\hat{H}, \hat{A}]|\Psi\rangle \tag{6.121}$$

This theorem makes it clear that the expectation value of any operator that commutes with the Hamiltonian is a constant of the motion, that is, its time derivative vanishes. Therefore, it is the expectation value of an observable that is conserved in quantum physics, not the observable itself. Moreover, the expectation value of the Hamiltonian is always a constant of the motion. This is the quantum mechanical statement of energy conservation.

Suppose \hat{A} is a time-independent Hermitian operator and that $|\Psi\rangle$ in Equation 6.121 is a stationary state. For consistency with the notation of this chapter we therefore let $|\Psi\rangle \rightarrow |\alpha\rangle$, an eigenvector of the Hamiltonian with eigenvalue α . Under these conditions Equation 6.121 becomes

$$\begin{aligned}
\frac{d\langle\hat{A}\rangle}{dt} &= \frac{i}{\hbar} \langle\alpha| [\hat{H}, \hat{A}] |\alpha\rangle \\
&= \frac{i}{\hbar} \langle\alpha| \hat{H} \hat{A} |\alpha\rangle - \frac{i}{\hbar} \langle\alpha| \hat{A} \hat{H} |\alpha\rangle \\
&= \frac{i\alpha}{\hbar} \{ \langle\alpha| \hat{A} |\alpha\rangle - \langle\alpha| \hat{A} |\alpha\rangle \} \\
&= 0
\end{aligned} \tag{6.122}$$

Thus, if \hat{A} is time-independent, then the time derivative of its expectation value on a stationary state vanishes.

Using Equation 6.120 it is a relatively simple matter to derive the first and second Ehrenfest equations of Section 4.1. The generalized form of these equations is

$$\begin{aligned}
\frac{d\langle\mathbf{r}\rangle}{dt} &= \frac{\langle\hat{\mathbf{p}}\rangle}{m} \\
\frac{d\langle\hat{\mathbf{p}}\rangle}{dt} &= -\langle\nabla U(\mathbf{r})\rangle
\end{aligned} \tag{6.123}$$

The Virial Theorem

The virial theorem in classical mechanics was developed at the end of the nineteenth century by Clausius. For a single particle, the time rate of change of the quantity $\mathbf{p} \bullet \mathbf{r}$ was determined. The key step was to show that for bounded motion (not necessarily periodic motion) the average value of this time derivative vanishes. He thus obtained a relationship between the average value of the kinetic energy T and the average value of the gradient of the potential energy, the force

$$2\langle T \rangle = -\frac{1}{2} \langle \nabla U \cdot \mathbf{r} \rangle \tag{6.124}$$

He named the right-hand side of Equation 6.124 the *virial*.

The quantum mechanical derivation follows the same approach, but, because average values are involved, it is convenient to begin with Equation 6.121 and let $\hat{A} \rightarrow \hat{\mathbf{p}} \bullet \mathbf{r} = \hat{p}_x x + \hat{p}_y y + \hat{p}_z z$. We have

$$\frac{d\langle\hat{\mathbf{p}} \cdot \mathbf{r}\rangle}{dt} = \frac{i}{\hbar} \langle\Psi| [\hat{H}, \hat{\mathbf{p}} \cdot \mathbf{r}] |\Psi\rangle \tag{6.125}$$

To evaluate the expression on the right-hand side we require the following commutators:

$$\begin{aligned}
 [\hat{H}, \hat{p}_x x] &= [\hat{H}, \hat{p}_x] x - \hat{p}_x [x, \hat{H}] \\
 [\hat{H}, \hat{p}_x] &= \frac{\hbar}{i} \left[\left\{ \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} + U(x, y, z) \right\}, \frac{\partial}{\partial x} \right] \\
 &= -\frac{\hbar}{i} \frac{\partial U(x, y, z)}{\partial x} \\
 [\hat{H}, x] &= \frac{\hbar}{i} \left[\left\{ \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} + \hat{U}(x, y, z) \right\}, x \right] \\
 &= \left(\frac{\hbar}{i} \right) \frac{\hat{p}_x}{m}
 \end{aligned} \tag{6.126}$$

where, again, we have used the commutation relations $[x_i, \hat{p}_j] = i\hbar\delta_{ij}$. Inserting these identities into Equation 6.125 we have

$$\begin{aligned}
 \frac{d\langle \hat{\mathbf{p}} \cdot \mathbf{r} \rangle}{dt} &= \left\langle -\frac{\partial U(x, y, z)}{\partial x} \hat{x} + \dots - \hat{p}_x \left(-\frac{\hat{p}_x}{m} \right) - \dots \right\rangle \\
 &= -\langle \nabla U(\mathbf{r}) \cdot \mathbf{r} \rangle + \left\langle \frac{\hat{p}^2}{m} \right\rangle \\
 &= -\langle \nabla U(\mathbf{r}) \cdot \mathbf{r} \rangle + 2\langle \hat{T} \rangle
 \end{aligned} \tag{6.127}$$

Now, if the state of the system over which the operator $\hat{\mathbf{p}} \cdot \mathbf{r}$ is averaged is a stationary state, then the time derivative in Equation 6.127 vanishes and

$$2\langle \hat{T} \rangle = \langle \nabla U(\mathbf{r}) \cdot \mathbf{r} \rangle \tag{6.128}$$

which is the quantum mechanical analog of the classical virial theorem, Equation 6.124. An important special case of the virial theorem is for a spherically symmetric potential $U(r) \propto r^k$. In this case we find that

$$\begin{aligned}
 2\langle \hat{T} \rangle &= \left\langle r \frac{dU(r)}{dr} \right\rangle \\
 &= k \langle U(r) \rangle
 \end{aligned} \tag{6.129}$$

6.4 Relation Between the State Vector and the Wave Function

In this chapter we have been dealing with the abstract kets that are state vectors or eigenvectors of an operator. We wish to relate the kets that represent state vectors to the wave functions of the Schrödinger picture. Since, previously, we dealt exclusively with wave functions in coordinate space (rather than momentum space) we will limit our discussion to the relation between the state vector $|\psi\rangle$ and the wave

function $\psi(x)$. To cast $|\psi\rangle$ into the coordinate representation we must expand it on the complete set of eigenvectors of the position operator \hat{x} which we designate with a hat to distinguish it from its eigenvalue. Writing the eigenvalue equation for this operator we have

$$\hat{x} |x\rangle = x |x\rangle \quad (6.130)$$

where x and $|x\rangle$ are the eigenvalue and eigenvector, respectively. Because, however, we are dealing with the position operator, the eigenvalues and eigenvectors are continuous rather than the discrete sets that we have encountered previously. To expand the state vector $|\psi\rangle$ on the complete set of eigenvectors $|x\rangle$ we must use integrals instead of summations. Thus, Equation 6.58 adapted to this case becomes

$$|\psi\rangle = \int dx |x\rangle \langle x| \psi\rangle \quad (6.131)$$

If we now assume that $|\psi\rangle$ is normalized and take the inner product of each side of Equation 6.131 with $\langle\psi|$ we have

$$\begin{aligned} 1 &= \int dx \langle\psi |x\rangle \langle x| \psi\rangle \\ &= \int dx |\langle x | \psi\rangle|^2 \end{aligned} \quad (6.132)$$

Comparing Equation 6.132 to the equation that defines normalization of the wave function

$$1 = \int dx |\psi(x)|^2 \quad (6.133)$$

it is clear that

$$\psi(x) = \langle x | \psi\rangle \quad (6.134)$$

In this book we will make a distinction between the state vector $|\psi\rangle$ and the corresponding wave function $\psi(x)$ [or $\phi(p)$] by employing the symbol $\hat{=}$, which, as noted in Section 5.6.1, stands for “corresponds to.” Thus, we write

$$\psi(x) \hat{=} |\psi\rangle \quad (6.135)$$

We may formalize the concept of parity of eigenfunctions that has been discussed in connection with several of the one-dimensional potentials for which the TISE was solved. To do this we introduce the parity operator. Generalizing to three dimensions and designating wave functions by $\psi(\mathbf{r})$ and $\phi(\mathbf{r})$ the parity operator $\hat{\phi}$ is defined as

$$\hat{\phi}\psi(\mathbf{r}) = \psi(-\mathbf{r}) \quad (6.136)$$

It is easily shown that $\hat{\phi}$ has only two (real) eigenvalues, ± 1 . That is, if $\hat{\phi} \psi(\mathbf{r}) = \lambda \psi(\mathbf{r})$,

$$\begin{aligned} \hat{\phi}^2 \psi(\mathbf{r}) &= \hat{\phi} \psi(-\mathbf{r}) = \psi(\mathbf{r}) \\ &= \lambda \hat{\phi} \psi(-\mathbf{r}) = \lambda^2 \psi(\mathbf{r}) \end{aligned} \quad (6.137)$$

so $\lambda = \pm 1$. Thus, the eigenfunctions of $\hat{\phi}$ are either even or odd.

The real eigenvalues suggest that $\hat{\phi}$ is Hermitian, but this can be proved. Using bra and ket notation we have

$$\langle \phi(\mathbf{r}) | (\hat{\phi} | \psi(\mathbf{r}) \rangle) = \pm \langle \phi(\mathbf{r}) | \psi(\mathbf{r}) \rangle \quad (6.138)$$

while

$$(\langle \phi(\mathbf{r}) | \hat{\phi}^\dagger) | \psi(\mathbf{r}) \rangle = \pm \langle \phi(\mathbf{r}) | \psi(\mathbf{r}) \rangle \quad (6.139)$$

which shows that $\hat{\phi} = \hat{\phi}^\dagger$.

If the parity operator commutes with the Hamiltonian, then the energy eigenfunctions have definite parity, that is, they are also eigenfunctions of $\hat{\phi}$. We already know that this occurs in one-dimension if the potential is even (see Section 2.9).

6.5 The Heisenberg Picture

We have seen that the time evolution operator converts a state vector at a given time, $|\Psi(t=t_0)\rangle = |\Psi\rangle$, into the state vector at the time t , $|\Psi(t)\rangle$. The state vector is often referred to as the state ket and it must be distinguished from the eigenvectors (eigenkets) which, according to Postulate IV, may serve as a basis set upon which to expand the state vector. To compute the time dependence of the expectation value of an operator \hat{A} , we must use time-dependent state vectors $|\Psi(t)\rangle$. Thus,

$$\langle \hat{A}(t) \rangle = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle \quad (6.140)$$

Replacing $|\Psi(t)\rangle$ (and its complex conjugate $\langle \Psi(t)|$) using Equation 6.112 we have

$$\langle \hat{A}(t) \rangle = \langle \Psi(t_0) | \hat{U}^\dagger(t, t_0) \hat{A} \hat{U}(t, t_0) | \Psi(t_0) \rangle \quad (6.141)$$

Now, suppose that in Equation 6.141 we group the operators on the right-hand side. In essence, we have converted the time-independent operator \hat{A} into a time-dependent operator $\hat{A}(t)$ according to the prescription

$$\begin{aligned}\hat{A}(t) &= \hat{U}^\dagger(t, t_0) \hat{A} \hat{U}(t, t_0) \\ &= e^{i\hat{H}(t-t_0)/\hbar} \hat{A} e^{-i\hat{H}(t-t_0)/\hbar}\end{aligned}\quad (6.142)$$

where the absence of a noted time dependence associated with \hat{A} implies its time *independence*. Thus, there are two ways of representing the time-dependent expectation value of a quantum mechanical observable, one using time-dependent state vectors and time-independent operators and the other using time-independent state vectors with time-dependent operators. So far in this book we have used time-dependent state vectors and time-independent operators. This formulation of quantum mechanics is known as the Schrödinger picture. The alternative formulation in which the state vectors remain fixed in time and the operators move is known as the Heisenberg picture. The Schrödinger picture is the most frequently used formulation of quantum physics, but the Heisenberg picture is equivalent.

In the Heisenberg picture it is the time dependence of the observables, operators, that describes the physical system. State vectors are of little consequence since they are evaluated at a fixed time. Of course, the possible results of a measurement, the eigenvalues, must be the same in both pictures, but the eigenvectors change with time in the Heisenberg picture. This may be shown by beginning with the eigenvalue equation for an operator \hat{A} in the Schrödinger picture. The corresponding Heisenberg picture operator is $\hat{A}(t)$. Denoting the eigenkets of \hat{A} in the Schrödinger picture by $|\alpha_i\rangle$, the eigenvalue equation in the Schrödinger picture at a fixed time, $t = 0$ for simplicity, is

$$\hat{A} |\alpha_i\rangle = \alpha_i |\alpha_i\rangle \quad (6.143)$$

Letting $\hat{U}(t, t_0 = 0) = \hat{U}$, we now operate on Equation 6.143 with \hat{U}^\dagger and insert $\hat{U}\hat{U}^\dagger \equiv \hat{I}$ in front of the ket $|\alpha_i\rangle$ on the left-hand side to obtain

$$\begin{aligned}\hat{U}^\dagger \hat{A} (\hat{U} \hat{U}^\dagger) |\alpha_i\rangle &= \alpha_i \hat{U}^\dagger |\alpha_i\rangle \\ (\hat{U}^\dagger \hat{A} \hat{U}) (\hat{U}^\dagger |\alpha_i\rangle) &= \alpha_i (\hat{U}^\dagger |\alpha_i\rangle) \\ \hat{A}(t) (\hat{U}^\dagger |\alpha_i\rangle) &= \alpha_i (\hat{U}^\dagger |\alpha_i\rangle)\end{aligned}\quad (6.144)$$

The last equation is clearly the eigenvalue equation for the operator $\hat{A}(t)$ with eigenvectors $\hat{U}^\dagger |\alpha_i\rangle$. The eigenvalues α_i are the same as those in the Schrödinger picture which is consistent with Postulate I because the possible results of a measurement of the observable A cannot depend upon the representation (picture). The eigenvectors in Equation 6.144 are, however, time-dependent. Thus, while the eigenvectors of the operator \hat{A} in the Schrödinger picture are the time-independent kets $|\alpha_i\rangle$, in the Heisenberg picture the eigenvectors are the time-dependent kets $\hat{U}^\dagger |\alpha_i\rangle$. In the Schrödinger picture the state vectors move while those in the Heisenberg representation are stationary. Thus, we must make a distinction between the state vector and

Table 6.1 Contrast between the Schrödinger and Heisenberg pictures. The time dependences are denoted by “fixed” for time-independent and “moving” for time-dependent

Entity	Significance	Schrödinger	Heisenberg
operator	observable	\hat{A} fixed	$\hat{A}(t)$ moving
state vector	system state	$ \Psi(t)\rangle$ moving	$ \Psi\rangle$ fixed
eigenvectors	basis vectors	$ \alpha_i\rangle$ fixed	$\hat{U}^\dagger \alpha_i\rangle$ moving

the eigenvectors. The time dependences of these quantities in each of the pictures are summarized in Table 6.1.

In the Schrödinger picture the time evolution of the quantum mechanical system is dictated by the TDSE, Equation 6.88. This is the equation of motion of the time-dependent state vector $|\Psi\rangle$. In the Heisenberg picture we require an equation of motion for the time-dependent operators $\hat{A}(t)$. To obtain this equation of motion we simply take the total time derivative of Equation 6.142. For simplicity, we assume the usual case in which the operator $\hat{A}(t)$ has no explicit time dependence so that $\partial \hat{A}(t) / \partial t \equiv 0$. Also, because we assume that the Hamiltonian operator does not contain the time explicitly it is not necessary to make any distinction between the Schrödinger and Heisenberg versions of this operator because $\hat{U} \hat{H} \hat{U}^\dagger = \hat{H}$ which is true because \hat{H} commutes with itself. We have

$$\begin{aligned}
 \frac{d\hat{A}(t)}{dt} &= \frac{i\hat{H}}{\hbar} \left[e^{i\hat{H}(t-t_0)/\hbar} \hat{A} e^{-i\hat{H}(t-t_0)/\hbar} \right] \\
 &\quad - \left[e^{i\hat{H}(t-t_0)/\hbar} \hat{A} e^{-i\hat{H}(t-t_0)/\hbar} \right] \frac{i\hat{H}}{\hbar} \\
 &= \frac{i}{\hbar} (\hat{H} \hat{A}(t) - \hat{A}(t) \hat{H}) \\
 &= \frac{i}{\hbar} [\hat{H}, \hat{A}(t)]
 \end{aligned} \tag{6.145}$$

Equation 6.145 is the Heisenberg equation of motion from which we see immediately that if $\hat{A}(t)$ commutes with the Hamiltonian, then it is a constant of the motion because its time derivative vanishes. In this case \hat{H} and $\hat{A}(t)$ can have simultaneous eigenvectors, the physical consequence of which is that these two observables, energy and A , may be measured simultaneously. That is, the measurement of one does not interfere with the measurement of the other. Moreover, if we take $\hat{A}(t) = \hat{H}$, it is seen immediately that the (total) time derivative of the Hamiltonian vanishes, thus confirming energy conservation.

From the Heisenberg equation of motion, Equation 6.145, we can immediately derive the Ehrenfest theorem, Equation 6.121 (we again assume that the operator $\hat{A}(t)$ does not contain any explicit time dependence). Since the Heisenberg state vectors are fixed in time we simply take the expectation value of Equation 6.145 with the Heisenberg state vector $|\Psi\rangle$ and its complex conjugate. The left-hand side of Equation 6.145, $\langle d\hat{A}(t)/dt \rangle$, is simply

$$\left\langle \frac{d\hat{A}(t)}{dt} \right\rangle = \frac{d\langle \hat{A}(t) \rangle}{dt} \quad (6.146)$$

Next we determine the right-hand side, the expectation value of the commutator in the Schrödinger picture:

$$\begin{aligned} \frac{i}{\hbar} \langle [\hat{H}, \hat{A}(t)] \rangle &= \frac{i}{\hbar} \langle \Psi | [\hat{H}, \hat{A}(t)] | \Psi \rangle \\ &= \frac{i}{\hbar} \langle \Psi | [\hat{H}, \hat{U}^\dagger \hat{A} \hat{U}] | \Psi \rangle \\ &= \frac{i}{\hbar} \langle \Psi | [\hat{H} \hat{U}^\dagger \hat{A} \hat{U} - \hat{U}^\dagger \hat{A} \hat{U} \hat{H}] | \Psi \rangle \\ &= \frac{i}{\hbar} \langle \Psi | [\hat{U}^\dagger \hat{U} \hat{H} \hat{U}^\dagger \hat{A} \hat{U} - \hat{U}^\dagger \hat{A} \hat{U} \hat{H} \hat{U}^\dagger \hat{U}] | \Psi \rangle \\ &= \frac{i}{\hbar} (\langle \Psi | \hat{U}^\dagger) [\hat{U} \hat{H} \hat{U}^\dagger \hat{A} - \hat{A} \hat{U} \hat{H} \hat{U}^\dagger] (\hat{U} | \Psi) \\ &= \frac{i}{\hbar} \langle \Psi(t) | [\hat{H} \hat{A} - \hat{A} \hat{H}] | \Psi(t) \rangle \\ &= \frac{i}{\hbar} \langle \Psi(t) | [\hat{H}, \hat{A}] | \Psi(t) \rangle \end{aligned} \quad (6.147)$$

which, when equated to the result from Equation 6.146, is Equation 6.121, the Ehrenfest theorem.

As stated above, most problems in quantum physics are attacked using the Schrödinger picture. Why then even bother with the Heisenberg picture? Of course, there is the aesthetic beauty attendant to proving that the two pictures are equivalent. Another reason is that the Heisenberg picture makes the connection between classical and quantum physics clearer than does the Schrödinger picture. After all, wave functions and state vectors have no classical analog. On the other hand, the observables in classical physics are usually time-dependent quantities so the Heisenberg equation of motion for an observable (Hermitian operator) is indeed analogous. Moreover, there is a close connection between this equation and Hamilton's equations of classical motion as well as a relationship between the Poisson brackets of classical physics and the commutator of quantum physics. We will not pursue these correspondences further in this book, but clearly Bohr's correspondence principle is at work here. Let us examine the time evolution of the position and momentum operators for a particle of mass m under the influence of an arbitrary one-dimensional potential $U(x)$. The Hamiltonian in the Heisenberg picture is

$$\hat{H} = \frac{\hat{p}_x(t)^2}{2m} + U\{\hat{x}(t)\} \quad (6.148)$$

where we have placed a hat over x to emphasize its operator status. To use the Heisenberg picture we must compute the commutators $[\hat{H}, \hat{x}(t)]$ and $[\hat{H}, \hat{p}_x(t)]$ and insert them into Equation 6.145. An important point in this calculation is to note that the commutators in the Heisenberg picture have exactly the same form as in the Schrödinger picture (see Problem 7). We may therefore use the relations listed as Equations 6.42 and 6.43 for this computation. Thus

$$\begin{aligned} \left[\hat{x}(t), \frac{\hat{p}_x(t)^2}{2m} \right] &= \frac{i\hbar}{2m} \frac{\partial \{ \hat{p}_x(t)^2 \}}{\partial x} \\ &= i\hbar \frac{\hat{p}_x(t)}{m} \end{aligned} \quad (6.149)$$

and

$$[\hat{p}_x(t), U\{\hat{x}(t)\}] = -i\hbar \frac{\partial U\{\hat{x}(t)\}}{\partial p_x(t)} \quad (6.150)$$

The Heisenberg equations of motion are then

$$\frac{d\hat{x}(t)}{dt} = \frac{\hat{p}_x(t)}{m} \quad (6.151)$$

and

$$\frac{d\hat{p}_x(t)}{dt} = -\frac{\partial U\{\hat{x}(t)\}}{\partial p_x(t)} \quad (6.152)$$

These are the familiar relations of nonrelativistic classical physics, the momentum is mass times velocity, and the time rate of change of the momentum is the force (Newton's second law).

The harmonic oscillator in the Heisenberg picture

We can illustrate the use of the Heisenberg picture by returning to an old friend, the harmonic oscillator. We will obtain the time dependences of the quantum mechanical operators $\hat{x}(t)$ and $\hat{p}_x(t)$ using this picture. We begin by applying Equation 6.152 to the potential energy function $U\{\hat{x}(t)\} = \frac{1}{2}m\omega^2\hat{x}(t)^2$. Of course, Equation 6.151 does not depend upon the potential energy. For simplicity of notation we

eliminate the subscript on the momentum since this is a one-dimensional problem. The two equations of motion are therefore

$$\frac{d\hat{x}(t)}{dt} = \frac{\hat{p}(t)}{m} \quad (6.153)$$

and

$$\frac{d\hat{p}(t)}{dt} = -m\omega^2\hat{x}(t) \quad (6.154)$$

Uncoupling these two first-order differential equations we obtain two second-order equations,

$$\frac{d^2\hat{x}(t)}{dt^2} = -\omega^2\hat{x}(t) \quad (6.155)$$

and

$$\frac{d^2\hat{p}(t)}{dt^2} = -\omega^2\hat{p}(t) \quad (6.156)$$

the solutions to which are

$$\hat{x}(t) = \hat{x}(0) \cos \omega t + \frac{\hat{p}(0)}{m\omega} \sin \omega t \quad (6.157)$$

and

$$\hat{p}(t) = -m\omega\hat{x}(0) \sin \omega t + \hat{p}(0) \cos \omega t \quad (6.158)$$

where the constants of integration have been evaluated at $t = 0$, that is, $\hat{x}(0) = \hat{x}(t=0)$ and $\hat{p}(0) = \hat{p}(t=0)$.

We see then that the Heisenberg operators oscillate exactly as the classical quantities $x(t)$ and $p(t)$. In this context, however, they are not classical quantities, they are quantum mechanical operators, Heisenberg operators. In contrast, the operators $\hat{x}(t=0)$ and $\hat{p}(t=0)$ obtained from the boundary conditions are stationary operators. They are the Schrödinger operators. Moreover, the commutator $[\hat{x}(t), \hat{p}(t)] = i\hbar$ and it is independent of time (see Problem 11).

6.6 Spreading of Wave Packets

6.6.1 Spreading in the Heisenberg Picture

Because the Heisenberg operators are time-dependent, they are ideally suited for reexamining the spreading of wave packets as in Section 4.5. We examine Case I

from that section, the case of a Gaussian wave packet subject to no external forces, a free particle. Recall that in this case we began with a minimum uncertainty wave packet and found that it spreads in time. We can employ Equation 6.109 with $A \rightarrow x(t)$ and $B \rightarrow \hat{x}(0)$ (which was called x_0 in Section 4.5). We therefore require the commutator $[\hat{x}(t), \hat{x}(0)]$. Before evaluating this commutator we must first find the equations of motion for a free particle in the Heisenberg picture.

Using Equations 6.151 and 6.152 we find that

$$\frac{d\hat{x}(t)}{dt} = \frac{\hat{p}(t)}{m} \quad \text{and} \quad \frac{d\hat{p}(t)}{dt} = 0 \quad (6.159)$$

which lead to

$$\hat{x}(t) = \hat{x}(0) + \frac{\hat{p}(0)}{m}t \quad \text{and} \quad \hat{p}(t) = \hat{p}(0) \quad (6.160)$$

The commutator $[\hat{x}(t), \hat{x}(0)]$ is easily found to be

$$\begin{aligned} [\hat{x}(t), \hat{x}(0)] &= \left[\left\{ \hat{x}(0) + \frac{\hat{p}(0)}{m}t \right\}, \hat{x}(0) \right] \\ &= [\hat{p}_x(0), \hat{x}(0)] \frac{t}{m} \\ &= -\frac{i\hbar}{m}t \end{aligned} \quad (6.161)$$

We can use this result in Equation 6.109 to obtain the standard deviation, the uncertainty, as a function of time $\Delta x(t)$. Let us clarify the meaning of the quantity ΔA in the present context. It is the standard deviation of the wave packet as a function of time beyond the initial standard deviation which at $t = 0$ is $\Delta x(0) = \Delta x_0$. Therefore, we will call the uncertainty in position that corresponds to ΔA in Equation 6.109 $\Delta x'(t)$ with the understanding that the $\Delta x(t)$ of Equation 4.74 is given by

$$\Delta x(t)^2 = \Delta x'(t)^2 + \Delta x_0^2 \quad (6.162)$$

Note that it is the variances, the squares of the standard deviations, that add, not the standard deviations themselves. We have then

$$\begin{aligned} \{\Delta x'(t)\}^2 \{\Delta x(0)\}^2 &\geq -\frac{1}{4} \left\langle -\frac{i\hbar}{m}t \right\rangle^2 \\ &\geq \left(\frac{\hbar}{2m} \right)^2 t^2 \end{aligned} \quad (6.163)$$

and

$$\begin{aligned}\{\Delta x'(t)\}^2 \{\Delta x(0)\}^2 &\geq -\frac{1}{4} \left\langle -\frac{i\hbar}{m} t \right\rangle^2 \\ \Delta x'(t)^2 &\geq \frac{1}{\Delta x(0)^2} \left(\frac{\hbar}{2m} \right)^2 t^2\end{aligned}\quad (6.164)$$

At $t = 0$ we had a minimum uncertainty wave packet so that $\Delta x'(t = 0) = 0$. Therefore, we must use the equal sign in Equation 6.164. Inserting this into Equation 6.162 we have

$$\Delta x(t)^2 = \frac{1}{\Delta x(0)^2} \left(\frac{\hbar}{2m} \right)^2 t^2 + \Delta x(0)^2 \quad (6.165)$$

$$= \Delta x(0)^2 \left\{ 1 + \frac{1}{\Delta x(0)^4} \left(\frac{\hbar}{2m} \right)^2 t^2 \right\} \quad (6.166)$$

from which we obtain

$$\Delta x(t) = \Delta x_0 \sqrt{1 + \left(\frac{\hbar}{2m\Delta x_0^2} \right)^2 t^2} \quad (6.167)$$

which is indeed the same as Equation 4.74. As noted in Section 4.5, this time dependence of the uncertainty shows that a Gaussian wave packet subjected to no forces will rapidly expand in time.

When studying Case III, the case of a Gaussian wave packet subjected to a harmonic oscillator force, it was shown that the wave packet oscillates, but does not change shape. Thus, there should be no time dependence of the uncertainty product $\Delta x(t) \Delta p(t)$. We can verify this by finding the uncertainty product using the Heisenberg equations of motion, Equations 6.157 and 6.158.

First, the packet used in Case III, the wave function of which at $t = 0$, was given by Equation 4.95, which we reproduce here, is

$$\Psi(x, 0) = \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-\alpha^2(x-x_0)^2/2} \quad (6.168)$$

has initial momentum zero and initial displacement x_0 . Therefore, the expectation values of momentum and position at $t = 0$ are given by

$$\langle \hat{x}(0) \rangle = x_0 \quad \text{and} \quad \langle \hat{p}(0) \rangle = 0 \quad (6.169)$$

The uncertainties are then

$$\Delta \hat{x}(t)^2 = \langle \hat{x}(t)^2 \rangle - \langle \hat{x}(t) \rangle^2 \quad \text{and} \quad \Delta \hat{p}(t)^2 = \langle \hat{p}(t)^2 \rangle - \langle \hat{p}(t) \rangle^2 \quad (6.170)$$

where, from Equation 6.158,

$$\langle \hat{p}(t) \rangle = -m\omega \langle \hat{x}(0) \rangle \sin \omega t \quad (6.171)$$

and, from Equation 6.157,

$$\langle \hat{x}(t) \rangle = \langle \hat{x}(0) \rangle \cos \omega t = x_0 \cos \omega t \quad (6.172)$$

Also,

$$\Delta \hat{x}(0)^2 = \langle \hat{x}(0)^2 \rangle - x_0^2 \quad \text{and} \quad \Delta \hat{p}(0)^2 = \langle \hat{p}(0)^2 \rangle \quad (6.173)$$

Next we compute $\langle \hat{p}(t)^2 \rangle$:

$$\begin{aligned} \langle \hat{p}(t)^2 \rangle &= \langle \hat{p}(0)^2 \rangle \cos^2 \omega t + m^2 \omega^2 \langle \hat{x}(0)^2 \rangle \\ &\quad - m\omega \sin \omega t \cos \omega t \langle \hat{p}(0) \hat{x}(0) + \hat{x}(0) \hat{p}(0) \rangle \\ &= \langle \hat{p}(0)^2 \rangle \cos^2 \omega t + m^2 \omega^2 \langle \hat{x}(0)^2 \rangle \\ &\quad - m\omega \sin \omega t \cos \omega t \langle 2\hat{x}(0) \hat{p}(0) - i\hbar \rangle \end{aligned} \quad (6.174)$$

where we have used the commutator $[\hat{x}(0), \hat{p}(0)] = i\hbar$.

Now, it can be shown that $\langle 2\hat{x}(0) \hat{p}(0) - i\hbar \rangle = 0$ (see Problem 12) so that

$$\Delta \hat{p}(t)^2 = \langle \hat{p}(0)^2 \rangle \cos^2 \omega t + m^2 \omega^2 \langle \hat{x}(0)^2 \rangle \sin^2 \omega t - m^2 \omega^2 \langle \hat{x}(0) \rangle^2 \sin^2 \omega t \quad (6.175)$$

which may be written in terms of the uncertainties

$$\begin{aligned} \Delta \hat{p}(t)^2 &= \Delta \hat{p}(0)^2 \cos^2 \omega t + \{ \langle \hat{x}(0)^2 \rangle - \langle \hat{x}(0) \rangle^2 \} m^2 \omega^2 \sin^2 \omega t \\ &= \Delta \hat{p}(0)^2 \cos^2 \omega t + \Delta \hat{x}(0)^2 m^2 \omega^2 \sin^2 \omega t \end{aligned} \quad (6.176)$$

Because, however, the wave packet had minimum uncertainty at $t = 0$ we must have

$$\Delta \hat{x}(0)^2 \Delta \hat{p}(0)^2 = \frac{\hbar^2}{4} \quad (6.177)$$

which we may use to eliminate $\Delta \hat{p}(0)$ from Equation 6.176 leading to

$$\Delta \hat{p}(t)^2 = \frac{\hbar^2}{4\Delta \hat{x}(0)^2} \cos^2 \omega t + \Delta \hat{x}(0)^2 m^2 \omega^2 \sin^2 \omega t \quad (6.178)$$

Now, it is easily shown that (see Problem 14)

$$\Delta \hat{x}(0)^2 = \frac{1}{2\alpha^2} \quad (6.179)$$

so that (using $\alpha^2 = m\omega/\hbar$)

$$\begin{aligned}\Delta\hat{p}(t)^2 &= \frac{\hbar^2}{4} (2\alpha^2) \cos^2 \omega t + \left(\frac{1}{2\alpha^2}\right) m^2 \omega^2 \sin^2 \omega t \\ &= \frac{\hbar^2 \alpha^2}{2}\end{aligned}\tag{6.180}$$

Returning now to $\Delta x(t)$ we have

$$\begin{aligned}\Delta\hat{x}(t)^2 &= \langle \hat{x}(t)^2 \rangle - \langle \hat{x}(t) \rangle^2 \\ &= \langle \hat{x}(0)^2 \rangle \cos^2 \omega t + \frac{\langle \hat{p}(0)^2 \rangle}{m^2 \omega^2} \sin^2 \omega t - \langle \hat{x}(0) \rangle^2 \cos^2 \omega t \\ &= \{ \langle \hat{x}(0)^2 \rangle - \langle \hat{x}(0) \rangle^2 \} \cos^2 \omega t + \left(\frac{\hbar^2 \alpha^2}{2} \right) \frac{1}{\hbar^2 \alpha^4} \sin^2 \omega t \\ &= \Delta\hat{x}(0)^2 \cos^2 \omega t + \frac{1}{2\alpha^2} \sin^2 \omega t \\ &= \frac{1}{2\alpha^2}\end{aligned}\tag{6.181}$$

where we have again used the fact that $\langle 2\hat{x}(0)\hat{p}(0) - i\hbar \rangle = 0$ and used Equation 6.179. Combining Equations 6.180 and 6.181 we can write the time dependence of the uncertainty product $\Delta\hat{x}(t)\Delta\hat{p}(t)$. We have

$$\Delta\hat{x}(t)\Delta\hat{p}(t) = \frac{\hbar}{2}\tag{6.182}$$

which is independent of time.

These results show that not only is the uncertainty product constant in time (see Problem 11), but so too are the individual uncertainties. That is, neither $\Delta\hat{x}(t)$ nor $\Delta\hat{p}(t)$ contains the time. This means that the spread in both position and momentum remain constant for a Gaussian packet subject to a harmonic force. Of course, we have already deduced this in Section 4.5 (see Equation 4.106), but the use of the Heisenberg picture presents a more nearly classical approach.

6.6.2 Spreading in the Schrödinger Picture

Because the time evolution operator converts a wave function at a fixed time to its time-dependent form, the new wave function is necessarily a representation in the Schrödinger picture. As an exercise in the use of the time evolution operator, in this section we will use it to derive the probability densities for the free particle wave packet and the wave packet under the influence of a constant force, Cases I and II in Section 4.5. Calculation of the time evolution operator for a harmonic oscillator potential is beyond the intended scope of this book so we defer reexamination of

Case III until Section 7.2 when we will have the tools to circumvent the use of this operator.

The Free Particle

It was shown in Section 6.3.2, Postulate VI that the state ket $|\Psi(x, t)\rangle$ may be obtained by applying the time evolution operator, $e^{-i\hat{H}(t-t_0)/\hbar}$ (see Equation 6.116) to the state ket at a fixed time $|\Psi(x, t_0)\rangle$. Therefore, if we consider the free particle Gaussian wave packet (Case I of Section 4.5.1) we may apply the time evolution operator to the wave function at $t = 0$ and compare the result with that obtained in Section 4.5.1. In terms of wave functions

$$\begin{aligned}\Psi(x, t) &= \langle x | \Psi(x, t) \rangle \\ &= e^{-i\hat{p}^2 t / (2m\hbar)} \Psi(x, 0)\end{aligned}\quad (6.183)$$

The first-order of business is to convert the initial momentum wave function $\Phi(p, 0)$ of Equation 4.66 to the coordinate space wave function $\Psi(x, 0)$. This can be done by taking the Fourier transform. The present calculation will be simplified by using the wave function in the form of the Fourier transformed wave functions given in Equations 4.60 and 4.61. Moreover, it was assumed in Section 4.5.1 that the initial state has $p(0) = p_0$ and $x(0) = 0$, but the calculation can be further simplified by assuming that both $p(0)$ and $x(0)$ vanish. Comparison with the previous results will not suffer from this simplification. The initial wave function in coordinate space is therefore

$$\Psi(x, 0) = \frac{1}{\pi^{1/4}} \left(\frac{1}{2^{1/4} \sqrt{\Delta x_0}} \right) e^{-x^2 / 4\Delta x_0^2} \quad (6.184)$$

The second thing that we must do is to determine the action of the time evolution operator $\hat{U}(t, 0)$ on $\Psi(x, 0)$. Letting $p \rightarrow (\hbar/i) \partial/\partial x$ to convert $\hat{U}(t, 0)$ to coordinate space representation, this operator is

$$\begin{aligned}\hat{U}(t, 0) &= e^{-i\hat{p}^2 t / (2m\hbar)} \\ &= \exp \left(\frac{i\hbar t}{2m} \frac{\partial^2}{\partial x^2} \right)\end{aligned}\quad (6.185)$$

which is difficult to apply to an arbitrary wave function. Because, however, the initial wave packet has Gaussian form, it has been shown that the action of $\hat{U}(t, 0)$ can be deduced using an ingenious mathematical trick [1]. Letting $\Delta x_0^2 = z$ to simplify Equation 6.184, it can be verified that

$$\frac{\partial^2}{\partial x^2} \left[\frac{1}{\sqrt{z}} e^{-x^2/4z} \right] = \frac{\partial}{\partial z} \left[\frac{1}{\sqrt{z}} e^{-x^2/4z} \right] \quad (6.186)$$

Expressing $\Psi(x, 0)$ in terms of z and Δx_0 we have

$$\Psi(x, 0) = \frac{\sqrt{\Delta x_0}}{(2\pi)^{1/4}} \frac{1}{\sqrt{z}} e^{-x^2/4z} \quad (6.187)$$

Now, using the identity given in Equation 6.186 we are in a position to apply the time evolution operator to $\Psi(x, 0)$:

$$\begin{aligned} \hat{U}(t, 0) \Psi(x, 0) &= \frac{\sqrt{\Delta x_0}}{(2\pi)^{1/4}} \exp\left(\frac{i\hbar t}{2m} \frac{\partial^2}{\partial x^2}\right) \left[\frac{1}{\sqrt{z}} e^{-x^2/4z} \right] \\ &= \frac{\sqrt{\Delta x_0}}{(2\pi)^{1/4}} \left[\exp\left(\frac{i\hbar t}{2m} \frac{\partial}{\partial z}\right) \right] \left[\frac{1}{\sqrt{z}} e^{-x^2/4z} \right] \end{aligned} \quad (6.188)$$

Comparing the last line of Equation 6.188 with the translation operator as given in Equation L.11 we see that $i\hbar t/(2m) = x_0$, the distance by which the translation is made. We see then that the action of the free particle time development operator, Equation 6.185, operating on an arbitrary function $f(x)$ is

$$\begin{aligned} \hat{U}(t, 0) f(x) &= e^{-i\hat{p}^2 t/(2m\hbar)} f(x) \\ &= \exp\left[\left(-\frac{i\hbar t}{2m}\right) \frac{\partial}{\partial x}\right] f(x) \\ &= f\left(x + \frac{i\hbar t}{2m}\right) \end{aligned} \quad (6.189)$$

Letting z return to Δx_0^2 we see that $\Psi(x, t)$ is found by letting $z \rightarrow \Delta x_0^2 + i\hbar t/(2m)$ after applying the translation operator. We have

$$\begin{aligned} \Psi(x, t) &= \frac{\sqrt{\Delta x_0}}{(2\pi)^{1/4}} \frac{1}{\sqrt{\Delta x_0^2 + \frac{i\hbar t}{2m}}} \exp\left[-\frac{x^2}{4\left(\Delta x_0^2 + \frac{i\hbar t}{2m}\right)}\right] \\ &= \frac{1}{(2\pi)^{1/4} \sqrt{\Delta x_0}} \frac{1}{\sqrt{1 + \frac{i\hbar t}{2m\Delta x_0^2}}} \exp\left[-\frac{x^2}{4\left(\Delta x_0^2 + \frac{i\hbar t}{2m}\right)}\right] \end{aligned} \quad (6.190)$$

Setting $\Delta x_0 = 1/(\sqrt{2}\beta)$ in Equation 6.190 and $p_0 = 0$ in Equation 4.68 makes it clear that the present treatment is consistent with our earlier formulation.

Constant Field

In Section 4.5.2, Case II, a wave packet under the influence of a constant field, we derived the probability density and the spreading of the packet in momentum space. In this section we will treat the same problem, but we will use the time evolution operator and derive the probability density in coordinate space. For simplicity, we begin with the initial wave function given in Equation 6.184. We will follow the treatment of Robinett [2].

The Hamiltonian is

$$\hat{H} = \frac{\hat{p}^2}{2m} - Fx \quad (6.191)$$

so the time evolution operator is

$$\hat{U}(t, 0) = \exp \left[-i \left(\frac{\hat{p}^2}{2m} - Fx \right) \left(\frac{t}{\hbar} \right) \right] \quad (6.192)$$

Because \hat{p} and x are operators we cannot naively apply the usual rules of algebra to this exponential expression. Rather, we must use the BCH formula of Appendix L in the form of Equation L.1 and L.2:

$$e^{\hat{A}} e^{\hat{B}} = e^{\hat{C}} \quad (6.193)$$

where

$$\hat{C} = \hat{A} + \hat{B} + \frac{1}{2} [\hat{A}, \hat{B}] + \frac{1}{12} \{ [[\hat{A}, \hat{B}], \hat{B}] + [\hat{A}, [\hat{A}, \hat{B}]] \} + \dots \quad (6.194)$$

Notice that when one of the commutators vanishes, all subsequent commutators vanish. In the special case in which $[\hat{A}, \hat{B}] = 0$ the usual rules of exponents apply. Unfortunately, in the present case $[\hat{A}, \hat{B}] \neq 0$ so we must use Equation 6.194.

Letting

$$\hat{A} = -i \frac{tFx}{\hbar} \quad \text{and} \quad \hat{B} = -i \frac{\hat{H}t}{\hbar} = -i \frac{t}{\hbar} \left(\frac{\hat{p}^2}{2m} - Fx \right) \quad (6.195)$$

so that

$$[\hat{A}, \hat{B}] = -i \frac{Ft^2}{m\hbar} \hat{p} \quad \text{and} \quad [[\hat{A}, \hat{B}], \hat{B}] = -i \frac{F^2 t^3}{m\hbar} = [\hat{A}, [\hat{A}, \hat{B}]] \quad (6.196)$$

Because $[[\hat{A}, \hat{B}], \hat{B}] \propto \hat{p}$, the remaining commutators vanish. Therefore,

$$\hat{C} = -i \frac{\hat{p}^2 t}{2m\hbar} - i \frac{Ft^2}{2m\hbar} \hat{p} - \frac{1}{6} \left(i \frac{F^2 t^3}{m\hbar} \right) \quad (6.197)$$

To find the time development operator for a wave packet subjected to a constant force we multiply Equation 6.193 on the left by $e^{-\hat{A}}$ to obtain

$$\begin{aligned}
 e^{-i\hat{H}t/\hbar} &= e^{\hat{B}} \\
 &= e^{-\hat{A}} e^{\hat{C}} \\
 &= e^{iFtx/\hbar} \exp \left[-i \frac{\hat{p}^2 t}{2m\hbar} - i \frac{Ft^2}{2m\hbar} \hat{p} - \frac{1}{6} \left(i \frac{F^2 t^3}{m\hbar} \right) \right] \\
 &= \exp \left[i \frac{Ft}{\hbar} \left(x - \frac{Ft^2}{6m} \right) \right] \cdot \exp \left[-i \frac{Ft^2}{2m\hbar} \hat{p} \right] \cdot \exp \left[-i \frac{\hat{p}^2 t}{2m\hbar} \right] \quad (6.198)
 \end{aligned}$$

An operator (\hat{p} in this case) commutes with any function of that operator, so the exponential containing \hat{p} may be written as a simple product.

Now, this time evolution operator looks somewhat formidable, but we have already done most of the work required to apply it. The exponential containing \hat{p}^2 is simply the free particle time evolution operator, Equation 6.189. As shown above, it causes a free particle to spread in time. This spreading is effected by making the conversion $\Delta x_0^2 \rightarrow \Delta x_0^2 + i\hbar t/(2m)$ in Equation 6.184. Moreover, the exponential that contains the first power of the momentum is also a translation operator (see above and Appendix L). This operator causes the conversion $x \rightarrow x - Ft^2/(2m\hbar)$. The effect of the time development operator on the initial wave function, Equation 6.184, results in Equation 6.190 so we have

$$\begin{aligned}
 \Psi(x, t) &= \exp \left[i \frac{Ft}{\hbar} \left(x - \frac{Ft^2}{6m} \right) \right] \cdot \exp \left[-i \frac{Ft^2}{2m\hbar} \hat{p} \right] \\
 &\quad \times \frac{1}{(2\pi)^{1/4} \sqrt{\Delta x_0}} \frac{1}{\sqrt{1 + \frac{i\hbar t}{2m\Delta x_0^2}}} \exp \left[-\frac{x^2}{4 \left(\Delta x_0^2 + \frac{i\hbar t}{2m} \right)} \right] \\
 &= \exp \left[i \frac{Ft}{\hbar} \left(x - \frac{Ft^2}{6m} \right) \right] \frac{1}{(2\pi)^{1/4} \sqrt{\Delta x_0}} \frac{1}{\sqrt{1 + \frac{i\hbar t}{2m\Delta x_0^2}}} \\
 &\quad \times \exp \left[-\frac{\left(x - \frac{Ft^2}{2m\hbar} \right)^2}{4\Delta x_0^2 \left(1 + \frac{i\hbar t}{2m\Delta x_0^2} \right)} \right] \quad (6.199)
 \end{aligned}$$

Notice that because x and \hat{p} do not commute, the exponential operator in Equation 6.198 remains to the left of the exponential operators containing \hat{p} . As a consequence, the x in that operator does not get shifted by the other operators.

Squaring Equation 6.199, the probability density is

$$\begin{aligned}
 |\Psi(x, t)|^2 &= \frac{1}{\sqrt{2\pi}\Delta x_0} \frac{1}{\sqrt{1 + \left(\frac{t}{t_0}\right)^2}} \exp \left[-\frac{\left(x - \frac{Ft^2}{2m\hbar}\right)^2}{2\Delta x_0^2 \left(1 + \left(\frac{t}{t_0}\right)^2\right)} \right] \\
 &= \frac{1}{\sqrt{2\pi}\Delta x(t)} \exp \left[-\frac{\left(x - \frac{Ft^2}{2m\hbar}\right)^2}{2\Delta x(t)^2} \right] \quad (6.200)
 \end{aligned}$$

where, as in Section 4.5,

$$t_0 = \frac{2m}{\hbar} \Delta x_0^2 \quad \text{and} \quad \Delta x(t) = \Delta x_0 \sqrt{1 + \left(\frac{t}{t_0}\right)^2} \quad (6.201)$$

Clearly Equation 6.201 is identical with the result obtained previously using Fourier transforms, Equation 4.94.

6.7 Retrospective

While a great deal of time and effort has been spent in this chapter on the properties of operators, especially Hermitian operators, the most important point for understanding quantum physics is the introduction of the postulates and their consequences. Although the discussion of the postulates may seem rather abstract and, in some cases, off the point of the chapter, the introduction of quantum mechanical concepts within the framework of abstract vector spaces makes it possible to reexamine problems treated in earlier chapters of this book with new insight. Moreover, once having mastered the formulation of quantum mechanics within the framework of vector spaces, many problems become simpler to solve, a good example being the harmonic oscillator as formulated in the next chapter of this book.

While the Schrödinger picture is the most often used in quantum mechanical calculations at the level of this book, the Heisenberg picture provides a clearer link between classical and quantum physics. This is because the time-dependent operators (the observables) of the Heisenberg picture are closely related to their classical analogs, while the wave functions of the Schrödinger picture have no classical counterpart. The equivalence of the two pictures should make the results obtained using the Schrödinger picture more credible to the student, especially the first time around the quantum mechanical block.

6.8 References

1. S. M. Blinder, "Evolution of a Gaussian wavepacket," Am. J. Phys., **36**, 525-526 (1968).
2. R. W. Robinett, "Quantum mechanical time-development operator for the uniformly accelerated particle," Am. J. Phys., **64**, 803-808 (1996).

Problems

1. Show that the unit vectors $1/\sqrt{2}(\hat{i} + \hat{j})$; $1/\sqrt{2}(\hat{i} - \hat{j})$; \hat{k} given in Equation 6.3 constitute an orthonormal basis set.
2. Show that $[\hat{A}, \hat{B}^{-1}] = -\hat{B}^{-1}[\hat{A}, \hat{B}]\hat{B}^{-1}$. Begin with $[\hat{A}, \hat{B}\hat{B}^{-1}] = [\hat{A}, \hat{I}] = 0$.
3. Show that the product of two Hermitian operators \hat{A} and \hat{B} is non-Hermitian unless $[\hat{A}, \hat{B}] = 0$.
4. Show that the expectation value of a Hermitian operator is real.
5. Show that the projection operator is Hermitian.
6. For the time evolution operator $e^{-i\hat{H}t/\hbar}$
 - (a) Show that the eigenvectors are the same as those of the Hamiltonian.
 - (b) What are the eigenvalues of $e^{-i\hat{H}t/\hbar}$?
 - (c) Are the eigenvalues of $e^{-i\hat{H}t/\hbar}$ necessarily real? If not, why not?
7. Show that if the Schrödinger operators \hat{A} and \hat{B} obey $[\hat{A}, \hat{B}] = \hat{C}$, then the Heisenberg operators $\hat{A}(t)$ and $\hat{B}(t)$ obey $[\hat{A}(t), \hat{B}(t)] = \hat{C}(t)$.
8. Show that the eigenvectors of the Hamiltonian are also eigenvectors of the time evolution operator $e^{-i\hat{H}t/\hbar}$. What are the eigenvalues?
9. Verify Equation 6.157 for the time dependence of the $\hat{x}(t)$ for the harmonic oscillator using the fundamental definition of a Heisenberg operator in terms of the time evolution operator and the equivalent Schrödinger operator. That is, show that

$$\begin{aligned}\hat{x}(t) &= e^{i\hat{H}t/\hbar}\hat{x}(t=0)e^{-i\hat{H}t/\hbar} \\ &= \hat{x}(t=0)\cos\omega t + \frac{\hat{p}_x(t=0)}{m\omega}\sin\omega t\end{aligned}$$

The Baker–Campbell–Hausdorff lemma, which will be needed, is

$$e^{i\lambda\hat{C}}\hat{A}e^{-i\lambda\hat{C}} = \hat{A} + i\lambda[\hat{C}, \hat{A}] + \frac{i^2\lambda^2}{2!}[\hat{C}, [\hat{C}, \hat{A}]] + \dots$$

10. Using $[x, \hat{p}_x] = i\hbar\hat{I}$ and mathematical induction show that

$$[x, \hat{p}_x^n] = i\hbar n\hat{p}_x^{n-1}$$

11. Show that the commutator $[\hat{x}(t), \hat{p}(t)] = i\hbar$ for the harmonic oscillator.

12. Show that the term $\langle 2\hat{x}(0)\hat{p}(0) - i\hbar \rangle$ in Equation 6.174 vanishes for the wave packet $\Psi(x, 0) = (\sqrt{\alpha}/\pi^{1/4}) e^{-\alpha^2(x-x_0)^2/2}$.
13. Assuming that the potential energy is a function of position only, evaluate the commutators $[\hat{H}, x]$ and $[\hat{H}, \hat{p}]$. Use one-dimension.
14. Show that for the wave packet $\Psi(x, 0) = (\sqrt{\alpha}/\pi^{1/4}) e^{-\alpha^2(x-x_0)^2/2}$ the uncertainty in position is given by $\Delta x(0)^2 = 1/2\alpha^2$ and thus that it is independent of the initial displacement x_0 .
15. A Hamiltonian $\hat{H}(x, y)$ is the sum $\hat{H}(x, y) = \hat{H}_x(x) + \hat{H}_y(y)$. Show that the eigenfunctions of $\hat{H}(x, y)$ are products of the eigenfunctions of $\hat{H}_x(x)$ and $\hat{H}_y(y)$ and the energy eigenvalues are the sums of the eigenvalues of $\hat{H}_x(x)$ and $\hat{H}_y(y)$. Assume that you know the eigenfunctions and energy eigenvalues of $\hat{H}_x(x)$ and $\hat{H}_y(y)$. That is, assume that you know

$$\hat{H}_x(x)\varphi(x) = E_x\varphi(x) \quad \text{and} \quad \hat{H}_y(y)\eta(y) = E_y\eta(y)$$

so you must show that the eigenfunctions of $\hat{H}(x, y)$ are $\psi(x, y) = \varphi(x)\eta(y)$ and their eigenvalues are $E = E_x + E_y$. Clearly this pattern will hold for any number of variables for which the Hamiltonian can be written as a sum of Hamiltonians, each consisting of a single variable.

16. Derive the Ehrenfest equations, Equations 4.7 and 4.10, using the generalized Ehrenfest theorem, Equation 6.120.
17. A Gaussian wave packet with initial displacement x_0 and initial momentum p_0 is subjected to the linear potential

$$U(x) = -Fx; \quad -\infty < x < \infty$$

where F is a constant force. Find the time dependence of the operators x and \hat{p} in the Heisenberg representation.

18. Verify the identity in Equation 6.186.
19. Show that the identities given in Equation 6.196 are correct. That is, show that

$$[\hat{A}, \hat{B}] = -i\frac{Ft^2}{m\hbar}\hat{p} \quad \text{and} \quad [[\hat{A}, \hat{B}], \hat{B}] = i\frac{F^2t^3}{m\hbar} = [\hat{A}, [\hat{A}, \hat{B}]]$$

20. Show that application of the time evolution operator for a wave packet under the influence of a constant force produces the same momentum space probability density for the initial packet given by Equation 4.77 as that obtained in Section 4.5, Equation 4.85. [Hint: Reverse the roles of the operators \hat{A} and \hat{B} from that used to derive the probability density in coordinate space in Section 6.6.2.

Chapter 7

Harmonic Oscillator Solution Using Operator Methods

We have already discussed the quantum mechanical harmonic oscillator several times in this book including Sections 3.1.2 and 6.5. In this chapter we will examine it yet again, this time using operator formalism, a method that is sometimes characterized as algebraic. We will show that the energy eigenvalues are obtainable without actually solving a differential equation, using only the Hamiltonian operator and the commutation relations between \hat{x} and \hat{p} . This powerful method of solution, due to Dirac, has consequences far beyond an exercise in elementary quantum physics. The operators are used in many problems in physics.

7.1 The Algebraic Method

7.1.1 The Schrödinger Picture

We define a new operator in terms of the position and momentum operators \hat{x} and \hat{p} . In this section we will be using the Schrödinger picture so the operators are time-independent. Because we are using operator methods, we retain the hat on the position operator. For simplicity we again drop the subscript on the momentum operator inasmuch as this is a one-dimensional problem. The new operator and its Hermitian conjugate are

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + \frac{i}{m\omega} \hat{p} \right) = \frac{1}{\sqrt{2}} \left(\alpha \hat{x} + i \frac{1}{\alpha \hbar} \hat{p} \right) \quad (7.1)$$

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i}{m\omega} \hat{p} \right) = \frac{1}{\sqrt{2}} \left(\alpha \hat{x} - i \frac{1}{\alpha \hbar} \hat{p} \right) \quad (7.2)$$

where $\alpha = \sqrt{m\omega/\hbar}$ as in Equation 3.25. Notice that these operators are *not* Hermitian operators. They therefore need not have real eigenvalues and do not qualify as observables. In the form written in Equations 7.1 and 7.2 \hat{a} and \hat{a}^\dagger are dimensionless. To exploit these new operators to solve the TISE we must do some preliminary work to derive relations between them and other quantum mechanical operators.

We first show that $[\hat{a}, \hat{a}^\dagger] = 1$ by invoking the $[\hat{x}, \hat{p}] = i\hbar$:

$$\begin{aligned}
 [\hat{a}, \hat{a}^\dagger] &= \frac{1}{2} \left[\left(\alpha \hat{x} + i \frac{1}{\alpha \hbar} \hat{p} \right), \left(\alpha \hat{x} - i \frac{1}{\alpha \hbar} \hat{p} \right) \right] \\
 &= \frac{1}{2} \left\{ \left(-\frac{i}{\hbar} \right) [\hat{x}, \hat{p}] + \left(\frac{i}{\hbar} \right) [\hat{p}, \hat{x}] \right\} \\
 &= \frac{-i}{2\hbar} \{2 [\hat{x}, \hat{p}]\} \\
 &= 1
 \end{aligned} \tag{7.3}$$

Next we express the Hamiltonian in terms of a and \hat{a}^\dagger by solving Equations 7.1 and 7.2 for \hat{x} and \hat{p} . We obtain

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a} + \hat{a}^\dagger) = \frac{1}{\sqrt{2\alpha}} (\hat{a} + \hat{a}^\dagger) \tag{7.4}$$

and

$$\hat{p} = -i\sqrt{\frac{m\omega\hbar}{2}} (\hat{a} - \hat{a}^\dagger) = -i\frac{\alpha\hbar}{\sqrt{2}} (\hat{a} - \hat{a}^\dagger) \tag{7.5}$$

The Hamiltonian then has the simple form

$$\begin{aligned}
 \hat{H} &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \\
 &= -\frac{\hbar\omega}{4} (\hat{a} - \hat{a}^\dagger)^2 + \frac{\hbar\omega}{4} (\hat{a} + \hat{a}^\dagger)^2 \\
 &= \frac{\hbar\omega}{4} \{ -(\hat{a}\hat{a} - \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} + \hat{a}^\dagger\hat{a}^\dagger) + (\hat{a}\hat{a} + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} + \hat{a}^\dagger\hat{a}^\dagger) \} \\
 &= \frac{\hbar\omega}{2} (\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger)
 \end{aligned} \tag{7.6}$$

We can put this in a slightly different form by adding and subtracting $\hat{a}^\dagger\hat{a}$ in the parentheses in this last equation and taking advantage of the commutation relation derived above and $[\hat{a}, \hat{a}^\dagger] = 1$. We obtain

$$\hat{H} = \hbar\omega \left(\hat{a}^\dagger\hat{a} + \frac{1}{2} \right) \tag{7.7}$$

In this form the Hamiltonian is the sum of two terms, one the operator $\hat{a}^\dagger\hat{a}$ and the other the constant $\hbar\omega/2$. The solution of the eigenvalue problem then becomes one of solving the eigenvalue equation for the operator $\hat{a}^\dagger\hat{a}$ and adding the constant

term to $\hbar\omega$ times their eigenvalues to find the energies. Note that the operator $\hat{a}^\dagger\hat{a}$ is Hermitian as it must be to be a term in the Hamiltonian. It therefore qualifies as an observable. Moreover, because it obviously commutes with the Hamiltonian, a measurement of this observable can be made simultaneously with a measurement of the energy, and these two operators can have simultaneous eigenvectors.

It is often convenient to express \hat{a} and \hat{a}^\dagger in terms of dimensionless operators. To do this we simply rescale \hat{x} and \hat{p} . Using Equations 7.1 and 7.2 as a guide we let

$$\hat{x} = \frac{1}{\alpha} \hat{X} \quad \text{and} \quad \hat{p} = \alpha \hbar \hat{P} \quad (7.8)$$

so that

$$\hat{a} = \frac{1}{\sqrt{2}} (\hat{X} + i \hat{P}) \quad (7.9)$$

and

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}} (\hat{X} - i \hat{P}) \quad (7.10)$$

This choice of scaling constants also preserves the “equality” of $\Delta\hat{X}$ and $\Delta\hat{P}$ as discussed in Section 4.5. Notice that \hat{X} is equivalent to the reduced coordinate $\xi = \alpha x$ of Section 3.1.2.

Now, what is the observable $\hat{a}^\dagger\hat{a}$? Being blessed with knowledge of the answer we will designate this operator with the symbol \hat{N} so that

$$\hat{N} = \hat{a}^\dagger\hat{a} \quad (7.11)$$

and we seek to solve the eigenvalue equation

$$\hat{N} |n\rangle = n |n\rangle \quad (7.12)$$

where n and $|n\rangle$ are the eigenvalues and eigenvectors of \hat{N} (as well as \hat{H} because \hat{N} and \hat{H} commute). We may write the energy eigenvalue equation in terms of the eigenvectors and eigenvalues of \hat{N} :

$$\begin{aligned} \hat{H} |n\rangle &= \hbar\omega \left(\hat{N} + \frac{1}{2} \right) |n\rangle \\ &= \hbar\omega \left(n + \frac{1}{2} \right) |n\rangle \end{aligned} \quad (7.13)$$

bearing in mind that we are pretending that we do not yet know the nature of the eigenvalue n . One thing we know, however, is that n is unitless because \hat{a} and \hat{a}^\dagger are dimensionless.

We now undertake the crucial task of identifying the nature of the observable \hat{N} by examining the properties of the eigenvalue n . We will require the commutation relations

$$[\hat{N}, \hat{a}] = -\hat{a} \quad (7.14)$$

and

$$[\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger \quad (7.15)$$

which are easy to prove (see Problem 2). To determine the nature of n , we begin by operating on the vector $\hat{a} |n\rangle$ with \hat{N} , use Equation 7.14, regroup the operators, and use the commutator in Equation 7.3. We obtain

$$\begin{aligned} \hat{N} \hat{a} |n\rangle &= (-\hat{a} + \hat{a} \hat{N}) |n\rangle \\ \hat{N} \{\hat{a} |n\rangle\} &= (-\hat{a} + \hat{a} n) |n\rangle \\ &= (n - 1) \{\hat{a} |n\rangle\} \end{aligned} \quad (7.16)$$

Equation 7.16 shows two important characteristics of the eigenvalues and eigenfunctions of \hat{N} . First, the quantity $\{\hat{a} |n\rangle\}$ is also an eigenvector of \hat{N} and, second, its eigenfunction is $(n - 1)$. We have therefore deduced a relationship between $\hat{a} |n\rangle$ and $|n - 1\rangle$, in particular

$$\hat{a} |n\rangle = c_1 |n - 1\rangle \quad (7.17)$$

where c_1 is a constant. In a similar manner we operate on $\hat{a}^\dagger |n\rangle$ with \hat{N} and employ the commutation relation in Equation 7.15 to obtain (see Problem 3)

$$\hat{a}^\dagger |n\rangle = c_2 |n + 1\rangle \quad (7.18)$$

We must now evaluate the constants c_1 and c_2 . To do this we use the fact that these eigenvectors must be normalized. Thus,

$$\begin{aligned} 1 &= \langle n - 1 | n - 1 \rangle \\ &= \frac{1}{|c_1|^2} \langle n | \hat{a}^\dagger \hat{a} | n \rangle \\ &= \frac{1}{|c_1|^2} \langle n | \hat{N} | n \rangle \\ &= \frac{n}{|c_1|^2} \end{aligned} \quad (7.19)$$

It is conventional to choose c_1 to be real in which case $c_1 = \sqrt{n}$ and the effect of \hat{a} operating on $|n\rangle$ is given by

$$\hat{a} |n\rangle = \sqrt{n} |n-1\rangle \quad (7.20)$$

In an analogous manner (see Problem 4) we find that

$$\hat{a}^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle \quad (7.21)$$

Equations 7.17 and 7.18 show that the effect of \hat{a} or \hat{a}^\dagger on one of the simultaneous eigenvectors of \hat{H} and \hat{N} is to lower it or raise it (respectively) to the next eigenvector. Equations 7.20 and 7.21 specify the “length” of the vectors that result from the action of each of these operators. The operators \hat{a} and \hat{a}^\dagger are known as ladder operators, raising and lowering operators, or creation and annihilation operators.

Now, what about the nature of n itself? Because the absolute square of $\hat{a} |n\rangle$ must be positive we know that

$$\begin{aligned} \langle n | \hat{a}^\dagger \hat{a} | n \rangle &= \langle n | \hat{N} | n \rangle \\ &= n \geq 0 \end{aligned} \quad (7.22)$$

Moreover, n cannot be negative so it must be impossible to lower an eigenvector to make its eigenvalue negative. The only way this is possible is if the n are positive integers. Now, clearly, there must be a minimum value of n , call it n_{\min} , to avoid negative values. Lowering the eigenket that has this minimum value, call it $|n_{\min}\rangle$, must obliterate it. That is,

$$\hat{a} |n_{\min}\rangle = 0 \quad (7.23)$$

Operating on Equation 7.23 with \hat{a}^\dagger leads to

$$\begin{aligned} \hat{a}^\dagger \hat{a} |n_{\min}\rangle &= \hat{N} |n_{\min}\rangle \\ &= 0 \end{aligned} \quad (7.24)$$

which shows that the minimum eigenvalue of \hat{N} must be zero, $n_{\min} = 0$. Thus, n can be any positive integer or zero. For this reason \hat{N} is called the number operator. These restrictions on the eigenvalue n together with Equation 7.13 make it clear that we have recovered the same equation for the energy eigenvalues as we derived by solving the TISE in Section 3.1.2. That is, from Equation 7.13, the energy eigenvalues are given by

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega \quad n = 0, 1, 2, \dots \quad (7.25)$$

We can also obtain the eigenfunctions given in Equation 3.45 using operator techniques. If we can find the eigenvector corresponding to the lowest eigenvalue, we can simply operate on it with the raising operator \hat{a}^\dagger until we have reached the desired eigenvector. Obviously this is an inferior method to simply looking up the

wave function, but it shows that any wave function can be obtained once one of them is known. To obtain the lowest eigenfunction we begin by lowering it out of existence, that is, employing Equation 7.23. To convert eigenkets into eigenfunctions we make use of Equation 6.134 so the ground state eigenfunction $\psi_0(x)$ is $\langle X | 0 \rangle$. Writing Equation 7.23 in the coordinate representation we have

$$\begin{aligned}\hat{a}\psi_0(x) &= 0 \\ &= \sqrt{\frac{m\omega}{2\hbar}} \left(x + \frac{i}{m\omega} \hat{p} \right) \psi_0(x) \\ &= \sqrt{\frac{m\omega}{2\hbar}} \left(x + \frac{\hbar}{m\omega} \frac{d}{dx} \right) \psi_0(x)\end{aligned}\quad (7.26)$$

which is a linear first-order differential equation for $\psi_0(x)$. This equation is separable and yields the normalized solution

$$\psi_0(x) = \left(\frac{\alpha^2}{\pi} \right)^{1/4} e^{-\alpha^2 x^2 / 2} \quad (7.27)$$

where $\alpha = \sqrt{m\omega/\hbar}$. It must be remembered that an arbitrary harmonic oscillator state vector (wave function) is time-dependent. The time dependence is obtained by operating on $|\psi\rangle$ with the time evolution operator. This has the same effect as multiplying each eigenvector in the expansion of the state vector by the appropriate exponential containing the eigenvalue. In terms of the eigenkets $|n\rangle$, an arbitrary state ket is

$$|\Psi\rangle = \sum_{i=0}^{\infty} a_i e^{-iE_i/\hbar} |i\rangle \quad (7.28)$$

A summary of the relations pertaining to the algebraic solution of the harmonic oscillator is given in Table 7.1.

7.1.2 Matrix Elements

It is useful to know the matrix elements of the ladder operators because powers of \hat{x} and \hat{p} may be written in terms of them (see Table 7.1). From Equations 7.20 and 7.21 it is clear that

$$\langle m | \hat{a} | n \rangle = \sqrt{n} \delta_{m,n-1} \quad (7.29)$$

and

$$\langle m | \hat{a}^\dagger | n \rangle = \sqrt{n+1} \delta_{m,n+1} \quad (7.30)$$

Table 7.1 Relations involving the raising and lowering operators, \hat{a}^\dagger and \hat{a} , of the harmonic oscillator

$$\begin{aligned}
\hat{x} &= \frac{1}{\alpha} \hat{X} \\
\hat{p} &= \alpha \hbar \hat{P} \\
\hat{a} &= \frac{1}{\sqrt{2}} \left(\alpha \hat{x} + i \frac{1}{\alpha \hbar} \hat{p} \right) = \frac{1}{\sqrt{2}} (\hat{X} + i \hat{P}) \\
\hat{a}^\dagger &= \frac{1}{\sqrt{2}} \left(\alpha \hat{x} - i \frac{1}{\alpha \hbar} \hat{p} \right) = \frac{1}{\sqrt{2}} (\hat{X} - i \hat{P}) \\
\hat{x} &= \frac{1}{\sqrt{2}\alpha} (\hat{a} + \hat{a}^\dagger) \\
\hat{p} &= -i \frac{\alpha \hbar}{\sqrt{2}} (\hat{a} - \hat{a}^\dagger) \\
\hat{X} &= \frac{1}{\sqrt{2}} (\hat{a} + \hat{a}^\dagger) \\
\hat{P} &= \frac{-i}{\sqrt{2}} (\hat{a} - \hat{a}^\dagger) \\
\hat{N} &= \hat{a}^\dagger \hat{a} \\
\hat{H} &= \hbar \omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) = \hbar \omega \left(\hat{N} + \frac{1}{2} \right) \\
[\hat{a}, \hat{a}^\dagger] &= 1 \\
[\hat{N}, \hat{a}] &= -\hat{a} \implies [\hat{H}, \hat{a}] = -\hbar \omega \hat{a} \\
[\hat{N}, \hat{a}^\dagger] &= \hat{a}^\dagger \implies [\hat{H}, \hat{a}^\dagger] = \hbar \omega \hat{a}^\dagger \\
\hat{a} |n\rangle &= \sqrt{n} |n-1\rangle \\
\hat{a}^\dagger |n\rangle &= \sqrt{n+1} |n+1\rangle
\end{aligned}$$

Because we already know \hat{x} and \hat{p} in terms of the ladder operators, Equations 7.4 and 7.5, we can easily find the matrix elements $\langle m | \hat{x} | n \rangle$ and $\langle m | \hat{p} | n \rangle$:

$$\begin{aligned}
\langle m | \hat{x} | n \rangle &= \frac{1}{\sqrt{2}\alpha} \langle m | (\hat{a} + \hat{a}^\dagger) | n \rangle \\
&= \frac{1}{\sqrt{2}\alpha} \left(\sqrt{n} \delta_{m,n-1} + \sqrt{n+1} \delta_{m,n+1} \right)
\end{aligned} \tag{7.31}$$

and

$$\begin{aligned}
\langle m | \hat{p} | n \rangle &= -i \frac{\alpha \hbar}{\sqrt{2}} \langle m | (\hat{a} - \hat{a}^\dagger) | n \rangle \\
&= -i \frac{\alpha \hbar}{\sqrt{2}} \left(\sqrt{n} \delta_{m,n-1} - \sqrt{n+1} \delta_{m,n+1} \right)
\end{aligned} \tag{7.32}$$

We can calculate the matrix elements of higher powers of \hat{x} by repetitive application of the ladder operators (see Problem 7). There is, however, another method which, while offering no particular advantage for low powers of \hat{x} , is more convenient for higher powers. We illustrate this method by evaluating a low power, $\langle m | \hat{x}^2 | n \rangle$. We write

$$\begin{aligned}
\langle m | \hat{x}^2 | n \rangle &= \langle m | \hat{x} \hat{x} | n \rangle \\
&= \sum_{k=0}^{\infty} \langle m | \hat{x} | k \rangle \langle k | \hat{x} | n \rangle
\end{aligned} \tag{7.33}$$

where the last step was effected using the identity operator (see Equation 6.58). Inserting the matrix elements from Equation 7.31 we have

$$\begin{aligned}
\langle m | \hat{x}^2 | n \rangle &= \frac{1}{2\alpha^2} \sum_{k=0}^{\infty} \left[\left(\sqrt{k} \delta_{m,k-1} + \sqrt{k+1} \delta_{m,k+1} \right) \right. \\
&\quad \left. \times \left(\sqrt{n} \delta_{k,n-1} + \sqrt{n+1} \delta_{k,n+1} \right) \right]
\end{aligned} \tag{7.34}$$

or

$$\begin{aligned}
\langle m | \hat{x}^2 | n \rangle &= \frac{1}{2\alpha^2} \sum_{k=0}^{\infty} \left[\sqrt{kn} \delta_{m,k-1} \delta_{k,n-1} + \sqrt{k(n+1)} \delta_{m,k-1} \delta_{k,n+1} \right. \\
&\quad \left. + \sqrt{n(k+1)} \delta_{m,k+1} \delta_{k,n-1} \right. \\
&\quad \left. + \sqrt{(n+1)(k+1)} \delta_{m,k+1} \delta_{k,n+1} \right]
\end{aligned} \tag{7.35}$$

To simplify this expression we must combine the Kronecker deltas, a process that we illustrate by considering the first term on the right-hand side of Equation 7.35. The only term of this summation that survives is the one for which $m = k - 1$ and for which $n = k + 1$ so that $m = n - 2$. Then

$$\begin{aligned}
\sum_{k=0}^{\infty} \sqrt{kn} \delta_{m,k-1} \delta_{k,n-1} &= \sqrt{n(m+1)} \delta_{m+1,n-1} \\
&= \sqrt{n(n-1)} \delta_{m,n-2}
\end{aligned} \tag{7.36}$$

where, for the sake of tidiness, we have made the first index on the Kronecker delta m . The remaining terms are treated the same way and we arrive at

$$\begin{aligned}
\langle m | \hat{x}^2 | n \rangle &= \frac{1}{2\alpha^2} \left[\sqrt{n(n-1)} \delta_{m,n-2} \right. \\
&\quad \left. + (2n+1) \delta_{m,n} + \sqrt{(n+1)(n+2)} \delta_{m,n+2} \right]
\end{aligned} \tag{7.37}$$

Similarly, we can obtain $\langle m | \hat{x}^3 | n \rangle$. After some labor we arrive at

$$\begin{aligned}
\langle m | \hat{x}^3 | n \rangle = \frac{1}{2\sqrt{2}\alpha^3} & \left[\sqrt{(n+1)(n+2)(n+3)}\delta_{m,n+3} \right. \\
& + 3\sqrt{(n+1)^3}\delta_{m,n+1} + 3\sqrt{n^3}\delta_{m,n-1} \\
& \left. + \sqrt{n(n-1)(n-2)}\delta_{m,n-3} \right]
\end{aligned} \tag{7.38}$$

Comparing the two odd powers of \hat{x} with the even powers, we see that $\delta_{m,n}$ occurs only in $(\hat{x}^2)_{mn}$. This term is missing from the odd powers. This is understandable in terms of the actual eigenfunctions which, recall, have definite parity. Therefore, if $m = n$, the diagonal matrix elements must vanish for the odd powers of \hat{x} while they are present in the even powers.

7.1.3 The Heisenberg Picture

We have already worked out the details of the solution to the harmonic oscillator in the Heisenberg representation in Section 6.5. In that section we obtained the time dependences of the observables $\hat{x}(t)$ and $\hat{p}(t)$. We now show that these solutions can be obtained using the ladder operators.

Although they are not themselves observables because they are not Hermitian, we may insert \hat{a} and \hat{a}^\dagger into the Heisenberg equation of motion, Equation 6.145, to convert them to Heisenberg operators. Of course, we could also apply the unitary transformation using the evolution operator. Using the equation of motion we have

$$\frac{d\hat{a}(t)}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{a}(t)] \tag{7.39}$$

and

$$\frac{d\hat{a}^\dagger(t)}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{a}^\dagger(t)] \tag{7.40}$$

From Problem 1 we know that

$$[\hat{H}, \hat{a}(t)] = -\hbar\omega\hat{a}(t) \quad \text{and} \quad [\hat{H}, \hat{a}^\dagger(t)] = \hbar\omega\hat{a}^\dagger(t) \tag{7.41}$$

because commutation relations between Schrödinger operators and Heisenberg operators are invariant (see Problem 7, Chapter 6). We thus have a differential equation for each operator:

$$\frac{d\hat{a}(t)}{dt} = -i\omega\hat{a}(t) \tag{7.42}$$

and

$$\frac{d\hat{a}^\dagger(t)}{dt} = i\omega\hat{a}^\dagger(t) \quad (7.43)$$

the solutions to which are

$$\begin{aligned} \hat{a}(t) &= \hat{a}(0)e^{-i\omega t} \\ \hat{a}^\dagger(t) &= \hat{a}^\dagger(0)e^{i\omega t} \end{aligned} \quad (7.44)$$

Using Equations 7.4 and 7.5 we have

$$\begin{aligned} \left\{ \hat{x}(t) + \frac{i}{m\omega} \hat{p}(t) \right\} &= \left\{ \hat{x}(0) + \frac{i}{m\omega} \hat{p}(0) \right\} e^{-i\omega t} \\ \left\{ \hat{x}(t) - \frac{i}{m\omega} \hat{p}(t) \right\} &= \left\{ \hat{x}(0) - \frac{i}{m\omega} \hat{p}(0) \right\} e^{i\omega t} \end{aligned} \quad (7.45)$$

Adding these two equations yields $\hat{x}(t)$ and $\hat{p}(t)$, respectively:

$$\begin{aligned} \hat{x}(t) &= \hat{x}(0) \left\{ \frac{e^{-i\omega t} + e^{i\omega t}}{2} \right\} + \frac{1}{m\omega} \hat{p}(0) \left\{ \frac{e^{-i\omega t} - e^{i\omega t}}{2i} \right\} \\ &= \hat{x}(0) \cos \omega t + \frac{1}{m\omega} \hat{p}(0) \sin \omega t \\ &= \hat{x}(0) \cos \omega t + \frac{1}{\alpha^2 \hbar} \hat{p}(0) \sin \omega t \end{aligned} \quad (7.46)$$

and

$$\begin{aligned} \hat{p}(t) &= \hat{p}(0) \cos \omega t - m\omega \hat{x}(0) \sin \omega t \\ &= \hat{p}(0) \cos \omega t - \alpha \hbar \hat{x}(0) \sin \omega t \end{aligned} \quad (7.47)$$

Thus, the equations of motion for the position and momentum operators that we have derived are identical with those already obtained, Equations 6.157 and 6.158.

We have seen that the commutation rules for Heisenberg operators are the same as those for Schrödinger operators (Problem 7, Chapter 6). How about commutators involving Heisenberg operators at different times? To investigate this we examine the commutator $[\hat{x}(t), \hat{p}(0)]$ for the harmonic oscillator. Using Equation 7.46 we have

$$\begin{aligned} [\hat{x}(t), \hat{p}(0)] &= \left[\left\{ \hat{x}(0) \cos \omega t - \frac{1}{\alpha^2 \hbar} \hat{p}(0) \sin \omega t \right\}, \hat{p}(0) \right] \\ &= [\hat{x}(0), \hat{p}(0)] \cos \omega t \\ &= i\hbar \cos \omega t \end{aligned} \quad (7.48)$$

For the harmonic oscillator we also have (see Problem 6).

$$\begin{aligned} [\hat{p}(t), \hat{p}(0)] &= -i m \omega \hbar \sin \omega t \\ [\hat{x}(t), \hat{x}(0)] &= -\frac{i \hbar}{m \omega} \sin \omega t \end{aligned} \quad (7.49)$$

7.2 Coherent States of the Harmonic Oscillator

After deducing his now-famous equation, Schrödinger searched for a way to relate quantum mechanical parameters to classical physics. In particular, he was looking for a way to quantum mechanically represent the motion of a classical particle. In 1926 he was led to what we may refer to as the Schrödinger coherent state [1]. He found that certain linear combinations of harmonic oscillator eigenfunctions produced Gaussian wave packets that did not spread in time. Moreover, he also noted that if the uncertainties in position and time were equal, as discussed in Section 4.5, the resulting packet would be as close a representation of a classical particle as could be obtained within the bounds of the uncertainty principle.

We have seen in Sections 4.5 and 6.6.1 the uncertainty product for a Gaussian wave packet has the minimum value $\hbar/2$. The ground state of the harmonic oscillator, being a Gaussian form, has minimum uncertainties

$$\Delta x = \frac{1}{\sqrt{2}\alpha} \quad \text{and} \quad \Delta p = \frac{\hbar\alpha}{\sqrt{2}} \quad (7.50)$$

and these uncertainties are equal. Although the ground state of the harmonic oscillator has these magical properties, we cannot relate it to a moving classical particle because it represents a stationary state. We can, however, translate the ground state Gaussian shape to some other equilibrium position, say x_0 , and release the particle (for simplicity with zero momentum). Clearly the wave packet will have the same properties as the ground state wave function, but, because this displaced Gaussian is not an eigenstate, it will move in time. This is the displaced ground state discussed in Section 4.5. It is the best that we can do to quantum mechanically simulate the motion of a classical particle because the uncertainties in position and momentum remain minimized *and* equal. We can, in fact, define this Schrödinger coherent state as one for which the uncertainty product $\Delta x \Delta p$ is minimized and for which the individual uncertainties are equal. Note that it is possible to retain the minimum uncertainty product without the condition that the uncertainties are equal. In such a case we have a “squeezed state,” a subject of contemporary research.

We have already constructed the Schrödinger coherent state in Section 4.5.3. It is precisely Case III, the Gaussian wave packet under the influence of a harmonic oscillator potential. The initial wave function is given by Equation 4.95 and the time-dependent probability by Equation 4.107. The probability distribution showed clearly that the packet oscillates with the same frequency as the classical oscillator. Moreover, it does not spread in time.

To construct these coherent states we take a clue from Equation 7.23 which exhibits the property of the annihilation operator, that, when it operates on the ground state of the harmonic oscillator, it obliterates it. This equation may be viewed as an eigenvalue equation, a particularly simple one, but an eigenvalue equation nonetheless. That is,

$$\hat{a} |0\rangle = 0 \cdot |0\rangle \quad (7.51)$$

Thus, $|0\rangle$, which has Gaussian shape in both coordinate and momentum spaces, is an eigenvector of the lowering operator with eigenvalue zero. This suggests that other eigenvectors of \hat{a} might have similar properties. Indeed they do, but these eigenstates are not eigenstates of the Hamiltonian and the number operator. In general, letting $|z\rangle$ represent an eigenvector of \hat{a} , we have

$$\hat{a} |z\rangle = \left(\frac{\alpha}{\sqrt{2}} \zeta \right) |z\rangle \quad (7.52)$$

where the eigenvalue ζ need not be real because \hat{a} is not Hermitian. The factor $\alpha/\sqrt{2}$ has been inserted to make the result dimensionally appealing when compared with Equation 4.107.

To investigate the nature of these eigenvalues we solve Equation 7.52 in coordinate space. In this case $\langle x | z \rangle = \Psi(x, 0)$ and we have the differential equation

$$\sqrt{\frac{1}{2}} \left[\alpha x + i \frac{1}{\alpha \hbar} \left(\hbar \frac{d}{dx} \right) \right] \Psi(x, 0) = \frac{\alpha}{\sqrt{2}} \zeta \Psi(x, 0) \quad (7.53)$$

the solution to which is

$$\Psi(x, 0) = M e^{-\alpha^2(x-\zeta)^2/2} \quad (7.54)$$

where M is the normalization constant. Recalling that the eigenvalue ζ may be a complex number, we let $\zeta = \text{Re } \zeta + i \text{Im } \zeta$ and normalize. Equation 7.54 is

$$\begin{aligned} \Psi(x, 0) &= M \exp \left[-\frac{\alpha^2}{2} (x - \text{Re } \zeta - i \text{Im } \zeta)^2 \right] \\ &= M \exp \left\{ -\frac{\alpha^2}{2} [(x - \text{Re } \zeta)^2 - (\text{Im } \zeta)^2] \right\} \cdot \exp [i \alpha^2 (x - \text{Re } \zeta) \cdot \text{Im } \zeta] \end{aligned} \quad (7.55)$$

Then

$$\begin{aligned}
 1 &= \int_{-\infty}^{\infty} \Psi^*(x, 0) \Psi(x, 0) dx \\
 &= |M|^2 \int_{-\infty}^{\infty} \exp \left\{ -\alpha^2 \left[(x - \operatorname{Re} \zeta)^2 - (\operatorname{Im} \zeta)^2 \right] \right\} dx \\
 &= |M|^2 \exp \left[\alpha^2 (\operatorname{Im} \zeta)^2 \right] \frac{\sqrt{\pi}}{\alpha}
 \end{aligned} \tag{7.56}$$

so that

$$M = \frac{\sqrt{\alpha}}{\pi^{1/4}} \exp \left[-\frac{\alpha^2}{2} (\operatorname{Im} \zeta)^2 \right] \tag{7.57}$$

The eigenfunction represented by Equation 7.54 makes it clear that the eigenvectors of the lowering operator lead to nonstationary states that are nonetheless Gaussian wave packets centered at $x = \operatorname{Re} \zeta$ at $t = 0$. Moreover, the uncertainty product $\Delta x \Delta p$ is minimized and the individual uncertainties are equal. They are not eigenstates of the Hamiltonian and the number operator, but they may be expanded in terms of their eigenstates. These displaced ground states are indeed the Schrödinger coherent states.

To write the eigenket of \hat{a} in terms of the harmonic oscillator eigenkets $|n\rangle$ we write the usual expansion on the complete set

$$|z\rangle = \sum_{n=0}^{\infty} b_n |n\rangle \tag{7.58}$$

Applying the annihilation operator to Equation 7.58, using Equation 7.52 and Equation 7.20, we have

$$\begin{aligned}
 \frac{\alpha}{\sqrt{2}} \zeta |z\rangle &= \sum_{n=0}^{\infty} b_n \hat{a} |n\rangle \\
 &= \sum_{n=1}^{\infty} b_n \sqrt{n} |n-1\rangle
 \end{aligned} \tag{7.59}$$

We now replace $|z\rangle$ with the expansion of Equation 7.58, but change the index on the summation on the right-hand side by letting $n \rightarrow (n+1)$ which makes the two summations have compatible ranges, namely, $0 \rightarrow \infty$.

$$\frac{\alpha}{\sqrt{2}} \zeta \sum_{n=0}^{\infty} b_n |n\rangle = \sum_{n=0}^{\infty} b_{n+1} \sqrt{n+1} |n\rangle \tag{7.60}$$

Because the summations are identical, the coefficients of $|n\rangle$ must be identical and we obtain the recursion relation

$$\frac{\alpha}{\sqrt{2}} \zeta b_n = b_{n+1} \sqrt{n+1} \Rightarrow b_{n+1} = \frac{\alpha}{\sqrt{2}} \frac{\zeta}{\sqrt{n+1}} b_n \quad (7.61)$$

Applying this recursion relation n times to the first expansion coefficient b_0 we have

$$\begin{aligned} b_1 &= \left(\frac{\alpha}{\sqrt{2}} \right) \left(\frac{\zeta}{\sqrt{1}} b_0 \right) \\ b_2 &= \left(\frac{\alpha}{\sqrt{2}} \right) \frac{\zeta}{\sqrt{2}} b_1 = \left(\frac{\alpha}{\sqrt{2}} \right)^2 \left(\frac{\zeta^2}{\sqrt{1 \cdot 2}} b_0 \right) \\ &\vdots \\ b_n &= \left(\frac{\alpha}{\sqrt{2}} \right)^n \left(\frac{\zeta^n}{\sqrt{n!}} \right) b_0 \end{aligned} \quad (7.62)$$

which we can now insert in Equation 7.58 to obtain

$$|z\rangle = b_0 \sum_{n=0}^{\infty} \left(\frac{\alpha}{\sqrt{2}} \right)^n \frac{\zeta^n}{\sqrt{n!}} |n\rangle \quad (7.63)$$

To find b_0 we normalize $|z\rangle$. Taking advantage of the orthonormality of the $|n\rangle$ we have

$$\begin{aligned} \langle z | z \rangle &= |b_0|^2 \sum_{n=0}^{\infty} \left(\frac{\alpha^2}{2} \right)^n \frac{(\zeta^*)^n \zeta^n}{n!} \\ &= |b_0|^2 \sum_{n=0}^{\infty} \left(\frac{\alpha^2 |\zeta|^2}{2} \right)^n \frac{1}{n!} \end{aligned} \quad (7.64)$$

The summation is the Taylor series for $e^{\alpha^2 |\zeta|^2 / 2}$ so b_0 is given by

$$b_0 = e^{-\alpha^2 |\zeta|^2 / 4} \quad (7.65)$$

and

$$b_n = \left(\frac{\alpha}{\sqrt{2}} \right)^n \frac{\zeta^n}{\sqrt{n!}} e^{-\alpha^2 |\zeta|^2 / 4} \quad (7.66)$$

The coherent state, Equation 7.58, is therefore

$$|z\rangle = e^{-\alpha^2 |\zeta|^2 / 4} \sum_{n=0}^{\infty} \left(\frac{\alpha}{\sqrt{2}} \right)^n \zeta^n \frac{1}{\sqrt{n!}} |n\rangle \quad (7.67)$$

which may be shown to be an eigenvector of \hat{a} with eigenvalue $(\alpha\zeta/\sqrt{2})$ (see Problem 12).

We may now put in the time dependence by applying the time evolution operator to $|z\rangle$ which has the effect of multiplying each term in the expansion of Equation 7.67 by $\exp[-i(n + 1/2)\omega t]$. Thus, the coherent state including the time dependence is

$$|z(t)\rangle = e^{-\alpha^2|\zeta|^2/4} e^{-i\omega t/2} \sum_{n=0}^{\infty} \left(\frac{\alpha}{\sqrt{2}}\right)^n (\zeta e^{-i\omega t})^n \frac{1}{\sqrt{n!}} |n\rangle \quad (7.68)$$

It is seen that, to obtain the time dependence of the Schrödinger coherent state, it is only necessary to make the substitution $\zeta \rightarrow \zeta e^{-i\omega t}$ in Equation 7.67 and multiply the entire expression by the phase factor representing the zero point energy of the oscillator, $e^{-i\omega t/2}$. Notice that, as remarked in Section 4.5, this is only possible because the energy levels of the harmonic oscillator are equally spaced.

We know that initially the wave packet was a minimum uncertainty packet. That is,

$$\Delta x \Delta p = \frac{\hbar}{2} \quad (7.69)$$

so we can examine the time evolution of the individual uncertainties by finding the uncertainties for $t = 0$ and then make the substitution $\zeta \rightarrow \zeta e^{-i\omega t}$ in $\Psi(x, 0)$. We begin by calculating Δp and leave the determination of Δx as an exercise (see Problem 15).

The expectation values of \hat{p} and \hat{p}^2 are conveniently calculated using the ladder operators, Equation 7.52, and \hat{p} in the form given in Equation 7.5. We have

$$\begin{aligned} \langle \hat{p} \rangle &= \left(-i \frac{\alpha \hbar}{\sqrt{2}}\right) \langle z | (\hat{a} - \hat{a}^\dagger) | z \rangle \\ &= \left(-i \frac{\alpha \hbar}{\sqrt{2}}\right) (\langle z | \hat{a} | z \rangle - \langle z | \hat{a}^\dagger | z \rangle) \\ &= \left(-i \frac{\alpha \hbar}{\sqrt{2}}\right) \left(\frac{\alpha}{\sqrt{2}}\right) (\zeta - \zeta^*) \\ &= \left(-i \frac{\alpha^2 \hbar}{2}\right) 2i \operatorname{Im} \zeta \\ &= \alpha^2 \hbar \operatorname{Im} \zeta \end{aligned} \quad (7.70)$$

where the second inner product was performed using the complex conjugate of Equation 7.52. We also require $\langle \hat{p}^2 \rangle$ which may be calculated in an analogous manner:

$$\begin{aligned}
\langle \hat{p}^2 \rangle &= \left(-i \frac{\alpha \hbar}{\sqrt{2}} \right)^2 \langle z | (\hat{a} - \hat{a}^\dagger) (\hat{a} - \hat{a}^\dagger) | z \rangle \\
&= - \left(\frac{\alpha \hbar}{\sqrt{2}} \right)^2 \langle z | \left[\hat{a}^2 - \hat{a} \hat{a}^\dagger - \hat{a}^\dagger \hat{a} - (\hat{a}^\dagger)^2 \right] | z \rangle
\end{aligned} \tag{7.71}$$

We know that the inner product $\langle z | \hat{a}^\dagger \hat{a} | z \rangle = \zeta^* \zeta \alpha^2 / 2$, but how about $\langle z | \hat{a} \hat{a}^\dagger | z \rangle$? We can easily evaluate this using the commutation relation given in Equation 7.3. Replacing the operator $\hat{a} \hat{a}^\dagger$ with $(1 + \hat{a}^\dagger \hat{a})$ leads to

$$\begin{aligned}
\langle \hat{p}^2 \rangle &= - \left(\frac{\alpha \hbar}{\sqrt{2}} \right)^2 \langle z | \left[\hat{a}^2 - 1 - 2\hat{a}^\dagger \hat{a} - (\hat{a}^\dagger)^2 \right] | z \rangle \\
&= - \left(\frac{\alpha \hbar}{\sqrt{2}} \right)^2 \left(\zeta^2 - 2\zeta^* \zeta + \zeta^{*2} \right) \left(\frac{\alpha}{\sqrt{2}} \right)^2 + \left(\frac{\alpha \hbar}{\sqrt{2}} \right)^2 \\
&= - \left(\frac{\alpha^4 \hbar^2}{4} \right) (2i \operatorname{Im} \zeta)^2 + \frac{\alpha^2 \hbar^2}{2} \\
&= \alpha^4 \hbar^2 (\operatorname{Im} \zeta)^2 + \frac{\alpha^2 \hbar^2}{2}
\end{aligned} \tag{7.72}$$

Therefore,

$$\begin{aligned}
(\Delta p)^2 &= \langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2 \\
&= \alpha^4 \hbar^2 (\operatorname{Im} \zeta)^2 + \frac{\alpha^2 \hbar^2}{2} - (\alpha^2 \hbar \operatorname{Im} \zeta)^2 \\
&= \frac{\alpha^2 \hbar^2}{2}
\end{aligned} \tag{7.73}$$

Notice that it is not possible to make the substitution $\zeta \rightarrow \zeta e^{-i\omega t}$ in the expression for $(\Delta p)^2$, Equation 7.73, in order to determine its time dependence since it is independent of ζ and therefore independent of time.

In a similar manner we find (see Problem 16)

$$\langle \hat{x} \rangle = \operatorname{Re} \zeta \quad \text{and} \quad \langle \hat{x}^2 \rangle = (\operatorname{Re} \zeta)^2 + \frac{1}{2\alpha^2} \tag{7.74}$$

so that

$$(\Delta x)^2 = \frac{1}{2\alpha^2} \tag{7.75}$$

which is also independent of time. The uncertainty product is therefore given *at all times* by that of the minimum uncertainty wave packet

$$(\Delta x)^2 (\Delta p)^2 = \frac{\hbar^2}{4} \quad (7.76)$$

Comparison of the values obtained for the expectation values $\langle \hat{x} \rangle$ and $\langle \hat{p} \rangle$, Equations 7.70 and 7.74, leads to a physical interpretation of the complex eigenvalue $(\alpha/\sqrt{2})\zeta$. From Equations 4.58 and 4.59 for a Gaussian wave packet with initial displacement x_0 and initial momentum p_0 , we know that $\langle \hat{x} \rangle = x_0$ and $\langle \hat{p} \rangle = p_0$ (see Problem 4 of Chapter 4). We are therefore led to write

$$\begin{aligned} \zeta &= \text{Re } \zeta + i \text{Im } \zeta \\ &= \langle \hat{x} \rangle + i \frac{\langle \hat{p} \rangle}{\alpha^2 \hbar} \\ &= x_0 + i \frac{p_0}{\alpha^2 \hbar} \end{aligned} \quad (7.77)$$

so that

$$\text{Re } \zeta = x_0 \quad \text{and} \quad \text{Im } \zeta = \frac{p_0}{\alpha^2 \hbar} \quad (7.78)$$

Inserting ζ in this form into Equation 7.55 we may write $\Psi(x, 0)$ in the form

$$\Psi(x, 0) = M \exp \left\{ -\frac{\alpha^2}{2} \left[(x - x_0)^2 - \left(\frac{p_0}{\alpha^2 \hbar} \right)^2 \right] \right\} \cdot \exp \left[i \alpha^2 (x - x_0) \cdot \frac{p_0}{\alpha^2 \hbar} \right] \quad (7.79)$$

where, using Equations 7.57 and 7.78, the normalization constant is

$$M = \frac{\sqrt{\alpha}}{\pi^{1/4}} \exp \left[-\frac{1}{2} \frac{p_0^2}{\alpha^2 \hbar} \right] \quad (7.80)$$

It was remarked in Section 6.6.2 that we would reexamine the time development of a Gaussian packet under the influence of a harmonic oscillator potential, an exercise that will now be undertaken. We wish to find the time-dependent wave function $\Psi(x, t)$ so we may compare $|\Psi(x, t)|^2$ with the corresponding probability density of Case III of Section 4.5 Equation 4.107 to verify that the wave packet of Section 4.5 is indeed a Schrödinger coherent state. To obtain the time dependence of a coherent state it is natural to begin by applying the time evolution operator, Equation 6.115, so that in the current notation

$$\Psi(x, t) = e^{-i\hat{H}t/\hbar} \Psi(x, 0) \quad (7.81)$$

As noted in Section 6.6.2, however, this is a nontrivial exercise because the Hamiltonian consists of two noncommuting terms (see the BCH formula in Appendix L). We can circumvent the necessity of using the time evolution operator because we found that $|z\rangle$ could be converted to $|z(t)\rangle$ by making the substitution $\zeta \rightarrow \zeta e^{-i\omega t}$

and multiplying the entire expression by $e^{-i\omega t/2}$ (see Equation 7.68). We therefore take that approach here to effect the conversion $\Psi(x, 0) \rightarrow \Psi(x, t)$. Making the substitution $\zeta \rightarrow (\text{Re } \zeta + i \text{Im } \zeta) e^{-i\omega t}$ in Equation 7.79 and substituting for the real and imaginary parts of ζ using Equation 7.78 we have

$$\begin{aligned} \Psi(x, t) = N e^{-i\omega t/2} \exp \left\{ -\frac{\alpha^2}{2} \left[(x - x_0 e^{-i\omega t})^2 - \left(\frac{p_0}{\alpha^2 \hbar} e^{-i\omega t} \right)^2 \right] \right\} \\ \times \exp \left[-2i (x - x_0 e^{-i\omega t}) \frac{p_0}{\alpha^2 \hbar} e^{-i\omega t} \right] \end{aligned} \quad (7.82)$$

Adapting Equation 7.82 to the conditions of Case III of Section 4.5, namely, initial momentum $p_0 = 0$, we have

$$\begin{aligned} \Psi(x, t) = \frac{\sqrt{\alpha}}{\pi^{1/4}} \exp \left\{ \left[-\frac{\alpha^2}{2} (x - x_0 \cos \omega t)^2 \right] \right\} \\ \times \exp [-i (x - x_0 \cos \omega t) x_0 \sin \omega t] \end{aligned} \quad (7.83)$$

and the probability distribution is

$$|\Psi(x, t)|^2 = \frac{\alpha}{\sqrt{\pi}} \exp [-\alpha^2 (x - x_0 \cos \omega t)^2] \quad (7.84)$$

We see that, indeed, we have reproduced the probability distribution of Equation 4.107 so that the Schrödinger coherent state of this section is identical with the Gaussian wave packet under the influence of a harmonic oscillator potential.

7.3 Retrospective

The algebraic method of solving the harmonic oscillator problem is a concise and elegant method of obtaining the energy eigenvalues and eigenfunctions. It provides a method of solving quantum mechanical problems using the commutator rules that are a unique feature of quantum physics. Because the harmonic oscillator is the starting point for the quantal description of a great many physical problems, for example, molecular vibrations and nuclear structure, the formulation in terms of the ladder operators is invaluable. Moreover, ladder operators of other operators are employed throughout quantum physics.

7.4 Reference

1. E. Schrödinger, *Naturwissenschaften*, **28**, 664-666 (1926). The English translation of this paper is contained in E. Schrödinger, *Collected Papers on Wave Mechanics* (Chelsea Publishing Co., New York, 3rd ed., 1982), pp. 41-44.

Problems

1. Show that $[\hat{H}, \hat{a}] = -\hbar\omega\hat{a}$ and $[\hat{H}, \hat{a}^\dagger] = \hbar\omega\hat{a}^\dagger$.
2. Prove Equations 7.14 and 7.15. That is, prove $[\hat{N}, \hat{a}] = -\hat{a}$ and $[\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger$.
3. Show that $\hat{a}^\dagger |n\rangle = c_2 |n+1\rangle$.
4. Beginning with $\hat{a}^\dagger |n\rangle = c_2 |n+1\rangle$, show that $\hat{a}^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle$.
5. The state vector at $t = 0$ for a particle subject to a harmonic oscillator potential is given by

$$|\Psi(x, 0)\rangle = \frac{1}{\sqrt{3}} |1\rangle + \sqrt{\frac{2}{3}} |2\rangle$$

where the $|n\rangle$ are eigenvectors of the Hamiltonian and the number operator.

- (a) Find the state vector as a function of time $|\Psi(x, t)\rangle$.
 - (b) Find the expectation value of the energy as a function of time.
 - (c) Find the expectation value of the position as a function of time.
6. Show that for the harmonic oscillator $[\hat{p}(t), \hat{p}(0)] = -im\omega\hbar \sin\omega t$ and $[\hat{x}(t), \hat{x}(0)] = -\frac{i\hbar}{m\omega} \sin\omega t$.
 7. Show that

$$\begin{aligned} \langle m | \hat{x}^2 | n \rangle = \frac{1}{2\alpha^2} & \left[\sqrt{n(n-1)}\delta_{m,n-2} \right. \\ & \left. + (2n+1)\delta_{m,n} + \sqrt{(n+1)(n+2)}\delta_{m,n+2} \right] \end{aligned}$$

by writing x in terms of the ladder operators and operating on $|n\rangle$.

8. Obtain the matrix element $\langle m | \hat{x} | n \rangle$, Equation 7.31, by direct integration using the wave functions given in Equation 3.49.
9. Obtain the matrix element $\langle m | \hat{x}^2 | n \rangle$ in terms of the quantum number m by applying the same technique to Equation 7.37 as that employed to obtain Equation 7.35. Of course, the answer will be the same as that in Problem 7, but show that the δ -functions at each end interchange. [Hint: Make sure that the second index in all the δ -functions is n .]
10. Obtain the matrix element $\langle m | \hat{x}^3 | n \rangle$ Equation 7.38:

$$\begin{aligned} \langle m | \hat{x}^3 | n \rangle = \frac{1}{2\sqrt{2}\alpha^3} & \left[\sqrt{(n+1)(n+2)(n+3)}\delta_{m,n+3} \right. \\ & + 3\sqrt{(n+1)^3}\delta_{m,n+1} + 3\sqrt{n^3}\delta_{m,n-1} \\ & \left. + \sqrt{n(n-1)(n-2)}\delta_{m,n-3} \right] \end{aligned}$$

11. Find the expectation value of \hat{x}^4 for arbitrary state of the harmonic oscillator.
12. Show that the time-dependent Schrödinger coherent state in the form given in Equation 7.68

$$|z(t)\rangle = e^{-\alpha^2|z|^2/4} e^{-i\omega t/2} \sum_{n=0}^{\infty} \left(\frac{\alpha z e^{-i\omega t}}{\sqrt{2}} \right)^n \frac{1}{\sqrt{n!}} |n\rangle$$

is an eigenstate of the annihilation operator \hat{a} with eigenvalue $(\alpha z e^{-i\omega t} / \sqrt{2})$ which shows that $|z(t)\rangle$ remains an eigenvector of \hat{a} for all time.

13. Show that the wave function at $t = 0$ for Case III in Chapter 4, Equation 4.95, is an eigenstate of the annihilation operator with eigenvalue $\alpha x_0 / \sqrt{2}$.
14. Show that the Schrödinger coherent state

$$|z\rangle = e^{-|z|^2/2} \sum_{n=0}^{\infty} \frac{z^n}{\sqrt{n!}} |n\rangle$$

can be written in the form

$$|z\rangle = e^{-|z|^2/2} e^{z\hat{a}^\dagger} |0\rangle$$

15. Show that $(\Delta x)^2 = 1/2\alpha^2$ for the Schrödinger coherent state of Equation 7.67.
16. Show that Δx is independent of time using Equations 7.44.
17. A particle of mass m is in the ground state of a harmonic oscillator potential $U(x) = (1/2)m\omega^2 x^2$. At $t = 0$ the force center is suddenly shifted to a point along the x -axis $x = x_0$. The shift is so sudden that the wave function does not change.
 - (a) Show that the state of the system after the shift is a Schrödinger coherent state.
 - (b) If the energy is measured immediately after the change, what values of the energy can be measured and with what probabilities?

Chapter 8

Quantum Mechanics in Three Dimensions—Angular Momentum

It is now time to attack problems in three dimensions. This is not merely a threefold extension of one-dimensional problems because we must now deal with angular momentum. In classical physics angular momentum is usually designated \mathbf{L} and defined as

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (8.1)$$

In quantum physics the term angular momentum has a much more general meaning. The most common perception of angular momentum is that of the momentum associated with some angular motion. In quantum physics, however, *an* angular momentum is defined as any operator $\hat{\mathbf{J}}$ that represents a vector observable and for which the components obey the commutation rule

$$[\hat{J}_i, \hat{J}_j] = i\hbar \hat{J}_k \epsilon_{ijk} \quad (8.2)$$

where any of the i , j , and k represent x , y , and z . The quantity ϵ_{ijk} is known as the Levi-Cevita symbol. If the indexes i , j and k are in cyclic order (for example jki), $\epsilon_{ijk} = +1$. If they are out of order (such as kji), then $\epsilon_{ijk} = -1$. If any two indexes are the same, $\epsilon_{ijk} = 0$. Any operator that obeys the commutation rule given in Equation 8.2 is called a generalized angular momentum.

The quantum mechanical angular momentum that corresponds to the classical angular momentum of Equation 8.1, which we will refer to as *orbital* angular momentum and designate the corresponding operator as $\hat{\mathbf{L}}$ is a special case of the more general entity as defined by Equation 8.2. It is unfortunate that physicists often use the term angular momentum without specifying which angular momentum it is to which they refer. To the beginner, angular momentum usually means \mathbf{L} . There are, however, other angular momenta, and these angular momenta may have nothing at all to do with $\mathbf{r} \times \mathbf{p}$. Indeed, *an* angular momentum may be a very abstract observable quantity. This is an important concept in quantum physics so we will delve into it in some detail.

Let us first examine the special case for which $\hat{\mathbf{J}} = \hat{\mathbf{L}}$ because we know the form of the operators $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ so we can show that the components of $\hat{\mathbf{L}}$ obey the commutation rule given in Equation 8.2. Note that, having completed our study

of the formal aspects of quantum mechanics, we revert to the unhatted coordinate operators. We must be careful with the ordering of the operators \mathbf{r} and $\hat{\mathbf{p}}$ in the cross product. The easiest way to do this is to remember that we are dealing with $\mathbf{r} \times \hat{\mathbf{p}}$, and not $\hat{\mathbf{p}} \times \mathbf{r}$. Therefore, the components of \mathbf{r} always come first. Using the determinant to evaluate the cross product we have

$$\begin{aligned}\hat{\mathbf{L}} &= \mathbf{r} \times \hat{\mathbf{p}} \\ &= \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ x & y & z \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix} \\ &= (y\hat{p}_z - z\hat{p}_y)\hat{\mathbf{i}} + (z\hat{p}_x - x\hat{p}_z)\hat{\mathbf{j}} + (x\hat{p}_y - y\hat{p}_x)\hat{\mathbf{k}} \end{aligned} \quad (8.3)$$

Notice that the coordinate operator is always first in each of the six terms in Equation 8.3. Using the coordinates of angular momentum in this equation we have

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= [(y\hat{p}_z - z\hat{p}_y), (z\hat{p}_x - x\hat{p}_z)] \\ &= [y\hat{p}_z, z\hat{p}_x] - [y\hat{p}_z, x\hat{p}_z] - [z\hat{p}_y, z\hat{p}_x] + [z\hat{p}_y, x\hat{p}_z] \end{aligned} \quad (8.4)$$

To evaluate this commutator it is necessary to use commutator identities of the type given in Appendix K. Noting that only two of the commutators in Equation 8.4 are nonvanishing and applying the identity given in Equation K.5 we have

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= y[\hat{p}_z, z]\hat{p}_x + x[z, \hat{p}_z]\hat{p}_y \\ &= y(-i\hbar)\hat{p}_x + x(i\hbar)\hat{p}_y \\ &= i\hbar(x\hat{p}_y - y\hat{p}_x) \\ &= i\hbar\hat{L}_z \end{aligned} \quad (8.5)$$

Cyclic permutation of the components reveals that, indeed, orbital angular momentum qualifies as an angular momentum.

8.1 Commutation Relations

Returning now to a discussion of generalized angular momenta, we saw in Chapter 6 that, for operators corresponding to observable quantities, a nonvanishing commutator indicates that the two operators represent observable quantities that are incompatible. That is, they cannot be measured simultaneously because the operators cannot have simultaneous eigenvectors. Thus, it is clear from Equation 8.2 that only one component of an angular momentum may be specified. Measurement of another component disturbs the measurement of the first. Traditionally, the component that is chosen to be the known component is the z -component. But, how about the magnitude of the angular momentum? Can it be determined if we know the value of \hat{J}_z ? To make this determination we must examine the commutation relation between $\hat{\mathbf{J}}$

and the magnitude of the angular momentum, subject to the commutation relation of Equation 8.2. It is easiest to work with the square of the magnitude \hat{J}^2 which is, necessarily, a scalar operator ($\hat{J}^2 = \hat{\mathbf{J}} \bullet \hat{\mathbf{J}}$). Thus,

$$[\hat{J}^2, \hat{J}_z] = [\hat{J}_x^2, \hat{J}_z] + [\hat{J}_y^2, \hat{J}_z] + [\hat{J}_z^2, \hat{J}_z] \quad (8.6)$$

where the last term clearly vanishes. Using the identity Equation K.4 we find that

$$\begin{aligned} [\hat{J}_x^2, \hat{J}_z] &= [\hat{J}_x, \hat{J}_z] \hat{J}_x + \hat{J}_x [\hat{J}_x, \hat{J}_z] \\ &= -i\hbar (\hat{J}_y \hat{J}_x + \hat{J}_x \hat{J}_y) \end{aligned} \quad (8.7)$$

and

$$[\hat{J}_y^2, \hat{J}_z] = +i\hbar (\hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x) \quad (8.8)$$

so that

$$[\hat{J}^2, \hat{J}_z] = 0 \quad (8.9)$$

It is clear from the equivalence of the components that

$$[\hat{J}^2, \hat{J}_i] = 0 \quad \text{where } i = x, y \text{ or } z \quad (8.10)$$

Therefore, the *magnitude* of the angular momentum can be specified together with any of the components of $\hat{\mathbf{J}}$. Because, however, the components do not commute, only one of them can be specified, customarily chosen to be \hat{J}_z .

8.2 Angular Momentum Ladder Operators

8.2.1 Definitions and Commutation Relations

Angular momentum ladder operators are a very important class of operators. They are very similar to the harmonic oscillator ladder operators introduced in Chapter 7. As for the harmonic oscillator, they are also referred to as ladder operators or raising and lowering operators. Another term for them is shift operators. For a generalized angular momentum the angular momentum ladder operators are defined as

$$\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y \quad (8.11)$$

Clearly

$$\hat{J}_{\pm} = \hat{J}_{\mp}^{\dagger} \quad (8.12)$$

Table 8.1 Angular momentum commutation relations

$$\begin{aligned}
[\hat{J}_i, \hat{J}_j] &= i\hbar \hat{J}_k \epsilon_{ijk} \\
[\hat{J}^2, \hat{J}_i] &= 0 \quad i = x, y, \text{ or } z \\
[\hat{J}_+, \hat{J}_-] &= 2\hbar \hat{J}_z \\
[\hat{J}_\pm, \hat{J}_z] &= \mp \hbar \hat{J}_\pm \\
[\hat{J}_\pm, \hat{J}^2] &= 0
\end{aligned}$$

The commutation relations with other angular momentum operators are useful. For example,

$$\begin{aligned}
[\hat{J}_+, \hat{J}_-] &= -i [\hat{J}_x, \hat{J}_y] + i [\hat{J}_y, \hat{J}_x] \\
&= -i (i\hbar \hat{J}_z) + i (-i\hbar \hat{J}_z) \\
&= 2\hbar \hat{J}_z
\end{aligned} \tag{8.13}$$

where we have used the fundamental definition of an angular momentum, Equation 8.2.

Other commutation relations can be easily derived. For example (see Problem 2),

$$[\hat{J}_\pm, \hat{J}_z] = \mp \hbar \hat{J}_\pm \tag{8.14}$$

and

$$[\hat{J}_\pm, \hat{J}^2] = 0 \tag{8.15}$$

A few of the angular momentum commutation relations including some with the ladder operators are summarized in Table 8.1.

8.2.2 Angular Momentum Eigenvalues

We can, with the aid of the ladder operators, find the eigenvalues of the generalized angular momentum operators \hat{J}^2 and \hat{J}_z . Because \hat{J}^2 commutes with its components, we know that \hat{J}^2 and any one of its components can have simultaneous eigenvalues.

We assume that the eigenstates are denoted by two quantum numbers, j and m , where j is associated with \hat{J}^2 and m with \hat{J}_z . The eigenvectors are represented by the ket $|jm\rangle$ so the eigenvalue equation for \hat{J}_z may be written

$$\hat{J}_z |jm\rangle = m\hbar |jm\rangle \tag{8.16}$$

where the \hbar has been inserted for convenience, because we have the luxury of knowing the answer. The only thing we know about m is that it is a real number (because

\hat{J}_z is a Hermitian operator). The ket $|jm\rangle$ must also be an eigenket of the total angular momentum operator \hat{J}^2 because $[\hat{J}^2, \hat{J}_z] = 0$. We therefore write

$$\hat{J}^2 |jm\rangle = \hbar^2 f(j, m) |jm\rangle \quad (8.17)$$

where $f(j, m)$ is presumed to be a function of the quantum number m and some other quantum number j that is unique to the *total* angular momentum. We have inserted \hbar^2 in the eigenvalue, again for convenience. This eigenvalue must also be real, but it must also be positive because \hat{J}^2 represents the *square* of the angular momentum. Moreover, the expectation value of the difference between \hat{J}^2 and \hat{J}_z^2 may be written

$$\begin{aligned} \langle (\hat{J}^2 - \hat{J}_z^2) \rangle &= \langle jm | (\hat{J}^2 - \hat{J}_z^2) | jm \rangle \\ &= \hbar^2 [f(j, m) - m^2] \end{aligned} \quad (8.18)$$

Because $f(j, m)$ is manifestly positive we have obtained a relationship between $f(j, m)$ and m^2 :

$$f(j, m) \geq m^2 \quad (8.19)$$

Now we operate on the eigenvalue equation, Equation 8.17, with \hat{J}_\pm :

$$\hat{J}_\pm \hat{J}^2 |jm\rangle = \hbar^2 f(j, m) \hat{J}_\pm |jm\rangle \quad (8.20)$$

Noting that the \hat{J}_\pm commutes with \hat{J}^2 we rewrite Equation 8.20 in the form

$$\hat{J}^2 \{ \hat{J}_\pm |jm\rangle \} = \hbar^2 f(j, m) \{ \hat{J}_\pm |jm\rangle \} \quad (8.21)$$

which makes it clear that the kets $\{ \hat{J}_\pm |jm\rangle \}$ are eigenkets of \hat{J}^2 . Moreover, the $\{ \hat{J}_\pm |jm\rangle \}$ have the same eigenvalue as \hat{J}^2 , $\hbar^2 f(j, m)$. Therefore, since \hat{J}^2 represents the magnitude of the angular momentum, the $\{ \hat{J}_\pm |jm\rangle \}$ eigenkets have the same magnitude as $|jm\rangle$.

To examine further the effects of \hat{J}_\pm on $|jm\rangle$ we could try the same approach using \hat{J}_z . This is not fruitful, however, because \hat{J}_z and \hat{J}_\pm do not commute. Instead, we apply \hat{J}_z to the eigenket of \hat{J}^2 , $\{ \hat{J}_\pm |jm\rangle \}$. Using the commutation relations of Table 8.1 we have

$$\begin{aligned} \hat{J}_z \{ \hat{J}_\pm |jm\rangle \} &= [\hat{J}_z \hat{J}_\pm + (\hat{J}_\pm \hat{J}_z - \hat{J}_\pm \hat{J}_z)] |jm\rangle \\ &= ([\hat{J}_z, \hat{J}_\pm] + \hat{J}_\pm \hat{J}_z) |jm\rangle \\ &= (\pm \hbar \hat{J}_\pm + \hat{J}_\pm m \hbar) |jm\rangle \\ &= \hbar(m \pm 1) \{ \hat{J}_\pm |jm\rangle \} \end{aligned} \quad (8.22)$$

Thus, $\{\hat{J}_\pm |jm\rangle\}$ is an eigenvector of \hat{J}_z . From Equation 8.22 it is seen that the action of \hat{J}_\pm on $|jm\rangle$ is to raise/lower the quantum number m by unity so we have

$$\hat{J}_\pm |jm\rangle = \hbar C_{jm}^\pm |j(m \pm 1)\rangle \quad (8.23)$$

where C_{jm}^\pm is a constant.

Inasmuch as the \hat{J}_\pm change only m , and because $f(j, m) \geq m^2$, these operators cannot be applied indefinitely. That is, there must be maximum and minimum values of m so we must have

$$\hat{J}_+ |jm_{\max}\rangle = 0 \quad (8.24)$$

and

$$\hat{J}_- |jm_{\min}\rangle = 0 \quad (8.25)$$

Applying \hat{J}_- to Equation 8.24 we obtain

$$\begin{aligned} 0 &= (\hat{J}_- \hat{J}_+) |jm_{\max}\rangle \\ &= (\hat{J}_x - i\hat{J}_y) (\hat{J}_x + i\hat{J}_y) |jm_{\max}\rangle \\ &= (\hat{J}_x^2 + \hat{J}_y^2 + i\hat{J}_x\hat{J}_y - i\hat{J}_y\hat{J}_x) |jm_{\max}\rangle \\ &= (\hat{J}_x^2 + \hat{J}_y^2 + i[\hat{J}_x, \hat{J}_y]) |jm_{\max}\rangle \\ &= (\hat{J}_x^2 + \hat{J}_y^2 - \hbar\hat{J}_z) |jm_{\max}\rangle \\ &= (\hat{J}^2 - \hat{J}_z^2 - \hbar\hat{J}_z) |jm_{\max}\rangle \end{aligned} \quad (8.26)$$

Therefore,

$$\begin{aligned} \hat{J}^2 |jm_{\max}\rangle &= (\hat{J}_z^2 + \hbar\hat{J}_z) |jm_{\max}\rangle \\ &= \{m_{\max}^2 \hbar^2 + \hbar(m_{\max} \hbar)\} |jm_{\max}\rangle \\ &= m_{\max} (m_{\max} + 1) \hbar^2 |jm_{\max}\rangle \end{aligned} \quad (8.27)$$

Comparing this last relation with Equation 8.17 we see that

$$f(j, m_{\max}) = m_{\max} (m_{\max} + 1) \quad (8.28)$$

Equation 8.28 makes it clear that the magnitude of the angular momentum is determined by the maximum value of m because $f(j, m)$ is the eigenvalue of \hat{J}^2 . We may therefore rename $m_{\max} = j$ and Equation 8.28 becomes

$$\hat{J}^2 |jm\rangle = j(j+1) \hbar^2 |jm\rangle \quad (8.29)$$

We still know nothing about j and m (other than the fact that they are real). We do not know if they are integers or fractions. Indeed, we do not even know if they are continuously distributed. Furthermore, we do not know the limits on them, although we know that they cannot go on forever. Before obtaining such information about j and m , we must evaluate the constants C_{jm}^{\pm} in Equation 8.23. To do this we find the matrix element $\langle jm | (\hat{J}_- \hat{J}_+) | jm \rangle$ in two different ways and equate the results. Using the form of $\hat{J}_- \hat{J}_+$ derived in Equation 8.26 we have

$$\begin{aligned} \langle jm | (\hat{J}_- \hat{J}_+) | jm \rangle &= \langle jm | (\hat{J}^2 - \hat{J}_z^2 - \hbar \hat{J}_z) | jm \rangle \\ &= \hbar^2 [j(j+1) - m^2 - m] \end{aligned} \quad (8.30)$$

$$= \hbar^2 [j(j+1) - m(m+1)] \quad (8.31)$$

Now, operating on $\hat{J}_+ | jm \rangle$ as given in Equation 8.23 with \hat{J}_-

$$\begin{aligned} \langle jm | (\hat{J}_- \hat{J}_+) | jm \rangle &= \langle jm | \hat{J}_- \hbar C_{jm}^+ | j(m+1) \rangle \\ &= \hbar C_{jm}^+ \langle jm | \hbar C_{j(m+1)}^- | jm \rangle \\ &= \hbar^2 C_{jm}^+ C_{j(m+1)}^- \end{aligned} \quad (8.32)$$

The successive operations with $\hat{J}_- \hat{J}_+$ were carried out to the right so that neither of the constants has been complex conjugated. Comparing Equations 8.31 and 8.32 we have

$$C_{jm}^+ C_{j(m+1)}^- = j(j+1) - m(m+1) \quad (8.33)$$

Now to find the relationship between C_{jm}^+ and $C_{j(m+1)}^-$ we find the matrix element $\langle jm | \hat{J}_- | j(m+1) \rangle$ which, using Equation 8.12, is

$$\langle jm | \hat{J}_- | j(m+1) \rangle = \langle j(m+1) | \hat{J}_+ | jm \rangle^* \quad (8.34)$$

Performing the operations on each side of Equation 8.34 by operating to the right we have

$$C_{j(m+1)}^- = (C_{jm}^+)^* \quad (8.35)$$

so that Equation 8.33 becomes

$$|C_{jm}^+|^2 = j(j+1) - m(m+1) \quad (8.36)$$

The constant C_{jm}^+ is, by convention, chosen to be real and positive so that

$$\begin{aligned} C_{jm}^+ &= \sqrt{j(j+1) - m(m+1)} \\ &= \sqrt{(j-m)(j+m+1)} \end{aligned} \quad (8.37)$$

Letting $m \rightarrow m-1$ in Equation 8.35 we find that $C_{jm}^- = C_{j(m-1)}^+$ so that

$$\begin{aligned} C_{jm}^- &= \sqrt{j(j+1) - m(m-1)} \\ &= \sqrt{(j+m)(j-m+1)} \end{aligned} \quad (8.38)$$

Putting these values into Equation 8.23 we see that we have determined the detailed action of the ladder operators on the simultaneous eigenkets of \hat{J}^2 and \hat{J}_z . We have

$$\begin{aligned} \hat{J}_+ |jm\rangle &= \hbar \sqrt{j(j+1) - m(m+1)} |j(m+1)\rangle \\ &= \hbar \sqrt{(j-m)(j+m+1)} |j(m+1)\rangle \end{aligned} \quad (8.39)$$

and

$$\begin{aligned} \hat{J}_- |jm\rangle &= \hbar \sqrt{j(j+1) - m(m-1)} |j(m-1)\rangle \\ &= \hbar \sqrt{(j+m)(j-m+1)} |j(m-1)\rangle \end{aligned} \quad (8.40)$$

Now that we know the actions of \hat{J}_+ and \hat{J}_- on $|jm\rangle$, we can pursue further the restrictions of j and m . Application of \hat{J}_- to the eigenstate having the lowest value of m , $|jm_{\min}\rangle$, must obliterate this eigenstate. Using Equation 8.40 with $m = m_{\min}$ and taking the inner product with $\langle j(m_{\min}-1)|$ which, for this purpose, we pretend exists, we have

$$\langle j(m_{\min}-1)| \hat{J}_- |jm_{\min}\rangle = 0 \quad (8.41)$$

We can, however, operate to the left with \hat{J}_- so that its action is that of \hat{J}_+ (see Equation 8.39) and obtain

$$\hbar \sqrt{j(j+1) - m_{\min}(m_{\min}-1)} \langle jm_{\min} | jm_{\min}\rangle = 0 \quad (8.42)$$

from which we find a relation between j and m_{\min} , specifically, $m_{\min} = -j$. We already know that $m_{\max} = j$ so that

$$-j \leq m \leq j \quad (8.43)$$

The inequality in Equation 8.43 leads to a very important conclusion. Careful inspection of this relation between j and m shows that there are only two ways it can be valid, j must be either an integer or a half-integer.

8.3 Vector Operators

There is a broad class of operators in quantum mechanics that are referred to as vector operators or class T operators. They are defined by their commutation properties with any angular momentum operator $\hat{\mathbf{J}}$. An operator $\hat{\mathbf{T}}$ is a vector operator if its Cartesian components obey the commutation rule

$$[\hat{J}_i, \hat{T}_j] = i\hbar \hat{T}_k \epsilon_{ijk} \quad (8.44)$$

Comparison of this definition with Equation 8.2 shows immediately that $\hat{\mathbf{J}}$ is itself a vector operator. Moreover, \mathbf{r} and $\hat{\mathbf{p}}$ are also vector operators. Additionally, linear combinations of vector operators are vector operators, so the ladder operators are vector operators.

We may also define ladder operators corresponding to any vector operator. The raising operator is defined by

$$\hat{T}_+ = \hat{T}_x + i\hat{T}_y \quad (8.45)$$

from which we have the relations (see Problem 7)

$$\begin{aligned} [\hat{J}_z, \hat{T}_+] &= \hbar \hat{T}_+ \\ [\hat{J}_+, \hat{T}_z] &= -\hbar \hat{T}_+ \\ [\hat{J}^2, \hat{T}_+] &= 2\hbar (\hat{T}_+ \hat{J}_z - \hat{T}_z \hat{J}_+) + 2\hbar^2 \hat{T}_+ \end{aligned} \quad (8.46)$$

Now let us examine the action of \hat{T}_+ on an angular momentum eigenstate for which $m = j$, a ket $|jj\rangle$. The eigenvalue equation is

$$\hat{J}^2 |jj\rangle = j(j+1)\hbar^2 |jj\rangle \quad (8.47)$$

Multiplying on the left by \hat{T}_+ we have

$$\hat{T}_+ \hat{J}^2 |jj\rangle = j(j+1)\hbar^2 \hat{T}_+ |jj\rangle \quad (8.48)$$

We may also evaluate $\hat{T}_+ \hat{J}^2 |jj\rangle$ using the last commutation rule in Equation 8.46. We operate on the eigenvalue equation, Equation 8.47, with $[\hat{J}^2, \hat{T}_+]$ recalling that

$$\hat{J}_+ |jj\rangle = 0 \quad (8.49)$$

and arrive at

$$\begin{aligned} \hat{T}_+ \hat{J}^2 |jj\rangle &= \{ \hat{J}^2 \hat{T}_+ - 2\hbar (\hat{T}_+ \hat{J}_z - \hat{T}_z \hat{J}_+) - 2\hbar^2 \hat{T}_+ \} |jj\rangle \\ &= \hat{J}^2 \hat{T}_+ |jj\rangle - 2\hbar \hat{T}_+ \hat{J}_z |jj\rangle - 2\hbar^2 \hat{T}_+ |jj\rangle \\ &= \hat{J}^2 \hat{T}_+ |jj\rangle - 2\hbar j \hat{T}_+ |jj\rangle - 2\hbar^2 \hat{T}_+ |jj\rangle \end{aligned} \quad (8.50)$$

Equating the results in Equations 8.50 and 8.48 we find that

$$(\hat{J}^2 - 2\hbar^2 j - 2\hbar^2) \{\hat{T}_+ |jj\rangle\} = j(j+1)\hbar^2 \{\hat{T}_+ |jj\rangle\} \quad (8.51)$$

or

$$\begin{aligned} \hat{J}^2 \{\hat{T}_+ |jj\rangle\} &= [j(j+1)\hbar^2 + 2\hbar^2 j + 2\hbar^2] \{\hat{T}_+ |jj\rangle\} \\ &= (j^2 + 3j + 2)\hbar^2 \{\hat{T}_+ |jj\rangle\} \\ &= (j+1)(j+2)\hbar^2 \{\hat{T}_+ |jj\rangle\} \end{aligned} \quad (8.52)$$

which shows that the action of \hat{T}_+ on $|jj\rangle$ is to convert it into a constant times $|(j+1)(j+1)\rangle$. That is,

$$\hat{T}_+ |jj\rangle = C_{\hat{T}} |(j+1)(j+1)\rangle \quad (8.53)$$

where $C_{\hat{T}}$ is a constant that depends upon the particular vector operator. In short, \hat{T}_+ is a raising operator for any angular momentum eigenfunction for which $m = j$.

Is this result consistent with Equation 8.49? As noted above, any angular momentum vector qualifies as a vector operator so the angular momentum ladder operator should obey Equation 8.53 with $\hat{T}_+ \rightarrow \hat{J}_+$. We have already deduced the action of \hat{J}_+ on an arbitrary ket $|jm\rangle$. The result is given in Equation 8.39 from which we deduce that

$$\begin{aligned} \hat{J}_+ |jj\rangle &= C_{\hat{J}} |(j+1)(j+1)\rangle \\ &= \hbar\sqrt{(j-j)(j+j+1)} |(j+1)(j+1)\rangle \\ &= 0 \cdot |(j+1)(j+1)\rangle \end{aligned} \quad (8.54)$$

In other words, for $\hat{T}_+ = \hat{J}_+$ the constant $C_{\hat{J}} \equiv 0$ so Equation 8.53 is satisfied.

Using the first of Equations 8.46 we can investigate the z -component of the angular momentum of the eigenket $\{\hat{T}_+ |jj\rangle\}$. We have

$$\begin{aligned} \hat{J}_z \{\hat{T}_+ |jj\rangle\} &= (\hat{T}_+ \hat{J}_z + \hbar \hat{T}_+) |jj\rangle \\ &= (j+1)\hbar \{\hat{T}_+ |jj\rangle\} \end{aligned} \quad (8.55)$$

so $\{\hat{T}_+ |jj\rangle\}$ is an eigenket of \hat{J}_z with eigenvalue $(j+1)$. It is seen, then, that the operator \hat{T}_+ is indeed a ladder operator inasmuch as it raises the eigenkets of \hat{J}^2 and \hat{J}_z by one unit of angular momentum.

It is easily shown that $[\hat{J}, \hat{T}^2] = 0$ (see Problem 8). Hence, \hat{T}^2 commutes with each component of \hat{J} as well as \hat{J}^2 . Therefore, operation on $|jj\rangle$ with \hat{T}^2 has no effect on this state.

Table 8.2 Some useful commutation relations of vector operators with angular momentum

$$\begin{aligned}
[\hat{J}_i, \hat{T}_j] &= i\hbar \hat{T}_k \epsilon_{ijk} \\
[\hat{T}_\pm, \hat{J}_z] &= \mp \hbar \hat{T}_\pm \\
[\hat{T}_\pm, \hat{J}_x] &= \pm \hbar \hat{T}_z \\
[\hat{T}_\pm, \hat{J}_y] &= i\hbar \hat{T}_z \\
[\hat{T}_\pm, \hat{J}_\pm] &= 0 \\
[\hat{T}_\pm, \hat{J}_\mp] &= \pm 2\hbar \hat{T}_z \\
[\hat{T}_z, \hat{J}_\pm] &= \pm \hbar \hat{T}_\pm \\
[\hat{J}, (\hat{T}_1 \bullet \hat{T}_2)] &= 0 \implies [\hat{J}, \hat{T}^2] = 0 \\
[\hat{J}^2, [\hat{J}^2, \hat{T}]] &= 2\hbar^2 (\hat{J}^2 \hat{T} + \hat{T} \hat{J}^2) - 4\hbar^2 \hat{J} (\hat{J} \bullet \hat{T})
\end{aligned}$$

$$\begin{aligned}
\hat{J}^2 \{ \hat{T}^2 |jj\rangle \} &= \hat{T}^2 \hat{J}^2 |jj\rangle \\
&= j(j+1)\hbar^2 \{ \hat{T}^2 |jj\rangle \}
\end{aligned} \tag{8.56}$$

which shows that $\{ \hat{T}^2 |jj\rangle \}$ remains an eigenket of \hat{J}^2 with the same eigenvalue, $j(j+1)$. A similar conclusion holds for \hat{J}_z . Note, however, if there are other quantum numbers besides j and m , that \hat{T}^2 might have an effect on them. For convenience, Table 8.2 is a listing of some useful commutation relations involving vector and angular momentum operators.

8.4 Orbital Angular Momentum Eigenfunctions—Spherical Harmonics

When the angular momentum is the *orbital* angular momentum the eigenvalues have very nearly their classical meaning. Moreover, we can readily find the eigenfunctions in coordinate space. For orbital angular momentum it is customary to designate the total angular momentum quantum number by ℓ . Thus, in the equations that have been derived we will let $j \rightarrow \ell$. We will retain the quantum number m for the z -component of angular momentum, although when there is more than one angular momentum to consider, their z -component quantum numbers will be differentiated by an appropriate subscript. In the case of orbital angular momentum we use m_ℓ . It will not, however, be necessary to use the subscript in this section.

Because we can write the components of the operator $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ in coordinate space, we can find explicit eigenfunctions of \hat{L}_z and \hat{L}^2 in terms of these coordinates. We therefore seek these functions, and their relation to the eigenvalues. We begin with the ladder operators \hat{L}_\pm in coordinate space. We then use a technique similar to that employed in Section 7.1.1 to obtain the ground state of the harmonic oscillator. In particular, given the known limits on m , $-\ell \leq m \leq \ell$, we know that applying the raising operator to the ket $|\ell\ell\rangle$ will obliterate it. Because we will have an expression for \hat{L}_+ in coordinate space, we will have a partial differential equation for

the eigenfunction $Y_{\ell\ell}(\theta, \phi) = \langle \mathbf{r} | \ell\ell \rangle$ which is referred to as the “top of the ladder” eigenfunction. It is best to work in spherical coordinates for reasons that will become apparent in the next chapter. The symbol $Y_{\ell m}(\theta, \phi)$ is the universal symbol for these functions. They are called spherical harmonics. Successive application of \hat{L}_- to the top of the ladder spherical harmonic, $|\ell\ell\rangle$, produces all eigenfunctions for a given ℓ . We can then use the same technique on kets of the form $|(\ell - m)(\ell - m)\rangle$ to obtain the eigenfunctions for all values of the quantum numbers ℓ and m .

To work in spherical coordinates it is necessary to convert the Cartesian components of $\hat{\mathbf{L}}$ into spherical coordinates. To obtain the functional forms of \hat{L}_x , \hat{L}_y and \hat{L}_z , we must convert the derivatives and coordinates in the Cartesian forms of these operators to spherical coordinates. A relatively simple way to obtain the relationship between the derivatives is to compare the coordinates of the known expressions for the operator ∇ in each coordinate system after casting both expressions in terms of the Cartesian unit vectors. We begin by writing the equations of the transformation from Cartesian to spherical coordinates. These can be obtained analytically or they can be obtained graphically from Fig. 8.1.

The transformation equations are

$$\begin{aligned}x &= r \sin \theta \cos \phi \\y &= r \sin \theta \sin \phi \\z &= r \cos \theta\end{aligned}\tag{8.57}$$

and the operator ∇ in each of these coordinate systems is

$$\nabla = \hat{\mathbf{i}} \frac{\partial}{\partial x} + \hat{\mathbf{j}} \frac{\partial}{\partial y} + \hat{\mathbf{k}} \frac{\partial}{\partial z} \quad \text{Cartesian} \tag{8.58}$$

$$\nabla = \hat{\mathbf{a}}_r \frac{\partial}{\partial r} + \hat{\mathbf{a}}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\mathbf{a}}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \quad \text{Spherical} \tag{8.59}$$

where $\hat{\mathbf{a}}_r$, $\hat{\mathbf{a}}_\theta$, and $\hat{\mathbf{a}}_\phi$ are the unit vectors in spherical coordinates. In terms of the Cartesian unit vectors the spherical coordinate unit vectors are

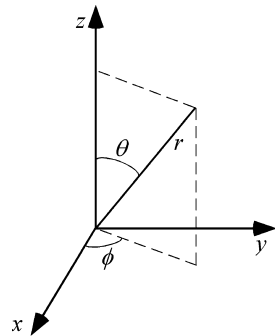


Fig. 8.1 Relationship between Cartesian coordinates and spherical coordinates

$$\begin{aligned}
\hat{\mathbf{a}}_r &= \sin \theta \cos \phi \hat{\mathbf{i}} + \sin \theta \sin \phi \hat{\mathbf{j}} + \cos \theta \hat{\mathbf{k}} \\
\hat{\mathbf{a}}_\theta &= \cos \theta \cos \phi \hat{\mathbf{i}} + \cos \theta \sin \phi \hat{\mathbf{j}} - \sin \theta \hat{\mathbf{k}} \\
\hat{\mathbf{a}}_\phi &= -\sin \phi \hat{\mathbf{i}} + \cos \phi \hat{\mathbf{j}}
\end{aligned} \tag{8.60}$$

Now replace $\hat{\mathbf{a}}_r$, $\hat{\mathbf{a}}_\theta$, and $\hat{\mathbf{a}}_\phi$ in Equation 8.59 with the expressions for the unit vectors in Equation 8.60 to obtain

$$\begin{aligned}
\nabla &= \left(\sin \theta \cos \phi \hat{\mathbf{i}} + \sin \theta \sin \phi \hat{\mathbf{j}} + \cos \theta \hat{\mathbf{k}} \right) \frac{\partial}{\partial r} \\
&+ \left(\cos \theta \cos \phi \hat{\mathbf{i}} + \cos \theta \sin \phi \hat{\mathbf{j}} - \sin \theta \hat{\mathbf{k}} \right) \frac{1}{r} \frac{\partial}{\partial \theta} \\
&+ \left(-\sin \phi \hat{\mathbf{i}} + \cos \phi \hat{\mathbf{j}} \right) \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}
\end{aligned} \tag{8.61}$$

Comparing the $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$, and $\hat{\mathbf{k}}$ components in Equations 8.58 and 8.61 we may write immediately

$$\begin{aligned}
\frac{\partial}{\partial x} &= \sin \theta \cos \phi \frac{\partial}{\partial r} + \cos \theta \cos \phi \frac{1}{r} \frac{\partial}{\partial \theta} - \frac{\sin \phi}{r \sin \theta} \frac{\partial}{\partial \phi} \\
\frac{\partial}{\partial y} &= \sin \theta \sin \phi \frac{\partial}{\partial r} + \cos \theta \sin \phi \frac{1}{r} \frac{\partial}{\partial \theta} + \frac{\cos \phi}{r \sin \theta} \frac{\partial}{\partial \phi} \\
\frac{\partial}{\partial z} &= \cos \theta \frac{\partial}{\partial r} - \sin \theta \frac{1}{r} \frac{\partial}{\partial \theta}
\end{aligned} \tag{8.62}$$

Now we write the Cartesian components of $\hat{\mathbf{L}}$ in coordinate space letting $\hat{p}_i \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x_i}$ using the determinant method. As discussed in connection with Equation 8.3, when using the determinant to find the components of $\hat{\mathbf{L}}$ in coordinate space, the linear momentum operator is always the second operator. Its components are therefore the entries in the third row of the determinant:

$$\begin{aligned}
\hat{\mathbf{L}} &= \mathbf{r} \times \hat{\mathbf{p}} \\
&= \left(\frac{\hbar}{i} \right) \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix} \\
&= \left(\frac{\hbar}{i} \right) \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \hat{\mathbf{i}} \\
&\quad + \left(\frac{\hbar}{i} \right) \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \hat{\mathbf{j}} \\
&\quad + \left(\frac{\hbar}{i} \right) \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \hat{\mathbf{k}}
\end{aligned} \tag{8.63}$$

The hats have been omitted from the coordinate operators because we are working in coordinate space and because it avoids confusion with the unit vectors. Inserting Equations 8.57 and 8.62 into each component in Equation 8.63 we obtain the desired result:

$$\begin{aligned}\hat{L}_x &= -\frac{\hbar}{i} \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \\ \hat{L}_y &= \frac{\hbar}{i} \left(\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \\ \hat{L}_z &= \frac{\hbar}{i} \frac{\partial}{\partial \phi}\end{aligned}\tag{8.64}$$

Combining \hat{L}_x and \hat{L}_y and using the exponential form of the sines and cosines we arrive at the ladder operators in spherical coordinates:

$$\begin{aligned}\hat{L}_+ &= \hbar e^{i\phi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) \\ \hat{L}_- &= -\hbar e^{-i\phi} \left(\frac{\partial}{\partial \theta} - i \cot \theta \frac{\partial}{\partial \phi} \right)\end{aligned}\tag{8.65}$$

Note that \hat{L}_- is not simply the complex conjugate of \hat{L}_+ . The Hermitian conjugate and the complex conjugate are the same only when all operators are Hermitian. The equation we must solve to obtain the top of the ladder eigenfunction $Y_{\ell\ell}(\theta, \phi)$ is then

$$\begin{aligned}\hat{L}_+ |\ell\ell\rangle &= 0 \\ e^{i\phi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) Y_{\ell\ell}(\theta, \phi) &= 0\end{aligned}\tag{8.66}$$

To solve this equation we use separation of variables with the substitution

$$Y_{\ell\ell}(\theta, \phi) = \Theta(\theta) \Phi(\phi)\tag{8.67}$$

which yields

$$\frac{\tan \theta}{\Theta(\theta)} \frac{d\Theta(\theta)}{d\theta} = -i \frac{1}{\Phi} \frac{d\Phi(\phi)}{d\phi}\tag{8.68}$$

The derivatives in Equation 8.68 are now total derivatives of $\Theta(\theta)$ and $\Phi(\phi)$. Inasmuch as the left side of Equation 8.68 contains only θ and the right side only ϕ , each side must be equal to a constant, the same constant which we call κ . We have

$$\Phi(\phi) = -K e^{i\kappa\phi}\tag{8.69}$$

where K is a constant of integration. The solution to the θ part of the equation is

$$\Theta(\theta) = K' \sin^\kappa \theta \quad (8.70)$$

which may be checked by substitution (see Problem 10). Finally then

$$Y_{\ell\ell}(\theta, \phi) = K'' e^{i\kappa\phi} \sin^\kappa \theta \quad (8.71)$$

We still do not know anything about the constant κ , the separation constant. To find κ in terms of known quantities we invoke the necessity that $|\ell\ell\rangle$ is an eigenvector of \hat{L}_z . The eigenvalue equation is

$$\hat{L}_z Y_{\ell\ell}(\theta, \phi) = \ell \hbar Y_{\ell\ell}(\theta, \phi) \quad (8.72)$$

which may also be written in terms of the solution of Equation 8.71 as

$$\begin{aligned} \hat{L}_z Y_{\ell\ell}(\theta, \phi) &= \frac{\hbar}{i} \frac{\partial}{\partial \phi} Y_{\ell\ell}(\theta, \phi) \\ &= \frac{\hbar}{i} \frac{\partial}{\partial \phi} (K'' e^{i\kappa\phi} \sin^\kappa \theta) \\ &= \frac{\hbar}{i} (i\kappa) Y_{\ell\ell}(\theta, \phi) \end{aligned} \quad (8.73)$$

Comparing Equations 8.73 with Equation 8.71 we see that $\kappa = \ell$. Thus, $Y_{\ell\ell}(\theta, \phi)$ is

$$Y_{\ell\ell}(\theta, \phi) = K'' e^{i\ell\phi} \sin^\ell \theta \quad (8.74)$$

A similar calculation starting at the bottom of the ladder yields

$$Y_{\ell-\ell}(\theta, \phi) = K'' e^{-i\ell\phi} \sin^\ell \theta \quad (8.75)$$

In principle, we are able to obtain all of the remaining eigenfunctions and eigenvalues by applying \hat{L}_- to $Y_{\ell\ell}(\theta, \phi)$ as many times as needed [or by applying \hat{L}_+ to $Y_{\ell-\ell}(\theta, \phi)$]. There are, however, restrictions on the quantum numbers ℓ and m that are not present for generalized angular momenta. These restrictions are the result of \hat{L} being a specific operator that represents the orbital angular momentum. We learn more about the quantum number m by solving the z -component eigenvalue equation for any value of m using the specific form of \hat{L}_z . From Equation 8.16 with $\hat{J}_z \rightarrow \hat{L}_z$, letting $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ and substituting for \hat{L}_z from Equation 8.64.

$$\frac{\hbar}{i} \frac{\partial}{\partial \phi} \Theta(\theta) \Phi(\phi) = m \hbar \Theta(\theta) \Phi(\phi) \quad (8.76)$$

The solution of this equation is

$$\Phi(\phi) = Ne^{im\phi} \quad (8.77)$$

where N is a constant. Comparing this expression for $\Phi(\phi)$ with $Y_{\ell\ell}(\theta, \phi)$, Equation 8.74, we see that the ℓ quantum number is associated with only the θ coordinate. We may therefore also write the eigenfunction $Y_{\ell m}(\theta, \phi)$ as

$$Y_{\ell m}(\theta, \phi) = Ne^{im\phi}\Theta(\theta) \quad (8.78)$$

So far so good, but the values of the quantum numbers ℓ and m are limited to integers. Half-integers, allowed for generalized angular momenta, are prohibited. To see this examine first the ϕ part of the eigenfunction. It is often remarked that a physically acceptable wave function must be single valued. That is, if we increase (or decrease) ϕ by 2π , we should get the same wave function. This is only true if m , and therefore ℓ , is an integer. There are, however, instances in which the wave function need not be single valued, but this is not one of them because the single-valuedness of the wave function is actually only valid if the wave function is a function of space coordinates only [1]. Therefore, the conclusion that m and ℓ must be integers for orbital angular momentum is indeed correct. Note, however, that the probability density, the absolute square of the wave function, must always be single valued.

There are other methods of proving that ℓ and m must be integral for orbital angular momentum [2]. One relatively simple method is to examine the eigenfunction with respect to a reflection through the xy -plane. Because this reflection has no effect on the ϕ part of $Y_{\ell m}(\theta, \phi)$ we need only examine the θ part. This reflection is effected by making the substitution $\theta \rightarrow \pi - \theta$, equivalent to letting $x \rightarrow x$, $y \rightarrow y$, and $z \rightarrow -z$. First, consider the symmetry of the top and bottom of the ladder states. The transformation $\theta \rightarrow \pi - \theta$ on $\sin \theta$ produces no change. Thus, the top and bottom states are even with respect to this reflection. We must now examine the effects of this reflection on the raising and lowering operations. Applying these operators to an arbitrary $Y_{\ell m}(\theta, \phi)$ we have

$$\begin{aligned} \hat{L}_{\pm} Y_{\ell m}(\theta, \phi) &= \hbar \sqrt{j(j+1) - m(m \pm 1)} Y_{\ell, m \pm 1}(\theta, \phi) \\ &= \hbar e^{\pm i\phi} \left(\frac{\partial}{\partial \theta} \pm i \cot \theta \frac{\partial}{\partial \phi} \right) [Ne^{im\phi} \Theta(\theta)] \\ &= \hbar e^{\pm i\phi} Ne^{im\phi} \left[\frac{d\Theta(\theta)}{d\theta} \mp m \cot \theta \Theta(\theta) \right] \\ &= Ne^{i(m \pm 1)\phi} \left[\frac{d}{d\theta} \mp m \cot \theta \right] \Theta(\theta) \end{aligned} \quad (8.79)$$

Now, the differentiation operation changes this symmetry of $\Theta(\theta)$ with respect to the x - y plane because of the minus sign in the transformation $\theta \rightarrow \pi - \theta$. Because $\cot \theta$ is odd under this reflection, the effect of the ladder operators is to change the symmetry of the state upon which they operate. Thus, the θ part of orbital angular momentum states alternate in reflection symmetry with the end states being even.

There must therefore be an odd number of states between the top and bottom. This condition is possible only if $2\ell + 1$ is odd so ℓ must be zero or an integer. Also, it can easily be shown that raising $Y_{\frac{1}{2}-\frac{1}{2}}(\theta, \phi)$ as given by Equation 8.75 does not produce $Y_{\frac{1}{2}\frac{1}{2}}(\theta, \phi)$ as given by Equation 8.74 (see Problem 11). The fact that the orbital angular momentum can be zero is in contrast to the Bohr model where the minimum value of the angular momentum was found to be \hbar (see Section 1.2.1)

Because of their importance, we will examine the spherical harmonics in some detail. These functions are simultaneous eigenfunctions of the commuting operators \hat{L}_z and \hat{L}^2 . We will see in the next chapter that for central potentials, $U(\mathbf{r}) = U(r)$, the spherical harmonics are always the angular portion of the energy eigenfunctions. Therefore, to solve central potential problems it is only necessary to solve the radial part of the three-dimensional TISE to obtain the complete eigenfunctions. The spherical harmonics are products of $e^{im\phi}$ and the associated Legendre functions designated $P_\ell^m(\cos \theta)$ which, in retrospect, are the functions $\Theta(\theta)$. The $P_\ell^m(\mu)$ are given by

$$P_\ell^m(\mu) = \frac{(1-\mu)^{m/2}}{2^\ell \ell!} \frac{d^{\ell+m}}{d\mu^{\ell+m}} (\mu^2 - 1)^\ell \quad (8.80)$$

Ordinary Legendre polynomials may be obtained using the Legendre polynomial generating function $g(t, \mu)$:

$$\begin{aligned} g(t, \mu) &= (1 - 2\mu t + t^2)^{-1/2} \\ &= \sum_{\ell=0}^{\infty} P_\ell(\mu) t^\ell \quad |t| < 1 \end{aligned} \quad (8.81)$$

or they may be obtained from the relation

$$P_\ell(\mu) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{d\mu^\ell} (\mu^2 - 1)^\ell \quad (8.82)$$

Substitution of Equation 8.82 into Equation 8.80 shows that the associated Legendre functions may also be written

$$P_\ell^m(\mu) = (1 - \mu)^{m/2} \frac{d^m}{d\mu^m} P_\ell(\mu) \quad (8.83)$$

Clearly $P_\ell^0(\mu) = P_\ell(\mu)$. The associated Legendre functions are orthogonal as given by the orthogonality integral:

$$\int_0^\pi d\theta \sin \theta P_\ell^m(\cos \theta) P_{\ell'}^m(\cos \theta) = \left(\frac{2}{2\ell + 1} \right) \cdot \frac{(\ell + m)!}{(\ell - m)!} \delta_{\ell\ell'} \quad (8.84)$$

While the entire set of (unnormalized) spherical harmonics can be generated by successive applications of \hat{L}_{\pm} to $Y_{\ell\mp\ell}(\theta, \phi)$, in practice, tables of spherical harmonics are used. These tables include the proper normalization. Spherical harmonics are orthogonal. The orthogonality and normalization relation is

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta Y_{\ell m}(\theta, \phi) [Y_{\ell' m'}(\theta, \phi)]^* = \delta_{mm'} \delta_{\ell\ell'} \quad (8.85)$$

In addition to orthogonality there are several other relations involving the spherical harmonics, a few of which are listed in Table 8.3.

There is yet another way to generate the spherical harmonics. We can make use of the properties of vector operators discussed in Section 8.3. Noting that

$$\begin{aligned} \mathbf{r} &= r_x \hat{\mathbf{i}} + r_y \hat{\mathbf{j}} + r_z \hat{\mathbf{k}} \\ &= x \hat{\mathbf{i}} + y \hat{\mathbf{j}} + z \hat{\mathbf{k}} \end{aligned} \quad (8.86)$$

is a vector operator we may form

$$r_+ = x + iy \quad (8.87)$$

The discussion in Section 8.3 assures us that application of \hat{r}_+ to $Y_{\ell\ell}(\theta, \phi)$ will raise both indexes (see the discussion leading up to Equation 8.53). In equation form

$$(x + iy) Y_{\ell\ell}(\theta, \phi) = C_{\hat{r}} Y_{\ell+1\ell+1}(\theta, \phi) \quad (8.88)$$

where $C_{\hat{r}}$ may be a function of r . Subsequent application of \hat{L}_- to $Y_{\ell+1\ell+1}(\theta, \phi)$ generates all of the spherical harmonics having angular momentum quantum number $(\ell + 1)$.

In the remainder of this book we will make extensive use of the normalized spherical harmonics. To facilitate this use Table 8.4 is a listing of the normalized spherical harmonics up to $\ell = 2$. For convenience, they are displayed in both spherical and Cartesian coordinates. An important property of the spherical harmonics is that the

Table 8.3 Some spherical harmonic relations

$Y_{\ell m}(\theta, \phi) = (-)^m [Y_{\ell -m}(\theta, \phi)]^*$
$\cos\theta Y_{\ell m}(\theta, \phi) = \sqrt{\frac{(\ell+m+1)(\ell-m+1)}{(2\ell+1)(2\ell+3)}} Y_{\ell+1 m}(\theta, \phi)$
$+ \sqrt{\frac{(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)}} Y_{\ell-1 m}(\theta, \phi)$
$\sin\theta e^{\pm i\phi} Y_{\ell m}(\theta, \phi) = \mp \sqrt{\frac{(\ell \pm m+1)(\ell \pm m+2)}{(2\ell+1)(2\ell+3)}} Y_{\ell+1 m \pm 1}(\theta, \phi)$
$\pm \sqrt{\frac{(\ell \mp m)(\ell \mp m-1)}{(2\ell+1)(2\ell-1)}} Y_{\ell-1 m \pm 1}(\theta, \phi)$

Table 8.4 Some spherical harmonics in spherical and Cartesian coordinates

$Y_{\ell m}(\theta, \phi)$	Spherical	Cartesian
$Y_{00}(\theta, \phi)$	$\sqrt{\frac{1}{4\pi}}$	$\sqrt{\frac{1}{4\pi}}$
$Y_{10}(\theta, \phi)$	$\sqrt{\frac{3}{4\pi}} \cos \theta$	$\sqrt{\frac{3}{4\pi}} \left(\frac{z}{r}\right)$
$Y_{1\pm 1}(\theta, \phi)$	$\mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$	$\mp \sqrt{\frac{3}{8\pi}} \left(\frac{x \pm iy}{r}\right)$
$Y_{20}(\theta, \phi)$	$\sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$	$\sqrt{\frac{5}{16\pi}} \left(\frac{3z^2 - r^2}{r^2}\right)$
$Y_{2\pm 1}(\theta, \phi)$	$\mp \sqrt{\frac{15}{8\pi}} \cos \theta \sin \theta e^{\pm i\phi}$	$\mp \sqrt{\frac{15}{8\pi}} \left[\frac{(x \pm iy)z}{r^2}\right]$
$Y_{2\pm 2}(\theta, \phi)$	$\sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$	$\sqrt{\frac{15}{32\pi}} \left(\frac{x \pm iy}{r}\right)^2$

value of ℓ determines the parity, odd ℓ means that $Y_{\ell m}(\theta, \phi)$ is an odd function. This may be seen in Table 8.4.

8.4.1 The Addition Theorem for Spherical Harmonics

The addition theorem for spherical harmonics is useful when two directions are specified as indicated by the spherical coordinates (θ_1, ϕ_1) and (θ_2, ϕ_2) . Figure 8.2 shows the geometry. The angle between the two directions as specified by the vectors \mathbf{r}_1 and \mathbf{r}_2 is γ .

The theorem gives the Legendre polynomial for the angle γ in terms of the spherical harmonics for each of the directions. Specifically,

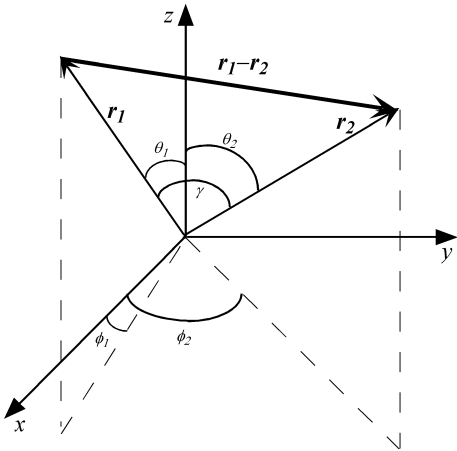


Fig. 8.2 Coordinates for the addition theorem for spherical harmonics. The angle between the two specified directions in space is γ

$$P_\ell(\cos \gamma) = \frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\theta_1, \phi_1) Y_{\ell m}^*(\theta_2, \phi_2) \quad (8.89)$$

Unsold's theorem

The addition theorem for spherical harmonics can be used to prove another useful theorem, Unsöld's theorem. Referring to Fig. 8.2, let $\theta_1 = \theta_2 = \theta$ and $\phi_1 = \phi_2 = \phi$, in which case the angle $\gamma = 0$. According to the addition theorem,

$$P_\ell(1) = \frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\theta, \phi) Y_{\ell m}^*(\theta, \phi) \quad (8.90)$$

But, the function $P_\ell(1) = 1$ for any value of ℓ [3] so

$$\sum_{m=-\ell}^{\ell} |Y_{\ell m}(\theta, \phi)|^2 = \frac{2\ell + 1}{4\pi} \quad (8.91)$$

Now, if a system is in an eigenstate of \hat{L}^2 , but not \hat{L}_z , then the wave function may be written

$$\psi_\ell(\theta, \phi) = \sum_{m=-\ell}^{\ell} a_m Y_{\ell m}(\theta, \phi) \quad (8.92)$$

If the m -states are equally populated, then $\psi_\ell(\theta, \phi)$ is an equal admixture of all of the m -states. Because there are $2\ell + 1$ m -states this expansion coefficient must be

$$a_m = \sqrt{\frac{1}{2\ell + 1}} \quad (8.93)$$

In this circumstance Unsöld's theorem assures us that the resulting probability density is independent of θ and ϕ and is therefore spherically symmetric. That is, because of orthogonality of the spherical harmonics, the probability density is

$$\begin{aligned} |\psi_\ell(\theta, \phi)|^2 &= \left(\frac{1}{\sqrt{2\ell + 1}} \right)^2 \sum_{m=-\ell}^{\ell} |Y_{\ell m}(\theta, \phi)|^2 \\ &= \frac{1}{4\pi} \end{aligned} \quad (8.94)$$

The factor $1/(4\pi)$ appears because the probability density integrated over all angles is unity. The important point is that the probability density is independent of θ and ϕ . This theorem has important consequences in atomic physics.

The function $1/|\mathbf{r}_1 - \mathbf{r}_2|$

Although slightly off the immediate subject of spherical harmonics, it is worthwhile at this point to examine the function $1/|\mathbf{r}_1 - \mathbf{r}_2|$ (see Fig. 8.2) because it has many physical applications. Using the law of cosines we can write this function in terms of the angle γ as

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = (r_1^2 + r_2^2 - 2r_1r_2 \cos \gamma)^{-1/2} \quad (8.95)$$

For convenience, \mathbf{r}_1 is often placed along the z -axis so γ becomes the spherical coordinate θ . Now, suppose that $r_2 > r_1$. Factoring $1/r_2$ out of the parentheses in Equation 8.95 we obtain

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{r_2} \left[1 + \left(\frac{r_1}{r_2} \right)^2 - 2 \left(\frac{r_1}{r_2} \right) \cos \gamma \right]^{-1/2} \quad (8.96)$$

Letting $\cos \gamma = \mu$ and the ratio $r_1/r_2 = t$, we see that Equation 8.96 contains the generating function for $P_\ell(\mu)$, Equation 8.81, so we may write

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{r_2} \sum_{\ell=0}^{\infty} P_\ell(\mu) \left(\frac{r_1}{r_2} \right)^\ell \quad (8.97)$$

If, instead of $r_2 > r_1$, we had $r_1 > r_2$, then the subscripts in Equation 8.97 would be reversed. This representation of the function $1/|\mathbf{r}_1 - \mathbf{r}_2|$ in terms of Legendre polynomials is usually displayed as

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{r_{>}} \sum_{\ell=0}^{\infty} P_\ell(\mu) \left(\frac{r_{<}}{r_{>}} \right)^\ell \quad (8.98)$$

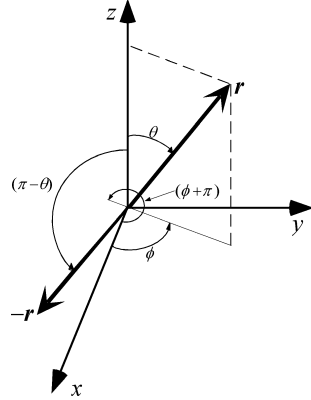
where $r_{>}$ and $r_{<}$ designate the larger and smaller, respectively, of r_1 and r_2 .

8.4.2 Parity

The parity of the spherical harmonics was discussed in connection with the determination that the quantum numbers ℓ and m are integers. We can, however, examine parity in more detail by employing the parity operator $\hat{\phi}$ to determine how the spherical harmonics behave under a parity inversion. Figure 8.3 illustrates the inversion caused by the action of the parity operator.

For simplicity we examine a point in the first octant as represented by the tip of the vector \mathbf{r} . The transformation $\mathbf{r} \rightarrow -\mathbf{r}$ places the vector in the eighth octant. Figure 8.3 shows that the coordinates undergo the transformations

Fig. 8.3 Spherical coordinates under parity inversion



$$r \rightarrow r \quad \theta \rightarrow \pi - \theta \quad \phi \rightarrow \phi + \pi \quad (8.99)$$

Therefore,

$$\begin{aligned} \hat{\mathcal{O}} Y_{\ell m}(\theta, \phi) &= \hat{\mathcal{O}} [e^{im\phi} P_{\ell}^m(\cos \theta)] \\ &= e^{im\phi} e^{im\pi} P_{\ell}^m[\cos(\pi - \theta)] \\ &= e^{im\phi} (-)^m P_{\ell}^m(-\cos \theta) \end{aligned} \quad (8.100)$$

From the properties of associated Legendre functions [3] we find that

$$P_{\ell}^m(-\cos \theta) = (-)^{\ell+m} P_{\ell}^m(\cos \theta) \quad (8.101)$$

so that

$$\begin{aligned} \hat{\mathcal{O}} Y_{\ell m}(\theta, \phi) &= (-)^{\ell+2m} [e^{im\phi} P_{\ell}^m(\cos \theta)] \\ &= (-)^{\ell} Y_{\ell m}(\theta, \phi) \end{aligned} \quad (8.102)$$

Therefore, from Equation 8.102 it is clear that the $Y_{\ell m}(\theta, \phi)$ do indeed have definite parity, the same as the parity of ℓ .

8.4.3 The Rigid Rotor

Imagine a quantum mechanical system consisting of a point mass μ attached to a rigid massless stick of length a that is pivoted at one end. This system is the rigid rotor. (We use μ for the mass to avoid confusion with the \hat{L}_z quantum number.) The mass can rotate on the sphere defined by $r = a$, but, if a and μ are of microscopic dimensions, then this system is subject to the laws of quantum physics and the available energy states and eigenvalues must be obtained by solving the TISE. The Hamiltonian is the TME which, for this system, is purely kinetic energy. There is no

potential energy. For a rotating body the kinetic energy is simply the square of the orbital angular momentum divided by twice the moment of inertia $I = \mu a^2$. This is the rotational analog of the translational energy being equal to $\frac{1}{2}mv^2$. Replacing the square of the angular momentum with the operator equivalent, the Hamiltonian is

$$\hat{H} = \frac{\hat{L}^2}{2I} \quad (8.103)$$

We need not go any further to solve the TISE. We have already solved it. The eigenfunctions of this Hamiltonian are the spherical harmonics. Moreover, the energy eigenvalues can be immediately written. They are

$$E_\ell = \frac{\ell(\ell+1)\hbar^2}{2\mu a^2} \quad (8.104)$$

The first thing we notice about this expression for the energy is that it is independent of the quantum number m . This is a degeneracy that occurs because the kinetic energy is independent of the direction in which the mass rotates. We also notice that the more massive the rotor, the smaller the separation between adjacent energy eigenvalues. Now we might ask if this can represent any physical system. The answer is a resounding yes. For example, the rigid rotor is a first approximation to a rotating diatomic molecule. We can estimate typical energy level spacings of diatomic molecule rotational levels. The energy separation between adjacent levels is

$$\begin{aligned} \Delta E_{\ell,\ell-1} &= \frac{\hbar^2}{2\mu a^2} [\ell(\ell+1) - \ell(\ell-1)] \\ &= \frac{\ell\hbar^2}{\mu a^2} \end{aligned} \quad (8.105)$$

Taking the Bohr radius as a typical internuclear separation $\Delta E_{\ell-1,\ell}$ may be written in terms of the ground state energy of the hydrogen atom $E_1 \sim 10\text{eV}$ as

$$\Delta E_{\ell-1,\ell} = 2\ell \left(\frac{m_e}{\mu} \right) E_1 \quad (8.106)$$

Thus, typical rotational level spacings in a diatomic molecule are roughly $(m_e/\mu) E_1 \sim 10^{-3} E_1$ for hydrogen molecules which may be compared with vibrational spacing which are proportional to $\sqrt{m_e/\mu} E_1 \sim (1/40) E_1$, Equation 5.43. Transitions between rotational levels are therefore usually in the far infrared or microwave regions of the spectrum. Indeed, operation of a microwave oven depends upon a rotational transition of the water molecule at 2.45GHz or $\sim 10\text{ cm}$.

8.5 Another Form of Angular Momentum—Spin

In contrast to orbital angular momentum, spin angular momentum is an angular momentum that cannot be described in terms of spatial coordinates. It represents the *intrinsic* magnetic moment of the electron. That is, it represents a magnetic moment that the electron possesses even if it were completely isolated in space. The electron is a bar magnet! This revolutionary notion was proposed by S. Goudsmit and G. E. Uhlenbeck in 1925 who, inexplicably, never won the Nobel Prize. Ironically, however, their discovery of spin was confirmed by Wolfgang Pauli's exclusion principle (to be discussed in Section 8.6.2) for which Pauli was awarded the 1945 Nobel Prize "for the discovery of the Exclusion Principle, also called the Pauli Principle."

We saw in Section 1.2.1 that an orbiting electron constitutes an electric current and therefore produces a magnetic field. Thus, the orbital motion of the electron in the Bohr model demands that the hydrogen atom behave as a bar magnet with magnetic moment designated μ_ℓ . This is not the same bar magnet as that associated with spin. As shown in Section 1.2.1, the Bohr magneton μ_B is simply μ_ℓ *when the electron is in the ground state of a hydrogen atom* (see Equation 1.44). Calculation of the Bohr magneton is based solely on the orbital motion of the electron about the nucleus. The fact that an electron has an intrinsic magnetic moment, the spin, means that in the Bohr model there is an electrically charged bar magnet revolving about the nucleus. Therefore, the total magnetic moment of the hydrogen atom is the vector sum of the orbital magnetic moment μ_ℓ and the spin magnetic moment μ_s .

Magnetic moments, being observable quantities, are represented in quantum mechanics by Hermitian operators. The operator that represents the orbital magnetic moment, μ_ℓ , is referred to as the orbital magnetic moment and is designated by the symbol $\hat{\mu}_\ell$. It is given by

$$\hat{\mu}_\ell = -\frac{g_\ell \mu_B}{\hbar} \hat{\mathbf{L}} \quad (8.107)$$

where g_ℓ is called the orbital g -factor. As it happens, $g_\ell = 1$, but it is included in the definition of μ_ℓ because the g -factors of other magnetic moments differ from unity. Equation 8.107 illustrates the direct relationship between the orbital magnetic moment and the orbital angular momentum.

To explain the occurrence of two spectral lines where only a single line was expected, Goudsmit and Uhlenbeck introduced the concept of the intrinsic magnetic moment. These line doublets were assumed to arise because one (or both) of the atomic energy levels involved in the transition that produced the radiation was split into two closely spaced energy levels. The splitting was postulated to arise from the interaction of the intrinsic magnetic moment of the electron with the magnetic field, B_{orbit} , produced by the orbital magnetic moment of the electron. Of course, in the electron's frame of reference it is the nucleus that is rotating and produces the magnetic field that is experienced by the electron spin. We will, however, continue to refer to the orbital magnetic moment of the electron as given in Equation 8.107.

Fig. 8.4 Schematic representation of the intrinsic magnetic moment of the electron as represented by a bar magnet oriented in opposite directions with respect to the magnetic field B_{orbit} produced by the orbital motion

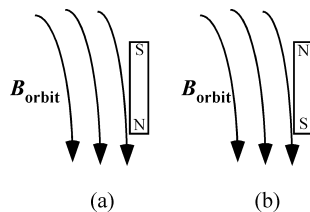
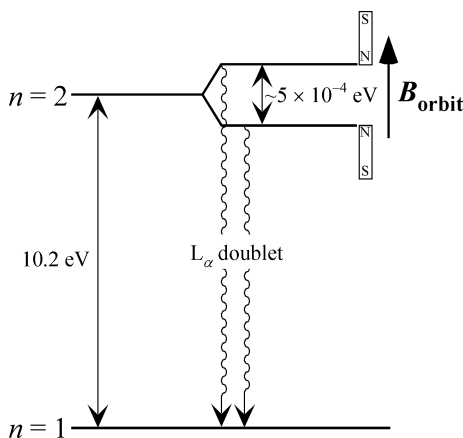


Figure 8.4 is a simplified illustration of the energy difference between the two states that arise from the different orientations of the spin magnetic moment with respect to the magnetic field that originates from the orbital motion B_{orbit} . In Fig. 8.4a the spin magnetic moment, represented by the bar magnet, is aligned in the general direction of B_{orbit} and is thus a state of lower energy than the depiction in Fig. 8.4b where the bar magnet is in the opposite direction.

The Lyman series of hydrogen, which, in emission, comprises all transitions to the ground state, affords an uncomplicated emission system that will aid in understanding the consequences of spin. The orbital angular momentum of the electron in the ground state is zero so that, according to Equation 8.107, there will be no B -field from the orbital motion. On the other hand, many of the excited states of hydrogen have nonzero orbital angular momenta that do indeed produce B -fields. The effects of spin on the ground state and the first excited state of hydrogen are illustrated in Fig. 8.5. The ground state is not split because there is no B -field arising from orbital angular momentum. The $n = 2$ state is, however, split by a very small amount compared with the separation between the Bohr energies. This splitting is due to the interaction of the intrinsic magnetic moment of the electron with the B -field that results from the orbital motion of the electron. It is referred to as fine structure and, as will be seen in Section 13.1.1, it depends upon the square of α , the fine structure constant. This effect manifests itself as a splitting of the L_α line into two lines of nearly equal wavelengths.

Fig. 8.5 Schematic energy level diagram of the $n = 1$ and $n = 2$ levels of hydrogen showing the splitting of the $n = 2$ level due to the interaction of the intrinsic magnetic moment of the electron with the B -field caused by the orbital motion of the electron, B_{orbit} . The L_α doublet with wavelengths near 121.5 nm are shown



To treat spin within the framework of quantum physics it is assumed, by analogy with Equation 8.107, that this magnetic moment μ_s is proportional to an angular momentum $\hat{\mathbf{S}}$ so

$$\hat{\boldsymbol{\mu}}_s = -\frac{g_e \mu_B}{\hbar} \hat{\mathbf{S}} \quad (8.108)$$

where g_e is the electron spin g -factor. For an electron it is found that $g_e = 2$ as will be discussed below. The quantum numbers associated with the angular momentum operator $\hat{\mathbf{S}}$ are

$$\begin{aligned} j &\rightarrow s = \frac{1}{2} \\ m &\rightarrow m_s = \pm \frac{1}{2} \end{aligned} \quad (8.109)$$

so the magnitude of the total spin angular momentum is always $\sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$ and there are only two possible z -components, “spin up” and “spin down.” Because it is found that the components of $\hat{\mathbf{S}}$ commute according to the rule given in Equation 8.2:

$$[\hat{S}_i, \hat{S}_j] = i\hbar \hat{S}_k \epsilon_{ijk} \quad (8.110)$$

$\hat{\mathbf{S}}$ qualifies as an angular momentum! Never mind that we cannot visualize some rotational motion that corresponds to this observable. The electron spin manifests itself as an intrinsic magnetic moment (see Equation 8.108) that is proportional to $\hat{\mathbf{S}}$.

Before proceeding with the mathematical details of this new angular momentum, we digress to discuss the origin of the term spin. After all, we have stated that in nonrelativistic quantum mechanics particles are point objects, they have no finite extent. How then does a point spin? Of course, it doesn't, but the pioneers of quantum mechanics, Goudsmit and Uhlenbeck in this case, visualized the effects that they were attempting to describe. They imagined that the electron is a spherical shell having total charge e uniformly smeared over its surface, reminiscent of the model used to derive the classical radius of the electron in Section 1.2.5. This spinning sphere creates a magnetic moment identical with that of a bar magnet. Is this model consistent with the classical radius of the electron? No—as can be seen by equating the angular momentum of the spinning sphere to $\hbar/2$. Solving for the speed of a point on the sphere leads to a speed that is roughly one hundred times the speed of light (see Problem 15). Thus, the manipulations that were performed in Section 1.2.5 that led to the expression for the classical radius of the electron, Equation 1.59, are suspect. Nevertheless, the concept of the classical radius of the electron remains in the physics jargon. It is the eigenvalues of the spin angular momentum that are correct as verified by observation.

Magnetic moments are, in many applications, specified in terms of their gyro-magnetic ratios which are defined as the ratio of the magnetic dipole moment to the angular momentum. For example, for an electron

$$\hat{\mu}_S = \gamma_e \hat{S} \quad (8.111)$$

so, comparing with Equation 8.108, we have

$$\begin{aligned} \gamma_e &= \frac{g_e \mu_B}{\hbar} \\ &= \frac{g_e e}{2m_e} \end{aligned} \quad (8.112)$$

with analogous expressions for any other magnetic moment.

Because we now have two angular momenta, orbital and spin, there is yet a third, the *total* angular momentum, which is traditionally designated by the operator $\hat{\mathbf{J}}$ with associated quantum number j . Now, however, we must modify our designation of the z -component of the angular momentum because we have z -components associated with three different angular momenta. In our discussion of orbital angular momentum we used the symbol m for this quantum number. It is now necessary to attach a subscript to clarify which z -component is meant. Table 8.5 is a listing of the quantum number designations for the different angular momenta.

For spin there is only one value of the total spin quantum number, $s = \frac{1}{2}$. If we designate the (simultaneous) eigenkets of \hat{S}^2 and \hat{S}_z by $|\chi_s m_s\rangle$, we have

$$\begin{aligned} \hat{S}^2 |\chi_s m_s\rangle &= s(s+1) \hbar^2 |\chi_s m_s\rangle \\ &= \frac{3}{4} \hbar^2 |\chi_s m_s\rangle \end{aligned} \quad (8.113)$$

and

$$\begin{aligned} \hat{S}_z |\chi_{sm_s}\rangle &= m_s \hbar |\chi_s m_s\rangle \\ &= \pm \frac{1}{2} \hbar |\chi_s m_s\rangle \end{aligned} \quad (8.114)$$

Because there is only one value of the quantum number s , it is useful to use a simpler designation for the two possible eigenkets. The notation is not, however, universal. Some of the common designations are

Table 8.5 Angular momentum quantum numbers

Ang. Momentum	z -component	
Total	j	m_j
Orbital	ℓ	m_ℓ
Spin	s	m_s

$$\begin{aligned} \left| \chi_s = \frac{1}{2}; m_s = \frac{1}{2} \right\rangle &= |\alpha\rangle = |\uparrow\rangle = |+\rangle = \left| \frac{1}{2} \right\rangle = \alpha = \text{spin up} \\ \left| \chi_s = \frac{1}{2}; m_s = -\frac{1}{2} \right\rangle &= |\beta\rangle = |\downarrow\rangle = |-\rangle = \left| -\frac{1}{2} \right\rangle = \beta = \text{spin down} \end{aligned} \quad (8.115)$$

In this section we elect to use $|\alpha\rangle$ and $|\beta\rangle$ for the eigenkets of \hat{S}^2 and \hat{S}_z ; later in this book when two electrons are involved, we will use $\frac{1}{2}$ and $-\frac{1}{2}$ inside the kets to specify spin up and spin down.

Now, $|\alpha\rangle$ and $|\beta\rangle$ must be orthogonal because \hat{S}_z is Hermitian (it corresponds to an observable). We assume that they are also normalized so

$$\begin{aligned} \langle\alpha|\alpha\rangle &= \langle\beta|\beta\rangle = 1 \\ \langle\alpha|\beta\rangle &= 0 \end{aligned} \quad (8.116)$$

Note that the spin angular momentum is not included in the TDSE so it must be added to the coordinate space or momentum space wave functions “by hand.”

8.5.1 Matrix Representation of the Spin Operators and Eigenkets

Because there are only two possible values of m_s , we can represent the unit vectors in spin space, $|\alpha\rangle$ and $|\beta\rangle$, by two-component column matrices called spinors. That is,

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (8.117)$$

The operators \hat{S}^2 and \hat{S}_z must be represented by diagonal 2×2 matrices because $|\alpha\rangle$ and $|\beta\rangle$ are their eigenkets. To comply with the eigenvalue Equations 8.113 and 8.114 we must have

$$\hat{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad \hat{S}_z = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (8.118)$$

To find the matrix representation of the operators \hat{S}_x and \hat{S}_y we first examine the effects of the spin ladder operators on the eigenkets $|\alpha\rangle$ and $|\beta\rangle$. Then, using these results, we determine the effect of operating on $|\alpha\rangle$ and $|\beta\rangle$ with \hat{S}_x and \hat{S}_y because

$$\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-) \quad \text{and} \quad \hat{S}_y = \frac{1}{2i}(\hat{S}_+ - \hat{S}_-) \quad (8.119)$$

For example,

$$\begin{aligned}
 \hat{S}_- |\alpha\rangle &= \hbar \sqrt{(s + m_s)(s - m_s + 1)} |\beta\rangle \\
 &= \hbar \sqrt{\left(\frac{1}{2} + \frac{1}{2}\right)} |\beta\rangle \\
 &= \hbar |\beta\rangle
 \end{aligned} \tag{8.120}$$

and

$$\hat{S}_+ |\beta\rangle = \hbar |\alpha\rangle \tag{8.121}$$

so that

$$\begin{aligned}
 \hat{S}_x |\alpha\rangle &= \frac{1}{2} (\hat{S}_+ |\alpha\rangle + \hat{S}_- |\alpha\rangle) \\
 &= \frac{1}{2} (0 + \hbar |\beta\rangle) \\
 &= \frac{1}{2} \hbar |\beta\rangle
 \end{aligned} \tag{8.122}$$

For convenience, the actions of the three components of the spin operator as well as the actions of the ladder operators on $|\alpha\rangle$ and $|\beta\rangle$ are tabulated in Table 8.6.

Now we can find the matrix representations of \hat{S}_x and \hat{S}_y . Let us look at the \hat{S}_y matrix in detail. We have the relation

$$\hat{S}_y |\alpha\rangle = \frac{i}{2} \hbar |\beta\rangle \tag{8.123}$$

which, when written in matrix notation, is

$$\begin{pmatrix} (S_y)_{11} & (S_y)_{12} \\ (S_y)_{21} & (S_y)_{22} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{i}{2} \hbar \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{8.124}$$

Table 8.6 The actions of the components of the spin operator and of the ladder operators on $|\alpha\rangle$ and $|\beta\rangle$, the eigenkets of \hat{S}_z and \hat{S}^2

$\hat{S}_x \alpha\rangle = \frac{1}{2} \hbar \beta\rangle$	$\hat{S}_x \beta\rangle = \frac{1}{2} \hbar \alpha\rangle$
$\hat{S}_y \alpha\rangle = \frac{i}{2} \hbar \beta\rangle$	$\hat{S}_y \beta\rangle = -\frac{i}{2} \hbar \alpha\rangle$
$\hat{S}_z \alpha\rangle = \frac{1}{2} \hbar \alpha\rangle$	$\hat{S}_z \beta\rangle = -\frac{1}{2} \hbar \beta\rangle$
$\hat{S}_+ \alpha\rangle = 0$	$\hat{S}_+ \beta\rangle = \hbar \alpha\rangle$
$\hat{S}_- \alpha\rangle = \hbar \beta\rangle$	$\hat{S}_- \beta\rangle = 0$

Multiplying the matrices and equation elements on each side of the equation we find

$$(S_y)_{11} = 0 \quad \text{and} \quad (S_y)_{21} = \frac{i}{2}\hbar \quad (8.125)$$

Using

$$\hat{S}_y |\beta\rangle = -\frac{i}{2}\hbar |\alpha\rangle \quad (8.126)$$

we obtain the remaining matrix elements

$$(S_y)_{12} = -\frac{i}{2}\hbar \quad \text{and} \quad (S_y)_{22} = 0 \quad (8.127)$$

so the matrix that represents \hat{S}_y is

$$\hat{S}_y = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (8.128)$$

Using the same technique we find that

$$\hat{S}_x = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (8.129)$$

From the matrices that represent \hat{S}_x and \hat{S}_y , we find that the matrices that represent the spin ladder operators \hat{S}_{\pm} are

$$\hat{S}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad \hat{S}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \quad (8.130)$$

We now have the matrix representations for all three of the components of the spin angular momentum operator $\hat{\mathbf{S}}$ and the spin ladder operators. To simplify computations, an operator $\hat{\sigma}$ is defined that avoids the necessity of continually writing the $\frac{1}{2}\hbar$ in these spin operators:

$$\hat{\sigma} = \frac{2}{\hbar} \hat{\mathbf{S}} \quad (8.131)$$

The components of $\hat{\sigma}$ are called the Pauli spin matrices and are given by

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (8.132)$$

and the corresponding ladder operators are

$$\hat{\sigma}_+ = 2 \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}; \quad \hat{\sigma}_- = 2 \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \quad (8.133)$$

Note the difference of a factor of 2 between the conventional spin ladder operators, Equation 8.130, and the Pauli ladder operators, Equation 8.133. Although the entries are essentially the same as those of Table 8.6, we present in Table 8.7 the effects of operation with the Pauli matrices.

We are now in a position to find the eigenkets of \hat{S}_x and \hat{S}_y in terms of $|\alpha\rangle$ and $|\beta\rangle$. The eigenvalue equation for the operator $\hat{\sigma}_x$ in matrix form is

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \lambda \begin{pmatrix} a \\ b \end{pmatrix} \quad (8.134)$$

where λ represents the eigenvalues of $\hat{\sigma}_x$. We can simplify things because we know that, except for the fact that we have *chosen* \hat{S}_z to be the component that commutes with \hat{S}^2 , \hat{S}_x and \hat{S}_y are no different than \hat{S}_z . Therefore, the eigenvalues of \hat{S}_x and \hat{S}_y are the same as those of \hat{S}_z so that in Equation 8.134 $\lambda = \pm 1$. Multiplying the matrices on the left side of this equation and equating matrix elements on each side of it we have

$$b = \pm a \quad \text{and} \quad a = \pm b \quad (8.135)$$

Thus, the matrix elements of the eigenkets either have the same sign or the opposite sign. The eigenkets are to be normalized so the one corresponding to the positive eigenvalue must be

$$\begin{aligned} |\alpha\rangle_x &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} |\alpha\rangle + \frac{1}{\sqrt{2}} |\beta\rangle \end{aligned} \quad (8.136)$$

Table 8.7 The actions of the Pauli spin matrices on the spin up and spin down eigenvectors

$\hat{\sigma}_x \alpha\rangle = \beta\rangle$	$\hat{\sigma}_x \beta\rangle = \alpha\rangle$
$\hat{\sigma}_y \alpha\rangle = i \beta\rangle$	$\hat{\sigma}_y \beta\rangle = -i \alpha\rangle$
$\hat{\sigma}_z \alpha\rangle = \alpha\rangle$	$\hat{\sigma}_z \beta\rangle = - \beta\rangle$
$\hat{\sigma}_+ \alpha\rangle = 0$	$\hat{\sigma}_+ \beta\rangle = 2 \alpha\rangle$
$\hat{\sigma}_- \alpha\rangle = 2 \beta\rangle$	$\hat{\sigma}_- \beta\rangle = 0$

and that the negative eigenvalue is

$$\begin{aligned} |\beta\rangle_x &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} |\alpha\rangle - \frac{1}{\sqrt{2}} |\beta\rangle \end{aligned} \quad (8.137)$$

The subscripts on the kets in Equations 8.136 and 8.137 indicate that they correspond to spin up and spin down with respect to \hat{S}_x . Because we have chosen \hat{S}_z to commute with \hat{S}^2 we omit any subscript from the eigenkets of \hat{S}_z . The eigenkets of \hat{S}_y can be obtained in an analogous manner. The result is

$$\begin{aligned} |\alpha\rangle_y &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} |\alpha\rangle + \frac{i}{\sqrt{2}} |\beta\rangle \end{aligned} \quad (8.138)$$

and

$$\begin{aligned} |\beta\rangle_y &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} |\alpha\rangle - \frac{i}{\sqrt{2}} |\beta\rangle \end{aligned} \quad (8.139)$$

We have thus found the eigenkets of the operators \hat{S}_x and \hat{S}_y in terms of the eigenkets of \hat{S}_z . This is a sensible procedure since, being eigenkets of a Hermitian operator, $|\alpha\rangle$ and $|\beta\rangle$ form a complete set.

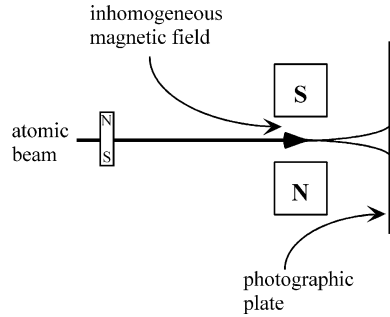
8.5.2 The Stern–Gerlach Experiment

The discussion of spin may seem very abstract, but it has important consequences in quantum physics. In a famous experiment performed in 1922, O. Stern and W. Gerlach observed directly the effects of quantized angular momentum. Their experiment, the apparatus for which is shown schematically in Fig. 8.6, was based on the fact that a nonuniform magnetic field applied to a bar magnet produces a net force on the bar magnet. To see this we write the potential energy U of a magnetic dipole moment $\boldsymbol{\mu}$ in a magnetic field \mathbf{B}

$$U = -\boldsymbol{\mu} \cdot \mathbf{B} \quad (8.140)$$

If $\boldsymbol{\mu}$ is constant and \mathbf{B} is inhomogeneous, there will be a force on the magnetic dipole. The force on the dipole in the z -direction is

Fig. 8.6 Schematic diagram of the Stern–Gerlach apparatus. The (uncharged) particles in the beam are assumed to have magnetic moments that are randomly oriented in space. The magnetic moment of one of these atoms is represented by the bar magnet



$$\begin{aligned} F_z &= -(\nabla U)_z \\ &= \mu_z \frac{dB_z(z)}{dz} \end{aligned} \quad (8.141)$$

The beam of electrically neutral atoms with randomly oriented angular momenta, an unpolarized beam, enters an inhomogeneous magnetic field and is, according to Equation 8.141, deflected. Particles emerging from the inhomogeneous field are detected on the photographic plate. If the magnitudes of the z -components of the magnetic moments of the atoms in the beam vary continuously, then the pattern on the photographic plate should be a continuous smear between the extreme values. On the other hand, if the magnetic moments are quantized, then a number of distinct lines should be observed corresponding to the discrete values of the z -components of the angular momentum. The number of lines will be the same as the number of possible z -components of the magnetic moment. For example, if the total angular momentum of the particle is 2, then there will be five z -components, -2 , -1 , 0 , 1 , 2 , and five lines should appear on the screen. Obviously, if the total angular momentum quantum number is an integer, there will always be an odd number of z -components and therefore lines. On the other hand, if the total angular momentum is half-integral, then there will be an even number of lines.

Stern and Gerlach performed the experiment with Ag atoms and observed two well-defined lines. We now know that in the ground state the total orbital angular momentum of Ag atoms is zero, but the total spin angular momentum is $\frac{1}{2}$. Without the existence of half-integral spin the observation of any even number of lines cannot be explained. It was Goudsmit and Uhlenbeck who postulated the existence of spin angular momentum that adequately explained the Stern–Gerlach result. Clearly this experiment can be performed with any atom (or molecule). It can be performed with electrons provided an electric field is imposed on the apparatus to oppose the Lorentz force that will deflect the electrons, irrespective of the magnetic deflection due to the intrinsic magnetic moment. For the present purpose it is simplest to imagine the Stern–Gerlach (SG) experiment as being performed with uncharged electrons. That is, we simply ignore the charge on the electron and treat only its magnetic moment. Identical results would be obtained using any atom for which

the total orbital angular momentum is zero and the total spin angular momentum is one-half, for example hydrogen atoms in the ground state.

The z -component of the magnetic moment is

$$\mu_z = -m_s g_e \mu_B \quad (8.142)$$

which we may insert in Equation 8.141 and the resulting equation solved for g_e . The variation of the B -field with z is an experimentally known parameter so, in this way, g_e can be measured. The result is that $g_e = 2$. It should be noted, however, that when relativistic effects are taken into account it is predicted that $g_e = 2.0023$ which is consistent with QED. The deviation from $g_e = 2$ is one of the triumphs of QED. For our purposes, however, we will assume $g_e = 2$.

Let us now examine, mathematically, the effects of sending the electron beam through one or more SG apparatuses. Suppose we pass an unpolarized beam of electrons through an SG apparatus with magnetic field in the z -direction, an SG $_z$ apparatus. The normalized ket that represents the spin of this unpolarized state is

$$|\chi\rangle = \frac{1}{\sqrt{2}}|\alpha\rangle + \frac{1}{\sqrt{2}}|\beta\rangle \quad (8.143)$$

The experimental result is that, for unpolarized electrons the SG $_z$ apparatus splits the beam into two equal beams, spin up ($m_s = \frac{1}{2}$) and spin down ($m_s = -\frac{1}{2}$). If now, only one of the beams emerging from the SG $_z$ apparatus, say the spin up beam, is passed through another SG $_z$ apparatus we get only a single beam, spin up. This is illustrated in Fig. 8.7.

Mathematically, the succession of SG apparatuses illustrated in Fig. 8.7 is equivalent to operating twice in succession with the operator \hat{S}_z , first on the unpolarized beam and then on the spin up (in the z -direction) beam. That is,

$$\begin{aligned} \hat{S}_z |\chi\rangle &= \left(\frac{\hbar}{2}\right) \left(\frac{1}{\sqrt{2}}|\alpha\rangle - \frac{1}{\sqrt{2}}|\beta\rangle \right) \\ \hat{S}_z |\alpha\rangle &= \left(\frac{\hbar}{2}\right) \frac{1}{\sqrt{2}}|\alpha\rangle \end{aligned} \quad (8.144)$$

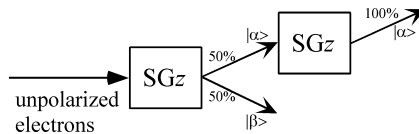


Fig. 8.7 Illustration of the results of an unpolarized beam passing through an SG $_z$ apparatus followed by passing the spin up output beam of the first SG $_z$ apparatus through a second one. It is imagined that the electrons are uncharged for this Gedanken experiment

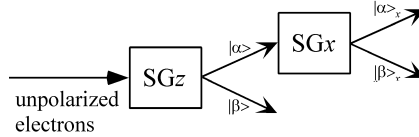


Fig. 8.8 The results of an unpolarized beam passing through an SGz apparatus followed by passing the spin up output beam of the first SGz apparatus through an SGx apparatus. As in Fig. 8.7, it is imagined that the electrons are uncharged for this Gedanken experiment

Suppose now that we replace the second SGz apparatus in Fig. 8.7 with an SGx apparatus, an apparatus with the magnetic field in the x -direction. This is equivalent to operating on $|\alpha\rangle$ with \hat{S}_x . Solving Equations 8.136 and 8.137 for $|\alpha\rangle$ in terms of $|\alpha\rangle_x$ and $|\beta\rangle_x$ we see that

$$\begin{aligned}\hat{S}_x |\alpha\rangle &= \hat{S}_x \left(\frac{1}{\sqrt{2}} |\alpha\rangle_x + \frac{1}{\sqrt{2}} |\beta\rangle_x \right) \\ &= \left(\frac{\hbar}{2} \right) \left(\frac{1}{\sqrt{2}} |\alpha\rangle_x - \frac{1}{\sqrt{2}} |\beta\rangle_x \right)\end{aligned}\quad (8.145)$$

from which it is clear that the SGx apparatus sorts the $|\alpha\rangle$ beam into two equal beams, spin up and down in the x -direction, $|\alpha\rangle_x$ and $|\beta\rangle_x$ as shown in Fig. 8.8.

We can continue this process, each time operating with the appropriate spin component on the chosen beam. For example, we might pass the $|\beta\rangle_x$ beam that is the output of the SGx apparatus in Fig. 8.8 through a second SGz apparatus, thus requiring operation on $|\beta\rangle_x$ with \hat{S}_z (see Problem 19).

8.6 Addition of Angular Momenta

We have studied two different types of angular momenta, orbital and spin. We can see in the simple diagram of Fig. 8.5 that the splitting of the $n = 2$ level of hydrogen is due to the interaction of these two angular momenta. Since it is possible to have more than one angular momentum in a given system, it is important to understand how to add these vector operators. Our discussion will be general so, rather than work with $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$, we will consider the addition, or “coupling,” of two generalized angular momenta, $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$.

There will be quantum numbers associated with each of these angular momenta, (j_1, m_{j1}) and (j_2, m_{j2}) . In classical physics it is the *total* angular momentum that is conserved, not necessarily the individual angular momenta. Therefore, we must examine the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$ and determine what operators, or combination of operators, lead to a set of quantum numbers that may be used to characterize the system. Such sets of quantum numbers are usually referred to as

“good” quantum numbers. For example, in our study of orbital angular momentum we found that the quantum numbers ℓ and m_ℓ determined the eigenvalues and the eigenfunctions of the commuting operators \hat{L}^2 and \hat{L}_z . Thus, for a system having only orbital angular momentum, ℓ and m_ℓ are good quantum numbers. As might be expected, if a set of quantum numbers does not characterize a system, these are bad quantum numbers. We will find that there are two sets of mutually commuting operators that produce good quantum numbers. Part of our art in performing quantum mechanical calculations is to determine which set will make the calculations the simplest and the most revealing.

We have introduced the total angular momentum operator $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$, but we do not know whether it qualifies as an angular momentum. To qualify, it must satisfy the commutation rules given in Equation 8.2. It can be shown that $\hat{\mathbf{J}}$ is indeed an angular momentum so we designate the quantum numbers of \hat{J}^2 and \hat{J}_z as (j, m_j) (see Problem 20). Now we must ask which of the quantum numbers that we have delineated $(j_1, m_{j1}, j_2, m_{j2}, j, m_j)$ are required to fully describe a system. This is tantamount to asking which sets of operators are commuting sets because the quantum numbers of commuting sets of operators are good quantum numbers. Clearly the operators $(\hat{J}_1^2, \hat{J}_{1z}, \hat{J}_2^2, \hat{J}_{2z})$ constitute a mutually commuting set because the commuting pairs $(\hat{J}_1^2, \hat{J}_{1z})$ and $(\hat{J}_2^2, \hat{J}_{2z})$ operate on different coordinates. Thus, each set of quantum numbers is good and we may characterize simultaneous eigenkets of these four operators by their respective quantum numbers. This set of simultaneously commuting operators constitutes what is commonly referred to as the uncoupled representation. The eigenkets of these operators are designated

$$|j_1, m_{j1}; j_2, m_{j2}\rangle \quad (8.146)$$

and are collectively referred to as the uncoupled set.

Now we turn our attention to the total angular momentum to determine the quantum numbers that constitute the other set, the coupled set. The operators $(\hat{J}^2, \hat{J}_1^2, \hat{J}_2^2, \hat{J}_z)$ are mutually commuting. For example,

$$\begin{aligned} [\hat{J}_1^2, \hat{J}_z] &= [\hat{J}_1^2, (\hat{J}_{1z} + \hat{J}_{2z})] \\ &= 0 \end{aligned} \quad (8.147)$$

Therefore, describing a system in terms of the eigenkets of these mutually commuting operators is called the coupled representation, an eigenket of which is written

$$|j_1, j_2; j, m_j\rangle \quad (8.148)$$

Before proceeding let us inquire into the usefulness of these two sets of eigenkets. Because both the coupled and uncoupled sets constitute complete sets, any arbitrary ket may be written as a linear combination of either set. If the linear combination is say the uncoupled set, we obtain information about the individual

angular momenta, but none about the total angular momentum. Remember that the square of the expansion coefficient of a given basis ket represents the probability of measuring simultaneously the parameters specified by the quantum numbers of this eigenket. Expanding the wave function on the coupled set gives information about the magnitudes of the individual and total angular momenta and the z -component of the total angular momentum. Can we also obtain information on the individual z -components from the coupled set? To answer this question we must investigate the commutators of \hat{J}_{1z} and \hat{J}_{2z} with the set of operators that specify the coupled set, namely, $(\hat{J}^2, \hat{J}_1^2, \hat{J}_2^2, \hat{J}_z)$. If we find one commutator that does not vanish, then m_{j1} and m_{j2} are not good quantum numbers in the coupled representation. Evaluating the commutator $[\hat{J}_{1z}, \hat{J}^2]$ we have

$$\begin{aligned}
 [\hat{J}_{1z}, \hat{J}^2] &= [\hat{J}_{1z}, (\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2)] \\
 &= [\hat{J}_{1z}, \hat{J}_x^2] + [\hat{J}_{1z}, \hat{J}_y^2] + [\hat{J}_{1z}, \hat{J}_z^2] \\
 &= [\hat{J}_{1z}, (\hat{J}_{1x} + \hat{J}_{2x})^2] + [\hat{J}_{1z}, (\hat{J}_{1y} + \hat{J}_{2y})^2] + 0 \\
 &= [\hat{J}_{1z}, (\hat{J}_{1x}^2 + 2\hat{J}_{1x}\hat{J}_{2x})] + [\hat{J}_{1z}, (\hat{J}_{1y}^2 + 2\hat{J}_{1y}\hat{J}_{2y})] \\
 &= [\hat{J}_{1z}, (\hat{J}_{1x}^2 + \hat{J}_{1y}^2)] + 2[\hat{J}_{1z}, \hat{J}_{1x}]\hat{J}_{2x} + 2[\hat{J}_{1z}, \hat{J}_{1y}]\hat{J}_{2y} \\
 &= [\hat{J}_{1z}, (\hat{J}_1^2 - \hat{J}_{1z}^2)] + 2i\hbar(\hat{J}_{1y}\hat{J}_{2x} - \hat{J}_{1x}\hat{J}_{2y}) \\
 &\neq 0
 \end{aligned} \tag{8.149}$$

Inasmuch as $[\hat{J}_{1z}, \hat{J}^2] \neq 0$ and, obviously, $[\hat{J}_{2z}, \hat{J}^2] \neq 0$ the z -components of the individual angular momenta cannot be specified using the coupled representation.

The next thing we must do is to determine the relationship between the quantum numbers in the two representations. We already know the relationships between the uncoupled quantum numbers:

$$-j_1 \leq m_{j1} \leq j_1 \quad \text{and} \quad -j_2 \leq m_{j2} \leq j_2 \tag{8.150}$$

Operating on an uncoupled ket with \hat{J}_z we find the relationship between m_j , m_{j1} , and m_{j2} :

$$\begin{aligned}
 \hat{J}_z |j_1, m_{j1}; j_2, m_{j2}\rangle &= (\hat{J}_{1z} + \hat{J}_{2z}) |j_1, m_{j1}; j_2, m_{j2}\rangle \\
 &= (m_{j1} + m_{j2}) \hbar |j_1, m_{j1}; j_2, m_{j2}\rangle
 \end{aligned} \tag{8.151}$$

Also, however,

$$\hat{J}_z |j_1, m_{j1}; j_2, m_{j2}\rangle = m_j \hbar |j_1, m_{j1}; j_2, m_{j2}\rangle \tag{8.152}$$

so, comparing Equation 8.152 with Equation 8.151, we find that

$$m_j = m_{j1} + m_{j2} \tag{8.153}$$

Additionally,

$$\begin{aligned}
 (m_j)_{\max} &= (m_{j_1})_{\max} + (m_{j_2})_{\max} \\
 &= j_1 + j_2 \\
 &= j
 \end{aligned} \tag{8.154}$$

so that m_j takes on the values $(j_1 + j_2) \geq m_j \geq -(j_1 + j_2)$.

We must also be sure that there are an equal number of states in each representation. This can be somewhat confusing because there are multiple ways to obtain a given quantum number. For example, the quantum number $(m_j)_{\max} = j_1 + j_2$ is unique, but $m_j = j_1 + j_2 - 1$ is not because it can be formed by adding j_1 to $j_2 - 1$ or j_2 to $j_1 - 1$. The total number of states N in the coupled representation is clearly the product of the number of states possible for each value of j which corresponds to the total number of m -states for a given j , namely, $(2j + 1)$. Therefore,

$$N = (2j_1 + 1) \cdot (2j_2 + 1) \tag{8.155}$$

and we should get the same total using the uncoupled representation. To facilitate this computation we present in Table 8.8 the total number of states for each possible value of j . It is assumed that $j_1 > j_2$.

To find N we simply add the number of states that are listed in the last column of the table. We have, again assuming that $j_1 > j_2$,

$$\begin{aligned}
 N &= \{2(j_1 + j_2) + 1\} + \{2(j_1 + j_2 - 1) + 1\} + \dots + \{2(j_1 - j_2) + 1\} \\
 &= \sum_{n=0}^{2j_2} \{2(j_1 + j_2 - n) + 1\} \\
 &= 2j_1 \sum_{n=0}^{2j_2} 1 + 2j_2 \sum_{n=0}^{2j_2} 1 - 2 \sum_{n=0}^{2j_2} n + \sum_{n=0}^{2j_2} 1
 \end{aligned} \tag{8.156}$$

The validity of the limits of the summation in Equation 8.156 can be checked by noting that there are $(2j_2 + 1)$ terms in the sum ranging from $(j_1 + j_2)$ to $(j_1 - j_2)$.

Table 8.8 Uncoupled quantum numbers and numbers of states for two angular momenta

j	m_j	Number of states
$j_1 + j_2$	$(j_1 + j_2), (j_1 + j_2 - 1), \dots$ $\dots, -(j_1 - j_2 + 1), -(j_1 - j_2)$	$2(j_1 + j_2) + 1$
$j_1 + j_2 - 1$	$(j_1 + j_2 - 1), (j_1 + j_2 - 2), \dots$ $\dots, -(j_1 - j_2 + 2), -(j_1 - j_2 + 1)$	$2(j_1 + j_2 - 1) + 1$
\vdots	\vdots	\vdots
$j_1 - j_2$	$(j_1 - j_2), (j_1 - j_2 - 1), \dots$ $\dots, -(j_1 - j_2 + 1), -(j_1 - j_2)$	$2(j_1 - j_2) + 1$

To evaluate the third term in this summation we use the well-known summation of successive integers known as “Gauss’ trick” which Carl Friedrich Gauss as a schoolchild is purported to have invented as a time saver when a teacher gave his class the wearisome task of adding the first one hundred numbers. Gauss noted that by combining them in pairs, $0 + 100$, $1 + 99$, \dots , $49 + 51$, he had 50 pairs, each of which added to 100 with a single 50 left over. Thus, the answer to the teacher’s posed question was almost immediately given by Gauss, 5050. This trick, in more sophisticated mathematical language (see Appendix I.3), is written (try it!)

$$\sum_{n=0}^M n = \frac{M(M+1)}{2} \quad (8.157)$$

Now, back to the summation in Equation 8.156:

$$\begin{aligned} N &= 2j_1 \sum_{n=0}^{2j_2} 1 + 2j_2 \sum_{n=0}^{2j_2} 1 - 2 \sum_{n=0}^{2j_2} n + \sum_{n=0}^{2j_2} 1 \\ &= 2j_1 (2j_2 + 1) + 2j_2 (2j_2 + 1) - 2 \frac{2j_2 (2j_2 + 1)}{2} + (2j_2 + 1) \\ &= (2j_2 + 1)(2j_1 + 2j_2 - 2j_2 + 1) \\ &= (2j_1 + 1) \cdot (2j_2 + 1) \end{aligned} \quad (8.158)$$

This is the same as the number of states in the uncoupled representation.

8.6.1 Examples of Angular Momentum Coupling

Example: $j_1 = 1$; $j_2 = 1/2$

Consider a Bohr atom in the $n = 2$ state, Fig. 8.5 with $\ell = 1$ and spin angular momentum $s = 1/2$. There are a total of $N = 6$ states. In the uncoupled representation the kets are, with $j_1 = \ell$ and $j_2 = s = 1/2$,

$$\begin{aligned} |j_1, m_{j1}; j_2, m_{j2}\rangle &= |\ell, m_\ell; s, m_s\rangle \\ &= |1, m_\ell; \tfrac{1}{2}, m_s\rangle \end{aligned} \quad (8.159)$$

while the kets in the coupled representation are

$$\begin{aligned} |j_1, j_2; j, m_j\rangle &= |\ell, s; j, m_j\rangle \\ &= |1, \tfrac{1}{2}; j, m_j\rangle \end{aligned} \quad (8.160)$$

In this discussion we have elected to designate m_s by the actual value of the quantum number, $1/2$ and $-1/2$, rather than using a code such as the α and β notation used in Section 8.5.

Now, each representation comprises a complete set of kets upon which any arbitrary ket may be expanded. It is, however, possible to expand a ket in one representation on the set of kets in the other representation so it is possible to express, for example, an uncoupled ket in terms of the coupled kets. In general, such an expansion will consist of more than a single ket, although there are cases in which there is a one-to-one correlation between the coupled and uncoupled kets.

Table 8.9 is a listing of the six possible states in each representation. The listing in the right-hand column shows the uncoupled kets that correlate with the coupled ket in the left-hand column. For example, the coupled ket with $(j = 3/2, m_j = 1/2)$ must contain the uncoupled kets having $(m_\ell = 1, m_s = -1/2)$ and $(m_\ell = 0, m_s = +1/2)$ because both of these uncoupled kets correspond to $m_j = m_\ell + m_s = 1/2$. On the other hand, the coupled ket with $(j = 3/2, m_j = 3/2)$ is identical with the uncoupled ket having $(m_\ell = 1, m_s = 1/2)$ because this is the only combination of m_ℓ and m_s that can combine to give $m_j = 3/2$. This is called a top of the ladder state. Obviously the ket having $(j = 3/2, m_j = -3/2)$ is a bottom of the ladder state. Note that the right-hand column, although it contains ten entries, has only six different states.

Because we know that the coupled ket $|1, 1/2; 3/2, 1/2\rangle$ is a linear combination of two uncoupled kets we write, using subscripts *c* for coupled and *u* for uncoupled on the kets for clarity,

$$|1, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}\rangle_c = C_1 |1, 0; \frac{1}{2}, \frac{1}{2}\rangle_u + C_2 |1, 1; \frac{1}{2}, -\frac{1}{2}\rangle_u \quad (8.161)$$

The constants C_1 and C_2 in Equation 8.161 are called Clebsch–Gordan coefficients. Of course, the particular values of C_1 and C_2 pertain only to the case $j_1 = 1, j_2 = \frac{1}{2}$. Of what use is the fact that a ket in one representation may be expressed in terms

Table 8.9 Coupled and uncoupled states for an electron with orbital angular momentum 1. The left-hand column is a listing of the possible coupled states. The right-hand column contains the uncoupled states that correlate with the adjacent coupled states. Therefore, in the right-hand column, some uncoupled states are listed more than once

Coupled $ 1, \frac{1}{2}; j, m_j\rangle$	Uncoupled $ 1, m_\ell; \frac{1}{2}, m_s\rangle$
$ 1, \frac{1}{2}; \frac{3}{2}, \frac{3}{2}\rangle$	$ 1, 1; \frac{1}{2}, \frac{1}{2}\rangle$
$ 1, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}\rangle$	$ 1, 1; \frac{1}{2}, -\frac{1}{2}\rangle$
	$ 1, 0; \frac{1}{2}, \frac{1}{2}\rangle$
$ 1, \frac{1}{2}; \frac{3}{2}, -\frac{1}{2}\rangle$	$ 1, -1; \frac{1}{2}, \frac{1}{2}\rangle$
	$ 1, 0; \frac{1}{2}, -\frac{1}{2}\rangle$
$ 1, \frac{1}{2}; \frac{3}{2}, -\frac{3}{2}\rangle$	$ 1, -1; \frac{1}{2}, -\frac{1}{2}\rangle$
$ 1, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle$	$ 1, 0; \frac{1}{2}, \frac{1}{2}\rangle$
	$ 1, 1; \frac{1}{2}, -\frac{1}{2}\rangle$
$ 1, \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle$	$ 1, -1; \frac{1}{2}, \frac{1}{2}\rangle$
	$ 1, 0; \frac{1}{2}, -\frac{1}{2}\rangle$

of the other representation? Suppose we know that an electron in an atom is characterized by the total quantum numbers ($j = 3/2, m_j = 1/2$) so that it is in an eigenstate represented by the ket $|1, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}\rangle_c$ in Equation 8.161 and we wish to determine the probability that a measurement of the z -components of the individual angular momenta will yield ($m_\ell = 0, m_s = +1/2$). If we knew the value of C_1 in Equation 8.161, we would have the answer. Assuming that the wave function in this equation is normalized the answer is $|C_1|^2$.

In practice, tables of Clebsch–Gordan coefficients are used when it is necessary to express a ket in one representation in terms of the other, especially for cases that are more complicated than the one for which ($\ell = 1, s = 1/2$). The Clebsch–Gordan coefficients that are the entries in the tables are calculated making use of the one-to-one correlation of the extreme states in each representation. For example, to find C_1 and C_2 in Equation 8.161 we make use of top of the ladder state

$$|1, \frac{1}{2}; \frac{3}{2}, \frac{3}{2}\rangle_c = |1, 1; \frac{1}{2}, \frac{1}{2}\rangle_u \quad (8.162)$$

and operate on both sides with the lowering operator. Using Equation 8.40 we have

$$\begin{aligned} \hat{J}_- |1, \frac{1}{2}; \frac{3}{2}, \frac{3}{2}\rangle_c &= (\hat{L}_- + \hat{S}_-) |1, 1; \frac{1}{2}, \frac{1}{2}\rangle_u \\ \sqrt{3} |1, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}\rangle_c &= \hat{L}_- |1, 1; \frac{1}{2}, \frac{1}{2}\rangle_u + \hat{S}_- |1, 1; \frac{1}{2}, \frac{1}{2}\rangle_u \\ &= \sqrt{2} |1, 0; \frac{1}{2}, \frac{1}{2}\rangle_u + |1, 1; \frac{1}{2}, -\frac{1}{2}\rangle_u \end{aligned} \quad (8.163)$$

We see then that $C_1 = \sqrt{2/3}$ and $C_2 = 1/\sqrt{3}$ so

$$|1, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}\rangle_c = \sqrt{\frac{2}{3}} |1, 0; \frac{1}{2}, \frac{1}{2}\rangle_u + \frac{1}{\sqrt{3}} |1, 1; \frac{1}{2}, -\frac{1}{2}\rangle_u \quad (8.164)$$

and we have calculated the Clebsch–Gordan coefficients for this case. To complete the task of calculating all coefficients for this case we judiciously apply the ladder operators. By judiciously it is meant, for example, we could obtain $|1, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}\rangle_c$ by lowering the ket we just found in Equation 8.164, but this would be more work than simply raising the bottom of the ladder kets, $|1, \frac{1}{2}; \frac{3}{2}, -\frac{3}{2}\rangle_c = |1, -1; \frac{1}{2}, -\frac{1}{2}\rangle_u$. The results of these calculations are summarized in Table 8.10.

To recover Equation 8.164 from the table we read down the fourth column which represents the coupled ket $|1, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}\rangle_c$; the rows having nonzero entries are the coefficients of uncoupled kets that are designated by the entries in the first two columns. It is seen that these entries match Equation 8.164. The final two columns, those representing the $j = 1/2$ states, may be generated to within a phase $e^{i\delta}$ by invoking normality and orthogonality with the $j = 3/2$ states. Since, however, it is the squares of the expansion coefficients that represent probabilities, the relative phase is of no consequence. The phases (signs) in all tables in this book conform with those given in most references.

Table 8.10 Clebsch–Gordan coefficients for $j_1 = \ell = 1$ and $j_2 = 1/2$

$j_1 = 1; j_2 = 1/2$		$j = 3/2$				$j = 1/2$	
m_ℓ	m_s	3/2	1/2	-1/2	-3/2	1/2	-1/2
1	1/2	1					
1	-1/2		$\sqrt{1/3}$			$\sqrt{2/3}$	
0	1/2		$\sqrt{2/3}$			$-\sqrt{1/3}$	
0	-1/2			$\sqrt{2/3}$			$\sqrt{1/3}$
-1	1/2			$\sqrt{1/3}$			$-\sqrt{2/3}$
-1	-1/2				1		

Table 8.10 can be generalized for any value of j_1 , integral or half-integral, with $j_2 = s = 1/2$. Table 8.11 is a more commonly seen compilatin of Clebsch–Gordan coefficients. To recover Equation 8.164 from this table we let $j_1 = 1$ and $m_j = 1/2$ in the row that represents $j_1 + 1/2$. Note that values of m_{j_1} are not explicitly used in this table; they are determined by the choice of m_j and m_s . For example, the uncoupled ket $|1, 0; 1/2, 1/2\rangle_u$ has $m_{j_1} = m_j - m_s = 1/2 - 1/2 = 0$.

Example: $j_1 = 1/2 ; j_2 = 1/2$

Table 8.11 can be specialized for the case of two spin- $\frac{1}{2}$ particles. This is of great importance in both atomic and nuclear physics. In this case, we change the notation for the coupled state quantum numbers to conform to commonly used notation. The total angular momentum j and its z -component m_j are designated by S and M , respectively. Using this notation we can convert Table 8.11 to this notation for two spin- $\frac{1}{2}$ particles. The result is Table 8.12.

There are only two possible values of the total spin, $S = 0, 1$. For $S = 0$ there is only one possible z -component, $M = 0$. For $S = 1$, however, there are three possible z -components, $M = 0, \pm 1$. For this reason, when the two spins are aligned resulting in $S = 1$, this state (actually, three states) is referred to as the triplet state. Similarly, $S = 0$ is the singlet state. The coupled kets may be written in terms of the

Table 8.11 Clebsch–Gordan coefficients for any value of j_1 and $j_2 = 1/2$

j	$m_s = 1/2$	$m_s = -1/2$
$j_1 + 1/2$	$\sqrt{(j_1 + 1/2 + m_j) / (2j_1 + 1)}$	$\sqrt{(j_1 + 1/2 - m_j) / (2j_1 + 1)}$
$j_1 - 1/2$	$-\sqrt{(j_1 + 1/2 - m_j) / (2j_1 + 1)}$	$\sqrt{(j_1 + 1/2 + m_j) / (2j_1 + 1)}$

Table 8.12 Clebsch–Gordan coefficients for two spin-1/2 particles

S	$m_{s_2} = 1/2$	$m_{s_2} = -1/2$
1	$\sqrt{(1 + M) / 2}$	$\sqrt{(1 - M) / 2}$
0	$-1 / \sqrt{2}$	$1 / \sqrt{2}$

uncoupled kets with the aid of Table 8.12. Using the notation $|SM\rangle$ for coupled kets and $|m_{s1}m_{s2}\rangle$ for the uncoupled we have

$$\begin{aligned}
 |11\rangle &= \left|\frac{1}{2}, \frac{1}{2}\right\rangle \\
 |10\rangle &= \frac{1}{\sqrt{2}} \left|-\frac{1}{2}, \frac{1}{2}\right\rangle + \frac{1}{\sqrt{2}} \left|\frac{1}{2}, -\frac{1}{2}\right\rangle \\
 |1-1\rangle &= \left|-\frac{1}{2}, -\frac{1}{2}\right\rangle \\
 |00\rangle &= -\frac{1}{\sqrt{2}} \left|-\frac{1}{2}, \frac{1}{2}\right\rangle + \frac{1}{\sqrt{2}} \left|\frac{1}{2}, -\frac{1}{2}\right\rangle
 \end{aligned} \tag{8.165}$$

In writing the kets $|SM\rangle$ and $|m_{s1}m_{s2}\rangle$ we have not included the individual spin angular momenta s_1 and s_2 , because they are common to every such ket. To obtain the triplet states in Equations 8.165 we use the first row of Table 8.12, changing the value of M each time. Bear in mind that the value of M together with the value of m_{s2} determines the value of m_{s1} , that is, $m_{s1} = M - m_{s2}$. Note that these four kets form an orthonormal set. The singlet state is specified by the second row of Table 8.12. For future reference we point out that the triplet states are symmetric under an interchange of particles, while the singlet state is antisymmetric. For example, upon interchange of particles $|00\rangle \rightarrow -|00\rangle$.

Application: Coupling of proton and electron spins in a hydrogen atom

The importance of choosing the most convenient coupling scheme can be illustrated by considering the interaction between the magnetic moments of the proton and the electron in a hydrogen atom. For simplicity we consider only the ground state, $n = 1$, for which there is no orbital angular momentum and therefore no B -field due to the orbital motion of the electron. There are, however, two other B -fields, one due to the intrinsic magnetic moment of the electron and the other the intrinsic magnetic moment of the proton. We may regard the energy of interaction as that due to one of the magnetic moments in the B -field of the other. From Electricity and Magnetism, however, we know that the interaction of two magnetic dipoles is proportional to the dot product of their dipole moments. The intrinsic magnetic moment of the electron is given in Equation 8.108 and may be written

$$\begin{aligned}
 \hat{\mu}_s &= -\frac{g_e}{\hbar} \mu_B \hat{S} \\
 &= -\frac{g_e}{\hbar} \left(\frac{e\hbar}{2m_e} \right) \hat{S}
 \end{aligned} \tag{8.166}$$

The magnetic moment of the proton $\hat{\mu}_p$ will have an analogous form,

$$\begin{aligned}\hat{\mu}_p &= -\frac{g_p}{\hbar}\mu_B\hat{S} \\ &= -\frac{g_e}{\hbar}\left(\frac{e\hbar}{2m_p}\right)\hat{S}\end{aligned}\quad (8.167)$$

Because the mass of the proton, $m_p = 1836m_e$, we see that, all other factors being equal, $\hat{\mu}_p$ should be ~ 2000 times smaller than $\hat{\mu}_s$. In fact, it is only about 650 times smaller because the $g_p = 5.585$. Nonetheless, this energy is referred to as hyperfine splitting. It is of great importance in modern physics research, especially radio astronomy. For our current purpose we may simply write the interaction Hamiltonian for the hyperfine interaction in terms of the spins as

$$\hat{H}_{HF} = \frac{2\kappa}{\hbar^2}\hat{S}_1 \cdot \hat{S}_2 \quad (8.168)$$

where \hat{S}_1 and \hat{S}_2 represent the spins of the electron and proton and the constant has been judiciously chosen. Additionally, it is known that the constant $\kappa > 0$. It doesn't matter which spin operator corresponds to a particular particle since interchange of them does not change the Hamiltonian. In general, Equation 8.168 represents only a portion of the dipole–dipole interaction. There is yet another term in the Hamiltonian, but for $\ell = 0$ this term makes no contribution. The portion of the Hamiltonian given in Equation 8.168 is referred to as the contact term [5] because it only contributes at the origin when the electron and the proton are “in contact” ($\ell = 0$).

Our goal is to calculate the energy eigenvalues (and eigenkets) of \hat{H}_{HF} . This will yield the hyperfine splitting of the ground state of hydrogen. We can use either the coupled or the uncoupled representation. Before choosing between the two representations, we rewrite \hat{H}_{HF} in terms of the total spin operator $\hat{S} = \hat{S}_1 + \hat{S}_2$. Noting that

$$\begin{aligned}\hat{S}^2 &= (\hat{S}_1 + \hat{S}_2) \cdot (\hat{S}_1 + \hat{S}_2) \\ &= \hat{S}_1^2 + 2\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2^2\end{aligned}\quad (8.169)$$

we can solve for $\hat{S}_1 \cdot \hat{S}_2$ so that

$$\hat{H}_{HF} = \frac{\kappa}{\hbar^2}(\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2) \quad (8.170)$$

Because Equation 8.170 contains only the squares of the total and the individual angular momenta, it is clear that the coupled set designated $|SM\rangle$ as in Section 8.6 are the eigenkets of \hat{H}_{HF} . Moreover, there is no operator in \hat{H}_{HF} that will produce the quantum number M , so the triplet states $|1M\rangle$ all have the same energy. The energies are trivially obtained by applying \hat{H}_{HF} to the coupled kets. For the triplet we have

$$\begin{aligned}
 \hat{H}_{HF} |1M\rangle &= \frac{\kappa}{\hbar^2} (\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2) |1M\rangle \\
 &= \kappa [1(1+1) - 1/2(1/2+1) - 1/2(1/2+1)] |1M\rangle \\
 &= \frac{\kappa}{2} |1M\rangle
 \end{aligned} \tag{8.171}$$

while for the singlet we have

$$\begin{aligned}
 \hat{H}_{HF} |00\rangle &= \frac{\kappa}{\hbar^2} (\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2) |00\rangle \\
 &= \kappa [0 - 1/2(1/2+1) - 1/2(1/2+1)] |00\rangle \\
 &= -\frac{3}{2}\kappa |00\rangle
 \end{aligned} \tag{8.172}$$

Thus, the interaction between the electron and proton spins splits the energy of the $n = 1$ state of the hydrogen atom, the singlet decreasing the energy and the triplet increasing it. The total splitting is 2κ which is shown in Fig. 8.9.

The value of κ has been found to be $5.9 \times 10^{-6} \text{ eV}$, a very tiny fraction of the energy difference between the ground state and the first excited state, $\sim 10 \text{ eV}$. Using the formula given in Equation 1.10 we can calculate the wavelength of radiation given off in a transition between these two levels:

$$\begin{aligned}
 \lambda_{HF} &= \frac{1240}{5.9 \times 10^{-6}} \text{ nm} \\
 &= 21 \text{ cm}
 \end{aligned} \tag{8.173}$$

This wavelength is in the radio region of the electromagnetic spectrum. Observation of the 21-cm line by radio astronomy has provided a means of detecting interstellar hydrogen by detecting a wavelength other than a visible Balmer line. Moreover, it also permitted verification of the redshift measurements made in the visible region of the spectrum.

We can also obtain the energy eigenvalues of \hat{H}_{HF} using the uncoupled representation, but it is a bit more complicated. To illustrate the wisdom of using the most convenient basis set for a particular problem we will work out the details of the

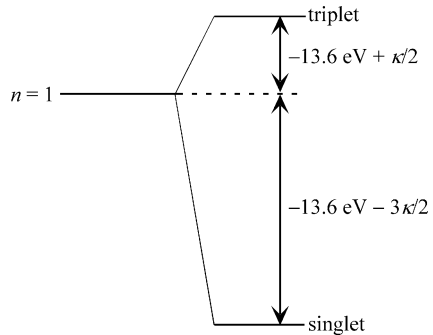


Fig. 8.9 Hyperfine splitting of the ground state of the hydrogen atom

calculation using the “wrong” basis set, the uncoupled set. To do so we first convert the eigenkets to this representation which is easily done using Table 8.12. Following Equations 8.165 in Section 8.6 we have

$$\begin{aligned}
 |11\rangle &= \left| \frac{1}{2}, \frac{1}{2} \right\rangle \\
 |10\rangle &= \frac{1}{\sqrt{2}} \left(\left| -\frac{1}{2}, \frac{1}{2} \right\rangle + \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \right) \\
 |1-1\rangle &= \left| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\
 |00\rangle &= -\frac{1}{\sqrt{2}} \left(\left| -\frac{1}{2}, \frac{1}{2} \right\rangle - \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \right)
 \end{aligned} \tag{8.174}$$

Now we must write \hat{H}_{HF} in terms of operators that will operate on the uncoupled kets. To do this we must cast $\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$ into a form that contains operators that, when operating on the uncoupled kets, yield known results. Using Equation 8.119 which gives \hat{S}_x and \hat{S}_y in terms of the ladder operators we have

$$\begin{aligned}
 \hat{H}_{HF} &= \frac{2\kappa}{\hbar^2} (\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z}) \\
 &= \frac{\kappa}{2\hbar^2} [(\hat{S}_{1+} + \hat{S}_{1-})(\hat{S}_{2+} + \hat{S}_{2-}) - (\hat{S}_{1+} - \hat{S}_{1-})(\hat{S}_{2+} - \hat{S}_{2-})] \\
 &\quad + \frac{2\kappa}{\hbar^2} \hat{S}_{1z}\hat{S}_{2z} \\
 &= \frac{\kappa}{\hbar^2} (\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+}) + \frac{2\kappa}{\hbar^2} \hat{S}_{1z}\hat{S}_{2z}
 \end{aligned} \tag{8.175}$$

This form is suitable because the uncoupled kets are eigenkets of \hat{S}_{1z} and \hat{S}_{2z} and because we know the actions of the ladder operators on the uncoupled kets (see Table 8.6). It simplifies matters to write \hat{H}_{HF} in terms of the Pauli spin matrices (see Section 8.5.1). We have

$$\begin{aligned}
 \hat{H}_{HF} &= \frac{\kappa}{\hbar^2} (\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+}) + \frac{2\kappa}{\hbar^2} \hat{S}_{1z}\hat{S}_{2z} \\
 &= \kappa \left[\left(\frac{1}{4} \right) (\hat{\sigma}_{1+}\hat{\sigma}_{2-} + \hat{\sigma}_{1-}\hat{\sigma}_{2+}) + 2 \left(\frac{1}{4} \right) \hat{\sigma}_{1z}\hat{\sigma}_{2z} \right] \\
 &= \frac{\kappa}{2} \left\{ \frac{1}{2} [(\hat{\sigma}_{1+}\hat{\sigma}_{2-} + \hat{\sigma}_{1-}\hat{\sigma}_{2+})] + \hat{\sigma}_{1z}\hat{\sigma}_{2z} \right\}
 \end{aligned} \tag{8.176}$$

Applying \hat{H}_{HF} to each of the uncoupled kets in Equation 8.174 produces the same eigenvalues that we obtained for the coupled kets. For example, with the aid of Table 8.7 we evaluate $\hat{H}_{HF} |10\rangle$. We obtain

$$\begin{aligned}
\frac{2}{\kappa} \hat{H}_{HF} |1\ 0\rangle &= \frac{1}{2} [(\hat{\sigma}_{1+}\hat{\sigma}_{2-} + \hat{\sigma}_{1-}\hat{\sigma}_{2+})] \left\{ \frac{1}{\sqrt{2}} (|-\frac{1}{2}, \frac{1}{2}\rangle + |\frac{1}{2}, -\frac{1}{2}\rangle) \right\} \\
&\quad + \hat{\sigma}_{1z}\hat{\sigma}_{2z} \left\{ \frac{1}{\sqrt{2}} (|-\frac{1}{2}, \frac{1}{2}\rangle + |\frac{1}{2}, -\frac{1}{2}\rangle) \right\} \\
&= \frac{1}{2} \frac{1}{\sqrt{2}} [4 |\frac{1}{2}, -\frac{1}{2}\rangle + 4 |-\frac{1}{2}, \frac{1}{2}\rangle] \\
&\quad + \frac{1}{\sqrt{2}} [(-1) |-\frac{1}{2}, \frac{1}{2}\rangle + (-1) |-\frac{1}{2}, \frac{1}{2}\rangle] \\
&= 2 \frac{1}{\sqrt{2}} [| \frac{1}{2}, -\frac{1}{2}\rangle + |-\frac{1}{2}, \frac{1}{2}\rangle] \\
&\quad - \frac{1}{\sqrt{2}} [| \frac{1}{2}, -\frac{1}{2}\rangle + |-\frac{1}{2}, \frac{1}{2}\rangle] \\
&= \frac{1}{\sqrt{2}} [| \frac{1}{2}, -\frac{1}{2}\rangle + |-\frac{1}{2}, \frac{1}{2}\rangle] \\
&= |1\ 0\rangle
\end{aligned} \tag{8.177}$$

so, indeed, the eigenvalue of $|1\ 0\rangle$ is $\kappa/2$. Of course, application of \hat{H}_{HF} as given in Equation 8.176 to the remaining three coupled kets produces the other two triplet eigenvalues, $\kappa/2$, $\kappa/2$ and the singlet eigenvalue $-3\kappa/2$. The problem can also be formulated in matrix notation (see Problem 22).

Evidently, the singlet state, in which the spins are antiparallel, carries a lower energy. In this state the magnetic moments are aligned. This is perhaps contrary to what one might think because the lower energy state of two magnets corresponds to antialignment of the magnetic moments. The lowest energy state of hydrogen has zero orbital angular momentum and the electron has some probability of being within the nucleus. This means that the magnetic interaction is dominated by the “contact term.” If the magnetic dipole is represented by an infinitesimal current loop, the contact term is due to the field within the loop, where it is in the same direction as the magnetic moment, the opposite direction of the field at all other points in the plane perpendicular to magnetic moment. This term has the opposite sign of the analogous term in the electric dipole interaction [5] and results in the lower energy of the aligned magnetic dipoles.

8.6.2 Spin and Identical Particles

In quantum physics particles of the same type are indistinguishable. For example, all electrons are the same and they cannot be tagged. One is the same as another and, indeed, they are indistinguishable. They are referred to as identical particles. Electrons are not the only particles that exhibit this indistinguishability. Protons, neutrons, and the other more exotic elementary particles are identical. Evidently nature made them so.

The key characteristic of identical particles is that interchange of them cannot be detected by a measurement. Therefore, indistinguishability demands that the probability distributions be unchanged upon interchange of the particles. Interchange can be effected by exchanging the coordinates of the particles, spatial and spin. This requirement imposes a symmetry on the state vectors that may be described in terms of an operator \hat{P}_{ij} , the particle exchange operator. When operating on a state vector, this operator exchanges all coordinates of the i th and j th particles. For simplicity we consider two identical noninteracting particles. A ket that specifies the two-particle state may be written

$$|a b\rangle = |a\rangle_1 |b\rangle_2 \quad (8.178)$$

where in the composite ket on the left, a and b designate the state of each particle and their position in the ket specifies the particle under the assumption that they can be tagged. In the product of individual particle kets on the right-hand side of Equation 8.178 a and b still designate the state, but the particular particle is designated by the subscript. Therefore, in Equation 8.178 particle #1 is in state a and particle #2 is in state b . It is important to remember that the state designations a and b include all coordinates, space and spin. If we now operate on this state vector with the exchange operator, we have

$$\begin{aligned} \hat{P}_{12} |a b\rangle &= |b a\rangle \\ &= |b\rangle_1 |a\rangle_2 \end{aligned} \quad (8.179)$$

Having defined the action of the operator we must now investigate the nature of the acceptable state vectors. That is, while the ket $|a b\rangle$ specifies the state of a two-particle system, we have no assurance that this represents an *acceptable* state. Clearly the ket in Equation 8.178 is *not* acceptable because exchanging the particles leads to a different state. So, what is an acceptable state? Let us designate an acceptable state by $|\psi\rangle$. The particles are indistinguishable so operating on $|\psi\rangle$ with the exchange operator cannot change the physical result. Therefore, the action of \hat{P}_{12} on $|\psi\rangle$ can only multiply it by a phase factor $e^{i\zeta}$, leaving $\langle\psi|\psi\rangle$ invariant. We have

$$\hat{P}_{12} |\psi\rangle = e^{i\zeta} |\psi\rangle \quad (8.180)$$

which is an eigenvalue equation for the particle exchange operator with eigenvalue $e^{i\zeta}$. Operating a second time with \hat{P}_{12} must return the original state vector so that

$$\begin{aligned} (\hat{P}_{12})^2 |\psi\rangle &= (e^{i\zeta})^2 |\psi\rangle \\ &= |\psi\rangle \end{aligned} \quad (8.181)$$

and the eigenvalue $e^{i\zeta} = \pm 1$. Therefore, $|\psi\rangle$ is an eigenket of \hat{P}_{12} with eigenvalues ± 1 . To find $|\psi\rangle$ in terms of the basis kets $|a b\rangle$ and $|b a\rangle$ we must solve the eigenvalue equation to find the expansion coefficients of $|a b\rangle$ and $|b a\rangle$. This is equivalent

to diagonalizing the matrix representing the operator \hat{P}_{12} using the basis set $|a b\rangle$ and $|b a\rangle$. We already know the eigenvalues are ± 1 , but we insert the eigenvalues as λ so we can find it later:

$$\begin{pmatrix} \langle a b | \hat{P}_{12} | a b \rangle & \langle a b | \hat{P}_{12} | b a \rangle \\ \langle b a | \hat{P}_{12} | a b \rangle & \langle b a | \hat{P}_{12} | b a \rangle \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \lambda \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad (8.182)$$

In Equation 8.182 the column matrix represents the ket

$$|\psi\rangle = c_1 |a b\rangle + c_2 |b a\rangle \quad (8.183)$$

and the unit matrix has been inserted for clarity. The basis vectors are orthonormal so the diagonal elements of \hat{P}_{12} vanish and the off-diagonal elements are each equal to unity. Transposing everything to the left-hand side we have

$$\begin{pmatrix} -\lambda & 1 \\ 1 & -\lambda \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad (8.184)$$

which represents two simultaneous equations for c_1 and c_2 . Solution of the secular equation (see Section 6.2.2) yields $\lambda = \pm 1$ which we already knew. (It is comforting to know that our method recovers the eigenvalues that we already deduced because it gives us confidence that the eigenvectors we seek will be correct.)

Inserting first $\lambda = +1$ in Equation 8.184 and multiplying the matrices we obtain $c_1 = c_2$. When we insert $\lambda = -1$ we arrive at $c_1 = -c_2$ so we have two acceptable eigenstates of the exchange operator. Normalized, they are

$$\begin{aligned} |\psi\rangle_s &= \frac{1}{\sqrt{2}} (|a b\rangle + |b a\rangle) \\ &= \frac{1}{\sqrt{2}} (|a\rangle_1 |b\rangle_2 + |b\rangle_1 |a\rangle_2) \end{aligned} \quad (8.185)$$

for $\lambda = +1$

$$\begin{aligned} |\psi\rangle_a &= \frac{1}{\sqrt{2}} (|a b\rangle - |b a\rangle) \\ &= \frac{1}{\sqrt{2}} (|a\rangle_1 |b\rangle_2 - |b\rangle_1 |a\rangle_2) \end{aligned} \quad (8.186)$$

for $\lambda = -1$.

The subscript designations “s” and “a” denote symmetric and antisymmetric eigenkets since the action of the exchange operator is to convert each into either itself (symmetric) or minus itself (antisymmetric). Neither of these exchanges produces a different probability distribution so they are acceptable states for identical particles. Note the contrast between these kets and that in Equation 8.178.

The above deductions about the nature of the acceptable state vectors may be stated in a slightly different way. Clearly the Hamiltonian that describes identical particles must be invariant under particle interchange. Thus, the Hamiltonian commutes with the exchange operator and the acceptable eigenstates are represented by kets that are simultaneous eigenkets of *both* operators. For example, while $|a b\rangle$ may be an eigenket of the Hamiltonian, it clearly is not an eigenket of the exchange operator. The defining relation for \hat{P}_{12} , Equation 8.179 assures us of this. On the other hand, $|\psi\rangle_s$ and $|\psi\rangle_a$ in Equations 8.185 and 8.186 are eigenkets of both \hat{P}_{12} and \hat{H} .

Particles fall into one of two types, fermions and bosons. Fermions have half-integral spin and are characterized by antisymmetric state vectors while bosons have integral spin (including zero) and are described by symmetric state vectors. Examples of fermions are electrons, protons and neutrons. Examples of bosons are photons and some of the exotic elementary particles. Composite particles are also subject to symmetry restrictions. For example, the nucleus of heavy hydrogen, known as a deuteron (see Section 9.4), consists of a proton and a neutron, both fermions. These half-integral spins, however, add in this case making the spin of the deuteron $+1$. It is therefore a boson. The nuclei of ordinary helium, α particles, are also bosons, but the isotope of helium having only one neutron in the nucleus is a fermion.

Let us examine the situation if both particles are placed in the same state so that $|a b\rangle \rightarrow |a a\rangle$. Clearly $|a a\rangle$ is an eigenket of the Hamiltonian, but, while $|\psi\rangle_s \rightarrow \sqrt{2}|a a\rangle$, $|\psi\rangle_a \equiv 0$. This is the Pauli exclusion principle which may be stated:

Two identical fermions may not occupy the same quantum state.

Again, it must be emphasized that a complete description of the quantum state includes spatial *and* spin coordinates. More fundamentally, however, the Pauli principle is

Systems of identical fermions are described by antisymmetric state vectors.

Interestingly, Pauli formulated this principle in 1925 in terms of quantum numbers of individual electrons in atoms.

No two electrons can have the same set of quantum numbers.

This formulation predated the discovery of electron spin and, indeed, even the formulation of the TDSE. Pauli invented a quantum number that could take on one of two values that, in fact, fulfilled the function of $m_s = \pm\frac{1}{2}$.

Suppose now that there are more than two identical particles in the system. For N identical fermions an antisymmetric state vector can be constructed using the Slater determinant

$$|\psi\rangle_a = \frac{1}{\sqrt{N!}} \begin{vmatrix} |a\rangle_1 & |b\rangle_1 & \cdots & \\ |a\rangle_2 & |b\rangle_2 & & \\ \vdots & \vdots & \ddots & \vdots \\ |a\rangle_N & |b\rangle_N & \cdots & \ddots \end{vmatrix} \quad (8.187)$$

where we use the individual ket notation of Equation 8.178 so that, for example, $|c\rangle_3$ represents particle #3 in quantum state c . As we will see in the example below, the Slater determinant guarantees a function that is antisymmetric under particle exchange, but this function may not be an *acceptable* wave function (see the example below). Expansion of the Slater determinant using only plus signs leads to an antisymmetric state vector.

Example: Two noninteracting fermions

In this example we examine the effects of properly symmetrizing the wave function on a simple system, two noninteracting fermions. Although the particles do not interact with each other, they are both subject to the same potential energy. We will determine the state vectors and energies for the ground state and the first excited state. Because the particles do not interact, the Hamiltonian is the sum of two individual Hamiltonians, one for each particle. The state vectors may therefore be kets of the form $|q m_s\rangle_i |p m_s\rangle_j$, where i, j stand for the number of the particle, 1 or 2, and q and p represent all spatial quantum numbers. Of course, $i \neq j$. The quantum numbers (q, p) and m_s represent the spatial and spin quantum states, respectively. The eigenkets are products of the individual eigenkets and the total energy is the sum of the energy eigenvalues of each of the particles. Additionally, because the energy does not depend upon the spin we may write $|n m_s\rangle_i = |n\rangle_i |m_s\rangle_i$. In this section, for each particle, we let $m_s = +\frac{1}{2} = \alpha$ or $m_s = -\frac{1}{2} = \beta$. Clearly the lowest energy state will be that for which each particle has the ground state energy E_1 . Thus, the total ground state energy is $2E_1$. We can use the Slater determinant to find the ground state eigenket. Denoting the spatial quantum numbers, q and p , by integers 0, 1, 2 . . . the state kets $|a\rangle_i$ and $|b\rangle_i$ are

$$\begin{aligned} |a\rangle_i &\triangleq |1\rangle_i |\alpha\rangle_i \\ |b\rangle_i &\triangleq |1\rangle_i |\beta\rangle_i \end{aligned} \quad (8.188)$$

These are the only choices for the ground state. The Slater determinant for the ground state $|\psi\rangle_0$ is

$$\begin{aligned}
|\psi\rangle_0 &= \frac{1}{\sqrt{2}} \begin{pmatrix} |1\rangle_1 |\alpha\rangle_1 |1\rangle_1 |\beta\rangle_1 \\ |1\rangle_2 |\alpha\rangle_2 |1\rangle_2 |\beta\rangle_2 \end{pmatrix} \\
&= \frac{1}{\sqrt{2}} (|1\rangle_1 |\alpha\rangle_1 |1\rangle_2 |\beta\rangle_2 - |1\rangle_2 |\alpha\rangle_2 |1\rangle_1 |\beta\rangle_1) \\
&= \frac{1}{\sqrt{2}} \{|1\rangle_1 |1\rangle_2\} \{|\alpha\rangle_1 |\beta\rangle_2 - |\alpha\rangle_2 |\beta\rangle_1\} \quad (8.189)
\end{aligned}$$

which is an acceptable eigenket because it is a product of space and spin kets, one of which (spin) is antisymmetric and the other (space) is symmetric. Therefore, their product is antisymmetric. In the language of Section 8.6.1, this is a singlet spin state. Clearly $S = 0$ and, consequently, $M = 0$.

The first excited state comprises states in which one electron is in the spatial state $q = 1$ and the other $p = 2$. Thus, the energy of the first excited state is $E_1 + E_2$. In this case m_s can take on either value α or β . There are, therefore, four possible individual electron states, but they must occur in pairs because the only combinations of states that can occur for the first excited states are states for which one spatial quantum number is 1 while the other is 2. Writing these out explicitly we let

$$\begin{aligned}
|a\rangle_i &\triangleq |1\rangle_i |\alpha\rangle_i; & |b\rangle_i &\triangleq |2\rangle_i |\alpha\rangle_i \\
|c\rangle_i &\triangleq |1\rangle_i |\beta\rangle_i; & |d\rangle_i &\triangleq |2\rangle_i |\beta\rangle_i
\end{aligned} \quad (8.190)$$

Such states are referred to as spin orbitals because the spatial part of atomic wave functions are called orbitals. Only four pairs of these spin orbitals lead to the energy of the first excited state. They may be designated

$$|a\rangle_i |b\rangle_j \delta_{ij}; \quad |a\rangle_i |d\rangle_j \delta_{ij}; \quad |c\rangle_i |b\rangle_j \delta_{ij}; \quad |c\rangle_i |d\rangle_j \delta_{ij} \quad i, j = 1, 2 \quad (8.191)$$

In this case we have four different 2×2 Slater determinants because the first excited state is four-fold degenerate, there are four ways of forming the energy $E_1 + E_2$. Inserting each of these pairs of states into the Slater determinant produces four degenerate state vectors. They are

$$|\psi\rangle_{1ab} = \frac{1}{\sqrt{2}} |\alpha\rangle_1 |\alpha\rangle_2 \{|1\rangle_1 |2\rangle_2 - |1\rangle_2 |2\rangle_1\} \quad (8.192)$$

$$|D\rangle_{1ad} = \frac{1}{\sqrt{2}} (|1\rangle_1 |\alpha\rangle_1 |2\rangle_2 |\beta\rangle_2 - |1\rangle_2 |\alpha\rangle_2 |2\rangle_1 |\beta\rangle_1) \quad (8.193)$$

$$|D\rangle_{1cb} = \frac{1}{\sqrt{2}} (|1\rangle_1 |\beta\rangle_1 |2\rangle_2 |\alpha\rangle_2 - |1\rangle_2 |\beta\rangle_2 |2\rangle_1 |\alpha\rangle_1) \quad (8.194)$$

$$|\psi\rangle_{1cd} = \frac{1}{\sqrt{2}} |\beta\rangle_1 |\beta\rangle_2 \{|1\rangle_1 |2\rangle_2 - |1\rangle_2 |2\rangle_1\} \quad (8.195)$$

Now, we must ask if these kets are acceptable eigenkets? The answer is that two of them, $|\psi\rangle_{1ab}$ and $|\psi\rangle_{1cd}$, are acceptable and two of them, $|D\rangle_{1ad}$ and $|D\rangle_{1cb}$, are not. Equations 8.192 and 8.195 clearly represent the triplet $M = \pm 1$ states (see Section 8.6.1). There is, however, (almost always) another requirement that must be met for a ket to be an acceptable eigenket. The Hamiltonian is of the form

$$\hat{H} = \hat{H}_{space} + \hat{H}_{spin} \quad (8.196)$$

so that, writing the particle interchange operator as the product of two operators,

$$\hat{P}_{12} = \hat{P}_{12}^{(space)} \hat{P}_{12}^{(spin)} \quad (8.197)$$

it is clear that each of these operators must have eigenvalues ± 1 , and that the particular eigenvalue of one determines the eigenvalue of the other. For example, if an exchange of spatial coordinates indicates an antisymmetric spatial part of the wave function, then the spin part of the wave function must be symmetric. Thus, symmetric spin and spatial kets are allowed, but not in the same eigenket. This infers that the acceptable kets must be products in the form $|space\rangle \times |spin\rangle$. This is also clear from the separability of the Hamiltonian as given in Equation 8.196.

It is seen that $|D\rangle_{1ad}$ and $|D\rangle_{1cb}$ do not qualify as acceptable eigenkets because they are not expressible as products of space and spin kets [4]. On the other hand, $|\psi\rangle_{1ab}$ and $|\psi\rangle_{1cd}$ are in product form and do qualify. To obtain acceptable eigenkets from $|D\rangle_{1ad}$ and $|D\rangle_{1cb}$ we must take linear combinations of them since linear combinations of symmetric or antisymmetric functions retain their symmetry under particle exchange. It is clear that the coefficients of $|D\rangle_{1ad}$ and $|D\rangle_{1cb}$ in the linear combinations must have the same magnitude to put them in proper form. We therefore deduce that

$$\begin{aligned} |\psi\rangle_{1\pm} &= \frac{1}{\sqrt{2}} |D\rangle_{1ad} \pm |D\rangle_{1cb} \\ &= \frac{1}{\sqrt{2}} \{ |1\rangle_1 |2\rangle_2 \mp |1\rangle_2 |2\rangle_1 \} \{ |\alpha\rangle_1 |\beta\rangle_2 \pm |\alpha\rangle_2 |\beta\rangle_1 \} \end{aligned} \quad (8.198)$$

Notice that the upper sign in Equation 8.198 must correspond to $M = 0$ of the triplet state, because it corresponds to a symmetric spin state, $S = 1$ (see Equations 8.165). We have therefore deduced the correct eigenkets for two noninteracting fermions and found that the spin parts of them are the same as those obtained by the addition of two spin- $\frac{1}{2}$ angular momenta as in Section 8.6.1. These properly symmetrized eigenkets are listed in Table 8.13. It is interesting that the symmetry requirements imposed by the indistinguishability criterion leads to differences in the average values of their separations. Despite the fact that the Hamiltonian does not contain the spin explicitly, it is found that the expectation value of the interparticle separation is greater for the triplet state than it is for the singlet state (see Problem 24). This effect has important consequences on the ordering of quantum mechanical states as will be seen in Section 13.3.2.

Table 8.13 The singlet and triplet states for two non-interacting fermions

Singlet
$\frac{1}{\sqrt{2}} \{ 1\rangle_1 2\rangle_2 + 1\rangle_2 2\rangle_1 \} \{ \alpha\rangle_1 \beta\rangle_2 - \alpha\rangle_2 \beta\rangle_1 \}$
Triplets
$\frac{1}{\sqrt{2}} \{ 1\rangle_1 2\rangle_2 - 1\rangle_2 2\rangle_1 \} \alpha\rangle_1 \alpha\rangle_2$
$\frac{1}{\sqrt{2}} \{ 1\rangle_1 2\rangle_2 - 1\rangle_2 2\rangle_1 \} \{ \alpha\rangle_1 \beta\rangle_2 + \alpha\rangle_2 \beta\rangle_1 \}$
$\frac{1}{\sqrt{2}} \{ 1\rangle_1 2\rangle_2 - 1\rangle_2 2\rangle_1 \} \beta\rangle_1 \beta\rangle_2$

8.7 The Vector Model of Angular Momentum

It has been emphasized that any vector operator having components that obey the commutation rules given in Equation 8.2 qualifies as an angular momentum even if it cannot be envisioned as such in the traditional sense. In the case in which an angular momentum operator does represent a quantity that has more than abstract meaning, we can construct a vector model to represent it. This vector model is particularly useful for understanding orbital angular momentum and for envisioning the coupling of two such angular momenta.

Figure 8.10 illustrates the vector model for a total angular momentum quantum number $j = 2$ and all of the $(2j + 1)$ possible z -components. The magnitude of the total angular momentum is $\sqrt{j(j+1)}\hbar$, while the maximum value that the $|m_j|$ can have is j . Therefore, the total angular momentum and its z -component can never be aligned (there is that pesky uncertainty principle again). The angular momentum vector will be oriented such that its z -component is the eigenvalue of \hat{J}_z , $m_j\hbar$. But nothing can be known about the x - and y -components. Therefore, all we know about the position of the *total* angular momentum vector is that it lies somewhere on a right circular cone, the altitude of which is known, $m_j\hbar$, with slant height $\sqrt{j(j+1)}\hbar$. It is a common misconception that the total angular momentum vector rotates, thus sweeping out the cone. This is not true! The total angular momentum vector lies somewhere *on* the cone, but the uncertainty principle, as embodied in the

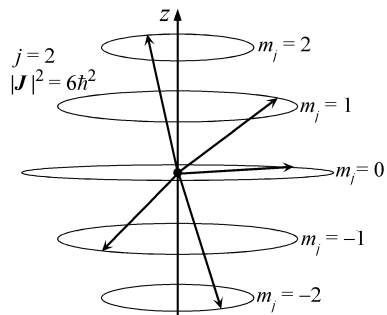
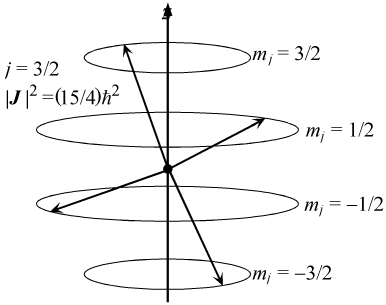


Fig. 8.10 Vector model of angular momentum for $j = 2$. Note that the plane in which the angular momentum vector lies when $m_j = 0$ is the xy -plane

Fig. 8.11 Vector model of angular momentum for $j = 3/2$. Notice that the total angular momentum vector cannot lie in the xy -plane



commutation properties of the components of angular momentum, prohibits precise knowledge of its position.

The vector model for a half-integral total angular momentum is slightly different from that for an integral total angular momentum because there is no zero z -component. That is, $m_j \neq 0$ for total spin that is half-integral. Fig. 8.11 illustrates this for $j = 3/2$.

The vector model of angular momentum is also useful when visualizing the coupling of angular momenta. Figure 8.12 illustrates the uncoupled representation showing how two different orientations of the individual angular momenta \mathbf{J}_1 and \mathbf{J}_2 can add vectorially to give different total angular momenta \mathbf{J} . The fact that different orientations of \mathbf{J}_1 and \mathbf{J}_2 produce different total angular momentum vectors illustrates that in the uncoupled representation, knowledge of total angular momentum is not possible.

Figure 8.13 illustrates the coupled representation. It shows two different individual angular momenta \mathbf{J}_1 and \mathbf{J}_2 that add to produce the same total angular momentum \mathbf{J} . Because, in this representation, the z -components of the individual angular momenta, m_{j1} and m_{j2} , are not known, the z -component of total angular momentum m_j is known.

Fig. 8.12 Illustration of the uncoupled representation. Two different possible orientations of the individual angular momenta \mathbf{J}_1 and \mathbf{J}_2 that lead to different total angular momentum vectors \mathbf{J}

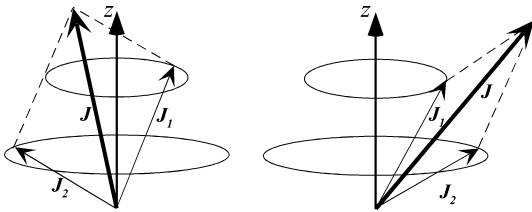
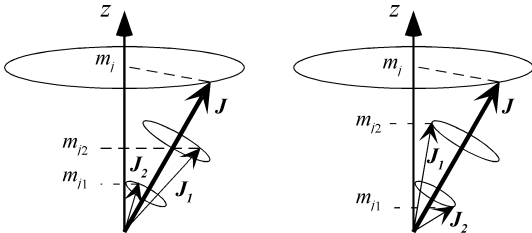


Fig. 8.13 Illustration of the coupled representation. Two different individual angular momenta \mathbf{J}_1 and \mathbf{J}_2 that produce the same total angular momentum vectors \mathbf{J}



8.8 Retrospective

While this chapter dealt in detail with angular momentum operator manipulation, perhaps the most important general concept for a beginning student of quantum mechanics is that angular momentum does not necessarily mean angular momentum as it was defined in classical mechanics. An angular momentum operator (an observable), as defined in quantum physics, obeys a very stringent criterion, namely that the commutator of its components obey Equation 8.2. Thus, except for orbital angular momentum, most angular momentum operators do not have any classical analogs. It is proper to refer to such an operator as *an* angular momentum.

8.9 References

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Problems

1. Find $[\hat{J}_x, \hat{J}_y, \hat{J}_z]$.
2. Show that $[\hat{J}_\pm, \hat{J}_z] = \mp \hbar \hat{J}_\pm$.
3. Show that $\hat{J}_+ \hat{J}_- = \hat{J}^2 - \hat{J}_z^2 + \hbar \hat{J}_z$.
4. Show that $\hat{\mathbf{J}} \times \hat{\mathbf{J}} = i\hbar \hat{\mathbf{J}}$. Classically, this is nonsense, but because of the commutation rules for angular momentum, it is perfectly reasonable quantum mechanically.
5. Find $\langle \hat{J}_x \rangle$ and $\langle \hat{J}_x^2 \rangle$ for eigenstates of \hat{J}^2 and \hat{J}_z .
6. Find the uncertainties $\Delta \hat{J}_x$, $\Delta \hat{J}_y$, and $\Delta \hat{J}_z$ for eigenstates of \hat{J}^2 and \hat{J}_z . and verify that they are consistent with the basic commutation rule of angular momentum, $[\hat{J}_i, \hat{J}_j] = i\hbar \hat{J}_k \epsilon_{ijk}$, and the uncertainty principle as given in Equation 6.109. You may use the results of Problem 5.
7. Verify the identities given in Equations 8.46.
8. Show that $[\hat{\mathbf{J}}, \hat{T}^2] = 0$. Working it out for one component is sufficient.
9. Show that the unit vector in the r -direction in spherical coordinates may be written in terms of the spherical harmonics as

$$\hat{\mathbf{a}}_r = \sqrt{\frac{4\pi}{3}} \left[\frac{-\hat{\mathbf{i}} + i\hat{\mathbf{j}}}{\sqrt{2}} Y_{11}(\theta, \phi) + \frac{\hat{\mathbf{i}} + i\hat{\mathbf{j}}}{\sqrt{2}} Y_{1-1}(\theta, \phi) + \hat{\mathbf{k}} Y_{10}(\theta, \phi) \right]$$

10. Show that $\Theta(\theta) = K' \sin^\kappa \theta$ is a solution to

$$\frac{\tan \theta}{\Theta(\theta)} \frac{d\Theta(\theta)}{d\theta} = \kappa$$

11. Show that using Equations 8.74 and 8.75 for the top and bottom of the ladder orbital angular momentum states and applying \hat{L}_+ to $Y_{\frac{1}{2}-\frac{1}{2}}(\theta, \phi)$ does not produce the known top state $Y_{\frac{1}{2}\frac{1}{2}}(\theta, \phi)$.
12. Use the operator $\hat{r}_+ = x + iy$ to find the spherical harmonic $Y_{11}(\theta, \phi)$. Do not normalize.
13. Verify Unsöld's theorem for $\ell = 0$ and $\ell = 1$.
14. A system is in a state such that the normalized angular part of the wave function is given by

$$\psi_{\ell m}(\theta, \phi) = \sqrt{\frac{1}{14}} \sqrt{\frac{1}{4\pi}} \left[1 + 2\sqrt{3} \cos \theta + 3\sqrt{\frac{5}{4}} (3 \cos^2 \theta - 1) \right]$$

- (a) If a measurement is made of the total angular momentum, what are the possible values that could be measured and with what probability of each?
- (b) If a measurement is made of the z -component of the angular momentum, what are the possible values that could be measured and with what probability of each?
- (c) What are the expectation values of \hat{L}_z and \hat{L}^2 ? Are the answers sensible?
15. For a spinning shell with radius equal to the classical radius of the electron $R_e \approx \alpha^2 a_0$, equate the angular momentum $I\omega$ to $\frac{1}{2}\hbar$ to show that the speed of a point on the rim would be about one hundred times the speed of light.
16. If the $|\beta\rangle_x$ beam in Fig. 8.8 is passed through a second SG $_z$ apparatus, what is the result? What percentage of the original unpolarized beam will be the spin up output of the second SG $_z$ apparatus?

apparatus which is $\frac{1}{2}$ of the input of the first SG $_z$ apparatus. Therefore, the $|\beta\rangle_x$ output beam is 1/8 of the intensity of the original unpolarized beam.

17. Find the matrices that are analogous to the electron spin matrices in Section 8.5.1 for the case of $\ell = 1$. That is, choose $[\hat{L}_z, \hat{L}^2] = 0$ and find the matrices that represent all components of angular momentum, the ladder operators and \hat{L}^2 .

Partial answer:

$$\hat{L}_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

18. A system has total angular momentum $\ell = 1$.

- (a) If a measurement of \hat{L}_x is made, what are the possible values that might be measured?
- (b) Find the eigenkets of \hat{L}_x .
- (c) If a system is in the eigenstate $|1 - 1\rangle$, what are the probabilities of measuring each of the permitted values of \hat{L}_x ?
19. Suppose the $|\beta\rangle_x$ beam that is the output of the SG_x apparatus in Fig. 8.8 is passed through an SG_z apparatus. How many beams will emerge from the SG_z apparatus and with what relative intensities? Demonstrate mathematically.
20. Show that the total angular momentum operator $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$ qualifies as a true angular momentum because its components obey the defining commutation rule, $[\hat{J}_i, \hat{J}_j] = i\hbar\hat{J}_k\epsilon_{ijk}$.
21. Use the result given in Equation 8.175 to show that the eigenvalue of the triplet and singlet coupled kets are $-3\kappa/2$ and $\kappa/2$ respectively.
22. Solve the eigenvalue problem to find the hyperfine energies using matrices. Use the uncoupled representation! Begin by writing the matrix that represents \hat{H}_{HF} using the basis set $|s_1s_2\rangle$, that is,

$$\left| \frac{1}{2}, \frac{1}{2} \right\rangle, \left| \frac{1}{2}, -\frac{1}{2} \right\rangle, \left| -\frac{1}{2}, \frac{1}{2} \right\rangle, \left| -\frac{1}{2}, -\frac{1}{2} \right\rangle$$

so the matrix is

$$\hat{H}_{HF} = \frac{2\kappa}{\hbar^2} \begin{pmatrix} \frac{1}{2}\frac{1}{2}\hat{H}_{\frac{1}{2}\frac{1}{2}} & \frac{1}{2}\frac{1}{2}\hat{H}_{\frac{1}{2}-\frac{1}{2}} & \frac{1}{2}\frac{1}{2}\hat{H}_{-\frac{1}{2}\frac{1}{2}} & \frac{1}{2}\frac{1}{2}\hat{H}_{-\frac{1}{2}-\frac{1}{2}} \\ \frac{1}{2}-\frac{1}{2}\hat{H}_{\frac{1}{2}\frac{1}{2}} & \frac{1}{2}-\frac{1}{2}\hat{H}_{\frac{1}{2}-\frac{1}{2}} & \frac{1}{2}-\frac{1}{2}\hat{H}_{-\frac{1}{2}\frac{1}{2}} & \frac{1}{2}-\frac{1}{2}\hat{H}_{-\frac{1}{2}-\frac{1}{2}} \\ -\frac{1}{2}\frac{1}{2}\hat{H}_{\frac{1}{2}\frac{1}{2}} & -\frac{1}{2}\frac{1}{2}\hat{H}_{\frac{1}{2}-\frac{1}{2}} & -\frac{1}{2}\frac{1}{2}\hat{H}_{-\frac{1}{2}\frac{1}{2}} & -\frac{1}{2}\frac{1}{2}\hat{H}_{-\frac{1}{2}-\frac{1}{2}} \\ -\frac{1}{2}-\frac{1}{2}\hat{H}_{\frac{1}{2}\frac{1}{2}} & -\frac{1}{2}-\frac{1}{2}\hat{H}_{\frac{1}{2}-\frac{1}{2}} & -\frac{1}{2}-\frac{1}{2}\hat{H}_{-\frac{1}{2}\frac{1}{2}} & -\frac{1}{2}-\frac{1}{2}\hat{H}_{-\frac{1}{2}-\frac{1}{2}} \end{pmatrix}$$

23. Apply \hat{H}_{FS} to the top and bottom of the ladder triplet states to obtain the eigenvalues $\kappa/2$ for the hyperfine energy.
24. Assuming that the potential to which the two noninteracting fermions in Example 8.6.2 are subjected is a one-dimensional harmonic oscillator, show that for the first excited state, the expectation value of the interelectron distance is greater for the triplet than the singlet. It is easier to work with the squares of the difference $(x_2 - x_1)$.

Chapter 9

Central Potentials

In general, the potential energy depends upon all three space coordinates, however we will consider cases for which the potential depends only upon the distance from some force center and not upon the direction. These are called central potentials. Mathematically we may define a central potential in terms of spherical coordinates $U(r, \theta, \phi) = U(r)$. It is obvious that spherical coordinates are ideal for describing such potentials. We note that central potentials have a built-in symmetry. Because the magnitude of the potential energy is independent of the direction, rotation of the coordinate system cannot change the physics. Therefore, the energy cannot depend upon any quantum number that establishes a direction in space.

The Hamiltonian is, as always, written as the sum of kinetic and potential energies. We ignore time-dependent Hamiltonians. Therefore, for a particle of mass m subject to a central potential $U(r)$ the Hamiltonian is

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(r) \quad (9.1)$$

We will follow custom and use the symbol m to designate the mass and also the quantum number associated with the z -component of angular momentum.

Now, just because $U(r)$ does not contain θ or ϕ does not mean that the kinetic energy term $\hat{p}^2/2m$ does not contain these coordinates. Indeed, because this is a three-dimensional problem $\hat{\mathbf{p}}$ is a vector operator that, in Cartesian coordinates, is

$$\hat{\mathbf{p}} = \frac{\hbar}{i} \left(\hat{\mathbf{i}} \frac{\partial}{\partial x} + \hat{\mathbf{j}} \frac{\partial}{\partial y} + \hat{\mathbf{k}} \frac{\partial}{\partial z} \right) \quad (9.2)$$

so the first term in Equation 9.1 is, in Cartesian coordinates,

$$\begin{aligned} \frac{\hat{p}^2}{2m} &= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \\ &= -\frac{\hbar^2}{2m} \nabla^2 \end{aligned} \quad (9.3)$$

The Hamiltonian for a central potential in coordinate space is therefore

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(r) \quad (9.4)$$

We can write ∇^2 in any coordinate system we please, but $U(r)$ is most conveniently written in spherical coordinates, so we concentrate on that system.

Let us now examine the orbital angular momentum operator \hat{L}^2 in spherical coordinates. One way to do this is to express ∇^2 in terms of its Cartesian components and then substitute Equations 8.64. A somewhat simpler method is to take advantage of the angular momentum ladder operators using the identity (see Problem 1)

$$\hat{L}^2 = \hat{L}_\pm \hat{L}_\mp + \hat{L}_z^2 \mp \hbar \hat{L}_z \quad (9.5)$$

Using Equations 8.65 for \hat{L}_\pm in spherical coordinates and letting \hat{L}^2 operate on some arbitrary function $f = f(\theta, \phi)$, it can be shown (see Problem 3) that

$$\hat{L}^2 f(\theta, \phi) = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] f(\theta, \phi) \quad (9.6)$$

Now, $\nabla^2 f$ in spherical coordinates is given by

$$\begin{aligned} \nabla^2 &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{r^2 \hbar^2} \end{aligned} \quad (9.7)$$

from which we see that the Hamiltonian for a central potential may be expressed in terms of the angular momentum as

$$\hat{H} = -\left(\frac{\hbar^2}{2m} \right) \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2mr^2} + U(r) \quad (9.8)$$

9.1 Separation of the Schrödinger Equation

Using the Hamiltonian given in Equation 9.8 we may write the TISE for any central potential as

$$\hat{H}(r, \theta, \phi) \psi(r, \theta, \phi) = \left[-\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2mr^2} + U(r) \right] \psi(r, \theta, \phi) \quad (9.9)$$

Because the operator \hat{L}^2 does not contain the spherical coordinate r , it is clear that \hat{L}^2 commutes with the Hamiltonian. Moreover, \hat{L}_z also commutes with \hat{H} . Therefore, the eigenfunctions $\psi(r, \theta, \phi)$ must be simultaneous eigenfunctions of \hat{L}^2 and

\hat{L}_z . From Section 8.4 we already know that simultaneous eigenfunctions of \hat{L}^2 and \hat{L}_z are the spherical harmonics $Y_{\ell m}(\theta, \phi)$, so it is reasonable to try to solve the TISE for an arbitrary central potential by separation of variables. Therefore, we write

$$\psi(r, \theta, \phi) = R(r) Y_{\ell m}(\theta, \phi) \quad (9.10)$$

which, when inserted in the TISE using the Hamiltonian in the form of Equation 9.9, yields

$$\left\{ -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2mr^2} + U(r) \right\} R(r) Y_{\ell m}(\theta, \phi) = E R(r) Y_{\ell m}(\theta, \phi) \quad (9.11)$$

Carrying out the differentiations leads to

$$Y_{\ell m}(\theta, \phi) \left[-\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + U(r) \right] R(r) + R(r) \frac{\hat{L}^2 Y_{\ell m}(\theta, \phi)}{2mr^2} = E R(r) Y_{\ell m}(\theta, \phi) \quad (9.12)$$

Dividing both sides of Equation 9.12 by $R(r) Y_{\ell m}(\theta, \phi)$, multiplying by $2mr^2$, and rearranging leads to

$$\frac{2mr^2}{R(r)} \left[-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + U(r) \right] R(r) - 2mr^2 E = -\frac{1}{Y_{\ell m}(\theta, \phi)} \hat{L}^2 Y_{\ell m}(\theta, \phi) \quad (9.13)$$

where the partial derivatives with respect to r have been replaced by total derivatives. The left-hand side of Equation 9.13 is a function of r only, while the right-hand side is a function of θ and ϕ . Each side must therefore be equal to a constant, the same constant. The angular equation is, however, the eigenvalue equation for \hat{L}^2 . Moreover, we know the eigenvalues of the $Y_{\ell m}(\theta, \phi)$ are $\ell(\ell+1)\hbar^2$ so we know the separation constant. The general equation for $R(r)$ is therefore

$$\frac{2mr^2}{R(r)} \left[-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + U(r) \right] R(r) - 2mr^2 E = -\ell(\ell+1)\hbar^2 \quad (9.14)$$

or, rearranging to cast it as an eigenvalue equation,

$$\left[-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + U(r) \right] R(r) = E R(r) \quad (9.15)$$

We see that the technique of separation of variables works again, in this case using spherical coordinates. When it does work, the equation on which it worked is said to be separable in the coordinate system. The energy eigenvalues are determined by the radial TISE, Equation 9.15, so it is clear that, in addition to an energy quantum number that will evolve from solution of this equation (usually designated n), the energy will also depend upon the angular momentum quantum number ℓ because it appears in the radial equation. There are, however, potential functions for which the energy eigenvalues are independent of ℓ . Because of this independence on ℓ the energy eigenvalues for such potentials will have a degree of degeneracy beyond that associated with any spherically symmetric potential. This feature of central potentials will be discussed in more detail in Section 9.1.2.

As discussed above, it is clear from Equation 9.8 that \hat{L}^2 commutes with the Hamiltonian for any central potential as do all the components of the orbital angular momentum because they individually commute with \hat{L}^2 (see Equation 8.10). Because the operators representing the components of angular momentum contain only angular coordinates they also commute with the first term of \hat{H} , the one containing only the coordinate r . Inasmuch as \hat{L}_z is chosen as the component of angular momentum that has simultaneous eigenfunctions we conclude that \hat{H} , \hat{L}^2 , and \hat{L}_z constitute a set of mutually commuting operators. They therefore have simultaneous eigenfunctions, the spherical harmonics. Note that the radial part of the eigenfunctions are trivially eigenfunctions of \hat{L}^2 and \hat{L}_z because these operators do not contain any radial coordinates. Thus, whenever the TISE is solved for a central potential using spherical coordinates the set of mutually commuting operators employed is \hat{H} , \hat{L}^2 , and \hat{L}_z . Moreover, the spherical harmonics, $Y_{\ell m}(\theta, \phi)$, are always the angular part of the eigenfunction in spherical coordinates.

9.1.1 The Effective Potential

It is seen that there is a great simplification in central force problems because we already know the angular parts of the eigenfunctions for *any* central potential, the spherical harmonics. Thus, to solve a central potential problem in its entirety we need only solve the radial TISE equation, Equation 9.15, to obtain the rest of the eigenfunction $R(r)$.

It is often convenient to make the same substitution that is made in classical mechanics to make this differential equation more tractable. In particular, if we let

$$u(r) = rR(r) \quad (9.16)$$

Equation 9.15 becomes

$$-\frac{\hbar^2}{2m} \frac{d^2 u(r)}{dr^2} + \left\{ \frac{\ell(\ell+1)\hbar^2}{2mr^2} + U(r) \right\} u(r) = Eu(r) \quad (9.17)$$

With the one-dimensional potential energy replaced by the term in curly brackets, Equation 9.17 has the same form as the one-dimensional TISE. For this reason it is sometimes convenient to solve for the radial part of the eigenfunction $R(r)$ by first solving Equation 9.17 for $u(r)$. The term in brackets is called the effective potential $U_{eff}(r)$. That is,

$$U_{eff}(r, \ell) = \frac{\ell(\ell+1)\hbar^2}{2mr^2} + U(r) \quad (9.18)$$

The effective potential contains the effects of orbital angular momentum, the centrifugal potential $\ell(\ell+1)\hbar^2/2mr^2$ as noted earlier in Section 5.6.6. It is traditional to omit the ℓ as a reminder that the effective potential depends on both r and ℓ so it is most often seen as $U_{eff}(r)$.

The independent variable r in Equation 9.17 is restricted to positive values, which is equivalent to a one-dimensional potential with an infinitely hard wall at $x \leq 0$. There are, however, significant differences between $U_{eff}(r)$ and a one-dimensional potential that are caused by the centrifugal term. Figure 9.1 illustrates the effects of the centrifugal term. It shows graphs of the Morse potential for four different values of the orbital angular momentum quantum number ℓ . The behavior of the Morse potential is typical of the substantial modification of $U(r)$ that transforms it into $U_{eff}(r)$ for $\ell \neq 0$.

The centrifugal term is positive definite so the effect of adding it to $U(r)$ is to raise the potential energy, ultimately making it positive as is apparent in Fig. 9.1 for $\ell = 4$ and $\ell = 6$. Clearly there will be different sets of eigenvalues and eigenfunctions for each value of ℓ . We will, later in this chapter, find the eigenvalues for the

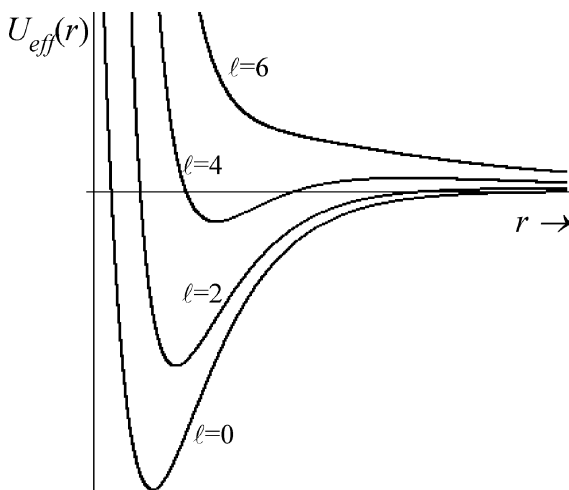


Fig. 9.1 The effective potential $U_{eff}(r)$ of the Morse potential for four different values of the orbital angular momentum quantum number ℓ

three-dimensional Morse potential for an arbitrary angular momentum and contrast them to those found in Section 5.4 which are relevant for $\ell = 0$.

While the Morse potential was used to illustrate the dramatic differences between $U(r)$ and $U_{eff}(r)$, it should be recalled that the Morse potential represents the potential energy for a diatomic molecule. As such, the potential is that experienced by a particle having the reduced mass of the atom–atom system. Thus, while most of the potential energy functions examined in this book are, implicitly, if not explicitly, those to which an electron is subjected, the Morse potential is not. To emphasize this distinction, symbols other than ℓ are usually used to designate the angular momentum of the reduced mass particle.

9.1.2 Degeneracy

When the rigid rotor was examined in Section 8.4.3 it was found that there was an energy degeneracy because the energy eigenvalues did not depend upon the quantum number m . Actually, *all* central potentials exhibit a similar degeneracy. We have seen that the TISE is separable in spherical coordinates for any central potential and that the angular part of the eigenfunction is always the spherical harmonics $Y_{\ell m}(\theta, \phi)$. It is, therefore, the radial equation that determines the energy. Solution of the radial equation will provide another quantum number that may be regarded as the energy quantum number or the radial quantum number in the same way that ℓ designates the total angular momentum and m the z -component of the angular momentum.

Examination of the radial equation, either Equation 9.15 or 9.17, reveals that, while the radial eigenfunction does not depend upon the quantum number m , it does, in general, depend upon ℓ . Therefore, the energy eigenvalue will, in general, depend upon the energy quantum number, usually designated n , and ℓ . Because it is independent of m , all m -states will be degenerate except the ones for which $\ell = 0$. The degree of degeneracy is simply the number of states that correspond to the same eigenvalue. For any value of ℓ there are $(2\ell + 1)$ values of m (see Section 8.7) so the solution of the TISE for any central potential exhibits (at least) a $(2\ell + 1)$ -fold degeneracy. Of course, there are other observables that can be degenerate, but we will concentrate our attention on energy degeneracies.

What is the source of this $(2\ell + 1)$ -fold degeneracy? Degeneracies always result from symmetries in the problem. In this case it is the spherical symmetry of a central potential. That is why the degeneracy exists for *any* central potential. Such potentials are invariant under rotations. This means that you can rotate the axes about the origin in any way you please and the potential at a given point in space remains the same. It is clear then that the energy cannot depend upon the orientation of the angular momentum vector. Therefore, the energy must also be invariant with respect to rotations. The symmetry responsible for this degeneracy is referred to as a spatial symmetry. Symmetries in quantum mechanical problems are always related to conserved quantities in classical mechanics. The $(2\ell + 1)$ -fold degeneracy

is related to the fact that, classically, angular momentum is conserved for any central potential. This conservation law is responsible for the fact that Keplerian orbits are always in a plane. It also accounts for Kepler's second law, the law of equal areas, which does not depend upon the gravitational potential. It pertains to any central potential.

There are other degeneracies that can exist for central potential problems. In such cases there exists a symmetry beyond the spatial symmetry that accounts for the universal $(2\ell + 1)$ -fold degeneracy for central potentials. Frequently the extra symmetry is difficult to envision (although some physicists claim that they can visualize them). The most notable example of such a supersymmetry is that of the hydrogen atom to be discussed in detail in the next chapter. Recalling that the Bohr energy, Equation 1.36, depends upon only a single quantum number n , we see that it must be independent of ℓ (as well as m) and therefore it has a higher degree of degeneracy than the required $(2\ell + 1)$. Recall that the Bohr energies are the same as the eigenvalues obtained by solving the TISE (see Section 1.2.1). Another problem that has a similarly higher symmetry than the spatial symmetry is the three-dimensional isotropic harmonic oscillator to be treated later in this chapter.

Degeneracies beyond the $(2\ell + 1)$ -fold degeneracy are often referred to as "accidental" degeneracies. It is clear now that there is nothing accidental about them. They result from higher symmetries. Nonetheless, we will conform with tradition and refer to them as accidental degeneracies. Although group theory can be invoked to better understand them, it is not required to accept their existence.

As noted above, the symmetries that are responsible for degeneracies always correspond to some classically conserved quantity. The quantum mechanical analog of a conserved quantity, one that remains constant in time, is an operator that commutes with the Hamiltonian. This may be seen by examining the Heisenberg equation of motion, Equation 6.145:

$$\begin{aligned}\frac{d\hat{A}(t)}{dt} &= \frac{i}{\hbar} [\hat{H}, \hat{A}(t)] \\ &= 0\end{aligned}\tag{9.19}$$

We will see that the accidental degeneracy of the hydrogen atom is due to a rather obscure classically conserved vector, the Lenz vector.

One final point about accidental degeneracies is worth noting. When they occur, the TISE is separable in at least one other coordinate system. Therefore, for a central potential that has supersymmetry, there is at least one other coordinate system, in addition to spherical coordinates, in which the TISE can be separated. The sets of eigenfunctions obtained using each of these coordinate systems are complete, so any eigenfunction in one coordinate system may be written as a linear combination of the eigenfunctions in the other system.

9.1.3 Behavior of the Wave Function for Small and Large Values of r

It is helpful to know the behavior of the wave function at the extreme values of r . Our interest will focus on bound states although near the origin this restriction is unnecessary. To obtain the general form on the wave function near $r = 0$, we examine the radial TISE, Equation 9.17. If the r -dependence of $U(r)$ is not stronger than $1/r^2$, then, near the origin, the centrifugal term dominates so that as $r \rightarrow 0$ the radial equation behaves as

$$-\frac{d^2 u(r)}{dr^2} + \frac{\ell(\ell+1)}{r^2} u(r) = 0 \quad (9.20)$$

We try a solution $u(r) = r^s$ which leads to

$$s(s-1) = \ell(\ell+1) \quad (9.21)$$

the solutions of which are $s = -\ell$ and $s = (\ell+1)$. From these solutions we might infer that near the origin $u(r)$ may be of the form $r^{\ell+1}$ and $r^{-\ell}$. In the vicinity of the origin, however, $r^{-\ell}$ is unacceptable because it blows up, so we conclude as $r \rightarrow 0$

$$u(r) \sim r^{\ell+1} \quad \text{and} \quad R(r) \sim r^\ell \quad (\text{near } r = 0) \quad (9.22)$$

Turning our attention to the behavior for large r we see that, assuming $U(r)$ can support bound states, Equation 9.17 becomes

$$\frac{d^2 u(r)}{dr^2} - \kappa^2 u(r) = 0 \quad (9.23)$$

where $\kappa = \sqrt{-2mE/\hbar^2}$. For bound states $E < 0$ so the solutions are $e^{\pm\kappa r}$ where κ is a real number. Of course, the positive exponential is prohibited because it blows up at infinity so we have

$$u(r) \rightarrow e^{-\kappa r} \quad \Longrightarrow \quad R(r) \rightarrow \frac{e^{-\kappa r}}{r} \quad (\text{as } r \rightarrow \infty) \quad (9.24)$$

For continuum states, that is, positive energy states $E > 0$, κ is imaginary so we let $\kappa \rightarrow k$ and the solutions are

$$u(r) \rightarrow e^{\pm ikr} \quad \Longrightarrow \quad R(r) \rightarrow \frac{e^{\pm ikr}}{r} \quad (\text{as } r \rightarrow \infty) \quad (9.25)$$

Notice that neither sign in the exponentials can be discarded on physical grounds since neither diverges for large r .

9.2 The Free Particle in Three Dimensions

In three dimensions the free particle exhibits features not available in one-dimension. In particular, in three dimensions, the particle can have angular momentum. Therefore, the effective potential reduces to the centrifugal term and the TISE for $R(r)$ for all values of r is

$$\left[-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} \right] R(r) = E R(r) \quad (9.26)$$

or

$$\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} + k^2 \right] R(r) = 0 \quad (9.27)$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad (9.28)$$

In solving the radial TISE it is often convenient to rescale the length which, in this problem, we accomplish with the substitution $\rho = kr$. With this rescaling the TISE becomes

$$\left\{ \frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} + \left[1 - \frac{\ell(\ell+1)}{\rho^2} \right] \right\} R(\rho) = 0 \quad (9.29)$$

While formidable looking, Equation 9.29 is a well-known differential equation, the spherical Bessel equation. The solutions of the spherical Bessel equation are special functions, spherical Bessel functions $j_\ell(\rho)$ and spherical Neumann functions $n_\ell(\rho)$. There are also linear combinations of $j_\ell(\rho)$ and $n_\ell(\rho)$ called Hankel functions that will be useful, but for now we concentrate on spherical Bessel and Neumann functions. This group of functions is known collectively as spherical Bessel functions even though one of them, $j_\ell(\rho)$, is itself called a spherical Bessel function. Table 9.1 contains the first few spherical Bessel and Neumann functions. The group of spherical Bessel functions are related to (cylindrical) Bessel functions of half-integral order, but this is of little concern here. In general, the solution to Equation 9.29 is a linear combination of $j_\ell(\rho)$ and $n_\ell(\rho)$ so

Table 9.1 The first three spherical Bessel and Neumann functions

ℓ	$j_\ell(x)$	$n_\ell(x)$
0	$\frac{\sin x}{x}$	$-\frac{\cos x}{x}$
1	$\frac{\sin x}{x^2} - \frac{\cos x}{x}$	$-\frac{\cos x}{x^2} - \frac{\sin x}{x}$
2	$\left(\frac{3}{x^3} - \frac{1}{x} \right) \sin x - \frac{3}{x^2} \cos x$	$-\left(\frac{3}{x^3} - \frac{1}{x} \right) \cos x - \frac{3}{x^2} \sin x$

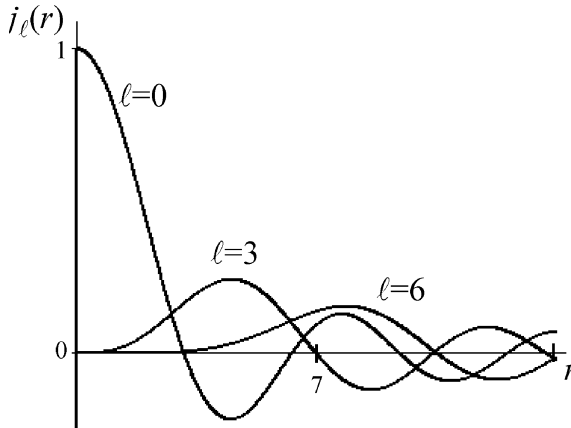


Fig. 9.2 Three spherical Bessel functions showing how the higher angular momentum states are prevented from coming near the origin

$$R(r) = A j_\ell(kr) + B n_\ell(kr) \quad (9.30)$$

Figures 9.2 and 9.3 are plots of three spherical Bessel and Neumann functions for $\ell = 0, 3$ and 6 . In both graphs it is seen that the higher the state of angular momentum the farther away from the origin are these functions. The divergence of the Neumann functions at the origin is also evident. It is also evident that $j_\ell(0) = 0$ for $\ell \neq 0$.

It is clear that if the region of interest includes the origin, the wave function cannot contain $n_\ell(kr)$ because it diverges. If, however, the origin is not included, then both functions must be included, subject to the wave function having the correct asymptotic behavior. For such a free particle this behavior must be characterized by a wave function that is a linear combination of e^{ikr}/r and e^{-ikr}/r as discussed in Section 9.1.3. We must, therefore, examine the asymptotic behavior of $j_\ell(kr)$ and $n_\ell(kr)$. Table 9.2 is a listing of the asymptotic forms of the spherical Bessel functions, as well as their behavior near the origin.

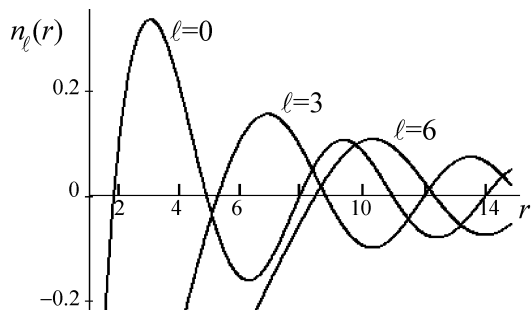


Fig. 9.3 Three spherical Neumann functions showing that they diverge at the origin

Table 9.2 Limiting forms of the spherical Bessel and Neumann functions

limit	$j_\ell(x)$	$n_\ell(x)$
$x \rightarrow \infty$	$\frac{1}{x} \sin\left(x - \ell \frac{\pi}{2}\right)$	$-\frac{1}{x} \cos\left(x - \ell \frac{\pi}{2}\right)$
$x \rightarrow 0$	$\frac{x^\ell}{1 \cdot 3 \cdot 5 \cdots (2\ell + 1)}$	$\frac{1 \cdot 3 \cdot 5 \cdots (2\ell - 1)}{x^{\ell+1}}$

The behavior of $n_\ell(x)$ near the origin shown in Table 9.2 emphasizes the irregularity of this function near the origin, and clearly shows that if the region of interest contains the origin the Neumann function cannot be included. Let us suppose that there is a hard sphere at $r = a$ so the particle cannot be found at $r < a$. The potential is therefore

$$\begin{aligned} U(r) &= \infty & r < a \\ &= 0 & r > a \end{aligned} \quad (9.31)$$

The Neumann function cannot now be precluded from the solution. Therefore, $u(r)$ is of the form given in Equation 9.30. Additionally, there is no reason to exclude $j_\ell(\rho)$. On the other hand, we must make sure that the solution exhibits the correct asymptotic behavior. It is clear from Table 9.2 that neither $j_\ell(\rho)$ nor $n_\ell(\rho)$ behaves properly as $r \rightarrow \infty$. It is, however, possible to construct a linear combination of them that does give the correct behavior. In particular, we can write

$$\begin{aligned} j_\ell(\rho) \pm i n_\ell(\rho) &\rightarrow \frac{1}{\rho} \left[\sin\left(\rho - \ell \frac{\pi}{2}\right) \mp i \cos\left(\rho - \ell \frac{\pi}{2}\right) \right] \\ &= \mp \frac{i}{\rho} \left[\cos\left(\rho - \ell \frac{\pi}{2}\right) \pm i \sin\left(\rho - \ell \frac{\pi}{2}\right) \right] \\ &= \mp \frac{i}{\rho} e^{\pm i\rho} \cdot e^{-\ell\pi/2} \end{aligned} \quad (9.32)$$

which does indeed have the correct asymptotic form. The positive exponential represents an outgoing spherical wave while the negative exponential represents an incoming spherical wave.

As noted above, the linear combinations of $j_\ell(\rho)$ and $n_\ell(\rho)$ also have names, spherical Hankel functions, $h_\ell(\rho)$. There are two different forms of $h_\ell(\rho)$ which are designated $h_\ell^{(1)}(\rho)$ and $h_\ell^{(2)}(\rho)$, and referred to as spherical Hankel functions of the first and second kind, respectively. The asymptotic forms of these spherical Hankel functions are precisely the linear combinations of $j_\ell(\rho)$ and $n_\ell(\rho)$ in Equation 9.32 which we rewrite for convenience

$$\begin{aligned}
\lim_{\rho \rightarrow \infty} h_{\ell}^{(1)}(\rho) &= -\frac{i}{\rho} e^{i\rho} \cdot e^{-\ell\pi/2} \\
\lim_{\rho \rightarrow \infty} h_{\ell}^{(2)}(\rho) &= \frac{i}{\rho} e^{-i\rho} \cdot e^{-\ell\pi/2}
\end{aligned} \tag{9.33}$$

The kinetic energy of a free particle, E , is always greater than the potential energy (zero) so that k , as given in Equation 9.28, is always positive and the wave function, the Hankel function, oscillates.

9.3 The Infinite Spherical Square Well

The first central potential that we will examine is the three-dimensional analog of the one-dimensional a -box. The potential energy function is

$$\begin{aligned}
U(r) &= 0 \quad r < a \\
&= \infty \quad r > a
\end{aligned} \tag{9.34}$$

Thus, we have a spherical cavity with impenetrable walls. The particle cannot get out and the particle's motion inside the cavity is rigorously restricted to the region $r < a$. For this problem, the radial TISE inside the well is identical with Equation 9.26. Because the origin is included, the spherical Neumann functions are excluded and the solution for $r < a$ is

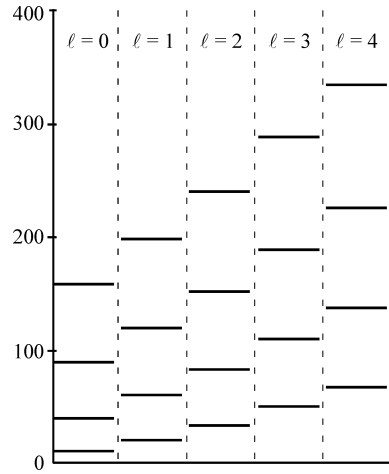
$$\begin{aligned}
R_{\ell}^{(1)}(r) &= C j_{\ell}(kr) \quad r < a \\
R_{\ell}^{(2)}(r) &= 0 \quad r < a
\end{aligned} \tag{9.35}$$

The bound state energies are defined by the condition that $R(r)$ must vanish both at the origin and at the wall of the sphere, and are determined from the condition $j_{\ell}(ka) = 0$. Evidently we require the zeros of the spherical Bessel functions, a listing of which for $0 \leq \ell \leq 4$ is contained in Table 9.3. The quantum number n designates the order of the zero. For example, the first zero of $\ell = 3$ occurs when the argument is 6.99 (see Fig. 9.2). Because $j_{\ell}(kr)$ undulates about the abscissa forever,

Table 9.3 Zeros of spherical Bessel functions $j_{\ell}(kr)$ for $\ell = 0 - 4$ not including $j_{\ell}(0)$ for which all spherical Bessel functions vanish except $j_0(kr)$

n	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
1	3.14	4.49	5.76	6.99	8.18
2	6.28	7.73	9.10	10.42	11.71
3	9.42	10.94	12.32	13.70	15.04
4	12.57	14.01	15.52	16.93	18.30

Fig. 9.4 The lowest four energies $E_{n\ell}$ for a particle enclosed in an infinite spherical well for $\ell = 0 - 4$. The units of energy are $\hbar^2 / (2ma^2)$



there are an infinite number of zeros. Therefore, there are an infinite number of energy levels that can fit into this spherical well for each value of the orbital angular momentum.

To determine the energies, which will be characterized by quantum numbers n and ℓ , we set

$$k_{n\ell}a = \zeta_{n\ell} \quad (9.36)$$

where $\zeta_{n\ell}$ is the n th zero of the ℓ th spherical Bessel function. After substituting for k from Equation 9.28 we have

$$E_{n\ell} = \left(\frac{\hbar^2}{2ma^2} \right) [\zeta_{n\ell}]^2 \quad (9.37)$$

Figure 9.4 shows the energy levels for each of the five values of ℓ listed in Table 9.3 in units of $\hbar^2 / (2ma^2)$. The lowest level in each column corresponds to $n = 1$, the second level in each column to $n = 2$, and so on.

9.4 The Finite Spherical Square Well

The potential energy function in this case is

$$\begin{aligned} U(r) &= -U_0 & r < a \\ &= 0 & r > a \end{aligned} \quad (9.38)$$

The transition from the infinite well to the finite well requires the same technique as was applied in the one-dimensional case. It is, however, a bit more complicated because of the presence of angular momentum. The TISE for $r < a$ is

$$\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} - \frac{2m}{\hbar^2} U_0 \right] R(r) = E R(r) \quad (9.39)$$

or

$$\begin{aligned} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} - \frac{2m}{\hbar^2} (E + U_0) \right] R(r) &= 0 \\ \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} + k^2 \right] R(r) &= 0 \end{aligned} \quad (9.40)$$

where

$$k = \sqrt{\frac{2m(E + U_0)}{\hbar^2}} \quad (9.41)$$

Note that, for bound states, $-U_0 < E < 0$, so k , as defined in Equation 9.41, is real. Now, Equation 9.40 is identical to Equation 9.27, so inside the well we have the same solution as that in Section 9.3. That is, $R(r)$ consists only of $j_\ell(kr)$ because $n_\ell(kr)$ blows up at the origin. Therefore, in terms of the coordinate r , the wave function for $r < a$ is

$$R_\ell(r) = C_1 j_\ell(kr); \quad r < a \quad (9.42)$$

where C_1 is a constant.

Because the potential energy is zero for $r > a$, the TISE outside the well is the same as the suitably modified TISE of a free particle. The suitable modification is associated with the fact that the character of the wave function for $r > a$ must be exponentially decreasing because $E < 0$. Thus, using the same notation as that in Section 5.3 we have

$$\kappa = \sqrt{\frac{2m(-E)}{\hbar^2}} \quad (9.43)$$

where κ is real because $E < 0$. The outcome of this is that we must let $k \rightarrow i\kappa$ so that $\rho \rightarrow i\kappa r$ for $r > a$.

For $r > a$ we already know that the solution is a linear combination of $h_\ell^{(1)}(\rho)$ and $h_\ell^{(2)}(\rho)$. Making the substitution $k \rightarrow i\kappa$ in the asymptotic forms of the Hankel functions, Equations 9.33, we have

$$\begin{aligned}
\lim_{\rho \rightarrow \infty} h_\ell^{(1)}(i\kappa r) &= -\frac{1}{\kappa r} e^{-\kappa r} \cdot e^{-\ell\pi/2} \\
\lim_{\rho \rightarrow \infty} h_\ell^{(2)}(i\kappa r) &= \frac{1}{\kappa r} e^{\kappa r} \cdot e^{-\ell\pi/2}
\end{aligned} \tag{9.44}$$

This is a bound state problem, so we know immediately that the spherical Hankel function of the second kind must be excluded from the solution and we have

$$R_\ell(r) = C_2 h_\ell^{(1)}(i\kappa r); \quad a < r \tag{9.45}$$

It is comforting that the asymptotic form of $h_\ell^{(1)}(i\kappa r)$ conforms with the known asymptotic form of the wave function, Equation 9.24 for bound states.

In contrast to the infinite well, we cannot require that $R(ka)$ vanish. Instead, we must demand continuity of $R(kr)$ and its derivative at this boundary which we accomplish using the logarithmic derivative (see Section 5.3). From Equations 9.42 and 9.45 we have

$$\left[\frac{1}{j_\ell(ka)} \right] \left[\frac{dj_\ell(kr)}{dr} \right]_{r=a} = \left[\frac{1}{h_\ell^{(1)}(i\kappa a)} \right] \left[\frac{dh_\ell^{(1)}(i\kappa r)}{dr} \right]_{r=a} \tag{9.46}$$

This equation will, in general, lead to a transcendental equation, the solutions of which give the quantized energies in an analogous manner to the transcendental equations that were encountered in the case of the one-dimensional finite well of Section 5.3. The choice of mass m and the range of the force a determines the energies and their spacing. As discussed in Section 3.1.1, if $m = m_e$ and $a \approx a_0$, the level spacing is the order of that of atomic energy levels, that is, $\sim \text{eV}$. On the other hand, if the mass is that of a nucleon, $m \approx 2000m_e$, and the range that of nuclear forces, $a \approx 10^{-5}a_0$, then the energies will be the order of MeV.

Application: The deuteron

We may use the finite square well to approximate the potential energy that binds a neutron and a proton to form a deuteron. The force that binds these two particles is the strong, or nuclear, force which acts over only a very short range, $\sim 10^{-15}\text{m} = 1\text{fm}$. The unit of length used in nuclear physics is the fm, the femtometer often called the Fermi in recognition of the many contributions of Enrico Fermi to nuclear physics for which he received the Nobel Prize in Physics in 1938 “for his demonstrations of the existence of new radioactive elements produced by neutron irradiation, and for his related discovery of nuclear reactions brought about by slow neutrons”. Fortunately, there is enough known experimentally about the deuteron to permit the square well potential to give a reasonable approximation to reality. For example, we know that there is only one bound state of a deuteron and we know that it is very weakly bound, only about 2.2MeV, small by nuclear standards. The binding energy is easily calculated using the parameters in Table 9.4 in which the

Table 9.4 Masses and magnetic moments of the indicated particles

	Mass (MeV)	μ_j (μ_N)
Proton	938.78899	2.79
Neutron	939.571448	-1.91
Deuteron	1876.126013	0.86

mass of each of the three particles is given in MeV and the magnetic moments μ_j [$j = n(\text{neutron}), p(\text{proton}), d(\text{deuteron})$] are in units of the nuclear magneton μ_N . By analogy with the Bohr magneton, Equation 1.44, μ_N is defined as

$$\mu_N = \frac{e\hbar}{2m_p} \quad (9.47)$$

where m_p is the mass of the proton.

The binding energy of the proton to the neutron in the deuteron, E_d , is simply the difference of their individual rest masses. Therefore,

$$\begin{aligned} E_d &= m_p c^2 + m_n c^2 - m_d c^2 \\ &= 2.2 \text{ MeV} \end{aligned} \quad (9.48)$$

where m_p , m_n , and m_d are the masses of the proton, neutron and deuteron respectively.

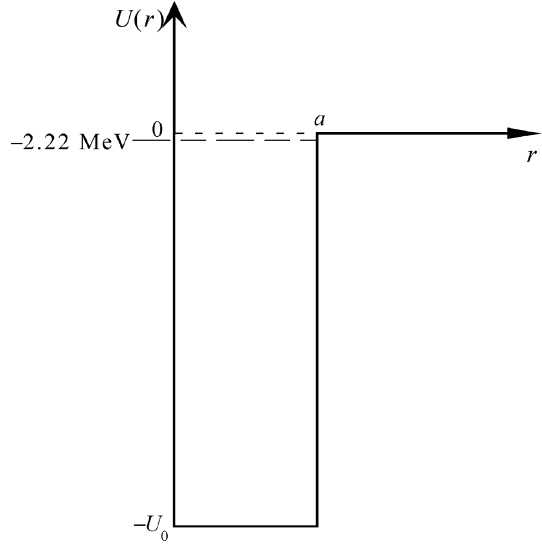
We can infer the nature of the ground state by examining the magnetic moments in Table 9.4. Before doing so let us note a couple of interesting points about these values, although these particular points are not germane to the problem at hand. First, the magnetic moment of the proton is not μ_N , it is nearly three times larger. Second, the magnetic moment of the neutron, despite the fact that it is uncharged, is not zero. It is negative and therefore opposite to the neutron spin angular momentum. The seemingly anomalous magnetic moments of the proton and neutron strongly indicate that they are not point particles, and that they have structure. This is in contrast to the electron for which the magnetic moment of the electron is very nearly one Bohr magneton.

Returning to the problem at hand, we deduce the orbital angular momentum of the neutron and proton in the deuteron ground state by comparing their magnetic moments with that of the deuteron. Using vectors for rigor,

$$\boldsymbol{\mu}_d = \boldsymbol{\mu}_p + \boldsymbol{\mu}_n + \boldsymbol{\mu}_\ell \quad (9.49)$$

where $\boldsymbol{\mu}_\ell$ represents the magnetic moment arising from orbital motion. From Table 9.4 we see that the algebraic sum of μ_p and μ_n essentially accounts for the magnetic moment of the deuteron. We therefore conclude that $\boldsymbol{\mu}_\ell \approx 0$. This is very good news because it means that the ground state is one for which $\ell = 0$, so the radial TISE does not contain a centrifugal term. There is more. From the magnetic moments we also know that the ground state is a triplet spin state because μ_d is the

Fig. 9.5 Schematic diagram of the three-dimensional square well for the deuteron. The single bound state is shown to be very near to the continuum of energy states for which $E > 0$. It is therefore very weakly bound



algebraic sum of μ_p and μ_n . Recall that the spin angular momentum and the magnetic moment of the neutron are in opposite directions, so the proton and neutron spins are parallel, a triplet. As in the discussion of magnetic moments above, this information is not needed in the calculation.

Because we already know the bound state energy, our goal is to work the problem in reverse from our usual procedure. Figure 9.5 illustrates the approximation to the potential with the lone bound state shown very close to $U(r) = 0$.

We seek to determine the depth of the well U_0 . Actually, we can only determine the product $U_0 a^2$, the strength of the well, but the nuclear force that glues the neutron to the proton is known to be of very short range $\sim 10^{-6} \text{ nm} = 1 \text{ fm}$. With $\ell = 0$, Equation 9.17 becomes

$$\begin{aligned} \frac{d^2 u(r)}{dr^2} + \frac{2\mu}{\hbar^2} (U_0 - E) u(r) &= 0 \quad r < a \\ \frac{d^2 u(r)}{dr^2} - \frac{2\mu}{\hbar^2} E u(r) &= 0 \quad r > a \end{aligned} \quad (9.50)$$

where μ is the reduced mass of the neutron and proton (not the magnetic moment), roughly $\frac{1}{2}m_p$. Bearing in mind that for a bound state $E < 0$, we make the usual substitutions

$$\begin{aligned} k &= \sqrt{\frac{2\mu(U_0 - E)}{\hbar^2}} \\ \kappa &= \sqrt{\frac{2\mu(-E)}{\hbar^2}} \end{aligned} \quad (9.51)$$

and obtain

$$\begin{aligned}\frac{d^2u(r)}{dr^2} + k^2u(r) &= 0 & r < a \\ \frac{d^2u(r)}{dr^2} - \kappa^2Eu(r) &= 0 & r > a\end{aligned}\quad (9.52)$$

which are identical with Equations 5.23 for the one-dimensional finite well. We can, therefore, use the same technique that was employed to solve the resulting transcendental equation in Section 5.3 with one important difference. We need not concern ourselves with the even solutions because they do not vanish at the origin. Thus, the three-dimensional problem is equivalent to a one-dimensional square well of the form (see Problem 5).

$$\begin{aligned}U(r) &= \infty & r < 0 \\ &= -U_0 & 0 < r < a \\ &= 0 & r > a\end{aligned}\quad (9.53)$$

As a consequence, we can use the same substitutions and graphs as those used to solve the transcendental equation for the odd wave functions in one-dimension. Letting

$$\eta = ka; \quad \zeta = \kappa a \quad (9.54)$$

so that

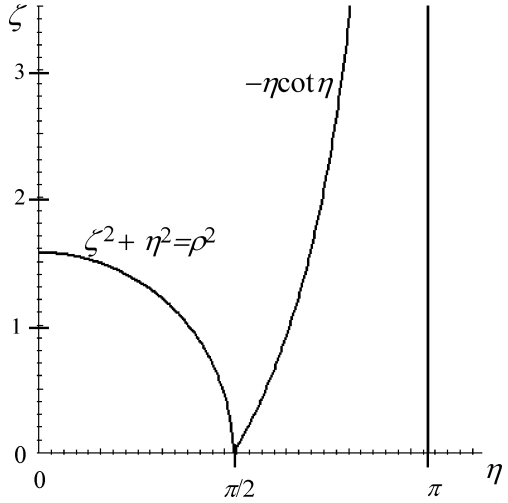
$$\begin{aligned}\eta^2 + \zeta^2 &= \frac{2\mu(U_0a^2)}{\hbar^2} \\ &= \rho^2\end{aligned}\quad (9.55)$$

and we arrive at the same equation for the energy as Equation 5.36:

$$\zeta = -\eta \cot \eta \quad (9.56)$$

Now, we could solve the transcendental equation, but we are, after all, making an extreme approximation by assuming that the attractive nuclear force that binds the proton and neutron is a spherical square well. Because we know that the binding energy is very weak, we expect that the energy of the ground state is only slightly negative. Under this assumption, and within the spirit of the square well approximation (another spherical horse), we may assume the extreme case as illustrated in Fig. 9.6, where $\rho = \pi/2$. Because $\zeta = 0$ when $-\eta \cot \eta = \pi/2$ there will be no intersection for $\rho^2 < \pi^2/4$, and there will be no bound states.

Fig. 9.6 Graphical solution of Equations 9.55 and 9.56. The value of ρ^2 was chosen so that it intersects the abscissa at $\pi/2$, the lower limit of ρ for the existence of a bound state



We may therefore calculate an upper limit on $U_0 a^2$, the strength of the well, by setting

$$\rho^2 = \frac{2\mu (U_0 a^2)}{\hbar^2} = \frac{\pi^2}{4} \quad (9.57)$$

Solving for $U_0 a^2$ we obtain

$$U_0 a^2 = \frac{\pi^2 (\hbar c)^2}{4 m_p c^2} \quad (9.58)$$

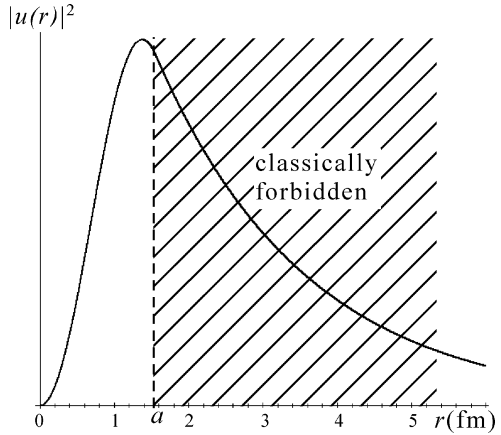
where we have substituted $\mu = m_p/2$ and multiplied top and bottom by c^2 to facilitate using the energy equivalent. Inserting $m_p c^2 \approx 939 \text{ MeV}$ and $\hbar c = 197.33 \text{ MeV} \cdot \text{F}$ we find

$$U_0 a^2 \approx 100 \text{ MeV} \cdot \text{fm}^2 \quad (9.59)$$

Note that for a bound state to actually exist there must be an intersection of the two curves in Fig. 9.6 so that, in reality, the strength of the well is less than $100 \text{ MeV} \cdot \text{fm}^2$. Nonetheless, in the spirit of the square well approximation, this upper limit permits reasonable estimates of U_0 and a .

The nuclear force has a very short range, $\sim 1 - 2 \text{ fm}$. If we choose $a \sim 1.6 \text{ fm}$, the required well depth for a bound state of -2.2 MeV is $\sim 40 \text{ MeV}$. An exact calculation shows it to be closer to 50 MeV , but, because of the approximations made, the discrepancy is not unreasonable. Figure 9.7 is a graph of $|u(r)|^2 = |rR(r)|^2$ for the single bound state of the deuteron using the square well approximation and $a = 1.6 \text{ fm}$. Note that plotting $|u(r)|^2$ does indeed give the proper probability

Fig. 9.7 The radial probability density of the bound state of the deuteron in the approximation that the potential is a finite square well



density because the factor r^2 in the the volume element in spherical coordinates is automatically included.

The wave function used in graphing the probability in Fig. 9.7 was calculated using $a = 1.4\text{fm}$. U_0 was adjusted to give the correct binding energy, 2.22MeV , and found to be 48MeV , in good agreement with the above calculation. Because the bound state is so close to the top of the well, it is not surprising that the proton and neutron have very high probability of being found far beyond the limits of the well.

9.5 The Isotropic Harmonic Oscillator

In Section 3.1.2 we studied the one-dimensional harmonic oscillator in detail. Here we will examine the three-dimensional analog of that problem. The major difference is that in three dimensions the orbital angular momentum must be included. To be very general we might write the potential energy function in Cartesian coordinates as

$$U(x, y, z) = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2 + \frac{1}{2}k_z z^2 \quad (9.60)$$

where the spring constants in x , y , and z are different, but this would not be a central force potential because we cannot write the potential as $U(r)$. If, however, all the spring constants are the same, that is,

$$k_x = k_y = k_z = k \quad (9.61)$$

the potential may indeed be written

$$\begin{aligned} U(r) &= \frac{1}{2}kr^2 \\ &= \frac{1}{2}\mu\omega^2r^2 \end{aligned} \quad (9.62)$$

where in this discussion we use μ for the mass to avoid confusion with the spherical coordinate quantum number m . In this case the harmonic oscillator potential is said to be isotropic because it is the same in all directions in space. We imagine a particle of mass μ attached to the end of a spring that is fixed at the origin. The particle is free to vibrate and rotate in the same manner in all directions. Because the potential is central we know immediately that, in spherical coordinates, the angular eigenfunctions are the spherical harmonics. We must solve the radial equation to obtain $R(r)$ and the energy eigenvalues. Before doing so, however, we notice that the TISE can be (easily) solved in Cartesian coordinates. Recalling our discussion of degeneracy, Section 9.1.2, we therefore expect to find an accidental degeneracy because we know that the TISE for central potential $U(r) = \frac{1}{2}kr^2$ can be separated in spherical coordinates.

9.5.1 Cartesian Coordinates

The Hamiltonian in Cartesian coordinates is

$$\begin{aligned} \hat{H}(x, y, z) &= \frac{p_x^2}{2\mu} + \frac{p_y^2}{2\mu} + \frac{p_z^2}{2\mu} + \frac{1}{2}\mu\omega^2x^2 + \frac{1}{2}\mu\omega^2y^2 + \frac{1}{2}\mu\omega^2z^2 \\ &= \left(\frac{p_x^2}{2\mu} + \frac{1}{2}\mu\omega^2x^2 \right) + \left(\frac{p_y^2}{2\mu} + \frac{1}{2}\mu\omega^2y^2 \right) + \left(\frac{p_z^2}{2\mu} + \frac{1}{2}\mu\omega^2z^2 \right) \\ &= \hat{H}_x(x) + \hat{H}_y(y) + \hat{H}_z(z) \end{aligned} \quad (9.63)$$

Because the Hamiltonian can be written as the sum of three Hamiltonians, each of which contains only a single coordinate, we know immediately that the eigenfunctions are the products of the individual eigenfunctions and the eigenvalues are the sums (Problem 15, Chapter 6). Notice that the TISE can be separated in Cartesian coordinates even if the potential is not isotropic. We are interested only in the isotropic case so, using Equation 3.49, the eigenfunctions are

$$\begin{aligned} \psi_{n_x n_y n_z}(x, y, z) &= \frac{1}{\sqrt{2^n n_x! n_y! n_z!}} e^{-\alpha^2(x^2+y^2+z^2)/2} H_{n_x}(x) H_{n_y}(y) H_{n_z}(z) \\ &= \frac{1}{\sqrt{2^n n_x! n_y! n_z!}} e^{-\alpha^2 r^2/2} H_{n_x}(x) H_{n_y}(y) H_{n_z}(z) \end{aligned} \quad (9.64)$$

where the $H_{n_i}(x_i)$ are Hermite polynomials and, as usual,

$$\alpha = \sqrt{\frac{\mu\omega}{\hbar}} \quad (9.65)$$

In Cartesian coordinates, then, the three mutually commuting operators that are employed are the individual Hamiltonians $\hat{H}_x(x)$, $\hat{H}_y(y)$, and $\hat{H}_z(z)$ and their simultaneous eigenfunctions are the $\psi_{n_x n_y n_z}(x, y, z)$. The energy eigenvalues are

$$\begin{aligned} E_{n_x n_y n_z} &= \left(n_x + \frac{1}{2}\right) \hbar\omega + \left(n_y + \frac{1}{2}\right) \hbar\omega + \left(n_z + \frac{1}{2}\right) \hbar\omega \\ &= (n_x + n_y + n_z + 3/2) \hbar\omega \\ &= (n + 3/2) \hbar\omega \end{aligned} \quad (9.66)$$

where

$$n = n_x + n_y + n_z \quad (9.67)$$

It is clear from Equation 9.66 that there is a degeneracy for all energy levels except for the ground state for which $n = 0$. Note that the zero point energy for the isotropic oscillator is $(3/2) \hbar\omega$, $(1/2) \hbar\omega$ for each coordinate.

The degeneracy g_n for a given energy level is the number of combinations of the (n_x, n_y, n_z) that can form the energy quantum number n . If we fix n_x , there will be $(n - n_x + 1)$ possible combinations of (n_y, n_z) that, together with n_x , “will add up to n . Therefore, if we sum $(n - n_x + 1)$ from $n_x = 0$ to $n_x = n$ we will obtain g_n . For a given n we have

$$\begin{aligned} g_n &= \sum_{n_x=0}^n (n - n_x + 1) \\ &= n \sum_{n_x=0}^n 1 - \sum_{n_x=0}^n n_x + \sum_{n_x=0}^n 1 \\ &= n(n+1) - \frac{n(n+1)}{2} + (n+1) \\ &= (n+1) \left[n - \frac{n}{2} + 1 \right] \\ &= \frac{(n+1)(n+2)}{2} \end{aligned} \quad (9.68)$$

where we used Gauss’ trick, Equation 8.157, to evaluate the summation of n_x .

9.5.2 Spherical Coordinates

The TISE

The mutually commuting operators that are used to effect this solution are the Hamiltonian \hat{H} , \hat{L}^2 , and \hat{L}_z . The eigenfunctions of the last two operators are the spherical harmonics which contain the information on the angular momentum states. Notice that solving the TISE in Cartesian coordinates did not provide any angular momentum information. This is because \hat{L}^2 and \hat{L}_z are not included in the mutually commuting operators that are used in the Cartesian coordinate separation.

Of course, the energies and their degeneracies are independent of the coordinate system, but the radial eigenfunctions will be different from the Cartesian coordinate eigenfunctions, Equation 9.66. Using the radial TISE for $u(r)$, Equation 9.17, we have

$$\begin{aligned} \frac{d^2 u(r)}{dr^2} - \frac{2\mu}{\hbar^2} \left\{ \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} + \frac{1}{2}\mu\omega^2 r^2 \right\} u(r) &= -\frac{2\mu}{\hbar^2} E u(r) \\ \left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} - \alpha^4 r^2 + \epsilon \right] u(r) &= 0 \end{aligned} \quad (9.69)$$

where, as before, $\alpha = \sqrt{\mu\omega/\hbar}$ and we have scaled the energy with the substitution

$$\epsilon = \frac{2\mu E}{\hbar^2} \quad (9.70)$$

From the solution to the isotropic oscillator in Cartesian coordinates, Equation 9.64, we know that, asymptotically, the wave function approaches $e^{-\alpha^2 r^2/2}$. Moreover, we also know that near the origin $u(r) \sim r^{\ell+1}$ (see Section 9.1.3). Therefore, using an approach similar to that applied to the differential equation for the one-dimensional oscillator, we write

$$u(r) = r^{\ell+1} e^{-\alpha^2 r^2/2} f(r) \quad (9.71)$$

It is $f(r)$ that we will eventually replace by a power series, but, in contrast to the one-dimensional case, there is an additional factor, $r^{\ell+1}$, in our trial solution because of the known behavior of $u(r)$ near the origin. Therefore, we must recognize that there will be some differences between the one-dimensional solution in Cartesian coordinates and the solution of the radial TISE in spherical coordinates. For this reason we will work out the three-dimensional solution in detail. It is also good practice for the important problem of the hydrogen atom that we will attack in the next chapter.

Equation 9.71 must be substituted in Equation 9.69 to obtain a differential equation for $f(r)$. The algebra is tedious, but may be simplified by first letting

$$F(r) = r^{\ell+1} f(r) \quad (9.72)$$

so that

$$u(r) = e^{-\alpha^2 r^2/2} F(r) \quad (9.73)$$

with the stipulation that

$$\lim_{r \rightarrow \infty} r^{\ell+1} f(r) < e^{\alpha^2 r^2/2} \quad (9.74)$$

We already know that this restriction on $F(r)$ will not be met if the series representing it is permitted to be an infinite series. We know this because in Section 9.5.1 we used the solution to the one-dimensional harmonic oscillator which contains the condition that the series must terminate. This termination led to energy quantization and, because the energy cannot be different, we must obtain the spherical coordinate solution using the same physics.

Substituting Equation 9.73 into Equation 9.69 we obtain

$$\frac{d^2 F}{dr^2} - 2\alpha^2 r \frac{dF}{dr} + \left[\epsilon - \alpha^2 - \frac{\ell(\ell+1)}{r^2} \right] F = 0 \quad (9.75)$$

and substituting Equation 9.72 into Equation 9.75 we arrive at

$$\frac{d^2 f}{dr^2} + 2 \left[\frac{(\ell+1)}{r} - \alpha^2 r \right] \frac{df}{dr} - [\alpha^2 (2\ell+3) - \epsilon] f = 0 \quad (9.76)$$

We attempt a series solution for $f(r)$ writing

$$f(r) = \sum_{p=0}^{\infty} a_p r^p \quad (9.77)$$

We must, however, stipulate that $a_0 \neq 0$ because, if it were, it would cause the leading term in $f(r)$ to be r^1 , thus violating the known r dependence near the origin, Equation 9.22. Substituting Equation 9.77 into Equation 9.76 we have

$$\begin{aligned} \sum_{p=2}^{\infty} p(p-1) a_p r^{p-2} + 2 \left[\frac{(\ell+1)}{r} - \alpha^2 r \right] \sum_{p=1}^{\infty} p a_p r^{p-1} \\ - [\alpha^2 (2\ell+3) - \epsilon] \sum_{p=0}^{\infty} a_p r^p = 0 \end{aligned} \quad (9.78)$$

or

$$\begin{aligned} & \sum_{p=2}^{\infty} p(p-1)a_p r^{p-2} + 2(\ell+1) \sum_{p=1}^{\infty} p a_p r^{p-2} \\ & - 2\alpha^2 \sum_{p=1}^{\infty} a_p p r^p - [\alpha^2(2\ell+3) - \epsilon] \sum_{p=0}^{\infty} a_p r^p = 0 \end{aligned} \quad (9.79)$$

Our goal is to convert Equation 9.79 to the form

$$\sum_{p=0}^{\infty} h(p, a_p, \ell) r^p = 0 \quad (9.80)$$

so that we may use the linear independence of the powers of r to set the function $h(p, a_p, \ell) = 0$ which, at least in the one-dimensional case, led to a recursion relation for the expansion coefficients, the a_p . Thus, we must change the indexes so all summations begin at $p = 0$ and all four terms contain r^p .

Let us examine each of the four summations in Equation 9.79. The first is easily converted to the desired form by making the substitution $p \rightarrow p + 2$ and the last requires no action. Clearly the second summation in Equation 9.79 requires $p \rightarrow p + 2$ to make the power of r correct, but then the summation begins with $p = -1$. Writing out the second summation after making the substitution $p \rightarrow p + 2$ and isolating the first term in the summation, the $p = -1$ term, we have

$$\sum_{p=-1}^{\infty} (p+2)a_{p+2}r^p = (1)a_1r^{-1} + \sum_{p=0}^{\infty} (p+2)a_{p+2}r^p \quad (9.81)$$

The presence of any powers of r less than unity is prohibited by the known behavior of $u(r)$ near the origin, Equation 9.22. This behavior is already built into our trial $u(r)$, Equation 9.71, by the inclusion of the factor $r^{\ell+1}$. Therefore, we must demand that $a_1 \equiv 0$ and the second summation in Equation 9.79 therefore becomes

$$\sum_{p=1}^{\infty} p a_p r^{p-2} \rightarrow \sum_{p=0}^{\infty} (p+2) a_{p+2} r^p \quad (9.82)$$

The third summation is easily converted to begin at $p = 0$ because $p r^p$ vanishes for $p = 0$. Therefore, beginning this summation at $p = 0$ merely adds a zero to the summation.

Equation 9.79 can now be written with the summation covering the range $0 \rightarrow \infty$. We have

$$\sum_{p=0}^{\infty} \{ [(p+2)(p+1) + 2(\ell+1)(p+2)] a_{p+2} - [2\alpha^2 p + \epsilon - \alpha^2(2\ell+3)] a_p \} r^p = 0 \quad (9.83)$$

so, setting the coefficient of r^p equal to zero, we obtain the desired recursion relation,

$$a_{p+2} = \frac{\alpha^2(2p+2\ell+3) - \epsilon}{(p+2)(p+2\ell+3)} a_p \quad (9.84)$$

Before analyzing the form of this relation let us note that, together with our deduction that $a_1 = 0$, it demands that *all* odd expansion coefficients vanish. Therefore, the power series $f(r)$ has even parity and the parity of the radial wave function is the parity of the quantity $(\ell+1)$.

Energy eigenvalues

To obtain the energy eigenvalues we proceed as in the one-dimensional harmonic oscillator. We have the series solution, but we know that if the series is permitted to be an infinite series, the wave function will not be normalizable. Although we have already treated this problem in one-dimension, we examine the recursion relation for the three-dimensional problem, Equation 9.84. Taking the ratio of successive terms we have

$$\begin{aligned} \lim_{p \rightarrow \infty} \frac{a_{p+2}}{a_p} &= \frac{2p\alpha^2}{p^2} \\ &= \frac{\alpha^2}{(p/2)} \end{aligned} \quad (9.85)$$

From our experience with the one-dimensional harmonic oscillator in Section 3.1.2, we conjecture that the p in the denominator indicates that the a_p will contain $p!$ in the denominator which suggests an exponential function. Because there are no odd terms in $f(r)$, it is likely that the series will involve $e^{(Kr)^2}$ where K is a real constant because the ratio of successive terms is positive. We therefore compare our asymptotic form of the expansion coefficient with those of such a series.

$$\begin{aligned} e^{(Kr)^2} &= 1 + \frac{(Kr)^2}{1!} + \frac{(Kr)^4}{2!} + \dots \\ &= \sum_{k=0}^{\infty} \frac{(Kr)^{2k}}{k!} \end{aligned} \quad (9.86)$$

The ratio of successive terms in the series representation of $e^{K^2 r^2}$ is therefore

$$\begin{aligned} \lim_{k \rightarrow \infty} \frac{K^{2(k+1)} / (k+1)!}{K^{2k} / k!} &= \lim_{k \rightarrow \infty} \frac{K^2}{k+1} \\ &= \frac{K^2}{k} \end{aligned} \quad (9.87)$$

Comparing Equation 9.87 with Equation 9.85, we identify K with α and k with $p/2$. Because the k can be any integer or zero and the index p can only be an even integer, the correlation is perfect. We conclude that the series part of our solution approaches $e^{\alpha^2 r^2}$ asymptotically which overpowers the $e^{-\alpha^2 r^2/2}$ in Equation 9.71, thus forcing $u(r)$ to diverge. To prevent this catastrophe we terminate the numerator of the recursion relation, Equation 9.84, after some value of $p = p_f$ and obtain

$$\alpha^2 (2p_f + 2\ell + 3) - \epsilon = 0 \quad (9.88)$$

After substituting for α and ϵ using Equations 9.65 and 9.70 we arrive at an expression for the quantized energies.

$$E_{p_f, \ell} = \hbar\omega (p_f + \ell + 3/2) \quad (9.89)$$

Now p_f must be an even integer or zero and we already know that ℓ can be any integer or zero. Therefore, the sum $(p_f + \ell)$ can take on any integral value or zero so we designate it by n . That is,

$$n = p_f + \ell \quad (9.90)$$

Finally, our expression for the energy is

$$E_n = \hbar\omega (n + 3/2) \quad (9.91)$$

which is identical to the energy obtained using Cartesian coordinates, Equation 9.66. Note that, while it appears that the quantum number ℓ determines the energy, this is not so because p_f changes to make n a constant for a given set of the allowed values of ℓ .

Degeneracy

It is again clear that the system has a greater degree of degeneracy than that of a central potential because the energy eigenvalues do not depend upon the quantum number ℓ . Therefore, for a given value of n there will be $\frac{1}{2}(n+1)(n+2)$ states having the same energy. Let us compute the degeneracy using spherical coordinate

quantum numbers and compare the result with that obtained using Cartesian coordinates (it had better be the same).

First, for a given value of n , the maximum allowable value of ℓ is n (see Equation 9.90). Also, p_f must be an even integer, so odd n implies odd ℓ and even n implies even ℓ . Therefore, for a given value of n , about half of the possible values of ℓ are excluded. Because each state that is designated by ℓ is $(2\ell + 1)$ -fold degenerate we can sum these degeneracies over the allowed values of ℓ . We consider odd and even values of n separately.

For even n there are $(n/2) + 1$ possible values of p_f because $p_f \leq n$ and it is even. (The $+1$ accounts for $p = 0$.) According to Equation 9.90 for each value of p_f there are $n - p_f$ possible values of ℓ . We may therefore sum the available m -states over all possible values of p_f and, to simplify the notation, we now let $p_f \rightarrow p$. Using

$$(2\ell + 1) = 2(n - p) + 1 \quad (9.92)$$

and Gauss' trick, Equation 8.157, we have

$$\begin{aligned} g_n^{\text{even}} &= \sum_{p/2=0}^{n/2} [2(n - p) + 1] \\ &= (2n + 1) \sum_{p/2=0}^{n/2} 1 - 2 \sum_{p/2=0}^{n/2} p \\ &= (2n + 1) \left(\frac{n}{2} + 1 \right) - 2 \left(\frac{n}{2} \right) \left(\frac{n}{2} + 1 \right) \\ &= \frac{1}{2} (n + 1)(n + 2) \end{aligned} \quad (9.93)$$

which is indeed the same as Equation 9.68. If n is odd, there will be $(n + 1)/2$ possible values of p ranging from $p = 0$ to $(n - 1)/2$ so, using the same approach,

$$\begin{aligned} g_n^{\text{odd}} &= \sum_{p/2=0}^{(n-1)/2} [2(n - p) + 1] \\ &= (2n + 1) \sum_{p/2=0}^{(n-1)/2} 1 - 2 \sum_{p/2=0}^{(n-1)/2} p \\ &= (2n + 1) \left[\frac{(n - 1)}{2} + 1 \right] - 2 \left(\frac{n - 1}{2} \right) \left(\frac{n - 1}{2} + 1 \right) \\ &= \frac{1}{2} (n + 1)(n + 2) \end{aligned} \quad (9.94)$$

we again get the correct degeneracy.

Relationship between n and ℓ

Because p_f is even, we know, from Equation 9.90, that n and ℓ must have the same parity. From this same equation we also know that the maximum value of ℓ (for a given n) is n . To understand better the nature of the relationship between n and ℓ we examine Fig. 9.8, which shows the effective potential for the isotropic harmonic oscillator. As was seen for the Morse potential, Fig. 9.1, increasing the angular momentum increases both the minimum value of the effective potential $U_{eff}(r)$ and r_0 , the position of this minimum.

Because the minimum in $U_{eff}(r, \ell = 0)$ is at $r = 0$, the graphs of $U_{eff}(r)$ versus r are qualitatively different from those shown in Fig. 9.1. The quantities r_0 and $U_{eff}(r_0, \ell)$ are easily found to be

$$r_0 = \left[\frac{\ell(\ell+1)\hbar^2}{\mu^2\omega^2} \right]^{1/4} \quad (9.95)$$

and

$$U_{eff}(r_0) = \sqrt{\ell(\ell+1)}\hbar\omega \quad (9.96)$$

(see Problem 8). Table 9.5 is a listing of the values of $U_{eff}(r_0)$ for each value of ℓ up to $\ell = 6$ in Equation 9.96 as well as the energy eigenvalues E_n in units of $\hbar\omega$. We see that this table is consistent with our deduction that $\ell \leq n$ because the minimum in the effective potential must always be lower than that of an allowed energy level.

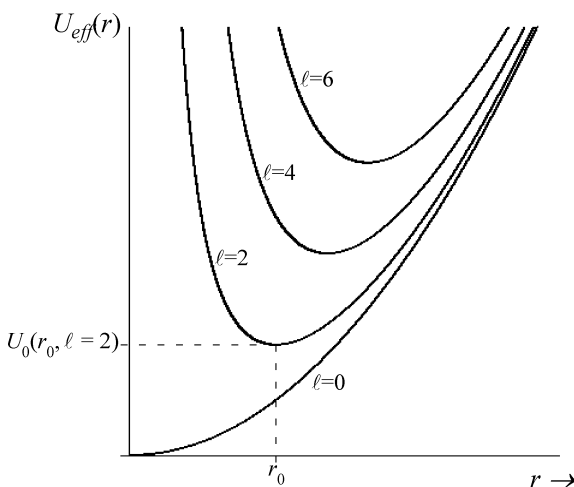


Fig. 9.8 The effective potential $U_{eff}(r)$ of the isotropic harmonic oscillator potential for four different values of the orbital angular momentum quantum number ℓ .

Table 9.5 Energies for $n = 0 - 6$ for the isotropic harmonic oscillator and the positions of the minima in $U_{eff}(r)$ for $\ell = 0 - 6$

n	$E_n(\hbar\omega)$	ℓ	$U_{eff}(r_0)(\hbar\omega)$
0	1.5	0	0
1	2.5	1	1.41
2	3.5	2	2.45
3	4.5	3	3.46
4	5.5	4	4.47
5	6.5	5	5.48
6	7.5	6	6.48

The relationship between E_n and $U_{eff}(r_0)$ is illustrated graphically in Fig. 9.9 for even ℓ . The ordinate is energy in units of $\hbar\omega$ and the abscissa is r in units of $\alpha^{-1} = \sqrt{\hbar/(\mu\omega)}$. When the value of $U_{eff}(r_0)$ for a given value of ℓ exceeds the energy of a level E_n , then that value of ℓ is inconsistent with E_n . Using the example of $\ell = 6$ as above, we see that all levels below $n = 4$ are excluded. Therefore, $n = 4$ is incompatible with $\ell = 6$ and we see that the maximum value of ℓ for $n = 4$ is $\ell = 4$. Note that $\ell = 5$ is excluded because n and ℓ must have the same parity. Of course, we would reach the same conclusion had we used odd values of ℓ for our example.

It is interesting that the zero point energy for $\ell = 0$ is $(3/2)\hbar\omega$ while that for higher values of the angular momentum is lower. In fact, the zero point energy is always slightly greater than $\hbar\omega$ as may be seen from Table 9.5. The reason for the

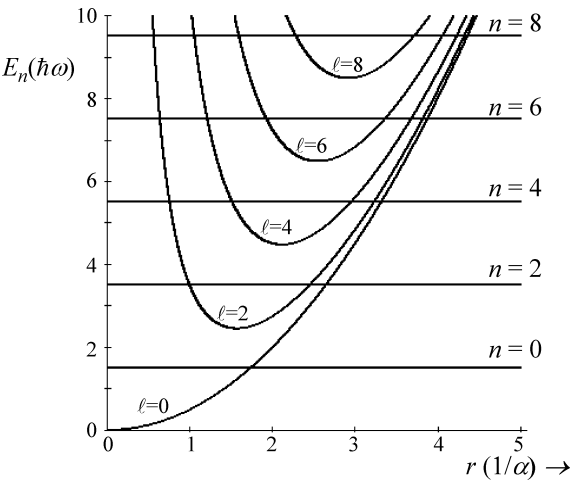


Fig. 9.9 The effective potential $U_{eff}(r)$ of the isotropic harmonic oscillator potential for four different even values of the orbital angular momentum quantum number ℓ . Also shown are the energy eigenvalues for the first five levels of even n

difference in the zero point energies is that for $\ell = 0$, all of the energy is radial in the three degrees of freedom, while, for nonzero ℓ , there must be rotational energy as well. The amount of rotational energy is just $U_{eff}(r_0)$ as given by Equation 9.96 so the zero point energy is the difference between the lowest energy state for a given value of ℓ , that is, $n = \ell$ (see Fig. 9.9) and $U_{eff}(r_0)$. This difference is

$$\begin{aligned}
 E_n - U_{eff}(r_0)|_{\ell=n} &= \left(n + \frac{3}{2}\right) \hbar\omega - \sqrt{n(n+1)} \hbar\omega \\
 &= \left(n + \frac{3}{2}\right) \hbar\omega - (n+1) \sqrt{\frac{n}{n+1}} \hbar\omega \\
 &= \left(n + \frac{3}{2}\right) \hbar\omega - (n+1) \sqrt{\frac{1}{1+1/n}} \hbar\omega \\
 &\approx \left(n + \frac{3}{2}\right) \hbar\omega - (n+1) \left(1 - \frac{1}{2n}\right) \hbar\omega \\
 &\approx \left(1 + \frac{1}{2n}\right) \hbar\omega
 \end{aligned} \tag{9.97}$$

It is seen that this energy difference is always greater than $\hbar\omega$ and it approaches this value as $n \rightarrow \infty$.

Energy eigenfunctions: associated Laguerre polynomials

To obtain the remaining portion of the radial wave function it is necessary to solve the differential equation for the series $f(r)$, Equation 9.76. Fortunately this equation can be put in the form of a differential equation having known solutions, the associated Laguerre polynomials. To convert Equation 9.76 to the standard form of the equation for which these special functions are the solutions, we make the substitution

$$z = \alpha^2 r^2 \tag{9.98}$$

which leads to

$$\left\{ z \frac{d^2}{dz^2} + \left[\left(\ell + \frac{1}{2} \right) + (1-z) \right] \frac{d}{dz} + \left[\frac{(n-\ell)}{2} \right] \right\} f(z) = 0 \tag{9.99}$$

This equation is of the form

$$\left\{ z \frac{d^2}{dz^2} + [q + (1 - z)] \frac{d}{dz} + p \right\} L_p^q(z) = 0 \quad (9.100)$$

where $L_v^q(z)$ are associated Laguerre polynomials [2]. These functions are defined in terms of the ordinary Laguerre polynomials $L_v(z)$. Comparing Equation 9.100 with Equation 9.99 we see that the functions $f(z)$ are the associated Laguerre polynomials $L_{(n-\ell)/2}^{\ell+\frac{1}{2}}(z)$ with

$$p = (n - \ell)/2 \quad \text{and} \quad q = \left(\ell + \frac{1}{2} \right) \quad (9.101)$$

The lower index is always an integer because n and ℓ must have the same parity, but the upper index is always half-integral. There is, however, no prohibition on half-integral upper indexes in the definition of the associated Laguerre polynomials.

It is important to bear in mind when working with Laguerre polynomials and associated Laguerre polynomials that there is not unanimity in the definitions of these special functions. One difference originates from two different definitions of the ordinary Laguerre polynomial from which the associated Laguerre polynomials are derived. In this book we adopt the conventions of Reference [1]. We begin by specifying that the ordinary Laguerre polynomials $L_v(z)$ are polynomials of degree v and are defined by the Rodrigues formula

$$L_v(z) = \frac{e^z}{v!} \frac{d^v}{dz^v} (z^v e^{-z}) \quad (9.102)$$

The other common definition of the ordinary Laguerre polynomial is identical, but $v!$ is omitted.

The associated Laguerre polynomial is often defined [1] as

$$L_v^q(z) = (-)^q \frac{d^q}{dz^q} L_{v+q}(z) \quad (9.103)$$

This definition, however, restricts the upper index to be an integer which is not the case here. We therefore use the Rodrigues formula for the associated Laguerre polynomial

$$L_v^q(z) = \frac{e^z z^{-q}}{v!} \frac{d^v}{dz^v} (z^{v+q} e^{-z}) \quad (9.104)$$

This definition includes the possibility of nonintegral upper indexes, but it reduces to Equation 9.103 when q is an integer [2].

The different definitions of the ordinary Laguerre polynomial are relatively easy to handle because they differ by only a constant multiplicative factor. There is, however, further confusion because there are, at least, two different definitions of the associated Laguerre polynomial. Both definitions occur in the literature so we will obtain the relationship between them. Assuming the same definition for the ordinary polynomial $L_\nu(z)$ as that in Equation 9.102, the alternative definition of the associated Laguerre polynomial to that of Equation 9.103 is

$$\mathcal{L}_\mu^q(z) = \frac{d^q}{dz^q} L_\mu(z) \quad (9.105)$$

where we have designated by $\mathcal{L}_\mu^q(z)$ the associated Laguerre polynomial as defined in Equation 9.105 to distinguish it from $L_\nu^q(z)$ as defined in Equation 9.103. Letting $\mu = \nu + q$ to eliminate μ from Equation 9.105 and multiplying both sides of this equation by $(-)^q$ makes the right-hand sides of Equations 9.103 and 9.105 identical. Therefore, the relation between the two definitions is

$$L_\nu^q(z) = (-)^q \mathcal{L}_{\nu+q}^q(z) \quad (9.106)$$

We will continue to use $L_\nu^q(z)$ as defined in Equation 9.104 and follow the convention of Reference [1].

Table 9.6 lists a few of the ordinary Laguerre polynomials. Because much of the confusion in the different definitions of these polynomials is the factorial in Equation 9.102, this factor is shown explicitly in Table 9.6.

Table 9.7 contains a few of the associated Laguerre polynomials. Only functions having half-integral upper indexes, those pertinent to the isotropic harmonic oscillator, are included. These functions are adjacent the state for which they are part of the eigenfunction, as designated by the quantum numbers n and ℓ . In the next chapter we will encounter associated Laguerre polynomials again, but this time both indexes will be integers.

The complete radial energy eigenfunctions for the isotropic oscillator in spherical coordinates are

$$R_{n\ell}(r) = N r^\ell e^{-\alpha^2 r^2/2} L_{(n-\ell)/2}^{\ell+\frac{1}{2}}(\alpha^2 r^2) \quad (9.107)$$

Table 9.6 The first seven Laguerre polynomials $L_\nu(z)$

$\nu! L_\nu^q(z)$
$0! L_0(z) = 1$
$1! L_1(z) = -z + 1$
$2! L_2(z) = z^2 - 4z + 2$
$3! L_3(z) = -z^3 + 9z^2 - 18z + 6$
$4! L_4(z) = z^4 - 16z^3 + 72z^2 - 96z + 24$
$5! L_5(z) = -z^5 + 25z^4 - 200z^3 + 600z^2 - 600z + 120$
$6! L_6(z) = z^6 - 36z^5 + 450z^4 - 2400z^3 + 5400z^2 - 4320z + 720$

Table 9.7 The associated Laguerre polynomials for the indicated quantum numbers of the isotropic harmonic oscillator

n	ℓ	$L_{(n-\ell)/2}^{\ell+\frac{1}{2}}(z)$
0	0	$L_0^{1/2}(z) = 1$
1	1	$L_0^{3/2}(z) = 1$
2	0	$L_1^{1/2}(z) = -z + \frac{3}{2}$
	2	$L_0^{5/2}(z) = 1$
3	1	$L_1^{3/2}(z) = -z + \frac{5}{2}$
	3	$L_0^{7/2}(z) = 1$
4	0	$L_2^{1/2}(z) = \frac{1}{2}z^2 - \frac{5}{2}z + \frac{15}{8}$
	2	$L_1^{5/2}(z) = -z + \frac{7}{2}$
	4	$L_0^{9/2}(z) = 1$

where the indexes on the associated Laguerre polynomial are in accord with Equations 9.101. To find N we use the orthogonality integral of the associated Laguerre polynomials. These functions are orthogonal over the interval $(0, \infty)$ if a weighting factor is inserted into the integral. The orthogonality integral is

$$\int_0^\infty [e^{-z} z^q] L_{\nu'}^q(z) L_\nu^q(z) dz = \frac{[\Gamma(\nu + q + 1)]}{\Gamma(\nu + 1)} \delta_{\nu\nu'} \quad (9.108)$$

where the weighting function is in square brackets; $\Gamma(\nu + q + 1)$ and $\Gamma(\nu + 1)$ are Γ -functions (see Appendix G). Taking the absolute square of $\psi(r, \theta, \phi)$ in Equation 9.107 and using the integral in Equation 9.108 leads to the value of the normalization constant N . Using $q = (\ell + \frac{1}{2})$ and $\nu = (n - \ell)/2$ we obtain (see Problem 10)

$$|N|^2 = 2\alpha^{2\ell+3} \frac{\Gamma[(n - \ell)/2 + 1]}{\Gamma[(n + \ell)/2 + 3/2]} \quad (9.109)$$

To clarify the nature of the radial eigenfunctions we show graphs of $R_{n\ell}(r)$ and the radial probability density $r^2 |R_{n\ell}(r)|^2 = |u(r)|^2$ in Fig. 9.10 for $n = 2$ and both permitted values of ℓ , 0 and 2. In accord with the behavior of the eigenfunctions discussed in Section 9.1.3, $R_{20}(r)$ is finite at the origin, but $R_{22}(r)$ vanishes at the origin. In contrast, both radial probability densities vanish at the origin because of the factor r^2 . Thus, the probability of actually finding the particle in an arbitrarily small volume ΔV about the origin is

$$\text{probability} = |R_{n\ell}(0)|^2 \Delta V \quad (9.110)$$

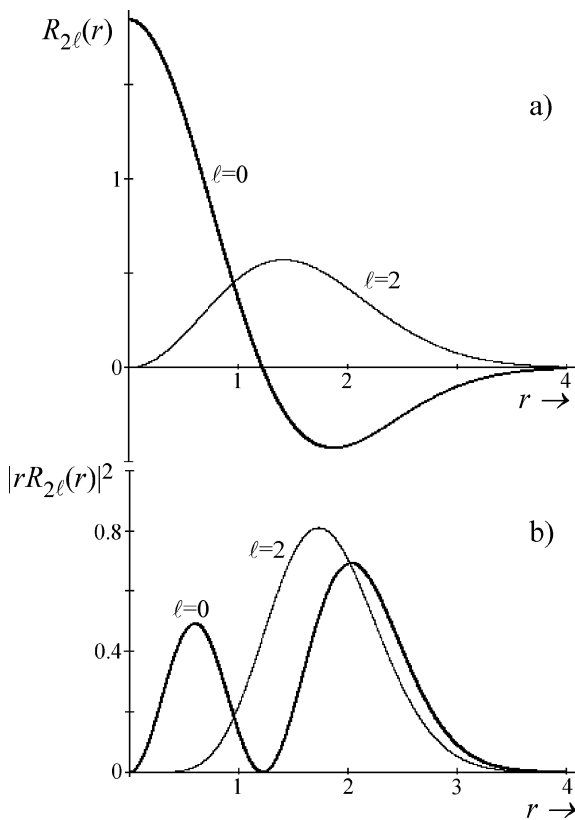


Fig. 9.10 (a) Graphs of the radial eigenfunctions $R_{20}(r)$ and $R_{22}(r)$. (b) Graphs of the radial probability distributions $|rR_{20}(r)|^2$ and $|rR_{22}(r)|^2$. The abscissas on both graphs are in units of $1/\alpha$

which vanishes for any nonzero value of ℓ . As noted previously, in all central force problems, the $\ell = 0$ state penetrates the force center. An easy way to rationalize this is that, classically, the orbital angular momentum is given by $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ so zero angular momentum with nonzero linear momentum implies that $\mathbf{r} = 0$.

The radial eigenfunctions shown in Fig. 9.10 exemplify the character of the radial isotropic harmonic oscillator wave functions. The structure of the eigenfunctions, and hence the probability distributions, becomes more complex as the difference between n and ℓ increases. This is because the number of nodes of the associated Laguerre polynomial is equal to the order of the polynomial, the lower index. Therefore, when $\ell = 0$ the number of nodes in the radial wave function is the maximum value. When $\ell \neq 0$ there is an additional node at the origin due to the r^ℓ factor in the radial wave function (see Equation 9.107), but, for the sake of uniformity, we consider the number of nodes to be those in the range $0 < r < \infty$. That is, we

include neither the node at the origin nor the node at infinity. Of course, the radial distribution function $|r R_{n\ell}(0)|^2$ always vanishes at the origin.

For reference, Table 9.8 is a listing of the lowest energy eigenfunctions of the isotropic oscillator. Figure 9.11 shows probability densities for eigenstates of the isotropic harmonic oscillator in the range $n = 0 - 4$. Each depiction of the designated state is a slice through the $y - z$ plane. The states are designated (n, ℓ, m) with the angular momentum quantum number ℓ denoted by the universally used spectroscopic designations.

For historical reasons, in this scheme the ℓ quantum number is represented by the lowercase letters with $\ell = 0, 1, 2, 3, \dots$ corresponding to s, p, d, f, g, \dots , respectively. Following f the sequence is alphabetical as shown in Table 9.9. While the correlation between ℓ and the letter designations is not obvious, nor is it even logical, it has been in use since the early days of atomic spectroscopy when the nature of the states was unknown. The last column lists the original meanings of the letter designations. These designations described the primary characteristic of each of the lines that were observed in atomic spectra (see Section 1.1.3). Despite the fact that these designations were invented for atomic spectroscopy, they transcend that field and apply to any orbital angular momentum.

Ladder operators

Because the one-dimensional harmonic oscillator eigenfunctions can be readily obtained by multiple application of the raising operator \hat{a}^\dagger to the ground state eigenfunction, it is natural to consider that possibility for the three-dimensional case. In Cartesian coordinates such a procedure is an extension of the one-dimensional procedure. In three dimensions we merely define raising operators corresponding to each of the coordinates. We may define a *vector* operator $\hat{\mathbf{a}}^\dagger$ in terms of these coordinate raising operators as

$$\hat{\mathbf{a}}^\dagger = \hat{a}_x^\dagger \hat{\mathbf{i}} + \hat{a}_y^\dagger \hat{\mathbf{j}} + \hat{a}_z^\dagger \hat{\mathbf{k}}$$
 (9.111)

Note that the operator $\hat{\mathbf{a}}^\dagger$ is distinguished from the one-dimensional raising operator, now designated \hat{a}_x^\dagger , by boldface to designate its vector status.

Table 9.8 Complete eigenfunctions for the isotropic harmonic oscillator in spherical coordinates

$(n \ell m)$	$\psi_{n\ell m}(r, \theta, \phi)$	Energy ($\hbar\omega$)
(0 0 0)	$2 \frac{\alpha^{3/2}}{\pi^{1/4}} e^{-\alpha^2 r^2/2} Y_{00}(\theta, \phi)$	$\frac{3}{2}$
(1 1 m)	$\sqrt{\frac{8}{3}} \cdot \frac{\alpha^{5/2}}{\pi^{1/4}} r e^{-\alpha^2 r^2/2} Y_{1m}(\theta, \phi)$	$\frac{5}{2}$
(2 0 0)	$\sqrt{6} \cdot \frac{\alpha^{3/2}}{\pi^{1/4}} \left(1 - \frac{2}{3} \alpha^2 r^2\right) e^{-\alpha^2 r^2/2} Y_{00}(\theta, \phi)$	$\frac{7}{2}$
(2 2 m)	$\frac{4}{\sqrt{15}} \cdot \frac{\alpha^{7/2}}{\pi^{1/4}} r^2 e^{-\alpha^2 r^2/2} Y_{2m}(\theta, \phi)$	$\frac{7}{2}$

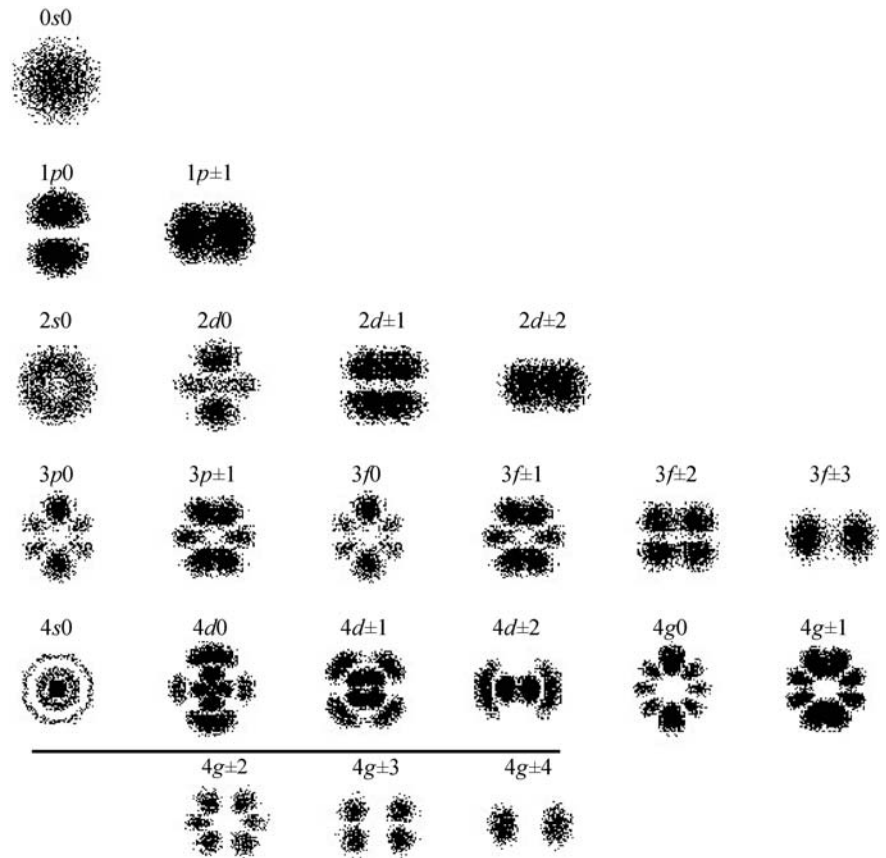


Fig. 9.11 Probability densities for eigenstates of the isotropic harmonic oscillator. The pictures are a slice through the $y - z$ plane and symmetric about the z -axis which is vertical and in the plane of the paper. The scale is proportional to n^2

Table 9.9 Correlation between the letter designations and the orbital angular momentum quantum number

ℓ	designation	meaning
0	s	sharp
1	p	principal
2	d	diffuse
3	f	fundamental
4	g	alphabetical
5	h	alphabetical

Now, $\hat{\mathbf{a}}^\dagger$ is indeed a vector operator since it is a linear combination of \mathbf{r} and $\hat{\mathbf{p}}$, both of which are vector operators. We may therefore construct the operator [3]

$$\hat{a}_+^\dagger = \hat{a}_x^\dagger + i\hat{a}_y^\dagger \quad (9.112)$$

as in Section 8.3. From that discussion we know that if \hat{a}_+^\dagger is applied to any of the eigenkets of the isotropic oscillator for which $m = \ell$, it will raise both of these quantum numbers. That is,

$$\hat{a}_+^\dagger |\ell\ell\rangle = C_a |(\ell+1)(\ell+1)\rangle \quad (9.113)$$

To investigate the effect of \hat{a}_+^\dagger on the remaining quantum number n we evaluate $[\hat{H}, \hat{a}_+^\dagger]$ using Table 7.1 and find

$$\begin{aligned} [\hat{H}, \hat{a}_+^\dagger] &= [\hat{H}, \hat{a}_x^\dagger] + i[\hat{H}, \hat{a}_y^\dagger] \\ &= \hbar\omega\hat{a}_+^\dagger \end{aligned} \quad (9.114)$$

Thus,

$$\hbar\omega\hat{a}_+^\dagger |n\ell\ell\rangle = \hat{H}\hat{a}_+^\dagger |n\ell\ell\rangle - \hat{a}_+^\dagger \hat{H} |n\ell\ell\rangle \quad (9.115)$$

or

$$\begin{aligned} \hat{H} \left\{ \hat{a}_+^\dagger |n\ell\ell\rangle \right\} &= \hbar\omega\hat{a}_+^\dagger |n\ell\ell\rangle + \hat{a}_+^\dagger \left(n + \frac{3}{2} \right) \hbar\omega |n\ell\ell\rangle \\ &= \left[(n+1) + \frac{3}{2} \right] \left\{ \hat{a}_+^\dagger |n\ell\ell\rangle \right\} \end{aligned} \quad (9.116)$$

Therefore, $\left\{ \hat{a}_+^\dagger |n\ell\ell\rangle \right\}$ is an eigenket of the Hamiltonian with eigenvalue $[(n+1) + 3/2]$. In other words, in addition to raising the angular momentum quantum numbers by unity, \hat{a}_+^\dagger also raises n by unity, and hence the energy, by one quantum. We have then

$$\hat{a}_+^\dagger |n\ell\ell\rangle = C_a |(n+1)(\ell+1)(\ell+1)\rangle \quad (9.117)$$

so that, starting with $|n\ell\ell\rangle = |000\rangle$, the ket representing the ground state of the isotropic harmonic oscillator, we can generate all eigenkets having $n = \ell = m$. Beginning with the eigenfunction corresponding to the ground state is not terribly presumptuous because, from the Cartesian coordinate solution, it is easily obtainable. Ignoring the normalization which can be calculated at any time, we apply \hat{a}_+^\dagger to $|000\rangle$ a total of p times:

$$\left(\hat{a}_+^\dagger\right)^p |000\rangle \propto |ppp\rangle \quad (9.118)$$

Now, consider the effect of the operator $\left(\hat{\mathbf{a}}^\dagger\right)^2$ on an arbitrary eigenket $|n\ell m\rangle$ where we have retained the boldface to distinguish $\hat{\mathbf{a}}^\dagger$ from the one dimensional raising operator. Because

$$\left[\hat{L}, \left(\hat{\mathbf{a}}^\dagger\right)^2\right] = 0 \quad (9.119)$$

(See Table 8.2) application of the operator $\left(\hat{\mathbf{a}}^\dagger\right)^2$ to an arbitrary eigenket leaves the angular momentum quantum numbers untouched, but raises the energy by two quanta, that is, $n \rightarrow (n + 2)$ so

$$\left(\hat{\mathbf{a}}^\dagger\right)^2 |n\ell m\rangle \propto |(n + 2) \ell m\rangle \quad (9.120)$$

Thus, successive application of $\left(\hat{\mathbf{a}}^\dagger\right)^2$ provides a means of changing only the quantum number n . It remains then to apply \hat{a}_+^\dagger and \hat{L}_- a suitable number of times to reach the desired $|n\ell m\rangle$ as shown below.

To convert $|000\rangle$ to $|n\ell m\rangle$ we begin by applying the operator $\left(\hat{\mathbf{a}}^\dagger\right)^2$ to $|000\rangle$ the appropriate number of times, $(n - \ell)/2$, which leads to

$$\left[\left(\hat{\mathbf{a}}^\dagger\right)^2\right]^{(n-\ell)/2} |000\rangle \propto |(n - \ell) 0 0\rangle \quad (9.121)$$

We are assured that $(n - \ell)/2$ is an integer because n and ℓ must have the same parity. Because application of \hat{a}_+^\dagger raises all three quantum numbers by unity, we see that ℓ applications of it will produce $|n\ell\ell\rangle$

$$\left(\hat{a}_+^\dagger\right)^\ell \left\{ \left[\left(\hat{\mathbf{a}}^\dagger\right)^2\right]^{(n-\ell)/2} |000\rangle \right\} \propto |n\ell\ell\rangle \quad (9.122)$$

To lower m to the desired value we simply apply \hat{L}_- to Equation 9.122 $(\ell - m)$ times so a general eigenket may be obtained from the prescription

$$\hat{L}_-^{\ell-m} \left(\hat{a}_+^\dagger\right)^\ell \left[\left(\hat{\mathbf{a}}^\dagger\right)^2\right]^{(n-\ell)/2} |000\rangle \propto |n\ell\ell_m\rangle \quad (9.123)$$

Application: The shell model of the nucleus

In Section 9.4 we used the finite square well to estimate the parameters of the deuteron, a nucleus consisting of a single proton and a single neutron. In the same spirit, we may use the isotropic harmonic oscillator as an approximation of the true internuclear potential of more complicated nuclei. Nuclei are composed of positively charged protons, charge $+e$, and neutral neutrons, collectively known as nucleons. The number of protons is the atomic number Z , while the number of neutrons is indicated by N . The total number of nucleons, protons plus neutrons, is the mass number $A = Z + N$. In nuclear physics, a given nucleus is often designated by the symbol AX , where X represents the chemical symbol of the element. Of course, this designation assumes that knowledge of the chemical symbol implies knowledge of Z so, for those of us who do not readily know or remember the number of protons in, for example, the nucleus of tellurium (Te), nuclei are often designated ${}_Z^AX$, for example ${}_{52}^{126}\text{Te}$.

As noted in Section 9.4, the force that binds nucleons in the nucleus is called the strong force or the nuclear force; it is of very short range, ~ 1 fm. It is 137 (yes, $1/\alpha$) times stronger than the electromagnetic force. Moreover, the strong force is always attractive. It was discovered empirically that if Z or N is one of the numbers

$$2, 8, 20, 28, 50, 82, 126$$

then the nucleus is particularly stable. These numbers are called “magic numbers.” What is more, if a nucleus is such that Z and N are magic numbers, then the nucleus is said to be “doubly magic” and the nucleus is even more stable than if it had a single magic number. Examples of doubly magic nuclei are ${}_2^4\text{He}$ (also known as an α -particle) and ${}_{82}^{208}\text{Pb}$.

Now, what is meant by nuclear stability? If a nucleus is particularly stable, then the energy required to remove one nucleon, the separation energy, is high. The separation energy is analogous to the ionization potential in atoms, Section 1.2.1, the energy required to liberate an electron from an atom. Thus, if we were to plot the ground state energies of the nuclei, we expect there to be groupings of nuclei as suggested in Fig. 9.12. In this figure the hypothetical levels are arranged so that the nucleus having atomic number Z is farther away from that having $Z + 1$ than from the nucleus having $Z - 1$ so the nucleus having atomic number Z is, in this fictitious example, magic. The occurrence of magic numbers suggests a filling of “shells” by the nucleons. The shells are presumed to be filled by the nucleons, but, because protons and neutrons are fermions, no two protons and no two neutrons can have the same set of quantum numbers in accord with the Pauli principle (see Section 8.6.2). The highest ground state of a given shell is far removed from the lowest ground state of the next shell as illustrated in Fig. 9.12.

In an effort to explain the apparent shell structure of nuclei, the isotropic harmonic oscillator potential was used to simulate the potential to which each nucleon is subjected as a result of all the other nucleons. For this reason the shell model of the nucleus is sometimes referred to as the single particle model. To investigate the

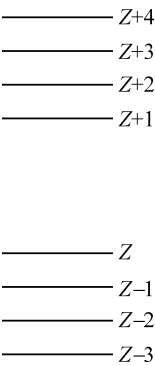


Fig. 9.12 Schematic diagram of the ground state energies of hypothetical nuclei, each represented by its atomic number. As illustrated, the nucleus having atomic number Z has a magic number

relationship to the magic numbers, we make a table of the number of states that can have given values of n and ℓ , bearing in mind that there is another factor of two that must be considered because each nucleon can have “spin up” or “spin down.” Thus, we require twice the degeneracy of the isotropic oscillator, Equation 9.94, or $(n + 1)(n + 2)$. Table 9.10 contains a listing of the possible states for each value of n . Also included in the table is the total number of states up to, and including, n (last column). It can be seen that the states up to $n = 2$ reproduce the first three magic numbers. The proton *and* the neutron each have a set of such states available to them so that, either or both can occupy a completed shell.

This would be the end of the story if all magic numbers were reproduced by simply considering the degeneracy of the oscillator. Is the partial agreement we have seen fortuitous or are there other factors to consider? In 1949 Maria Goeppert-Mayer and, independently, J. Hans D. Jensen included an interaction between the spin angular momentum and the motion of each of the nucleons to refine the shell structure of the basic shell model described above. For this work they were awarded the Nobel Prize in Physics in 1963 the citation for which reads “for their discoveries concerning nuclear shell structure”. The interaction they included is referred to as spin–orbit coupling. To remove the degeneracy for a given n in the basic model a more complete Hamiltonian must be employed. This is referred to as “breaking the

Table 9.10 Number of states N (including spin) for each isotropic harmonic oscillator state $n\ell$ together with the cumulative number of states N_T

n	ℓ	N	N_T
0	0	2	2
1	1	6	8
2	0, 2	12	20
3	1, 3	20	40
4	0, 2, 4	30	70
5	1, 3, 5	42	112
6	0, 2, 4, 6	56	168

degeneracy.” Although all levels having the same value of n have the same energy, these levels are “split” by terms added to the Hamiltonian. These terms lead to an additional angular momentum quantum number $j = \ell \pm \frac{1}{2}$ for each nucleon which has, as usual, $2j + 1$ values of m_j , the quantum number designating the z -component of j . In most cases, terms added to the Hamiltonian make it impossible to solve the TISE exactly, so approximation methods must be employed. This is a subject which will be covered later in this book (see Chapters 12 and 13, specifically Section 13.2), but for now we simply illustrate the result of the Mayer and Jensen treatments.

First, we alter our notation so it conforms with the commonly used designations of nuclear states. The angular momentum quantum number ℓ is represented by the letter designations listed in Table 9.9. Nuclear states are also assigned a number that corresponds to the order of appearance of a particular value of ℓ . Thus, for example, a $1d$ nuclear state is the first state having $\ell = 2$. Of course, this must correspond to $n = 2$, which is the lowest quantum number n for which ℓ can be 2. A following subscript j is appended to the state designation, but this is simply the $j = \ell \pm \frac{1}{2}$. As an aid in correlating the quantum numbers that arise from the spherical coordinate separation of the TISE with the common nuclear physics state designations, Table 9.11 contains the first few states in each notation.

Figure 9.13 shows the first four degenerate isotropic oscillator levels on the left. The isotropic oscillator potential is an approximation to the actual potential, so it likely overestimates the degeneracy. Therefore, in the center of the diagram are the levels for a central potential based on interpolation between a spherical square well and the isotropic oscillator. These levels need not concern us. The key point is that the inclusion of strong spin–orbit coupling, as shown on the right side of the diagram, “explains” the magic numbers. Also shown on the right side are the total number of states up to and including the one designated. As was seen above, breaking of the degeneracy of the levels is not necessary to explain the nuclear shell structure until the $n = 3$ level. According to the figure, spin–orbit coupling lowers one of the $1f$ states, the one for which the spin and orbital angular momentum are in the same direction (subscript $7/2$), to such a degree that this level is isolated from the other $n = 3$ states as well as the $n = 2$ states. The isolated $1f_{7/2}$ state thus constitutes a shell that accounts for the magic number 28 because there are $2(7/2) + 1 = 8$ states included in the $1f_{7/2}$ state. Notice that the total number of $n = 3$ states is $8 + 6 + 4 + 2 = 20$ which is indeed $(n + 1)(n + 2)$, consistent

Table 9.11 Correlation between the quantum numbers arising from solving the TISE in spherical coordinates for the isotropic oscillator and the common designation of states used in nuclear physics

$n\ell$	Nuclear physics
$0s$	$1s$
$1p$	$1p$
$2s$	$2s$
$2d$	$1d$
$3p$	$2p$
$3f$	$1f$

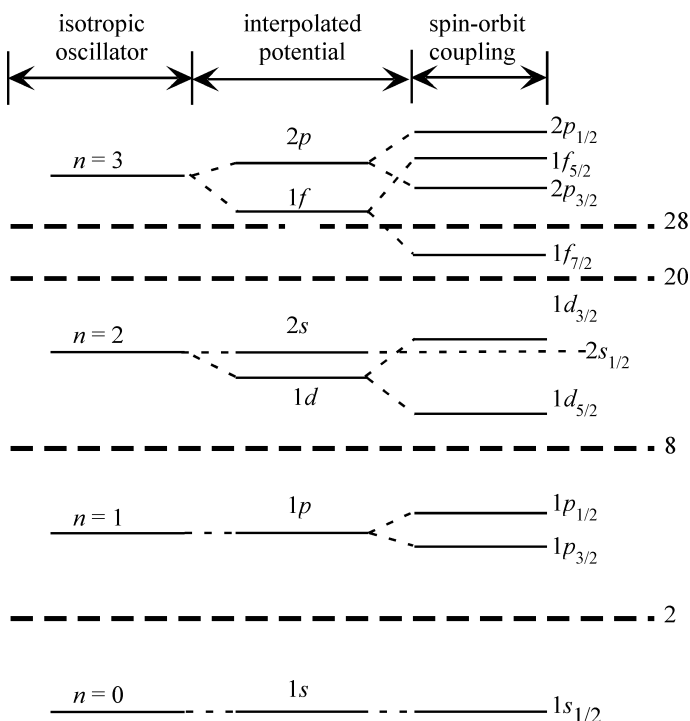


Fig. 9.13 Schematic diagram showing the degenerate isotropic oscillator levels up to $n = 3$. These degenerate levels are then split by the spin-orbit coupling. This scheme rationalizes the shell structure of the nucleus. The resulting shells are separated by heavy dashed lines. The diagram is not to scale

with the known degeneracy of this level. In Chapter 13 we will examine the effects of spin-orbit coupling in atomic systems. Incidentally, the fact that the spin-orbit coupling is “strong” is evidenced by the fact that the level shifts due to it are of the order of the separations between the unshifted levels. This is in contrast to the atomic case where the spin-orbit interaction is a small fraction of the gross energy separation.

9.6 The Morse Potential in Three Dimensions

In Section 5.4 we solved the TISE for the Morse potential [4], a potential energy function that has been widely used to describe diatomic molecules. The solution was predicated on our assumption that the molecule was not rotating, so we could treat the problem in one-dimension. If now we allow for rotation, we must add the centrifugal term to the potential to form the effective potential

$$U_{eff}(r) = D_e [e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}] + \frac{j(j+1)\hbar^2}{2\mu r^2} \quad (9.124)$$

where, as in Section 5.4, r is the internuclear separation; D_e and α are constants that are peculiar to each diatomic molecule as is r_e , the equilibrium internuclear separation when the molecule is not rotating. The reduced mass of the two nuclei is μ and the quantum number ℓ has been replaced by j , the customary designation for the quantum number associated with molecular rotation.

The solution in Section 5.4 is identical to the solution of the radial solution to the TISE using the effective potential of Equation 9.124 for $j = 0$. To consider nonzero values of j , we could make the simple approximation that the internuclear separation r_e does not change appreciably, even for excited rotational levels. This is the rigid rotor approximation discussed in Section 8.4.3. In this approximation we simply replace the coordinate r by the constant r_e in the centrifugal term. This amounts to adding a constant energy to the Hamiltonian, but the eigenfunctions do not change. For our purpose the rigid rotor approximation is too much of a simplification because it uncouples the vibrational and rotational motions. We wish to find the changes in the energy eigenvalues of Section 5.4 due to the interaction between the vibrational and rotational degrees of freedom.

Morse, in his original paper [4], and later Pekeris [5], showed how to obtain an improved approximation to the energy of a rotating molecule subjected to a Morse potential. In what follows we arrive at the same answer, but using a modification of their method [6]. The effect of the centrifugal term on a bound state potential such as the rotationless Morse potential is to increase the equilibrium position and to raise the minimum as shown in Fig. 9.1. Figure 9.14 is a similar illustration, but the notation has been adapted to conform with that of the present section. In terms of diatomic molecules, for $j \neq 0$ the internuclear separation has been stretched by the rotation. Moreover, the position of the minimum, D_e for $j \neq 0$, has been raised.

Our approach to approximating the energy of rotation on the molecule is to find the new equilibrium position $r_e^{(j)}$, and the new minimum energy $D_e^{(j)}$. We then use these parameters to construct a new Morse potential as though it represented

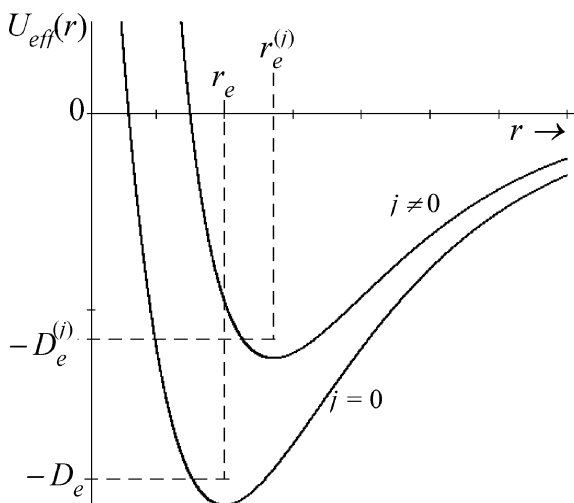


Fig. 9.14 The effective potential for the Morse potential showing the effects of rotation

a different rotationless molecule. The new potential contains the effects of rotation through $r_e^{(j)}$ and $D_e^{(j)}$.

Differentiating Equation 9.124 and setting it equal to zero to find $r_e^{(j)}$ leads to a transcendental equation. It is necessary, therefore, to make approximations to obtain a closed form for $r_e^{(j)}$ (and hence $D_e^{(j)}$). Of course, a computer solution can always be obtained, but even an approximate analytic solution can provide more insight into the nature of the problem. We begin by letting

$$x = \frac{r - r_e}{r_e} \quad (9.125)$$

which is the fraction by which the original equilibrium internuclear separation is stretched. The amount of stretching is small, that is, x is small. The problem now reduces to finding x_e , the value of x corresponding to $r = r_e^{(j)}$. The effective potential, Equation 9.124, in terms of x is

$$U_{eff}(x) = D_e [e^{-2\alpha r_e x} - 2e^{-\alpha r_e x}] + B \frac{1}{(1+x)^2} \quad (9.126)$$

where B is the rigid rotor energy given by

$$B = \frac{j(j+1)\hbar^2}{2\mu r_e^2} \quad (9.127)$$

Differentiating, we have

$$\frac{dU_{eff}(x)}{dx} = (-2\alpha D_e) [e^{-2\alpha r_e x} - e^{-\alpha r_e x}] - 2B \frac{1}{(1+x)^3} \quad (9.128)$$

which may be expanded in a Taylor series to

$$\frac{dU_{eff}(x)}{dx} = (-2\alpha r_e D_e) \left[-(\alpha r_e x) + \frac{3}{2} (\alpha r_e x)^2 \right] - 2B + 6Bx - 12Bx^2 \dots \quad (9.129)$$

Setting this derivative equal to zero and dropping terms higher than the first power in x leads to

$$x_e^{(j)} \simeq \left(\frac{1}{\alpha r_e} \right)^2 \left(\frac{B}{D_e} \right) \quad (9.130)$$

where $x_e^{(j)}$ is the value of x at $r = r_e^{(j)}$. Notice that $x_e^{(j)}$ is, as required, dimensionless and that it is small because the rotational energy is much smaller than the rotationless minimum in the Morse curve D_e . Thus,

$$\begin{aligned} r_e^{(j)} &= r_e (1 + x_e^{(j)}) \\ &= r_e \left(1 + \frac{B}{\alpha^2 r_e^2 D_e} \right) \end{aligned} \quad (9.131)$$

To find $D_e^{(j)}$ we evaluate

$$U_{eff}(r = r_e^{(j)}) = D_e [e^{-2\alpha r_e x_e} - 2e^{-\alpha r_e x_e}] + B \frac{1}{(1 + x_e)^2} \quad (9.132)$$

which, as was done for the derivative, we expand. Retaining terms up to the second power of x_e we have

$$\begin{aligned} -D_e^{(j)} &= U_{eff}(r = r_e^{(j)}) \\ &\simeq D_e [-1 + (\alpha r_e x_e)^2] + B (1 - 2x_e + 3x_e^2) \\ &= -D_e + B \left[1 - \frac{1}{\alpha^2 r_e^2} \left(\frac{R}{D_e} \right) \right] \end{aligned} \quad (9.133)$$

Thus, the minimum value of the Morse curve for $j \neq 0$ has been raised by an amount $B (1 - B/\alpha^2 r_e^2 D_e)$ and the position of the minimum in this curve has been shifted by $[B/(\alpha^2 r_e^2 D_e)] r_e$. We may therefore approximate the effective potential by simply making the substitutions

$$r_e \rightarrow r_e^{(j)} \quad \text{and} \quad D_e \rightarrow D_e^{(j)} \quad (9.134)$$

in the (rotationless) Morse function given by Equation 9.124. The energy eigenvalues, including rotational energy, can be calculated to this level of approximation by making the substitution $D_e \rightarrow D_e^{(j)}$ into the expression for the rotationless eigenvalues, Equation 5.67. As noted above, this approximation includes the effects of rotation because $D_e^{(j)}$ contains these effects. In terms of the frequency of the harmonic oscillator, which is the first approximation to the Morse potential, Equation 5.45,

$$\omega_0 = \sqrt{\frac{2D_e}{\mu}} \alpha \quad (9.135)$$

the total energy, including rotation and vibration, is

$$\begin{aligned} E_{nj} &= -D_e + \left(n + \frac{1}{2} \right) \hbar \omega_0 \left[1 - \frac{1}{4D_e} \left(n + \frac{1}{2} \right) \hbar \omega_0 \right] \\ &\quad - \left[\frac{j(j+1)\hbar^2}{4\mu r_e^2 D_e} \right] \left(n + \frac{1}{2} \right) \hbar \omega_0 \\ &\quad + \frac{j(j+1)\hbar^2}{2\mu r_e^2} \left[1 - \frac{\hbar^2 j(j+1)}{\mu^2 r_e^4 \omega_0^2} \right] \end{aligned} \quad (9.136)$$

Care should be taken in comparing this expression to that in the original paper by Morse because the customary symbol for frequency in radians/second, ω , is used to denote the frequency in cycles/second in the original paper. The first two terms in Equation 9.136 are identical to the energy eigenvalue deduced for the rotationless

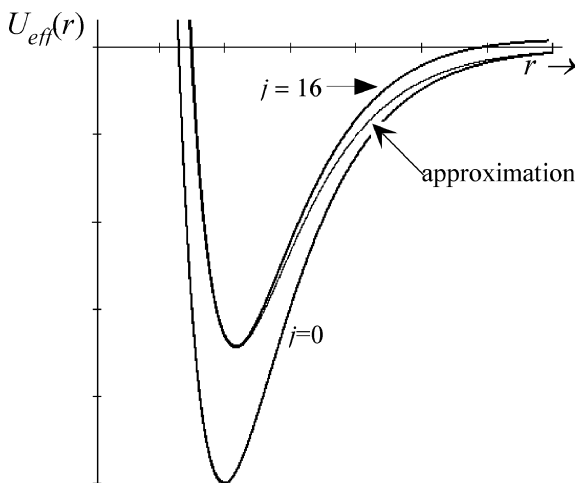


Fig. 9.15 Morse curves for $j = 0$ (for reference) and $j = 16$ (heavy lines). The curve marked approximation was constructed using $r_e^{(j=16)}$ and $D_e^{(j=16)}$ as parameters for a “rotationless” Morse function

Morse oscillator (see Equation 5.67). Therefore, these terms reflect only the effects of vibration. The last term contains only the quantum number j so, clearly, it arises from rotation. The only quantum number contained in the term on the third line is j , suggesting that this term is due to rotation only. Indeed, the first factor containing j is merely B , the rigid rotor energy. This term cannot include the effects of vibration. The term proportional to $[j(j+1)]^2$ might be regarded as a purely rotational term. This is not so because the vibrational motion is hiding in ω_0^2 . The most interesting term is the cross term, the term on the second line. This term is proportional to the product $(n + \frac{1}{2})j(j+1)$ so it clearly represents the coupling between the vibrational and rotational degrees of freedom. Moreover, it contains rotational parameters (μr_e^2) and vibrational parameters ($\mu \omega_0$).

Finally, we examine graphically the approximations in which the original equilibrium internuclear separation and the dissociation energy are replaced by their values obtained from the effective potential, that is, the values for which $r_e \rightarrow r_e^{(j)}$ and $D_e \rightarrow D_e^{(j)}$. Figure 9.15 shows these curves. An unusually high value was chosen for j in order to emphasize the difference between the actual effective potential and the approximate one since for low values, where the approximation is most valid, the curves are virtually indistinguishable.

9.7 Retrospective

For central potentials, separation of the TISE in spherical coordinates is possible because \hat{H} , \hat{L}^2 , and \hat{L}_z form a mutually commuting set. Because they commute with the Hamiltonian, the magnitude of the angular momentum and its z -component are

constants of the motion (see Equation 6.145) along with the TME. Indeed, this is also the case in classical mechanics where, for any central potential, angular momentum is conserved. In general, classical constants of the motion correspond to quantum mechanical operators that commute with \hat{H} . When a fourth commuting operator exists for a given potential energy function, the TISE can be separated in two coordinate systems, spherical and one other.

9.8 References

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Problems

1. Prove the identity given in Equation 9.5 that was used to deduce the correlation between \hat{L}^2 and ∇^2 . That is, show that $\hat{J}_\pm \hat{J}_\mp = \hat{J}^2 - \hat{J}_z^2 \pm \hbar \hat{J}_z$.
2. Show that

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) = \cot \theta \frac{\partial f}{\partial \theta} + \frac{\partial^2 f}{\partial \theta^2}$$

3. Use the identity in Problem 1 together with Equations 8.64, 8.65 and the result in Problem 2 to show that

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

4. A particle of mass m is subject to an unknown central potential $U(r)$ that vanishes as $r \rightarrow \infty$. One (unnormalized) eigenfunction in the usual spherical coordinates is $\psi(r, \theta, \phi) = e^{-\beta r} r^{3/2} \cos \theta$ where β is a real positive constant. Atomic units are recommended for convenience.
 - (a) Does this state have definite angular momentum? If so, why and what is the total angular momentum and the z -component of the angular momentum of this state?
 - (b) What is the energy eigenvalue of this state? Is the state bound or free? [Hint: Because $\lim_{r \rightarrow \infty} U(r) = 0$ all the energy at $r = \infty$ is kinetic energy.]
 - (c) What is the potential energy?

5. An impenetrable sphere of radius a is at the center of a spherical cavity of radius $b > a$. The walls of the cavity are also impenetrable. A particle of mass m is confined in the space between the inner sphere and the cavity wall. Find the eigenfunctions and the energy eigenvalues for $\ell = 0$.
6. For the deuteron, assume that the radius of the spherical square well $a = 1.5$ fm, the well depth is $U_0 = 40\text{MeV}$, and the deuteron binding energy is $E = -2\text{MeV}$.
 - (a) Show that $k \approx \sqrt{2\mu U_0/\hbar^2}$ and that the ratio $\kappa^2/k^2 \approx 0.05$.
 - (b) Show that $\kappa a \approx 0.23$.
 - (c) Using these approximations find the probability that the fraction of the time that the neutron and the proton spend outside $r = a$ the range of the nuclear force. What does this suggest about the deuteron?
7. A particle of mass m is trapped in a cube of side L that has impenetrable walls, a three-dimensional L -box.
 - (a) Find the energy eigenfunctions in Cartesian coordinates.
 - (b) Find the energy eigenvalues. How does the ground state energy compare with that of the one-dimensional L -box?
 - (c) What are the degeneracies of the first three energy levels?
8. Show that r_0 and $U_{eff}(\ell)$ as given in Equations 9.95 and 9.96 are correct.
9. Consider the isotropic harmonic oscillator to be a one-dimensional problem with potential given by the effective potential.
 - (a) By expanding the effective potential as a Taylor series about the position of the minimum r_0 show that the frequency of oscillation in the harmonic approximation is 2ω when $\ell \neq 0$.
 - (b) Show that the energy levels in this approximation depend upon both n and ℓ and are given by $E_{n\ell} = [(2n+1) + \sqrt{\ell(\ell+1)}]\hbar\omega$.
10. For the isotropic harmonic oscillator:
 - (a) Derive the normalization constant for the eigenfunctions, Equation 9.109.
 - (b) Show that this normalization constant gives the correct value for $\psi_{200}(r, \theta, \phi)$.
11. For the isotropic harmonic oscillator show the following:

$$(a) \quad r R_{00}(r) = \sqrt{\frac{3}{2}} \frac{1}{\alpha} R_{11}(r)$$

$$(b) \quad r R_{11}(r) = \frac{1}{\alpha} \left[\sqrt{\frac{3}{2}} R_{00}(r) - R_{20}(r) \right]$$

$$(c) \quad r R_{11}(r) = \frac{1}{\alpha} \sqrt{\frac{5}{2}} R_{22}(r)$$

12. Show that for an isotropic harmonic oscillator

$$\langle n\ell m | z | 000 \rangle = \frac{1}{\sqrt{2}\alpha} \delta_{n1} \delta_{\ell 1} \delta_{m0}$$

One of the results of Problem 11 should be helpful.

13. Calculate the energy eigenvalues for the n th state of the isotropic oscillator using the virial theorem and known expectation values. The result of Problem 7 will be helpful.
14. Prove the commutator relation of Equation 9.119.
15. A collection of isotropic oscillators having the same natural frequency ω is in a superposition of states at $t = 0$ that is given by

$$|\psi(\mathbf{r}, t = 0)\rangle = \sum_k a_k |n\ell m\rangle$$

where k stands for all combinations of isotropic oscillator quantum numbers $(n\ell m)$. Find $|\psi(\mathbf{r}, t)\rangle$ the state vector as a function of time.

Chapter 10

The Hydrogen Atom

Although the Bohr model of the atom correctly produced the energy levels of hydrogen, there are many discrepancies. For example, there is no provision in the Bohr model for zero orbital angular momentum. Fortunately, the TISE can be solved exactly for the Coulomb potential that binds the electron and the proton. While this is yet another example of a central potential, it is so important that it merits a separate chapter. The Coulomb potential is, however, not just another central potential. Like the isotropic harmonic oscillator discussed in Section 9.5, it exhibits an accidental degeneracy. That is, it is degenerate beyond the $2\ell + 1$ -fold degeneracy associated with any central potential, as discussed in Section 9.1.2. Consequently, the TISE can also be separated in parabolic coordinates. We will, however, study only the spherical coordinate solution. The angular portions of the wave functions are, of course, the spherical harmonics, so our task is to solve the radial equation. We will obtain the solution for the “one-electron atom,” an atom having Z protons in the nucleus, but only a single electron so that $Z = 1$ corresponds to a hydrogen atom. Nonetheless, we will continue to refer to it as the hydrogen atom even though Z will appear in many of the formulas.

10.1 The Radial Equation—Energy Eigenvalues

The Coulomb potential for the one-electron atom is

$$\begin{aligned} U(r) &= -\frac{Ze^2}{4\pi\epsilon_0} \cdot \frac{1}{r} \\ &= -Z(\alpha\hbar c) \cdot \frac{1}{r} \end{aligned} \quad (10.1)$$

where α is the fine structure constant, Equation 1.35, and c is the speed of light. As we have seen in Chapter 9, the effects of the centrifugal term are very important, so it is imperative that we examine the effective potential

$$\begin{aligned}
 U_{eff}(r) &= -Z[(\alpha c)\hbar] \cdot \frac{1}{r} + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2} \\
 &= -\frac{Z}{r} + \frac{\ell(\ell+1)}{2r^2} \quad (\text{a.u.})
 \end{aligned}
 \tag{10.2}$$

We will use the symbol m_e for the reduced mass of the electron–proton system because they are virtually the same due to the three-order-of-magnitude difference between the proton and electron masses. This approximation is even better if $Z > 1$. Also, in addition to the usual SI units, we will use atomic units (a.u.) as described in Section 1.3.

The form of the effective potential is similar to that already encountered for the Morse potential, but there are differences, so it is worth examining the hydrogen atom effective potential carefully. Figure 10.1 shows the effective potential for $\ell = 0 - 4$. The graph is plotted in a.u., so the abscissa has units of Bohr radii while each division on the ordinate is 0.1 a.u. (of energy) ≈ 2.72 eV.

As with the effective potential for a Morse function, increasing angular momentum raises the minimum of the well while moving the coordinate of the minimum to larger values of r . A major difference between these two effective potentials is that the Coulomb potential that binds the electron and the proton(s) becomes infinitely negative at $r = 0$ for $\ell = 0$. Thus, a particle in a bound state that is supported by the $\ell = 0$ Coulomb potential can pass through the origin and must have zero angular momentum. Indeed, because the radial wave function depends upon r^ℓ for small r (see Section 9.1.3) the wave function can be finite at $r = 0$. Classically, the particle

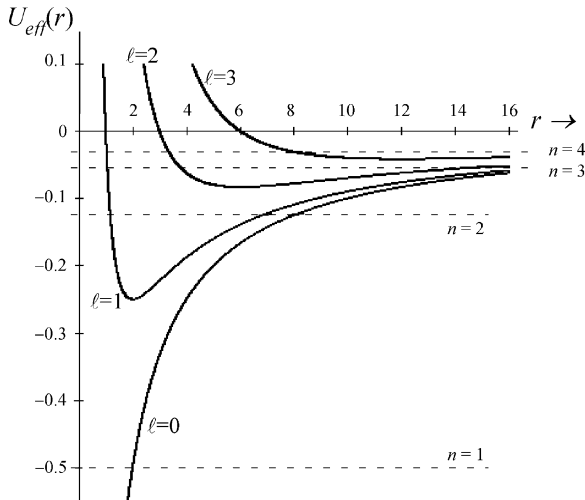


Fig. 10.1 The effective potential for the hydrogen atom for the lowest four values of orbital angular momentum. The horizontal dashed lines are the Bohr energies of the lowest four levels

can (actually “must”) pass through the origin because the angular momentum is zero. Notice that each Bohr energy is precluded from having $\ell = n$ so that $0 \leq \ell \leq n - 1$.

Figure 10.2 is similar to Fig. 10.1, but the vertical scale has been expanded to show more detail. In this figure we can easily see that the effective potential for $\ell = 3$ does indeed have a minimum (at $r = 12$ a.u., see Problem 2). Note that the effective potential for $\ell = 0$ has no minimum—it is a pure Coulomb potential.

To solve the radial equation, we begin with the usual substitution $u(r) = rR(r)$ and the radial equation for $u(r)$ in SI units, Equation 9.17, is

$$-\frac{\hbar^2}{2m_e} \frac{d^2 u(r)}{dr^2} + \left\{ -\frac{Ze^2}{4\pi\epsilon_0} \cdot \frac{1}{r} + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2} \right\} u(r) = E u(r) \quad (10.3)$$

Remembering that we seek the bound state energies, E will be a negative number, so we simplify Equation 10.3 with the substitution

$$r = \sqrt{-\frac{\hbar^2}{8m_e E}} \rho \quad (10.4)$$

which amounts to rescaling r and converting it to a dimensionless quantity. This substitution yields

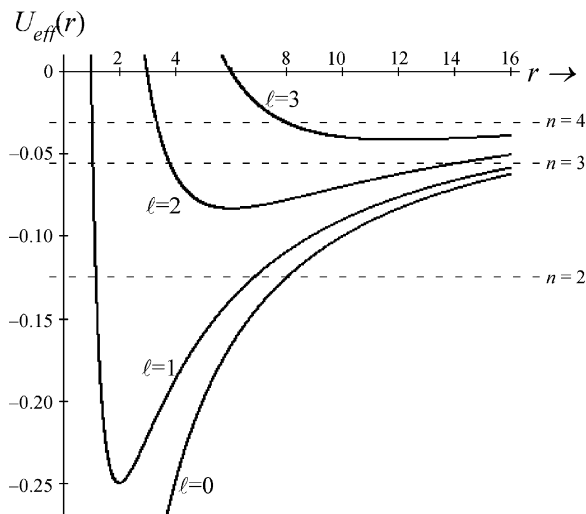


Fig. 10.2 The effective potential for a hydrogen atom as in Fig. 10.1, but the vertical scale has been expanded to show detail such as the minimum in $U_{eff}(r)$ for $\ell = 3$

$$\frac{d^2 u(\rho)}{d\rho^2} + \left\{ \frac{Ze^2}{4\pi\epsilon_0\hbar} \left(-\frac{m_e}{2E}\right)^{\frac{1}{2}} \cdot \frac{1}{\rho} - \frac{\ell(\ell+1)\hbar^2}{\rho^2} - \frac{1}{4} \right\} u(\rho) = 0 \quad (10.5)$$

Equation 10.5 is further simplified with the substitution

$$\begin{aligned} \lambda &= \frac{Ze^2}{4\pi\epsilon_0\hbar} \left(-\frac{m_e}{2E}\right)^{\frac{1}{2}} \\ &= Z\alpha \left(-\frac{m_e c^2}{2E}\right)^{\frac{1}{2}} \end{aligned} \quad (10.6)$$

with which we arrive at

$$\frac{d^2 u(\rho)}{d\rho^2} + \left\{ \frac{\lambda}{\rho} - \frac{\ell(\ell+1)}{\rho^2} - \frac{1}{4} \right\} u(\rho) = 0 \quad (10.7)$$

Notice that the energy eigenvalues are concealed in λ .

Let us reiterate a few points that have been made previously. There is nothing in what we have done (yet) that imposes any condition that will force the energy eigenvalues to be quantized. Indeed, although we will not treat the problem here, if we permit positive values of E , these positive energy eigenvalues will not be quantized. Of course, positive energies correspond to unbound states so the kinetic energy of the electron can be anything it pleases. We will see that in order to bind the electron to the nucleus only very specific energies (which we know are the Bohr energies, Equation 1.33) are permitted.

Now let us solve Equation 10.7. We know from Section 9.1.3 that if the potential energy does not decrease faster than $1/r^2$ as $r \rightarrow 0$, then, near the origin,

$$u(r) \sim r^{\ell+1} \quad \text{and} \quad R(r) \sim r^\ell \quad (10.8)$$

The Coulomb potential fits this condition, so, indeed, Equation 10.8 must represent the behavior of these functions near the origin. Moreover, as $\rho \rightarrow \infty$ Equation 10.7 is

$$\frac{d^2 u(\rho)}{d\rho^2} - \frac{1}{4} u(\rho) = 0 \quad (10.9)$$

the solutions of which are

$$u(\rho) \propto e^{\pm\rho/2} \quad (10.10)$$

The eigenfunctions must be square integrable (see Section 2.9), so we dismiss the increasing exponential because these bound state wave functions cannot diverge at infinity. Using these extreme forms of the function $u(r)$ to guide our choice of a possible solution we write

$$u(\rho) = \rho^{\ell+1} f(\rho) e^{-\rho/2} \quad (10.11)$$

where $f(\rho)$ represents the portion of the eigenfunction between $\rho \approx 0$ and $\rho \rightarrow \infty$. We now employ the same technique used in the solutions of the TISE for the harmonic oscillator and Morse potentials and expand $f(\rho)$ in a power series

$$f(\rho) = \sum_{j=0}^{\infty} a_j \rho^j \quad (10.12)$$

subject to the condition

$$\lim_{\rho \rightarrow \infty} \rho^{\ell+1} f(\rho) < e^{\rho/2} \quad (10.13)$$

Substituting into Equation 10.7 we obtain

$$\sum_{j=0}^{\infty} \{[j(j+1) + 2(\ell+1)(j+1)]a_{j+1} + (\lambda - \ell - 1 - j)a_j\} \rho^j \quad (10.14)$$

By now the procedure is familiar. We take advantage of the linear independence of the powers of ρ and force the coefficient of each power of ρ to vanish, thus obtaining a recursion relation between successive coefficients:

$$a_{j+1} = \frac{(j + \ell + 1 - \lambda)}{(j + 1)(j + 2\ell + 2)} a_j \quad (10.15)$$

Being seasoned veterans of solving the TISE we know that we had better check convergence before proceeding. From our experience with the harmonic oscillator and the Morse potentials, we suspect that we are going to have to terminate the series to impose physics on the mathematical solution of Equation 10.7. In other words, past experience suggests that the infinite series represented by the recursion relation in Equation 10.15 will cause the wave function to diverge so its termination will be required. Taking the limit, which is the same if the $\rho^{\ell+1}$ is included, we have

$$\lim_{j \rightarrow \infty} \frac{a_{j+1}}{a_j} = \frac{1}{j} \quad (10.16)$$

This limit is the same limit as that for the function e^ρ (see Problem 9 of Chapter 5) so, for large ρ , the series that represents $f(\rho)$ behaves as e^ρ . The condition set forth in Equation 10.13 is therefore not met, so we terminate the series. The only way that it can terminate is if λ in the numerator of Equation 10.15 is an integer, which we designate by n (good choice). We have then

$$\begin{aligned}\lambda &= n \\ &= Z\alpha \left(-\frac{m_e c^2}{2E} \right)^{\frac{1}{2}}\end{aligned}\quad (10.17)$$

and, solving for n , the principal quantum number, yields the energy which we now specify with a subscript:

$$\begin{aligned}E_n &= -Z^2 (m_e c^2) \alpha^2 \cdot \frac{1}{2n^2} \\ &= -\left(\frac{Z^2 e^2}{4\pi \epsilon_0} \right) \frac{1}{2n^2 a_0}\end{aligned}\quad (10.18)$$

This is precisely the Bohr energy that was derived in Section 1.2.1. Recall that writing the Bohr energy in terms of the fine structure constant is particularly convenient because the rest energy of the electron is well known to physics students, 0.511 MeV, so, with $Z = 1$, $E_1 = -13.6$ eV. Additionally, because the quantity $\alpha c \equiv 1$ in atomic units, the Bohr energy is

$$E_n = -Z \frac{1}{2n^2} \text{ (a.u.)} \quad (10.19)$$

Setting

$$n = j + \ell + 1 \quad (10.20)$$

in Equation 10.15 is equivalent to terminating the series given in Equation 10.12 after j terms. This provides a relationship between n and ℓ because the minimum value that j can have is zero. Therefore,

$$\ell \leq n - 1 \quad (10.21)$$

as was seen from examination of Fig. 10.1. The value of j that signifies the number of terms in the series after which the series is terminated is usually designated n_r and referred to as the radial quantum number so that

$$n = n_r + \ell + 1 \quad (10.22)$$

10.2 Degeneracy of the Energy Eigenvalues

Noting that the energy eigenvalues for the hydrogen atom are independent of the quantum number ℓ , we see immediately that there is an accidental degeneracy. This is similar to the extra degree of degeneracy encountered with the isotropic harmonic oscillator (see Section 9.5.2). To find the degree of this degeneracy g_H we must sum

the ℓ -states for a given principal quantum number n over all possible values of m , the quantum number associated with the z -component of angular momentum:

$$\begin{aligned}
 g_H &= \sum_{\text{all } \ell} m \\
 &= \sum_{\ell=0}^{n-1} (2\ell + 1) \\
 &= 2(n-1) \left(\frac{n}{2} \right) + n \\
 &= n^2
 \end{aligned} \tag{10.23}$$

where we have used Gauss' trick introduced in Section 8.6. Note that the degeneracy of the hydrogen atom is actually $2n^2$ because, in each state, the electron may have spin up or spin down. Because the TDSE, being a nonrelativistic equation, does not contain the spin, it must be put in "by hand" which accounts for the additional factor of 2 in the degeneracy.

The independence of the energy on ℓ as well as the restriction on the values of ℓ , Equation 10.21, are illustrated in Figs. 10.1 and 10.2. For example, it can be seen that the energy E_3 can be associated with any of the effective potentials corresponding to $\ell = 0, 1$, or 2 , but it falls below the minimum of the effective potential for $\ell = 3$. Therefore, the $n = 3$ state cannot have $\ell = 3$. This is a specific example of the restriction on the ℓ -values deduced in Section 10.1.

Because degeneracies are associated with classically conserved quantities, the operators that correspond to these classically conserved quantities commute with the Hamiltonian. Thus, in addition to the angular momentum there must be another classically conserved quantity that commutes with \hat{H} . This constant of the motion is the Lenz vector which will be discussed in the next chapter. For now it is sufficient to know that the Lenz vector A points along the major axis of the closed elliptical orbit that results from the bound state solution of the Kepler problem, the potential for which is

$$U_{\text{classical}}(r) = -\frac{k}{r} \tag{10.24}$$

where k is a constant. In the Kepler problem, $U_{\text{classical}}(r)$ is the gravitational potential, which has the same r -dependence as the Coulomb potential. The fact that A is a constant of the motion assures us that the major axis remains fixed in space and the elliptical orbit does not precess. (The celebrated precession of the perihelion of the orbit of the planet Mercury is due to effects other than the gravitational potential.) Fixed orbits occur classically for only two central potentials, the gravitation/Coulomb potential and the isotropic harmonic oscillator potential (which is related to the accidental degeneracy in the oscillator). Fixed orbits are thus related to the classical degeneracy that correlates to the quantum mechanical degeneracy. The energy eigenvalues of both the hydrogen atom and isotropic oscillator systems are

independent of the angular momentum, just as in their classical analogs. The independence of the energy on the angular momentum in the classical Kepler problem manifests itself as an independence of the energy on the length of the semiminor axis b which depends upon the angular momentum [1]. The classical energy depends only upon the semimajor axis a which does *not* depend upon the angular momentum. Thus, there are an infinite number of elliptical orbits, all having the same semimajor axis, but each having a different value of b (and, hence, angular momentum). The classical energy is given by

$$E = -\frac{k}{2a} \quad (10.25)$$

As discussed in Section 9.1.2, when accidental degeneracies occur, the TISE can be separated in more than one coordinate system. For hydrogen this additional system is parabolic coordinates. For the isotropic oscillator it is Cartesian coordinates.

10.3 The Radial Equation—Energy Eigenfunctions

Although we have determined the energy eigenvalues and their degeneracies, we have yet to actually solve the radial TISE for the energy eigenfunctions. The general form of these eigenfunctions is given by Equation 10.11, but we must find $f(\rho)$. To this end we insert $u(\rho)$ from Equation 10.11 into Equation 10.7 with $\lambda = n$. This leads to a differential equation for $f(\rho)$:

$$\rho \frac{d^2 f(\rho)}{d\rho^2} + [2(\ell + 1) - \rho] \frac{df(\rho)}{d\rho} + (n - 1 - \ell) f(\rho) = 0 \quad (10.26)$$

Equation 10.26 is of the same form as Equation 9.100 provided

$$q = 2\ell + 1 \quad \text{and} \quad p = n - \ell - 1 \quad (10.27)$$

Therefore,

$$f(\rho) = L_{n-\ell-1}^{2\ell+1}(\rho) \quad (10.28)$$

the associated Laguerre polynomial. The radial wave function is therefore

$$R(\rho) = N \rho^\ell e^{-\rho/2} L_{n-\ell-1}^{2\ell+1}(\rho) \quad (10.29)$$

where $\rho = 2Zr/(na_0)$ (see Problem 1) and N is the normalization factor.

The associated Laguerre polynomials were discussed in Section 9.5.2. In that case our interest was on half-integer upper indexes. For hydrogen, both indexes are integers. Table 10.1 lists a few associated Laguerre polynomials for low-lying states.

Table 10.2 contains some relations involving these polynomials including the general formulas for those having lower indexes 0–2.

Table 10.1 The associated Laguerre polynomials for n and ℓ

n	ℓ	$L_{n-\ell-1}^{2\ell+1}(\rho)$
1	0	$1!L_0^1 = 1$
2	0	$2!L_1^1 = 4 - 2\rho$
	1	$3!L_0^3 = 6$
3	0	$3!L_2^1 = 3\rho^2 - 18\rho + 18$
	1	$4!L_1^3 = 96 - 24\rho$
	2	$5!L_0^5 = 120$

Table 10.2 Some special properties of associated Laguerre polynomials having integer indexes

$$\begin{aligned}
L_v^0(\rho) &= L_v(\rho) \\
L_0^q(z) &= 1 \\
L_1^q(\rho) &= -\rho + q + 1 \\
L_2^q(\rho) &= \frac{\rho^2}{2} - (q+2)\rho + \frac{(q+1)(q+2)}{2} \\
\int_0^\infty [e^{-z}\rho^q] L_v^q(\rho) L_{v'}^q(\rho) d\rho &= \frac{[(v+q)!]}{v!} \delta_{vv'} \\
\rho L_v^q(\rho) &= (2v+q+1) L_v^q(\rho) - (v+1) L_{v+1}^q(\rho) - (v+q) L_{v-1}^q(\rho)
\end{aligned}$$

To find the normalization constant N in Equation 10.29, we use the normalization condition for $R_{n\ell}(r)$. That is,

$$\int_0^\infty |R_{n\ell}(r)|^2 r^2 dr = 1 \quad (10.30)$$

After substituting the energy E_n from Equation 10.18 it can be shown (see Problem 1) that

$$\rho = \frac{2Z}{n} \left(\frac{r}{a_0} \right) \quad (10.31)$$

so, isolating the desired constant N , we have

$$\begin{aligned}
|N|^{-2} &= \left(\frac{na_0}{2Z} \right)^3 \int_0^\infty \rho^{2\ell} e^{-\rho} [L_{n-\ell-1}^{2\ell+1}(\rho)]^2 (\rho^2 d\rho) \\
&= \left(\frac{na_0}{2Z} \right)^3 \int_0^\infty \rho^{2\ell+1} e^{-\rho} [\rho L_{n-\ell-1}^{2\ell+1}(\rho)] [L_{n-\ell-1}^{2\ell+1}(\rho)] d\rho \\
&= \left(\frac{na_0}{2Z} \right)^3 \int_0^\infty \rho^q e^{-\rho} [\rho L_v^q(\rho)] L_v^q(\rho) d\rho
\end{aligned} \quad (10.32)$$

where $q = (2\ell + 1)$ and $v = (n - \ell - 1)$. The orthogonality relation is given in Table 10.2, but, unfortunately, it differs from Equation 10.32 which has an extra ρ . There are, however, a number of recurrence relations for the associated Laguerre

polynomials, one of which is extremely helpful here. The one we require is listed in Table 10.2, last line. When substituted in Equation 10.32 we obtain two extra integrals, both of which vanish because of orthogonality. The remaining integral is of the form of the orthogonality integral, Equation 9.108, and is reprised in Table 10.2, second line from the bottom. This procedure leads to

$$\begin{aligned} |N|^{-2} &= \left(\frac{2Z}{na_0} \right)^3 (2\nu + q + 1) \frac{[(\nu + q)!]}{\nu!} \\ &= \left(\frac{2Z}{na_0} \right)^3 2n \frac{[(n + \ell)!]}{(n - \ell - 1)!} \end{aligned} \quad (10.33)$$

so that

$$N = \sqrt{\frac{1}{2n} \left(\frac{2Z}{na_0} \right)^3 \frac{(n - \ell - 1)!}{(n + \ell)!}} \quad (10.34)$$

and the normalized radial wave function is

$$R_{n\ell}(r) = \left[\frac{1}{2n} \left(\frac{2Z}{na_0} \right)^3 \frac{(n - \ell - 1)!}{(n + \ell)!} \right]^{1/2} \left(\frac{2Zr}{na_0} \right)^\ell e^{-Zr/na_0} L_{n-\ell-1}^{2\ell+1} \left(\frac{2Zr}{na_0} \right) \quad (10.35)$$

Note that in some books the factor $(n + \ell)!$ in the denominator of the radical in Equation 10.34 is cubed. If so, this indicates that the alternative definition of the ordinary Laguerre polynomials, as discussed in Section 9.5.2, has been used. That is, the factorial in the denominator of Equation 9.102 has been omitted. Moreover, when the “other” convention on associated Laguerre polynomials is employed, it changes the lower index. Rather than $(n - \ell - 1)$ it is $(n + \ell)$. This difference provides a convenient way of determining which definition is being used in a particular reference. The first few radial eigenfunctions are tabulated in Table 10.3 using the convention adopted in this book. They are listed in a way such that the exponent is kept intact in the polynomials.

The radial wave functions $R_{n\ell}(r)$, and the probability distributions, the radial distribution functions $|R(r)|^2 r^2 dr$, are shown in Fig. 10.3 for all states having $n = 1 - 3$. These graphs illustrate many of the general features of $R_{n\ell}(r)$ and $|R(r)|^2 r^2 dr$. Comparing all of the radial wave functions for which $\ell = 0$ with those for which $\ell \neq 0$ we see that the $R_{n0}(r)$ are the only ones for which the magnitude of $R(r)$ at the origin is nonzero. This is required, inasmuch as the wave function must behave as r^ℓ near the origin.

Let us examine the number of nodes, points at which the function crosses the abscissa, in these functions. When counting nodes, we ignore those at $r = 0$ and $r = \infty$. For example, in Fig. 10.3 it is seen that for $n = 3$, $\ell = 2$ there are no nodes. One attraction of using the definition of associated Laguerre polynomials employed here is that the lower index, $(n - \ell - 1)$, is the number of nodes.

Table 10.3 A few radial hydrogen atom eigenfunctions

$R_{10}(r) = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$
$R_{20}(r) = 2 \left(\frac{Z}{2a_0} \right)^{3/2} \left(1 - \frac{Zr}{2a_0} \right) e^{-Zr/2a_0}$
$R_{21}(r) = \frac{2}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \left(\frac{Zr}{2a_0} \right) e^{-Zr/2a_0}$
$R_{30}(r) = 2 \left(\frac{Z}{3a_0} \right)^{3/2} \left[1 - 2 \left(\frac{Zr}{3a_0} \right) + \frac{2}{3} \left(\frac{Zr}{3a_0} \right)^2 \right] e^{-Zr/3a_0}$
$R_{31}(r) = \frac{4\sqrt{2}}{3} \left(\frac{Z}{3a_0} \right)^{3/2} \left(\frac{Zr}{3a_0} \right) \left[1 - \frac{1}{2} \left(\frac{Zr}{3a_0} \right) \right] e^{-Zr/3a_0}$
$R_{32}(r) = \frac{2}{3} \sqrt{\frac{2}{5}} \left(\frac{Z}{3a_0} \right)^{3/2} \left(\frac{Zr}{3a_0} \right)^2 e^{-Zr/3a_0}$

According to the definition of the radial quantum number n_r (see Equation 10.22), the lower index on the associated Laguerre is n_r . Thus, n_r represents the number of nodes in the radial wave function. It is seen that when ℓ has its maximum value, $(n - 1)$, the radial wave function is nodeless. In such cases the maximum in the radial distribution function r_{\max} occurs at precisely the Bohr radius for that value of n , that is, $r_{\max} = n^2 a_0$, which is the most probable value of r at which the electron

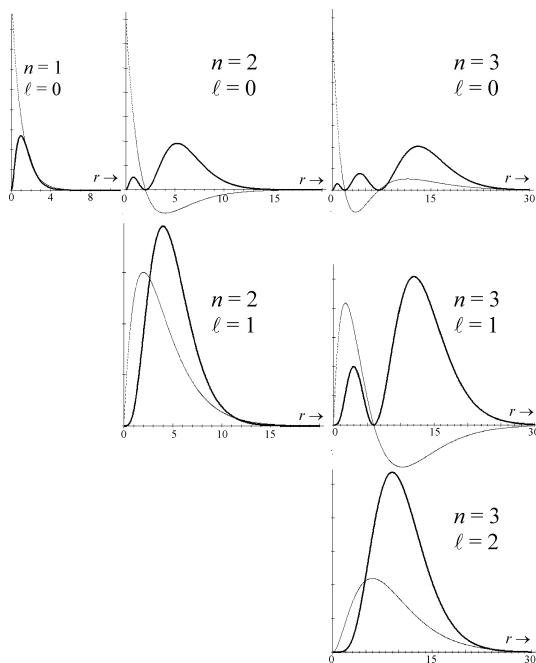


Fig. 10.3 The radial eigenfunctions $R_{n\ell}(r)$ (thin line) and the radial distribution functions $|rR_{n\ell}(r)|^2$ (heavy line) for all states of hydrogen for $n = 1 - 3$. The ordinate scales have been adjusted to best display the graphs, but the abscissa scales are all in a.u., that is, Bohr radii a_0 . Note the different horizontal scales for each column

will be found (see Problem 7). The fact that the most probable distance from the nucleus at which the electron will be found coincides with the Bohr radius for that particular value of n , shows how insightful the Bohr model was, especially since neither the TDSE nor the Heisenberg uncertainty principle had yet been formulated. Of course, the uncertainty principle prohibits the well-defined orbits of the Bohr model, but if one envisions a smearing of these Bohr orbits into a probability distribution, it is not difficult to imagine that the result would be similar to those predicted by the solution of the radial TISE. Despite the imprecise language, states for which $\ell = n - 1$ are often referred to as circular states by analogy with the classical Kepler problem. When the angular momentum has its maximum value (for a given energy) the ellipse is one of zero eccentricity, a circle (see, for example, Reference [1]).

It should be clear that the Bohr model of the atom, although not consistent with wave mechanics, is valuable because the orders of magnitude it predicts are correct and because physical quantities such as the most probable value of r scale in accord with it. In a sense, the atomic system of units is based on the parameters of the Bohr model. Recall that the unit of length in a.u. is the Bohr radius. Thus, the scales of the abscissas in Fig. 10.3 are a.u.

We may contrast r_{\max} with the average or expectation value $\langle r \rangle$ which is defined by

$$\langle r^s \rangle \equiv \int_0^\infty r^s [|R_{n\ell}(r)|^2 r^2] dr \quad (10.36)$$

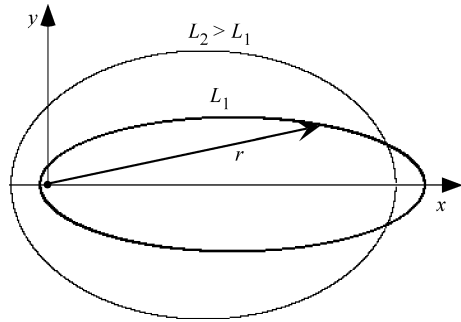
with $s = 1$. The calculation yields

$$\langle r \rangle = \frac{3}{2}n^2a_0 - \frac{\ell(\ell+1)}{2}a_0 \quad (10.37)$$

which shows that, for $\ell = 0$, $\langle r \rangle > r_{\max}$, as expected from the shape of the radial distribution functions (see Fig. 10.3). Notice that $\langle r \rangle$ decreases with increasing angular momentum. This may be understood by again appealing to the classical Kepler problem discussed in Section 10.2. A given energy, E , is independent of the value of the semiminor axis b and depends only upon the value of the semimajor axis a . The force center is at one focus of the ellipse and is thus the origin of polar coordinates. For low angular momentum, L , the apogee is larger than for higher values of L as depicted in Fig. 10.4. Thus, the average value of the distance from the origin is greater at low angular momenta.

The expectation values of many integral powers of r , including negative powers, are important for calculations and estimations of atomic effects. Although integrals of the type in Equation 10.36 are required, we can use a recursion relation between them known as Kramer's relation. If s is an integer such that $s > -2\ell - 1$, Kramer's relation is:

Fig. 10.4 Elliptical orbits having the same semi-major axis, but different semi-minor axes as characterized by their respective angular momenta, L_1 and L_2 . The foci of the two ellipses coincide at the origin of coordinates



$$\frac{(s+1)}{n^2} \langle r^s \rangle - (2s+1) a_0 \langle r^{s-1} \rangle + \frac{s}{4} a_0^2 [(2\ell+1)^2 - s^2] \langle r^{s-2} \rangle = 0 \quad (10.38)$$

The proof is not difficult, but it is somewhat lengthy (see Problem 9).

Kramer's relation makes it unnecessary to evaluate *any* integrals. For example, if we take $s = 0$, then it follows immediately from Equation 10.38 that $\langle r^{-1} \rangle = 1/(n^2 a_0)$ because $\langle r^0 \rangle \equiv 1$. To obtain $\langle r \rangle$ we choose $s = 1$ in Equation 10.38 we have

$$\frac{2}{n^2} \langle r \rangle - 3a_0 \langle r^0 \rangle + \frac{1}{4} a_0^2 [(2\ell+1)^2 - 1] \langle r^{-1} \rangle = 0 \quad (10.39)$$

Inserting the known value of $\langle r^{-1} \rangle$ and $\langle r^0 \rangle = 1$, $\langle r \rangle$ follows (see Problem 10). Table 10.4 is a listing of some useful expressions for expectation values of powers of r for one-electron atoms.

Table 10.4 Expectation values of r^s for one-electron atoms

$\langle r^2 \rangle = \left(\frac{a_0}{Z}\right)^2 \left\{ \frac{n^2}{2} [5n^2 + 1 - 3\ell(\ell+1)] \right\}$
$\langle r \rangle = \left(\frac{a_0}{Z}\right) \left\{ \frac{1}{2} [3n^2 - \ell(\ell+1)] \right\}$
$\langle r^{-1} \rangle = \frac{1}{(a_0/Z)} \left(\frac{1}{n^2} \right)$
$\langle r^{-2} \rangle = \frac{1}{(a_0/Z)^2} \left\{ \frac{1}{n^3 (\ell + 1/2)} \right\}$
$\langle r^{-3} \rangle = \frac{1}{(a_0/Z)^3} \left\{ \frac{1}{n^3 \ell (\ell + \frac{1}{2}) (\ell + 1)} \right\}$
$\langle r^{-4} \rangle = \frac{1}{(a_0/Z)^4} \left(\frac{1}{2} \right) \left\{ \frac{[3n^2 - \ell(\ell+1)]}{n^5 \ell (\ell - \frac{1}{2}) (\ell + \frac{1}{2}) (\ell + 1) (\ell + 3/2)} \right\}$

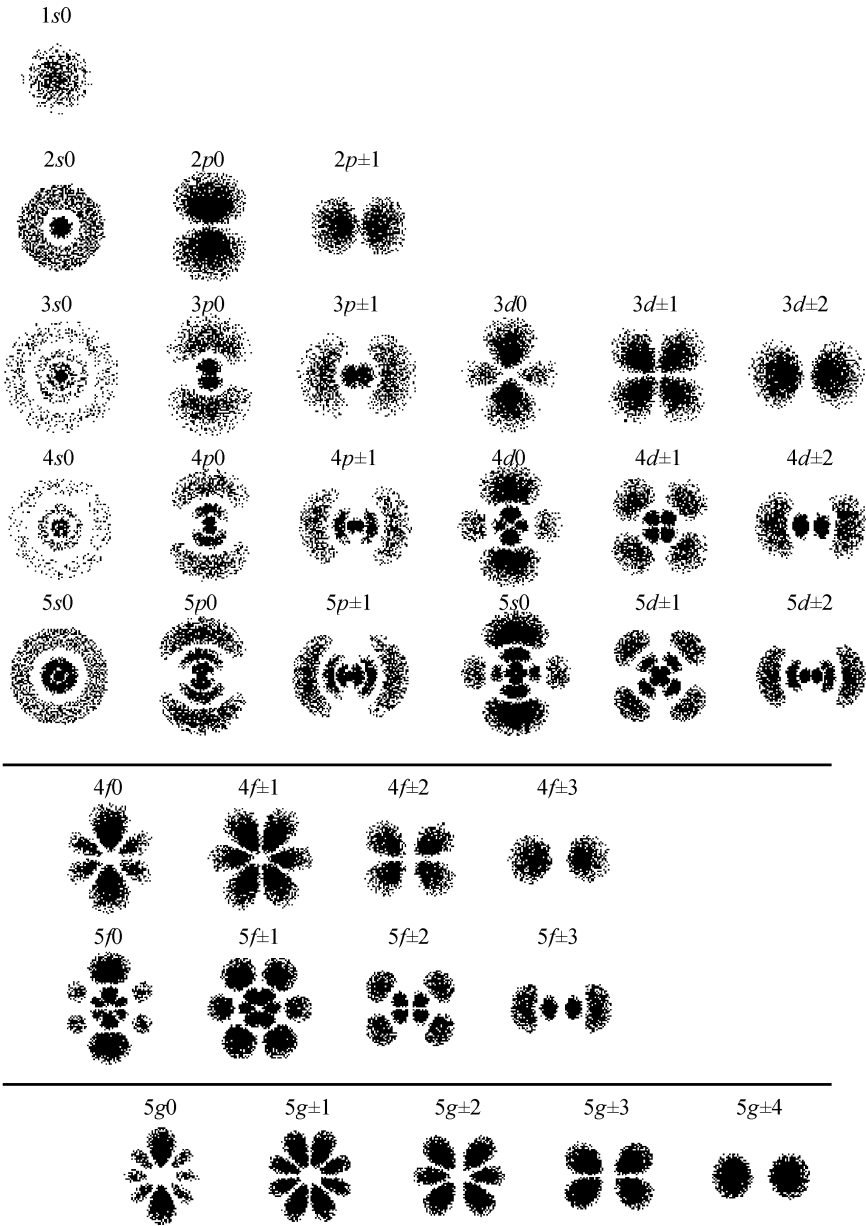


Fig. 10.5 Probability densities for eigenstates of hydrogen. The pictures are a slice through the $y - z$ plane and symmetric about the z -axis which is vertical and in the plane of the paper. The scale is proportional to n^2

10.4 The Complete Energy Eigenfunctions

The complete eigenfunctions for the hydrogen atom in spherical coordinates are given by

$$\psi_{n\ell m}(r, \theta, \phi) = Y_{\ell m}(\theta, \phi) R_{n\ell}(r) \quad (10.40)$$

The spin of the electron does not appear in the TISE and thus the effects of spin must be inserted “by hand.” The complete set of quantum numbers is then $(n \ell m_\ell s m_s)$, where we now use subscripts to differentiate between the quantum numbers representing the z -components of orbital and spin angular momenta. Clearly this set of quantum numbers represents the uncoupled set of energy eigenfunctions. We can also imagine using the coupled basis set in which the quantum numbers would be $(n j m_j \ell s)$. These produce eigenfunctions in which neither of the z -components of angular momentum are specified. By giving up these z -components we are rewarded with knowledge of the value of the total angular momentum and its z -component, j and m_j .

Because we already know that the angular portions of the one-electron wave functions are the spherical harmonics, we tabulate the first few complete one-electron atom eigenfunctions in Table 10.5. The spectroscopic notation introduced in Section 9.5.2 that is used to designate the orbital angular momentum quantum number is indicated. States of hydrogen are often designated by the principal quantum number n followed by this letter denoting the angular momentum. This designation ignores spin, which, when included, is attached as a following subscript, $j = \ell \pm \frac{1}{2}$.

Table 10.5 The first few complete wave functions for one-electron atoms

n	ℓ	m	$\psi_{n\ell m}(r, \theta, \phi)$
1	0 (s)	0	$\frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0 (s)	0	$\frac{1}{2\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$
2	1 (p)	1	$-\frac{1}{4\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{2a_0}\right) e^{-Zr/2a_0} \sin \theta e^{i\phi}$
2	1 (p)	0	$\frac{1}{2\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{2a_0}\right) e^{-Zr/2a_0} \cos \theta$
2	1 (p)	-1	$\frac{1}{4\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{2a_0}\right) e^{-Zr/2a_0} \sin \theta e^{-i\phi}$

10.5 Retrospective

The hydrogen atom is the paradigm for all atoms so a complete understanding of the solution to the TISE is required for further study of atomic physics. The mathematical details of the solution are both important and interesting and the accidental degeneracy of the states of atomic hydrogen illustrates the special nature of the Coulomb potential, the extra symmetry beyond the spatial symmetry associated with any central potential. This additional symmetry, which manifests itself classically as an additional constant of the motion, provides another operator that commutes with the Hamiltonian, a commuting operator in addition to \hat{L}^2 and \hat{L}_z . Because only three commuting operators are required to effect a separation of the TISE, the additional commuting operator makes it possible to separate the TISE in a coordinate system other than spherical coordinates, parabolic coordinates. The result of this dual separation is that there are two different sets of eigenfunctions, each of which is a complete set. Thus, an eigenfunction in one set can be expressed as a linear combination of eigenfunctions of the other set, making the degeneracy transparent.

10.6 References

1. S. T. Thornton and J. B. Marion, *Classical Dynamics of Particles and Systems* (Harcourt Brace Jovanovich, New York, 1995).

Problems

1. Show that the substitution $r = \sqrt{-\hbar^2/(8mE)}\rho$ is equivalent to scaling r and converting it to a dimensionless quantity. That is, show that $\rho = 2Zr/(na_0)$.
2. Show that the minimum in the effective potential for a one-electron atom occurs at $r_{\min} = \ell(\ell + 1)/Z$ a.u.
3. Find the boundaries of the classically allowed region for the electron in a hydrogen atom for any value of angular momentum ℓ . Use atomic units.
4. Find $\delta r_c = (r_c)_{\max} - (r_c)_{\min}$, the width of the classically allowed region for a hydrogen atom, as a function of n and ℓ . For which values of ℓ will δr_c be a minimum and a maximum for a given value of n ? Use atomic units, but convert the answers back to SI units.
5. Use the orthogonality relation for associated Laguerre polynomials to determine $\langle r^{-1} \rangle$ for a one-electron atom.
6. What is the probability of finding the electron in a ground state hydrogen atom in the classically forbidden region? Atomic units will be helpful.
7. Show that the maximum in the radial distribution function for a circular orbit of a hydrogen atom occurs for $r_{\max} = n^2 a_0$.
8. Find $\langle x \rangle_{n\ell m}$ for the hydrogen atom. Based on the answer for $\langle x \rangle$ what are $\langle y \rangle$ and $\langle z \rangle$? If you insist on working out the integrals for $\langle y \rangle$ and $\langle z \rangle$, a glance at Table 8.3 will be helpful.

9. Prove Kramer's relation for expectation values

$$\frac{(s+1)}{n^2} \langle r^s \rangle - (2s+1) a_0 \langle r^{s-1} \rangle + \frac{s}{4} a_0^2 [(2\ell+1)^2 - s^2] \langle r^{s-2} \rangle = 0$$

To do this first convert the radial equation, Equation 10.3, to the form

$$\frac{d^2 u(r)}{dr^2} + \left[\frac{2}{ra_0} - \frac{\ell(\ell+1)}{r^2} - \frac{1}{a_0^2 n^2} \right] u(r) = 0$$

Then multiply through by $u(r) r^s dr$ and integrate from $0 \rightarrow \infty$ using integration by parts. Your result should have all expectation values except one pesky integral, $\int_0^\infty r^s [u'(r)]^2 dr$, where the prime signifies differentiation with respect to r . To eliminate this integral multiply the TISE through by $u'(r) r^{s+1} dr$ and integrate from $0 \rightarrow \infty$. Again there will be all expectation values except for the same annoying integral. This integral is not so annoying at this point because you can equate the two expressions for it and obtain Kramer's relation. The integration by parts that is required will be facilitated by using the relations $u'(r) u(r) = \frac{1}{2} [u^2(r)]'$ and $u'(r) u''(r) = \frac{1}{2} \{[u'(r)]^2\}'$.

10. Evaluate $\langle r \rangle$ using Kramer's relation with $s = 1$ and show that the answer is that given in Table 10.4.
11. For what values of ℓ will $\langle r \rangle$ and Δr have their maximum and minimum values? Are the conclusions consistent with Fig. 10.3?
12. Evaluate $\langle r \rangle$ and Δr for the two extremes of angular momentum, $\ell = 0$ and $\ell = n - 1$, and relate them.
13. Calculate the energy eigenvalues for the n th state of the hydrogen atom using the virial theorem and known expectation values. Atomic units are recommended.
14. The triton is a nucleus of heavy hydrogen ${}^3_1\text{H}$ (see Section 9.5.2). It is radioactive with one of the decay products being the nucleus ${}^3_2\text{He}$. An atom consisting of a triton with a bound electron, which is called tritium, can therefore decay to a singly ionized atom ${}^3_2\text{He}^+$ provided the triton retains the electron after the radioactive decay. If the tritium is initially in the ground state, what is the probability that the ${}^3_2\text{He}^+$ decay product is also in the ground state? Atomic units are recommended.
15. Alkali atoms, those in the first column of the periodic table, have a single electron outside a spherically symmetric core of electrons and therefore behave much as hydrogen atoms. The effects of core penetration by the outer electron may be approximated by a potential $U(r)$ which is given in a.u. by

$$U(r) = -\frac{1}{r} - \frac{b}{r^2}; \quad b/r \ll 1$$

Solve the radial part of the TISE by combining b/r^2 with the centrifugal term and show that the energy eigenvalues may be written as the Bohr energy plus

a correction term that depends upon both n and ℓ . The energy in a.u. is approximately

$$E_{n\ell} \approx -\frac{1}{2n^2} - \frac{b}{n^3 \left(\ell + \frac{1}{2}\right)}$$

16. A hydrogen atom is in a superposition of states at $t = 0$ that is given by

$$|\psi(\mathbf{r}, t = 0)\rangle = \sum_k a_k |n\ell m\rangle$$

where k stands for all combinations of hydrogen atom quantum numbers $(n\ell m)$.

Find $|\psi(\mathbf{r}, t)\rangle$ the state vector as a function of time.

17. The state vector for a hydrogen atom at $t = 0$ is given by

$$|\psi(\mathbf{r}, t = 0)\rangle = \frac{1}{\sqrt{3}} |100\rangle + \frac{1}{\sqrt{6}} |210\rangle + \frac{1}{\sqrt{2}} |320\rangle$$

- (a) Find $|\psi(\mathbf{r}, t)\rangle$ the state vector as a function of time.
- (b) Find the expectation values $\langle E \rangle$, $\langle \hat{L}^2 \rangle$, and $\langle \hat{L}_z \rangle$ as functions of time.
- (c) Why are these expectation values independent of time?

Chapter 11

Angular Momentum—Encore

In our discussion of the accidental degeneracy of the hydrogen atom in Section 10.2 it was noted that this degeneracy is the consequence of an additional symmetry of the system, a symmetry beyond that associated with a central potential. This additional symmetry manifests itself classically as an additional constant of the motion and quantum mechanically as another operator that commutes with the Hamiltonian. In this chapter we will discuss the properties of this operator and its effect on the energy eigenfunctions of the TISE. We will also discuss its relationship to angular momentum. First, however, we will synopsise the classical Kepler problem.

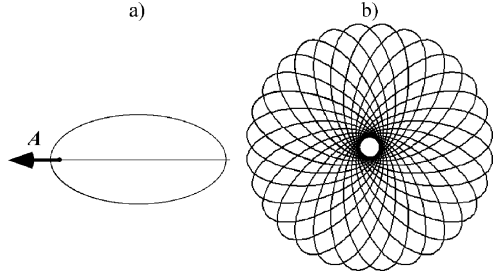
11.1 The Classical Kepler Problem

The mathematical description of planetary orbits is called the Kepler problem because it was Kepler who deduced, purely empirically, that the planets travel around the sun in elliptical orbits. Newton solved the problem mathematically by ignoring the other planets so his solution of the two-body problem is analogous to that of the classical hydrogen atom. When a particle is subject to a central force its motion is confined to a plane because the angular momentum \mathbf{L} is conserved. Moreover, if the particle is bound, this planar motion is confined between two values of r . The motion is not necessarily periodic inasmuch as it may never retrace itself. If, however, the force is an attractive inverse square force, a $1/r$ potential, then the bound motion *is* periodic and the particle executes a closed elliptical orbit. The uniqueness of a classical Keplerian orbit is illustrated in Fig. 11.1.

In Fig. 11.1(a), the potential is an attractive $1/r$ potential while in Fig. 11.1(b) a small non-Keplerian term has been added to the $1/r$ potential. The effect of the added term is to cause a precession of the ellipse so that, except in special circumstances, the particle trajectory never retraces itself. Thus, if the plot of the precessing ellipses were permitted to run for a very long time, the annular region between the minimum and maximum distances from the force center would be completely black.

An additional constant of the motion is responsible for the special properties of the Kepler problem. This constant is a vector that goes by a variety of names [1][2]. For simplicity, we refer to it as the Lenz vector. Consider first a *general* central

Fig. 11.1 (a) A fixed elliptical orbit resulting from a Kepler potential. The vector \mathbf{A} is the Lenz vector. (b) Trajectory of a particle under the influence of a nearly Keplerian potential. The ellipse precesses and, in general, never retraces itself



potential $U(r)$ such that the force is $f(r)\hat{\mathbf{a}}_r$ where $\hat{\mathbf{a}}_r = \mathbf{r}/r$ is the unit direction in the \mathbf{r} direction[3]. Newton's second law may be written in terms of the linear momentum \mathbf{p} :

$$\dot{\mathbf{p}} = f(r)\hat{\mathbf{a}}_r \quad (11.1)$$

Taking the cross product $\dot{\mathbf{p}} \times \mathbf{L}$ where $\mathbf{L} = \mathbf{r} \times m\dot{\mathbf{r}}$ we have

$$\begin{aligned} \dot{\mathbf{p}} \times \mathbf{L} &= mf(r) \left[\frac{\mathbf{r}}{r} \times (\mathbf{r} \times \dot{\mathbf{r}}) \right] \\ &= mf(r)r^2 \left[\frac{\dot{\mathbf{r}}\mathbf{r}}{r^2} - \frac{\dot{\mathbf{r}}}{r} \right] \end{aligned} \quad (11.2)$$

where we have used the vector identity for the triple cross product as well as the relation

$$\dot{\mathbf{r}} \bullet \mathbf{r} = \frac{1}{2} \frac{d}{dt} (\mathbf{r} \bullet \mathbf{r}) = \dot{r}r \quad (11.3)$$

to arrive at Equation 11.2. Because we are dealing with a central force, \mathbf{L} is a constant so we may rewrite Equation 11.2 as

$$\frac{d}{dt} (\mathbf{p} \times \mathbf{L}) = -mf(r)r^2 \frac{d\hat{\mathbf{a}}_r}{dt} \quad (11.4)$$

Inserting Coulomb's law into Equation 11.4 we find that the additional constant of the motion, the Lenz vector \mathbf{A} , is:

$$\begin{aligned} \mathbf{A} &= \left[(\mathbf{p} \times \mathbf{L}) - \left(\frac{me^2}{4\pi\epsilon_0} \right) \hat{\mathbf{a}}_r \right] \\ &= \mathbf{p} \times \mathbf{L} - \hat{\mathbf{a}}_r \quad \text{a.u.} \end{aligned} \quad (11.5)$$

As defined in Equation 11.5, the vector \mathbf{A} lies in the plane of the orbit and points along the major axis of the ellipse toward the perigee. Because it is in the plane of the orbit, it is perpendicular to the angular momentum so that

$$\mathbf{A} \bullet \mathbf{L} = 0 \quad (11.6)$$

For the Kepler potential the time rate of change of the Lenz vector $\dot{\mathbf{A}} = 0$ (see Problem 1) and it is a constant of the motion. The effect of the small non-Keplerian term is to rotate the Lenz vector, thus producing the precession. In the case of the precession of the orbit of the planet Mercury, the precession is due in large part to the effects of other planets, but this accounts for only a portion of the observed rate of precession. The remainder is a relativistic effect that adds additional powers of $(1/r)$ to the potential.

11.2 The Quantum Mechanical Kepler Problem

Frequently, when solving a problem in quantum physics the Hermitian operators look the same as their classical counterparts. For example, the Hamiltonian is simply $\hat{p}^2/2m + U(r)$. If the classical quantity is a vector, however, often there is a problem in that the corresponding operator is not Hermitian. Such is the case with the Lenz vector. If the defining quantities are simply made into operators, the resulting operator $\hat{\mathbf{A}}$ is not Hermitian. The formulation was rescued by Pauli who showed how to convert the classical Lenz vector into a Hermitian operator by symmetrizing it to produce

$$\hat{\mathbf{A}} = \frac{1}{2} (\hat{\mathbf{p}} \times \hat{\mathbf{L}} - \hat{\mathbf{L}} \times \hat{\mathbf{p}}) - \hat{\mathbf{a}}_r \quad (11.7)$$

Atomic units are used to simplify the calculations. Note that, because they are operators $\hat{\mathbf{p}} \times \hat{\mathbf{L}} \neq -\hat{\mathbf{L}} \times \hat{\mathbf{p}}$. It is outside our interest to prove that $[\hat{\mathbf{A}}, \hat{H}] = 0$ or many of the other properties of the Lenz vector, but there are discussions of this elsewhere[4]. Table 11.1 is a listing of some important commutation relations involving the Lenz vector operator; ϵ_{ijk} is the Levi-Cevita symbol. The second relation is the quantum mechanical equivalent of the classical perpendicularity of \mathbf{A} and \mathbf{L} , Equation 11.6. The third shows that $\hat{\mathbf{A}}$ is *not* an angular momentum, but the fourth shows that it does fit the definition of a vector operator, Equation 8.44.

Table 11.1 Some useful relations involving the Lenz vector operator $\hat{\mathbf{A}}$ in atomic units

1. $[\hat{H}, \hat{\mathbf{A}}] = 0$
2. $\hat{\mathbf{A}} \bullet \hat{\mathbf{L}} = 0$
3. $[\hat{A}_i, \hat{A}_j] = -2i \hat{L}_k \hat{H} \epsilon_{ijk}$
4. $[\hat{L}_i, \hat{A}_j] = i \hat{A}_k \epsilon_{ijk}$
5. $\hat{A}^2 = 2(\hat{L}^2 + 1)\hat{H} + 1$
6. $\hat{A}_z = -\frac{1}{2}(\hat{L}_- \hat{A}_+ + \hat{A}_- \hat{L}_+) - \hat{A}_z \hat{L}_z$

Now, incredible as it may seem, it is possible to obtain the Bohr energy without actually solving the TISE. Pauli did this using operator methods one year before Schrödinger's paper describing the TDSE was published. To obtain the Bohr energies we take advantage of our knowledge of (and our proficiency with) *generalized* angular momentum (see Chapter 8). Although the third relation in Table 11.1 clearly shows that \hat{A} is *not* an angular momentum, it is possible to construct linear combinations of \hat{A} and \hat{L} that *are* angular momentum operators. First we define a new operator

$$\hat{A} = \sqrt{-2\hat{H}}\hat{A}' \quad (11.8)$$

This is a peculiar-looking operator, the use of which is not obvious, but if we restrict the functions upon which it operates to energy eigenfunctions of the hydrogen atom, then we can replace the Hamiltonian under the radical with the Bohr energy which, recall, we are attempting to derive. With this restriction the new operator \hat{A}' is simply a scaled Lenz vector

$$\hat{A}' = \sqrt{-\frac{1}{2E}}\hat{A} \quad (11.9)$$

In terms of \hat{A}' relations 3 and 4 in Table 11.1 are

$$\begin{aligned} [\hat{A}'_i, \hat{A}'_j] &= i\hat{L}_k \epsilon_{ijk} \\ [\hat{L}_i, \hat{A}'_j] &= i\hat{A}'_k \epsilon_{ijk} \end{aligned} \quad (11.10)$$

We now define two new vector operators

$$\begin{aligned} \hat{I} &= \frac{1}{2}(\hat{L} + \hat{A}') \\ \hat{K} &= \frac{1}{2}(\hat{L} - \hat{A}') \end{aligned} \quad (11.11)$$

and evaluate the commutators of these operators with each other and with the Hamiltonian. Using the relations in Table 11.1 and Equation 11.11, we can evaluate the commutators of \hat{I} and \hat{K} with each other and with the Hamiltonian (see Problem 2). We have

$$[\hat{I}, \hat{H}] = 0 = [\hat{K}, \hat{H}] = [\hat{I}, \hat{K}] \quad (11.12)$$

Moreover,

$$\begin{aligned} [\hat{I}_i, \hat{I}_j] &= i \hat{I}_k \epsilon_{ijk} \\ [\hat{K}_i, \hat{K}_j] &= i \hat{K}_j \epsilon_{ijk} \end{aligned} \quad (11.13)$$

from which it is clear that $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$ are angular momenta (see Problem 3). Because $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$ are angular momenta, we immediately know the eigenvalues of their squares. That is,

$$\hat{I}^2 |i\rangle = i(i+1) |i\rangle \quad \text{and} \quad \hat{K}^2 |k\rangle = k(k+1) |k\rangle \quad (11.14)$$

where $|i\rangle$ and $|k\rangle$ are eigenkets of \hat{I}^2 and \hat{K}^2 , respectively. The quantum numbers i and k must assume the values

$$i, k = 0, 1/2, 1, 3/2, 2, 5/2, 3, \dots \quad (11.15)$$

Because $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$ commute with each other and the Hamiltonian, \hat{I}^2 and \hat{K}^2 must commute with each other and the Hamiltonian (see Problem 4). Therefore, we know that we can find a set of eigenfunctions that are simultaneously eigenfunctions of \hat{I}^2 , \hat{K}^2 , and \hat{H} . We designate the eigenkets by

$$|i, m_i; k, m_k\rangle \quad (11.16)$$

where m_i and m_k are the eigenvalues of \hat{I}_z and \hat{K}_z , respectively. Again because they are angular momenta, we know the action of the ladder operators $I_{\pm} = I_x \pm iI_y$ and $K_{\pm} = K_x \pm iK_y$ on the eigenfunctions. They will raise and lower m_i and m_k without affecting i and k . Squaring $\hat{\mathbf{I}}$ and using the fact that $\hat{\mathbf{A}}' \bullet \hat{\mathbf{L}} = 0$ we obtain

$$\begin{aligned} \hat{I}^2 &= \frac{1}{4} (\hat{L}^2 + \hat{A}^2) \\ &= \hat{K}^2 \end{aligned} \quad (11.17)$$

from which we deduce that the quantum numbers are equal, $i = k$ (see Equation 11.14).

It is helpful to cast the Hamiltonian in terms of the scaled Lenz vector and the angular momentum operator. Inserting the definition of $\hat{\mathbf{A}}'$, Equation 11.8 into relation 4 in Table 11.1 we obtain

$$-2\hat{H}\hat{A}'^2 = 2(\hat{L}^2 + 1)\hat{H} + 1 \quad (11.18)$$

which may be rearranged using Equation 11.17 and the fact that $[\hat{H}, \hat{L}^2] = 0 = [\hat{H}, \hat{K}^2]$ to obtain

$$\begin{aligned}
1 + 2\hat{H}(\hat{A}'^2 + \hat{L}^2) + 2\hat{H} &= 0 \\
1 + 2(4\hat{K}^2 + 1)\hat{H} &= 0
\end{aligned}
\tag{11.19}$$

Now we operate on a ket $|\Phi\rangle$ that is presumed to be one of the simultaneous eigenkets of \hat{H} and \hat{K}^2 (because $[\hat{H}, \hat{K}^2] = 0$):

$$[1 + 2(4\hat{K}^2 + 1)\hat{H}]|\Phi\rangle = 0 \tag{11.20}$$

Carrying out the operations we obtain

$$1 + 2[4k(k+1) + 1]E = 0 \tag{11.21}$$

or, solving for E ,

$$E = -\frac{1}{2} \cdot \frac{1}{(2k+1)^2} \tag{11.22}$$

But, k must be zero, an integer, or a half-integer so the quantity $(2k+1)$ represents the set of integers beginning with unity. Naturally we designate this integer by n and obtain the Bohr energy for the hydrogen atom in atomic units.

It is remarkable that, using only the properties of generalized angular momenta, one can deduce the energy eigenvalues for the hydrogen atom. Note that the nature of the eigenket $|\Phi\rangle$ is still unknown. In fact, in this derivation, a coordinate system was not even specified so $\langle \mathbf{r} | \Phi \rangle$ is an eigenfunction in coordinate space while $\langle \mathbf{p} | \Phi \rangle$ is an eigenfunction in momentum space.

We can do more using only operators and angular momentum. By adding the definitions of $\hat{\mathbf{L}}$ and $\hat{\mathbf{K}}$, Equations 11.11, we find that

$$\hat{\mathbf{L}} = \hat{\mathbf{I}} + \hat{\mathbf{K}} \tag{11.23}$$

From the restrictions on the quantum numbers i and k , the quantum number ℓ is limited to

$$\ell = (i+k), (i+k-1), (i+k-2), \dots, |i-k| \tag{11.24}$$

Recall that $\hat{\mathbf{L}}$ is surely an angular momentum so $\ell \geq 0$. Moreover, as we have seen $i = k$ and $n = (2k+1)$ which leads to

$$\begin{aligned}
\ell_{\max} &= (2k), (2k-1), (2k-2), \dots, 0 \\
&= (n-1), (n-2), \dots, 0
\end{aligned}
\tag{11.25}$$

which are precisely the limitations imposed on ℓ that were obtained by solving the TISE.

We can even obtain the degree of degeneracy using these operators. Because $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$ are angular momenta, their z -components \hat{I}_z and \hat{K}_z commute with the Hamiltonian. Consequently, the eigenkets of these operators are also simultaneous eigenkets of \hat{H} , \hat{I}^2 , and \hat{K}^2 . We know that each state that is characterized by the quantum numbers i and k has $(2i + 1) \cdot (2k + 1)$ substates, the z -components of $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$. The degeneracy is therefore

$$g_H = (2i + 1) \cdot (2k + 1) \quad (11.26)$$

But $i = k$ and $n = (2k + 1)$ so, as was found in spherical coordinates, the degree of degeneracy is n^2 (excluding spin).

11.3 The Action of \hat{A}_+

Because we know that $\hat{\mathbf{A}}$ is a vector operator, we know that $\hat{A}_+ = \hat{A}_x + i\hat{A}_y$ is a ladder operator (see Section 8.3) and that

$$\hat{A}_+ |n\ell\ell\rangle = C_{\hat{A}} |n(\ell + 1)(\ell + 1)\rangle \quad (11.27)$$

where $|n\ell m\rangle$ is an eigenket of the hydrogen atom in spherical coordinates. Of course, in addition to being an energy eigenket, it is also an eigenket of \hat{L}^2 and \hat{L}_z . It is not, however, an eigenket of $\hat{\mathbf{A}}$ or any of its components because these operators are not part of the mutually commuting set that is used to solve the problem in spherical coordinates. On the other hand, separation of the TISE in parabolic coordinates produces a different set of eigenfunctions which, in effect, are the result of using the mutually commuting set of operators \hat{H} , \hat{L}_z , and \hat{A}_z . Thus, when solving the hydrogen atom problem in parabolic coordinates the good quantum numbers are n and m as in spherical coordinates, but the other quantum number is reflective of the eigenvalues of \hat{A}_z ; ℓ is no longer a good quantum number. The fact that there are four mutually commuting operators for this problem is at the root of the accidental degeneracy and the concomitant separability of the TISE in more than one coordinate system.

In addition to \hat{A}_+ , there are other combinations of the components of $\hat{\mathbf{A}}$ that produce useful relations when acting on the spherical coordinate eigenkets of the hydrogen atom. The ability of the \hat{L}_{\pm} to change only the m quantum number when operating on a general spherical eigenket $|n\ell m\rangle$ is a consequence of the spherical symmetry of any central potential. Changing m merely changes the z -component of the orbital angular momentum, leaving the total angular momentum and the energy unaffected. The spherical symmetry is associated with the total angular momentum without regard to the direction of it (as is indicated by the value of m). The components of $\hat{\mathbf{A}}$ acting on a spherical eigenket of hydrogen can produce additional useful relations. For reference, Table 11.2 contains a listing of the actions of \hat{A}_z and \hat{A}_+ on spherical hydrogen eigenkets $|n\ell m\rangle$ and $|n\ell\ell\rangle$. The fact that $\hat{A}_z |n\ell m\rangle$ yields a linear

Table 11.2 The action of \hat{A}_\pm and \hat{A}_z on the indicated spherical eigenkets $|n\ell m\rangle$

$$\begin{aligned}
\hat{A}_\pm |n\ell m\rangle &= \mp \frac{1}{n} \sqrt{\frac{[n^2 - (\ell + 1)^2](\ell \pm m + 1)(\ell \pm m + 2)}{(2\ell + 1)(2\ell + 3)}} |n(\ell + 1)(m \pm 1)\rangle \\
&\quad \pm \frac{1}{n} \sqrt{\frac{(n^2 - \ell^2)(\ell \mp m)(\ell \mp m - 1)}{(2\ell - 1)(2\ell + 1)}} |n(\ell - 1)(m \pm 1)\rangle \\
\hat{A}_\pm |n\ell\ell\rangle &= -\frac{1}{n} \sqrt{\frac{2(\ell + 1)}{(2\ell + 3)}} [n^2 - (\ell + 1)^2] |n(\ell + 1)(\ell + 1)\rangle \\
\hat{A}_z |n\ell m\rangle &= \frac{1}{n} \sqrt{\frac{[n^2 - (\ell + 1)^2](\ell + m + 1)(\ell - m + 1)}{(2\ell + 1)(2\ell + 3)}} |n(\ell + 1)m\rangle \\
&\quad + \frac{1}{n} \sqrt{\frac{(n^2 - \ell^2)(\ell + m)(\ell - m)}{(2\ell - 1)(2\ell + 1)}} |n(\ell - 1)m\rangle \\
\hat{A}_z |n\ell\ell\rangle &= \frac{1}{n} \sqrt{\frac{[n^2 - (\ell + 1)^2]}{(2\ell + 3)}} |n(\ell + 1)\ell\rangle
\end{aligned}$$

combination of two different eigenkets clearly shows that the spherical eigenkets are not eigenkets of \hat{A}_z .

11.4 Retrospective

Aside from the interesting aspects of the classical Kepler problem, the discussion in this chapter was intended to illustrate, with a concrete example, the concept of a *generalized* angular momentum. Recall that an operator is *an* angular momentum if its components obey the commutation rules given in Equation 8.2. There need not be any correlation between the operator and the classical definition of angular momentum. Indeed, spin is such an angular momentum, but its name suggests rotational angular motion in the classical sense. Such a visualization is preposterous for a point particle. The operators $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$ introduced in this chapter, while qualifying as quantum mechanical angular momenta, have no classical counterparts, preposterous or otherwise.

11.5 References

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Problems

1. Starting with Equation 11.4 derive an expression for dA/dt for a hydrogen atom.

2. Show that the operators $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$ commute with the Hamiltonian and with each other.
3. Show that $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$ are angular momenta.
4. Show that the commutator

$$[\hat{H}, \hat{\mathbf{I}}] = 0 = [\hat{H}, \hat{\mathbf{K}}]$$

assures us that

$$[\hat{H}, \hat{\mathbf{I}}^2] = 0 = [\hat{H}, \hat{\mathbf{K}}^2]$$

Chapter 12

Time-Independent Approximation Methods

To this point we have, with two exceptions, dealt with potential energy functions for which the TISE could be solved exactly. The WKB method of approximation was introduced in Section 5.6 in the natural progression of studying one-dimensional problems. Later, in Section 9.6, we reexamined diatomic molecules for which the Morse potential is a good approximation to the potential energy between the two nuclei. This time, however, we permitted the molecule to rotate as well as vibrate and this additional degree of freedom rendered the TISE unsolvable. For this problem it was possible to make some approximations concerning the relative magnitudes of the molecular parameters, thus enabling us to obtain an approximation to the vibrational-rotational energy levels. In this chapter we will develop more general methods for dealing with potentials for which the TISE cannot be solved exactly. Our goal is to obtain methods of approximating the energy eigenvalues and eigenfunctions. Because we are not concerned with the time development of any system, these approximation methods are termed time-independent.

In the first approximation method that we will study, perturbation theory, it is assumed that the true Hamiltonian that describes the system differs only slightly from another Hamiltonian for which the TISE can be solved exactly. In the second method that we will study, the variational technique, we will obtain only the energy eigenvalue, usually of the ground state, and seek no information about the energy eigenfunction. As we shall see, using this method we must guess the form of the energy eigenfunction to obtain the desired energy eigenvalue. The better the guess, the more accurate the energy that we obtain.

12.1 Perturbation Theory

12.1.1 Nondegenerate Perturbation Theory

We assume that the true Hamiltonian for the system is given by

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1 \quad (12.1)$$

where \hat{H}_0 is referred to as the unperturbed Hamiltonian and \hat{H}_1 the perturbing Hamiltonian. The parameter λ has been inserted to facilitate keeping track of the level of approximation. It is assumed that the eigenkets and energy eigenvalues of \hat{H}_0 are known, and that to each eigenket there is one energy eigenvalue. All energy eigenvalues are assumed different so that, indeed, we are dealing with the nondegenerate case. The eigenkets and energy eigenvalues are designated $|\psi_n^{(0)}\rangle$ and $E_n^{(0)}$, respectively, so that

$$\hat{H}_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle \quad (12.2)$$

The $|\psi_n^{(0)}\rangle$ are assumed to constitute an orthonormal set. The eigenkets of \hat{H} are designated $|\psi_n\rangle$ and we assume that we can write them to as great an accuracy as we please as follows:

$$\begin{aligned} |\psi_n\rangle &= \sum_k \lambda^k |\psi_n^{(k)}\rangle \\ &= \lambda^0 |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots \end{aligned} \quad (12.3)$$

where the superscript designates the level of approximation. Therefore, for the zeroth level the “correction” is merely the eigenket of \hat{H}_0 , which we assume we already know. The energy eigenvalues of \hat{H} , E_n , are written in an analogous way:

$$E_n = \sum_k \lambda^k E_n^{(k)} \quad (12.4)$$

$$= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (12.5)$$

Therefore, the true TISE is

$$\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle \quad (12.6)$$

Note that the kets $|\psi_n^{(j)}\rangle$ and energies $E_n^{(j)}$ are the j th correction terms, not the corrected kets and energy eigenvalues. These corrected quantities are obtained by adding as many $|\psi_n^{(j)}\rangle$ and $E_n^{(j)}$ to $|\psi_n^{(0)}\rangle$ and $E_n^{(0)}$ as is required for the degree of accuracy desired.

To determine the corrections to $|\psi_n^{(0)}\rangle$ and $E_n^{(0)}$ we write the TISE, Equation 12.6, in terms of Equations 12.1, 12.3, and 12.4:

$$(\hat{H}_0 + \lambda \hat{H}_1) \sum_k \lambda^k |\psi_n^{(k)}\rangle = \left(\sum_j \lambda^j E_n^{(j)} \right) \left(\sum_k \lambda^k |\psi_n^{(k)}\rangle \right) \quad (12.7)$$

where the two summations on the right-hand side are independent. Recall that λ is an arbitrary parameter that was inserted to keep track of the level of approximation.

Therefore, if, after multiplying the terms, we collect terms according to powers of λ , we will have an equation that has the form

$$c_0\lambda^0 + c_1\lambda^1 + c_2\lambda^2 + \dots = 0 \quad (12.8)$$

Because λ is arbitrary, the coefficients of each power of λ must vanish. This leads to

$$\begin{aligned} \lambda^0 : \hat{H}_0 |\psi_n^{(0)}\rangle &= E_n^{(0)} |\psi_n^{(0)}\rangle \\ \lambda^1 : \hat{H}_0 |\psi_n^{(1)}\rangle + \hat{H}_1 |\psi_n^{(0)}\rangle &= E_n^{(0)} |\psi_n^{(1)}\rangle + E_n^{(1)} |\psi_n^{(0)}\rangle \\ \lambda^2 : \hat{H}_0 |\psi_n^{(2)}\rangle + \hat{H}_1 |\psi_n^{(1)}\rangle &= E_n^{(0)} |\psi_n^{(2)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(2)} |\psi_n^{(0)}\rangle \end{aligned} \quad (12.9)$$

which are the zeroth-, first-, and second-order corrections.

Now, how do we use these equations? To get the first-order correction to the energy we take the inner product of the second equation with the bra $\langle\psi_k^{(0)}|$ and obtain

$$\langle\psi_k^{(0)}| \hat{H}_0 |\psi_n^{(1)}\rangle + \langle\psi_k^{(0)}| \hat{H}_1 |\psi_n^{(0)}\rangle = E_n^{(0)} \langle\psi_k^{(0)}| \psi_n^{(1)}\rangle + E_n^{(1)} \langle\psi_k^{(0)}| \psi_n^{(0)}\rangle \quad (12.10)$$

or, using orthonormality of the zeroth-order kets and the complex conjugate of Equation 12.2 we have

$$\left(E_k^{(0)} - E_n^{(0)}\right) \langle\psi_k^{(0)}| \psi_n^{(1)}\rangle + \langle\psi_k^{(0)}| \hat{H}_1 |\psi_n^{(0)}\rangle = E_n^{(1)} \delta_{kn} \quad (12.11)$$

Thus, if $k = n$, we immediately obtain the first-order correction to the energy of the n th state. It is

$$E_n^{(1)} = \langle\psi_n^{(0)}| \hat{H}_1 |\psi_n^{(0)}\rangle \quad (12.12)$$

so the rule is

The first-order correction to the energy is the expectation value of the perturbing Hamiltonian on the unperturbed state.

To obtain the first-order correction to the eigenket we return to Equation 12.10 and examine the case for which $k \neq n$. We expand $|\psi_n^{(1)}\rangle$ on the complete set of $|\psi_n^{(0)}\rangle$ which is easily done using the projection operator, Equation 6.61a, and the identity operator, Equation 6.58:

$$\begin{aligned} |\psi_n^{(1)}\rangle &= \sum_k \left(|\psi_k^{(0)}\rangle \langle\psi_k^{(0)}| \right) |\psi_n^{(1)}\rangle \\ &= \sum_k \langle\psi_k^{(0)}| \psi_n^{(1)}\rangle |\psi_k^{(0)}\rangle \end{aligned} \quad (12.13)$$

Then, for $k \neq n$ Equation 12.10 becomes

$$\left(E_k^{(0)} - E_n^{(0)}\right) \left\langle \psi_k^{(0)} \left| \psi_n^{(1)} \right\rangle + \left\langle \psi_k^{(0)} \left| \hat{H}_1 \right| \psi_n^{(0)} \right\rangle = 0 \quad (12.14)$$

because only the term in the summation that survives the inner product with $\left\langle \psi_k^{(0)} \right|$ is the k th. The expansion coefficient for the k th term in the expansion of $\left| \psi_n^{(1)} \right\rangle$ is therefore given by

$$\left\langle \psi_k^{(0)} \left| \psi_n^{(1)} \right\rangle = \frac{\left\langle \psi_k^{(0)} \left| \hat{H}_1 \right| \psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)} \quad (12.15)$$

Splitting off the $k = n$ term in Equation 12.13 we have

$$\left| \psi_n^{(1)} \right\rangle = c_n \left| \psi_n^{(0)} \right\rangle + \sum_{k \neq n} \frac{\left\langle \psi_k^{(0)} \left| \hat{H}_1 \right| \psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)} \left| \psi_k^{(0)} \right\rangle \quad (12.16)$$

where we have let

$$c_n = \left\langle \psi_n^{(0)} \left| \psi_n^{(1)} \right\rangle \quad (12.17)$$

We now have all the expansion coefficients in Equation 12.13 except c_n . To find this coefficient we use the normalization of the eigenkets of \hat{H} , the $\left| \psi_n \right\rangle$. Using Equation 12.3 we have

$$\begin{aligned} \langle \psi_n | \psi_n \rangle &= 1 \\ &= \left(\langle \psi_n^{(0)} | + \lambda \langle \psi_n^{(1)} | + \lambda^2 \langle \psi_n^{(2)} | + \dots \right) \\ &\quad \times \left(| \psi_n^{(0)} \rangle + \lambda | \psi_n^{(1)} \rangle + \lambda^2 | \psi_n^{(2)} \rangle + \dots \right) \\ &= 1 + \lambda \left(\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle \right) + \lambda^2 \left(\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \dots \right) \\ &= 1 + \lambda \left(c_n^* + c_n \right) + \lambda^2 \left(\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \dots \right) \end{aligned} \quad (12.18)$$

Because λ is arbitrary, the coefficients of each power of λ must vanish. For the first power we have

$$\begin{aligned} c_n^* + c_n &= 2 \operatorname{Re}(c_n) \\ &= 0 \end{aligned} \quad (12.19)$$

which means that c_n is an imaginary number which we write as $c_n = ic$, where c is real. Splitting off the term for which $k = n$, the first-order correction to the energy eigenket is

$$|\psi_n^{(1)}\rangle = \lambda i c |\psi_n^{(0)}\rangle + \lambda \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} |\psi_k^{(0)}\rangle \quad (12.20)$$

and the eigenket of \hat{H} correct to first-order is

$$\begin{aligned} |\psi_n\rangle &= |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle \\ |\psi_n\rangle &= (1 + i c \lambda) |\psi_n^{(0)}\rangle + \lambda \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} |\psi_k^{(0)}\rangle \\ &\approx e^{i c \lambda} |\psi_n^{(0)}\rangle + \lambda \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} |\psi_k^{(0)}\rangle \end{aligned} \quad (12.21)$$

It is seen, then, that the only effect of c_n is to change the phase of the unperturbed ket $|\psi_n^{(0)}\rangle$ in the expansion of $|\psi_n\rangle$. Unless c vanishes, the perturbed ket will not reduce to the unperturbed ket in the event that $\hat{H}_1 = 0$. We must therefore choose $c = 0$ and we have

$$\begin{aligned} c_n &= i c \\ &= i \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle \\ &= 0 \end{aligned} \quad (12.22)$$

so the corrected ket is

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} |\psi_k^{(0)}\rangle \quad (12.23)$$

where we have let $\lambda = 1$ since it is no longer needed and the first-order correction is given by

$$|\psi_n^{(1)}\rangle = \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} |\psi_k^{(0)}\rangle \quad (12.24)$$

Finally, we will obtain the second-order correction to the energy $E_n^{(2)}$. This correction is important because often the first-order correction vanishes. This happens in one-dimensional problems if the unperturbed potential is an even function and the perturbation is odd. In this case the unperturbed energy eigenfunctions

corresponding to $|\psi_n^{(0)}\rangle$ have definite parity, so the integral that leads to $E_n^{(1)}$ in Equation 12.12 vanishes.

As we might anticipate, to obtain $E_n^{(2)}$, we must use the coefficient of λ^2 . Taking the inner product of this coefficient (given in Equation 12.9) with $\langle\psi_n^{(0)}|$ we have

$$\begin{aligned}\langle\psi_n^{(0)}|\hat{H}_0|\psi_n^{(2)}\rangle + \langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(1)}\rangle &= E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle \\ &\quad + E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(2)} \\ &= 0\end{aligned}\tag{12.25}$$

or

$$\langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(1)}\rangle = E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(2)}\tag{12.26}$$

Solving for $E_n^{(2)}$ and substituting Equation 12.24 for $|\psi_n^{(1)}\rangle$ we have

$$\begin{aligned}E_n^{(2)} &= \langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(1)}\rangle - E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle \\ &= \sum_{k \neq n} \frac{\langle\psi_k^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})} \langle\psi_n^{(0)}|\hat{H}_1|\psi_k^{(0)}\rangle \\ &= \sum_{k \neq n} \frac{|\langle\psi_k^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle|^2}{(E_n^{(0)} - E_k^{(0)})}\end{aligned}\tag{12.27}$$

The last term in the first equation of Equation 12.27 vanishes because the $k = n$ is excluded from the summation.

Equation 12.27 is the important result of second-order perturbation theory. The term in the numerator is the matrix element of the perturbing Hamiltonian on the set of unperturbed wave functions. If these matrix elements are of roughly the same magnitude, it is seen that the biggest contribution to $E_n^{(2)}$ is from those states that are nearest to the level of interest, the one designated by n , because the denominator is small. These nearby levels are called the perturbing levels. If the major perturbing levels are above the state n , then the denominator is negative and $E_n^{(2)}$ lowers the unperturbed energy. The opposite is true if the perturbing levels lie above the unperturbed level. This is the origin of the expression that the levels repel.

Example: Charged harmonic oscillator in a constant electric field

Imagine an electron at the end of a one-dimensional (quantum mechanical) spring. In the absence of any fields, the unperturbed Hamiltonian \hat{H}_0 is that of the harmonic oscillator and the unperturbed eigenkets are, as usual, designated $|n\rangle$ with energy eigenvalues $E_n = (n + \frac{1}{2})\hbar\omega$. If, however, a constant electric field F is applied,

we can treat the potential energy associated with this field as the perturbation. Thus, we have

$$\hat{H}_1 = eFx \quad (12.28)$$

and we seek the first- and second-order corrections to the energy as well as the first-order correction to the unperturbed kets. While this problem illustrates many of the features of both first- and second-order nondegenerate perturbation theory, the TISE can be solved exactly for the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_1$ (see Problem 1). Nonetheless, in this section we treat it by perturbation theory.

The first-order correction vanishes. This is easily seen by noting that the eigenfunctions must have definite parity and the perturbation is an odd power of x . Therefore,

$$\langle n | \hat{H}_1 | n \rangle = 0 \quad (12.29)$$

Before going on to the second-order correction, let us examine the expectation value from a different viewpoint. We know from Section 7.1.2 that the diagonal matrix elements for odd powers of x vanish. This is easily seen because, from Equation 7.4, we know that we may write x in terms of the ladder operators

$$\hat{x} = \frac{1}{\sqrt{2}\alpha} (\hat{a} + \hat{a}^\dagger) \quad \text{with} \quad \alpha = \sqrt{\frac{m\omega}{\hbar}} \quad (12.30)$$

so

$$\begin{aligned} \langle n | \hat{H}_1 | n \rangle &= \frac{eF}{\sqrt{2}\alpha} \langle n | (\hat{a} + \hat{a}^\dagger) | n \rangle \\ &= \frac{eF}{\sqrt{2}\alpha} (\langle n | \hat{a} | n \rangle + \langle n | \hat{a}^\dagger | n \rangle) \\ &= 0 \end{aligned} \quad (12.31)$$

Now, to proceed to second-order perturbation theory, we must evaluate the matrix elements $eF \langle m | x | n \rangle$ which we accomplish using the ladder operators. The matrix element $\langle m | x | n \rangle$ is given in Equation 7.31:

$$\begin{aligned} \langle m | \hat{H}_1 | n \rangle &= eF \langle m | x | n \rangle \\ &= \frac{eF}{\sqrt{2}\alpha} \left(\sqrt{n} \delta_{m,n-1} + \sqrt{n+1} \delta_{m,n+1} \right) \end{aligned} \quad (12.32)$$

so that only two terms survive the summation. We have

$$\begin{aligned}
 E_n^{(2)} &= \sum_{m \neq n} \frac{|\langle m | \hat{H}_1 | n \rangle|^2}{(E_n^{(0)} - E_m^{(0)})} \\
 &= \left(\frac{eF}{\sqrt{2}\alpha} \right)^2 \left[\frac{n}{(E_n - E_{n-1})} + \frac{n+1}{(E_n - E_{n+1})} \right] \\
 &= \frac{e^2 F^2}{2} \left(\frac{\hbar}{m\omega} \right) \left[\frac{n}{\hbar\omega} + \frac{n+1}{-\hbar\omega} \right] \\
 &= -\frac{e^2 F^2}{2m\omega^2}
 \end{aligned} \tag{12.33}$$

12.1.2 Degenerate Perturbation Theory

Examination of Equations 12.24 and 12.27 reveals a serious problem if an unperturbed level is degenerate. That is, suppose an unperturbed eigenvalue, $E_m^{(0)}$, corresponds to two (or more) unperturbed kets $|\psi_m^{(0)}\rangle$ and $|\psi_{m'}^{(0)}\rangle$. Then, when the summations in these equations are executed the denominator of one term vanishes. The underlying reason for this is that the eigenfunctions corresponding to a degenerate level are not unique as discussed in Section 6.2.1. To handle this situation we assume that, although some set of unperturbed kets are degenerate, the eigenkets of the true Hamiltonian, $\hat{H}_0 + \lambda \hat{H}_1$, are nondegenerate. The jargon that accompanies this condition is that “the perturbation removes the degeneracy,” although in many cases the perturbation only partially removes the degeneracy. Figure 12.1 illustrates the contrast between the nondegenerate and degenerate cases. For the nondegenerate case each unperturbed state evolves into another nondegenerate state, but for the degenerate case the group of degenerate states on the left is split into a group of nondegenerate states. In the illustration the degenerate state is fivefold degenerate and one of those states is not shifted by application of the perturbation.

Recalling that any linear combination of the degenerate eigenkets is also an eigenket, we must construct a linear combination of the degenerate kets of \hat{H}_0 that are also eigenkets of \hat{H}_1 . That is, we seek a particular linear combination of the q degenerate kets $|\psi_j^{(0)}\rangle$

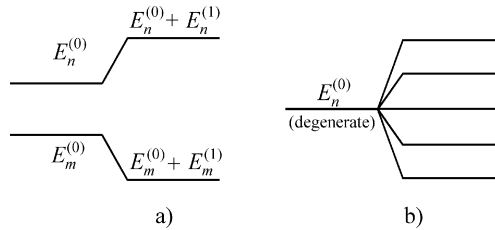


Fig. 12.1 Illustration of the effects of a perturbation on (a) a nondegenerate level and (b) a degenerate level

$$\left| \phi_i^{(0)} \right\rangle = \sum_{j=1}^q c_{ij} \left| \psi_j^{(0)} \right\rangle \quad (12.34)$$

to serve as our unperturbed ket such that

$$\hat{H}_1 \left| \phi_i^{(0)} \right\rangle = E_i^{(1)} \left| \phi_i^{(0)} \right\rangle \quad (12.35)$$

Because it is always possible to construct an orthonormal set (see Section 6.2.1, Theorem 6.2.1), we assume that the set of $\left| \psi_j^{(0)} \right\rangle$, which are not unique, are indeed orthonormal. Let us carefully examine the symbols in Equation 12.34. This state is q -fold degenerate, so there are q different linear combinations $\left| \phi_i^{(0)} \right\rangle$, one corresponding to each degenerate state. All, however, have the same energy eigenvalue, $E_q^{(0)}$. The kets $\left| \phi_i^{(0)} \right\rangle$ are sometimes referred to as the select linear combination of degenerate unperturbed kets and we have used the symbol ϕ to distinguish the select kets from the kets $\left| \psi_j^{(0)} \right\rangle$ that are not eigenkets of \hat{H}_1 .

To determine the select linear combinations we substitute $\left| \phi_i^{(0)} \right\rangle$ for $\left| \psi_n^{(0)} \right\rangle$, Equation 12.34, into the second of Equations 12.9, the coefficient of λ^1 :

$$\hat{H}_0 \left| \psi_i^{(1)} \right\rangle + \hat{H}_1 \left| \phi_i^{(0)} \right\rangle = E_i^{(0)} \left| \psi_i^{(1)} \right\rangle + E_i^{(1)} \left| \phi_i^{(0)} \right\rangle \quad (12.36)$$

Because the eigenkets that have been corrected to first-order are nondegenerate we may expand the $\left| \psi_i^{(1)} \right\rangle$ on the original unperturbed set $\left| \psi_j^{(0)} \right\rangle$:

$$\left| \psi_i^{(1)} \right\rangle = \sum_{j=1}^{\infty} a_{ij} \left| \psi_j^{(0)} \right\rangle \quad (12.37)$$

where we assume that in the summation the first q terms, $j = 1 \rightarrow q$, are the degenerate eigenkets $\left| \psi_j^{(0)} \right\rangle$. Inserting this expansion into Equation 12.36 we obtain

$$\sum_{j=1}^{\infty} a_{ij} E_j^{(0)} \left| \psi_j^{(0)} \right\rangle + \hat{H}_1 \sum_{j=1}^q c_{ij} \left| \psi_j^{(0)} \right\rangle = E_i^{(0)} \sum_{j=1}^{\infty} a_{ij} \left| \psi_j^{(0)} \right\rangle + E_i^{(1)} \sum_{j=1}^q c_{ij} \left| \psi_j^{(0)} \right\rangle \quad (12.38)$$

For the $j = 1 \rightarrow q$ terms of the expansions $E_j^{(0)} = E_i^{(0)} = E_q^{(0)}$ so Equation 12.38 becomes

$$\sum_{j>q}^{\infty} a_{ij} E_j^{(0)} \left| \psi_j^{(0)} \right\rangle + \hat{H}_1 \sum_{j=1}^q c_{ij} \left| \psi_j^{(0)} \right\rangle = E_q^{(0)} \sum_{j>q}^{\infty} a_{ij} \left| \psi_j^{(0)} \right\rangle + E_i^{(1)} \sum_{j=1}^q c_{ij} \left| \psi_j^{(0)} \right\rangle \quad (12.39)$$

because the first q terms in the first summation on each side of the equation cancel. Multiplying on the left by an unperturbed degenerate bra $\langle \psi_k^{(0)} |$, that is, a bra for which $k \leq q$, we have

$$\sum_{j=1}^q c_{ij} \langle \psi_k^{(0)} | \hat{H}_1 | \psi_j^{(0)} \rangle = E_i^{(1)} c_{ik} \quad k < q \quad (12.40)$$

Equation 12.40 may be written in matrix notation. The degenerate eigenkets $|\psi_i^{(0)}\rangle$ are not eigenkets of \hat{H}_1 so the matrix of the perturbing Hamiltonian is not diagonal on this basis set (see Section 6.1.3). It is, however, diagonal on the $|\phi_j^{(0)}\rangle$ basis. This makes clear the reason for constructing the select set $|\phi_i^{(0)}\rangle$. Note that the matrix representing the unperturbed Hamiltonian, \hat{H}_0 , is diagonal on both basis sets. To clarify the nature of the matrices we illustrate schematically the $q \times q$ matrix representation of the complete Hamiltonian, $\hat{H} = \hat{H}_0 + \hat{H}_1$, on each of these basis sets. On the $|\psi_i^{(0)}\rangle$ set we have

$$\begin{aligned} \hat{H} &= \hat{H}_0 + \hat{H}_1 \\ &\begin{pmatrix} E_q^{(0)} & 0 & 0 & 0 \\ 0 & E_q^{(0)} & 0 & 0 \\ 0 & 0 & E_q^{(0)} & 0 \\ 0 & 0 & 0 & \dots \end{pmatrix} \\ &+ \begin{pmatrix} (\hat{H}_1)_{11} & (\hat{H}_1)_{12} & (\hat{H}_1)_{13} & \dots \\ (\hat{H}_1)_{21} & (\hat{H}_1)_{22} & (\hat{H}_1)_{23} & \dots \\ (\hat{H}_1)_{31} & (\hat{H}_1)_{32} & (\hat{H}_1)_{33} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \end{aligned} \quad (12.41)$$

where $(\hat{H}_1)_{ij} = \langle \psi_i^{(0)} | \hat{H}_1 | \psi_j^{(0)} \rangle$. This matrix representation of \hat{H}_1 is not, in general, diagonal, so it is not useful for determination of the first-order corrections to the energy, the $E_i^{(1)}$. If, however, some of the off-diagonal matrix elements ($i \neq j$) vanish, then the corresponding diagonal elements are the first-order correction to the eigenvalues as for nondegenerate perturbations. Thus, if part of a matrix is diagonal, we need diagonalize only the submatrix that is not.

To diagonalize the matrix we must use the select set, the $|\phi_j^{(0)}\rangle$, as the basis set and the matrix representation of \hat{H} is

$$\begin{aligned}
\langle \phi_k^{(0)} | \hat{H} | \phi_i^{(1)} \rangle &= \langle \phi_k^{(0)} | \hat{H}_0 | \phi_i^{(1)} \rangle + \langle \phi_k^{(0)} | \hat{H}_1 | \phi_i^{(1)} \rangle \\
&= \begin{pmatrix} E_q^{(0)} & 0 & 0 & 0 \\ 0 & E_q^{(0)} & 0 & 0 \\ 0 & 0 & E_q^{(0)} & 0 \\ 0 & 0 & 0 & \dots \end{pmatrix} + \begin{pmatrix} E_1^{(1)} & 0 & 0 & 0 \\ 0 & E_2^{(1)} & 0 & 0 \\ 0 & 0 & E_3^{(1)} & 0 \\ 0 & 0 & 0 & \dots \end{pmatrix} \\
&= \begin{pmatrix} E_q^{(0)} + E_1^{(1)} & 0 & 0 & 0 \\ 0 & E_q^{(0)} + E_3^{(1)} & 0 & 0 \\ 0 & 0 & E_q^{(0)} + E_3^{(1)} & 0 \\ 0 & 0 & 0 & \dots \end{pmatrix} \quad (12.42)
\end{aligned}$$

where $(\hat{H}_1)_{ij} = \langle \phi_i^{(0)} | \hat{H}_1 | \phi_j^{(0)} \rangle$. It should now be clear why most degenerate perturbation problems are solved by using matrices to represent the Hamiltonians and the eigenkets. An example will serve to illustrate the method.

Example: A perturbed isotropic oscillator

Cartesian coordinates

We examine the effects of a perturbation $\hat{H}_1 = \varepsilon xy$ on the first excited state of an isotropic harmonic oscillator. The form of \hat{H}_1 suggests that we work in Cartesian coordinates, but this is not actually necessary. In Cartesian coordinates the unperturbed Hamiltonian is $\hat{H}_0 = \frac{1}{2}m\omega^2(x^2 + y^2 + z^2)$. Recall from the discussion of this oscillator in Section 9.5 that the ground state is nondegenerate, but that the first excited state, the state having quantum number $n = 1$, is threefold degenerate. We seek the first-order correction to the unperturbed energy

$$E_1^{(0)} = \frac{5}{2}\hbar\omega \quad (12.43)$$

Clearly $E_1^{(0)}$ is formed from the quantum numbers (n_x, n_y, n_z) using the combinations $(1, 0, 0)$, $(0, 1, 0)$, or $(0, 0, 1)$. We can therefore immediately write the matrix representation for \hat{H}_0 using the corresponding kets, which we designate as $|n_x n_y n_z\rangle$, as a basis set. Of course, in this representation \hat{H}_0 is diagonal:

$$\hat{H}_0 = \frac{5}{2}\hbar\omega \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (12.44)$$

Now we must find the \hat{H}_1 using the same basis set so its matrix is given by

$$\hat{H}_1 = \varepsilon \begin{pmatrix} \langle 100|_{xy}|100\rangle & \langle 100|_{xy}|010\rangle & \langle 100|_{xy}|001\rangle \\ \langle 010|_{xy}|100\rangle & \langle 010|_{xy}|010\rangle & \langle 010|_{xy}|001\rangle \\ \langle 001|_{xy}|100\rangle & \langle 001|_{xy}|010\rangle & \langle 001|_{xy}|001\rangle \end{pmatrix} \quad (12.45)$$

To find the entries in this matrix we use the matrix elements determined in Section 7.1.2. From Equation 7.31 we have

$$\begin{aligned} \langle m_x m_y m_z | \hat{H}_1 | n_x n_y n_z \rangle &= \varepsilon \langle m_x m_y m_z | xy | n_x n_y n_z \rangle \\ &= \frac{\varepsilon}{2\alpha^2} \left(\sqrt{n_x} \delta_{m_x, n_x-1} + \sqrt{n_x+1} \delta_{m_x, n_x+1} \right) \\ &\quad \times \left(\sqrt{n_y} \delta_{m_y, n_y-1} + \sqrt{n_y+1} \delta_{m_y, n_y+1} \right) \end{aligned} \quad (12.46)$$

and we see immediately that, because none of the Kronecker deltas have the same indexes, all diagonal elements of the perturbation matrix vanish. This is the same as noting that x is an odd function so all diagonal elements of \hat{H}_1 vanish. They also vanish because y is an odd function. Also, again because of the Kronecker deltas, any matrix elements for which the value of n_x and n_y is the same, vanish. That is, $\langle 001|_{xy}|100\rangle = \langle 100|_{xy}|001\rangle = 0$ and $\langle 010|_{xy}|100\rangle = \langle 010|_{xy}|100\rangle = 0$. Thus, the only nonzero matrix elements are $\langle 100|_{xy}|010\rangle = \langle 010|_{xy}|100\rangle$, those for which n_x and n_y differ by unity, and we have

$$\begin{aligned} \langle 001|_{xy}|010\rangle &= \frac{\varepsilon}{2\alpha^2} (1+0) \times (0+1) \\ &= \frac{\varepsilon}{2\alpha^2} \end{aligned} \quad (12.47)$$

Therefore, the matrix representation of \hat{H}_1 on the $|n_x n_y n_z\rangle$ basis set is

$$\hat{H}_1 = \frac{\varepsilon}{2\alpha^2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (12.48)$$

Because the only off-diagonal elements occur between state $|001\rangle$ and $|010\rangle$ only the upper left 2×2 submatrix need be diagonalized as discussed above. We therefore diagonalize the matrix

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (12.49)$$

to find the corrections to the unperturbed energies, as well as the select linear combination of unperturbed kets. Performing all the steps we have

$$\frac{\varepsilon}{2\alpha^2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E_1^{(1)} \begin{pmatrix} a \\ b \end{pmatrix} \quad (12.50)$$

or

$$\begin{pmatrix} -E_1^{(1)} & \frac{\varepsilon}{2\alpha^2} \\ \frac{\varepsilon}{2\alpha^2} & -E_1^{(1)} \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0 \quad (12.51)$$

This equation represents two homogeneous linear equations with the variables a and b . A nontrivial solution will exist if the determinant of coefficients vanishes. Note that this will not (yet) determine the select kets. Rather, we will obtain the allowable values of $E_1^{(1)}$ from which we will be able to determine the select kets. Setting the determinant equal to zero we obtain the secular equation

$$\left[E_1^{(1)} \right]^2 - \left(\frac{\varepsilon}{2\alpha^2} \right)^2 = 0 \quad (12.52)$$

from which it is clear that the eigenvalues of \hat{H}_1 , which are also the corrections to the unperturbed energy, are

$$\begin{aligned} E_{1\pm}^{(1)} &= \pm \frac{\varepsilon}{2\alpha^2} \\ &= \pm \frac{\varepsilon \hbar}{2m\omega} \end{aligned} \quad (12.53)$$

and the corrected energy is

$$E_{1\pm} = \frac{5}{2}\hbar\omega \pm \frac{\varepsilon \hbar}{2m\omega} \quad (12.54)$$

It is clear from this equation that, indeed, application of the perturbation has split the degenerate levels $(1, 0, 0)$ and $(0, 1, 0)$ and thus removed the $n = 1$ degeneracy.

The kets that represent these split states are the select kets which may be found by inserting the two values of $E_{1\pm}^{(1)}$ into Equation 12.50 and solving for a and b . Using the 3×3 matrix, we have

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \pm \begin{pmatrix} a \\ b \\ c \end{pmatrix} \quad (12.55)$$

so that

$$b = \pm a; \quad c = 0 \quad (12.56)$$

In terms of the unperturbed kets the normalized select kets are therefore

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \pm \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad (12.57)$$

or, designating the select kets a $|+\rangle$ and $|-\rangle$,

$$|\pm\rangle = \frac{1}{\sqrt{2}} |1\ 0\ 0\rangle \pm \frac{1}{\sqrt{2}} |0\ 1\ 0\rangle \quad (12.58)$$

Of course, the unperturbed ket $|0\ 0\ 1\rangle$ is unaffected by the perturbation, so the eigenvalue of this ket is not shifted. The levels and the kets are shown in Fig. 12.2.

Spherical coordinates

Working this problem in spherical coordinates is a bit more involved, but not much. Doing so provides practice in solving degenerate perturbation problems so we work out the details. The eigenfunctions and their eigenvalues in spherical coordinates are already known (see Section 9.5.2). For the first excited state the quantum numbers are $n = 1$, $\ell = 1$, $m = 0, \pm 1$ so, as for Cartesian coordinates, this state is threefold degenerate. In spherical coordinates the perturbing Hamiltonian is

$$\hat{H}_1 = \varepsilon r^2 \sin^2 \theta \cos \phi \sin \phi \quad (12.59)$$

and, from Table 9.8, the three unperturbed eigenfunctions are

$$\psi_{11m}(r, \theta, \phi) = \sqrt{\frac{8}{3}} \cdot \frac{\alpha^{5/2}}{\pi^{1/4}} r e^{-\alpha^2 r^2/2} Y_{1m}(\theta, \phi) \quad (12.60)$$

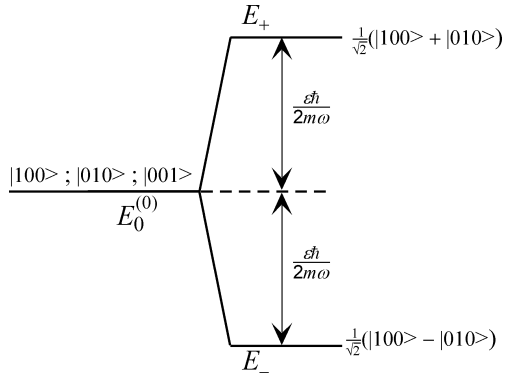


Fig. 12.2 The effects of the perturbation $\hat{H}_1 = \varepsilon xy$ on the $n = 1$ states of an isotropic oscillator

Because the three spherical eigenfunctions all have the same values of n and ℓ , we designate the corresponding kets by only their values of m . The matrix representing the unperturbed Hamiltonian is the diagonal matrix displayed in Equation 12.44. We must now find the matrix representation of \hat{H}_1 in the representation of the spherical basis. We are free to choose the order of the matrix elements, so we elect to use

$$\hat{H}_1 = \varepsilon \begin{pmatrix} \langle -1 | \hat{H}_1 | -1 \rangle & \langle -1 | \hat{H}_1 | 0 \rangle & \langle -1 | \hat{H}_1 | 1 \rangle \\ \langle 0 | \hat{H}_1 | -1 \rangle & \langle 0 | \hat{H}_1 | 0 \rangle & \langle 0 | \hat{H}_1 | 1 \rangle \\ \langle 1 | \hat{H}_1 | -1 \rangle & \langle 1 | \hat{H}_1 | 0 \rangle & \langle 1 | \hat{H}_1 | 1 \rangle \end{pmatrix} \quad (12.61)$$

Three integrals are required to compute each matrix element. These ϕ -integrals have the form

$$I_\phi(m, m') = \int_0^{2\pi} (e^{im\phi})^* e^{im'\phi} \cos \phi \sin \phi d\phi \quad (12.62)$$

If $m = m'$, this integral vanishes, so all diagonal elements of the matrix in Equation 12.61 are zero. Moreover, if *either* m or m' is zero, then the integral also vanishes. Thus, the only nonvanishing matrix elements are $\langle 1 | \hat{H}_1 | -1 \rangle$ and $\langle -1 | \hat{H}_1 | 1 \rangle$. Because $\langle 1 | \hat{H}_1 | -1 \rangle = \langle -1 | \hat{H}_1 | 1 \rangle^*$ it is necessary to evaluate only one integral. We obtain (see Problem 10)

$$\langle 1 | \hat{H}_1 | -1 \rangle = -\frac{i\varepsilon}{2\alpha^2} \quad (12.63)$$

so the matrix that we must diagonalize is

$$\hat{H}_1 = \frac{i\varepsilon}{2\alpha^2} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} \quad (12.64)$$

Clearly we could have arranged the order of the kets to obtain a matrix of the form of that in Equation 12.48 so that a 2×2 submatrix was obvious. Nonetheless, the secular equation is

$$\begin{vmatrix} -E_1^{(1)} & 0 & \frac{i\varepsilon}{2\alpha^2} \\ 0 & -E_1^{(1)} & 0 \\ -\frac{i\varepsilon}{2\alpha^2} & 0 & -E_1^{(1)} \end{vmatrix} = 0 \quad (12.65)$$

or

$$\left[-E_1^{(1)}\right]^3 + \left(\frac{i\varepsilon}{2\alpha^2}\right) \left[-\left(E_1^{(1)} \frac{i\varepsilon}{2\alpha^2}\right)\right] = 0 \quad (12.66)$$

from which we find

$$\begin{aligned} E_1^{(1)} &= 0, \pm \left(\frac{\varepsilon}{2\alpha^2} \right) \\ &= 0, \pm \left(\frac{\varepsilon \hbar}{2m\omega} \right) \end{aligned} \quad (12.67)$$

which agrees with the result obtained using Cartesian coordinates, Equation 12.53.

12.2 The Variational Method

As noted, this method provides only the energy eigenvalue, but we can obtain these energies to any precision that we desire. We assume that we know the true Hamiltonian and pretend that we can solve the problem which may be written symbolically as

$$\hat{H} |\phi_n\rangle = E_n |\phi_n\rangle \quad (12.68)$$

where the $|\phi_n\rangle$ eigenkets form a complete orthonormal set. The E_n are the corresponding energy eigenvalues; we seek E_0 . The only thing we actually know in Equation 12.68 is the Hamiltonian.

We now assume some arbitrary normalized wave function that we refer to as a trial wave function $|\psi\rangle$ and expand it on the complete, but unknown, set of orthonormal eigenkets $|\phi_n\rangle$:

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n |\phi_n\rangle \quad (12.69)$$

Of course, it is sensible to begin with a trial function that matches the boundary conditions. For example, if we are attempting to find the ground state energy of a hydrogen atom, it would not be wise to choose a trial wave function that vanishes at $r = 0$ (see Fig. 10.3).

Now we write an expression for the expectation value of the energy in the state represented by $|\psi\rangle$:

$$\begin{aligned} \langle E \rangle &= \langle \psi | \hat{H} | \psi \rangle \\ &= \sum_{n=0}^{\infty} |c_n|^2 \langle \phi_n | \hat{H} | \phi_n \rangle \\ &= \sum_{n=0}^{\infty} |c_n|^2 E_n \end{aligned} \quad (12.70)$$

The ground state energy, E_0 , is lower in magnitude than any of the other eigenvalues so, if we let $E_n = E_0$ in Equation 12.70, we obtain an inequality

$$\begin{aligned}\langle E \rangle &\geq E_0 \sum_{n=0}^{\infty} |c_n|^2 \\ &\geq E_0\end{aligned}\tag{12.71}$$

where, because $|\psi\rangle$ is normalized, the summation in Equation 12.71 is unity. If the trial wave function is not normalized, we merely divide by $\langle \psi | \psi \rangle$ and we have

$$\begin{aligned}\langle E \rangle &= \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= \frac{\int \psi^*(\mathbf{r}) \hat{H} \psi(\mathbf{r}) dV}{\int \psi^*(\mathbf{r}) \psi(\mathbf{r}) dV} \\ &\geq E_0\end{aligned}\tag{12.72}$$

Now, let us examine the ramifications of Equation 12.71. If we are working in coordinate space, this inequality is

$$\begin{aligned}\langle E \rangle &= \int \psi^*(\mathbf{r}) \hat{H} \psi(\mathbf{r}) dV \\ &\geq E_0\end{aligned}\tag{12.73}$$

so we can take any trial wave function, compute the integral in Equation 12.73, and be assured that the result will be greater than the true ground state energy. To make our result more precise we can insert parameters in the wave function and minimize $\langle E \rangle$ with respect to these parameters. No matter how many parameters we include in our trial wave function we are assured that $\langle E \rangle$ will be greater than the true ground state energy. Thus, it can be seen that if many parameters are chosen, using modern computers it is possible to evaluate the expectation value and minimize $\langle E \rangle$, thus obtaining the ground state to virtually any accuracy we please.

Example: Ground state energy of a one-dimensional harmonic oscillator

Let us assume that we do not know either the ground state eigenfunction or the ground state energy of a one-dimensional harmonic oscillator, $E_0 = \frac{1}{2}\hbar\omega$. To approximate the ground state energy we guess at a trial wave function. We can, however, make an educated guess. For example, we know that the potential energy is given by Equation 3.22, which is an even function of x . Therefore, the ground state eigenfunction must be an even function. We choose one of the form

$$\psi(x) = \frac{1}{\beta^2 + x^2} \quad (12.74)$$

where β is a parameter that we can vary to minimize $\langle E \rangle$. This trial wave function is not normalized so we will have to use Equation 12.72. We expect that both integrals in Equation 12.72 will depend upon β . Using Equation H.8 we have

$$\begin{aligned} \langle \psi | \psi \rangle &= \int_{-\infty}^{\infty} \frac{1}{(\beta^2 + x^2)^2} dx \\ &= \frac{\pi}{2\beta^3} \end{aligned} \quad (12.75)$$

and

$$\langle \psi | \hat{H} | \psi \rangle = \int_{-\infty}^{\infty} \frac{1}{(\beta^2 + x^2)} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 \right) \frac{1}{(\beta^2 + x^2)} dx \quad (12.76)$$

Using the integrals given in Equations H.8, H.9, and H.10,

$$\langle \psi | \hat{H} | \psi \rangle = \frac{\pi \hbar^2}{8m\beta^5} + \frac{\pi m \omega^2}{4\beta} \quad (12.77)$$

so that

$$\langle E \rangle = \frac{\hbar^2}{4m\beta^2} + \frac{m\omega^2}{2} \beta^2 \quad (12.78)$$

We wish to minimize this expression with respect to β to obtain β_0 , the value of β that minimizes $\langle E \rangle$. Therefore,

$$\begin{aligned} \frac{d \langle E \rangle}{d\beta} &= 0 \\ &= -\frac{\hbar^2}{2m\beta_0^3} + m\omega^2 \beta_0 \end{aligned} \quad (12.79)$$

so that

$$\beta_0^2 = \frac{\hbar}{\sqrt{2} m \omega} \quad (12.80)$$

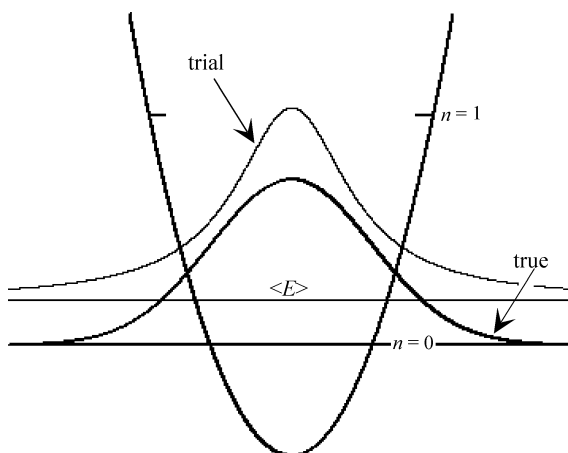


Fig. 12.3 The trial wave function and true eigenfunction for the ground state of the harmonic oscillator plotted on the same graph as the potential energy function. These wave functions are plotted at the energies to which they correspond

which, when inserted in Equation 12.78, leads to

$$\langle E \rangle = \frac{1}{\sqrt{2}} \hbar \omega \quad (12.81)$$

This approximation is clearly not very close to the correct value, $\frac{1}{2} \hbar \omega$, since it is in error by roughly forty percent.

Figure 12.3 shows the true eigenfunction and the trial wave function. The zero of the trial wave function is the calculated approximate energy $\langle E \rangle$ (see Equation 12.81). Despite the fact that the calculated energy is not a very close approximation to the actual energy, this simple example illustrates the power of the method because, as seen in Fig. 12.3, the trial wave function is not a very good likeness of the true ground state wave function. In principle, we could include a large number of adjustable parameters in our trial wave function, minimizing $\langle E \rangle$ with respect to each of them. As a consequence, with the availability of modern computers it is possible to obtain an approximation to virtually any energy with unlimited precision.

Problems

1. A particle of mass m is trapped in a one-dimensional harmonic oscillator potential with a constant electric field F superimposed.
 - (a) Show that the TISE can be solved exactly.
 - (b) Compare the answer with that obtained in the example in Section 12.1.1. What can be said about the perturbation corrections higher than second-order?

2. A δ -function spike in the potential energy, $U_0\delta(x)$, is inserted in an a -box at $x = 0$. Find the first-order correction to the energy of the n th state. Why is there no first-order correction for even quantum numbers n ?
3. An electron is confined to an L -box with a superimposed electric field that is associated with the potential energy $U(x) = eFx$. The field is such that $eFL \ll E_1^{(0)}$, the unperturbed ground state energy.
 - (a) Find the first-order correction to the ground state energy of the L -box.
 - (b) Find the first-order correction to the ground state eigenfunction of the L -box. Evaluate only the first term in the summation. Why is this term the leading term?
4. A particle of mass m is confined to an L -box, the parameters of which are such that $mc^2 \gg E_n^{(0)}$ for low values of n .
 - (a) Find $E_n^{(1)}$ the first-order correction to the energy due to the relativistic kinetic energy of the particle. Write $E_n^{(1)}$ in terms of $E_n^{(0)}$, the nonrelativistic energy for an L -box. [Note that the *total* relativistic energy of a particle of mass m is given by $E^2 = \hat{p}^2c^2 + m^2c^4$.]
 - (b) For a particle-in-a-box the usual nonrelativistic energy eigenfunctions are also eigenfunctions of the relativistic Hamiltonian. Find the exact relativistic energy and show that for $mc^2 \gg E_n^{(0)}$ the solution reduces to the perturbation theory result.
5. Treat the rotationless Morse oscillator, Equation 5.44, using perturbation theory and obtain the first nonvanishing correction to the n th state of a one-dimensional harmonic oscillator due to the first anharmonic term. Use β in place of α in the Morse potential to avoid confusion with $\alpha^2 = m\omega/\hbar$. The matrix element given in Equation 7.38 may be helpful.
6. Suppose the square of the natural frequency of a harmonic oscillator is written as the sum of two squared frequencies so that $\omega^2 \rightarrow \omega^2 + \omega_1^2$ where $\omega_1^2 \ll \omega^2$.
 - (a) Calculate the energy shifts using perturbation theory with $\hat{H}_1 = \frac{1}{2}m\omega_1^2$ through second-order.
 - (b) Compare the perturbation result with the exact energies.
7. Find the first-order correction to the energy of a particle in the ground state of a quartic oscillator having potential energy $U(x) = Cx^4$ (C is a positive constant) using a harmonic oscillator as the unperturbed system. [Hint: Add and subtract $\frac{1}{2}m\omega^2x^2$ to the Hamiltonian.]
8. A matrix that has been constructed on an orthonormal basis set and represents the Hamiltonian of a particular system is given by

$$\hat{H} = \begin{pmatrix} 1 & \epsilon & 0 \\ \epsilon & 2 & 0 \\ 0 & 0 & 3 - \epsilon \end{pmatrix}$$

- (a) Write this matrix as the sum of two matrices $\hat{H} = \hat{H}_0 + \hat{H}_1$ for the purpose of applying perturbation theory to approximate the eigenvalues of \hat{H} .
- (b) Find the eigenvalues to second-order.
- (c) Solve the problem exactly and compare with the perturbation theory result.
9. Show that the first-order corrections to the energy of the isotropic oscillator due to the perturbation $\hat{H}_1 = \epsilon xy$, Equation 12.53, do indeed have units of energy.
10. Verify the matrix element $\langle 1 | \hat{H}_1 | -1 \rangle = -i\epsilon / (2\alpha^2)$ (see Equation 12.63) where $\hat{H}_1 = \epsilon r^2 \sin^2 \theta \cos \phi \sin \phi$.
11. An electron trapped in an isotropic harmonic oscillator potential has applied to it an electric field $\mathbf{F} = F\hat{\mathbf{k}}$. Use perturbation theory to find the first nonvanishing correction to the ground state energy:
- (a) in Cartesian coordinates
- (b) in spherical coordinates
12. Suppose the matrix representing the Hamiltonian \hat{H} in Problem 8 is modified so the middle entry is unity:

$$\hat{H} = \begin{pmatrix} 1 & \epsilon & 0 \\ \epsilon & 1 & 0 \\ 0 & 0 & 6 \end{pmatrix}$$

- (a) Find the select basis set and show that these select eigenvectors diagonalize \hat{H} .
- (b) Show that the select set diagonalizes \hat{H} and therefore show that the eigenvalues are $(1 \pm \epsilon)$ and 6.
- (c) Show that \hat{H} operating on the select eigenvectors produces the eigenvalues.
- (d) Solve the problem exactly and compare with the perturbation theory result.
13. A particle of mass m is trapped in a quartic oscillator having potential energy $U(x) = Cx^4$ where C is a positive constant.
- (a) Using the variational technique estimate the ground state energy using the trial wave function $\psi(x) = Ae^{-\beta^2 x^2/2}$ where $A = \text{constant}$. Use β as the adjustable parameter.
- (b) Compare the variational technique answer with the perturbation result found in Problem 7.
14. Use the trial wave function $\psi(x) = Ae^{-\beta^2 x^2}$ to estimate the ground state energy of a harmonic oscillator and show that the value of β that minimizes $\langle \psi | \hat{H} | \psi \rangle$ is $\alpha/\sqrt{2}$ where $\alpha = \sqrt{m\omega/\hbar}$.
15. Using the variational technique, estimate the ground state energy of a particle of mass m trapped in a half harmonic oscillator (see Problem 19 of Chapter 3):

$$\begin{aligned} U(x) &= \frac{1}{2}m\omega^2 x^2 & x > 0 \\ &= \infty & x \leq 0 \end{aligned}$$

using the trial wave function with β as a parameter:

$$\begin{aligned}\psi(x) &= Axe^{-\beta x} & x > 0; A = \text{constant} \\ &= 0 & x \leq 0\end{aligned}$$

Compare the answer with the exact answer. Why was the trial wave function chosen to vanish at $x = 0$?

16. A particle of mass m is trapped in a linear potential

$$\begin{aligned}U(x) &= eFx & x > 0 \\ &= \infty & x \leq 0\end{aligned}$$

- (a) Using the variational technique estimate the ground state energy using the trial wave function $\psi(x) = Axe^{-\beta x}$; $A = \text{constant}$.
- (b) Show that the energy calculated using the variational principle is greater than the exact energy calculated in Section 5.5.

Chapter 13

Applications of Time-Independent Approximation Methods

The examples of the approximation methods discussed in Chapter 12 were chosen primarily to illustrate the methods, and not necessarily for their relevance to physical problems. In this chapter we will concentrate on application of these methods to real problems. We begin with the hydrogen atom. When relativistic effects are included in the Hamiltonian, the accidental degeneracy is broken, so we will examine these effects. We will then study the helium atom as an example of atoms having more than one electron. Because the three body problem cannot be solved exactly the approximation methods used to understand the helium atom serve as a paradigm for all multielectron atoms.

13.1 Hydrogen Atoms

13.1.1 Breaking the Degeneracy—Fine Structure

The first corrections to the Bohr energy are called fine structure. They are all relativistic in nature. To understand the magnitudes of the corrections that relativistic effects make to the degenerate Bohr energies, we write this energy in terms of the fine structure constant α , Equation 1.36:

$$E_n^{(0)} = -\frac{1}{2}\alpha^2 \frac{(m_e c^2)}{n^2} \quad (13.1)$$

where, for consistency with the notation of Chapter 12, we have designated the Bohr energy as $E_n^{(0)}$. This energy is proportional to the rest energy of the electron multiplied by α^2 . We will see that the next level of correction is proportional to the rest energy times α^4 . Therefore, the fine structure corrections to the Bohr energy $E_n^{(1)} = E_{FS}$ are such that

$$E_{FS} \propto \alpha^2 E_n^{(0)} \quad (13.2)$$

It is because $\alpha^4 \approx 5 \times 10^{-5} \cdot \alpha^2$ that these corrections are known as fine structure. To obtain the fine structure corrections rigorously, the Dirac equation, an inherently relativistic equation, must be solved. Because it is a relativistic equation, the Dirac equation supersedes the Schrödinger equation.

We have already studied hyperfine structure as an example of angular momentum coupling in Section 8.6.1 where, in the notation of that section, we found that the energy splitting due to the magnetic interaction between the proton and the electron on the $n = 1$ state is $2\kappa = E_{HF}$ (see Fig. 8.9). It can be shown that the magnitude of this splitting is given by

$$\begin{aligned} E_{HF} &= \frac{4}{3} \left[\frac{m_e}{m_p} g_p \right] \left[\alpha^2 g_e \left(\frac{1}{2} \alpha^2 m_e c^2 \right) \right] \\ &\propto \frac{m_e}{m_p} E_{FS} \end{aligned} \quad (13.3)$$

where $g_p = 5.586$ is the proton spin g -factor and m_e/m_p is the ratio of the electron to proton mass. Since this ratio is $\sim 1/2000$ it is clear that the hyperfine splitting is more than three orders of magnitude smaller than the fine structure splitting.

There is yet another shift in energy, this one roughly proportional to α^3 times the Bohr energy. This energy shift cannot be derived from even the Dirac equation. Rather, it is a consequence of quantum electrodynamics (QED). When this shift, known as the Lamb shift, was measured, it validated QED and represents a triumph for that theory for which W. E. Lamb, Jr. shared the 1955 Nobel prize with Polykarp Kusch. The citation for Lamb's portion of the prize reads: "for his discoveries concerning the fine structure of the hydrogen spectrum." Kusch's award was for his precision measurements of magnetic moments. The citation for Kusch's portion of the prize reads: "for his precision determination of the magnetic moment of the electron." We will, however, concentrate our efforts on fine structure.

The exact energy eigenvalues obtained from the Dirac equation for the Coulomb potential, when expanded, yield the Bohr energy and the fine structure corrections as well as higher order corrections. These higher order corrections are of little consequence because they are smaller than the Lamb Shift, which is not part of the solution of the Dirac equation. An alternative method of examining the hydrogen atom is to first expand the Dirac Hamiltonian. This procedure permits identification of the physical origin of the individual terms and, thus, provides insight into the physical basis for these corrections. We will see, however, that in one case the source of the terms is vague at best.

Expanding the Dirac Hamiltonian and retaining terms up to α^4 leads to

$$\hat{H}_{\text{Dirac}} = m_e c^2 + \left[\frac{\hat{p}^2}{2m_e} - \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{r} \right] + \hat{H}_T + \hat{H}_{SO} + \hat{H}_D \quad (13.4)$$

where

$$\hat{H}_T = -\frac{\hat{p}^4}{8m_e^3c^2} \quad (13.5)$$

$$\hat{H}_{SO} = \left(\frac{e^2}{4\pi\epsilon_0}\right) \left(\frac{1}{2m_e^2c^2}\right) \frac{1}{r^3} \hat{\mathbf{L}} \bullet \hat{\mathbf{S}} \quad (13.6)$$

$$\hat{H}_D = \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{\hbar^2\pi}{2m_e^2c^2} \delta(\mathbf{r}) \quad (13.7)$$

Each of the Hamiltonians, \hat{H}_T , \hat{H}_{SO} , and \hat{H}_D , produces a correction to the Bohr energy that is of the order $\alpha^2 E_n^{(0)}$ so their sum constitutes the fine structure Hamiltonian \hat{H}_{FS} . We will evaluate the corrections due to each of these perturbing Hamiltonians, and then add the results to obtain the complete fine structure correction. Notice that the leading term in the expansion of \hat{H}_{Dirac} , Equation 13.4, is the rest energy of the electron, a constant. This is not a very mathematically interesting Hamiltonian, but, quite naturally, it leads to the correct rest mass. This term is proportional to α^0 . The term in brackets is the familiar unperturbed nonrelativistic Schrödinger Hamiltonian \hat{H}_0 , the energy eigenvalues of which are the Bohr energies $E_n^{(0)} \propto \alpha^2 m_e c^2$. The sources of the first two of the remaining three terms, \hat{H}_T and \hat{H}_{SO} , are easily understood. The first term, \hat{H}_T , corresponds to the correction to the unperturbed energy resulting from proper inclusion of the relativistic velocity of the electron. The second, \hat{H}_{SO} , represents the interaction between the spin and orbital magnetic moments. The last term is the Darwin correction, named for Charles Galton Darwin, grandson of the famous biologist. Physical interpretation of the origin of the Darwin term is of dubious value. It is said to originate from a “shaking motion” of the electron that smears its probability distribution. As a consequence of the δ -function, it affects only $\ell = 0$ states (s -states) because all other angular momentum states vanish at the origin. Despite the vagueness of the meaning of this term, it represents a real effect. Each of the three Hamiltonians \hat{H}_T , \hat{H}_{SO} , and \hat{H}_D is proportional to α^4 and they are therefore treated as the perturbation Hamiltonians for determination of the fine structure. Often the expansion of the Dirac Hamiltonian assumes that the unperturbed energy is the leading term, so the perturbing Hamiltonians are said to be proportional to α^2 rather than α^4 . We will attempt to express the energies in a way that clearly shows the relationship between the energy corrections and the unperturbed energy.

Relativistic motion of the electron

We consider first the relativistic motion of the electron. Although the highest electronic velocity as estimated from the Bohr model of the atom, Equation 1.41, is more than two orders of magnitude smaller than the speed of light, relativistic effects must be considered to accurately assess the fine structure. That is, inclusion of relativity in describing the electronic velocity leads to a correction to $E_n^{(0)}$ that is proportional to α^2 . The effect is identical with that encountered in Problem 4,

Chapter 12 for an L -box, but not quite as simple. The relativistic kinetic energy operator \hat{T}_{rel} is

$$\begin{aligned}\hat{T}_{rel} &= \sqrt{\hat{p}^2 c^2 + (m_e c^2)^2} - m_e c^2 \\ &= m_e c^2 \left(1 + \frac{\hat{p}^2}{m_e^2 c^2} \right)^{1/2} - m_e c^2 \\ &= \frac{\hat{p}^2}{2m_e} - \frac{\hat{p}^4}{8m_e^3 c^2} \dots\end{aligned}\quad (13.8)$$

The first term in Equation 13.8 is simply the nonrelativistic kinetic energy that is part of the Schrödinger Hamiltonian, but the second is the first-order correction due to relativistic motion of the electron \hat{H}_T which we treat as the perturbing Hamiltonian. Both terms are present in the Dirac Hamiltonian given in Equation 13.4. Retaining the first two terms in the expansion of \hat{T}_{rel} in Equation 13.8, we may express \hat{T}_{rel} in terms of the nonrelativistic kinetic energy, $\hat{T}_0 = \hat{p}^2 / (2m_e)$:

$$\hat{T}_{rel} = \hat{T}_0 \left(1 - \hat{T}_0 \frac{1}{2m_e c^2} \right) \quad (13.9)$$

so that we may write

$$\hat{H}_T = -\frac{\hat{T}_0^2}{2m_e c^2} \quad (13.10)$$

and the first-order correction to the Bohr energy due to the relativistic motion of the electron is

$$\begin{aligned}E_{T(n\ell m)}^{(1)} &= \langle n\ell m | \hat{H}_T | n\ell m \rangle \\ &= \langle \hat{H}_T \rangle_{n\ell m}\end{aligned}\quad (13.11)$$

Before evaluating the first-order correction to the energy that is caused by \hat{H}_T , we may estimate its value relative to the unperturbed energy. For the Coulomb potential, the virial theorem in the form given in Equation 6.129 is applicable and we have

$$\begin{aligned}2\langle \hat{T}_0 \rangle &= -\langle U \rangle \\ &= -[E_n^{(0)} - \langle \hat{T}_0 \rangle]\end{aligned}\quad (13.12)$$

or

$$\langle \hat{T}_0 \rangle = -E_n^{(0)} \quad (13.13)$$

so that we may estimate the magnitude of the correction term, the second term on the right-hand side of Equation 13.9, by taking the ratio

$$\begin{aligned} \left| \frac{\langle \hat{H}_T \rangle}{\langle \hat{H}_0 \rangle} \right| &= \frac{(\hat{T}_0^2/2m_e c^2)}{E_n^{(0)}} \\ &\propto \alpha^2/n^2 \end{aligned} \quad (13.14)$$

which is the criterion for the correction to be a fine structure correction.

To evaluate this correction we write this expectation value in Equation 13.11 in the form

$$\begin{aligned} E_{T(n\ell m)}^{(1)} &= -\frac{1}{2m_e c^2} \langle \hat{T}_0^2 \rangle_{n\ell m} \\ &= -\frac{1}{2m_e c^2} \langle n\ell m | [\hat{H}_0 - \langle U \rangle] [\hat{H}_0 - \langle U \rangle] | n\ell m \rangle \\ &= -\frac{1}{2m_e c^2} \langle n\ell m | \left[E_n^{(0)} + (\hbar c \alpha) \frac{1}{r} \right] \left[E_n^{(0)} + (\hbar c \alpha) \frac{1}{r} \right] | n\ell m \rangle \\ &= -\frac{1}{2m_e c^2} \left[(E_n^{(0)})^2 + 2E_n^{(0)} (\hbar c \alpha) \left\langle \frac{1}{r} \right\rangle_{n\ell m} + (\hbar c \alpha)^2 \left\langle \frac{1}{r^2} \right\rangle_{n\ell m} \right] \\ &= -\frac{1}{2m_e c^2} \left\{ \left(\frac{1}{2} \frac{m_e c^2 \alpha^2}{n^2} \right)^2 + 2 \left(-\frac{1}{2} \frac{m_e c^2 \alpha^2}{n^2} \right) (\hbar c \alpha) \left(\frac{m_e c \alpha}{n^2 \hbar} \right) \right. \\ &\quad \left. + (\hbar c \alpha)^2 \left(\frac{m_e c \alpha}{\hbar} \right)^2 \left[\frac{2}{n^3 (2\ell + 1)} \right] \right\} \\ &= \left(-\frac{m_e c^2 \alpha^2}{2n^2} \right) \frac{\alpha^2}{n^2} \left[\frac{n}{(\ell + 1/2)} - \frac{3}{4} \right] \\ &= E_n^{(0)} \frac{\alpha^2}{n^2} \left[\frac{n}{(\ell + 1/2)} - \frac{3}{4} \right] \end{aligned} \quad (13.15)$$

where we have used the expectation values from Table 10.4 and $a_0 = \hbar/m_e c \alpha$ from Table 1.1. Because the factor $n/(\ell + \frac{1}{2}) > 1$ for a one-electron atom and $E_n^{(0)} < 0$, it is clear that the effect of \hat{H}_T is always to lower the energy. We must, however, bear in mind that this is only a portion of the fine structure correction.

Spin-orbit coupling

In the discussion of the Bohr magneton in Section 1.2.1, the magnitude of the magnetic moment μ that is a consequence of the electronic orbital motion was derived. Of course, this orbital magnetic moment has associated with it a magnetic field B , a field that mimics that of a bar magnet. As we saw in Section 8.5, the electron, by virtue of its spin, possesses an intrinsic magnetic moment and, therefore, it too behaves as a bar magnet. The spin-orbit Hamiltonian may be envisioned as the energy of orientation of this intrinsic magnetic moment in the field produced by the orbital motion of the electron so

$$\hat{H}_{SO} = -\hat{\boldsymbol{\mu}}_S \bullet \mathbf{B}_{\text{orbital}} \quad (13.16)$$

where $\hat{\boldsymbol{\mu}}_S$ is the spin magnetic moment given by Equation 8.108 and \mathbf{B} is the magnetic field produced by the orbiting electron. Of course, assuming that the orbiting electron is a bar magnet in the field of the spinning electron will produce the same effect.

A simple way of looking at this is to imagine being on the electron and seeing the orbiting proton. In this frame of reference it is the motion of the proton that produces the B -field in which the electron spin magnetic moment resides. We will calculate this B -field from this point of view, but we will find that the answer is incorrect by a factor of $\frac{1}{2}$. This factor is known as the Thomas precession factor. It corrects the naive assumption that the electron is traveling with constant velocity. Because the electron is accelerating, the rest frame of the electron is not an inertial frame. Proper consideration of the relativistic problem led Llewellyn Thomas to the now-famous correction. We will simply insert it. Note, however, that \hat{H}_{SO} as obtained from the Dirac equation (see Equation 13.6) is correct.

For this not so rigorous calculation we assume that the B -field is that of the circling proton having speed v , so that we require the field at the center of a plane circular loop of radius r . From elementary electromagnetic theory,

$$\begin{aligned} B_{\text{orbital}} &= \frac{\mu_0 i}{2r} \\ &= \frac{i}{\epsilon_0 c^2 2r} \end{aligned} \quad (13.17)$$

where the magnetic permeability of free space, μ_0 , has been eliminated in favor of electric permittivity of free space ϵ_0 using $\mu_0 \epsilon_0 = 1/c^2$. The “current” i is given by

$$i = \frac{ev}{2\pi r} \quad (13.18)$$

so we have

$$\begin{aligned} B_{\text{orbital}} &= \left(\frac{1}{4\pi \epsilon_0} \right) \frac{e}{c^2 r^2} \cdot \frac{(m_e v r)}{m_e} \\ &= \left(\frac{1}{4\pi \epsilon_0} \right) \frac{e}{m_e c^2 r^3} \hat{L} \end{aligned} \quad (13.19)$$

which was written in a way that is meant to emphasize that B is proportional to the electronic angular momentum $L = m_e v r$, which, as usual, is replaced by its quantum mechanical operator \hat{L} . The direction of B is specified by the direction of the angular momentum. Inserting $\hat{\boldsymbol{\mu}}_S$ from Equations 1.44 and 8.108 into Equation 13.16 we have

$$\hat{H}_{SO} = \left(\frac{1}{4\pi\epsilon_0} \right) \frac{g_e e^2}{2m_e^2 c^2 r^3} (\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}) \quad (13.20)$$

Inserting the Thomas factor, which is equivalent to dividing Equation 13.20 by 2, cancels $g_e = 2$ in the numerator so we obtain

$$\hat{H}_{SO} = \left(\frac{1}{4\pi\epsilon_0} \right) \frac{e^2}{2m_e^2 c^2 r^3} (\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}) \quad (13.21)$$

A more general and electrostatically rigorous derivation of \hat{H}_{SO} than is required here shows that the $1/r^3$ in Equation 13.21 actually results from a term involving the potential energy. We may therefore write

$$\hat{H}_{SO} = \frac{1}{2m_e^2 c^2} \left[\frac{1}{r} \frac{dU(r)}{dr} \right] (\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}) \quad (13.22)$$

for any central potential. It is customary to represent the coefficient of $\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}$ by $\xi(r)$ so that

$$\hat{H}_{SO} = \xi(r) (\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}) \quad (13.23)$$

where

$$\xi(r) = \frac{1}{2m_e^2 c^2} \left[\frac{1}{r} \frac{dU(r)}{dr} \right] \quad (13.24)$$

Before proceeding, let us estimate the magnitude of this correction in a manner similar to that employed to obtain Equation 13.14 by noting that the magnitudes of the orbital and spin angular momenta are roughly \hbar while $r \sim a_0$, the Bohr radius. Making these substitutions we find that (see Problem 1)

$$\left| \frac{\langle \hat{H}_{SO} \rangle}{\langle \hat{H}_0 \rangle} \right| \sim \alpha^2 \quad (13.25)$$

so the spin-orbit correction does indeed qualify as a fine structure correction. It is interesting to note that the order of magnitude for the ratio of energies given in Equation 13.25 is almost trivially derived using atomic units (see Problem 1).

The first-order spin-orbit correction to the Bohr energy is

$$E_{SO}^{(1)} = \langle \hat{H}_{SO} \rangle \quad (13.26)$$

but we have not specified the quantum numbers in Equation 13.26 because the appropriate ones are yet to be determined. To evaluate $\langle \hat{H}_{SO} \rangle_{n\ell m_\ell}$ we must evaluate $\langle 1/r^3 \rangle_{n\ell m_\ell}$, which requires only the radial part of the wave function. Note that

the quantum number that represents the z -component of orbital angular momentum has been designated m_ℓ to distinguish it from the analogous spin quantum number m_s because spin will be an important part of this calculation. There is no other r -dependence in \hat{H}_{SO} so we can use the $\langle 1/r^3 \rangle_{n\ell m_\ell}$, as listed in Table 10.4. There is, however, a problem if we attempt to use these uncoupled kets, $|n \ell m_\ell m_s\rangle$, in the computation of $\langle \hat{\mathbf{L}} \bullet \hat{\mathbf{S}} \rangle = \langle \hat{L}_x \hat{S}_x \rangle + \langle \hat{L}_y \hat{S}_y \rangle + \langle \hat{L}_z \hat{S}_z \rangle$ because m_ℓ and m_s are not good quantum numbers with respect to the operator $\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}$. That is, neither \hat{L}_z nor \hat{S}_z commute with $\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}$ (see Problem 3). Thus, these uncoupled kets are not eigenkets of \hat{H}_{SO} , so we must diagonalize this perturbation. Fortunately, we have already done this because the uncoupled kets, $|n j m_j \ell s\rangle$, are the select eigenkets of \hat{H}_{SO} because \hat{J}^2 and \hat{J}_z commute with this perturbing Hamiltonian (see Problem 4). Therefore, we may use the coupled kets, $|n j m_j \ell s\rangle$, for which both \hat{H}_0 and \hat{H}_{SO} are diagonal. Incidentally, the eigenkets of \hat{H}_0 and \hat{H}_T are the same, so \hat{H}_T was already diagonal in the basis set of \hat{H}_0 eigenkets and we could use either set of kets. Note that the only quantum numbers that appear in Equation 13.15 are n and ℓ , both of which are good in either representation.

To use the coupled set we must express $\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}$ in terms of the mutually commuting operators, in particular \hat{J}^2 , \hat{L}^2 , and \hat{S}^2 . The first of these is

$$\hat{J}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{S}}) \bullet (\hat{\mathbf{L}} + \hat{\mathbf{S}}) \quad (13.27)$$

so the cross term provides the necessary relationship

$$\hat{\mathbf{L}} \bullet \hat{\mathbf{S}} = \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2) \quad (13.28)$$

Therefore, the expectation value is

$$\begin{aligned} \langle \hat{\mathbf{L}} \bullet \hat{\mathbf{S}} \rangle &= \langle n j m_j \ell s | (\hat{J}^2 - \hat{L}^2 - \hat{S}^2) | n j m_j \ell s \rangle \\ &= \frac{1}{2} [j(j+1) - \ell(\ell+1) - 3/4] \hbar^2 \end{aligned} \quad (13.29)$$

Inserting Equation 13.29 into Equation 13.26 we obtain the spin-orbit correction which we now designate $(E_{SO}^{(1)})_{nj\ell}$:

$$\begin{aligned} (E_{SO}^{(1)})_{nj\ell} &= \frac{1}{2m_e^2 c^2} \left[\left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r^3} \right\rangle \right] \langle \hat{\mathbf{L}} \bullet \hat{\mathbf{S}} \rangle \\ &= \frac{1}{2m_e^2 c^2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{a_0^3} \left\{ \frac{[j(j+1) - \ell(\ell+1) - 3/4]}{2n^3 \ell (\ell + \frac{1}{2}) (\ell + 1)} \hbar^2 \right\} \\ &= -\frac{1}{2n} \alpha^2 E_n^{(0)} \frac{[j(j+1) - \ell(\ell+1) - 3/4]}{[\ell (\ell + \frac{1}{2}) (\ell + 1)]} \end{aligned} \quad (13.30)$$

For hydrogen j can take on only two values, $\ell \pm \frac{1}{2}$, so we may express the spin-orbit correction in terms of ℓ for each of these values of j . We have

$$\left(E_{SO}^{(1)}\right)_{n j=\ell+\frac{1}{2}} = -\frac{1}{2n}\alpha^2 E_n^{(0)} \frac{1}{\left[\left(\ell+\frac{1}{2}\right)(\ell+1)\right]} \quad (13.31)$$

$$\left(E_{SO}^{(1)}\right)_{n j=\ell-\frac{1}{2}} = \frac{1}{2n}\alpha^2 E_n^{(0)} \frac{1}{\left[\ell\left(\ell+\frac{1}{2}\right)\right]} \quad (13.32)$$

The Darwin term

The spin-orbit coupling Hamiltonian was found to be proportional to $\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}$ so it follows that for s -states, $\ell = 0$ states, $\left(E_{SO}^{(1)}\right)_{nj0} = 0$. To examine the validity of this statement we return to Equation 13.30. Noting that for $\ell = 0$, $j = s$ so that $\left(E_{SO}^{(1)}\right)_{j\ell}$ is proportional to zero divided by zero. We conclude therefore that Equation 13.30 is not valid for $\ell = 0$. The culprit in making Equation 13.30 indeterminate is $\langle 1/r^3 \rangle$ because it provides the zero in the denominator. There is nothing wrong with the expression for $\langle 1/r^3 \rangle$! The problem is that the spin-orbit term that was derived using magnetic moments is incomplete when compared with the terms arising from the Dirac equation. If the Dirac equation is carried out to the next level of expansion, there appears a term that “softens” the divergence of $1/r^3$ at the origin [1]. Thus, in place of $\langle 1/r^3 \rangle$ there is a function that is finite at the origin that makes the spin-orbit correction zero for $\ell = 0$. For our purpose Equation 13.30 is valid for all $\ell \neq 0$.

While the spin-orbit term vanishes for s -states, the Darwin term is valid *only* for s -states because of the δ -function. Therefore, the uncoupled kets $|n 0 0\rangle$ are eigenkets of \hat{H}_D and

$$E_D^{(1)} = \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{\hbar^2\pi}{2m_e^2c^2} \langle n 0 0 | \delta(r) | n 0 0 \rangle \quad (13.33)$$

where the argument of the δ -function has been changed to spherical coordinate r because there is no angular dependence of the eigenfunctions for s -states. To evaluate the integral that is the expectation value of the δ -function we use the sifting property of the δ -function. Using Equation 10.40 and knowledge that $Y_{00}(\theta, \phi) = 1/\sqrt{4\pi}$ we write

$$\begin{aligned} \langle n 0 0 | \delta(r) | n 0 0 \rangle &= |\psi_{n00}(r, \theta, \phi)|^2 \\ &= \frac{1}{4\pi} |R_{n0}(0)|^2 \end{aligned} \quad (13.34)$$

From Equation 10.35 we have

$$\begin{aligned}
R_{n0}(r) &= \left[\frac{1}{2n} \left(\frac{2}{na_0} \right)^3 \frac{(n-1)!}{n!} \right]^{1/2} L_{n-1}^1(0) \\
&= \left[\frac{1}{2n^2} \left(\frac{2}{na_0} \right)^3 \right]^{1/2} L_{n-1}^1(0)
\end{aligned} \tag{13.35}$$

Fortunately, there is a general expression [2] for $L_p^q(0)$:

$$L_p^q(0) = \frac{(p+q)!}{p!q!} \implies L_{n-1}^1(0) = \frac{n!}{(n-1)!} = n \tag{13.36}$$

so that we have

$$\begin{aligned}
(E_D^{(1)})_n &= \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{\hbar^2\pi}{2m_e^2c^2} \frac{1}{4\pi} \left[\frac{1}{2n^2} \left(\frac{2}{na_0} \right)^3 \right] (n^2) \\
&= \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{\hbar^2}{2m_e^2c^2} \left(\frac{1}{na_0} \right)^3 \\
&= \left(\frac{\hbar}{a_0m_e c} \right)^2 \left[\left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{2n^2a_0} \right] \left(\frac{1}{n} \right) \\
&= -\frac{\alpha^2}{n} E_n^{(0)}
\end{aligned} \tag{13.37}$$

Because $(E_D^{(1)})_n$ is proportional to $\alpha^2 E_n^{(0)}$, it qualifies as a fine structure correction.

Although they are valid for mutually exclusive values of ℓ , we nevertheless compare the Darwin correction with that obtained for the spin-orbit interaction. We take the limit of $(E_{SO}^{(1)})_{j=\ell+\frac{1}{2}}$, Equation 13.31, as $\ell \rightarrow 0$. According to the discussion above, however, this is not really legitimate because Equation 13.31 is not valid as $\ell \rightarrow 0$. Nonetheless, we will take this limit. Note that there is no point in evaluating $(E_{SO}^{(1)})_{j=\ell-\frac{1}{2}}$ as $\ell \rightarrow 0$ because $j < 0$ is forbidden. We have

$$\begin{aligned}
\lim_{\ell \rightarrow 0} (E_{SO}^{(1)})_{j=\ell+\frac{1}{2}} &= -\frac{1}{2n} \alpha^2 E_n^{(0)} \lim_{\ell \rightarrow 0} \frac{1}{[(\ell + \frac{1}{2})(\ell + 1)]} \\
&= -\frac{1}{n} \alpha^2 E_n^{(0)} \\
&= E_D^{(1)}
\end{aligned} \tag{13.38}$$

and we see that, indeed, our effort was worth it. The Darwin result, Equation 13.37, follows if the limit $\ell \rightarrow 0$ is taken in the expression for the $(E_{SO}^{(1)})_{j=\ell+\frac{1}{2}}$. This

means that we can use the formula for the $(\ell + \frac{1}{2})$ spin-orbit energy for *all* values of ℓ . While this seems to be an accident, it is not, as will be discussed below.

The total fine structure correction

Adding the relativistic correction, Equation 13.15, to the spin-orbit correction, Equation 13.32, gives the total fine structure correction, $(E_{FS}^{(1)})$, which is valid for all values of ℓ :

$$(E_{FS}^{(1)})_{j=\ell+\frac{1}{2}} = \frac{\alpha^2}{n^2} E_n^{(0)} \left[\frac{n}{(\ell+1)} - \frac{3}{4} \right] \quad (13.39)$$

$$(E_{FS}^{(1)})_{j=\ell-\frac{1}{2}} = \frac{\alpha^2}{n^2} E_n^{(0)} \left[\frac{n}{\ell} - \frac{3}{4} \right] \quad (13.40)$$

The quantities in the square brackets in Equations 13.39 and 13.40 cannot be negative because $n \geq \ell + 1$. Therefore, because $E_n^{(0)}$ is manifestly negative, the fine structure correction *always* lowers the Bohr energy as is illustrated in Fig. 13.1, which shows the fine structure corrections to the first two Bohr levels of hydrogen. Conventional coupled ket notation is used to label the states. That is, a given state is denoted as $n\ell_j$, where the orbital angular momentum ℓ is designated by lowercase letters according to the scheme in Table 9.9.

The units of energy used in Fig. 13.1 are GHz (gigahertz). These units are derived from the Planck relation $E = h\nu \approx (4.14 \times 10^{-15} \text{ eVs}) \nu$. Therefore, $1 \text{ eV} = 2.42 \times 10^5 \text{ GHz}$ and the separation between the fine structure levels of the hydrogen atom is roughly $0.5 \times 10^{-5} \text{ eV}$. Because $\alpha^2 \approx 5 \times 10^{-5}$, we see that this separation is indeed of order $\alpha^2 E_n^{(0)}$. Notice that the $n = 1$ level is lowered more than the

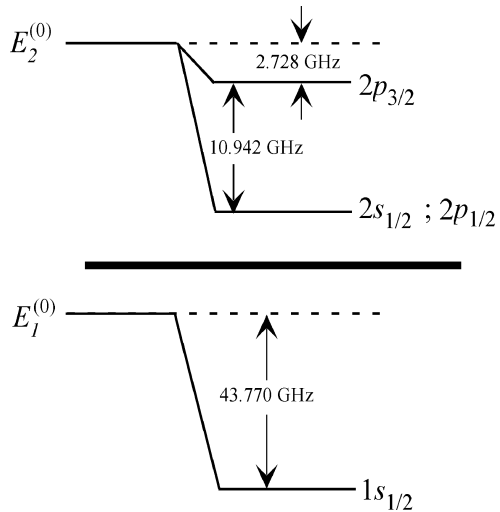


Fig. 13.1 The fine structure splittings of the $n = 1$ and $n = 2$ levels of hydrogen

$n = 2$ levels because of the n -dependence of the fine structure correction as shown in Equations 13.39 and 13.40.

The fine structure correction can be stated in terms of the quantum number j . Interestingly, as is obvious from Equations 13.39 and 13.40, when $\ell = j \mp \frac{1}{2}$ is inserted for each value of ℓ it is found that a single expression represents the total fine structure correction. We obtain

$$\left(E_{FS}^{(1)}\right)_j = \frac{\alpha^2}{n^2} E_n^{(0)} \left[\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right] \quad (13.41)$$

The inclusion of the fine structure Hamiltonian \hat{H}_{FS} in the TISE breaks the accidental degeneracy that is present in the solution of the nonrelativistic Schrödinger hydrogen Hamiltonian—almost. Notice in Fig. 13.1 that the $2s_{\frac{1}{2}}$ and the $2p_{\frac{1}{2}}$ states are degenerate, even after the fine structure correction has been applied. It is not even broken by the Dirac Hamiltonian. It is left for QED to resolve this degeneracy which, when split, is the Lamb shift. Fig. 13.2 shows the fine structure levels of $n = 2$, together with the Lamb shift corrections. Notice that the Lamb shift in hydrogen, at its largest, is about an order of magnitude smaller than the fine structure corrections.

Fine structure and the Dirac equation

As discussed above, the Dirac equation can be solved exactly for the Coulomb potential. The method of solution employs boundary conditions and the restriction that a bound state wave function must be localized. Electron spin is an inherently

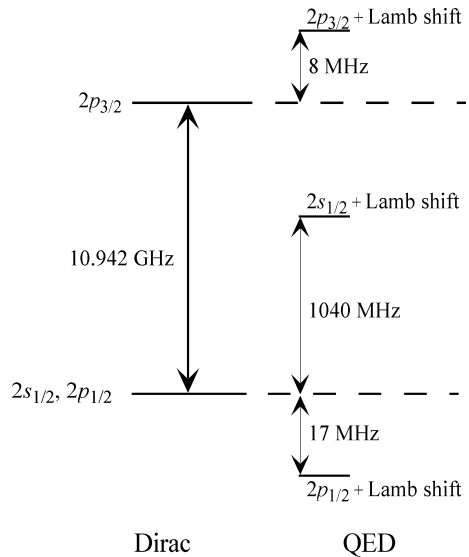


Fig. 13.2 Energy level diagram of the $n = 2$ states of hydrogen showing the fine structure splitting and the Lamb shift

relativistic attribute, so the Dirac equation necessarily includes these effects. It is therefore expected (actually, “demanded” is a better word) that the quantized hydrogen energies that arise from solution of the Dirac equation will contain terms that originate from electron spin. The exact expression for the Dirac equation energy eigenvalues is

$$E_{nj} = \frac{m_e c^2}{\sqrt{1 + \frac{(Z\alpha)^2}{[n - (j + \frac{1}{2})] + \sqrt{(j + \frac{1}{2})^2 - (Z\alpha)^2}}}} \quad (13.42)$$

where we have set $\alpha \rightarrow Z\alpha$ to show the effects of the nuclear charge on the one-electron energy. Expanding this exact expression for the energy (with $z = 1$) we obtain

$$E_{nj} = m_e c^2 + E_n^{(0)} + \frac{\alpha^2}{n^2} E_n^{(0)} \left[\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right] + \dots \quad (13.43)$$

The third term in Equation 13.43 is the same as the fine structure correction of Equation 13.41.

Because the Dirac Hamiltonian was not expanded to find the exact energy eigenvalues, it is not possible to identify the origins of the individual terms as being from the relativistic kinetic energy, spin–orbit, or Darwin corrections. The energy eigenvalues that arise from the exact solution of the Dirac equation are relativistic in nature and individual physical interactions cannot be recovered. It is for this reason that the spin–orbit term reduces to the Darwin term in the limit; they have the same source—relativity. As discussed above, the eigenvalues of hydrogen obtained from the exact solution to the Dirac equation do not include the Lamb shift or the effects of hyperfine structure. Both of these energy corrections are larger than $\alpha^4 E_n^{(0)}$, so computation of the remaining terms in any expansion of Equation 13.42 is of little value.

13.2 Spin–Orbit Coupling and the Shell Model of the Nucleus

Spin–orbit interactions are not restricted to electrons in atoms. Indeed, as was noted in Section 9.5.2, spin–orbit interactions are responsible for the spacing of the nuclear levels that causes the magic numbers to occur. It was shown that breaking of the degeneracy is not required to explain the nuclear shell structure until the $n = 3$ level, but after $n = 3$ the level spacing must be adjusted to account for the observed magic numbers. Although the spin–orbit coupling in the case of nucleons is strong, we can use the formalism developed above to better understand its effects.

The potential to which each nucleon is subjected, including spin–orbit coupling, may be written

$$U'(r) = U(r) + \xi(r) (\hat{\ell} \bullet \hat{s}) \quad (13.44)$$

where $U(r)$ is often approximated by the isotropic oscillator potential, but for our purpose we assume that the levels resulting from it are as shown in the middle of Fig. 9.13. Lowercase letters are used to designate the orbital and spin angular momentum operators in the spin–orbit term. As was seen in the case of spin–orbit coupling for the hydrogen atom, the eigenkets of the spin–orbit Hamiltonian must be the coupled kets for which $j = \ell \pm \frac{1}{2}$. In other words the select set of eigenkets are the coupled kets which we designate $|j m_j \ell s\rangle$. Also, experimentally, it is found that $\xi(r)$ is attractive and may be considered constant, so we write, for convenience, $\xi(r) = -2\beta/\hbar^2$ where β is a positive constant. (Nuclear physicists often use α instead of β , but α is tired so we use β instead.)

By analogy with Equation 13.29, we know that the unperturbed energies, the energy excluding spin–orbit coupling, are split by the spin–orbit interaction according to

$$E_{SO}^{(1)}(j, \ell) = \beta \left(j(j+1) - \ell(\ell+1) - \frac{3}{4} \right) \quad (13.45)$$

or

$$E_{SO}^{(1)} \left(j = \ell + \frac{1}{2} \right) = -\beta\ell \quad (13.46)$$

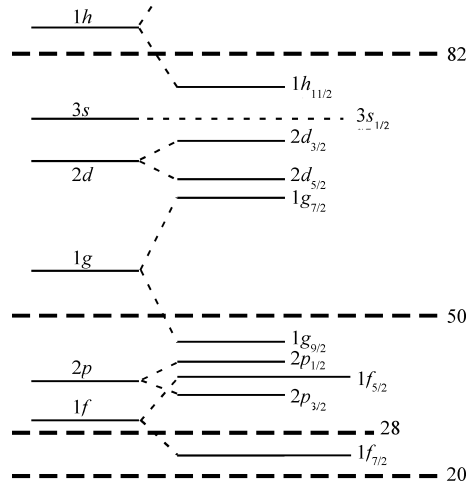
$$E_{SO}^{(1)} \left(j = \ell - \frac{1}{2} \right) = \beta(\ell+1) \quad (13.47)$$

from which it is seen that the energy is lower when the orbital and spin angular momenta are parallel, $j = \ell + \frac{1}{2}$. Of course, the m -degeneracy is not broken. Nonetheless, the energy separation between states having the same values of j and ℓ is

$$\Delta E_{SO}(j, \ell) = \beta(2\ell+1) \quad (13.48)$$

from which we see that the splitting increases with increasing ℓ . Thus, the lowest level of a high orbital angular momentum group of states can be depressed in a way that it joins a group of states of lower values of ℓ and principal quantum number n . This is illustrated in Fig. 9.13 and again in Fig. 13.3, which extends to higher levels than Fig. 9.13 in order to show the large splitting of the higher orbital angular momentum levels.

Fig. 13.3 Schematic diagram showing the groupings of states that lead to the magic numbers. The shells are delineated by heavy dashed lines



It can be seen that, indeed, spin-orbit coupling lowers $1g_{9/2}$ and $1h_{11/2}$ from the degenerate $1g$ and $1h$ states to the extent that each joins a lower manifold of states, thus producing the magic numbers 50 and 82. The dashed lines in the figure denote the magic numbers that result from this regrouping of the states. Notice that there are 32 substates associated with the 5 states that lie between 50 and 82 nucleons. Above the $1h_{11/2}$ state there is a wide gap before the next grouping of states. In this way the groupings of states can be understood and the magic numbers follow.

13.3 Helium Atoms

13.3.1 The Ground State

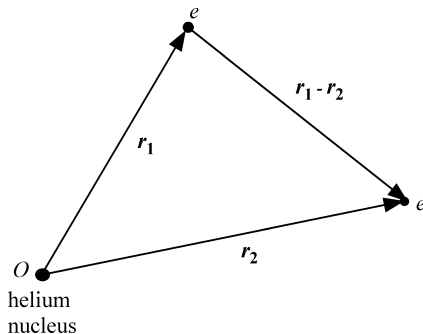
Helium atoms have two protons and two neutrons in the nucleus and two electrons surrounding the nucleus. To study the helium atom we assume that the nucleus is an entity of its own (actually, in the parlance of nuclear physics, it is an α -particle) and we treat the electrons as identical particles (see Section 8.6.2). Setting the origin of coordinates at the nucleus, we designate the vectors to the electrons as shown in Fig. 13.4.

The Hamiltonian is

$$\hat{H} = \frac{\hat{p}_1^2}{2m_e} + \frac{\hat{p}_2^2}{2m_e} - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_1} - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (13.49)$$

where $Z = 2$ and \hat{p}_i is the momentum of the i th electron. The negative terms are the potential energy of the nucleus and each electron and the remaining term represents the interelectron repulsion. It is convenient to solve the problem in atomic units (see

Fig. 13.4 Coordinates used in the helium atom calculations



Section 1.3) in which the Hamiltonian is

$$\hat{H} = \frac{\hat{p}_1^2}{2} + \frac{\hat{p}_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (13.50)$$

The Hamiltonian may also be written as

$$\begin{aligned} \hat{H} &= \hat{H}_{01} + \hat{H}_{02} + \hat{H}_1 \\ &= \hat{H}_0 + \hat{H}_1 \end{aligned} \quad (13.51)$$

where

$$\hat{H}_{0i} = \frac{\hat{p}_i^2}{2} - \frac{Z}{r_i} \quad \text{and} \quad \hat{H}_1 = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{r_{12}} \quad (13.52)$$

Because the unperturbed Hamiltonians, \hat{H}_{01} and \hat{H}_{02} , contain only coordinates of a single electron, the eigenfunctions of the unperturbed Hamiltonian \hat{H}_0 are products of one-electron eigenfunctions. For helium $Z = 2$, but we retain Z in the Hamiltonian for convenience.

Because \hat{H}_0 contains no interaction between the individual electrons, it represents a Hamiltonian of two isolated electrons, each under the influence of the same nucleus. In the unperturbed state, each electron behaves as if it were the electron in the ground state of a helium ion (a helium nucleus and *one* electron) provided they have opposite spins. We can therefore immediately write the unperturbed ket that represents the spatial part of the ground state. It is the product of the one-electron ground state eigenkets of \hat{H}_{01} and \hat{H}_{02} with $Z = 2$. Moreover, the unperturbed eigenvalues are the sums of the ground state eigenvalues of these two operators which are simply Z^2 times the ground state Bohr energy. In this unperturbed state, the quantum numbers for each electron will be $(n_1 \ell_1 m_{\ell 1} m_{s 1}) = (100\alpha)$ and $(n_2 \ell_2 m_{\ell 2} m_{s 2}) = (100\beta)$, so we designate the unperturbed spatial kets and their eigenvalues as

$$|1s1s\rangle_{space} = |100\rangle_1 |100\rangle_2 \quad \text{and} \quad E_1^{(0)} = E_{11}^{(0)} + E_{11}^{(0)} \quad (13.53)$$

where the ket on the left represents $|n\ell n'\ell'\rangle$ with the unprimed quantum numbers representing electron 1 (by virtue of being in the first position), and the primed quantum numbers, particle 2.

Let us examine the magnitude of the unperturbed energy and the significance of this energy. In atomic units the Bohr energy for a one-electron atom is

$$E_n^{(0)} = -\frac{Z^2}{2n^2} \quad (13.54)$$

so the unperturbed energy for the ground state of the helium atom is twice this with $Z = 2$ and $n = 1$. Thus, the unperturbed ground state energy of a helium atom is $E_1^{(0)} = -Z^2 = -4$ a.u. This is a large (negative) energy, -108.8 eV. It is twice the ionization potential of two He^+ ions, one to remove each electron. It is known from experiments that the total energy of the ground state helium atom is actually -2.90 a.u. $= -78.9$ eV. Thus, the correction that we seek from perturbation theory is ~ 30 eV! This can hardly be considered to be a “small” perturbation. Nonetheless, as will be seen below, perturbation theory provides a reasonable approximation to reality. Before performing this perturbation theory calculation we must return to the task of determining the total eigenket.

The spatial part of the ket in Equation 13.53 is clearly symmetric under particle interchange. The example in Section 8.6.2 is identical to the problem of the helium atom inasmuch as we didn’t specify a particular potential in the example, only a two-electron system. Whatever the potential, it will determine the spatial part of the eigenkets, but the spin parts will be identical to those in the example. Therefore, we can immediately write the spin part of the ket. It must be a singlet state, the antisymmetric state, so the complete ground state ket is

$$\begin{aligned} |1s1s\rangle &= |1s1s\rangle_{\text{space}} |\text{spin}\rangle \\ &= |100\rangle_1 |100\rangle_2 \left\{ \frac{1}{\sqrt{2}} (|\alpha\rangle_1 |\beta\rangle_2 - |\beta\rangle_1 |\alpha\rangle_2) \right\} \\ &= |100\rangle_1 |100\rangle_2 \left\{ \frac{1}{\sqrt{2}} (|\alpha\beta\rangle - |\beta\alpha\rangle) \right\} \end{aligned} \quad (13.55)$$

In the last line of Equation 13.55 we have reverted to the notation that the first position in the spin kets refers to particle 1 and the second to particle 2.

We have gone as far as we can go without using the actual wave functions. Our goal is to now compute $E_1^{(1)}$, the first order correction to $E_1^{(0)}$. This requires evaluation of the integral

$$E_1^{(1)} = {}_2 \langle 100 | {}_1 \langle 100 | \left(\frac{1}{r_{12}} \right) | 100 \rangle_1 | 100 \rangle_2 \quad (13.56)$$

Because the perturbing Hamiltonian does not contain spin, normalization of the spin part of the eigenket leads to unity, and is omitted from Equation 13.56. The

perturbation $1/r_{12}$ is spatial in nature so $E_1^{(1)}$ must be evaluated in coordinate space. Thus, in coordinate space, Equation 13.56 is

$$E_1^{(1)} = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \psi^*(\mathbf{r}_1) \psi^*(\mathbf{r}_2) \left(\frac{1}{r_{12}} \right) \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) \quad (13.57)$$

where the $d^3\mathbf{r}_i$ are the volume elements in each of the coordinates \mathbf{r}_1 and \mathbf{r}_2 , and the $\psi(\mathbf{r}_i)$ are the eigenfunctions for each coordinate. Notice that we can use ψ to represent both electronic wave functions inasmuch as they are in the same (unperturbed) state.

The integrals in Equation 13.57 permit a physical interpretation of the interaction. Each of the functions $\psi^*(\mathbf{r}_i) \psi(\mathbf{r}_i)$ is the probability density of finding electron i in a volume surrounding \mathbf{r}_i . Because the electronic charge is unity in atomic units, these probability densities also the charge densities due to each electron. Therefore, $E_1^{(1)}$ is simply the electrostatic interaction energy of two overlapping charge densities. It is denoted by J_{1s1s} , where the subscripts indicate the quantum state of each electron in the unperturbed state, in this case both are in their ground states. The integral $J_{n\ell n'\ell'}$ is called the Coulomb integral

The ground state eigenfunction for the one-electron atom is, in atomic units (see Table 10.3),

$$\psi_{100}(r, \theta, \phi) = 2Z^{3/2} e^{-Zr} Y_{00}(\theta, \phi) \quad (13.58)$$

so the integral that must be evaluated is

$$\begin{aligned} J_{1s1s} &= \frac{2^4 Z^6}{(\sqrt{4\pi})^4} \int e^{-2Z(r_1+r_2)} \left(\frac{1}{r_{12}} \right) \\ &\quad \times (r_1^2 \sin \theta_1 d\theta_1 dr_1) (4\pi r_2^2 \sin \theta_2 d\theta_2 dr_2) \\ &= \frac{Z^6}{\pi^2} \int e^{-2Z(r_1+r_2)} \left(\frac{1}{r_{12}} \right) \\ &\quad \times (r_1^2 \sin \theta_1 dr_1 d\theta_1 d\phi_1) (r_2^2 \sin \theta_2 dr_2 d\theta_2 d\phi_2) \end{aligned} \quad (13.59)$$

where it is understood that the volume integral extends over all space. Note that the $(1/\sqrt{4\pi})$ is $Y_{00}(\theta, \phi)$. This appears to be a formidable integral, but, with the aid of the mathematics developed in Section 8.4.1, it simplifies considerably. The function $1/|\mathbf{r}_1 - \mathbf{r}_2|$ can be written in terms of Legendre polynomials, Equation 8.98:

$$\begin{aligned}
\frac{1}{r_{12}} &= \frac{1}{r_{>}} \sum_{\ell=0}^{\infty} P_{\ell}(\cos \gamma) \left(\frac{r_{<}}{r_{>}} \right)^{\ell} \\
&= \frac{4\pi}{2\ell+1} \left(\frac{1}{r_{>}} \right) \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\theta_1, \phi_1) Y_{\ell m}^*(\theta_2, \phi_2) \left(\frac{r_{<}}{r_{>}} \right)^{\ell} \quad (13.60)
\end{aligned}$$

where we have replaced $P_{\ell}(\cos \gamma)$ using the addition theorem for spherical harmonics, Equation 8.89. At first glance this does not seem to be a simplification, but, noticing that the only angular dependence other than that from $1/r_{12}$ in Equation 13.59 is contained in the volume element, we see that the only part of the angular integral that survives the summation is the term for which $\ell = 0$ and $m = 0$ because $Y_{00}(\theta, \phi) = 1/\sqrt{4\pi}$, a constant. Thus, using the normalization integral for spherical harmonics, Equation 8.85, we have

$$\int_0^{2\pi} d\phi_i \int_0^{\theta} d\theta \sin \theta_i \left\{ \sqrt{4\pi} Y_{00}(\theta_i, \phi_i) \right\} [Y_{\ell m}(\theta_i, \phi_i)]^* = \sqrt{4\pi} \quad (13.61)$$

for each of the angular integrations. Notice that the quantity in curly brackets in Equation 13.61 is unity. Putting this back into Equation 13.59 and performing the integration we have

$$\begin{aligned}
J_{1s1s} &= (4\pi)^2 \frac{Z^6}{\pi^2} \int e^{-2Z(r_1+r_2)} r_1^2 dr_1 r_2^2 dr_2 \\
&= 16Z^6 \int_0^{\infty} \left[\int_0^{r_1} e^{-2Z(r_1+r_2)} r_2^2 dr_2 + \int_{r_1}^{\infty} e^{-2Z(r_1+r_2)} r_2^2 dr_2 \right] r_1^2 dr_1 \\
&= \frac{5}{8} Z \quad (13.62)
\end{aligned}$$

As expected this correction to the ground state energy is positive reflecting the interelectron *repulsion*. For the helium atom, for which $Z = 2$, the correction is ~ 34 eV, surprisingly close to the needed correction of 30 eV. The final result of the perturbation theory treatment is that the total energy of a helium atom in the ground state is $-2^2 + 5/4 = -2.75 = -74.8$ eV, still about five percent too low.

From perturbation theory, we conclude that the total energy of the two-electron atom in a.u. is

$$E_1^P(Z) = -Z^2 + \frac{5}{8}Z \quad (13.63)$$

This expression is good for any two-electron atom having Z protons in the nucleus. Equation 13.63 shows that the effect of interelectron repulsion on the total energy decreases with increasing atomic number because the unperturbed energy decreases as Z^2 , while the perturbation correction increases only as Z . The reason for this is that each electron is screened from “seeing” the full $Z = 2$ charge on the nucleus by

the other electron. This suggests that we consider an effective charge of the nucleus to be smaller than Z due to this screening. This concept suggests that we might be able to obtain a better approximation to the total energy using the variational method with a trial wave function (see Section 12.2) that includes an adjustable parameter that represents the screened nuclear charge. For simplicity, we choose the one-electron wave function, the radial part of which is given in Equation 13.58, but with Z replaced by an adjustable parameter ζ that will be used to minimize the expectation value of the energy. We expect the optimum value of ζ for helium to be somewhat less than 2. The calculation is relatively straightforward, except that it will contain both ζ and Z so we must make sure to keep them straight. The reason that Z is still in the problem is that the Hamiltonian is still that of Equation 13.50 because there really are Z protons in the nucleus. The screened nuclear charge concept enters only in the trial wave function which we write as $\langle \mathbf{r}_1, \mathbf{r}_2 | \psi_t \rangle$ (see Section 6.4):

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \psi_t \rangle = [2\zeta^{3/2} e^{-\zeta r_1} Y_{00}(\theta_1, \phi_1)] [2\zeta^{3/2} e^{-\zeta r_2} Y_{00}(\theta_2, \phi_2)] \quad (13.64)$$

In accord with Equation 12.72 we must minimize the expectation value of the entire Hamiltonian with respect to the adjustable parameter. We do not have to worry about normalization because the wave function in Equation 13.58 is already normalized. Using the notation of Equation 13.51 we have

$$\begin{aligned} \langle \hat{H} \rangle &= \langle \psi_t | \hat{H} | \psi_t \rangle \\ &= \langle \psi_t | \hat{H}_0 | \psi_t \rangle + \langle \psi_t | \hat{H}_1 | \psi_t \rangle \end{aligned} \quad (13.65)$$

The second term has already been evaluated. It is J_{1s1s} as given in Equation 13.62, but we must make the substitution $Z \rightarrow \zeta$ because \hat{H}_1 does not contain the nuclear charge, screened or otherwise. The origin of the Z in the expression for J_{1s1s} is the wave function, which we are changing for this variational calculation by substituting ζ for Z . In the first integral, however, the trial wave functions that contain ζ are not eigenfunctions of \hat{H}_0 because \hat{H}_0 contains Z not ζ . To compensate for this we add and subtract the potential energy term using ζ to make part of the integrand an operator for which $|\psi_t\rangle$ is an eigenket:

$$\begin{aligned} \langle \hat{H} \rangle &= \langle \psi_t | \frac{\hat{p}_1^2}{2} + \frac{\hat{p}_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} | \psi_t \rangle + \langle \psi_t | \hat{H}_1 | \psi_t \rangle \\ &= \langle \psi_t | \frac{\hat{p}_1^2}{2} + \frac{\hat{p}_2^2}{2} - \frac{\zeta}{r_1} - \frac{\zeta}{r_2} | \psi_t \rangle \\ &\quad + \langle \psi_t | \left[\frac{(\zeta - Z)}{r_1} + \frac{(\zeta - Z)}{r_2} \right] | \psi_t \rangle + \frac{5}{8}\zeta \\ &= 2E_1^{(0)} + (\zeta - Z) \left[\left\langle \frac{1}{r_1} \right\rangle + \left\langle \frac{1}{r_2} \right\rangle \right] + \frac{5}{8}\zeta \end{aligned} \quad (13.66)$$

The expectation values are simply the expectation value of $1/r$ (see Table 10.4) with $Z \rightarrow \zeta$. Therefore

$$\langle \hat{H} \rangle = -2\frac{\zeta^2}{2} + 2(\zeta - Z)\zeta + \frac{5}{8}\zeta \quad (13.67)$$

Treating ζ as an adjustable parameter we set $d\langle \hat{H} \rangle/d\zeta = 0$ to find ζ_0 , the value of ζ that minimizes $\langle \hat{H} \rangle$. This yields

$$\zeta_0 = Z - \frac{5}{16} \quad (13.68)$$

which, as expected, is less than Z (see Problem 7). Inserting ζ_0 into Equation 13.67, we find that the total energy of the ground state obtained using the variational treatment is

$$E_1^V(Z) = -\left(Z - \frac{5}{16}\right)^2 \quad (13.69)$$

For helium this leads to a total energy of -2.85 a.u. $= -77.4$ eV, much closer to the actual value of 78.9 eV than that obtained from perturbation theory (see Problem 8). It is, however, not difficult to envision a computer program written to incorporate a trial wave function with many variable parameters. We need not even concern ourselves with the physical significance of these parameters as we did in the calculation above. The variational principle assures us that we will never obtain an energy lower than the true ground state energy so we can, in principle, obtain the energy to any desired accuracy.

13.3.2 Excited States

The first unperturbed excited state of the helium atom above the ground state is obtained by assuming that one electron is in the ground state of the He^+ ion, $n = 1$, and the other is in the first excited state $n = 2$. The unperturbed energy is therefore

$$\begin{aligned} E_{ns,n\ell} &= -\frac{Z^2}{2} - \frac{Z^2}{8} \\ &= -\frac{5}{8}Z^2 = -68 \text{ eV for } Z = 2 \end{aligned} \quad (13.70)$$

We know from the discussion of identical particles in Section 8.6.2 that the acceptable eigenkets must be antisymmetric under particle exchange and they must be products of spin and space kets. The structure of the eigenkets is identical with those deduced in the example of two noninteracting fermions discussed in Section

8.6.2. Using the results of that example we can immediately write the acceptable eigenkets for the first excited state of helium. To make the conversion we use the notation

$$|1\rangle \rightarrow |1s\rangle; \quad |2\rangle \rightarrow |2\ell\rangle \quad (13.71)$$

for the spatial kets. The perturbing Hamiltonian \hat{H}_1 is given by Equation 13.52 which does not contain ϕ (see Equation 8.98). Therefore, \hat{H}_1 commutes with \hat{L}_z . This means that the energy cannot contain the quantum number m_ℓ so, for simplicity, it has been omitted from the kets as was done for $|1s\rangle$; thus, $|2\ell m_\ell\rangle \rightarrow |2\ell\rangle$. Any integrals that are required may, for convenience, be evaluated for $m = 0$. For the spin kets we employ the standard notation $|S M\rangle$, where, in this case, $S = 0$ (singlet) or 1 (triplet). The kets from Table 8.13 transformed to the notation of this section are shown in Table 13.1.

The spatial kets in Table 13.1 diagonalize the permutation operator \hat{P}_{12} . There are, however, only two spatial kets, one symmetric and the other antisymmetric. Because the total ket must be antisymmetric, the spin kets are chosen accordingly. The symmetric and antisymmetric spatial parts of the eigenkets are

$$|\psi\rangle_\pm \rightarrow \frac{1}{\sqrt{2}} \{ |1s\rangle_1 |2\ell\rangle_2 \pm |1s\rangle_2 |2\ell\rangle_1 \} \quad (13.72)$$

Now, there are eight of the simple product kets of the type $|1s\rangle_i |2\ell\rangle_j$, where $i, j = 1$ or 2, with $i \neq j$. All eight are also eigenkets of \hat{H}_0 . As such, they are acceptable eigenkets of the unperturbed Hamiltonian. They are not, however, eigenkets of \hat{P}_{12} ,

Table 13.1 Singlet and triplet states of Table 8.13 converted to the notation of the current section

Singlet	
$\frac{1}{\sqrt{2}} \{ 1\rangle_1 2\rangle_2 + 1\rangle_2 2\rangle_1 \} \{ \alpha\rangle_1 \beta\rangle_2 - \alpha\rangle_2 \beta\rangle_1 \}$	
$\rightarrow \frac{1}{\sqrt{2}} \{ 1s\rangle_1 2\ell\rangle_2 + 1s\rangle_2 2\ell\rangle_1 \} 00\rangle$	
Triplets	
$\frac{1}{\sqrt{2}} \{ 1\rangle_1 2\rangle_2 - 1\rangle_2 2\rangle_1 \} \alpha\rangle_1 \alpha\rangle_2$	
$\rightarrow \frac{1}{\sqrt{2}} \{ 1s\rangle_1 2\ell\rangle_2 - 1s\rangle_2 2\ell\rangle_1 \} 11\rangle$	
$\frac{1}{\sqrt{2}} \{ 1\rangle_1 2\rangle_2 - 1\rangle_2 2\rangle_1 \} \{ \alpha\rangle_1 \beta\rangle_2 + \alpha\rangle_2 \beta\rangle_1 \}$	
$\rightarrow \frac{1}{\sqrt{2}} \{ 1s\rangle_1 2\ell\rangle_2 - 1s\rangle_2 2\ell\rangle_1 \} 10\rangle$	
$\frac{1}{\sqrt{2}} \{ 1\rangle_1 2\rangle_2 - 1\rangle_2 2\rangle_1 \} \beta\rangle_1 \beta\rangle_2$	
$\rightarrow \frac{1}{\sqrt{2}} \{ 1s\rangle_1 2\ell\rangle_2 - 1s\rangle_2 2\ell\rangle_1 \} 1-1\rangle$	

a fact that renders them unacceptable as kets for the two-electron system. The degeneracy of these kets suggests that the properly symmetrized kets constitute the select set. We must, however, examine the matrix that represents \hat{H}_1 to verify this assertion.

Using the properly symmetrized kets as a basis set for matrix representation of \hat{H}_1 we have

$$\hat{H}_1 = \begin{pmatrix} +\langle\psi|\hat{H}_1|\psi\rangle_+ & +\langle\psi|\hat{H}_1|\psi\rangle_- \\ -\langle\psi|\hat{H}_1|\psi\rangle_+ & -\langle\psi|\hat{H}_1|\psi\rangle_- \end{pmatrix} \quad (13.73)$$

Computation of the matrix elements (see Problem 9) shows that the off-diagonal elements vanish, so, indeed, the symmetrized kets are the select kets. The diagonal elements of \hat{H}_1 are

$$\begin{aligned} (\hat{H}_1)_{\pm\pm} &= {}_2\langle 2\ell|_1\langle 1s|\left(\frac{1}{r_{12}}\right)|1s\rangle_1|2\ell\rangle \pm {}_2\langle 2\ell|_1\langle 1s|\left(\frac{1}{r_{12}}\right)|2\ell\rangle_1|1s\rangle_2 \\ &= J_{1s2\ell} \pm K_{1s2\ell} \end{aligned} \quad (13.74)$$

where $J_{1s2\ell}$ is the Coulomb integral for these two electrons (see Section 13.3.1):

$$J_{1s2\ell} = {}_2\langle 2\ell|_1\langle 1s|\left(\frac{1}{r_{12}}\right)|1s\rangle_1|2\ell\rangle_2 \quad (13.75)$$

and $K_{1s2\ell}$, called the exchange integral, is

$$K_{1s2\ell} = {}_2\langle 2\ell|_1\langle 1s|\left(\frac{1}{r_{12}}\right)|2\ell\rangle_1|1s\rangle_2 \quad (13.76)$$

Because all off-diagonal elements vanish, \hat{H}_1 was already diagonal in the properly symmetrized spatial eigenkets, so degenerate perturbation theory is not required.

This is another way of seeing that \hat{H}_1 and \hat{P}_{12} commute and have simultaneous eigenkets. Since \hat{H}_1 is diagonal, the diagonal elements are the eigenvalues and the properly symmetrized kets are the eigenkets. That is, both \hat{H}_0 and \hat{H}_1 are diagonal in the representation of this select set of kets. It is seen that the use of nondegenerate perturbation theory, in which the energy corrections are the expectation values of the perturbing Hamiltonian using unperturbed kets, is equivalent to computing the diagonal elements of \hat{H}_1 . Thus, the correction to the unperturbed energy, Equation 13.70, is

$$E_{2\ell}^{(1)} = J_{1s2\ell} \pm K_{1s2\ell} \quad (13.77)$$

where the upper sign gives the eigenvalues of the symmetric spatial kets (singlet spin state) and the lower sign the eigenvalue of the antisymmetric spatial kets (triplet spin states).

As was the case for the ground state, the Coulomb integrals $J_{1s2\ell}$, each of which is a double integral, represent the electrostatic interaction energy of the two overlapping charge densities. The integrals $K_{1s2\ell}$ are, however, a different matter. They too are double integrals, each of which involves both spatial kets, but each state refers to a different electron. They, therefore, represent the overlap of the two states for a single electron. It is as if the electrons are indeed changing their designations, $1 \rightleftharpoons 2$, each “flitting” between the two states, as described in the discussion of Postulate IV in Section 6.3.2. This is the reason that the integrals $K_{n\ell n'\ell'}$ are referred to as exchange integrals. This term arises only because of the symmetrization requirement, the foundation of which is the demand of particle indistinguishability. The existence of the exchange integrals illustrates the interference effects alluded to in Section 6.3.2 because they raise and lower the electrostatic interaction energy. Note that for the ground state there is no exchange integral because both electrons occupy the same unperturbed spatial state and the properly symmetrized unperturbed spatial kets are the simple product $|1s\rangle_1 |1s\rangle_2$, which is symmetric.

The eigen *functions* in coordinate space are given by $\langle \mathbf{r}_1, \mathbf{r}_2 | \psi_{\pm} \rangle$. If we let $\mathbf{r}_1 \rightarrow \mathbf{r}_2$ to determine the probability of finding both electrons at the same point in space, we see that the antisymmetric spatial state $|\psi_{-}\rangle$ vanishes so, in this respect, the electrons avoid each other in an antisymmetric spatial state creating a hole in the probability density known as a Fermi hole. On the other hand, the symmetric state exhibits no such behavior. The symmetric space state favors a buildup of probability as $\mathbf{r}_1 \rightarrow \mathbf{r}_2$, as if there was an attraction between the two electrons. This attraction creates a Fermi heap. The “force” that creates these heaps and holes is known as the exchange force, but it is not a force in the traditional sense. The exchange force is due to the exchange symmetry restrictions placed on the wave function by the necessity of forcing the particles to be mathematically indistinguishable. The effect would exist even if the electrons carried no charge, provided that they remain fermions.

To calculate the correction to the unperturbed energy, Equation 13.77, we must evaluate the integrals $J_{1s2\ell}$ and $K_{1s2\ell}$. The calculation utilizes the Legendre expansion of Equation 8.98 as was done for the ground state so there is nothing new from a pedagogical point of view. We therefore list the results in Table 13.2. Because the value of the exchange integral is always less than that of the Coulomb integral, the correction, as expected, raises the energy for all four states. Both the Coulomb and the exchange integrals are positive, and $J > K$, so the unperturbed energy is raised by the combination of the interelectron repulsion, J , and the exchange energy, K .

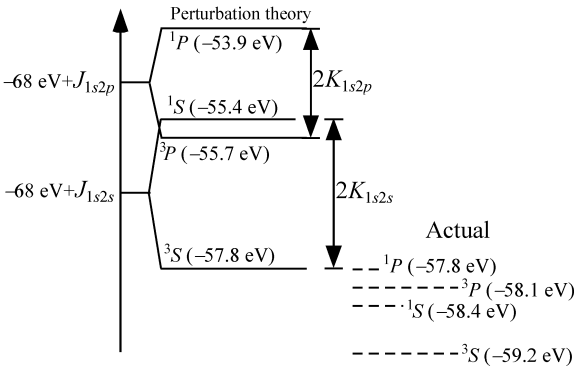
Table 13.2 Calculated values of the energy corrections due to the Coulomb and exchange integrals for helium

	a.u.	eV ($Z = 2$)
J_{1s2s}	$(17/81) Z$	11.4
K_{1s2s}	$(729/16) Z$	1.2
J_{1s2p}	$(59/243) Z$	13.2
K_{1s2p}	$(112/6561) Z$	0.9

Table 13.3 Calculated and actual energies of the first excited electron configuration of helium

State	Calculated (eV)	Actual (eV)
$2p\ ^1P$	-53.9	-57.8
$2p\ ^3P$	-55.7	-58.1
$2s\ ^1S$	-55.4	-58.4
$2s\ ^3S$	-57.8	-59.2

Fig. 13.5 Energy level diagram of the $n = 2$ states of helium comparing the perturbation theory results with the actual energies



Before continuing, let us pause to give these states their proper names. The naming scheme is that commonly used in atomic spectroscopy. For helium, the states (also referred to as terms) are designated $(1s)(n\ell)^{2S+1}L$ where $(1s)(n\ell)$ is known as the electron configuration. As we have seen, this indicates the unperturbed one-electron states. The individual terms $(n\ell)$ in the electron configuration are called subshells or orbitals. Often, the state designation for electrons in the lowest orbitals is omitted. The remaining symbols, L and S , are the total orbital angular momentum of all electrons and the total spin of all electrons, respectively. The quantity $2S + 1$ is known as the multiplicity of the state for reasons that will become apparent in the next section. The values of L and S are determined by vector addition. In the case of helium, the total angular momentum is simply the angular momentum of the excited electron because that of the other electron is zero. As we have seen, the value of S can be either 0 or 1, reflecting the possibility of singlet or triplet spin states. Finally, we note that electron configurations for helium of the type $(n\ell)(n'\ell')$ where both $n, n' \neq 1$ are possible, but these states have energy higher than the ionization potential. They are referred to as autoionizing states, but we will not consider them here.

Although the perturbation calculation includes the correct features, in particular the Coulomb and exchange integrals, it does not give the correct ordering of the states. Table 13.3 lists the observed and calculated energies and Fig. 13.5 shows them graphically.

First, we notice that the calculated energies are uniformly higher than the observed energies. Also, the calculated energy of the $2s\ ^1S$ is higher than the calculated energy of $2p\ ^3P$. This is contrary to the observed ordering of the levels, as shown in . Within the spirit of the approximation this is not a serious discrepancy.

13.4 Multielectron Atoms

The helium atom serves as a prototype for the study of the multielectron atoms that comprise the remainder of the periodic table. The model that is used for the zeroth-order description of these atoms is the same as that used in the perturbation theory treatment of the helium atom. That is, the eigenkets are treated as properly symmetrized products of one-electron kets, each of which is referred to as an orbital or a subshell. For this reason this model is often called the independent electron model. The electron configuration introduced in Section 13.3.2 for two electrons is extended to include all Z electrons. For example, the electron configuration for the ground state of the lithium atom is $(1s)^2(2s)^1$. The superscripts represent the number of electrons having the particular designation so the $(1s)^2$ means that there are two electrons in the $1s$ orbital. This is frequently (and incorrectly) read “ $1s$ squared.” Often, if there is only a single electron in a particular orbital the superscript is omitted.

By virtue of having two electrons in the $1s$ orbital, this orbital is full. Therefore, because the total orbital and spin angular momenta are both zero, the $(1s)^2$ is frequently omitted from the configuration. The ground state of the lithium atom might then be designated $\text{Li}(2s)$. Taking a more complicated example, the electron configuration of the magnesium atom ($Z = 12$) is $(1s)^2(2s)^2(2p)^6(3s)^2$. The reason that a p orbital accommodates at most six electrons is that there are only three possible values of m_ℓ for $\ell = 1$, each of which can have spin up or spin down. Any orbital that is full must have $2(2\ell + 1)$ electrons, twice the number of possible values of m_ℓ . Completely full orbitals always have the total orbital angular momentum $L = 0$ and the total spin $S = 0$.

Molecule formation depends upon two or more atoms sharing electrons in partially filled orbitals. Therefore, atoms for which all orbitals are full are not reactive, at least in their ground states. Thus, helium is the first of these inert gases (also referred to as rare gases or noble gases). The next is neon with an electron configuration $(1s)^2(2s)^2(2p)^6$. Another scheme for shortening the electron configuration designation is to use the inert gases. For example, the lithium electron configuration could be designated $[\text{He}]2s$ and that for magnesium $[\text{Ne}](3s)^2$.

The independent electron eigenfunctions, the orbitals, form a complete set, so they can serve as a basis set upon which any eigenfunction may be expanded. The assumption that the true eigenket is only a single independent electron orbital breaks down in varying degrees, depending upon the atom and the state. When the true eigenfunction is adequately described by a single basis function, it is referred to as a pure state. In many cases the true eigenfunction requires two or more independent electron basis functions or electron configurations. When this occurs it is said that these configurations interact and “configuration interaction” is present.

There is more than one way to designate a state of an atom. One way is by the electron configuration, but this is only a first (or zeroth) approximation. Refinement of the designation requires examination of the coupling between the different electronic angular momenta. Before discussing this let us ask why the designation of states is important. After all, they are just names. To answer this question we recall that atoms emit and absorb radiation as discussed in Section 1.1.3. For sim-

plicity, we illustrate using emission. We know photons are emitted in transitions between two states. Transitions between some pairs of states are highly favored, while transitions between other pairs rarely, if ever, occur. Transitions are therefore described as being “allowed” or “forbidden.” There are rules that govern whether a given transition is allowed or forbidden and these rules, known as selection rules, are based on the names of the states. Forbidden transitions can be strictly forbidden and *never* occur or merely forbidden, in which case transitions that do occur are weak. A weak emission is one for which the upper state of the transition has a very long lifetime. If we use a scheme for naming the states from which we can accurately deduce whether transitions between two states should be strong, weak, or not occur at all, then this scheme is useful. On the other hand, if there is no correlation between the names of the states and the selection rules, then we may as well call them Joe, Sam, and Pete. An example will clarify matters. One selection rule is that transitions between states of different multiplicity do not occur or, if they do occur, they are weak. In other words, an electron cannot change spin during a transition so that $\Delta S \neq 0$ is forbidden. The ground state of helium is a $(1s)^2\ ^1S$ and there are four $(1s)(2\ell)$ states, 1S , 1P , 3S , and 3P , the lowest lying of which is the 3S (see Fig. 13.5). According to this rule, transitions between triplets and singlets are forbidden and indeed, it is found that when they do occur they are weak. The transition between $(1s)(2s)\ ^3S$ and $(1s)^2\ ^1S$ is so weak that the lifetime of the $(1s)(2s)\ ^3S$ state is the order of months. (Compare this to the nanosecond lifetimes of states involved in allowed atomic transitions.) The prohibition on transitions between singlet and triplet states led early investigators to think that there are two kinds of helium, parahelium (singlets) and orthohelium (triplets), because helium atoms seemed to have two distinct sets of emissions. In contrast to the $(1s)(2s)\ ^3S \rightarrow (1s)^2\ ^1S$, we expect the $(1s)(2p)\ ^1P \rightarrow (1s)^2\ ^1S$ transition to be strong. Indeed it is, especially since, in addition to obeying $\Delta S = 0$, it obeys another of the selection rules, namely, that $\Delta L = 0, \pm 1$. Thus, if a naming scheme is to be useful, the designations of two states indicates whether transitions between them are allowed, or, in spectroscopic parlance, if they combine.

Naming schemes are based on the method by which the different angular momenta are coupled. They are therefore referred to as coupling schemes. The scheme that describes light atoms is called Russell Saunders or *LS*-coupling. In Russell Saunders coupling it is assumed that the orbital angular momentum of each electron interacts strongly with the other electronic orbital angular momenta, and that there is also a strong interaction between the electronic spin angular momenta. The vector sum of the orbital angular momenta of all electrons is designated by L , and S is the vector sum of all the spin angular momenta. The spin-orbit interaction between S and L is weaker and treated as a perturbation as was done in Section 13.1.1 for the single electron in a hydrogen atom. The vector sum of L and S is J which is added to the state designation $^{2S+1}L_J$ as a subscript. The good quantum numbers are therefore presumed to be L , S , M_L , M_S , and J . A complete *LS*-coupling state designation is therefore

$$(\text{electron configuration})^{2S+1}L_J \quad (13.78)$$

where the electron configuration might be any of the types discussed in Section 13.3.2. Such designations are often called spectroscopic terms. For two electrons outside completed orbitals, total orbital angular momentum can take on the values

$$L = |\ell_1 + \ell_2|, |\ell_1 + \ell_2 - 1|, \dots, |\ell_1 - \ell_2| \quad (13.79)$$

while the total spin values are 0 and 1. Extension to more than two eligible electrons is obvious.

The *jj*-coupling scheme is based on the opposite to the assumptions made in the *LS*-coupling scheme. It is assumed that the orbital and spin angular momenta of each electron interact strongly so the resulting total angular momenta of each electron serve to designate the states. This scheme is valid for the heaviest of the atoms. We shall not discuss it further since the *LS*-coupling scheme is, by far, the most prevalent.

We can illustrate the way in which the different angular momenta combine in *LS*-coupling by considering the carbon atom. The ground state of C has the electron configuration $(1s)^2(2s)^2(2p)^2$; however, to avoid dealing with the Pauli principle, we first consider an excited electron configuration, $(1s)^2(2s)^2(2p)(3p)$. The total orbital and spin angular momenta of the $(1s)^2(2s)^2$ part of this configuration both vanish so we need consider only the two *p*-electrons. Therefore, the possible values of the total orbital angular momentum *L* are 0, 1, and 2 which correspond to *S*, *P*, and *D*-states. It is important to note that this *S*-state refers to *orbital* angular momentum and should not be confused with the total *spin* quantum number *S*. Combining the two possible multiplicities with the three possible values of total angular momentum we arrive at the possible states

$$^1S \ ^1P \ ^1D \ ^3S \ ^3P \ ^3D \quad (13.80)$$

The orbital and spin angular momenta can also combine vectorially to form the total angular momentum *J*. For example, the 3P state for which $L = 1$ and $S = 1$ can have $J = 0, 1$, and 2. We may therefore list all of the states of this excited carbon atom as

$$^1S_0 \ ^1P_1 \ ^1D_2 \ ^3S_1 \ ^3P_{0,1,2} \ ^3D_{1,2,3} \quad (13.81)$$

This enumeration of the possible states for the configuration $(2p)(3p)$, or, indeed, for any configuration of the type $(np)(n'p)$, makes it clear why the superscript is referred to as the multiplicity. The number of *J*-substates associated with any term ^{2S+1}L is the multiplicity. Most of the time $2S + 1$ is the multiplicity. As is clear from the 3S_1 state, which has only one *J*-substate, this rule can be broken. It is broken any time that $S > L$ because, in this case, the number of *J*-substates is $2L + 1$ rather than $2S + 1$. A term such as 1P is called a singlet *P*-state while 3P is a triplet *P*-state. Often, in conversation, even when $S > L$, the superscript is referred to as singlet, triplet, doublet ($S = \frac{1}{2}$), etc. For example, the 3S_1 state may be referred to as a triplet *S*-state even though there is only one *J* substate. In general, however, each

LS combination designated ^{2S+1}L is called a multiplet, the multiplicity of which is the total number of possible J -states.

Now, back to the ground state of C. While the states arising from the $(2p)^2$ configuration might be thought to be identical to those arising from $(2p)(3p)$, this is not the case because of the Pauli exclusion principle. Care must be taken to make sure that the electrons do not have the same sets of quantum numbers. This condition is automatically fulfilled when the electrons occupy different orbitals. When electrons occupy the same orbital they are referred to as equivalent electrons, otherwise they are non-equivalent. In the present example it should be clear that the allowed states for $(2p)^2$ should be a subset of the allowed states for the $(2p)(3p)$ configuration. There is a simple way to decide which of the allowed $(2p)(3p)$ states are also allowed for $(2p)^2$. For any two equivalent electrons the rule is

*For two equivalent electrons the only allowed states
are those for which the sum $(L + S)$ is even.*

Unfortunately, there is no such rule that applies when there are more than two equivalent electrons. The easiest way to find the allowed terms for more than two equivalent electrons is to use a table of equivalent electrons [6]. Using the rule stated above, the only possible states for the ground state electron configuration of C are 1S_0 , 1D_2 , and $^3P_{0,1,2}$.

Because the total spin and the total orbital angular momenta vanish for closed shells, the term symbol for an atom with a completely filled shell, a noble gas, is 1S_0 . Suppose we take the term symbols that are possible for the ground state of C and add four more $2p$ electrons. This must result in a 1S_0 state. Thus, if we consider the atom for which the ground state configuration is $(1s)^2(2s)^2(2p)^4$, the O atom, the allowed states must be such that, when the angular momenta are added vectorially to those of the ground state of C, the result is 1S_0 . To achieve this, the possible spins and angular momenta of the O atom must be identical with those of the C atom. Thus, we may treat the vacancies in an orbital, “holes,” as though they were actually electrons to deduce the correct terms. Indeed, the possible states for the ground state configurations of C and O are identical. This is a general rule for all orbitals.

For a given ground state electron configuration the states can be ordered with respect to their energies using two empirically deduced, but quantum mechanically sound, rules known as Hund’s rules. These rules apply to atoms for which LS -coupling applies. For our purposes, we state Hund’s rules as follows.

Rule 1: *For states composed of equivalent electrons,
the state of highest S lies lowest.*

Rule 2: *For a given S within the same configuration of equivalent
electrons, the state with the highest L lies lowest.*

In practice, the rules apply to the ground state only because the electrons must be in the same orbital, that is, equivalent electrons. Hund’s rules are, however, often

applied to excited configurations with only modest success. Frequently the requirement that the electrons must be equivalent is omitted from the statement of Hund's rules. Since the rules have been found to work unequivocally for ground states and only occasionally for excited configurations [3] we include the stipulation that the electrons be equivalent. Also, the two rules above are often given as a single rule [4].

We have already discussed the physical reason for the first of Hund's rules, Fermi holes and heaps (see Section 13.3.2). The root of the second rule also lies in the relative values of the interelectron Coulomb repulsion. Imagine two electrons orbiting the nucleus with nonzero total orbital angular momentum L , and individual orbital angular momenta ℓ_1 and ℓ_2 . To get a physical feeling for Rule #2 using this Gedanken experiment it is best to envision both electrons having nonzero angular momenta. When L has its lowest possible value, $\ell_2 - \ell_1$, the individual electronic orbital angular momentum vectors are in opposite directions, indicative of electrons revolving in the opposite sense to each other. They, therefore, pass each other and r_{12} can be quite small, thereby raising the interelectron energy considerably. On the other hand, when L has the highest possible value, $\ell_2 + \ell_1$, the electrons are rotating in the same sense, more or less rigidly, thus keeping them apart and, consequently, the interelectron repulsion is small. While these rules may seem to be based on highly qualitative arguments, they actually work for a wide class of atoms.

Returning to the carbon atom, according to Hund's rules, the 3P term of the ground state configuration of C lies lowest. Next lowest is the 1D_2 and the highest energy state of the three is the 1S_0 state. The 3P has, however, three J -substates, so it is necessary to determine the ordering of these sublevels. In LS -coupling the energy associated with any of states ^{2S+1}L is determined by the individual angular momenta, spin and orbital, and by the symmetry requirements. It is assumed that the orbital angular momenta of the electrons interact strongly with each other, leading to a grand L . Similarly, there is a strong interaction between the spin angular momenta that leads to the total spin S . Thus, the energy of the states ^{2S+1}L is determined by interelectron Coulomb repulsion and the symmetry requirements. The spin-orbit coupling, $\mathbf{L} \bullet \mathbf{S}$, further splits the levels according to their J -values and is the major contributor to fine structure splitting in multielectron atoms.

As was the case for hydrogen, we treat the spin-orbit coupling term $\mathbf{L} \bullet \mathbf{S}$ as a perturbation letting

$$\hat{H}_1 = A \hat{\mathbf{L}} \bullet \hat{\mathbf{S}} \quad (13.82)$$

where A is a constant that depends upon L and S . In terms of the individual angular momenta we have

$$\hat{\mathbf{L}} \bullet \hat{\mathbf{S}} = \frac{1}{2} (\hat{J}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2) \quad (13.83)$$

and, because L , S , and J are good quantum numbers in LS -coupling, the spin-orbit energy correction is

$$E^{(1)}(J, L, S) = \frac{A}{2} [J(J+1) - L(L+1) - S(S+1)] \quad (13.84)$$

Within a given multiplet, say 3P_J , the values of L and S are the same so the difference in energy between successive J -levels, J and $J-1$, is

$$\begin{aligned} E^{(1)}(J) - E^{(1)}(J-1) &= \frac{A}{2} [J(J+1) - J(J-1)] \\ &= AJ \end{aligned} \quad (13.85)$$

Equation 13.85 is known as the Landé interval rule. It states that, for a given multiplet, the energy interval between two successive J -values is proportional to the greater of the J 's.

The Landé interval rule leads to a rule that gives the ordering of the J -states in a given multiplet. This rule is often stated as one of Hund's rules, but we separate it from them. It is found empirically that when a particular atomic orbital is less than half-full, the constant A is positive. Consequently, the lowest J -state has the lowest energy. On the other hand, when the atomic orbital is more than half-full, it is found that A is negative. The spin-orbit interaction is one between magnetic moments so the reversal of sign for orbitals that are more than half-full can be envisioned as the same spin-orbit interaction for the same number of holes as there are electrons in the less-than-half-full orbital. It is reasonable to think of the holes as having magnetic moments in the opposite direction to that of the electrons, thus reversing the sign of A . Therefore, if an atomic orbital is more than half-full, the energies of the J -states are reversed and the multiplet is said to be inverted. For inverted multiplets the highest value of J lies lowest. The rule for ordering the substates in a multiplet is therefore

For a given multiplicity and value of L , the state having the lowest J lies lowest for subshells that are less than half-full. If the subshell is more than half-full the state having the highest value of J lies lowest.

It is interesting that for a level that is half-filled, the spin-orbit coupling is zero. This can be seen by noting that a half-full orbital can be regarded as half-full or half-empty. Thus, the spin-orbit coupling energy for half-full should be of opposite sign to spin-orbit coupling for half empty. This can only be true if the spin-orbit coupling is zero.

13.5 Retrospective

While the study of the hydrogen atom in Chapter 10 provided an elegant solution to the TISE, this solution was, sadly, incomplete because the Schrödinger equation does not contain relativistic effects such as spin. Indeed, the Dirac equation comes closer to providing a complete solution, but it too is incomplete because it does not

contain some important effects such as those of QED. It is, however, possible to circumvent the Dirac equation by proper use of perturbation theory. Thus, the study of perturbation theory in Chapter 12 is crucial to the study of quantum physics. Moreover, approximation methods such as perturbation theory and the variational technique are required to describe multielectron atoms because the three-body problem is not solvable. Therefore, a seemingly simple system like the helium atom requires application of these approximation techniques.

Because the hydrogen atom contains only a single electron it is not necessary to confront the concept of identical particles when studying it. The helium atom, however, requires proper attention to this very important quantum mechanical concept, a concept that leads to an extra “force,” the exchange force, as manifested through the exchange integral K . The effect of the exchange integral is to raise the Coulomb energy by K for the singlet states and lower it by K for the triplet states as dictated by Equation 13.77. Were it not for the quantum mechanical requirement of indistinguishability, the corrected energy would be simply the unperturbed energy plus the energy of the Coulomb integrals. The reason that the triplet states are lowered in energy is because the triplet is characterized by a probability distribution that represents a Fermi hole which keeps the electrons away from each other. Because the interelectron repulsion depends upon $1/r_{12}$, the triplet state energy is lower than the corresponding singlet, the probability density of which is that of a Fermi heap for which the electrons are close to each other and, consequently, the interelectron repulsive energy is higher than for the triplet.

13.6 References

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Problems

1. Show that the ratio $|\langle \hat{H}_{SO} \rangle / \langle \hat{H}_0 \rangle| \sim \alpha^2$ first using SI units and then using atomic units.
2. Show that for the hydrogen atom the expectation value of the spin–orbit Hamiltonian, Equation 13.21, is given by

$$\begin{aligned} \langle \hat{H}_{SO} \rangle &= \frac{1}{2m_e^2 c^2 \hbar^2} \left(\frac{1}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r^3} \right\rangle \langle \hat{\mathbf{L}} \bullet \hat{\mathbf{S}} \rangle \\ &= -\frac{1}{n} \alpha^2 E_n^{(0)} \frac{1}{\left[\ell \left(\ell + \frac{1}{2} \right) (\ell + 1) \right]} \frac{\langle \hat{\mathbf{L}} \bullet \hat{\mathbf{S}} \rangle}{\hbar^2} \end{aligned}$$

3. Show that neither \hat{L}_z nor \hat{S}_z commute with $\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}$.
4. Show that \hat{J}^2 and \hat{J}_z commute with $\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}$.
5. Assume that nucleons are bound by an isotropic oscillator potential $U(r) = \frac{1}{2}m\omega^2 r^2$.
 - (a) Use perturbation theory to solve for the energy level splitting by the spin-orbit interaction.
 - (b) What is the splitting of s -states?
6. Solve for the hyperfine eigenvalues found in Section 8.6.1 and Problem 22 of Chapter 8 using degenerate perturbation theory and compare with the exact answers.
7. Show that minimization of $\langle \hat{H} \rangle$ in Equation 13.67 leads to $\zeta_0 = Z - 5/16$, the value of ζ that minimizes $\langle \hat{H} \rangle$ which yields Equation 13.69 for the minimized expectation value of the energy.
8. Using Equations 13.63 and 13.69 show that the energy obtained from the variational treatment is lower than that obtained from perturbation theory and is therefore closer to reality. By how much lower is the energy obtained from the variational treatment in eV?
9. Using the degenerate product kets $|1s\rangle_1 |2\ell\rangle_2$ and $|1s\rangle_2 |2\ell\rangle_1$ to represent the $1s2\ell$ electron configuration of helium, diagonalize \hat{H}_1 and obtain the correction to the unperturbed energy and the select eigenkets that diagonalize \hat{H}_1 .
10. Show that using the properly symmetrized eigenkets, the select eigenkets, for the $1sn\ell$ excited states of helium, the perturbing Hamiltonian $\hat{H}_1 = 1/r_{12}$ is diagonal.
11. The ground state electron configuration of the boron atom is $(1s)^2 (2s)^2 2p$.
 - (a) Using LS notation list all possible states in order of increasing energy.
 - (b) List all possible states of the first excited configuration of boron $(1s)^2 2s (2p)^2$ using LS notation. Include all possible J -states.
12. One excited electron configuration of Ca atoms is $[\text{Ar}](3d)^2$.
 - (a) What are the allowed LS terms?
 - (b) A particular multiplet of this configuration is observed to have the energy spacing between three adjacent J -levels, $J, J \pm 1$ such that $E(J) - E(J-1) = E_0$ and $E(J+1) - E(J) = (4/3)E_0$ where E_0 is a constant. What is the LS term designation of the multiplet for which the energy level spacing is as given?

Chapter 14

Atoms in External Fields

We have seen that fine structure effects break the accidental degeneracy of the hydrogen atom. These effects, however, leave untouched the spatial degeneracy that is due to the central potential. This degeneracy may be broken by spoiling the spherical symmetry of the central potential. One way to do this is to impose an external field on the atom, thus establishing a direction in space. Of course, either an electric field or a magnetic field will do.

In 1896, at the suggestion of Hendrik Antoon Lorentz, under whom he had previously studied, Pieter Zeeman began experimental investigations of the effects of magnetic fields on atomic spectra. This led to the discovery of the Zeeman effect. In 1902 Zeeman and Lorentz shared the Nobel Prize in Physics, the citation for which reads, “in recognition of the extraordinary service they rendered by their researches into the influence of magnetism upon radiation phenomena.”

The study of atoms in external magnetic fields predated the analogous study with electric fields largely because high electrical fields cause electrical breakdown, thus making the experiments more difficult. In 1913, however, Johannes Stark and, independently, Antonino Lo Surdo observed splittings of the hydrogen spectral lines by an external electric field. Interestingly, only Stark received the Nobel Prize for the work which was awarded in 1919. The citation reads: “for his discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric fields.” The effect is commonly known as the Stark effect, but is often referred to as the Stark–Lo Surdo effect.

14.1 Hydrogen Atoms in External Fields

14.1.1 Electric Fields—the Stark Effect

Quadratic Stark Effect—The Ground State

The energy of orientation of any charge distribution is the dot product of the electric dipole moment (if it has one) and the field. Thus, we take the perturbing Hamiltonian, which we designate by $\hat{H}_1 = \hat{H}_S$, to be of the form

$$\hat{H}_S = -\hat{\mathbf{p}} \bullet \mathbf{F} \quad (14.1)$$

where $\hat{\mathbf{p}} = e\mathbf{r}$ is the electric dipole moment and \mathbf{F} is the applied electric field. We choose the field to be constant and in the z -direction, $\mathbf{F} = F\hat{\mathbf{k}}$, so that

$$\hat{H}_S = -eFz \quad (14.2)$$

Electronic spin is not important here because spin is a magnetic quantity.

It is assumed that the perturbing Hamiltonian is small enough compared with \hat{H}_0 that we can employ perturbation theory. We therefore restrict our attention to weak fields. What is a weak field? From a practical standpoint, it is a field that makes the problem tractable so it may serve as a suitable example of perturbation theory. For this purpose we restrict the field strength to being weak enough so the energy splitting that it causes is much smaller than the spacing between adjacent n -levels, $\Delta E_n^{(0)}$, but strong enough that this splitting is much greater than the fine structure splitting for a given n , $\Delta E_{FS}(n)$. We can then ignore fine structure and assume the unperturbed energy to be the Bohr energy, $E_n^{(0)}$. In terms of the Bohr energy

$$\Delta E_n^{(0)} \gg eFz \gg \Delta E_{FS}(n) \quad (14.3)$$

We may assume that the dimension over which the field acts is roughly the size of an atom in the n th state, $\sim n^2 a_0$. From Equation 13.41 and the Bohr energy, we have, after rearranging the inequality in Equation 14.3,

$$\frac{\alpha^2}{4} \left(\frac{e}{4\pi\epsilon_0 a_0^2} \right) \frac{1}{n^5} \ll F \ll \left(\frac{e}{4\pi\epsilon_0 a_0^2} \right) \frac{1}{n^5} \quad (14.4)$$

As displayed in Equation 14.4 the quantities in parentheses are the atomic unit of electric field (see Table 1.2).

If the only energy eigenfunctions were those obtained by solving the TISE in spherical coordinates, then the atom could *not* have a permanent electric dipole moment in an eigenstate because of the symmetry of the probability distributions. Recall from Section 8.4 that the spherical harmonics have definite parity and the parity is determined solely by ℓ . The parabolic coordinate eigenfunctions are another matter. Many of these do lead to electronic probability densities for which there *is* a permanent dipole moment because they produce asymmetric electronic charge distributions. This can be understood by noting that any linear combination of eigenfunctions that have the same eigenvalue is also an eigenfunction. Thus, we may form an eigenfunction as a linear combination of spherical (or parabolic) eigenfunctions, and arrange the expansion coefficients to make the resulting electronic probability distribution as asymmetric as we please. Because each set of eigenfunctions is complete, any of the parabolic eigenfunctions can be expressed as a linear combination of spherical eigenfunctions (and vice versa). The consequence of this is that excited eigenstates of the hydrogen atom can, and do, have permanent electric dipole moments because of the accidental degeneracy. Being nondegenerate, however, the ground state does not have a permanent dipole moment. This is

reflected in the fact that the ground state eigenfunctions in spherical and parabolic coordinates are identical. We first consider the ground state for which we need use only nondegenerate perturbation theory.

The first-order correction to the ground state energy $\left(E_S^{(1)}\right)_{100}$ is

$$\langle \hat{H}_S \rangle_{100} = eF \langle 100 | z | 100 \rangle \quad (14.5)$$

which vanishes because it represents an integral with an odd integrand. We must therefore proceed to second-order perturbation theory for which the energy correction to the ground state is

$$\left(E_S^{(2)}\right)_{100} = (eF)^2 \sum_{n\ell m \neq 100} \frac{|\langle 100 | z | n\ell m \rangle|^2}{E_1^{(0)} - E_n^{(0)}} \quad (14.6)$$

This sum can actually be evaluated exactly, but doing so is of limited pedagogical value so we simply estimate it. We obtain an upper bound to $\left(E_S^{(2)}\right)_{100}$ by letting all of the $E_n^{(0)} = E_2^{(0)}$. We have then

$$\left(E_S^{(2)}\right)_{100} < \frac{(eF)^2}{E_1^{(0)} - E_2^{(0)}} \sum_{n\ell m \neq 100} |\langle 100 | z | n\ell m \rangle|^2 \quad (14.7)$$

We can let the summation run over all $n\ell m$ because the first term will vanish anyway. The summation in Equation 14.7 can be evaluated by expanding it as

$$\begin{aligned} \sum_{n\ell m} |\langle 100 | z | n\ell m \rangle|^2 &= \sum_{n\ell m} \langle 100 | z | n\ell m \rangle \langle n\ell m | z | 100 \rangle \\ &= \langle 100 | z^2 | 100 \rangle \end{aligned} \quad (14.8)$$

Note the presence of the identity operator. Also, this is the expectation value of z^2 , not z , so this integral does not vanish. Now, the ground state is spherically symmetric so $\langle z^2 \rangle = (1/3) \langle r^2 \rangle$. Using Table 10.4 to evaluate $\langle r^2 \rangle$ for $n = 1$ we find

$$\left(E_S^{(2)}\right)_{100} < -(4\pi\epsilon_0) \left(\frac{8}{3}\right) a_0^3 F^2 \quad (14.9)$$

while the exact answer is

$$\left(E_S^{(2)}\right)_{100} = -\frac{9}{4} (4\pi\epsilon_0) a_0^3 F^2 \quad (14.10)$$

In atomic units this is

$$\left(E_S^{(2)}\right)_{100} = -\frac{9}{4} F^2 \quad (14.11)$$

The important point about this expression is that it is proportional to the square of the electric field. It is therefore referred to as the quadratic Stark effect. Why is it proportional to the square of the electric field? The reason is that there is no permanent electric dipole moment in the nondegenerate ground state. The probability distribution for this state is spherically symmetric. The field, however, induces a dipole moment. The propensity of a charge distribution to be polarized by a field is called the dipole polarizability and, regrettably, is designated by the Greek letter α . We use α_d to avoid confusion with the fine structure constant. The induced dipole moment p_{in} is given by

$$p_{in} = \alpha_d F \quad \Longrightarrow \quad \alpha_d = \frac{dp_{in}}{dF} \quad (14.12)$$

In general, the dipole moment is the change in energy E with respect to the field so

$$p_{in} = -\frac{dE}{dF} \quad \Longrightarrow \quad \alpha_d = -\frac{d^2E}{dF^2} \quad (14.13)$$

from which it is clear that for the ground state of hydrogen

$$\begin{aligned} \alpha_d &= \frac{9}{2} (4\pi\epsilon_0) a_0^3 \\ &= \frac{9}{2} \text{ (a.u.)} \end{aligned} \quad (14.14)$$

The Linear Stark effect—Excited States

We now turn our attention to the excited states, focusing on $n = 2$ because it minimizes the algebra. We have already solved a similar problem when we examined the perturbed isotropic harmonic oscillator in Section 12.1.2. In the present case, the $n = 2$ state of hydrogen is fourfold degenerate, not counting spin, which can be ignored because spin is a magnetic property. The matrix that represents the unperturbed Hamiltonian, \hat{H}_0 , is diagonal; the diagonal elements of which are all the Bohr energy for $n = 2$, in perturbation theory terms $E_2^{(0)}$.

The perturbing Hamiltonian, \hat{H}_1 , is not, however, diagonal, so we must find the linear combinations of spherical eigenfunctions that diagonalize it. We represent the unperturbed eigenstates in spherical coordinates for $n = 2$ by the kets $|\ell m\rangle$ where, because spin is not affected, we have dropped the subscript on the m quantum number. We therefore write the matrix representing \hat{H}_1 as

$$\hat{H}_1 = eF \begin{pmatrix} \langle 00|z|00\rangle & \langle 00|z|10\rangle & \langle 00|z|11\rangle & \langle 00|z|1-1\rangle \\ \langle 10|z|00\rangle & \langle 10|z|10\rangle & \langle 10|z|11\rangle & \langle 10|z|1-1\rangle \\ \langle 11|z|00\rangle & \langle 11|z|10\rangle & \langle 11|z|11\rangle & \langle 11|z|1-1\rangle \\ \langle 1-1|z|00\rangle & \langle 1-1|z|10\rangle & \langle 1-1|z|11\rangle & \langle 1-1|z|1-1\rangle \end{pmatrix} \quad (14.15)$$

Symmetry considerations will eliminate most of these matrix elements. First, it is clear that the diagonal elements vanish because \hat{H}_1 is an odd function. Second, again because \hat{H}_1 is odd, and because ℓ determines the parity of the spherical harmonics, any matrix element for which both values of ℓ are the same vanishes. Therefore, the only possible nonzero matrix elements are those in the first column and the first row. Finally, those matrix elements for which the quantum numbers m are different, vanish because there will be a factor $e^{i(m-m')\phi}$ in the integral and $z = r \cos \theta$ does not contain ϕ . The factor $e^{i(m-m')\phi}$, when integrated from 0 to 2π , vanishes.

We see that the only nonzero matrix elements are $\langle 10|z|00\rangle = \langle 00|z|10\rangle^*$ so we need diagonalize only the 2×2 submatrix in the upper left-hand corner of Equation 14.15. These matrix elements may be evaluated with the help of the eigenfunctions listed in Table 10.5. We have

$$\begin{aligned}
 \langle 10|z|00\rangle &= eF \int_0^\infty R_{21}^*(r) R_{20}(r) r^3 dr \\
 &\quad \times \int_0^\pi Y_{10}^*(\theta, \phi) \cos \theta Y_{10}(\theta, \phi) \sin \theta d\theta \int_0^{2\pi} d\phi \\
 &= eF \frac{1}{8a_0^3} \int_0^\infty \left(\frac{r}{a_0}\right) \left(1 - \frac{r}{2a_0}\right) r^3 dr \int_0^\pi \sin \theta \cos^2 \theta d\theta \\
 &= -3eFa_0
 \end{aligned} \tag{14.16}$$

The eigenvalue equation for the 2×2 submatrix is

$$\begin{pmatrix} 0 & -3eFa_0 \\ -3eFa_0 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E_2^{(1)} \begin{pmatrix} a \\ b \end{pmatrix} \tag{14.17}$$

so the secular equation is

$$\begin{vmatrix} -E_2^{(1)} & -3eFa_0 \\ -3eFa_0 & -E_2^{(1)} \end{vmatrix} = 0 \implies \left[E_2^{(1)}\right]^2 - (3eFa_0)^2 = 0 \tag{14.18}$$

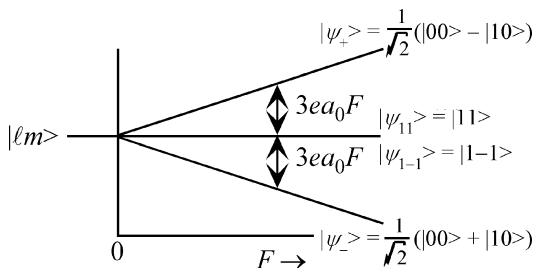
and the energy splittings due to application of the field are

$$E_2^{(1)} = 0, 0, \pm 3eFa_0 \tag{14.19}$$

The unshifted values are associated with the $|11\rangle$ and $|1-1\rangle$ states which are part of the select set. The $|10\rangle$ and $|00\rangle$ states are, however, destroyed by the perturbation, although they reappear in linear combinations that constitute the select states. These select states are (see Problem 1)

$$|\psi\rangle_\pm = \frac{1}{\sqrt{2}} (|00\rangle \mp |10\rangle) \tag{14.20}$$

Fig. 14.1 Energy level diagram showing the linear Stark effect on the $n = 2$ states of hydrogen



Therefore, only part of the degeneracy is removed by application of the electric field. The energy is split as shown in Fig. 14.1, which also shows the associated select eigenkets. It is said that the perturbation mixes the $|10\rangle$ and $|00\rangle$ states.

Notice that the energy correction is proportional to the first power of the field, so the Stark effect for excited states of hydrogen is the *linear* Stark effect in contrast to the ground state which exhibits the quadratic Stark effect. We might say that in the quadratic Stark effect one power of the field is required to induce the dipole while the remaining power determines the energy of orientation of the dipole in the field.

Interestingly, the kets that are the eigenkets of the shifted energies are precisely the kets that are obtained if the TISE is separated and solved in parabolic coordinates. This is because the TISE for the hydrogen atom in a weak electric field is separable in parabolic coordinates, the eigenfunctions being the same as the parabolic eigenfunctions obtained for $F = 0$. For this reason the parabolic eigenfunctions are often referred to as Stark eigenfunctions.

14.1.2 Magnetic Fields—The Zeeman Effect

The energy of orientation of a magnetic dipole in a magnetic field is analogous to that of an electric dipole in an electric field, Equation 14.1. Letting the magnetic moment of the atom be

$$\boldsymbol{\mu} = \boldsymbol{\mu}_\ell + \boldsymbol{\mu}_s \quad (14.21)$$

the Hamiltonian for the Zeeman effect \hat{H}_B is

$$\begin{aligned} \hat{H}_B &= -(\boldsymbol{\mu}_\ell + \boldsymbol{\mu}_s) \cdot \mathbf{B} \\ &= \left(\frac{g_\ell \mu_B}{\hbar} \hat{\mathbf{L}} + \frac{g_s \mu_B}{\hbar} \hat{\mathbf{S}} \right) \cdot \mathbf{B} \\ &= \frac{\mu_B}{\hbar} (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{B} \end{aligned} \quad (14.22)$$

where the g -factors are $g_\ell = 1$ and $g_s = 2$ (see Section 8.5). The spin of the proton has been ignored inasmuch as its magnetic moment is tiny compared with the orbital and spin magnetic moments. For convenience, the direction of the external field is

again chosen to be in the z -direction so that

$$\hat{H}_B = \frac{\mu_B}{\hbar} B (\hat{L}_z + 2\hat{S}_z) \quad (14.23)$$

To treat the problem using perturbation theory, we must compare the magnitudes of the various energies. The total Hamiltonian may be written in terms of the constituent Hamiltonians:

$$\hat{H} = \hat{H}_{\text{Coul}} + \hat{H}_{FS} + \hat{H}_B \quad (14.24)$$

where \hat{H}_{FS} is the fine structure Hamiltonian and \hat{H}_{Coul} is the field-free Hamiltonian. We need consider only the spin-orbit part of the fine structure Hamiltonian because the spin-orbit energy is in competition with the energy associated with the externally applied magnetic field. The contribution to the fine structure of the relativistic energy of the electron remains unchanged with application of the external field.

A weak external field is defined as one that causes splitting that is small compared with the spin-orbit splitting. A strong external field leads to splitting that is greater than the spin-orbit splitting. Therefore, for a weak field, \hat{H}_B is treated as the perturbation while for strong fields \hat{H}_{FS} is the perturbation. In the absence of the external field the magnitude of the spin-orbit portion of the fine structure splitting is determined by the magnitude of the internal magnetic field, B_{orbital} , as given in Equation 13.19. We may therefore compare the magnitudes of the respective fields, internal and external, to assess the two effects. In terms of the Bohr magneton (see Equation 1.44) the internal field B_{orbital} is

$$B_{\text{orbital}} = \left(\frac{1}{4\pi\epsilon_0} \right) \left(\frac{2}{c^2 r^3} \right) \mu_B \ell \quad (14.25)$$

where we have replaced the angular momentum by $\ell\hbar$. For $n = 2$ the internal field is approximately $B_{\text{orbital}} \approx 1\text{T}$. We may therefore consider 1T as the dividing line between weak and strong fields. In the vicinity of 1T the fine structure splittings and the Zeeman effect splittings are comparable so that to properly use the weak field approximation the external field should be substantially less than 1T. In fact, the problem can be solved exactly for hydrogen [1, 2], thus eliminating the necessity of defining a boundary between weak and strong fields. We will not, however, work out the details of the exact case here. It is customary to use SI units when treating the Zeeman effect, a convention we will follow.

Strong Fields

For the strong field case the unperturbed Hamiltonian is

$$\hat{H}_0 = \hat{H}_{\text{Coul}} + \frac{\mu_B}{\hbar} B (\hat{L}_z + 2\hat{S}_z) \quad (14.26)$$

Because \hat{L}_z and \hat{S}_z commute with \hat{H}_{Coul} , the quantum numbers (ℓ, m_ℓ, s, m_s) remain good quantum numbers. Therefore, the unperturbed eigenkets for the strong field case are the uncoupled set $|n \ell m_\ell; \frac{1}{2} m_s\rangle$. The coupled set $|n j m_j \ell s\rangle$ are not eigenkets of \hat{H}_0 because j and m_j are not good quantum numbers. From Equation 14.26 it is clear that the unperturbed energy in the presence of a strong B -field, $E_n^{(0)}(B)$, is

$$E_n^{(0)}(B) = E_n^{(0)} + \mu_B B (m_\ell + 2m_s) \quad (14.27)$$

which makes it clear that the degenerate Bohr energy $E_n^{(0)}$ is split by application of the field. This is precisely what was expected because application of the field destroys the spherical symmetry that is partially responsible for the field-free degeneracy. Incidentally, Equation 14.27 also makes clear the reason that m_ℓ and m_s are referred to as magnetic quantum numbers. There does, however, remain some degeneracy. States for which m_ℓ and m_s are different, but for which the sum $(m_\ell + 2m_s)$ is the same, are degenerate.

To find the correction to the energy, Equation 14.27, we must find the expectation value of the fine structure Hamiltonian in the presence of the externally applied field. As noted above, the relativistic correction will be insensitive to this field, but the spin-orbit term $\hat{\mathbf{L}} \bullet \hat{\mathbf{S}}$ is indeed affected by its presence. We must therefore reevaluate $\langle \hat{H}_{SO} \rangle$ as given in Equation 13.21. This expectation value can be put in the form (see Problem 2, Chapter 13)

$$\langle \hat{H}_{SO} \rangle = -\frac{1}{n} \alpha^2 E_n^{(0)} \left\{ \frac{1}{[\ell(\ell + \frac{1}{2})(\ell + 1)]} \right\} \frac{\langle \hat{\mathbf{L}} \bullet \hat{\mathbf{S}} \rangle}{\hbar^2} \quad (14.28)$$

The uncoupled kets are the unperturbed kets so we must use them to evaluate $\langle \hat{\mathbf{L}} \bullet \hat{\mathbf{S}} \rangle$. To do this we employ the identity (see Problem 2)

$$\hat{\mathbf{L}} \bullet \hat{\mathbf{S}} = \hat{L}_z \hat{S}_z + \frac{1}{2} (\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+) \quad (14.29)$$

Because of orthogonality, the expectation values involving the ladder operators vanish from $\langle \hat{\mathbf{L}} \bullet \hat{\mathbf{S}} \rangle$ and we have

$$\langle \hat{\mathbf{L}} \bullet \hat{\mathbf{S}} \rangle = m_\ell m_s \hbar^2 \quad (14.30)$$

Adding $\langle \hat{H}_{SO} \rangle$ to the relativistic energy, Equation 13.15, we obtain the fine structure correction in the presence of a strong external magnetic field B to be

$$\begin{aligned}
E_{FS}^{(1)} &= -\frac{1}{n}\alpha^2 E_n^{(0)} \left(\frac{m_\ell m_s}{\left[\ell\left(\ell + \frac{1}{2}\right)(\ell + 1)\right]} \right) + E_n^{(0)} \frac{\alpha^2}{n^2} \left[\frac{n}{(\ell + 1/2)} - \frac{3}{4} \right] \\
&= -E_n^{(0)} \left(\frac{\alpha^2}{n} \right) \left\{ \frac{3}{4n} - \left[\frac{\ell(\ell + 1) - m_\ell m_s}{\ell\left(\ell + \frac{1}{2}\right)(\ell + 1)} \right] \right\} \quad (14.31)
\end{aligned}$$

Notice that this expression is indeterminate for $\ell = 0$ in which case it can be shown that the term in square brackets is unity. Adding this energy to that in the second term in Equation 14.27 gives the total Zeeman energy resulting from application of the strong field E_Z :

$$E_Z^{(1)} = \mu_B B (m_\ell + 2m_s) - E_n^{(0)} \left(\frac{\alpha^2}{n} \right) \left\{ \frac{3}{4n} - \left[\frac{\ell(\ell + 1) - m_\ell m_s}{\ell\left(\ell + \frac{1}{2}\right)(\ell + 1)} \right] \right\} \quad (14.32)$$

Weak Fields

In this case we take \hat{H}_B as the perturbing Hamiltonian so that

$$\hat{H}_0 = \hat{H}_{\text{Coul}} + \hat{H}_{FS} \quad (14.33)$$

Therefore, the unperturbed eigenkets are the coupled kets so, to obtain the correction to the unperturbed energy, we must evaluate the expectation value $\langle \hat{H}_B \rangle$ using these kets. We can simplify this task slightly by eliminating \hat{L}_z from Equation 14.23 using $\hat{J}_z = \hat{L}_z + \hat{S}_z$. We have

$$\hat{H}_B = \frac{\mu_B}{\hbar} B (\hat{J}_z + \hat{S}_z) \quad (14.34)$$

The coupled kets are eigenkets of \hat{J}_z , but not of \hat{S}_z . We are therefore left with the task of evaluating

$$\begin{aligned}
\langle \hat{S}_z \rangle &= \langle n j m_j \ell s | \hat{S}_z | n j m_j \ell s \rangle \\
&= \left\langle \left(\ell \pm \frac{1}{2} \right) m_j \left| \hat{S}_z \right| \left(\ell \pm \frac{1}{2} \right) m_j \right\rangle \quad (14.35)
\end{aligned}$$

where the notation in the last line of Equation 14.35 has been truncated. Because the coupled kets are not eigenkets of \hat{S}_z we must write them as linear combinations of the uncoupled kets which are indeed eigenkets of \hat{S}_z . Of course, the expansion coefficients in these linear combinations are the Clebsch–Gordan coefficients which we may read from Table 14.1 which is a modified version of Table 8.11 is that has been adapted to conform to the present notation.

Table 14.1 Clebsch–Gordan coefficients for $j_1 = \ell$ and $j_2 = 1/2$

j	$m_s = \frac{1}{2}$	$m_s = -\frac{1}{2}$
$\ell + \frac{1}{2}$	$\sqrt{(\ell + \frac{1}{2} + m_j) / (2\ell + 1)}$	$\sqrt{(\ell + \frac{1}{2} - m_j) / (2\ell + 1)}$
$\ell - \frac{1}{2}$	$-\sqrt{(\ell + \frac{1}{2} - m_j) / (2\ell + 1)}$	$\sqrt{(\ell + \frac{1}{2} + m_j) / (2\ell + 1)}$

Designating the uncoupled kets as $|\ell \ m_\ell \ m_s\rangle$, where $m_s = \alpha$ (spin up) or β (spin down), the desired expansions are

$$\left| \left(\ell + \frac{1}{2} \right) m_j \right\rangle = \sqrt{\frac{(\ell + \frac{1}{2} + m_j)}{(2\ell + 1)}} |\ell \ m_\ell \ \alpha\rangle + \sqrt{\frac{(\ell + \frac{1}{2} - m_j)}{(2\ell + 1)}} |\ell \ m_\ell \ \beta\rangle \quad (14.36)$$

and

$$\left| \left(\ell - \frac{1}{2} \right) m_j \right\rangle = -\sqrt{\frac{(\ell - m_j + \frac{1}{2})}{(2\ell + 1)}} |\ell \ m_\ell \ \alpha\rangle + \sqrt{\frac{(\ell + m_j + \frac{1}{2})}{(2\ell + 1)}} |\ell \ m_\ell \ \beta\rangle \quad (14.37)$$

Note that the value of m_ℓ is fixed for a given one of these expansion coefficients by the value of $m_j = m_\ell + m_s$. For example, in the coefficients of $|\ell \ m_\ell \ \alpha\rangle$ we must have $m_\ell = m_j - \frac{1}{2}$, while the coefficients of $|\ell \ m_\ell \ \beta\rangle$ must have $m_\ell = m_j + \frac{1}{2}$. Using these expansions, the expectation value $\langle \hat{S}_z \rangle$ is

$$\begin{aligned} \langle \hat{S}_z \rangle &= \frac{\hbar}{2} \left[\frac{(\ell + \frac{1}{2} \pm m_j)}{(2\ell + 1)} - \frac{(\ell + \frac{1}{2} \mp m_j)}{(2\ell + 1)} \right] \\ &= \pm \frac{m_j \hbar}{(2\ell + 1)} \end{aligned} \quad (14.38)$$

The first-order correction to the energy in the weak field case is thus

$$\begin{aligned} E_B^{(1)} &= \langle \hat{H}_B \rangle \\ &= \mu_B B m_j \left[1 \pm \frac{1}{(2\ell + 1)} \right]; \quad j = \ell \pm \frac{1}{2} \end{aligned} \quad (14.39)$$

The quantity in brackets in Equation 14.39 is called the Landé g -factor. For simplicity, it is usually expressed in terms of j and ℓ because it can be represented as a single expression. That is, for either value $j = \ell \pm \frac{1}{2}$ it can be shown that the Landé g -factor is (see Problem 4)

$$g(j, \ell) = \left[1 + \frac{j(j+1) - \ell(\ell+1) + 3/4}{2j(j+1)} \right] \quad (14.40)$$

so the energy due to the field $E_B^{(1)}$ is simply

$$E_B^{(1)} = \mu_B B m_j g(j, \ell) \quad (14.41)$$

Under our definition of weak field, the fine structure is unaffected, so the total correction due to application of the B -field is $E_B^{(1)}$. Adding the fine structure correction to $E_B^{(1)}$ we obtain the total energy, not including the Bohr energy:

$$E_{FS}^{(1)} + E_B^{(1)} = \frac{\alpha^2}{n^2} E_n^{(0)} \left[\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right] + \mu_B B m_j g(j, \ell); \quad j = \ell \pm \frac{1}{2} \quad (14.42)$$

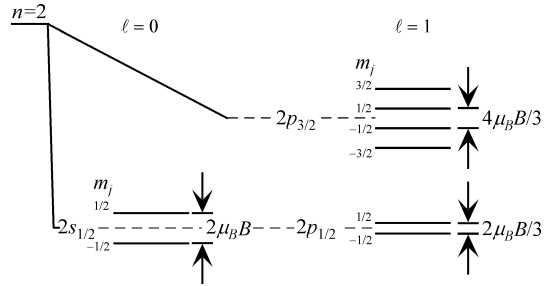
To illustrate the breaking of the degeneracy that is caused by application of an external magnetic field we examine the fine structure levels of the $n = 2$ state of hydrogen (see Figs. 13.1 and 13.2). While the fine structure correction removes some of the degeneracy, it does not remove the degeneracy between the $2s_{1/2}$ and the $2p_{1/2}$ states. It is left to the Lamb shift to do this. Table 14.2 contains a listing of the g -factors for the $n = 2$ states of hydrogen. Also included in the table are the values of $E_B^{(1)}$, in units of $\mu_B B$, for each of the $n = 2$ substates. Now, the Bohr magneton, $\mu_B = 9.274 \times 10^{-24} \text{J/T} = 1.39 \times 10^4 \text{MHz/T}$ (see Table C.1), so that an external field of 1T leads to a Zeeman splitting comparable with that of the $2p_{3/2} - 2p_{1/2}/2s_{1/2}$ fine structure splitting (see Fig. 13.1). Thus, as suggested above, a field substantially below 1T safely coincides with our definition of a weak field since it leads to Zeeman splittings that are smaller than the fine structure splittings. On the other hand, for simplicity, we would like our hypothetically applied external field to produce a splitting that is sufficiently large compared with the Lamb shift (1057 MHz) and the hyperfine splitting (177 MHz for $n = 2$ [1]) that we need not concern ourselves with these effects. Thus, we assume that the applied field is in the approximate range $0.2\text{T} < B < 0.8\text{T}$.

Using the entries in Table 14.2 we can construct a schematic energy level diagram for the $n = 2$ state of hydrogen. Figure 14.2 shows the $n = 2$ level together with the fine structure splitting (see Fig. 13.1), their combination being the unperturbed energy for the weak field case. This figure has been constructed with the assumption that the external magnetic field is sufficiently weak so that, indeed, the Zeeman splitting is smaller than the fine structure splitting. It is seen that application of the field completely removes the degeneracy that persisted even when fine structure is included. The four $2p_{3/2}$ states are now separated. Note that, because the g -factors

Table 14.2 Landé g -factors for the fine structure states of the $n = 2$ level of hydrogen

State	ℓ	m_j	$g(j, \ell)$	$E_B^{(1)}(\mu_B B)$
$2s_{1/2}$	0	$\pm 1/2$	2	± 1
$2p_{1/2}$	1	$\pm 1/2$	$2/3$	$\pm 1/3$
$2p_{3/2}$	1	$\pm 1/2$	$4/3$	± 2
$2p_{3/2}$	1	$\pm 3/2$	$4/3$	$\pm 2/3$

Fig. 14.2 Energy splittings of $n = 2$ states of the hydrogen atom due to application of a weak magnetic field B



for the $2s_{1/2}$ and the $2p_{1/2}$ are different (see Table 14.2), application of the external field causes different Zeeman splittings, thus breaking the degeneracy.

The unperturbed kets used in the perturbation theory treatment of the Zeeman effect were different in the cases of strong and weak fields. For strong fields it was necessary to use the uncoupled kets while for weak fields the coupled kets were required. These kets are, however, identical at the top and bottom of the ladder. That is, when $m_j = j$ the top of the ladder state designations are

$$|j m_j = j; s \ell\rangle = \left| \ell m_\ell = \ell; \frac{1}{2} m_s = \frac{1}{2} \right\rangle \quad (14.43)$$

because, to have $m_j = j$, we must have $m_\ell = \ell$ and $m_s = +\frac{1}{2}$. This is the only way these combinations can be formed so the kets are identical. We see then that, because the uncoupled ket is an eigenket of \hat{H}_B , Equation 14.23, the corresponding coupled ket must also be an eigenket. In this case,

$$\hat{H}_B |j m_j = j; s \ell\rangle = \mu_B B (\ell + 1) \left| \ell m_\ell = \ell; \frac{1}{2} m_s = \frac{1}{2} \right\rangle \quad (14.44)$$

Since, however, $j = \ell + \frac{1}{2}$ we may also write

$$\begin{aligned} \hat{H}_B \left| \ell m_\ell = \ell; \frac{1}{2} m_s = \frac{1}{2} \right\rangle &= \frac{\mu_B B}{\hbar} [(\hat{L}_z + \hat{S}_z) + \hat{S}_z] \left| \ell m_\ell = \ell; \frac{1}{2} m_s = \frac{1}{2} \right\rangle \\ &= \mu_B B \left(j + \frac{1}{2} \right) \left| \ell m_\ell = \ell; \frac{1}{2} m_s = \frac{1}{2} \right\rangle \quad (14.45) \end{aligned}$$

14.2 Multielectron Atoms in External Magnetic Fields

Although the Zeeman effect was observed in 1896 it was not completely understood until 1926 when electron spin was postulated. In the intervening 30 years, attempts to explain the effect met with only limited success. These attempts to explain the Zeeman effect ignored the intrinsic magnetic moment of the electron because it had not yet been discovered. Multielectron atoms were considered in the context of the

Bohr model with quantized orbital angular momenta and energy levels that could accommodate specific numbers of electrons. According to the model, each state that is characterized by a total orbital angular momentum quantum number L splits, upon immersion in an external magnetic field, into $2L + 1$ magnetic substates, one for each value of M_L . Thus, the model ignored a substantial part of the total atomic magnetic moment. It was successful only when the total spin was zero, as it is for parahelium and the singlet states of other atoms. When $S = 0$ the Zeeman effect is referred to as the normal Zeeman effect. Note that $S = 0$ is not a very common occurrence. Nonetheless, this is the normal Zeeman effect because it is the only one that could be understood for 30 years. This understanding was based on classical physics. Experiments showed, however, that the most commonly observed effect was the anomalous Zeeman effect which, as we will see, could be understood only in terms of quantum physics using the concept of spin. Because hydrogen has only a single electron the total spin is always $\frac{1}{2}$ and the anomalous Zeeman effect is observed.

To formulate the problem for multielectron atoms we take an approach similar to that taken for hydrogen, but we must make some approximations that were not required in that case. We treat the weak field case and assume that the unperturbed Hamiltonian is the sum of the Coulomb Hamiltonian and the spin-orbit Hamiltonian:

$$\hat{H}_0 = \hat{H}_{\text{Coul}} + \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \quad (14.46)$$

so the unperturbed kets are the coupled kets. The perturbing Hamiltonian is then \hat{H}_B as in Equation 14.34:

$$\hat{H}_B = \frac{\mu_B}{\hbar} (\hat{\mathbf{J}} + \hat{\mathbf{S}}) \cdot \mathbf{B} \quad (14.47)$$

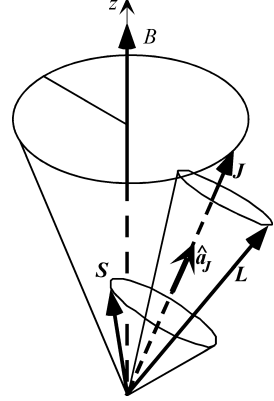
and, assuming that the applied field is in the z -direction, the correction to the energy is

$$\begin{aligned} E_B^{(1)} &= \langle \hat{H}_B \rangle \\ &= \frac{\mu_B}{\hbar} B (M_J \hbar + \langle \hat{S}_z \rangle) \end{aligned} \quad (14.48)$$

Unfortunately, $\langle \hat{S}_z \rangle$ is not as readily evaluated as it was for the hydrogen atom because for hydrogen $s = \frac{1}{2}$. We can, however, make a good approximation for the weak field case. Figure 14.3 shows the relationship between the three angular momenta and the applied field. The vectors \mathbf{S} and \mathbf{L} precess about \mathbf{J} while \mathbf{J} precesses about \mathbf{B} as shown in Fig. 14.3. If the field is weak, then the precession rate of \mathbf{J} will be slow and the average values of \mathbf{S} and \mathbf{L} in the direction of \mathbf{J} provide the *effective* magnetic moment.

The components of \mathbf{S} and \mathbf{L} that are perpendicular to \mathbf{J} will average to zero so the averaging is over only the components that are parallel to \mathbf{J} . The component of

Fig. 14.3 Diagram of the relationship between the various angular momenta



S in the direction of J , S_{\parallel} , is the projection of S in the direction of J :

$$\begin{aligned} S_{\parallel} &= (S \cdot \hat{a}_j) \hat{a}_j \\ &= \left[S \cdot \left(\frac{J}{\sqrt{J(J+1)\hbar}} \right) \right] \left(\frac{J}{\sqrt{J(J+1)\hbar}} \right) \end{aligned} \quad (14.49)$$

where \hat{a}_j is the unit vector in the J -direction. (The denominator $\sqrt{J(J+1)\hbar}$ is simply the magnitude of the total angular momentum vector J .) To calculate $E_B^{(1)}$ we require $\langle \hat{H}_B \rangle$ so, replacing \hat{S} in Equation 14.47 with S_{\parallel} , we have

$$\begin{aligned} \langle \hat{H}_B \rangle &= \frac{\mu_B}{\hbar} \langle \hat{J} + (\hat{S} \cdot \hat{a}_j) \hat{a}_j \rangle \cdot B \\ &= \frac{\mu_B}{\hbar} \left\langle \left[\hat{J} + \frac{(\hat{S} \cdot \hat{J})}{J(J+1)\hbar^2} \hat{J} \right] \cdot B \right\rangle \\ &= \frac{\mu_B}{\hbar} \left\langle \left[1 + \frac{(\hat{S} \cdot \hat{J})}{J(J+1)\hbar^2} \right] (\hat{J} \cdot B) \right\rangle \end{aligned} \quad (14.50)$$

Now, because the external field is in the z -direction, $\hat{J} \cdot B = B \hat{J}_z$. Also, we may evaluate $\hat{S} \cdot \hat{J}$ using the relationship between the three angular momenta:

$$\begin{aligned} \hat{L} \cdot \hat{L} &= (\hat{J} - \hat{S}) \cdot (\hat{J} - \hat{S}) \\ &= \hat{J}^2 + \hat{S}^2 - 2\hat{S} \cdot \hat{J} \end{aligned} \quad (14.51)$$

Therefore,

$$\hat{S} \cdot \hat{J} = \frac{1}{2} (\hat{J}^2 + \hat{S}^2 - \hat{L}^2) \quad (14.52)$$

so that

$$E_B^{(1)} = \frac{\mu_B}{\hbar} \left\langle \left[1 + \frac{(\hat{J}^2 + \hat{S}^2 - \hat{L}^2)}{2J(J+1)\hbar^2} \right] B \hat{J}_z \right\rangle \quad (14.53)$$

The unperturbed kets are coupled kets so the quantum numbers corresponding to all operators in the expectation value are easily evaluated. We have

$$\begin{aligned} E_B^{(1)} &= \mu_B B M_J \left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right] \\ &= \mu_B B M_J g(J, L, S) \end{aligned} \quad (14.54)$$

where

$$g(J, L, S) = \left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right] \quad (14.55)$$

is the Landé g -factor, as in Equation 14.40. Indeed, $g(J, L, S)$ for multielectron atoms reduces to $g(j, \ell)$ for the hydrogen atom.

It is easily seen that the Landé g -factor is unity when $S = 0$, because in that case $J = L$. Therefore, the normal Zeeman effect is observed. That is, the splittings for levels of any value of L are the same, $\mu_B B$, which is the criterion for the normal Zeeman effect. Thus, the splitting of a singlet state such as those in parahelium depend only upon the magnitude of the applied field as indicated on the left side of Fig. 14.4 for $L = 1$ and $L = 2$.

Also shown in Fig. 14.4 are the level splittings resulting from the anomalous Zeeman effect for the same values of L . It is seen that the splittings of the triplet states are different from those of the singlet states and, indeed, different from each other.

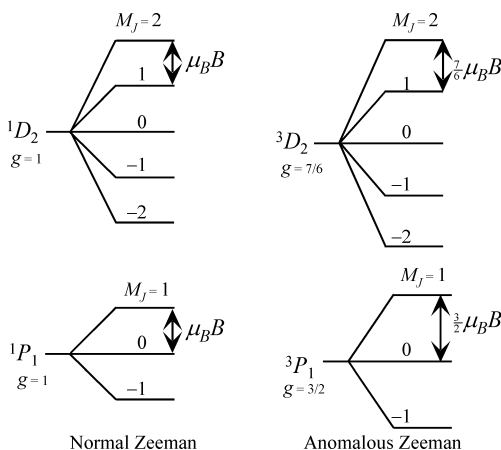


Fig. 14.4 The normal Zeeman effect for 1P_1 and 1D_2 states and the anomalous Zeeman effect for 3P_1 and 3D_2 states

14.3 Retrospective

Historically, the study of the behavior of atoms in external fields provided valuable insight into the nature of the subatomic world in which quantum physics rules. Of particular importance was the notion that an electron has an intrinsic magnetic moment, the spin. This innovative concept was a direct consequence of the failure of classical physics to describe the anomalous Zeeman effect. Subsequently, it was found that the electron is not alone in possessing an intrinsic magnetic moment. A great many other particles, including the proton and neutron, have spin, so this property of fundamental particles pervades quantum physics. Moreover, the differences between particles having half-integral spin and those having integral spin are the basis for the distinction between fermions and bosons. It is probably safe to say that without the data on the anomalous Zeeman effect the breakthrough in thinking that led Goudsmit and Uhlenbeck to formulate the notion of spin would have been delayed by many years.

From the standpoint of atomic physics, the Stark effect is of less importance than the Zeeman effect. Unlike the Zeeman effect, however, it is not possible to formulate the problem classically. (Recall that the *normal* Zeeman effect can be understood using classical physics.) Because understanding of the Stark effect required the principles of quantum physics, its explanation ca. 1920 was a triumph for this emerging scientific discipline.

14.4 References

1. C. E. Burkhardt and J. J. Leventhal, Topics in Atomic Physics (Springer, New York, 2005).
2. D. J. Griffiths, Introduction to Quantum Mechanics (Prentice-Hall, Upper Saddle River, NJ, 2nd ed., 2004).

Problems

1. Show that the eigenkets for the $n = 2$ levels of hydrogen in a weak electric field F are

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2}} (|00\rangle \mp |10\rangle)$$

where the kets on the right are the spherical $n = 2$ kets designated $|\ell m\rangle$.

2. Show that $\hat{\mathbf{L}} \bullet \hat{\mathbf{S}} = \hat{L}_z \hat{S}_z + \frac{1}{2} (\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+)$.
3. Find the Stark effect on the energy levels of a rigid rotor of radius a , mass μ , and electrical charge q that is confined to the xy -plane if the constant electric field F is in the x -direction.
4. Show that the Landé g -factor

$$g = \left[1 \pm \frac{1}{(2\ell + 1)} \right]; \quad j = \ell \pm \frac{1}{2}$$

can be written

$$g(j, \ell) = \left[1 + \frac{j(j+1) - \ell(\ell+1) + 3/4}{2j(j+1)} \right]$$

for both $j = \ell \pm \frac{1}{2}$.

5. Show that for hydrogen the sums of the fine structure and Zeeman corrections to the energy for strong and weak fields are the same for the top of the ladder state and are given by

$$E_{FS}^{(1)} + E_B^{(1)} = \frac{\alpha^2}{n^2} E_n^{(0)} \left[\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right] + \mu_B B \left(j = \frac{1}{2} \right)$$

6. A constant magnetic field $\mathbf{B} = B\hat{\mathbf{k}}$ is applied to a hydrogen atom and the Zeeman effect on the hyperfine levels of the ground state is examined.
- (a) Write the Hamiltonian that describes this Zeeman effect in terms of the Pauli spin matrices and the Bohr magneton. Use the notation of Section 8.6.1.
- (b) Ignoring the interaction of the proton spin magnetic moment with the external field, find the exact eigenvalues of this Hamiltonian. Do not find the eigenkets. Why is it permissible to ignore the proton interaction with the field? Make sure that the final answer is correct for $B = 0$.
7. Show that the Landé g -factor $g(J, L, S)$ is unity for all singlet states and is 2 for all S -states.
8. Determine the weak field Zeeman splittings for 3S_1 , 3P_2 , and $^4D_{5/2}$ states. Make a diagram similar to those in Fig. 14.4 illustrating the relative magnitudes of the splittings for these states.
9. Show that there is no weak field Zeeman effect for a $^4D_{1/2}$ state.

Chapter 15

Time-Dependent Perturbations

It was noted in Section 3.3 that, although the emphasis in introductory courses in quantum physics is, necessarily, on stationary states and the solution of the TISE for various potential energy functions, physical systems do not typically “live” in stationary states. Generally, they are in a time-dependent superposition of states that, as long as the potential energy is independent of time, can be determined by applying the time evolution operator to the wave function at some specific time (see the discussion of Postulate VI in Section 6.3.2).

Now, suppose at some time, say $t = 0$, a perturbation is applied to the system. We wish to describe the reaction of the system to the perturbation. An example of such a perturbation might be one such that at $t = 0$ a constant field, electric or magnetic, is applied. Because the field is turned on at a particular time the perturbation is time-dependent, so we expect the time dependence of the state vector to be altered. To determine how the system evolves in time, we must solve the TDSE. Indeed, in a limited number of cases, this is possible. When it is not possible to solve the problem exactly we must find approximate solutions. One such approximation method is time-dependent perturbation theory. We begin the discussion with the exact solution to the TDSE and then elaborate on the approximations that can be made in given physical situations.

15.1 Time Dependence of the State Vector

To this point we have dealt only with Hamiltonians that do not contain time. Before studying time-dependent perturbation theory we examine the time evolution of a system when the Hamiltonian contains the time. To do this we assume that the Hamiltonian $\hat{H}(\mathbf{r}, t)$ can be separated into the sum of two terms, \hat{H}_0 a time-independent Hamiltonian and $\hat{W}(t)$ which depends upon time, although it may depend upon other observables as well. It is also assumed that $\hat{W}(t)$ is turned on at $t = 0$. Thus,

$$\hat{H}(\mathbf{r}, t) = \hat{H}_0(\mathbf{r}) + \lambda \hat{W}(t) \quad (15.1)$$

where λ is a parameter that is used to keep track of the order of the approximation. It may be set equal to unity at any time. As in time-independent perturbation theory, we assume that the eigenkets and energy eigenvalues of \hat{H}_0 are known and that to each eigenket there is one energy eigenvalue. These eigenkets and eigenvalues are designated $|\psi_n\rangle$ and E_n , respectively. We do not require superscripts as in the case of time-independent perturbation theory because we will use the $|\psi_n\rangle$ as a basis set throughout. That is, the only possible final states will be one of the $|\psi_n\rangle$. It is the probability of finding the system in one of these eigenstates that is affected by the time-dependent perturbation. The TISE is

$$\hat{H}_0 |\psi_n\rangle = E_n |\psi_n\rangle \quad (15.2)$$

and we seek the ket $|\Psi(\mathbf{r}, t)\rangle$ that is the superposition of the $|\psi_n\rangle$ states that result from the perturbation $\hat{W}(t)$. This superposition may be written as a linear combination of the time-independent eigenkets with time-dependent expansion coefficients. Thus,

$$|\Psi(\mathbf{r}, t)\rangle = \sum_n c_n(t) |\psi_n\rangle \exp\left(-i \frac{E_n}{\hbar} t\right) \quad (15.3)$$

where the time dependence of the Hamiltonian has been accounted for by making the expansion coefficients functions of time. Note that we cannot use the time evolution operator because the Hamiltonian is not independent of time. Clearly the probability of measuring the system to be in a given stationary state, say $|\psi_m\rangle$, is $|c_m(t)|^2$, which is time-dependent.

The state vector, $|\Psi(\mathbf{r}, t)\rangle$, is determined by the TDSE

$$\hat{H}(\mathbf{r}, t) |\Psi(\mathbf{r}, t)\rangle = i\hbar \frac{\partial}{\partial t} |\Psi(\mathbf{r}, t)\rangle \quad (15.4)$$

Substituting Equations 15.1 and 15.3 into the TDSE we have

$$\begin{aligned} [\hat{H}_0(\mathbf{r}) + \lambda \hat{W}(t)] \sum_n c_n(t) |\psi_n\rangle \exp\left(-i \frac{E_n}{\hbar} t\right) \\ = i\hbar \frac{\partial}{\partial t} \sum_n c_n(t) |\psi_n\rangle \exp\left(-i \frac{E_n}{\hbar} t\right) \end{aligned} \quad (15.5)$$

Using Equation 15.2 and regrouping we have

$$\lambda \sum_n c_n(t) \hat{W}(t) |\psi_n\rangle \exp\left(-i \frac{E_n}{\hbar} t\right) = i\hbar \sum_n \dot{c}_n(t) |\psi_n\rangle \exp\left(-i \frac{E_n}{\hbar} t\right) \quad (15.6)$$

where $\dot{c}_n(t)$ is the time derivative of c_n . Taking the inner product with $\langle\psi_k|$, multiplying by $\exp(i E_k t / \hbar)$ and solving for $\dot{c}_k(t)$ we have

$$i \hbar \dot{c}_k(t) = \lambda \sum_n \hat{W}_{kn} \exp(i \omega_{kn} t) c_n(t) \quad (15.7)$$

where

$$\omega_{kn} = \frac{E_k - E_n}{\hbar} \quad (15.8)$$

and

$$\hat{W}_{kn} = \langle \psi_k | \hat{W}(t) | \psi_n \rangle \quad (15.9)$$

Note that if there is no time-dependent perturbation, that is, $\hat{W}(t) = 0$, then $\dot{c}_k(t) = 0$ in Equation 15.7 and all of the expansion coefficients, the c_k , are constants. In the general case, however, the transition probability, the probability that the system will be found in the k th state, is given by

$$P_k = |c_k(t)|^2 \quad (15.10)$$

Equation 15.7 is a set of differential equations for each of the expansion coefficients $c_k(t)$. To better appreciate the structure of these differential equations we can write them in matrix form:

$$i \hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \\ \dot{c}_3 \\ \vdots \end{pmatrix} = \begin{pmatrix} \hat{W}_{11} & \hat{W}_{12} e^{i \omega_{12} t} & \hat{W}_{13} e^{i \omega_{13} t} & \cdots \\ \hat{W}_{21} e^{i \omega_{21} t} & \hat{W}_{22} & \hat{W}_{23} e^{i \omega_{23} t} & \cdots \\ \hat{W}_{31} e^{i \omega_{31} t} & \hat{W}_{32} e^{i \omega_{32} t} & \hat{W}_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} \quad (15.11)$$

Notice that the matrix elements are not independent. The off-diagonal matrix elements are related because $\hat{W}_{ij} = \hat{W}_{ji}^*$ and $\omega_{ij} = -\omega_{ji}$.

We stress once more that Equations 15.11 are exact. The matrix form makes it clear that there are, in principle, an infinite number of differential equations and that each differential equation can have an infinite number of terms. For most cases it is impossible to solve these equations exactly so approximations are required. We will apply Equation 15.6 to several problems of interest after first attacking a problem that *can* be solved exactly, the two-state problem. It should also be borne in mind that the matrix representation for the total Hamiltonian, $\hat{H}(\mathbf{r}, t)$ (see Equation 15.1), is the same as that for $\hat{W}(t)$ with the energy eigenvalues of $\hat{H}_0(\mathbf{r})$ subtracted from each of the diagonal elements.

15.2 Two-State Systems

Although a two-state system might at first seem to be a gross oversimplification, it actually has many applications. Additionally, it can be solved exactly (or almost exactly) in a few cases so it serves as a benchmark for comparison with solutions obtained using approximation methods.

For two states $|\psi_1\rangle$ and $|\psi_2\rangle$, with energy eigenvalues E_1 and E_2 , Equation 15.11 becomes

$$i\hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \end{pmatrix} = \begin{pmatrix} \hat{W}_{11} & \hat{W}_{12}e^{i\omega_{12}t} \\ \hat{W}_{21}e^{i\omega_{21}t} & \hat{W}_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad (15.12)$$

For simplicity we assume that $E_2 > E_1$ and we let

$$\omega_0 = (E_2 - E_1)/\hbar = \omega_{21} = -\omega_{12} \quad (15.13)$$

the Bohr frequency. Equation 15.12 represents the two coupled differential equations

$$i\hbar \dot{c}_1(t) = \hat{W}_{11}c_1(t) + \hat{W}_{12}e^{-i\omega_0 t}c_2(t) \quad (15.14)$$

and

$$i\hbar \dot{c}_2(t) = \hat{W}_{21}e^{i\omega_0 t}c_1(t) + \hat{W}_{22}c_2(t) \quad (15.15)$$

where we have explicitly shown the time dependence of the expansion coefficients, $c_1(t)$ and $c_2(t)$. We assume that initially all systems are in the lower state so that

$$c_1(0) = 1 \quad \text{and} \quad c_2(0) = 0 \quad (15.16)$$

Our task is to solve these simultaneous equations for particular time-dependent perturbations $\hat{W}(t)$, subject to the initial conditions given in Equation 15.16.

15.2.1 Harmonic Perturbation—Rotating Wave Approximation

An important case is that of a two-state system immersed in a sinusoidally varying electromagnetic field, a harmonic perturbation, which we write in the form

$$\begin{aligned} \hat{W}(t) &= \hat{W} \cos(\omega t) \\ &= \hat{W} \left(\frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) \end{aligned} \quad (15.17)$$

where \hat{W} is the time-independent operator amplitude of the sinusoidal perturbation and ω is the frequency of the applied field, which is distinctly different from the

natural frequency of the system ω_0 . Note that \hat{W} may contain other observables as long as there is no explicit dependence on time. Inserting this into Equations 15.14 and 15.15 and using Equation 15.13 we have

$$\begin{aligned} i\hbar\dot{c}_1(t) &= \hat{W}_{11} \left(\frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) c_1(t) + \hat{W}_{12} \left(\frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) e^{-i\omega_0 t} c_2(t) \\ i\hbar\dot{c}_2(t) &= \hat{W}_{21} \left(\frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) e^{i\omega_0 t} c_1(t) + \hat{W}_{22} \left(\frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) c_2(t) \end{aligned} \quad (15.18)$$

or

$$\begin{aligned} i\hbar\dot{c}_1(t) &= \hat{W}_{11} \left(\frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) c_1(t) + \hat{W}_{12} \left(\frac{e^{i(\omega-\omega_0)t} + e^{-i(\omega+\omega_0)t}}{2} \right) c_2(t) \\ i\hbar\dot{c}_2(t) &= \hat{W}_{12}^\dagger \left(\frac{e^{i(\omega+\omega_0)t} + e^{-i(\omega-\omega_0)t}}{2} \right) c_1(t) + \hat{W}_{22} \left(\frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) c_2(t) \end{aligned} \quad (15.19)$$

These formidable-looking differential equations can be simplified by making the first approximation of this chapter. It is known as the rotating wave approximation (RWA), and is based on the fact that terms involving the applied frequency ω , or the sum $(\omega + \omega_0)$, will oscillate very rapidly compared with terms involving the difference of frequencies, $(\omega - \omega_0)$. For long times, these high-frequency oscillations will average to zero and make no contribution to the expansion coefficients. Retaining only the difference terms we have

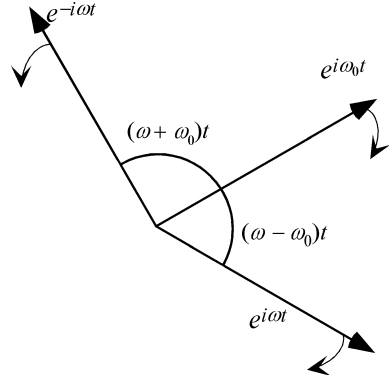
$$\begin{aligned} \dot{c}_1(t) &= \left(\frac{e^{i(\omega-\omega_0)t}}{2i\hbar} \right) \hat{W}_{12} c_2(t) \\ \dot{c}_2(t) &= \left(\frac{e^{-i(\omega-\omega_0)t}}{2i\hbar} \right) \hat{W}_{12}^\dagger c_1(t) \end{aligned} \quad (15.20)$$

The applied field can be represented by two phasors, each rotating in the opposite sense (see Equation 15.17). The terms retained in Equations 15.20 correspond to phase angle *differences* between the applied field and that of the two-state transition, $\omega_0 t$, when they are rotating in the same sense. The neglected terms correspond to phasors that are rotating in opposite directions. The relationships between these phasors are illustrated in Fig. 15.1.

We can solve these coupled differential equations by differentiating one of them, say the second, with respect to time and eliminating $\dot{c}_1(t)$ in the first. Letting $\delta = \omega - \omega_0$, the detuning from resonance of the applied frequency, we have for the second of these equations

$$\ddot{c}_2(t) + i\delta\dot{c}_2(t) + \frac{|\hat{W}_{12}|^2}{4\hbar^2} c_2(t) = 0 \quad (15.21)$$

Fig. 15.1 Phasor diagram depicting the rotating wave approximation



Solving this differential equation by letting $c_1(t) = e^{mt}$ we find that

$$m = -\frac{i}{2}\delta \pm \frac{i}{2}\sqrt{\delta^2 + \frac{|\hat{W}_{12}|^2}{\hbar^2}} \quad (15.22)$$

We now introduce the Rabi flopping frequency ω_R which is defined as

$$\omega_R = \frac{1}{2}\sqrt{\delta^2 + \frac{|\hat{W}_{12}|^2}{\hbar^2}} \quad (15.23)$$

and named for Isidor Isaac Rabi who was awarded the Nobel Prize in Physics in 1944 “for his resonance method for recording the magnetic properties of atomic nuclei”. The solution to Equation 15.21 is a linear combination of two solutions so we have

$$c_2(t) = e^{-i\delta t/2} (Ae^{i\omega_R t} + Be^{-i\omega_R t}) \quad (15.24)$$

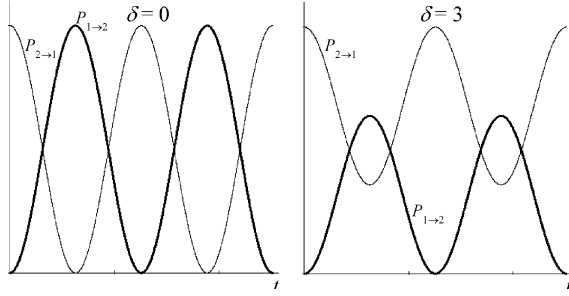
where A and B are constants that can be evaluated using the initial conditions given in Equation 15.16. The result is

$$c_2(t) = \frac{\hat{W}_{21}}{2i\hbar\omega_R} e^{-i\delta t/2} \sin(\omega_R t) \quad (15.25)$$

so the probability of a transition from the lower to the upper state is

$$\begin{aligned} P_{1 \rightarrow 2} &= |c_2(t)|^2 \\ &= \frac{|\hat{W}_{21}|^2}{|\hat{W}_{21}|^2 + (\hbar\delta)^2} \sin^2(\omega_R t) \end{aligned} \quad (15.26)$$

Fig. 15.2 Probabilities of transitions for a two-state system subjected to a harmonic perturbation for two sets of values of the matrix element \hat{W}_{12} and detuning frequency δ . The values of \hat{W}_{12} and δ have been adjusted to keep the Rabi frequency ω_R the same in the two graphs



Using conservation of probability we also have

$$\begin{aligned} P_{2 \rightarrow 1} &= 1 - |c_2(t)|^2 \\ &= \cos^2(\omega_R t) + \left(\frac{\delta}{2\omega_R} \right)^2 \sin^2(\omega_R t) \end{aligned} \quad (15.27)$$

These equations show that the system oscillates, or “flops,” between the states with frequency ω_R . Figure 15.2 shows the $P_{1 \rightarrow 2}$ and $P_{2 \rightarrow 1}$ as functions of time for two different values of the parameters, but with the same value of ω_R .

For the resonant case, $\delta = 0$, as is clear from Equation 15.26, the probability flops between zero and unity. In the off-resonant case, however, the nonzero detuning attenuates the amplitude of $P_{1 \rightarrow 2}$ so that the upper level is never fully populated. Commensurately, the lower level is never depleted when $\delta \neq 0$.

15.2.2 Constant Perturbation Turned On at $t = 0$

A constant perturbation might not seem to be within the scope of this chapter, but the fact that we are assuming that this perturbation is turned on at some time, $t = 0$, does indeed qualify it as a time-dependent problem. Thus, the perturbation is a step function.

Because the harmonic perturbation was taken to be in the form of a cosine, Equation 15.17, it is a simple matter to alter the treatment for a harmonic perturbation to apply to a constant perturbation by properly letting $\omega = 0$. We therefore take $\hat{W}(t)$ to be independent of time, although it may contain other operators corresponding to quantum mechanical observables. We begin by letting $\omega = 0$ in the differential equations for the harmonic perturbation before the RWA was applied, Equations 15.19:

$$\begin{aligned} i\hbar \dot{c}_1(t) &= \hat{W}_{11}c_1(t) + \hat{W}_{12}e^{-i\omega_0 t}c_2(t) \\ i\hbar \dot{c}_2(t) &= \hat{W}_{12}^\dagger e^{i\omega_0 t}c_1(t) + \hat{W}_{22}c_2(t) \end{aligned} \quad (15.28)$$

The algebra required to solve these equations is tedious, so we merely outline the solution which employs the method that is commonly used to solve normal mode problems in classical mechanics [2]. We assume a solution of the form

$$c_1(t) = Ae^{-i\omega t} \quad \text{and} \quad c_2(t) = Be^{-i(\omega-\omega_0)t} \quad (15.29)$$

where A and B are constants to be determined, as is ω .

After substituting into Equations 15.28 we arrive at two simultaneous homogeneous equations for A and B . Because the equations are homogeneous, we solve the secular equation and find two solutions for ω :

$$\hbar\omega_{\pm} = \frac{1}{2}\hbar\gamma + \hat{W}_{11} \pm \hbar\beta \quad (15.30)$$

where

$$\hbar\gamma = \hat{W}_{22} - \hat{W}_{11} + \hbar\omega_0 \quad (15.31)$$

and

$$\hbar\beta = \sqrt{\left(\frac{\hbar\gamma}{2}\right)^2 + |\hat{W}_{12}|^2} \quad (15.32)$$

Using the solutions ω_{\pm} , we obtain a relationship between the constants A and B , but there are now four such constants, one set of two constants for each sign. After obtaining this relationship we can evaluate the constants by applying the boundary conditions, Equation 15.16, and arrive at the probability for a transition from the lower state to the upper state:

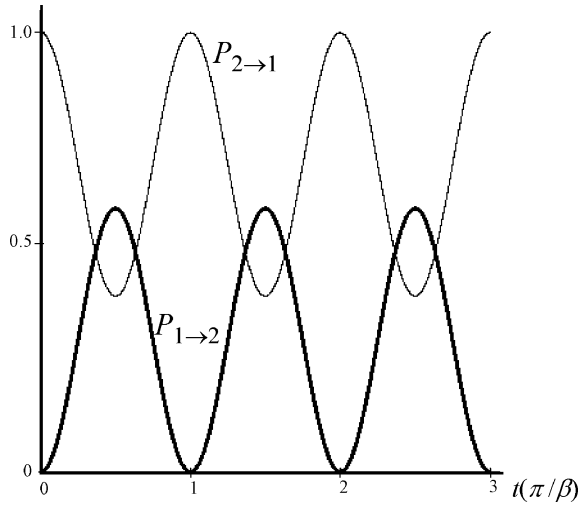
$$P_{1 \rightarrow 2} = \frac{|\hat{W}_{12}|^2}{\left(\frac{\hbar\gamma}{2}\right)^2 + |\hat{W}_{12}|^2} \sin^2 \beta t \quad (15.33)$$

and

$$P_{2 \rightarrow 1} = 1 - \frac{|\hat{W}_{12}|^2}{\left(\frac{\hbar\gamma}{2}\right)^2 + |\hat{W}_{12}|^2} \sin^2 \beta t \quad (15.34)$$

Equations 15.33 and 15.34 are exact. No approximations have been made. The transition probability oscillates sinusoidally with frequency 2β . (The frequency is 2β rather than β because it depends upon the square of the sine.) The amplitude of these oscillations is always less than unity except when the difference between the diagonal matrix elements $\hat{W}_{11} - \hat{W}_{22} = \hbar\omega_0$, the Bohr frequency (see Equation

Fig. 15.3 Probabilities of transitions for a two-state system subjected to a constant perturbation under the assumption that $(\hbar\gamma/2)^2 = (2/3) |\hat{W}_{12}|^2$. The units of the abscissa are the frequency of the probabilities



15.31), thus making $\gamma = 0$. When this occurs $\hbar\beta \rightarrow \hat{W}_{12}$, so the oscillation frequency is $2\hat{W}_{12}/\hbar$. Figure 15.3 is a plot of these probabilities for the case in which the amplitude is taken to be $3/5$.

15.3 Time-Dependent Perturbation Theory

We saw in the previous section that, using the exact equations for the expansion coefficients, we could (almost) solve the two-state problem exactly. This is not the usual case so it is necessary to formulate a method of approximation. This is time-dependent perturbation theory. We begin with the Hamiltonian as given in Equation 15.1, and use the same designations for the eigenkets and the time-dependent wave function as were used in Section 15.1 to arrive at Equation 15.7. Inasmuch as this equation is exact, we may begin there.

We assume that the expansion coefficient, $c_k(t)$, can be expanded in powers of some parameter λ :

$$c_k(t) = \lambda^0 c_k^{(0)}(t) + \lambda^1 c_k^{(1)}(t) + \lambda^2 c_k^{(2)}(t) + \dots \quad (15.35)$$

Substituting Equation 15.35 into Equation 15.7 and equating coefficients of like powers of λ leads to the solution for each of the orders of the expansion coefficient. From the zeroth-order approximation

$$\lambda^0 : \quad \dot{c}_k^{(0)}(t) = 0 \quad \implies \quad c_k^{(0)} = \text{constant} \quad (15.36)$$

we see that, to this order, the expansion coefficients are time-independent. The *first*-order approximation is the one that we will use. The coefficient of λ^1 is

$$\lambda^1 : \dot{c}_k^{(1)}(t) = \frac{1}{i\hbar} \sum_n \hat{W}_{kn} \exp(i\omega_{kn}t) c_n^{(0)} \quad (15.37)$$

where $\omega_{kn} = \omega_k - \omega_n$. Equations 15.37 and 15.36 illustrate a common feature of perturbation theory. Each approximation depends upon the next lower level of approximation. Thus, Equation 15.36, the zeroth-order solution, which simply depends upon the initial conditions, is used to determine the first-order solution. This bootstrapping procedure continues through the higher orders of perturbation theory.

We assume that at $t = 0$, the system is in a particular one of the unperturbed eigenstates, the eigenket of which we designate $|\psi_i\rangle$. Therefore, $c_i(0) = 1$ and all the other expansion coefficients are zero at $t = 0$. From the zeroth-order approximation, Equation 15.36, we have, using the Kronecker delta,

$$c_n^{(0)} = \delta_{ni} \quad (15.38)$$

Inserting these values into the first-order approximation, Equation 15.37, we obtain

$$\dot{c}_k^{(1)}(t) = \frac{1}{i\hbar} \sum_n \hat{W}_{kn} \exp(i\omega_{kn}t) \delta_{ni} \quad (15.39)$$

The only term in the summation that survives is the one for which $n = i$ so we have

$$\dot{c}_k^{(1)}(t) = \frac{1}{i\hbar} \hat{W}_{ki} \exp(i\omega_{ki}t) \quad (15.40)$$

For $k = i$, integration of Equation 15.40 is trivial. Assuming that the perturbation is turned on at $t = t_0$ we obtain

$$c_i^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^t \hat{W}_{ii}(t') dt' \quad (15.41)$$

where we have used the dummy variable of integration t' . Inserting Equations 15.41 and 15.38 into Equation 15.35, setting $\lambda = 1$ and retaining only the first two terms we have

$$\begin{aligned} c_i(t) &\approx 1 + \frac{1}{i\hbar} \int_{t_0}^t \hat{W}_{ii}(t') dt' \\ &\approx \exp \left[\frac{1}{i\hbar} \int_{t_0}^t \hat{W}_{ii}(t') dt' \right] \end{aligned} \quad (15.42)$$

Thus, to first-order, the population of the initially populated state $|c_i(t)|^2$ is unity. The initially populated state is *never* depleted to this level of approximation.

If, however, $k \neq i$, integration of Equation 15.40 yields

$$c_k^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^t \hat{W}_{ki}(t') e^{i\omega_{ki}t'} dt' \quad (15.43)$$

so that the probability of finding the system in the k th state is

$$\begin{aligned} P_{i \rightarrow k}^{(1)} &= \left| c_k^{(1)}(t) \right|^2 \\ &= \frac{1}{\hbar^2} \left| \int_{t_0}^t \hat{W}_{ki}(t') e^{i\omega_{ki}t'} dt' \right|^2 \end{aligned} \quad (15.44)$$

which is the fundamental result of first-order time-dependent perturbation theory. The matrix element, $\hat{W}_{ki} = \langle \psi_k | \hat{W}(t) | \psi_i \rangle$, is called the matrix element connecting the initial and final states. If it were zero, then the perturbation could not cause the transition from the initial state to the final state. Note that, to first-order, $c_k^{(1)}(t)$ must be small for $k \neq i$ because the initially populated state is not depleted.

The notion that the population of the initial state remains at unity while other states acquire nonzero populations after $t = 0$ seems to defy conservation of probability. Indeed, it does violate this obvious conservation law! It is as if we are manufacturing atoms. We started with all of them in the i th state, none of them leave this state, yet other levels acquire atoms. The problem is the approximation. For time-dependent perturbation theory to be efficacious, the transition probability for the k th state must be small so that $|c_i(t)|^2 = 1 - |c_k(t)|^2 \approx 1$. Thus, the deviation of $|c_i(t)|^2$ from unity is insignificant (compared with unity), but the small population acquired by the k th level, which began with zero population, is significant (compared with zero). The validity of the approximation depends upon the assumption that the expansion coefficients will not deviate substantially from their initial values as time advances. Thus, it is expected that the approximation will break down for long times.

15.4 Two-state Systems Using Perturbation Theory

15.4.1 Harmonic Perturbation

When only two states are important, this simple system provides a convenient test of perturbation theory. Because the RWA is a nearly exact treatment of the same problem this comparison is an aid in determining the limits of the perturbation treatment. Using the same notation as in Section 15.2 and letting $t_0 = 0$ we apply Equation 15.43 and obtain

$$\begin{aligned} c_2^{(1)}(t) &= \frac{\hat{W}_{21}}{2i\hbar} \int_0^t \left[e^{i(\omega+\omega_0)t'} + e^{-i(\omega-\omega_0)t'} \right] dt' \\ &= \frac{\hat{W}_{21}}{2i\hbar} \left[\frac{1 - e^{i(\omega+\omega_0)t}}{(\omega + \omega_0)} - \frac{1 - e^{-i(\omega-\omega_0)t}}{(\omega - \omega_0)} \right] \end{aligned} \quad (15.45)$$

It is clear from Equation 15.45 that near resonance, $\omega \approx \omega_0$, the transition probability $P_{1 \rightarrow 2} = |c_2(t)|^2$ will depend predominantly upon the second term so the perturbation theory result may be approximated as

$$\begin{aligned}
 P_{1 \rightarrow 2}^{(1)} &= |c_2^{(1)}(t)|^2 \\
 &= \frac{|\hat{W}_{21}|^2}{\hbar^2} \cdot \frac{1}{(\omega - \omega_0)^2} \left| e^{-i(\omega - \omega_0)t/2} \left[\frac{e^{i(\omega - \omega_0)t/2} - e^{-i(\omega - \omega_0)t/2}}{2i} \right] \right|^2 \\
 &= \frac{|\hat{W}_{21}|^2}{\hbar^2} \cdot \frac{\sin^2[(\omega - \omega_0)t/2]}{(\omega - \omega_0)^2} \quad (15.46)
 \end{aligned}$$

where the superscript has been inserted in the probability to distinguish it from those calculated using methods other than perturbation theory. The probability of the transition is highly dependent on the frequency of the applied field, ω , as may be seen from the graph of Equation 15.46, Fig. 15.4. Clearly the probability decreases strongly as ω deviates from resonance at ω_0 .

Now let us examine the time dependence of the probability for a fixed value of ω . In particular, we wish to assess the time interval during which perturbation theory is valid. There must be a lower limit on t . That is, there is a time interval after $t = 0$ during which the perturbation theory treatment cannot be applied because the sinusoidal perturbation must be permitted to act long enough for the system to perceive it as being sinusoidal. In other words, the perturbation must have been “on” long enough to wiggle so we must have $t > 2\pi/\omega$. As discussed at the end of Section 15.3, however, the perturbation theory result is only valid for “short” times. Thus, there is some upper time limit after which we expect the perturbation theory treatment to be invalid. To determine this upper time boundary we examine the limit of Equation 15.46 as $t \rightarrow 0$ by writing $P_{1 \rightarrow 2}$ in the form

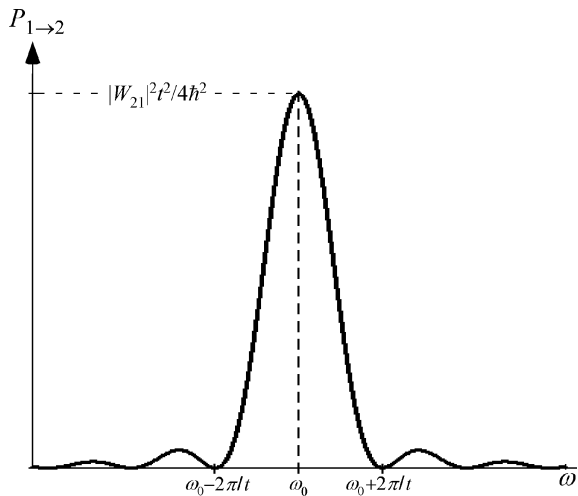


Fig. 15.4 Graph of the probability $P_{1 \rightarrow 2}$ as a function of the frequency ω of the applied field for a fixed time t

$$\begin{aligned}
 \lim_{t \rightarrow 0} P_{1 \rightarrow 2}^{(1)} &= \frac{|\hat{W}_{21}|^2}{\hbar^2} \lim_{t \rightarrow 0} \left\{ \left(\frac{t}{2} \right)^2 \frac{\sin^2 [(\omega - \omega_0) t / 2]}{[(\omega - \omega_0) t / 2]^2} \right\} \\
 &= \frac{|\hat{W}_{21}|^2}{4\hbar^2} t^2
 \end{aligned} \tag{15.47}$$

from which it is clear that we must impose the condition $t^2 < 4\hbar^2 / |\hat{W}_{21}|^2$ just to conserve probability. That is, $P_{1 \rightarrow 2}^{(1)}$ cannot exceed unity. Because, however, $P_{1 \rightarrow 2}^{(1)}$ increases quadratically, it represents only the first term in a Taylor series expansion of the RWA solution, Equation 15.26 (see Problem 2). Therefore, we must require that

$$t \ll \frac{|\hat{W}_{21}|}{\hbar} \tag{15.48}$$

Figure 15.5 illustrates the time interval during which perturbation theory is valid. The heavy lines are $P_{1 \rightarrow 2}$, as calculated from the RWA and from time-dependent perturbation theory $P_{1 \rightarrow 2}^{(1)}$. Also shown superposed on these probabilities are the oscillations of the applied field of frequency ω to illustrate that there is necessarily a minimum value of the time during which the perturbation must act.

Reexamining Fig. 15.4 with knowledge of the limits of t for perturbation theory to be applicable, we see that, within these limits, the probability of a transition increases with increasing time. Moreover, because the value of the absolute maximum is proportional to t^2 , while the first minima after the absolute maximum occur at $2\pi/t$, the area under the central maximum increases at the first power in t .

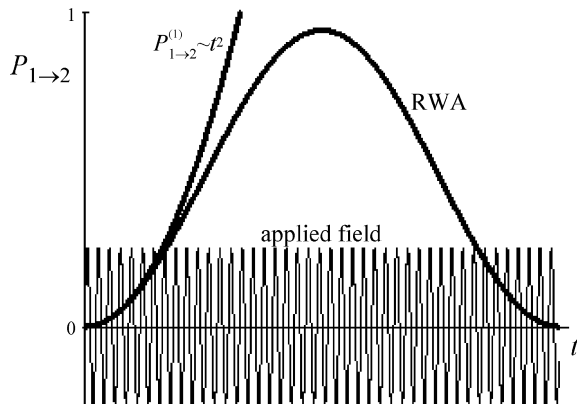


Fig. 15.5 Illustration of the range of time during which perturbation theory, the curve $\sim t^2$, will be valid. The high-frequency sinusoidal variations represent the applied field. The time scale is in units of the period associated with the Rabi frequency

15.4.2 Constant Perturbation Turned On at $t = 0$

To apply perturbation theory to the two-state problem with a constant perturbation (actually, a step function), we return to Equation 15.45 for $c_2^{(1)}(t)$. We cannot work with the function $\left|c_2^{(1)}(t)\right|^2$ of Equation 15.46 because it was evaluated *after* the approximation $(\omega + \omega_0) \gg (\omega - \omega_0)$ was made. Setting $\omega = 0$ in Equation 15.45 we have

$$\begin{aligned} c_2^{(1)}(t, \omega = 0) &= \frac{\hat{W}_{21}}{2i\hbar} \left[\frac{1 - e^{i\omega_0 t}}{\omega_0} + \frac{1 - e^{i\omega_0 t}}{\omega_0} \right] \\ &= \frac{\hat{W}_{21}}{2i(\hbar\omega_0)} [2(1 - e^{i\omega_0 t})] \\ &= \frac{2\hat{W}_{21}}{(\hbar\omega_0)} \left[e^{-i\omega_0 t/2} \left(\frac{e^{i\omega_0 t/2} - e^{-i\omega_0 t/2}}{2i} \right) \right] \end{aligned} \quad (15.49)$$

which leads to

$$P_{1 \rightarrow 2}^{(1)} = \frac{4|\hat{W}_{21}|^2}{(\hbar\omega_0)^2} \sin^2(\omega_0 t/2) \quad (15.50)$$

We may compare this result with the exact answer, Equation 15.33, determined in Section 15.2.2 where it was found that

$$P_{1 \rightarrow 2} = \frac{|\hat{W}_{12}|^2}{\left(\frac{\hbar\gamma}{2}\right)^2 + |\hat{W}_{12}|^2} \sin^2 \beta t \quad (15.51)$$

To cast the exact expression for the probability, Equation 15.51, into a form suitable for comparison with the perturbation theory result, Equation 15.50, we must convert the parameters in Equation 15.51 to conform with the restrictions on perturbation theory. In particular, weak perturbations are demanded, so all matrix elements of \hat{W} must be assumed to be small. Therefore,

$$\begin{aligned} \hbar\gamma &= \hat{W}_{22} - \hat{W}_{11} + \hbar\omega_0 \\ &\approx \hbar\omega_0 \end{aligned} \quad (15.52)$$

and

$$\begin{aligned}\hbar\beta &= \sqrt{\left(\frac{\hbar\omega_0}{2}\right)^2 + |\hat{W}_{12}|^2} \\ &\approx \left(\frac{\hbar\omega_0}{2}\right)\end{aligned}\quad (15.53)$$

Inserting these values into Equation 15.51 we have

$$P_{1\rightarrow 2} \rightarrow \frac{|\hat{W}_{12}|^2}{\left(\frac{\hbar\omega_0}{2}\right)^2} \sin^2(\omega_0 t/2) \rightarrow P_{1\rightarrow 2}^{(1)} \quad (15.54)$$

That is, the converted exact result is identical to Equation 15.50. Graphs of Equation 15.54 are shown in Fig. 15.6. These curves are very similar to the curve shown in Fig. 15.4 except that they are centered at $\omega_0 = 0$. Thus, the probability of a transition is maximum when $E_1 \approx E_2$, that is, when the energy states are degenerate. Moreover, the probability becomes narrower for longer times, signifying that for longer times the near degeneracy criterion is more stringent.

Comparing the transition probability due to a harmonic perturbation, Equation 15.46, with that resulting from a step perturbation, Equation 15.50, we see that they have the same form, namely, $\sin^2 x/x^2$. The difference is that the peak in the transition probability for the harmonic perturbation occurs when the frequency of the applied field is the same as the Bohr frequency, while the peak for the step

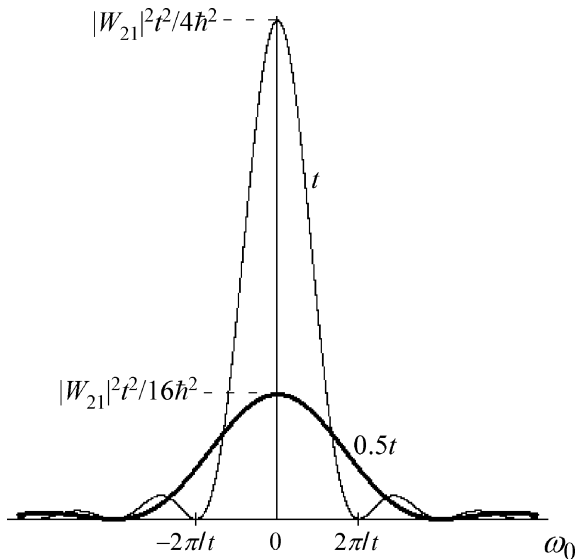


Fig. 15.6 Transition probability in Equation 15.54 plotted versus ω_0 at fixed times t_0 and $0.5t_0$

perturbation occurs when the two states have the same energy. Both exhibit the resonance phenomenon characteristic of quantum systems.

What is the meaning of the term “weak perturbation” in this case? The matrix element $\hat{W}_{12} = \langle \psi_1 | \hat{W} | \psi_2 \rangle$ represents the coupling between the states. Because it occurs in the numerator of the exact expression for the probability, Equation 15.51, there can be no transition if this matrix element vanishes. Even if it is merely weak the probability of transition is nonzero.

15.5 Extension to Multistate Systems

15.5.1 Harmonic Perturbation

If a system has many possible final states, the perturbation theory results can be derived from consideration of the two-state results above. For a harmonic perturbation, however, it is necessary to consider the possibility of transitions both up and down from the initially populated state. Thus, either term in Equation 15.45 can be important, but (usually) not both. For this case we will use notation that reflects the multistate nature of the system, letting i designate the initial state and f the final state. The expansion coefficients are then $c_i^{(1)}(t)$ and $c_f^{(1)}(t)$ and $\omega_0 \rightarrow \omega_{fi}$. Equation 15.45 becomes

$$c_f^{(1)}(t) = \frac{\hat{W}_{fi}}{2i\hbar} \left[\frac{1 - e^{i(\omega_{fi} + \omega)t}}{(\omega_{fi} + \omega)} + \frac{1 - e^{i(\omega_{fi} - \omega)t}}{(\omega_{fi} - \omega)} \right] \quad (15.55)$$

Recalling that $\hbar\omega_{fi} = E_f - E_i$, Equation 15.8, we see that if $E_f < E_i$ then $\omega_{fi} < 0$ and the first term in Equation 15.55 dominates. We may therefore ignore the second term. In this case the system is “stimulated” to undergo a transition from the higher state of energy E_i to the lower state of energy E_f . To conserve energy, a quantum of energy, $\hbar\omega_{if}$, is emitted and the process is called stimulated emission. The “se” in the word laser comes from this term. On the other hand, if $E_f > E_i$, then $\hbar\omega_{fi} > 0$, and the system absorbs a quantum of energy $\hbar\omega_{fi}$ from the perturbing field. This is absorption which, for symmetry, should perhaps be called “stimulated absorption,” but, as will be seen below, this is not necessary. There is a third process, this one called spontaneous emission, that can occur. When a system decays from a higher state to a lower state, seemingly without an external perturbation, this is spontaneous emission because, consistent with Bohr’s postulate II (see Section 1.2.1), energy in the amount of $\hbar\omega_{if}$ is emitted. Because the analogous absorption process, spontaneous absorption, is nonsense (even in quantum mechanics), stimulated absorption is referred to only by its surname. Thus, absorption and spontaneous emission are the processes responsible for absorption and emission spectroscopy discussed in Section 1.1.3.

According to the above discussion, only one of the terms in the brackets in Equation 15.55 will dominate for a given frequency. We may therefore write the transition probabilities for stimulated emission and absorption as

$$P_{i \rightarrow f}^{(1)} = \frac{|\hat{W}_{fi}|^2}{\hbar^2} \cdot \frac{\sin^2[(\omega \pm \omega_{fi})t/2]}{(\omega \pm \omega_{fi})^2} \quad (15.56)$$

Equation 15.56 represents the probability for stimulated emission (upper sign) for which $\omega_{fi} < 0$ or absorption (lower sign) for which $\omega_{fi} > 0$. It is seen that the maximum probability will occur when the applied frequency $\omega \approx \pm \omega_{fi}$. Of course, the value of \hat{W}_{fi} , the matrix element connecting the initial and final states, is also crucial in determining the transition rate, $dP_{i \rightarrow f}/dt$. In particular, if this matrix element always vanishes, then the transition is prohibited. We will derive selection rules for transitions by deducing the conditions under which $\hat{W}_{fi} \equiv 0$.

15.5.2 Constant Perturbation Turned On at $t = 0$

Extension of the results for a constant perturbation are quite simple. Beginning with Equation 15.49 rather than letting $\omega = 0$ in Equation 15.56, we have

$$c_f^{(1)}(t, \omega = 0) = \frac{2\hat{W}_{fi}}{(\hbar\omega_{if})} \left[e^{-i\omega_{fi}t/2} \left(\frac{e^{i\omega_{fi}t/2} - e^{-i\omega_{fi}t/2}}{2i} \right) \right] \quad (15.57)$$

from which we obtain

$$P_{i \rightarrow f}^{(1)} = \frac{4|\hat{W}_{fi}|^2}{\hbar^2} \cdot \frac{\sin^2(\omega_{fi}t/2)}{\omega_{fi}^2} \quad (15.58)$$

or, in terms of the energies,

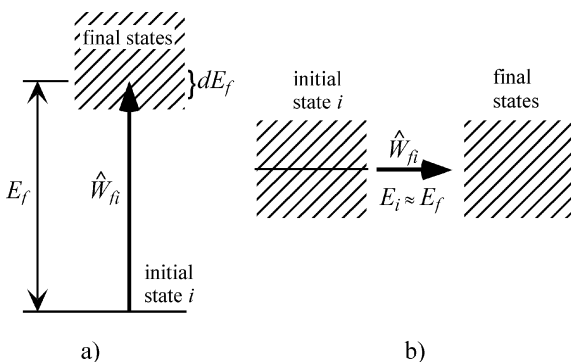
$$P_{i \rightarrow f}^{(1)} = 4|\hat{W}_{fi}|^2 \cdot \frac{\sin^2 \left[\frac{(E_f - E_i)t}{2\hbar} \right]}{(E_f - E_i)^2} \quad (15.59)$$

Therefore, the transition probability maximizes when the energy of the final state $E_f \approx E_i$. This degeneracy condition becomes more stringent for longer times, as discussed in conjunction with Fig. 15.6.

15.5.3 Transitions to a Continuum of States—The Golden Rule

We have focused most of our attention on two-state systems, but even in the extension to multistate systems, it was tacitly assumed that the states were discrete in nature. Suppose, however, that the energy of the transition places the system in a

Fig. 15.7 Illustration of transition from an initial state to a continuum of final states. (a) Ionization of a discrete state is effected by supplying external energy in the amount E_f to a continuum of final states (b) Energy is internally converted from a bound state embedded in a continuum of states to one of the continuum states (autoionization)



region where the states form a continuum. One example of such a system is an atom that is ionized by, for example, a photon (a harmonic perturbation), as illustrated in Fig. 15.7a. If the photon energy is greater than the ionization potential of the atom, the atomic electron will be liberated, and the excess energy converted to kinetic energy. Such final states are part of a continuum of states because there are no restrictions on the TME associated with fitting de Broglie waves. The process is called photoionization.

Another example of a process having a continuum of final states is one in which there is a bound state embedded in a continuum of states. This configuration of states can occur in atoms if the bound state energy is higher than the ionization potential. Helium provides a simple example because there exist bound states in which *both* electrons are in excited orbitals, for example, a $2s2p$ configuration. The energies of the states that arise from this configuration are around 60 eV, well in excess of the 24.6 eV ionization potential of helium. Thus, these discrete states, being degenerate with continuum states, can convert the neutral, but highly excited atom into a He^+ ion and a free electron, the kinetic energy of which is equal to the difference in energy between the ionization potential and that of the doubly excited state. This process is called autoionization and is illustrated in Fig. 15.7b.

Because these states are continuously distributed, they must be specified by a density of states function, $\rho_f(E_f)$, the dimensions of which are number of (final) states per energy interval dE_f . Thus, $\rho_f(E_f) dE_f$ represents the number of final states in the energy interval dE_f . If we were computing the probability of a transition from a single initial state, i , to more than one discrete final state, say n possible final states, then this probability would be

$$\begin{aligned}
 P_{i \rightarrow \Sigma f}^{(1)} &= P_{i \rightarrow f_1} + P_{i \rightarrow f_2} + \cdots \\
 &= \sum_{j=1}^n P_{i \rightarrow f_j}
 \end{aligned} \tag{15.60}$$

where Σf in the subscript means any of the n possible (discrete) final states. If, however, the final states are continuously distributed, then we must integrate over

the final state distribution. Thus, applying Equation 15.56 to the case of a transition from the initial state to any of a *group* of continuously distributed final states, each having energy E'_f , we find the probability of a transition to a group of final states in the neighborhood of the state designated by the subscript f to be

$$\begin{aligned} P_{i \rightarrow f}^{(1)} &= 4 \int_{-\infty}^{\infty} |\hat{W}_{fi}|^2 \frac{\sin^2 \left[\left(E'_f - E_i - \hbar\omega \right) (t/2\hbar) \right]}{(+E_i)^2} \rho_f(E'_f) dE'_f \\ &= \frac{t^2}{\hbar^2} \int_{-\infty}^{\infty} |\hat{W}_{fi}|^2 \frac{\sin^2 \left[\left(\omega'_{fi} - \omega \right) (t/2) \right]}{\left[\left(\omega'_{fi} - \omega \right) (t/2) \right]^2} \rho_f(E'_f) dE'_f \quad (15.61) \end{aligned}$$

where we have multiplied and divided by t^2 to make the denominator the same as the argument of the sine function.

To investigate the important region near E'_f , we reexamine the curves in Fig. 15.6 because the plotted function is part of the integrand of Equation 15.61. For the present purpose $\omega_0 \rightarrow \omega'_{fi} - \omega$. After a long time (not too long because we are using perturbation theory) the width of the central maximum peak is quite narrow. We therefore assume that t is long enough so the width of the central maximum, $4\pi/t$, is much smaller than the width of the density of states in the region $E_f - E_i$. We also assume that the matrix element connecting these states is slowly varying in this vicinity. This leads to

$$P_{i \rightarrow f}^{(1)} = \frac{t^2}{\hbar^2} |\hat{W}_{fi}|^2 \rho_f(E_f) \int_{-\infty}^{\infty} \frac{\sin^2 \left[\left(\omega - \omega'_{fi} \right) (t/2) \right]}{\left[\left(\omega - \omega'_{fi} \right) (t/2) \right]^2} dE'_f \quad (15.62)$$

Now, the remaining integral can be evaluated as $t \rightarrow \infty$ for a fixed value of the applied frequency. Letting $x = \left(\omega - \omega'_{fi} \right) t/2$ so that

$$\begin{aligned} dE'_f &= \hbar d \left(\omega - \omega'_{fi} \right) \\ &= \hbar \frac{2}{t} d \left[\left(\omega - \omega'_{fi} \right) (t/2) \right] \\ &= \hbar \frac{2}{t} dx \quad (15.63) \end{aligned}$$

and, using

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = \pi \quad (15.64)$$

we have

$$\int_{-\infty}^{\infty} \frac{\sin^2 \left[\left(\omega - \omega'_{fi} \right) (t/2) \right]}{\left[\left(\omega - \omega'_{fi} \right) (t/2) \right]^2} dE'_f = \hbar \frac{2}{t} \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = \frac{2\pi \hbar}{t} \quad (15.65)$$

which leads to

$$P_{i \rightarrow f}^{(1)} = \frac{2\pi t}{\hbar} |\hat{W}_{fi}|^2 \rho_f(E_f) \quad (15.66)$$

Equation 15.66 is known as Fermi's Golden Rule.

Our interest is in the transition *rate* (probability per unit time). Designating this rate by w_{if} , differentiation of Equation 15.66 yields

$$w_{if} = \frac{dP_{i \rightarrow f}}{dt} = \frac{2\pi}{\hbar} |\hat{W}_{fi}|^2 \rho_f(E_f) \quad (15.67)$$

The validity of Equation 15.67 depends upon two assumptions. First, we require the time to be long enough so that $\hbar(4\pi/t)$ is small compared with the effective width of $\rho_f(E'_f \approx E_f)$, see Equation 15.66. Thus, denoting this effective width as $\hbar\Delta\omega$, we may write

$$\hbar\Delta\omega \gg \frac{4\pi \hbar}{t} \implies \frac{4\pi}{\Delta\omega} \ll t \quad (15.68)$$

Second, because we are using perturbation theory we must require that the probability of the transition is small, a condition that, according to Equation 15.62, depends upon the ratio

$$\frac{t^2 |\hat{W}_{fi}|^2}{\hbar^2} \ll 1 \implies t \ll \frac{\hbar}{\hat{W}_{fi}} \quad (15.69)$$

We may therefore state the limits of validity on the time during which the Golden Rule is applicable as

$$\frac{4\pi}{\Delta\omega} \ll t \ll \frac{\hbar}{\hat{W}_{fi}} \quad (15.70)$$

15.6 Interactions of Atoms with Radiation

The importance of atomic (and molecular) spectroscopy to the development of quantum physics cannot be overemphasized, nor can its continuing importance to modern

technology. It is therefore important to understand the basic features of spectroscopy using the tools at our disposal.

15.6.1 The Nature of Electromagnetic Transitions

Let us return to the question of why electrons that are bound to a nucleus, and are therefore subject to some form of acceleration, do not radiate away their energy (see Section 1.2.1). Assume an atom is in an eigenstate of a time-independent Hamiltonian. The energy eigenfunctions are products of the spatial eigenfunctions and the exponential time factors, so the total wave function, including time, is given by

$$\Psi_q(\mathbf{r}, t) = \psi_q(\mathbf{r}) e^{-iE_q t/\hbar} \quad (15.71)$$

where the subscript q refers to all spatial quantum numbers and E_q is the energy eigenvalue corresponding to the eigenfunction $\psi_q(\mathbf{r})$. The electronic charge density $\rho(\mathbf{r}, t)$ associated with this atom is, in atomic units

$$\begin{aligned} \rho(\mathbf{r}, t) &= |\Psi_q(\mathbf{r}, t)|^2 \\ &= |\psi_q(\mathbf{r})|^2 e^{-iE_q t/\hbar} \cdot e^{iE_q t/\hbar} \\ &= |\psi_q(\mathbf{r})|^2 \end{aligned} \quad (15.72)$$

The charge density is independent of time! Such charge distributions do not radiate energy. Now suppose that the atom is in a superposition of, for convenience, two states $\Psi_q(\mathbf{r}, t)$ and $\Psi_p(\mathbf{r}, t)$, so the wave function is

$$\Psi(\mathbf{r}, t) = A\psi_q(\mathbf{r}) e^{-iE_q t/\hbar} + B\psi_p(\mathbf{r}) e^{-iE_p t/\hbar} \quad (15.73)$$

where A and B are in general complex constants but, for simplicity, we assume they are real. The charge density $\rho(\mathbf{r}, t)$ associated with this non-stationary state is

$$\rho(\mathbf{r}, t) = |A\psi_q(\mathbf{r})|^2 + |B\psi_p(\mathbf{r})|^2 + 2AB \cos[(E_q - E_p)t/\hbar] \quad (15.74)$$

Thus, unlike the stationary state case, the charge distribution for an atom in a superposition of states is an oscillating function of time and, classically, such an oscillating distribution radiates electromagnetic energy. It radiates at the frequency of the oscillations of the charge distribution. Incidentally, the Greek letter ρ is used repeatedly in physics, usually to represent a density of some kind. We have already used it for density of states in Section 15.5.3 and are using it here, as is virtually universal, as a charge density. Indeed, we will use it again, in another context, simply because it is the commonly used symbol. It is anticipated that the reader can compensate for the different uses of ρ .

Let us assume that the atom is in the upper state q . Because it is a stationary state the electronic charge distribution is static. Now apply a perturbation to this atom, a perturbation that “connects” the state q to the lower state p . The perturbation causes the system to be in a superposition of the two states the electronic charge density of which oscillates as in Equation 15.74 and thus radiates. In fact, it radiates at frequency $\omega_{qp} = [(E_q - E_p)/\hbar]$ which is precisely the Bohr frequency. Thus, the name “stationary state” for the energy eigenstates is indeed an appropriate designation.

15.6.2 The Transition Rate

We have seen in this chapter that the probability of a transition always depends upon the square of the matrix element, $|\hat{W}_{12}|^2$, connecting the states involved. We may therefore begin our excursion into spectroscopy by examining the conditions under which transitions *cannot* occur. This means that we wish to find the conditions under which $\hat{W}_{12} \equiv 0$. These conditions are referred to as selection rules. We will examine them for the hydrogen atom, but, as will be discussed, with suitable modifications, they apply to a wide class of atoms.

We begin by assuming that an atom is immersed in an electromagnetic field in the form of a monochromatic plane wave of wavelength λ and frequency $\omega = 2\pi c/\lambda$. Such a wave is a transverse wave with electric and magnetic components given by [1]

$$\mathbf{F}(\mathbf{r}, t) = \hat{\mathbf{e}} F_0 \cos(\mathbf{k} \bullet \mathbf{r} - \omega t) \quad (15.75)$$

and

$$\mathbf{B}(\mathbf{r}, t) = (\mathbf{k} \times \hat{\mathbf{e}}) (F_0/c) \cos(\mathbf{k} \bullet \mathbf{r} - \omega t) \quad (15.76)$$

where $|\mathbf{k}| = \omega/c$ in the direction of propagation. The direction of polarization is given by the unit polarization vector, $\hat{\mathbf{e}}$. Again we use F to denote the electric field to avoid confusion with energy. Because electromagnetic waves are transverse waves, $\hat{\mathbf{e}}$ is perpendicular to \mathbf{k} . We make two approximations. First, we observe that transitions between atomic states typically emit or absorb radiation of wavelength the order of hundreds of nm. For example, the shortest of the Balmer lines (see Section 1.1.3) is $\sim 365\text{nm}$. The “size” of an atom is, however, $\sim a_0 = 0.5\text{nm}$. As we have learned in this chapter, transitions can only occur when there is resonance or near-resonance between the applied radiation and the Bohr frequency, so we ignore spatial variations of the wave over the dimensions of the atom. This is called the dipole approximation. If one considers the atom to be a distribution of electric and magnetic multipoles, in the dipole approximation only the electric dipole moments are retained.

We can, however, simplify things further. Because we are retaining only the dipole terms, we may estimate the ratio of the magnetic to the electric interaction energies. From Section 14.1.1 we have

$$\begin{aligned} E_{\text{electric}} &= -\hat{\mathbf{p}} \bullet \mathbf{F} \\ &\approx (ea_0) F_0 \\ &= \frac{1}{\alpha} \left(\frac{e\hbar}{m_e c} \right) F_0 \end{aligned} \quad (15.77)$$

where $\hat{\mathbf{p}} = e\mathbf{r}$ is the electric dipole moment. From Section 14.1.2, Equation 14.22, we may write

$$\begin{aligned} E_{\text{magnetic}} &= -\hat{\boldsymbol{\mu}} \bullet \mathbf{B} \\ &\approx \mu_B B_0 \\ &= \left(\frac{e\hbar}{2m_e} \right) \left(\frac{F_0}{c} \right) \end{aligned} \quad (15.78)$$

where $\hat{\boldsymbol{\mu}}$ is the magnetic dipole moment, μ_B is the Bohr magneton, and, from Equation 15.76, $B_0 \sim F_0/c$. The ratio is therefore

$$\frac{E_{\text{magnetic}}}{E_{\text{electric}}} \sim \alpha \quad (15.79)$$

so the magnetic dipole energy is lower than the electric dipole energy by a factor of 137. We may therefore ignore the magnetic interaction and simply write the interaction Hamiltonian as

$$\hat{W}_{ft} = -e\mathbf{r} \bullet \hat{\boldsymbol{\epsilon}} F_0 \cos(\omega t) \quad (15.80)$$

For simplicity, in what follows we will obtain the transition rate for absorption, so we will use the lower sign in Equation 15.56 which means that $\omega_{fi} > 0$. Inserting Equation 15.80 into Equation 15.56 we have

$$P_{i \rightarrow f}^{(1)} = \frac{e^2 F_0^2 |\langle \psi_i | \mathbf{r} \bullet \hat{\boldsymbol{\epsilon}} | \psi_f \rangle|^2}{\hbar^2} \cdot \frac{\sin^2[(\omega - \omega_{fi})t/2]}{(\omega - \omega_{fi})^2} \quad (15.81)$$

Note that this expression for the probability pertains to a single frequency, ω , of the applied field. The radiation is never of a single frequency, even if one imagines that it is being provided by a laser beam. Even laser light is distributed over a (very small) range of frequencies. To account for this distribution we must consider the density of states of the radiation in much the same way that the density of continuum states was treated in Section 15.5.3. In short, we must integrate over all frequencies using an appropriate weighting function to account for the actual distribution of frequencies. This distribution is called the spectral distribution function and is designated by

$\rho(\omega)$ (there is that often used ρ again), such that $\int_{\omega_1}^{\omega_2} \rho(\omega) d\omega$ represents the energy density between the frequencies ω_1 and ω_2 . Notice that this energy density depends upon the nature of the source of the external radiation. It might be blackbody radiation, as was used in early experiments on absorption spectroscopy, or it might be a very sharply peaked density function such as that of a laser beam.

Fortunately, the probability in Equation 15.81 already contains the energy density. As is known from electromagnetic theory, the energy density is $\epsilon_0 E_0^2/2$, which we may identify with $\int_{\omega_1}^{\omega_2} \rho(\omega) d\omega$, so we have

$$P_{i \rightarrow f}^{(1)} = \frac{2e^2 |\langle \psi_i | \mathbf{r} \bullet \hat{\mathbf{e}} | \psi_f \rangle|^2}{\epsilon_0 \hbar^2} \int_0^\infty \frac{\sin^2[(\omega - \omega_{fi})t/2]}{(\omega - \omega_{fi})^2} \rho(\omega) d\omega \quad (15.82)$$

Although $\rho(\omega)$ can have any shape, the other term in the integrand is narrow and peaked at ω_{fi} . Therefore, we may let $\omega \rightarrow \omega_{fi}$ in $\rho(\omega)$ and remove it from the integral. Using Equation 15.64 we find

$$P_{i \rightarrow f}^{(1)} = \frac{\pi e^2 |\langle \psi_i | \mathbf{r} \bullet \hat{\mathbf{e}} | \psi_f \rangle|^2}{\epsilon_0 \hbar^2} \rho(\omega_{fi}) t \quad (15.83)$$

To further simplify the calculation we will (temporarily) assume that the radiation is polarized in the x -direction. In this case

$$\langle \psi_i | \mathbf{r} \bullet \hat{\mathbf{e}} | \psi_f \rangle = \langle \psi_i | x | \psi_f \rangle \quad (15.84)$$

and Equation 15.83 becomes

$$P_{i \rightarrow f}^{(1)} = \frac{\pi e^2 |x_{if}|^2}{\epsilon_0 \hbar^2} \rho(\omega_{fi}) t \quad (15.85)$$

To generalize this result to the case in which the radiation is randomly polarized and is incident on the atoms from all directions, we simply include contributions to the probability from y_{if} and z_{if} , dividing by 3 because each direction of polarization contributes 1/3 to the energy density. Taking the derivative we obtain the rate $w_{i \rightarrow f}^{(1)}$

$$w_{i \rightarrow f}^{(1)} = \frac{\pi e^2}{3\epsilon_0 \hbar^2} (|x_{if}|^2 + |y_{if}|^2 + |z_{if}|^2) \rho(\omega_{fi}) \quad (15.86)$$

From Equation 15.86 we arrive at the sensible conclusion that the absorption rate is proportional to the energy density of the incident radiation evaluated at the resonant

frequency ω_{fi} . As usual, the transition rate depends upon the square of the matrix element connecting the initial and final states, in this case the electric dipole operator $e\mathbf{r}$.

15.6.3 The Einstein Coefficients—Spontaneous Emission

So far, we have discussed only stimulated emission as a means for a system to undergo a transition to a lower state. There is, however, another process that can occur—spontaneous emission. Suppose an atom (the physical system) is in a given eigenstate. Yes, we stated that systems do not generally live in eigenstates, but the problem is easier to formulate this way. If there is no perturbation to cause these transitions, then the atom would stay in the initial eigenstate forever. According to QED, however, there is always an electromagnetic field present. While this subject is beyond the scope of this book, it is not unreasonable to think of the modes of oscillation of an electromagnetic wave as being described by a harmonic oscillator potential. Indeed, this is QED! The fact that harmonic oscillators must have a zero point energy to be consistent with the uncertainty principle leads to the concept of a zero point field, even in field-free space. This provides the perturbation that is required to cause the excited state to decay to a lower state, seemingly in the absence of a perturbation. Such a transition is called spontaneous emission. It is spontaneous emission that leads to the concept of a lifetime of a state. If undisturbed, an atom in an excited state will ultimately decay.

Because spontaneous emission is a QED effect, its transition rate cannot be derived using the nonrelativistic quantum physics discussed in this book. To the rescue, though, was Einstein who showed the connection between the stimulated emission and absorption rates, both of which can be obtained nonrelativistically, and the spontaneous emission rate. The importance of this result leads us to present it here.

Einstein assumed a two-level system as depicted in Fig. 15.8. The separation between the two levels is $\hbar\omega = (E_2 - E_1)/\hbar$ and the numbers of atoms in each state at a given time are designated $N_1(t)$ and $N_2(t)$. The degeneracies of the levels are g_1 and g_2 . The entire system is bathed in blackbody radiation. The three single arrows represent spontaneous emission, stimulated emission, and absorption from

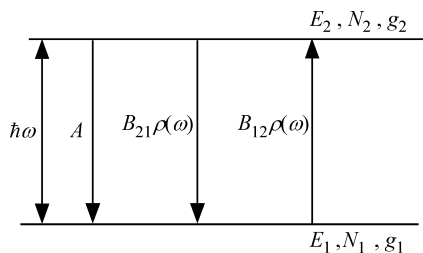


Fig. 15.8 Two-state energy level diagram showing the parameters used in Einstein's derivation

left to right in the figure. The quantities A , B_{21} , and B_{12} are known as the Einstein coefficients. Beware! The units of A and the units of the B 's are different. This is because the spontaneous emission rate, the Einstein A coefficient, must have units of s^{-1} which means transitions per second. This rate is independent of the external perturbation and does not depend upon the intensity of the external radiation. The B 's, however, depend upon this intensity of the external radiation that is being absorbed, or that is causing the stimulated emission. Therefore, the rates for absorption and stimulated emission are given by the product of B and the density of incident radiation, $B\rho(\omega)$, the units of which are s^{-1} . Einstein assumed this radiation to be characterized by the Planck blackbody distribution so $\rho(\omega)$ is the Planck distribution.

Einstein simply added the rates of the three processes to determine the rate of change of the number of atoms in a particular state. At equilibrium the total rate must vanish because, although atoms are arriving and leaving each state, the total population of each level remains constant. This is the meaning of "equilibrium." Therefore, at equilibrium

$$\dot{N}_1(t) = N_2 A + N_2 B_{21} \rho(\omega) - N_1 B_{12} \rho(\omega) = 0 \quad (15.87)$$

where we have dropped the designation of the time dependence of the populations N_1 and N_2 because at equilibrium they are constants. We now solve Equation 15.87 for $\rho(\omega)$ and find

$$\rho(\omega) = \frac{A}{(N_1/N_2) B_{12} - B_{21}} \quad (15.88)$$

The ratio of the populations, N_1/N_2 , is given by the ratio of the degeneracies multiplied by the Boltzmann factor, $\exp(\hbar\omega/kT)$ where k is the Boltzmann constant. Therefore,

$$\frac{N_1}{N_2} = \left(\frac{g_1}{g_2} \right) \exp \left(\frac{\hbar\omega}{kT} \right) \quad (15.89)$$

and we can replace the ratio N_1/N_2 in Equation 15.88 with Equation 15.89 to yield an expression for $\rho(\omega)$ in terms of the properties of the system, the Einstein coefficients, and the degeneracies of the levels. This expression must be the blackbody distribution which is given by

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{\exp \left(\frac{\hbar\omega}{kT} \right) - 1} \quad (15.90)$$

so, comparing Equation 15.90 with Equation 15.88 we obtain the relationships between the Einstein coefficients:

$$B_{12} = \left(\frac{g_1}{g_2} \right) B_{21} \quad (15.91)$$

and

$$A = \frac{\hbar \omega^3}{\pi^2 c^3} B_{12} \quad (15.92)$$

Equation 15.91 shows that calculation of one of the B -coefficients, perhaps using perturbation theory, leads to the remaining B -coefficient. Moreover, Equation 15.92 shows that the spontaneous emission rate can be calculated without employing QED. Notice that A is proportional to ω^3 times the B coefficient. This shows that, other things being equal, higher frequency transitions are more likely than lower frequency transitions. In terms of the Einstein coefficients, the transition rate for absorption is given by

$$w_{i \rightarrow f} = B_{12} \rho(\omega_{fi}) \quad (15.93)$$

where we have designated the initial state as 1 and the final state as 2. Additionally, because the transitions occur at or near resonance $\omega \approx \omega_{fi}$, we have evaluated the energy density at $\omega \approx \omega_{fi}$ in Equation 15.93. Comparing this equation with Equation 15.86 we find that

$$B_{12} = \frac{\pi e^2}{3\epsilon_0 \hbar^2} \left(|x_{if}|^2 + |y_{if}|^2 + |z_{if}|^2 \right) \quad (15.94)$$

which provides the link between quantum mechanical perturbation theory and the thermodynamic argument of Einstein. From Equation 15.92 the spontaneous emission rate is therefore

$$\begin{aligned} A &= \frac{e^2 \omega_{fi}^3}{3\pi \epsilon_0 \hbar c^3} \left(|x_{if}|^2 + |y_{if}|^2 + |z_{if}|^2 \right) \\ &= \frac{4}{3} \frac{\omega_{fi}^3}{c^3} \left(|x_{if}|^2 + |y_{if}|^2 + |z_{if}|^2 \right) \quad (\text{a.u.}) \end{aligned} \quad (15.95)$$

It must be remembered, however, that these expressions for the rates are subject to the limitations of first-order time-dependent perturbation theory. In what follows we will assume that these conditions have been met.

If, at some time $t = 0$, a collection of N_0 atoms has been excited to a particular state, how long will they stay there before spontaneously decaying? Assuming no external radiation is present (other than the zero-point field energy), and that there are only two states to consider, the rate of decay from the initial state i to the final state f having lower energy is

$$\frac{dN_i(t)}{dt} = -A_{if} N_i(t) \quad (15.96)$$

where A_{if} is the Einstein spontaneous decay coefficient for these two states. The solution of Equation 15.96 yields the time-dependent population of the initial state

$$N_i(t) = N_0 e^{-A_{if}t} \quad (15.97)$$

so that we may identify the time required to deplete the population to N_0/e as the spontaneous decay lifetime τ . The lifetime is therefore the time required for the initial population of excited atoms to be reduced by one e -fold. That is,

$$\tau = \frac{1}{A_{if}} \quad (15.98)$$

where the units of A are transitions/s, while those of τ are s/transition. Note that “transitions” is not officially a unit, but it is convenient to carry it for dimensional analysis.

If there is more than one lower state to which an excited state can decay, then Equation 15.96 would have additional terms on the right-hand side. For example, if the upper state could decay to states $j = 1, 2, \dots$, then

$$\frac{dN_i(t)}{dt} = - \left(\sum_j A_{ij} \right) N_i(t) \quad (15.99)$$

in which case the lifetime is

$$\tau = \left(\sum_j A_{ij} \right)^{-1} \quad (15.100)$$

In other words, the initial state might have a low spontaneous decay coefficient to a particular state, but a high one to another. Clearly the spontaneous decay rate out of the initial state is the sum of the individual (state-to-state) coefficients.

15.6.4 Selection Rules

Selection rules are based on determination of what cannot happen rather than what can happen. Thus, we wish to determine the conditions under which the transition rates vanish so we know which transitions are forbidden, at least within the electric dipole approximation. The key quantity to examine is the square of the matrix element that connects the two states, $|\hat{W}_{fi}|^2 = |\langle \psi_i | \mathbf{r} | \psi_f \rangle|^2$, as discussed in Section 15.6.1. The selection rules so derived pertain to absorption, stimulated emission,

and spontaneous emission because all of these processes depend upon the square of the matrix element connecting the states.

Because the electric dipole approximation ignores any magnetic interactions, we can immediately deduce our first selection rule. For an electric dipole transition there can be no change in the spin as was alluded to in Section 13.4. This is because spin is a magnetic property of the electron so to alter it a magnetic interaction is required. Thus, spin flips must occur via a magnetic interaction, the strongest of which is a magnetic dipole interaction. The rule is stated $\Delta S = 0$, where we have used a capital letter to designate spin because the rule transcends one-electron atoms.

For states of hydrogen we take the final state to be represented by primed quantum numbers. This matrix element is designated

$$\begin{aligned} \mathbf{r}_{n\ell m}^{n'\ell' m'} &= \langle n' \ell' m' | \mathbf{r} | n \ell m \rangle \\ &= \langle n' \ell' | r | n \ell \rangle \langle \ell' m' | \hat{a}_r | \ell m \rangle \\ &= R_{n\ell}^{n'\ell'} \langle \ell' m' | \hat{a}_r | \ell m \rangle \end{aligned} \quad (15.101)$$

where \hat{a}_r is the unit vector in the \mathbf{r} -direction. The radial part of this integral is

$$R_{n\ell}^{n'\ell'} = \langle n' \ell' | r | n \ell \rangle \quad (15.102)$$

Because these radial integrals never vanish, there is no selection rule associated with the principal quantum number. Therefore, the angular integrals determine the selection rules. For this reason other atoms are subject to the same selection rules as those associated with the hydrogen atom. All that is required is that the atomic electrons are subject to a *central* potential, or a nearly central potential, because we know that the spherical harmonics are always the angular portion of the eigenfunctions for central potentials. It should be stressed that, while the radial integrals are not involved in determination of the selection rules, they must be evaluated when the actual transition rates are calculated.

The eigenfunctions corresponding to the kets, $|\ell m\rangle$, in Equation 15.101 are the spherical harmonics. In Section 8.4 it was seen that these functions have definite parity, the parity of ℓ . We must therefore insist that, for the integral to be nonzero, the initial and final states have opposite parity because $\hat{\mathbf{r}}$ and its components are odd. Thus, we obtain a second selection rule. Transitions only occur between states of opposite parity. In spectroscopist jargon, “states of the same parity cannot combine.” This is known as the Laporte rule.

To obtain the remaining selection rules, we must examine further the integrals, which we do using the Cartesian components of \mathbf{r} in their spherical coordinate representation. This facilitates the computation because the quantum numbers, $n\ell m$, are spherical coordinate quantum numbers. Beginning with the z -component we have

$$\begin{aligned} z_{n\ell m}^{n'\ell' m'} &= \langle n' \ell' m' | z | n \ell m \rangle \\ &= R_{n\ell}^{n'\ell'} \langle \ell' m' | \cos \theta | \ell m \rangle \end{aligned} \quad (15.103)$$

The radial integral $\langle n\ell | r | n'\ell' \rangle = R_{n\ell}^{n'\ell'}$ is common to all three components. First, we concentrate on the angular integrals. Because the angular portions of the eigenfunctions are spherical harmonics (see Section 8.4), it is possible to obtain a general formula for the angular integrals in the matrix element. We consider an arbitrary pair of states $|n\ell m\rangle = |n\ell\rangle |\ell m\rangle$ and $|n'\ell' m'\rangle = |n'\ell'\rangle |\ell' m'\rangle$. Using the second of the relations in Table 8.3, we may write the angular integral in Equation 15.103 as

$$\begin{aligned} \langle \ell' m' | \cos \theta | \ell m \rangle &= \sqrt{\frac{(\ell + m + 1)(\ell - m + 1)}{(2\ell + 1)(2\ell + 3)}} \langle \ell' m' | (\ell + 1) m \rangle \\ &+ \sqrt{\frac{(\ell + m)(\ell - m)}{(2\ell + 1)(2\ell - 1)}} \langle \ell' m' | (\ell - 1) m \rangle \quad (15.104) \end{aligned}$$

From the orthogonality relation for spherical harmonics, Equation 8.85, it is clear that

$$\langle (\ell + 1) m | \cos \theta | \ell m \rangle = \sqrt{\frac{(\ell + m + 1)(\ell - m + 1)}{(2\ell + 1)(2\ell + 3)}} \quad (15.105)$$

and

$$\langle (\ell - 1) m | \cos \theta | \ell m \rangle = \sqrt{\frac{(\ell + m)(\ell - m)}{(2\ell + 1)(2\ell - 1)}} \quad (15.106)$$

are the only nonzero matrix elements. Therefore,

$$z_{n\ell m}^{n'(\ell+1)m'} = \sqrt{\frac{(\ell + m + 1)(\ell - m + 1)}{(2\ell + 1)(2\ell + 3)}} R_{n\ell}^{n'(\ell+1)} \quad (15.107)$$

$$z_{n\ell m}^{n'(\ell-1)m'} = \sqrt{\frac{(\ell + m)(\ell - m)}{(2\ell + 1)(2\ell - 1)}} R_{n\ell}^{n'(\ell-1)} \quad (15.108)$$

Equations 15.107 and 15.108 establish additional selection rules. First, we see that the orbital angular momentum quantum numbers must differ by ± 1 in order for the z -component of the matrix element to be nonzero. We therefore have the selection rule

$$\Delta\ell = \ell - \ell' = \pm 1 \quad (15.109)$$

which is consistent with the Laporte rule. Equations 15.107 and 15.108 also establish a portion of the selection rule on m . In particular, we see that the matrix element of z vanishes unless $\Delta m = 0$. The remaining selection rules on m come from the other components of \mathbf{r} .

Rather than obtain the analogous relation for the other two matrix elements we take advantage of the relationship between spherical and Cartesian coordinates. We may write the square of the matrix element $|\mathbf{r}_{n\ell m}^{n'\ell'm'}|^2$ in the form

$$\begin{aligned} \sum_{m'=-\ell'}^{\ell'} |\mathbf{r}_{n\ell m}^{n'\ell'm'}|^2 &= \sum_{m'=-\ell'}^{\ell'} \left(|x_{n\ell m}^{n'\ell'm'}|^2 + |y_{n\ell m}^{n'\ell'm'}|^2 + |z_{n\ell m}^{n'\ell'm'}|^2 \right) \\ &= |R_{n\ell}^{n'\ell'}|^2 \sum_{m'=-\ell'}^{\ell'} \left(\frac{1}{2} |x_{n\ell m}^{n'\ell'm'} + iy_{n\ell m}^{n'\ell'm'}|^2 \right. \\ &\quad \left. + \frac{1}{2} |x_{n\ell m}^{n'\ell'm'} - iy_{n\ell m}^{n'\ell'm'}|^2 + |z_{n\ell m}^{n'\ell'm'}|^2 \right) \end{aligned} \quad (15.110)$$

which permits us to exploit the relations

$$x + iy = r \sin \theta e^{i\phi} \quad \text{and} \quad x - iy = r \sin \theta e^{-i\phi} \quad (15.111)$$

We use the third relation in Table 8.3 to complete our evaluation of $|\mathbf{r}_{n\ell m}^{n'\ell'm'}|^2$. Because of orthogonality, the only matrix elements that survive the summation are

$$(x + iy)_{n\ell m}^{n'(\ell+1)(m+1)} = \sqrt{\frac{(\ell + m + 1)(\ell + m + 2)}{(2\ell + 1)(2\ell + 3)}} R_{n\ell}^{n'(\ell+1)} \quad (15.112)$$

$$(x + iy)_{n\ell m}^{n'(\ell-1)(m+1)} = -\sqrt{\frac{(\ell - m - 1)(\ell - m)}{(2\ell + 1)(2\ell - 1)}} R_{n\ell}^{n'(\ell-1)} \quad (15.113)$$

$$(x - iy)_{n\ell m}^{n'(\ell+1)(m-1)} = -\sqrt{\frac{(\ell - m + 1)(\ell - m + 2)}{(2\ell + 1)(2\ell + 3)}} R_{n\ell}^{n'(\ell+1)} \quad (15.114)$$

$$(x - iy)_{n\ell m}^{n'(\ell-1)(m-1)} = \sqrt{\frac{(\ell + m - 1)(\ell + m)}{(2\ell + 1)(2\ell - 1)}} R_{n\ell}^{n'(\ell-1)} \quad (15.115)$$

These relations confirm, but do not add to, the selection rule on ℓ . They do, however, provide the remaining selection rules on m since it is clear from them that m and m' must differ by unity. Mathematically, this results from the $e^{\pm i\phi}$ in the identity for $\sin \theta e^{\pm i\phi} |\ell m\rangle$ in Table 8.3. The selection rules for m are then

$$\Delta m = m - m' = 0, \pm 1 \quad (15.116)$$

These three possible Δm transitions correspond to emission or absorption of linearly polarized ($\Delta m = 0$) and circularly polarized light ($\Delta m = \pm 1$).

15.6.5 Transition Rates and Lifetimes

In practice, one often speaks of excited states in terms of the lifetimes, τ , rather than transition probabilities, A_{if} . As discussed in Section 15.6.3, calculation of the lifetime of a state requires knowledge of each of the state-to-state Einstein coefficients (see Equation 15.100). In this section we will examine emissions of the Balmer series of hydrogen which, it may be recalled, terminate in $n = 2$ (see Section 1.1.3). The allowed electric dipole transitions are shown in Fig. 15.9. In accord with the selection rules, there are three allowed transitions for each Balmer line because the lower states are $2s$ and $2p$. The wavelengths of the components of H_α and H_β differ slightly due to fine structure corrections, but we will ignore these differences here.

To calculate the lifetime of the $n = 3$ state of hydrogen, the three A coefficients corresponding to the three H_α lines (see Fig. 15.9) are needed as well as $A_{3p \rightarrow 1s}$ because $3p \rightarrow 1s$ is an escape route for atoms in the $3p$ state. Actually, $A_{3p \rightarrow 1s}$ is larger than any of the three spontaneous transition rates for H_α as a consequence of the ω^3 factor in Equation 15.95. We calculate $A_{3d \rightarrow 2p}$ and $A_{4d \rightarrow 2p}$ and compare them. In principle, this means that we have two angular integrals and two radial integrals to evaluate. It is, however, relatively simple to determine general formulas for the angular integral so we present this derivation.

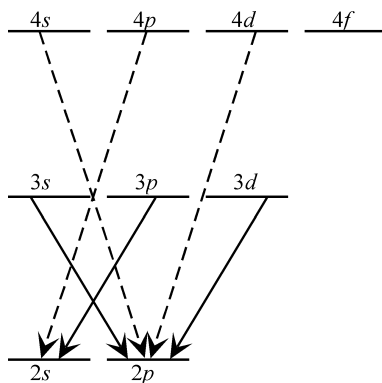
Consider first the transitions $\ell \rightarrow \ell + 1$. Using Equations 15.107, 15.112, and 15.114, the general expression for $\left| \mathbf{r}_{n\ell m}^{n'(\ell+1)m'} \right|^2$, Equation 15.110, summed over all possible m' states (in accord with the selection rule given in Equation 15.116) is

$$\begin{aligned}
 \left| \mathbf{r}_{n\ell m}^{n'(\ell+1)m'} \right|^2 &= \sum_{m' = -(\ell+1)}^{(\ell+1)} \left| \mathbf{r}_{n\ell m}^{n'(\ell+1)m'} \right|^2 \\
 &= \frac{1}{2} \left| (x + iy)_{n\ell m}^{n'(\ell+1)(m+1)} \right|^2 + \frac{1}{2} \left| (x - iy)_{n\ell m}^{n'(\ell+1)(m-1)} \right|^2 \\
 &\quad + \left| z_{n\ell m}^{n'(\ell+1)m} \right|^2 \\
 &= \left[R_{n\ell}^{n'(\ell+1)} \right]^2 [(2\ell + 1)(2\ell + 3)]^{-1} \left[\frac{1}{2} (\ell + m + 1)(\ell + m + 2) \right. \\
 &\quad \left. + \frac{1}{2} (\ell - m + 1)(\ell - m + 2) + (\ell + m + 1)(\ell - m + 1) \right] \\
 &= \left(\frac{\ell + 1}{2\ell + 1} \right) \left| R_{n\ell}^{n'(\ell+1)} \right|^2 \tag{15.117}
 \end{aligned}$$

Using an identical technique for $\ell \rightarrow \ell - 1$ transitions we find (see Problem 6)

$$\left| \mathbf{r}_{n\ell}^{n'(\ell-1)} \right|^2 = \left(\frac{\ell}{2\ell + 1} \right) \left| R_{n\ell}^{n'(\ell-1)} \right|^2 \tag{15.118}$$

Fig. 15.9 Schematic diagram of the orbital angular momentum states of the $n = 2, 3$, and 4 states of hydrogen showing the electric dipole allowed transitions that lead to H_α (solid) and H_β (dashed)



Equations 15.117 and 15.118 are noteworthy because they are independent of the initial magnetic quantum number m .

We require the $3d \rightarrow 2p$ and $4d \rightarrow 2p$ matrix elements so the angular parts of the required matrix elements for these transitions are the same. Note that we may use either the uncoupled set $|nlm_\ell m_s\rangle$ or the coupled set $|nljm_j\rangle$, because the integrals do not include spin. It is, however, easier (by far) to use the uncoupled set. We are therefore justified in simplifying the notation by letting $m_\ell = m$ and ignoring m_s .

To calculate the transition rates we use atomic units so A_{if} will have units of (atomic units of time) $^{-1}$, which can be converted to s^{-1} using Table 1.2. According to Equation 15.95, $A_{3d \rightarrow 2p}$ in atomic units is given by

$$A_{3d \rightarrow 2p} = \frac{4}{3} \frac{\omega_{32}^3}{c^3} |\mathbf{r}_{3d}^{2p}|^2 \quad (15.119)$$

The transition is $\ell \rightarrow \ell - 1$, so the square of the matrix element is given by Equation 15.118. For $3d \rightarrow 2p$ the square of the matrix element is

$$|\mathbf{r}_{3d}^{2p}|^2 = \left(\frac{2}{5}\right) |R_{3d}^{2p}|^2 \quad (15.120)$$

so we must calculate R_{3d}^{2p} as given in Equation 15.102. Using the radial eigenfunctions in Table 10.3 with $Z = 1$ for hydrogen and $a_0 = 1$ to convert to atomic units we have

$$\begin{aligned} R_{3d}^{2p} &= \int_0^\infty R_{21}(r) R_{32}^*(r) r^3 dr \\ &= \int_0^\infty \left[\left(\frac{1}{2\sqrt{6}} \right) (r e^{-r/2}) \right] \left[\left(\frac{4}{81\sqrt{30}} \right) (r^2 e^{-r/3}) \right] r^3 dr \\ &= \frac{2^6}{15\sqrt{5}} \left(\frac{6}{5} \right)^5 = 4.75 \end{aligned} \quad (15.121)$$

where we used the definite integral given in Equation H.2. In atomic units $\omega_{32} = (5/72)$ and $c = 137$. Because this transition is $d \rightarrow p$ we use Equation 15.118 in Equation 15.119 and obtain

$$\begin{aligned} A_{3d \rightarrow 2p} &= \left(\frac{4}{3}\right) \left(\frac{1}{137^3}\right) \left(\frac{5}{72}\right)^3 \left[\left(\frac{2}{5}\right) (4.75)^2\right] \text{ a.u.} \\ &= 0.65 \times 10^8 \text{ s}^{-1} \end{aligned} \quad (15.122)$$

For the $4d \rightarrow 2p$ transition

$$R_{4d}^{2p} = 1.71 \quad (15.123)$$

from which we determine (see Problem 8)

$$A_{4d \rightarrow 2p} = 0.21 \times 10^8 \text{ s}^{-1} \quad (15.124)$$

Let us examine the two competing factors that determine the A coefficients for the Balmer series (see Equation 15.119 and Problem 8). On the one hand, as the principal quantum number of the upper state increases, ω^3 increases, thus increasing A . On the other hand, however, the overlap of $R_{nd}(r)$ with $R_{2p}(r)$ decreases with increasing n because the electron samples a wider region of space in the more highly excited states. This is clear in Fig. 15.10 which contains plots of the relevant radial functions and clearly shows that, because the $4d$ electron samples a wider region of space than does the $3d$ electron, $R_{4d}^{2p} < R_{3d}^{2p}$. This is because the $2p - 3d$ overlap is greater than the $2p - 4d$ overlap. Moreover, because $R_{4d}(r)$ has a node, part of the R_{4d}^{2p} integrand is negative, further contributing to making $R_{4d}^{2p} < R_{3d}^{2p}$. Note that,

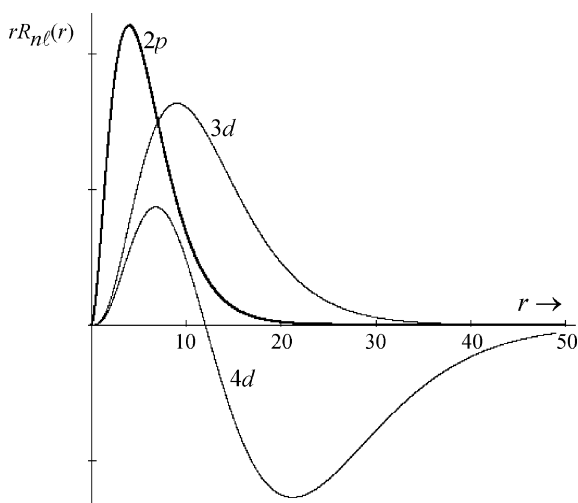
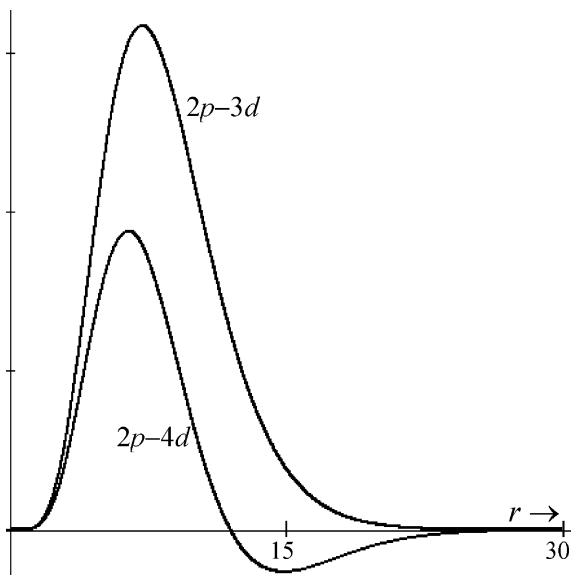


Fig. 15.10 The radial hydrogen atom eigenfunctions $R_{21}(r)$, $R_{32}(r)$, and $R_{42}(r)$

Fig. 15.11 The integrands, $R_{21}(r) R_{32}^*(r) r^3$ and $R_{21}(r) R_{42}^*(r) r^3$ of R_{3d}^{2p} and R_{4d}^{2p}



because both the $2p$ and $3d$ states are states for which $\ell = n - 1$, their product is manifestly positive. Thus, despite the larger ω for the transition from $n = 4$, $A_{4d \rightarrow 2p} < A_{3d \rightarrow 2p}$, and this trend continues as n increases. These considerations are illustrated in Fig. 15.11 which shows the plots of the integrands of R_{4d}^{2p} and R_{3d}^{2p} .

15.7 References

1. D. J. Griffiths, Introduction to Electrodynamics (Prentice-Hall, Upper Saddle River, NJ, 1999).
2. S. T. Thornton and J. B. Marion, Classical Dynamics of Particles and Systems (Harcourt Brace Jovanovich, New York, 1995).

Problems

1. Show that applying the boundary conditions given in Equation 15.16 to the general solution of the differential equation given in Equation 15.24 leads to Equation 15.25.
2. Show that the perturbation theory result for $P_{1 \rightarrow 2}^{(1)}$ as given in Equation 15.47 is the first term in the Taylor series expansion of the RWA solution, Equation 15.26.
3. An electron subject to a one-dimensional harmonic oscillator potential is in the ground state. At a time $t = -\infty$ a time-dependent electric field $F(t)$ is turned on. The field is constant in space and is given by

$$\mathbf{F}(t) = F_0 e^{-(t/\tau)^2} \hat{\mathbf{i}}$$

where τ is a constant. Use first-order time-dependent perturbation theory to find the probability that the electric field will cause the system to undergo a transition to the first excited state after a long time, $t = +\infty$.

4. A particle in a one-dimensional harmonic oscillator potential is in the ground state. At $t = 0$ a perturbation

$$\hat{W}(t) = Ax^3 e^{-t/\tau}$$

where A and τ are constants is applied. Use first-order time-dependent perturbation theory to find the probability that the system will undergo a transition to *all* excited states after a long time, $t = +\infty$. What are the units of A ? Do the calculated probabilities have the correct units?

5. At $t = 0$ a collection of hydrogen atoms, all in the $n = 1$ state, is subjected to a time-dependent electric field $F(t)$ in the z -direction. The time dependence is given by

$$F(t) = F_0 e^{-t/\tau}$$

where τ is a constant. Use first-order time-dependent perturbation theory to find the probability that the electric field will cause the system to undergo a transition to the $n = 2$ state after a long time, $t = +\infty$.

6. Show that for hydrogen the matrix element $|\langle n'(\ell-1)m' | \mathbf{r} | n\ell m \rangle|^2 = \left| \mathbf{r}_{n\ell m}^{n'(\ell-1)m'} \right|^2$ (Equation 15.118) is given by

$$\left| \mathbf{r}_{n\ell m}^{n'(\ell-1)m'} \right|^2 = \left[R_{n\ell}^{n'(\ell-1)} \right]^2 \left(\frac{\ell}{2\ell+1} \right)$$

7. Show that for hydrogen $A_{2p \rightarrow 1s} \approx 1.6 \times 10^{-8}$ (a.u. of time) $^{-1}$. What is the lifetime of the $2p$ state in seconds?
8. Verify that $A_{4d \rightarrow 2p} = 0.21 \times 10^8 \text{s}^{-1}$.
9. Show that for an isotropic oscillator the spontaneous decay rate from the $(n = 1, \ell = 1)$ state to the $(n = 0, \ell = 0)$ state is

$$A_{1p \rightarrow 0s} = \left(\frac{1}{4\pi\epsilon_0} \right) \left(\frac{2}{3} \right) \frac{e^2 \omega^2}{mc^3}$$

Show that the answer has the correct units.

10. Using a harmonic oscillator with charge e show that in the classical limit, the Larmor formula, Equation 1.17, and the Einstein A coefficient, Equation 15.95, agree. [Hint: Take the average of the classical power radiated during one cycle.]

Appendix A

Answers to Problems

Chapter 1

- $W = 2.28\text{ eV}$, sodium
- 253.1 nm
- (a) The Lyman and Balmer lines are:

$(n \rightarrow m)$	$\Delta E_{n \rightarrow m} \text{ (eV)}$	Designation	$\lambda \text{ (nm)}$
$4 \rightarrow 1$	12.75	L_γ	97.3
$3 \rightarrow 1$	9.06	L_β	136.9
$2 \rightarrow 1$	10.2	L_α	121.6
$5 \rightarrow 2$	2.86	H_γ	433.6
$4 \rightarrow 2$	2.55	H_β	486.3
$3 \rightarrow 2$	1.89	H_α	656.1

- (b) Lyman 91.2 nm ; Balmer 364.7 nm
- $a_{0\mu} = a_0/180$; αc ; $\approx 2450\text{ eV}$
- (a) $\approx 1.2 \times 10^{-15}\text{ m}$
(b) $44 \times 10^{-7}\text{ nm}$ (γ rays)

Chapter 2

- (a) $U(x) = \frac{\hbar^2 \alpha^4}{2m} x^2$
(b) $F = -(\hbar^2 \alpha^4 / m) x$
(c) $A = \sqrt{\alpha / \sqrt{\pi}}$
- (a) $P(x) dx = \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 x^2} dx$
(b) 1

4. (a) $j(x, t) = \frac{\hbar k}{m} |A|^2$
 (b) amplitude increases to $\sqrt{2}A$

5. (a) Acceptable
 (b) Unacceptable
 (c) Acceptable
 (d) Acceptable
 (c) Acceptable
 (e) Unacceptable

6. (a)

$$\Psi(x, 0) = \frac{1}{2}\psi_1(x) + \frac{1}{\sqrt{3}}\psi_2(x) + \sqrt{\frac{5}{12}}\psi_3(x)$$

- (b)

$$\begin{aligned}\Psi(x, t) = & \frac{1}{2}\psi_1(x)e^{-iE_1t/\hbar} + \frac{1}{\sqrt{3}}\psi_2(x)e^{-iE_2t/\hbar} \\ & + \sqrt{\frac{5}{12}}\psi_3(x)e^{-iE_3t/\hbar}\end{aligned}$$

- (c)

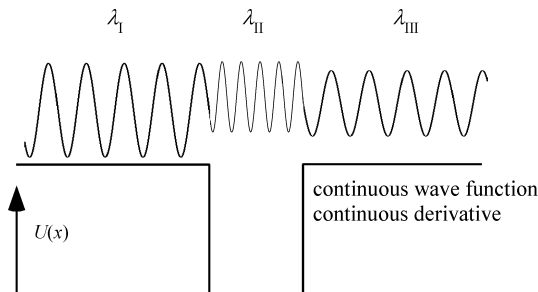
$$\langle E \rangle = \frac{1}{4}E_1 + \frac{1}{3}E_2 + \frac{5}{12}E_3$$

- (d)

$$\langle E \rangle = \frac{1}{4}E_1 + \frac{1}{3}E_2 + \frac{5}{12}E_3$$

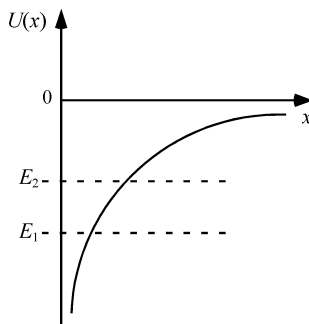
7.

$$\lambda_I = \frac{h}{\hbar k_I} = \frac{2\pi}{k_I} = k_{II}; \quad \lambda_{II} < \lambda_I \text{ because } k_{II} > k_I$$



Problem 7 of Chapter 2

8. (a) $E_1 = -\frac{E_0}{1^2}; E_2 = -\frac{E_0}{2^2}; E_3 = -\frac{E_0}{3^2}$
- (b) $\frac{2}{9}; \frac{1}{9}; \frac{6}{9}$ for states 1, 2, and 3
- (c) $\langle E \rangle = -0.32E_0$
- (d) $3Q_0$
9. (a) Yes, it can support bound states having $\text{TME} < 0$.



Problem 9 of Chapter 2

- (b) $\psi_2(x)$
- (c) $1/2$
- (d) $3/2$ a.u.

Chapter 3

2. $A = \sqrt{2/L}$
3. $(1/2\sqrt{2})\lambda_c$
6. (a) $\langle E \rangle = 3 \frac{\pi^2 \hbar^2}{2mL^2}$
- (b) $\Psi(x, t) = \frac{1}{\sqrt{3}}\psi_1(x)e^{-\omega_1 t} + \sqrt{\frac{2}{3}}\psi_2(x)e^{-\omega_2 t}$
7. $\langle E \rangle = \frac{4^2 \pi^2 \hbar^2}{2mL^2} = E_4$

8. (a) $P_{cl}(x) \Delta x = \Delta x / L$

(b) $\langle x^2 \rangle_{\text{classical}} = L^2/3; \langle x^2 \rangle_n = \frac{L^2}{3} \left[1 - \frac{3}{2(n\pi)^2} \right]$

9. $\Delta x_0 = 1/\sqrt{2}\alpha$

10. (a) zero

(b) $\langle \hat{p}^2 \rangle = \left(\frac{n\pi\hbar}{L} \right)^2$

11. $(\Delta x)^2 = L^2 \left(\frac{1}{12} - \frac{1}{2\pi^2 n^2} \right)$

12. (a) ≈ 0.36

(b) 0.5

13. (a) $K = \frac{\sqrt{210}}{2a^{3/2}}$

(b) $P_n = \frac{24^2 \cdot 105}{\pi^6} \cdot \frac{1}{n^6} \quad n \text{ even}; P(n=1) = 0; P(n=2) = 0.983$

(c) 1

(d) $\langle E \rangle = \frac{42}{(2^2\pi^2)} E_2$

14. (a) ≈ 0.36

(b) zero

(c) The initial wave functions in the two problems are different. There is no symmetry in Problem 12 while the initial wave function in this problem is symmetric.

16. $\Delta x \Delta p = \frac{1}{2} \hbar \omega$

17. $P_{\text{out}}(n=1) = 0.111$

19. $E_n = \left(n + \frac{1}{2} \right) \hbar \omega$ where $n = 1, 3, 5, \dots$ and corresponding eigenfunctions

20. (a) $E_n = \left(n + \frac{1}{2} \right) \hbar \omega$ with $\omega = \sqrt{\frac{2k}{m}}$

(b) ≈ 0.985

(c) zero

22. (a) $P = \frac{2\alpha\beta}{\alpha^2 + \beta^2}$

23. (a) Eigenfunctions are the same with $x \rightarrow x + eF/(m_e\omega^2)$. Eigenvalues are $E_n = (n + 1/2)\hbar\omega - eF/(m_e\omega^2)$

(b) $P = \exp\left[-\frac{1}{2} \frac{e^2 F^2}{m_e \hbar \omega^3}\right]$

Chapter 4

9. (a) $\Psi(x, 0) = K\delta(x)$

(b) Probability of measuring any odd state is zero. Normalization not recommended because the probabilities of measuring any even state are all the same.

(c) No odd states. No even eigenfunction should contribute more than another.

(d) $\Psi(x, t) = \frac{2}{a} \sum_{n \text{ odd}}^{\infty} e^{-iE_n t/\hbar} \sin\left(\frac{n\pi x}{L}\right)$

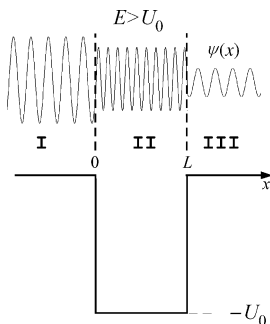
10. $\phi_n(p) = \sqrt{\frac{1}{2^n n!}} \left(\frac{1}{\pi \alpha^2 \hbar^2}\right)^{1/4} H_n\left(\frac{1}{\sqrt{m\omega\hbar}} p\right) e^{-p^2/(2\alpha^2 \hbar^2)}$

Chapter 5

1. $R = \frac{1}{1 + \left(\frac{\hbar^2 k}{mU_0}\right)^2}; T = \frac{1}{1 + \left(\frac{mU_0}{\hbar^2 k}\right)^2}$

2. $E = -\frac{mU_0^2}{2\hbar^2}$

3. (a)



Problem 3 (a) of Chapter 5

- (b) $T_{E>U_0} = \frac{4E(E + U_0)}{4E(E + U_0) + U_0^2 \sin^2 \left(\frac{L}{\hbar} \sqrt{2m(E + U_0)} \right)}$
5. The eigenfunctions are the odd eigenfunctions for the finite square well because they are the ones with a node at $x = 0$ which is demanded by the infinity in the potential.
7. $E = -\frac{2mU_0^2 a^2}{\hbar^2}$
8. (a) $\frac{P_{in}}{P_{out}} = \frac{e^{-2\kappa a}}{\sin^2 ka} \left(1 - \frac{\sin 2ka}{2ka} \right) \frac{\kappa a}{e^{-2\kappa a}}$
- (b) A state just above $E = 0$, a continuum state.
11. $n + 1/2 = 20/\sqrt{2} = 14.14$
15. $E_n = \left(n + \frac{1}{2} \right) \hbar \omega$
16. $E_n = -\frac{m}{2 \left(n + \frac{1}{2} \right)^2 \hbar^2} \cdot \left(\frac{e^2}{4\pi\epsilon_0} \right)^2$
17. $T = \exp \left[-\sqrt{\frac{2m}{E}} \frac{KZZ'e^2\pi}{\hbar} \right]$. As E increases the exponent decreases so T increases.
18. $T = \exp \left[-\frac{4W^{3/2}\sqrt{2m}}{3\hbar eF} \right]$

Chapter 6

6. (b) $e^{-iE_n t/\hbar}$
- (c) No, because the operator $e^{-i\hat{H}t/\hbar}$ is not Hermitian.
13. $[\hat{H}, x] = -i\hbar \frac{\hat{p}}{m}; [\hat{H}, \hat{p}] = i\hbar \frac{dU(x)}{dx}$
17. $x(t) = \frac{F}{2m}t^2 + \frac{p_0}{m}t + x_0; \hat{p}(t) = Ft + p_0$

Chapter 7

$$5. (a) |\Psi(x, t)\rangle = \frac{1}{\sqrt{3}} |1\rangle e^{-(3/2)i\omega t} + \sqrt{\frac{2}{3}} |2\rangle e^{-(5/2)i\omega t}$$

$$(b) \langle E \rangle = \left(\frac{13}{6} \hbar \omega \right)$$

$$(c) \langle \hat{x}(t) \rangle = \sqrt{\frac{\hbar}{m\omega}} \frac{\sqrt{2}}{3} 2 \cos \omega t$$

$$11. \langle n | \hat{x}^4 | n \rangle = \frac{3}{4\alpha^4} (2n^2 + 2n + 1)$$

$$17. (b) P_N = \left[\left(\frac{\alpha}{\sqrt{2}} x_0 \right)^N \frac{e^{-|\alpha^2 x_0^2|/2}}{\sqrt{N!}} \right]^2$$

Chapter 8

$$1. [\hat{J}_x \hat{J}_y, \hat{J}_z] = i \hbar (\hat{J}_x^2 - \hat{J}_y^2)$$

$$5. \langle \hat{J}_x \rangle = 0; \langle \hat{J}_x^2 \rangle = \frac{\hbar^2}{2} [j(j+1) - m^2]$$

$$14. (a) 0, \sqrt{2}\hbar, \sqrt{6}\hbar$$

$$(b) \text{ zero}$$

$$(c) \langle \hat{L}_z \rangle = 0; \langle \hat{L}^2 \rangle = \frac{\hbar^2}{14} (8 + 54) \approx 4.43 \hbar^2$$

$$16. 12.5\%$$

$$17. \hat{L}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}; \hat{L}^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix};$$

$$\hat{L}_+ = \hbar \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}; \hat{L}_- = \hbar \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix};$$

$$\hat{L}_y = \frac{i\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

18. (a) $\hbar, 0, -\hbar$

$$(b) |\uparrow\rangle_x = \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}; |\rightarrow\rangle_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}; |\downarrow\rangle_x = \frac{1}{2} \begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix}$$

a. The probabilities of measuring $\hbar, 0, -\hbar$ for \hat{L}_x are then $1/4, 1/2, 1/4$, respectively.

19. Two beams of equal intensity

Chapter 9

4. (a) It does have definite angular momentum. $\ell = 1$ and $m = 0$.

(b) $\frac{1}{2}\beta^2$; bound

$$(c) U(r) = -\frac{5\beta}{2r} + \frac{7}{8r^2}$$

$$5. E_n = \frac{n^2\pi^2\hbar^2}{2m(b-a)^2}; \psi_{n00}(r, \theta, \phi) = \frac{1}{\sqrt{4\pi}} \sqrt{\frac{2}{(b-a)}} \left(\frac{1}{r}\right) \sin\left[\frac{(r-a)}{(b-a)}\pi\right]$$

6. (c) ≈ 0.74

$$7. (a) \psi(x, y, z) = \left(\sqrt{\frac{2}{L}}\right)^3 \sin\left(\frac{n_x\pi}{L}x\right) \sin\left(\frac{n_y\pi}{L}y\right) \sin\left(\frac{n_z\pi}{L}z\right)$$

$$(b) E_{n_x n_y n_z} = \frac{\pi^2\hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2). \text{ Three times larger.}$$

(c) $g_1 = 1; g_2 = 3; g_3 = 6$

$$15. |\psi(\mathbf{r}, t)\rangle = \sum_j a_j e^{-iE_j t/\hbar} |n\ell m\rangle$$

Chapter 10

$$3. r_c = n^2 \left(1 \pm \sqrt{1 - \frac{\ell(\ell+1)}{n^2}} \right)$$

$$4. (\delta r_c)_{\max} = 2(n^2 a_0); (\delta r_c)_{\min} = 2(n^2 a_0) \sqrt{\frac{1}{n}}$$

6. ≈ 0.24

$$8. \langle x \rangle_{n\ell m} = 0 = \langle y \rangle_{n\ell m} = \langle z \rangle_{n\ell m}$$

11. $\ell = 0$

12. For $\ell = 0$: $\langle r \rangle = \frac{3}{2} (a_0 n^2)$; $\langle \Delta r \rangle = \frac{a_0}{2} n \sqrt{n^2 + 2}$

For $\ell = n - 1$: $\langle r \rangle = a_0 n \left(n + \frac{1}{2} \right)$; $\langle \Delta r \rangle = a_0 n \sqrt{\frac{1}{2} \left(n + \frac{1}{2} \right)}$

14. ≈ 0.70

17. (a) $|\psi(\mathbf{r}, t)\rangle = \frac{1}{\sqrt{3}} e^{-iE_1 t/\hbar} |100\rangle + \frac{1}{\sqrt{6}} e^{-iE_2 t/\hbar} |210\rangle + \frac{1}{\sqrt{2}} e^{-iE_3 t/\hbar} |320\rangle$

(b) $\langle E \rangle = -\frac{(mc^2)\alpha^2}{2} \left(\frac{89}{144} \right)$; $\langle \hat{L}^2 \rangle = \frac{13}{3} \hbar^2$; $\langle \hat{L}_z \rangle = 0$

(c) As specified by Ehrenfest's theorem (see Section 6.3.3), in particular Equation 6.120)

Chapter 11

1. $\dot{\mathbf{A}} = \left[(\mathbf{p} \times \mathbf{L}) - \left(\frac{me^2}{4\pi\epsilon_0} \right) \hat{\mathbf{r}} \right]$

Chapter 12

1. (a) $E_n = \left(n + \frac{1}{2} \right) \hbar\omega - \frac{e^2 F^2}{2m\omega^2}$

(b) Second-order perturbation theory result is the same as the exact solution.

2. $E_{\text{nodd}}^{(1)} = \frac{2}{a} U_0$; $E_{\text{neven}}^{(1)} = 0$

3. $E_{\text{nodd}}^{(1)} = \frac{2}{a} U_0$; $E_{\text{neven}}^{(1)} = 0$. There is a node at the perturbation for n even.

(a) $E_1^{(1)} = \frac{eFL}{2}$

(b) $\psi_1^{(1)}(x) \approx \frac{32}{27\pi^2} \frac{E_1^{(1)}}{E_1^{(0)}} \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$

(c) $E_n^{(1)} = \frac{1}{2mc^2} (E_n^{(0)})^2$

(d) $E_n^{(\text{rel})} = E_n^{(0)} - \frac{1}{2} \left(\frac{1}{mc^2} \right) (E_n^{(0)})^2 + \dots$

$$4. E_n^{(2)} = - \left(\frac{15}{8} \right) \left(\frac{1}{4D_e} \right) (\hbar\omega)^2 [(n^2 + n + 11/30)]$$

$$(a) E_1^{(1)} = \frac{1}{2} \left(\frac{\omega_1}{\omega} \right)^2 \left(n + \frac{1}{2} \right) \hbar\omega; E_n^{(2)} = -\frac{1}{8} \frac{\omega_1^4}{\omega^4} \left(n + \frac{1}{2} \right) \hbar\omega$$

(b) The first three terms in the expansion of the exact result are $E_n^{(0)}$, $E_1^{(1)}$, and $E_n^{(2)}$.

$$5. E_0^{(1)} = \frac{1}{4\alpha^2} \left(\frac{3C}{\alpha^2} - m\omega^2 \right)$$

$$(a) \hat{H}_0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 3 \end{pmatrix}; \hat{H}_1 = \begin{pmatrix} 0 & \epsilon & 0 \\ \epsilon & 0 & 0 \\ 0 & 0 & -\epsilon \end{pmatrix}$$

$$(b) E_1^{(1)} = 0; E_2^{(1)} = 0; E_3^{(1)} = -\epsilon; E_1^{(2)} = -\epsilon^2; E_2^{(2)} = \epsilon^2; E_3^{(2)} = 0$$

(c) The exact result reduces to the second-order perturbation theory result.

$$11. (a) E_{000}^{(2)} = -\frac{1}{2} \frac{e^2 F^2}{m_e \omega^2}$$

$$(b) E_{000}^{(2)} = -\frac{1}{2} \frac{e^2 F^2}{m_e \omega^2}$$

$$12. (a) |1^{(s)}\rangle = \frac{1}{\sqrt{2}} (|1^{(0)}\rangle + |2^{(0)}\rangle); |2^{(s)}\rangle = \frac{1}{\sqrt{2}} (|1^{(0)}\rangle - |2^{(0)}\rangle); \\ |3^{(s)}\rangle = |3^{(0)}\rangle$$

$$13. (a) E_{\text{variational}} = \frac{3}{8} \left(6 \frac{C\hbar^4}{m^2} \right)^{1/3}$$

$$15. E_{\text{variational}} = \sqrt{3}\hbar\omega$$

$$16. (a) E_{\text{variational}} = \frac{3^{5/3}}{2^{4/3}} \left(\frac{e^2 F^2 \hbar^2}{2m} \right)^{1/3}$$

Chapter 13

$$5. (a) E_{SO}^{(1)} \left(j = \ell + \frac{1}{2} \right) = \frac{(\hbar\omega)^2}{4mc^2} \left(\frac{\ell}{2} \right);$$

$$E_{SO}^{(1)} \left(j = \ell - \frac{1}{2} \right) = -\frac{(\hbar\omega)^2}{4mc^2} \left(\frac{\ell+1}{2} \right)$$

(b) zero

8. 2.6 eV

$$9. E_{1s2\ell}^{(1)} = J_{1s2\ell} \pm K_{1s2\ell}; |\psi_{\pm}\rangle = \frac{1}{\sqrt{2}} \{ |1s\rangle_1 |n\ell\rangle_2 \pm |1s\rangle_2 |2\ell\rangle_1 \}$$

11. (a) ${}^2P_{1/2}$ and at higher energy ${}^2P_{3/2}$ (b) ${}^2S_{1/2}; {}^2P_{3/2,1/2}; D_{5/2,3/2}$ 12. (a) ${}^1S; {}^1D; {}^1G; {}^3P; {}^3F$ (b) 3F

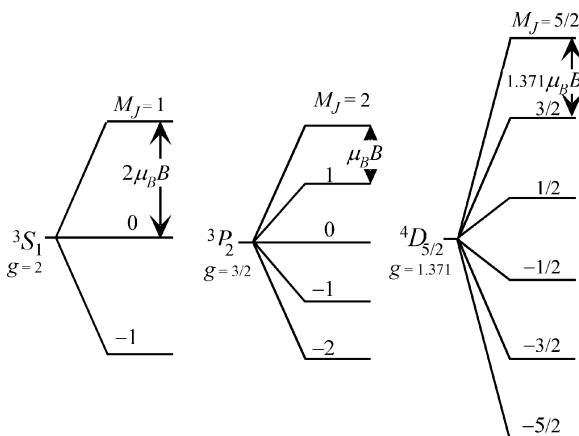
Chapter 14

$$3. E_m^{(0)} = \frac{(m\hbar)^2}{2\mu a^2}; E_m^{(2)} = \frac{\mu q^2 a^4 F^2}{\hbar^2} \left(\frac{1}{4m^2 - 1} \right)$$

$$6. (a) \hat{H} = \hat{\mu}_S \cdot \mathbf{B} + \hat{\mu}_p \cdot \mathbf{B} + \frac{2\kappa}{\hbar^2} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$$

(b) $E_{\pm} = -\frac{\kappa}{2} \pm (\kappa^2 + \mu_B B)^{1/2}$; The proton magnetic moment is tiny compared with that of the electron.

8.



Problem 8 of Chapter 14

Chapter 15

$$3. P_{0 \rightarrow 1}^{(1)} = \frac{(eF_0)^2}{2m\hbar\omega} \pi e^{-\omega^2\tau^2/2} \tau^2$$

4. Transitions to all states vanish except $n = 1$ and 3.

$$P_{0 \rightarrow 1}^{(1)} = |A|^2 \frac{9}{8} \frac{\hbar}{m^3\omega^3} \frac{1}{(\omega^2 + 1/\tau^2)}$$

$$P_{0 \rightarrow 3}^{(1)} = |A|^2 \frac{3}{4} \frac{\hbar}{m^3\omega^3} \frac{1}{(9\omega^2 + 1/\tau^2)}$$

$$5. P_{1 \rightarrow 2}^{(1)} = \frac{e^2 F_0^2}{\hbar^2} \left(\frac{2^{15}}{3^{10}} a_0^2 \right) \left(\frac{1}{\omega_{21}^2 + 1/\tau^2} \right)$$

Appendix B Useful Constants

Table B.1 A few physical constants listed to a limited number of significant figures

Constant	Symbol	Value
speed of light	c	$3 \times 10^8\text{m/s}$
elementary charge	e	$1.6 \times 10^{-19}\text{C}$
electronic mass	m_e	$9.1 \times 10^{-31}\text{kg}$
Bohr magneton	μ_B	$9.27 \times 10^{-24}\text{J/T}$
nuclear magneton	μ_N	$5.05 \times 10^{-27}\text{J/T}$
fine structure constant	α	$1/137$
Rydberg constant	R_∞	$1.09 \times 10^7\text{m}^{-1}$
Bohr radius	a_0	0.053nm

Appendix C

Energy Units

Because of the wide variation of the magnitudes of energies encountered in quantum physics, energies are often specified in convenient units that are tailored to a given physical problem. For example, while electron volts (eV) are convenient units for dealing with electronic levels of atoms and molecules, they are not particularly suited to describe fine structure intervals. Below is a table that gives the relationship between the electron-volt and some commonly used units. Only a few significant figures are included because the table is meant to demonstrate the orders of magnitude of these relationships.

Table C.1 The relationship between electron-volts and other commonly used units of energy

$1\text{eV} = 1 \times 10^{-6}\text{MeV}$	$1\text{MeV} = 1 \times 10^6\text{eV}$
$1\text{eV} = 1.6 \times 10^{-19}\text{J}$	$1\text{J} = 6.24 \times 10^{18}\text{eV}$
$1\text{eV} = 8065.6\text{ cm}^{-1}$	$1\text{ cm}^{-1} = 1.24 \times 10^{-4}\text{eV}$
$1\text{eV} = 2.42 \times 10^8\text{MHz}$	$1\text{MHz} = 4.12 \times 10^{-9}\text{eV}$
$1\text{eV} = 3.68 \times 10^{-2}\text{ hartree}$	$1\text{ hartree} = 27.21\text{eV}$

Appendix D

Useful Formulas

Table D.1 Some key formulas in SI units and atomic units

Quantity	Symbol	SI Units	a.u.
Fine structure constant	α	$\left(\frac{1}{4\pi\epsilon_0}\right)\frac{e^2}{\hbar c}$	$\frac{1}{c}$
Bohr energy	E_n	$-\frac{1}{2}\frac{\alpha^2 m_e c^2}{n^2}$	$\frac{-1}{2n^2}$
Bohr radius	a_0	$\frac{1}{\alpha}\left(\frac{\hbar}{m_e c}\right)$	1
Compton wavelength—electron	λ_c	$\frac{\hbar}{m_e c} = \alpha a_0$	$\sim \frac{1}{c}$
Classical radius—electron	R_e	$\sim \alpha^2 a_0$	$\sim \frac{1}{c^2}$
Bohr magneton	μ_B	$\frac{e\hbar}{2m_e}$	$\frac{1}{2}$

Appendix E

Greek Alphabet

Table E.1 The letters of the Greek alphabet. Where appropriate, their primary usage in this book is indicated. U. C. refers to uppercase

L. C.	U. C.	Name	Usage in this book
α	<i>A</i>	Alpha	fine structure constant, harmonic oscillator, spin up
β	<i>B</i>	Beta	general parameter, spin down
γ	Γ	Gamma	Γ function (U. C.), square root of transmission coefficient T (U. C.)
δ	Δ	Delta	Dirac δ -function, small increment, difference (U. C.)
ϵ, ε	<i>E</i>	Epsilon	unitless energy parameter, small quantity
ζ	<i>Z</i>	Zeta	general parameter
η	<i>H</i>	Eta	general parameter
θ, ϑ	Θ	Theta	polar angle, function (U. C.)
ι	<i>I</i>	Iota	—
κ	<i>K</i>	Kappa	real exponent, hyperfine energy
λ	Λ	Lambda	wavelength
μ	<i>M</i>	Mu	general parameter, mass
ν	<i>N</i>	Nu	frequency (radians/s)
ξ	Ξ	Xi	unitless length harmonic oscillator
o	<i>O</i>	Omicron	—
π	Π	Pi	—
ρ	<i>P</i>	Rho	parameter, unitless length hydrogen
σ	Σ	Sigma	Pauli matrices, summation
τ	<i>T</i>	Tau	increment of time
υ	<i>Y</i>	Upsilon	—
ϕ	Φ	Phi	azimuthal angle, function (U. C.)
χ	<i>X</i>	Chi	spin state
ψ	Ψ	Psi	wave function (L. C. and U. C.)
ω	Ω	Omega	frequency (radians/s) (L. C.), Bohr frequency $\omega_{nm} = (E_n - E_m) / \hbar$ (not just hydrogen)
	<i>F</i>	Digamma	function

Appendix F

Acronyms

Table F.1 Some acronyms used in this book

Acronym	Meaning
RWA	rotating wave approximation
TDSE	time-dependent Schrödinger equation
TISE	time-independent Schrödinger equation
TME	total mechanical energy (the “energy”)
WKB	Wentzel, Kramers, Brillouin approximation

Appendix G

Γ -Functions

G.1 Integral Γ -Functions

$$\Gamma(n+1) = n\Gamma(n) = n! \quad n = 1, 2, 3, \dots \quad (\text{G.1})$$

$$\Gamma(1) = 1 \quad (\text{G.2})$$

$$\Gamma(2) = 1 \quad (\text{G.3})$$

$$\Gamma(3) = 2 \quad (\text{G.4})$$

$$\Gamma(4) = 3! = 6 \quad (\text{G.5})$$

$$\Gamma(5) = 4! = 24 \quad (\text{G.6})$$

G.2 Half-Integral Γ -Functions

$$\Gamma(m+1) = \frac{1 \cdot 3 \cdot 5 \cdots (2m-1)}{2^m} \sqrt{\pi} \quad m = 1, 2, 3, \dots \quad (\text{G.7})$$

$$\Gamma(1/2) = \sqrt{\pi} \quad (\text{G.8})$$

$$\Gamma(3/2) = \frac{\sqrt{\pi}}{2} \quad (\text{G.9})$$

$$\Gamma(5/2) = \frac{3\sqrt{\pi}}{4} \quad (\text{G.10})$$

$$\Gamma(7/2) = \frac{15\sqrt{\pi}}{8} \quad (\text{G.11})$$

Appendix H

Useful Integrals

$$\int x^2 e^{-ax} dx = \frac{e^{-ax}}{-a} \left(x^2 + \frac{2x}{a} + \frac{2}{a^2} \right) \quad (\text{H.1})$$

$$\int_0^\infty x^m e^{-ax} dx = \frac{\Gamma[(m+1)]}{a^{m+1}} = \frac{m!}{a^{m+1}} \quad (\text{H.2})$$

$$\int_{-\infty}^\infty e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \quad (\text{H.3})$$

$$\int_{-\infty}^\infty e^{-(ax^2+bx+c)} dx = \sqrt{\frac{\pi}{a}} e^{(b^2-4ac)/4a} \quad (\text{H.4})$$

$$\int_0^\infty x^m e^{-ax^2} dx = \frac{\Gamma[(m+1)/2]}{2a^{(m+1)/2}} \quad (\text{H.5})$$

$$\int_0^1 \sqrt{\frac{1}{x} - 1} dx = \frac{\pi}{2} \quad (\text{H.6})$$

$$\int \sqrt{a^2 - x^2} dx = \frac{x\sqrt{a^2 - x^2}}{2} + \frac{a^2}{2} \sin^{-1} \frac{x}{a} \quad (\text{H.7})$$

$$\int \frac{dx}{(x^2 + a^2)^2} = \frac{x}{2a^2(x^2 + a^2)} + \frac{1}{2a^3} \tan^{-1} \left(\frac{x}{a} \right) \quad (\text{H.8})$$

$$\int \frac{dx}{(x^2 + a^2)^n} dx = \frac{x}{2(n-1)a^2(x^2 + a^2)^{n-1}} + \frac{2n-3}{(2n-2)a^2} \int \frac{dx}{(x^2 + a^2)^{n-1}} dx \quad (\text{H.9})$$

$$\int \frac{x^m dx}{(x^2 + a^2)^n} dx = \int \frac{x^{m-2} dx}{(x^2 + a^2)^{n-1}} dx - a^2 \int \frac{x^{m-2} dx}{(x^2 + a^2)^n} dx \quad (\text{H.10})$$

Appendix I

Useful Series

I.1 Taylor Series

A Taylor series expansion of a function $f(x)$ about a point $x = a$ is

$$\begin{aligned} f(x) &= f(a) + \frac{(x-a)}{1!} f'(a) + \frac{(x-a)^2}{2!} f''(a) + \cdots \\ &= \sum_{n=0}^{\infty} \frac{(x-a)^n}{n!} f^{(n)}(a) \end{aligned} \quad (\text{I.1})$$

where the primes signify differentiation with respect to x . Therefore, for example, $f''(a)$ is the second derivative of the function $f(x)$ with respect to x evaluated at $x = a$.

There are at least four Taylor series that every physics student should have at their command:

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \quad (\text{I.2})$$

$$\sin x = \frac{x}{1!} - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots \quad (\text{I.3})$$

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots \quad (\text{I.4})$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots \quad (\text{I.5})$$

I.2 Binomial Expansion

Binomial series are special cases of Taylor series for $f(x) = (1+x)^m$ and $a = 0$. The exponent m may be positive or negative and is not restricted to being an integer. The general form of the binomial expansion is, in three equivalent forms,

$$\begin{aligned}
(1+x)^m &= 1 + mx + \frac{m(m-1)}{2!}x^2 + \frac{m(m-1)(m-2)}{3!}x^3 + \dots \\
&= \sum_{n=0}^{\infty} \frac{m!}{n!(m-n)!} x^n \\
&= \sum_{n=0}^{\infty} \binom{m}{n} x^n
\end{aligned} \tag{I.6}$$

where

$$\binom{m}{n} \equiv \frac{m!}{n!(m-n)!} \tag{I.7}$$

is called the binomial coefficient. A few of the most common binomial expansions are listed below:

$$(1+x)^{-1} = 1 - x + x^2 - x^3 + \dots \tag{I.8}$$

$$(1+x)^{-2} = 1 - 2x + 3x^2 - 4x^3 + \dots \tag{I.9}$$

$$(1+x)^{1/2} = 1 + \frac{1}{2}x - \frac{1}{2 \cdot 4}x^2 + \frac{1}{2 \cdot 4 \cdot 6}x^3 + \dots \tag{I.10}$$

$$(1+x)^{-1/2} = 1 - \frac{1}{2}x + \frac{1 \cdot 3}{2 \cdot 4}x^2 - \frac{1 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6}x^3 + \dots \tag{I.11}$$

I.3 Gauss' Trick

Because Gauss' trick is useful in quantum physics, we show a simple method of deriving an expression for the sum of the first M integers. We write this sum in two different ways. First,

$$\sum_{n=0}^M n = 1 + 2 + 3 + \dots + (M-2) + (M-1) + M \tag{I.12}$$

and, second, by simply reversing the order of summation:

$$\sum_{n=0}^M n = M + (M-1) + (M-2) + \dots + 3 + 2 + 1 \tag{I.13}$$

Now add these sums term by term and obtain

$$2 \sum_{n=0}^M n = (M+1) + (M-1+2) + (M-2+3) + \cdots + (M+1) \quad (\text{I.14})$$

Examination of Equation I.14 reveals that the right-hand side comprises $(M+1)$ added to itself M times, the sum of which is $M(M+1)$. Solving for $\sum_{n=0}^M n$ we obtain Gauss' trick, Equation 8.157:

$$\sum_{n=0}^M n = \frac{M(M+1)}{2} \quad (\text{I.15})$$

Appendix J

Fourier Integrals

A function $f(x)$ that is periodic on an interval $-L \leq x \leq L$ can be expanded in a Fourier series

$$f(x) = \sum_{n=0}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=0}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right) \quad (\text{J.1})$$

where a_n and b_n are constants, but functions of n . This representation of $f(x)$ can be put in more concise form by substituting the Euler forms of the sine and cosine:

$$\cos \theta = \frac{e^{i\theta} + e^{-i\theta}}{2}; \quad \sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i} \quad (\text{J.2})$$

Combining the constants and renaming them B_n and C_n we have

$$f(x) = \sum_{n=0}^{\infty} B_n e^{in\pi x/L} + \sum_{n=0}^{\infty} C_n e^{-in\pi x/L} \quad (\text{J.3})$$

By extending the summation to $n = -\infty$ we can write Equation J.3 as a single term

$$f(x) = \sum_{n=-\infty}^{\infty} D_n e^{in\pi x/L} \quad (\text{J.4})$$

where D_n is the new constant.

The functions $e^{in\pi x/L}$ and $e^{im\pi x/L}$ are orthogonal, but not orthonormal, as may be seen from the integral

$$\int_{-L}^L e^{i(n-m)\pi x/L} dx = 2L\delta_{nm} \quad (\text{J.5})$$

where δ_{nm} is the Kronecker delta. By taking advantage of the orthogonality relation we may determine the constant A_n if $f(x)$ is known. Multiplying both sides of Equation J.4 by $e^{-im\pi x/L}$ and integrating over the interval we have

$$D_m = \frac{1}{2L} \int_{-L}^L f(x) e^{-im\pi x/L} dx \quad (\text{J.6})$$

Our goal is to extend the infinite series that represents a periodic function to an expression that represents a nonperiodic function. In preparation for this extension we make the substitution

$$k_n = \frac{n\pi}{L} \quad (\text{J.7})$$

from which we see that

$$\Delta k = \frac{\pi}{L} \Delta n \quad (\text{J.8})$$

If Δn is the difference between successive integers, then it is unity so it may be inserted in Equation J.4 without affecting the equation:

$$\begin{aligned} f(x) &= \sum_{n=-\infty}^{\infty} D_n e^{in\pi x/L} \Delta n \\ &= \sum_{n=-\infty}^{\infty} D_n e^{in\pi x/L} \left(\frac{L}{\pi} \right) \Delta k \end{aligned} \quad (\text{J.9})$$

The conversion from periodic to nonperiodic function can be effected by letting $L \rightarrow \infty$, in which case k becomes a continuous variable, $\Delta k \rightarrow dk$, $D_n \rightarrow D(k)$, and $\sum_{n=-\infty}^{\infty} \rightarrow \int_{-\infty}^{\infty}$. Also, to conform with the common notation of quantum physics we make the change $f(x) \rightarrow \psi(x)$. With these substitutions Equation J.9 becomes

$$\psi(x) = \frac{L}{\pi} \int_{-\infty}^{\infty} D(k) e^{ikx} dk \quad (\text{J.10})$$

Now we rescale $D(k)$ according to

$$D(k) = \sqrt{\frac{\pi}{2}} \frac{A(k)}{L} \quad (\text{J.11})$$

and obtain

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{ikx} dk \quad (\text{J.12})$$

Now let us return to Equation J.6 for the Fourier coefficients using Equation J.11:

$$A_n = \frac{1}{\sqrt{2\pi}} \int_{-L}^L \psi(x) e^{-ik_n x/L} dx \quad (\text{J.13})$$

Again letting $L \rightarrow \infty$ we have

$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx/L} dx \quad (\text{J.14})$$

In summary, the equations

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{ikx} dk \quad (\text{J.15})$$

$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx/L} dx \quad (\text{J.16})$$

are the Fourier transforms. That is, $\psi(x)$ is the Fourier transform of $A(k)$, and $A(k)$ is the Fourier transform of $\psi(x)$. In quantum mechanics the variable x is space and k is the wave number. Thus, the wave function in coordinate space is $\psi(x)$ and the wave function in k -space is $A(k)$. Often it is desirable to have the wave function in terms of the momentum $p = \hbar k$. That is,

$$\begin{aligned} \phi(p) &\equiv \frac{1}{\sqrt{\hbar}} A(k) \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x) e^{-ipx/\hbar} dx \end{aligned} \quad (\text{J.17})$$

Appendix K

Commutator Identities

K.1 General Identities

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \quad (\text{K.1})$$

$$[\hat{A}, \hat{A}] = 0 \quad (\text{K.2})$$

$$[\hat{A}, \hat{B}\hat{C}] \equiv [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] \quad (\text{K.3})$$

$$[\hat{A}\hat{B}, \hat{C}] \equiv [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}] \quad (\text{K.4})$$

$$\begin{aligned} [\hat{A}\hat{B}, \hat{C}\hat{D}] &\equiv [\hat{A}, \hat{C}]\hat{B}\hat{D} + \hat{A}[\hat{B}, \hat{C}]\hat{D} \\ &\quad + \hat{C}[\hat{A}, \hat{D}]\hat{B} + \hat{C}\hat{A}[\hat{B}, \hat{D}] \end{aligned} \quad (\text{K.5})$$

K.2 Quantum Mechanical Identities

$$[x, \hat{p}] = i\hbar \quad (\text{K.6})$$

$$[x, \hat{p}_x^n] = i\hbar n \hat{p}_x^{n-1} \quad (\text{K.7})$$

$$[\hat{J}_i, \hat{J}_j] = i\hbar \hat{J}_k \epsilon_{ijk} \quad (\text{K.8})$$

Appendix L

Miscellaneous Operator Relations

L.1 Baker–Campbell–Hausdorff (BCH) Formula

Depending upon the reference source consulted, there are two formulas that are referred to in the literature as the Baker–Campbell–Hausdorff formula, theorem, or lemma. Both are used in this book, so we will discuss them in this appendix. The proof of the first is somewhat involved and is of limited pedagogical value in a course on quantum physics, so it will not be presented. The proof of the second is considerably simpler and offers a good exercise in exponentiated operators, so we give this proof below.

First, let us state the one that we will not prove. Given that \hat{A} , \hat{B} , and \hat{C} are operators, then the product of two exponentiated operators is

$$e^{\hat{A}}e^{\hat{B}} = e^{\hat{C}} \quad (\text{L.1})$$

where

$$\hat{C} = \hat{A} + \hat{B} + \frac{1}{2} [\hat{A}, \hat{B}] + \frac{1}{12} \{ [[\hat{A}, \hat{B}], \hat{B}] + [\hat{A}, [\hat{A}, \hat{B}]] \} + \cdots \quad (\text{L.2})$$

where we have truncated the series after the terms that are necessary for the work described in this book.

For the second formula we assume two operators, \hat{A} and \hat{B} , that do not commute and write

$$e^{\hat{A}}\hat{B}e^{-\hat{A}} = \hat{A} + \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!} [\hat{A}, [\hat{A}, \hat{B}]] + \frac{1}{3!} [\hat{A}, [\hat{A}, [\hat{A}, \hat{B}]]] + \cdots \quad (\text{L.3})$$

Proof:

Define the product on the left-hand side in terms of an arbitrary parameter λ .

$$f(\lambda) = e^{\lambda\hat{A}}\hat{B}e^{-\lambda\hat{A}} \quad (\text{L.4})$$

Now we strive to write a Taylor expansion of $f(\lambda)$ about $\lambda = 0$. To do so will require the derivatives of $f(\lambda)$, the first few of which we tabulate bearing in mind that $[\hat{A}, e^{\pm\lambda\hat{A}}] = 0$:

$$\begin{aligned} \frac{df(\lambda)}{d\lambda} &= e^{\lambda\hat{A}} [\hat{A}, \hat{B}] e^{-\lambda\hat{A}} \\ \frac{d^2f(\lambda)}{d\lambda^2} &= e^{\lambda\hat{A}} [\hat{A}, [\hat{A}, \hat{B}]] e^{-\lambda\hat{A}} \\ &\vdots \\ \frac{d^n f(\lambda)}{d\lambda^n} &= e^{\lambda\hat{A}} [\hat{A}, \dots [\hat{A}, [\hat{A}, \hat{B}]] \dots] e^{-\lambda\hat{A}} \end{aligned} \quad (\text{L.5})$$

Using these derivatives to write the Taylor expansion we have

$$e^{\lambda\hat{A}} \hat{B} e^{-\lambda\hat{A}} = \hat{A} + \hat{B} + [\hat{A}, \hat{B}] \frac{\lambda}{1!} + [\hat{A}, [\hat{A}, \hat{B}]] \frac{\lambda^2}{2!} + [\hat{A}, [\hat{A}, [\hat{A}, \hat{B}]]] \frac{\lambda^3}{3!} + \dots \quad (\text{L.6})$$

Because λ is arbitrary, we may set it equal to unity and obtain Equation L.3.

L.2 Translation Operator

We will derive the form of the translation operator, also known as the displacement operator, or the propagator. This latter term is often used for a Green's function, so it is advisable to use one of the first two appellations. We begin by writing the Taylor expansion for a function $f(x)$ about the point $x = a$:

$$f(x) = \sum_{n=0}^{\infty} \frac{d^n f(x)}{dx^n} \bigg|_{x=a} \frac{(x-a)^n}{n!} \quad (\text{L.7})$$

Then, letting $x \rightarrow x + x_0$, and continuing to expand about $x = a$ we have

$$\begin{aligned} f(x + x_0) &= \sum_{n=0}^{\infty} \frac{d^n f(x + x_0)}{d(x + x_0)^n} \bigg|_{(x+x_0)=a} \frac{[(x + x_0) - a]^n}{n!} \\ &= \sum_{n=0}^{\infty} \frac{d^n f(x)}{dx^n} \bigg|_{x=a} \frac{[(x + x_0) - a]^n}{n!} \end{aligned} \quad (\text{L.8})$$

because

$$\frac{d^n f(x + x_0)}{d(x + x_0)^n} \bigg|_{(x+x_0)=a} = \frac{d^n f(x)}{dx^n} \bigg|_{x=a} \quad (\text{L.9})$$

Now let $a \rightarrow x$ in Equation L.8 and obtain

$$\begin{aligned} f(x + x_0) &= \sum_{n=0}^{\infty} \left[\frac{x_0^n}{n!} \frac{d^n}{dx^n} \right] f(x) \\ &= \left[1 + \frac{x_0^1}{1!} \frac{d}{dx} + \frac{x_0^2}{2!} \frac{d^2}{dx^2} + \frac{x_0^3}{3!} \frac{d^3}{dx^3} + \cdots \right] f(x) \quad (\text{L.10}) \end{aligned}$$

$$= \exp \left[x_0 \frac{d}{dx} \right] f(x) \quad (\text{L.11})$$

which shows that application of the operator, $\exp \left[x_0 \frac{d}{dx} \right]$, to an arbitrary function $f(x)$, effects a translation $x \rightarrow x + x_0$.

We can cast the translation operator in terms of the momentum operator using Equation 2.28 to make the identification

$$\frac{d}{dx} \rightarrow \frac{i \hat{p}}{\hbar} \quad (\text{L.12})$$

we see that

$$\begin{aligned} f(x + x_0) &= \left\{ \sum_{n=0}^{\infty} \frac{1}{n!} \left(x_0 \frac{i \hat{p}}{\hbar} \right)^n \right\} f(x) \\ &= e^{i p x_0 / \hbar} f(x) \quad (\text{L.13}) \end{aligned}$$

We can also derive the action of the translation operator by beginning with the Fourier transforms, Equations 4.33 and 4.31. This will provide the action of the translation operator on $\psi(x)$ and $\phi(x)$. Multiplying Equations 4.33 by $e^{i p x_0 / \hbar}$ we have

$$\begin{aligned} e^{i p x_0 / \hbar} \psi(x) &= \frac{1}{\sqrt{2\pi \hbar}} \int_{-\infty}^{\infty} \phi(p) e^{i p (x + x_0) / \hbar} dp \\ &= \psi(x + x_0) \quad (\text{L.14}) \end{aligned}$$

Multiplying Equations 4.31 by $e^{i p_0 x / \hbar}$ we find that

$$\begin{aligned} e^{i p_0 x / \hbar} \phi(p) &= \frac{1}{\sqrt{2\pi \hbar}} \int_{-\infty}^{\infty} \psi(x) e^{-i (p + p_0) x / \hbar} dx \\ &= \phi(p + p_0) \quad (\text{L.15}) \end{aligned}$$

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