

Atomic Spectroscopy

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1. INTRODUCTION

This article outlines the main concepts of atomic structure, with some emphasis on terminology and notation. Atomic radiation is discussed, in particular the wavelengths, intensities, and shapes of spectral lines, and a few remarks are made regarding continuous spectra. We include updated tabulations of ionization energies for the neutral atoms and transition probabilities for persistent lines of selected neutral atoms. Some sources of additional atomic spectroscopic data are mentioned.

Experimental techniques and the details of atomic theoretical methods are not covered in this article; these and a number of other subjects pertinent to atomic spectroscopy are treated in one or more of at least fifteen chapters in the volume *Atomic, Molecular, and Optical Physics Handbook*, G.W.F. Drake, Ed. (AIP Press, Woodbury, NY, 1996) and in references below.

2. FREQUENCY, WAVENUMBER, WAVELENGTH

The photon energy due to an electron transition between an upper atomic level k (of energy E_k) and a lower level i is

$$\Delta E = E_k - E_i = h\nu = hc\sigma = hc/\lambda_{\text{vac}} \quad (1)$$

where ν is the frequency, σ the wavenumber in vacuum, and λ_{vac} the wavelength in vacuum. The most accurate spectroscopic measurements are determinations of transition frequencies, the unit being the Hertz (1 Hz = cycle/sec) or one of its multiples. A measurement of any one of the entities frequency, wavenumber, or wavelength (in vacuum) is an equally accurate determination of the others since the speed of light is exactly defined. The most common wavelength units are the nanometer (nm), the Ångström (1 = 10^{-1} nm) and the micrometer (μm). The SI wavenumber unit is the inverse meter, but in practice wavenumbers are usually expressed in inverse centimeters: $1 \text{ cm}^{-1} = 10^2 \text{ m}^{-1}$, equivalent to $2.997\,924\,58 \times 10^4 \text{ MHz}$.

In addition to frequency and wavenumber units, atomic energies are often expressed in electron volts (eV). One eV is the energy associated with each of the following quantities:

$$\begin{aligned} &2.417\,988\,4(7) \times 10^{14} \text{ Hz} \\ &8\,065.541\,0(24) \text{ cm}^{-1} \\ &1\,239.842\,44(37) \text{ nm} \\ &11\,604.45(10) \text{ K (kelvin)} \\ &1.602\,177\,3(5) \times 10^{-19} \text{ J (joule)} \end{aligned}$$

We note that the basic unit of temperature, the kelvin, is equivalent to about 0.7 cm^{-1} , i.e., the value of the Boltzmann constant k expressed in wavenumber units per kelvin is $0.695\,039(6) \text{ cm}^{-1}/\text{K}$. One reason for citing this particular equivalency involving the internationally accepted symbol for the kelvin (K) [1] is to suggest that use of the letter K as a symbol for 1 cm^{-1} (1 kayser) should be discontinued.

The unit of energy in the system of atomic units (a.u.) often used for theoretical calculations is the hartree, which is equal to 2 rydbergs. The rydberg for an atom having nuclear mass M is

$$1 \text{ Ry} = R_M = M(M + m_e)^{-1} R_\infty \quad (2)$$

with

$$R_\infty = m_e c \alpha^2 / (2h) = 10\,973\,731.568\,62(9) \text{ m}^{-1} \quad (3)$$

which is equivalent to $13.605\,698(4) \text{ eV}$. The Rydberg constant R_∞ is thus the limit value for infinite nuclear mass.

3. ATOMIC STATES, SHELLS, AND CONFIGURATIONS

A one-electron atomic *state* is defined by the quantum numbers $nlm_j m_s$ or $nlj m_j$, with n and l representing the principal quantum number and the orbital angular momentum quantum number, respectively. The allowed values of n are the positive integers, and $l = 0, 1, \dots, n-1$. The quantum number j represents the angular momentum obtained by coupling the orbital and spin angular momenta of an electron, i.e., $j = l + s$, so that $j = l \pm 1/2$. The magnetic quantum numbers m_l , m_s , and m_j represent the projections of the corresponding angular momenta along a particular direction; thus, for example, $m_l = -l, -l+1 \dots l$ and

$$m_s = \pm 1/2.$$

The central field approximation for a many-electron atom leads to wave functions expressed in terms of products of such one-electron states [2], [3]. Those electrons having the same principal quantum number n belong to the *shell* for that number. Electrons having both the same n value and l value belong to a *subshell*, all electrons in a particular subshell being *equivalent*. The notation for a *configuration* of N equivalent electrons is nl^N , the superscript usually being omitted for $N = 1$. A configuration of several subshells is written as $nl^N n'l'^M \dots$. The numerical values of l are replaced by letters in writing a configuration, according to the code s, p, d for $l = 0, 1, 2$ and $f, g, h \dots$ for $l = 3, 4, 5 \dots$, the letter j being omitted.

The Pauli exclusion principle prohibits atomic states having two electrons with all four quantum numbers the same. Thus the maximum number of equivalent electrons is $2(2l + 1)$. A subshell having this number of electrons is *full*, *complete*, or *closed*, and a subshell having a smaller number of electrons is *unfilled*, *incomplete*, or *open*. The $3p^6$ configuration thus represents a full subshell and $3s^2 3p^6 3d^{10}$ represents a full shell for $n = 3$.

The *parity* of a configuration is *even* or *odd* according to whether $\sum_i l_i$ is even or odd, the sum being taken over all electrons (in practice only those in open subshells need be considered).

4. HYDROGEN AND HYDROGEN-LIKE IONS

The quantum numbers n, l , and j are appropriate [4]. A particular *level* is denoted either by nl_j or by nl^2L_J with $L = l$ and $J = j$. The latter notation is somewhat redundant for one-electron spectra, but is useful for consistency with more complex structures. The L values are written with the same letter code used for l values, but with roman capital letters. The *multiplicity* of the L term is equal to $2S + 1 = 2s + 1 = 2$. Written as a superscript, this number expresses the *doublet* character of the structure: each term for $L \geq 1$ has two levels, with $J = L \pm 1/2$, respectively.

The Coulomb interaction between the nucleus and the single electron is dominant, so that the largest energy separations are associated with levels having different n . The hyperfine splitting of the $^1\text{H } 1s$ ground level [1420.405 751 766 7(10) MHz] results from the interaction of the proton and electron magnetic moments and gives rise to the famous 21 cm line. The separations of the $2n - 1$ excited levels having the same n are largely determined by relativistic contributions, including the spin-orbit interaction, with the result that each of the $n - 1$ pairs of levels having the same j value is almost degenerate; the separation of the two levels in each pair is mainly due to relatively small Lamb shifts.

5. ALKALIS AND ALKALI-LIKE SPECTRA

In the central field approximation there exists no angular-momentum coupling between a closed subshell

and an electron outside the subshell, since the net spin and orbital angular momenta of the subshell are both zero. The nlj quantum numbers are, then, again appropriate for a single electron outside closed subshells. However, the electrostatic interactions of this electron with the core electrons and with the nucleus yield a strong l -dependence of the energy levels [5]. The differing extent of "core penetration" for ns and np electrons can in some cases, for example, give an energy difference comparable to or exceeding the difference between the np and $(n + 1)p$ levels. The spin-orbit fine-structure separation between the nl ($l > 0$) levels having $j = l - 1/2$ and $l + 1/2$, respectively, is relatively small.

6. HELIUM AND HELIUM-LIKE IONS; LS COUPLING

The energy structure of the normal $1snl$ configurations is dominated by the electron-nucleus and electron-electron Coulomb contributions [4]. In helium and in helium-like ions of the lighter elements, the separations of levels having the same n and having $l = s, p$, or d are mainly determined by direct and exchange electrostatic interactions between the electrons - the spin-orbit, spin-other orbit, and other relativistic contributions are much smaller. This is the condition for LS coupling, in which:

(a) The orbital angular momenta of the electrons are coupled to give a total orbital angular momentum $\mathbf{L} = \sum_i \mathbf{l}_i$.

(b) The spins of the electrons are coupled to give a total spin $\mathbf{S} = \sum_i \mathbf{s}_i$.

The combination of a particular S value with a particular L value comprises a spectroscopic *term*, the notation for which is ^{2S+1}L . The quantum number $2S + 1$ is the *multiplicity* of the term. The \mathbf{S} and \mathbf{L} vectors are coupled to obtain the total angular momentum, $\mathbf{J} = \mathbf{S} + \mathbf{L}$, for a *level* of the term; the level is denoted as $^{2S+1}L_J$.

For $1snl$ configurations, $L = l$ and $S = 0$ or 1 , i.e., the terms are *singlets* ($S = 0$) or *triplets* ($S = 1$). As examples of the He I structure, the ionization energy (energy required to remove one of the $1s$ electrons in the $1s^2$ ground configuration) is 24.5874 eV, the $1s2s\ ^3S - ^1S$ separation is 0.7962 eV, the $1s2p\ ^3P^\circ - ^1P^\circ$ separation is 0.2539 eV, and the $1s2p\ ^3P^\circ_2 - ^3P^\circ_0$ fine-structure spread is only 1.32×10^{-4} eV.

7. HIERARCHY OF ATOMIC STRUCTURE IN LS COUPLING

The centrality of LS coupling in the analysis and theoretical interpretation of atomic spectra has led to the acceptance of notations and nomenclature well adapted to discussions of particular structures and spectra [2]. The main elements of the nomenclature are shown in the table below, most of the structural entities having already been defined in the above discussions of simple spectra. The quantum numbers in the table represent a full description for complex configurations, and the accepted names for transitions between

the structural elements are also given.

Atomic structural hierarchy in *LS* coupling and names for the groups of all transitions between structural entities.

Structural entity	Quantum numbers ^a	Group of all transitions
Configuration	$(n,l_i)^{N_i}$	Transition array
Polyad	$(n,l_i)^{N_i} \gamma S_I L_I n l S L, S L' \dots$	Supermultiplet
Term	$(n,l_i)^{N_i} \gamma S L$	Multiplet
Level	$(n,l_i)^{N_i} \gamma S L J$	Line
State	$(n,l_i)^{N_i} \gamma S L J M$	Line component

^aThe configuration may include several open subshells, as indicated by the *i* subscripts. The letter γ represents any additional quantum numbers, such as ancestral terms, necessary to specify a particular term.

As an example, the Ca I $3d4p\ ^3D^\circ_2$ *level* belongs to the $^3D^\circ$ *term* which, in turn, belongs to the $3d4p\ ^3(P^\circ D^\circ F^\circ)$ triplet *triad*. The $3d4p$ *configuration* also has a $^1(P^\circ D^\circ F^\circ)$ singlet *triad*. The $3d4s$ configuration has only *monads*, one 1D and one 3D . The $3d4s\ ^3D_2 - 3d4p\ ^3D^\circ_3$ *line* belongs to the corresponding $^3D - ^3D^\circ$ triplet *multiplet*, and this multiplet belongs to the great Ca I $3d4s\ ^3D - 3d4p\ ^3(P^\circ D^\circ F^\circ)$ *supermultiplet* of three triplet multiplets discussed by Russell and Saunders in their classic paper on the alkaline-earth spectra [6]. The $3d4s - 3d4p$ *transition array* includes both the singlet and triplet supermultiplets, as well as any (*LS*-forbidden) *intercombination* or *intersystem* lines arising from transitions between levels of the singlet *system* and those of the triplet *system*. The order of the two terms in the transitions as written above, with the lower-energy term on the left, is standard in atomic spectroscopy. Examples of notations for complex configurations are given in [Notations for Different Coupling Schemes](#).

8. ALLOWED TERMS OR LEVELS FOR EQUIVALENT ELECTRONS

• *LS* Coupling

The allowed *LS* terms of a configuration consisting of two nonequivalent groups of electrons are obtained by coupling the *S* and *L* vectors of the groups in all possible ways, and the procedure may be extended to any number of such groups. Thus the allowed terms for any configuration can be

obtained from a table of the allowed terms for groups of equivalent electrons.

The configuration l^N has more than one allowed term of certain LS types if $l > 1$ and $2 < N < 4l$ ($d^3 - d^7, f^3 - f^{11}$, etc.). The recurring terms of a particular LS term type from d^N and f^N configurations are assigned sequential index numbers in the tables of Nielson and Koster [7]; the index numbers stand for additional numbers having group-theoretical significance that serve to differentiate the recurring terms, except for a few terms of f^5 and f^9, f^6 and f^8 , and f^7 . These remaining terms, which occur only in pairs, are further labeled A or B to indicate Racah's separation of the two terms.

The index numbers of Nielson and Koster are in practice the most frequently used labels for the recurring terms of f^N configurations. Use of their index numbers for the recurring terms of d^N configurations has perhaps the disadvantage of substituting an arbitrary number for a quantum number (the seniority) that itself distinguishes the recurring terms in all cases. The actual value of the seniority number is rarely needed, however, and a consistent notation for the d^N and f^N configurations is desirable. A table of the allowed LS terms of the l^N electrons for $l \leq 3$ is given in Ref. [8], with all recurring terms having the index numbers of Nielson and Koster as a following on-line integer. The theoretical group labels are also listed. Thus the $d^3 {}^2D$ term having seniority 3 is designated 2D_2 , instead of 2D , in this scheme; and the level having $J = 3/2$ is designated ${}^2D_{3/2}$.

• *jj* Coupling

The allowed J values for a group of N equivalent electrons having the same j value, l_j^N , are given in the table below for $j = 1/2, 3/2, 5/2$, and $7/2$ (sufficient for $l \leq 3$). The $l_{7/2}^4$ group has two allowed levels for each of the J values 2 and 4. The subscripts distinguishing the two levels in each case are the seniority numbers [9].

Allowed J values for l_j^N equivalent electrons (jj coupling).

l_j^N	Allowed J values
$l_{1/2}$	$1/2$
$l_{1/2}^2$	0
$l_{3/2}$ and $l_{3/2}^3$	$3/2$
$l_{3/2}^2$	0, 2
$l_{3/2}^4$	0
$l_{5/2}$ and $l_{5/2}^5$	$5/2$
$l_{5/2}^2$ and $l_{5/2}^4$	0, 2, 4
$l_{5/2}^3$	$3/2, 5/2, 9/2$
$l_{5/2}^6$	0
$l_{7/2}$ and $l_{7/2}^7$	$7/2$
$l_{7/2}^2$ and $l_{7/2}^6$	0, 2, 4, 6
$l_{7/2}^3$ and $l_{7/2}^5$	$3/2, 5/2, 7/2, 9/2, 11/2, 15/2$
$l_{7/2}^4$	0, $2^2, 4^2, 2^4, 4^4, 5, 6, 8$
$l_{7/2}^8$	0

The allowed levels of the configuration nl^N may be obtained by dividing the electrons into sets of two groups $nl_{i+1/2}^Q nl_{i-1/2}^R$, $Q + R = N$. The possible sets run from $Q = N - 2l$ (or zero if $N < 2l$) up to $Q = N$ or $Q = 2l + 2$, whichever is smaller. The (degenerate) levels for a set with both Q and R nonzero have wave functions defined by the quantum numbers $(\alpha J_1, \beta J_2) J$, with J_1 and J_2 deriving from the Q and R groups, respectively. The symbols α and β represent any additional quantum numbers required to identify levels. The J values of the allowed levels for each $(\alpha J_1, \beta J_2)$ subset are obtained by combining J_1 and J_2 in the usual way.

9. NOTATIONS FOR DIFFERENT COUPLING SCHEMES

The following examples make clear the meaning of the different coupling-scheme notations. Not all the

configurations in the examples have been identified experimentally, and some of the examples of a particular coupling scheme given for heuristic purposes may be physically inappropriate. Cowan [3] describes the physical conditions for the different coupling schemes and gives experimental examples.

• *LS* Coupling (Russell-Saunders Coupling)

Some of the examples given below indicate notations bearing on the order of coupling of the electrons.

1. $3d^7\ ^4F_{7/2}$
2. $3d^7(^4F)4s4p(^3P^\circ)\ ^6F^\circ_{9/2}$
3. $4f^7(^8S^\circ)6s6p^2(^4P)\ ^{11}P^\circ_5$
4. $3p^5(^2P^\circ)3d^2(^1G)\ ^2F^\circ_{7/2}$
5. $4f^{10}(^3K2)6s6p(^1P^\circ)\ ^3L^\circ_6$
6. $4f^7(^8S^\circ)5d\ (^7D^\circ)6p\ ^8F^\circ_{13/2}$
7. $4f^7(^8S^\circ)5d\ (^9D^\circ)6s\ (^8D^\circ)7s\ ^9D^\circ_5$
8. $4f^7(^8S^\circ)5d\ (^9D^\circ)6s6p(^3P^\circ)\ ^{11}F_8$
9. $4f^7(^8S^\circ)5d\ ^2(^1G)\ (^8G^\circ)6p\ ^7F_0$
10. $4f(^2F^\circ)5d\ ^2(^1G)6s\ (^2G)\ ^1P^\circ_1$

In the second example, the seven $3d$ electrons couple to give a 4F term, and the $4s$ and $4p$ electrons couple to form the $^3P^\circ$ term; the final $^6F^\circ$ term is one of nine possible terms obtained by coupling the 4F grandparent and $^3P^\circ$ parent terms. The next three examples are similar to the second. The meaning of the index number 2 following the 3K symbol in the fifth example is explained in the section [LS Coupling](#).

The coupling in example 6 is appropriate if the interaction of the $5d$ and $4f$ electrons is sufficiently stronger than the $5d$ - $6p$ interaction. The $^7D^\circ$ parent term results from coupling the $5d$ electron to the $^8S^\circ$ grandparent, and the $6p$ electron is then coupled to the $^7D^\circ$ parent to form the final 8F term. A space is inserted between the $5d$ electron and the $^7D^\circ$ parent to emphasize that the latter is formed by coupling a term ($^8S^\circ$) listed to the left of the space. Example 7 illustrates a similar coupling order carried to a further stage; the $^8D^\circ$ parent term results from the coupling of the $6s$ electron to the $^9D^\circ$ grandparent.

Example 8 is similar to examples 2 through 5, but in 8 the first of the two terms that couple to form the final ^{11}F term, i.e., the $^9D^\circ$ term, is itself formed by the coupling of the $5d$ electron to the $^8S^\circ$ core term. Example 9 shows an $^8G^\circ$ parent term formed by coupling the $^8S^\circ$ and 1G grandparent terms. A space is again used to emphasize that the following ($^8G^\circ$) term is formed by the coupling of terms listed before the space.

A different order of coupling is indicated in the final example, the $5d^2\ ^1G$ term being coupled first to the external $6s$ electron instead of directly to the $4f$ core electron. The $4f(^2F^\circ)$ core term is

isolated by a space to denote that it is coupled (to the $5d^2(^1G)6s^2G$ term) only after the other electrons have been coupled. The notation in this particular case (with a single $4f$ electron) could be simplified by writing the $4f$ electron after the 2G term to which it is coupled. It appears more important, however, to retain the convention of giving the core portion of the configuration first.

The notations in examples 1 through 5 are in the form recommended by Russell, Shenstone, and Turner [10], and used in both the *Atomic Energy States* [11] and *Atomic Energy Levels* [8], [12] compilations. The spacings used in the remaining examples allow different orders of coupling of the electrons to be indicated without the use of additional parentheses, brackets, etc.

Some authors assign a short name to each (final) term, so that the configuration can be omitted in tables of classified lines, etc. The most common scheme distinguishes the low terms of a particular *SL* type by the prefixes *a*, *b*, *c*, ..., and the high terms by *z*, *y*, *x*, ... [12].

• *jj* Coupling of Equivalent Electrons

This scheme is used, for example, in relativistic calculations. The lower-case *j* indicates the angular momentum of one electron ($j = l \pm 1/2$) or of each electron in an l_j^N group. Various ways of indicating which of the two possible *j* values applies to such a group without writing the *j*-value subscript have been used by different authors; we give the *j* values explicitly in the examples below. We use the symbols J_i and *J* to represent total angular momenta.

1. $(6p^2_{1/2})_0$
2. $(6p^2_{1/2} 6p^2_{3/2})^\circ_{3/2}$
3. $(6p^2_{1/2} 6p^2_{3/2})_2$
4. $4d^3_{5/2} 4d^2_{3/2} (^{9/2}, 2)_{11/2}$

The relatively large spin-orbit interaction of the $6p$ electrons produces *jj*-coupling structures for the $6p^2$, $6p^3$, and $6p^4$ ground configurations of neutral Pb, Bi, and Po, respectively; the notations for the ground levels of these atoms are given as the first three examples above. The configuration in the first example shows the notation for equivalent electrons having the same *j* value l_j^N , in this case two $6p$ electrons each having $j = 1/2$. A convenient notation for a particular level ($J = 0$) of such a group is also indicated. The second example extends this notation to the case of a $6p^3$ configuration divided into two groups according to the two possible *j* values. A similar notation is shown for the $6p^4$ level in the third example; this level might also be designated $(6p^{-2}_{3/2})_2$, the negative superscript indicating the two $6p$ holes. The $(J_1, J_2)_J$ term and level notation shown on the right in the fourth example is convenient because each of the two electron groups $4d^3_{5/2}$ and $4d^2_{3/2}$ has more than one allowed total J_i value. The assumed convention is that J_1 applies to the group on the left ($J_1 = 9/2$ for the $4d^3_{5/2}$ group) and J_2 to that on the right.

• $J_1 j$ or $J_1 J_2$ Coupling

1. $3d^9(^2D_{5/2})4p_{3/2} (^{5/2}, ^{3/2})^\circ_3$
2. $4f^{11}(^2H^\circ_{9/2} 2)6s6p(^3P^\circ_1) (^{9/2}, 1)_{7/2}$
3. $4f^9(^6H^\circ)5d (^7H^\circ_8)6s6p(^3P^\circ_0) (8,0)_8$
4. $4f^{12}(^3H_6) 5d(^2D)6s6p(^3P^\circ) (^4F^\circ_{3/2}) (6, ^{3/2})^\circ_{13/2}$
5. $5f^4(^5I_4)6d_{3/2} (4, ^{3/2})_{11/2} 7s7p(^1P^\circ_1) (^{11/2}, 1)^\circ_{9/2}$
6. $5f^4_{7/2} 5f^5_{5/2} (8, ^{5/2})^\circ_{21/2} 7p_{3/2} (^{21/2}, ^{3/2})_{10}$
7. $5f^3_{7/2} 5f^3_{5/2} (^{9/2}, ^{9/2})_9 7s7p(^3P^\circ_2) (9,2)^\circ_7$

The first five examples all have core electrons in LS coupling, whereas jj coupling is indicated for the $5f$ core electrons in the last two examples. Since the J_1 and J_2 values in the final (J_1, J_2) term have already been given as subscripts in the configuration, the (J_1, J_2) term notations are redundant in all these examples. Unless separation of the configuration and final term designations is desired, as in some data tables, one may obtain a more concise notation by simply enclosing the entire configuration in brackets and adding the final J value as a subscript. Thus, the level in the first example can be designated as $[3d^9(^2D_{5/2}) 4p_{3/2}]^\circ_3$. If the configuration and coupling order are assumed to be known, still shorter designations may be used; for example, the fourth level above might then be given as $[(^3H_6) (^3P^\circ) (^4F^\circ_{3/2})]_{13/2}$ or $(^3H_6, ^3P^\circ, ^4F^\circ_{3/2})_{13/2}$. Similar economies of notation are of course possible, and often useful, in all coupling schemes.

• $J_1 l$ or $J_1 L_2$ Coupling ($J_1 K$ Coupling)

1. $3p^5(^2P^\circ_{1/2})5g \ ^2[{}^9/2]^\circ_5$
2. $4f^2(^3H_4)5g \ ^2[3]_{5/2}$
3. $4f^{13}(^2F^\circ_{7/2})5d^2(^1D) \ ^1[{}^7/2]^\circ_{7/2}$
4. $4f^{13}(^2F^\circ_{5/2})5d6s(^3D) \ ^3[{}^9/2]^\circ_{11/2}$

The final terms in the first two examples result from coupling a parent-level J_1 to the orbital angular momentum of a $5g$ electron to obtain a resultant K , the K value being enclosed in brackets. The spin of the external electron is then coupled with the K angular momentum to obtain a pair of J values, $J = K \pm 1/2$ (for $K \neq 0$). The multiplicity (2) of such pair terms is usually omitted from the term symbol, but other multiplicities occur in the more general $J_1 L_2$ coupling (examples 3 and 4). The last two examples are straightforward extensions of $J_1 l$ coupling, with the L_2 and S_2 momenta of the "external" term (1D and 3D in examples 3 and 4, respectively) replacing the l and s momenta of a single external electron.

• LS_1 Coupling (LK Coupling)

1. $3s^23p(^2P^\circ)4f\ G\ ^2[7/2]_3$
2. $3d^7(^4P)4s4p(^3P^\circ)\ D^\circ\ ^3[5/2]^\circ_{7/2}$

The orbital angular momentum of the core is coupled with the orbital angular momentum of the external electron(s) to give the total orbital angular momentum L . The letter symbol for the final L value is listed with the configuration because this angular momentum is then coupled with the spin of the core (S_1) to obtain the resultant K angular momentum of the final term (in brackets). The multiplicity of the $[K]$ term arises from the spin of the external electron(s).

• **Coupling Schemes and Term Symbols**

The coupling schemes outlined above include those now most frequently used in calculations of atomic structure [3]. Any term symbol gives the values of two angular momenta that may be coupled to give the total electronic angular momentum of a level (indicated by the J value). For configurations of more than one unfilled subshell, the angular momenta involved in the final coupling derive from two groups of electrons (either group may consist of only one electron). These are often an inner group of coupled electrons and an outer group of coupled electrons, respectively. In any case the quantum numbers for the two groups can be distinguished by subscripts 1 and 2, so that quantum numbers represented by capital letters without subscripts are total quantum numbers for both groups. Thus, the quantum numbers for the two vectors that couple to give the final J are related to the term symbol as follows:

Coupling Scheme	Quantum numbers for vectors that couple to give J	Term Symbol
LS	L, S	$2S+1_L$
$J_1 J_2$	J_1, J_2	(J_1, J_2)
$J_1 L_2(\rightarrow K)$	K, S_2	$2S_2+1[K]$
$LS_1(\rightarrow K)$	K, S_2	$2S_2+1[K]$

The parity is indicated by appended degree symbols on odd parity terms.

10. EIGENVECTOR COMPOSITION OF LEVELS

The wave functions of levels are often expressed as eigenvectors that are linear combinations of basis states in one of the standard coupling schemes. Thus, the wave function $\Psi(\alpha J)$ for a level labeled αJ might be expressed in terms of normalized LS coupling basis states $\Phi(\gamma SLJ)$:

$$\Psi(\alpha J) = \sum_{\gamma SL} c(\gamma SLJ) \Phi(\gamma SLJ). \quad (4)$$

The $c(\gamma SLJ)$ are expansion coefficients, and

$$\sum_{\gamma SL} |c(\gamma SLJ)|^2 = 1. \quad (5)$$

The squared expansion coefficients for the various γSL terms in the composition of the αJ level are conveniently expressed as percentages, whose sum is 100%. Thus the percentage contributed by the pure Russell-Saunders state γSLJ is equal to $100 \times |c(\gamma SLJ)|^2$. The notation for Russell-Saunders basis states has been used only for concreteness; the eigenvectors may be expressed in any coupling scheme, and the coupling schemes may be different for different configurations included in a single calculation (with configuration interaction). "Intermediate coupling" conditions for a configuration are such that calculations in both LS and jj coupling yield some eigenvectors representing significant mixtures of basis states.

The largest percentage in the composition of a level is called the *purity* of the level in that coupling scheme. The coupling scheme (or combination of coupling schemes if more than one configuration is involved) that results in the largest average purity for all the levels in a calculation is usually best for naming the levels. With regard to any particular calculation, one does well to remember that, as with other calculated quantities, the resulting eigenvectors depend on a specific theoretical model and are subject to the inaccuracies of whatever approximations the model involves.

Theoretical calculations of experimental energy level structures have yielded many eigenvectors having significantly less than 50% purity in any coupling scheme. Since many of the corresponding levels have nevertheless been assigned names by spectroscopists, some caution is advisable in the acceptance of level designations found in the literature.

11. GROUND LEVELS AND IONIZATION ENERGIES FOR THE NEUTRAL ATOMS

Table of Ground Levels and Ionization Energies for the Neutral Atoms

When using the above table, be sure to use your "[Back](#)" button to return to this document.

The ground-state electron configurations of elements heavier than neon are shortened in the table by using rare-gas element symbols in brackets to represent the corresponding electrons. The ground levels of all neutral atoms have reasonably meaningful LS -coupling names, the corresponding eigenvector percentages lying in the range from ~55 % to 100 %. These names are listed in the table, except for Pa, U, and Np; the lowest few ground-configuration levels of these atoms comprise better $5f^N(L_1 S_1 J_1)$, $6d;7s^2(J_1 j)$ terms than LS -coupling terms. The relatively large spin-orbit interaction of the $6p$ electrons produces jj -coupling structures for the $(6p^2_{1/2})_0$, $(6p^2_{1/2}6p_{3/2})^o_{3/2}$, and $(6p^2_{1/2}6p^2_{3/2})_2$ ground levels of the $6p^2$, $6p^3$, and $6p^4$ configurations of neutral Pb, Bi, and Po, respectively. As noted in the section [jj Coupling of Equivalent Electrons](#), the jj -coupling names are more appropriate for these atoms than the alternative LS -coupling designations in the table.

The ionization energies in the table are based on a recent survey of the literature [\[13\]](#). The uncertainties

are mainly in the range from less than one to several units in the last decimal place, but a few of the values may be in error by 20 or more units in the final place; i.e., the error of some of the two place values could be greater than 0.2 eV. Estimated uncertainties of the ionization energies are usually given in the references. Although no more than four decimal places are given, the accuracies of some of the better known values would, in eV units, be limited only by the uncertainty in the conversion factor, $1.239\,842\,44(37) \times 10^{-4} \text{ eV/cm}^{-1}$.

12. ZEEMAN EFFECT

The Zeeman effect for "weak" magnetic fields (the anomalous Zeeman effect) is of special interest because of the importance of Zeeman data in the analysis and theoretical interpretation of complex spectra. In a weak field, the J value remains a good quantum number although in general a level is split into magnetic sublevels [3]. The g value of such a level may be defined by the expression for the energy shift of its magnetic sublevel having magnetic quantum number M , which has one of the $2J + 1$ values, $-J, -J + 1, \dots, J$:

$$\Delta E = gM \mu_B B \quad . \quad (6)$$

The magnetic flux density is B , and μ_B is the Bohr magneton ($\mu_B = e\hbar/2m_e$).

The wavenumber shift $\Delta\sigma$ corresponding to this energy shift is

$$\Delta\sigma = gM(0.466\,86\,B \text{ cm}^{-1}) \quad , \quad (7)$$

with B representing the numerical value of the magnetic flux density in teslas. The quantity in parentheses, the Lorentz unit, is of the order of 1 or 2 cm^{-1} for typical flux densities used to obtain Zeeman-effect data with classical spectroscopic methods. Accurate data can be obtained with much smaller fields, of course, by using higher-resolution techniques such as laser spectroscopy. Most of the g values now available for atomic energy levels were derived by application of the above formula (for each of the two combining levels) to measurements of optical Zeeman patterns. A single transverse-Zeeman-effect pattern (two polarizations, resolved components, and sufficiently complete) can yield the J value and the g value for each of the two levels involved.

Neglecting a number of higher-order effects, we can evaluate the g value of a level βJ belonging to a pure LS -coupling term using the formula

$$g_{\beta SLJ} = 1 + (g_e - 1) \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad . \quad (8)$$

The independence of this expression from any other quantum numbers (represented by β) such as the configuration, etc., is important. The expression is derived from vector coupling formulas by assuming a g value of unity for a pure orbital angular momentum and writing the g value for a pure electron spin as g_e [14]. A value of 2 for g_e yields the Landé formula. If the anomalous magnetic moment of the electron is taken into account, the value of g_e is 2.002 319 3. "Schwinger" g values obtained with this more accurate value for g_e are given for levels of SL terms in Ref. [8].

The usefulness of g_{SLJ} values is enhanced by their relation to the g values in intermediate coupling. In the notation used in Eq. (4) for the wave function of a level βJ in intermediate coupling, the corresponding g value is given by

$$g_{\beta J} = \sum_{\gamma SL} g_{SLJ} |c(\gamma SLJ)|^2, \quad (9)$$

where the summation is over the same set of quantum numbers as for the wave function. The $g_{\beta J}$ value is thus a weighted average of the Landé g_{SLJ} values, the weighting factors being just the corresponding component percentages.

Formulas for magnetic splitting factors in the $J_1 J_2$ and $J_1 L_2$ coupling schemes are given in Refs. [8] and [14]. Some higher-order effects that must be included in more accurate Zeeman-effect calculations are treated by Bethe and Salpeter [4] and by Wybourne [14], for example. High precision calculations for helium are given in Ref. [15].

13. TERM SERIES, QUANTUM DEFECTS, AND SPECTRAL-LINE SERIES

The Bohr energy levels for hydrogen or for a hydrogenic (one-electron) ion are given by

$$E_n = -\frac{Z^2}{n^2}, \quad (10)$$

in units of R_M , the Rydberg for the appropriate nuclear mass. For a multielectron atom, the deviations of a series of (core) nl levels from hydrogenic E_n values may be due mainly to core penetration by the nl electron (low l -value series), or core polarization by the nl electron (high l -value series), or a combination of the two effects. In either case it can be shown that these deviations can be approximately represented by a constant quantum defect δ_l in the Rydberg formula,

$$E_{nl} = -\frac{Z_c^2}{(n - \delta_l)^2} = -\frac{Z_c^2}{(n^*)^2}, \quad (11)$$

where Z_c is the charge of the core and $n^* = n - \delta$ is the effective principal quantum number. If the core includes only closed subshells, the E_{nl} values are with respect to a value of zero for the (core) 1S_0 level, i.e., the 1S_0 level is the limit of the (core) nl series. If the quantities in Eq. (11) are taken as positive, they represent term values or ionization energies; the term value of the ground level of an atom or ion with respect to the ground level of the next higher ion is thus the principal ionization energy.

If the core has one or more open subshells, the series limit may be the baricenter of the entire core configuration, or any appropriate sub-structure of the core, down to and including a single level. The E_{nl} values refer to the series of corresponding (core) nl structures built on the particular limit structure. The value of the quantum defect depends to some extent on which (core) nl structures are represented by the series formula.

The quantum defect in general also has an energy dependence that must be taken into account if lower members of a series are to be accurately represented by Eq. (11). For an unperturbed series, this

dependence can be expressed by the extended Ritz formula

$$\delta = n - n^* \quad (12)$$

$$= \delta_0 + \frac{a}{(n - \delta_0)^2} + \frac{b}{(n - \delta_0)^4} + \dots,$$

with δ_0, a, b, \dots constants for the series (δ_0 being the limit value of the quantum defect for high series members) [16]. The value of a is usually positive for core-penetration series and negative for core-polarization series. A discussion of the foundations of the Ritz expansion and application to high precision calculations in helium is given in Ref. [17].

A spectral-line series results from either emission or absorption transitions involving a common lower level and a series of successive (core) nl upper levels differing only in their n values. The principal series of Na I, $3s^2S_{1/2} - np^2P^{\circ}_{1/2,3/2}$ ($n \geq 3$) is an example. The regularity of successive upper term values with increasing n [Eqs. (11), (12)] is of course observed in line series; the intervals between successive lines decrease in a regular manner towards higher wavenumbers, and the series of increasing wavenumbers converges towards the term value of the lower level as a limit.

14. SEQUENCES

Several types of sequences of elements and/or ionization stages are useful because of regularities in the progressive values of parameters relating to structure and other properties along the sequences. All sequence names may refer either to the atoms and/or ions of the sequence or to their spectra.

• Isoelectronic Sequence

A neutral atom and those ions of other elements having the same number of electrons as the atom comprise an isoelectronic sequence. (Note that a negative ion having this number of electrons is a member of the sequence.) An isoelectronic sequence is named according to its neutral member; for example, the Na I isoelectronic sequence.

• Isoionic, Isonuclear, and Homologous Sequences

An isoionic sequence comprises atoms or ions of different elements having the same charge. Such sequences have probably been most useful along the d - and f -shell rows of the periodic table. Isoionic analyses have also been carried out along p -shell rows, however, and a fine-structure regularity covering spectra of the p -shell atoms throughout the periodic table is known [18].

The atom and successive ions of a particular element comprise the isonuclear sequence for that element.

The elements of a particular column and subgroup in the periodic table are homologous. Thus the C, Si, Ge, Sn, and Pb atoms belong to a homologous sequence having np^2 ground configurations (see [Table of Ground Levels and Ionization Energies for the Neutral Atoms](#)). The singly ionized atoms of

these elements comprise another example of a homologous sequence.

15. SPECTRAL WAVELENGTH RANGES, DISPERSION OF AIR

The ranges of most interest for optical atomic spectroscopy are:

~ 2 - 20 μm	mid-infrared (ir)
700 - 2000 nm	near ir
400 - 700 nm	visible
200 - 400 nm	near ultraviolet (uv)
100 - 200 nm	vacuum uv or far uv
10 - 100 nm	extreme uv (euv or xuv)
< 10 nm	soft x-ray, x-ray

The above correspondence of names to ranges should not be taken as exact; the variation as to the extent of some of the named ranges found in the literature is considerable.

Wavelengths in standard air are often tabulated for the region longer than 200 nm. These wavelengths can be related to energy-level differences by conversion to the corresponding (vacuum) wavenumbers or frequencies [19].

16. WAVELENGTH (FREQUENCY) STANDARDS

In 1992 the Comité International des Poids et Mesures recommended values for six frequencies for the absorbing molecule $^{127}\text{I}_2$ (515 nm to 640 nm), one frequency for the ^{40}Ca atom (657 nm), and one for methane (3.39 μm) as standards for suitably stabilized lasers [20]. These frequencies range from 88 376 181.600 18 MHz (3.392 231 397 327 μm , fractional uncertainty 3×10^{-12}) for a particular hyperfine-structure (hfs) component in methane to 582 490 603.37 MHz (514.673 466 4 nm, fractional uncertainty 2.5×10^{-10}) for a particular hfs component in $^{127}\text{I}_2$. Reference [20] also gives accurate values for hfs frequency intervals in $^{127}\text{I}_2$ that connect each of the six standard frequencies to other hfs components of the same or nearby transitions.

Extensive tables of wavenumbers for molecular transitions in the mid-ir range 2.3 μm to 20.5 μm are included in a calibration atlas published in 1991 [21]. Measurements of U and Th lines (575 to 692 nm)

suitable for wavenumber calibration at uncertainty levels of 0.0003 cm⁻¹ or 0.0004 cm⁻¹ were reported in Ref. [22]. Comprehensive tables of lines for U [23], Th [24], and I₂ [25] are useful for calibration at uncertainty levels of 0.002 cm⁻¹ to 0.003 cm⁻¹, the atlas of the Th spectrum extending down to 278 nm.

A 1974 compilation gives reference wavelengths for some 5400 lines of 38 elements covering the range 1.5 nm to 2.5 μm, with most uncertainties between 10⁻⁵ and 2 × 10⁻⁴ nm [26]. Norlén's tables of Ar I and Ar II wavelengths range from 156 nm to 2.4 μm, with uncertainties of 1 to 3 × 10⁻⁵ nm for the more accurate wavelengths shorter than ~ 850 nm [27]. The wavelengths for some 1100 Fe lines selected from the Fe/Ne hollow-cathode spectrum have been recommended for reference standards over the range 183 nm to 4.2 μm, with wavenumber uncertainties 0.001 cm⁻¹ to 0.002 cm⁻¹ [28]. Wavelengths for about 3000 vuv and uv lines (110 to 400 nm) from a Pt/Ne hollow-cathode lamp have been determined with uncertainties of 0.0002 nm or less [29].

17. SPECTRAL LINES: SELECTION RULES, INTENSITIES, TRANSITION PROBABILITIES, VALUES, AND LINE STRENGTHS

Selection rules for discrete transitions.

		Electric dipole (E1) ("allowed")	Magnetic dipole (M1) ("forbidden")	Electric quadrupole (E2) ("forbidden")
Rigorous rules	1.	$\Delta J = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta J = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta J = 0, \pm 1, \pm 2$ (except $0 \nleftrightarrow 0$, $1/2 \nleftrightarrow 1/2$, $0 \nleftrightarrow 1$)
	2.	$\Delta M = 0, \pm 1$ (except $0 \nleftrightarrow 0$ when $\Delta J = 0$)	$\Delta M = 0, \pm 1$ (except $0 \nleftrightarrow 0$ when $\Delta J = 0$)	$\Delta M = 0, \pm 1, \pm 2$
	3.	Parity change	No parity change	No parity change
With negligible configuration interaction	4.	One electron jumping, with $\Delta l = \pm 1$, Δn arbitrary	No change in electron configuration; i.e., for all electrons, $\Delta l = 0$, $\Delta n = 0$	No change in electron configuration; <i>or</i> one electron jumping with $\Delta l = 0, \pm 2$, Δn arbitrary
For <i>LS</i> coupling only	5.	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
	6.	$\Delta L = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta L = 0$ $\Delta J = \pm 1$	$\Delta L = 0, \pm 1, \pm 2$ (except $0 \nleftrightarrow 0$, $0 \nleftrightarrow 1$)

• Emission Intensities (Transition Probabilities)

The total power ϵ radiated in a spectral line of frequency ν per unit source volume and per unit solid angle is

$$\epsilon_{\text{line}} = (4\pi)^{-1} h\nu A_{ki} N_k, \quad (13)$$

where A_{ki} is the atomic transition probability and N_k the number per unit volume (number density) of excited atoms in the upper (initial) level k . For a homogeneous light source of length l and for the optically thin case, where all radiation escapes, the total emitted line intensity (SI quantity: radiance) is

$$\begin{aligned} I_{\text{line}} &= \epsilon_{\text{line}} l = \int_0^{+\infty} I(\lambda) d\lambda \\ &= (4\pi)^{-1} (hc/\lambda_0) A_{ki} N_k l, \end{aligned} \quad (14)$$

where $I(\lambda)$ is the specific intensity at wavelength λ , and λ_0 the wavelength at line center.

• Absorption f values

In absorption, the reduced absorption

$$W(\lambda) = [I(\lambda) - P(\lambda)]/I(\lambda) \quad (15)$$

is used, where $I(\lambda)$ is the incident intensity at wavelength λ , e.g., from a source providing a continuous background, and $P(\lambda)$ the intensity after passage through the absorbing medium. The reduced line intensity from a homogeneous and optically thin absorbing medium of length l follows as

$$W_{ik} = \int_0^{+\infty} W(\lambda) d\lambda = \frac{e^2}{4\epsilon_0 m_e c^2} \lambda_0^2 N_i f_{ik} l, \quad (16)$$

where f_{ik} is the atomic (absorption) oscillator strength (dimensionless).

• Line Strengths

A_{ki} and f_{ik} are the principal atomic quantities related to line intensities. In theoretical work, the *line strength* S is also widely used (see *Atomic, Molecular, & Optical Physics Handbook*, Chap. 21, ed. by G.W.F. Drake (AIP, Woodbury, NY, 1996):

$$S = S(i, k) = S(k, i) = |R_{ik}|^2, \quad (17)$$

$$R_{ik} = \langle \psi_k | P | \psi_i \rangle, \quad (18)$$

where ψ_i and ψ_k are the initial- and final-state wave functions and R_{ik} is the *transition matrix element* of the appropriate multipole operator P (R_{ik} involves an integration over spatial and spin coordinates of all N electrons of the atom or ion).

• Relationships between A , f , and S

The relationships between A , f , and S for electric dipole (E1, or allowed) transitions in SI units (A in s^{-1} , λ in m, S in $m^2 C^2$) are

$$A_{ki} = \frac{2\pi e^2}{m_e c \epsilon_0 \lambda^2} \frac{g_i}{g_k} f_{ik} = \frac{16\pi^3}{3h \epsilon_0 \lambda^3 g_k} S, \quad (19)$$

Numerically, in customary units (A in s^{-1} , λ in Å, S in atomic units),

$$A_{ki} = \frac{6.6702 \times 10^{15}}{\lambda^2} \frac{g_i}{g_k} f_{ik} = \frac{2.0261 \times 10^{18}}{\lambda^3 g_k} S, \quad (20)$$

and for S and ΔE in atomic units,

$$f_{ik} = \frac{2}{3} (\Delta E / g_i) S. \quad (21)$$

g_i and g_k are the statistical weights, which are obtained from the appropriate angular momentum quantum numbers. Thus for the lower (upper) level of a spectral line, $g_{i(k)} = 2J_{i(k)} + 1$, and for the lower (upper) term of a multiplet,

$$\begin{aligned} \bar{g}_{i(k)} &= \sum_{i(k)} (2J_{i(k)} + 1) \\ &= (2L_{i(k)} + 1) (2S_{i(k)} + 1). \end{aligned} \quad (22)$$

The A_{ki} values for strong lines of [selected elements](#) are given. For comprehensive numerical tables of A , f , and S , including forbidden lines (see [Sources of Spectroscopic Data](#)).

Experimental and theoretical methods to determine A , f , or S values as well as atomic lifetimes are discussed in *Atomic, Molecular, & Optical Physics Handbook*, Chaps. 17, 18, and 21, ed. by G.W.F. Drake (AIP, Woodbury, NY, 1996).

Conversion relations between S and A_{ki} for the most common forbidden transitions

	SI units ^a	Numerically, in customary units ^b
Electric quadrupole	$A_{ki} = \frac{16\pi^5}{15h \epsilon_0 \lambda^5 g_k} S$	$A_{ki} = \frac{1.1199 \times 10^{18}}{g_k \lambda^5} S$
Magnetic dipole	$A_{ki} = \frac{16\pi^3 \mu_0}{3h \lambda^3 g_k} S$	$A_{ki} = \frac{2.697 \times 10^{13}}{g_k \lambda^3} S$

^aA in s⁻¹, λ in m. Electric quadrupole: S in m⁴ C². Magnetic dipole: S in J² T⁻².

^bA in s⁻¹, λ in Å. S in atomic units: $a_0^4 e^2 = 2.013 \times 10^{-79}$ m⁴ C² (electric quadrupole), $e^2 \hbar^2 / 16\pi^2 m_e^2 = \mu_B^2 = 8.601 \times 10^{-47}$ J² T⁻² (magnetic dipole). μ_B is the Bohr magneton.

Oscillator strengths f are not used for forbidden transitions, i.e., magnetic dipole (M1), electric quadrupole (E2), etc.

[Numerical example: For the $1s2p\ ^1P_1 - 1s3d\ ^1D_2$ (allowed) transition in He I at 6678.15 Å: $g_i = 3$; $g_k = 5$; $A_{ki} = 6.38 \times 10^7$ s⁻¹; $f_{ik} = 0.711$; $S = 46.9 a_0^2 e^2$.]

• Relationships between Line and Multiplet Values

The relations between the total strength and f value of a multiplet (M) and the corresponding quantities for the lines of the multiplet (allowed transitions) are

$$S_M = \sum S_{\text{line}} \quad , \quad (23)$$

$$f_M = (\bar{\lambda} \bar{g}_i)^{-1} \sum_{J_k, J_i} g_i \lambda(J_i, J_k) f(J_i, J_k) \quad . \quad (24)$$

$\bar{\lambda}$ is the weighted ("multiplet") wavelength in vacuum:

$$\bar{\lambda} = n \bar{\lambda}_{\text{air}} = hc / \overline{\Delta E} \quad , \quad (25)$$

where

$$\overline{\Delta E} = \overline{E_k} - \overline{E_i} = (\bar{g}_k)^{-1} \sum_{J_k} g_k E_k - (\bar{g}_i)^{-1} \sum_{J_i} g_i E_i \quad , \quad (26)$$

and n is the refractive index of standard air.

• Relative Strengths for Lines of Multiplets in LS Coupling

This table lists relative line strengths for frequently encountered symmetrical ($P \rightarrow P$, $D \rightarrow D$) and normal ($S \rightarrow P$, $P \rightarrow D$) multiplets in LS coupling. The strongest, or principal, lines are situated along the main diagonal of the table and are called x_1 , x_2 , etc. Their strengths normally diminish along the diagonal. The satellite lines y_n and z_n are usually weaker and deviate more from the LS values than the stronger diagonal lines when departures from LS coupling are encountered. The total multiplet strengths S_M are also listed in this table. A discussion of their normalization as well as more extensive tables are given in Ref. [30].

Relative Strengths for Lines of Multiplets in LS Coupling

Normal multiplets S - P, P - D, D - F, etc.						Symmetrical multiplets P - P, D - D, etc.					
	J_m	$J_m - 1$	$J_m - 2$	$J_m - 3$	$J_m - 4$		J_m	$J_m - 1$	$J_m - 2$	$J_m - 3$	
$J_m - 1$	x_1	y_1	z_1			J_m	x_1	y_1			
$J_m - 2$		x_2	y_2	z_2		$J_m - 1$	y_1	x_2	y_2		
$J_m - 3$			x_3	y_3	z_3	$J_m - 2$		y_2	x_3	y_3	
$J_m - 4$				x_4	y_4	$J_m - 3$			y_3	x_4	

Multiplicity						Multiplicity					
	1	2	3	4	5		1	2	3	4	5
S - P						D - D					
$S_M =$	3	6	9	12	15	$S_M =$	25	50	75	100	125
x_1	3.00	4.00	5.00	6.00	7.00	x_1	25.00	28.00	31.11	34.29	37.50
y_1		2.00	3.00	4.00	5.00	x_2		18.00	17.36	17.29	17.50
z_1			1.00	2.00	3.00	x_3			11.25	8.00	6.25
						x_4				5.00	1.25
P - P						y_1		2.00	3.89	5.71	7.50
$S_M =$	9	18	27	36	45	y_2			3.75	7.00	10.00
x_1	9.00	10.00	11.25	12.60	14.00	y_3				5.00	8.75
x_2		4.00	2.25	1.60	1.25	y_4					5.00
x_3				1.00	2.25						
						D - F					
y_1		2.00	3.75	5.40	7.00	$S_M =$	35	70	105	140	175
y_2			3.00	5.00	6.75	x_1	35.00	40.00	45.00	50.00	55.00

P - D											
$S_M =$	15	30	45	60	75		x_2	28.00	31.11	34.29	37.50
							x_3		21.00	22.40	24.00
							x_4			14.00	14.00
x_1	15.00	18.00	21.00	24.00	27.00		x_5				7.00
x_2		10.00	11.25	12.60	14.00						
x_3			5.00	5.00	5.25		y_1	2.00	3.89	5.71	7.50
							y_2		3.89	7.31	10.50
y_1		2.00	3.75	5.40	7.00		y_3			5.60	10.00
y_2			3.75	6.40	8.75		y_4				7.00
y_3				5.60	6.75						
							z_1		.11	.29	.50
z_1			.25	.60	1.00		z_2			.40	1.00
z_2				1.00	2.25		z_3				1.00
z_3					3.00						

18. ATOMIC LIFETIMES

The radiative lifetime τ_k of an atomic level k is related to the sum of transition probabilities to all levels i lower in energy than k :

$$\tau_k = \left(\sum_i A_{ki} \right)^{-1} .$$

(27)

The *branching* ratio of a particular transition, say to state i' , is defined as

$$A_{ki'} / \sum_i A_{ki} = A_{ki'} \tau_k .$$

(28)

If only one branch (i') exists (or if all other branches may be neglected), one obtains $A_{ki'} \tau_k = 1$, and

$$\tau_k = 1/A_{ki'} .$$

(29)

Precision lifetime measurement techniques are discussed in *Atomic, Molecular, & Optical Physics Handbook*, Chaps. 17 and 18, ed. by G.W.F. Drake (AIP, Woodbury, NY, 1996).

19. REGULARITIES AND SCALING

• Transitions in Hydrogenic (One-Electron) Species

The nonrelativistic *energy* of a hydrogenic transition [Eqs. (1), (10)] is

$$(\Delta E)_Z = (E_k - E_i)_Z = R_M h c Z^2 (1/n_i^2 - 1/n_k^2). \quad (30)$$

Hydrogenic Z scaling. The spectroscopic quantities for a hydrogenic ion of nuclear charge Z are related to the equivalent quantities in hydrogen ($Z = 1$) as follows (neglecting small differences in the values of R_M):

$$(\Delta E)_Z = Z^2 (\Delta E)_H, \quad (31)$$

$$(\lambda_{\text{vac}})_Z = Z^{-2} (\lambda_{\text{vac}})_H, \quad (32)$$

$$S_Z = Z^{-2} S_H, \quad (33)$$

$$f_Z = f_H, \quad (34)$$

$$A_Z = Z^4 A_H, \quad (35)$$

For large values of Z , roughly $Z > 20$, relativistic corrections become noticeable and must be taken into account.

f-value trends. f values for high series members (large n' values) of hydrogenic ions decrease according to

$$f(n, l \rightarrow n', l \pm 1) \propto (n')^{-3}. \quad (36)$$

Data for some lines of the main spectral series of hydrogen are given in the table below.

Some transitions of the main spectral series of hydrogen

Transition	Customary name ^a	λ^b (Å)	g_i^c	g_k	A_{ki} (10^8 s^{-1})
1-2	(L $_{\alpha}$)	1 215.67	2	8	4.699
1-3	(L $_{\beta}$)	1 025.73	2	18	5.575(-1) ^d
1-4	(L $_{\gamma}$)	972.537	2	32	1.278(-1)
1-5	(L $_{\delta}$)	949.743	2	50	4.125(-2)
1-6	(L $_{\epsilon}$)	937.80	2	72	1.644(-2)
2-3	(H $_{\alpha}$)	6 562.80	8	18	4.410(-1)
2-4	(H $_{\beta}$)	4 861.32	8	32	8.419(-2)
2-5	(H $_{\gamma}$)	4 340.46	8	50	2.530(-2)
2-6	(H $_{\delta}$)	4 101.73	8	72	9.732(-3)
2-7	(H $_{\epsilon}$)	3 970.07	8	98	4.389(-3)
3-4	(P $_{\alpha}$)	18 751.0	18	32	8.986(-2)
3-5	(P $_{\beta}$)	12 818.1	18	50	2.201(-2)
3-6	(P $_{\gamma}$)	10 938.1	18	72	7.783(-3)
3-7	(P $_{\delta}$)	10 049.4	18	98	3.358(-3)
3-8	(P $_{\epsilon}$)	9 545.97	18	128	1.651(-3)

^aL $_{\alpha}$ is often called Lyman α , H $_{\alpha}$ = Balmer α , P $_{\alpha}$ = Paschen α , etc.

^bWavelengths below 2000 Å are in vacuum; values above 2000 Å are in air.

^cFor transitions in hydrogen, $g_{i(k)} = 2(n_{i(k)})^2$, where $n_{i(k)}$ is the principal quantum number of the lower (upper) electron shell.

^dThe number in parentheses indicates the power of 10 by which the value has to be multiplied.

• Systematic Trends and Regularities in Atoms and Ions with Two or More Electrons

Nonrelativistic atomic quantities for a given state or transition in an *isoelectronic sequence* may be expressed as power series expansions in Z^{-1} :

$$Z^{-2} E = E_0 + E_1 Z^{-1} + E_2 Z^{-2} + \dots, \quad (37)$$

$$Z^2 S = S_0 + S_1 Z^{-1} + S_2 Z^{-2} + \dots, \quad (38)$$

$$f = f_0 + f_1 Z^{-1} + f_2 Z^{-2} + \dots, \quad (39)$$

where E_0 , f_0 , and S_0 are hydrogenic quantities. For transitions in which n does not change ($n_i = n_k$), $f_0 = 0$, since states i and k are degenerate.

For equivalent transitions of *homologous atoms*, f values vary gradually. Transitions to be compared in the case of the "alkalis" are [31]

$$(nl - n'l')_{\text{Li}} \rightarrow [(n+1)l - (n'+1)l']_{\text{Na}} \\ \rightarrow [(n+2)l - (n'+2)l']_{\text{Cu}} \rightarrow \dots$$

Complex atomic structures, as well as cases involving strong cancellation in the integrand of the transition integral, generally do not adhere to this regular behavior.

20. SPECTRAL LINE SHAPES, WIDTHS, AND SHIFTS

Observed spectral lines are always broadened, partly due to the finite resolution of the spectrometer and partly due to intrinsic physical causes. The principal physical causes of spectral line broadening are Doppler and pressure broadening. The theoretical foundations of line broadening are discussed in *Atomic, Molecular, & Optical Physics Handbook*, Chaps. 19 and 57, ed. G.W.F. Drake (AIP, Woodbury, NY, 1996).

• Doppler Broadening

Doppler broadening is due to the thermal motion of the emitting atoms or ions. For a Maxwellian velocity distribution, the line shape is *Gaussian*; the full width at half maximum intensity (FWHM) is, in Å,

$$\Delta\lambda_{1/2}^D = (7.16 \times 10^{-7}) \lambda (T/M)^{1/2} \quad (40)$$

T is the temperature of the emitters in K, and M the atomic weight in atomic mass units (amu).

• Pressure Broadening

Pressure broadening is due to collisions of the emitters with neighboring particles [see also *Atomic, Molecular, & Optical Physics Handbook*, Chaps. 19 and 57, ed. G.W.F. Drake (AIP, Woodbury, NY, 1996)]. Shapes are often approximately Lorentzian, i.e., $I(\lambda) \propto \{1 + [(\lambda - \lambda_0)/\Delta\lambda_{1/2}]^2\}^{-1}$. In the following formulas, all FWHM's and wavelengths are expressed in Å, particle densities N in cm^{-3} , temperatures T in K, and energies E or I in cm^{-1} .

Resonance broadening (self-broadening) occurs only between identical species and is confined to lines with the upper or lower level having an electric dipole transition (resonance line) to the ground state. The FWHM may be estimated as

$$\Delta\lambda_{1/2}^R \simeq 8.6 \times 10^{-30} (g_i/g_k)^{1/2} \lambda^2 \lambda_r f_r N_i \quad (41)$$

where λ is the wavelength of the observed line. f_r and λ_r are the oscillator strength and wavelength of the resonance line; g_k and g_i are the statistical weights of its upper and lower levels. N_i is the ground state number density.

For the $1s2p \ ^1P_1^o - 1s3d \ ^1D_2$ transition in He I [$\lambda = 6678.15 \text{ Å}$; $\lambda_r (1s^2 \ ^1S_0 - 1s2p \ ^1P_1^o) = 584.334 \text{ Å}$; $g_i = 1$; $g_k = 3$; $f_r = 0.2762$] at $N_i = 1 \times 10^{18} \text{ cm}^{-3}$: $\Delta\lambda_{1/2}^R = 0.036 \text{ Å}$.

Van der Waals broadening arises from the dipole interaction of an excited atom with the induced

dipole of a ground state atom. (In the case of foreign gas broadening, both the perturber and the radiator may be in their respective ground states.) An approximate formula for the FWHM, strictly applicable to hydrogen and similar atomic structures only, is

$$\Delta\lambda_{1/2}^W \simeq 3.0 \times 10^{16} \lambda^2 C_6^{2/5} (T/\mu)^{3/10} N, \quad (42)$$

where μ is the atom-perturber reduced mass in units of u , N the perturber density, and C_6 the interaction constant. C_6 may be roughly estimated as follows: $C_6 = C_k - C_i$, with $C_{i(k)} = (9.8 \times 10^{10}) (\alpha_d R_{i(k)}^2) \alpha_d$ in cm^3 , R^2 in a_0^2 . Mean atomic polarizability $\alpha_d \approx (6.7 \times 10^{-25}) (3I_H/4E^*)^2 \text{ cm}^3$, where I_H is the ionization energy of hydrogen and E^* the energy of the first excited level of the perturber atom. $R_{i(k)}^2 \approx 2.5 [I_H/(I-E_{i(k)})]^2$, where I is the ionization energy of the radiator. Van der Waals broadened lines are red shifted by about one-third the size of the FWHM.

For the $1s2p \ ^1P_1^\circ - 1s3d \ ^1D_2$ transition in He I, and with He as perturber: $\lambda = 6678.15 \text{ \AA}$; $I = 198\,311 \text{ cm}^{-1}$; $E^* = E_i = 171\,135 \text{ cm}^{-1}$; $E_k = 186\,105 \text{ cm}^{-1}$; $\mu = 2$. At $T = 15\,000 \text{ K}$ and $N = 1 \times 10^{18} \text{ cm}^{-3}$: $\Delta\lambda_{1/2}^W = 0.044 \text{ \AA}$.

Stark broadening due to charged perturbers, i.e., ions and electrons, usually dominates resonance and van der Waals broadening in discharges and plasmas. The FWHM for hydrogen lines is

$$\Delta\lambda_{1/2}^{S,H} = (2.50 \times 10^{-9}) \alpha_{1/2} N_e^{2/3}, \quad (43)$$

where N_e is the electron density. The half-width parameter $\alpha_{1/2}$ for the H_β line at 4861 \AA , widely used for plasma diagnostics, is tabulated in the table below for some typical temperatures and electron densities [30]. This reference also contains $\alpha_{1/2}$ parameters for other hydrogen lines, as well as Stark width and shift data for numerous lines of other elements, i.e., neutral atoms and singly charged ions (in the latter, Stark widths and shifts depend linearly on N_e). Other tabulations of complete hydrogen Stark profiles exist.

Values of Stark-broadening parameter $\alpha_{1/2}$ for the H_β line of hydrogen (4861 \AA) for various temperatures and electron densities.

$N_e \text{ (cm}^{-3}\text{)}$				
$T(\text{K})$	10^{15}	10^{16}	10^{17}	10^{18}
5 000	0.0787	0.0808	0.0765	...
10 000	0.0803	0.0840	0.0851	0.0781
20 000	0.0815	0.0860	0.0902	0.0896
30 000	0.0814	0.0860	0.0919	0.0946

21. SPECTRAL CONTINUUM RADIATION

• Hydrogenic Species

Precise quantum-mechanical calculations exist only for hydrogenic species. The total power ϵ_{cont} radiated (per unit source volume and per unit solid angle, and expressed in SI units) in the wavelength interval $\Delta\lambda$ is the sum of radiation due to the recombination of a free electron with a bare ion (free-bound transitions) and bremsstrahlung (free-free transitions):

$$\begin{aligned}
 \epsilon_{\text{cont}} = & \frac{\epsilon_0^6}{2\pi \epsilon_0^3 (6\pi m_e)^{3/2}} N_e N_Z Z^2 \\
 & \times \frac{1}{(kT)^{1/2}} \exp\left(-\frac{hc}{\lambda kT}\right) \frac{\Delta\lambda}{\lambda^2} \\
 & \times \left\{ \frac{2Z^2 I_H}{kT} \sum_{n \geq (Z^2 I_H \lambda / hc)^{1/2}}^{n'} \frac{\gamma_{\text{fb}}}{n^3} \exp\left(\frac{Z^2 I_H}{n^2 kT}\right) \right. \\
 & \left. + \bar{\gamma}_{\text{fb}} \left[\exp\left(\frac{Z^2 I_H}{(n' + 1)^2 kT}\right) - 1 \right] + \gamma_{\text{ff}} \right\}
 \end{aligned} \tag{44}$$

where N_e is the electron density, N_Z the number density of hydrogenic (bare) ions of nuclear charge Z , I_H the ionization energy of hydrogen, n' the principal quantum number of the lowest level for which adjacent levels are so close that they approach a continuum and summation over n may be replaced by an integral. (The choice of n' is rather arbitrary; n' as low as 6 is found in the literature.) γ_{fb} and γ_{ff} are the Gaunt factors, which are generally close to unity. (For the higher free-bound continua, starting with $n' + 1$, an average Gaunt factor $\bar{\gamma}_{\text{fb}}$ is used.) For neutral hydrogen, the recombination continuum forming H^- becomes important, too [32].

In the equation above, the value of the constant factor is $6.065 \times 10^{-55} \text{ W m}^4 \text{ J}^{1/2} \text{ sr}^{-1}$. [Numerical

example: For atomic hydrogen ($Z = 1$), the quantity ϵ_{cont} has the value $2.9 \text{ W m}^{-3} \text{ sr}^{-1}$ under the following conditions: $\lambda = 3 \times 10^{-7} \text{ m}$; $\Delta\lambda = 1 \times 10^{-10} \text{ m}$; $N_e (= N_{Z=1}) = 1 \times 10^{21} \text{ m}^{-3}$; $T = 12\,000 \text{ K}$. The lower limit of the summation index n is 2; the upper limit n' has been taken to be 10. All Gaunt factors γ_{fb} , $\bar{\gamma}_{fb}$, γ_{ff} have been assumed to be unity.]

• Many-Electron Systems

For many-electron systems, only approximate theoretical treatments exist, based on the quantum-defect method (for results of calculations for noble gases, see, e.g., Ref. [33]). Experimental work is centered on the noble gases [34]. Modifications of the continuum by autoionization processes must also be considered.

Near the ionization limit, the f values for bound-bound transitions of a spectral series ($n' \rightarrow \infty$) make a smooth connection to the differential oscillator strength distribution $df/d\epsilon$ in the continuum [35].

22. SOURCES OF SPECTROSCOPIC DATA

A few data compilations have been cited above [8], [12], [30], and [Wavelength \(Frequency\) Standards](#) includes additional references for wavelength tables. A compilation of energy levels and other spectroscopic data for the actinide elements is also available [36]. Major recent compilations of atomic transition probabilities cover C, N and O [37] and the Fe-group elements [38]. A fairly comprehensive bibliographic review of compilations of data on atomic energy levels, wavelengths, transition probabilities, and spectral line shapes and shifts was published in 1992 [39]. Extensive data from compilations and other sources, as well as bibliographies, are included in the holdings of the [NIST Atomic Spectra Database](#).

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