

Many-Electron Atoms

11.1 The Hartree–Fock Self-Consistent-Field Method

For the hydrogen atom, the exact wave function is known. For helium and lithium, very accurate wave functions have been calculated by including interelectronic distances in the variation functions. For atoms of higher atomic number, one way to find an accurate wave function is to first find an approximate wave function using the Hartree–Fock procedure, which we shall outline in this section. The Hartree–Fock method is the basis for the use of atomic and molecular orbitals in many-electron systems.

The Hamiltonian operator for an n -electron atom is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (11.1)$$

where an infinitely heavy point nucleus was assumed (Section 6.6). The first sum in (11.1) contains the kinetic-energy operators for the n electrons. The second sum is the potential energy (6.58) for the attractions between the electrons and the nucleus of charge Ze . For a neutral atom, $Z = n$. The last sum is the potential energy of the interelectronic repulsions. The restriction $j > i$ avoids counting each interelectronic repulsion twice and avoids terms like $e^2/4\pi\epsilon_0 r_{ii}$. The Hamiltonian (11.1) is incomplete, because it omits spin–orbit and other interactions. The omitted terms are small (except for atoms with high Z) and will be considered in Sections 11.6 and 11.7.

The Hartree SCF Method

Because of the interelectronic repulsion terms $e^2/4\pi\epsilon_0 r_{ij}$, the Schrödinger equation for an atom is not separable. Recalling the perturbation treatment of helium (Section 9.3), we can obtain a zeroth-order wave function by neglecting these repulsions. The Schrödinger equation would then separate into n one-electron hydrogenlike equations. The zeroth-order wave function would be a product of n hydrogenlike (one-electron) orbitals:

$$\psi^{(0)} = f_1(r_1, \theta_1, \phi_1) f_2(r_2, \theta_2, \phi_2) \cdots f_n(r_n, \theta_n, \phi_n) \quad (11.2)$$

where the hydrogenlike orbitals are

$$f = R_{nl}(r) Y_l^m(\theta, \phi) \quad (11.3)$$

For the ground state of the atom, we would feed two electrons with opposite spin into each of the lowest orbitals, in accord with the Pauli exclusion principle, giving the ground-state configuration. Although the approximate wave function (11.2) is qualitatively useful, it is gravely lacking in quantitative accuracy. For one thing, all the orbitals

use the full nuclear charge Z . Recalling our variational treatments of helium and lithium, we know we can get a better approximation by using different effective atomic numbers for the different orbitals to account for screening of electrons. The use of effective atomic numbers gives considerable improvement, but we are still far from having an accurate wave function. The next step is to use a variation function that has the same form as (11.2) but is not restricted to hydrogenlike or any other particular form of orbitals. Thus we take

$$\phi = g_1(r_1, \theta_1, \phi_1) g_2(r_2, \theta_2, \phi_2) \cdots g_n(r_n, \theta_n, \phi_n) \quad (11.4)$$

and we look for the functions $g_1, g_2, \dots, g_n$ that minimize the variational integral $\langle \phi | \hat{H} | \phi \rangle / \langle \phi | \phi \rangle$. Our task is harder than in previous variational calculations, where we guessed a trial function that included some parameters and then varied the *parameters*. In (11.4) we must vary the *functions* g_i . [After we have found the best possible functions g_i , Eq. (11.4) will still be only an approximate wave function. The many-electron Schrödinger equation is not separable, so the true wave function cannot be written as the product of n one-electron functions.]

To simplify matters somewhat, we approximate the best possible atomic orbitals with orbitals that are the product of a radial factor and a spherical harmonic:

$$g_i = h_i(r_i) Y_{l_i}^{m_i}(\theta_i, \phi_i) \quad (11.5)$$

This approximation is generally made in atomic calculations.

The procedure for finding the functions g_i was introduced by Hartree in 1928 and is called the **Hartree self-consistent-field (SCF) method**. Hartree arrived at the SCF procedure by intuitive physical arguments. The proof that Hartree's procedure gives the best possible variation function of the form (11.4) was given by Slater and by Fock in 1930. [For the proof and a review of the SCF method, see S. M. Blinder, *Am. J. Phys.*, **33**, 431 (1965).]

Hartree's procedure is as follows. We first guess a product wave function

$$\phi_0 = s_1(r_1, \theta_1, \phi_1) s_2(r_2, \theta_2, \phi_2) \cdots s_n(r_n, \theta_n, \phi_n) \quad (11.6)$$

where each s_i is a normalized function of r multiplied by a spherical harmonic. A reasonable guess for ϕ_0 would be a product of hydrogenlike orbitals with effective atomic numbers. For the function (11.6), the probability density of electron i is $|s_i|^2$. We now focus attention on electron 1 and regard electrons 2, 3, $\dots$, n as being smeared out to form a fixed distribution of electric charge through which electron 1 moves. We are thus averaging out the instantaneous interactions between electron 1 and the other electrons. The potential energy of interaction between point charges Q_1 and Q_2 is $V_{12} = Q_1 Q_2 / 4\pi\epsilon_0 r_{12}$ [Eq. (6.58)]. We now take Q_2 and smear it out into a continuous charge distribution such that ρ_2 is the charge density, the charge per unit volume. The infinitesimal charge in the infinitesimal volume dv_2 is $\rho_2 dv_2$, and summing up the interactions between Q_1 and the infinitesimal elements of charge, we have

$$V_{12} = \frac{Q_1}{4\pi\epsilon_0} \int \frac{\rho_2}{r_{12}} dv_2$$

For electron 2 (with charge $-e$), the charge density of the hypothetical charge cloud is $\rho_2 = -e|s_2|^2$, and for electron 1, $Q_1 = -e$. Hence

$$V_{12} = \frac{e^2}{4\pi\epsilon_0} \int \frac{|s_2|^2}{r_{12}} dv_2$$

Adding in the interactions with the other electrons, we have

$$V_{12} + V_{13} + \cdots + V_{1n} = \sum_{j=2}^n \frac{e^2}{4\pi\epsilon_0} \int \frac{|s_j|^2}{r_{1j}} dv_j$$

The potential energy of interaction between electron 1 and the other electrons and the nucleus is then

$$V_1(r_1, \theta_1, \phi_1) = \sum_{j=2}^n \frac{e^2}{4\pi\epsilon_0} \int \frac{|s_j|^2}{r_{1j}} dv_j - \frac{Ze^2}{4\pi\epsilon_0 r_1} \quad (11.7)$$

We now make a further approximation beyond assuming the wave function to be a product of one-electron orbitals. We assume that the effective potential acting on an electron in an atom can be adequately approximated by a function of r only. This *central-field approximation* can be shown to be generally accurate. We therefore average $V_1(r_1, \theta_1, \phi_1)$ over the angles to arrive at a potential energy that depends only on r_1 :

$$V_1(r_1) = \frac{\int_0^{2\pi} \int_0^\pi V_1(r_1, \theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1}{\int_0^{2\pi} \int_0^\pi \sin \theta d\theta d\phi} \quad (11.8)$$

We now use $V_1(r_1)$ as the potential energy in a one-electron Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m_e} \nabla_1^2 + V_1(r_1) \right] t_1(1) = \epsilon_1 t_1(1) \quad (11.9)$$

and solve for $t_1(1)$, which will be an improved orbital for electron 1. In (11.9), ϵ_1 is the energy of the orbital of electron 1 at this stage of the approximation. Since the potential energy in (11.9) is spherically symmetric, the angular factor in $t_1(1)$ is a spherical harmonic involving quantum numbers l_1 and m_1 (Section 6.1). The radial factor $R_1(1)$ in t_1 is the solution of a one-dimensional Schrödinger equation of the form (6.17). We get a set of solutions $R_1(1)$, where the number of nodes k interior to the boundary points ($r = 0$ and ∞) starts at zero for the lowest energy and increases by 1 for each higher energy (Section 4.2). We now *define* the quantum number n as $n \equiv l + 1 + k$, where $k = 0, 1, 2, \dots$. We thus have $1s$, $2s$, $2p$, and so on, orbitals (with orbital energy ϵ increasing with n) just as in hydrogenlike atoms, and the number of interior radial nodes ($n - l - 1$) is the same as in hydrogenlike atoms (Section 6.6). However, since $V_1(r_1)$ is not a simple Coulomb potential, the radial factor $R_1(r_1)$ is not a hydrogenlike function. Of the set of solutions $R_1(r_1)$, we take the one that corresponds to the orbital we are improving. For example, if electron 1 is a $1s$ electron in the beryllium $1s^2 2s^2$ configuration, then $V_1(r_1)$ is calculated from the guessed orbitals of one $1s$ electron and two $2s$ electrons, and we use the radial solution of (11.9) with $k = 0$ to find an improved $1s$ orbital.

We now go to electron 2 and regard it as moving in a charge cloud of density

$$-e[|t_1(1)|^2 + |s_3(3)|^2 + |s_4(4)|^2 + \dots + |s_n(n)|^2]$$

due to the other electrons. We calculate an effective potential energy $V_2(r_2)$ and solve a one-electron Schrödinger equation for electron 2 to get an improved orbital $t_2(2)$. We continue this process until we have a set of improved orbitals for all n electrons. Then we go back to electron 1 and repeat the process. We continue to calculate improved orbitals until there is no further change from one iteration to the next. The final set of orbitals gives the Hartree self-consistent-field wave function.

How do we get the energy of the atom in the SCF approximation? It seems natural to take the sum of the orbital energies of the electrons, $\epsilon_1 + \epsilon_2 + \dots + \epsilon_n$, but this is wrong. In calculating the orbital energy ϵ_1 , we iteratively solved the one-electron Schrödinger equation (11.9). The potential energy in (11.9) includes, in an average way, the energy of the repulsions between electrons 1 and 2, 1 and 3, $\dots$, 1 and n . When we

solve for ε_2 , we solve a one-electron Schrödinger equation whose potential energy includes repulsions between electrons 2 and 1, 2 and 3, $\dots$, 2 and n . If we take $\sum_i \varepsilon_i$, we will count each interelectronic repulsion twice. To correctly obtain the total energy E of the atom, we must take

$$E = \sum_{i=1}^n \varepsilon_i - \sum_{i=1}^{n-1} \sum_{j=i+1}^n \iint \frac{e^2 |g_i(i)|^2 |g_j(j)|^2}{4\pi\epsilon_0 r_{ij}} dv_i dv_j \quad (11.10)$$

$$E = \sum_i \varepsilon_i - \sum_i \sum_{j>i} J_{ij}$$

where the average repulsions of the electrons in the Hartree orbitals of (11.4) were subtracted from the sum of the orbital energies, and where the notation J_{ij} was used for Coulomb integrals [Eq. (9.99)].

The set of orbitals belonging to a given principal quantum number n constitutes a **shell**. The $n = 1, 2, 3, \dots$ shells are the $K, L, M, \dots$ shells, respectively. The orbitals belonging to a given n and a given l constitute a **subshell**. Consider the sum of the Hartree probability densities for the electrons in a filled subshell. Using (11.5), we have

$$2 \sum_{m=-l}^l |h_{n,l}(r)|^2 |Y_l^m(\theta, \phi)|^2 = 2 |h_{n,l}(r)|^2 \sum_{m=-l}^l |Y_l^m(\theta, \phi)|^2 \quad (11.11)$$

where the factor 2 comes from the pair of electrons in each orbital. The spherical-harmonic addition theorem (Merzbacher, Section 9.7) shows that the sum on the right side of (11.11) equals $(2l + 1)/4\pi$. Hence the sum of the probability densities is $[(2l + 1)/2\pi] |h_{n,l}(r)|^2$, which is independent of the angles. A closed subshell gives a spherically symmetric probability density, a result called *Unsöld's theorem*. For a half-filled subshell, the factor 2 is omitted from (11.11), and here also we get a spherically symmetric probability density.

The Hartree–Fock SCF Method

The alert reader may have realized that there is something fundamentally wrong with the Hartree product wave function (11.4). Although we have paid some attention to spin and the Pauli exclusion principle by putting no more than two electrons in each spatial orbital, any approximation to the true wave function should include spin explicitly and should be antisymmetric to interchange of electrons (Chapter 10). Hence, instead of the spatial orbitals, we must use spin-orbitals and must take an antisymmetric linear combination of products of spin-orbitals. This was pointed out by Fock (and by Slater) in 1930, and an SCF calculation that uses antisymmetrized spin-orbitals is called a **Hartree–Fock calculation**. We have seen that a Slater determinant of spin-orbitals provides the proper antisymmetry. For example, to carry out a Hartree–Fock calculation for the lithium ground state, we start with the function (10.54), where f and g are guesses for the $1s$ and $2s$ orbitals. We then carry out the SCF iterative process until we get no further improvement in f and g . This gives the lithium ground-state Hartree–Fock wave function.

The differential equations for finding the Hartree–Fock orbitals have the same general form as (11.9):

$$\hat{F}u_i = \varepsilon_i u_i, \quad i = 1, 2, \dots, n \quad (11.12)$$

where u_i is the i th spin-orbital, the operator $\hat{F}$, called the **Fock** (or **Hartree–Fock**) **operator**, is the effective Hartree–Fock Hamiltonian, and the eigenvalue ε_i is the **orbital energy** of spin-orbital i . However, the Hartree–Fock operator $\hat{F}$ has extra terms as compared with the effective Hartree Hamiltonian given by the bracketed terms in (11.9). The

Hartree–Fock expression for the total energy of the atom involves exchange integrals K_{ij} in addition to the Coulomb integrals that occur in the Hartree expression (11.10). See Section 14.3. [Actually, Eq. (11.12) applies only when the Hartree–Fock wave function can be written as a single Slater determinant, as it can for closed-subshell atoms and atoms with only one electron outside closed subshells. When the Hartree–Fock wave function contains more than one Slater determinant, the Hartree–Fock equations are more complicated than (11.12).]

The orbital energy ε_i in the Hartree–Fock equations (11.12) can be shown to be a good approximation to the negative of the energy needed to ionize a closed-subshell atom by removing an electron from spin-orbital i (Koopmans' theorem; Section 15.5).

Originally, Hartree–Fock atomic calculations were done by using numerical methods to solve the Hartree–Fock differential equations (11.12), and the resulting orbitals were given as tables of the radial functions for various values of r . [The Numerov method (Sections 4.4 and 6.9) can be used to solve the radial Hartree–Fock equations for the radial factors in the Hartree–Fock orbitals; the angular factors are spherical harmonics. See D. R. Hartree, *The Calculation of Atomic Structures*, Wiley, 1957; C. Froese Fischer, *The Hartree–Fock Method for Atoms*, Wiley, 1977.]

In 1951, Roothaan proposed representing the Hartree–Fock orbitals as linear combinations of a complete set of known functions, called **basis functions**. Thus for lithium we would write the Hartree–Fock $1s$ and $2s$ spatial orbitals as

$$f = \sum_i b_i \chi_i, \quad g = \sum_i c_i \chi_i \quad (11.13)$$

where the χ_i functions are some complete set of functions, and where the b_i 's and c_i 's are expansion coefficients that are found by the SCF iterative procedure. Since the χ_i (chi i) functions form a complete set, these expansions are valid. The Roothaan expansion procedure allows one to find the Hartree–Fock wave function using matrix algebra (see Section 14.3 for details). The Roothaan procedure is readily implemented on a computer and is often used to find atomic Hartree–Fock wave functions and nearly always used to find molecular Hartree–Fock wave functions.

A commonly used set of basis functions for atomic Hartree–Fock calculations is the set of **Slater-type orbitals** (STOs) whose normalized form is

$$\frac{(2\zeta/a_0)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r/a_0} Y_l^m(\theta, \phi) \quad (11.14)$$

The set of all such functions with n , l , and m being integers obeying (6.96)–(6.98) but with ζ having all possible positive values forms a complete set. The parameter ζ is called the **orbital exponent**. To get a truly accurate representation of the Hartree–Fock orbitals, we would have to include an infinite number of Slater orbitals in the expansions. In practice, one can get very accurate results by using only a few judiciously chosen Slater orbitals. (Another possibility is to use Gaussian-type basis functions; see Section 15.4.)

Clementi and Roetti did Hartree–Fock calculations for the ground state and some excited states of the first 54 elements of the periodic table [E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (1974); Bunge and co-workers have recalculated these wave functions; C. F. Bunge et al., *At. Data Nucl. Data Tables*, **53**, 113 (1993); *Phys. Rev. A*, **46**, 3691 (1992); these atomic wave functions can be found at www.ccl.net/cca/data/atomic-RHF-wavefunctions/index.shtml]. For example, consider the Hartree–Fock ground-state wave function of helium, which has the form [see Eq. (10.41)]

$$f(1)f(2) \cdot 2^{-1/2} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

Clementi and Roetti expressed the $1s$ orbital function f as the following combination of five $1s$ Slater-type orbitals:

$$f = \pi^{-1/2} \sum_{i=1}^5 c_i \left(\frac{\zeta_i}{a_0} \right)^{3/2} e^{-\zeta_i r/a_0}$$

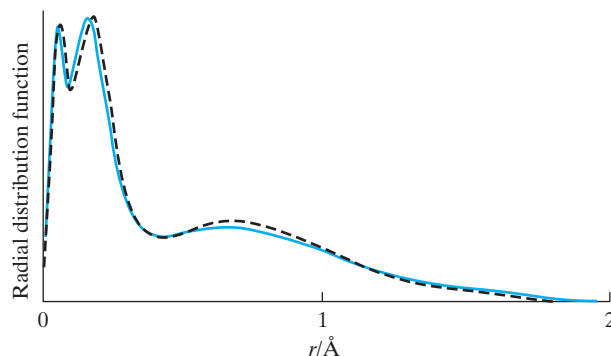
where the expansion coefficients c_i are $c_1 = 0.76838$, $c_2 = 0.22346$, $c_3 = 0.04082$, $c_4 = -0.00994$, $c_5 = 0.00230$ and where the orbital exponents ζ_i are $\zeta_1 = 1.41714$, $\zeta_2 = 2.37682$, $\zeta_3 = 4.39628$, $\zeta_4 = 6.52699$, $\zeta_5 = 7.94252$. [The largest term in the expansion has an orbital exponent that is similar to the orbital exponent (9.62) for the simple trial function (9.56).] The Hartree–Fock energy is -77.9 eV, as compared with the true nonrelativistic energy, -79.0 eV. The $1s$ orbital energy corresponding to f was found to be -25.0 eV, as compared with the experimental helium ionization energy of 24.6 eV.

For the lithium ground state, Clementi and Roetti used a basis set consisting of two $1s$ STOs (with different orbital exponents) and four $2s$ STOs (with different orbital exponents). The lithium $1s$ and $2s$ Hartree–Fock orbitals were each expressed as a linear combination of all six of these basis functions. The Hartree–Fock energy is -202.3 eV, as compared with the true energy -203.5 eV.

Electron densities calculated from Hartree–Fock wave functions are quite accurate. **Figure 11.1** compares the radial distribution function of argon (found by integrating the electron density over the angles θ and ϕ and multiplying the result by r^2) calculated by the Hartree–Fock method with the experimental radial distribution function found by electron diffraction. (Recall from Section 6.6 that the radial distribution function is proportional to the probability of finding an electron in a thin spherical shell at a distance r from the nucleus.) Note the electronic shell structure in Fig. 11.1. The high nuclear charge in ^{18}Ar makes the average distance of the $1s$ electrons from the nucleus far less than in H or He. Thus there is only a moderate increase in atomic size as we go down a given group in the periodic table. Calculations show that the radius of a sphere containing 98% of the Hartree–Fock electron probability density gives an atomic radius in good agreement with the empirically determined van der Waals radius. [See C. W. Kammeyer and D. R. Whitman, *J. Chem. Phys.*, **56**, 4419 (1972).]

Although the radial distribution function of an atom shows the shell structure, the electron probability density integrated over the angles and plotted versus r does not oscillate. Rather, for ground-state atoms this probability density is a maximum at the nucleus (because of the s electrons) and continually decreases as r increases. Similarly, in molecules the maxima in electron probability density usually occur at the nuclei; see, for example, Fig. 13.7. [For further discussion, see H. Weinstein, P. Politzer, and S. Srebnik, *Theor. Chim. Acta*, **38**, 159 (1975).]

FIGURE 11.1 Radial distribution function in Ar as a function of r . The broken line is the result of a Hartree–Fock calculation. The solid line is the result of electron-diffraction data. [Reprinted figure with permission from L.S. Bartell and L. O. Brockway, *Physical Review Series II*, Vol 90, 833, 1953. Copyright 1953 by the American Physical Society.]



Accurate representation of a many-electron atomic orbital (AO) requires a linear combination of several Slater-type orbitals. For rough calculations, it is convenient to have simple approximations for AOs. We might use hydrogenlike orbitals with effective nuclear charges, but Slater suggested an even simpler method: to approximate an AO by a single function of the form (11.14) with the orbital exponent ζ taken as

$$\zeta = (Z - s)/n \quad (11.15)$$

where Z is the atomic number, n is the orbital's principal quantum number, and s is a screening constant calculated by a set of rules (see Prob. 15.62). A Slater orbital replaces the polynomial in r in a hydrogenlike orbital with a single power of r . Hence a single Slater orbital does not have the proper number of radial nodes and does not represent well the inner part of an orbital.

A lot of computation is required to perform a Hartree–Fock SCF calculation for a many-electron atom. Hartree did several SCF calculations in the 1930s, when electronic computers were not in existence. Fortunately, Hartree's father, a retired engineer, enjoyed numerical computation as a hobby and helped his son. Nowadays computers have replaced Hartree's father.

11.2 Orbitals and the Periodic Table

The orbital concept and the Pauli exclusion principle allow us to understand the periodic table of the elements. An orbital is a one-electron spatial wave function. We have used orbitals to obtain approximate wave functions for many-electron atoms, writing the wave function as a Slater determinant of one-electron spin-orbitals. In the crudest approximation, we neglect all interelectronic repulsions and obtain hydrogenlike orbitals. The best possible orbitals are the Hartree–Fock SCF functions. We build up the periodic table by feeding electrons into these orbitals, each of which can hold a pair of electrons with opposite spin.

Latter [R. Latter, *Phys. Rev.*, **99**, 510 (1955)] calculated approximate orbital energies for the atoms of the periodic table by replacing the complicated expression for the Hartree–Fock potential energy in the Hartree–Fock radial equations by a much simpler function obtained from the Thomas–Fermi–Dirac method, which uses ideas of statistical mechanics to get approximations to the effective potential-energy function for an electron and the electron-density function in an atom (*Bethe and Jackiw*, Chapter 5). **Figure 11.2** shows Latter's resulting orbital energies for neutral ground-state atoms. These AO energies are in pretty good agreement with both Hartree–Fock and experimentally found orbital energies (see J. C. Slater, *Quantum Theory of Matter*, 2nd ed., McGraw-Hill, 1968, pp. 146, 147, 325, 326).

Orbital energies change with changing atomic number Z . As Z increases, the orbital energies decrease because of the increased attraction between the nucleus and the electrons. This decrease is most rapid for the inner orbitals, which are less well-shielded from the nucleus.

For $Z > 1$, orbitals with the same value of n but different l have different energies. For example, for the $n = 3$ orbital energies, we have $\epsilon_{3s} < \epsilon_{3p} < \epsilon_{3d}$ for $Z > 1$. The splitting of these levels, which are degenerate in the hydrogen atom, arises from the interelectronic repulsions. (Recall the perturbation treatment of helium in Section 9.7.) In the limit $Z \rightarrow \infty$, orbitals with the same value of n are again degenerate, because the interelectronic repulsions become insignificant in comparison with the electron–nucleus attractions.

The relative positions of certain orbitals change with changing Z . Thus in hydrogen the $3d$ orbital lies below the $4s$ orbital, but for Z in the range from 7 through 20 the $4s$ is below the $3d$. For large values of Z , the $3d$ is again lower. At $Z = 19$, the $4s$ is lower; hence ${}_{19}\text{K}$ has the ground-state configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s$. Recall that s orbitals are more

states of a given electron configuration, instead of by minimizing the energy of each individual state of the configuration. The average orbitals obtained differ only slightly from the true Hartree–Fock orbitals for a given state of the configuration.

For each of the atoms ${}_1\text{H}$ to ${}_{19}\text{K}$, Vanquickenborne and co-workers calculated the $3d$ average orbital energy ϵ_{3d} for the electron configuration in which one electron is removed from the highest-occupied orbital of the ground-state electron configuration and put in the $3d$ orbital; they calculated ϵ_{4s} for these atoms in a similar manner. In agreement with Fig. 11.2, they found $\epsilon_{3d} < \epsilon_{4s}$ for atomic numbers $Z < 6$ and $\epsilon_{4s} < \epsilon_{3d}$ for $Z = 7$ to 19 for neutral atoms.

For discussion of the transition elements with Z from 21 to 29, Fig. 11.2 is inadequate because it gives only a single value for ϵ_{3d} for each element, whereas ϵ_{3d} (and ϵ_{4s}) for a given atom depend on which orbitals are occupied. This is because the electric field experienced by an electron depends on which orbitals are occupied. Vanquickenborne and co-workers calculated ϵ_{3d} and ϵ_{4s} for each of the valence-electron configurations $3d^n 4s^2$, $3d^{n+1} 4s^1$, and $3d^{n+2} 4s^0$ and found $\epsilon_{3d} < \epsilon_{4s}$ in each of these configurations of the neutral atoms and the +1 and +2 ions of the transition elements ${}_{21}\text{Sc}$ through ${}_{29}\text{Cu}$ (which is the order shown in Fig. 11.2).

Since $3d$ lies below $4s$ for Z above 20, one might wonder why the ground-state configuration of, say, ${}_{21}\text{Sc}$ is $3d^1 4s^2$, rather than $3d^3$. Although $\epsilon_{3d} < \epsilon_{4s}$ for each of these configurations, this does not mean that the $3d^3$ configuration has the lower sum of orbital energies. When an electron is moved from $4s$ into $3d$, ϵ_{4s} and ϵ_{3d} are increased. An orbital energy is found by solving a one-electron Hartree–Fock equation that contains potential-energy terms for the average repulsions between the electron in orbital i and the other electrons in the atom, so ϵ_i depends on the values of these repulsions and hence on which orbitals are occupied. For the first series of transition elements, the $4s$ orbital is much larger than the $3d$ orbital. For example, Vanquickenborne and co-workers found the following $\langle r \rangle$ values in Sc: $\langle r \rangle_{3d} = 0.89 \text{ \AA}$ and $\langle r \rangle_{4s} = 2.09 \text{ \AA}$ for $3d^1 4s^2$; $\langle r \rangle_{3d} = 1.11 \text{ \AA}$ and $\langle r \rangle_{4s} = 2.29 \text{ \AA}$ for $3d^2 4s^1$. Because of this size difference, repulsions involving $4s$ electrons are substantially less than repulsions involving $3d$ electrons, and we have $(4s, 4s) < (4s, 3d) < (3d, 3d)$, where $(4s, 3d)$ denotes the average repulsion between an electron distributed over the $3d$ orbitals and an electron in a $4s$ orbital. (These repulsions are expressed in terms of Coulomb and exchange integrals.) When an electron is moved from $4s$ into $3d$, the increase in interelectronic repulsion that is a consequence of the preceding inequalities raises the orbital energies ϵ_{3d} and ϵ_{4s} . For example, for ${}_{21}\text{Sc}$, the $3d^1 4s^2$ configuration has $\epsilon_{3d} = -9.35 \text{ eV}$ and $\epsilon_{4s} = -5.72 \text{ eV}$, whereas the $3d^2 4s^1$ configuration has $\epsilon_{3d} = -5.23 \text{ eV}$ and $\epsilon_{4s} = -5.06 \text{ eV}$. For the $3d^1 4s^2$ configuration, the sum of valence-electron orbital energies is $-9.35 \text{ eV} + 2(-5.72 \text{ eV}) = -20.79 \text{ eV}$, whereas for the $3d^2 4s^1$ configuration, this sum is $2(-5.23 \text{ eV}) - 5.06 \text{ eV} = -15.52 \text{ eV}$. Thus, despite the fact that $\epsilon_{3d} < \epsilon_{4s}$ for each configuration, transfer of an electron from $4s$ to $3d$ raises the sum of valence-electron orbital energies in Sc. [As we saw in Eq. (11.10) for the Hartree method and will see in Section 14.3 for the Hartree–Fock method, the Hartree and Hartree–Fock expressions for the energy of an atom contain terms in addition to the sum of orbital energies, so we must look at more than the sum of orbital energies to see which configuration is most stable.]

For the +2 ions of the transition metals, the reduction in screening makes the valence $3d$ and $4s$ electrons feel a larger effective nuclear charge Z_{eff} than in the neutral atoms. By analogy to the H-atom equation $E = -(Z^2/n^2)(e^2/8\pi\epsilon_0 a)$ [Eq. (6.94)], the orbital energies ϵ_{3d} and ϵ_{4s} are each roughly proportional to Z_{eff}^2 and the energy difference $\epsilon_{4s} - \epsilon_{3d}$ is roughly proportional to Z_{eff}^2 . The difference $\epsilon_{4s} - \epsilon_{3d}$ is thus much larger in the transition-metal ions than in the neutral atoms; the increase in valence-electron repulsion is no longer

enough to make the $4s$ to $3d$ transfer energetically unfavorable; and the $+2$ ions have ground-state configurations with no $4s$ electrons.

For further discussion of electron configurations, see W. H. E. Schwarz, *J. Chem. Educ.*, **87**, 444 (2010); Schwarz and R. L. Rich, *ibid.*, **87**, 435.

Figure 11.2 shows that the separation between ns and np orbitals is much less than that between np and nd orbitals, giving the familiar ns^2np^6 stable octet.

The orbital concept is the basis for most qualitative discussions of the chemistry of atoms and molecules. The use of orbitals, however, is an approximation. To reach the true wave function, we must go beyond a Slater determinant of spin-orbitals.

11.3 Electron Correlation

Energies calculated by the Hartree–Fock method are typically in error by about $\frac{1}{2}\%$ for light atoms. On an absolute basis this is not much, but for the chemist it is too large. For example, the total energy of the carbon atom is about -1000 eV, and $\frac{1}{2}\%$ of this is 5 eV. Chemical single-bond energies run about 5 eV. Calculating a bond energy by taking the difference between Hartree–Fock molecular and atomic energies, which are in error by several electronvolts for light atoms, is an unreliable procedure. We must seek a way to improve Hartree–Fock wave functions and energies. (Our discussion will apply to molecules as well as atoms.)

A Hartree–Fock SCF wave function takes into account the interactions between electrons only in an average way. Actually, we must consider the instantaneous interactions between electrons. Since electrons repel each other, they tend to keep out of each other's way. For example, in helium, if one electron is close to the nucleus at a given instant, it is energetically more favorable for the other electron to be far from the nucleus at that instant. One sometimes speaks of a *Coulomb hole* surrounding each electron in an atom. This is a region in which the probability of finding another electron is small. The motions of electrons are correlated with each other, and we speak of **electron correlation**. We must find a way to introduce the instantaneous electron correlation into the wave function.

Actually, a Hartree–Fock wave function does have some instantaneous electron correlation. A Hartree–Fock function satisfies the antisymmetry requirement. Therefore [Eq. (10.20)], it vanishes when two electrons with the same spin have the same spatial coordinates. For a Hartree–Fock function, there is little probability of finding electrons of the same spin in the same region of space, so a Hartree–Fock function has some correlation of the motions of electrons with the same spin. This makes the Hartree–Fock energy lower than the Hartree energy. One sometimes refers to a *Fermi hole* around each electron in a Hartree–Fock wave function, thereby indicating a region in which the probability of finding another electron with the same spin is small.

The **correlation energy** E_{corr} is the difference between the exact nonrelativistic energy E_{nonrel} and the (nonrelativistic) Hartree–Fock energy E_{HF} :

$$E_{\text{corr}} \equiv E_{\text{nonrel}} - E_{\text{HF}} \quad (11.16)$$

where E_{nonrel} and E_{HF} should both either include corrections for nuclear motion or omit these corrections. For the He atom, the (nonrelativistic) Hartree–Fock energy uncorrected for nuclear motion is $-2.86168(e^2/4\pi\epsilon_0a_0)$ [E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (1974)] and variational calculations (Section 9.4) give the exact nonrelativistic energy uncorrected for nuclear motion as $-2.90372(e^2/4\pi\epsilon_0a_0)$. Therefore, $E_{\text{corr, He}} = -2.90372(e^2/4\pi\epsilon_0a_0) + 2.86168(e^2/4\pi\epsilon_0a_0) = -0.04204(e^2/4\pi\epsilon_0a_0) = -1.14$ eV. For atoms and molecules where E_{nonrel} cannot be accurately calculated,

one combines the experimental energy with estimates for relativistic and nuclear-motion corrections to get E_{nonrel} . For neutral ground-state atoms, $|E_{\text{corr}}|$ has been found to increase roughly linearly with the number n of electrons:

$$E_{\text{corr}} \approx -0.0170n^{1.31}(e^2/4\pi\epsilon_0 a_0) = -0.0170n^{1.31}(27.2 \text{ eV})$$

[E. Clementi and G. Corongiu, *Int. J. Quantum Chem.*, **62**, 571 (1997)]. The percentage $(E_{\text{corr}}/E_{\text{nonrel}}) \times 100\%$ decreases with increasing atomic number. Some values are 0.6% for Li, 0.4% for C, 0.2% for Na, and 0.1% for K.

We have already indicated two of the ways in which we may provide for instantaneous electron correlation. One method is to introduce the interelectronic distances r_{ij} into the wave function (Section 9.4).

Another method is configuration interaction. We found (Sections 9.3 and 10.4) the zeroth-order wave function for the helium-atom $1s^2$ ground state to be $1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}$. We remarked that first- and higher-order corrections to the wave function will mix in contributions from excited configurations, producing **configuration interaction** (CI), also called **configuration mixing** (CM).

The most common way to do a configuration-interaction calculation on an atom or molecule uses the variation method. One starts by choosing a basis set of one-electron functions χ_i . In principle, this basis set should be complete. In practice, one is limited to a basis set of finite size. One hopes that a good choice of basis functions will give a good approximation to a complete set. For atomic calculations, STOs [Eq. (11.14)] are often chosen as the basis functions.

The SCF atomic (or molecular) orbitals ϕ_i are written as linear combinations of the basis-set members [see (11.13)], and the Hartree–Fock equations (11.12) are solved to give the coefficients in these linear combinations. The number of atomic (or molecular) orbitals obtained equals the number of basis functions used. The lowest-energy orbitals are the occupied orbitals for the ground state. The remaining unoccupied orbitals are called **virtual orbitals**.

Using the set of occupied and virtual spin-orbitals, one can form antisymmetric many-electron functions that have different orbital occupancies. For example, for helium, one can form functions that correspond to the electron configurations $1s^2$, $1s2s$, $1s2p$, $2s^2$, $2s2p$, $2p^2$, $1s3s$, and so on. Moreover, more than one function can correspond to a given electron configuration. Recall the functions (10.27) to (10.30) corresponding to the helium $1s2s$ configuration. Each such many-electron function Φ_i is a Slater determinant or a linear combination of a few Slater determinants. Use of more than one Slater determinant is required for certain open-shell functions such as (10.44) and (10.45). Each Φ_i is called a **configuration state function** or a **configuration function** or simply a “configuration.” (This last name is unfortunate, since it leads to confusion between an electron configuration such as $1s^2$ and a configuration function such as $|1s \bar{1}s|$.)

As we saw in perturbation theory, the true atomic (or molecular) wave function ψ contains contributions from configurations other than the one that makes the main contribution to ψ , so we express ψ as a linear combination of the configuration functions Φ_i :

$$\psi = \sum_i c_i \Phi_i \quad (11.17)$$

We then regard (11.17) as a linear variation function (Section 8.5). Variation of the coefficients c_i to minimize the variational integral leads to the equation

$$\det(H_{ij} - ES_{ij}) = 0 \quad (11.18)$$

where $H_{ij} \equiv \langle \Phi_i | \hat{H} | \Phi_j \rangle$ and $S_{ij} \equiv \langle \Phi_i | \Phi_j \rangle$. Commonly, the Φ_i functions are orthonormal, but if they are not orthogonal, they can be made so by the Schmidt method. [Only

configuration functions whose angular-momentum eigenvalues are the same as those of the state ψ will contribute to the expansion (11.17); see Section 11.5.]

Because the many-electron configuration functions Φ_i are ultimately based on a one-electron basis set that is a complete set, the set of all possible configuration functions is a complete set for the many-electron problem: Any antisymmetric many-electron function (including the exact wave function) can be expressed as a linear combination of the Φ_i functions. (For a proof of this, see *Szabo and Ostlund*, Section 2.2.7.) Therefore, if one starts with a complete one-electron basis set and includes all possible configuration functions, a CI calculation will give the exact atomic (or molecular) wave function ψ for the state under consideration. In practice, one is limited to a finite, incomplete basis set, rather than an infinite, complete basis set. Moreover, even with a modest-size basis set, the number of possible configuration functions is extremely large, and one usually does not include all possible configuration functions. Part of the “art” of the CI method is choosing those configurations that will contribute the most.

Because it generally takes very many configuration functions to give a truly accurate wave function, configuration-interaction calculations for systems with more than a few electrons are time-consuming, even on supercomputers. Other methods for allowing for electron correlation are discussed in Chapter 16.

In summary, to do a CI calculation, we choose a one-electron basis set χ_i , iteratively solve the Hartree–Fock equations (11.12) to determine one-electron atomic (or molecular) orbitals ϕ_i as linear combinations of the basis set, form many-electron configuration functions Φ_i using the orbitals ϕ_i , express the wave function ψ as a linear combination of these configuration functions, solve (11.18) for the energy, and solve the associated simultaneous linear equations for the coefficients c_i in (11.17). [In practice, (11.18) and its associated simultaneous equations are solved by matrix methods; see Section 8.6.]

As an example, consider the ground state of beryllium. The Hartree–Fock SCF method would find the best forms for the $1s$ and $2s$ orbitals in the Slater determinant $|1s\bar{1}s2s\bar{2}s|$ and use this for the ground-state wave function. [We are using the notation of Eq. (10.47).] Going beyond the Hartree–Fock method, we would include contributions from excited configuration functions (for example, $|1s\bar{1}s3s\bar{3}s|$) in a linear variation function for the ground state. Bunge did a CI calculation for the beryllium ground state using a linear combination of 650 configuration functions [C. F. Bunge, *Phys. Rev. A*, **14**, 1965 (1976)]. The Hartree–Fock energy is $-14.5730(e^2/4\pi\epsilon_0a_0)$, Bunge’s CI result is $-14.6669(e^2/4\pi\epsilon_0a_0)$, and the exact nonrelativistic energy is $-14.6674(e^2/4\pi\epsilon_0a_0)$. Bunge was able to obtain 99.5% of the correlation energy.

A detailed CI calculation for the He atom is shown in Section 16.2.

11.4 Addition of Angular Momenta

For a many-electron atom, the operators for individual angular momenta of the electrons do not commute with the Hamiltonian operator, but their sum does. Hence we want to learn how to add angular momenta.

Suppose we have a system with two angular-momentum vectors $\mathbf{M}_1$ and $\mathbf{M}_2$. They might be the orbital angular-momentum vectors of two electrons in an atom, or they might be the spin angular-momentum vectors of two electrons, or one might be the spin and the other the orbital angular momentum of a single electron. The eigenvalues of $\hat{M}_1^2$, $\hat{M}_2^2$, $\hat{M}_{1z}$, and $\hat{M}_{2z}$ are $j_1(j_1 + 1)\hbar^2$, $j_2(j_2 + 1)\hbar^2$, $m_1\hbar$, and $m_2\hbar$, where the quantum numbers obey the usual restrictions. The components of $\hat{\mathbf{M}}_1$ and $\hat{\mathbf{M}}_2$ obey the angular-momentum commutation relations [Eqs. (5.46), (5.48), and (5.107)]

$$[\hat{M}_{1x}, \hat{M}_{1y}] = i\hbar\hat{M}_{1z}, \text{ etc.} \quad [\hat{M}_{2x}, \hat{M}_{2y}] = i\hbar\hat{M}_{2z}, \text{ etc.} \quad (11.19)$$

We define the **total angular momentum** $\mathbf{M}$ of the system as the vector sum

$$\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2 \quad (11.20)$$

$\mathbf{M}$ is a vector with three components:

$$\mathbf{M} = M_x \mathbf{i} + M_y \mathbf{j} + M_z \mathbf{k} \quad (11.21)$$

The vector equation (11.20) gives the three scalar equations

$$M_x = M_{1x} + M_{2x}, \quad M_y = M_{1y} + M_{2y}, \quad M_z = M_{1z} + M_{2z} \quad (11.22)$$

For the operator $\hat{M}^2$, we have

$$\hat{M}^2 = \hat{\mathbf{M}} \cdot \hat{\mathbf{M}} = \hat{M}_x^2 + \hat{M}_y^2 + \hat{M}_z^2 \quad (11.23)$$

$$\hat{M}^2 = (\hat{\mathbf{M}}_1 + \hat{\mathbf{M}}_2) \cdot (\hat{\mathbf{M}}_1 + \hat{\mathbf{M}}_2)$$

$$\hat{M}^2 = \hat{M}_1^2 + \hat{M}_2^2 + \hat{\mathbf{M}}_1 \cdot \hat{\mathbf{M}}_2 + \hat{\mathbf{M}}_2 \cdot \hat{\mathbf{M}}_1 \quad (11.24)$$

If $\hat{\mathbf{M}}_1$ and $\hat{\mathbf{M}}_2$ refer to different electrons, they will commute with each other, since each will affect only functions of the coordinates of one electron and not the other. Even if $\hat{\mathbf{M}}_1$ and $\hat{\mathbf{M}}_2$ are the orbital and spin angular momenta of the same electron, they will commute, as one will affect only functions of the spatial coordinates while the other will affect functions of the spin coordinates. Thus (11.24) becomes

$$\hat{M}^2 = \hat{M}_1^2 + \hat{M}_2^2 + 2\hat{\mathbf{M}}_1 \cdot \hat{\mathbf{M}}_2 \quad (11.25)$$

$$\hat{M}^2 = \hat{M}_1^2 + \hat{M}_2^2 + 2(\hat{M}_{1x}\hat{M}_{2x} + \hat{M}_{1y}\hat{M}_{2y} + \hat{M}_{1z}\hat{M}_{2z}) \quad (11.26)$$

We now show that the components of the total angular momentum obey the usual angular-momentum commutation relations. We have [Eq. (5.4)]

$$\begin{aligned} [\hat{M}_x, \hat{M}_y] &= [\hat{M}_{1x} + \hat{M}_{2x}, \hat{M}_{1y} + \hat{M}_{2y}] \\ &= [\hat{M}_{1x}, \hat{M}_{1y} + \hat{M}_{2y}] + [\hat{M}_{2x}, \hat{M}_{1y} + \hat{M}_{2y}] \\ &= [\hat{M}_{1x}, \hat{M}_{1y}] + [\hat{M}_{1x}, \hat{M}_{2y}] + [\hat{M}_{2x}, \hat{M}_{1y}] + [\hat{M}_{2x}, \hat{M}_{2y}] \end{aligned}$$

Since all components of $\hat{\mathbf{M}}_1$ commute with all components of $\hat{\mathbf{M}}_2$, we have

$$\begin{aligned} [\hat{M}_x, \hat{M}_y] &= [\hat{M}_{1x}, \hat{M}_{1y}] + [\hat{M}_{2x}, \hat{M}_{2y}] = i\hbar\hat{M}_{1z} + i\hbar\hat{M}_{2z} \\ [\hat{M}_x, \hat{M}_y] &= i\hbar\hat{M}_z \end{aligned} \quad (11.27)$$

Cyclic permutation of x , y , and z gives

$$[\hat{M}_y, \hat{M}_z] = i\hbar\hat{M}_x, \quad [\hat{M}_z, \hat{M}_x] = i\hbar\hat{M}_y \quad (11.28)$$

The same commutator algebra used to derive (5.109) gives

$$[\hat{M}^2, \hat{M}_x] = [\hat{M}^2, \hat{M}_y] = [\hat{M}^2, \hat{M}_z] = 0 \quad (11.29)$$

Thus we can simultaneously quantize M^2 and one of its components, say M_z . Since the components of the total angular momentum obey the angular-momentum commutation relations, the work of Section 5.4 shows that the eigenvalues of $\hat{M}^2$ are

$$J(J+1)\hbar^2, \quad J = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots \quad (11.30)$$

and the eigenvalues of $\hat{M}_z$ are

$$M_J\hbar, \quad M_J = -J, -J+1, \dots, J-1, J \quad (11.31)$$

We want to find out how the total-angular-momentum quantum numbers J and M_J are related to the quantum numbers j_1, j_2, m_1, m_2 of the two angular momenta we are adding in (11.20). We also want the eigenfunctions of $\hat{M}^2$ and $\hat{M}_z$. These eigenfunctions are characterized by the quantum numbers J and M_J , and, using ket notation (Section 7.3), we write them as $|JM_J\rangle$. Similarly, let $|j_1 m_1\rangle$ denote the eigenfunctions of $\hat{M}_1^2$ and $\hat{M}_{1z}$ and $|j_2 m_2\rangle$ denote the eigenfunctions of $\hat{M}_2^2$ and $\hat{M}_{2z}$. Now it is readily shown (Prob. 11.10) that

$$[\hat{M}_x, \hat{M}_1^2] = [\hat{M}_y, \hat{M}_1^2] = [\hat{M}_z, \hat{M}_1^2] = [\hat{M}^2, \hat{M}_1^2] = 0 \quad (11.32)$$

with similar equations with $\hat{M}_2^2$ replacing $\hat{M}_1^2$. Hence we can have simultaneous eigenfunctions of all four operators $\hat{M}_1^2, \hat{M}_2^2, \hat{M}^2, \hat{M}_z$, and the eigenfunctions $|JM_J\rangle$ can be more fully written as $|j_1 j_2 JM_J\rangle$. However, one finds that $\hat{M}^2$ does not commute with $\hat{M}_{1z}$ or $\hat{M}_{2z}$ (Prob. 11.12), so the eigenfunctions $|j_1 j_2 JM_J\rangle$ are not necessarily eigenfunctions of $\hat{M}_{1z}$ or $\hat{M}_{2z}$.

If we take the complete set of functions $|j_1 m_1\rangle$ for particle 1 and the complete set $|j_2 m_2\rangle$ for particle 2 and form all possible products of the form $|j_1 m_1\rangle |j_2 m_2\rangle$, we will have a complete set of functions for the two particles. Each unknown eigenfunction $|j_1 j_2 JM_J\rangle$ can then be expanded using this complete set:

$$|j_1 j_2 JM_J\rangle = \sum C(j_1 j_2 JM_J; m_1 m_2) |j_1 m_1\rangle |j_2 m_2\rangle \quad (11.33)$$

where the expansion coefficients are the $C(j_1 \cdots m_2)$'s. The functions $|j_1 j_2 JM_J\rangle$ are eigenfunctions of the commuting operators $\hat{M}_1^2, \hat{M}_2^2, \hat{M}^2$, and $\hat{M}_z$ with the following eigenvalues:

$\hat{M}_1^2$	$\hat{M}_2^2$	$\hat{M}^2$	$\hat{M}_z$
$j_1(j_1 + 1)\hbar^2$	$j_2(j_2 + 1)\hbar^2$	$J(J + 1)\hbar^2$	$M_J\hbar$

The functions $|j_1 m_1\rangle |j_2 m_2\rangle$ are eigenfunctions of the commuting operators $\hat{M}_1^2, \hat{M}_{1z}, \hat{M}_2^2, \hat{M}_{2z}$ with the following eigenvalues:

$\hat{M}_1^2$	$\hat{M}_{1z}$	$\hat{M}_2^2$	$\hat{M}_{2z}$
$j_1(j_1 + 1)\hbar^2$	$m_1\hbar$	$j_2(j_2 + 1)\hbar^2$	$m_2\hbar$

Since the function $|j_1 j_2 JM_J\rangle$ being expanded in (11.33) is an eigenfunction of $\hat{M}_1^2$ with eigenvalue $j_1(j_1 + 1)\hbar^2$, we include in the sum only terms that have the same j_1 value as in the function $|j_1 j_2 JM_J\rangle$. (See Theorem 3 at the end of Section 7.3.) Likewise, only terms with the same j_2 value as in $|j_1 j_2 JM_J\rangle$ are included in the sum. Hence the sum goes over only the m_1 and m_2 values. Also, using $\hat{M}_z = \hat{M}_{1z} + \hat{M}_{2z}$, we can prove (Prob. 11.11) that the coefficient C vanishes unless

$$m_1 + m_2 = M_J \quad (11.34)$$

To find the total-angular-momentum eigenfunctions, one must evaluate the coefficients in (11.33). These are called *Clebsch–Gordan* or *Wigner* or *vector addition* coefficients. For their evaluation, see *Merzbacher*, Section 16.6.

Thus each total-angular-momentum eigenfunction $|j_1 j_2 JM_J\rangle$ is a linear combination of those product functions $|j_1 m_1\rangle |j_2 m_2\rangle$ whose m values satisfy $m_1 + m_2 = M_J$.

We now find the possible values of the total-angular-momentum quantum number J that arise from the addition of angular momenta with individual quantum numbers j_1 and j_2 .

Before discussing the general case, we consider the case with $j_1 = 1, j_2 = 2$. The possible values of m_1 are $-1, 0, 1$, and the possible values of m_2 are $-2, -1, 0, 1, 2$. If we

describe the system by the quantum numbers j_1, j_2, m_1, m_2 , then the total number of possible states is fifteen, corresponding to three possibilities for m_1 and five for m_2 . Instead, we can describe the system using the quantum numbers j_1, j_2, J, M_J , and we must have the same number of states in this description. Let us tabulate the fifteen possible values of M_J using (11.34):

$m_1 = -1$	0	1	
-3	-2	-1	$-2 = m_2$
-2	-1	0	-1
-1	0	1	0
0	1	2	1
1	2	3	2

where each M_J value in the table is the sum of the m_1 and m_2 values at the top and side. The number of times each value of M_J occurs is

value of M_J	3	2	1	0	-1	-2	-3
number of occurrences	1	2	3	3	3	2	1

The highest value of M_J is +3. Since M_J ranges from $-J$ to $+J$, the highest value of J must be 3. Corresponding to $J = 3$, there are seven values of M_J ranging from -3 to $+3$. Eliminating these seven values, we are left with

value of M_J	2	1	0	-1	-2
number of occurrences	1	2	2	2	1

The highest remaining value, $M_J = 2$, must correspond to $J = 2$. For $J = 2$, we have five values of M_J , which when eliminated leave

value of M_J	1	0	-1
number of occurrences	1	1	1

These remaining values of M_J clearly correspond to $J = 1$. Thus, for the individual angular-momentum quantum numbers $j_1 = 1, j_2 = 2$, the possible values of the total angular-momentum quantum number J are 3, 2, and 1.

Now consider the general case. There are $2j_1 + 1$ values of m_1 (ranging from $-j_1$ to $+j_1$) and $2j_2 + 1$ values of m_2 . Hence there are $(2j_1 + 1)(2j_2 + 1)$ possible states $|j_1 m_1\rangle |j_2 m_2\rangle$ with fixed j_1 and j_2 values. The highest possible values of m_1 and m_2 are j_1 and j_2 , respectively. Therefore, the maximum possible value of $M_J = m_1 + m_2$ is $j_1 + j_2$ [Eq. (11.34)]. Since M_J ranges from $-J$ to $+J$, the maximum possible value of J must also be $j_1 + j_2$:

$$J_{\max} = j_1 + j_2 \quad (11.35)$$

The second-highest value of M_J is $j_1 + j_2 - 1$, which arises in two ways: $m_1 = j_1 - 1, m_2 = j_2$ and $m_1 = j_1, m_2 = j_2 - 1$. Linear combinations of these two states must give one state with $J = j_1 + j_2, M_J = j_1 + j_2 - 1$ and one state with $J = j_1 + j_2 - 1, M_J = j_1 + j_2 - 1$. Continuing in this manner, we find that the possible values of J are

$$j_1 + j_2, \quad j_1 + j_2 - 1, \quad j_1 + j_2 - 2, \quad \dots, \quad J_{\min}$$

where $J_{\min}$ is the lowest possible value of J .

We determine $J_{\min}$ by the requirement that the total number of states be $(2j_1 + 1)(2j_2 + 1)$. For a particular value of J , there are $2J + 1$ M_J values, and so $2J + 1$ states correspond to each value of J . The total number of states $|j_1 j_2 J M_J\rangle$ for fixed j_1 and j_2 is found by summing the number of states $2J + 1$ for each J from $J_{\min}$ to $J_{\max}$:

$$\text{number of states} = \sum_{J=J_{\min}}^{J_{\max}} (2J + 1) \quad (11.36)$$

This sum goes from $J_{\min}$ to $J_{\max}$. Let us now take the lower limit of the sum to be $J = 0$ instead of $J_{\min}$. This change adds to the sum terms with J values of $0, 1, 2, \dots, J_{\min} - 1$. To compensate, we must subtract the corresponding sum that goes from $J = 0$ to $J = J_{\min} - 1$. Therefore, (11.36) becomes

$$\text{number of states} = \sum_{J=0}^{J_{\max}} (2J + 1) - \sum_{J=0}^{J_{\min}-1} (2J + 1)$$

Problem 6.16 gives $\sum_{l=0}^{n-1} (2l + 1) = n^2$. Replacing $n - 1$ with b , we get $\sum_{j=0}^b (2J + 1) = (b + 1)^2$. Therefore,

$$\text{number of states} = (J_{\max} + 1)^2 - J_{\min}^2 = J_{\max}^2 + 2J_{\max} + 1 - J_{\min}^2$$

Replacing $J_{\max}$ by $j_1 + j_2$ [Eq. (11.35)] and equating the number of states to $(2j_1 + 1)(2j_2 + 1) = 4j_1 j_2 + 2j_1 + 2j_2 + 1$, we have

$$(j_1 + j_2)^2 + 2(j_1 + j_2) + 1 - J_{\min}^2 = 4j_1 j_2 + 2j_1 + 2j_2 + 1$$

$$J_{\min}^2 = j_1^2 - 2j_1 j_2 + j_2^2 = (j_1 - j_2)^2$$

$$J_{\min} = \pm (j_1 - j_2) \quad (11.37)$$

If $j_1 = j_2$, then $J_{\min} = 0$. If $j_1 \neq j_2$, then one of the values in (11.37) is negative and must be rejected [Eq. (11.30)]. Thus

$$J_{\min} = |j_2 - j_1| \quad (11.38)$$

To summarize, we have shown that *the addition of two angular momenta characterized by quantum numbers j_1 and j_2 results in a total angular momentum whose quantum number J has the possible values*

$$J = j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2| \quad (11.39)$$

EXAMPLE

Find the possible values of the total-angular-momentum quantum number resulting from the addition of angular momenta with quantum numbers $j_1 = 2$ and $j_2 = 3$.

The maximum and minimum J values are given by (11.39) as $j_1 + j_2 = 2 + 3 = 5$ and $|j_1 - j_2| = |2 - 3| = 1$. The possible J values (11.39) are therefore $J = 5, 4, 3, 2, 1$.

EXERCISE Find the possible values of the total-angular-momentum quantum number resulting from the addition of angular momenta with quantum numbers $j_1 = 3$ and $j_2 = \frac{3}{2}$. (Answer: $J = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$.)

EXAMPLE

Find the possible J values when angular momenta with quantum numbers $j_1 = 1$, $j_2 = 2$, and $j_3 = 3$ are added.

To add more than two angular momenta, we apply (11.39) repeatedly. Addition of $j_1 = 1$ and $j_2 = 2$ gives the possible quantum numbers 3, 2, and 1. Addition of j_3 to each of these values gives the following possibilities for the total-angular-momentum quantum number:

$$6, 5, 4, 3, 2, 1, 0; \quad 5, 4, 3, 2, 1; \quad 4, 3, 2 \quad (11.40)$$

We have one set of states with total-angular-momentum quantum number 6, two sets of states with $J = 5$, three sets with $J = 4$, and so on.

EXERCISE Find the possible J values when angular momenta with quantum numbers $j_1 = 1$, $j_2 = 1$, and $j_3 = 1$ are added. (Answer: $J = 3, 2, 2, 1, 1, 1, 0$.)

11.5 Angular Momentum in Many-Electron Atoms

Total Electronic Orbital and Spin Angular Momenta

The **total electronic orbital angular momentum** of an n -electron atom is defined as the vector sum of the orbital angular momenta of the individual electrons:

$$\mathbf{L} = \sum_{i=1}^n \mathbf{L}_i \quad (11.41)$$

Although the individual orbital-angular-momentum operators $\hat{\mathbf{L}}_i$ do not commute with the atomic Hamiltonian (11.1), one can show (*Bethe and Jackiw*, pp. 102–103) that $\hat{\mathbf{L}}$ does commute with the atomic Hamiltonian [provided spin–orbit interaction (Section 11.6) is neglected]. We can therefore characterize an atomic state by a quantum number L , where $L(L + 1)\hbar^2$ is the square of the magnitude of the total electronic orbital angular momentum. The electronic wave function ψ of an atom satisfies $\hat{L}^2\psi = L(L + 1)\hbar^2\psi$. The total-electronic-orbital-angular-momentum quantum number L of an atom is specified by a code letter, as follows:

L	0	1	2	3	4	5	6	7	8
letter	<i>S</i>	<i>P</i>	<i>D</i>	<i>F</i>	<i>G</i>	<i>H</i>	<i>I</i>	<i>K</i>	<i>L</i>

(11.42)

The total orbital angular momentum is designated by a capital letter, while lowercase letters are used for orbital angular momenta of individual electrons.

EXAMPLE

Find the possible values of the quantum number L for states of the carbon atom that arise from the electron configuration $1s^2 2s^2 2p 3d$.

The s electrons have zero orbital angular momentum and contribute nothing to the total orbital angular momentum. The $2p$ electron has $l = 1$ and the $3d$ electron has $l = 2$. From the angular-momentum addition rule (11.39), the total-orbital-angular-momentum quantum number ranges from $1 + 2 = 3$ to $|1 - 2| = 1$; the possible values of L are $L = 3, 2, 1$. The configuration $1s^2 2s^2 2p 3d$ gives rise to P , D , and F states. [The Hartree–Fock central-field approximation has each electron moving in a central-field potential, $V = V(r)$. Hence, within this approximation, the individual electronic orbital angular momenta are constant, giving rise to a wave function composed of a single

configuration that specifies the individual orbital angular momenta. When we go beyond the SCF central-field approximation, we mix in other configurations so we no longer specify precisely the individual orbital angular momenta. Even so, we can still use the rule (11.39) for finding the possible values of the total orbital angular momentum.]

EXERCISE Find the possible values of L for states that arise from the electron configuration $1s^2 2s^2 2p^6 3s^2 3p 4p$. (Answer: 2, 1, 0.)

The **total electronic spin angular momentum** $\mathbf{S}$ of an atom is defined as the vector sum of the spins of the individual electrons:

$$\mathbf{S} = \sum_{i=1}^n \mathbf{S}_i \quad (11.43)$$

The atomic Hamiltonian $\hat{H}$ of (11.1) (which omits spin-orbit interaction) does not involve spin and therefore commutes with the total-spin operators $\hat{S}^2$ and $\hat{S}_z$. The fact that $\hat{S}^2$ commutes with $\hat{H}$ is not enough to show that the atomic wave functions ψ are eigenfunctions of $\hat{S}^2$. The antisymmetry requirement means that each ψ must be an eigenfunction of the exchange operator $\hat{P}_{ik}$ with eigenvalue -1 (Section 10.3). Hence $\hat{S}^2$ must also commute with $\hat{P}_{ik}$ if we are to have simultaneous eigenfunctions of $\hat{H}$, $\hat{S}^2$, and $\hat{P}_{ik}$. Problem 11.19 shows that $[\hat{S}^2, \hat{P}_{ik}] = 0$, so the atomic wave functions are eigenfunctions of $\hat{S}^2$. We have $\hat{S}^2\psi = S(S+1)\hbar^2\psi$, and each atomic state can be characterized by a total-electronic-spin quantum number S .

EXAMPLE

Find the possible values of the quantum number S for states that arise from the electron configuration $1s^2 2s^2 2p 3d$.

Consider first the two $1s$ electrons. To satisfy the exclusion principle, one of these electrons must have $m_s = +\frac{1}{2}$ while the other has $m_s = -\frac{1}{2}$. If M_S is the quantum number that specifies the z component of the total spin of the $1s$ electrons, then the only possible value of M_S is $\frac{1}{2} - \frac{1}{2} = 0$ [Eq. (11.34)]. This single value of M_S clearly means that the total spin of the two $1s$ electrons is zero. Thus, although in general when we add the spins $s_1 = \frac{1}{2}$ and $s_2 = \frac{1}{2}$ of two electrons according to the rule (11.39), we get the two possibilities $S = 0$ and $S = 1$, the restriction imposed by the Pauli principle leaves $S = 0$ as the only possibility in this case. Likewise, the spins of the $2s$ electrons add up to zero. The exclusion principle does not restrict the m_s values of the $2p$ and $3d$ electrons. Application of the rule (11.39) to the spins $s_1 = \frac{1}{2}$ and $s_2 = \frac{1}{2}$ of the $2p$ and $3d$ electrons gives $S = 0$ and $S = 1$. These are the possible values of the total spin quantum number, since the $1s$ and $2s$ electrons do not contribute to S .

EXERCISE Find the possible values of S for states that arise from the electron configuration $1s^2 2s^2 2p^6 3s^2 3p 4p$. (Answer: 0 and 1.)

Atomic Terms

A given electron configuration gives rise in general to several different atomic states, some having the same energy and others having different energies, depending on whether the interelectronic repulsions are the same or different for the states. For example, the $1s2s$ configuration of helium gives rise to four states: The three states with zeroth-order wave functions (10.27) to (10.29) all have the same energy; the single state (10.30) has a different energy. The $1s2p$ electron configuration gives rise to twelve states: The nine states obtained by replacing $2s$ in (10.27) to (10.29) by $2p_x$, $2p_y$, or $2p_z$ have the same energy; the three states obtained by replacing $2s$ in (10.30) by $2p_x$, $2p_y$, or $2p_z$ have the same energy, which differs from the energy of the other nine states.

Thus the atomic states that arise from a given electron configuration can be grouped into sets of states that have the same energy. One can show that states that arise from the same electron configuration and that have the same energy (with spin-orbit interaction neglected) will have the same value of L and the same value of S (see *Kemble*, Section 63a). A set of equal-energy atomic states that arise from the same electron configuration and that have the same L value and the same S value constitutes an atomic **term**. For a fixed L value, the quantum number M_L (where $M_L\hbar$ is the z component of the total electronic orbital angular momentum) takes on $2L + 1$ values ranging from $-L$ to $+L$. For a fixed S value, M_S takes on $2S + 1$ values. The atomic energy does not depend on M_L or M_S , and each term consists of $(2L + 1)(2S + 1)$ atomic states of equal energy. The degeneracy of an atomic term is $(2L + 1)(2S + 1)$ (spin-orbit interaction neglected).

Each term of an atom is designated by a **term symbol** formed by writing the numerical value of the quantity $2S + 1$ as a left superscript on the code letter (11.42) that gives the L value. For example, a term that has $L = 2$ and $S = 1$ has the term symbol ${}^3D$, since $2S + 1 = 3$.

EXAMPLE

Find the terms arising from each of the following electron configurations: (a) $1s2p$; (b) $1s^22s^22p3d$. Give the degeneracy of each term.

(a) The $1s$ electron has quantum number $l = 0$ and the $2p$ electron has $l = 1$. The addition rule (11.39) gives $L = 1$ as the only possibility. The code letter for $L = 1$ is P . Each electron has $s = \frac{1}{2}$, and (11.39) gives $S = 1, 0$ as the possible S values. The possible values of $2S + 1$ are 3 and 1. The possible terms are thus ${}^3P$ and ${}^1P$. The ${}^3P$ term has quantum numbers $L = 1$ and $S = 1$, and its degeneracy is $(2L + 1)(2S + 1) = 3(3) = 9$. The ${}^1P$ term has $L = 1$ and $S = 0$, and its degeneracy is $(2L + 1)(2S + 1) = 3(1) = 3$. [The nine states of the ${}^3P$ term are obtained by replacing $2s$ in (10.27) to (10.29) by $2p_x, 2p_y$, or $2p_z$. The three states of the ${}^1P$ term are obtained by replacing $2s$ in (10.30) by $2p$ functions.]

(b) In the two previous examples in this section, we found that the configuration $1s^22s^22p3d$ has the possible L values $L = 3, 2, 1$ and has $S = 1, 0$. The code letters for these L values are F, D, P , and the terms are

$${}^1P, \quad {}^3P, \quad {}^1D, \quad {}^3D, \quad {}^1F, \quad {}^3F \quad (11.44)$$

The degeneracies are found as in (a) and are 3, 9, 5, 15, 7, and 21, respectively.

Derivation of Atomic Terms

We now examine how to systematically derive the terms that arise from a given electron configuration.

First consider configurations that contain only completely filled subshells. In such configurations, for each electron with $m_s = +\frac{1}{2}$ there is an electron with $m_s = -\frac{1}{2}$. Let the quantum number specifying the z component of the total electronic spin angular momentum be M_S . The only possible value for M_S is zero ($M_S = \sum_i m_{si} = 0$). Hence S must be zero. For each electron in a closed subshell with magnetic quantum number m , there is an electron with magnetic quantum number $-m$. For example, for a $2p^6$ configuration we have two electrons with $m = +1$, two with $m = -1$, and two with $m = 0$. Denoting the quantum number specifying the z component of the total electronic orbital angular momentum by M_L , we have $M_L = \sum_i m_i = 0$. We conclude that L must be zero. In summary, a configuration of closed subshells gives rise to only one term: ${}^1S$. For configurations consisting of closed subshells and open subshells, the closed subshells make no contribution to L or S and may be ignored in finding the terms.

We now consider two electrons in different subshells; such electrons are called **non-equivalent**. Nonequivalent electrons have different values of n or l or both, and we need not worry about any restrictions imposed by the exclusion principle when we derive the terms. We simply find the possible values of L from l_1 and l_2 according to (11.39); combining s_1 and s_2 gives $S = 0, 1$. We previously worked out the pd case, which gives the terms in (11.44). If we have more than two nonequivalent electrons, we combine the individual l 's to find the values of L , and we combine the individual s 's to find the values of S . For example, consider a pdf configuration. The possible values of L are given by (11.40). Combining three spin angular momenta, each of which is $\frac{1}{2}$, gives $S = \frac{3}{2}, \frac{1}{2}, \frac{1}{2}$. Each of the three possibilities in (11.40) with $L = 3$ may be combined with each of the two possibilities for $S = \frac{1}{2}$, giving six ${}^2F$ terms. Continuing in this manner, we find that the following terms arise from a pdf configuration: ${}^2S(2), {}^2P(4), {}^2D(6), {}^2F(6), {}^2G(6), {}^2H(4), {}^2I(2), {}^4S, {}^4P(2), {}^4D(3), {}^4F(3), {}^4G(3), {}^4H(2), {}^4I$, where the number of times each type of term occurs is in parentheses.

Now consider two electrons in the same subshell (**equivalent** electrons). Equivalent electrons have the same value of n and the same value of l , and the situation is complicated by the necessity to avoid giving two electrons the same four quantum numbers. Hence not all the terms derived for nonequivalent electrons are possible. As an example, consider the terms arising from two equivalent p electrons, an np^2 configuration. (The carbon ground-state configuration is $1s^2 2s^2 2p^2$.) The possible values of m and m_s for the two electrons are listed in Table 11.1, which also gives M_L and M_S .

Note that certain combinations are missing from this table. For example, $m_1 = 1, m_{s1} = \frac{1}{2}, m_2 = 1, m_{s2} = \frac{1}{2}$ is missing, since it violates the exclusion principle. Another missing combination is $m_1 = 1, m_{s1} = -\frac{1}{2}, m_2 = 1, m_{s2} = \frac{1}{2}$. This combination differs from $m_1 = 1, m_{s1} = \frac{1}{2}, m_2 = 1, m_{s2} = -\frac{1}{2}$ (row 1) solely by interchange of electrons 1 and 2. Each row in Table 11.1 stands for a Slater determinant, which when expanded

TABLE 11.1 Quantum Numbers for Two Equivalent p Electrons

m_1	m_{s1}	m_2	m_{s2}	$M_L = m_1 + m_2$	$M_S = m_{s1} + m_{s2}$
1	$\frac{1}{2}$	1	$-\frac{1}{2}$	2	0
1	$\frac{1}{2}$	0	$\frac{1}{2}$	1	1
1	$\frac{1}{2}$	0	$-\frac{1}{2}$	1	0
1	$-\frac{1}{2}$	0	$\frac{1}{2}$	1	0
1	$-\frac{1}{2}$	0	$-\frac{1}{2}$	1	-1
1	$\frac{1}{2}$	-1	$\frac{1}{2}$	0	1
1	$\frac{1}{2}$	-1	$-\frac{1}{2}$	0	0
1	$-\frac{1}{2}$	-1	$\frac{1}{2}$	0	0
1	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	0	-1
0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0
0	$\frac{1}{2}$	-1	$\frac{1}{2}$	-1	1
0	$\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	0
0	$-\frac{1}{2}$	-1	$\frac{1}{2}$	-1	0
0	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	-1
-1	$\frac{1}{2}$	-1	$-\frac{1}{2}$	-2	0

contains terms for all possible electron interchanges among the spin-orbitals. Two rows that differ from each other solely by interchange of two electrons correspond to the same Slater determinant, and we include only one of them in the table.

The highest value of M_L in Table 11.1 is 2, which must correspond to a term with $L = 2$, a D term. The $M_L = 2$ value occurs in conjunction with $M_S = 0$, indicating that $S = 0$ for the D term. Thus we have a ^1D term corresponding to the five states

$$\begin{array}{cccccc} M_L = & 2 & 1 & 0 & -1 & -2 \\ M_S = & 0 & 0 & 0 & 0 & 0 \end{array} \quad (11.45)$$

The highest value of M_S in Table 11.1 is 1, indicating a term with $S = 1$. $M_S = 1$ occurs in conjunction with $M_L = 1, 0, -1$, which indicates a P term. Hence we have a ^3P term corresponding to the nine states

$$\begin{array}{ccccccccc} M_L = & 1 & 1 & 1 & 0 & 0 & 0 & -1 & -1 & -1 \\ M_S = & 1 & 0 & -1 & 1 & 0 & -1 & 1 & 0 & -1 \end{array} \quad (11.46)$$

Elimination of the states of (11.45) and (11.46) from Table 11.1 leaves only a single state, which has $M_L = 0, M_S = 0$, corresponding to a ^1S term. Thus a p^2 configuration gives rise to the terms $^1S, ^3P, ^1D$. (In contrast, two nonequivalent p electrons give rise to six terms: $^1S, ^3S, ^1P, ^3P, ^1D, ^3D$.)

Table 11.2a lists the terms arising from various configurations of equivalent electrons. These results may be derived in the same way that we found the p^2 terms, but this procedure can become quite involved. To derive the terms of the f^7 configuration would require a table with 3432 rows. More efficient methods exist [R. F. Curl and J. E. Kilpatrick, *Am. J. Phys.*, **28**, 357 (1960); K. E. Hyde, *J. Chem. Educ.*, **52**, 87 (1975)].

TABLE 11.2 Terms Arising from Various Electron Configurations

Configuration	Terms
(a) <i>Equivalent electrons</i>	
$s^2; p^6; d^{10}$	^1S
$p; p^5$	^2P
$p^2; p^4$	$^3P, ^1D, ^1S$
p^3	$^4S, ^2D, ^2P$
$d; d^9$	^2D
$d^2; d^8$	$^3F, ^3P, ^1G, ^1D, ^1S$
$d^3; d^7$	$^4F, ^4P, ^2H, ^2G, ^2F, ^2D(2), ^2P$
$d^4; d^6$	$\begin{cases} ^5D, ^3H, ^3G, ^3F(2), ^3D, ^3P(2) \\ ^1I, ^1G(2), ^1F, ^1D(2), ^1S(2) \end{cases}$
d^5	$\begin{cases} ^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G(2) \\ ^2F(2), ^2D(3), ^2P, ^2S \end{cases}$
(b) <i>Nonequivalent electrons</i>	
ss	$^1S, ^3S$
sp	$^1P, ^3P$
sd	$^1D, ^3D$
pp	$^3D, ^1D, ^3P, ^1P, ^3S, ^1S$

Note from Table 11.2a that the terms arising from a subshell containing N electrons are the same as the terms for a subshell that is N electrons short of being full. For example, the terms for p^2 and p^4 are the same. We can divide the electrons of a closed subshell into two groups and find the terms for each group. Because a closed subshell gives only a ^1S term, the terms for each of these two groups must be the same. Table 11.2b gives the terms arising from some nonequivalent electron configurations.

To deal with a configuration containing both equivalent and nonequivalent electrons, we first find separately the terms from the nonequivalent electrons and the terms from the equivalent electrons. We then take all possible combinations of the L and S values of these two sets of terms. For example, consider an sp^3 configuration. From the s electron, we get a ^2S term. From the three equivalent p electrons, we get the terms ^2P , ^2D , and ^4S (Table 11.2a). Combining the L and S values of these terms, we have as the terms of an sp^3 configuration

$$^3P, ^1P, ^3D, ^1D, ^5S, ^3S \quad (11.47)$$

Hund's Rule

To decide which one of the terms arising from a given electron configuration is lowest in energy, we use the empirical **Hund's rule**: *For terms arising from the same electron configuration, the term with the largest value of S lies lowest. If there is more than one term with the largest S , then the term with the largest S and the largest L lies lowest.*

EXAMPLE

Use Table 11.2 to predict the lowest term of (a) the carbon ground-state configuration $1s^22s^22p^2$; (b) the configuration $1s^22s^22p^63s^23p^63d^24s^2$.

(a) Table 11.2a gives the terms arising from a p^2 configuration as ^3P , ^1D , and ^1S . The term with the largest S will have the largest value of the left superscript $2S + 1$. Hund's rule predicts ^3P as the lowest term. (b) Table 11.2a gives the d^2 terms as ^3F , ^3P , ^1G , ^1D , ^1S . Of these terms, ^3F and ^3P have the highest S . ^3F has $L = 3$; ^3P has $L = 1$. Therefore, ^3F is predicted to be lowest.

EXERCISE Predict the lowest term of the $1s^22s2p^3$ configuration using (11.47). (Answer: ^5S .)

Hund's rule works very well for the ground-state configuration, but occasionally fails for an excited configuration (Prob. 11.30).

Hund's rule gives only the lowest term of a configuration and should not be used to decide the order of the remaining terms. For example, for the $1s^22s2p^3$ configuration of carbon, the observed order of the terms is

$$^5S < ^3D < ^3P < ^1D < ^3S < ^1P$$

The ^3S term lies above the ^1D term, even though ^3S has the higher spin S .

It is not necessary to consult Table 11.2a to find the lowest term of a partly filled subshell configuration. We simply put the electrons in the orbitals so as to give the greatest number of parallel spins. Thus, for a d^3 configuration, we have

$$m: \begin{array}{ccccc} \uparrow & \uparrow & \uparrow & _ & _ \\ +2 & +1 & 0 & -1 & -2 \end{array} \quad (11.48)$$

The lowest term thus has three parallel spins, so $S = \frac{3}{2}$, giving $2S + 1 = 4$. The maximum value of M_L is 3, corresponding to $L = 3$, an F term. Hund's rule thus predicts ^4F as the lowest term of a d^3 configuration.

The traditional explanation of Hund's rule is as follows: Electrons with the same spin tend to keep out of each other's way (recall the idea of Fermi holes), thereby minimizing the Coulombic repulsion between them. The term that has the greatest number of parallel spins (that is, the greatest value of S) will therefore be lowest in energy. For example, the ^3S term of the helium $1s2s$ configuration has an antisymmetric spatial function that vanishes when the spatial coordinates of the two electrons are equal. Hence the ^3S term is lower than the ^1S term.

This traditional explanation turns out to be wrong in most cases. It is true that the probability that the two electrons are very close together is smaller for the helium ^3S $1s2s$ term than for the ^1S $1s2s$ term. However, calculations with accurate wave functions show that the probability that the two electrons are very far apart is also less for the ^3S term. The net result is that the average distance between the two electrons is slightly less for the ^3S term than for the ^1S term, and the interelectronic repulsion is slightly greater for the ^3S term. The calculations show that the ^3S term lies below the ^1S term because of a substantially greater electron–nucleus attraction in the ^3S term as compared with the ^1S term. Similar results are found for terms of the atoms beryllium and carbon. [See J. Katriel and R. Pauncz, *Adv. Quantum Chem.*, **10**, 143 (1977).] The following explanation of these results has been proposed [I. Shim and J. P. Dahl, *Theor. Chim. Acta*, **48**, 165 (1978)]. The Pauli “repulsion” between electrons of like spin makes the average angle between the radius vectors of the two electrons larger for the ^3S term than for the ^1S term. This reduces the electronic screening of the nucleus and allows the electrons to get closer to the nucleus in the ^3S term, making the electron–nucleus attraction greater for the ^3S term. [See also R. E. Boyd, *Nature*, **310**, 480 (1984); T. Oyamada et al., *J. Chem. Phys.*, **133**, 164113 (2010).]

Eigenvalues of Two-Electron Spin Functions

The helium atom $1s2s$ configuration gives rise to the term ^3S with degeneracy $(2L + 1)(2S + 1) = 1(3) = 3$ and to the term ^1S with degeneracy $1(1) = 1$. The three helium zeroth-order wave functions (10.27) to (10.29) must correspond to the triply degenerate ^3S term, and the single function (10.30) must correspond to the ^1S term. Since $S = 1$ and $M_S = 1, 0, -1$ for the ^3S term, the three spin functions in (10.27) to (10.29) should be eigenfunctions of $\hat{S}^2$ with eigenvalue $S(S + 1)\hbar^2 = 2\hbar^2$ and eigenfunctions of $\hat{S}_z$ with eigenvalues $M_S\hbar = \hbar, 0$, and $-\hbar$. The spin function in (10.30) should be an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$ with eigenvalue zero in each case, since $S = 0$ and $M_S = 0$ here. We now verify these assertions.

From Eq. (11.43), the total-electron-spin operator is the sum of the spin operators for each electron:

$$\hat{S} = \hat{S}_1 + \hat{S}_2 \quad (11.49)$$

Taking the z components of (11.49), we have

$$\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z} \quad (11.50)$$

$$\begin{aligned} \hat{S}_z \alpha(1)\alpha(2) &= \hat{S}_{1z} \alpha(1)\alpha(2) + \hat{S}_{2z} \alpha(1)\alpha(2) \\ &= \alpha(2)\hat{S}_{1z} \alpha(1) + \alpha(1)\hat{S}_{2z} \alpha(2) \\ &= \frac{1}{2}\hbar\alpha(1)\alpha(2) + \frac{1}{2}\hbar\alpha(1)\alpha(2) \\ \hat{S}_z \alpha(1)\alpha(2) &= \hbar\alpha(1)\alpha(2) \end{aligned} \quad (11.51)$$

where Eq. (10.7) has been used. Similarly, we find

$$\hat{S}_z \beta(1)\beta(2) = -\hbar\beta(1)\beta(2) \quad (11.52)$$

$$\hat{S}_z[\alpha(1)\beta(2) + \beta(1)\alpha(2)] = 0 \quad (11.53)$$

$$\hat{S}_z[\alpha(1)\beta(2) - \beta(1)\alpha(2)] = 0 \quad (11.54)$$

Consider now $\hat{S}^2$. We have [Eq. (11.26)]

$$\hat{S}^2 = (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2) \cdot (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2) = \hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z}) \quad (11.55)$$

$$\begin{aligned} \hat{S}^2\alpha(1)\alpha(2) &= \alpha(2)\hat{S}_1^2\alpha(1) + \alpha(1)\hat{S}_2^2\alpha(2) + 2\hat{S}_{1x}\alpha(1)\hat{S}_{2x}\alpha(2) \\ &\quad + 2\hat{S}_{1y}\alpha(1)\hat{S}_{2y}\alpha(2) + 2\hat{S}_{1z}\alpha(1)\hat{S}_{2z}\alpha(2) \end{aligned}$$

Using Eqs. (10.7) to (10.9) and (10.72) and (10.73), we find

$$\hat{S}^2\alpha(1)\alpha(2) = 2\hbar^2\alpha(1)\alpha(2) \quad (11.56)$$

Hence $\alpha(1)\alpha(2)$ is an eigenfunction of $\hat{S}^2$ corresponding to $S = 1$. Similarly, we find

$$\hat{S}^2\beta(1)\beta(2) = 2\hbar^2\beta(1)\beta(2)$$

$$\hat{S}^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] = 2\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\hat{S}^2[\alpha(1)\beta(2) - \beta(1)\alpha(2)] = 0$$

Thus the spin eigenfunctions in (10.27) to (10.30) correspond to the following values for the total spin quantum numbers:

	S	M_S	
triplet $\left\{ \begin{array}{l} \alpha(1)\alpha(2) \\ 2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \beta(1)\beta(2) \end{array} \right.$	1	1	(11.57)
	1	0	(11.58)
	1	-1	(11.59)
singlet $\{ 2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$	0	0	(11.60)

[In the notation of Section 11.4, we are dealing with the addition of two angular momenta with quantum numbers $j_1 = \frac{1}{2}$ and $j_2 = \frac{1}{2}$ to give eigenfunctions with total angular-momentum quantum numbers $J = 1$ and $J = 0$. The coefficients in (11.57) to (11.60) correspond to the coefficients C in (11.33) and are examples of Clebsch–Gordan coefficients.]

Figure 11.3 shows the vector addition of $\mathbf{S}_1$ and $\mathbf{S}_2$ to form $\mathbf{S}$. It might seem surprising that the spin function (11.58), which has the z components of the spins of the two electrons pointing in opposite directions, could have total spin quantum number $S = 1$. Figure 11.3 shows how this is possible.

Atomic Wave Functions

In Section 10.6, we showed that two of the four zeroth-order wave functions of the $1s2s$ helium configuration could be written as single Slater determinants, but the other two functions had to be expressed as linear combinations of two Slater determinants. Since $\hat{L}^2$ and $\hat{S}^2$ commute with the Hamiltonian (11.1) and with the exchange operator $\hat{P}_{ik}$, the zeroth-order functions should be eigenfunctions of $\hat{L}^2$ and $\hat{S}^2$. The Slater determinants D_2 and D_3 of Section 10.6 are not eigenfunctions of these operators and so are not suitable zeroth-order functions. We have just shown that the linear combinations (10.44) and (10.45) are eigenfunctions of $\hat{S}^2$, and they can also be shown to be eigenfunctions of $\hat{L}^2$.

For a configuration of closed subshells (for example, the helium ground state), we can write only a single Slater determinant. This determinant is an eigenfunction of $\hat{L}^2$ and $\hat{S}^2$ and is the correct zeroth-order function for the nondegenerate ^1S term. A configuration

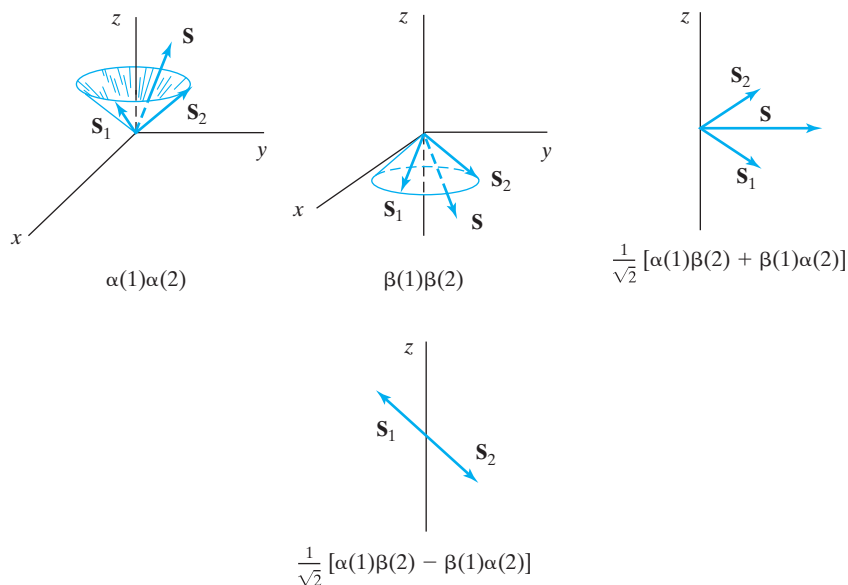


FIGURE 11.3 Vector addition of the spins of two electrons. For $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$, the projections of $\mathbf{S}_1$ and $\mathbf{S}_2$ in the xy plane make an angle of 90° with each other (Prob. 11.18c).

with one electron outside closed subshells (for example, the boron ground configuration) gives rise to only one term. The Slater determinants for such a configuration differ from one another only in the m and m_s values of this electron and are the correct zeroth-order functions for the states of the term. When all the electrons in singly occupied orbitals have the same spin (either all α or all β), the correct zeroth-order function is a single Slater determinant [for example, see (10.42)]. When this is not true, one has to take a linear combination of a few Slater determinants to obtain the correct zeroth-order functions, which are eigenfunctions of $\hat{L}^2$ and $\hat{S}^2$. The correct linear combinations can be found by solving the secular equation of degenerate perturbation theory or by operator techniques. Tabulations of the correct combinations for various configurations are available (*Slater, Atomic Structure*, Vol. II). Hartree–Fock calculations of atomic term energies use these linear combinations and find the best possible orbital functions for the Slater determinants.

Each wave function of an atomic term is an eigenfunction of $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_z$, and $\hat{S}_z$. Therefore, when one does a configuration-interaction calculation, only configuration functions that have the same $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_z$, and $\hat{S}_z$ eigenvalues as the state under consideration are included in the expansion (11.17). For example, the helium $1s^2$ ground term is ^1S , which has $L = 0$ and $S = 0$. The electron configuration $1s2p$ produces ^1P and ^3P terms only and so gives rise to states with $L = 1$ only. No configuration functions arising from the $1s2p$ configuration can occur in the CI wave function (11.17) for the He ground state.

Parity of Atomic States

Consider the atomic Hamiltonian (11.1). We showed in Section 7.5 that the parity operator $\hat{\Pi}$ commutes with the kinetic-energy operator. The quantity $1/r_i$ in (11.1) is $r_i^{-1} = (x_i^2 + y_i^2 + z_i^2)^{-1/2}$. Replacement of each coordinate by its negative leaves $1/r_i$ unchanged. Also

$$r_{ij}^{-1} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{-1/2}$$

and inversion has no effect on $1/r_{ij}$. Thus $\hat{\Pi}$ commutes with the atomic Hamiltonian, and we can choose atomic wave functions to have definite parity.

For a one-electron atom, the spatial wave function is $\psi = R(r)Y_l^m(\theta, \phi)$. The radial function is unchanged on inversion, and the parity is determined by the angular factor. In Prob. 7.29 we showed that Y_l^m is an even function when l is even and is an odd function when l is odd. Thus the states of one-electron atoms have even or odd parity according to whether l is even or odd.

Now consider an n -electron atom. In the Hartree–Fock central-field approximation, we write the wave function as a Slater determinant (or linear combination of Slater determinants) of spin-orbitals. The wave function is the sum of terms, the spatial factor in each term having the form

$$R_1(r_1) \cdots R_n(r_n) Y_{l_1}^{m_1}(\theta_1, \phi_1) \cdots Y_{l_n}^{m_n}(\theta_n, \phi_n)$$

The parity of this product is determined by the spherical-harmonic factors. We see that the product is an even or odd function according to whether $l_1 + l_2 + \cdots + l_n$ is an even or odd number. Therefore, the parity of an atomic state is found by adding the l values of the electrons in the electron configuration that gives rise to the state: If $\sum_i l_i$ is an even number, then ψ is an even function; if $\sum_i l_i$ is odd, ψ is odd. For example, the configuration $1s^2 2s 2p^3$ has $\sum_i l_i = 0 + 0 + 0 + 1 + 1 + 1 = 3$, and all states arising from this electron configuration have odd parity. (Our argument was based on the SCF approximation to ψ , but the conclusions are valid for the true ψ .)

Total Electronic Angular Momentum and Atomic Levels

The **total electronic angular momentum** $\mathbf{J}$ of an atom is the vector sum of the total electronic orbital and spin angular momenta:

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (11.61)$$

The operator $\hat{\mathbf{J}}$ for the total electronic angular momentum commutes with the atomic Hamiltonian, and we may characterize an atomic state by a quantum number J , which has the possible values [Eq. (11.39)]

$$L + S, L + S - 1, \dots, |L - S| \quad (11.62)$$

We have $\hat{J}^2 \psi = J(J + 1) \hbar^2 \psi$.

For the atomic Hamiltonian (11.1), all states that belong to the same term have the same energy. However, when spin–orbit interaction (Section 11.6) is included in $\hat{H}$, one finds that the value of the quantum number J affects the energy slightly. Hence states that belong to the same term but that have different values of J will have slightly different energies. The set of states that belong to the same term and that have the same value of J constitutes an atomic **level**. The energies of different levels belonging to the same term are slightly different. (See Fig. 11.6 in Section 11.7.) To denote the level, one adds the J value as a right subscript on the term symbol. Each level is $(2J + 1)$ -fold degenerate, corresponding to the $2J + 1$ values of M_J , where $M_J \hbar$ is the z component of the total electronic angular momentum $\mathbf{J}$. Each level consists of $2J + 1$ **states** of equal energy.

EXAMPLE

Find the levels of a ^3P term and give the degeneracy of each level.

For a ^3P term, $2S + 1 = 3$ and $S = 1$; also, from (11.42), $L = 1$. With $L = 1$ and $S = 1$, (11.62) gives $J = 2, 1, 0$. The levels are $^3P_2$, $^3P_1$, and $^3P_0$.

The $^3P_2$ level has $J = 2$ and has $2J + 1 = 5$ values of M_J , namely, $-2, -1, 0, 1$, and 2 . The $^3P_1$ level is 5-fold degenerate. The $^3P_1$ level is $2(1) + 1 = 3$ -fold degenerate. The $^3P_0$ level has $2J + 1 = 1$ and is nondegenerate.

The total number of states for the three levels ${}^3P_2$, ${}^3P_1$, and ${}^3P_0$ is $5 + 3 + 1 = 9$. When spin-orbit interaction was neglected, we had a ${}^3P$ term that consisted of $(2L + 1)(2S + 1) = 3(3) = 9$ equal-energy states. With spin-orbit interaction, the 9-fold-degenerate term splits into three closely spaced levels: ${}^3P_2$ with five states, ${}^3P_1$ with three states, and ${}^3P_0$ with one state. The total number of states is the same for the term ${}^3P$ as for the three levels arising from this term.

EXERCISE Find the levels of a ${}^2D$ term and give the level degeneracies. (Answer: ${}^2D_{5/2}$, ${}^2D_{3/2}$; 6, 4.)

The quantity $2S + 1$ is called the **electron-spin multiplicity** (or the *multiplicity*) of the term. If $L \geq S$, the possible values of J in (11.62) range from $L + S$ to $L - S$ and are $2S + 1$ in number. If $L < S$, the values of J range from $S + L$ to $S - L$ and are $2L + 1$ in number. In this case, the spin multiplicity is greater than the number of levels. For example, if $L = 0$ and $S = 1$ (a ${}^3S$ term), the spin multiplicity is 3, but there is only one possible value for J , namely, $J = 1$. For $2S + 1 = 1, 2, 3, 4, 5, 6, \dots$, the words **singlet**, **doublet**, **triplet**, **quartet**, **quintet**, **sextet**, $\dots$, are used to designate the spin multiplicity. The level symbol ${}^3P_1$ is read as “triplet P one.”

For light atoms, the spin-orbit interaction is very small and the separation between levels of a term is very small. Note from Fig. 11.6 in Section 11.7 that the separations between the ${}^3P_0$, ${}^3P_1$, and ${}^3P_2$ levels of the helium $1s2p$ ${}^3P$ term are far, far less than the separation between the ${}^1P$ and ${}^3P$ terms of the $1s2p$ configuration.

Terms and Levels of Hydrogen and Helium

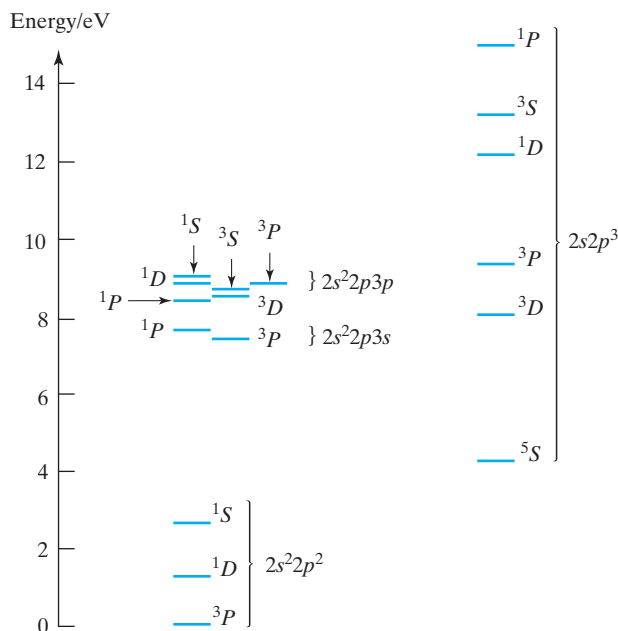
The hydrogen atom has one electron. Hence $L = l$ and $S = s = \frac{1}{2}$. The possible values of J are $L + \frac{1}{2}$ and $L - \frac{1}{2}$, except for $L = 0$, where $J = \frac{1}{2}$ is the only possibility. Each electron configuration gives rise to only one term, which is composed of one level if $L = 0$ and two levels if $L \neq 0$. The ground-state configuration $1s$ gives the term ${}^2S$, which is composed of the single level ${}^2S_{1/2}$; the level is twofold degenerate ($M_J = -\frac{1}{2}, \frac{1}{2}$). The $2s$ configuration also gives a ${}^2S_{1/2}$ level. The $2p$ configuration gives rise to the levels ${}^2P_{3/2}$ and ${}^2P_{1/2}$; the ${}^2P_{3/2}$ level is fourfold degenerate, and the ${}^2P_{1/2}$ level is twofold degenerate. There are $2 + 4 + 2 = 8$ states with $n = 2$, in agreement with our previous work.

The helium ground-state configuration $1s^2$ is a closed subshell and gives rise to the single level ${}^1S_0$, which is nondegenerate ($M_J = 0$). The $1s2s$ excited configuration gives rise to the two terms ${}^1S$ and ${}^3S$, each of which has one level. The ${}^1S_0$ level is nondegenerate; the ${}^3S_1$ level is threefold degenerate. The $1s2p$ configuration gives rise to the terms ${}^1P$ and ${}^3P$. The levels of ${}^3P$ are ${}^3P_2$, ${}^3P_1$, and ${}^3P_0$; ${}^1P$ has the single level ${}^1P_1$.

Tables of Atomic Energy Levels

The spectroscopically determined energy levels for atoms with atomic number less than 90 are given in the tables of C. E. Moore and others: C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular 467, vols. I, II, and III, 1949, 1952, and 1958, Washington D.C.; these have been reprinted as Natl. Bur. Stand. Publ. NSRDS-NBS 35, 1971; W. C. Martin et al., *Atomic Energy Levels—The Rare-Earth Elements*, Natl. Bur. Stand. Publ. NSRDS-NBS 60, Washington, D.C., 1978. The atomic-energy-level data in Moore’s tables and subsequent revisions are available online at the NIST Atomic Spectra Database at www.nist.gov/pml/data/asd.cfm.

These tables also list the levels of many atomic ions. Spectroscopists use the symbol I to indicate a neutral atom, the symbol II to indicate a singly ionized atom, and so on. To view the energy level data for the C^{2+} ion in the NIST online database, click on Levels and then enter C III after Spectrum.

FIGURE 11.4 Some term energies of the carbon atom.

The tables take the zero level of energy at the lowest energy level of the atom and list the level energies E_i as E_i/hc in cm^{-1} , where h and c are Planck's constant and the speed of light. The difference in E/hc values for two levels gives the wavenumber [Eq. (4.64)] of the spectral transition between the levels (provided the transition is allowed). An energy E of 1 eV corresponds to $E/hc = 8065.544 \text{ cm}^{-1}$ (Prob. 11.29).

Figure 11.4 shows some of the term energies of the carbon atom. The separations between levels of each term are too small to be visible in this figure.

11.6 Spin–Orbit Interaction

The atomic Hamiltonian (11.1) does not involve electron spin. In reality, the existence of spin adds an additional term, usually small, to the Hamiltonian. This term, called the **spin–orbit interaction**, splits an atomic term into levels. Spin–orbit interaction is a relativistic effect and is properly derived using Dirac's relativistic treatment of the electron. This section gives a qualitative discussion of the origin of spin–orbit interaction.

If we imagine ourselves riding on an electron in an atom, from our viewpoint, the nucleus is moving around the electron (as the sun appears to move around the earth). This apparent motion of the nucleus produces a magnetic field that interacts with the intrinsic (spin) magnetic moment of the electron, giving the spin–orbit interaction term in the Hamiltonian. The interaction energy of a magnetic moment $\mathbf{m}$ with a magnetic field $\mathbf{B}$ is given by (6.131) as $-\mathbf{m} \cdot \mathbf{B}$. The electron's spin magnetic moment $\mathbf{m}_s$ is proportional to its spin $\mathbf{S}$ [Eq. (10.57)], and the magnetic field arising from the apparent nuclear motion is proportional to the electron's orbital angular momentum $\mathbf{L}$. Therefore, the spin–orbit interaction is proportional to $\mathbf{L} \cdot \mathbf{S}$. The dot product of $\mathbf{L}$ and $\mathbf{S}$ depends on the relative orientation of these two vectors. The total electronic angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ also depends on the relative orientation of $\mathbf{L}$ and $\mathbf{S}$, and so the spin–orbit interaction energy depends on J [Eq. (11.67)].

When a proper relativistic derivation of the spin–orbit-interaction term $\hat{H}_{\text{S.O.}}$ in the atomic Hamiltonian is carried out, one finds that for a one-electron atom (see *Bethe and Jackiw*, Chapters 8 and 23)

$$\hat{H}_{\text{s.o.}} = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \quad (11.63)$$

where V is the potential energy experienced by the electron in the atom and c is the speed of light. One way to calculate $\hat{H}_{\text{s.o.}}$ for a many-electron atom is first to neglect $\hat{H}_{\text{s.o.}}$ and do an SCF calculation (Section 11.1) using the central-field approximation to get an effective potential energy $V_i(r_i)$ for each electron i in the field of the nucleus and the other electrons viewed as charge clouds [Eqs. (11.7) and (11.8)]. One then sums (11.63) over the electrons to get

$$\hat{H}_{\text{s.o.}} \approx \frac{1}{2m_e^2 c^2} \sum_i \frac{1}{r_i} \frac{dV_i(r_i)}{dr_i} \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i = \sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i \quad (11.64)$$

where the definition of $\xi_i(r_i)$ is obvious and $\hat{\mathbf{L}}_i$ and $\hat{\mathbf{S}}_i$ are the operators for orbital and spin angular momenta of electron i .

Calculating the spin–orbit interaction energy $E_{\text{s.o.}}$ by finding the eigenfunctions and eigenvalues of the operator $\hat{H}_{(11.1)} + \hat{H}_{\text{s.o.}}$, where $\hat{H}_{(11.1)}$ is the Hamiltonian of Eq. (11.1), is difficult. One therefore usually estimates $E_{\text{s.o.}}$ by using perturbation theory. Except for heavy atoms, the effect of $\hat{H}_{\text{s.o.}}$ is small compared with the effect of $\hat{H}_{(11.1)}$, and first-order perturbation theory can be used to estimate $E_{\text{s.o.}}$.

Equation (9.22) gives $E_{\text{s.o.}} \approx \langle \psi | \hat{H}_{\text{s.o.}} | \psi \rangle$, where ψ is an eigenfunction of $\hat{H}_{(11.1)}$. For a one-electron atom,

$$E_{\text{s.o.}} \approx \langle \psi | \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | \psi \rangle \quad (11.65)$$

We have

$$\begin{aligned} \mathbf{J} \cdot \mathbf{J} &= (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S} \\ \mathbf{L} \cdot \mathbf{S} &= \frac{1}{2}(J^2 - L^2 - S^2) \\ (\hat{\mathbf{L}} \cdot \hat{\mathbf{S}})\psi &= \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)\psi = \frac{1}{2}[J(J+1) - L(L+1) - S(S+1)]\hbar^2\psi \end{aligned}$$

since the unperturbed ψ is an eigenfunction of $\hat{L}^2$, $\hat{S}^2$, and $\hat{J}^2$. Therefore,

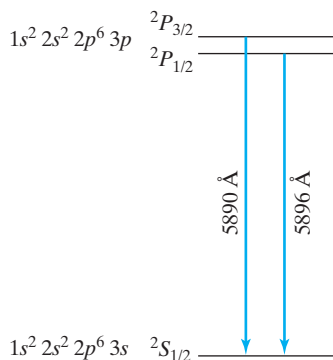
$$E_{\text{s.o.}} \approx \frac{1}{2} \langle \xi \rangle \hbar^2 [J(J+1) - L(L+1) - S(S+1)] \quad (11.66)$$

For a many-electron atom, it can be shown (*Bethe and Jackiw*, p. 164) that the spin–orbit interaction energy is

$$E_{\text{s.o.}} \approx \frac{1}{2} A \hbar^2 [J(J+1) - L(L+1) - S(S+1)] \quad (11.67)$$

where A is a constant for a given term; that is, A depends on L and S but not on J . Equation (11.67) shows that when we include the spin–orbit interaction, the energy of an atomic state depends on its total electronic angular momentum J . Thus each atomic term is split into levels, each level having a different value of J . For example, the $1s^2 2s^2 2p^6 3p$ configuration of sodium has the single term ^2P , which is composed of the two levels $^2P_{3/2}$ and $^2P_{1/2}$. The splitting of these levels gives the observed *fine structure* of the sodium D line (**Fig. 11.5**). The levels of a given term are said to form its *multiplet structure*.

What about the order of levels within a given term? Since L and S are the same for such levels, their relative energies are determined, according to Eq. (11.67), by $AJ(J+1)$. If A is positive, the level with the lowest value of J lies lowest, and the multiplet is said to be **regular**. If A is negative, the level with the highest value of J lies lowest, and the multiplet is said to be **inverted**. The following rule usually applies to a configuration with only one partly filled subshell: *If this subshell is less than half filled, the multiplet is regular; if this*

FIGURE 11.5 Fine structure of the sodium D line.

subshell is more than half filled, the multiplet is inverted. (A few exceptions exist.) For the half-filled case, see Prob. 11.28.

EXAMPLE

Find the ground level of the oxygen atom.

The ground electron configuration is $1s^2 2s^2 2p^4$. Table 11.2 gives ^1S , ^1D , and ^3P as the terms of this configuration. By Hund's rule, ^3P is the lowest term. [Alternatively, a diagram like (11.48) could be used to conclude that ^3P is the lowest term.] The ^3P term has $L = 1$ and $S = 1$, so the possible J values are 2, 1, and 0. The levels of ^3P are $^3P_2$, $^3P_1$, and $^3P_0$. The $2p$ subshell is more than half filled, so the rule just given predicts the multiplet is inverted, and the $^3P_2$ level lies lowest. This is the ground level of O.

EXERCISE Find the ground level of the Cl atom. (Answer: $^2P_{3/2}$.)

11.7 The Atomic Hamiltonian

The Hamiltonian operator of an atom can be divided into three parts:

$$\hat{H} = \hat{H}^0 + \hat{H}_{\text{rep}} + \hat{H}_{\text{S.O.}} \quad (11.68)$$

where $\hat{H}^0$ is the sum of hydrogenlike Hamiltonians,

$$\hat{H}^0 = \sum_{i=1}^n \left(-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) \quad (11.69)$$

$\hat{H}_{\text{rep}}$ consists of the interelectronic repulsions,

$$\hat{H}_{\text{rep}} = \sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (11.70)$$

and $\hat{H}_{\text{S.O.}}$ is the spin-orbit interaction (11.64):

$$\hat{H}_{\text{S.O.}} = \sum_{i=1}^n \xi_i \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i \quad (11.71)$$

If we consider just $\hat{H}^0$, all atomic states corresponding to the same electronic *configuration* are degenerate. Adding in $\hat{H}_{\text{rep}}$, we lift the degeneracy between states with different L or S or both, thus splitting each configuration into *terms*. Next, we add in $\hat{H}_{\text{S.O.}}$, which splits each term into *levels*. Each level is composed of *states* with the same value of J and is $(2J + 1)$ -fold degenerate, corresponding to the possible values of M_J .

We can remove the degeneracy of each level by applying an external magnetic field (the *Zeeman effect*). If $\mathbf{B}$ is the applied field, we have the additional term in the Hamiltonian [Eq. (6.131)]

$$\hat{H}_B = -\hat{\mathbf{m}} \cdot \mathbf{B} = -(\hat{\mathbf{m}}_L + \hat{\mathbf{m}}_S) \cdot \mathbf{B} \quad (11.72)$$

where both the orbital and spin magnetic moments have been included. Using $\mathbf{m}_L = -(e/2m_e)\mathbf{L}$, $\mathbf{m}_S = -(e/m_e)\mathbf{S}$, and $\mu_B \equiv e\hbar/2m_e$ [Eqs. (6.128), (10.55) with $g_e \approx 2$, and (6.130)], we have

$$\hat{H}_B = \mu_B \hbar^{-1} (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{B} = \mu_B \hbar^{-1} (\hat{\mathbf{J}} + \hat{\mathbf{S}}) \cdot \mathbf{B} = \mu_B B \hbar^{-1} (\hat{J}_z + \hat{S}_z) \quad (11.73)$$

where μ_B is the Bohr magneton and the z axis is taken along the direction of the field. If the external field is reasonably weak, its effect will be less than that of the spin-orbit interaction, and the effect of the field can be calculated by use of first-order perturbation theory. Since $\hat{J}_z \psi = M_J \hbar \psi$, the energy of interaction with the applied field is

$$E_B = \langle \psi | \hat{H}_B | \psi \rangle = \mu_B B M_J + \mu_B B \hbar^{-1} \langle S_z \rangle$$

Evaluation of $\langle S_z \rangle$ (Bethe and Jackiw, p. 169) gives as the final weak-field result:

$$E_B = \mu_B g B M_J \quad (11.74)$$

where g (the *Landé g factor*) is given by

$$g = 1 + \frac{[J(J+1) - L(L+1) + S(S+1)]}{2J(J+1)} \quad (11.75)$$

Thus the external field splits each level into $2J+1$ states, each state having a different value of M_J .

Figure 11.6 shows what happens when we consider successive interactions in an atom, using the $1s2p$ configuration of helium as the example.

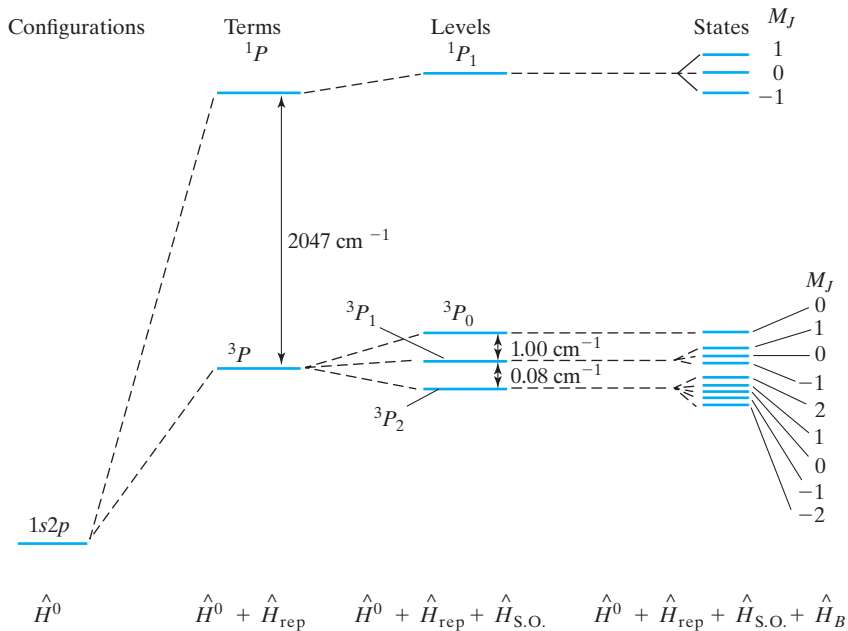


FIGURE 11.6 Effect of inclusion of successive terms in the atomic Hamiltonian for the $1s2p$ helium configuration. $\hat{H}_B$ is not part of the atomic Hamiltonian but is due to an applied magnetic field.

We have based the discussion on a scheme in which we first added the individual electronic orbital angular momenta to form a total-orbital-angular-momentum vector and did the same for the spins: $\mathbf{L} = \sum_i \mathbf{L}_i$ and $\mathbf{S} = \sum_i \mathbf{S}_i$. We then combined $\mathbf{L}$ and $\mathbf{S}$ to get $\mathbf{J}$. This scheme is called **Russell–Saunders coupling** (or *L–S coupling*) and is appropriate where the spin–orbit interaction energy is small compared with the interelectronic repulsion energy. The operators $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ commute with $\hat{H}^0 + \hat{H}_{\text{rep}}$, but when $\hat{H}_{\text{S.O.}}$ is included in the Hamiltonian, $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ no longer commute with $\hat{H}$. ($\hat{\mathbf{J}}$ does commute with $\hat{H}^0 + \hat{H}_{\text{rep}} + \hat{H}_{\text{S.O.}}$.) If the spin–orbit interaction is small, then $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ “almost” commute with $\hat{H}$, and *L–S coupling* is valid.

As the atomic number increases, the average speed v of the electrons increases. As v/c increases, relativistic effects such as the spin–orbit interaction increase. For atoms with very high atomic number, the spin–orbit interaction exceeds the interelectronic repulsion energy, and we can no longer consider $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ to commute with $\hat{H}$; the operator $\hat{\mathbf{J}}$, however, still commutes with $\hat{H}$. In this case we first add in $\hat{H}_{\text{S.O.}}$ to $\hat{H}^0$ and then consider $\hat{H}_{\text{rep}}$. This corresponds to first combining the spin and orbital angular momenta of each electron to give a total angular momentum $\mathbf{j}_i$ for each electron: $\mathbf{j}_i = \mathbf{L}_i + \mathbf{S}_i$. We then add the $\mathbf{j}_i$ ’s to get the total electronic angular momentum: $\mathbf{J} = \sum_i \mathbf{j}_i$. This scheme is called *j–j coupling*. For most heavy atoms, the situation is intermediate between *j–j* and *L–S coupling*, and computations are difficult.

Several other effects should be included in the atomic Hamiltonian. The finite size of the nucleus and the effect of nuclear motion slightly change the energy (*Bethe and Salpeter*, pp. 102, 166, 351). There is a small relativistic term due to the interaction between the spin magnetic moments of the electrons (*spin–spin interaction*). We should also take into account the relativistic change of electronic mass with velocity. This effect is significant for inner-shell electrons of heavy atoms, where average electronic speeds are not negligible in comparison with the speed of light.

If the nucleus has a nonzero spin, the nuclear spin magnetic moment interacts with the electronic spin and orbital magnetic moments, giving rise to atomic *hyperfine structure*. The *nuclear spin angular momentum* $\mathbf{I}$ adds vectorially to the total electronic angular momentum $\mathbf{J}$ to give the *total angular momentum* $\mathbf{F}$ of the atom: $\mathbf{F} = \mathbf{I} + \mathbf{J}$. For example, consider the ground state of the hydrogen atom. The spin of a proton is $\frac{1}{2}$, so $I = \frac{1}{2}$; also, $J = \frac{1}{2}$. Hence the quantum number F can be 0 or 1, corresponding to the proton and electron spins being antiparallel or parallel. The transition $F = 1 \rightarrow 0$ gives a line at 1420 MHz, the 21-cm line emitted by hydrogen atoms in outer space. In 1951, Ewen and Purcell stuck a horn-shaped antenna out the window of a Harvard physics laboratory and detected this line. The frequency of the hyperfine splitting in the ground state of hydrogen is one of the most accurately measured physical constants: $1420.405751768 \pm 0.000000002$ MHz [S. G. Karshenboim, *Can. J. Phys.*, **78**, 639 (2000); arxiv.org/abs/physics/0008051].

11.8 The Condon–Slater Rules

In the Hartree–Fock approximation, the wave function of an atom (or molecule) is a Slater determinant or a linear combination of a few Slater determinants [for example, Eq. (10.44)]. A configuration-interaction wave function such as (11.17) is a linear combination of many Slater determinants. To evaluate the energy and other properties of atoms and molecules using Hartree–Fock or configuration-interaction wave functions, we must be able to evaluate integrals of the form $\langle D' | \hat{B} | D \rangle$, where D and D' are Slater determinants of orthonormal spin-orbitals and $\hat{B}$ is an operator.

Each spin-orbital u_i is a product of a spatial orbital θ_i and a spin function σ_i , where σ_i is either α or β . We have $u_i = \theta_i \sigma_i$ and $\langle u_i(1) | u_j(1) \rangle = \delta_{ij}$, where $\langle u_i(1) | u_j(1) \rangle$ involves a sum over the spin coordinate of electron 1 and an integration over its spatial coordinates. If u_i and u_j have different spin functions, then (10.12) ensures the orthogonality

of u_i and u_j . If u_i and u_j have the same spin function, their orthogonality is due to the orthogonality of the spatial orbitals θ_i and θ_j .

For an n -electron system, D is

$$D = \frac{1}{\sqrt{n!}} \begin{vmatrix} u_1(1) & u_2(1) & \dots & u_n(1) \\ u_1(2) & u_2(2) & \dots & u_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ u_1(n) & u_2(n) & \dots & u_n(n) \end{vmatrix} \quad (11.76)$$

An example with $n = 3$ is Eq. (10.40). D' has the same form as D except that $u_1, u_2, \dots, u_n$ are replaced by $u'_1, u'_2, \dots, u'_n$.

We shall assume that the columns of D and D' are arranged so as to have as many as possible of their left-hand columns match. For example, if we were working with the Slater determinants $|1s\bar{1}s2s3p_0|$ and $|1s\bar{1}s3p_04s|$, we would interchange the third and fourth columns of the first determinant (thereby multiplying it by -1) and let $D = |1s\bar{1}s3p_02s|$ and $D' = |1s\bar{1}s3p_04s|$.

The operator $\hat{B}$ typically has the form

$$\hat{B} = \sum_{i=1}^n \hat{f}_i + \sum_{i=1}^{n-1} \sum_{j>i} \hat{g}_{ij} \quad (11.77)$$

where the *one-electron operator* $\hat{f}_i$ involves only coordinate and momentum operators of electron i and the *two-electron operator* $\hat{g}_{ij}$ involves electrons i and j . For example, if $\hat{B}$ is the atomic Hamiltonian operator (11.1), then $\hat{f}_i = -(\hbar^2/2m_e)\nabla_i^2 - Ze^2/4\pi\epsilon_0 r_i$ and $\hat{g}_{ij} = e^2/4\pi\epsilon_0 r_{ij}$.

Condon and Slater showed that the n -electron integral $\langle D' | \hat{B} | D \rangle$ can be reduced to sums of certain one- and two-electron integrals. The derivation of these Condon–Slater formulas uses the determinant expression of Prob. 8.22 together with the orthonormality of the spin-orbitals. (See Parr, pp. 23–27 for the derivation.) Table 11.3 gives the Condon–Slater formulas.

In Table 11.3, each matrix element of $\hat{g}_{12}$ involves summation over the spin coordinates of electrons 1 and 2 and integration over the full range of the spatial coordinates of electrons 1 and 2. Each matrix element of $\hat{f}_1$ involves summation over the spin coordinate of electron 1 and integration over its spatial coordinates. The variables in the sums and definite integrals are dummy variables.

TABLE 11.3 The Condon–Slater Rules

D and D' differ by	$\left\langle D' \left \sum_{i=1}^n \hat{f}_i \right D \right\rangle$	$\left\langle D' \left \sum_{i=1}^{n-1} \sum_{j>i} \hat{g}_{ij} \right D \right\rangle$
no spin-orbitals	$\sum_{i=1}^n \langle u_i(1) \hat{f}_1 u_i(1) \rangle$	$\sum_{i=1}^{n-1} \sum_{j>i} [\langle u_i(1) u_j(2) \hat{g}_{12} u_i(1) u_j(2) \rangle - \langle u_i(1) u_j(2) \hat{g}_{12} u_j(1) u_i(2) \rangle]$
one spin-orbital $u'_n \neq u_n$	$\langle u'_n(1) \hat{f}_1 u_n(1) \rangle$	$\sum_{j=1}^{n-1} [\langle u'_n(1) u_j(2) \hat{g}_{12} u_n(1) u_j(2) \rangle - \langle u'_n(1) u_j(2) \hat{g}_{12} u_j(1) u_n(2) \rangle]$
two spin-orbitals $u'_n \neq u_n, u'_{n-1} \neq u_{n-1}$	0	$\langle u'_n(1) u'_{n-1}(2) \hat{g}_{12} u_n(1) u_{n-1}(2) \rangle - \langle u'_n(1) u'_{n-1}(2) \hat{g}_{12} u_{n-1}(1) u_n(2) \rangle$
three or more spin-orbitals	0	0

If the operators $\hat{f}_i$ and $\hat{g}_{ij}$ do not involve spin, the expressions in Table 11.3 can be further simplified. We have $u_i = \theta_i \sigma_i$ and

$$\begin{aligned} \langle u_i(1) | \hat{f}_1 | u_i(1) \rangle &= \int \theta_i^*(1) \hat{f}_1 \theta_i(1) dv_1 \sum_{m_{s1}} \sigma_i^*(1) \sigma_i(1) \\ &= \int \theta_i^*(1) \hat{f}_1 \theta_i(1) dv_1 = \langle \theta_i(1) | \hat{f}_1 | \theta_i(1) \rangle \end{aligned}$$

since σ_i is normalized. Using this result and the orthonormality of σ_i and σ_j , we get for the case $D = D'$ (Prob. 11.37)

$$\left\langle D \left| \sum_{i=1}^n \hat{f}_i \right| D \right\rangle = \sum_{i=1}^n \langle \theta_i(1) | \hat{f}_1 | \theta_i(1) \rangle \quad (11.78)$$

$$\left\langle D \left| \sum_{i=1}^{n-1} \sum_{j>1} \hat{g}_{ij} \right| D \right\rangle =$$

$$\sum_{i=1}^{n-1} \sum_{j>1} [\langle \theta_i(1) \theta_j(2) | \hat{g}_{12} | \theta_i(1) \theta_j(2) \rangle - \delta_{m_{s,i} m_{s,j}} \langle \theta_i(1) \theta_j(2) | \hat{g}_{12} | \theta_j(1) \theta_i(2) \rangle] \quad (11.79)$$

where $\delta_{m_{s,i} m_{s,j}}$ is 0 or 1 according to whether $m_{s,i} \neq m_{s,j}$ or $m_{s,i} = m_{s,j}$. Similar equations hold for the other integrals.

Let us apply these equations to evaluate $\langle D | \hat{H} | D \rangle$, where $\hat{H}$ is the Hamiltonian of an n -electron atom with spin-orbit interaction neglected and D is a Slater determinant of n spin-orbitals. We have $\hat{H} = \sum_i \hat{f}_i + \sum_i \sum_{j>i} \hat{g}_{ij}$, where $\hat{f}_i = -(\hbar^2/2m_e) \nabla_i^2 - Ze^2/4\pi\epsilon_0 r_i$ and $\hat{g}_{ij} = e^2/4\pi\epsilon_0 r_{ij}$. Introducing the Coulomb and exchange integrals (9.99) and (9.100) and using (11.78) and (11.79), we have

$$\langle D | \hat{H} | D \rangle = \sum_{i=1}^n \langle \theta_i(1) | \hat{f}_1 | \theta_i(1) \rangle + \sum_{i=1}^{n-1} \sum_{j>1} (J_{ij} - \delta_{m_{s,i} m_{s,j}} K_{ij}) \quad (11.80)$$

$$J_{ij} = \langle \theta_i(1) \theta_j(2) | e^2/4\pi\epsilon_0 r_{12} | \theta_i(1) \theta_j(2) \rangle, K_{ij} = \langle \theta_i(1) \theta_j(2) | e^2/4\pi\epsilon_0 r_{12} | \theta_j(1) \theta_i(2) \rangle \quad (11.81)$$

$$\hat{f}_1 = -(\hbar^2/2m_e) \nabla_1^2 - Ze^2/4\pi\epsilon_0 r_1 \quad (11.82)$$

The Kronecker delta in (11.80) results from the orthonormality of the one-electron spin functions.

As an example, consider Li. The SCF approximation to the ground-state ψ is the Slater determinant $D = |1s\bar{1}s2s|$. The spin-orbitals are $u_1 = 1s\alpha$, $u_2 = 1s\beta$, and $u_3 = 2s\alpha$. The spatial orbitals are $\theta_1 = 1s$, $\theta_2 = 1s$, and $\theta_3 = 2s$. We have $J_{12} = J_{1s1s}$ and $J_{13} = J_{23} = J_{1s2s}$. Since $m_{s1} \neq m_{s2}$ and $m_{s2} \neq m_{s3}$, the only exchange integral that appears in the energy expression is $K_{13} = K_{1s2s}$. We get exchange integrals only between spin-orbitals with the same spin. Equation (11.80) gives the SCF energy as

$$E = \langle D | \hat{H} | D \rangle = 2 \langle 1s(1) | \hat{f}_1 | 1s(1) \rangle + \langle 2s(1) | \hat{f}_1 | 2s(1) \rangle + J_{1s1s} + 2J_{1s2s} - K_{1s2s}$$

The terms involving $\hat{f}_1$ are hydrogenlike energies, and their sum equals $E^{(0)}$ in Eq. (10.49). The remaining terms equal $E^{(1)}$ in Eq. (10.51). As noted at the beginning of Section 9.4, $E^{(0)} + E^{(1)}$ equals the variational integral $\langle D | \hat{H} | D \rangle$, so the Condon-Slater rules have been checked in this case.

For an atom with closed subshells only (for example, ground-state Be with a $1s^2 2s^2$ configuration), the n electrons reside in $n/2$ different spatial orbitals, so $\theta_1 = \theta_2$, $\theta_3 = \theta_4$, and so on. Let $\phi_1 \equiv \theta_1 = \theta_2$, $\phi_2 \equiv \theta_3 = \theta_4$, $\dots$, $\phi_{n/2} \equiv \theta_{n-1} = \theta_n$. If one rewrites

(11.80) using the ϕ 's instead of the θ 's, one finds (Prob. 11.38) for the SCF energy of the ^1S term produced by a closed-subshell configuration

$$E = \langle D | \hat{H} | D \rangle = 2 \sum_{i=1}^{n/2} \langle \phi_i(1) | \hat{f}_1 | \phi_i(1) \rangle + \sum_{j=1}^{n/2} \sum_{i=1}^{n/2} (2J_{ij} - K_{ij}) \quad (11.83)$$

where $\hat{f}_1$ is given by (11.82) and where J_{ij} and K_{ij} have the forms in (11.81) but with θ_i and θ_j replaced by ϕ_i and ϕ_j . Each sum in (11.83) goes over all the $n/2$ different spatial orbitals.

For example, consider the $1s^2 2s^2$ electron configuration. We have $n = 4$ and the two different spatial orbitals are $1s$ and $2s$. The double sum in Eq. (11.83) is equal to $2J_{1s1s} - K_{1s1s} + 2J_{1s2s} - K_{1s2s} + 2J_{2s1s} - K_{2s1s} + 2J_{2s2s} - K_{2s2s}$. From the definition (11.81), it follows that $J_{ii} = K_{ii}$. The labels 1 and 2 in (11.81) are dummy variables, and interchanging them can have no effect on the integrals. Interchanging 1 and 2 in J_{ij} converts it to J_{ji} ; therefore, $J_{ij} = J_{ji}$. The same reasoning gives $K_{ij} = K_{ji}$. Thus

$$J_{ii} = K_{ii}, \quad J_{ij} = J_{ji}, \quad K_{ij} = K_{ji} \quad (11.84)$$

Use of (11.84) gives the Coulomb- and exchange-integrals expression for the $1s^2 2s^2$ configuration as $J_{1s1s} + J_{2s2s} + 4J_{1s2s} - 2K_{1s2s}$. Between the two electrons in the $1s$ orbital, there is only one Coulombic interaction, and we get the term J_{1s1s} . Each $1s$ electron interacts with two $2s$ electrons, for a total of four $1s$ - $2s$ interactions, and we get the term $4J_{1s2s}$. As noted earlier, exchange integrals occur only between spin-orbitals of the same spin. There is an exchange integral between the $1s\alpha$ and $2s\alpha$ spin-orbitals and an exchange integral between the $1s\beta$ and $2s\beta$ spin-orbitals, which gives the $-2K_{1s2s}$ term.

The magnitude of the exchange integrals is generally much less than the magnitude of the Coulomb integrals [for example, see Eq. (9.111)].

Summary

The Hartree SCF method approximates the atomic wave function as a product of one-electron spatial orbitals [Eq. (11.2)] and finds the best possible forms for the orbitals by an iterative calculation in which each electron is assumed to move in the field produced by the nucleus and a hypothetical charge cloud due to the other electrons.

The more accurate Hartree-Fock method approximates the wave function as an antisymmetrized product (Slater determinant or determinants) of one-electron spin-orbitals and finds the best possible forms for the spatial orbitals in the spin-orbitals. Hartree-Fock calculations are usually done by expanding each orbital as a linear combination of basis functions and iteratively solving the Hartree-Fock equations (11.12). The Slater-type orbitals (11.14) are often used as the basis functions in atomic calculations. The difference between the exact nonrelativistic energy and the Hartree-Fock energy is the correlation energy of the atom (or molecule).

To go beyond the Hartree-Fock approximation and approach the true wave function and energy, we can use configuration interaction (CI), expressing ψ as a linear combination of configuration functions corresponding to various electron configurations [Eq. (11.17)].

Let $\mathbf{M}_1$ and $\mathbf{M}_2$ be two angular momenta with quantum numbers j_1, m_1 and j_2, m_2 , and let $\mathbf{M}$ be their sum: $\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2$. We showed that, for the angular-momentum sum, $\hat{M}^2$ has eigenvalues $J(J+1)\hbar^2$ and $\hat{M}_z$ has eigenvalues $M_J\hbar$, where the possible values of J and M_J are $J = j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2|$ and $M_J = J, J-1, \dots, -J$.

For a many-electron atom where spin-orbit interaction is small, the individual electronic orbital angular momenta add to give a total electronic orbital angular momentum ($\mathbf{L} = \sum_i \mathbf{L}_i$), and similarly for the spin angular momenta ($\mathbf{S} = \sum_i \mathbf{S}_i$). The eigenvalues

of the operators $\hat{L}^2$ and $\hat{S}^2$ for the squares of the magnitudes of the total electronic orbital and spin angular momenta are $L(L + 1)\hbar^2$ and $S(S + 1)\hbar^2$, respectively. For nonequivalent electrons (electrons in different subshells), the possible L values arising from a given electron configuration are readily found by using the angular-momentum addition rule (11.39), ignoring any closed subshells. For equivalent electrons, the possible L values can be found by consulting Table 11.2a. The possible S values are found using (11.39), ignoring all electrons that are paired.

With spin–orbit interaction neglected, atomic states that have the same energy have the same L value and the same S value. A set of equal-energy states with the same L and the same S constitutes a term. The term is denoted by the term symbol $^{2S+1}(L)$, where $2S + 1$ is called the spin multiplicity and (L) is a code letter that gives the L value [see (11.42)]. The degeneracy of an atomic term is $(2L + 1)(2S + 1)$.

When spin–orbit interaction is included, each term is split into a number of levels, each level having a different value of the total-electronic-angular-momentum quantum number J . The total electronic angular momentum is $\mathbf{J} = \mathbf{L} + \mathbf{S}$, and the eigenvalues of $\hat{J}^2$ are $J(J + 1)\hbar^2$, where J ranges from $L + S$ to $|L - S|$ in integral steps. The symbol for a level is $^{2S+1}(L)_J$. Each level is $(2J + 1)$ -fold degenerate, corresponding to the $2J + 1$ values of M_J , which range from J to $-J$. The degeneracy of an atomic level can be removed by application of an external magnetic field, which splits each level into $2J + 1$ states of slightly different energies.

In summary,

Configurations $\xrightarrow[\text{repulsions}]{\text{interelectronic}}$ Terms $\xrightarrow[\text{interaction}]{\text{spin-orbit}}$ Levels $\xrightarrow[\text{field}]{\text{external}}$ States

The Condon–Slater rules give the values of one- and two-electron integrals involving Slater determinants and can be used to evaluate properties (such as the energy) for a wave function that is a linear combination of Slater determinants.

Problems

Sec.	11.1	11.2	11.3	11.4	11.5	11.6
Probs.	11.1–11.4	11.5–11.6	11.7	11.8–11.12	11.13–11.32	11.33–11.35

Sec.	11.7	11.8	general
Probs.	11.36	11.37–11.39	11.40–11.42

- 11.1** How many electrons can be put in each of the following: (a) a shell with principal quantum number n ; (b) a subshell with quantum numbers n and l ; (c) an orbital; (d) a spin-orbital?
- 11.2** Without consulting the text, write the Hamiltonian operator for the lithium atom without using any sum symbols. Assume an infinitely heavy nucleus (and omit spin–orbit interaction).
- 11.3** If $R(r_1)$ is the radial factor in the function t_1 in the Hartree differential equation (11.9), write the differential equation satisfied by R .
- 11.4** Which STOs have the same form as hydrogenlike AOs?
- 11.5** Estimate the nonrelativistic $1s$ orbital energy in Ar. Check with Fig. 11.2.
- 11.6** At what atomic number does the second crossing of the $3d$ and $4s$ orbital energies occur in Fig. 11.2? Take account of the logarithmic scale. (Atomic spectral data show that the crossing actually occurs between 20 and 21.)
- 11.7** (a) Use the Clementi–Corongiu formula to estimate the correlation energy in the ground-state He atom and compare the result with the true value. (b) Use the Clementi–Corongiu formula to estimate the correlation energy in the ground-state N atom. Find the ground-state energy of the N atom by using data in the online reference in Sec. 10.5 to add up all the ionization energies of N. About what percentage of the true energy is the correlation energy in N?

- 11.8** Give the possible values of the total-angular-momentum quantum number J that result from the addition of angular momenta with quantum numbers (a) $\frac{3}{2}$ and 4; (b) 2, 3, and $\frac{1}{2}$.
- 11.9** True or false? The angular-momentum addition rule (11.39) shows that the number of values of J obtained by adding j_1 and j_2 is always $2j_{<} + 1$, where $j_{<}$ is the smaller of j_1 and j_2 or is j_1 if $j_1 = j_2$.
- 11.10** Verify the angular-momentum commutation relations (11.32).
- 11.11** Prove that $m_1 + m_2 = M_J$ [Eq. (11.34)], as follows: Apply $\hat{M}_z = \hat{M}_{1z} + \hat{M}_{2z}$ to (11.33), substitute (11.33) in the resulting equation, combine terms, and use the linear independence of the functions involved to deduce (11.34).
- 11.12** Show that $[\hat{M}^2, \hat{M}_{1z}] = 2i\hbar(\hat{M}_{1x}\hat{M}_{2y} - \hat{M}_{1y}\hat{M}_{2x})$, where $\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2$.
- 11.13** True or false? (Answer without looking at Chapter 11 tables.) (a) The terms arising from the $1s^2 2s^2 2p 3p$ configuration are the same as the terms arising from $1s^2 2s^2 2p^2$. (b) The terms arising from a $3d^3$ configuration are the same as those from a $3d^7$ configuration.
- 11.14** Verify the terms in Table 11.2b.
- 11.15** Find the terms that arise from each of the following electron configurations: (a) $1s^2 2s^2 2p^6 3s^2 3p 5g$; (b) $1s^2 2s^2 2p 3p 3d$; (c) $1s^2 2s^2 2p^4 4d$. You may use Table 11.2a for part (c).
- 11.16** Which of the following electron configurations will contribute configuration functions to a CI calculation of the ground state of He? (a) $1s 2s$; (b) $1s 2p$; (c) $2s^2$; (d) $2s 2p$; (e) $2p^2$; (f) $3d^2$.
- 11.17** Verify the spin-eigenfunction equations (11.52) to (11.54), (11.56), and the three equations following (11.56).
- 11.18** (a) Calculate the angle in Fig. 11.3 between the z axis and $\mathbf{S}$ for the spin function $\alpha(1)\alpha(2)$. (b) Calculate the angle between $\mathbf{S}_1$ and $\mathbf{S}_2$ for each of the functions (11.57) to (11.60). [Hint: Use $\mathbf{S} \cdot \mathbf{S} = (\mathbf{S}_1 + \mathbf{S}_2) \cdot (\mathbf{S}_1 + \mathbf{S}_2)$.] (c) If a vector $\mathbf{A}$ has components (A_x, A_y, A_z) , what are the components of the projection of $\mathbf{A}$ in the xy plane? Use the answer to this question to find the angle between the projections of $\mathbf{S}_1$ and $\mathbf{S}_2$ in the xy plane for the function $\alpha(1)\alpha(2)$.
- 11.19** (a) If $\hat{S}^2 = (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 + \cdots) \cdot (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 + \cdots)$, show that $[\hat{S}^2, \hat{P}_{ik}] = 0$, where $\hat{P}_{ik}$ is the exchange operator. (b) Show that $[\hat{L}^2, \hat{P}_{ik}] = 0$, where $\mathbf{L}$ is the total electronic orbital angular momentum.
- 11.20** Of the atoms with $Z \leq 10$, which have ground states of odd parity?
- 11.21** Give the number of states that belong to each of the following terms: (a) ^4F ; (b) ^1S ; (c) ^3P ; (d) ^2D .
- 11.22** How many states belong to each of the following carbon configurations? (a) $1s^2 2s^2 2p^2$; (b) $1s^2 2s^2 2p 3p$.
- 11.23** Give the possible spin multiplicities of the terms that arise from each of the following electron configurations: (a) f ; (b) f^2 ; (c) f^3 ; (d) f^7 ; (e) f^{12} ; (f) f^{13} .
- 11.24** Give the levels that arise from each of the following terms, and give the degeneracy of each level: (a) ^1S ; (b) ^2S ; (c) ^3F ; (d) ^4D .
- 11.25** For a state belonging to a $^3D_3$ level, give the magnitude of (a) the total electronic orbital angular momentum; (b) the total electronic spin angular momentum; (c) the total electronic angular momentum.
- 11.26** Give the symbol for the ground level of each of the atoms with $Z \leq 10$.
- 11.27** Give the symbol for the ground level of each of the atoms with $21 \leq Z \leq 30$. Which one of these atoms has the most degenerate ground level?
- 11.28** (a) Use a diagram like (11.48) to show that the lowest term of a single half-filled-subshell configuration has $L = 0$. (b) How many levels arise from a term with $L = 0$? Explain why no rule is needed to find the lowest level of the lowest term of a half-filled-subshell configuration.
- 11.29** Verify that if $E = 1$ eV, then $E/hc = 8065.54 \text{ cm}^{-1}$.
- 11.30** Consult Moore's table of atomic energy levels (Section 11.5) to find at least three electron configurations of the neutral carbon atom for which Hund's rule does not correctly predict the lowest term.

- 11.31** Selection rules for spectral transitions of atoms where Russell–Saunders coupling is valid are (*Bethe and Jackiw*, Chapter 11) $\Delta L = 0, \pm 1$; $\Delta S = 0$; $\Delta J = 0, \pm 1$ (but $J = 0$ to $J = 0$ is forbidden); $\Delta(\sum_i l_i) = \pm 1$, meaning that the change in configuration must change the sum of the l values of the electrons by ± 1 . For most atomic spectral lines, only one electron changes its subshell; here the $\Delta(\sum_i l_i) = \pm 1$ rule becomes $\Delta l = \pm 1$ for the electron making the transition.

For the carbon atom, the levels that arise from the $1s^2 2s^2 2p^2$ configuration are

Level	$^3P_0$	$^3P_1$	$^3P_2$	$^1D_2$	$^1S_0$
$(E/hc)/\text{cm}^{-1}$	0	16.4	43.4	10192.6	21648.0

and the energy levels of the $1s^2 2s 2p^3$ configuration are

$^5S_2$	$^3D_3$	$^3D_1$	$^3D_2$	$^3P_1$	$^3P_2$	$^3P_0$
33735.2	64086.9	64089.8	64090.9	75254.0	75255.3	75256.1

$^1D_2$	$^3S_1$	$^1P_1$
97878	105798.7	119878

Use the above selection rules to find the wavenumbers of all the transitions that are allowed between pairs of these 15 levels.

- 11.32** Go to www.nist.gov/pml/data/asd.cfm, click on Levels, enter C I in Spectrum, and click Retrieve Data to find the energy levels of the $2s^2 2p^3 s$ configuration of C. Then use the selection rules given in Prob. 11.31 to find the wavenumbers and wavelengths of all allowed transitions between the levels of $2s^2 2p^3 s$ and the levels of $2s^2 2p^2$ given in Prob. 11.31. Check your wavelengths by clicking on Lines instead of Levels.
- 11.33** Use Eq. (11.66) to calculate the separation between the $^2P_{3/2}$ and $^2P_{1/2}$ levels of the hydrogen-atom $2p$ configuration. (Because of other relativistic effects, the result will not agree accurately with experiment.)
- 11.34** Does Fig. 11.6 contain a violation of the rule given in Section 11.6 for determining whether a multiplet is regular or inverted?
- 11.35** Draw a diagram similar to Fig. 11.6 for the carbon $1s^2 2s^2 2p^2$ configuration. (The ^1S term is the highest.)
- 11.36** Use Eq. (11.74) to calculate the energy separation between the $M_J = \frac{1}{2}$ and $M_J = -\frac{1}{2}$ states of the $2p^2 P_{1/2}$ hydrogen-atom level, if a magnetic field of 0.200 T is applied.
- 11.37** (a) Derive Eq. (11.78). (b) Derive (11.79).
- 11.38** For a closed-subshell configuration, (a) show that the double sum in (11.80) equals

$$\sum_{j>i} \sum_{i=1}^{n/2} (4J_{ij} - 2K_{ij}) + \sum_{i=1}^{n/2} J_{ii}$$

where the Coulomb and exchange integrals are defined in terms of the $n/2$ different spatial orbitals ϕ_i ; (b) use (11.84) and the result of part (a) to derive (11.83).

- 11.39** Use the Condon–Slater rules to prove the orthonormality of two n -electron Slater determinants of orthonormal spin-orbitals.
- 11.40** Explain why it would be incorrect to calculate the experimental ground-state energy of lithium by taking $-(E_{2s} + 2E_{1s})$, where E_{2s} is the experimental energy needed to remove the $2s$ electron from lithium and E_{1s} is the experimental energy needed to remove a $1s$ electron from lithium.
- 11.41** The total magnetic moment $\mathbf{m}$ of an atom contains contributions from the magnetic moments $\mathbf{m}_L$, $\mathbf{m}_S$, and $\mathbf{m}_I$ associated with the total electronic orbital angular momentum $\mathbf{L}$, the total electronic spin angular momentum $\mathbf{S}$, and the nuclear spin angular momentum $\mathbf{I}$. (a) For an

atom with $\mathbf{L}$, $\mathbf{S}$, and $\mathbf{I}$ all nonzero, which one of these three contributions to $\mathbf{m}$ is by far the smallest? (b) For the ^{87}Rb ground electronic state (used in the Bose–Einstein condensation experiment of Section 10.5), which one of these three contributions is zero?

- 11.42** True or false? (a) The spin multiplicity of every term of an atom with an odd number of electrons must be an even number. (b) The spin multiplicity of every term of an atom with an even number of electrons must be an odd number. (c) The spin multiplicity of a term is always equal to the number of levels of that term. (d) In the Hartree SCF method, the energy of an atom equals the sum of the orbital energies of the electrons. (e) The Hartree–Fock method is capable of giving the exact nonrelativistic energy of a many-electron atom.