

# Atomic Structure | 4

“That’s like saying you’re the most important electron in the hydrogen atom.  
‘Cause you see, there’s only one electron in a hydrogen atom.”

—Sheldon Cooper (*Big Bang Theory*)

## 4.1 THE HYDROGEN ATOM

The goal of this chapter is to solve the Schrödinger equation for the one electron in the hydrogen atom. This electron experiences an electrostatic attraction for the nucleus which is distance dependent and which has a potential energy term given by Coulomb’s law. The time-independent Schrödinger equation for the hydrogen atom is given in Equation (4.1), where  $Z$  is the atomic number ( $Z = 1$  for H) and  $e$  is the charge on an electron. Because of the spherical symmetry for the potential energy term, it is more convenient to switch from Cartesian to polar coordinates, as shown in Figure 4.1. The conversions are given in the figure caption.

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi \quad (4.1)$$

After substituting the polar coordinates for Cartesian coordinates and a very lengthy application of the chain rule, Equation (4.1) becomes Equation (4.2) in spherical polar coordinates.

$$-\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi \quad (4.2)$$

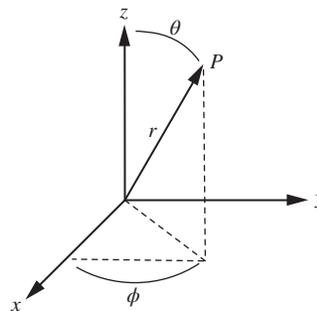
This equation can be separated into a radial part and an angular part, such that the wave function  $\psi$  can be taken as the product of a radial function  $R$  and an angular function  $Y$ , as shown in Equation (4.3). Multiplication of both sides of Equation (4.2) by  $2mr^2$ , followed by the method of separation of variables yields the slightly more manageable form of the Schrödinger equation for the hydrogen atom given in Equation (4.4), where  $\beta$  is the separation constant and we have incorporated  $\hbar$  in with  $\beta$ .

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \quad (4.3)$$

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**FIGURE 4.1**

The point  $P$  is expressed in Cartesian units as  $P(x, y, z)$  and in spherical polar coordinates as  $P(r, \theta, \phi)$ , where  $x = r \sin\theta \cos\phi$ ,  $y = r \sin\theta \sin\phi$ , and  $z = r \cos\theta$ .



$$\frac{1}{R(r)} \left[ \frac{d}{dR} \left( r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0 r} + E \right) R(r) \right] = -Y(\theta, \phi) \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial Y}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 Y}{\partial\phi^2} \right] = \beta \quad (4.4)$$

Neither of the differential equations in Equation (4.4) is particularly easy to solve. Owing to the separation of variables, however, each solution will consist of two parts: a radial wave function  $R(r)$  and an angular wave function  $Y(\theta, \phi)$ . The solutions to the angular part are referred to as the *spherical harmonics*, a fairly common type of function in a wide variety of physical problems. Furthermore, because there are three variables, the solutions to Equation (4.4) will be subject to three different quantum numbers (Q.N.):  $n$ ,  $l$ , and  $m_l$ . The three quantum numbers can only assume the values given and have the designations listed at the right. Thus, for instance, when  $n = 3$ ,  $l$  can equal 0, 1, or 2. If  $l = 2$ ,  $m_l$  can be  $-2, -1, 0, 1$ , or 2.

$n = 1, 2, 3, \dots$	Principal Q.N.
$l = 0, 1, 2, \dots, n - 1$	Azimuthal Q.N.
$m_l = 0, \pm 1, \pm 2, \dots, \pm l$	Magnetic Q.N.

The solutions to the Schrödinger equation for the hydrogen atom are shown in Table 4.1 for the first few sets of quantum numbers. By analogy to the Bohr model of the hydrogen atom, each set of three quantum numbers specifies a particular orbital, instead of an orbit. An *orbital* is nothing more than one of the allowed wave function solutions to the Schrödinger equation for an electron in the hydrogen atom. Each orbital is given a symbol, such as the  $2p_z$  orbital, where the numeral indicates the value of the principal quantum number, the letter indicates the value of the azimuthal quantum number ( $l = 0, 1, 2$ , and 3 correspond with the letters  $s, p, d$ , and  $f$ ), and the subscript has to do with the magnetic quantum number. To a first approximation, the principal quantum number determines an orbital's size, the azimuthal quantum number is reflective of its shape, and the magnetic quantum number indicates its relative orientation in space.

### 4.1.1 The Radial Wave Functions

The radial wave functions all show an exponential decay as the radius increases. The exponential decay is slower with increasing  $n$  because the denominator in the exponential term contains a factor of  $na_0$ . Thus, the average radius (or size) of an orbital also increases with  $n$ . For  $n > 1$ , the radial functions all have at least one radial

**TABLE 4.1** Mathematical forms of the radial wave functions,  $R(r)$ , and angular wave functions,  $Y(\theta, \phi)$ , for the hydrogen atom for the first few sets of allowed quantum numbers, where  $a_0 = 52.9$  pm, the Bohr radius.

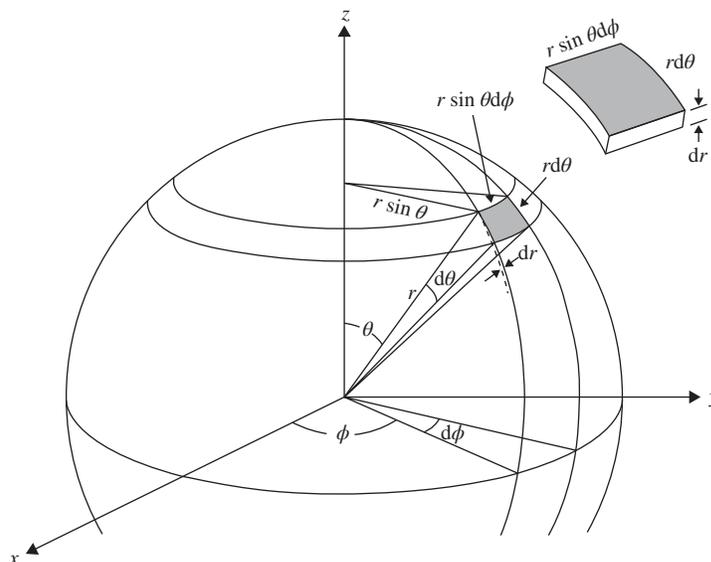
$n, l, m_l$	$R(r)$	$Y(\theta, \phi)$	Orbital
1, 0, 0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$	$\left(\frac{1}{4\pi}\right)^{1/2}$	1s
2, 0, 0	$\left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$	$\left(\frac{1}{4\pi}\right)^{1/2}$	2s
2, 1, 0	$\frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$	$\left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$	$2p_0$
2, 1, 1	$\frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$	$\left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{i\phi}$	$2p_{+1}$
2, 1, -1	$\frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$	$\left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{-i\phi}$	$2p_{-1}$
3, 0, 0	$\frac{2}{27}\left(\frac{Z}{3a_0}\right)^{3/2} \left(27 - \frac{18Zr}{a_0} + \frac{2Z^2r^2}{a_0^2}\right) e^{-\frac{Zr}{3a_0}}$	$\left(\frac{1}{4\pi}\right)^{1/2}$	3s
3, 1, 0	$\frac{1}{81\sqrt{3}}\left(\frac{2Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-\frac{Zr}{3a_0}}$	$\left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$	$3p_0$
3, 1, 1	$\frac{1}{81\sqrt{3}}\left(\frac{2Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-\frac{Zr}{3a_0}}$	$\left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{i\phi}$	$3p_{+1}$
3, 1, -1	$\frac{1}{81\sqrt{3}}\left(\frac{2Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-\frac{Zr}{3a_0}}$	$\left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{-i\phi}$	$3p_{-1}$
3, 2, 0	$\frac{1}{81\sqrt{15}}\left(\frac{2Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$	$\left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$3d_0$
3, 2, 1	$\frac{1}{81\sqrt{15}}\left(\frac{2Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$	$\left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{i\phi}$	$3d_{+1}$
3, 2, -1	$\frac{1}{81\sqrt{15}}\left(\frac{2Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$	$\left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{-i\phi}$	$3d_{-1}$
3, 2, 2	$\frac{1}{81\sqrt{15}}\left(\frac{2Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$	$\left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{2i\phi}$	$3d_{+2}$
3, 2, -2	$\frac{1}{81\sqrt{15}}\left(\frac{2Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$	$\left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{-2i\phi}$	$3d_{-2}$

node. For the 2s orbital, for instance, which has the quantum numbers  $n=2$ ,  $l=0$ ,  $m_l=0$ , the radial node occurs when  $r=2a_0/Z$  because this makes the second term in the parentheses zero ( $a_0 = 52.9$  pm, the Bohr radius). A general rule is that there are  $n - l - 1$  radial nodes. Thus, a 2s orbital has one radial node, while a 2p orbital has no radial nodes.

When a wave function or a product of wave functions is integrated over all space, the volume element in Cartesian coordinates is  $d\tau = dx dy dz$ . In polar coordinates,

**FIGURE 4.2**

Definition of the volume element  $d\tau$  in polar coordinates:  $d\tau = dV = r^2 \sin\theta \, dr \, d\theta \, d\phi$ . [© University Science Books, Mill Valley, CA. Used with permission. All rights reserved. McQuarrie, D. A.; Simon, J. D. *Physical Chemistry: A Molecular Approach*, 1997.]



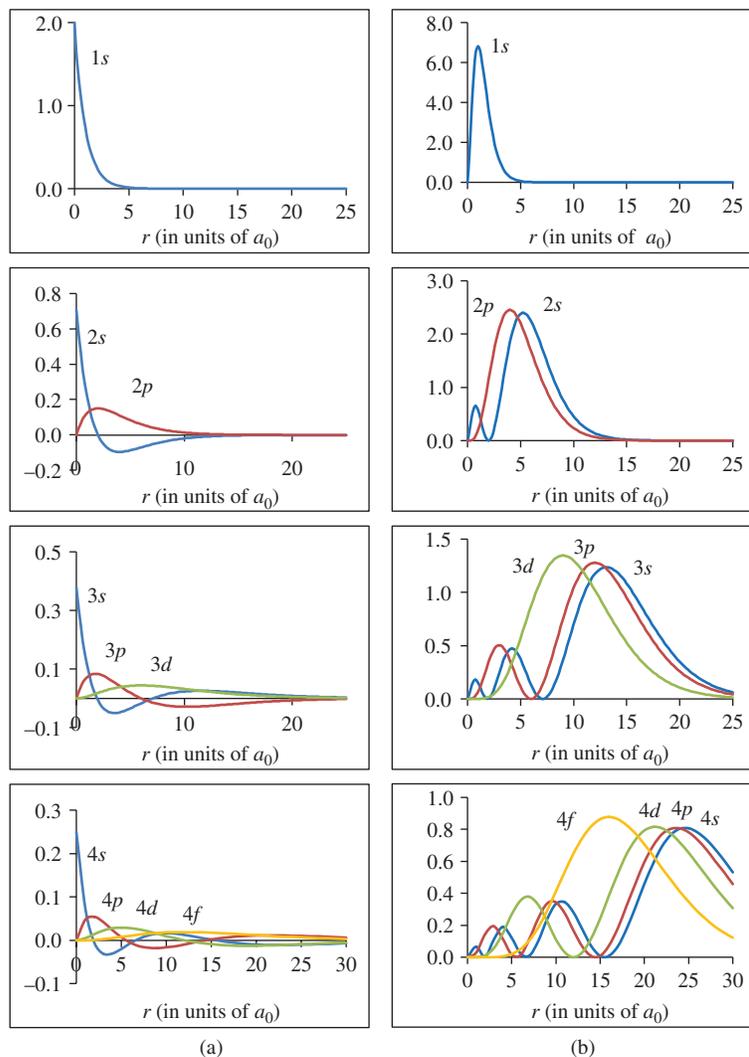
however, the volume element becomes  $d\tau = dV = r^2 \sin\theta \, dr \, d\theta \, d\phi$ , as shown in Figure 4.2.

A more useful quantity than the radial wave function is the radial distribution function, also called the *radial probability function*. The *radial distribution function* is the probability that the electron will exist in a thin volume element  $dV$  at a distance  $r$  from the nucleus. One way of visualizing this is to think of the volume element as a thin spherical shell, similar to one of the layers in an onion skin, existing at a distance  $r$  away from the nucleus. The volume element  $dV$  shown in Figure 4.2 represents a fraction of this “onion skin.” Because the probability of finding an electron in a given region of space goes as the square of the wave function (the Born interpretation), the radial distribution function is equal to  $R(r)^2 \, dV$ . The volume of a sphere is  $V = (4/3)\pi r^3$ , and therefore  $dV/dr = 4\pi r^2$ . Following substitution, the radial distribution function is defined as  $4\pi r^2 R(r)^2 \, dr$ . Plots of the radial distribution function for the first several types of orbitals in the hydrogen atom are shown in Figure 4.3. The presence of the radial nodes is clearly indicated on the diagram. A second noteworthy feature is that the probability of the electron being close to the nucleus for a given value of  $n$  decreases in the order  $s > p > d > f$ . In other words, the  $s$  orbital “penetrates” the nucleus better than a  $p$  orbital having the same principal quantum number. This fact is of utmost importance in the forthcoming section of shielding and influences a large number of an element’s chemical properties.

**Example 4-1.** Use Equation (3.18) to prove that the Bohr radius  $a_0$  has a value of 52.9 pm when  $n = 1$ .

**Solution.** Using Equation (3.18) and solving for  $r$  yields:

$$\begin{aligned} r &= \frac{4\pi\epsilon_0 n^2 h^2}{4\pi^2 m e^2} = \frac{(1.113 \times 10^{-10} \text{ C}^2/\text{Jm})(6.626 \times 10^{-34} \text{ Js})^2}{4(3.1416)^2(9.109 \times 10^{-31} \text{ kg})(1.602 \times 10^{-19} \text{ C})^2} \\ &= 5.29 \times 10^{-11} \text{ m} = 52.9 \text{ pm} \end{aligned}$$

**FIGURE 4.3**

The radial function  $R(r)$  (a) and the radial distribution function (b) for several types of orbitals in the hydrogen atom. The y-scale varies from one orbital to the next.

**Example 4-2.** Show that the most probable radius for an electron in the  $1s$  orbital of hydrogen is equal to the Bohr radius,  $a_0$ .

**Solution.** The most probable radius can be obtained from the highest peak in the radial distribution function, because this function is a measure of the probability of finding an electron in a volume element at a certain distance from the nucleus. Because the radial distribution function for a  $1s$  orbital has a single peak, the radius at which this peak occurs can be calculated by taking the first derivative of the function with respect to  $r$  and setting it equal to zero. For a  $1s$  orbital,  $R(r)$  and the first derivative of the radial probability function are

$$R(r) = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-\frac{Zr}{a_0}}$$

$$\begin{aligned}\frac{d(4\pi^2r^2R^2)}{dr} &= \frac{d}{dr} \left[ 16\pi^2 \left( \frac{Z}{a_0} \right)^3 r^2 e^{-\frac{2Zr}{a_0}} \right] \\ &= 16\pi^2 \left( \frac{Z}{a_0} \right)^3 \left[ 2r e^{-\frac{2Zr}{a_0}} - \frac{2Z}{a_0} r^2 e^{-\frac{2Zr}{a_0}} \right] = 0\end{aligned}$$

which implies that  $\left[ 2r - \frac{2Z}{a_0} r^2 \right] = 0$

Hence,  $r = a_0/Z$ . Because  $Z = 1$  for H,  $r = a_0 = 52.9$  pm, the same result as in the Bohr model of the atom.

**Example 4-3.** At what distance from the nucleus does the radial node in a 2s orbital occur?

**Solution.** The radial wave function for a 2s orbital is given here:

$$\left( \frac{Z}{2a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right)^{3/2} e^{-\frac{Zr}{2a_0}}$$

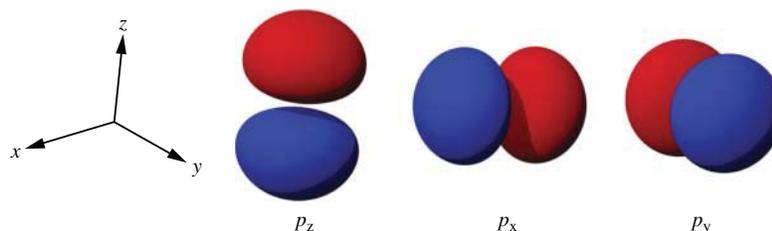
Setting the middle term equal to zero, we find that  $2 = \frac{Zr}{a_0}$  and hence  $r = \frac{2a_0}{Z} = 106$  pm.

### 4.1.2 The Angular Wave Functions

The solutions to the angular part of the hydrogen atom are known as the *spherical harmonics*. The angular wave functions  $Y(\theta, \phi)$  depend on two variables and are therefore governed by the quantum numbers  $l$  and  $m_l$ . It is these quantum numbers that dictate the shape of the atomic orbitals. Thus, for example, all of the s orbitals are spherical regardless of their principal quantum number and they each have the same angular dependence on  $\theta$  and  $\phi$ . Because  $l = 0$  for s orbitals,  $m_l$  can only be zero; therefore, only one type of s orbital exists for any given value of  $n$ . By contrast, there are three different kinds of p orbitals because  $m_l$  can take values of  $-1$ ,  $0$ , or  $+1$ . The shapes of these orbitals are shown in Figure 4.4, where the orbital boundary indicates a 90% or greater probability of finding the electron in the enclosed region of space. When  $m_l = 0$ , the angular wave function is real, and the shape of the orbital consists of two lobes that lie along the z coordinate axis. Because its lobes lie along the z-axis, the  $p_0$  orbital is also known as the  $p_z$  orbital. The sign of the wave function before squaring is also indicated in the figure. Notice that one of the lobes is positive while the other is negative and therefore an angular nodal surface exists in

**FIGURE 4.4**

Shapes of the three p orbitals. [Modified from [http://en.wikipedia.org/wiki/Atomic\\_orbital](http://en.wikipedia.org/wiki/Atomic_orbital) (accessed November 30, 2013).]



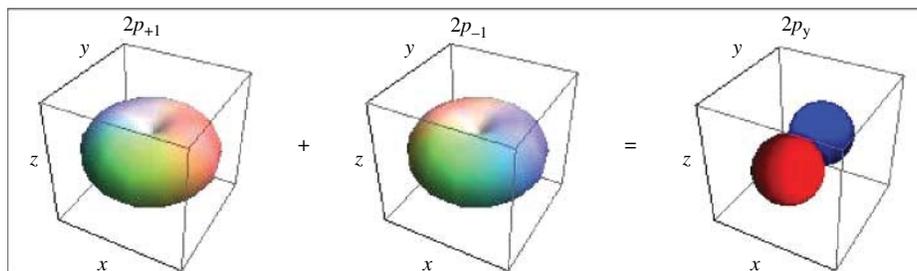
**FIGURE 4.5**

Illustration of how a linear combination of the  $2p_{+1}$  and  $2p_{-1}$  orbitals can be used to construct the more familiar  $2p_y$  orbital. [Images by Lisa M. Goss. Used by permission.]

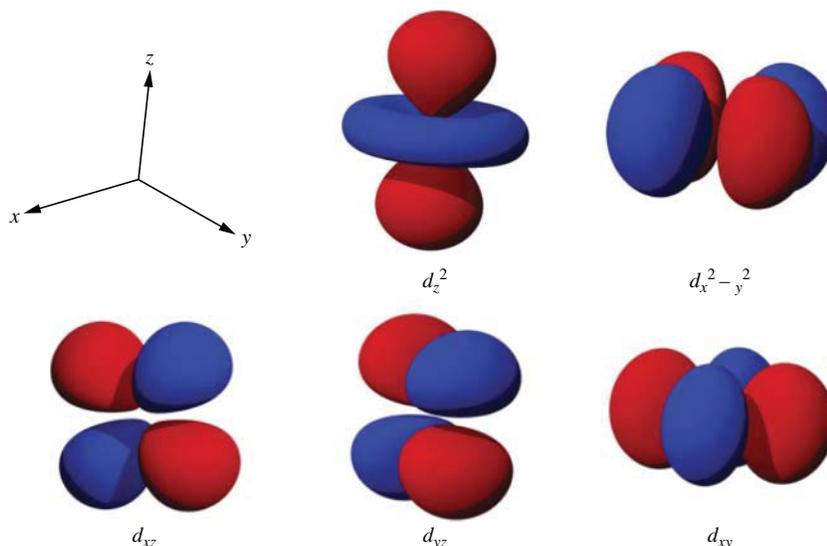
the  $xy$  plane. As a rule, every orbital will exhibit  $l$  angular nodal surfaces, which can be either planar or conical in shape. Thus, all three of the  $p$  orbitals will have a single angular nodal plane. Likewise, each  $d$  orbital will have two angular nodal surfaces and each  $f$  orbital will have three.

Although the angular wave functions of orbitals having  $|m_l| > 0$  all contain imaginary components in their exponential terms, the product  $Y^*Y$  is real and can therefore be plotted. The angular dependence of the  $2p$  orbitals having  $m_l = -1$  and  $m_l = +1$  are identical. Both orbitals take on the shape of a donut with the  $z$ -axis passing through the center of the donut hole. The only difference between the two orbitals is that the electron is moving in opposite directions in each of them. Because of the requirement that all quantum mechanical operators be linear and Hermitian, any linear combination of two degenerate wave functions will also be an acceptable solution to the Schrödinger equation. When the positive linear combination  $Y(1,1) + Y(1,-1)$  is taken, as shown in Equation (4.6), where the numbers in parentheses refer to  $l$  and  $m_l$ , respectively, the equation for the familiar  $p_y$  orbital is obtained after normalization, as shown in Figure 4.5. When the negative linear combination  $Y(1,1) - Y(1,-1)$  is taken, as shown in Equation (4.7), the equation for the  $p_x$  orbital results after normalization. This process is also known as the *hybridization* of atomic orbitals. As shown in Figure 4.4, the  $p_x$  hybrid orbital has its lobes lying along the  $x$ -axis, while the  $p_y$  hybrid has its lobes lying along the  $y$ -axis. According to quantum theory, the hybrid orbitals must also be orthogonal to one another. These particular linear combinations ensure that all three  $p$  orbitals will have the same shape with their lobes pointing along the three orthogonal Cartesian axes.

$$Y(1,1)^* Y(1,1) = Y(1,-1)^* Y(1,-1) = \frac{3}{8\pi} \sin^2 \theta \quad (4.5)$$

Normalization means that the integral of  $Y^*Y$  over all space must equal unity. Because each of the original wave functions  $Y(1,1)$  and  $Y(1,-1)$  are normalized and have integrals of one, the integral of the positive linear combination must equal two. Therefore,  $N=2$  in the normalization equation and the normalizing coefficient is  $c = 1/2^{1/2}$ .

$$\begin{aligned} p_x &= \frac{1}{\sqrt{2}}(Y(1,1) + Y(1,-1)) = \frac{1}{\sqrt{2}} \left( \frac{3}{8\pi} \right)^{1/2} [\sin \theta e^{i\phi} + \sin \theta e^{-i\phi}] = \\ & \frac{1}{\sqrt{2}} \left( \frac{3}{8\pi} \right)^{1/2} \sin \theta [\cos \phi + i \sin \phi + \cos \phi - i \sin \phi] = \frac{1}{\sqrt{2}} \left( \frac{3}{8\pi} \right)^{1/2} \sin \theta \cos \phi \end{aligned} \quad (4.6)$$

**FIGURE 4.6**

Shapes of the five  $d$  orbitals. [Modified from [http://en.wikipedia.org/wiki/Atomic\\_orbital](http://en.wikipedia.org/wiki/Atomic_orbital) (accessed November 30, 2013).]

For normalization of the negative linear combination, the  $i$  factors out in the determination of the normalizing coefficient because of the complex conjugate in Equation (3.54), such that:

$$\begin{aligned}
 p_y &= \frac{-i}{\sqrt{2}}(Y(1, 1) - Y(1, -1)) = -\frac{i}{\sqrt{2}}\left(\frac{3}{8\pi}\right)^{1/2} [\sin \theta e^{i\phi} - \sin \theta e^{-i\phi}] = \\
 &= -\frac{i}{\sqrt{2}}\left(\frac{3}{8\pi}\right)^{1/2} \sin \theta [\cos \phi + i \sin \phi - \cos \phi + i \sin \phi] = \frac{1}{\sqrt{2}}\left(\frac{3}{8\pi}\right)^{1/2} \sin \theta \sin \phi
 \end{aligned}
 \tag{4.7}$$

The five different kinds of  $d$  orbitals are shown in Figure 4.6.

When  $m_l = 0$ , the  $d_z^2$  orbital results. This orbital has two lobes of the same sign pointing along the  $z$ -axis, with a donut-shaped lobe of the opposite sign in the  $xy$  plane. Notice that there are two conical nodes, each beginning at the origin and pointing in a different direction along the  $z$ -axis. When  $|m_l| = 1$ , the product  $Y^*Y$  yields a probability function containing two donuts centered on the  $z$ -axis, where one lies above the  $xy$  plane and the other lies beneath it. When  $|m_l| = 2$ , the product  $Y^*Y$  looks similar to a single hollow donut lying in the  $xy$  plane, as shown in Figure 4.7. Taking the positive and negative linear combinations of  $Y(2, 1)$  with  $Y(2, -1)$  yields the  $d_{xz}$  and the  $d_{yz}$  orbitals shown in Figure 4.6. Both of these orbitals contain four lobes (as in a four-leaf clover) of alternating sign of the wave function and lying in the  $xz$  and  $yz$  planes, respectively. Each of the four lobes lies between the coordinate axes. Likewise, linear combinations of the  $Y(2, 2)$  and  $Y(2, -2)$  wave functions yield the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals shown in Figure 4.6. Both orbitals lie in the  $xy$  plane and have the same alternating four-leaf clover shape. However, the  $d_{xy}$  orbital has its lobes pointing between the coordinate axes, while the  $d_{x^2-y^2}$  orbital's lobes lie squarely on the coordinate axes. The names and shapes of the five  $d$ -orbitals are especially important in the field of coordination chemistry and should be memorized by the student at this time.

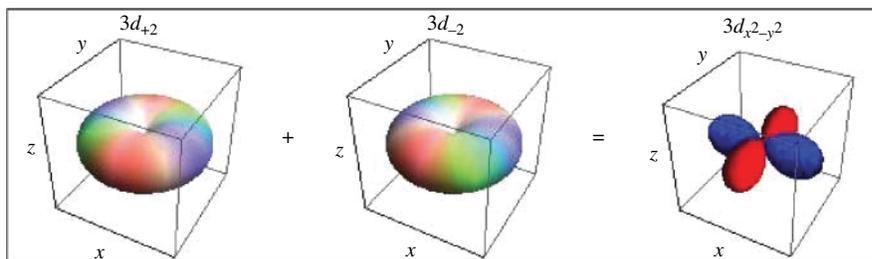
**FIGURE 4.7**

Illustration of how a linear combination of the  $3d_{+2}$  and  $3d_{-2}$  orbitals can be used to construct the more familiar  $3d_{x^2-y^2}$  orbital. [Images by Lisa M. Goss. Used by permission.]

**Example 4-4.** Write the mathematical form of the angular part of the wave function for the  $d_{xz}$  and  $d_{yz}$  orbitals by taking the positive and negative linear combinations of  $Y(2,1)$  with  $Y(2,-1)$ , respectively.

**Solution.** The positive linear combination ( $d_{xz}$ ) of  $Y(2,1)$  with  $Y(2,-1)$  is given by

$$\begin{aligned} d_{xz} &= \frac{1}{\sqrt{2}}(Y(2,1) + Y(2,-1)) = \frac{1}{\sqrt{2}} \left( \frac{15}{8\pi} \right)^{1/2} \\ &\quad [\sin \theta \cos \theta (\cos \phi + i \sin \phi + \cos \phi - i \sin \phi)] \\ &= \left( \frac{15}{4\pi} \right)^{1/2} \sin \theta \cos \theta \cos \phi \end{aligned}$$

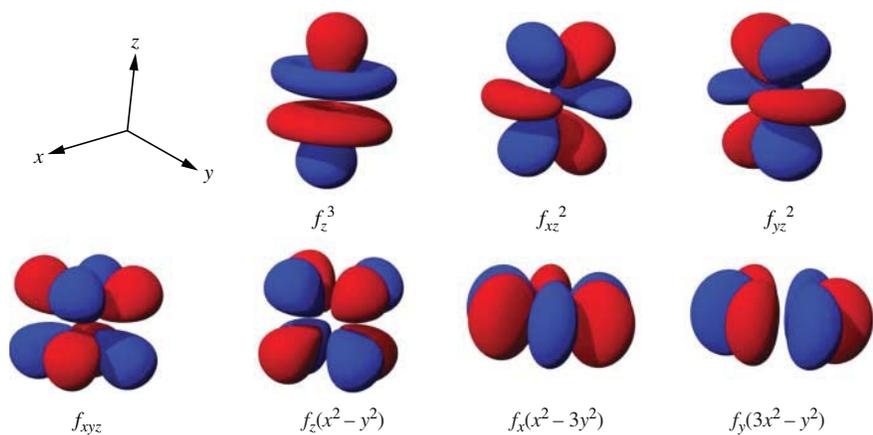
The negative linear combination ( $d_{yz}$ ) of  $Y(2,1)$  with  $Y(2,-1)$  is given by

$$\begin{aligned} d_{yz} &= -\frac{i}{\sqrt{2}}(Y(2,1) - Y(2,-1)) = -\frac{i}{\sqrt{2}} \left( \frac{15}{8\pi} \right)^{1/2} \\ &\quad [\sin \theta \cos \theta (\cos \phi + i \sin \phi - \cos \phi + i \sin \phi)] \\ &= \left( \frac{15}{4\pi} \right)^{1/2} \sin \theta \cos \theta \sin \phi \end{aligned}$$

The shapes of the seven f orbitals are shown in Figure 4.8. When  $m_l = 0$ , the  $f_z^3$  orbital results, which has lobes of opposite sign along the z-axis and two donuts encircling that axis that also have opposite signs. For  $|m_l| = 1$ , the positive and negative linear combinations  $Y(3,1) \pm Y(3,-1)$  yield the  $f_{xz}^2$  and  $f_{yz}^2$  orbitals, which have six lobes each lying in the xz and yz planes, respectively. For  $|m_l| = 2$ , the two hybrids are the  $f_{xyz}$  and  $f_{z(x^2-y^2)}$  orbitals. Both of these orbitals have eight lobes forming a cubic shape, with the former lying between the x- and y-axes and the latter lying on the coordinate axes. Lastly, for  $|m_l| = 3$ , the hybrid orbitals are the  $f_{x(x^2-3y^2)}$  and  $f_{y(3x^2-y^2)}$  orbitals, which have six lobes each lying in the xy plane. The shapes of the seven f-orbitals are typically unimportant in chemical bonding and do not need to be memorized.

Several features common to all of the atomic orbitals are as follows:

- For any given value of  $l$ , the summation of the electron density probabilities for the complete set of orbitals will be a sphere. This is known as *Unsold's theorem*. Thus, for example, the sum of the electron density for the  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbitals is a sphere, as is the case for the lone  $2s$  orbital.

**FIGURE 4.8**

Shapes of the seven  $f$  orbitals, with  $|m_l|$  increasing from left to right in the diagram. [Modified from [http://en.wikipedia.org/wiki/Atomic\\_orbital](http://en.wikipedia.org/wiki/Atomic_orbital) (accessed November 30, 2013).]

- The absolute value of  $m_l$  is the number of angular nodes that present themselves when the orbital is viewed from either direction along the  $z$ -axis. Thus, a  $p_z$  orbital ( $m_l = 0$ ), when viewed from the “top” of the  $z$ -axis, will present with a positive lobe. The negative lobe that lies beneath this will not be observed from this vantage point. However, the  $p_x$  and  $p_y$  orbitals ( $|m_l| = 1$ ) will each present one angular nodal plane when viewed along the  $z$ -axis.
- The symmetry of the atomic orbitals with respect to inversion alternates in a regular pattern. The inversion operation means that if one takes any point  $(x, y, z)$  back through the origin an equal distance to point  $(-x, -y, -z)$ , the probability density will be identical in magnitude and sign. All  $s$  and  $d$  orbitals are symmetric (or *gerade*) with respect to inversion. All  $p$  and  $f$  orbitals are antisymmetric (or *ungerade*) with respect to inversion (they have the opposite sign). More generally, whenever  $l$  is odd, the atomic orbitals will be *gerade* and whenever  $l$  is even, they will be *ungerade*.

**Example 4-5.** Prove that the total probability density for the three  $2p$  orbitals is a sphere.

**Solution.** The sum of the squares of the angular components of the wave functions for the three  $2p$  orbitals is

$$\left(\frac{3}{4\pi}\right) [\cos^2\theta + \sin^2\theta\cos^2\phi + \sin^2\theta\sin^2\phi] = \left(\frac{3}{4\pi}\right) [\cos^2\theta + \sin^2\theta(\cos^2\phi + \sin^2\phi)]$$

We can ignore the coefficient in front just as we ignored the radial part of the wave function because these just relate to the radius of the orbital summation and have nothing to do with its shape. We can also use the trigonometric identity that  $\cos^2(a) + \sin^2(a) = 1$ . Thus, the equation reduces to

$$[\cos^2\theta + \sin^2\theta(1)] = [\cos^2\theta + \sin^2\theta] = 1$$

Because the total angular component is a constant, there is no net angular dependence and the overall shape is that of a sphere.

## 4.2 POLYELECTRONIC ATOMS

Whenever two or more electrons are present in an atom or ion, an exact solution to the Schrödinger equation cannot be obtained because of the *electron correlation problem*. Consider any given electron in a polyelectronic atom. The electrostatic field experienced by this electron cannot be known exactly because of the Heisenberg uncertainty principle, which states that the exact position of other electrons cannot be measured precisely. In order to circumvent this problem, an approximation method is used. The most common approximation technique is known as the *self-consistent field (SCF) method*. Using this procedure, a reasonable wave function is used as a first approximation for all but one of the electrons. Then, the force field felt by this one electron is calculated to obtain a wave function for the electron. Next, a second electron is chosen and the wave function just obtained for the first electron is used in the calculation of the force field that the second electron experiences. This method is repeated for each of the electrons in an iterative process until the force field for each electron begins to converge to a single value; or in other words, when a SCF results. This field is then used to calculate the approximate wave function solutions (known as the *Hartree–Fock equations*) to the polyelectronic Schrödinger equation.

The following is an example of the SCF method in practice in the treatment of the two electrons present in a helium atom. Because helium has two electrons orbiting a +2 nucleus, it presents itself as the three-body problem shown in Figure 4.9, where the nucleus is presumed to be at rest and therefore sits at the origin of the coordinate system. The Hamiltonian for the helium atom includes three potential energy terms: an attractive force between electron 1 and the nucleus ( $r_1$ ), an attractive force between electron 2 and the nucleus ( $r_2$ ), and the electron–electron repulsion between the two electrons ( $r_{12}$ ), as shown in Equation (4.8).

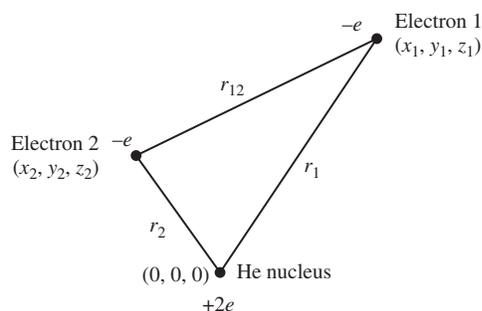
$$\hat{H} = \left[ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right] \quad (4.8)$$

We allow the overall wave function to be a product of two wave functions, one for each individual electron, as shown in Equation (4.9). The effective Hamiltonian for electron 1 can then be calculated using Equation (4.10), where  $V_1^{\text{eff}}$  is the effective potential energy that electron 1 feels with respect to electron 2 and is given by Equation (4.11).

$$\psi(r_1, r_2) = \phi(r_1)\phi(r_2) \quad (4.9)$$

$$\hat{H}_1^{\text{eff}}(r_1) = \left[ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} + V_1^{\text{eff}} \right] \quad (4.10)$$

$$V_1^{\text{eff}}(r_1) = \int \phi^*(r_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \phi(r_2) dr_2 \quad (4.11)$$



**FIGURE 4.9**

Definition of the different potential energy interactions between the two electrons and the +2 nucleus in a helium atom.

There are, of course, two additional equations corresponding to Equations (4.10) and (4.11) for the second electron. We begin by assuming a reasonable wave function (such as a 1s hydrogen wave function) for the second electron  $\phi(r_2)$  and then using this wave function to evaluate the effective potential energy that electron 1 experiences according to Equation (4.11). This will allow a suitable effective Hamiltonian to be calculated for electron 1 using Equation (4.10). Next, we solve the Schrödinger equation using our effective Hamiltonian for electron 1, as shown by Equation (4.12)

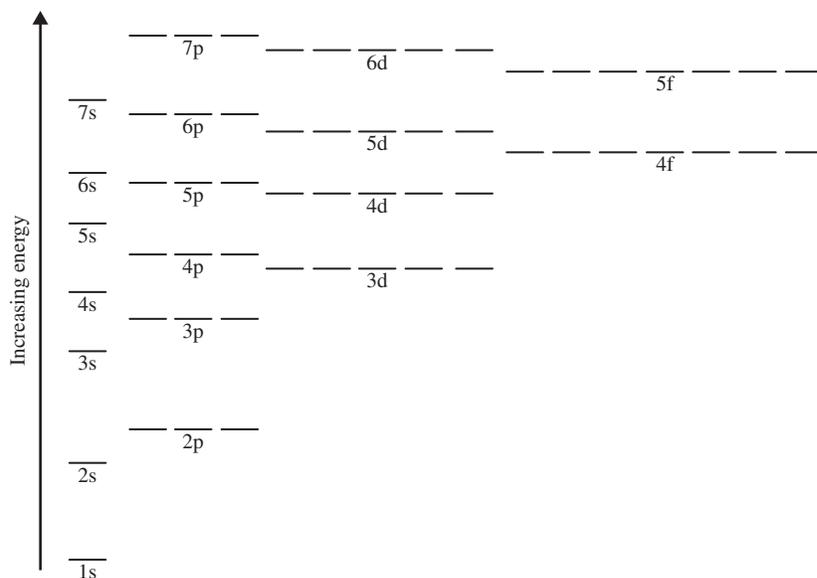
$$\hat{H}_1^{\text{eff}}(r_1)\phi(r_1) = E_1\phi(r_1) \quad (4.12)$$

We then substitute the resulting value for  $\phi(r_1)$  into the effective potential energy equation for electron 2. This value is then used in the equation that corresponds to Equation (4.10) to determine the effective Hamiltonian for electron 2. Then the Schrödinger equation corresponding to Equation (4.12) for electron 2 is solved in order to determine a new value for  $\phi(r_2)$ . The whole process is repeated in an iterative manner until the wave functions for  $\phi(r_1)$  and  $\phi(r_2)$  no longer change with time. We call this a SCF and the two resulting wave functions obtained by this method are known as the *Hartree–Fock orbitals*.

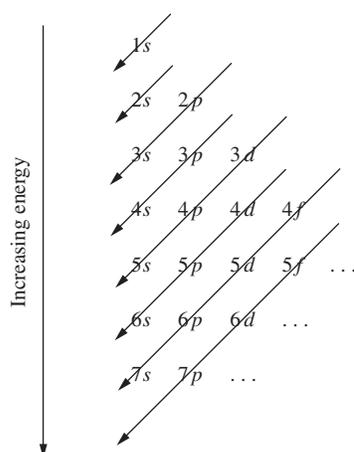
It is fortunate that whenever the SCF method is employed for any element or ion having more than one electron, the resulting wave functions always tend to resemble those of the hydrogen atom. Hence, the probability electron densities for the other elements can be compared to the *hydrogenic* orbital shapes. However, these wave functions are not identical to those of hydrogen, and the following differences should be noted:

- All of the hydrogenic orbitals contract as  $Z$  increases.
- Unlike the hydrogen atom, where the energies of the orbitals depend only on the principal quantum number, the energies of the hydrogenic orbitals also depend on the magnitude of  $l$ . For any given value of  $n$ , the energies of the hydrogenic orbitals for a polyelectronic atom increase in the order:  $s < p < d < f$ . The lowered degeneracy is a direct result of the differing degrees of penetration of the nucleus that the electrons in these orbitals exhibit. Comparing the radial distribution functions for a 3d, 3p, and 3s electron in Figure 4.3, it is apparent that an electron in the 3s orbital will have a higher probability of residing closer to the nucleus than will a 3p or a 3d electron. Thus, an electron in a 3d orbital of iron, for instance, will be somewhat shielded (or screened) from feeling the full effect of the +26 charge of the nucleus by any electrons that have a higher probability of lying closer to the nucleus. Therefore, the *effective nuclear charge* that the 3d electron feels will be less than that of a 3p or a 3s electron. Consequently, a 3d electron will be held less tightly by the nucleus than a 3s or 3p electron and will therefore lie at higher energy, as shown in Figure 4.10.
- As a result of the different energies of the s, p, d, and f hydrogenic orbitals having the same value of  $n$ , some overlapping of orbital energies between different principal quantum numbers occurs. *Madelung's rule* (also known as *Klechkowski's rule*) states that, as a general principle, hydrogenic orbital filling proceeds from the lowest available sum of  $n + l$ . If there is more than one combination yielding the same value of  $n + l$ , then the filling will occur first for the smallest value of  $n$ . Using Madelung's rule, where  $n + l$  is shown in parentheses, the order of filling for the one-electron hydrogenic orbitals (ignoring electron–electron repulsions) is

$$1s(1) < 2s(2) < 2p(3) < 3s(3) < 3p(4) < 4s(4) < 3d(5) < 4p(5) < 5s(5) < 4d(6) < 5p(6) < 6s(6) < 4f(7) < 5d(7) < 6p(7) < 7s(7) < 5f(8) < 6d(8) < 7p(8)$$

**FIGURE 4.10**

Energy ordering of the hydrogenic orbitals in a polyelectronic atom. [Reproduced from [http://en.wikibooks.org/wiki/High\\_School\\_Chemistry/Families\\_on\\_the\\_Periodic\\_Table](http://en.wikibooks.org/wiki/High_School_Chemistry/Families_on_the_Periodic_Table) (accessed November 30, 2013).]

**FIGURE 4.11**

Moeller's rubric for the general order of orbital filling using the one-electron hydrogenic orbitals.

The same ordering is obtained if one employs *Moeller's rubric*, which is shown in Figure 4.11. This general ordering of the hydrogenic orbitals neatly mimics the pattern of the periodic properties of the elements that were first discovered in the late 1860s by Dmitri Mendeleev and J. Lothar Meyer. A version of the periodic table showing its correlation with orbital filling is shown in Figure 4.12.

### 4.3 ELECTRON SPIN AND THE PAULI PRINCIPLE

A fourth quantum number, called the *spin quantum number*, is required when the relativistic effects of electronic motion are taken into consideration. The concept of *electron spin* was first postulated by Goudsmit and Uhlenbeck in 1925 in order to explain the fine structure (or splitting) of the line spectra of several of the alkali metals. For example, the yellowish glow of many incandescent lights found in large city parking lots is actually due to two very closely spaced lines in the emission spectrum of Na. The two sodium D-lines, which arise from a transition between 3p and 3s hydrogenic orbitals, have wavelengths of 588.9950 and 589.5924 nm. The

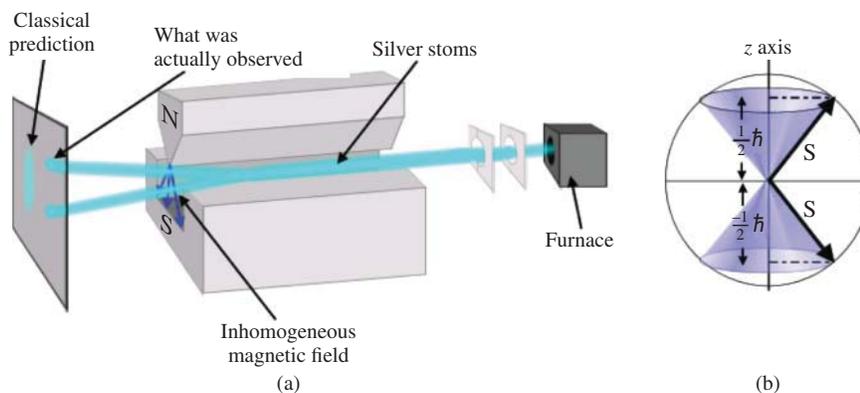
		s-block			d-block		
		p-block			f-block		
1s							1s
2s							2p
3s							3p
4s			3d				4p
5s			4d				5p
6s			5d				6p
7s			6d				7p
					4f		
					5f		

**FIGURE 4.12**

Periodic table showing the correlation with Moeller's rubric for orbital filling.

**FIGURE 4.13**

(a,b) Schematic diagram of the Stern–Gerlach experiment, showing how a beam of Ag atoms can be split by an inhomogeneous magnetic field into two different trajectories as a result of the different spin states they possess. [(a,b) Attributed to Theresa Knott, reproduced from [http://en.wikipedia.org/wiki/Stern%E2%80%93Gerlach\\_experiment](http://en.wikipedia.org/wiki/Stern%E2%80%93Gerlach_experiment) (accessed November 30, 2013).]



*Stern–Gerlach experiment*, depicted in Figure 4.13, provided the first experimental confirmation for the quantization of electron spin. In their 1922 experiment, Otto Stern and Walther Gerlach showed that a beam of silver atoms could be split into two beams by passing it through an inhomogeneous magnetic field. In addition to electrons, many nuclei also exhibit spin, forming the basis of nuclear magnetic resonance (NMR) and electron spin resonance (ESR) analytical techniques.

In 1928, Paul Dirac developed a relativistic theory of quantum mechanics from which the concept of spin arose naturally. The inclusion of a fourth variable (time) required the presence of a fourth quantum number. According to Dirac's derivation, an electron possesses both orbital ( $L$ ) and spin ( $S$ ) angular momentum. The total angular momentum ( $J$ ) is a linear combination of the two, as shown in Equation (4.13).

$$\hat{J} = \hat{L} + \hat{S} = -i\hbar \frac{\partial}{\partial \phi} \pm \frac{\hbar}{2} \quad (4.13)$$

The spin angular momentum vector  $S$  can take values of  $\pm m_s \hbar/2$ , where  $m_s$  can take values of  $+1/2$  ( $\alpha$ ) or  $-1/2$  ( $\beta$ ), depending on whether it aligns against or with the external magnetic field, respectively. The usual classical picture of electron spin, where the electron can be considered as a top spinning on its axis either in the

clockwise or the counterclockwise direction, is only useful as a conceptual tool. In actuality, spin is strictly a quantum mechanical phenomenon and it has no classical analogy.

The introduction of a fourth quantum number to account for the spin angular momentum of an electron also necessitates the introduction of a sixth fundamental postulate of quantum mechanics.

*Postulate 6:* The total wave function must be antisymmetric with respect to the interchange of all coordinates of one fermion with those of another. The *Pauli exclusion principle*, which states that no two electrons within an atom can have the same set of quantum numbers, is a direct result of this antisymmetry principle.

Another way of thinking about the Pauli exclusion principle is to give each electron in an atom its own electronic (e-mail) address. For instance, at one point in time, my e-mail address was brpfennig@vaxsar.vassar.edu. One could think of my e-mail address as consisting of four quantum numbers. The principal quantum number here would be the .edu domain, which identifies this electron (me) as belonging to the realm of educational institutions. The second quantum number in my e-mail address gets a little more specific and identifies me at Vassar College, where I used to teach. The third quantum number is even more specific, sending my junk mail to the Vaxsar server (clever, huh?) at the college. Finally, the mail is delivered specifically to me. Just as there are no two people in the world having the exact same email address, there are no two electrons within an atom that can have the same set of all four quantum numbers:  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ .

Returning to the helium atom, suppose that electrons 1 and 2 occupy the two states  $a$  and  $b$ , respectively. The wave function in Equation (4.14) would be unacceptable because the two electrons are distinguishable upon interchange. Taking linear combinations of the product of the two states, however, provides two acceptable wave functions because now the electrons become indistinguishable upon interchange, as shown in Equations (4.15) and (4.16). The former of these equations is symmetric with respect to electron exchange (it yields the same mathematical expression), while the latter is antisymmetric.

$$\psi = \psi_a(1)\psi_b(2) \neq \psi_a(2)\psi_b(1) \quad (4.14)$$

$$\psi_+ = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)] \quad (4.15)$$

$$\psi_- = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] \quad (4.16)$$

For the same pair of electrons, the spins of the two electrons could be both positive  $[\alpha(1)\alpha(2)]$ , both negative  $[\beta(1)\beta(2)]$ , or some linear combination of the two:  $1/\sqrt{2}[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$  or  $1/\sqrt{2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$ . The former three spin functions are symmetric with respect to interchange, while the latter is antisymmetric. Because it is the total wave function (spatial plus spin) that must be antisymmetric according to the Pauli principle, of the eight possible combinations between the two spatial wave functions given in Equations (4.15) and (4.16) with the four spin wave functions, only the following are antisymmetric overall:

$$\psi_+ = \frac{1}{2}[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (4.17)$$

$$\psi_- = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)][\alpha(1)\alpha(2)] \quad (4.18)$$

$$\psi_- = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)][\beta(1)\beta(2)] \quad (4.19)$$

$$\psi_- = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)][\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (4.20)$$

Any two electrons occupying the same orbital would have a symmetric spatial wave function. Therefore, their spin wave functions must be antisymmetric, as is the case for Equation (4.17). In other words, the Pauli exclusion principle states that no two electrons in the same atom may have all four quantum numbers the same. Each electron in an atom must possess a unique set of quantum numbers. As a result, every hydrogenic orbital in a polyelectronic atom can hold at most two electrons, and then if and only if their electron spins are opposite. Hence, the sets of *s*, *p*, *d*, and *f* orbitals for a given value of *n* can hold a maximum of 2, 6, 10, and 14 electrons, as suggested by the blocks of elements shown in Figure 4.12.

#### 4.4 ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

The *Aufbau* (or “building up”) principle uses one-electron (hydrogenic) atomic orbital energies to predict the electron configurations of polyelectronic atoms. The electrons are placed into the orbitals one at a time to form the lowest energy configuration that is consistent with the Pauli exclusion principle and Hund’s rule of maximum multiplicity. *Hund’s rule* requires that the electrons be placed in a degenerate set of orbitals in such a way as to maximize the spin multiplicity. The *spin multiplicity* is defined as  $2S + 1$ , where *S* is the sum of the  $m_s$  values for all of the electrons. Because  $S = 0$  for any combination of paired electrons, the spin multiplicity is solely determined by the number of unpaired electrons. Using the Aufbau principle, along with Madelung’s rule, the electron configuration of *N* is  $1s^2 2s^2 2p^3$ . Hund’s rule implies that the three electrons in the  $2p$  orbitals all have identical spins and are unpaired. Any atom that has unpaired electrons will be *paramagnetic* and will be strongly attracted by a magnetic field. Atoms that have all their electrons paired are *diamagnetic* and are weakly repelled by a magnetic field. The electron configurations for the 118 elements are shown in Table 4.2. In order to avoid having to write out lengthy descriptions for the entire electron configuration of the heavier elements, a short-hand method is used whereby a set of square brackets containing the symbol for the most recent noble gas is used to abbreviate the electron configuration.

The astute reader will notice that there are quite a few exceptions to the electron configurations predicted by the Aufbau principle. This is because the hydrogenic orbitals only have meaning for one-electron systems. Whenever there is more than one electron, electron–electron repulsions must also be considered. Consider the case of the two electrons discussed, electrons 1 and 2, occupying the states *a* and *b*. There were four allowed wave functions for this particular case, given by Equations (4.17)–(4.20). The energies of the unperturbed wave functions are shown in Figure 4.14 at left. Because both of the electrons are negatively charged, there exists a coulombic repulsion between them whenever the electrons are in different regions of space. As a result of this repulsion, which is given by the Coulomb integral *J*, the total energy of the system will be raised as shown in Figure 4.14, center.

When the two electrons occupy the same region of space (the overlap region), the energies of the four different wave functions are no longer degenerate. When the electrons are all paired,  $S = 0$  and the spin multiplicity is 1, forming a singlet state, *S*, which is singly degenerate. The wave function that describes this state is the one given by Equation (4.17), where the spatial portion of the total wave function is symmetric with respect to interchange. The spatially symmetric state tends to bring the electrons together into the same region of space. Therefore, the energy of the singlet state will be raised even further in Figure 4.14 as a result of the larger

TABLE 4.2 Electron configurations for the elements in terms of the one-electron, hydrogenic orbitals.

Symbol	Z	Configuration	Symbol	Z	Configuration
H	1	1s <sup>1</sup>	Nd	60	[Xe]6s <sup>2</sup> 4f <sup>4</sup>
He	2	1s <sup>2</sup>	Pm	61	[Xe]6s <sup>2</sup> 4f <sup>5</sup>
Li	3	[He]2s <sup>1</sup>	Sm	62	[Xe]6s <sup>2</sup> 4f <sup>6</sup>
Be	4	[He]2s <sup>2</sup>	Eu	63	[Xe]6s <sup>2</sup> 4f <sup>7</sup>
B	5	[He]2s <sup>2</sup> 2p <sup>1</sup>	Gd*	64	[Xe]6s <sup>2</sup> 4f <sup>7</sup> 5d <sup>1</sup>
C	6	[He]2s <sup>2</sup> 2p <sup>2</sup>	Tb	65	[Xe]6s <sup>2</sup> 4f <sup>9</sup>
N	7	[He]2s <sup>2</sup> 2p <sup>3</sup>	Dy	66	[Xe]6s <sup>2</sup> 4f <sup>10</sup>
O	8	[He]2s <sup>2</sup> 2p <sup>4</sup>	Ho	67	[Xe]6s <sup>2</sup> 4f <sup>11</sup>
F	9	[He]2s <sup>2</sup> 2p <sup>5</sup>	Er	68	[Xe]6s <sup>2</sup> 4f <sup>12</sup>
Ne	10	[He]2s <sup>2</sup> 2p <sup>6</sup>	Tm	69	[Xe]6s <sup>2</sup> 4f <sup>13</sup>
Na	11	[Ne]3s <sup>1</sup>	Yb	70	[Xe]6s <sup>2</sup> 4f <sup>14</sup>
Mg	12	[Ne]3s <sup>2</sup>	Lu	71	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>1</sup>
Al	13	[Ne]3s <sup>2</sup> 3p <sup>1</sup>	Hf	72	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>2</sup>
Si	14	[Ne]3s <sup>2</sup> 3p <sup>2</sup>	Ta	73	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>3</sup>
P	15	[Ne]3s <sup>2</sup> 3p <sup>3</sup>	W	74	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>4</sup>
S	16	[Ne]3s <sup>2</sup> 3p <sup>4</sup>	Re	75	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>5</sup>
Cl	17	[Ne]3s <sup>2</sup> 3p <sup>5</sup>	Os	76	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>6</sup>
Ar	18	[Ne]3s <sup>2</sup> 3p <sup>6</sup>	Ir	77	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>7</sup>
K	19	[Ar]4s <sup>1</sup>	Pt*	78	[Xe]6s <sup>1</sup> 4f <sup>14</sup> 5d <sup>9</sup>
Ca	20	[Ar]4s <sup>2</sup>	Au*	79	[Xe]6s <sup>1</sup> 4f <sup>14</sup> 5d <sup>10</sup>
Sc	21	[Ar]4s <sup>2</sup> 3d <sup>1</sup>	Hg	80	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup>
Ti	22	[Ar]4s <sup>2</sup> 3d <sup>2</sup>	Tl	81	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>1</sup>
V	23	[Ar]4s <sup>2</sup> 3d <sup>3</sup>	Pb	82	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>2</sup>
Cr*	24	[Ar]4s <sup>1</sup> 3d <sup>5</sup>	Bi	83	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>3</sup>
Mn	25	[Ar]4s <sup>2</sup> 3d <sup>5</sup>	Po	84	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>4</sup>
Fe	26	[Ar]4s <sup>2</sup> 3d <sup>6</sup>	At	85	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>5</sup>
Co	27	[Ar]4s <sup>2</sup> 3d <sup>7</sup>	Rn	86	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>6</sup>
Ni	28	[Ar]4s <sup>2</sup> 3d <sup>8</sup>	Fr	87	[Rn]7s <sup>1</sup>
Cu*	29	[Ar]4s <sup>1</sup> 3d <sup>10</sup>	Ra	88	[Rn]7s <sup>2</sup>
Zn	30	[Ar]4s <sup>2</sup> 3d <sup>10</sup>	Ac*	89	[Rn]7s <sup>2</sup> 6d <sup>1</sup>
Ga	31	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>1</sup>	Th*	90	[Rn]7s <sup>2</sup> 6d <sup>2</sup>
Ge	32	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup>	Pa*	91	[Rn]7s <sup>2</sup> 5f <sup>2</sup> 6d <sup>1</sup>
As	33	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>3</sup>	U*	92	[Rn]7s <sup>2</sup> 5f <sup>3</sup> 6d <sup>1</sup>
Se	34	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>4</sup>	Np*	93	[Rn]7s <sup>2</sup> 5f <sup>4</sup> 6d <sup>1</sup>
Br	35	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>5</sup>	Pu	94	[Rn]7s <sup>2</sup> 5f <sup>6</sup>
Kr	36	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>6</sup>	Am	95	[Rn]7s <sup>2</sup> 5f <sup>7</sup>
Rb	37	[Kr]5s <sup>1</sup>	Cm*	96	[Rn]7s <sup>2</sup> 5f <sup>7</sup> 6d <sup>1</sup>
Sr	38	[Kr]5s <sup>2</sup>	Bk	97	[Rn]7s <sup>2</sup> 5f <sup>9</sup>
Y	39	[Kr]5s <sup>2</sup> 4d <sup>1</sup>	Cf*	98	[Rn]7s <sup>2</sup> 5f <sup>9</sup> 6d <sup>1</sup>
Zr	40	[Kr]5s <sup>2</sup> 4d <sup>2</sup>	Es	99	[Rn]7s <sup>2</sup> 5f <sup>11</sup>
Nb*	41	[Kr]5s <sup>1</sup> 4d <sup>4</sup>	Fm	100	[Rn]7s <sup>2</sup> 5f <sup>12</sup>
Mo*	42	[Kr]5s <sup>1</sup> 4d <sup>5</sup>	Md	101	[Rn]7s <sup>2</sup> 5f <sup>13</sup>
Tc	43	[Kr]5s <sup>2</sup> 4d <sup>5</sup>	No	102	([Rn]7s <sup>2</sup> 5f <sup>14</sup> )
Ru*	44	[Kr]5s <sup>1</sup> 4d <sup>7</sup>	Lr*	103	[Rn]7s <sup>2</sup> 5f <sup>14</sup> 7p <sup>1</sup>
Rh*	45	[Kr]5s <sup>1</sup> 4d <sup>8</sup>	Rf	104	[Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>2</sup>
Pd*	46	[Kr]4d <sup>10</sup>	Db	105	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>3</sup> )
Ag*	47	[Kr]5s <sup>1</sup> 4d <sup>10</sup>	Sg	106	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>4</sup> )
Cd	48	[Kr]5s <sup>2</sup> 4d <sup>10</sup>	Bh	107	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>5</sup> )
In	49	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>1</sup>	Hs	108	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>6</sup> )
Sn	50	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>2</sup>	Mt	109	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>7</sup> )
Sb	51	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>3</sup>	Ds*	110	([Rn]7s <sup>1</sup> 5f <sup>14</sup> 6d <sup>9</sup> )
Te	52	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>4</sup>	Rg*	111	([Rn]7s <sup>1</sup> 5f <sup>14</sup> 6d <sup>10</sup> )
I	53	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>5</sup>	Cn	112	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>10</sup> )
Xe	54	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>6</sup>	Uut	113	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>10</sup> 7p <sup>1</sup> )

(continued)

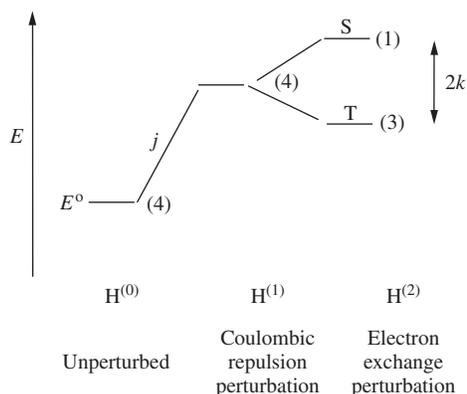
TABLE 4.2 (Continued)

Symbol	Z	Configuration	Symbol	Z	Configuration
Cs	55	[Xe]6s <sup>1</sup>	Fl	114	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>10</sup> 7p <sup>2</sup> )
Ba	56	[Xe]6s <sup>2</sup>	Uup	115	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>10</sup> 7p <sup>3</sup> )
La*	57	[Xe]6s <sup>2</sup> 5d <sup>1</sup>	Lv	116	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>10</sup> 7p <sup>4</sup> )
Ce*	58	[Xe]6s <sup>2</sup> 4f <sup>1</sup> 5d <sup>1</sup>	Uus	117	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>10</sup> 7p <sup>5</sup> )
Pr	59	[Xe]6s <sup>2</sup> 4f <sup>3</sup>	Uuo	118	([Rn]7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>10</sup> 7p <sup>6</sup> )

Exceptions to the Aufbau principle are noted with an asterisk. Values in parentheses are calculated, not experimental.

FIGURE 4.14

Energy diagram for a two-electron, two-state system, showing the changes in energy and the degeneracies (in parentheses) that result from the electron–electron repulsions.



electron–electron repulsion. The remaining three wave functions, which possess an antisymmetric spatial component, form a triplet state, *T*, which is triply degenerate. In the antisymmetric spatial wave function, the electrons tend to avoid each other. This natural tendency of the electrons to stay away from each other decreases the amount of electron–electron repulsion. Therefore, the triplet state will be lower in energy than the singlet state, as shown in Figure 4.14 at the right. This observation is the basis for Hund's rule of maximum multiplicity, which would also predict that the triplet state should be more stable than the singlet state. The energy difference between the two states is given by twice the exchange integral *k*. The magnitude of the exchange integral, in turn, is proportional to  $N(N-1)$ , where *N* is the number of unpaired electrons. For those electron configurations that are exceptions to the Aufbau principle, the exception is usually a result of the increased exchange energy that results when there are a large number of unpaired electrons. For example, the electron configuration of Cr is [Ar]4s<sup>1</sup>3d<sup>5</sup> instead of the predicted [Ar]4s<sup>2</sup>3d<sup>4</sup>. The added stability of the former electron configuration over the latter is due in large part to the larger number of unpaired electrons that it possesses.

## 4.5 ATOMIC TERM SYMBOLS

The electron configurations of polyelectronic atoms given by the one-electron hydrogenic orbitals are an incomplete description of the ways that the electrons can occupy these orbitals. When the electron configuration of Fe, for instance, is said to be [Ar]4s<sup>2</sup>3d<sup>6</sup> using Madelung's rule, this ignores the contribution that the electron–electron repulsions make to the one-electron hydrogenic orbital energies. For the *d*<sup>6</sup> configuration in Fe, there are actually 210 different ways that the six electrons can occupy the five *d* orbitals. Some of these 210 microstates will have the same values of *j* and *k* and therefore have the same energy, while

other combinations will have different energies. Each energy level describes a *state*, or a *term*. It is more realistic for us to think about the electron configurations of polyelectronic atoms in terms of the energies of their terms instead of the one-electron hydrogenic orbital energies. The energies of these terms depend on three factors: (i) the average energy of the one-electron hydrogenic orbitals from which they are derived,  $E^{\circ}$ ; (ii) the magnitude of the Coulomb integral  $j$ ; and (iii) the magnitude of the exchange integral  $k$ .

The following method can be used to extract the *term symbols* (which are used to describe electronic transitions) from all of the different microstates that the electrons in an atom can assume. Consider the carbon atom, for example. Carbon has the electron configuration  $1s^2 2s^2 2p^2$ . The occupation of the filled  $1s$  and  $2s$  orbitals is unambiguous. According to the Pauli exclusion principle, there is only one way that the electrons can occupy each of these singly degenerate orbitals: one with  $m_s = +1/2$  and the other with  $m_s = -1/2$ . However, there are 15 different ways to place two electrons into the triply degenerate  $2p$  subshell. These 15 possibilities are called *microstates* and are shown in Figure 4.15, where the 15 sets are  $p$  orbitals arranged vertically. The  $m_l$  quantum number for each  $p$  orbital is listed at the left in the diagram.

In general, the number of Pauli-allowed microstates (M.S.) can be calculated using the formula given by Equation (4.21), where  $n_o$  is the number of degenerate orbitals and  $n_e$  is the number of electrons to be placed in those orbitals.

$$\#M.S. = \frac{(2n_o)!}{n_e!(2n_o - n_e)!} \quad (4.21)$$

Applying this formula to the carbon atom ( $n_o = 3$ ,  $n_e = 2$ ), 15 Pauli-allowed microstates are predicted. For the  $3d^2$  configuration in  $V^{3+}$  (g), there are 45 possible microstates ( $n_o = 5$ ,  $n_e = 2$ ). In the case of electron configurations such as  $[Ar]4s^1 3d^5$ , the probabilities are multiplicative. The number of allowed microstates for the  $s^1$  configuration is 2, while that for the  $d^5$  configuration is 252. Thus, there are 504 possible microstates for a gaseous Cr atom!

As a result of electron–electron repulsions, not all of the microstates for a given electron configuration will necessarily have the same energy. In the case of carbon, for instance, it is logical to conclude that the microstates where both electrons are paired in the same orbital will have a greater coulombic repulsion than those that are unpaired. Thus, our goal is to take the Pauli-allowed microstates and to extract from them all those combinations that have the same energy. These are collectively referred to as *states*. Each *state*, or collection of microstates, has its own energy and can be assigned a symbol, known as a *term symbol* that characterizes some of the properties of the state (or *term*). In general, there are two formalisms for extracting term symbols from the microstates: Russell–Saunders (RS) coupling and *jj* coupling. Each method is discussed individually.

+1	↑↓			↑	↑		↓	↓		↑	↑	↓		↓	
0		↑↓		↑		↑	↓		↓	↓		↑	↑		↓
-1			↑↓		↑	↑		↓	↓		↓		↓	↑	↑

**FIGURE 4.15**

The 15 ways (microstates) that two electrons can occupy the three  $2p$  orbitals.

### 4.5.1 Extracting Term Symbols Using Russell–Saunders Coupling

Every electron has both orbital ( $L$ ) and spin ( $S$ ) angular momentum. The RS or LS coupling scheme, which is generally valid for the lighter elements ( $Z < 30$ ), provides a mechanism whereby the orbital angular momenta  $l$  of the individual electrons couple together to produce a total orbital angular momentum  $L$  and the individual spin angular momenta  $s$  couple together to yield a total spin angular momentum  $S$ , as shown in Equation (4.22):

$$L = \sum_i l_i \text{ and } S = \sum_i s_i \quad (4.22)$$

Just as the orbital angular momentum  $l$  can take on  $2l + 1$  components having  $m_l = -l, -l + 1, \dots, l - 1, l$ , the total orbital angular momentum  $L$  will also have  $2L + 1$  components having  $M_L = -L, -L + 1, \dots, L - 1, L$ . Similarly, the states described by  $L = 0, 1, 2, 3$ , and so on, will have symbols reflecting the shape of their orbital angular momenta, namely  $S, P, D$ , and  $F$ . It is common practice to use lower case symbols to represent “one-electron” orbitals and upper case symbols for polyelectronic states. For a given value of  $S$ , there will be  $2S + 1$  spin states having values of  $M_S$  ranging from  $-S$  to  $+S$  in integral steps. The value of  $2S + 1$  is known as the *spin multiplicity*. States having  $2S + 1 = 1$  are called *singlets*, while those having a spin multiplicity of three are known as *triplets*.

The procedure for extracting term symbols from the microstates using the RS coupling scheme is as follows:

- Determine the number of allowed microstates and sketch a microstate table similar to the one shown earlier for carbon.
- Add a row across the top of the microstate table that calculates the  $M_L$  as the sum of the individual  $m_l$ 's. Add a similar row across the bottom that calculates  $M_S$  as the sum of the individual  $m_s$ 's. The microstate table for carbon should now look similar to the one in Figure 4.16:
- Count the number of microstates that have the same values of  $M_L$  and  $M_S$  and organize them into a new table similar to the one shown in Figure 4.17. Note that this form of the microstate table will always be symmetric about its center, a fact that can be used to simplify the amount of work involved in the table's construction.
- Remove the first term symbol from the chart by choosing the maximum value of  $M_L$ . If there is more than one entry having the same value, then maximize the value of  $M_S$  as a secondary consideration. In this case, the entry with the largest value of  $M_L$  is indicated by an asterisk in Figure 4.18. This entry has  $M_L = 2$  and  $M_S = 0$ . These are the maximum values for the total orbital and total spin angular momentum components, and they therefore correspond with  $L = 2$  and  $S = 0$ . The extracted term is a D-term, because  $L = 2$  has the same orbital angular momentum as a hydrogenic  $d$ -orbital ( $l = 2$ ). The spin multiplicity of the term is  $2S + 1$ , in this case, a singlet. The singlet-D term symbol is written as  $^1D$ . It has a degeneracy equal to  $(2L + 1)(2S + 1) = 5$ . Thus, in the extraction of the  $^1D$  term symbol, we must remove a total of five microstates. Obviously, the one that is asterisked in the table must be included in the extraction. The remaining four microstates to be removed are underlined. They are chosen in such a manner that the center of symmetry in the table following extraction will be preserved.
- After removal of the five degenerate microstates that comprise the singlet-D term, the microstate table is reduced as follows (Figure 4.18(b)).

$M_L =$	2	0	-2	1	0	-1	1	0	-1	1	0	-1	1	0	-1
$m_l$	+1	↑↓	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑
$m_l$	0	↑↓	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑
$m_l$	-1	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑
$M_S =$	0	0	0	1	1	1	-1	-1	-1	0	0	0	0	0	0

FIGURE 4.16

Microstate table for carbon, with the  $M_L$  and  $M_S$  values tabulated across the top and bottom, respectively.

$M_L \backslash M_S$	1	0	-1
2	0	1	0
1	1	2	1
0	1	3	1
-1	1	2	1
-2	0	1	0

FIGURE 4.17

Table for a  $p^2$  electron configuration showing the numbers of microstates having the corresponding values of  $M_L$  and  $M_S$ .

- The extraction process is repeated until all of the microstates have been assigned to term symbols. The next extraction removes a term with  $L=1$  and  $S=1$ , or a triplet-P term. The degeneracy of the  $^3P$  state is  $(2L+1)(2S+1)=9$ . Thus, nine microstates must be removed from the table in a symmetrical manner. The table now reduces to Figure 4.18(c). The final term has  $L=0$  and  $S=0$ , or  $^1S$ , and is singly degenerate.

Using the RS coupling scheme, it was determined that there are three different energy levels for the  $1s^2 2s^2 2p^2$  electron configuration of carbon, having the degeneracies listed in parentheses:  $^1D$  (5),  $^3P$  (9), and  $^1S$  (1). As required by the formula given in Equation (4.21), there are a total of 15 Pauli-allowed microstates. However, these 15 configurations exist in states that have three separate energy levels.

- We can use Hund's rules to determine the ground-state term. First, we choose the term with the maximum spin multiplicity and then (if necessary) the term with the largest total orbital angular momentum  $L$ . In the case of the C atom, the ground-state term is the  $^3P$  state. Hund's rules can only be

$M_L \backslash M_S$	1	0	-1
2	0	<u>1</u> *	0
1	1	<u>2</u>	1
0	1	<u>3</u>	1
-1	1	<u>2</u>	1
-2	0	<u>1</u>	0
		$^1D$	
		(a)	

$M_L \backslash M_S$	1	0	-1
2	0	0	0
1	<u>1</u>	<u>1</u>	<u>1</u>
0	<u>1</u>	<u>2</u>	<u>1</u>
-1	<u>1</u>	<u>1</u>	<u>1</u>
-2	0	1	0
		$^3P$	
		(b)	

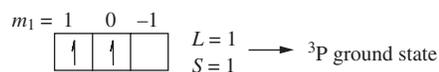
$M_L \backslash M_S$	1	0	-1
2	0	0	0
1	0	0	0
0	0	<u>1</u> *	0
-1	0	0	0
-2	0	0	0
		$^1S$	
		(c)	

FIGURE 4.18

(a–c) Extracting the term symbols from the  $p^2$  microstate table.

**FIGURE 4.19**

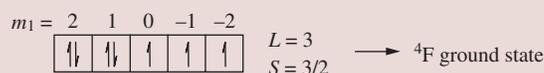
The shortcut method for determining the ground-state term symbol for a  $p^2$  electron configuration.



applied to the ground state. We still have no idea whether the  ${}^1D$  or  ${}^1S$  state will be the lowest energy excited state of carbon. If one is only interested in the ground-state term, there is an easy shortcut that can be used. Sketch the electron configuration by filling in the orbital “boxes” such that the electrons fill in unpaired first beginning with the orbital having the largest value of  $m_l$ . Then, it is a simple matter to calculate  $L$  and  $S$  from the individual angular momenta in order to determine the ground-state term. The example for C is shown in Figure 4.19.

**Example 4-6.** Determine the ground-state term symbol for the  $d^7$  electron configuration.

**Solution.** Using the given figure, the sum of the  $m_l$  values is 3 such that  $L = 3$  ( $F$ ) and  $S = 3/2$  so the spin multiplicity is 4. Thus, the ground-state term symbol is  ${}^4F$  and has a degeneracy of  $(2L + 1)(2S + 1)$  or 28.



The term symbols for a variety of possible electron configurations are shown in Table 4.3. For each entry, the ground-state term symbol is listed first. Note that the completely filled subshells  $s^2$ ,  $p^6$ , and  $d^{10}$  are all spherically symmetric, as required by Unsöld’s theorem and have the  ${}^1S$  term. Half-filled subshells (such as  $p^3$  or  $d^5$  are also spherically symmetric. The term symbols for the pairs:  $p^1$  and  $p^5$ ,  $p^2$  and  $p^4$ ,  $d^2$  and  $d^8$ , and so on, are identical to one another because the  $p^5$  electron configuration, for instance, can be viewed equivalently as a  $p^1$  (hole) configuration.

#### 4.5.2 Extracting Term Symbols Using $jj$ Coupling

For the heavier elements ( $Z \geq 30$ ), the total orbital  $L$  and spin  $S$  angular momentum quantum numbers are no longer valid. Instead, the orbital  $l$  and spin  $s$  angular momentum of each individual electron couple together first, as shown by Equation (4.23), to produce a new quantum number  $j$ . The directional components of  $j$  are given by the quantum number  $m$  and range from  $j \rightarrow -j$  in integral increments, as shown in Equation (4.24).

$$j_i = l_i \pm s_i \quad (4.23)$$

$$m_i = -j_i, -j_i + 1, \dots, j_i - 1, j_i \quad (4.24)$$

The individual  $j$ ’s then couple together to yield the total angular momentum  $J$ , according to Equation (4.25). The components of  $J$  can range from  $-J$  to  $+J$ , as shown by Equation (4.26).

$$J = \sum_i j_i \quad (4.25)$$

$$M = \sum_i m_i = -J, -J + 1, \dots, J - 1, J \quad (4.26)$$

**TABLE 4.3** Term symbols for common electron configurations.*Equivalent electrons*

$s^2, p^6, d^{10}$	$^1S$
$p^1, p^5$	$^2P$
$p^2, p^4$	$^3P, ^1D, ^1S$
$p^3$	$^4S, ^2D, ^2P$
$d^1, d^9$	$^2D$
$d^2, d^8$	$^3F, ^3P, ^1G, ^1D, ^1S$
$d^3, d^7$	$^4F, ^4P, ^2H, ^2G, ^2F, ^2D, ^2D, ^2P$
$d^4, d^6$	$^5D, ^3H, ^3G, ^3F, ^3F, ^3D, ^3P, ^3P, ^1I, ^1G, ^1G, ^1F, ^1D, ^1D, ^1S, ^1S$
$d^5$	$^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G, ^2G, ^2F, ^2F, ^2D, ^2D, ^2D, ^2P, ^2S$

*Nonequivalent electrons*

$s s$	$^1S, ^3S$
$s p$	$^1P, ^3P$
$s d$	$^1D, ^3D$
$p p$	$^3D, ^1D, ^3P, ^1P, ^3S, ^1S$
$p d$	$^3F, ^1F, ^3D, ^1D, ^3P, ^1P$
$d d$	$^3G, ^1G, ^3F, ^1F, ^3D, ^1D, ^3P, ^1P, ^3S, ^1S$

Consider the  $p^2$  electron configuration of lead (earlier we had used C for the  $p^2$  configuration, but carbon's atomic number is less than 30, so here we will use Pb instead). Because  $l = 1$  for a  $p$ -electron and  $s = \pm 1/2$ ,  $j = 3/2$  or  $1/2$ . When the values of  $jj'$  are  $3/2, 3/2$ , the combinations of  $mm'$  quantum numbers possible are shown in Table 4.4. For  $j = 3/2$ ,  $m = 3/2, 1/2, -1/2$ , or  $-3/2$ . Certain combinations, such as  $(3/2, 3/2)$  are Pauli-excluded because  $j = j'$  and  $m = m'$ . Likewise, only one combination of pairs such as  $(3/2, 1/2), (1/2, 3/2)$  is allowed because of configurational exclusion. For this particular set of  $jj'$ , there are six possible microstates, as shown in Table 4.4.

In order to extract the terms from these microstates, one must first maximize  $M$  and then select  $2J + 1$  microstates to remove. Thus, the first term to be extracted will have  $J = 2$  and is fivefold degenerate ( $M = 2, 1, 0, -1, \text{ and } -2$ ). This leaves one remaining microstate in the table, having  $J = 0$  and where  $M = 0$  (singly-degenerate). Consequently, there are two terms from this table:  $J = 2$  (5) and  $J = 0$  (1), where the degeneracy of each term is shown in parentheses. For the combination  $jj' = 3/2, 1/2$ , eight combinations of  $mm'$  are allowed, as shown in Table 4.5. In this case,  $m$  can equal  $m'$ , because  $j \neq j'$ . Extraction of the terms from Table 4.5 yields:  $J = 2$  (5),  $J = 1$  (3). For  $jj' = 1/2, 1/2$ , there is only one possible microstate ( $m = 1/2, m' = -1/2$ ). Because  $j = j'$ , the Pauli exclusion principle states that  $m \neq m'$ . Hence, the combinations  $mm' = 1/2, 1/2$  or  $-1/2, -1/2$  are not allowed. The combination  $-1/2, 1/2$  is

**TABLE 4.4** Microstates having  $jj' = 3/2, 3/2$ .

$m_1$	$m_2$	$M$
3/2	1/2	2
3/2	-1/2	1
3/2	-3/2	0
1/2	-1/2	0
1/2	-3/2	-1
-1/2	-3/2	-2

TABLE 4.5 Microstates having  $jj' = 3/2, 1/2$ .

$m_1$	$m_2$	$M$
3/2	1/2	2
3/2	-1/2	1
1/2	1/2	1
1/2	-1/2	0
-1/2	1/2	0
-1/2	-1/2	-1
-3/2	1/2	-1
-3/2	-1/2	-2

configurationally excluded. Extraction of the final term yields  $J = 0$  (1). In summary, applying the  $jj$  coupling scheme to the  $p^2$  configuration of Pb yields a total of 15 possible microstates (6 from  $jj' = 3/2, 3/2$ ; 8 from  $jj' = 3/2, 1/2$ ; and 1 from  $jj' = 1/2, 1/2$ ) and five terms ( $J = 2, J = 0, J = 2, J = 1$ , and  $J = 0$ ).

### 4.5.3 Correlation Between RS (LS) Coupling and $jj$ Coupling

For elements having atomic numbers that are intermediate between the extremes of RS coupling and  $jj$  coupling, there is a one-to-one correspondence between the terms. For every RS term symbol, one can introduce a spin-orbit perturbation that further splits these terms into different energies by introducing the quantum number  $J$ . For intermediate cases,  $J = |L + S| \rightarrow |L - S|$ . Consider the  $p^2$  electron configuration as an example. In this case, the RS term symbols are  $^3P$  (9),  $^1D$  (5), and  $^1S$  (1). For the  $^3P$  term, where  $L = 1$  and  $S = 1$ ,  $J$  can take values of 2, 1, or 0. Thus, the  $^3P$  term will split into three different energy levels, each having a degeneracy of  $2J + 1$ , as follows:  $^3P_2$  (5),  $^3P_1$  (3), and  $^3P_0$  (1). The revised RS term symbol lists the quantum number  $J$  as a subscript following the term. As before, the number in parentheses represents the degeneracy of the modified term. Note that the total number of microstates both before and after spin-orbit coupling is the same (in this case, 9). Likewise, the  $^1D$  (5) term will become  $^1D_2$  (5) as a result of the spin-orbit perturbation and the  $^1S$  (1) term will become  $^1S_0$  (1). Figure 4.20 shows the one-to-one correspondence between terms in the RS coupling scheme and those in the  $jj$  coupling scheme for the  $p^2$  electron configuration.

In progressing from the RS term symbol to the spin-orbit modified terms, a *barycenter* of energy must be maintained. In other words, the total energy of the microstates before and after the perturbation must be equivalent. The energies of

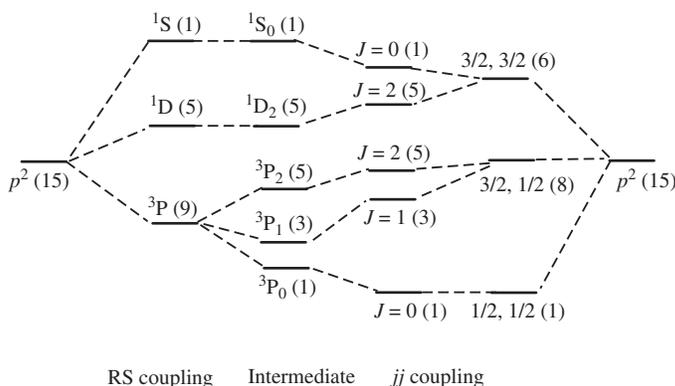


FIGURE 4.20

There is a one-to-one correspondence between terms in the RS coupling scheme and terms in the  $jj$  coupling scheme.

the spin-orbit perturbed states (relative to each unperturbed RS term) are given by Equation (4.27), where  $\lambda$  is the spin-orbit coupling constant:

$$E_{s.o.} = (\lambda/2)[J(J+1) - L(L+1) - S(S+1)] \quad (4.27)$$

For the  $^3P$  term, the energy of the perturbed  $^3P_2$ ,  $^3P_1$ , and  $^3P_0$  states are  $+\lambda$ ,  $-\lambda$ , and  $-2\lambda$ , respectively, according to the given equation. Although the magnitude of  $\lambda$  is a function of the element, it always increases with increasing atomic number. Hence, the degree of spin-orbit coupling will increase with  $Z$ . Because the  $^3P_2$  state is fivefold degenerate, it is destabilized with respect to the unperturbed term by  $5(+\lambda)$ , or  $+5\lambda$ . The triply degenerate  $^3P_1$  state and the singly degenerate  $^3P_0$  state are stabilized by  $3(-\lambda)$  and  $1(-2\lambda)$ , respectively. Thus, the total energy of the  $^3P_2$ ,  $^3P_1$ , and  $^3P_0$  terms are  $+5(+\lambda) + 3(-\lambda) + 1(-2\lambda) = 0$ , relative to the unperturbed  $^3P$  state. Note that the total energy is conserved following the spin-orbit perturbation. The very important concept of term symbols will be revisited in a later section of this text when the spectroscopy of coordination compounds is discussed.

## 4.6 SHIELDING AND EFFECTIVE NUCLEAR CHARGE

One of the largest differences between hydrogen and polyelectronic atoms is that the nuclear charge that an outer electron feels in a polyelectronic atom will be reduced by the electron–electron repulsions of all the inner electrons. Thus, the nuclear charge  $Z$  should be replaced by the effective nuclear charge  $Z^*$ . As mentioned previously, for a given value of  $n$ , the ability of an electron to penetrate the nucleus decreases in the order  $s > p > d > f$ . Therefore, the  $ns$  and  $np$  electrons are particularly good at shielding (or screening) the  $nd$  or  $nf$  electrons from feeling the full effect of the nuclear charge. The effective nuclear charge is equal to the difference between the nuclear charge  $Z$  and a shielding parameter  $\sigma$ , as shown in Equation (4.28). The shielding parameter depends on the electron configuration of the atom and the electron of interest.

$$Z^* = Z - \sigma \quad (4.28)$$

In 1930, Slater developed a set of empirical rules for calculating the magnitude of the shielding parameter:

- The electron configuration is written in groups with increasing values of  $n$  according to the paradigm given here:

$$(1s)(2s, 2p)(3s, 3p)(3d)(4s, 4p)(4d)(4f)(5s, 5p)(5d)(5f) \dots$$

- The electron of interest and any electrons that lie to the right of that electron in the paradigm will contribute zero to the shielding parameter.
- For  $s$  and  $p$  electrons, any other electron in the same group contributes 0.35 each (exception: if the electron of interest lies in the  $1s$  orbital, any other  $1s$  electron will contribute only 0.30). Electrons in the  $n-1$  group contribute 0.85 each and all other groups lying to the left contribute 1.00 each to the shielding parameter.
- For  $d$  or  $f$  electrons, any electron in the same group contributes 0.35 each and all other electrons to the left contribute 1.00 each. This is a result of the fact that the  $s$  and  $p$  orbitals are better screeners than are  $d$  and  $f$  orbitals.

**Example 4-7.** Calculate the effective nuclear charge that the outermost electron in K would feel if: (a) it was placed into the 4s orbital, and (b) it was instead placed into a 3d orbital.

**Solution.** The electron configuration of the first 18 electrons in K using the paradigm is  $(1s)^2(2s, 2p)^8(3s, 3p)^8$ .

(a) If the electron of interest is placed into a 4s orbital, the shielding parameter and effective nuclear charge calculated using Slater's rules are

$$\sigma = 0(0.35) + 8(0.85) + 10(1.00) = 16.8$$

$$Z^* = Z - \sigma = 19.0 - 16.8 = 2.2$$

(b) If the electron of interest is placed into a 3d orbital, the shielding parameter and effective nuclear charge calculated using Slater's rules are

$$\sigma = 0(0.35) + 18(1.00) = 18.0$$

$$Z^* = Z - \sigma = 19.0 - 18.0 = 1.0$$

Because of the larger value of  $Z^*$ , Slater's rules predict correctly that the 19th electron of K will fill the 4s orbital instead of the 3d orbital.

To a first approximation, the ionization energy (I.E.) of an atom is equal to the negative of the energy of the electron ( $E_{el}$ ) that is being removed. This is known as *Koopman's theorem*. Because electron energies are always negative, the ionization energy will always be positive. The I.E. can be calculated from Equation (4.29), where  $Z^*$  is the effective nuclear charge calculated using Slater's rules and  $n$  is the principal quantum number for the outermost electron.

$$\text{I.E.} = -E_{el} = -2.179 \times 10^{-18} \text{ J} (6.022 \times 10^{23} \text{ mol}^{-1}) \frac{Z^*}{n^2} \quad (4.29)$$

**Example 4-8.** Calculate the effective nuclear charge for: (a) a 3d electron in Ni and (b) for a 4s electron in Ni. Which electron will have the smaller first ionization energy?

**Solution.** The electron configuration for Ni using the Slater paradigm is  $(1s)^2(2s, 2p)^8(3s, 3p)^8(3d)^8(4s, 4p)^2$ .

(a) If the electron of interest is a 3d electron, the shielding parameter and effective nuclear charge calculated using Slater's rules are

$$\sigma = 7(0.35) + 18(1.00) = 20.45$$

$$Z^* = Z - \sigma = 28.00 - 20.45 = 7.55$$

(b) If the electron of interest is a 4s electron, the shielding parameter and effective nuclear charge calculated using Slater's rules are

$$\sigma = 1(0.35) + 16(0.85) + 10(1.00) = 23.95$$

$$Z^* = Z - \sigma = 28.00 - 23.95 = 4.05$$

Slater's rules predict that the 3d electron will experience a stronger effective nuclear charge than will the 4s electron. Therefore, the 4s electron will have the smaller first ionization energy. Thus, the electron configuration of Ni<sup>+</sup> is [Ar]4s<sup>1</sup>3d<sup>8</sup>, not [Ar]4s<sup>2</sup>3d<sup>7</sup>. Likewise, the electron configuration of Ni<sup>2+</sup> is [Ar]4s<sup>0</sup>3d<sup>8</sup>. It is a general property of the transition metals that the hydrogenic ns orbitals typically fill before the (n-1)d orbitals fill; and the ns orbitals also ionize (or empty) before the (n-1)d orbitals do.

**Example 4-9.** Calculate the theoretical ionization energy for a 2p electron in the N atom using Equation (4.29). Then, calculate the ionization energy if the effects of shielding had not been considered (using just Z instead of Z\*). Compare both answers to the experimental ionization energy of 1.4 MJ/mol.

**Solution.** The electron configuration of N using the Slater paradigm is (1s)<sup>2</sup>(2s, 2p)<sup>5</sup>. The electron of interest is a 2p electron. The shielding parameter and effective nuclear charge can be calculated using Slater's rules:

$$\sigma = 4(0.35) + 2(0.85) = 3.1$$

$$Z^* = Z - \sigma = 7.0 - 3.1 = 3.9$$

The first ionization energy using Equation (4.29) is

$$\text{I.E.} = -E_{\text{el}} = -2.179 \times 10^{-18} \text{ J} (6.022 \times 10^{23} \text{ mol}^{-1}) \frac{3.9}{2^2} \left( \frac{1 \text{ MJ}}{10^6 \text{ J}} \right) = 1.3 \text{ MJ/mol}$$

Ignoring shielding, one obtains:

$$\text{I.E.} = -E_{\text{el}} = -2.179 \times 10^{-18} \text{ J} (6.022 \times 10^{23} \text{ mol}^{-1}) \frac{7}{2^2} \left( \frac{1 \text{ MJ}}{10^6 \text{ J}} \right) = 2.3 \text{ MJ/mol}$$

Clearly, the answer that includes shielding is closer to the experimental value.

The periodic properties of the elements, including the first ionization energy, are discussed in the next chapter. Almost all of these properties will ultimately depend on three simple factors: (i) the electron configuration of the atom, (ii) the principal quantum number of the outermost electron, and (iii) the effective nuclear charge. Therefore, a quantitative understanding of Slater's rules is an important tool in the prediction of the chemical reactivity of the elements.

## EXERCISES

- 4.1. How far from the hydrogen nucleus will the radial node for an electron in the 3p orbital reside?
- 4.2. How many radial nodes and how many angular nodal planes will a 4f orbital possess?
- 4.3. Write the mathematical form of the angular part of the wave function for the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals by taking the positive and negative linear combinations of  $Y(2,2)$  with  $Y(2,-2)$ , respectively.
- 4.4. Write the complete electron configurations (no shorthand notation) for each of the following: (a) Fe, (b) Fe<sup>3+</sup>, (c) O<sup>-</sup>, (d) Pb, (e) Mn<sup>2+</sup>, (f) Sc, (g) Zn<sup>2+</sup>, (h) Tl, (i) Pu, and (j) Re<sup>+</sup>.

- 4.5. Which atoms or ions in Problem 4.4 are paramagnetic and which are diamagnetic?
- 4.6. Determine the term symbols for the N atom. Show all work. (a) Determine the number of possible microstates. (b) Write out all the possible combinations of the electrons in a microstates table. (c) Extract the term symbols and determine the degeneracy of each term. (d) Determine the ground-state term symbol using Hund's rule of maximum multiplicity.
- 4.7. Determine the spin-orbit splitting for each of the RS term symbols for the P atom and use Equation (4.27) to calculate their energies relative to the barycenter of each term.
- 4.8. Determine the ground-state term symbol for each of the following: (a) O, (b) Ni, (c)  $\text{Fe}^{2+}$ , (d) Co, and (e) Pu.
- 4.9. Using Slater's rules, calculate  $Z^*$  for: (a)  $2p$  electron in F, (b)  $4s$  electron in Cu, and (c)  $3d$  electron in Cu.
- 4.10. When Cu is oxidized by one electron, will the electron be removed from the  $4s$  or the  $3d$  orbital first? Explain your answer.
- 4.11. The stabilization of a half-filled  $d$ -subshell is greater than that for a half-filled  $p$ -subshell. Explain why.
- 4.12. Calculate the first ionization energy for P in units of megajoule per mole.

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