

# The Hydrogen Atom

## 6.1 The One-Particle Central-Force Problem

Before studying the hydrogen atom, we shall consider the more general problem of a single particle moving under a central force. The results of this section will apply to any central-force problem. Examples are the hydrogen atom (Section 6.5) and the isotropic three-dimensional harmonic oscillator (Prob. 6.3).

A **central force** is one derived from a potential-energy function that is spherically symmetric, which means that it is a function only of the distance of the particle from the origin:  $V = V(r)$ . The relation between force and potential energy is given by (5.31) as

$$\mathbf{F} = -\nabla V(x, y, z) = -\mathbf{i}(\partial V/\partial x) - \mathbf{j}(\partial V/\partial y) - \mathbf{k}(\partial V/\partial z) \quad (6.1)$$

The partial derivatives in (6.1) can be found by the chain rule [Eqs. (5.53)–(5.55)]. Since  $V$  in this case is a function of  $r$  only, we have  $(\partial V/\partial \theta)_{r,\phi} = 0$  and  $(\partial V/\partial \phi)_{r,\theta} = 0$ . Therefore,

$$\left(\frac{\partial V}{\partial x}\right)_{y,z} = \frac{dV}{dr} \left(\frac{\partial r}{\partial x}\right)_{y,z} = \frac{x}{r} \frac{dV}{dr} \quad (6.2)$$

$$\left(\frac{\partial V}{\partial y}\right)_{x,z} = \frac{y}{r} \frac{dV}{dr}, \quad \left(\frac{\partial V}{\partial z}\right)_{x,y} = \frac{z}{r} \frac{dV}{dr} \quad (6.3)$$

where Eqs. (5.57) and (5.58) have been used. Equation (6.1) becomes

$$\mathbf{F} = -\frac{1}{r} \frac{dV}{dr} (x\mathbf{i} + y\mathbf{j} + z\mathbf{k}) = -\frac{dV(r)}{dr} \frac{\mathbf{r}}{r} \quad (6.4)$$

where (5.33) for  $\mathbf{r}$  was used. The quantity  $\mathbf{r}/r$  in (6.4) is a unit vector in the radial direction. A central force is radially directed.

Now we consider the quantum mechanics of a single particle subject to a central force. The Hamiltonian operator is

$$\hat{H} = \hat{T} + \hat{V} = -(\hbar^2/2m)\nabla^2 + V(r) \quad (6.5)$$

where  $\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$  [Eq. (3.46)]. Since  $V$  is spherically symmetric, we shall work in spherical coordinates. Hence we want to transform the Laplacian operator to these coordinates. We already have the forms of the operators  $\partial/\partial x$ ,  $\partial/\partial y$ , and  $\partial/\partial z$  in these coordinates [Eqs. (5.62)–(5.64)], and by squaring each of these operators and

then adding their squares, we get the Laplacian. This calculation is left as an exercise. The result is (Prob. 6.4)

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2} \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (6.6)$$

Looking back to (5.68), which gives the operator  $\hat{L}^2$  for the square of the magnitude of the orbital angular momentum of a single particle, we see that

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{1}{r^2 \hbar^2} \hat{L}^2 \quad (6.7)$$

The Hamiltonian (6.5) becomes

$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{1}{2mr^2} \hat{L}^2 + V(r) \quad (6.8)$$

In classical mechanics a particle subject to a central force has its angular momentum conserved (Section 5.3). In quantum mechanics we might ask whether we can have states with definite values for both the energy and the angular momentum. To have the set of eigenfunctions of  $\hat{H}$  also be eigenfunctions of  $\hat{L}^2$ , the commutator  $[\hat{H}, \hat{L}^2]$  must vanish. We have

$$\begin{aligned} [\hat{H}, \hat{L}^2] &= [\hat{T}, \hat{L}^2] + [\hat{V}, \hat{L}^2] \\ [\hat{T}, \hat{L}^2] &= \left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{1}{2mr^2} \hat{L}^2, \hat{L}^2 \right] \\ [\hat{T}, \hat{L}^2] &= -\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}, \hat{L}^2 \right] + \frac{1}{2m} \left[ \frac{1}{r^2} \hat{L}^2, \hat{L}^2 \right] \end{aligned} \quad (6.9)$$

Recall that  $\hat{L}^2$  involves only  $\theta$  and  $\phi$  and not  $r$  [Eq. (5.68)]. Hence it commutes with every operator that involves only  $r$ . [To reach this conclusion, we must use relations like (5.47) with  $x$  and  $z$  replaced by  $r$  and  $\theta$ .] Thus the first commutator in (6.9) is zero. Moreover, since any operator commutes with itself, the second commutator in (6.9) is zero. Therefore,  $[\hat{T}, \hat{L}^2] = 0$ . Also, since  $\hat{L}^2$  does not involve  $r$ , and  $V$  is a function of  $r$  only, we have  $[\hat{V}, \hat{L}^2] = 0$ . Therefore,

$$[\hat{H}, \hat{L}^2] = 0 \quad \text{if } V = V(r) \quad (6.10)$$

$\hat{H}$  commutes with  $\hat{L}^2$  when the potential-energy function is independent of  $\theta$  and  $\phi$ .

Now consider the operator  $\hat{L}_z = -i\hbar \partial/\partial \phi$  [Eq. (5.67)]. Since  $\hat{L}_z$  does not involve  $r$  and since it commutes with  $\hat{L}^2$  [Eq. (5.50)], it follows that  $\hat{L}_z$  commutes with the Hamiltonian (6.8):

$$[\hat{H}, \hat{L}_z] = 0 \quad \text{if } V = V(r) \quad (6.11)$$

We can therefore have a set of simultaneous eigenfunctions of  $\hat{H}$ ,  $\hat{L}^2$ , and  $\hat{L}_z$  for the central-force problem. Let  $\psi$  denote these common eigenfunctions:

$$\hat{H}\psi = E\psi \quad (6.12)$$

$$\hat{L}^2\psi = l(l+1)\hbar^2\psi, \quad l = 0, 1, 2, \dots \quad (6.13)$$

$$\hat{L}_z\psi = m\hbar\psi, \quad m = -l, -l+1, \dots, l \quad (6.14)$$

where Eqs. (5.104) and (5.105) were used.

Using (6.8) and (6.13), we have for the Schrödinger equation (6.12)

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} \right) + \frac{1}{2mr^2} \hat{L}^2 \psi + V(r) \psi = E \psi$$

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} \right) + \frac{l(l+1)\hbar^2}{2mr^2} \psi + V(r) \psi = E \psi \quad (6.15)$$

The eigenfunctions of  $\hat{L}^2$  are the spherical harmonics  $Y_l^m(\theta, \phi)$ , and since  $\hat{L}^2$  does not involve  $r$ , we can multiply  $Y_l^m$  by an arbitrary function of  $r$  and still have eigenfunctions of  $\hat{L}^2$  and  $\hat{L}_z$ . Therefore,

$$\psi = R(r)Y_l^m(\theta, \phi) \quad (6.16)$$

Using (6.16) in (6.15), we then divide both sides by  $Y_l^m$  to get an ordinary differential equation for the unknown function  $R(r)$ :

$$-\frac{\hbar^2}{2m} \left( R'' + \frac{2}{r} R' \right) + \frac{l(l+1)\hbar^2}{2mr^2} R + V(r)R = ER(r) \quad (6.17)$$

We have shown that, for any one-particle problem with a spherically symmetric potential-energy function  $V(r)$ , the stationary-state wave functions are  $\psi = R(r)Y_l^m(\theta, \phi)$ , where the radial factor  $R(r)$  satisfies (6.17). By using a specific form for  $V(r)$  in (6.17), we can solve it for a particular problem.

## 6.2 Noninteracting Particles and Separation of Variables

Up to this point, we have solved only one-particle quantum-mechanical problems. The hydrogen atom is a two-particle system, and as a preliminary to dealing with the H atom, we first consider a simpler case, that of two noninteracting particles.

Suppose that a system is composed of the noninteracting particles 1 and 2. Let  $q_1$  and  $q_2$  symbolize the coordinates  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$  of particles 1 and 2. Because the particles exert no forces on each other, the classical-mechanical energy of the system is the sum of the energies of the two particles:  $E = E_1 + E_2 = T_1 + V_1 + T_2 + V_2$ , and the classical Hamiltonian is the sum of Hamiltonians for each particle:  $H = H_1 + H_2$ . Therefore, the Hamiltonian operator is

$$\hat{H} = \hat{H}_1 + \hat{H}_2$$

where  $\hat{H}_1$  involves only the coordinates  $q_1$  and the momentum operators  $\hat{p}_1$  that correspond to  $q_1$ . The Schrödinger equation for the system is

$$(\hat{H}_1 + \hat{H}_2)\psi(q_1, q_2) = E\psi(q_1, q_2) \quad (6.18)$$

We try a solution of (6.18) by separation of variables, setting

$$\psi(q_1, q_2) = G_1(q_1)G_2(q_2) \quad (6.19)$$

We have

$$\hat{H}_1 G_1(q_1)G_2(q_2) + \hat{H}_2 G_1(q_1)G_2(q_2) = EG_1(q_1)G_2(q_2) \quad (6.20)$$

Since  $\hat{H}_1$  involves only the coordinate and momentum operators of particle 1, we have  $\hat{H}_1[G_1(q_1)G_2(q_2)] = G_2(q_2)\hat{H}_1 G_1(q_1)$ , since, as far as  $\hat{H}_1$  is concerned,  $G_2$  is a constant. Using this equation and a similar equation for  $\hat{H}_2$ , we find that (6.20) becomes

$$G_2(q_2)\hat{H}_1 G_1(q_1) + G_1(q_1)\hat{H}_2 G_2(q_2) = EG_1(q_1)G_2(q_2) \quad (6.21)$$

$$\frac{\hat{H}_1 G_1(q_1)}{G_1(q_1)} + \frac{\hat{H}_2 G_2(q_2)}{G_2(q_2)} = E \quad (6.22)$$

Now, by the same arguments used in connection with Eq. (3.65), we conclude that each term on the left in (6.22) must be a constant. Using  $E_1$  and  $E_2$  to denote these constants, we have

$$\begin{aligned} \frac{\hat{H}_1 G_1(q_1)}{G_1(q_1)} &= E_1, & \frac{\hat{H}_2 G_2(q_2)}{G_2(q_2)} &= E_2 \\ E &= E_1 + E_2 \end{aligned} \quad (6.23)$$

Thus, when the system is composed of two noninteracting particles, we can reduce the two-particle problem to two separate one-particle problems by solving

$$\hat{H}_1 G_1(q_1) = E_1 G_1(q_1), \quad \hat{H}_2 G_2(q_2) = E_2 G_2(q_2) \quad (6.24)$$

which are separate Schrödinger equations for each particle.

Generalizing this result to  $n$  noninteracting particles, we have

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \cdots + \hat{H}_n$$

$$\psi(q_1, q_2, \dots, q_n) = G_1(q_1) G_2(q_2) \cdots G_n(q_n) \quad (6.25)$$

$$E = E_1 + E_2 + \cdots + E_n \quad (6.26)$$

$$\hat{H}_i G_i = E_i G_i, \quad i = 1, 2, \dots, n \quad (6.27)$$

*For a system of noninteracting particles, the energy is the sum of the individual energies of each particle and the wave function is the product of wave functions for each particle. The wave function  $G_i$  of particle  $i$  is found by solving a Schrödinger equation for particle  $i$  using the Hamiltonian  $\hat{H}_i$ .*

These results also apply to a single particle whose Hamiltonian is the sum of separate terms for each coordinate:

$$\hat{H} = \hat{H}_x(\hat{x}, \hat{p}_x) + \hat{H}_y(\hat{y}, \hat{p}_y) + \hat{H}_z(\hat{z}, \hat{p}_z)$$

In this case, we conclude that the wave functions and energies are

$$\begin{aligned} \psi(x, y, z) &= F(x)G(y)K(z), & E &= E_x + E_y + E_z \\ \hat{H}_x F(x) &= E_x F(x), & \hat{H}_y G(y) &= E_y G(y), & \hat{H}_z K(z) &= E_z K(z) \end{aligned}$$

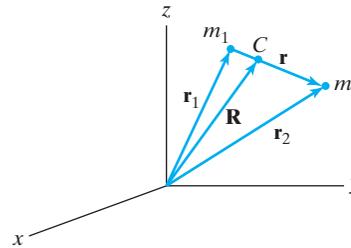
Examples include the particle in a three-dimensional box (Section 3.5), the three-dimensional free particle (Prob. 3.42), and the three-dimensional harmonic oscillator (Prob. 4.20).

## 6.3 Reduction of the Two-Particle Problem to Two One-Particle Problems

The hydrogen atom contains two particles, the proton and the electron. For a system of two particles 1 and 2 with coordinates  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$ , the potential energy of interaction between the particles is usually a function of only the relative coordinates  $x_2 - x_1$ ,  $y_2 - y_1$ , and  $z_2 - z_1$  of the particles. In this case the two-particle problem can be simplified to two separate one-particle problems, as we now prove.

Consider the classical-mechanical treatment of two interacting particles of masses  $m_1$  and  $m_2$ . We specify their positions by the radius vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$  drawn from the origin

**FIGURE 6.1** A two-particle system with center of mass at  $C$ .



of a Cartesian coordinate system (Fig. 6.1). Particles 1 and 2 have coordinates  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$ . We draw the vector  $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$  from particle 1 to 2 and denote the components of  $\mathbf{r}$  by  $x$ ,  $y$ , and  $z$ :

$$x = x_2 - x_1, \quad y = y_2 - y_1, \quad z = z_2 - z_1 \quad (6.28)$$

The coordinates  $x$ ,  $y$ , and  $z$  are called the **relative** or **internal coordinates**.

We now draw the vector  $\mathbf{R}$  from the origin to the system's center of mass, point  $C$ , and denote the coordinates of  $C$  by  $X$ ,  $Y$ , and  $Z$ :

$$\mathbf{R} = \mathbf{i}X + \mathbf{j}Y + \mathbf{k}Z \quad (6.29)$$

The definition of the center of mass of this two-particle system gives

$$X = \frac{m_1x_1 + m_2x_2}{m_1 + m_2}, \quad Y = \frac{m_1y_1 + m_2y_2}{m_1 + m_2}, \quad Z = \frac{m_1z_1 + m_2z_2}{m_1 + m_2} \quad (6.30)$$

These three equations are equivalent to the vector equation

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \quad (6.31)$$

We also have

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 \quad (6.32)$$

We regard (6.31) and (6.32) as simultaneous equations in the two unknowns  $\mathbf{r}_1$  and  $\mathbf{r}_2$  and solve for them to get

$$\mathbf{r}_1 = \mathbf{R} - \frac{m_2}{m_1 + m_2} \mathbf{r}, \quad \mathbf{r}_2 = \mathbf{R} + \frac{m_1}{m_1 + m_2} \mathbf{r} \quad (6.33)$$

Equations (6.31) and (6.32) represent a transformation of coordinates from  $x_1, y_1, z_1, x_2, y_2, z_2$  to  $X, Y, Z, x, y, z$ . Consider what happens to the Hamiltonian under this transformation. Let an overhead dot indicate differentiation with respect to time. The velocity of particle 1 is [Eq. (5.34)]  $\mathbf{v}_1 = d\mathbf{r}_1/dt = \dot{\mathbf{r}}_1$ . The kinetic energy is the sum of the kinetic energies of the two particles:

$$T = \frac{1}{2}m_1|\dot{\mathbf{r}}_1|^2 + \frac{1}{2}m_2|\dot{\mathbf{r}}_2|^2 \quad (6.34)$$

Introducing the time derivatives of Eqs. (6.33) into (6.34), we have

$$\begin{aligned} T &= \frac{1}{2}m_1\left(\dot{\mathbf{R}} - \frac{m_2}{m_1 + m_2}\dot{\mathbf{r}}\right) \cdot \left(\dot{\mathbf{R}} - \frac{m_2}{m_1 + m_2}\dot{\mathbf{r}}\right) \\ &\quad + \frac{1}{2}m_2\left(\dot{\mathbf{R}} + \frac{m_1}{m_1 + m_2}\dot{\mathbf{r}}\right) \cdot \left(\dot{\mathbf{R}} + \frac{m_1}{m_1 + m_2}\dot{\mathbf{r}}\right) \end{aligned}$$

where  $|\mathbf{A}|^2 = \mathbf{A} \cdot \mathbf{A}$  [Eq. (5.24)] has been used. Using the distributive law for the dot products, we find, after simplifying,

$$T = \frac{1}{2}(m_1 + m_2)|\dot{\mathbf{R}}|^2 + \frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} |\dot{\mathbf{r}}|^2 \quad (6.35)$$

Let  $M$  be the total mass of the system:

$$M \equiv m_1 + m_2 \quad (6.36)$$

We define the **reduced mass**  $\mu$  of the two-particle system as

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \quad (6.37)$$

Then

$$T = \frac{1}{2} M |\dot{\mathbf{R}}|^2 + \frac{1}{2} \mu |\dot{\mathbf{r}}|^2 \quad (6.38)$$

The first term in (6.38) is the kinetic energy due to translational motion of the whole system of mass  $M$ . **Translational motion** is motion in which each particle undergoes the same displacement. The quantity  $\frac{1}{2} M |\dot{\mathbf{R}}|^2$  would be the kinetic energy of a hypothetical particle of mass  $M$  located at the center of mass. The second term in (6.38) is the kinetic energy of internal (relative) motion of the two particles. This internal motion is of two types. The distance  $r$  between the two particles can change (vibration), and the direction of the  $\mathbf{r}$  vector can change (rotation). Note that  $|\dot{\mathbf{r}}| = |d\mathbf{r}/dt| \neq d|\mathbf{r}|/dt$ .

Corresponding to the original coordinates  $x_1, y_1, z_1, x_2, y_2, z_2$ , we have six linear momenta:

$$p_{x_1} = m_1 \dot{x}_1, \quad \dots, \quad p_{z_2} = m_2 \dot{z}_2 \quad (6.39)$$

Comparing Eqs. (6.34) and (6.38), we define the six linear momenta for the new coordinates  $X, Y, Z, x, y, z$  as

$$\begin{aligned} p_X &\equiv M\dot{X}, & p_Y &\equiv M\dot{Y}, & p_Z &\equiv M\dot{Z} \\ p_x &\equiv \mu\dot{x}, & p_y &\equiv \mu\dot{y}, & p_z &\equiv \mu\dot{z} \end{aligned}$$

We define two new momentum vectors as

$$\mathbf{p}_M \equiv \mathbf{i}M\dot{X} + \mathbf{j}M\dot{Y} + \mathbf{k}M\dot{Z} \quad \text{and} \quad \mathbf{p}_\mu \equiv \mathbf{i}\mu\dot{x} + \mathbf{j}\mu\dot{y} + \mathbf{k}\mu\dot{z}$$

Introducing these momenta into (6.38), we have

$$T = \frac{|\mathbf{p}_M|^2}{2M} + \frac{|\mathbf{p}_\mu|^2}{2\mu} \quad (6.40)$$

Now consider the potential energy. We make the restriction that  $V$  is a function *only* of the relative coordinates  $x, y$ , and  $z$  of the two particles:

$$V = V(x, y, z) \quad (6.41)$$

An example of (6.41) is two charged particles interacting according to Coulomb's law [see Eq. (3.53)]. With this restriction on  $V$ , the Hamiltonian function is

$$H = \frac{p_M^2}{2M} + \left[ \frac{p_\mu^2}{2\mu} + V(x, y, z) \right] \quad (6.42)$$

Now suppose we had a system composed of a particle of mass  $M$  subject to no forces and a particle of mass  $\mu$  subject to the potential-energy function  $V(x, y, z)$ . Further suppose that there was no interaction between these particles. If  $(X, Y, Z)$  are the coordinates of the particle of mass  $M$ , and  $(x, y, z)$  are the coordinates of the particle of mass  $\mu$ , what is the Hamiltonian of this hypothetical system? Clearly, it is identical with (6.42).

The Hamiltonian (6.42) can be viewed as the sum of the Hamiltonians  $p_M^2/2M$  and  $p_\mu^2/2\mu + V(x, y, z)$  of two hypothetical noninteracting particles with masses  $M$  and  $\mu$ . Therefore, the results of Section 6.2 show that the system's quantum-mechanical energy is the sum of energies of the two hypothetical particles [Eq. (6.23)]:  $E = E_M + E_\mu$ . From Eqs. (6.24) and (6.42), the translational energy  $E_M$  is found by solving the Schrödinger equation  $(\hat{p}_M^2/2M)\psi_M = E_M\psi_M$ . This is the Schrödinger equation for a free particle of mass  $M$ , so its possible eigenvalues are all nonnegative numbers:  $E_M \geq 0$  [Eq. (2.31)]. From (6.24) and (6.42), the energy  $E_\mu$  is found by solving the Schrödinger equation

$$\left[ \frac{\hat{p}_\mu^2}{2\mu} + V(x, y, z) \right] \psi_\mu(x, y, z) = E_\mu \psi_\mu(x, y, z) \quad (6.43)$$

We have thus separated the problem of two particles interacting according to a potential-energy function  $V(x, y, z)$  that depends on only the relative coordinates  $x, y, z$  into two separate one-particle problems: (1) the translational motion of the entire system of mass  $M$ , which simply adds a nonnegative constant energy  $E_M$  to the system's energy, and (2) the relative or internal motion, which is dealt with by solving the Schrödinger equation (6.43) for a hypothetical particle of mass  $\mu$  whose coordinates are the relative coordinates  $x, y, z$  and that moves subject to the potential energy  $V(x, y, z)$ .

For example, for the hydrogen atom, which is composed of an electron ( $e$ ) and a proton ( $p$ ), the atom's total energy is  $E = E_M + E_\mu$ , where  $E_M$  is the translational energy of motion through space of the entire atom of mass  $M = m_e + m_p$ , and where  $E_\mu$  is found by solving (6.43) with  $\mu = m_e m_p / (m_e + m_p)$  and  $V$  being the Coulomb's law potential energy of interaction of the electron and proton; see Section 6.5.

## 6.4 The Two-Particle Rigid Rotor

Before solving the Schrödinger equation for the hydrogen atom, we will first deal with the two-particle rigid rotor. This is a two-particle system with the particles held at a fixed distance from each other by a rigid massless rod of length  $d$ . For this problem, the vector  $\mathbf{r}$  in Fig. 6.1 has the constant magnitude  $|\mathbf{r}| = d$ . Therefore (see Section 6.3), the kinetic energy of internal motion is wholly rotational energy. The energy of the rotor is entirely kinetic, and

$$V = 0 \quad (6.44)$$

Equation (6.44) is a special case of Eq. (6.41), and we may therefore use the results of the last section to separate off the translational motion of the system as a whole. We will concern ourselves only with the rotational energy. The Hamiltonian operator for the rotation is given by the terms in brackets in (6.43) as

$$\hat{H} = \frac{\hat{p}_\mu^2}{2\mu} = -\frac{\hbar^2}{2\mu} \nabla^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad (6.45)$$

where  $m_1$  and  $m_2$  are the masses of the two particles. The coordinates of the fictitious particle of mass  $\mu$  are the relative coordinates of  $m_1$  and  $m_2$  [Eq. (6.28)].

Instead of the relative Cartesian coordinates  $x, y, z$ , it will prove more fruitful to use the relative spherical coordinates  $r, \theta, \phi$ . The  $r$  coordinate is equal to the magnitude of

the  $\mathbf{r}$  vector in Fig. 6.1, and since  $m_1$  and  $m_2$  are constrained to remain a fixed distance apart, we have  $r = d$ . Thus the problem is equivalent to a particle of mass  $\mu$  constrained to move on the surface of a sphere of radius  $d$ . Because the radial coordinate is constant, the wave function will be a function of  $\theta$  and  $\phi$  only. Therefore the first two terms of the Laplacian operator in (6.8) will give zero when operating on the wave function and may be omitted. Looking at things in a slightly different way, we note that the operators in (6.8) that involve  $r$  derivatives correspond to the kinetic energy of radial motion, and since there is no radial motion, the  $r$  derivatives are omitted from  $\hat{H}$ .

Since  $V = 0$  is a special case of  $V = V(r)$ , the results of Section 6.1 tell us that the eigenfunctions are given by (6.16) with the  $r$  factor omitted:

$$\psi = Y_J^m(\theta, \phi) \quad (6.46)$$

where  $J$  rather than  $l$  is used for the rotational angular-momentum quantum number.

The Hamiltonian operator is given by Eq. (6.8) with the  $r$  derivatives omitted and  $V(r) = 0$ . Thus

$$\hat{H} = (2\mu d^2)^{-1} \hat{L}^2$$

Use of (6.13) gives

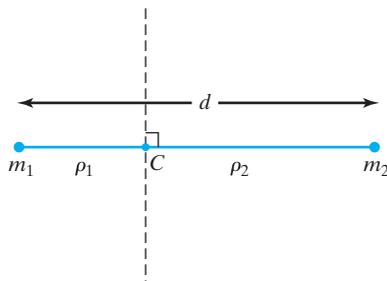
$$\begin{aligned} \hat{H}\psi &= E\psi \\ (2\mu d^2)^{-1} \hat{L}^2 Y_J^m(\theta, \phi) &= E Y_J^m(\theta, \phi) \\ (2\mu d^2)^{-1} J(J+1) \hbar^2 Y_J^m(\theta, \phi) &= E Y_J^m(\theta, \phi) \\ E &= \frac{J(J+1) \hbar^2}{2\mu d^2}, \quad J = 0, 1, 2, \dots \end{aligned} \quad (6.47)$$

The **moment of inertia**  $I$  of a system of  $n$  particles about some particular axis in space as defined as

$$I \equiv \sum_{i=1}^n m_i \rho_i^2 \quad (6.48)$$

where  $m_i$  is the mass of the  $i$ th particle and  $\rho_i$  is the perpendicular distance from this particle to the axis. The value of  $I$  depends on the choice of axis. For the two-particle rigid rotor, we choose our axis to be a line that passes through the center of mass and is perpendicular to the line joining  $m_1$  and  $m_2$  (Fig. 6.2). If we place the rotor so that the center of mass, point  $C$ , lies at the origin of a Cartesian coordinate system and the line joining  $m_1$  and  $m_2$  lies on the  $x$  axis, then  $C$  will have the coordinates  $(0, 0, 0)$ ,  $m_1$  will have the coordinates  $(-\rho_1, 0, 0)$ , and  $m_2$  will have the coordinates  $(\rho_2, 0, 0)$ . Using these coordinates in (6.30), we find

$$m_1 \rho_1 = m_2 \rho_2 \quad (6.49)$$



**FIGURE 6.2** Axis (dashed line) for calculating the moment of inertia of a two-particle rigid rotor.  $C$  is the center of mass.

The moment of inertia of the rotor about the axis we have chosen is

$$I = m_1\rho_1^2 + m_2\rho_2^2 \quad (6.50)$$

Using (6.49), we transform Eq. (6.50) to (see Prob. 6.14)

$$I = \mu d^2 \quad (6.51)$$

where  $\mu \equiv m_1m_2/(m_1 + m_2)$  is the reduced mass of the system and  $d \equiv \rho_1 + \rho_2$  is the distance between  $m_1$  and  $m_2$ . The allowed energy levels (6.47) of the two-particle rigid rotor are

$$E = \frac{J(J + 1)\hbar^2}{2I}, \quad J = 0, 1, 2, \dots \quad (6.52)$$

The lowest level is  $E = 0$ , so there is no zero-point rotational energy. Having zero rotational energy and therefore zero angular momentum for the rotor does not violate the uncertainty principle; recall the discussion following Eq. (5.105). Note that  $E$  increases as  $J^2 + J$ , so the spacing between adjacent rotational levels increases as  $J$  increases.

Are the rotor energy levels (6.52) degenerate? The energy depends on  $J$  only, but the wave function (6.46) depends on  $J$  and  $m$ , where  $m\hbar$  is the  $z$  component of the rotor's angular momentum. For each value of  $J$ , there are  $2J + 1$  values of  $m$ , ranging from  $-J$  to  $J$ . Hence the levels are  $(2J + 1)$ -fold degenerate. The states of a degenerate level have different orientations of the angular-momentum vector of the rotor about a space-fixed axis.

The angles  $\theta$  and  $\phi$  in the wave function (6.46) are relative coordinates of the two point masses. If we set up a Cartesian coordinate system with the origin at the rotor's center of mass,  $\theta$  and  $\phi$  will be as shown in Fig. 6.3. This coordinate system undergoes the same translational motion as the rotor's center of mass but does not rotate in space.

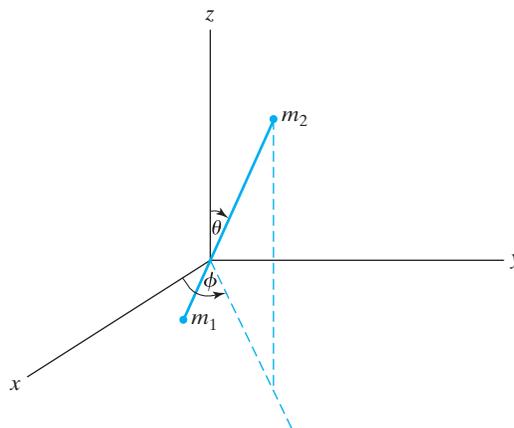
The rotational angular momentum  $[J(J + 1)\hbar^2]^{1/2}$  is the angular momentum of the two particles with respect to an origin at the system's center of mass  $C$ .

The rotational levels of a diatomic molecule can be well approximated by the two-particle rigid-rotor energies (6.52). It is found (*Levine, Molecular Spectroscopy*, Section 4.4) that when a diatomic molecule absorbs or emits radiation, the allowed pure-rotational transitions are given by the selection rule

$$\Delta J = \pm 1 \quad (6.53)$$

In addition, a molecule must have a nonzero dipole moment in order to show a pure-rotational spectrum. A *pure-rotational transition* is one where only the rotational

**FIGURE 6.3** Coordinate system for the two-particle rigid rotor.



quantum number changes. [Vibration–rotation transitions (Section 4.3) involve changes in both vibrational and rotational quantum numbers.] The spacing between adjacent low-lying rotational levels is significantly less than that between adjacent vibrational levels, and the pure-rotational spectrum falls in the microwave (or the far-infrared) region. The frequencies of the pure-rotational spectral lines of a diatomic molecule are then (approximately)

$$\nu = \frac{E_{J+1} - E_J}{h} = \frac{[(J+1)(J+2) - J(J+1)]h}{8\pi^2 I} = 2(J+1)B \quad (6.54)$$

$$B \equiv h/8\pi^2 I, \quad J = 0, 1, 2, \dots \quad (6.55)$$

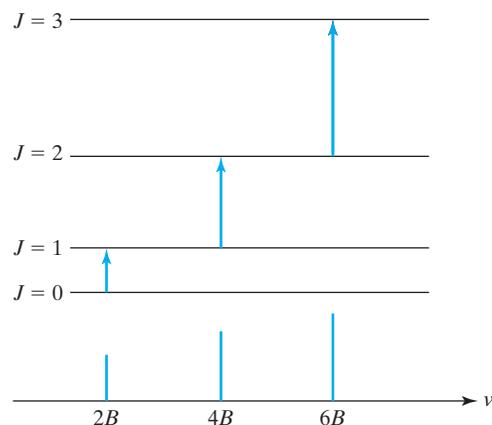
$B$  is called the **rotational constant** of the molecule.

The spacings between the diatomic rotational levels (6.52) for low and moderate values of  $J$  are generally less than or of the same order of magnitude as  $kT$  at room temperature, so the Boltzmann distribution law (4.63) shows that many rotational levels are significantly populated at room temperature. Absorption of radiation by diatomic molecules having  $J = 0$  (the  $J = 0 \rightarrow 1$  transition) gives a line at the frequency  $2B$ ; absorption by molecules having  $J = 1$  (the  $J = 1 \rightarrow 2$  transition) gives a line at  $4B$ ; absorption by  $J = 2$  molecules gives a line at  $6B$ ; and so on. See Fig. 6.4.

Measurement of the rotational absorption frequencies allows  $B$  to be found. From  $B$ , we get the molecule's moment of inertia  $I$ , and from  $I$  we get the bond distance  $d$ . The value of  $d$  found is an average over the  $v = 0$  vibrational motion. Because of the asymmetry of the potential-energy curve in Figs. 4.6 and 13.1,  $d$  is very slightly longer than the equilibrium bond length  $R_e$  in Fig. 13.1.

As noted in Section 4.3, isotopic species such as  $^1\text{H}^{35}\text{Cl}$  and  $^1\text{H}^{37}\text{Cl}$  have virtually the same electronic energy curve  $U(R)$  and so have virtually the same equilibrium bond distance. However, the different isotopic masses produce different moments of inertia and hence different rotational absorption frequencies.

Because molecules are not rigid, the rotational energy levels for diatomic molecules differ slightly from rigid-rotor levels. From (6.52) and (6.55), the two-particle rigid-rotor levels are  $E_{\text{rot}} = BhJ(J+1)$ . Because of the anharmonicity of molecular vibration (Fig. 4.6), the average internuclear distance increases with increasing vibrational quantum number  $v$ , so as  $v$  increases, the moment of inertia  $I$  increases and the rotational constant  $B$  decreases. To allow for the dependence of  $B$  on  $v$ , one replaces  $B$  in  $E_{\text{rot}}$  by  $B_v$ . The *mean rotational constant*  $B_v$  for vibrational level  $v$  is  $B_v = B_e - \alpha_e(v + 1/2)$ , where  $B_e$  is calculated using the equilibrium internuclear separation  $R_e$  at the bottom



**FIGURE 6.4** Two-particle rigid-rotor absorption transitions.

of the potential-energy curve in Fig. 4.6, and the *vibration-rotation coupling constant*  $\alpha_e$  is a positive constant (different for different molecules) that is much smaller than  $B_e$ . Also, as the rotational energy increases, there is a very slight increase in average internuclear distance (a phenomenon called *centrifugal distortion*). This adds the term  $-hDJ^2(J+1)^2$  to  $E_{\text{rot}}$ , where the centrifugal-distortion constant  $D$  is an extremely small positive constant, different for different molecules. For example, for  $^{12}\text{C}^{16}\text{O}$ ,  $B_0 = 57636$  MHz,  $\alpha_e = 540$  MHz, and  $D = 0.18$  MHz. As noted in Section 4.3, for lighter diatomic molecules, nearly all the molecules are in the ground  $v = 0$  vibrational level at room temperature, and the observed rotational constant is  $B_0$ .

For more discussion of nuclear motion in diatomic molecules, see Section 13.2. For the rotational energies of polyatomic molecules, see *Townes and Schawlow*, chaps. 2–4.

### EXAMPLE

The lowest-frequency pure-rotational absorption line of  $^{12}\text{C}^{32}\text{S}$  occurs at 48991.0 MHz. Find the bond distance in  $^{12}\text{C}^{32}\text{S}$ .

The lowest-frequency rotational absorption is the  $J = 0 \rightarrow 1$  line. Equations (1.4), (6.52), and (6.51) give

$$h\nu = E_{\text{upper}} - E_{\text{lower}} = \frac{1(2)\hbar^2}{2\mu d^2} - \frac{0(1)\hbar^2}{2\mu d^2}$$

which gives  $d = (h/4\pi^2\nu\mu)^{1/2}$ . Table A.3 in the Appendix gives

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{12(31.97207)}{(12 + 31.97207)} \frac{1}{6.02214 \times 10^{23}} \text{ g} = 1.44885 \times 10^{-23} \text{ g}$$

The SI unit of mass is the kilogram, and

$$d = \frac{1}{2\pi} \left( \frac{h}{\nu_{0 \rightarrow 1} \mu} \right)^{1/2} = \frac{1}{2\pi} \left[ \frac{6.62607 \times 10^{-34} \text{ J s}}{(48991.0 \times 10^6 \text{ s}^{-1})(1.44885 \times 10^{-26} \text{ kg})} \right]^{1/2} \\ = 1.5377 \times 10^{-10} \text{ m} = 1.5377 \text{ \AA}$$

**EXERCISE** The  $J = 1$  to  $J = 2$  pure-rotational transition of  $^{12}\text{C}^{16}\text{O}$  occurs at 230.538 GHz. (1 GHz =  $10^9$  Hz.) Find the bond distance in this molecule. (Answer:  $1.1309 \times 10^{-10}$  m.)

## 6.5 The Hydrogen Atom

The hydrogen atom consists of a proton and an electron. If  $e$  symbolizes the charge on the proton ( $e = +1.6 \times 10^{-19}$  C), then the electron's charge is  $-e$ .

A few scientists have speculated that the proton and electron charges might not be exactly equal in magnitude. Experiments show that the magnitudes of the electron and proton charges are equal to within one part in  $10^{21}$ . See G. Bressi et al., *Phys. Rev. A*, **83**, 052101 (2011) (available online at [arxiv.org/abs/1102.2766](http://arxiv.org/abs/1102.2766)).

We shall assume the electron and proton to be point masses whose interaction is given by Coulomb's law. In discussing atoms and molecules, we shall usually be considering isolated systems, ignoring interatomic and intermolecular interactions.

Instead of treating just the hydrogen atom, we consider a slightly more general problem: the **hydrogenlike atom**, which consists of one electron and a nucleus of charge  $Ze$ . For  $Z = 1$ , we have the hydrogen atom; for  $Z = 2$ , the  $\text{He}^+$  ion; for  $Z = 3$ , the  $\text{Li}^{2+}$  ion; and so on. The hydrogenlike atom is the most important system in quantum chemistry. An exact solution of the Schrödinger equation for atoms with more than one electron cannot be obtained because of the interelectronic repulsions. If, as a crude first approximation, we ignore these repulsions, then the electrons can be treated independently. (See Section 6.2.) The atomic wave function will be approximated by a product of one-electron functions, which will be hydrogenlike wave functions. A one-electron wave function (whether or not it is hydrogenlike) is called an **orbital**. (More precisely, an **orbital** is a one-electron spatial wave function, where the word *spatial* means that the wave function depends on the electron's three spatial coordinates  $x$ ,  $y$ , and  $z$  or  $r$ ,  $\theta$ , and  $\phi$ . We shall see in Chapter 10 that the existence of electron spin adds a fourth coordinate to a one-electron wave function, giving what is called a spin-orbital.) An orbital for an electron in an atom is called an **atomic orbital**. We shall use atomic orbitals to construct approximate wave functions for atoms with many electrons (Chapter 11). Orbitals are also used to construct approximate wave functions for molecules.

For the hydrogenlike atom, let  $(x, y, z)$  be the coordinates of the electron relative to the nucleus, and let  $\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$ . The Coulomb's law force on the electron in the hydrogenlike atom is [see Eq. (1.37)]

$$\mathbf{F} = -\frac{Ze^2}{4\pi\epsilon_0 r^2} \frac{\mathbf{r}}{r} \quad (6.56)$$

where  $\mathbf{r}/r$  is a unit vector in the  $\mathbf{r}$  direction. The minus sign indicates an attractive force.

The possibility of small deviations from Coulomb's law has been considered. Experiments have shown that if the Coulomb's-law force is written as being proportional to  $r^{-2+s}$ , then  $|s| < 10^{-16}$ . A deviation from Coulomb's law can be shown to imply a nonzero photon rest mass. No evidence exists for a nonzero photon rest mass, and data indicate that any such mass must be less than  $10^{-51}$  g; A. S. Goldhaber and M. M. Nieto, *Rev. Mod. Phys.*, **82**, 939 (2010) (arxiv.org/abs/0809.1003); G. Spavieri et al., *Eur. Phys. J. D*, **61**, 531 (2011) (www.epj.org/\_pdf/HP\_EPJD\_classical\_and\_quantum\_approaches.pdf).

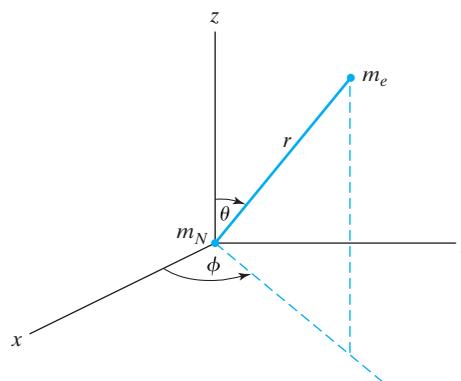
The force in (6.56) is central, and comparison with Eq. (6.4) gives  $dV(r)/dr = Ze^2/4\pi\epsilon_0 r^2$ . Integration gives

$$V = \frac{Ze^2}{4\pi\epsilon_0} \int \frac{1}{r^2} dr = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad (6.57)$$

where the integration constant has been taken as 0 to make  $V = 0$  at infinite separation between the charges. For any two charges  $Q_1$  and  $Q_2$  separated by distance  $r_{12}$ , Eq. (6.57) becomes

$$V = \frac{Q_1 Q_2}{4\pi\epsilon_0 r_{12}} \quad (6.58)$$

Since the potential energy of this two-particle system depends only on the relative coordinates of the particles, we can apply the results of Section 6.3 to reduce the problem to two one-particle problems. The translational motion of the atom as a whole simply adds some constant to the total energy, and we shall not concern ourselves

**FIGURE 6.5** Relative spherical coordinates.

with it. To deal with the internal motion of the system, we introduce a fictitious particle of mass

$$\mu = \frac{m_e m_N}{m_e + m_N} \quad (6.59)$$

where  $m_e$  and  $m_N$  are the electronic and nuclear masses. The particle of reduced mass  $\mu$  moves subject to the potential-energy function (6.57), and its coordinates  $(r, \theta, \phi)$  are the spherical coordinates of one particle relative to the other (Fig. 6.5).

The Hamiltonian for the internal motion is [Eq. (6.43)]

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \quad (6.60)$$

Since  $V$  is a function of the  $r$  coordinate only, we have a one-particle central-force problem, and we may apply the results of Section 6.1. Using Eqs. (6.16) and (6.17), we have for the wave function

$$\psi(r, \theta, \phi) = R(r)Y_l^m(\theta, \phi), \quad l = 0, 1, 2, \dots, \quad |m| \leq l \quad (6.61)$$

where  $Y_l^m$  is a spherical harmonic, and the radial function  $R(r)$  satisfies

$$-\frac{\hbar^2}{2\mu} \left( R'' + \frac{2}{r} R' \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} R - \frac{Ze^2}{4\pi\epsilon_0 r} R = ER(r) \quad (6.62)$$

To save time in writing, we define the constant  $a$  as

$$a \equiv \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} \quad (6.63)$$

and (6.62) becomes

$$R'' + \frac{2}{r} R' + \left[ \frac{8\pi\epsilon_0 E}{ae^2} + \frac{2Z}{ar} - \frac{l(l+1)}{r^2} \right] R = 0 \quad (6.64)$$

### Solution of the Radial Equation

We could now try a power-series solution of (6.64), but we would get a three-term rather than a two-term recursion relation. We therefore seek a substitution that will lead to a two-term recursion relation. It turns out that the proper substitution can be found by examining the behavior of the solution for large values of  $r$ . For large  $r$ , (6.64) becomes

$$R'' + \frac{8\pi\epsilon_0 E}{ae^2} R = 0, \quad r \text{ large} \quad (6.65)$$

which may be solved using the auxiliary equation (2.7). The solutions are

$$\exp[\pm(-8\pi\epsilon_0 E/ae^2)^{1/2}r] \quad (6.66)$$

Suppose that  $E$  is positive. The quantity under the square-root sign in (6.66) is negative, and the factor multiplying  $r$  is imaginary:

$$R(r) \sim e^{\pm i\sqrt{2\mu E}r/\hbar}, \quad E \geq 0 \quad (6.67)$$

where (6.63) was used. The symbol  $\sim$  in (6.67) indicates that we are giving the behavior of  $R(r)$  for large values of  $r$ ; this is called the *asymptotic* behavior of the function. Note the resemblance of (6.67) to Eq. (2.30), the free-particle wave function. Equation (6.67) does not give the complete radial factor in the wave function for positive energies. Further study (*Bethe and Salpeter*, pages 21–24) shows that the radial function for  $E \geq 0$  remains finite for all values of  $r$ , no matter what the value of  $E$ . Thus, just as for the free particle, all nonnegative energies of the hydrogen atom are allowed. Physically, these eigenfunctions correspond to states in which the electron is not bound to the nucleus; that is, the atom is ionized. (A classical-mechanical analogy is a comet moving in a hyperbolic orbit about the sun. The comet is not bound and makes but one visit to the solar system.) Since we get continuous rather than discrete allowed values for  $E \geq 0$ , the positive-energy eigenfunctions are called **continuum eigenfunctions**. The angular part of a continuum wave function is a spherical harmonic. Like the free-particle wave functions, the continuum eigenfunctions are not normalizable in the usual sense.

We now consider the *bound* states of the hydrogen atom, with  $E < 0$ . (For a **bound state**,  $\psi \rightarrow 0$  as  $x \rightarrow \pm\infty$ .) In this case, the quantity in parentheses in (6.66) is positive. Since we want the wave functions to remain finite as  $r$  goes to infinity, we prefer the minus sign in (6.66), and in order to get a two-term recursion relation, we make the substitution

$$R(r) = e^{-Cr}K(r) \quad (6.68)$$

$$C \equiv \left(-\frac{8\pi\epsilon_0 E}{ae^2}\right)^{1/2} \quad (6.69)$$

where  $e$  in (6.68) stands for the base of natural logarithms, and not the proton charge. Use of the substitution (6.68) will guarantee nothing about the behavior of the wave function for large  $r$ . The differential equation we obtain from this substitution will still have two linearly independent solutions. We can make any substitution we please in a differential equation; in fact, we could make the substitution  $R(r) = e^{+Cr}J(r)$  and still wind up with the correct eigenfunctions and eigenvalues. The relation between  $J$  and  $K$  would naturally be  $J(r) = e^{-2Cr}K(r)$ .

Proceeding with (6.68), we evaluate  $R'$  and  $R''$ , substitute into (6.64), multiply by  $r^2 e^{Cr}$ , and use (6.69) to get the following differential equation for  $K(r)$ :

$$r^2 K'' + (2r - 2Cr^2)K' + [(2Za^{-1} - 2C)r - l(l+1)]K = 0 \quad (6.70)$$

We could now substitute a power series of the form

$$K = \sum_{k=0}^{\infty} c_k r^k \quad (6.71)$$

for  $K$ . If we did we would find that, in general, the first few coefficients in (6.71) are zero. If  $c_s$  is the first nonzero coefficient, (6.71) can be written as

$$K = \sum_{k=s}^{\infty} c_k r^k, \quad c_s \neq 0 \quad (6.72)$$

Letting  $j \equiv k - s$ , and then defining  $b_j$  as  $b_j \equiv c_{j+s}$ , we have

$$K = \sum_{j=0}^{\infty} c_{j+s} r^{j+s} = r^s \sum_{j=0}^{\infty} b_j r^j, \quad b_0 \neq 0 \quad (6.73)$$

(Although the various substitutions we are making might seem arbitrary, they are standard procedure in solving differential equations by power series.) The integer  $s$  is evaluated by substitution into the differential equation. Equation (6.73) is

$$K(r) = r^s M(r) \quad (6.74)$$

$$M(r) = \sum_{j=0}^{\infty} b_j r^j, \quad b_0 \neq 0 \quad (6.75)$$

Evaluating  $K'$  and  $K''$  from (6.74) and substituting into (6.70), we get

$$r^2 M'' + [(2s + 2)r - 2Cr^2]M' + [s^2 + s + (2Za^{-1} - 2C - 2Cs)r - l(l + 1)]M = 0 \quad (6.76)$$

To find  $s$ , we look at (6.76) for  $r = 0$ . From (6.75), we have

$$M(0) = b_0, \quad M'(0) = b_1, \quad M''(0) = 2b_2 \quad (6.77)$$

Using (6.77) in (6.76), we find for  $r = 0$

$$b_0(s^2 + s - l^2 - l) = 0 \quad (6.78)$$

Since  $b_0$  is not zero, the terms in parentheses must vanish:  $s^2 + s - l^2 - l = 0$ . This is a quadratic equation in the unknown  $s$ , with the roots

$$s = l, \quad s = -l - 1 \quad (6.79)$$

These roots correspond to the two linearly independent solutions of the differential equation. Let us examine them from the standpoint of proper behavior of the wave function. From Eqs. (6.68), (6.74), and (6.75), we have

$$R(r) = e^{-Cr} r^s \sum_{j=0}^{\infty} b_j r^j \quad (6.80)$$

Since  $e^{-Cr} = 1 - Cr + \dots$ , the function  $R(r)$  behaves for small  $r$  as  $b_0 r^s$ . For the root  $s = l$ ,  $R(r)$  behaves properly at the origin. However, for  $s = -l - 1$ ,  $R(r)$  is proportional to

$$\frac{1}{r^{l+1}} \quad (6.81)$$

for small  $r$ . Since  $l = 0, 1, 2, \dots$ , the root  $s = -l - 1$  makes the radial factor in the wave function infinite at the origin. Many texts take this as sufficient reason for rejecting this root. However, this is not a good argument, since for the *relativistic* hydrogen atom, the  $l = 0$  eigenfunctions are infinite at  $r = 0$ . Let us therefore look at (6.81) from the standpoint of quadratic integrability, since we certainly require the bound-state eigenfunctions to be normalizable.

The normalization integral [Eq. (5.80)] for the radial functions that behave like (6.81) looks like

$$\int_0^{\infty} |R|^2 r^2 dr \approx \int_0^{\infty} \frac{1}{r^{2l}} dr \quad (6.82)$$

for small  $r$ . The behavior of the integral at the lower limit of integration is

$$\left. \frac{1}{r^{2l-1}} \right|_{r=0} \quad (6.83)$$

For  $l = 1, 2, 3, \dots$ , (6.83) is infinite, and the normalization integral is infinite. Hence we must reject the root  $s = -l - 1$  for  $l \geq 1$ . However, for  $l = 0$ , (6.83) is finite, and there is no trouble with quadratic integrability. Thus there is a quadratically integrable solution to the radial equation that behaves as  $r^{-1}$  for small  $r$ .

Further study of this solution shows that it corresponds to an energy value that the experimental hydrogen-atom spectrum shows does not exist. Thus the  $r^{-1}$  solution must be rejected, but there is some dispute over the reason for doing so. One view is that the  $1/r$  solution satisfies the Schrödinger equation everywhere in space except at the origin and hence must be rejected [Dirac, page 156; B. H. Armstrong and E. A. Power, *Am. J. Phys.*, **31**, 262 (1963)]. A second view is that the  $1/r$  solution must be rejected because the Hamiltonian operator is not Hermitian with respect to it (Merzbacher, Section 10.5). (In Chapter 7 we shall define Hermitian operators and show that quantum-mechanical operators are required to be Hermitian.) Further discussion is given in A. A. Khelashvili and T. P. Nadareishvili, *Am. J. Phys.*, **79**, 668 (2011) (see arxiv.org/abs/1102.1185) and in Y. C. Cantelaube, arxiv.org/abs/1203.0551.

Taking the first root in (6.79), we have for the radial factor (6.80)

$$R(r) = e^{-Cr} r^l M(r) \quad (6.84)$$

With  $s = l$ , Eq. (6.76) becomes

$$rM'' + (2l + 2 - 2Cr)M' + (2Za^{-1} - 2C - 2Cl)M = 0 \quad (6.85)$$

From (6.75), we have

$$M(r) = \sum_{j=0}^{\infty} b_j r^j \quad (6.86)$$

$$M' = \sum_{j=0}^{\infty} j b_j r^{j-1} = \sum_{j=1}^{\infty} j b_j r^{j-1} = \sum_{k=0}^{\infty} (k+1) b_{k+1} r^k = \sum_{j=0}^{\infty} (j+1) b_{j+1} r^j$$

$$M'' = \sum_{j=0}^{\infty} j(j-1) b_j r^{j-2} = \sum_{j=1}^{\infty} j(j-1) b_j r^{j-2} = \sum_{k=0}^{\infty} (k+1) k b_{k+1} r^{k-1}$$

$$M'' = \sum_{j=0}^{\infty} (j+1) j b_{j+1} r^{j-1} \quad (6.87)$$

Substituting these expressions in (6.85) and combining sums, we get

$$\sum_{j=0}^{\infty} \left[ j(j+1) b_{j+1} + 2(l+1)(j+1) b_{j+1} + \left( \frac{2Z}{a} - 2C - 2Cl - 2Cj \right) b_j \right] r^j = 0$$

Setting the coefficient of  $r^j$  equal to zero, we get the recursion relation

$$b_{j+1} = \frac{2C + 2Cl + 2Cj - 2Za^{-1}}{j(j+1) + 2(l+1)(j+1)} b_j \quad (6.88)$$

We now must examine the behavior of the infinite series (6.86) for large  $r$ . The result of the same procedure used to examine the harmonic-oscillator power series in (4.42) suggests that for large  $r$  the infinite series (6.86) behaves like  $e^{2Cr}$ . (See Prob. 6.20.) For large  $r$ , the radial function (6.84) behaves like

$$R(r) \sim e^{-Cr} r^l e^{2Cr} = r^l e^{Cr} \quad (6.89)$$

Therefore,  $R(r)$  will become infinite as  $r$  goes to infinity and will not be quadratically integrable. The only way to avoid this “infinity catastrophe” (as in the harmonic-oscillator case) is to have the series terminate after a finite number of terms, in which case the  $e^{-Cr}$  factor will ensure that the wave function goes to zero as  $r$  goes to infinity. Let the

last term in the series be  $b_k r^k$ . Then, to have  $b_{k+1}, b_{k+2}, \dots$  all vanish, the fraction multiplying  $b_j$  in the recursion relation (6.88) must vanish when  $j = k$ . We have

$$2C(k + l + 1) = 2Za^{-1}, \quad k = 0, 1, 2, \dots \quad (6.90)$$

$k$  and  $l$  are integers, and we now define a new integer  $n$  by

$$n \equiv k + l + 1, \quad n = 1, 2, 3, \dots \quad (6.91)$$

From (6.91) the quantum number  $l$  must satisfy

$$l \leq n - 1 \quad (6.92)$$

Hence  $l$  ranges from 0 to  $n - 1$ .

### Energy Levels

Use of (6.91) in (6.90) gives

$$Cn = Za^{-1} \quad (6.93)$$

Substituting  $C \equiv (-8\pi\epsilon_0 E/ae^2)^{1/2}$  [Eq. (6.69)] into (6.93) and solving for  $E$ , we get

$$E = -\frac{Z^2 e^2}{n^2 8\pi\epsilon_0 a} = -\frac{Z^2 \mu e^4}{8\epsilon_0^2 n^2 \hbar^2} \quad (6.94)$$

where  $a \equiv 4\pi\epsilon_0 \hbar^2 / \mu e^2$  [Eq. (6.63)]. These are the bound-state energy levels of the hydrogenlike atom, and they are discrete. **Figure 6.6** shows the potential-energy curve [Eq. (6.57)] and some of the allowed energy levels for the hydrogen atom ( $Z = 1$ ). The crosshatching indicates that all positive energies are allowed.

It turns out that all changes in  $n$  are allowed in light absorption and emission. The wavenumbers [Eq. (4.64)] of H-atom spectral lines are then

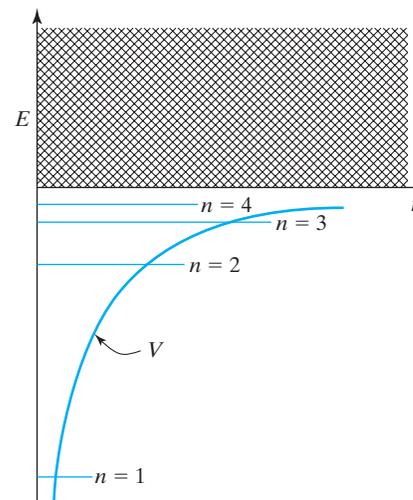
$$\tilde{\nu} \equiv \frac{1}{\lambda} = \frac{\nu}{c} = \frac{E_2 - E_1}{hc} = \frac{e^2}{8\pi\epsilon_0 \hbar c} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \equiv R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (6.95)$$

where  $R_H = 109677.6 \text{ cm}^{-1}$  is the *Rydberg constant* for hydrogen.

### Degeneracy

Are the hydrogen-atom energy levels degenerate? For the bound states, the energy (6.94) depends only on  $n$ . However, the wave function (6.61) depends on all three quantum numbers  $n$ ,  $l$ , and  $m$ , whose allowed values are [Eqs. (6.91), (6.92), (5.104), and (5.105)]

**FIGURE 6.6** Energy levels of the hydrogen atom.



$$n = 1, 2, 3, \dots \quad (6.96)$$

$$l = 0, 1, 2, \dots, n - 1 \quad (6.97)$$

$$m = -l, -l + 1, \dots, 0, \dots, l - 1, l \quad (6.98)$$

Hydrogen-atom states with different values of  $l$  or  $m$ , but the same value of  $n$ , have the same energy. The energy levels are degenerate, except for  $n = 1$ , where  $l$  and  $m$  must both be 0. For a given value of  $n$ , we can have  $n$  different values of  $l$ . For each of these values of  $l$ , we can have  $2l + 1$  values of  $m$ . The degree of degeneracy of an H-atom bound-state level is found to equal  $n^2$  (spin considerations being omitted); see Prob. 6.16. For the continuum levels, it turns out that for a given energy there is no restriction on the maximum value of  $l$ ; hence these levels are infinity-fold degenerate.

The radial equation for the hydrogen atom can also be solved by the use of ladder operators (also known as *factorization*); see Z. W. Salsburg, *Am. J. Phys.*, **33**, 36 (1965).

## 6.6 The Bound-State Hydrogen-Atom Wave Functions

### The Radial Factor

Using (6.93), we have for the recursion relation (6.88)

$$b_{j+1} = \frac{2Z}{na} \frac{j + l + 1 - n}{(j + 1)(j + 2l + 2)} b_j \quad (6.99)$$

The discussion preceding Eq. (6.91) shows that the highest power of  $r$  in the polynomial  $M(r) = \sum_j b_j r^j$  [Eq. (6.86)] is  $k = n - l - 1$ . Hence use of  $C = Z/na$  [Eq. (6.93)] in  $R(r) = e^{-Cr} r^l M(r)$  [Eq. (6.84)] gives the radial factor in the hydrogen-atom  $\psi$  as

$$R_{nl}(r) = r^l e^{-Zr/na} \sum_{j=0}^{n-l-1} b_j r^j \quad (6.100)$$

where  $a \equiv 4\pi\epsilon_0 \hbar^2 / \mu e^2$  [Eq. (6.63)]. The complete hydrogenlike bound-state wave functions are [Eq. (6.61)]

$$\psi_{nlm} = R_{nl}(r) Y_l^m(\theta, \phi) = R_{nl}(r) S_{lm}(\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (6.101)$$

where the first few theta functions are given in Table 5.1.

How many nodes does  $R(r)$  have? The radial function is zero at  $r = \infty$ , at  $r = 0$  for  $l \neq 0$ , and at values of  $r$  that make  $M(r)$  vanish.  $M(r)$  is a polynomial of degree  $n - l - 1$ , and it can be shown that the roots of  $M(r) = 0$  are all real and positive. Thus, aside from the origin and infinity, there are  $n - l - 1$  nodes in  $R(r)$ . The nodes of the spherical harmonics are discussed in Prob. 6.41.

### Ground-State Wave Function and Energy

For the ground state of the hydrogenlike atom, we have  $n = 1$ ,  $l = 0$ , and  $m = 0$ . The radial factor (6.100) is

$$R_{10}(r) = b_0 e^{-Zr/a} \quad (6.102)$$

The constant  $b_0$  is determined by normalization [Eq. (5.80)]:

$$|b_0|^2 \int_0^\infty e^{-2Zr/a} r^2 dr = 1$$

Using the Appendix integral (A.8), we find

$$R_{10}(r) = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a} \quad (6.103)$$

Multiplying by  $Y_0^0 = 1/(4\pi)^{1/2}$ , we have as the ground-state wave function

$$\psi_{100} = \frac{1}{\pi^{1/2}} \left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a} \quad (6.104)$$

The hydrogen-atom energies and wave functions involve the reduced mass, given by (6.59) as

$$\mu_{\text{H}} = \frac{m_e m_p}{m_e + m_p} = \frac{m_e}{1 + m_e/m_p} = \frac{m_e}{1 + 0.000544617} = 0.9994557m_e \quad (6.105)$$

where  $m_p$  is the proton mass and  $m_e/m_p$  was found from Table A.1. The reduced mass is very close to the electron mass. Because of this, some texts use the electron mass instead of the reduced mass in the H atom Schrödinger equation. This corresponds to assuming that the proton mass is infinite compared with the electron mass in (6.105) and that all the internal motion is motion of the electron. The error introduced by using the electron mass for the reduced mass is about 1 part in 2000 for the hydrogen atom. For heavier atoms, the error introduced by assuming an infinitely heavy nucleus is even less than this. Also, for many-electron atoms, the form of the correction for nuclear motion is quite complicated. For these reasons we shall assume in the future an infinitely heavy nucleus and simply use the electron mass in writing the Schrödinger equation for atoms.

If we replace the reduced mass of the hydrogen atom by the electron mass, the quantity  $a$  defined by (6.63) becomes

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529177 \text{ \AA} \quad (6.106)$$

where the subscript zero indicates use of the electron mass instead of the reduced mass.  $a_0$  is called the **Bohr radius**, since it was the radius of the circle in which the electron moved in the ground state of the hydrogen atom in the Bohr theory. Of course, since the ground-state wave function (6.104) is nonzero for all finite values of  $r$ , there is some probability of finding the electron at any distance from the nucleus. The electron is certainly not confined to a circle.

A convenient unit for electronic energies is the **electronvolt** (eV), defined as the kinetic energy acquired by an electron accelerated through a potential difference of 1 volt (V). Potential difference is defined as energy per unit charge. Since  $e = 1.6021766 \times 10^{-19} \text{ C}$  and  $1 \text{ V C} = 1 \text{ J}$ , we have

$$1 \text{ eV} = 1.6021766 \times 10^{-19} \text{ J} \quad (6.107)$$

#### EXAMPLE

Calculate the ground-state energy of the hydrogen atom using SI units and convert the result to electronvolts.

The H atom ground-state energy is given by (6.94) with  $n = 1$  and  $Z = 1$  as  $E = -\mu e^4 / 8h^2 \epsilon_0^2$ . Use of (6.105) for  $\mu$  gives

$$E = -\frac{0.9994557(9.109383 \times 10^{-31} \text{ kg})(1.6021766 \times 10^{-19} \text{ C})^4 Z^2}{8(6.626070 \times 10^{-34} \text{ J s})^2 (8.8541878 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)^2 n^2}$$

$$E = -(2.178686 \times 10^{-18} \text{ J})(Z^2/n^2)[(1 \text{ eV})/(1.6021766 \times 10^{-19} \text{ J})]$$

$$E = -(13.598 \text{ eV})(Z^2/n^2) = -13.598 \text{ eV} \quad (6.108)$$

a number worth remembering. The minimum energy needed to ionize a ground-state hydrogen atom is 13.598 eV.

**EXERCISE** Find the  $n = 2$  energy of  $\text{Li}^{2+}$  in eV; do the minimum amount of calculation needed. (Answer:  $-30.60 \text{ eV}$ .)

### EXAMPLE

Find  $\langle T \rangle$  for the hydrogen-atom ground state.

Equations (3.89) for  $\langle T \rangle$  and (6.7) for  $\nabla^2\psi$  give

$$\langle T \rangle = \int \psi^* \hat{T} \psi \, d\tau = -\frac{\hbar^2}{2\mu} \int \psi^* \nabla^2 \psi \, d\tau$$

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} - \frac{1}{r^2} \hat{L}^2 \psi = \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r}$$

since  $\hat{L}^2 \psi = l(l+1)\hbar^2 \psi$  and  $l = 0$  for an  $s$  state. From (6.104) with  $Z = 1$ , we have  $\psi = \pi^{-1/2} a^{-3/2} e^{-r/a}$ , so  $\partial\psi/\partial r = -\pi^{-1/2} a^{-5/2} e^{-r/a}$  and  $\partial^2\psi/\partial r^2 = \pi^{-1/2} a^{-7/2} e^{-r/a}$ . Using  $d\tau = r^2 \sin\theta \, dr \, d\theta \, d\phi$  [Eq. (5.78)], we have

$$\begin{aligned} \langle T \rangle &= -\frac{\hbar^2}{2\mu} \frac{1}{\pi a^4} \int_0^{2\pi} \int_0^\pi \int_0^\infty \left( \frac{1}{a} e^{-2r/a} - \frac{2}{r} e^{-2r/a} \right) r^2 \sin\theta \, dr \, d\theta \, d\phi \\ &= -\frac{\hbar^2}{2\mu \pi a^4} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta \, d\theta \int_0^\infty \left( \frac{r^2}{a} e^{-2r/a} - 2r e^{-2r/a} \right) dr = \frac{\hbar^2}{2\mu a^2} = \frac{e^2}{8\pi\epsilon_0 a} \end{aligned}$$

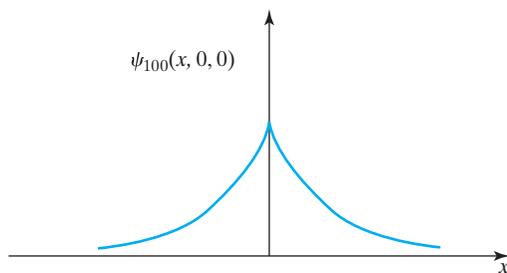
where Appendix integral A.8 and  $a = 4\pi\epsilon_0 \hbar^2 / \mu e^2$  were used. From (6.94),  $e^2/8\pi\epsilon_0 a$  is minus the ground-state H-atom energy, and (6.108) gives  $\langle T \rangle = 13.598 \text{ eV}$ . (See also Sec. 14.4.)

**EXERCISE** Find  $\langle T \rangle$  for the hydrogen-atom  $2p_0$  state using (6.113). (Answer:  $e^2/32\pi\epsilon_0 a = (13.598 \text{ eV})/4 = 3.40 \text{ eV}$ .)

Let us examine a significant property of the ground-state wave function (6.104). We have  $r = (x^2 + y^2 + z^2)^{1/2}$ . For points on the  $x$  axis, where  $y = 0$  and  $z = 0$ , we have  $r = (x^2)^{1/2} = |x|$ , and

$$\psi_{100}(x, 0, 0) = \pi^{-1/2} (Z/a)^{3/2} e^{-Z|x|/a} \quad (6.109)$$

**Figure 6.7** shows how (6.109) varies along the  $x$  axis. Although  $\psi_{100}$  is continuous at the origin, the slope of the tangent to the curve is positive at the left of the origin but negative



**FIGURE 6.7** Cusp in the hydrogen-atom ground-state wave function.

at its right. Thus  $\partial\psi/\partial x$  is discontinuous at the origin. We say that the wave function has a *cusp* at the origin. The cusp is present because the potential energy  $V = -Ze^2/4\pi\epsilon_0 r$  becomes infinite at the origin. Recall the discontinuous slope of the particle-in-a-box wave functions at the walls of the box.

We denoted the hydrogen-atom bound-state wave functions by three subscripts that give the values of  $n$ ,  $l$ , and  $m$ . In an alternative notation, the value of  $l$  is indicated by a letter:

|          |          |          |          |          |          |          |          |          |     |         |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----|---------|
| 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> | ... | (6.110) |
| <i>l</i> | 0        | 1        | 2        | 3        | 4        | 5        | 6        | 7        | ... |         |

The letters *s*, *p*, *d*, *f* are of spectroscopic origin, standing for sharp, principal, diffuse, and fundamental. After these we go alphabetically, except that *j* is omitted. Preceding the code letter for *l*, we write the value of  $n$ . Thus the ground-state wave function  $\psi_{100}$  is called  $\psi_{1s}$  or, more simply, *1s*.

### Wave Functions for $n = 2$

For  $n = 2$ , we have the states  $\psi_{200}$ ,  $\psi_{21-1}$ ,  $\psi_{210}$ , and  $\psi_{211}$ . We denote  $\psi_{200}$  as  $\psi_{2s}$  or simply as *2s*. To distinguish the three *2p* functions, we use a subscript giving the  $m$  value and denote them as  $2p_1$ ,  $2p_0$ , and  $2p_{-1}$ . The radial factor in the wave function depends on  $n$  and  $l$ , but not on  $m$ , as can be seen from (6.100). Each of the three *2p* wave functions thus has the same radial factor. The *2s* and *2p* radial factors may be found in the usual way from (6.100) and (6.99), followed by normalization. The results are given in **Table 6.1**. Note that the exponential factor in the  $n = 2$  radial functions is not the same as in the  $R_{1s}$  function. The complete wave function is found by multiplying the radial factor by the appropriate spherical harmonic. Using (6.101), Table 6.1, and Table 5.1, we have

$$2s = \frac{1}{\pi^{1/2}} \left(\frac{Z}{2a}\right)^{3/2} \left(1 - \frac{Zr}{2a}\right) e^{-Zr/2a} \quad (6.111)$$

$$2p_{-1} = \frac{1}{8\pi^{1/2}} \left(\frac{Z}{a}\right)^{5/2} r e^{-Zr/2a} \sin\theta e^{-i\phi} \quad (6.112)$$

**TABLE 6.1** Radial Factors in the Hydrogenlike-Atom Wave Functions

$$R_{1s} = 2 \left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$R_{2s} = \frac{1}{\sqrt{2}} \left(\frac{Z}{a}\right)^{3/2} \left(1 - \frac{Zr}{2a}\right) e^{-Zr/2a}$$

$$R_{2p} = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a}\right)^{5/2} r e^{-Zr/2a}$$

$$R_{3s} = \frac{2}{3\sqrt{3}} \left(\frac{Z}{a}\right)^{3/2} \left(1 - \frac{2Zr}{3a} + \frac{2Z^2 r^2}{27a^2}\right) e^{-Zr/3a}$$

$$R_{3p} = \frac{8}{27\sqrt{6}} \left(\frac{Z}{a}\right)^{3/2} \left(\frac{Zr}{a} - \frac{Z^2 r^2}{6a^2}\right) e^{-Zr/3a}$$

$$R_{3d} = \frac{4}{81\sqrt{30}} \left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a}$$

$$2p_0 = \frac{1}{\pi^{1/2}} \left( \frac{Z}{2a} \right)^{5/2} r e^{-Zr/2a} \cos \theta \quad (6.113)$$

$$2p_1 = \frac{1}{8\pi^{1/2}} \left( \frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta e^{i\phi} \quad (6.114)$$

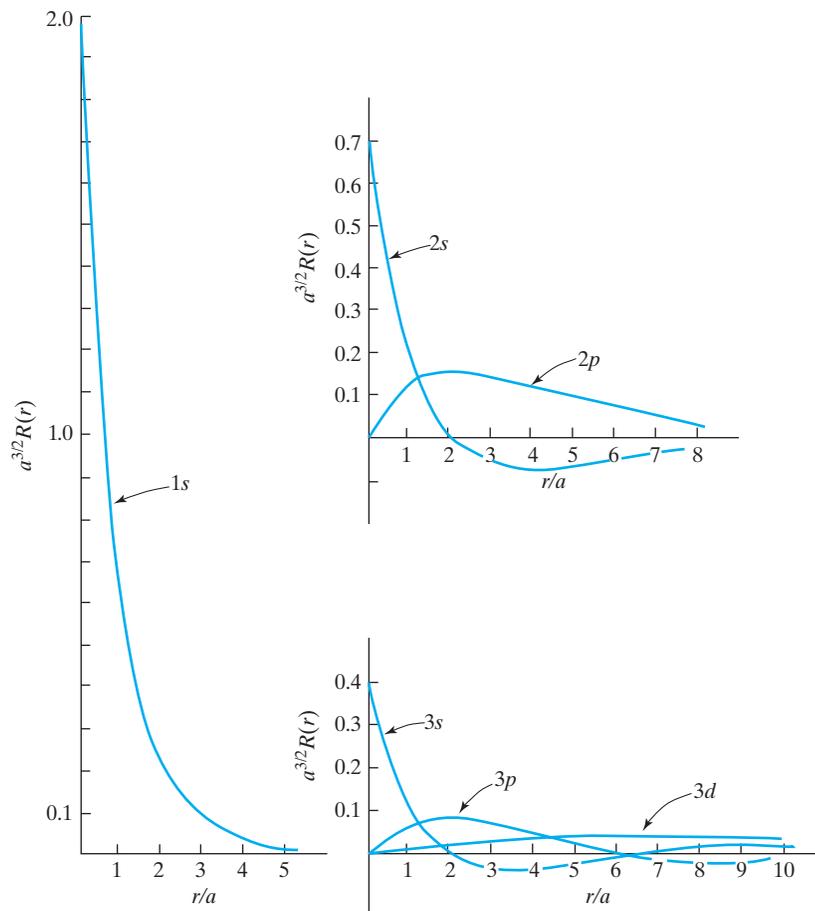
Table 6.1 lists some of the normalized radial factors in the hydrogenlike wave functions. **Figure 6.8** graphs some of the radial functions. The  $r^l$  factor makes the radial functions zero at  $r = 0$ , except for  $s$  states.

### The Radial Distribution Function

The probability of finding the electron in the region of space where its coordinates lie in the ranges  $r$  to  $r + dr$ ,  $\theta$  to  $\theta + d\theta$ , and  $\phi$  to  $\phi + d\phi$  is [Eq. (5.78)]

$$|\psi|^2 d\tau = [R_{nl}(r)]^2 |Y_l^m(\theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi \quad (6.115)$$

We now ask: What is the probability of the electron having its radial coordinate between  $r$  and  $r + dr$  with no restriction on the values of  $\theta$  and  $\phi$ ? We are asking for the probability of finding the electron in a thin spherical shell centered at the origin, of inner radius  $r$  and outer radius  $r + dr$ . We must thus add up the infinitesimal probabilities (6.115) for all



**FIGURE 6.8** Graphs of the radial factor  $R_{nl}(r)$  in the hydrogen-atom ( $Z = 1$ ) wave functions. The same scale is used in all graphs. (In some texts, these functions are not properly drawn to scale.)

possible values of  $\theta$  and  $\phi$ , keeping  $r$  fixed. This amounts to integrating (6.115) over  $\theta$  and  $\phi$ . Hence the probability of finding the electron between  $r$  and  $r + dr$  is

$$[R_{nl}(r)]^2 r^2 dr \int_0^{2\pi} \int_0^\pi |Y_l^m(\theta, \phi)|^2 \sin \theta d\theta d\phi = [R_{nl}(r)]^2 r^2 dr \quad (6.116)$$

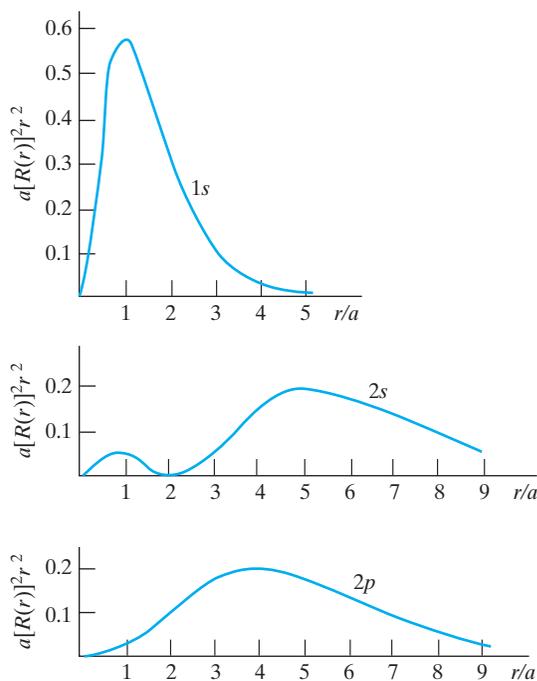
since the spherical harmonics are normalized:

$$\int_0^{2\pi} \int_0^\pi |Y_l^m(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1 \quad (6.117)$$

as can be seen from (5.72) and (5.80). The function  $R^2(r)r^2$ , which determines the probability of finding the electron at a distance  $r$  from the nucleus, is called the **radial distribution function**; see Fig. 6.9.

For the  $1s$  ground state of H, the probability density  $|\psi|^2$  is from Eq. (6.104) equal to  $e^{-2r/a}$  times a constant, and so  $|\psi_{1s}|^2$  is a maximum at  $r = 0$  (see Fig. 6.14). However, the radial distribution function  $[R_{1s}(r)]^2 r^2$  is zero at the origin and is a maximum at  $r = a$  (Fig. 6.9). These two facts are not contradictory. The probability density  $|\psi|^2$  is proportional to the probability of finding the electron in an infinitesimal box of volume  $dx dy dz$ , and this probability is a maximum at the nucleus. The radial distribution function is proportional to the probability of finding the electron in a thin spherical shell of inner and outer radii  $r$  and  $r + dr$ , and this probability is a maximum at  $r = a$ . Since  $\psi_{1s}$  depends only on  $r$ , the  $1s$  probability density is essentially constant in the thin spherical shell. If we imagine the thin shell divided up into a huge number of infinitesimal boxes each of volume  $dx dy dz$ , we can sum up the probabilities  $|\psi_{1s}|^2 dx dy dz$  of being in

**FIGURE 6.9** Plots of the radial distribution function  $[R_{nl}(r)]^2 r^2$  for the hydrogen atom.



each tiny box in the thin shell to get the probability of finding the electron in the thin shell as being  $|\psi_{1s}|^2 V_{\text{shell}}$ . The volume  $V_{\text{shell}}$  of the thin shell is

$$\frac{4}{3}\pi(r + dr)^3 - \frac{4}{3}\pi r^3 = 4\pi r^2 dr$$

where terms in  $(dr)^2$  and  $(dr)^3$  are negligible compared with the  $dr$  term. Therefore the probability of being in the thin shell is

$$|\psi_{1s}|^2 V_{\text{shell}} = R_{1s}^2 (Y_0^0)^2 4\pi r^2 dr = R_{1s}^2 [(4\pi)^{-1/2}]^2 4\pi r^2 dr = R_{1s}^2 r^2 dr$$

in agreement with (6.116). The  $1s$  radial distribution function is zero at  $r = 0$  because the volume  $4\pi r^2 dr$  of the thin spherical shell becomes zero as  $r$  goes to zero. As  $r$  increases from zero, the probability density  $|\psi_{1s}|^2$  decreases and the volume  $4\pi r^2 dr$  of the thin shell increases. Their product  $|\psi_{1s}|^2 4\pi r^2 dr$  is a maximum at  $r = a$ .

### EXAMPLE

Find the probability that the electron in the ground-state H atom is less than a distance  $a$  from the nucleus.

We want the probability that the radial coordinate lies between 0 and  $a$ . This is found by taking the infinitesimal probability (6.116) of being between  $r$  and  $r + dr$  and summing it over the range from 0 to  $a$ . This sum of infinitesimal quantities is the definite integral

$$\begin{aligned} \int_0^a R_{1s}^2 r^2 dr &= \frac{4}{a^3} \int_0^a e^{-2r/a} r^2 dr = \frac{4}{a^3} e^{-2r/a} \left( -\frac{r^2 a}{2} - \frac{2ra^2}{4} - \frac{2a^3}{8} \right) \Big|_0^a \\ &= 4[e^{-2}(-5/4) - (-1/4)] = 0.323 \end{aligned}$$

where  $R_{10}$  was taken from Table 6.1 and the Appendix integral A.7 was used.

**EXERCISE** Find the probability that the electron in a  $2p_1$  H atom is less than a distance  $a$  from the nucleus. Use a table of integrals or the website [integrals.wolfram.com](http://integrals.wolfram.com). (Answer: 0.00366.)

### Real Hydrogenlike Functions

The factor  $e^{im\phi}$  makes the spherical harmonics complex, except when  $m = 0$ . Instead of working with complex wave functions such as (6.112) and (6.114), chemists often use real hydrogenlike wave functions formed by taking linear combinations of the complex functions. The justification for this procedure is given by the theorem of Section 3.6: Any linear combination of eigenfunctions of a degenerate energy level is an eigenfunction of the Hamiltonian with the same eigenvalue. Since the energy of the hydrogen atom does not depend on  $m$ , the  $2p_1$  and  $2p_{-1}$  states belong to a degenerate energy level. Any linear combination of them is an eigenfunction of the Hamiltonian with the same energy eigenvalue.

One way to combine these two functions to obtain a real function is

$$2p_x \equiv \frac{1}{\sqrt{2}}(2p_{-1} + 2p_1) = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta \cos \phi \quad (6.118)$$

where we used (6.112), (6.114), and  $e^{\pm i\phi} = \cos \phi \pm i \sin \phi$ . The  $1/\sqrt{2}$  factor normalizes  $2p_x$ :

$$\begin{aligned} \int |2p_x|^2 d\tau &= \frac{1}{2} \left( \int |2p_{-1}|^2 d\tau + \int |2p_1|^2 d\tau + \int (2p_{-1})^* 2p_1 d\tau + \int (2p_1)^* 2p_{-1} d\tau \right) \\ &= \frac{1}{2}(1 + 1 + 0 + 0) = 1 \end{aligned}$$

Here we used the fact that  $2p_1$  and  $2p_{-1}$  are normalized and are orthogonal to each other, since

$$\int_0^{2\pi} (e^{-i\phi})^* e^{i\phi} d\phi = \int_0^{2\pi} e^{2i\phi} d\phi = 0$$

The designation  $2p_x$  for (6.118) becomes clearer if we note that (5.51) gives

$$2p_x = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a}\right)^{5/2} x e^{-Zr/2a} \quad (6.119)$$

A second way of combining the functions is

$$2p_y \equiv \frac{1}{i\sqrt{2}}(2p_1 - 2p_{-1}) = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a}\right)^{5/2} r \sin \theta \sin \phi e^{-Zr/2a} \quad (6.120)$$

$$2p_y = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a}\right)^{5/2} y e^{-Zr/2a} \quad (6.121)$$

The function  $2p_0$  is real and is often denoted by

$$2p_0 = 2p_z = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{2a}\right)^{5/2} z e^{-Zr/2a} \quad (6.122)$$

where capital  $Z$  stands for the number of protons in the nucleus, and small  $z$  is the  $z$  coordinate of the electron. The functions  $2p_x$ ,  $2p_y$ , and  $2p_z$  are mutually orthogonal (Prob. 6.42). Note that  $2p_z$  is zero in the  $xy$  plane, positive above this plane, and negative below it.

The functions  $2p_{-1}$  and  $2p_1$  are eigenfunctions of  $\hat{L}^2$  with the *same* eigenvalue:  $2\hbar^2$ . The reasoning of Section 3.6 shows that the linear combinations (6.118) and (6.120) are also eigenfunctions of  $\hat{L}^2$  with eigenvalue  $2\hbar^2$ . However,  $2p_{-1}$  and  $2p_1$  are eigenfunctions of  $\hat{L}_z$  with *different* eigenvalues:  $-\hbar$  and  $+\hbar$ . Therefore,  $2p_x$  and  $2p_y$  are not eigenfunctions of  $\hat{L}_z$ .

We can extend this procedure to construct real wave functions for higher states. Since  $m$  ranges from  $-l$  to  $+l$ , for each complex function containing the factor  $e^{-i|m|\phi}$  there is a function with the same value of  $n$  and  $l$  but having the factor  $e^{+i|m|\phi}$ . Addition and subtraction of these functions gives two real functions, one with the factor  $\cos(|m|\phi)$ , the other with the factor  $\sin(|m|\phi)$ . **Table 6.2** lists these real wave functions for the hydrogenlike atom. The subscripts on these functions come from similar considerations as for the  $2p_x$ ,  $2p_y$ , and  $2p_z$  functions. For example, the  $3d_{xy}$  function is proportional to  $xy$  (Prob. 6.37).

The real hydrogenlike functions are derived from the complex functions by replacing  $e^{im\phi}/(2\pi)^{1/2}$  with  $\pi^{-1/2} \sin(|m|\phi)$  or  $\pi^{-1/2} \cos(|m|\phi)$  for  $m \neq 0$ ; for  $m = 0$  the  $\phi$  factor is  $1/(2\pi)^{1/2}$  for both real and complex functions.

In dealing with molecules, the real hydrogenlike orbitals are more useful than the complex ones. For example, we shall see in Section 15.5 that the real atomic orbitals  $2p_x$ ,  $2p_y$ , and  $2p_z$  of the oxygen atom have the proper symmetry to be used in constructing a wave function for the  $\text{H}_2\text{O}$  molecule, whereas the complex  $2p$  orbitals do not.

**TABLE 6.2 Real Hydrogenlike Wave Functions**

$$1s = \frac{1}{\pi^{1/2}} \left( \frac{Z}{a} \right)^{3/2} e^{-Zr/a}$$

$$2s = \frac{1}{4(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{3/2} \left( 2 - \frac{Zr}{a} \right) e^{-Zr/2a}$$

$$2p_z = \frac{1}{4(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \cos \theta$$

$$2p_x = \frac{1}{4(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta \cos \phi$$

$$2p_y = \frac{1}{4(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta \sin \phi$$

$$3s = \frac{1}{81(3\pi)^{1/2}} \left( \frac{Z}{a} \right)^{3/2} \left( 27 - 18 \frac{Zr}{a} + 2 \frac{Z^2 r^2}{a^2} \right) e^{-Zr/3a}$$

$$3p_z = \frac{2^{1/2}}{81\pi^{1/2}} \left( \frac{Z}{a} \right)^{5/2} \left( 6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \cos \theta$$

$$3p_x = \frac{2^{1/2}}{81\pi^{1/2}} \left( \frac{Z}{a} \right)^{5/2} \left( 6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \sin \theta \cos \phi$$

$$3p_y = \frac{2^{1/2}}{81\pi^{1/2}} \left( \frac{Z}{a} \right)^{5/2} \left( 6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \sin \theta \sin \phi$$

$$3d_{z^2} = \frac{1}{81(6\pi)^{1/2}} \left( \frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} (3 \cos^2 \theta - 1)$$

$$3d_{xz} = \frac{2^{1/2}}{81\pi^{1/2}} \left( \frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin \theta \cos \theta \cos \phi$$

$$3d_{yz} = \frac{2^{1/2}}{81\pi^{1/2}} \left( \frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin \theta \cos \theta \sin \phi$$

$$3d_{x^2-y^2} = \frac{1}{81(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin^2 \theta \cos 2\phi$$

$$3d_{xy} = \frac{1}{81(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin^2 \theta \sin 2\phi$$

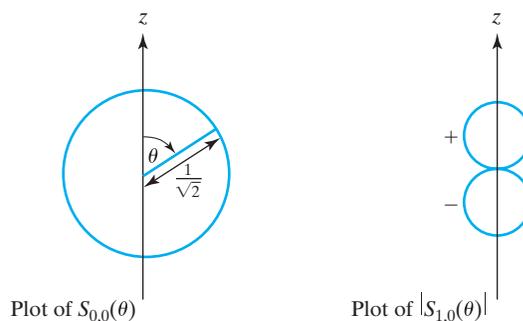
## 6.7 Hydrogenlike Orbitals

The hydrogenlike wave functions are one-electron spatial wave functions and so are hydrogenlike orbitals (Section 6.5). These functions have been derived for a one-electron atom, and we cannot expect to use them to get a truly accurate representation of the wave function of a many-electron atom. The use of the orbital concept to approximate many-electron atomic wave functions is discussed in Chapter 11. For now we restrict ourselves to one-electron atoms.

There are two fundamentally different ways of depicting orbitals. One way is to draw graphs of the functions; a second way is to draw contour surfaces of constant probability density.

First consider drawing graphs. To graph the variation of  $\psi$  as a function of the three independent variables  $r$ ,  $\theta$ , and  $\phi$ , we need four dimensions. The three-dimensional nature of our world prevents us from drawing such a graph. Instead, we draw graphs of the

**FIGURE 6.10** Polar graphs of the  $\theta$  factors in the  $s$  and  $p_z$  hydrogen-atom wave functions.



factors in  $\psi$ . Graphing  $R(r)$  versus  $r$ , we get the curves of Fig. 6.8, which contain no information on the angular variation of  $\psi$ .

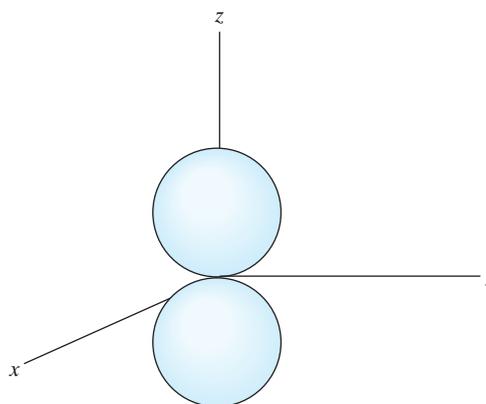
Now consider graphs of  $S(\theta)$ . We have (Table 5.1)

$$S_{0,0} = 1/\sqrt{2}, \quad S_{1,0} = \frac{1}{2}\sqrt{6} \cos \theta$$

We can graph these functions using two-dimensional Cartesian coordinates, plotting  $S$  on the vertical axis and  $\theta$  on the horizontal axis.  $S_{0,0}$  gives a horizontal straight line, and  $S_{1,0}$  gives a cosine curve. More commonly,  $S$  is graphed using plane polar coordinates. The variable  $\theta$  is the angle with the positive  $z$  axis, and  $S(\theta)$  is the distance from the origin to the point on the graph. For  $S_{0,0}$ , we get a circle; for  $S_{1,0}$  we obtain two tangent circles (Fig. 6.10). The negative sign on the lower circle of the graph of  $S_{1,0}$  indicates that  $S_{1,0}$  is negative for  $\frac{1}{2}\pi < \theta \leq \pi$ . Strictly speaking, in graphing  $\cos \theta$  we only get the upper circle, which is traced out twice; to get two tangent circles, we must graph  $|\cos \theta|$ .

Instead of graphing the angular factors separately, we can draw a single graph that plots  $|S(\theta)T(\phi)|$  as a function of  $\theta$  and  $\phi$ . We will use spherical coordinates, and the distance from the origin to a point on the graph will be  $|S(\theta)T(\phi)|$ . For an  $s$  state,  $ST$  is independent of the angles, and we get a sphere of radius  $1/(4\pi)^{1/2}$  as the graph. For a  $p_z$  state,  $ST = \frac{1}{2}(3/\pi)^{1/2} \cos \theta$ , and the graph of  $|ST|$  consists of two spheres with centers on the  $z$  axis and tangent at the origin (Fig. 6.11). No doubt Fig. 6.11 is familiar. Some texts say this gives the shape of a  $p_z$  orbital, which is wrong. Figure 6.11 is simply a graph of the angular factor in a  $p_z$  wave function. Graphs of the  $p_x$  and  $p_y$  angular factors give tangent spheres lying on the  $x$  and  $y$  axes, respectively. If we graph  $S^2T^2$  in spherical coordinates, we get surfaces with the familiar figure-eight cross sections; to repeat, these are graphs, not orbital shapes.

**FIGURE 6.11** Graph of  $|Y_1^0(\theta, \phi)|$ , the angular factor in a  $p_z$  wave function.



Now consider drawing contour surfaces of constant probability density. We shall draw surfaces in space, on each of which the value of  $|\psi|^2$ , the probability density, is constant. Naturally, if  $|\psi|^2$  is constant on a given surface,  $|\psi|$  is also constant on that surface. The contour surfaces for  $|\psi|^2$  and for  $|\psi|$  are identical.

For an  $s$  orbital,  $\psi$  depends only on  $r$ , and a contour surface is a surface of constant  $r$ , that is, a sphere centered at the origin. To pin down the size of an orbital, we take a contour surface within which the probability of finding the electron is, say, 95%; thus we want  $\int_V |\psi|^2 d\tau = 0.95$ , where  $V$  is the volume enclosed by the orbital contour surface.

Let us obtain the cross section of the  $2p_y$  hydrogenlike orbital in the  $yz$  plane. In this plane,  $\phi = \pi/2$  (Fig. 6.5), and  $\sin \phi = 1$ ; hence Table 6.2 gives for this orbital in the  $yz$  plane

$$|2p_y| = k^{5/2} \pi^{-1/2} r e^{-kr} |\sin \theta| \quad (6.123)$$

where  $k = Z/2a$ . To find the orbital cross section, we use plane polar coordinates to plot (6.123) for a fixed value of  $\psi$ ;  $r$  is the distance from the origin, and  $\theta$  is the angle with the  $z$  axis. The result for a typical contour (Prob. 6.44) is shown in Fig. 6.12. Since  $ye^{-kr} = y \exp[-k(x^2 + y^2 + z^2)^{1/2}]$ , we see that the  $2p_y$  orbital is a function of  $y$  and  $(x^2 + z^2)$ . Hence, on a circle centered on the  $y$  axis and parallel to the  $xz$  plane,  $2p_y$  is constant. Thus a three-dimensional contour surface may be developed by rotating the cross section in Fig. 6.12 about the  $y$  axis, giving a pair of distorted ellipsoids. The shape of a real  $2p$  orbital is two separated, distorted ellipsoids, and not two tangent spheres.

Now consider the shape of the two complex orbitals  $2p_{\pm 1}$ . We have

$$\begin{aligned} 2p_{\pm 1} &= k^{5/2} \pi^{-1/2} r e^{-kr} \sin \theta e^{\pm i\phi} \\ |2p_{\pm 1}| &= k^{5/2} \pi^{-1/2} e^{-kr} r |\sin \theta| \end{aligned} \quad (6.124)$$

and these two orbitals have the same shape. Since the right sides of (6.124) and (6.123) are identical, we conclude that Fig. 6.12 also gives the cross section of the  $2p_{\pm 1}$  orbitals in the  $yz$  plane. Since [Eq. (5.51)]

$$e^{-kr} r |\sin \theta| = \exp[-k(x^2 + y^2 + z^2)^{1/2}] (x^2 + y^2)^{1/2}$$

we see that  $2p_{\pm 1}$  is a function of  $z$  and  $x^2 + y^2$ ; so we get the three-dimensional orbital shape by rotating Fig. 6.12 about the  $z$  axis. This gives a doughnut-shaped surface.

Some hydrogenlike orbital surfaces are shown in Fig. 6.13. The  $2s$  orbital has a spherical node, which is not visible; the  $3s$  orbital has two such nodes. The  $3p_z$  orbital has a spherical node (indicated by a dashed line) and a nodal plane (the  $xy$  plane).

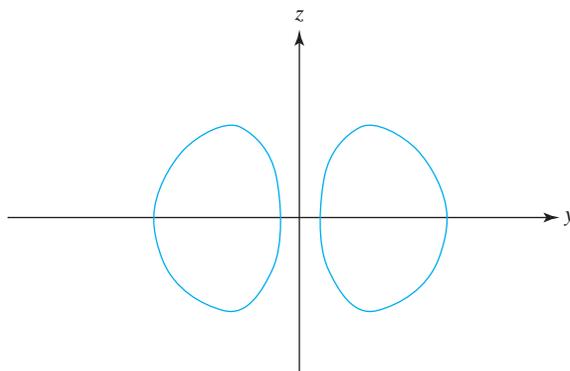
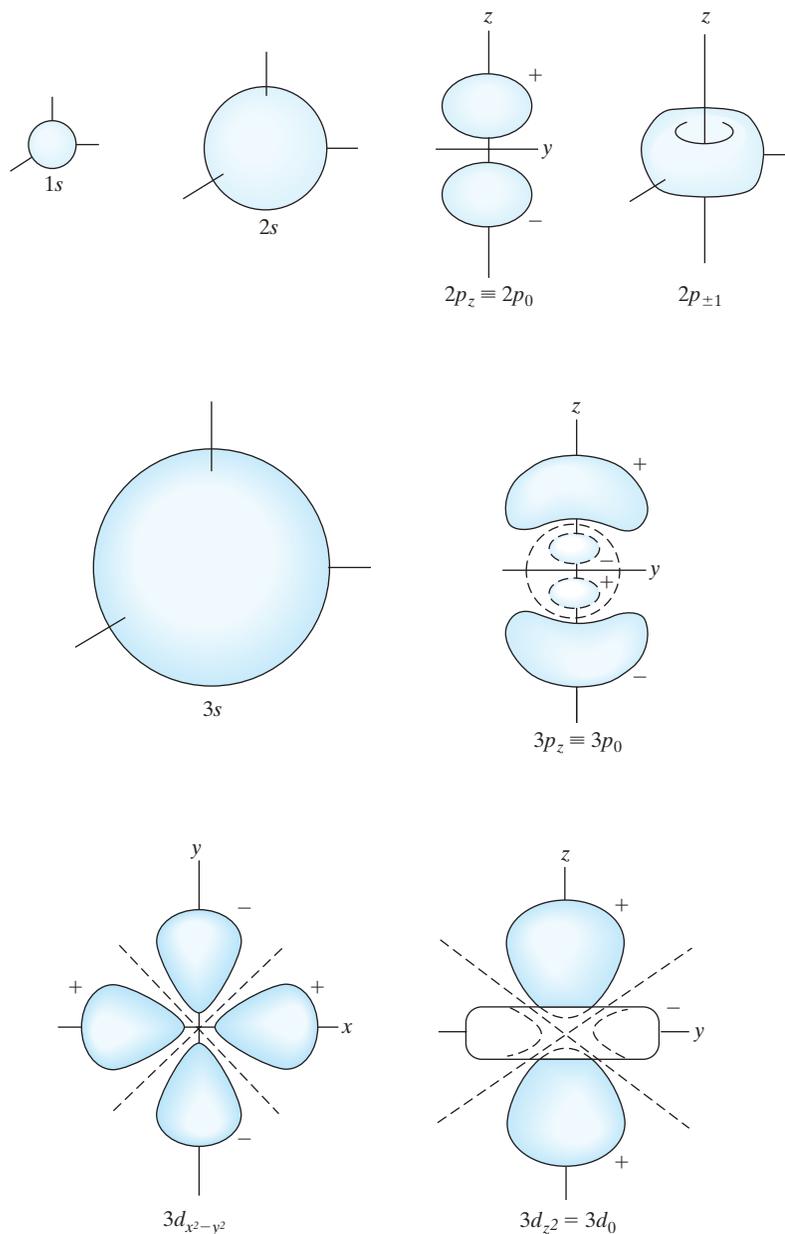
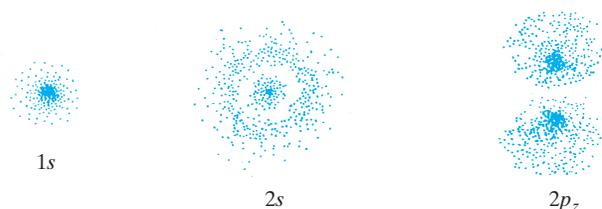


FIGURE 6.12 Contour of a  $2p_y$  orbital.

**FIGURE 6.13** Shapes of some hydrogen-atom orbitals.



The  $3d_{z^2}$  orbital has two nodal cones. The  $3d_{x^2-y^2}$  orbital has two nodal planes. Note that the view shown is not the same for the various orbitals. The relative signs of the wave functions are indicated. The other three real  $3d$  orbitals in Table 6.2 have the same shape as the  $3d_{x^2-y^2}$  orbital but have different orientations. The  $3d_{xy}$  orbital has its lobes lying between the  $x$  and  $y$  axes and is obtained by rotating the  $3d_{x^2-y^2}$  orbital by  $45^\circ$  about the  $z$  axis. The  $3d_{yz}$  and  $3d_{xz}$  orbitals have their lobes between the  $y$  and  $z$  axes and between the  $x$  and  $z$  axes, respectively. (Online three-dimensional views of the real hydrogenlike orbitals are at [www.falstad.com/qmatom](http://www.falstad.com/qmatom); these can be rotated using a mouse.)



**FIGURE 6.14** Probability densities for some hydrogen-atom states. [For accurate stereo plots, see D. T. Cromer, *J. Chem. Educ.*, **45**, 626 (1968).]

**Figure 6.14** represents the probability density in the  $yz$  plane for various orbitals. The number of dots in a given region is proportional to the value of  $|\psi|^2$  in that region. Rotation of these diagrams about the vertical ( $z$ ) axis gives the three-dimensional probability density. The  $2s$  orbital has a constant for its angular factor and hence has no angular nodes; for this orbital,  $n - l - 1 = 1$ , indicating one radial node. The sphere on which  $\psi_{2s} = 0$  is evident in Fig. 6.14.

Schrödinger's original interpretation of  $|\psi|^2$  was that the electron is "smeared out" into a charge cloud. If we consider an electron passing from one medium to another, we find that  $|\psi|^2$  is nonzero in both mediums. According to the charge-cloud interpretation, this would mean that part of the electron was reflected and part transmitted. However, experimentally one never detects a fraction of an electron; electrons behave as indivisible entities. This difficulty is removed by the Born interpretation, according to which the values of  $|\psi|^2$  in the two mediums give the *probabilities* for reflection and transmission. The orbital shapes we have drawn give the regions of space in which the total probability of finding the electron is 95%.

## 6.8 The Zeeman Effect

In 1896, Zeeman observed that application of an external magnetic field caused a splitting of atomic spectral lines. We shall consider this *Zeeman effect* for the hydrogen atom. We begin by reviewing magnetism.

Magnetic fields arise from moving electric charges. A charge  $Q$  with velocity  $\mathbf{v}$  gives rise to a magnetic field  $\mathbf{B}$  at point P in space, such that

$$\mathbf{B} = \frac{\mu_0}{4\pi} \frac{Q\mathbf{v} \times \mathbf{r}}{r^3} \quad (6.125)$$

where  $\mathbf{r}$  is the vector from  $Q$  to point P and where  $\mu_0$  (called the **permeability of vacuum** or the **magnetic constant**) is defined as  $4\pi \times 10^{-7} \text{ N C}^{-2} \text{ s}^2$ . [Equation (6.125) is valid only for a nonaccelerated charge moving with a speed much less than the speed of light.] The vector  $\mathbf{B}$  is called the **magnetic induction** or **magnetic flux density**. (It was formerly believed that the vector  $\mathbf{H}$  was the fundamental magnetic field vector, so  $\mathbf{H}$  was called the *magnetic field strength*. It is now known that  $\mathbf{B}$  is the fundamental magnetic vector.) Equation (6.125) is in SI units with  $Q$  in coulombs and  $\mathbf{B}$  in teslas (T), where  $1 \text{ T} = 1 \text{ N C}^{-1} \text{ m}^{-1} \text{ s}$ .

Two electric charges  $+Q$  and  $-Q$  separated by a small distance  $b$  constitute an electric dipole. The **electric dipole moment** is defined as a vector from  $-Q$  to  $+Q$  with magnitude  $Qb$ . For a small planar loop of electric current, it turns out that the magnetic field generated by the moving charges of the current is given by the same mathematical

expression as that giving the electric field due to an electric dipole, except that the electric dipole moment is replaced by the **magnetic dipole moment**  $\mathbf{m}$ ;  $\mathbf{m}$  is a vector of magnitude  $IA$ , where  $I$  is the current flowing in a loop of area  $A$ . The direction of  $\mathbf{m}$  is perpendicular to the plane of the current loop.

Consider the magnetic (dipole) moment associated with a charge  $Q$  moving in a circle of radius  $r$  with speed  $v$ . The current is the charge flow per unit time. The circumference of the circle is  $2\pi r$ , and the time for one revolution is  $2\pi r/v$ . Hence  $I = Qv/2\pi r$ . The magnitude of  $\mathbf{m}$  is

$$|\mathbf{m}| = IA = (Qv/2\pi r)\pi r^2 = Qvr/2 = Qrp/2m \quad (6.126)$$

where  $m$  is the mass of the charged particle and  $p$  is its linear momentum. Since the radius vector  $\mathbf{r}$  is perpendicular to  $\mathbf{p}$ , we have

$$\mathbf{m}_L = \frac{Q\mathbf{r} \times \mathbf{p}}{2m} = \frac{Q}{2m} \mathbf{L} \quad (6.127)$$

where the definition of orbital angular momentum  $\mathbf{L}$  was used and the subscript on  $\mathbf{m}$  indicates that it arises from the orbital motion of the particle. Although we derived (6.127) for the special case of circular motion, its validity is general. For an electron,  $Q = -e$ , and the magnetic moment due to its orbital motion is

$$\mathbf{m}_L = -\frac{e}{2m_e} \mathbf{L} \quad (6.128)$$

The magnitude of  $\mathbf{L}$  is given by (5.95), and the magnitude of the orbital magnetic moment of an electron with orbital-angular-momentum quantum number  $l$  is

$$|\mathbf{m}_L| = \frac{e\hbar}{2m_e} [l(l+1)]^{1/2} = \mu_B [l(l+1)]^{1/2} \quad (6.129)$$

The constant  $e\hbar/2m_e$  is called the *Bohr magneton*  $\mu_B$ :

$$\mu_B \equiv e\hbar/2m_e = 9.2740 \times 10^{-24} \text{ J/T} \quad (6.130)$$

Now consider applying an external magnetic field to the hydrogen atom. The energy of interaction between a magnetic dipole  $\mathbf{m}$  and an external magnetic field  $\mathbf{B}$  can be shown to be

$$E_B = -\mathbf{m} \cdot \mathbf{B} \quad (6.131)$$

Using Eq. (6.128), we have

$$E_B = \frac{e}{2m_e} \mathbf{L} \cdot \mathbf{B} \quad (6.132)$$

We take the  $z$  axis along the direction of the applied field:  $\mathbf{B} = B\mathbf{k}$ , where  $\mathbf{k}$  is a unit vector in the  $z$  direction. We have

$$E_B = \frac{e}{2m_e} B(L_x\mathbf{i} + L_y\mathbf{j} + L_z\mathbf{k}) \cdot \mathbf{k} = \frac{e}{2m_e} BL_z = \frac{\mu_B}{\hbar} BL_z$$

where  $L_z$  is the  $z$  component of orbital angular momentum. We now replace  $L_z$  by the operator  $\hat{L}_z$  to give the following additional term in the Hamiltonian operator, resulting from the external magnetic field:

$$\hat{H}_B = \mu_B B \hbar^{-1} \hat{L}_z \quad (6.133)$$

The Schrödinger equation for the hydrogen atom in a magnetic field is

$$(\hat{H} + \hat{H}_B)\psi = E\psi \quad (6.134)$$

where  $\hat{H}$  is the hydrogen-atom Hamiltonian in the absence of an external field. We readily verify that the solutions of Eq. (6.134) are the complex hydrogenlike wave functions (6.61):

$$(\hat{H} + \hat{H}_B)R(r)Y_l^m(\theta, \phi) = \hat{H}RY_l^m + \mu_B\hbar^{-1}B\hat{L}_zRY_l^m = \left(-\frac{Z^2}{n^2}\frac{e^2}{8\pi\epsilon_0 a} + \mu_B Bm\right)RY_l^m \quad (6.135)$$

where Eqs. (6.94) and (5.105) were used. Thus there is an additional term  $\mu_B Bm$  in the energy, and the external magnetic field removes the  $m$  degeneracy. For obvious reasons,  $m$  is often called the *magnetic quantum number*. Actually, the observed energy shifts do *not* match the predictions of Eq. (6.135) because of the existence of electron spin magnetic moment (Chapter 10 and Section 11.7).

In Chapter 5 we found that in quantum mechanics  $\mathbf{L}$  lies on the surface of a cone. A *classical*-mechanical treatment of the motion of  $\mathbf{L}$  in an applied magnetic field shows that the field exerts a torque on  $\mathbf{m}_L$ , causing  $\mathbf{L}$  to revolve about the direction of  $\mathbf{B}$  at a constant frequency given by  $|\mathbf{m}_L|B/2\pi|\mathbf{L}|$ , while maintaining a constant angle with  $\mathbf{B}$ . This gyroscopic motion is called *precession*. In quantum mechanics, a complete specification of  $\mathbf{L}$  is impossible. However, one finds that  $\langle \mathbf{L} \rangle$  precesses about the field direction (*Dicke and Wittke*, Section 12-3).

## 6.9 Numerical Solution of the Radial Schrödinger Equation

For a one-particle central-force problem, the wave function is given by (6.16) as  $\psi = R(r)Y_l^m(\theta, \phi)$  and the radial factor  $R(r)$  is found by solving the radial equation (6.17). The Numerov method of Section 4.4 applies to differential equations of the form  $\psi'' = G(x)\psi(x)$  [Eq. (4.66)], so we need to eliminate the first derivative  $R'$  in (6.17). Let us define  $F(r)$  by  $F(r) \equiv rR(r)$ , so

$$R(r) = r^{-1}F(r) \quad (6.136)$$

Then  $R' = -r^{-2}F + r^{-1}F'$  and  $R'' = 2r^{-3}F - 2r^{-2}F' + r^{-1}F''$ . Substitution in (6.17) transforms the radial equation to

$$-\frac{\hbar^2}{2m}F''(r) + \left[V(r) + \frac{l(l+1)\hbar^2}{2mr^2}\right]F(r) = EF(r) \quad (6.137)$$

$$F''(r) = G(r)F(r), \quad \text{where } G(r) \equiv \frac{m}{\hbar^2}(2V - 2E) + \frac{l(l+1)}{r^2} \quad (6.138)$$

which has the form needed for the Numerov method. In solving (6.137) numerically, one deals separately with each value of  $l$ . Equation (6.137) resembles the one-dimensional Schrödinger equation  $-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x)$ , except that  $r$  (whose range is 0 to  $\infty$ ) replaces  $x$  (whose range is  $-\infty$  to  $\infty$ ),  $F(r) \equiv rR(r)$  replaces  $\psi$ , and  $V(r) + l(l+1)\hbar^2/2mr^2$  replaces  $V(x)$ . We can expect that for each value of  $l$ , the lowest-energy solution will have 0 interior nodes (that is, nodes with  $0 < r < \infty$ ), the next lowest will have 1 interior node, and so on.

Recall from the discussion after (6.81) that if  $R(r)$  behaves as  $1/r^b$  near the origin, then if  $b > 1$ ,  $R(r)$  is not quadratically integrable; also, the value  $b = 1$  is not allowed, as noted after (6.83). Hence  $F(r) \equiv rR(r)$  must be zero at  $r = 0$ .

For  $l \neq 0$ ,  $G(r)$  in (6.138) is infinite at  $r = 0$ , which upsets most computers. To avoid this problem, one starts the solution at an extremely small value of  $r$  (for example,  $10^{-15}$  for the dimensionless  $r_r$ ) and approximates  $F(r)$  as zero at this point.

As an example, we shall use the Numerov method to solve for the lowest bound-state H-atom energies. Here,  $V = -e^2/4\pi\epsilon_0 r = -e'^2/r$ , where  $e' \equiv e/(4\pi\epsilon_0)^{1/2}$ . The radial equation (6.62) contains the three constants  $e'$ ,  $\mu$ , and  $\hbar$ , where  $e' \equiv e/(4\pi\epsilon_0)^{1/2}$  has SI units of  $\text{m N}^{1/2}$  (see Table A.1 of the Appendix) and hence has the dimensions  $[e'] = \text{L}^{3/2}\text{M}^{1/2}\text{T}^{-1}$ . Following the procedure used to derive Eq. (4.73), we find the H-atom reduced energy and reduced radial coordinate to be (Prob. 6.47)

$$E_r = E/\mu e'^4 \hbar^{-2}, \quad r_r = r/B = r/\hbar^2 \mu^{-1} e'^{-2} \quad (6.139)$$

Use of (6.139) and (4.76) and (4.77) with  $\psi$  replaced by  $F$  and  $B = \hbar^2 \mu^{-1} e'^{-2}$  transforms (6.137) for the H atom to (Prob. 6.47)

$$F_r'' = G_r F_r, \quad \text{where } G_r = l(l+1)/r_r^2 - 2/r_r - 2E_r \quad (6.140)$$

and where  $F_r = F/B^{-1/2}$ .

The bound-state H-atom energies are all less than zero. Suppose we want to find the H-atom bound-state eigenvalues with  $E_r \leq -0.04$ . Equating this energy to  $V_r$ , we have (Prob. 6.47)  $-0.04 = -1/r_r$  and the classically allowed region for this energy value extends from  $r_r = 0$  to  $r_r = 25$ . Going two units into the classically forbidden region, we take  $r_{r,\text{max}} = 27$  and require that  $F_r(27) = 0$ . We shall take  $s_r = 0.1$ , giving 270 points from 0 to 27 (more precisely, from  $10^{-15}$  to  $27 + 10^{-15}$ ).

$G_r$  in (6.140) contains the parameter  $l$ , so the program of Table 4.1 has to be modified to input the value of  $l$ . When setting up a spreadsheet, enter the  $l$  value in some cell and refer to this cell when you type the formula for cell B7 (Fig. 4.9) that defines  $G_r$ . Start column A at  $r_r = 1 \times 10^{-15}$ . Column C of the spreadsheet will contain  $F_r$  values instead of  $\psi_r$  values, and  $F_r$  will differ negligibly from zero at  $r_r = 1 \times 10^{-15}$ , and will be taken as zero at this point.

With these choices, we find (Prob. 6.48a) the lowest three H-atom eigenvalues for  $l = 0$  to be  $E_r = -0.4970$ ,  $-0.1246$ , and  $-0.05499$ ; the lowest two  $l = 1$  eigenvalues found are  $-0.1250$  and  $-0.05526$ . The true values [Eqs. (6.94) and (6.139)] are  $-0.5000$ ,  $-0.1250$ , and  $-0.05555$ . The mediocre accuracy can be attributed mainly to the rapid variation of  $G(r)$  near  $r = 0$ . If  $s_r$  is taken as 0.025 instead of 0.1 (giving 1080 points), the  $l = 0$  eigenvalues are improved to  $-0.4998$ ,  $-0.12497$ , and  $-0.05510$ . See also Prob. 6.48b.

## Summary

For a one-particle system with potential energy a function of  $r$  only [ $V = V(r)$ , a central-force problem], the stationary-state wave functions have the form  $\psi = R(r)Y_l^m(\theta, \phi)$ , where  $R(r)$  satisfies the radial equation (6.17) and  $Y_l^m$  are the spherical harmonics.

For a system of two noninteracting particles 1 and 2, the Hamiltonian operator is  $\hat{H} = \hat{H}_1 + \hat{H}_2$ , and the stationary-state wave functions and energies satisfy  $\psi = \psi_1(q_1)\psi_2(q_2)$ ,  $E = E_1 + E_2$ , where  $\hat{H}_1\psi_1 = E_1\psi_1$  and  $\hat{H}_2\psi_2 = E_2\psi_2$ ;  $q_1$  and  $q_2$  stand for the coordinates of particles 1 and 2.

For a system of two interacting particles 1 and 2 with Hamiltonian  $\hat{H} = \hat{T}_1 + \hat{T}_2 + \hat{V}$ , where  $V$  is a function of only the relative coordinates  $x, y, z$  of the particles, the energy is the sum of the energies of two hypothetical particles:  $E = E_M + E_\mu$ . One hypothetical particle has mass  $M \equiv m_1 + m_2$ ; its coordinates are the coordinates of the center of mass, and its energy  $E_M$  is that of a free particle. The second particle has mass  $\mu \equiv m_1 m_2 / (m_1 + m_2)$ ; its coordinates are the relative coordinates  $x, y, z$ , and its energy  $E_\mu$  is found by solving the Schrödinger equation for internal motion:  $[(-\hbar^2/2\mu)\nabla^2 + V]\psi(x, y, z) = E_\mu\psi(x, y, z)$ .

The two-particle rigid rotor consists of particles of masses  $m_1$  and  $m_2$  separated by a fixed distance  $d$ . Its energy is the sum of the energy  $E_M$  of translation and the energy  $E_\mu$  of rotation. Its stationary-state rotational wave functions are  $\psi = Y_J^m(\theta, \phi)$ , where  $\theta$  and  $\phi$  give the orientation of the rotor axis with respect to an origin at the rotor's center of mass, and the quantum numbers are  $J = 0, 1, 2, \dots$ , and  $m = -J, -J + 1, \dots, J - 1, J$ . The rotational energy levels are  $E_\mu = J(J + 1)\hbar^2/2I$ , where  $I = \mu d^2$ , with  $\mu = m_1 m_2 / (m_1 + m_2)$ . The selection rule for spectroscopic transitions is  $\Delta J = \pm 1$ .

The hydrogenlike atom has  $V = -Ze^2/4\pi\epsilon_0 r$ . With the translational energy separated off, the internal motion is a central-force problem and  $\psi = R(r)Y_l^m(\theta, \phi)$ . The continuum states have  $E \geq 0$  and correspond to an ionized atom. The bound states have the allowed energies  $E = -(Z^2/n^2)(e^2/8\pi\epsilon_0 a)$ , where  $a \equiv 4\pi\epsilon_0 \hbar^2 / \mu e^2$ . The bound-state radial wave function is (6.101). The bound-state quantum numbers are  $n = 1, 2, 3, \dots$ ;  $l = 0, 1, 2, \dots, n - 1$ ;  $m = -l, -l + 1, \dots, l - 1, l$ .

A one-electron spatial wave function is called an orbital. The shape of an orbital is defined by a contour surface of constant  $|\psi|$  that encloses a specified amount of probability.

The Numerov method can be used to numerically solve the radial Schrödinger equation for a one-particle system with a spherically symmetric potential energy.

## Problems

|        |           |         |           |           |           |           |
|--------|-----------|---------|-----------|-----------|-----------|-----------|
| Sec.   | 6.1       | 6.2     | 6.3       | 6.4       | 6.5       | 6.6       |
| Probs. | 6.1–6.4   | 6.5–6.6 | 6.7       | 6.8–6.14  | 6.15–6.21 | 6.22–6.42 |
| Sec.   | 6.7       | 6.8     | 6.9       | general   |           |           |
| Probs. | 6.43–6.45 | 6.46    | 6.47–6.51 | 6.52–6.56 |           |           |

- 6.1** True or false? (a) For a one-particle problem with  $V = br^3$ , where  $b$  is a positive constant, the stationary-state wave functions have the form  $\psi = f(r)Y_l^m(\theta, \phi)$ . (b) Every one-particle Hamiltonian operator commutes with  $\hat{L}^2$  and with  $\hat{L}_z$ .
- 6.2** The particle in a spherical box has  $V = 0$  for  $r \leq b$  and  $V = \infty$  for  $r > b$ . For this system: (a) Explain why  $\psi = R(r)f(\theta, \phi)$ , where  $R(r)$  satisfies (6.17). What is the function  $f(\theta, \phi)$ ? (b) Solve (6.17) for  $R(r)$  for the  $l = 0$  states. *Hints:* The substitution  $R(r) = g(r)/r$  reduces (6.17) to an easily solved equation. Use the boundary condition that  $\psi$  is finite at  $r = 0$  [see the discussion after Eq. (6.83)] and use a second boundary condition. Show that for the  $l = 0$  states,  $\psi = N[\sin(n\pi r/b)]/r$  and  $E = n^2\hbar^2/8mb^2$  with  $n = 1, 2, 3, \dots$ . (For  $l \neq 0$ , the energy-level formula is more complicated.)
- 6.3** If the three force constants in Prob. 4.20 are all equal, we have a three-dimensional isotropic harmonic oscillator. (a) State why the wave functions for this case can be written as  $\psi = f(r)G(\theta, \phi)$ . (b) What is the function  $G$ ? (c) Write a differential equation satisfied by  $f(r)$ . (d) Use the results found in Prob. 4.20 to show that the ground-state wave function does have the form  $f(r)G(\theta, \phi)$  and verify that the ground-state  $f(r)$  satisfies the differential equation in (c).
- 6.4** Verify Eq. (6.6) for the Laplacian in spherical coordinates. (This is a long, tedious problem, and you probably have better things to spend your time on.)
- 6.5** True or false? (a) For a system of  $n$  noninteracting particles, each stationary-state wave function has the form  $\psi = \psi_1(q_1) + \psi_2(q_2) + \dots + \psi_n(q_n)$ . (b) The energy of a system of noninteracting particles is the sum of the energies of the individual particles, where the energy of each particle is found by solving a one-particle Schrödinger equation.
- 6.6** For a system of two noninteracting particles of mass  $9.0 \times 10^{-26}$  g and  $5.0 \times 10^{-26}$  g in a one-dimensional box of length  $1.00 \times 10^{-8}$  cm, calculate the energies of the six lowest stationary states.

- 6.7** True or false? (a) The reduced mass of a two-particle system is always less than  $m_1$  and less than  $m_2$ . (b) When we solve a two-particle system (whose potential-energy  $V$  is a function of only the relative coordinates of the two particles) by dealing with two separate one-particle systems,  $V$  is part of the Hamiltonian operator of the fictitious particle with mass equal to the reduced mass.
- 6.8** True or false? (a) The degeneracy of the  $J = 4$  two-particle rigid-rotor energy level is 9. (b) The spacings between successive two-particle-rigid-rotor energy levels remain constant as  $J$  increases. (c) The spacings between successive two-particle-rigid-rotor absorption frequencies remain constant as the  $J$  of the lower level increases. (d) The molecules  $^1\text{H}^{35}\text{Cl}$  and  $^1\text{H}^{37}\text{Cl}$  have essentially the same equilibrium bond length. (e) The  $\text{H}_2$  molecule does not have a pure-rotational absorption spectrum.
- 6.9** The lowest observed microwave absorption frequency of  $^{12}\text{C}^{16}\text{O}$  is 115271 MHz. (a) Compute the bond distance in  $^{12}\text{C}^{16}\text{O}$ . (b) Predict the next two lowest microwave absorption frequencies of  $^{12}\text{C}^{16}\text{O}$ . (c) Predict the lowest microwave absorption frequency of  $^{13}\text{C}^{16}\text{O}$ . (d) For  $^{12}\text{C}^{16}\text{O}$  at  $25^\circ\text{C}$ , calculate the ratio of the  $J = 1$  population to the  $J = 0$  population. Repeat for the  $J = 2$  to  $J = 0$  ratio. Don't forget degeneracy.
- 6.10** The  $J = 2$  to 3 rotational transition in a certain diatomic molecule occurs at 126.4 GHz, where  $1 \text{ GHz} \equiv 10^9 \text{ Hz}$ . Find the frequency of the  $J = 5$  to 6 absorption in this molecule.
- 6.11** The  $J = 7$  to 8 rotational transition in gas-phase  $^{23}\text{Na}^{35}\text{Cl}$  occurs at 104189.7 MHz. The relative atomic mass of  $^{23}\text{Na}$  is 22.989770. Find the bond distance in  $^{23}\text{Na}^{35}\text{Cl}$ .
- 6.12** For a certain diatomic molecule, two of the pure-rotational absorption lines are at 806.65 GHz and 921.84 GHz, where  $1 \text{ GHz} \equiv 10^9 \text{ Hz}$ , and there are no pure-rotational lines between these two lines. Find the initial  $J$  value for each of these transitions and find the molecular rotational constant  $B$ .
- 6.13** (a) For  $^{12}\text{C}^{16}\text{O}$  in the  $v = 0$  vibrational level, the  $J = 0$  to 1 absorption frequency is 115271.20 MHz and the  $J = 4$  to 5 absorption frequency is 576267.92 MHz. Calculate the centrifugal distortion constant  $D$  for this molecule. (b) For  $^{12}\text{C}^{16}\text{O}$  in the  $v = 1$  level, the  $J = 0$  to 1 absorption is at 114221.74 MHz. Find the constant  $\alpha_e$  for this molecule.
- 6.14** Verify Eq. (6.51) for  $I$  of a two-particle rotor. Begin by multiplying and dividing the right side of (6.50) by  $m_1 m_2 / (m_1 + m_2)$ . Then use (6.49).
- 6.15** Calculate the ratio of the electrical and gravitational forces between a proton and an electron. Is neglect of the gravitational force justified?
- 6.16** (a) Explain why the degree of degeneracy of an H-atom energy level is given by  $\sum_{l=0}^{n-1} (2l + 1)$ . (b) Break this sum into two sums. Evaluate the first sum using the fact that  $\sum_{j=1}^k j = \frac{1}{2}k(k + 1)$ . Show that the degree of degeneracy of the H-atom levels is  $n^2$  (spin omitted). (c) Prove that  $\sum_{j=1}^k j = \frac{1}{2}k(k + 1)$  by adding corresponding terms of the two series  $1, 2, 3, \dots, k$  and  $k, k - 1, k - 2, \dots, 1$ .
- 6.17** (a) Calculate the wavelength and frequency for the spectral line that arises from an  $n = 6$  to  $n = 3$  transition in the hydrogen atom. (b) Repeat the calculations for  $\text{He}^+$ ; neglect the change in reduced mass from H to  $\text{He}^+$ .
- 6.18** Assign each of the following observed vacuum wavelengths to a transition between two hydrogen-atom levels:

$$656.47 \text{ nm}, \quad 486.27 \text{ nm}, \quad 434.17 \text{ nm}, \quad 410.29 \text{ nm} \quad (\text{Balmer series})$$

Predict the wavelengths of the next two lines in this series and the wavelength of the series limit. (Balmer was a Swiss mathematician who, in 1885, came up with an empirical formula that fitted lines of the hydrogen spectrum.)

- 6.19** Each hydrogen-atom line of Prob. 6.18 shows a very weak nearby satellite line. Two of the satellites occur at the vacuum wavelength 656.29 nm and 486.14 nm. (a) Explain their origin. (The person who first answered this question got a Nobel Prize.) (b) Calculate the other two satellite wavelengths.

- 6.20 Verify that for large values of  $j$ , the ratio  $b_{j+1}/b_j$  in (6.88) is the same as the ratio of the coefficient of  $r^{j+1}$  to that of  $r^j$  in the power series for  $e^{2Cr}$ .
- 6.21 For the particle in a box with infinitely high walls and for the harmonic oscillator, there are no continuum eigenfunctions, whereas for the hydrogen atom we do have continuum functions. Explain this in terms of the nature of the potential-energy function for each problem.
- 6.22 The positron has charge  $+e$  and mass equal to the electron mass. Calculate in electronvolts the ground-state energy of positronium—an “atom” that consists of a positron and an electron.
- 6.23 For the ground state of the hydrogenlike atom, show that  $\langle r \rangle = 3a/2Z$ .
- 6.24 Find  $\langle r \rangle$  for the  $2p_0$  state of the hydrogenlike atom.
- 6.25 Find  $\langle r^2 \rangle$  for the  $2p_1$  state of the hydrogenlike atom.
- 6.26 For a hydrogenlike atom in a stationary state with quantum numbers  $n$ ,  $l$ , and  $m$ , prove that 
$$\langle r \rangle = \int_0^\infty r^3 |R_{nl}|^2 dr.$$
- 6.27 Derive the  $2s$  and  $2p$  radial hydrogenlike functions.
- 6.28 For which hydrogen-atom states is  $\psi$  nonzero at the nucleus?
- 6.29 What is the value of the angular-momentum quantum number  $l$  for a  $t$  orbital?
- 6.30 If we were to ignore the interelectronic repulsion in helium, what would be its ground-state energy and wave function? (See Section 6.2.) Compute the percent error in the energy; the experimental He ground-state energy is  $-79.0$  eV.
- 6.31 For the ground state of the hydrogenlike atom, find the most probable value of  $r$ .
- 6.32 Where is the probability density a maximum for the hydrogen-atom ground state?
- 6.33 (a) For the hydrogen-atom ground state, find the probability of finding the electron farther than  $2a$  from the nucleus. (b) For the H-atom ground state, find the probability of finding the electron in the classically forbidden region.
- 6.34 A stationary-state wave function is an eigenfunction of the Hamiltonian operator  $\hat{H} = \hat{T} + \hat{V}$ . Students sometimes erroneously believe that  $\psi$  is an eigenfunction of  $\hat{T}$  and of  $\hat{V}$ . For the ground state of the hydrogen atom, verify directly that  $\psi$  is not an eigenfunction of  $\hat{T}$  or of  $\hat{V}$ , but is an eigenfunction of  $\hat{T} + \hat{V}$ . Can you think of a problem we solved where  $\psi$  is an eigenfunction of  $\hat{T}$  and of  $\hat{V}$ ?
- 6.35 Show that  $\langle T \rangle + \langle V \rangle = E$  for a stationary state.
- 6.36 For the hydrogen-atom ground state, (a) find  $\langle V \rangle$ ; (b) use the results of (a) and 6.35 to find  $\langle T \rangle$ ; then find  $\langle T \rangle / \langle V \rangle$ ; (c) use  $\langle T \rangle$  to calculate the root-mean-square speed  $\langle v^2 \rangle^{1/2}$  of the electron; then find the numerical value of  $\langle v^2 \rangle^{1/2} / c$ , where  $c$  is the speed of light.
- 6.37 (a) The  $3d_{xy}$  function is defined as  $3d_{xy} \equiv (3d_2 - 3d_{-2})/2^{1/2}i$ . Use Tables 6.1 and 5.1, Eq. (6.101), and an identity for  $\sin 2\phi$  to show that  $3d_{xy}$  is proportional to  $xy$ . (b) Express the other real  $3d$  functions of Table 6.2 as linear combinations of the complex functions  $3d_2, 3d_1, \dots, 3d_{-2}$ . (c) Use a trigonometric identity to show that  $3d_{x^2-y^2}$  contains the factor  $x^2 - y^2$ .
- 6.38 The hydrogenlike wave functions  $2p_1$ ,  $2p_0$ , and  $2p_{-1}$  can be characterized as those  $2p$  functions that are eigenfunctions of  $\hat{L}_z$ . What operators can we use to characterize the functions  $2p_x$ ,  $2p_y$ , and  $2p_z$ , and what are the corresponding eigenvalues?
- 6.39 Given that  $\hat{A}f = af$  and  $\hat{A}g = bg$ , where  $f$  and  $g$  are functions and  $a$  and  $b$  are constants, under what condition(s) is the linear combination  $c_1f + c_2g$  an eigenfunction of the linear operator  $\hat{A}$ ?
- 6.40 State which of the three operators  $\hat{L}^2$ ,  $\hat{L}_z$ , and the H-atom  $\hat{H}$  each of the following functions is an eigenfunction of: (a)  $2p_z$ ; (b)  $2p_x$ ; (c)  $2p_1$ .
- 6.41 For the *real* hydrogenlike functions: (a) What is the shape of the  $n - l - 1$  nodal surfaces for which the radial factor is zero? (b) The nodal surfaces for which the  $\phi$  factor vanishes are of the form  $\phi = \text{constant}$ . Thus they are planes perpendicular to the  $xy$  plane. How many such planes are there? (Values of  $\phi$  that differ by  $\pi$  are considered to be part of the same plane.) (c) It can be shown that there are  $l - m$  surfaces on which the  $\theta$  factor vanishes. What is the shape of these surfaces? (d) How many nodal surfaces are there for the real hydrogenlike wave functions?

- 6.42** Verify the orthogonality of the  $2p_x$ ,  $2p_y$ , and  $2p_z$  functions.
- 6.43** Find the radius of the sphere defining the  $1s$  hydrogen orbital using the 95% probability definition.
- 6.44** Show that the maximum value for  $2p_y$  [Eq. (6.123)] is  $k^{3/2}\pi^{-1/2}e^{-1}$ . Use Eq. (6.123) to plot the  $2p_y$  contour for which  $\psi = 0.316\psi_{\max}$ .
- 6.45** Sketch rough contours of constant  $|\psi|$  for each of the following states of a particle in a two-dimensional square box:  $n_x n_y = 11; 12; 21; 22$ . What are you reminded of?
- 6.46** (Answer this question based on Section 6.8, which omits the effects of electron spin.) How many energy levels is the  $n = 2$  H-atom energy level split into when an external magnetic field is applied? Give the degeneracy of each of these levels.
- 6.47** (a) Verify the equations (6.139) for the H-atom dimensionless  $E_r$  and  $r_r$ . (b) Verify (6.140) for  $F_r$ . (c) Verify that  $V_r = -1/r_r$  for the H atom.

For Probs. 6.48–6.51, use a modified version of the program in Table 4.1 or a spreadsheet or a computer algebra system.

- 6.48** (a) Verify the  $l = 0$  and  $l = 1$  Numerov-method H-atom energies given in Section 6.9 for 270 points and for 1080 points, with  $r_r$  going from  $10^{-15}$  to 27. You must uncheck the Make Unconstrained Variables Non-Negative box in the Solver Parameters box in Excel 2010. (b) For 1080 points and  $r_r$  going to 27, the  $n = 3, l = 0$  Numerov  $E_r$  of  $-0.05510$  is still substantially in error. Use the Numerov method to improve this energy significantly without decreasing  $s_r$ .
- 6.49** Use the Numerov method to calculate the lowest four  $l = 0$  energy eigenvalues and the lowest four  $l = 1$  eigenvalues of the three-dimensional isotropic harmonic oscillator, which has  $V = \frac{1}{2}kr^2$ . Compare with the exact results (Prob. 4.20).
- 6.50** Use the Numerov method to calculate and plot the reduced radial function  $R_r(r_r)$  for the lowest  $l = 0$  H-atom state. (See Prob. 6.48.) Explain why the value of  $R_r$  at  $r_r = 10^{-15}$  calculated from  $R_r = F_r/r_r$  [the equation corresponding to (6.136)] is wrong for this state.
- 6.51** For the particle in a spherical box (Prob. 6.2), use the Numerov method to find the lowest three  $l = 0$  energy eigenvalues and the lowest three  $l = 1$  eigenvalues. Compare your  $l = 0$  results with the exact results of Prob. 6.2.
- 6.52** For each of the following systems, give the expression for  $d\tau$  and give the limits of each variable in the equation  $\int |\psi|^2 d\tau = 1$ . (a) The particle in a one-dimensional box of length  $l$ . (b) The one-dimensional harmonic oscillator. (c) A one-particle, three-dimensional system where Cartesian coordinates are used. (d) Internal motion in the hydrogen atom, using spherical coordinates.
- 6.53** Find the  $n = 2$  to  $n = 1$  energy-level population ratio for a gas of hydrogen atoms at (a) 25°C; (b) 1000 K; (c) 10000 K.
- 6.54** Name a quantum-mechanical system for which the spacing between adjacent bound-state energy levels (a) remains constant as  $E$  increases; (b) increases as  $E$  increases; (c) decreases as  $E$  increases.
- 6.55** (a) Name two quantum-mechanical systems that have an infinite number of bound-state energy levels. (b) Name a quantum-mechanical system that has a finite number of bound-state energy levels. (c) Name a quantum-mechanical system that has no zero-point energy.
- 6.56** True or false? (a) The value zero is never allowed for an eigenvalue. (b) The function  $f = 0$  is never allowed as an eigenfunction. (c) The symbol  $e$  stands for the charge on an electron. (d) In the equation  $\langle B \rangle = \int \psi^* \hat{B} \psi d\tau$ , where  $d\tau = r^2 \sin \theta dr d\theta d\phi$ ,  $\hat{B}$  operates on  $\psi$  only and does not operate on  $r^2 \sin \theta$ . (e) In the  $n = 1$  state of an H atom, the electron moves on a circular orbit whose radius is the Bohr radius. (f) The electron probability density at the nucleus is zero for all H-atom states. (g) In the ground-state of an H atom, the electron is restricted to move on the surface of a sphere. (h) For the ground-state H atom, the electron probability density is greater than zero at all locations in the atom. (i) All the spherical harmonics  $Y_l^m$  are constant on the surface of a sphere centered at the origin.