16

The Electronic States of Atoms. I. The Hydrogen Atom and the Simple Orbital Approximation for Multielectron Atoms

OBJECTIVES

After studying this chapter, a student should:

1. understand the central-force problem, including the angular momentum properties of a central-force system;
2. be able to solve problems related to the angular momentum of a single particle;
3. understand the solution of the Schrödinger equation for the hydrogen atom and be able to solve problems related to it;
4. be familiar with the principal properties of the hydrogenlike orbitals and be able to solve problems related to them;
5. understand the possible states for multielectron atoms and be able to assign term symbols for different electron configurations of multielectron atoms.

PRINCIPAL FACTS AND IDEAS

1. The Schrödinger equation for the hydrogen atom is an example of the "central-force problem," in which the potential energy depends only on the distance between the two particles that make up the system.
2. In the central-force problem, the angular momentum of the system can have definite values if the system is in a state corresponding to an energy eigenfunction.
3. The Schrödinger equation for the hydrogen atom can be solved exactly, giving electronic wave functions called orbitals.
4. Electrons have intrinsic (spin) angular momentum in addition to the angular momentum of orbital motion. Spin orbitals describe both space and spin behavior.
5. Each electron in a multielectron atom occupies a hydrogenlike spin orbital if the simple orbital approximation is applied.
6. The wave function for a multielectron atom must be antisymmetric. That is, the wave function changes sign if the coordinates of two electrons are exchanged.
7. In an orbital wave function, every electron must occupy a different spin orbital (the Pauli exclusion principle).
8. The total orbital angular momentum and the total spin angular momentum correspond to the same pattern as other angular momenta, and are used to characterize the energy levels of multielectron atoms.

16.1 The Hydrogen Atom and the Central Force System. Angular Momentum

A hydrogen atom consists of a single electron with charge $-e$ and a nucleus containing a single proton with charge e, as depicted in Figure 16.1. The Hamiltonian operator for this system contains the potential energy function that corresponds to Coulomb's law

$$\mathscr{V}(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{16.1-1}$$

where ε_0 is the permittivity of the vacuum and where r is the distance between the particles. The hydrogen atom is a member of a class of systems called **central-force systems**, which consist of two particles separated by a distance r with a potential energy function $\mathscr{V}$ that depends only on r. The Schrödinger equation will be expressed in spherical polar coordinates, and the variables can be separated in this coordinate system. The solution for the θ and ϕ factors is the same for any central-force system. The results of this part will give us all of the information that can be obtained about the angular momentum of the hydrogen atom or any other central-force system. We will then proceed to the solution for the r factor, which is specific to the hydrogen atom.

To construct the Hamiltonian operator for any system we write the classical Hamiltonian function in cartesian coordinates and then make the replacements analogous to Eq. (15.3-5) to form the Hamiltonian operator. The cartesian coordinates of the nucleus are denoted by x_n, y_n, and z_n, and the cartesian coordinates of the electron are denoted by x_e, y_e, and z_e. However, the variables cannot be separated with these coordinates. We transform to relative coordinates and center-of-mass coordinates. The **relative coordinates**: x, y and z are

$$x = x_e - x_n \tag{16.1-2a}$$

$$y = y_e - y_n \tag{16.1-2b}$$

$$z = z_e - z_n \tag{16.1-2c}$$

The potential energy depends on the distance between the particles, which is

$$r = (x^2 + y^2 + z^2)^{1/2} \tag{16.1-3}$$

The coordinates of the center of mass are

$$X = \frac{m_e x_e + m_n x_n}{M} \tag{16.1-4a}$$

$$Y = \frac{m_e y_e + m_n y_n}{M} \tag{16.1-4b}$$

$$Z = \frac{m_e z_e + m_n z_n}{M} \tag{16.1-4c}$$

where the sum of the masses is denoted by M:

$$M = m_e + m_n \tag{16.1-5}$$

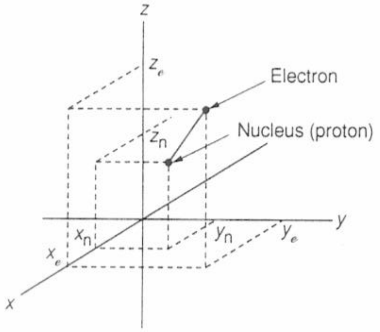

Figure 16.1. The System Consisting of a Nucleus and an Electron. This figure shows the cartesian coordinates of both particles, with a line segment drawn between the particles.

The classical Hamiltonian contains the kinetic energy in terms of momentum components. The kinetic energy in terms of the velocity of the center of mass and the relative velocity is given in Eq. (D-26) of Appendix D:

$$\mathcal{K} = \frac{M}{2}(V_x^2 + V_y^2 + V_z^2) + \frac{\mu}{2}(v_x^2 + v_y^2 + v_z^2) \tag{16.1-6}$$

where **V** and **v** are the velocity of the center of mass and the relative velocity, respectively. The **reduced mass** is denoted by μ:

$$\mu = \frac{m_\text{n} m_e}{m_\text{n} + m_e} \tag{16.1-7}$$

The momenta conjugate to the center-of-mass coordinates X, Y, and Z are

$$P_x = MV_x, \qquad P_y = MV_y, \qquad P_z = MV_z \tag{16.1-8a}$$

The momenta conjugate to the relative coordinates x, y, and z are

$$p_x = \mu v_x, \qquad p_y = \mu y_y, \qquad p_z = \mu v_z \tag{16.1-8b}$$

The classical Hamiltonian function is

$$H_\text{cl} = \frac{1}{M}(P_x^2 + P_y^2 + P_z^2) + \frac{1}{\mu}(p_x^2 + p_y^2 + p_z^2) + \mathcal{V}(r) \tag{16.1-9}$$

The Hamiltonian operator is obtained by the usual replacements for cartesian momentum components as in Eq. (15.3-5):

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right) - \frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \mathcal{V}(r) \\ &= -\frac{\hbar^2}{2M}\nabla_\text{c}^2 - \frac{\hbar^2}{2\mu}\nabla_\text{r}^2 + \mathcal{V}(r)\end{aligned} \tag{16.1-10}$$

where ∇^2 is the Laplacian operator defined in Eq. (14.4-25) and Eq. (B-40).

The first term in the Hamiltonian operator is the **center-of-mass Hamiltonian**:

$$\hat{H}_\text{c} = -\frac{\hbar^2}{2M}\nabla_\text{c}^2 \tag{16.1-11}$$

and the other two terms are the **relative Hamiltonian**.

$$\hat{H}_\text{r} = -\frac{\hbar^2}{2\mu}\nabla_\text{r}^2 + \mathcal{V}(r) \tag{16.1-12}$$

in

The time-dependent Schrödinger equation is

$$(\hat{H}_\text{c} + \hat{H}_\text{r})\Psi = E\Psi \tag{16.1-13}$$

This equation can be solved by the separation of variables. We assume the trial function

$$\Psi = \psi_\text{c}(X, Y, Z)\psi(x, y, z) \tag{16.1-14}$$

In previous chapters Ψ has represented a time-dependent wave function. We will use both Ψ and ψ for coordinate wave functions in the next several chapters, usually using Ψ for wave functions of more than one particle.

By separation of variables, Eq. (16.1-14) leads to the two equations

$$\hat{H}_\text{c}\psi_\text{c} = E_\text{c}\psi_\text{c} \tag{16.1-15}$$

$$\hat{H}\psi = E_\text{r}\psi \tag{16.1-16}$$

with the energy eigenvalue E,

$$E = E_c + E_r \tag{16.1-17}$$

Exercise 16.1

Carry out the steps to obtain Eq. (16.1-15)–(16.1-17).

Equation (16.1-15) for the center of mass is the same as the Schrödinger equation for a free particle. We can transcribe the energy eigenfunctions and energy eigenvalues from Chapter 14 with replacement of the symbol for the mass by M. We will return to the motion of the center of mass in Chapter 19 and will then also consider the possibility that the atom or molecule is contained in a box.

Solution of the Relative Schrödinger Equation

Equation (16.1-16) is the Schrödinger equation for the relative motion. It is mathematically equivalent to the problem of the motion of a particle of mass μ moving at distance r from a fixed origin under the effect of the potential energy $\mathcal{V}(r)$ (see Appendix D). Figure 16.2 depicts this equivalence. The vector from the nucleus, (labeled n) to the electron (labeled e) in Figure 16.2a is equal to the vector from a fixed origin to the fictitious particle of mass μ in Figure 16.2b. If one of the particles is much heavier than the other, as is the case in the hydrogen atom, the reduced mass is nearly equal to the mass of the lighter object, the center of mass is much closer to the heavier particle than to the other, and the motion is nearly the same as though the heavier particle were stationary with the lighter particle moving around it.

***Exercise 16.2**

The mass of the electron is 9.10939×10^{-31} kg and the mass of the proton is 1.672623×10^{-27} kg.

a. Calculate the ratio of the reduced mass of the hydrogen atom to the mass of the electron.

b. For a hydrogen atom with the electron at a distance 1.000×10^{-10} m from the nucleus, find

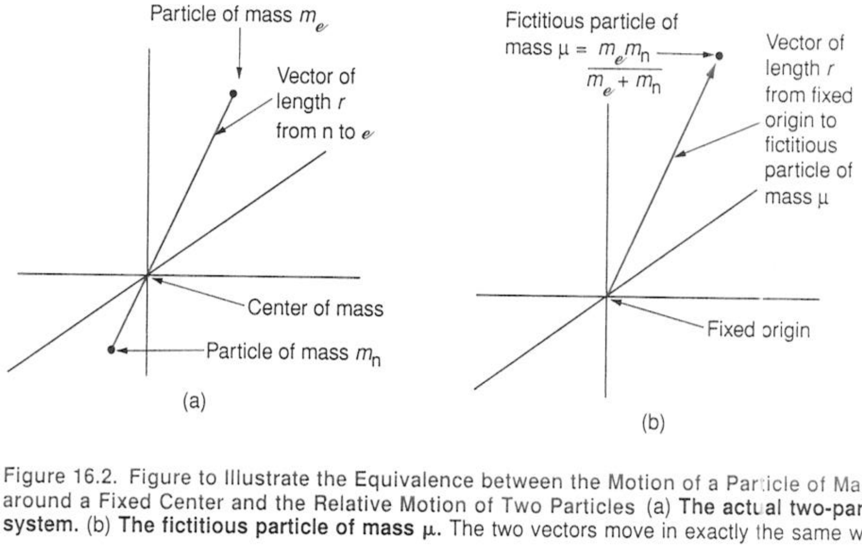

Figure 16.2. Figure to Illustrate the Equivalence between the Motion of a Particle of Mass μ around a Fixed Center and the Relative Motion of Two Particles (a) **The actual two-particle system.** (b) **The fictitious particle of mass μ.** The two vectors move in exactly the same way.

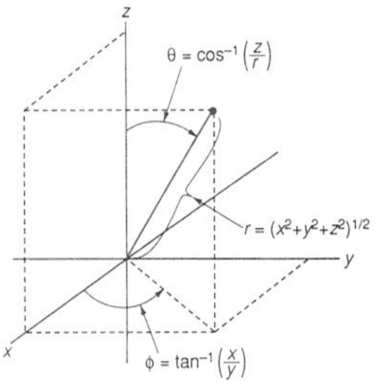

Figure 16.3. Spherical Polar Coordinates. These coordinates are used to simplify the solution of the Schrödinger equation.

the distance from the center of mass to the nucleus and to the electron. Hint: Assume that the particles are temporarily on the x axis.

We now transform the relative Schrödinger equation to spherical polar coordinates, in which r is one of the coordinates. These coordinates are shown in Figure 16.3. The expression for the Laplacian operator in spherical polar coordinates in Eq. (B-42) of Appendix B gives the relative Schrödinger equation:

$$\begin{aligned}\hat{H}_{\mathrm{r}}\psi &= -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2(\theta)}\frac{\partial^2\psi}{\partial\phi^2}\right]+\mathcal{V}(r)\psi \\ &= E_{\mathrm{r}}\psi \qquad (16.1\text{-}18)\end{aligned}$$

Comparison of this equation with Eq. (15.3-11) shows that the operator for the square of the angular momentum is contained in the Hamiltonian operator:

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{2\mu r^2}\hat{L}^2\psi+\mathcal{V}(r)\psi = E_{\mathrm{r}}\psi \qquad (16.1\text{-}19)$$

This equation can be solved by another separation of variables. We assume the trial solution

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \qquad (16.1\text{-}20)$$

The separation of variables is a little more difficult in this case than in previous cases since the coordinates do not occur only in separate terms in the Hamiltonian operator. We have to do it in two steps.

Since the operator $\hat{L}^2$ does not contain r, substitution of the trial solution into Eq. (16.1-19) gives

$$-\frac{\hbar^2}{2\mu}\left[Y\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+R\hat{L}^2Y\right]+(\mathcal{V}-E_{\mathrm{r}})RY = 0 \qquad (16.1\text{-}21)$$

We multiply this equation by $2\mu r^2/\hbar^2$ and divide by RY. This separates r from the other variables, giving

$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}(\mathcal{V}-E_{\mathrm{r}})+\frac{1}{\hbar^2}\frac{1}{Y}\hat{L}^2Y = 0 \qquad (16.1\text{-}22)$$

The Angular Factors in the Wave Function

The final term on the left-hand side of Eq. (16.1-22) contains no r and the other terms contain no θ or ϕ. The last term must be a constant function of θ and ϕ, which we set equal to the constant K. Multiplication by $\hbar^2 Y$ gives the equation

$$\hat{L}^2Y = \hbar^2KY \qquad (16.1\text{-}23)$$

which we can solve for the angular factor Y, which is also the eigenfunction of $\hat{L}^2$. The factor R in the eigenfunction will be different for different potential energy functions, but the factor Y will be the same for every potential energy function $\mathcal{V}$ that depends only on r.

Equation (16.1-23) can be written

$$-\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2(\theta)}\frac{\partial^2Y}{\partial\phi^2}\right] = \hbar^2KY \qquad (16.1\text{-}24)$$

To carry out a second separation for the variables θ and ϕ, we assume the trial solution

$$Y = \Theta(\theta)\Phi(\phi) \tag{16.1-25}$$

Substitution into Eq. (16.1-24) followed by division by $\Theta(\theta)\Phi(\phi)$ and multiplication by $\sin^2(\theta)$ gives

$$\frac{\sin(\theta)}{\Theta}\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -K\sin^2(\theta) \tag{16.1-26}$$

The last term on the left-hand side of this equation depends only on ϕ, so it must be a constant function of ϕ, which we call $-m^2$. If this choice for the constant is made, m will turn out to be a real integer. Multiplication by Φ gives the equation

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \tag{16.1-27}$$

Except for the symbols used, Eq. (16.1-27) is exactly the same as several equations already encountered, and its general solution can be written as in Eq. (14.5-21):

$$\Phi = Ae^{im\phi} + Be^{-im\phi} \tag{16.1-28}$$

where A and B are constants. The version of the general solution with sine and cosine functions could also have been used.

A wave function must be continuous. The variable ϕ ranges from 0 to 2π radians. Since $\phi = 0$ and $\phi = 2\pi$ refer to the same location for given values of r and θ,

$$\Phi(0) = \Phi(2\pi) \tag{16.1-29}$$

This condition is satisfied only if m is real and equal to an integer.

Exercise 16.3

Use the identity

$$e^{im\phi} = \cos(m\phi) + i\,\sin(m\phi)$$

to show that m is real and equal to an integer.

There are two standard forms of the function in Eq. (16.1-28). For the first form, we choose the values so that Φ is an eigenfunction of $\hat{L}_z$, given by Eq. (15.3-10):

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \tag{16.1-30}$$

We operate on Φ with $\hat{L}_z$:

$$\hat{L}_z\Phi = \frac{\hbar}{i}\left(imAe^{im\phi} - imBe^{-im\phi}\right) \tag{16.1-31}$$

We have an eigenfunction of $\hat{L}_z$ with eigenvalue $\hbar m$ if B is chosen to equal zero, or an eigenfunction of $\hat{L}_z$ with eigenvalue $-\hbar m$ if A is chosen to equal zero. It can be shown that $\hat{L}^2$ and $\hat{L}_z$ commute with each other and with $\hat{H}_r$, so that these three operators can have a set of common eigenfunctions. It is sometimes useful to have wave functions that are eigenfunctions of $\hat{L}_z$.

Exercise 16.4

Show that $\hat{H}_r$, $\hat{L}^2$, and $\hat{L}_z$ all commute.

With $B = 0$, the normalized Φ function is

$$\Phi = \Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\phi} \tag{16.1-32}$$

where we label the members of the set of functions with the quantum number m.

For the second standard form the constants A and B are chosen so that Φ is a real function. If A and B are equal,

$$\Phi = \Phi_{mx} = A\left(e^{im\phi} + e^{-im\phi}\right) = 2A\cos(m\phi)$$

In normalized form,

$$\Phi_{mx} = \frac{1}{\sqrt{\pi}}\cos(m\phi) \qquad (m \neq 0) \tag{16.1-33}$$

If $B = -A$, then

$$\Phi = \Phi_{my} = A\left(e^{im\phi} - e^{-im\phi}\right) = 2iA\sin(m\phi)$$

In normalized form,

$$\Phi_{my} = \frac{1}{\sqrt{\pi}}\sin(m\phi) \qquad (m \neq 0) \tag{16.1-34}$$

where the values of A and B are chosen for normalization. The complex Φ functions are eigenfunctions of the $\hat{L}_z$ operator. The real functions are not eigenfunctions of the $\hat{L}_z$ operator if $m \neq 0$, but sometimes it is convenient to have real wave functions.

Exercise 16.5

Show that Φ_{mx} and Φ_{my} are not eigenfunctions of $\hat{L}_z$ for $m \neq 0$.

After replacement of the constant term by $-m^2$ and multiplication by Θ, Eq. (16.1-26) becomes an equation that can be solved for the Θ function:

$$\sin(\theta)\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right) - m^2\Theta + K\sin^2(\theta)\,\Theta = 0 \tag{16.1-35}$$

This equation can be transformed into the **associated Legendre equation** by a change of variables:

$$y = \cos(\theta), \qquad P(y) = \Theta(\theta) \tag{16.1-36}$$

The equation is named for Adrien-Marie Legendre, 1752–1833, a famous French mathematician.

The associated Legendre equation and its solutions are given in Appendix F. The solutions are called **associated Legendre functions**, and are derivatives of polynomials known as **Legendre polynomials**.

For a solution to exist that obeys the relevant boundary conditions, the constant K must be equal to $l(l+1)$ where l is an integer at least as large as $|m|$. There is one solution for each set of values of the two quantum numbers l and m:

$$\Theta(\theta) = \Theta_{lm}(\theta) \tag{16.1-37}$$

The solutions are the same for a given value of m and its negative:

$$\Theta_{lm}(\theta) = \Theta_{l,-m}(\theta) \tag{16.1-38}$$

where we insert a comma to avoid confusing two subscripts having values l and $-m$ with a single subscript having a value equal to $(l-m)$.

The Y functions are called **spherical harmonic functions**. Each one is a product of a $\Theta_{lm}(\theta)$ function and a $\Phi_m(\phi)$ function having the same value of m as the Θ function:

$$Y = Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$$

Table 16.1 gives the normalized spherical harmonic functions for $l=0$, $l=1$, and $l=2$. Additional functions can be derived from formulas in Appendix F.

Table 16.1. Spherical harmonic functions $\psi_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$

Complex Φ functions, eigenfunctions of $\hat{L}_z$

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

Real Φ functions, not necessarily eigenfunctions of $\hat{L}_z$

$$\Phi_{mx}(\phi) = \frac{1}{\sqrt{\pi}}\cos(m\phi)$$

$$\Phi_{my}(\phi) = \frac{1}{\sqrt{\pi}}\sin(m\phi)$$

Θ functions

$$\Theta_{00}(\theta) = \frac{\sqrt{2}}{2}$$

$$\Theta_{10}(\theta) = \frac{\sqrt{6}}{2}\cos(\theta)$$

$$\Theta_{11}(\theta) = \Theta_{1,-1}(\theta) = \frac{\sqrt{3}}{2}\sin(\theta)$$

$$\Theta_{20}(\theta) = \frac{\sqrt{10}}{4}(3\cos^2(\theta)-1)$$

$$\Theta_{21}(\theta) = \Theta_{2,-1}(\theta) = \frac{\sqrt{15}}{2}\sin(\theta)\cos(\theta)$$

$$\Theta_{22}(\theta) = \Theta_{2,-2}(\theta) = \frac{\sqrt{15}}{4}\sin^2(\theta)$$

Additional Θ functions can be obtained from Appendix F.

Angular Momentum Values

The spherical harmonic functions, $Y_{lm}(\theta, \phi)$, are eigenfunctions of the operator for the square of the angular momentum with eigenvalue $\hbar^2 K$, as in Eq. (16.1-23). The fact that K must equal $l(l+1)$ where l is a nonnegative integer gives us the eigenvalues of the square of the angular momentum:

$$\hat{L}^2 Y_{lm} = \hat{L}^2\Theta_{lm}\Phi_m = \hbar^2 l(l+1)\Theta_{lm}\Phi_m \qquad (l = 0, 1, 2, \ldots) \tag{16.1-39}$$

The square of the angular momentum takes on the values

$$L^2 = 0,\quad 2\hbar^2,\quad 6\hbar^2,\quad 12\hbar^2,\quad 20\hbar^2,\quad \ldots \tag{16.1-40}$$

so that the magnitude of the angular momentum takes on the values

$$L = |\mathbf{L}| = 0, \quad \sqrt{2}\hbar, \quad \sqrt{6}\hbar, \quad \sqrt{12}\hbar, \quad \sqrt{20}\hbar, \ldots \tag{16.1-41}$$

Compare these mathematically generated values with the assumed values $\hbar$, $2\hbar$, $3\hbar, \ldots,$ in the Bohr theory of the hydrogen atom. Not only is the origin of the quantization different, but the values are different from those of the Bohr theory. The Bohr theory gave the correct value of the energy of the hydrogen atom, but not of the angular momentum.

The function Φ_m in Eq. (16.1-32) is an eigenfunction of $\hat{L}_z$ with eigenvalue $\hbar m$, so that Y_{lm} is also an eigenfunction:

$$\hat{L}_z Y_{lm} = \Theta_{lm}\hat{L}_z\Phi_m = \Theta_{lm}\hbar m\Phi_m \qquad (m = 0, \pm 1, \ldots, \pm l) \tag{16.1-42}$$

The possible values of L_z are

$$L_z = m\hbar = 0, \quad \pm\hbar, \quad \pm 2\hbar, \quad \pm 3\hbar, \quad \ldots \pm l\hbar \tag{16.1-43}$$

The magnitude of the angular momentum and the z component can simultaneously have predictable values. In order to specify completely the direction of the angular momentum vector, values of L_x and L_y would have to be specified as well as L_z. However, $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ do not commute with each other, so all three of these operators cannot have a full set of common eigenfunctions. Only one component of the angular momentum can have a predictable value for the full set of states, and the exact direction of the angular momentum vector cannot be determined.

Exercise 16.6

a. Use Eq. (15.4-24) and the expression for the commutator $[\hat{L}_x, \hat{L}_y]$ in Problem 15.36 to obtain an uncertainty relation for L_x and L_y. As the wave function in the integral, use the spherical harmonic function Y_{21}.

b. Repeat part (a) using the spherical harmonic function Y_{00}. Comment on your result.

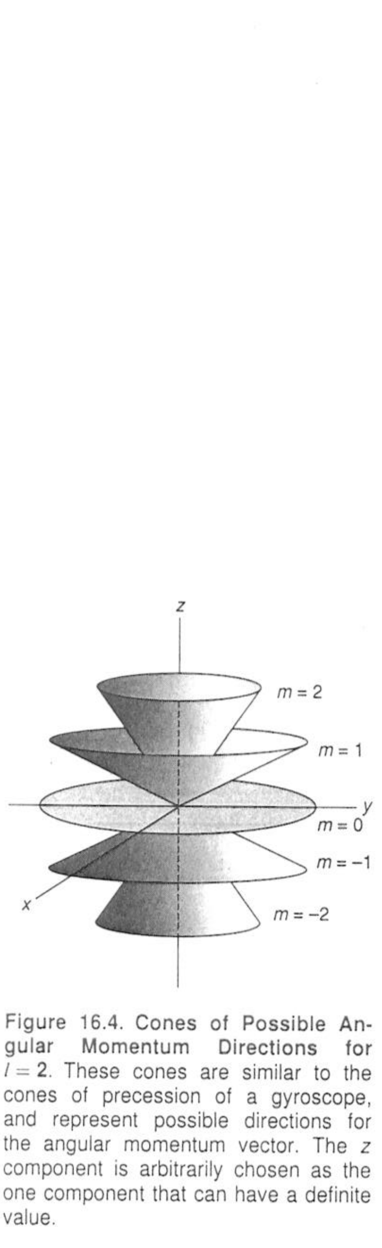

Figure 16.4. Cones of Possible Angular Momentum Directions for $l = 2$. These cones are similar to the cones of precession of a gyroscope, and represent possible directions for the angular momentum vector. The z component is arbitrarily chosen as the one component that can have a definite value.

Figure 16.4 depicts the case that $l = 2$, for which m can take on the values 2, 1, 0, -1, and -2. The magnitude of L is $\sqrt{6}\hbar = 2.4495\hbar$, and the possible values of L_z are $2\hbar$, $\hbar$, 0, $-\hbar$, and $-2\hbar$. The angular momentum vector can point anywhere on the five cones drawn in the figure. If the wave function is known to correspond to particular values of l and m, then it is known which cone applies, but the direction on that cone is not known. For any values of l, there are $2l + 1$ cones, one for each possible value of m. Notice the similarity between each cone on Figure 16.4 and the cone of directions around which a gyroscope axis precesses, as shown in Figure D-3 of Appendix D.

There is nothing unique about the z direction. One could choose $\hat{L}_x$ or $\hat{L}_y$ as a member of a set of commuting observables instead of $\hat{L}_z$. In that event, the Φ functions would be different, and would correspond to cones in Figure 16.4 that would be oriented around either the x axis or the y axis. We choose L_z since its operator is simpler in spherical polar coordinates than those of the other components.

***Exercise 16.7**

Transform the expression for $\Theta_{11}\Phi_{1x}$ to cartesian coordinates. Show that this function is an eigenfunction of the operator $\hat{L}_x$ and find its eigenvalue.

16.2 The Wave Functions of the Hydrogen Atom

In Section 16.1, we wrote the energy eigenfunction for any central-force system as

$$\Psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi) = R(r)\Theta_{lm}(\theta)\Phi_m(\phi) \tag{16.2-1}$$

The spherical harmonic functions $Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$ are the same functions for any central-force problem. The R function (the **radial factor**) is different for each choice of the potential energy function $\mathcal{V}(r)$. We replace $\hat{L}^2 Y$ by $\hbar^2 l(l+1)Y$ in Eq. (16.1-22), according to Eq. (16.1-39) and multiply the resulting equation by R to obtain the differential equation for R:

$$-\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}(\mathcal{V} - E)R + l(l+1)R = 0 \tag{16.2-2}$$

where we now omit the subscript r from the symbol for the relative energy. For the hydrogen atom, $\mathcal{V}(r)$ is given by the expression in Eq. (16.1-1). Expanding the derivative term into two terms gives

$$-r^2\frac{d^2R}{dr^2} - 2r\frac{dR}{dr} - \frac{2\mu r^2}{\hbar^2}\left(E + \frac{e^2}{4\pi\varepsilon_0 r}\right)R + l(l+1)R = 0 \tag{16.2-3}$$

We make the following substitutions:

$$\alpha^2 = -\frac{2\mu E}{\hbar^2}, \qquad \beta = \frac{\mu e^2}{4\pi\varepsilon_0\alpha\hbar^2}, \qquad \rho = 2\alpha r \tag{16.2-4}$$

This equation is named for Edmund Laguerre, 1834–1866, a famous French mathematician who solved the equation.

The resulting equation is divided by ρ^2, giving an equation that is known as the **associated Laguerre equation**:

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{R}{4} + \frac{\beta R}{\rho} - l(l+1)\frac{R}{\rho^2} = 0 \tag{16.2-5}$$

where we use the letter R for the function of ρ that is equal to $R(r)$.

Exercise 16.8

Carry out the manipulations to obtain Eq. (16.2-5) from Eq. (16.2-3).

The solution is written as

$$R(\rho) = G(\rho)e^{-\rho/2} \tag{16.2-6}$$

where $G(\rho)$ is a power series

$$G(\rho) = \sum_{j=0}^{\infty} a_j\rho^j \tag{16.2-7}$$

with constant coefficients $a_1, a_2, a_3, \ldots$. The solution of the equation, which we will not discuss, is reduced to the problem of determining these coefficients.

The Hydrogen Atom Energy Levels

As with the series in the harmonic oscillator solution, the series in Eq. (16.2-7) must terminate after a finite number of terms in order to keep the wave function from becoming infinite for large values of ρ, violating our boundary conditions.[1] The termination requires that the parameter β in Eq. (16.2-4) is equal to an integer n, which must be at least as large as $l + 1$. The minimum value of n is unity, and this value occurs only for $l = 0$. Solving the second equality in Eq. (16.2-4) for α, we obtain

$$\alpha = \frac{\mu e^2}{4\pi\varepsilon_0 \hbar^2 n} \tag{16.2-8}$$

From the first relation in Eq. (16.2-4) , the energy is quantized, with a value determined by the quantum number n:

$$E = E_n = -\frac{\hbar^2\alpha^2}{2\mu} = -\frac{\mu e^4}{2(4\pi\varepsilon_0 \hbar n)^2} \qquad (n = 1, 2, 3, \ldots) \tag{16.2-9}$$

The energy expression in Eq. (16.2-9) is identical with that of the Bohr theory. As in the case of the particle in a box and the harmonic oscillator, the energy is quantized by the nature of the Schrödinger equation and its boundary conditions, and not by arbitrary assumption as in the Bohr theory. These negative values of the energy eigenvalue E correspond to **bound states**, in which the system does not have sufficient relative energy for the electron to escape from the nucleus. There are also non-bound states called **scattering states** in which the energy is positive and in which the electron moves toward the nucleus, passes it, and continues on its way. We will not discuss these states, which do not have quantized energy values.[2]

Exercise 16.9

Substitute the values of the constants into Eq. (16.2-9) to show that the energy of relative motion of a hydrogen atom can take on the values

$$E = E_n = -\frac{2.1787 \times 10^{-18}\,\mathrm{J}}{n^2} = -\frac{13.60\,\mathrm{eV}}{n^2} \tag{16.2-10}$$

where 1 eV (electronvolt) is the energy required to move one electron through an electric potential difference of 1 volt, equal to 1.6022×10^{-19} J.

The parameter a is the same as the radius of the smallest orbit in the Bohr theory of the hydrogen atom in Eq. (14.3-14):

$$a = \frac{\hbar^2 4\pi\varepsilon_0}{\mu^2} = 5.2947 \times 10^{-11}\,\mathrm{m} = 52.947\,\mathrm{pm} = 0.52947\,\mathrm{\mathring{A}} \tag{16.2-11}$$

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[1] Frank L. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill, New York, 1968, pp. 151ff.

[2] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems*, Plenum, New York, 1977, pp. 21ff, pp. 32ff.

where Å represents the angstrom unit, 10^{-10} m. When we express the energy in terms of this parameter, we get

$$E = E_n = -\frac{\hbar^2 \alpha^2}{2\mu} = -\frac{e^2}{2(4\pi\varepsilon_0)an^2} \tag{16.2-12}$$

Exercise 16.10

Verify Eqs. (16.2-11) and (16.2-12).

In the (fictitious) limit that the nucleus is infinitely heavy compared to the electron, the electron moves about the stationary nucleus, and the reduced mass becomes

$$\lim_{m_n \to \infty} \mu = \lim_{m_n \to \infty} \left(\frac{m_e m_n}{m_e + m_n} \right) = m_e \tag{16.2-13}$$

where m_e is the mass of the electron. Equation (16.2-11) becomes

$$\lim_{m_n \to \infty} a = a_0 = \frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2} = 5.29198 \times 10^{-11}\ \mathrm{m} \tag{16.2-14}$$

For ordinary purposes, the distinction between relative motion of the nucleus and electron about their center of mass and electronic motion about a stationary nucleus is numerically unimportant, because the nucleus is so much more massive than the electron. We usually refer to the relative motion as electronic motion.

*Exercise 16.11

Calculate the percentage error in the hydrogen atom Bohr radius and in the hydrogen atom energy introduced by replacing the reduced mass by the mass of the electron.

The rules that the quantum numbers obey can be restated:

$$n = 1, 2, 3, \ldots \tag{16.2-15a}$$

$$l = 0, 1, 2, \ldots, n-1 \tag{16.2-15b}$$

$$m = 0, \pm 1, \pm 2, \ldots, \pm l \tag{16.2-15c}$$

The quantum number n is called the **principal quantum number**. The quantum number l has been called the **azimuthal quantum number**, but could also be called the **angular momentum quantum number**. The quantum number m has been called the **magnetic quantum number**, but could also be called the **angular momentum projection quantum number**. Since the energy eigenvalue depends only on the value of the principal quantum number, the energy levels are degenerate except for the $n = 1$ level.

EXAMPLE 16.1

Find an expression for the degeneracy of the hydrogen atom energy levels.

Solution

For a given value of n, the possible values of l range from 0 to $n-1$. For a given value of l, the values of m range from $-l$ to l. The number of possible values of m for a given value of l is $2l+1$, since m can have any of l positive values, any of l negative values, or can be equal to zero. The degeneracy g_n is

$$g_n = \sum_{l=0}^{n-1}(2l+1) = 2n\frac{0+n-1}{2} + n = n^2 \qquad (16.2\text{-}16)$$

where we have used the fact that the sum of a set of successive integers is the mean of the first and the last times the number of members of the set (a fact that Gauss reportedly discovered when he was seven years old).

Figure 16.5 shows the energy level diagram for the first few bound-state electronic energy levels of a hydrogen atom. Each state is represented by a horizontal line segment at the appropriate height for its energy level. There is also a continuous spectrum of unbound states of positive energy. The characteristic pattern for the degeneracies of the bound states is that increasing the value of n by unity makes one more value of l available while increasing the value of l by unity makes two more values of m available.

The Radial Factor of the Hydrogen Atom Wave Functions

The polynomial G in Eq. (16.2-6) is expressed as a function of ρ, which is proportional to r. From Eqs. (16.2-4), (16.2-8) and (16.2-11),

$$\rho = 2\alpha r = \frac{2r}{na} \qquad (16.2\text{-}17)$$

These polynomials are related to the **associated Laguerre functions**. Appendix F describes these functions and the **Laguerre polynomials** of which they are derivatives and gives formulas for generating the polynomials. There is a different R factor for each set of values of the quantum numbers n and l. Table 16.2 gives the R functions for $n = 1$, 2, and 3, and others can be written from the formulas for associated Laguerre functions given in Appendix F.

The energy eigenfunctions of relative motion in the hydrogen atom are called **orbitals**. Each orbital is obtained by multiplying a radial factor R_{nl} by a spherical harmonic function Y_{lm}, which must have the same value of l as the radial factor. The Y_{lm} factor consists of a $\Theta_{lm}(\theta)$ factor and a $\Phi_m(\phi)$ factor with the same value of m:

$$\Psi_{nlm} = R_{nl}Y_{lm} = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi)$$

To each one of these eigenfunctions there corresponds a stationary state of the electron, with predictable values of the energy and the square of the angular momentum. If the complex Φ functions are used, there is also a predictable value of the z component of the angular momentum. The energy, the square of the angular momentum, and the z component of the angular momentum are a complete set of commuting observables for the electronic motion of the hydrogen atom. That is, if each of these variables is measured, the system will afterwards be in a state corresponding to a known wave function.

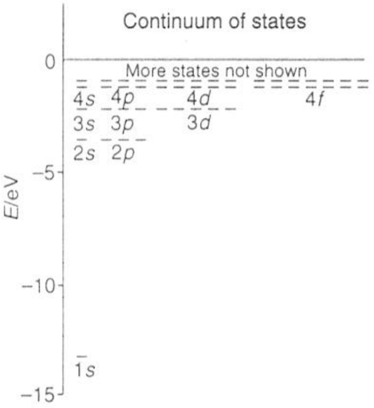


Figure 16.5. Energy Levels of the Hydrogen Atom. The bound-state energy levels are quantized.

Table 16.2. Radial Factors for Hydrogenlike Energy Eigenfunctions

$$R_{10}(r) = R_{1s}(r) = \left(\frac{Z}{a}\right)^{3/2} 2e^{-Zr/a}$$

$$R_{20}(r) = R_{2s}(r) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$$

$$R_{21}(r) = R_{2p}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}$$

$$R_{30}(r) = R_{3s}(r) = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2}\left[6 - \frac{4Zr}{a} + \left(\frac{2Zr}{3a}\right)^2\right]e^{-Zr/3a}$$

$$R_{31}(r) = R_{3p}(r) = \frac{2}{27\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{4Zr}{a} - \frac{2Z^2r^2}{3a^2}\right)e^{-Zr/3a}$$

$$R_{32}(r) = R_{3d}(r) = \frac{1}{9\sqrt{30}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{2Zr}{3a}\right)^2 e^{-Zr/3a}$$

Additional functions can be obtained from Appendix F.

The electronic energy levels of the hydrogen atom are called **shells**, because the expectation value of the distance of the electron from the nucleus is approximately the same for all states with the same value of n and is larger for larger values of n. The shells are labeled with the value of n, the principal quantum number. There is also an older notation in which the first shell is called the K shell, the second shell is called the L shell, etc. Within a given shell, the states with a given value of l constitute a **subshell**. The $l = 0$ state of a shell is called its *s* **subshell**. The three states in a shell with $l = 1$ constitute a *p* **subshell**. A *d* **subshell** consists of the five $l = 2$ states. An *f* **subshell** consists of the seven $l = 3$ states. As further subshells appear, they are given the letters *g*, *h*, *i*, etc. (alphabetical after *f*). The letters *s*, *p*, *d*, and *f* came from the spectroscopic terms "sharp", "principal," "diffuse", and "fundamental," but these names have no connection with the present usage. There are n subshells in the nth shell. The first shell has only the 1*s* subshell, while the seventh shell has the 7*s*, 7*p*, 7*d*, 7*f*, 7*g*, 7*h*, and 7*i* subshells.

***Exercise 16.12**

Give the value of each of the three quantum numbers for each state of the fourth shell.

The Hydrogenlike Atom

A He^+ ion or a Li^{2+} ion has a single electron, and must be similar to a hydrogen atom. We define a **hydrogenlike atom** to have one electron and a number Z of protons in its nucleus. The only change that we need to make in our discussion of the hydrogen atom is to replace the potential energy function in Eq. (16.1-1) by

$$\mathcal{V}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \qquad (16.2\text{-}18)$$

The energy eigenvalue of Eq. (16.2-12) is replaced by

$$E = E_n = -\frac{\hbar^2\alpha^2}{2\mu} = -\frac{Z^2e^2}{2(4\pi\varepsilon_0)an^2} = -(13.60\,\mathrm{eV})\frac{Z^2}{n^2} \tag{16.2-19}$$

and the variable ρ becomes

$$\rho = 2\alpha r = \frac{2Zr}{na} \tag{16.2-20}$$

Since ρ is proportional to Z, the effective radius of a shell is inversely proportional to Z. The first shell for a He^+ ion is closer to the nucleus than the first shell of a hydrogen atom, and so on. The orbital energy is directly proportional to Z^2 so that E_1 is larger in magnitude (more negative) for a He^+ ion than for a hydrogen atom, and so on.

Table 16.1 contains formulas for the first few spherical harmonic functions, and Table 16.2 contains formulas for the first few radial factors of the hydrogenlike atoms. Table 16.3 contains formulas for the real energy eigenfunctions for the first three shells (using Φ_{mx} and Φ_{my} instead of Φ_m and Φ_{-m}). The real Φ functions will often be more useful in describing chemical bonding, and the complex Φ functions will be more useful in discussing angular momentum values.

Instead of giving the value of the subscript l, we can give the letter of the subshell. The 210 function can be called the $2p0$ function and the 211 function can be called the $2p1$ function, etc. The $2p0$ function is also called the $2p_z$ function. The $2p$ function with Φ_{mx} is called the $2p_x$ function, and the $2p$ function with Φ_{mx} is called the $2p_y$ function. The labels on the real $3d$ functions can be seen in Table 16.3. The formulas in these tables can be applied to the hydrogen atom by letting $Z = 1$, to the He^+ ion by letting $Z = 2$, etc. Other wave functions can be constructed from formulas in Appendix F.

EXAMPLE 16.2

Write the formula for Ψ_{211}.

Solution

From Eq. (16.1-32),

$$\Phi_1 = \frac{1}{\sqrt{2\pi}}e^{i\phi}$$

From Table 16.1,

$$\Theta_{11} = \sqrt{\frac{3}{4}}\,\sin(\theta)$$

From Table 16.2,

$$R_{21}(\rho) = \left(\frac{Z}{a}\right)^{3/2}\frac{1}{2\sqrt{6}}\rho e^{-\rho/2}$$

The energy eigenfunction is

$$\psi_{211} = \left(\frac{Z}{a}\right)^{3/2}\frac{1}{8\sqrt{\pi}}\rho e^{-\rho/2}\sin(\theta)\,e^{i\phi} = \left(\frac{Z}{a}\right)^{3/2}\frac{1}{8\sqrt{\pi}}\frac{Zr}{a}e^{-Zr/2a}\sin(\theta)\,e^{i\phi}$$

It is important to have a grasp of the qualitative properties of the hydrogenlike orbitals. Figure 16.6 shows graphs of the R functions for the first three shells. The number of nodes in the R function increases by unity if n is increased by unity for fixed

Table 16.3. Real Hydrogenlike Energy Eigenfunctions

$$\psi_{10} = \psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$\psi_{20} = \psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$$

$$\psi_{21x} = \psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}\sin(\theta)\cos(\phi)$$

$$\psi_{21y} = \psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}\sin(\theta)\sin(\phi)$$

$$\psi_{210} = \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}\cos(\theta)$$

$$\psi_{300} = \psi_{3s} = \frac{1}{18\sqrt{3\pi}}\left(\frac{Z}{a}\right)^{3/2}\left[6 - \frac{4Zr}{a} + \left(\frac{2Zr}{3a}\right)^2\right]e^{-Zr/3a}$$

$$\psi_{310} = \psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{6Zr}{a} - \frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}\cos(\theta)$$

$$\psi_{31x} = \psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{6Zr}{a} - \frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}\sin(\theta)\cos(\phi)$$

$$\psi_{31y} = \psi_{3p_y} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{6Zr}{a} - \frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}\sin(\theta)\sin(\phi)$$

$$\psi_{320} = \psi_{3d_{z^2}} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^2 e^{-Zr/3a}[3\cos^2(\theta) - 1]$$

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

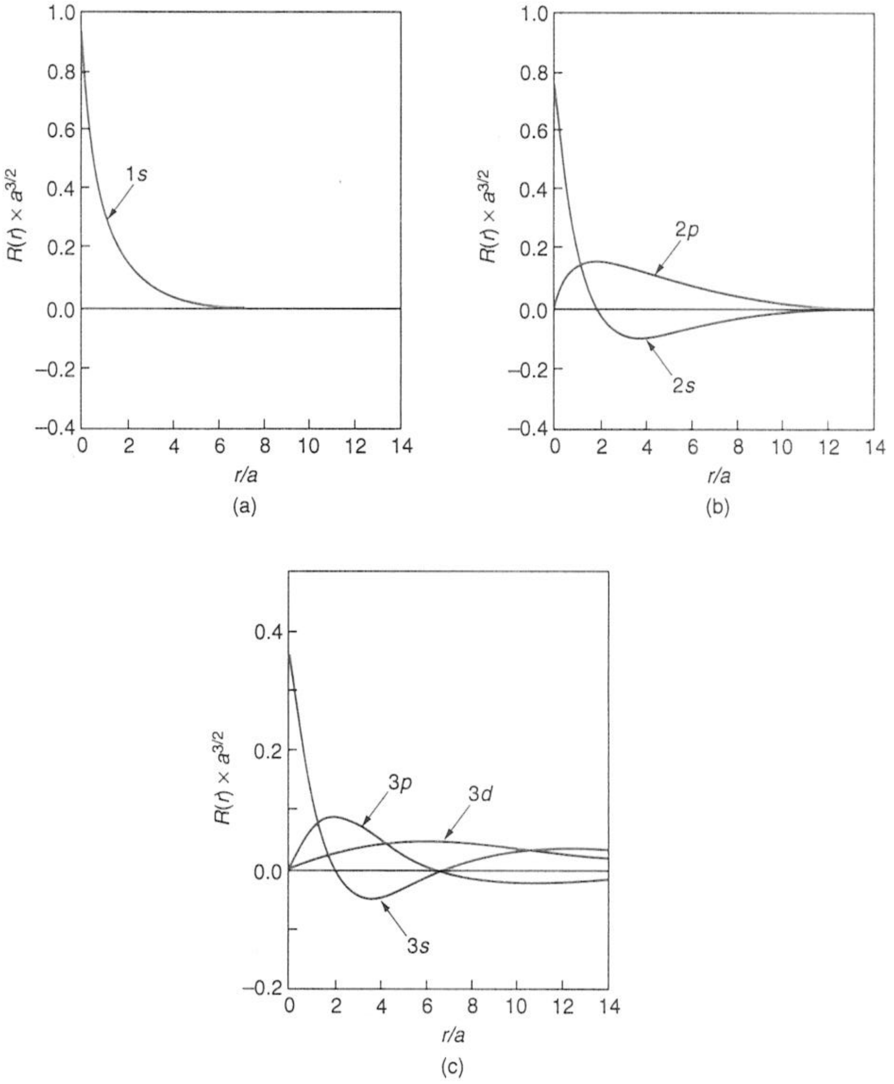
$$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^2 e^{-Zr/3a}\sin(\theta)\cos(\theta)\sin(\phi)$$

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

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

l, and decreases by unity if l is increased by unity for fixed n. The Θ_{00} function and the Φ_0 function for the s subshells are equal to constants. The orbitals in the s subshells depend only on r and are called **spherically symmetric** functions. The other Θ and Φ functions are more complicated, especially in the case of the complex Φ functions, which have a real and an imaginary part. Figure 16.7 shows graphs of several of these functions. The three spherical harmonic functions that occur in the $2p$ subshell are exactly the same as the three spherical harmonic functions that occur in the $3p$ subshell or any other p subshell, and those of the $3d$ subshell are the same as those of any other d subshell, and so on.

It is not possible to draw a graph representing a function of three independent variables, and it is also difficult to visualize the qualitative properties of the orbital by looking at three separate graphs for the R, Θ, and Φ functions. Therefore, we introduce the **orbital region**, which is the region in space where the magnitude of the orbital



(a)

(b)

(c)

Figure 16.6. Radial Factors for Hydrogenlike Energy Eigenfunctions. (a) $n = 1$. (b) $n = 2$. (c) $n = 3$. The pattern of numbers of nodal surfaces is important. As n is increased with l fixed, the number of spherical nodal surfaces increases. As l is increased with n fixed, the number of sperhical nodal surfaces decreases.

function is larger than some specified small value. Since the square of the orbital function is the probability density, the orbital region is the region inside which the electron is likely to be found. A common policy chooses a constant magnitude of the orbital at the boundary of the orbital regions such that 90% of the total probability of finding the electron is inside the orbital region. Pictures of orbital regions are seen in almost all elementary chemistry and organic chemistry textbooks, but sometimes the distinction between the orbital and the orbital region is not made clear. The orbital is a one-electron wave function, while the orbital region is a three-dimensional region in space inside of which the orbital is larger in magnitude than some small value. Figure 16.8 shows several orbital regions. The sign of the orbital function is indicated for the

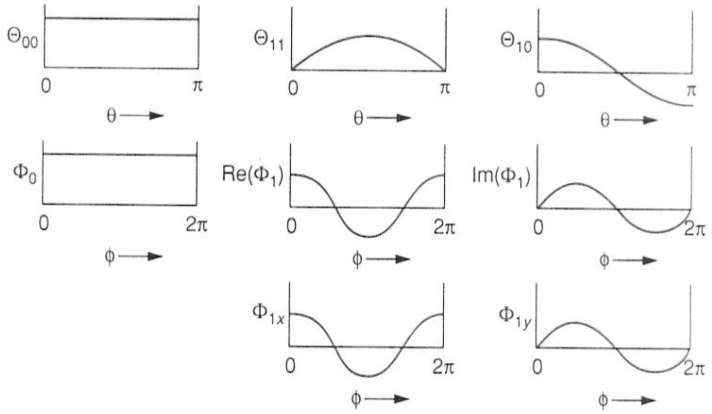
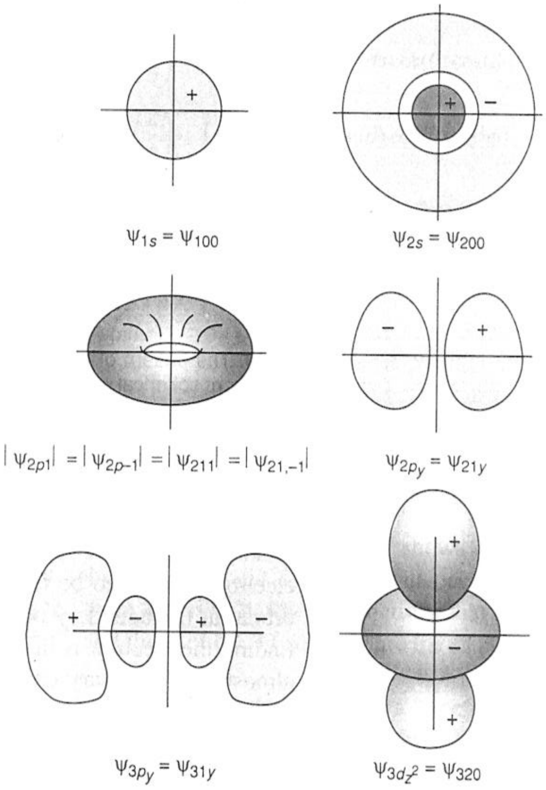


Figure 16.7. Some Factors of Spherical Harmonic Functions. These are the factors by which the radial functions must be multiplied to give the energy eigenfunctions.

real orbitals. Notice the differences between the orbital regions for the complex $2p$ and the real $2p$ orbitals. For the complex orbitals, we take the magnitude of the complex exponential $e^{im\phi}$ or $e^{-im\phi}$, which is a constant, while for the real orbitals we have either $\sin(m\phi)$ or $\cos(m\phi)$. The compactness of the orbital regions of the real p functions often makes them more useful than the complex p orbitals in discussing chemical bonding.


$\psi_{1s} = \psi_{100}$

$\psi_{2s} = \psi_{200}$

$|\psi_{2p1}| = |\psi_{2p-1}| = |\psi_{211}| = |\psi_{21,-1}|$

$\psi_{2p_y} = \psi_{21y}$

$\psi_{3p_y} = \psi_{31y}$

$\psi_{3d_{z^2}} = \psi_{320}$

Figure 16.8. Some Orbital Regions for Hydrogenlike Orbitals. The orbital region is the region in space inside which the orbital function differs significantly from zero.

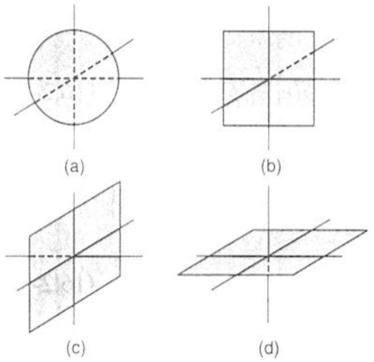


Figure 16.9. The Nodal Planes of the Real Energy Eigenfunctions of the Second Shell. (a) **The nodal sphere of the 2*s* wave function.** (b) **The nodal plane of the $2p_x$ wave function.** (c) **The nodal plane of the $2p_y$ wave function.** (d) **The nodal plane of the $2p_z$ wave function.** Each of these surfaces represents the points in space where the wave function vanishes.

The orbital regions can be approximately constructed from the pattern of the nodal surfaces in the R, Θ, and Φ functions. The orbital region cannot include any nodal surface, so any nodal surface divides the orbital region into two separate subregions, which are sometimes called "lobes". If there is a node in the R factor, the nodal surface is a sphere. If there is a node in the Φ factor the nodal surface is a cone, or a plane if the node occurs at $\theta = \pi/2$ (90°). If there is a node in a real Φ factor the nodal surface is a half-plane with edge at the z axis, which is always paired with another half-plane to make a nodal plane containing the z axis. The nodes in the real part of a complex Φ function are just like those of a real Φ function, and the nodes in the imaginary part of a complex Φ function are just like those of a different real Φ function. The number of nodal surfaces is always equal to $n - 1$ if the spherical nodal surface at $r \to \infty$ is excluded (and we will consistently exclude it). The 1*s* orbital has no nodal surfaces. Each of the orbitals in the second shell has one nodal surface, and each of the orbitals in the third shell has two nodal surfaces, and so on.

EXAMPLE 16.3

Describe the nodal surfaces for the real orbitals of the second shell.

Solution

We disregard the spherical nodal surface at $r \to \infty$ that occurs with each orbital. In each of the orbitals of the second shell there is one node. For the 2*s* function there is one node in the R function, producing a single spherical nodal surface. The $2p_z$ function has a node in the Θ function at $\theta = \pi/2$, producing a nodal plane in the x–y plane. The $2p_x$ function has nodes in the Φ function at $\phi = \pi/2$ and at $3\pi/2$, producing a nodal plane in the y–z plane. The $2p_y$ orbital has a nodal plane in the x–z plane. Figure 16.9 depicts the nodal surfaces in the real orbitals of the second shell.

Exercise 16.13

Describe the nodal surfaces for the real orbitals of the 3*d* subshell.

In general, a wave function with more nodes corresponds to a higher energy. This fact correlates with the fact that the de Broglie wavelength has a smaller value if there are more nodes. By Eq. (14.4-3), the de Broglie wavelength is inversely proportional to the speed, and thus has a smaller value when the kinetic energy is larger. With a particle in a one-dimensional box, the number of nodes was (in addition to the nodes at the ends of the box) equal to $n - 1$, where n was the quantum number. The energy was proportional to the square of n. With the harmonic oscillator, the number of nodes was equal to v, the quantum number, and the energy was proportional to $v + \frac{1}{2}$. In the real hydrogenlike orbitals, the number of nodal surfaces is equal to $n - 1$, where n is the principal quantum number, and the energy is also higher for larger values of n.

Normalization of the Hydrogenlike Orbitals

For motion of one particle in three dimensions, normalization in cartesian coordinates means

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi(x, y, z)^{*}\psi(x, y, z)\, dx\, dy\, dz = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x, y, z)|^{2}\, d^{3}\mathbf{r} = 1 \tag{16.2-21}$$

In spherical polar coordinates,

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi(r, \theta, \phi)|^2 r^2 \sin(\theta)\, d\phi\, d\theta\, dr = \int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi(r, \theta, \phi)|^2\, d^3\mathbf{r} = 1 \quad (16.2\text{-}22)$$

We abbreviate the volume element in any coordinate system by $d^3\mathbf{r}$ or by dq. The factor $r^2 \sin(\theta)$, which is called a **Jacobian**, is required to complete the element of volume in spherical polar coordinates.

$$d^3\mathbf{r} = r^2 \sin(\theta)\, d\phi\, d\theta\, dr \quad \text{(spherical polar coordinates)} \qquad (16.2\text{-}23)$$

The form of this Jacobian can be deduced from the fact that an infinitesimal length in the r direction is dr, an infinitesimal arc length in the θ direction is $r\,d\theta$, and an infinitesimal arc length in the ϕ direction is $r \sin(\theta)\, d\phi$. Since the lengths are infinitesimal, there is no distinction between arc lengths and linear lengths. The element of volume is the product of these mutually perpendicular infinitesimal lengths, giving Eq. (16.2-23).

The normalization integral for the hydrogen orbitals can be factored in spherical polar coordinates:

$$\int_0^\infty R^* R r^2\, dr \int_0^\pi \Theta^* \Theta \sin(\theta)\, d\theta \int_0^{2\pi} \Phi^* \Phi\, d\phi = 1 \qquad (16.2\text{-}24)$$

We make the additional normalization requirement that each of the three integrals in this equation equals unity. The constants in the formulas for the R, Θ, and Φ factors that we have introduced correspond to this requirement. These separate normalizations in Eq. (16.2-24) simplify the calculation of many expectation values.

EXAMPLE 16.4

Calculate the expectation values $\langle 1/r \rangle$ and $\langle \mathscr{V} \rangle$, where $\mathscr{V}$ is the potential energy, for a hydrogenlike atom in the $1s$ state.

Solution

Since the wave function is normalized, we can omit the denominator in the formula for the expectation value shown in Eq. (15.4-1). We can factor the integral:

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty R_{10}^* \frac{1}{r} R_{10} r^2\, dr \int_0^\pi \Theta_{00}^* \Theta_{00} \sin(\theta)\, d\theta \int_0^{2\pi} \Phi_0^* \Phi_0\, d\phi \qquad (16.2\text{-}25)$$

By our separate normalizations, the second and third integrals both equal unity, so that

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty R_{10}{}^* \frac{1}{r} R_{10} r^2\, dr = 4\left(\frac{Z}{a}\right)^3 \int_0^\infty e^{-2Zr/a} r\, dr$$
$$= 4\left(\frac{Z}{a}\right)^3 \left(\frac{a}{2Z}\right)^2 (1) = \frac{Z}{a} \qquad (16.2\text{-}26)$$

where we looked up the integral in Appendix C.

$$\langle \mathscr{V} \rangle = -\frac{Ze^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r} \right\rangle = -\frac{Z^2 e^2}{4\pi\varepsilon_0 a} \qquad (16.2\text{-}27)$$

Since the θ and the ϕ integrals in Eq. (16.2-25) both equal unity, we can omit them and use only the function R in calculating the expectation value of any function of r. The expectation value $\langle 1/r \rangle$ is proportional to Z, in agreement with the statement that the effective radius of a shell is inversely proportional to Z.

***Exercise 16.14**

Substitute the values of the constants into Eqs. (16.2-26) and (16.2-27) to obtain numerical values for $\langle 1/r \rangle$ and $\langle \mathscr{V} \rangle$ for a hydrogen atom.

As shown in Eq. (16.2-27) the expectation value of the potential energy of a hydrogenlike atom equals twice the total energy of Eq. (16.2-12). Therefore, the expectation value of the kinetic energy is half as large as the magnitude of the potential energy, and is equal in magnitude to the total energy (the kinetic energy must be positive while the total energy and the potential energy are negative). This behavior occurs in all systems of particles interacting only with the Coulomb potential energy, and is a consequence of the **virial theorem** of mechanics.[3]

The Radial Distribution Function

The **radial distribution function,** f_{r}, is defined as the probability per unit value of r for finding the electron at a distance r from the nucleus. That is,

$$f_{\mathrm{r}}\,dr = \begin{pmatrix}\text{Probability that the particle} \\ \text{lies at a distance from the} \\ \text{nucleus between } r \text{ and } r + dr\end{pmatrix} \tag{16.2-28}$$

The locations that lie at distances from the nucleus between r and $r + dr$ constitute a spherical shell of radius r and thickness dr, as shown in Figure 16.10a. The total probability of finding the electron in this shell is obtained by integrating over θ and ϕ:

$$f_{\mathrm{r}}\,dr = \left(\int_0^{\pi}\int_0^{2\pi} |\psi(r, \theta, \phi)|^2 r^2 \sin(\theta)\phi\, d\theta\right) dr \tag{16.2-29}$$

where r is not integrated. The integral can be factored, and the θ and ϕ integrals give factors of unity:

$$f_{\mathrm{r}}\,dr = R^*R\left(\int_0^{\pi} |\Theta|^2 \sin(\theta)\,d\theta \int_0^{2\pi} |\Phi|^2\,d\phi\right) r^2\,dr = R^*Rr^2\,dr \tag{16.2-30}$$

The expectation value of a quantity depending only on r can be computed using the radial distribution function. For example,

$$\left\langle \frac{1}{r} \right\rangle = \int_0^{\infty} \frac{1}{r} R^*Rr^2\,dr = \int_0^{\infty} \frac{1}{r} f_{\mathrm{r}}\,dr \tag{16.2-31}$$

Figure 16.10b shows graphs of the radial distribution function for several energy eigenfunctions. All of the states of a given subshell have the same radial distribution function because they have the same radial factor in their wave functions. Since the radial distribution function is proportional to r^2, each one vanishes at the nucleus, and since it is proportional to an exponential function, each one approaches zero for large values of r. Therefore, each radial distribution function goes through one or more relative maxima. The s orbitals are nonzero at the nucleus (the origin) but even their radial distribution functions vanish at the nucleus.

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[3] Ira N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall Englewood Cliffs, N.J., 1991, pp. 434ff.

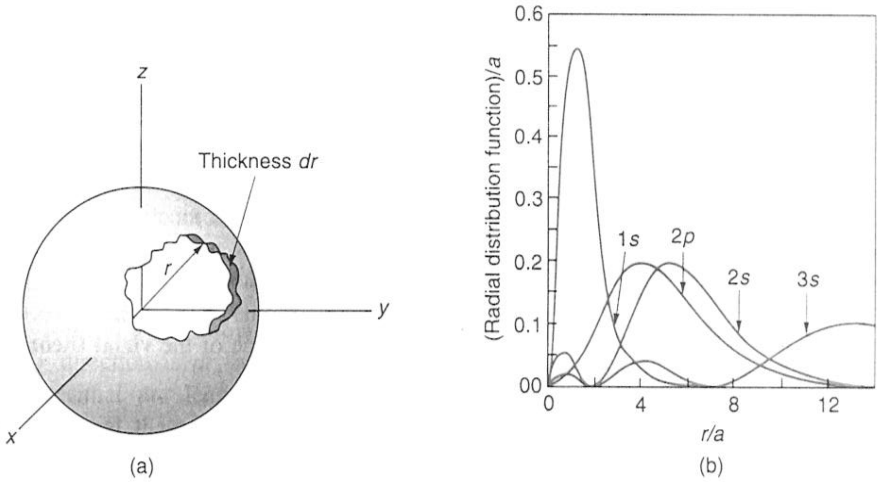

Figure 16.10. The Probability Distribution for Electron–Nucleus Distances. (a) **A spherical shell of radius r, and thickness dr.** This shell is centered on the origin, and contains the points that are at distances from the origin between r and $r + dr$. (b) **Radial distribution functions for hydrogenlike orbitals.** The radial distribution function is the probability density for finding the particle at a certain distance from the origin, irrespective of direction. It is somewhat analogous to the probability density for molecular speeds, although that probability density is a density in velocity space instead of coordinate space.

***Exercise 16.15**

a. Calculate the expectation value $\langle r \rangle$ for a hydrogenlike atom in the $1s$ state. Why is this not equal to $\langle 1/r \rangle^{-1}$?

b. Calculate $\langle r^2 \rangle$ for a hydrogenlike atom in the $1s$ state. Why is this not equal to $\langle r \rangle^2$?

c. Find the most probable value of r for a hydrogenlike atom in the $1s$ state. Why is this not equal to $\langle r \rangle$?

The Time-Dependent Wave Function of the Hydrogen Atom

We can now write the time-dependent wave function, using the three-dimensional analogue of Eq. (14.4-22):

$$\Psi_{nlm}(r, \theta, \phi, t) = \psi_{nlm}(r, \theta, \phi)e^{-iE_nt/\hbar} \qquad (16.2\text{-}32)$$

This represents a stationary state. The probability density for finding the electron is time-independent. The expectation value of any time-independent variable is time-independent, and can be calculated with the coordinate wave function.

Exercise 16.16

Show that the expectation value $\langle 1/r \rangle$ is exactly the same as in Example 16.4 when the time-dependent wave function Ψ_{100} is used instead of the coordinate wave function ψ_{100}.

The Intrinsic Angular Momentum of the Electron. "Spin"

It is found experimentally that in addition to the angular momentum included in the solution to the Schrödinger equation, electrons have an additional angular momentum. To obtain adequate agreement with experiment, this feature must be added to the Schrödinger theory. The angular momentum included in the Schrödinger theory is now called the **orbital angular momentum** and the additional angular momentum is called the **intrinsic angular momentum** or the **spin angular momentum**. The Schrödinger theory is nonrelativistic and cannot be correct when particles have speeds near the speed of light. There is a version of quantum mechanics that is compatible with special relativity, based on the Dirac equation rather than the Schrödinger equation. The intrinsic angular momentum occurs naturally in this theory.

EXAMPLE 16.5

Calculate the expectation value of the square of the speed of the electron in a hydrogen atom in the 1*s* state, and from this calculate the root-mean-square speed. Compare this speed with the speed of light.

Solution

We can obtain this quantity from the expectation value of the kinetic energy:

$$\begin{aligned}\langle \mathscr{K} \rangle &= E_1 - \langle \mathscr{V} \rangle = -2.18 \times 10^{-18}\,\mathrm{J} + \frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle \\ &= -2.18 \times 10^{-18}\,\mathrm{J} + 2(2.18 \times 10^{-18}\,\mathrm{J}) = 2.18 \times 10^{-18}\,\mathrm{J} \\ \langle v^2 \rangle &= \frac{2\langle \mathscr{K} \rangle}{m} = \frac{2(2.18 \times 10^{-18}\,\mathrm{kg\,m^2\,s^{-2}})}{9.11 \times 10^{-31}\,\mathrm{kg}} = 4.69 \times 10^{12}\,\mathrm{m^2\,s^{-2}} \\ v_{\mathrm{rms}} &= \langle v^2 \rangle^{1/2} = 2.16 \times 10^6\,\mathrm{m\,s^{-1}}\end{aligned}$$

which is smaller than the speed of light by a factor of roughly 100. Although relativistic corrections are not important for the hydrogen atom, they are important for atoms beyond the middle of the periodic table.

The z component of the intrinsic angular momentum takes on one of only two possible values, $\hbar/2$ and $-\hbar/2$. We denote the intrinsic angular momentum by **S** and write

$$S_z = \pm\frac{\hbar}{2} \qquad (16.2\text{-}33)$$

We assign a new quantum number, m_s, for the z component of the intrinsic angular momentum, with the values

$$m_s = \pm\frac{1}{2} \qquad (16.2\text{-}34)$$

The total angular momentum of an electron is the vector sum of the orbital and intrinsic angular momenta. The total angular momentum is denoted by **J** and its z component is denoted by J_z. It has values

$$J_z = m\hbar + m_s\hbar \qquad (16.2\text{-}35)$$

where m is the same quantum number as before.

The pattern of values of m_s is analogous to that of Eq. (16.1-43) for the orbital angular momentum if we assign a quantum number s for the square of the intrinsic angular momentum with a fixed value of $\frac{1}{2}$. If we allow half-integral values for quantum numbers, all angular momentum quantum numbers follow this pattern. The square of the intrinsic angular momentum has the fixed value

$$s^2 = \hbar^2 \frac{1}{2}\left(\frac{1}{2}+1\right) \tag{16.2-36}$$

following the same pattern as Eq. (16.1-40).

There are three principal differences between the orbital angular momentum and the intrinsic angular momentum. First, the orbital angular momentum occurred naturally in the nonrelativistic Schrödinger theory, while the intrinsic angular momentum is arbitrarily added to the theory in order to make it agree with experiment and with this aspect of relativistic quantum mechanics. Second, the intrinsic angular momentum has only one possible magnitude while the orbital angular momentum has variable (but quantized) magnitude. Third, this single magnitude corresponds to a quantum number that is a half-integer instead of an integer. Figure 16.11 shows the two cones of possible directions of the intrinsic angular momentum.

EXAMPLE 16.6

Find the angle between the z axis and the intrinsic angular momentum for $m_s = +\frac{1}{2}$.

Solution

$$\theta = \arccos\left(\frac{\hbar/2}{\hbar\sqrt{(1/2)(3/2)}}\right) = \arccos\left(\frac{1/2}{\sqrt{3/4}}\right)$$
$$= \arccos(0.57735) = 54.7356\ldots \text{ degrees} = 0.9553166\ldots \text{ radians}$$

It is natural to seek a classical interpretation for the intrinsic angular momentum. Although we have previously treated the electron as a mass point, and although it is not known what its internal structure is (if any), it is customary to ascribe the intrinsic angular momentum to rotation of the electron about its own axis, calling it **spin angular momentum**. The assumed motion is analogous to the rotation of the earth on its axis as it revolves about the sun. We will use this spin interpretation, although we could proceed if we wished without any mental picture of spinning motion, and there is no guarantee that it is physically accurate. We now have twice as many possible states of electronic motion in a hydrogenlike atom as we did before, since for every set of values of the quantum numbers n, l, and m, there are two possible values of m_s. We will call the state for $m_s = +\frac{1}{2}$ the "spin up" state and the state for $m_s = -\frac{1}{2}$ "spin down" state, corresponding to the direction of the intrinsic angular momentum vector.

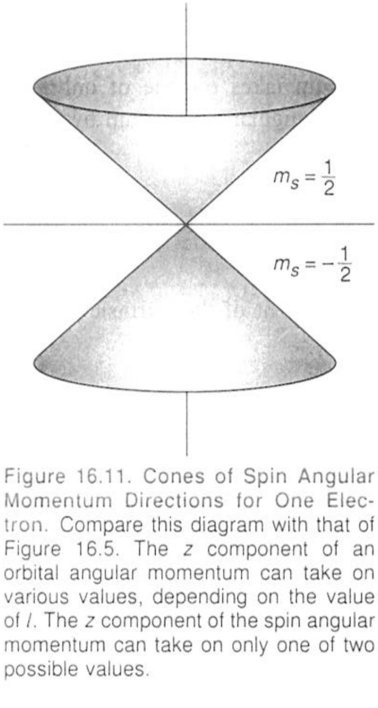

Figure 16.11. Cones of Spin Angular Momentum Directions for One Electron. Compare this diagram with that of Figure 16.5. The z component of an orbital angular momentum can take on various values, depending on the value of l. The z component of the spin angular momentum can take on only one of two possible values.

There are two different ways to include spin in our notation. The first is to attach another subscript to the orbital symbol, replacing nlm by $nlmm_s$. There is no need to include the value of s since it is fixed. The orbital is now called a **spin orbital**. The second way is to multiply the original orbital by a **spin function** that is called α for $m_s = +\frac{1}{2}$ and β for $m = -\frac{1}{2}$. The original orbital is now called a **space orbital** and the product is called a spin orbital. The spin function is thought of as being a function of some spin coordinates that are not explicitly represented. The two ways of writing a spin orbital are equivalent:

$$\psi_{nlm,1/2} = \psi_{nlm}\alpha, \qquad \psi_{nlm,-1/2} = \psi_{nlm}\beta \tag{16.2-37}$$

We define operators for the spin angular momentum that are analogous to the orbital angular momentum operators. We do not write any explicit mathematical forms for them, but assign their properties by definition. The spin functions α and β are defined to be eigenfunctions of $\hat{S}^2$, the operator for the square of the spin angular momentum:

$$\hat{S}^2\alpha = \hbar^2(1/2)(3/2)\alpha \tag{16.2-38}$$

$$\hat{S}^2\beta = \hbar^2(1/2)(3/2)\beta \tag{16.2-39}$$

They are also defined to be eigenfunctions of $\hat{S}_z$, the operator for the z component of the spin angular momentum:

$$\hat{S}_z\alpha = +\frac{\hbar}{2}\alpha \tag{16.2-40}$$

$$\hat{S}_z\beta = -\frac{\hbar}{2}\beta \tag{16.2-41}$$

The spin functions are defined to be normalized and to be orthogonal to each other.

Addition of the intrinsic angular momentum modifies the Schrödinger theory of the electron so that it agrees adequately with experiment for many purposes. Further modifications can be made to include additional aspects of relativistic quantum mechanics such as small differences between the energies of "spin up" and "spin down" states for states of nonzero orbital angular momentum. We will not discuss the **spin–orbit coupling** that produces this effect, although it is numerically important in heavy atoms.[4]

16.3 The Helium Atom in the "Zero-Order" Orbital Approximation

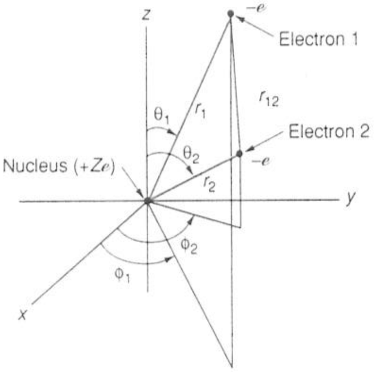

Figure 16.12. The Helium Atom System. The occurrence of two electrons makes it impossible to obtain an exact solution to the Schrödinger equation for this system.

The hydrogenlike atom is the only atom for which the Schrödinger equation can be solved without approximation. This does not invalidate the Schrödinger quantum theory for other atoms, since approximate treatments of other atoms have been carried out that give accurate agreement with experimental energy values. It does mean that the only way to proceed with other atoms is with approximations.

The Hamiltonian of a Heliumlike Atom

The helium atom contains two electrons and a nucleus containing two protons. We define a "heliumlike" atom with Z protons in the nucleus, so that $Z = 2$ represents the He atom, $Z = 3$ represents the Li^+ ion, etc. The system is shown in Figure 16.12. The three-body problem cannot be solved exactly, either in classical or in quantum

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[4] Pilar, *op. cit.*, pp. 301ff (Note 1); K. Balasubramanian, *J. Phys. Chem.*, 93, 6585 (1989).

mechanics, so we assume that the helium nucleus is stationary. This is a good approximation, as with the hydrogenlike atom. With a stationary nucleus, the classical Hamiltonian function is

$$H_{\mathrm{cl}} = \frac{1}{2m}p_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{4\pi\varepsilon_0}\left(-\frac{Ze^2}{r_2} - \frac{Ze^2}{r_1} + \frac{e^2}{r_{12}}\right) \tag{16.3-1}$$

where $\mathbf{p}_1$ is the vector momentum of electron 1, $\mathbf{p}_2$ is the vector momentum of electron 2, m is the electron mass, and the distances are as labeled in Figure 16.12. The Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \frac{1}{4\pi\varepsilon_0}\left(-\frac{Ze^2}{r_2} - \frac{Ze^2}{r_1} + \frac{e^2}{r_{12}}\right) \tag{16.3-2}$$

where ∇_1^2 and ∇_2^2 are the Laplacian operators for electrons 1 and 2.

The "Zero-Order" Orbital Approximation

The Hamiltonian operator of Eq. (16.3-2) gives a time-independent Schrödinger equation that has not been solved exactly. We begin with the **zero-order approximation**, which is obtained by neglecting the repulsion of the electrons for each other. It is not a good approximation, but it is a starting point for better approximations. The approximate Hamiltonian operator is now

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2} \tag{16.3-3}$$

where we add a superscript (0) to distinguish the approximate "zero-order" Hamiltonian from the correct Hamiltonian. It is a sum of hydrogenlike Hamiltonian operators:

$$\hat{H}^{(0)} = \hat{H}_{\mathrm{HL}}(1) + \hat{H}_{\mathrm{HL}}(2) \tag{16.3-4}$$

where the subscript HL stands for "hydrogenlike," and where we abbreviate the coordinates of a particle by writing only the particle index. The approximate time-independent Schrödinger equation is

$$\hat{H}^{(0)}\Psi^{(0)}(1,2) = \left[\hat{H}_{\mathrm{HL}}(1) + \hat{H}_{\mathrm{HL}}(2)\right]\Psi^{(0)}(1,2) = E^{(0)}\Psi^{(0)}(1,2) \tag{16.3-5}$$

where we attach a superscript (0) to the zero-order wave function and eigenvalue. Equation (16.3-5) can be solved by separation of variables, using the trial solution:

$$\Psi^{(0)}(1,2) = \psi_1(r_1,\theta_1,\phi_1)\psi_2(r_2,\theta_2,\phi_2) = \psi_1(1)\psi_2(2) \tag{16.3-6}$$

where ψ_1 and ψ_2 are two orbitals (functions of the coordinates of one electron). In the second version of the orbitals, each particle's coordinates are represented only by their subscript. A multielectron wave function that is a product of orbitals is called an **orbital wave function**.

We substitute the trial solution into Eq. (16.3-5) and use the fact that $\psi_1(1)$ is treated as a constant when $\hat{H}_{\mathrm{HL}}(2)$ operates and $\psi_2(2)$ is treated as a constant when $\hat{H}_{\mathrm{HL}}(1)$ operates. The result is

$$\psi_2(2)\hat{H}_{\mathrm{HL}}(1)\psi_1(1) + \psi_1(1)\hat{H}_{\mathrm{HL}}(2)\psi_2(2) = E^{(0)}\psi_1(1)\psi_2(2) \tag{16.3-7}$$

Division of this equation by $\psi_1(1)\psi_2(2)$ completes the separation of variables:

$$\frac{1}{\psi_1(1)}\hat{H}_{\text{HL}}(1)\psi_1(1) + \frac{1}{\psi_2(2)}\hat{H}_{\text{HL}}(2)\psi_2(2) = E^{(0)} \tag{16.3-8}$$

Each of the terms on the left-hand-side of the equation contains only a set of variables not occurring in the other term, and the right-hand side is a constant. The first term must be equal to a constant, which we call E_1, and the second term must be equal to a constant, E_2, such that

$$E_1 + E_2 = E^{(0)} \tag{16.3-9}$$

We now have two differential equations:

$$\hat{H}_{\text{HL}}(1)\psi_1(1) = E_1\psi_1(1) \tag{16.3-10}$$

$$\hat{H}_{\text{HL}}(2)\psi_2(2) = E_2\psi_2(2) \tag{16.3-11}$$

Equations (16.3-10) and (16.3-11) are two hydrogenlike Schrödinger equations. Therefore, E_1 and E_2 are hydrogenlike energies (orbital energies). The total electronic energy in the zero-order approximation is

$$E^{(0)}_{n_1 n_2} = E_{n_1}(\text{HL}) + E_{n_2}(\text{HL}) = -(13.60\,\text{eV})(Z^2)\left[\frac{1}{n_1^2} + \frac{1}{n_2^2}\right] \tag{16.3-12}$$

where n_1 and n_2 are two values of the principal quantum number for a hydrogenlike atom. The orbitals $\psi_1(1)$ and $\psi_2(2)$ are hydrogenlike orbitals:

$$\Psi^{(0)}(1,2) = \psi_1(1)\psi_2(2) = \psi_{n_1 l_1 m_1 m_{s1}}(1)\psi_{n_2 l_2 m_2 m_{s2}}(2) \tag{16.3-13}$$

The values of a given quantum number for the two orbitals are not necessarily equal, so we add a subscript on each subscript to distinguish them from each other. The notation with separate spin functions can also be used.

Probability Densities for Two Particles

For a system of two particles whose wave function is $\Psi(1,2)$, the probability of finding particle 1 in the volume element $d^3\mathbf{r}_1$ and finding particle 2 in the volume element $d^3\mathbf{r}_2$ is given by

$$(\text{Probability}) = \Psi^*(1,2)\Psi(1,2)\,d^3\mathbf{r}_1\,d^3\mathbf{r}_2 = |\Psi(1,2)|^2\,d^3\mathbf{r}_1\,d^3\mathbf{r}_2 \tag{16.3-14}$$

The square of the magnitude of the wave function is a probability density in a six-dimensional space. For the orbital wave function of Eq. (16.3-13), the probability density for two particles is the product of two one-particle probability densities:

$$|\Psi(1,2)|^2 = |\psi_1(1)|^2|\psi_2(2)|^2 \tag{16.3-15}$$

Since we have neglected the interaction between the electrons, it is reasonable that the probability densities of the two particles are independent of each other. If this probability density is normalized,

$$\int |\Psi(1,2)|^2\,d^3\mathbf{r}_1\,d^3\mathbf{r}_2 = 1 \tag{16.3-16}$$

We consider the inclusion of spin functions later.

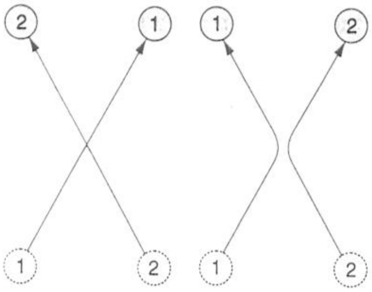

Figure 16.13. Two Encounters of Classical Particles. Since classical mechanics includes exact trajectories, we can "track" each particle exactly.

The Indistinguishability of Identical Particles

Although we have obtained a function that satisfies our approximate Schrödinger equation and the appropriate boundary conditions, it must be further modified to obtain agreement with experiment. It must conform to the condition: *Identical particles are inherently indistinguishable from each other*. This condition does not occur in classical mechanics and is an additional hypothesis that must be tested by comparing its consequences with experimental fact. It is plausible because of the uncertainty principle, which makes exact trajectories impossible to specify, so that if two identical particles approach each other closely it might not be possible to tell which is which after the encounter. Figure 16.13 shows two encounters that could be distinguished from each other if classical mechanics were valid, but which might not be distinguished according to quantum mechanics.

We must not build anything into our theory that would allow us to distinguish one particle from another of the same kind. In a helium atom, the probability of finding electron 1 at location 1 and finding electron 2 at location 2 must equal the probability of finding electron 1 at location 2 and finding electron 2 at location 1. Any difference in these two probabilities would give an illusory means of distinguishing the particles. The probability density in Eq. (16.3-14) must remain unchanged if the locations of the two electrons are interchanged:

$$\Psi(1,2)^*\Psi(1,2) = \Psi(2,1)^*\Psi(2,1) \qquad (16.3\text{-}17)$$

That is, the probability density $\Psi^*\Psi$ must be **symmetric** with respect to interchange of the two particles' locations. The probability density of two particles does not have to be symmetric if the particles are not identical. For example, the probability density for a hydrogen atom does not have to be symmetry with respect to interchange of the proton and the electron.

With real functions there are only two ways to satisfy Eq. (16.3-17). Either the wave function must be **symmetric** with respect to interchange of the particles:

$$\Psi(1,2) = \Psi(2,1) \qquad \text{(symmetric wave function)} \qquad (16.3\text{-}18)$$

or the wave function must be **antisymmetric** with respect to interchange of the particles (change sign if the locations of the particles are switched):

$$\Psi(1,2) = -\Psi(2,1) \qquad \text{(antisymmetric wave function)} \qquad (16.3\text{-}19)$$

Although our wave functions are not required to be real, they are also not required to be complex. We consider only these two possibilities.

Particles that obey Eq. (16.3-18) are called **bosons**, and particles that obey Eq. (16.3-19) are called **fermions**. Electrons are found experimentally to be fermions, so that our approximate two-electron wave function must be modified to obey Eq. (16.3-19). Protons and neutrons are also fermions. Photons are bosons. Atoms or molecules containing an even number of fermions are bosons, and molecules containing an odd number of fermions are fermions. The requirement that a two-electron wave function be antisymmetric is a requirement of the same sort as the requirement that a wave function be continuous, single-valued, and finite. These conditions, in addition to solution of the Schrödinger equation, must be applied to find an acceptable wave function.

The simplest way to obtain an antisymmetric two-electron orbital wave function is to add a second term that is the negative of the first term with the orbital labels interchanged, giving

$$\Psi(1,2) = C\left[\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)\right] \qquad (16.3\text{-}20)$$

We say that we have **antisymmetrized** the wave function. With this wave function it is not possible to say which electron occupies which orbital, because the labels are in one order in the first term of the antisymmetric wave function and in the other order in the second term.

Exercise 16.17

By explicit manipulation, show that the function of Eq. (16.3-20) obeys Eq. (16.3-19).

The Pauli Exclusion Principle

There is an important fact about fermions that we can see in Eq. (16.3-20). If the orbitals ψ_1 and ψ_2 are the same function, the two-particle wave function is the difference of two identical terms and vanishes. A vanishing wave function cannot represent any state of the system. Therefore, a given spin orbital cannot occur more than once in any term of a two-electron wave function. We will later construct orbital wave functions for more than two electrons. When antisymmetrized, these will consist of a sum of terms with different signs. Each term will be a product of spin orbitals, one for each electron. The **Pauli exclusion principle** is a generalization of our observations for two electrons: *In an orbital wave function, the same spin orbital cannot occur more than once in each term.* A spin orbital that occurs in an orbital wave function is said to be "occupied" by an electron. Another statement of the Pauli exclusion principle is: *In an orbital wave function, no two electrons can occupy the same spin orbital.*

The Pauli exclusion principle is named for Wolfgang Pauli, 1900–1958, who received the 1945 Nobel Prize in physics for his contributions to quantum mechanics.

The probability density for the antisymmetrized wave function of Eq. (16.3-20) is

$$\Psi(1,2)^*\Psi(1,2) = |C|^2\big[|\psi_1(1)|^2|\psi_2(2)|^2 + |\psi_2(1)|^2|\psi_1(2)|^2 - \psi_1(1)^*\psi_2(1)\psi_2(2)^*\psi_1(2) - \psi_2(1)^*\psi_1(1)\psi_1(2)^*\psi_2(2)\big] \quad (16.3\text{-}21)$$

where C is a normalizing constant. Each term in Eq. (16.3-21) gives an integral that factors into a product of two one-particle integrals. Each of the first two terms gives unity if the orbitals are normalized. Each of the last two terms gives zero if the orbitals are orthogonal to each other. To normalize the wave function,

$$1 = |C|^2[1+1] = 2|C|^2$$

or if C is taken to be real and positive,

$$C = \sqrt{\frac{1}{2}} \quad (16.3\text{-}22)$$

The probability of finding particle 1 in the volume element $d^3\mathbf{r}_1$ irrespective of the location of particle 2 is given by integrating the probability density in Eq. (16.3-14) over all positions of particle 2:

$$\begin{pmatrix}\text{Probability of finding}\\ \text{particle 1 in } d^3\mathbf{r}_1\end{pmatrix} = \left[\int \Psi(1,2)^*\Psi(1,2)\,d^3\mathbf{r}_2\right] d^3\mathbf{r}_1 \quad (16.3\text{-}23)$$

If the two-electron wave function is a one-term orbital wave function such as that of Eq. (16.3-6), the orbital function for electron 1 factors out of the integral:

$$\begin{pmatrix}\text{Probability of finding}\\ \text{particle 1 in } d^3\mathbf{r}_1\end{pmatrix} = \psi_1(1)^*\psi_1(1)\,d^3\mathbf{r}_1 \int \psi_2(2)^*\psi_2(2)\,d^3\mathbf{r}_2$$

If ψ_2 is normalized, the integral in this equation equals unity and

$$\begin{pmatrix}\text{Probability of finding}\\ \text{particle 1 in } d^3\mathbf{r}_1\end{pmatrix} = \psi_1(1)^*\psi_1(1)\,d^3\mathbf{r}_1 = |\psi_1(1)|^2\,d^3\mathbf{r}_1 \qquad (16.3\text{-}24)$$

The probability density for electron 1 is just that of its own orbital, independent of electron 2. An analogous equation can be written for electron 2.

If the antisymmetrized wave function of Eq. (16.3-21) is used, the expression must be integrated in the same way as Eq. (16.3-23) to obtain the probability density for particle 1. Only the first two terms in Eq. (16.3-21) survive, due to the orthogonality of the orbitals, and the result is

$$\begin{aligned}\begin{pmatrix}\text{Probability of finding}\\ \text{particle 1 in } d^3\mathbf{r}_1\end{pmatrix} &= |C|^2\left[|\psi_1(1)|^2 + |\psi_2(1)|^2\right]d^3\mathbf{r}_1\\ &= \frac{1}{2}\left[|\psi_1(1)|^2 + |\psi_2(1)|^2\right]d^3\mathbf{r}_1 \qquad (16.3\text{-}25)\end{aligned}$$

This probability is the average of what would occur if electron 1 occupied orbital 1 and what would occur if it occupied orbital 2. Since we cannot specify which orbital is occupied by the electron, this is a plausible result. An exactly analogous expression can be written for electron 2. The total probability of finding some electron in a volume $d^3\mathbf{r}$ is the sum of the probabilities for the two electrons:

$$\begin{aligned}\begin{pmatrix}\text{Probability of finding}\\ \text{an electron in } d^3\mathbf{r}_1\end{pmatrix} &= 2|C|^2\left[|\psi_1(\mathbf{r})|^2 + |\psi_2(\mathbf{r})|^2\right]d^3\mathbf{r}\\ &= \left[|\psi_1(\mathbf{r})|^2 + |\psi_2(\mathbf{r})|^2\right]d^3\mathbf{r} \qquad (16.3\text{-}26)\end{aligned}$$

When this probability density is multiplied by $-e$, the electron charge, it is the charge density (charge per unit volume) due to the electrons.

The Ground State of the Helium Atom

The lowest-energy state of a system is called its **ground state**. Since the subshell of lowest orbital energy, the $1s$ subshell, contains two spin orbitals (one space orbital), both electrons can be in the $1s$ subshell. Our approximate ground-state wave function is

$$\begin{aligned}\Psi^{(0)}_{1s1s}(1,2) &= \Psi_{1s,1/2;1s,-1/2}(1,2)\\ &= C[\psi_{100,1/2}(1)\psi_{100,-1/2}(2) - \psi_{100,-1/2}(1)\psi_{100,1/2}(2)] \qquad (16.3\text{-}27)\end{aligned}$$

where two sets of orbital subscripts are used because the orbital wave function contains two spin orbitals. This wave function is antisymmetric, and satisfies the Pauli exclusion principle. If the spin orbitals are written as products of space orbitals and spin functions, the spin part can be factored out:

$$\begin{aligned}\Psi^{(0)}(1,2) &= C\left[\psi_{100}(1)\alpha(1)\psi_{100}(2)\beta(2) - \psi_{100}(1)\beta(1)\psi_{100}(2)\alpha(2)\right]\\ &= C\psi_{100}(1)\psi_{100}(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \qquad (16.3\text{-}28)\end{aligned}$$

To normalize the wave function, the constant C must be such that

$$1 = C^*C\int \Psi^{(0)}(1,2)^*\Psi^{(0)}(1,2)\,dq_1'\,dq_2' \qquad (16.3\text{-}29)$$

where the coordinates of both particles are integrated. Since we have introduced spin functions, an integration over the independent variables of the spin functions as well as over the space coordinates is indicated. We regard dq_1' and dq_2' as representing both space and spin coordinates:

$$dq_1' = d^3\mathbf{r}_1\, d^s(1) \tag{16.3-30}$$

where $d^3\mathbf{r}_1$ is the volume element in ordinary space, and $d^s(1)$ is the "volume element" of the unspecified spin coordinates. We do not explicitly integrate over the unspecified spin coordinates, but define the spin functions α and β to be normalized and orthogonal to each other:

$$\int \alpha(1)^*\alpha(1)\, d^s(1) = \int \beta(1)^*\beta(1)\, d^s(1) = 1 \quad \text{(by definition)} \tag{16.3-31}$$

and

$$\int \beta(1)^*\alpha(1)\, d^s(1) = \int \alpha(1)^*\beta(1)\, d^s(1) = 0 \quad \text{(by definition)} \tag{16.3-32}$$

We use these definitions when an integration over spin coordinates is indicated instead of explicitly carrying out an integration.

The two-electron wave function in Eq. (16.3-28) is substituted into the normalization integral of Eq. (16.3-29). The integral can be factored, since the space and spin coordinates of each particle occur in separate factors:

$$\begin{aligned} 1 = C^*C &\int \psi_{100}(1)^*\psi_{100}(1)\, d^3\mathbf{r}_1 \int \psi_{100}(2)^*\psi_{100}(2)\, d^3\mathbf{r}_2 \\ &\times \int [\alpha(1)\beta(2) - \beta(1)\alpha(2)]^*[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\, d^s(1)\, d^s(2) \end{aligned} \tag{16.3-33}$$

Since the hydrogenlike orbitals are normalized, the integrals over the space coordinates equal unity, and we have, after multiplying out the terms and factoring the spin integrals:

$$\begin{aligned} 1 = C^*C\Bigg\{\Bigg[\Bigg[\int &\alpha(1)^*\alpha(1)\, d^s(1) \int \beta(2)^*\beta(2)\, d^s(2) \\ &+ \int \beta(1)\beta(1)\, d^s(1) \int \alpha(2)^*\alpha(2)\, d^s(2) \\ &- \int \alpha(1)^*\beta(1)\, d^s(1) \int \beta(2)^*\alpha(2)\, d^s(2) \\ &- \int \beta(1)^*\alpha(1)\, d^s(1) \int \alpha(2)^*\beta(2)\, d^s(2)\Bigg]\Bigg\} \end{aligned} \tag{16.3-34}$$

where we have factored the double integrals. Each of the first two terms in the final equation above gives unity because of the defined normalization of the spin functions. The last two terms give zero because of the defined orthogonality of the spin functions, so that if we choose C to be real and positive,

$$C = \sqrt{\frac{1}{2}} \tag{16.3-35}$$

The energy eigenvalue for our zero-order ground-state wave function is the sum of two hydrogenlike orbital energies:

$$E_{1s1s}^{(0)} = E_1(\mathrm{HL}) + E_1(\mathrm{HL}) = 2(-13.60\,\mathrm{eV})Z^2 \tag{16.3-36a}$$

For helium, $Z = 2$, so that

$$E_{1s1s}^{(0)} = -108.8\,\mathrm{eV} \tag{16.3-36b}$$

This approximate energy eigenvalue is seriously in error, since the experimental value is -79.0 eV. Since 1 eV is equivalent to 96.5 kJ mol^{-1}, an error of 30 eV is a very large error, larger than chemical bond energies. We obtain better approximations in the next chapter.

Excited States of the Helium Atom

States of higher energy than the ground state are called **excited states**. For excited states represented by orbital wave functions, there are two cases: (1) both electrons occupy the same space orbital with different spin functions, and (2) the two electrons occupy different space orbitals, either with the same or different spin functions. A statement of which orbitals are occupied is called the **electron configuration**. The **detailed configuration** is specified by writing the designation of each occupied space orbital with a right superscript giving the number of electrons occupying that space orbital. This superscript can equal either 1 or 2. The **subshell configuration** is specified by writing the designation of each subshell with a right superscript giving the number of electrons occupying orbitals of that subshell. The maximum value of this superscript is 2 for an s subshell, 6 for a p subshell, 10 for a d subshell, and so on. The configuration of the ground state of helium is $(1s)^2$ (subshell and detailed configurations are the same with s subshells). Two of the many possible excited configurations are $(1s)^1(2s)^1$ and $(1s)^1(2p0)^1$ (detailed) or $(1s)^1(2p)^1$ (subshell). A superscript equal to unity is often omitted, so that $(1s)(2s)$ means the same as $(1s)^1(2s)^1$.

If both electrons occupy the same space orbital, a wave function for an excited state is similar to that of the ground state, with the antisymmetric spin factor. For the configuration $(2s)^2$:

$$\Psi_{2s2s} = \frac{1}{\sqrt{2}}\psi_{2s}(1)\psi_{2s}(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{16.3-37}$$

For the configuration $(1s)^1(2s)^1$, there are four states, since each electron has two choices, spin up and spin down. Four antisymmetric wave functions are:

$$\Psi_1 = \frac{1}{\sqrt{2}}[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)]\alpha(1)\alpha(2) \tag{16.3-38a}$$

$$\Psi_2 = \frac{1}{\sqrt{2}}[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)]\beta(1)\beta(2) \tag{16.3-38b}$$

$$\Psi_3 = \frac{1}{2}[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)] \tag{16.3-38c}$$

$$\Psi_4 = \frac{1}{2}[\psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)\psi_{1s}(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{16.3-38d}$$

All of these functions are eigenfunctions of the $\hat{L}^2$ and $\hat{S}^2$ operators, although we do not prove that fact.

Exercise 16.18

Show that Ψ_3 and Ψ_4 satisfy the zero-order Schrödinger equation and find the energy eigenvalue. Show that these functions are normalized if the orbitals are normalized.

Angular Momentum in the Helium Atom. Russell–Saunders Coupling

It is a theorem of both classical and quantum mechanics that the total angular momentum of an isolated system is conserved. If no external forces act on the system, its total angular momentum does not change in time. A conserved quantity is called a **constant of the motion**. A quantum number determining the value of a conserved quantity is called a **good quantum number**, and the quantity itself is sometimes referred to by the same name. The total angular momentum is always a good quantum number for an isolated atom or molecule, and for atoms in the first part of the periodic table the orbital and spin angular momenta can be assumed to be good quantum numbers. This assumption is called **Russell–Saunders coupling**.

The sum of two angular momenta is a vector sum. Consider an atom with two electrons. Let $\mathbf{l}_1$ and $\mathbf{s}_1$ be the orbital and spin angular momenta of electron 1, and let $\mathbf{l}_2$ and $\mathbf{s}_2$ be the orbital and spin angular momenta of electron 2. We will now use lower-case letters for angular momenta of single electrons, and capital letters for angular momenta of multielectron atoms. The total orbital and spin angular momenta of the helium atom are vector sums of the contributions of the individual electrons:

$$\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 \tag{16.3-39}$$

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 \tag{16.3-40}$$

The total angular momentum of the atom is

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{16.3-41}$$

The eigenvalues of the $\hat{J}^2$, $\hat{J}_z$, $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$ operators follow the same pattern as other angular momenta:

$$\hat{J}^2\Psi = \hbar^2 J(J+1)\Psi \tag{16.3-42}$$

$$\hat{J}_z\Psi = \hbar M_J\Psi \tag{16.3-43}$$

$$\hat{L}^2\Psi = \hbar^2 L(L+1)\Psi \tag{16.3-44}$$

$$\hat{L}_z\Psi = \hbar M_L\Psi \tag{16.3-45}$$

$$\hat{S}^2\Psi = \hbar^2 S(S+1)\Psi \tag{16.3-46}$$

$$\hat{S}_z\Psi = \hbar M_S\Psi \tag{16.3-47}$$

Figure 16.14 illustrates how angular momentum vectors can add vectorially to produce some particular values of the quantum numbers L, M_L, S, and M_S. In each diagram, the tail of the second vector is placed at the head of the first vector, as is done in the geometric representation of vector addition.

In Russell–Saunders coupling, the energy levels are characterized by the values of L and S. The orbital angular momentum quantum number L is a nonnegative integer. The spin angular momentum quantum number S is a nonnegative integer or half-integer. Each set of states corresponding to a particular value of L and a particular value of S is called a **term**. A **Russell–Saunders term symbol** is assigned to each term. The principal part of the symbol is a letter giving the value of L, as follows:

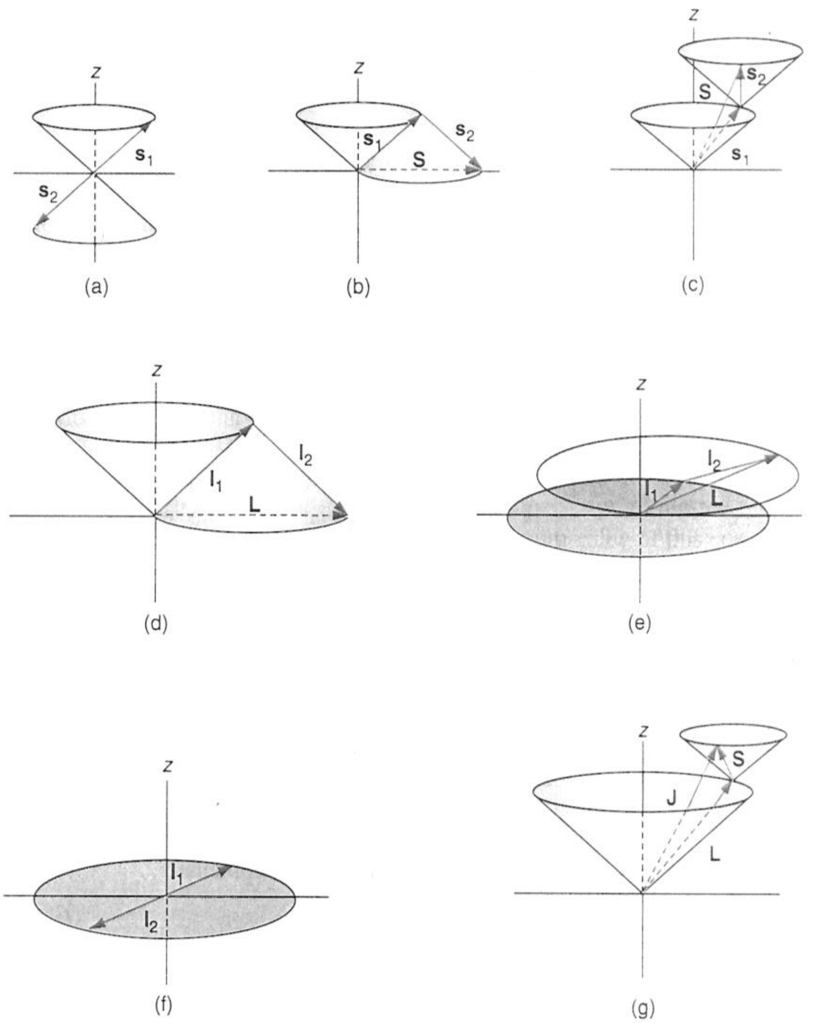

Figure 16.14. Examples of Vector Addition of Angular Momenta. These examples show how angular momenta add vectorially to give sums that follow the standard pattern for an angular momentum. (a) Two electron spins: $m_{s1} = 1/2$, $m_{s2} = -1/2$, $M_S = 0$, $S = 0$. (b) Two electron spins: $m_{s1} = 1/2$, $m_{s2} = -1/2$, $M_S = 0$, $S = 1$. (c) Two electron spins: $m_{s1} = 1/2$, $m_{s2} = 1/2$, $M_S = 1$, $S = 1$. (d) Two p electrons' orbital angular momenta: $l_1 = 1$, $m_1 = 1$, $l_2 = 1$, $m_2 = -1$, $M_L = 0$, $L = 1$. (e) Two p electrons' orbital angular momenta: $l_1 = 1$, $m_1 = 0$, $l_2 = 1$, $m_2 = 0$, $M_L = 0$, $L = 2$. (f) Two p electrons' orbital angular momenta: $m_1 = 0$, $l_1 = 1$, $m_2 = 0$, $l_2 = 1$, $M_L = 0$, $L = 0$. (g) Total orbital and spin angular momenta: $L = 1$, $M_L = 1$, $S = 1/2$, $M_S = 1/2$, $M_J = 3/2$, $J = 3/2$.

Value of L	Symbol
0	S
1	P
2	D
3	F
4	G
etc.	

From this point on the symbols are in alphabetical order.

A left superscript is attached that has the value $2S + 1$. For our two sets of states we will show that we have ${}^3S$ and ${}^1S$ (pronounced "triplet S" and "singlet S.") In addition to the terms "singlet" for $S = 0$ and "triplet" for $S = 1$, we use "doublet" for $S = 1/2$, "quartet" for $S = 3/2$, etc. The value of the left superscript is called the **multiplicity** of the term, and is equal to the number of values of M_S that occur since M_S ranges from S to $-S$. A right subscript giving the value of J is also sometimes used.

We now investigate the values of the quantum numbers for particular configurations. Since the angular momenta are vectors, their operators are expressed as vector sums. For two electrons,

$$\hat{L}^2 = (\hat{l}_{x1} + \hat{l}_{x2})^2 + (\hat{l}_{y1} + \hat{l}_{y2})^2 + (\hat{l}_{z1} + \hat{l}_{z2})^2 \tag{16.3-48}$$

$$\hat{L}_z = \hat{l}_{z1} + \hat{l}_{z2} \tag{16.3-49}$$

$$\hat{S}^2 = (\hat{s}_{x1} + \hat{s}_{x2})^2 + (\hat{s}_{y1} + \hat{s}_{y2})^2 + (\hat{s}_{z1} + \hat{s}_{z2})^2 \tag{16.3-50}$$

$$\hat{S}_z = \hat{s}_{z1} + \hat{s}_{z2} \tag{16.3-51}$$

The $\hat{L}_2$ and $\hat{S}^2$ expressions are not easy to use because they contain terms that do not commute with each other, and we will not obtain explicit expressions for them.[5] We can find the values of M_L and M_S, and from these infer the values of L and S using the fact that M_L ranges from $+L$ to $-L$ and that M_S ranges from $+S$ to $-S$. For two electrons, since the z components of two vectors add algebraically,

$$M_L = m_1 + m_2 \tag{16.3-52}$$

and

$$M_S = m_{s1} + m_{s2} \tag{16.3-53}$$

EXAMPLE 16.7

Find the values of the quantum numbers M_L and M_S for each of the wave functions in Eq. (16.3-38a)–(16.3-38d).

Solution

$$\begin{aligned}\hat{L}_z\Psi_1 &= \left(\hat{l}_{z1} + \hat{l}_{z2}\right)\Psi_1 = \frac{1}{\sqrt{2}}\left[\hat{l}_{z1}\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\hat{l}_{z2}\psi_{1s}(2)\right]\alpha(1)\alpha(2)\\ &= 0 + 0 = 0\end{aligned}$$

so that $M_L = 0$. All of the other wave functions also contain only s orbitals, so that $M_L = 0$ for all of them.

$$\begin{aligned}\hat{S}_z\Psi_1 &= (\hat{s}_{z1} + \hat{s}_{z2})\Psi_1\\ &= \frac{1}{\sqrt{2}}(\psi_{1s}(1)\psi_{1s}(2) - \psi_{1s}(1)\psi_{1s}(2))(\hat{s}_{z1}\alpha(1)\alpha(2) + \alpha(1)\hat{s}_{z2}\alpha(2))\\ &= \frac{1}{\sqrt{2}}(\psi_{1s}(1)\psi_{1s}(2) - \psi_{1s}(1)\psi_{1s}(2))\left(\frac{\hbar}{2}\alpha(1)\alpha(2) + \alpha(1)\frac{\hbar}{2}\alpha(2)\right)\\ &= \left(\frac{\hbar}{2} + \frac{\hbar}{2}\right)\Psi_1 = \hbar\Psi_1\end{aligned}$$

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[5] Levine, *op. cit.*, pp. 292ff (Note 3).

so that Ψ_1 corresponds to $M_S = 1$. We carried out the operations, but could have simply identified the m_s values and added them.

Similarly,

$$\hat{S}_z\Psi_2 = \left(-\frac{\hbar}{2} - \frac{\hbar}{2}\right)\Psi_2 = -\hbar\Psi_2$$

so that $M_S = -1$ for Ψ_2.

$$\begin{aligned}\hat{S}_z\Psi_3 &= \frac{1}{2}\left[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)\right]\\ &\quad\times\left[\hat{s}_{z1}\alpha(1)\beta(2) + \hat{s}_{z1}\beta(1)\alpha(2) + \alpha(1)\hat{s}_{z2}\beta(2) + \beta(1)\hat{s}_{z2}\alpha(2)\right]\\ &= \frac{1}{2}\left[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)\right]\\ &\quad\times\left[\left(\frac{\hbar}{2}\right)\alpha(1)\beta(2) + \left(\frac{-\hbar}{2}\right)\beta(1)\alpha(2) + \alpha(1)\left(\frac{-\hbar}{2}\right)\beta(2) + \beta(1)\left(\frac{\hbar}{2}\right)\alpha(2)\right]\\ &= 0\end{aligned}$$

so that $M_S = 0$ for Ψ_3. A similar calculation leads to the value $M_S = 0$ for Ψ_4. We wrote the operations and functions explicitly, but could simply have added the m values and the m_s values to obtain the same answers.

We have enough states that we can have a ^3S term ($L = 0$, $S = 1$), with $M_S = 1$, 0, and -1, plus a ^1S term ($L = 0$, $S = 0$) with $M_S = 0$. The wave functions in Eq. (16.3-38) are eigenfunctions of the $\hat{S}^2$ operator. We state the eigenvalues without proof:

$$\hat{S}^2\alpha(1)\alpha(2) = 2\hbar^2\alpha(1)\alpha(2) \tag{16.3-54}$$

$$\hat{S}^2\beta(1)\beta(2) = 2\hbar^2\beta(1)\beta(2) \tag{16.3-55}$$

$$\hat{S}^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] = 2\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \tag{16.3-56}$$

$$\hat{S}^2[\alpha(1)\beta(2) - \beta(1)\alpha(2)] = 0 \tag{16.3-57}$$

The first three functions correspond to the triplet term and the fourth corresponds to the singlet term. The symmetric spin factor in Eq. (16.3-56) belongs to the triplet, and the antisymmetric spin factor in Eq. (16.3-57) is the singlet. This is the general pattern.

We can infer the values of L and S as follows: Since the only value of M_L is zero, there are only S states, with $L = 0$. We begin with the largest value of M_S, which is 1 in this case. This means that the largest value of S is 1. A value of S equal to 1 requires values of M_S equal to 1, 0, and -1. We assign three states with these values to a ^3S (triplet S) term. There is only one state remaining, with $M_S = 0$. We assign it to a ^1S (singlet S) term. We always begin with the largest values of M_L and M_S and assign the states to the largest values of L and S first.

EXAMPLE 16.8

Enumerate the states in the ($1s$) ($2p$) configuration.

Solution

With the $1s$ orbital and one of the p orbitals, we can construct either a symmetric space factor or an antisymmetric space factor. For example, using the $2p1$ orbital we have

$$\Psi_s = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\psi_{2p1}(2) + \psi_{2p1}(1)\psi_{1s}(2)\right] \tag{16.3-58}$$

and

$$\Psi_{\mathrm{a}} = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\psi_{2p1}(2) - \psi_{2p1}(1)\psi_{1s}(2)\right] \tag{16.3-59}$$

There is only one antisymmetric spin factor, and it must be combined with the symmetric space factor, so the symmetric space factor leads to only one state, with $S = 0$. The three triplet spin factors are all symmetric, so the antisymmetric space factor can combine with any of these, leading to three states, with M_S equal to 1, 0 and -1, but with $S = 1$ for each one. The $2p0$ and the $2p, -1$ orbitals each combine with the $1s$ orbital in exactly the same way as the $2p1$ orbital, to make one symmetric space factor and one antisymmetric space factor. Each corresponds to four states for a total of 12 states.

The space factors of Eqs. (16.3-58) and (16.3-59) both correspond to $M_L = 1$. The analogous factors containing the $2p0$ orbital correspond to $M_L = 0$, and those containing the $2p, -1$ orbital correspond to $M_L = -1$. These three values of M_L correspond to $L = 1$ with no states left over, so that only P terms occur. Each triplet spin factor combines with each one of the three antisymmetric space factors to give the nine states of the ^{3}P term, and the singlet spin factor combines with each one of the symmetric space factors to give the three states of the ^{1}P term.

The states can be counted up more simply by listing all the possible combinations of m_1, m_2, m_{s1}, and m_{s2} that can occur, and then marking off enough states for each possible term. These entries are shown in Table 16.4. The actual states are linear combinations of the wave functions corresponding to the entries in this list, but the number of them is correctly counted. The largest values of M_L and M_S are identified, which must be equal to the largest values of L and S. The states with the appropriate values of M_L and M_S for this term are marked and then the largest remaining values of M_L and M_S are identified and marked off. The process is continued until all states have been assigned to terms. In this case, all states are assigned when the ^{3}P and ^{1}P terms are found.

Exercise 16.19

By explicit operation with $\hat{L}_z = \hat{L}_{z1} + \hat{L}_{z2}$, shows that the eigenvalues of the two space factors in Eq. (16.3-58) and Eq. (16.3-59) both equal $\hbar$, corresponding to $M_L = 1$.

Table 16.4. Terms for the $(1s)(2p)$ Configuration of the He Atom for Example 16.8

Values						Terms	
m_1	m_2	m_{s1}	m_{s2}	M_L	M_S	^{3}P	^{1}P
0	1	+1/2	+1/2	1	1	x	
0	1	+1/2	−1/2	1	0	x	
0	1	−1/2	+1/2	1	0		x
0	1	−1/2	−1/2	1	−1	x	
0	0	+1/2	+1/2	0	1	x	
0	0	+1/2	−1/2	0	0	x	
0	0	−1/2	+1/2	0	0		x
0	0	−1/2	−1/2	0	−1	x	
0	−1	+1/2	+1/2	−1	1	x	
0	−1	+1/2	−1/2	−1	0	x	
0	−1	−1/2	+1/2	−1	0		x
0	−1	−1/2	−1/2	−1	−1	x	

In order to finish characterizing our electronic states, we can give the values of J, the quantum number for the total angular momentum, and M_J, the quantum number for its z component. Since **J** is the sum of **L** and **S**,

$$\hat{J}_z = \hat{L}_z + \hat{S}_z \tag{16.3-60}$$

Therefore,

$$M_J = M_L + M_S \tag{16.3-61}$$

The possible values of J can be deduced by using the rule that for each value of J, the values of M_J range from $+J$ to $-J$. Since the largest value of M_J equals the largest value of M_L plus the largest value of M_S, the largest value of J is

$$J_{\text{max}} = L + S \tag{16.3-62}$$

The smallest value of J is

$$J_{\text{min}} = |L - S| \tag{16.3-63}$$

J must be nonnegative.

***Exercise 16.20**

Tabulate the M_L and M_S values of the 12 states of Example 16.8. Show that the following terms occur:

$$^1\text{P}_1, \quad ^3\text{P}_1, \quad ^3\text{P}_2, \quad ^3\text{P}_0$$

Hint: Use the list of quantum numbers in Table 16.4 and assign values of M_J. The largest value of M_J is equal to the largest value of J. Assign the states to the different values of J in the same way as was done in Example 16.8 with L and S.

16.4

Atoms with More Than Two Electrons

Our discussion of larger atoms will be similar to that of the helium atom, neglecting the electron–electron repulsion. In Chapter 17 we will describe the approximate inclusion of this repulsion.

The Lithium Atom in Zero Order

A lithium atom has three electrons and a nucleus with three protons. The Hamiltonian operator for a lithium atom with stationary nucleus is

$$\begin{aligned}\hat{H} = &-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) \\ &+ \frac{1}{4\pi\varepsilon_0}\left(-\frac{3e^2}{r_1} - \frac{3e^2}{r_2} - \frac{3e^2}{r_3} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}}\right)\end{aligned} \tag{16.4-1}$$

As in the helium atom treatment, the zero-order Hamiltonian omits the electron–electron repulsion terms, giving

$$\hat{H}^{(0)} = \hat{H}_{\text{HL}}(1) + \hat{H}_{\text{HL}}(2) + \hat{H}_{\text{HL}}(3) \tag{16.4-2}$$

where the hydrogenlike Hamiltonians correspond to $Z = 3$. The zero-order approximation always leads to a wave function that is a product of orbitals:

$$\Psi^{(0)} = \psi_1(1)\psi_2(2)\psi_3(3) \tag{16.4-3}$$

The three orbitals are hydrogenlike orbitals with $Z = 3$, so that the zero-order wave function without antisymmetrization but with inclusion of spin is

$$\Psi^{(0)} = \psi_{n_1 l_1 m_1 m_{s1}}(1)\psi_{n_2 l_2 m_2 m_{s2}}(2)\psi_{n_3 l_3 m_3 m_{s3}}(3) \tag{16.4-4}$$

The subscripts on the subscripts indicate the fact that the quantum numbers do not necessarily have the same value for each orbital.

The electronic energy of the atom is the sum of three hydrogenlike energy eigenvalues with $Z = 3$. From Eq. (16.2-19),

$$\begin{aligned} E^{(0)} &= E^{(0)}_{n_1 n_2 n_3} = E_{n_1}(\mathrm{HL}) + E_{n_2}(\mathrm{HL}) + E_{n_3}(\mathrm{HL}) \\ &= -(13.60\,\mathrm{eV})\left(\frac{3^2}{n_1^2} + \frac{3^2}{n_2^2} + \frac{3^2}{n_3^2}\right) \end{aligned} \tag{16.4-5}$$

Exercise 16.21

Carry out the steps to obtain Eqs. (16.4-4) and (16.4-5).

Antisymmetrization

The orbital wave function of Eq. (16.4-4) can be antisymmetrized by including one term corresponding to each possible order of the orbital labels for a fixed order of particle labels. Each term that is generated from the first term by one permutation of a pair of indexes has a negative sign, and each term that is generated by two permutations of pairs of indexes has a positive sign. The antisymmetrized function is

$$\begin{aligned} \Psi = \frac{1}{\sqrt{6}}[&\psi_1(1)\psi_2(2)\psi_3(3) - \psi_2(1)\psi_1(2)\psi_3(3) - \psi_1(1)\psi_3(2)\psi_2(3) \\ &- \psi_3(1)\psi_2(2)\psi_1(3) + \psi_3(1)\psi_1(2)\psi_2(3) + \psi_2(1)\psi_3(2)\psi_1(3)] \end{aligned} \tag{16.4-6}$$

where we abbreviate the quantum numbers by writing 1 instead of n_1, l_1, m_1, m_{s1}, etc.

Exercise 16.22

Show that the function produced by exchanging particle labels 1 and 3 in Eq. (16.4-6) is the negative of the original function. Choose another permutation and show the same thing.

If a spin orbital occurs more than once in each term in the wave function, the wave function vanishes (this is the Pauli exclusion principle).

EXAMPLE 16.9

If orbitals ψ_1 and ψ_3 are the same function, show that the wave function of Eq. (16.4-6) vanishes.

Solution

$$\begin{aligned}\Psi &= \frac{1}{\sqrt{6}}[\psi_1(1)\psi_2(3)\psi_1(3) - \psi_2(1)\psi_1(2)\psi_1(3) - \psi_1(1)\psi_1(2)\psi_2(3)\\ &\quad - \psi_1(1)\psi_2(2)\psi_1(3) + \psi_1(1)\psi_1(2)\psi_2(3) + \psi_2(1)\psi_1(2)\psi_1(3)]\\ &= 0\end{aligned}$$

Exercise 16.23

Show that the wave function of Eq. (16.4-6) is normalized if the orbitals are normalized and orthogonal to each other. The normalization integral is an integral over the coordinates of all three electrons. Each term will factor, but there will be 36 terms. Look for a way to write down the result of integrating each term without having to write all of the integrands, using the orthogonality and normalization of the orbitals.

Slater Determinants

There is another notation that can be used to write the antisymmetrized wave function of Eq. (16.4-6). A **determinant** is a quantity derived from a square matrix by a certain set of multiplications, additions and subtractions. If the elements of the matrix are constants, the determinant is equal to a single constant. If the elements of the matrix are orbitals, the determinant of that matrix is a single function of the coordinates on which the orbitals depend. The wave function of Eq. (16.4-6) is equal to the determinant:

$$\Psi = \frac{1}{\sqrt{6}}\begin{vmatrix} \psi_1(1) & \psi_1(2) & \psi_1(3) \\ \psi_2(1) & \psi_2(2) & \psi_2(3) \\ \psi_3(1) & \psi_3(2) & \psi_3(3) \end{vmatrix} \qquad (16.4\text{-}7)$$

which is called a **Slater determinant**. There is a brief introduction to matrices and determinants in Appendix B.

The Slater determinant is named after John C. Slater, 1900–1976, a prominent American physicist who made various contributions to atomic and molecular quantum theory.

Exercise 16.24

Use the rule of Eq. (B-89) of Appendix B for expanding a three-by-three determinant to show that the function of Eq. (16.4-7) is the same as that of Eq. (16.4-6):

Two properties of determinants presented in Appendix B relate to the properties of antisymmetrized orbital wave functions:

1. If one exchanges two columns or two rows of a determinant, the resulting determinant is the negative of the original determinant. Exchanging the locations of two particles is equivalent to exchanging two columns, so that the Slater determinant exhibits the necessary antisymmetry.

2. If two rows or two columns of a determinant are identical, the determinant vanishes. If two electrons occupy identical spin orbitals, two rows of the determinant in Eq. (16.4-7) are identical, and the determinant vanishes, in agreement with the Pauli exclusion principle.

For the ground state, we must choose three different spin orbitals with the minimum possible sum of orbital energies, since the zero-order energy is equal to the sum of the orbital energies. This practice of choosing the ground-state configuration with the minimum sum of orbital energies is called the **Aufbau principle**, from the German word for "building-up". For the lithium atom, we choose the two $1s$ spin orbitals and one spin orbital from the second shell. In zero order, all of the $2s$ and $2p$ orbitals have the same energy, but we anticipate the fact that higher-order calculations will give a lower energy for the $2s$ subshell than for the $2p$ subshell and choose one of the $2s$ spin orbitals. The zero-order energy of the ground state is, from Eq. (16.2-21),

$$\begin{aligned} E_{\text{gs}}^{(0)} &= E_{1s1s2s}^{(0)} = 2E_1(\text{HL}) + E_2(\text{HL}) \\ &= (-13.60\,\text{eV})\left(2\frac{3^2}{1^2} + \frac{3^2}{2^2}\right) = -275.4\,\text{eV} \end{aligned} \tag{16.4-8}$$

This value is seriously in error, as was the zero-order value for helium. It differs from the experimental value of -203.5 eV by 35%.

The antisymmetrized zero-order wave function can be written

$$\Psi^{(0)} = \frac{1}{\sqrt{6}}\begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(2)\alpha(2) & \psi_{1s}(3)\alpha(3) \\ \psi_{1s}(1)\beta(1) & \psi_{1s}(2)\beta(2) & \psi_{1s}(3)\beta(3) \\ \psi_{2s}(1)\alpha(1) & \psi_{2s}(2)\alpha(2) & \psi_{2s}(3)\alpha(3) \end{vmatrix} \tag{16.4-9}$$

The $2s$-spin-down orbital could have been chosen instead of the $2s$-spin-up orbital. We therefore have two states of equal energy instead of a single ground state. This doubly degenerate ground level corresponds to $S = 1/2$ (a doublet term), since the possible values of M_S are $+1/2$ and $-1/2$. Since $M_L = 0$, the value of L is 0, the only value of J is 1/2, and the ground term symbol of lithium is ${}^2S_{1/2}$.

Excited states of the lithium atom can correspond to various choices of orbitals. The values of M_L and M_S for these excited states can be calculated by algebraic addition. Using the rules that M_L ranges from $+L$ to $-L$ and that M_S ranges from $+S$ to $-S$, one can deduce the values of L and S that occur and can assign term symbols. Higher-order calculations must be used to determine the order of the energies of the excited states.

Exercise 16.25

Consider the excited-state configuration $(1s)(2s)(3s)$ for a lithium atom.

a. Show that quartet states with $S = 3/2$ can occur.

***b.** Write the term symbols for all terms that occur.

***c.** Find the zero-order energy eigenvalue for this configuration.

Atoms with More Than Three Electrons

The treatment of the other atoms in zero order is similar to the helium and lithium treatments. For an atom with atomic number Z (Z protons in the nucleus and Z electrons), the stationary-nucleus Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{Z}\nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0}\sum_{i=1}^{Z}\frac{1}{r_i} + \frac{e^2}{4\pi\varepsilon_0}\sum_{i=2}^{Z}\sum_{j=1}^{i-1}\frac{1}{r_{ij}} \tag{16.4-10}$$

where r_i is the distance from the nucleus to the ith electron and r_{ij} is the distance from the ith electron to the jth electron.

The first two sums in Eq. (16.4-10) are a sum of hydrogenlike one-electron Hamiltonian operators, and the double sum is a sum of terms like those that we have neglected with helium and lithium. The zero-order Hamiltonian operator is sum of hydrogenlike Hamiltonians (with those terms neglected):

$$\hat{H}^{(0)} = \sum_{i=1}^{Z} \hat{H}_{\mathrm{HL}}(i) \tag{16.4-11}$$

The time-dependent Schrödinger equation corresponding to this Hamiltonian can be solved by separation of variables, using the trial function

$$\Psi^{(0)} = \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\cdots\psi_Z(Z) = \prod_{i=1}^{Z} \psi_i(i) \tag{16.4-12}$$

where the symbol $\prod$ stands for a product of factors, just as the $\sum$ symbol stands for a sum of terms. Since the terms in the zero-order Hamiltonian are hydrogenlike Hamiltonians, the factors $\psi_1(1), \psi_2(2), \psi_3(3)$, etc. are all hydrogenlike orbitals and the energy eigenvalue is a sum of hydrogenlike orbital energies:

$$\psi_i(i) = \psi_{n_i l_i m_i m_{si}}(i) \tag{16.4-13}$$

$$E^{(0)} = E_{n_1}(\mathrm{HL}) + E_{n_2}(\mathrm{HL}) + \cdots = \sum_{i=1}^{Z} E_{n_i}(\mathrm{HL}) \tag{16.4-14}$$

where n_i, l_i, etc., are values of the quantum numbers for hydrogenlike orbitals. Just as with the helium and lithium atoms, the zero-order wave functions and energies of Eqs. (16.4-13) and (16.4-14) are very poor approximations.

We must antisymmetrize the orbital wave function of Eq. (16.4-12). This can be done by writing a Slater determinant with one row for each spin orbital and one column for each electron:

$$\Psi = \frac{1}{\sqrt{Z!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \psi_1(3) & \psi_1(4) & \cdots & \psi_1(Z) \\ \psi_2(1) & \psi_2(2) & \psi_2(3) & \psi_2(4) & \cdots & \psi_2(Z) \\ \psi_3(1) & \psi_3(2) & \psi_3(3) & \psi_3(4) & \cdots & \psi_3(Z) \\ \psi_4(1) & \psi_4(2) & \psi_4(3) & \psi_4(4) & \cdots & \psi_4(Z) \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \psi_Z(1) & \psi_Z(2) & \psi_Z(3) & \psi_Z(4) & \cdots & \psi_Z(Z) \end{vmatrix} \tag{16.4-15}$$

where the $1/\sqrt{Z!}$ factor normalizes the wave function, assuming that all orbitals are normalized and orthogonal to each other, and where we have abbreviated the quantum numbers. The Pauli exclusion principle must be followed. No two spin orbitals can be the same, or two rows of the determinant would be identical, causing the wave function to vanish.

The values of M_L, M_S, L, and S can be computed in the same way as with the helium and lithium atoms. The computation can be simplified by noting that the contributions to M_L and M_S for any completely filled subshell vanish. For example, the only term symbol that occurs for the ground state of an inert gas (He, Ne, Ar, etc.) is ^1S. Since the hydrogenlike orbitals in the same shell all have the same energy, many of the terms are degenerate in zero order, but will have different energies when better approximations are used.

In the next chapter, we will discuss approximations beyond the zero-order approximation that will give better values of atomic energies. We will usually use the orbital approximation. We will find that the orbitals in different subshells in the same shell do not correspond to the same energy, and will use the facts about the orbital energies to understand the periodic chart of the elements.

Summary of the Chapter

The time-independent Schrödinger equation for a general two-particle central-force system was separated into a one-particle Schrödinger equation for the motion of the center of mass of the two particles, and a one-particle Schrödinger equation for the motion of one particle relative to the other.

The Schrödinger equation for the relative motion was solved by separation of variables in spherical polar coordinates, assuming the trial function

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi)$$

The angular functions $Y_{lm}(\theta, \phi)$ are a set of functions called spherical harmonic functions. These functions are also eigenfunctions of the operator for the square of the orbital angular momentum and its z component, with eigenvalues given by

$$\hat{L}^2 Y_{lm} = \hbar l(l+1) Y_{lm}$$

and

$$\hat{L}_z Y_{lm} = \hbar m Y_{lm}$$

The solution to the equation for the radial factor $R(r)$ was presented for the hydrogen atom, giving a set of wave functions with two quantum numbers: n, the principal quantum number, and l, the same quantum number as in the spherical harmonic functions. The hydrogenlike atom was defined, with a single electron, but with Z protons in the nucleus. The energy eigenvalues of the hydrogenlike atom depend only on the principal quantum number:

$$E = E_n = -\frac{(13.60\,\text{eV})Z^2}{n^2}$$

where Z was the number of protons in the nucleus.

An intrinsic electronic angular momentum of the electron was introduced. This angular momentum corresponds to a spinning motion of the electron in addition to its orbital motion. It corresponds to fixed magnitude and two possible z projections, $\hbar/2$ and $-\hbar/2$.

In the "zero-order" approximation, the repulsions between electrons were neglected. The energy eigenfunctions of the helium atom were products of one hydrogenlike orbital for each electron. These orbital wave functions were antisymmetrized to conform to the physical indistinguishability of the electrons, producing the Pauli exclusion principle, which states that no two electrons can occupy the same orbital in any orbital wave function. Similar wave functions were discussed for multielectron atoms. By utilizing the Pauli exclusion principle, possible electron configurations and term symbols can be computed.