8

Quantum Mechanics in Three Dimensions

Chapter Outline

So far we have shown how quantum mechanics can be used to describe motion in one dimension. Although the one-dimensional case illustrates such basic features of systems as the quantization of energy, we need a full three-dimensional treatment for the applications to atomic, solid-state, and nuclear physics that we will meet in later chapters. In this chapter we extend the concepts of quantum mechanics from one to three dimensions and explore the predictions of the theory for the simplest of real systems—the hydrogen atom.

With the introduction of new degrees of freedom (and the additional coordinates needed to describe them) comes a disproportionate increase in the level of mathematical difficulty. To guide our inquiry, we shall rely on classical insights to help us identify the observables that are likely candidates for quantization. These must come from the ranks of the so-called *sharp observables* and, with few exceptions, are the same as the constants of the classical motion.

8.1 PARTICLE IN A THREE-DIMENSIONAL BOX

Let us explore the workings of wave mechanics in three dimensions through the example of a particle confined to a cubic "box." The box has edge length L and occupies the region $0 < x, y, z < L$, as shown in Figure 8.1. We assume the walls of the box are *smooth,* so they exert forces only perpendicular to the surface, and that collisions with the walls are elastic. A classical particle would

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rattle around inside such a box, colliding with the walls. At each collision, the component of particle momentum normal to the wall is reversed (changes sign), while the other two components of momentum are unaffected (Fig. 8.2). Thus, the collisions preserve the magnitude of each momentum component, in addition to the total particle energy. These four quantities—$|p_x|$, $|p_y|$, $|p_z|$, and E—then, are constants of the classical motion, and it should be possible to find quantum states for which all of them are sharp.[1]

The wavefunction Ψ in three dimensions is a function of **r** and *t*. Again the magnitude of Ψ determines the probability density $P(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2$, which is now a *probability per unit volume*. Multiplication by the volume element $dV(= dx\ dy\ dz)$ gives the probability of finding the particle within the volume element dV at the point **r** at time *t*.

Since our particle is confined to the box, the wavefunction Ψ must be zero at the walls and outside. The wavefunction inside the box is found from Schrödinger's equation,

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + U(\mathbf{r})\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{8.1}$$

We see that $\partial^2/\partial x^2$ in the one-dimensional case is replaced in three dimensions by the **Laplacian,**

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{8.2}$$

where $U(\mathbf{r})$ is still the potential energy but is now a function of all the space coordinates: $U(\mathbf{r}) = U(x, y, z)$. Indeed, the Laplacian together with its multiplying constant is just the kinetic energy operator of Table 6.2 extended to include the contributions to kinetic energy from motion in each of three mutually perpendicular directions:

$$-\frac{\hbar^2}{2m}\nabla^2 = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right) + \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\right) + \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\right)$$
$$= [K_x] + [K_y] + [K_z] \tag{8.3}$$

This form is consistent with our belief that the Cartesian axes identify independent but logically equivalent directions in space. With this identification of the kinetic energy operator in three dimensions, the left-hand side of Equation 8.1 is again the Hamiltonian operator $[H]$ applied to Ψ, and the right-hand side is the energy operator $[E]$ applied to Ψ (see Section 6.8). As it does in one dimension, Schrödinger's equation asserts the equivalence of these two operators when applied to the wavefunction of any physical system.

Stationary states are those for which all probabilities are constant in time, and are given by solutions to Schrödinger's equation in the separable form,

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[1]Recall from Section 6.7 that sharp observables are those for which there is no statistical distribution of measured values. Indeed, quantum wavefunctions typically are labeled by the sharp observables for that state. (For example, the oscillator states of Section 6.6 are indexed by the quantum number *n*, which specifies the sharp value of particle energy *E*. In this case, the sharp values of energy also are *quantized,* that is, limited to the discrete values $(n + \frac{1}{2})\hbar\omega$. It follows that any sharp observable is constant over time (unless the corresponding operator explicitly involves time). The converse—that quantum states exist for which all constants of the classical motion are sharp—is not always true but occurs frequently enough that it can serve as a useful rule of thumb.
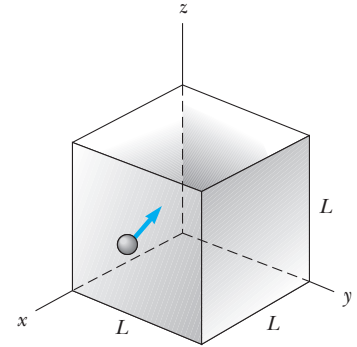

Figure 8.1 A particle confined to move in a cubic box of sides *L*. Inside the box $U = 0$. The potential energy is infinite at the walls and outside the box.

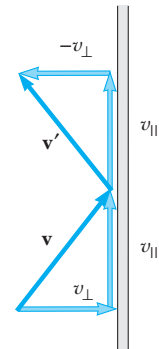**Schrödinger equation in three dimensions**

Figure 8.2 Change in particle velocity (or momentum) during collision with a wall of the box. For elastic collision with a smooth wall, the component normal to the wall is reversed, but the tangential components are unaffected.

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\, e^{-i\omega t} \tag{8.4}$$

With this time dependence, the right-hand side of Equation 8.1 reduces to $\hbar\omega\Psi$, leaving $\psi(\mathbf{r})$ to satisfy the **time-independent Schrödinger equation** for a particle whose energy is $E = \hbar\omega$:

The time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\,\nabla^2\psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{8.5}$$

Since our particle is free inside the box, we take the potential energy $U(\mathbf{r}) = 0$ for $0 < x, y, z < L$. In this case the spatial wavefunction also is separable; that is, solutions to Equation 8.5 with $U(\mathbf{r}) = 0$ can be found in product form:

$$\psi(\mathbf{r}) = \psi(x, y, z) = \psi_1(x)\psi_2(y)\psi_3(z) \tag{8.6}$$

Substituting Equation 8.6 into Equation 8.5 and dividing every term by the function $\psi(x, y, z)$ gives (for $U(\mathbf{r}) = 0$)

$$-\frac{\hbar^2}{2m\psi_1}\frac{d^2\psi_1}{dx^2} - \frac{\hbar^2}{2m\psi_2}\frac{d^2\psi_2}{dy^2} - \frac{\hbar^2}{2m\psi_3}\frac{d^2\psi_3}{dz^2} = E$$

In this form the independent variables are isolated: the first term on the left depends only on x, the second only on y, and the third only on z. To satisfy the equation *everywhere* inside the cube, each of these terms must reduce to a constant:

$$-\frac{\hbar^2}{2m\psi_1}\frac{d^2\psi_1}{dx^2} = E_1$$

$$-\frac{\hbar^2}{2m\psi_2}\frac{d^2\psi_2}{dy^2} = E_2 \tag{8.7}$$

$$-\frac{\hbar^2}{2m\psi_3}\frac{d^2\psi_3}{dz^2} = E_3$$

The stationary states for a particle confined to a cube are obtained from these three separate equations. The energies E_1, E_2, and E_3 are **separation constants** and represent the energy of motion along the three Cartesian axes x, y, and z. Consistent with this identification, the Schrödinger equation requires that $E_1 + E_2 + E_3 = E$.

The first of Equations 8.7 is the same as that for the infinite square well in one dimension. Independent solutions to this equation are $\sin k_1 x$ and $\cos k_1 x$, where $k_1 = \sqrt{2mE_1/\hbar^2}$ is the wavenumber of oscillation. Only $\sin k_1 x$ satisfies the condition that the wavefunction must vanish at the wall $x = 0$, however. Requiring the wavefunction to vanish also at the opposite wall $x = L$ implies $k_1 L = n_1\pi$, where n_1 is any positive integer. In other words, we must be able to fit an integral number of half-wavelengths into our box along the direction marked by x. It follows that the magnitude of particle momentum along this direction must be one of the special values

$$|p_x| = \hbar k_1 = n_1\frac{\pi\hbar}{L} \qquad n_1 = 1, 2, \ldots$$

Identical considerations applied to the remaining two equations show that the magnitudes of particle momentum in all three directions are similarly

quantized:

$$|p_x| = \hbar k_1 = n_1 \frac{\pi \hbar}{L} \qquad n_1 = 1, 2, \ldots$$

$$|p_y| = \hbar k_2 = n_2 \frac{\pi \hbar}{L} \qquad n_2 = 1, 2, \ldots \qquad (8.8)$$

$$|p_z| = \hbar k_3 = n_3 \frac{\pi \hbar}{L} \qquad n_3 = 1, 2, \ldots$$

Allowed values of momentum components for a particle in a box

Notice that $n_i = 0$ is not allowed, since that choice leads to a ψ_i that is also zero and a wavefunction $\psi(\mathbf{r})$ that vanishes everywhere. Since the momenta are restricted this way, the particle energy (all kinetic) is limited to the following discrete values:

$$E = \frac{1}{2m}(|p_x|^2 + |p_y|^2 + |p_z|^2) = \frac{\pi^2 \hbar^2}{2mL^2}\{n_1^2 + n_2^2 + n_3^2\} \qquad (8.9)$$

Discrete energies allowed for a particle in a box

Thus, confining the particle to the cube serves to quantize its momentum and energy according to Equations 8.8 and 8.9. Note that **three quantum numbers are needed to specify the quantum condition, corresponding to the three independent degrees of freedom for a particle in space.** These quantum numbers specify the values taken by the sharp observables for this system.

Collecting the previous results, we see that the stationary states for this particle are

$$\Psi(x, y, z, t) = A \sin(k_1 x)\sin(k_2 y)\sin(k_3 z)e^{-i\omega t} \qquad \text{for } 0 < x, y, z < L$$
$$= 0 \qquad \text{otherwise} \qquad (8.10)$$

The multiplier A is chosen to satisfy the normalization requirement. Example 8.1 shows that $A = (2/L)^{3/2}$ for the ground state, and this result continues to hold for the excited states as well.

EXAMPLE 8.1   Normalizing the Box Wavefunctions

Find the value of the multiplier A that normalizes the wavefunction of Equation 8.10 having the lowest energy.

Solution   The state of lowest energy is described by $n_1 = n_2 = n_3 = 1$, or $k_1 = k_2 = k_3 = \pi/L$. Since Ψ is nonzero only for $0 < x, y, z < L$, the probability density integrated over the volume of this cube must be unity:

$$1 = \int_0^L dx \int_0^L dy \int_0^L dz\, |\Psi(x, y, z, t)|^2$$

$$= A^2 \left\{\int_0^L \sin^2(\pi x/L)\, dx\right\}\left\{\int_0^L \sin^2(\pi y/L)\, dy\right\}$$

$$\times \left\{\int_0^L \sin^2(\pi z/L)\, dz\right\}$$

Using $2\sin^2\theta = 1 - \cos 2\theta$ gives

$$\int_0^L \sin^2(\pi x/L)\, dx = \frac{L}{2} - \frac{L}{4\pi}\sin(2\pi x/L)\Big|_0^L = \frac{L}{2}$$

The same result is obtained for the integrations over y and z. Thus, normalization requires

$$1 = A^2\left(\frac{L}{2}\right)^3$$

or

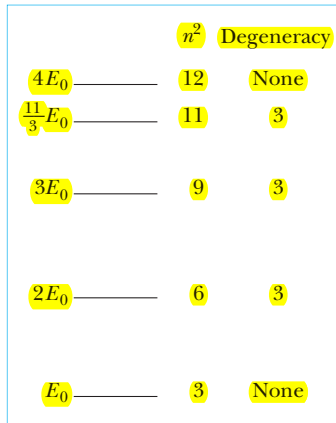$$A = \left(\frac{2}{L}\right)^{3/2}$$

Figure 8.3 An energy-level diagram for a particle confined to a cubic box. The ground-state energy is $E_0 = 3\pi^2\hbar^2/2mL^2$, and $n^2 = n_1^2 + n_2^2 + n_3^2$. Note that most of the levels are degenerate.

Exercise 1 With what probability will the particle described by the wavefunction of Example 8.1 be found in the volume $0 < x, y, z < L/4$?

Answer   0.040, or about 4%

Exercise 2 Modeling a defect trap in a crystal as a three-dimensional box with edge length 5.00 Å, find the values of momentum and energy for an electron bound to the defect site, assuming the electron is in the ground state.

Answer $|p_x| = |p_y| = |p_z| = 1.24$ keV/c; $E = 4.51$ eV

The ground state, for which $n_1 = n_2 = n_3 = 1$, has energy

$$E_{111} = \frac{3\pi^2\hbar^2}{2mL^2}$$

There are *three* first excited states, corresponding to the three different combinations of n_1, n_2, and n_3, whose squares sum to 6. That is, we obtain the same energy for the three combinations $n_1 = 2$, $n_2 = 1$, $n_3 = 1$, or $n_1 = 1$, $n_2 = 2$, $n_3 = 1$, or $n_1 = 1$, $n_2 = 1$, $n_3 = 2$. The first excited state has energy

$$E_{211} = E_{121} = E_{112} = \frac{6\pi^2\hbar^2}{2mL^2}$$

Note that each of the first excited states is characterized by a different wavefunction: ψ_{211} has wavelength L along the x-axis and wavelength $2L$ along the y- and z-axes, but for ψ_{121} and ψ_{112} the shortest wavelength is along the y-axis and the z-axis, respectively.

Whenever different states have the same energy, this energy level is said to be **degenerate.** In the example just described, the first excited level is three-fold (or triply) degenerate. This system has degenerate levels because of the high degree of symmetry associated with the cubic shape of the box. The degeneracy would be removed, or *lifted*, if the sides of the box were of unequal lengths (see Example 8.3). In fact, the extent of splitting of the originally degenerate levels increases with the degree of asymmetry.

Figure 8.3 is an energy-level diagram showing the first five levels of a particle in a cubic box; Table 8.1 lists the quantum numbers and degeneracies of the various levels. Computer-generated plots of the probability density $|\psi(x, y, z)|^2$ for the ground state and first excited states of a particle in a box are shown in Figure 8.4. Notice that the probabilities for the (degenerate) first excited states differ only in their orientation with respect to the coordinate axes, again a reflection of the cubic symmetry imposed by the box potential.

EXAMPLE 8.2   The Second Excited State

Determine the wavefunctions and energy for the second excited level of a particle in a cubic box of edge L. What is the degeneracy of this level?

Solution   The second excited level corresponds to the three combinations of quantum numbers $n_1 = 2$, $n_2 = 2$, $n_3 = 1$ or $n_1 = 2$, $n_2 = 1$, $n_3 = 2$ or $n_1 = 1$, $n_2 = 2$, $n_3 = 2$. The corresponding wavefunctions inside the box are

$$\Psi_{221} = A \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)e^{-iE_{221}t/\hbar}$$

$$\Psi_{212} = A \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{2\pi z}{L}\right)e^{-iE_{212}t/\hbar}$$

$$\Psi_{122} = A \sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right)\sin\left(\frac{2\pi z}{L}\right)e^{-iE_{122}t/\hbar}$$

The level is threefold degenerate, since each of these wavefunctions has the same energy,

$$E_{221} = E_{212} = E_{122} = \frac{9\pi^2\hbar^2}{2mL^2}$$

Table 8.1   Quantum Numbers and Degeneracies of the Energy Levels for a Particle Confined to a Cubic Box*

n_1	n_2	n_3	n^2	Degeneracy
1	1	1	3	None
1	1	2	6	
1	2	1	6	Threefold
2	1	1	6	
1	2	2	9	
2	1	2	9	Threefold
2	2	1	9	
1	1	3	11	
1	3	1	11	Threefold
3	1	1	11	
2	2	2	12	None

*Note: $n^2 = n_1^2 + n_2^2 + n_3^2$.

(a)   (b)   (c)
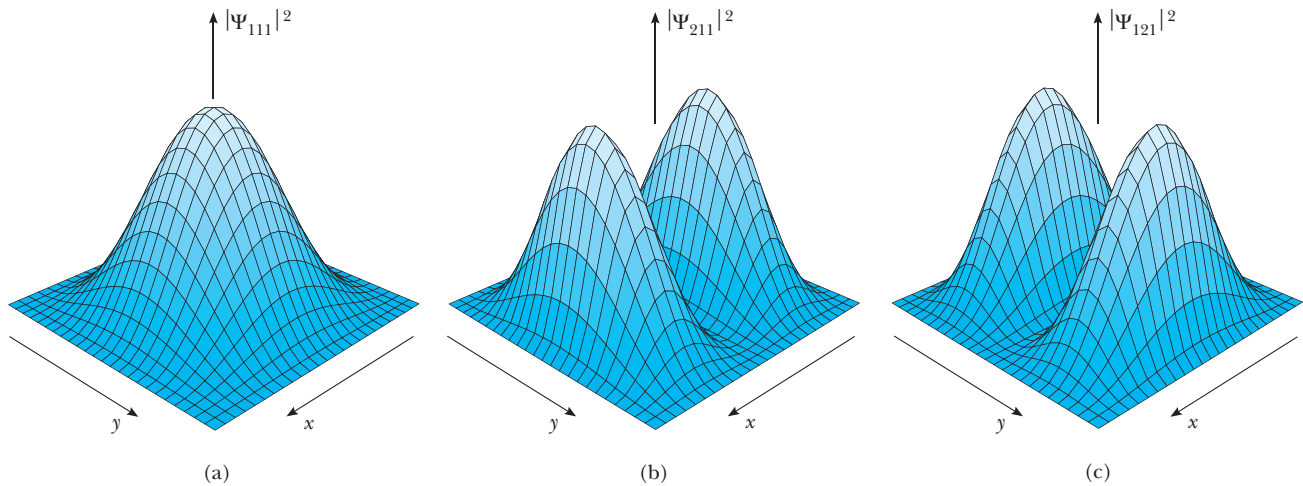
Figure 8.4   Probability density (unnormalized) for a particle in a box: (a) ground state, $|\Psi_{111}|^2$; (b) and (c) first excited states, $|\Psi_{211}|^2$ and $|\Psi_{121}|^2$. Plots are for $|\Psi|^2$ in the plane $z = \frac{1}{2}L$. In this plane, $|\Psi_{112}|^2$ (not shown) is indistinguishable from $|\Psi_{111}|^2$.

EXAMPLE 8.3 **Quantization in a Rectangular Box**

Obtain a formula for the allowed energies of a particle confined to a rectangular box with edge lengths L_1, L_2, and L_3. What is the degeneracy of the first excited state?

Solution For a box having edge length L_1 in the x direction, ψ will be zero at the walls if L_1 is an integral number of half-wavelengths. Thus, the magnitude of particle momentum in this direction is quantized as

$$|p_x| = \hbar k_1 = n_1 \frac{\pi\hbar}{L_1} \qquad n_1 = 1, 2, \ldots$$

Likewise, for the other two directions, we have

$$|p_y| = \hbar k_2 = n_2 \frac{\pi\hbar}{L_2} \qquad n_2 = 1, 2, \ldots$$

$$|p_z| = \hbar k_3 = n_3 \frac{\pi\hbar}{L_3} \qquad n_3 = 1, 2, \ldots$$

The allowed energies are

$$E = (|p_x|^2 + |p_y|^2 + |p_z|^2)/2m$$
$$= \frac{\pi^2\hbar^2}{2m}\left\{\left(\frac{n_1}{L_1}\right)^2 + \left(\frac{n_2}{L_2}\right)^2 + \left(\frac{n_3}{L_3}\right)^2\right\}$$

The lowest energy occurs again for $n_1 = n_2 = n_3 = 1$. Increasing one of the integers by 1 gives the next-lowest, or first, excited level. If L_1 is the largest dimension, then $n_1 = 2$, $n_2 = 1$, $n_3 = 1$ produces the smallest energy increment and describes the first excited state. Further, so long as both L_2 and L_3 are not equal to L_1, the first excited level is nondegenerate, that is, there is no other state with this energy. If L_2 or L_3 equals L_1, the level is doubly degenerate; if all three are equal, the level will be triply degenerate. Thus, the higher the symmetry, the more degeneracy we find.

8.2 CENTRAL FORCES AND ANGULAR MOMENTUM

The formulation of quantum mechanics in Cartesian coordinates is the natural way to generalize from one to higher dimensions, but often it is not the best suited to a given application. For instance, an atomic electron is attracted to the nucleus of the atom by the Coulomb force between opposite charges. This is an example of a **central force,** that is, one directed toward a fixed point. The nucleus is the center of force, and the coordinates of choice here are spherical coordinates r, θ, ϕ centered on the nucleus (Fig. 8.5). If the central force is conservative, the particle energy (kinetic plus potential) stays
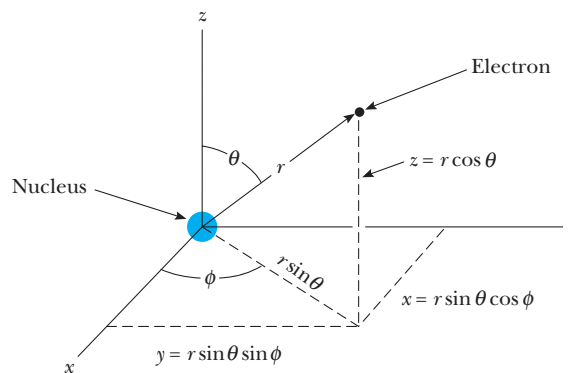

Figure 8.5 The central force on an atomic electron is one directed toward a fixed point, the nucleus. The coordinates of choice here are the spherical coordinates r, θ, ϕ centered on the nucleus.

constant and E becomes a candidate for quantization. In that case, the quantum states are stationary waves $\psi(\mathbf{r})\,e^{-i\omega t}$, with $\omega = E/\hbar$, where E is the sharp value of particle energy.

But for central forces, angular momentum $\mathbf{L}$ about the force center also is constant (a central force exerts no torque about the force center), and we might expect that wavefunctions can be found for which all three angular momentum components take sharp values. This imposes severe constraints on the form of the wavefunction. In fact, these constraints are so severe that it is impossible to find a wavefunction satisfying all of them at once; that is, not all components of angular momentum can be known simultaneously!

The dilemma is reminiscent of our inability to specify simultaneously the position and momentum of a particle. Indeed, if the direction of $\mathbf{L}$ were known precisely, the particle would be confined to the orbital plane (the plane perpendicular to the vector $\mathbf{L}$), and its coordinate in the direction normal to this plane would be accurately known (and unchanging) (Fig. 8.6). In that case, however, the particle could have no momentum out of the orbital plane, so that its linear momentum perpendicular to this plane also would be known (to be zero), in violation of the uncertainty principle. The argument just given may be refined to establish an uncertainty principle for angular momentum: **it is impossible to specify simultaneously any two components of angular momentum.** Alternatively, if one component of $\mathbf{L}$ is sharp, then the remaining two must be "fuzzy."[2]

Along with E and one component of $\mathbf{L}$, then, what else might be quantized, or sharp, for central forces? The answer is contained in the following observation: With only one component of $\mathbf{L}$ sharp, there is no redundancy in having the magnitude $|\mathbf{L}|$ sharp also. In this way, E, $|\mathbf{L}|$, and one component of $\mathbf{L}$, say L_z, become the sharp observables subject to quantization in the central force problem.

Wavefunctions for which $|\mathbf{L}|$ and L_z are both sharp follow directly from separating the variables in Schrödinger's equation for a central force. We take the time-independent wavefunction in spherical coordinates r, θ, ϕ to be the product

$$\psi(\mathbf{r}) = \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \tag{8.11}$$

and write Schrödinger's time-independent equation (Eq. 8.5) in these coordinates using the spherical coordinate form for the Laplacian[3]:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \left(\frac{2}{r}\right)\frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\,\frac{\partial}{\partial\theta} + \csc^2\theta\,\frac{\partial^2}{\partial\phi^2}\right]$$

Figure 8.6 The angular momentum $\mathbf{L}$ of an orbiting particle is perpendicular to the plane of the orbit. If the direction of $\mathbf{L}$ were known precisely, both the coordinate and momentum in the direction perpendicular to the orbit would be known, in violation of the uncertainty principle.

Uncertainty principle for angular momentum

Separation of variables for the stationary state wavefunction

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[2]Angular momentum is a notable exception to the argument that constants of the classical motion correspond to sharp observables in quantum mechanics. The failure is rooted in another maxim—the uncertainty principle—that takes precedence. The only instance in which two or more angular momentum components may be known exactly is the trivial case $L_x = L_y = L_z = 0$.

[3]The Laplacian in spherical coordinates is given in any more advanced scientific text or may be constructed from the Cartesian form by following the arguments of Section 8.4.
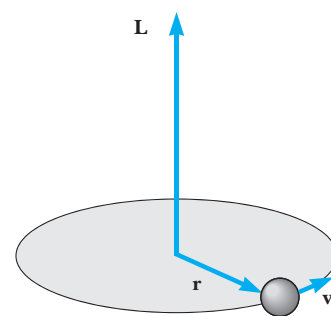
After dividing each term in Equation 8.5 by $R\Theta\Phi$, we are left with

$$\frac{-\hbar^2}{2mR}\left[\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right] - \frac{\hbar^2}{2m\Theta}\frac{1}{r^2}\left[\frac{d^2\Theta}{d\theta^2} + \cot\theta\,\frac{d\Theta}{d\theta}\right]$$

$$-\frac{\hbar^2}{2m\Phi}\frac{1}{r^2\sin^2\theta}\frac{d^2\Phi}{d\phi^2} + U(r) = E$$

Notice that ordinary derivatives now replace the partials and that $U(\mathbf{r})$ becomes simply $U(r)$ for a central force seated at the origin. We can isolate the dependence on ϕ by multiplying every term by $r^2\sin^2\theta$ to get, after some rearrangement,

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -\sin^2\theta\left\{\frac{r^2}{R}\left[\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right] + \frac{1}{\Theta}\left[\frac{d^2\Theta}{d\theta^2} + \cot\theta\,\frac{d\Theta}{d\theta}\right]\right.$$

$$\left. + \frac{2mr^2}{\hbar^2}[E - U(r)]\right\} \quad (8.12)$$

In this form the left side is a function only of ϕ while the right side depends only on r and θ. Because these are independent variables, equality of the two sides requires that each side reduce to a constant. Following convention, we write this separation constant as $-m_\ell^2$, where m_ℓ is the **magnetic quantum number.**[4]

Equating the left side of Equation 8.12 to $-m_\ell^2$ gives an equation for $\Phi(\phi)$:

$$\frac{d^2\Phi}{d\phi^2} = -m_\ell^2\Phi(\phi) \quad (8.13)$$

A solution to Equation 8.13 is $\Phi(\phi) = \exp(im_\ell\phi)$; this is periodic with period 2π if m_ℓ is restricted to integer values. Periodicity is necessary here because all physical properties that derive from the wavefunction should be unaffected by the replacement $\phi \to \phi + 2\pi$, both of which describe the same point in space (see Fig. 8.5).

Equating the right side of Equation 8.12 to $-m_\ell^2$ gives, after some further rearrangement,

$$\frac{r^2}{R}\left[\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right] + \frac{2mr^2}{\hbar^2}[E - U(r)] = -\frac{1}{\Theta}\left[\frac{d^2\Theta}{d\theta^2} + \cot\theta\,\frac{d\Theta}{d\theta}\right]$$

$$+ \frac{m_\ell^2}{\sin^2\theta} \quad (8.14)$$

In this form the variables r and θ are separated, the left side being a function only of r and the right side a function only of θ. Again, each side must reduce to a constant. This furnishes two more equations, one for each of the remaining functions $R(r)$ and $\Theta(\theta)$, and introduces a second separation

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[4]This seemingly peculiar way of writing the constant multiplier is based on the physical significance of the function $\Phi(\phi)$ and is discussed at length in (optional) Section 8.4. The student is referred there for a concise treatment of the quantum central force problem based on the operator methods of Section 6.8.

constant, which we write as $\ell(\ell + 1)$. Equating the right side of Equation 8.14 to $\ell(\ell + 1)$ requires $\Theta(\theta)$ to satisfy

$$\frac{d^2\Theta}{d\theta^2} + \cot\theta\,\frac{d\Theta}{d\theta} - m_\ell^2\,\csc^2\theta\,\Theta(\theta) = -\ell(\ell+1)\Theta(\theta) \qquad (8.15)$$

ℓ is called the **orbital quantum number.** For $\psi(\mathbf{r})$ to be an acceptable wavefunction, $\Theta(\theta)$ also must be bounded and single-valued, conditions which are met for functions satisfying Equation 8.15 only if ℓ is a nonnegative integer, and then only if m_ℓ is limited to absolute values not larger than ℓ. The resulting solutions $\Theta(\theta)$ are polynomials in $\cos\theta$ known as **associated Legendre polynomials.** A few of these polynomials are listed in Table 8.2 for easy reference. The products $\Theta(\theta)\Phi(\phi)$ specify the full angular dependence of the central force wavefunction and are known as **spherical harmonics,** denoted by $Y_\ell^{m_\ell}(\theta, \phi)$. Some spherical harmonics are given in Table 8.3. The constant prefactors are chosen to normalize these functions.[5]

Table 8.2   Some Associated Legendre Polynomials $P_\ell^{m_\ell}(\cos\theta)$

$P_0^0 = 1$
$P_1^0 = 2\cos\theta$
$P_1^1 = \sin\theta$
$P_2^0 = 4(3\cos^2\theta - 1)$
$P_2^1 = 4\sin\theta\cos\theta$
$P_2^2 = \sin^2\theta$
$P_3^0 = 24(5\cos^3\theta - 3\cos\theta)$
$P_3^1 = 6\sin\theta(5\cos^2\theta - 1)$
$P_3^2 = 6\sin^2\theta\cos\theta$
$P_3^3 = \sin^3\theta$

Table 8.3   The Spherical Harmonics $Y_\ell^{m_\ell}(\theta, \phi)$

$$Y_0^0 = \frac{1}{2\sqrt{\pi}}$$

$$Y_1^0 = \tfrac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\cos\theta$$

$$Y_1^{\pm1} = \mp\tfrac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\sin\theta\cdot e^{\pm i\phi}$$

$$Y_2^0 = \tfrac{1}{4}\sqrt{\frac{5}{\pi}}\cdot(3\cos^2\theta - 1)$$

$$Y_2^{\pm1} = \mp\tfrac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\sin\theta\cdot\cos\theta\cdot e^{\pm i\phi}$$

$$Y_2^{\pm2} = \tfrac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\sin^2\theta\cdot e^{\pm 2i\phi}$$

$$Y_3^0 = \tfrac{1}{4}\sqrt{\frac{7}{\pi}}\cdot(5\cos^3\theta - 3\cos\theta)$$

$$Y_3^{\pm1} = \mp\tfrac{1}{8}\sqrt{\frac{21}{\pi}}\cdot\sin\theta\cdot(5\cos^2\theta - 1)\cdot e^{\pm i\phi}$$

$$Y_3^{\pm2} = \tfrac{1}{4}\sqrt{\frac{105}{2\pi}}\cdot\sin^2\theta\cdot\cos\theta\cdot e^{\pm 2i\phi}$$

$$Y_3^{\pm3} = \mp\tfrac{1}{8}\sqrt{\frac{35}{\pi}}\cdot\sin^3\theta\cdot e^{\pm 3i\phi}$$

[5]The normalization is such that the integral of $|Y_\ell^{m_\ell}|^2$ over the surface of a sphere with unit radius is 1.

In keeping with our earlier remarks, the separation constants $\ell(\ell + 1)$ and m_ℓ should relate to the sharp observables $|\mathbf{L}|$, L_z, and E for central forces. The connection is established by the more detailed arguments of Section 8.4, with the result

Angular momentum and its *z* component are quantized

$$|\mathbf{L}| = \sqrt{\ell(\ell + 1)}\,\hbar \qquad \ell = 0, 1, 2, \ldots$$

$$L_z = m_\ell \hbar \qquad m_\ell = 0, \pm 1, \pm 2, \ldots, \pm\ell \qquad (8.16)$$

We see that the limitation on the magnetic quantum number m_ℓ to values between $-\ell$ and $+\ell$, obtained on purely mathematical grounds from separating variables, has an obvious physical interpretation: the z component of angular momentum, L_z, must never exceed the magnitude of the vector, $|\mathbf{L}|$! Notice, too, that ℓ and m_ℓ are quantum numbers for angular momentum only; their connection with particle energy E must depend on the potential energy function $U(r)$ and is prescribed along with the radial wavefunction $R(r)$ in the final stage of the separation procedure.

To obtain $R(r)$, we return to Equation 8.14 and equate the left side to $\ell(\ell + 1)$. Rearranging terms once more, we find that $R(r)$ must satisfy

Radial wave equation

$$-\frac{\hbar^2}{2m}\left[\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right] + \frac{\ell(\ell + 1)\hbar^2}{2mr^2}R(r) + U(r)R(r) = ER(r) \qquad (8.17)$$

This is the **radial wave equation;** it determines the radial part of the wavefunction ψ and the allowed particle energies E. As the equation contains the orbital quantum number ℓ, each angular momentum orbital is expected to give rise to a different radial wave and a distinct energy. By contrast, the magnetic quantum number m_ℓ appears nowhere in this equation. Thus, the radial wave and particle energy remain the same for different m_ℓ values consistent with a given value of ℓ. In particular, **for a fixed ℓ the particle energy E is independent of m_ℓ, and so is at least $2\ell + 1$-fold degenerate.** Such degeneracy—a property of all central forces—stems from the spherical symmetry of the potential and illustrates once again the deep-seated connection between symmetry and the degeneracy of quantum states.

The reduction from Schrödinger's equation to the radial wave equation represents enormous progress and is valid for any central force. Still, the task of solving this equation for a specified potential $U(r)$ is a difficult one, often requiring methods of considerable sophistication. In Section 8.5 we tackle this task for the important case of the electron in the hydrogen atom.

EXAMPLE 8.4   Orbital Quantum Number for a Stone

A stone with mass 1.00 kg is whirled in a horizontal circle of radius 1.00 m with a period of revolution equal to 1.00 s. What value of orbital quantum number ℓ describes this motion?

Solution   The speed of the stone in its orbit is

$$v = \frac{2\pi R}{T} = \frac{2\pi(1.00\ \text{m})}{1.00\ \text{s}} = 6.28\ \text{m/s}$$

The corresponding angular momentum has magnitude

$$|\mathbf{L}| = mvR = (1.00\ \text{kg})(6.28\ \text{m/s})(1.00\ \text{m})$$
$$= 6.28\ \text{kg} \cdot \text{m}^2/\text{s}$$

But angular momentum is quantized as $\sqrt{\ell(\ell + 1)}\,\hbar$, which is approximately $\ell\hbar$ when ℓ is large. Then

$$\ell \approx \frac{|\mathbf{L}|}{\hbar} = \frac{6.28\ \text{kg} \cdot \text{m}^2/\text{s}}{1.055 \times 10^{-34}\ \text{kg} \cdot \text{m}^2/\text{s}} = 5.96 \times 10^{34}$$

Again, we see that macroscopic objects are described by enormous quantum numbers, so that quantization is not evident on this scale.

EXAMPLE 8.5   The Bohr Atom Revisited

Discuss angular momentum quantization in the Bohr model. What orbital quantum number describes the electron in the first Bohr orbit of hydrogen?

Solution Angular momentum in the Bohr atom is quantized according to the Bohr postulate

$$|\mathbf{L}| = mvr = n\hbar$$

with $n = 1$ for the first Bohr orbit. Comparing this with the quantum mechanical result, Equation 8.14, we see that the two rules are incompatible! The magnitude $|\mathbf{L}|$ can never be an integral multiple of $\hbar$—the smallest nonzero value consistent with Equation 8.16 is $|\mathbf{L}| = \sqrt{2}\,\hbar$ for $\ell = 1$.

In fairness to Bohr, we should point out that the Bohr model makes no distinction between the quantization of $\mathbf{L}$ and quantization of its components along the coordinate axes. From the classical viewpoint, the coordinate system can always be oriented to align one of the axes, say the z-axis, along the direction of $\mathbf{L}$. In that case, $\mathbf{L}$ may be identified with $|L_z|$. The Bohr postulate in this form agrees with the quantization of L_z in Equation 8.16 and indicates $\ell = 1$ for the first Bohr orbit! This conflicting result derives from a false assertion, namely, that we may orient a coordinate axis along the direction of $\mathbf{L}$. The freedom to do so must be abandoned if the quantization rules of Equation 8.16 are correct! This stunning conclusion is one of the great mysteries of quantum physics and is implicit in the notion of space quantization that we discuss in the next section.

8.3   SPACE QUANTIZATION

For wavefunctions satisfying Equations 8.13 and 8.15, the orbital angular momentum magnitude $|\mathbf{L}|$, and L_z, the projection of $\mathbf{L}$ along the z-axis, are both sharp and quantized according to the restrictions imposed by the orbital and magnetic quantum numbers, respectively. Together, ℓ and m_ℓ specify the orientation of the angular momentum vector $\mathbf{L}$. The fact that the direction of $\mathbf{L}$ is quantized with respect to an arbitrary axis (the z-axis) is referred to as **space quantization.**

Let us look at the possible orientations of $\mathbf{L}$ for a given value of orbital quantum number ℓ. Recall that m_ℓ can have values ranging from $-\ell$ to $+\ell$. If $\ell = 0$, then $m_\ell = 0$ and $L_z = 0$. In fact, for this case $|\mathbf{L}| = 0$, so that all components of $\mathbf{L}$ are 0. If $\ell = 1$, then the possible values for m_ℓ are -1, 0, and $+1$, so that L_z may be $-\hbar$, 0, or $+\hbar$. If $\ell = 2$, m_ℓ can be $-2, -1, 0, +1,$ or $+2$, corresponding to L_z values of $-2\hbar, -\hbar, 0, +\hbar,$ or $+2\hbar$, and so on. A classical visualization of the algebra describing space quantization for the case $\ell = 2$ is shown in Figure 8.7a. Note that $\mathbf{L}$ can never be aligned with the z-axis, since L_z must be smaller than the total angular momentum L. From a three-dimensional perspective, $\mathbf{L}$ must lie on the surface of a cone that makes an angle θ with the z-axis, as shown in Figure 8.7b. From the figure, we see that θ also is quantized and that its values are specified by the relation

$$\cos\theta = \frac{L_z}{|\mathbf{L}|} = \frac{m_\ell}{\sqrt{\ell(\ell+1)}} \tag{8.18}$$

The orientations of L are restricted (quantized)

Classically, θ can take any value; that is, the angular momentum vector $\mathbf{L}$ can point in any direction whatsoever. According to quantum mechanics, the possible orientations for $\mathbf{L}$ are those consistent with Equation 8.18. Furthermore, these special directions have nothing to do with the forces acting on
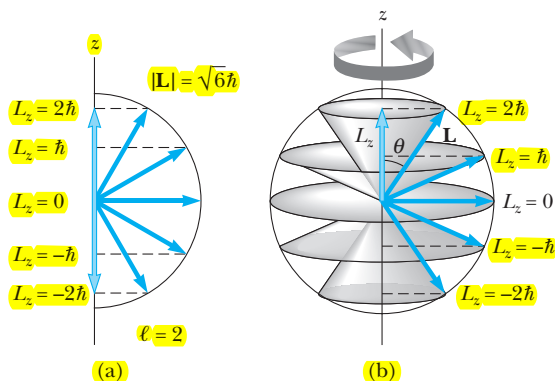
Figure 8.7 (a) The allowed projections of the orbital angular momentum for the case $\ell = 2$. (b) From a three-dimensional perspective, the orbital angular momentum vector **L** lies on the surface of a cone. The fuzzy character of L_x and L_y is depicted by allowing **L** to precess about the z-axis, so that L_x and L_y change continually while L_z maintains the fixed value $m_\ell \hbar$.

the particle, provided only that these forces are central. Thus, **the rule of Equation 8.18 does not originate with the law of force but derives from the structure of space itself,** hence the name *space quantization.*

  Figure 8.7 is misleading in showing **L** with a specific direction, for which all three components L_x, L_y, and L_z are known exactly. As we have mentioned, there is no quantum state for which this condition is true. If L_z is sharp, then L_x and L_y must be fuzzy. Accordingly, it is more proper to visualize the vector **L** of Figure 8.7b as precessing around the z-axis so as to trace out a cone in space. This allows the components L_x and L_y to change continually, while L_z maintains the fixed value $m_\ell \hbar$.[6]

EXAMPLE 8.6   Space Quantization for an Atomic Electron

Consider an atomic electron in the $\ell = 3$ state. Calculate the magnitude $|\mathbf{L}|$ of the total angular momentum and the allowed values of L_z and θ.

Solution With $\ell = 3$, Equation 8.16 gives

$$|\mathbf{L}| = \sqrt{3(3+1)}\,\hbar = 2\sqrt{3}\,\hbar$$

The allowed values of L_z are $m_\ell \hbar$, with $m_\ell = 0, \pm 1, \pm 2,$ and ± 3. This gives

$$L_z = -3\hbar, -2\hbar, -\hbar, 0, \hbar, 2\hbar, 3\hbar$$

Finally, we obtain the allowed values of θ from

$$\cos\theta = \frac{L_z}{|\mathbf{L}|} = \frac{m_\ell}{2\sqrt{3}}$$

Substituting the values for m_ℓ gives

$$\cos\theta = \pm 0.866, \quad \pm 0.577, \quad \pm 0.289, \quad \text{and} \quad 0$$

or

$$\theta = \pm 30°, \quad \pm 54.8°, \quad \pm 73.2°, \quad \text{and} \quad 90°$$

---

[6]This precession of the classical vector to portray the inherent fuzziness in L_x and L_y is meant to be suggestive only. In effect, we have identified the quantum averages $\langle L_x \rangle$ and $\langle L_y \rangle$ with their averages over *time* in a classical picture, but the two kinds of averaging in fact are quite distinct.

Exercise 3   Compare the minimum angles between **L** and the *z*-axis for the electron of Example 8.6 and for the 1.00-kg stone of Example 8.4.

Answer   30° for the electron but only 2.3×10^{-16} degrees for the stone

8.4   QUANTIZATION OF ANGULAR MOMENTUM AND ENERGY

We saw in Section 8.2 that angular momentum plays an essential role in the quantization of systems with spherical symmetry. Here we develop further the properties of angular momentum from the viewpoint of quantum mechanics and show in more detail how angular momentum considerations facilitate the solution to Schrödinger's equation for central forces.

Our treatment is based on the operator methods introduced in Section 6.8, which the reader should review at this time. In particular, the eigenvalue condition

$$[Q]\Psi = q\Psi \tag{8.19}$$

used there as a *test* for sharp observables becomes here a tool for discovering the form of the unknown wavefunction Ψ. (Recall that $[Q]$ denotes the operator for some observable Q and q is the sharp value of that observable when measured for a system described by the wavefunction Ψ.) We look on Equation 8.19 now as a *constraint* imposed on the wavefunction Ψ that guarantees that the observable Q will take the sharp value q in that state. The more sharp observables we can identify for some system, the more we can learn in advance about the wavefunction describing that system. **With few exceptions, the sharp observables are just those that are constants of the classical motion.** (See footnote 1.)

Consider the particle energy. If total energy is constant, we should be able to find wavefunctions Ψ for which E is a sharp observable. Otherwise, repeated measurements made on identical systems would reveal a statistical distribution of values for the particle energy, inconsistent with the idea of a quantity not changing over time. Thus, energy conservation suggests $\Delta E = 0$, which, in turn, requires Ψ to be an eigenfunction of the energy operator

$$[E]\Psi = E\Psi$$

Because $[E] = i\hbar\,\partial/\partial t$ this eigenvalue condition is met by the stationary waves $\psi(\mathbf{r})\,e^{-i\omega t}$, with $E = \hbar\omega$ the sharp value of particle energy.

The argument for energy applies equally well to other constants of the classical motion.[7] If the only forces are central, angular momentum about the force center is a constant of the motion. This is a vector quantity $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, whose rectangular components are expressed in terms of position and momentum components as

$$L_z = (\mathbf{r} \times \mathbf{p})_z = xp_y - yp_x$$

and so on. In the same way, the *operators* for angular momentum are found from the coordinate and momentum *operators*. From Chapter 6, the operator for *x* is just the

---

[7]Exceptions to this rule do exist. For instance, an atomic electron cannot have all three angular momentum components sharp at once, even though in this case all components are constant classically. For such *incompatible* observables, quantum mechanics adopts the broader interpretation of a conserved quantity as one whose *average value does not change over time*, no matter what may be the initial state of the system. With this definition, all components of angular momentum for an atomic electron remain constant, but no more than one can be sharp in a given state.

coordinate itself, and the operator for momentum in this direction is $(\hbar/i)\,\partial/\partial x$. Similar relations should apply to the directions labeled y and z,[8] so that the operator for L_z becomes

$$[L_z] = [x][p_y] - [y][p_x] = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{8.20}$$

Angular momentum finds its natural expression in the spherical coordinates of Figure 8.5. A little geometry applied to Figure 8.5 shows that the spherical-to-Cartesian coordinate transformation equations are

$$z = r\cos\theta$$
$$x = r\sin\theta\cos\phi \tag{8.21}$$
$$y = r\sin\theta\sin\phi$$

The inverse transformations are

$$r = \{x^2 + y^2 + z^2\}^{1/2}$$
$$\cos\theta = \frac{z}{r} = z\{x^2 + y^2 + z^2\}^{-1/2} \tag{8.22}$$
$$\tan\phi = \frac{y}{x}$$

The procedure for transcribing operators such as $[L_z]$ from Cartesian to spherical form is straightforward, but tedious. For instance, an application of the chain rule gives

$$\frac{\partial f}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial f}{\partial r} + \frac{\partial\theta}{\partial z}\frac{\partial f}{\partial\theta} + \frac{\partial\phi}{\partial z}\frac{\partial f}{\partial\phi}$$

for any function f. On the left we think of f expressed as a function of x, y, z, but on the right the same function is expressed in terms of r, θ, ϕ. The partial derivatives $\partial r/\partial z$, and so on, are to be taken with the aid of the transformation equations, holding x and y fixed. The simplest of these is $\partial\phi/\partial z$. From the inverse transformations in Equations 8.22, we see that ϕ is independent of z, so that $\partial\phi/\partial z = 0$. From the same equations we find that

$$\frac{\partial r}{\partial z} = \frac{1}{2}\{x^2 + y^2 + z^2\}^{-1/2}(2z) = \frac{z}{r} = \cos\theta$$

To obtain $\partial\theta/\partial z$ we differentiate the second of Equations 8.22 implicitly to get

$$-\sin\theta\,\frac{\partial\theta}{\partial z} = \frac{\partial\{\cos\theta\}}{\partial z} = z(-\tfrac{1}{2})\{x^2 + y^2 + z^2\}^{-3/2}(2z) + \{x^2 + y^2 + z^2\}^{-1/2}$$

Converting the right-hand side back to spherical coordinates gives

$$-\sin\theta\,\frac{\partial\theta}{\partial z} = -\frac{(r\cos\theta)^2}{r^3} + \frac{1}{r} = \frac{1 - \cos^2\theta}{r} = \frac{\sin^2\theta}{r}$$

or $\partial\theta/\partial z = -\sin\theta/r$. Collecting the previous results, we have

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial z}\frac{\partial}{\partial\theta} = \cos\theta\,\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}$$

---

[8]For the momentum operator along each axis we use the one-dimensional form from Chapter 6, ($[p_x] = (\hbar/i)\partial/\partial x$, etc.), consistent with the belief that Cartesian axes identify independent but logically equivalent directions in space.

In like fashion, we can obtain spherical representations for $\partial/\partial x$, $\partial/\partial y$ and ultimately for the angular momentum operators themselves:

$$[L_x] = i\hbar \left\{ \sin\phi \, \frac{\partial}{\partial\theta} + \cot\theta \cos\phi \, \frac{\partial}{\partial\phi} \right\}$$

$$[L_y] = -i\hbar \left\{ \cos\phi \, \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \, \frac{\partial}{\partial\phi} \right\} \qquad (8.23)$$

$$[L_z] = -i\hbar \, \frac{\partial}{\partial\phi}$$

Notice that the operators for angular momentum in spherical form do not contain the radial coordinate r—our reward for selecting the right system of coordinates! By insisting that angular momentum be sharp in the quantum state Ψ, and using the differential forms (Eqs. 8.23) for the angular momentum operators, we can discover how the wavefunction depends on the spherical angles θ and ϕ *without knowing the details of the central force.*

L_z Is Sharp: The Magnetic Quantum Number

For L_z to be sharp, our wavefunction $\Psi = \psi(r)e^{-i\omega t}$ must be an eigenfunction of $[L_z]$, or

$$-i\hbar \, \frac{\partial\psi}{\partial\phi} = L_z\psi \qquad (8.24)$$

with L_z the eigenvalue (a number). Equation 8.24 prescribes the functional dependence of ψ on the azimuthal angle ϕ to be

$$\psi(\mathbf{r}) = Ce^{iL_z\phi/\hbar} \qquad (8.25)$$

with C still any function of r and θ. The values taken by L_z must be restricted, however. Since increasing ϕ by 2π radians returns us to the same place in space (see Fig. 8.5), the wavefunction also should return to its initial value, that is, the solutions represented by Equation 8.25 must be periodic in ϕ with period 2π. This will be true if $L_z/\hbar$ is any integer, say, m_ℓ or $L_z = m_\ell\hbar$. The magnetic quantum number m_ℓ indicates the (sharp) value for the z component of angular momentum in the state described by ψ.

Because all components of $\mathbf{L}$ are constant for central forces, we should continue by requiring the wavefunction of Equation 8.25 also to be an eigenfunction of the operator for a second angular momentum component, say $[L_x]$, so that L_z and L_x might both be sharp in the state ψ. For ψ to be an eigenfunction of $[L_x]$ with eigenvalue L_x requires

$$i\hbar \left\{ \sin\phi \, \frac{\partial\psi}{\partial\theta} + \cot\theta \cos\phi \, \frac{\partial\psi}{\partial\phi} \right\} = L_x\psi$$

This relation must hold for all values of θ and ϕ. In particular, for $\phi = 0$ the requirement is

$$i\hbar \cot\theta \, \frac{\partial\psi}{\partial\phi} = L_x\psi$$

Because ψ varies exponentially with ϕ according to Equation 8.25, the indicated derivative may be taken and evaluated at $\phi = 0$ to get

$$(-L_z \cot\theta) \, \psi = L_x\psi$$

which can be satisfied for *all* θ only if $L_x = L_z = 0$ or if ψ vanishes identically. A similar difficulty arises if we attempt to make L_y sharp together with L_z. Therefore,

unless the angular momentum is exactly zero (all components), there is no wavefunction for which two or more components are simultaneously sharp!

|L| Is Sharp: The Orbital Quantum Number

To make further progress, we must look to other constants of the classical motion. In addition to each component of angular momentum, the magnitude $|\mathbf{L}|$ of the vector also is constant and becomes a candidate for an observable that can be made sharp together with L_z. Consider simply the squared-magnitude $L^2 = \mathbf{L} \cdot \mathbf{L}$. The operator for L^2 is

$$[L]^2 = [L_x]^2 + [L_y]^2 + [L_z]^2$$

Using Equation 8.23, we find the spherical coordinate form for $[L^2]$:

$$[L^2] = -\hbar^2 \left\{ \frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \csc^2\theta \frac{\partial^2}{\partial \phi^2} \right\} \tag{8.26}$$

For L^2 to be sharp requires $[L^2]\psi = |\mathbf{L}|^2\psi$ or

$$-\hbar^2 \left\{ \frac{\partial^2\psi}{\partial \theta^2} + \cot\theta \frac{\partial\psi}{\partial \theta} + \csc^2\theta \frac{\partial^2\psi}{\partial \phi^2} \right\} = |\mathbf{L}|^2\psi$$

But from Equation 8.24, we see that differentiating ψ with respect to ϕ is equivalent to multiplication by $iL_z/\hbar = im_\ell$, so that the last equation reduces to

$$-\hbar^2 \left\{ \frac{\partial^2\psi}{\partial \theta^2} + \cot\theta \frac{\partial\psi}{\partial \theta} - m_\ell^2 \csc^2\theta\, \psi \right\} = |\mathbf{L}|^2\psi \tag{8.27}$$

For wavefunctions satisfying Equation 8.27, the magnitude of angular momentum will be sharp at the value $|\mathbf{L}|$. The equation prescribes the dependence of ψ on the polar angle θ. The solutions are not elementary functions but can be investigated with the help of more advanced techniques. The results of such an investigation are reported in Section 8.2 and repeated here for completeness: Physically acceptable solutions to Equation 8.27 can be found provided $|\mathbf{L}| = \sqrt{\ell(\ell+1)}\,\hbar$, where ℓ, the orbital quantum number, must be a nonnegative integer. Furthermore, the magnetic quantum number, also appearing in Equation 8.27, must be limited as $|m_\ell| \le \ell$. With these restrictions, the solutions to Equation 8.27 are the associated Legendre polynomials in $\cos\theta$, denoted $P_\ell^{m_\ell}(\cos\theta)$. Several of these polynomials are listed in Table 8.2 for easy reference; you may verify by direct substitution that they satisfy Equation 8.27 for the appropriate values of ℓ and m_ℓ.

The associated Legendre polynomials may be multiplied by $\exp(im_\ell\phi)$ and still satisfy the orbital equation Equation 8.27. Indeed, the products $P_\ell^{m_\ell}(\cos\theta)\exp(im_\ell\phi)$ satisfy both Equations 8.24 and 8.27; thus, they represent waves for which $|\mathbf{L}|$ and L_z are simultaneously sharp. Except for a multiplicative constant, these are just the spherical harmonics $Y_\ell^{m_\ell}(\theta, \phi)$ introduced in Section 8.2.

E Is Sharp: The Radial Wave Equation

For energy to be constant, E should be a sharp observable. The stationary state form $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-i\omega t}$ results from imposing the eigenvalue condition for the energy operator $[E]$—but what of the other energy operator $[H] = [K] + [U]$ (the Hamiltonian)? In fact, requiring $[H]\Psi = E\Psi$ is equivalent to writing the time-independent Schrödinger equation for $\psi(\mathbf{r})$

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U(\mathbf{r})\psi = E\psi \tag{8.28}$$

because $[U] = U(\mathbf{r})$ and the kinetic energy operator $[K]$ in three dimensions is none other than

$$[K] = \frac{[p_x]^2 + [p_y]^2 + [p_z]^2}{2m} = \frac{(\hbar/i)^2\{(\partial/\partial x)^2 + (\partial/\partial y)^2 + (\partial/\partial z)^2\}}{2m} = -\frac{\hbar^2}{2m}\nabla^2$$

The spherical form of the Laplacian given in Section 8.2 may be used to write $[K]$ in spherical coordinates:

$$[K] = -\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta} + \csc^2\theta\frac{\partial^2}{\partial \phi^2}\right]\right\}$$

Comparing this with the spherical representation for $[L^2]$ from Equation 8.26 shows that $[K]$ is the sum of two terms,

$$[K] = [K_{\text{rad}}] + [K_{\text{orb}}] = [K_{\text{rad}}] + \frac{1}{2mr^2}[L^2] \qquad (8.29)$$

representing the separate contributions to the kinetic energy from the orbital and radial components of motion. The comparison also furnishes the spherical form for $[K_{\text{rad}}]$:

$$[K_{\text{rad}}] = -\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right\} \qquad (8.30)$$

These expressions for $[K]$ are completely general. When applied to waves for which $|\mathbf{L}|$ is sharp, however, the *operator* $[L^2]$ may be replaced with the *number* $|\mathbf{L}|^2 = \ell(\ell + 1)\hbar^2$. Therefore, the Schrödinger equation (Eq. 8.28) becomes

$$[K_{\text{rad}}]\psi(\mathbf{r}) + \frac{\ell(\ell + 1)\hbar^2}{2mr^2}\psi(\mathbf{r}) + U(r)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad (8.31)$$

For central forces, all terms in this equation, including $U(r)$, involve only the spherical coordinate r: the angle variables θ and ϕ have been eliminated from further consideration by the requirement that ψ be an eigenfunction of $[L^2]$! It follows that the solutions to Equation 8.31 take the form of a radial wave $R(r)$ multiplied by a spherical harmonic:

$$\psi(\mathbf{r}) = R(r)Y_\ell^{m_\ell}(\theta, \phi) \qquad (8.32)$$

The spherical harmonic may be divided out of each term in Equation 8.31, in effect replacing $\psi(\mathbf{r})$ by $R(r)$. The result is just the radial wave equation of Section 8.2; it determines the radial wavefunction $R(r)$ and the allowed particle energies E, once the potential energy function $U(r)$ is specified.

8.5   ATOMIC HYDROGEN AND HYDROGEN-LIKE IONS

In this section we study the hydrogen atom from the viewpoint of wave mechanics. Its simplicity makes atomic hydrogen the ideal testing ground for comparing theory with experiment. Furthermore, the hydrogen atom is the prototype system for the many complex ions and atoms of the heavier elements. Indeed, our study of the hydrogen atom ultimately will enable us to understand the periodic table of the elements, one of the greatest triumphs of quantum physics.

The object of interest is the orbiting electron, with its mass m and charge $-e$, bound by the force of electrostatic attraction to the nucleus, with its much larger mass M and charge $+Ze$, where Z is the atomic number. The

choice $Z = 1$ describes the hydrogen atom, while for singly ionized helium (He^+) and doubly ionized lithium (Li^{2+}), we take $Z = 2$ and $Z = 3$, respectively, and so on. Ions with only one electron, like He^+ and Li^{2+}, are called **hydrogen-like.** Because $M \gg m$, we will assume that the nucleus does not move but simply exerts the attractive force that binds the electron. This force is the coulomb force, with its associated potential energy

$$U(r) = \frac{k(+Ze)(-e)}{r} = -\frac{kZe^2}{r} \tag{8.33}$$

where k is the coulomb constant.

The hydrogen atom constitutes a central force problem; according to Section 8.2, the stationary states for any central force are

$$\Psi(r, \theta, \phi, t) = R(r) Y_\ell^{m_\ell}(\theta, \phi) e^{-i\omega t} \tag{8.34}$$

where $Y_\ell^{m_\ell}(\theta, \phi)$ is a spherical harmonic from Table 8.3. The radial wavefunction $R(r)$ is found from the radial wave equation of Section 8.2,

$$-\frac{\hbar^2}{2m}\left[\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right] + \frac{\ell(\ell + 1)\hbar^2}{2mr^2}R(r) + U(r)R(r) = ER(r) \tag{8.17}$$

$U(r)$ is the potential energy of Equation 8.33; the remaining terms on the left of Equation 8.17 are associated with the kinetic energy of the electron. The term proportional to $\ell(\ell + 1)\hbar^2 = (|\mathbf{L}^2|)$ is the orbital contribution to kinetic energy, K_{orb}. To see this, consider a particle in circular orbit, in which all the kinetic energy is in orbital form (since the distance from the center remains fixed). For such a particle $K_{\mathrm{orb}} = \frac{1}{2}mv^2$ and $|\mathbf{L}| = mvr$. Eliminating the particle speed v, we get

$$K_{\mathrm{orb}} = \frac{m}{2}\left(\frac{|\mathbf{L}|}{mr}\right)^2 = \frac{|\mathbf{L}|^2}{2mr^2} \tag{8.35}$$

Although it was derived for circular orbits, this result correctly represents the orbital contribution to kinetic energy of a mass m in general motion with angular momentum $\mathbf{L}$.[9]

The derivative terms in Equation 8.17 are the radial contribution to the kinetic energy, that is, they represent the contribution from electron motion toward or away from the nucleus. The leftmost term is just what we should write for the kinetic energy of a matter wave $\psi = R(r)$ associated with motion along the coordinate line marked by r. But what significance should we attach to the first derivative term dR/dr? In fact, the presence of this term is evidence that *the effective one-dimensional matter wave is not $R(r)$, but $rR(r)$.* In support of this claim we note that

$$\frac{d^2(rR)}{dr^2} = r\left[\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right]$$

Then the radial wave equation written for the effective one-dimensional matter wave $g(r) = rR(r)$ takes the same form as Schrödinger's equation in

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[9]For any planar orbit we may write $|\mathbf{L}| = rp_\perp$, where $p_\perp$ is the component of momentum in the orbital plane that is normal to the radius vector $\mathbf{r}$. The orbital part of the kinetic energy is then $K_{\mathrm{orb}} = p_\perp^2/2m = |\mathbf{L}|^2/2mr^2$.

one dimension,

$$-\frac{\hbar^2}{2m}\frac{d^2 g}{dr^2} + U_{\mathrm{eff}}(r)g(r) = Eg(r) \tag{8.36}$$

but with an *effective potential energy*

$$U_{\mathrm{eff}} = \frac{|\mathbf{L}|^2}{2mr^2} + U(r) = \frac{\ell(\ell+1)\hbar^2}{2mr^2} + U(r) \tag{8.37}$$

The magnitude of $g(r)$ also furnishes probabilities, as described later in this section.

The solution of Equation 8.36 with $U(r) = -kZe^2/r$ (for one-electron atoms or ions) requires methods beyond the scope of this text. Here, as before, we shall present the results and leave their verification to the interested reader. Acceptable wavefunctions can be found only if the energy E is restricted to be one of the following special values:

$$E_n = -\frac{ke^2}{2a_0}\left\{\frac{Z^2}{n^2}\right\} \qquad n = 1, 2, 3, \ldots \tag{8.38}$$

Allowed energies for hydrogen-like atoms

This result is in exact agreement with that found from the simple Bohr theory (see Chapter 4): $a_0 = \hbar^2/m_e ke^2$ is the Bohr radius, 0.529 Å, and $ke^2/2a_0$ is the Rydberg energy, 13.6 eV. The integer n is called the **principal quantum number.** Although n can be any positive integer, the orbital quantum number now is limited to values less than n; that is, ℓ can have only the values

$$\ell = 0, 1, 2, \ldots, (n-1) \tag{8.39}$$

Allowed values of ℓ

The cutoff at $(n-1)$ is consistent with the physical significance of these quantum numbers: The magnitude of orbital angular momentum (fixed by ℓ) cannot become arbitrarily large for a given energy (fixed by n). A semiclassical argument expressing this idea leads to $\ell_{\max} = n - 1$ (see Problem 20). In the same spirit, the restriction on the magnetic quantum number m_ℓ to values between $-\ell$ and $+\ell$ guarantees that the z component of angular momentum never exceeds the magnitude of the vector.

The radial waves $R(r)$ for hydrogen-like atoms are products of exponentials with polynomials in r/a_0. These radial wavefunctions are tabulated as $R_{n\ell}(r)$ in Table 8.4 for principal quantum numbers up to and including $n = 3$.

For hydrogen-like atoms, then, the quantum numbers are n, ℓ, and m_ℓ, associated with the sharp observables E, $|\mathbf{L}|$, and L_z, respectively. Notice that the energy E depends on n, but not at all on ℓ or m_ℓ. The energy is independent of m_ℓ because of the spherical symmetry of the atom, and this will be true for any central force that varies only with distance r. The fact that E also is independent of ℓ is a special consequence of the coulomb force, however, and is not to be expected in heavier atoms, say, where the force on any one electron includes the electrostatic repulsion of the remaining electrons in the atom, as well as the coulombic attraction of the nucleus.

For historical reasons, all states with the same principal quantum number n are said to form a **shell.** These shells are identified by the letters K, L, M, . . . , which designate the states for which $n = 1, 2, 3, \ldots$. Likewise, states

Principal quantum number n
$$n = 1, 2, 3, \ldots$$
Orbital quantum number ℓ
$$\ell = 0, 1, 2, \ldots, (n-1)$$

Magnetic quantum number m_ℓ
$$m_\ell = 0, \pm 1, \pm 2, \ldots, \pm\ell$$

Table 8.4   The Radial Wavefunctions $R_{n\ell}(r)$ of Hydrogen-like Atoms for $n = 1, 2,$ and 3

n	ℓ	$R_{n\ell}(r)$
1	0	$\left(\dfrac{Z}{a_0}\right)^{3/2} 2e^{-Zr/a_0}$
2	0	$\left(\dfrac{Z}{2a_0}\right)^{3/2}\left(2 - \dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$
2	1	$\left(\dfrac{Z}{2a_0}\right)^{3/2}\dfrac{Zr}{\sqrt{3}\,a_0}e^{-Zr/2a_0}$
3	0	$\left(\dfrac{Z}{3a_0}\right)^{3/2} 2\left[1 - \dfrac{2Zr}{3a_0} + \dfrac{2}{27}\left(\dfrac{Zr}{a_0}\right)^2\right]e^{-Zr/3a_0}$
3	1	$\left(\dfrac{Z}{3a_0}\right)^{3/2}\dfrac{4\sqrt{2}}{3}\dfrac{Zr}{a_0}\left(1 - \dfrac{Zr}{6a_0}\right)e^{-Zr/3a_0}$
3	2	$\left(\dfrac{Z}{3a_0}\right)^{3/2}\dfrac{2\sqrt{2}}{27\sqrt{5}}\left(\dfrac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$

having the same value of both n and ℓ are said to form a **subshell.** The letters $s, p, d, f,$ . . . are used to designate the states for which $\ell = 0, 1, 2, 3,$ . . . .[10] This **spectroscopic notation** is summarized in Table 8.5.

The shell (and subshell) energies for several of the lowest-lying states of the hydrogen atom are illustrated in the energy-level diagram of Figure 8.8. The figure also portrays a few of the many electronic transitions possible within the atom. Each such transition represents a change of energy for the atom and must be compensated for by emission (or absorption) of energy in some other form. For **optical transitions,** photons carry off the surplus energy, but not all energy-conserving optical transitions may occur. As it happens, photons also carry angular momentum. To conserve *total* angular momentum (atom + photon) in optical transitions, the angular momentum of the electron in the

Table 8.5   Spectroscopic Notation for Atomic Shells and Subhells

n	Shell Symbol	ℓ	Shell Symbol
1	K	0	s
2	L	1	p
3	M	2	d
4	N	3	f
5	O	4	g
6	P	5	h
. . .		. . .	

[10]*s, p, d, f* are one-letter abbreviations for *sharp, principal, diffuse,* and *fundamental.* The nomenclature is a throwback to the early days of spectroscopic observations, when these terms were used to characterize the appearance of spectral lines.
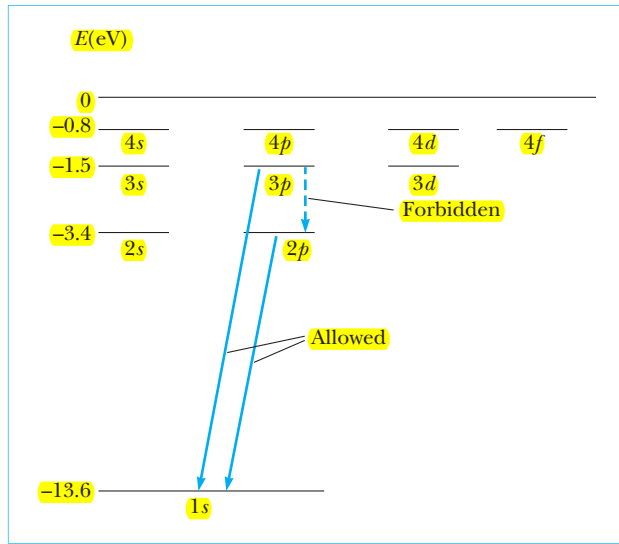
Figure 8.8   Energy-level diagram of atomic hydrogen. Allowed photon transitions are those obeying the selection rule $\Delta \ell = \pm 1$. The $3p \rightarrow 2p$ transition ($\Delta \ell = 0$) is said to be forbidden, though it may still occur (but only rarely).

initial and final states must differ by exactly one unit, that is

$$|\ell_f - \ell_i| = 1 \quad \text{or} \quad \Delta \ell = \pm 1 \quad\quad (8.40)$$

Selection rule for allowed transitions

Equation 8.40 expresses a **selection rule** that must be obeyed in optical transitions.[11] As Figure 8.8 indicates, the transitions $3p \rightarrow 1s$ and $2p \rightarrow 1s$ are **allowed** by the rule ($\Delta \ell = -1$), but the $3p \rightarrow 2p$ transition is said to be **forbidden** ($\Delta \ell = 0$). (Such transitions can occur, but with negligible probability compared with that of allowed transitions.) Clearly, selection rules play a vital role in the interpretation of atomic spectra.

EXAMPLE 8.7   The $n = 2$ Level of Hydrogen

Enumerate all states of the hydrogen atom corresponding to the principal quantum number $n = 2$, giving the spectroscopic designation for each. Calculate the energies of these states.

Solution   When $n = 2$, ℓ can have the values 0 and 1. If $\ell = 0$, m_ℓ can only be 0. If $\ell = 1$, m_ℓ can be -1, 0, or $+1$. Hence, we have a $2s$ state with quantum numbers

$$n = 2, \quad \ell = 0, \quad m_\ell = 0$$

and three $2p$ states for which the quantum numbers are

$$n = 2, \quad \ell = 1, \quad m_\ell = -1$$
$$n = 2, \quad \ell = 1, \quad m_\ell = 0$$
$$n = 2, \quad \ell = 1, \quad m_\ell = +1$$

Because all of these states have the same principal quantum number, $n = 2$, they also have the same energy, which can be calculated from Equation 8.38. For $Z = 1$ and $n = 2$, this gives

$$E_2 = -(13.6 \text{ eV})\{1^2/2^2\} = -3.4 \text{ eV}$$

---

[11]$\Delta \ell = 0$ also is allowed by angular momentum considerations but forbidden by parity conservation. Further, since the angular momentum of a photon is just $\pm \hbar$, the z component of the atom's angular momentum cannot change by more than $\pm \hbar$, giving rise to a *second selection rule*, $\Delta m_\ell = 0, \pm 1$.

Exercise 4   How many possible states are there for the $n = 3$ level of hydrogen? For the $n = 4$ level?

Answers   Nine states for $n = 3$, and 16 states for $n = 4$.

The Ground State of Hydrogen-like Atoms

The ground state of a one-electron atom or ion with atomic number Z, for which $n = 1$, $\ell = 0$, and $m_\ell = 0$, has energy

$$E_1 = -(13.6 \text{ eV}) Z^2 \tag{8.41}$$

The wavefunction for this state is

$$\psi_{100} = R_{10}(r) Y_0^0 = \pi^{-1/2} (Z/a_0)^{3/2} e^{-Zr/a_0} \tag{8.42}$$

The constants are such that ψ is normalized. Notice that ψ_{100} does not depend on angle, since it is the product of a radial wave with $Y_0^0 = 1/\sqrt{4\pi}$. In fact, all the $\ell = 0$ waves share this feature; that is, **all *s*-state waves are spherically symmetric.**

The electron described by the wavefunction of Equation 8.42 is found with a probability per unit volume given by

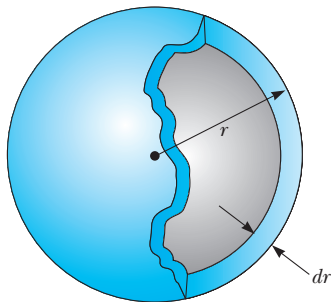$$|\psi_{100}|^2 = \frac{Z^3}{\pi a_0^3} e^{-2Zr/a_0}$$

Figure 8.9 $P(r) \, dr$ is the probability that the electron will be found in the volume of a spherical shell with radius r and thickness dr. The shell volume is just $4\pi r^2 \, dr$.

(Three-dimensional renditions of the probability per unit volume $|\psi(\mathbf{r})|^2$—often called electron "clouds"—are constructed by making the shading at every point proportional to $|\psi(\mathbf{r})|^2$.) The probability distribution also is spherically symmetric, as it would be for any *s*-state wave; that is, the likelihood for finding the electron in the atom is the same at all points equidistant from the center (nucleus). Thus, it is convenient to define another probability function, called the **radial probability distribution,** with its associated density $P(r)$, such that **$P(r) \, dr$ is the probability of finding the electron anywhere in the spherical shell of radius r and thickness dr** (Fig. 8.9). The shell volume is its surface area, $4\pi r^2$, multiplied by the shell thickness, dr. Since the probability density $|\psi_{100}|^2$ is the same everywhere in the shell, we have

$$P(r) \, dr = |\psi|^2 \, 4\pi r^2 \, dr$$

or, for the hydrogen-like 1*s* state,

$$P_{1s}(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0} \tag{8.43}$$

The same result is obtained for $P_{1s}(r)$ from the intensity of the effective one-dimensional matter wave $g(r) = rR(r)$:

The radial probability density for any state

$$P(r) = |g(r)|^2 = r^2 |R(r)|^2 \tag{8.44}$$

In fact, *Equation 8.44 gives the correct radial probability density for any state*; for the spherically symmetric *s*-states this is the same as $4\pi r^2 |\psi|^2$, since then $\psi(r) = (1/\sqrt{4\pi})R(r)$.[12]

A plot of the function $P_{1s}(r)$ is presented in Figure 8.10a; Figure 8.10b shows the 1*s* electron "cloud" or probability per unit volume $|\psi_{100}|^2$ from which $P_{1s}(r)$ derives. $P(r)$ may be loosely interpreted as the probability of finding the electron at distance *r* from the nucleus, irrespective of its angular position. Thus, the peak of the curve in Figure 8.10a represents the most probable distance of the 1*s* electron from the nucleus. Furthermore, the normalization condition becomes

$$1 = \int_0^\infty P(r) \, dr \tag{8.45}$$

where the integral is taken over all *possible* values of *r*. The average distance of the electron from the nucleus is found by weighting each possible distance with the probability that the electron will be found at that distance:

$$\langle r \rangle = \int_0^\infty r P(r) \, dr \tag{8.46}$$

The average distance of an electron from the nucleus

In fact, the average value of *any* function of distance $f(r)$ is obtained

$$P_{1s}(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$$

$$|\psi_{100}|^2 = \frac{Z^3}{\pi a_0^3} e^{-2Zr/a_0}$$
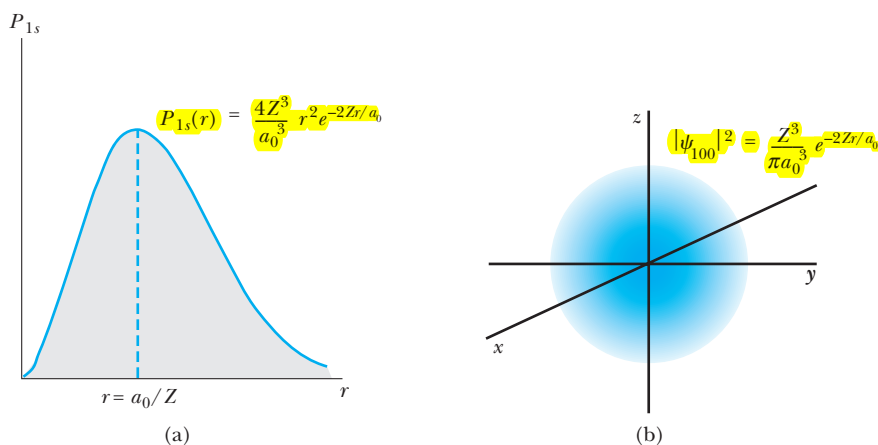
$r = a_0/Z$

(a)   (b)

Figure 8.10   (a) The curve $P_{1s}(r)$ representing the probability of finding the electron as a function of distance from the nucleus in a 1*s* hydrogen-like state. Note that the probability takes its maximum value when *r* equals a_0/Z. (b) The spherical electron "cloud" for a hydrogen-like 1*s* state. The shading at every point is proportional to the probability density $|\psi_{1s}(\mathbf{r})|^2$.

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[12]From its definition, $P(r) \, dr$ always may be found by integrating $|\psi|^2 = |R(r)|^2 |Y_\ell^{m_\ell}|^2$ over the volume of a spherical shell having radius *r* and thickness *dr*. Since the volume element in spherical coordinates is $dV = r^2 dr \sin\theta \, d\theta \, d\phi$, and the integral of $|Y_\ell^{m_\ell}|^2$ over angle is unity (see footnote 5), this leaves $P(r) = r^2 |R(r)|^2$.

by weighting the function value at every distance with the probability at that distance:

$$\langle f \rangle = \int_0^\infty f(r) P(r) \, dr \tag{8.47}$$

EXAMPLE 8.8 Probabilities for the Electron in Hydrogen

Calculate the probability that the electron in the ground state of hydrogen will be found outside the first Bohr radius.

Solution The probability is found by integrating the radial probability density for this state, $P_{1s}(r)$, from the Bohr radius a_0 to ∞. Using Equation 8.43 with $Z = 1$ for hydrogen gives

$$P = \frac{4}{a_0^3} \int_{a_0}^\infty r^2 e^{-2r/a_0} \, dr$$

We can put the integral in dimensionless form by changing variables from r to $z = 2r/a_0$. Noting that $z = 2$ when $r = a_0$, and that $dr = (a_0/2) \, dz$, we get

$$P = \frac{1}{2} \int_2^\infty z^2 e^{-z} dz = -\frac{1}{2} \{z^2 + 2z + 2\} e^{-z} \Big|_2^\infty = 5e^{-2}$$

This is about 0.677, or 67.7%.

EXAMPLE 8.9 The Electron–Proton Separation in Hydrogen

Calculate the most probable distance of the electron from the nucleus in the ground state of hydrogen, and compare this with the average distance.

Solution The most probable distance is the value of r that makes the radial probability $P(r)$ a maximum. The slope here is zero, so the most probable value of r is obtained by setting $dP/dr = 0$ and solving for r. Using Equation 8.43 with $Z = 1$ for the 1s, or ground, state of hydrogen, we get

$$0 = \left(\frac{4}{a_0^3} \right) \frac{d}{dr} \{r^2 e^{-2r/a_0}\} = \left(\frac{4}{a_0^3} \right) e^{-2r/a_0} \left\{ -\frac{2r^2}{a_0} + 2r \right\}$$

The right-hand side is zero for $r = 0$ and for $r = a_0$. Since $P(0) = 0$, $r = 0$ is a minimum of $P(r)$, not a maximum. Thus, the most probable distance is

$$r = a_0$$

The average distance is obtained from Equation 8.46, which in this case becomes

$$\langle r \rangle = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} \, dr$$

Again introducing $z = 2r/a_0$, we obtain

$$\langle r \rangle = \frac{a_0}{4} \int_0^\infty z^3 e^{-z} \, dz$$

The definite integral on the right is one of a broader class,

$$\int_0^\infty z^n e^{-z} dz = n!$$

whose value $n! = n(n-1) \ldots (1)$ is established by repeated integration by parts. Then

$$\langle r \rangle = \frac{a_0}{4} (3!) = \frac{3}{2} a_0$$

The average distance and the most probable distance are not the same, because the probability curve $P(r)$ is not symmetric about the peak distance a_0. Indeed, values of r greater than a_0 are weighted more heavily in Equation 8.46 than values smaller than a_0, so the average $\langle r \rangle$ actually exceeds a_0 for this probability distribution.

Excited States of Hydrogen-like Atoms

There are four first excited states for hydrogen-like atoms: ψ_{200}, ψ_{210}, ψ_{211}, and ψ_{21-1}. All have the same principal quantum number $n = 2$, hence the same total energy

$$E_2 = -(13.6 \text{ eV}) \frac{Z^2}{4}$$

Accordingly, the first excited level, E_2, is fourfold degenerate.

The 2s state, ψ_{200}, is again spherically symmetric. Plots of the radial probability density for this and several other hydrogen-like states are shown in Figure 8.11. Note that the plot for the 2s state has two peaks. In this case, the most probable distance $(\sim 5a_0/Z)$ is marked by the highest peak. An electron in the 2s state would be much farther from the nucleus (on the average) than an electron in the 1s state. Likewise, the most probable distances are even greater for an electron in any of the $n = 3$ states (3s, 3p, or 3d). Observations such as these continue to support the old idea of a shell structure for the atom, even in the face of the uncertainties inherent in the wave nature of matter.

The remaining three first excited states, ψ_{211}, ψ_{210}, and ψ_{21-1}, have $\ell = 1$ and make up the 2p subshell. These states are not spherically symmetric. All of them have the same radial wavefunction $R_{21}(r)$, but they are multiplied by different spherical harmonics and thus depend differently on the angles θ and ϕ. For example, the wavefunction ψ_{211} is

$$\psi_{211} = R_{21}(r)\,Y_1^1 = \pi^{-1/2}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{8a_0}\right)e^{-Zr/2a_0}\sin\theta\,e^{i\phi} \qquad (8.48)$$
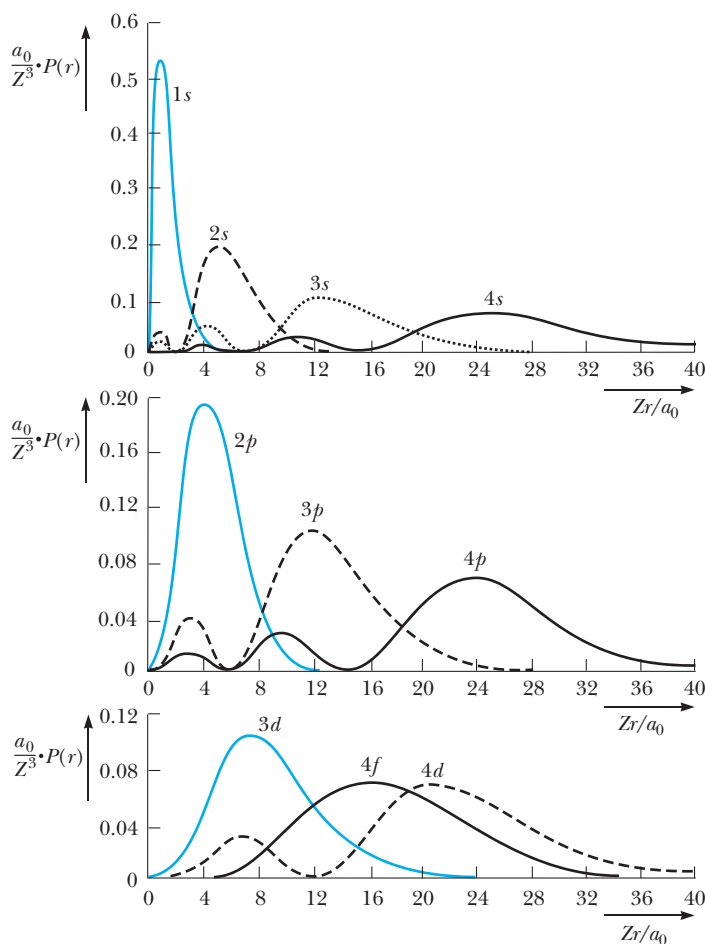

Figure 8.11   The radial probability density function for several states of hydrogen-like atoms.

$n = 2, \ell = 1, m_\ell = \pm 1$

(a)

$n = 3, \ell = 1, m_\ell = 0$

(b)

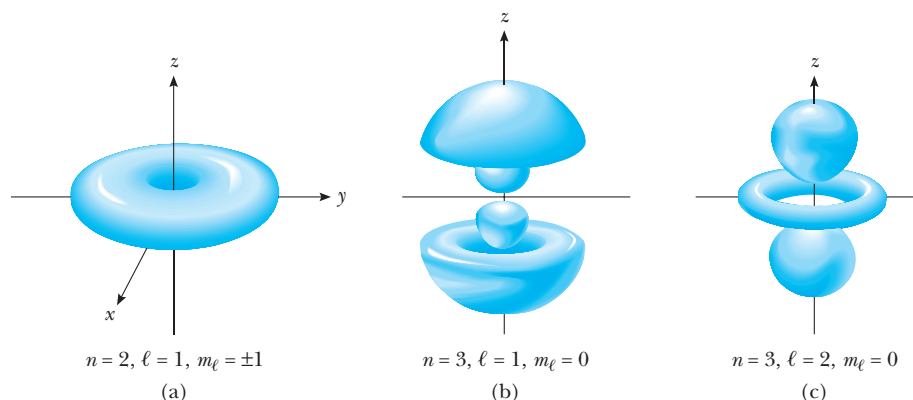$n = 3, \ell = 2, m_\ell = 0$

(c)

Figure 8.12 (a) The probability density $|\psi_{211}|^2$ for a hydrogen-like 2p state. Note the axial symmetry about the z-axis. (b) and (c) The probability densities $|\psi(\mathbf{r})|^2$ for several other hydrogen-like states. The electron "cloud" is axially symmetric about the z-axis for all the hydrogen-like states $\psi_{n\ell m_\ell}(\mathbf{r})$.

Notice, however, that the probability density $|\psi_{211}|^2$ is independent of ϕ and therefore is symmetric about the z-axis (Fig. 8.12a). Since $|e^{im_1\phi}|^2 = 1$, the same is true for all the hydrogen-like states $\psi_{n\ell m_\ell}$, as suggested by the remaining illustrations in Figure 8.12.

The ψ_{210} state

$$\psi_{210} = R_{21}(r) Y_1^0 = \pi^{-1/2} \left(\frac{Z}{2a_0} \right)^{3/2} \left(\frac{Zr}{2a_0} \right) e^{-Zr/2a_0} \cos\theta \qquad (8.49)$$

has distinct directional characteristics, as shown in Figure 8.13a, and is sometimes designated $[\psi_{2p}]_z$ to indicate the preference for the electron in this state to be found along the z-axis. Other highly directional states can be formed by combining the waves with $m_\ell = +1$ and $m_\ell = -1$. Thus, the wavefunctions

$$[\psi_{2p}]_x = \frac{1}{\sqrt{2}} \{\psi_{211} + \psi_{21-1}\} \qquad (8.50a)$$
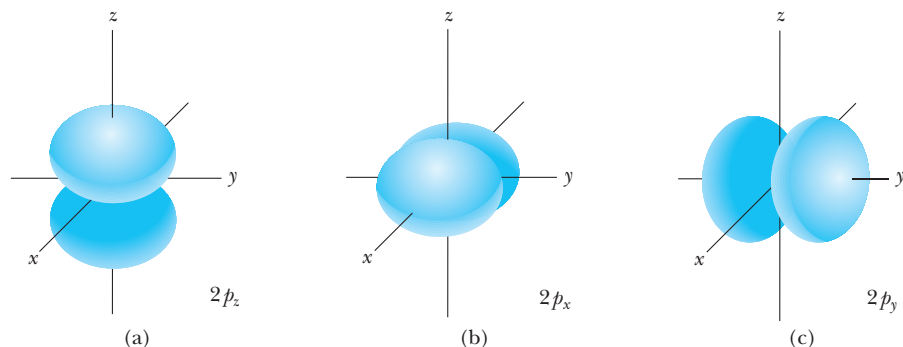

$2p_z$

(a)

$2p_x$

(b)

$2p_y$

(c)

Figure 8.13 (a) Probability distribution for an electron in the hydrogenlike 2p_z state, described by the quantum numbers $n = 2, \ell = 1, m_\ell = 0$. (b) and (c) Probability distributions for the 2p_x and 2p_y states. The three distributions 2p_x, 2p_y, and 2p_z have the same structure, but differ in their spatial orientation.

and

$$[\psi_{2p}]_y = \frac{1}{\sqrt{2}} \{\psi_{211} - \psi_{21-1}\} \tag{8.50b}$$

have large probability densities along the x- and y-axes, respectively, as shown in Figures 8.13b and 8.13c. The wavefunctions of Equations 8.50, formed as superpositions of first excited state waves with *identical* energies E_2, are themselves stationary states with this same energy; indeed, the three wavefunctions $[\psi_{2p}]_z$, $[\psi_{2p}]_x$, and $[\psi_{2p}]_y$ together constitute an equally good description of the $2p$ states for hydrogenlike atoms. Wavefunctions with a highly directional character, such as these, play an important role in chemical bonding, the formation of molecules, and chemical properties.

The next excited level, E_3, is ninefold degenerate; that is, there are nine different wavefunctions with this energy, corresponding to all possible choices for ℓ and m_ℓ consistent with $n = 3$. Together, these nine states constitute the third shell, with subshells $3s$, $3p$, and $3d$ composed of one, three, and five states, respectively. The wavefunctions for these states may be constructed from the entries in Tables 8.3 and 8.4. Generally, they are more complicated than their second-shell counterparts because of the increasing number of nodes in the radial part of the wavefunction.

The progression to higher-lying states leads to still more degeneracy and wavefunctions of ever-increasing complexity. The nth shell has energy

$$E_n = -(13.6 \text{ eV}) \frac{Z^2}{n^2}$$

and contains exactly n subshells, corresponding to $\ell = 0, 1, \ldots, n - 1$. Within the ℓth subshell there are $2\ell + 1$ orbitals. Altogether, the nth shell contains a total of n^2 states, all with the same energy, E_n; that is, **the energy level E_n is n^2 degenerate.** Equivalently, we say the nth shell can hold as many as n^2 electrons, assuming no more than one electron can occupy a given orbital. This argument underestimates the actual shell capacity by a factor of 2, owing to the existence of electron spin, as discussed in the next chapter.

8.6   ANTIHYDROGEN

The constituents of hydrogen atoms, protons and electrons, are abundant in the universe and among the elementary particles that make up all matter around us. But each of these elementary particles has a partner, its *antiparticle*, identical to the original in all respects other than carrying charge of the opposite sign.[13] The anti-electron, or positron, was discovered in 1932 by Carl Anderson.[14] The positron has the same mass as the electron but carries charge

[13]Strictly speaking, the antiparticle also has a magnetic moment opposite that of its companion particle. Magnetic moments are discussed in Chapter 9, and are intimately related to a new particle property called *spin*. The spin is the same for particle and antiparticle.

[14]The idea of antiparticles received a solid theoretical underpinning in 1928 with P. A. M. Dirac's relativistic theory of the electron. While furnishing an accurate quantum description of electrons with relativistic energies, Dirac's theory also included mysterious "negative energy" states. Eventually Dirac realized that these "negative energy" states actually describe antiparticles with positive energy. Dirac's conjecture was subsequently confirmed with the discovery of the positron in 1932. See Section 15.2.

$+e$. Because it cannot be produced without a powerful particle accelerator, the much more massive antiproton was not observed until 1955. Again, the antiproton has the same mass as the proton but is oppositely charged. Just as atoms and ordinary matter are made up of particles, it is easy to conceive of anti-atoms and all forms of antimatter built out of antiparticles. Indeed, on the face of it there would be no way to tell if we lived in an antimatter world and were ourselves composed entirely of antimatter!

The simplest such anti-atom is **antihydrogen,** the most fundamental neutral unit of antimatter. Antihydrogen consists of a positron bound electrically to an antiproton. Many physicists believe that the study of antihydrogen can answer the question of whether there is some fundamental, heretofore unknown difference between matter and antimatter and why our Universe seems to be composed almost exclusively of ordinary matter. For the reasons outlined here, the production of antihydrogen is fraught with difficulties, and it was not until the mid 1990s that two groups, one at CERN and the other at Fermilab, reported success in producing antihydrogen at high energies. In 2002, the CERN group reported antihydrogen production at the very low energies required for precision comparison measurements with ordinary hydrogen. Trapping the anti-atoms long enough so that experiments can be performed on them is much more difficult and has not yet been achieved.

When a particle and its antiparticle collide, both disappear in a burst of electromagnetic energy. This is **pair annihilation,** the direct conversion of mass into energy in accord with Einstein's famous relation $E = mc^2$. An electron and a positron combine to produce two (sometimes three) gamma-ray photons (one photon alone cannot conserve both energy *and* momentum). The collision of a proton and antiproton produces three or four other elementary particles called *pions*. The problem that experimentalists face is that their laboratories and measuring instruments are made of ordinary matter and antiparticles will self-destruct on first contact with the apparatus. A similar problem arises in the containment of plasmas, which are tamed using a magnetic trap, that is, a configuration of magnetic fields that exert forces on charged particles of the plasma to keep them confined. But neutral anti-atoms experience only weak magnetic forces and will quickly escape the trap unless they are moving very slowly. Thus, the antihydrogen atom must be *cold* if it is to survive long enough to be useful for precision experiments, and this presents yet another challenge. While positrons are readily available as decay products of naturally occurring radioactive species like ^{22}Na, antiprotons must be created artificially in particle accelerators by bombarding heavy targets (Be) with ultra-energetic (~GeV) protons. The positrons and antiprotons so produced are very energetic and must be slowed down enormously to form cold antihydrogen. The slowdown is achieved at the cost of lost particles in what is essentially an accelerator run backwards. The CERN experiment yields about 50,000 antihydrogen atoms starting from some 1.5 million antiprotons. And of these, only a small fraction is actually detected.

Detecting antihydrogen is a challenge in its own right. The existence of an antiproton is confirmed by the decay products (pions) it produces on annihilation with its antimatter counterpart, the proton. These decay products leave directional traces in the detectors that surround the anti-atom sample. From the directional traces, physicists are able to reconstruct the precise location of the annihilation event. To confirm the existence of antihydrogen, however, one must also

record electron–positron annihilation in the same place at the same time. The tell-tale gamma-ray photons produced in that annihilation can also be traced back to a point of origination. Thus, the signature of antihydrogen is the coincidence of multiple distinct detection events, as illustrated in Figure 8.14.

According to the theory presented in this chapter, the energy spectrum of antihydrogen should be identical to that of ordinary hydrogen. The hydrogen atom is the best known of all physical systems, and extremely precise measurements of its spectrum have been made, the best of which is accurate to about 2 parts in 10^{14}. Thus, comparing spectra of antihydrogen with ordinary hydrogen would allow a stringent test of the symmetry expected between matter and antimatter in atomic interactions. This symmetry is rooted in so-called CPT invariance, which states that if one were to take any lump of matter, reverse the sign of all the elementary charges (C), the direction of time's flow (T), and another property of particles called parity (P), the specimen would obey the same laws of physics. CPT invariance is a very general consequence of quantum theory and the covariance of quantum laws under Lorentz transformation demanded by special relativity and is the cornerstone for every modern theory of matter. If CPT invariance is violated, the whole of physical theory at the fundamental level will have to be rewritten. While nearly all physicists agree that is very unlikely, the prospect of CPT violation holds tantalizing possibilities and may shed light on one of the most perplexing problems of modern cosmology: why there is now a preponderance of matter in the Universe, when the Big Bang theory predicts that matter and antimatter should have been created in equal amounts. Furthermore, if antihydrogen responds differently to gravity, the theory of relativity in its present form would be compromised, a development that could point the way to the long-sought unification of relativity and quantum theory.

SUMMARY

In three dimensions, the matter wave intensity $|\Psi(\mathbf{r}, t)|^2$ represents the probability per unit volume for finding the particle at $\mathbf{r}$ at time t. Probabilities are found by integrating this probability density over the volume of interest.

The wavefunction itself must satisfy the Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + U(\mathbf{r})\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad (8.1)$$

Stationary states are solutions to this equation in separable form: $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-i\omega t}$ with $\psi(\mathbf{r})$ satisfying

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad (8.5)$$

This is the **time-independent Schrödinger equation,** from which we obtain the time-independent wavefunction $\psi(\mathbf{r})$ and the allowed values of particle energy E.

For a particle confined to a cubic box whose sides are L, the magnitudes of the components of particle momentum normal to the walls of the box can be made sharp, as can the particle energy. The sharp momentum values are quantized as
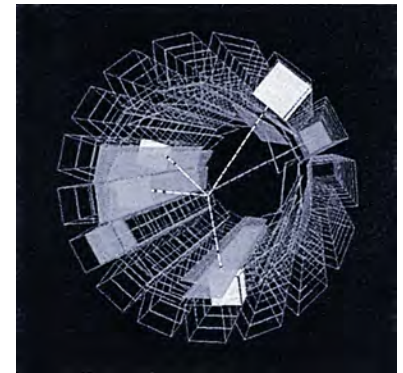

Figure 8.14 Antihydrogen is detected through its destruction in collisions with matter particles. The annihilation of the antiproton produces pions that, picked up in the surrounding detectors (light colored), can be traced back (four light colored dashed lines) to the annihilation point. Similarly, the annihilation of the positron produces a distinctive back-to-back two-photon signature (two dashed tracks at 180° to one another). Overlap of the two annihilation points signifies that the positron and antiproton were bound together in an atom of antihydrogen. (Adapted from *Nature*, 419, 456–459, October 3, 2002.)