FIGURE 1.14 The Born interpretation of the wavefunction. The probability density (the blue line) is given by the square of the wavefunction and depicted by the density of shading in the band beneath. Note that the probability density is zero at a node. A node is a point where the wavefunction (the orange line) passes through zero, not merely approaches zero.

Note the "passes through"; merely becoming zero is not enough to be considered a node.

The symbol V is commonly used to denote potential energy, rather than E_P, in this context.

Derivatives are reviewed in Appendix 1F.

FIGURE 1.15 Erwin Schrödinger (1887–1961), thinking about his equation.

nothing mysterious about the form of wavefunctions: they are just mathematical functions such as $\sin x$, a function that varies like a wave, and e^{-x}, a function that decays exponentially toward zero.

The German physicist Max Born suggested how the wavefunction should be interpreted physically. According to the **Born interpretation** of the wavefunction, *the probability of finding the particle in a region is proportional to the value of* ψ^2 (Fig. 1.14). To be precise, ψ^2 is a **probability density,** the probability that the particle will be found in a small region divided by the volume of the region. It follows that, to calculate the probability that the particle is in a small region of space, we multiply ψ^2 by the volume of the region. For instance, if $\psi^2 = 0.1 \text{ pm}^{-3}$ at a point, then the probability of finding the particle in a region of volume 2 pm^3 located at that point would be $(0.1 \text{ pm}^{-3}) \times (2 \text{ pm}^3) = 0.2$, or 1 chance in 5. According to the Born interpretation, wherever ψ^2 is large, the particle has a high probability density; wherever ψ^2 is small, the particle has only a low probability density.

Because the square of any number is positive, we don't have to worry about ψ having a negative sign in some regions of space (as a function such as $\sin x$ has): probability density is never negative. Wherever ψ, and hence ψ^2, is zero, there is zero probability density for the particle. A location where ψ passes through zero is called a **node** of the wavefunction; so we can say that a particle has zero probability density wherever the wavefunction has nodes.

The **Schrödinger equation** is an equation for calculating wavefunctions. We can see what the equation looks like in Fig. 1.15, which shows it emerging from Schrödinger's head. More formally, the equation for a particle of mass m moving in a region where the potential energy is $V(x)$ is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \tag{8a}$$

The Schrödinger equation is a "differential equation," an equation that relates derivatives of a function (in this case, a second derivative of ψ, $d^2\psi/dx^2$) to the value of the function at each point. It is impossible to solve exactly except in certain simple cases. However, in this text, we need only the form of some of its solutions, not how those solutions are found. The left-hand side of the Schrödinger equation is commonly written $H\psi$, where H is called the **hamiltonian** for the system, then the equation takes the deceptively simple form

$$H\psi = E\psi \tag{8b}*$$

One of the simplest examples of an actual wavefunction is that for a particle of mass m confined between two rigid walls a distance L apart, the so-called **particle in a box** (Fig. 1.16). The shapes of the wavefunctions for this one-dimensional system, some of which are shown in the illustration, make sense when we view the particle as a wave. Only certain wavelengths can exist in the box, just as a stretched string can support only certain wavelengths. Think of a guitar string: because it is tied down at each end, it can support only shapes like the ones shown in Fig. 1.16. The shapes of the wavefunctions are identical with the displacements of a stretched string when it vibrates, and their mathematical form is that of a standing wave:

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \qquad n = 1, 2, \ldots \tag{9}$$

The integer n labels the wavefunctions and is called a "quantum number." In general, a **quantum number** is an integer (sometimes, a half-integer) that labels a wavefunction, specifies a state, and can be used to calculate the value of a property of the system. For example, we can use n to find an expression for the energy corresponding to each wavefunction.

HOW DO WE DO THAT (LEVEL 1)?

The kinetic energy of a particle of mass m is related to its speed, v, by $E_K = \frac{1}{2}mv^2$. We can relate this energy to the wavelength of the particle by noting that the linear momentum is $p = mv$ and then using the de Broglie relation (Eq. 6b):

$$E_K = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$$

The potential energy of the particle is zero everywhere inside the box, and so the total energy, E, is given by the expression for E_K alone. At this point, we recognize that only waves have one bulge, two bulges, three bulges, and so forth, with each "bulge" a half-wavelength. That is, for a box of length L,

$$L = \frac{1}{2}\lambda, \lambda, \frac{3}{2}\lambda, \ldots = n \times \frac{1}{2}\lambda, \quad \text{with } n = 1, 2, \ldots$$

Therefore, the allowed wavelengths are

$$\lambda = 2L/n, \quad \text{with } n = 1, 2, \ldots$$

When this expression for λ is inserted into the expression for the energy, we obtain

$$E_n = \frac{n^2 h^2}{8mL^2}$$

HOW DO WE DO THAT (LEVEL 2)?

The more sophisticated—and more general—way of finding the energy levels of a particle in a box is to solve the Schrödinger equation. First, we note that the potential energy of the particle is zero everywhere inside the box; so $V(x) = 0$, and the equation that we have to solve is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

This equation has the solutions

$$\psi(x) = A \sin kx + B \cos kx$$

with A, B, and k constants, as may be verified by substituting the solutions into the differential equation and using $d(\sin kx)/dx = k \cos kx$ and $d(\cos kx)/dx = -k \sin kx$. Indeed, because

$$\frac{d^2\psi}{dx^2} = \frac{d^2}{dx^2}(A \sin kx + B \cos kx) = -k^2(A \sin kx + B \cos kx) = -k^2\psi$$

we can conclude, by substituting this relation into the Schrödinger equation, that

$$E = \frac{k^2\hbar^2}{2m} = \frac{k^2 h^2}{8\pi^2 m}$$

Now we have to find the constants A, B, and k. First, we note that the wavefunction is zero outside the box but must be continuous. Therefore, for a box of length L, $\psi(x)$ must be zero at the edges of the box, at $x = 0$ and $x = L$. We call these constraints "boundary conditions." If we set $x = 0$ and use $\sin 0 = 0$ and $\cos 0 = 1$ in $\psi(x) = A \sin kx + B \cos kx$, we find $\psi(0) = B$. However, $\psi(0) = 0$; so $B = 0$ and the wavefunction is

$$\psi(x) = A \sin kx$$

This expression already resembles that in Eq. 9. To find the value of k, we use the second boundary condition, that $\psi(L) = 0$; that is,
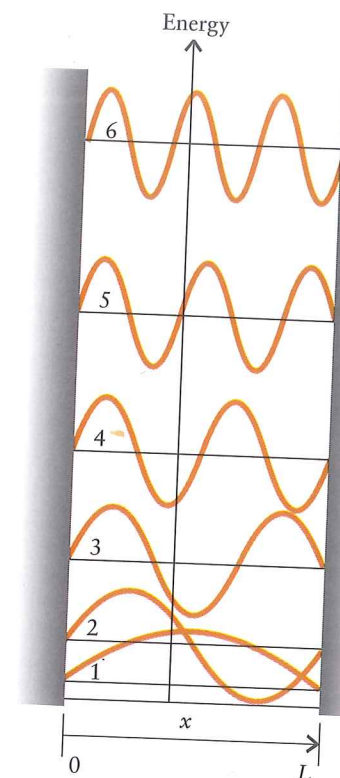
$$\psi(L) = A \sin kL = 0$$

FIGURE 1.16 The arrangement known as "a particle in a box," in which a particle of mass m is confined between two impenetrable walls a distance L apart. The first six wavefunctions and their energies are shown. The numbers on the left are values of the quantum number n. Note that there is a zero-point energy because n cannot be zero.

Setting $A = 0$ is unacceptable, because then $\psi(x)$ would be 0 everywhere, which would mean that the particle would be nowhere. Therefore, to guarantee that $\psi(L) = 0$, we use the relation $\sin n\pi = 0$ and set $kL = n\pi$, with $n = 1, 2, \ldots$. We now have

$$\psi(x) = A \sin \frac{n\pi x}{L} \qquad n = 1, 2, \ldots$$

To find the one remaining constant, A, we use the fact that the probability of finding the particle in a region of length dx at x is $\psi(x)^2 dx$, and therefore the total probability of finding the particle between $x = 0$ and $x = L$ is the sum (integral) of these probabilities and must be equal to 1 (the particle must be somewhere in the box). Therefore,

$$\int_0^L \psi(x)^2 dx = A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = 1$$

The integral evaluates to $L/2$; so $A = (2/L)^{1/2}$ and the final form of the wavefunction is that given in Eq. 9. Moreover, because k is limited to the values $n\pi/L$, it follows that the energy of the particle is limited to

$$E = \frac{(n\pi/L)^2 \hbar^2}{8\pi^2 m} = \frac{n^2 h^2}{8mL^2}$$

exactly as we found in level 1. We see that the quantization of energy (see following text) stems directly from the imposition of "boundary conditions" on the wavefunction, conditions that ψ must obey in order for it to be acceptable. In this example, the boundary conditions are that ψ must be zero at each wall of the box. The origin of quantization from the imposition of boundary conditions on the wavefunction is a general result for any system.

We have established that the allowed energies of a particle of mass m in a one-dimensional box of length L are

$$E_n = \frac{n^2 h^2}{8mL^2} \tag{10*}$$

A striking implication of this result is that the energy of the particle is **quantized**, meaning that it is restricted to a series of discrete values, called **energy levels**. According to classical mechanics, an object can have any total energy—high, low, and anything in between. For example, a particle in a box could bounce from wall to wall with any speed and hence any kinetic energy. According to quantum mechanics, however, the energy is quantized: only certain wavelengths fit into the box. Quantization is a little like pouring water into a bucket. Water seems to be a continuous fluid that can be transferred in any amount, no matter how small. However, the smallest amount of water that we can transfer is one H_2O molecule. Energy seems to be unrestricted on the macroscopic scale; but, on the subatomic scale, we can transfer only discrete amounts to the particle in a box and it can lose energy only in discrete amounts corresponding to the differences between the energy levels. As we saw in the derivation of Eq. 10, the existence of quantization stems from the **boundary conditions** on the wavefunction, the constraints that the wavefunction must satisfy at different points of space (such as fitting into a container correctly).

We can use Eq. 10 to calculate the energy separation between two neighboring levels with quantum numbers n and $n + 1$:

$$E_{n+1} - E_n = \frac{(n+1)^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2} = \frac{(2n+1)h^2}{8mL^2} \tag{11}$$

We see that, as L or m increases, the separation between neighboring energy levels decreases (Fig. 1.17). That is why no one noticed that energy is quantized until they investigated very small systems such as an electron in a hydrogen atom: the separation between levels is so small for ordinary particles in ordinary-sized vessels that it is completely undetectable. We can, in fact, ignore the quantization of the motion of the atoms of a gas in a typical flask.
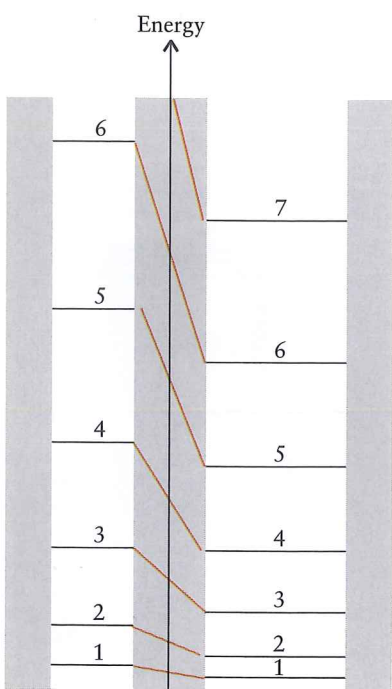

FIGURE 1.17 As the length of the box increases (compare boxes on left and right), the energy levels fall and move closer together.

EXAMPLE 1.5   Calculating the energies of a particle in a box

Treat a hydrogen atom as a one-dimensional box of length 150. pm (the approximate diameter of the atom) containing an electron and predict the wavelength of the radiation emitted when the electron falls to the lowest energy level from the next higher energy level.

STRATEGY   The lowest energy level has $n = 1$, and so we can use Eq. 11 with $n = 1$ and $m = m_e$, the mass of the electron. The energy difference is carried away as a photon of radiation; so we set the energy difference equal to $h\nu$ and express ν in terms of the corresponding wavelength by using Eq. 1 ($\lambda = c/\nu$). As usual, it is good practice to go as far as possible symbolically and then to insert numerical values at the last possible stage.

SOLUTION   According to Eq. 11, with $n = 1$:

$$h\nu = E_2 - E_1 = \frac{[(2 \times 1) + 1]h^2}{8 m_e L^2} = \frac{3h^2}{8 m_e L^2}$$

It follows that,

$$\text{from } h\nu = \frac{3h^2}{8 m_e L^2}, \qquad \nu = \frac{3h}{8 m_e L^2}$$

$$\text{and, from } \lambda\nu = c, \qquad \lambda = \frac{c}{\nu} = \frac{8 m_e c L^2}{3h}$$

Finally, insert the data:

$$\lambda = \frac{8 \times (9.109 \times 10^{-31}\, kg) \times (2.998 \times 10^8\, m \cdot s^{-1}) \times (1.50 \times 10^{-10}\, m)^2}{3 \times (6.626 \times 10^{-34}\, J \cdot s)}$$

$$= 2.47 \times 10^{-8} \frac{kg \times (m \cdot s^{-1}) \times m^2}{(kg \cdot m^2 \cdot s^{-2}) \times s} = 2.47 \times 10^{-8}\, m$$

Note how the complicated collection of units is treated: arriving at the correct units for the answer is a sign that you have set up the equation correctly. This wavelength corresponds to 24.7 nm. The experimental value for an electron in a hydrogen atom is 122 nm. Although there is a big discrepancy, the fact that the predicted wavelength has nearly the same order of magnitude as the actual value suggests that a quantum theory of the atom, based on a more realistic three-dimensional model, should give good agreement.

SELF-TEST 1.7A   Use the same model for helium but suppose that the box is 100. pm long, because the atom is smaller. Estimate the wavelength of the same transition.

[*Answer*: 11.0 nm]

SELF-TEST 1.7B   Use the same model for hydrogen and estimate the wavelength for the transition from the $n = 3$ energy level to the $n = 2$ level.

Another surprising implication of Eq. 10 is that *a particle in a container cannot have zero energy*. Because the lowest value of n is 1 (corresponding to a wave of one-half wavelength fitting into the box), the lowest energy is $E_1 = h^2/8mL^2$. This lowest possible energy is called the **zero-point energy**. The existence of a zero-point energy means that, according to quantum mechanics, a particle can never be perfectly still when it is confined between two walls: it must always possess an energy—in this case, a kinetic energy—of at least $h^2/8mL^2$. This result is consistent with the uncertainty principle. When a particle is confined between two walls, the uncertainty in its position cannot be larger than the distance between the two walls. Because the position is not *completely* uncertain, the linear momentum must be uncertain, too, and so we cannot say that the particle is completely still. The particle must therefore have some kinetic energy. The zero-point energy is a purely quantum mechanical phenomenon and is very small for macroscopic systems. For example, a billiard ball on a pool table has a completely negligible zero-point energy of about 10^{-67} J.
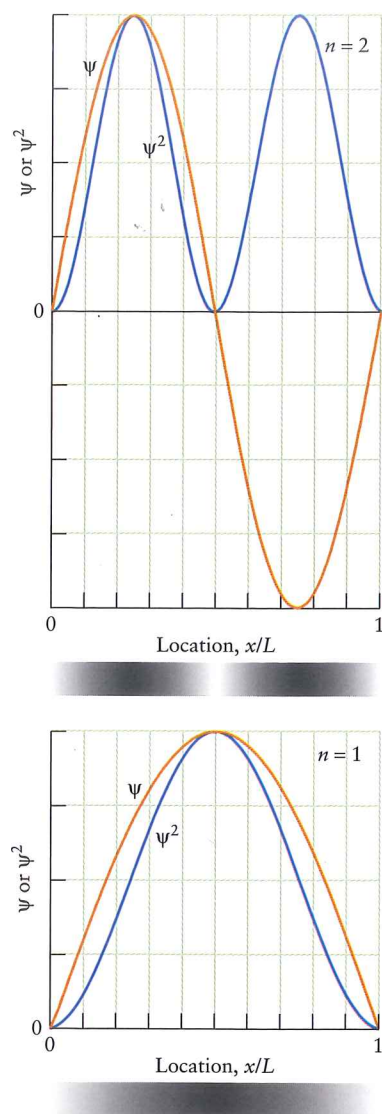
Finally, the shapes of the wavefunctions of a particle in a box also reveal some interesting information. Let's look at the two lowest energy wavefunctions, corresponding to $n = 1$ and $n = 2$. Figure 1.18 shows, by the density of shading, the likelihood of finding a particle: we see that when a particle is described by the wavefunction ψ_1 (and has energy $h^2/8mL^2$), then it is most likely to be found in the center of the box. Conversely, if the particle is described by the wavefunction ψ_2 (and has energy $h^2/2mL^2$), then it is most likely to be found in regions between the center and the walls and is unlikely to be found in the middle of the box. Remember that the wavefunction itself does not have any direct physical significance: we have to take the square of ψ before we can interpret it in terms of the probability of finding a particle somewhere.

EXAMPLE 1.6 Plotting the wavefunctions for a particle in a box

(a) Using the Living Graphs on the Web site for this book, plot the particle-in-a-box wavefunction for $n = 2$ and $L = 1$ m. (b) How many nodes does the wavefunction have? Where do these nodes occur? (c) Repeat parts (a) and (b) for $n = 3$. (d) What general conclusion can you draw about the relation between n and the number of nodes present in a wavefunction? (e) Convert the $n = 2$ plot into a probability density distribution: at what values of x is the particle most likely to be found? (f) Repeat part (e) for $n = 3$.

STRATEGY The wavefunctions for a particle in a box are given by Eq. 9. Use the Living Graphs "Particle-in-a-Box Wavefunctions" on the Web site for this book to plot them. (a) To plot the wavefunction, enter the parameters $L = 1$ m and $n = 2$, set the range for the entire box ($x = 0$ m to 1 m), check the $f(x)$ box, and hit New Plot. (b) The nodes are found where the curve passes through zero. To find the value of x at a point, click on the plot at that point. (c) Create a new plot as before, but set $n = 3$. (d) Look for the patterns in the number of nodes and the value of the quantum number n. (e) Repeat part (a) with the $f^2(x)$ box checked and look for the maxima in the probability density. (f) Repeat part (e) for $n = 3$.

SOLUTION

(a)
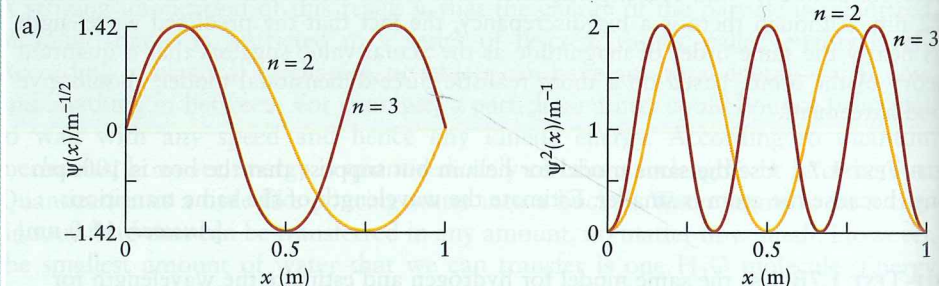
(b) The plot for $n = 2$ has one node at $x = 0.500$ m. (c) The plot for $n = 3$ has two nodes at $x = 0.333$ m and 0.667 m. (d) The number of nodes is equal to $n - 1$. (e) Maxima occur at $x = 0.25$ m and 0.75 m. (f) Maxima occur at $x = 0.17$ m, 0.50 m, and 0.83 m.

SELF-TEST 1.8A Verify the conclusion in part (d) of Example 1.6 by plotting the wavefunction for $n = 4$ and determining the number of nodes.

[*Answer:* Three nodes]

SELF-TEST 1.8B Verify the conclusion in part (d) of Example 1.6 by plotting the wavefunction for $n = 5$ and determining the number of nodes.

The probability density for a particle at a location is proportional to the square of the wavefunction at that point; the wavefunction is found by solving the Schrödinger equation for the particle. When the equation is solved subject to the appropriate boundary conditions, it is found that the particle can possess only certain discrete energies.
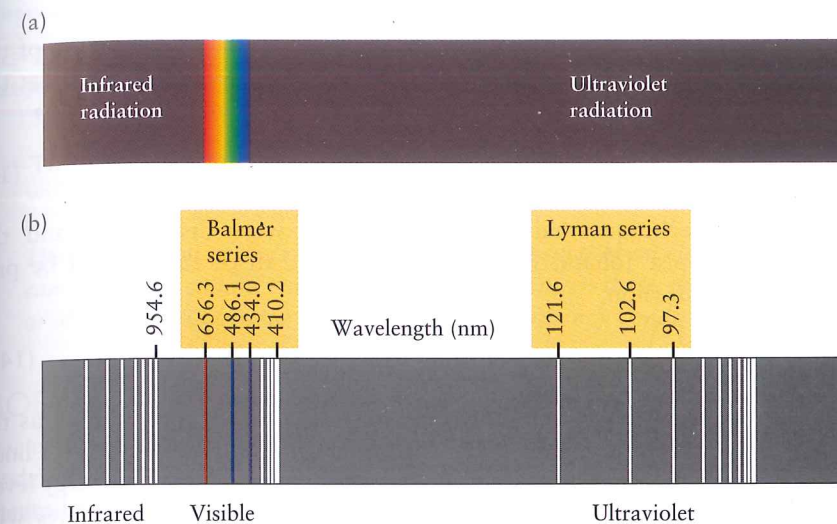
FIGURE 1.18 The two lowest energy wavefunctions (ψ, orange) for a particle in a box and the corresponding probability densities (ψ^2, blue). The probability densities are also shown by the density of shading of the bands beneath each wavefunction.

FIGURE 1.19 (a) The visible spectrum. (b) The complete spectrum of atomic hydrogen. The spectral lines have been assigned to various groups called series, two of which are shown with their names.

1.6 Atomic Spectra and Energy Levels

Compelling evidence for the validity of quantum mechanics came from its ability to explain atomic spectra. When an electric current is passed through a low-pressure sample of hydrogen gas, the sample emits light. The electric current, which is like a storm of electrons, breaks up the H_2 molecules and excites the free hydrogen atoms to higher energies. These excited atoms quickly discard their excess energy by giving off electromagnetic radiation; then they combine to form H_2 molecules again.

When white light is passed through a prism, a continuous spectrum of light results (Fig. 1.19a). However, when the light emitted by excited hydrogen atoms is passed through a prism, the radiation is found to consist of a number of components, or **spectral lines** (Fig. 1.19b). The brightest line (at 656 nm) is red, and the excited atoms in the gas glow with this red light. Excited hydrogen atoms also emit ultraviolet and infrared radiation, which are invisible to the eye but can be detected electronically and photographically.

The series of discrete lines making up the spectrum of atomic hydrogen was highly puzzling to early spectroscopists. They wondered how an atom could emit only particular frequencies of electromagnetic radiation and not all possible frequencies. The answer must be that an atom can lose energy only in certain discrete amounts. This answer, in turn, suggests that the electron in the atom can exist *only in a series of discrete energy levels,* just like a particle in a box. When an electron undergoes a **transition**, a change of state, in which its energy changes from a higher energy level to a lower one, the difference in energy, $\Delta E = E_{upper} - E_{lower}$, is carried away as a photon. Because the energy of a photon is $h\nu$, where h is Planck's constant, the frequency ν, of an individual line in a spectrum, is related to the energy difference between two energy levels (Fig. 1.20):

$$h\nu = E_{upper} - E_{lower} \qquad (12)*$$

This relation is called the **Bohr frequency condition.** Each spectral line arises from a specific transition. By analyzing the appearance of the spectrum, we can build a picture of the ladder of energy levels for the atom, which is called an **energy-level diagram** (Fig. 1.21).

FIGURE 1.20 When an atom undergoes a transition from a state of higher energy to one of lower energy, it loses energy that is carried away as a photon. The greater the energy loss (A compared with B), the higher the frequency (and the shorter the wavelength) of the radiation emitted.

The components of different frequency or wavelength are called lines because, in the early spectroscopic experiments, the radiation from the sample was passed through a slit and then through a prism; the image of the slit was then focused on a photographic plate, where it appeared as a line.

FIGURE 1.21 The spectrum of atomic hydrogen (reproduced on the right) tells us the arrangement of the energy levels of the atom because each line results from the transition of electrons between two specific states. The frequency of the radiation emitted in a transition is proportional to the energy difference between the two energy levels. The zero of energy corresponds to the completely separated proton and electron. The numbers on the right identify the energy levels: they are examples of quantum numbers.
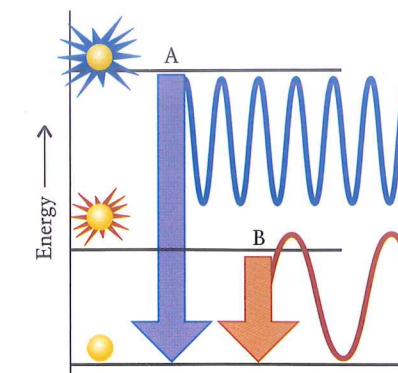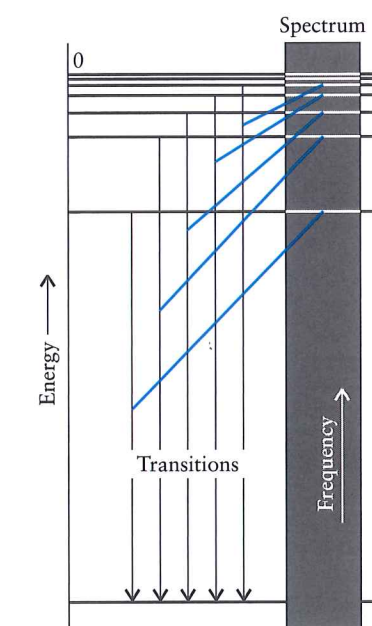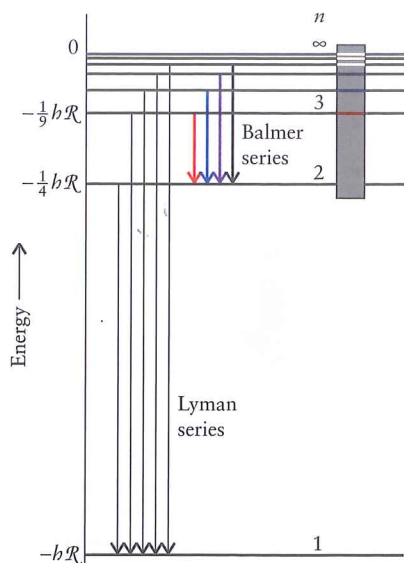
FIGURE 1.22 The permitted energy levels of a hydrogen atom as calculated from Eq. 14. The levels are labeled with the quantum number, n, which ranges from 1 (for the lowest state) to infinity (for the separated proton and electron).

The first person to identify a pattern in the lines of the visible region of the spectrum was Joseph Balmer, a Swiss schoolteacher. In 1885, he noticed that the frequencies of all the lines then known could be generated by the expression

$$\nu \propto \frac{1}{2^2} - \frac{1}{n^2} \qquad n = 3, 4, \ldots \tag{13}$$

As experimental techniques advanced, more lines were discovered, and the Swedish spectroscopist Johann Rydberg noticed that all of them could be predicted from the expression

$$\nu = \mathcal{R}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad n_1 = 1, 2, \ldots \quad n_2 = n_1 + 1, n_1 + 2, \ldots \tag{14}*$$

Here $\mathcal{R}$ is an empirical (experimentally determined) constant now known as the **Rydberg constant;** its value is 3.29×10^{15} Hz. This empirical formula for the lines, together with the Bohr frequency condition, strongly suggests that the energy levels themselves are proportional to $\mathcal{R}/n^2$. The **Balmer series** is the set of lines with $n_1 = 2$ (and $n_2 = 3, 4, \ldots$). The **Lyman series,** a set of lines in the ultraviolet region of the spectrum, has $n_1 = 1$ (and $n_2 = 2, 3, \ldots$) (Fig. 1.22).

Another consequence of quantization is that an atom can *absorb* radiation only of certain frequencies. The energy of the incoming photon excites electrons from one quantum level to another. If we pass light through a vapor composed of the atoms of an element, we see its *absorption spectrum,* a series of dark lines on an otherwise continuous spectrum (Fig 1.23). The absorption lines have the same frequencies as those of the lines in the emission spectrum. Absorption spectra are used by astronomers to identify elements in the outer layers of stars.

EXAMPLE 1.7   Identifying a line in the hydrogen spectrum

Calculate the wavelength of the radiation emitted by a hydrogen atom when an electron makes a transition between the levels with $n_2 = 3$ and $n_1 = 2$. Identify in Fig. 1.19b the spectral line produced by this transition.

STRATEGY   The frequency of a line arising from a transition is given by Eq. 14. Convert frequency into wavelength by using Eq. 1. The wavelength should match one of the lines in the Balmer series in Fig. 1.19b.

SOLUTION   For the transition from a level with $n_2 = 3$ to a level with $n_1 = 2$, from Eq. 14 with $n_1 = 2$ and $n_2 = 3$,

$$\nu = \mathcal{R}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5}{36}\mathcal{R}$$

From $\lambda\nu = c$,

$$\lambda = \frac{c}{\nu} = \frac{c}{(5/36)\mathcal{R}} = \frac{36c}{5\mathcal{R}}$$

Now substitute the values of c and $\mathcal{R}$:

$$\lambda = \frac{36 \times (2.998 \times 10^8 \text{ m·s}^{-1})}{5 \times (3.29 \times 10^{15} \text{ s}^{-1})} = \frac{36 \times 2.998 \times 10^8}{5 \times 3.29 \times 10^{15}} \text{ m} = 6.57 \times 10^{-7} \text{ m}$$

This wavelength, 657 nm, corresponds to the red line in the Balmer series of lines in the spectrum. Light of this wavelength is absorbed when the electron is promoted from the $n = 2$ level to the $n = 3$ level and is given off when the electron falls back to the $n = 2$ level.

FIGURE 1.23 When white light shines through an atomic vapor, radiation is absorbed at frequencies that correspond to excitation energies of the atoms. Here is a small section of the spectrum of the Sun, in which atoms in its outer layers absorb the radiation from the incandescence below. Many of the lines have been ascribed to hydrogen, showing that hydrogen is present in the cooler outer layers of the sun.
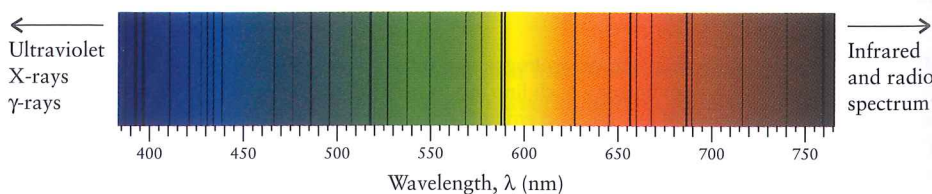
The observation of discrete spectral lines suggests that an electron in an atom can have only certain energies. Transitions between these energy levels generate or absorb photons in accord with the Bohr frequency condition.

MODELS OF ATOMS

Our next task is to combine the wavelike properties of electrons with the nuclear model of the atom and explain the strange ladder of energy levels observed experimentally in a hydrogen atom. We proceed in two steps. First, we develop the quantum mechanical model of a hydrogen atom. Then we use that model to account for the structures of atoms with more than one electron and see how a few simple ideas account not only for atomic spectra but also for the structure of the periodic table.

1.7   The Principal Quantum Number

An electron in an atom is like a particle in a box, in the sense that it is confined within the atom by the pull of the nucleus. We can therefore expect the electron's wavefunctions to obey certain boundary conditions, like the constraints we encountered when fitting a wave between the walls of a container. As we saw for a particle in a box, these constraints result in the quantization of energy and the existence of discrete energy levels.

We find the actual energy levels of an electron in a hydrogen atom by setting up and solving the appropriate Schrödinger equation. To set up the equation, we insert the appropriate expression for the potential energy, V, in Eq. 8. For an electron in a hydrogen atom, the Coulomb potential energy of the electron of charge $-e$ (Section A) varies with distance, r, from the nucleus of charge $+e$ as follows (as remarked earlier, V is commonly used rather than E_P in this context):

$$V(r) = \frac{(-e)(+e)}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{15}$$

Solving the Schrödinger equation for a particle with this potential energy is difficult, but Schrödinger himself achieved it in 1927. He found that the allowed energy levels are

$$E_n = -\frac{h\mathcal{R}}{n^2} \qquad \mathcal{R} = \frac{m_e e^4}{8h^3\varepsilon_0^2} \qquad n = 1, 2, \ldots \tag{16a}*$$

These energy levels have exactly the form suggested by the wavelengths of the lines measured spectroscopically, but now we have an expression for $\mathcal{R}$ in terms of more fundamental constants. When the fundamental constants are inserted into the expression for $\mathcal{R}$, the value obtained is 3.29×10^{15} Hz, the same as the experimental value of the Rydberg constant. This agreement is a triumph for Schrödinger's theory and for quantum mechanics. A very similar expression applies to other one-electron ions, such as He^+ and even C^{5+}, with atomic number Z:

$$E_n = -\frac{Z^2 h\mathcal{R}}{n^2} \tag{16b}$$

The greater the value of Z, the more tightly the electron is bound to a nucleus, and so these energies are more strongly negative for heavy atoms than for a hydrogen atom.

Figure 1.22 shows the energy levels calculated from Eq. 16. From the minus signs in Fig. 1.22 and in Eq. 16, we can see that the energy of an electron in a hydrogen atom is always lower than that of a free electron. The **principal quantum number,** n, is an integer that labels these energy levels, from $n = 1$ for the first (lowest, most negative) level, $n = 2$ for the second, continuing to infinity. The lowest energy possible for an electron in a hydrogen atom, $-h\mathcal{R}$, is obtained when $n = 1$. This lowest energy state is called the **ground state** of the atom. A hydrogen atom is normally found in its ground state, with its electron in the level with $n = 1$. The energy of the bound electron climbs up the ladder of levels as n increases. It reaches the top of the ladder, corresponding to $E = 0$ and freedom, when n reaches infinity. At that point, the electron has left the atom. This process is called **ionization.** The difference in energy between the ground state and the ionized state is the energy required to remove an electron from the neutral atom in its ground state.

> *The energy levels of a hydrogen atom, Eq. 16, are defined by the principal quantum number, $n = 1, 2, \ldots$, and form a converging series, as shown in Fig. 1.22.*
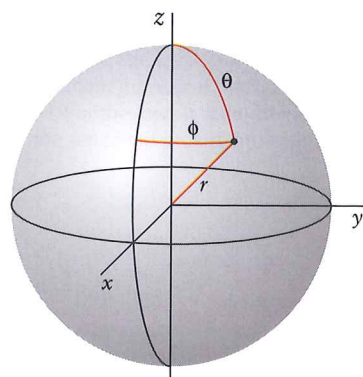
1.8 Atomic Orbitals

Wavefunctions of electrons in atoms are called **atomic orbitals.** The name was chosen to suggest something less definite than an "orbit" of an electron around a nucleus and to take into account the wave nature of the electron. The mathematical expressions for atomic orbitals—which are obtained as solutions of the Schrödinger equation—are more complicated than the sine functions for the particle in a box, but their essential features are quite simple. Moreover, we must never lose sight of their interpretation, that the *square* of a wavefunction tells us the probability density of an electron at each point. To visualize this probability density, imagine a cloud centered on the nucleus. The density of the cloud at each point represents the probability of finding an electron there. Denser regions of the cloud therefore represent locations where the electron is more likely to be found.

To interpret the information in each atomic orbital, we need a way to identify the location of each point around a nucleus. It is most convenient to describe these locations in terms of **spherical polar coordinates,** in which each point is labeled with three coordinates:

- r, the distance from the center of the atom;
- θ (theta), the angle from the positive z-axis (the "north pole"), which can be thought of as playing the role of the "latitude"; and
- ϕ (phi), the angle about the z-axis, the "longitude."

These coordinates are shown in Fig. 1.24. Each wavefunction, which in general varies from point to point, can be written as a function of the coordinates, $\psi(r,\theta,\phi)$. It turns out, however, that all the wavefunctions can be written as the product of a function that depends only on r and another function that depends only on the angles θ and ϕ. That is,

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \qquad (17)*$$

The function $R(r)$ is called the **radial wavefunction,** and the function $Y(\theta,\phi)$ is called the **angular wavefunction.** For example, the wavefunction corresponding to the ground state of the hydrogen atom is

$$\psi(r,\theta,\phi) = \overbrace{\frac{2e^{-r/a_0}}{a_0^{3/2}}}^{R(r)} \times \overbrace{\frac{1}{2\pi^{1/2}}}^{Y(\theta,\phi)} = \frac{e^{-r/a_0}}{(\pi a_0^3)^{1/2}} \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

The quantity a_0 is called the **Bohr radius;** when the values of the fundamental constants are inserted, we find $a_0 = 52.9$ pm. For this wavefunction, the angular

wavefunction Y is a constant, $1/2\pi^{1/2}$, independent of the angles, and the radial wavefunction R decays exponentially toward zero as r increases. One of the wavefunctions for the next higher energy level (at $E_2 = -\frac{1}{4}hR$) is

$$\psi(r,\theta,\phi) = \overbrace{\frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2} re^{-r/2a_0}}^{R(r)} \times \overbrace{\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi}^{Y(\theta,\phi)}$$
$$= \frac{1}{4}\left(\frac{1}{2\pi a_0^3}\right)^{1/2} re^{-r/2a_0}\sin\theta\cos\phi$$

Notice how this wavefunction depends on the angles θ and ϕ.

The expressions for a number of other atomic orbitals are shown in Table 1.2a (for R) and Table 1.2b (for Y). To understand these tables, we need to know that each wavefunction is labeled by *three* quantum numbers, n, l, and m_l. As we shall see, n is related to the *size* and *energy* of the orbital, l is related to its *shape*, and m_l is related to its *orientation* in space.

We have already encountered n, the principal quantum number, which specifies the energy of the orbital (through Eq. 16). In a hydrogen atom, all atomic orbitals with the same value of n have the same energy and are said to belong to the same **shell** of the atom.

The second quantum number needed to specify an orbital is l, the **orbital angular momentum quantum number.** This quantum number can take the values

$$l = 0, 1, 2, \ldots, n - 1$$

There are n different values of l for a given value of n. For instance, when $n = 3$, l can have any of the three values 0, 1, and 2. The orbitals of a shell with principal quantum number n therefore fall into n groups (each identified by a different value of l), which are called **subshells** of the shell. There is only one subshell in the $n = 1$ level ($l = 0$), two in the $n = 2$ level ($l = 0$ and 1), three in the $n = 3$ level

TABLE 1.2 Hydrogen Wavefunctions (Atomic Orbitals), $\psi = RY$

(a) Radial wavefunctions, $R_{nl}(r)$			(b) Angular wavefunctions, $Y_{lm_l}(\theta,\phi)$		
n	l	$R_{nl}(r)$	l	"m_l"*	$Y_{lm_l}(\theta,\phi)$
1	0	$2\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	0	0	$\left(\dfrac{1}{4\pi}\right)^{1/2}$
2	0	$\dfrac{1}{2\sqrt{2}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2 - \dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$	1	x	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
	1	$\dfrac{1}{2\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(\dfrac{Zr}{a_0}\right)e^{-Zr/2a_0}$		y	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
3	0	$\dfrac{1}{9\sqrt{3}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(3 - \dfrac{2Zr}{a_0} + \dfrac{2Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$		z	$\left(\dfrac{3}{4\pi}\right)^{1/2}\cos\theta$
	1	$\dfrac{2}{27\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2 - \dfrac{Zr}{3a_0}\right)e^{-Zr/3a_0}$	2	xy	$\left(\dfrac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos 2\phi$
	2	$\dfrac{4}{81\sqrt{30}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(\dfrac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$		yz	$\left(\dfrac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\sin\phi$
				zx	$\left(\dfrac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\cos\phi$
				$x^2 - y^2$	$\left(\dfrac{15}{16\pi}\right)^{1/2}\sin^2\theta\sin 2\phi$
				z^2	$\left(\dfrac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$

Note: In each case, $a_0 = 4\pi\varepsilon_0^2/m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.
*In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l.

The names come from the fact that spectroscopic lines were once classified as sharp, principal, diffuse, and fundamental.

($l = 0$, 1, and 2), and so on. All orbitals with $l = 0$ are called s-orbitals, those with $l = 1$ are called p-orbitals, those with $l = 2$ are called d-orbitals, and those with $l = 3$ are called f-orbitals. Although higher values of l (corresponding to g-, h-, . . . orbitals) are possible, the lower values of l (0, 1, 2, and 3) are the only ones that chemists need in practice.

Just as the value of n can be used to calculate the energy of an electron, the value of l can be used to calculate another physical property. As its name suggests, l tells us the **orbital angular momentum** of the electron, a measure of the rate at which the electron circulates round the nucleus:

$$\text{Orbital angular momentum} = \{l(l + 1)\}^{1/2}\hbar \qquad (18)^*$$

An s-electron, for which $l = 0$, has zero orbital angular momentum. That means that we should imagine it not as circulating around the nucleus but simply as distributed around it. An electron in a p-orbital has nonzero orbital angular momentum (of magnitude $2^{1/2}\hbar$); so it can be thought of as circulating around the nucleus. An electron in a d-orbital has a higher orbital angular momentum ($6^{1/2}\hbar$), one in an f-orbital has an even higher angular momentum ($12^{1/2}\hbar$), and so on.

An important feature of the hydrogen atom is that all the orbitals of a given shell have the same energy, regardless of the value of their orbital angular momentum (we see from Eq.16 that l does not appear in the expression for the energy). We say that the orbitals of a shell in a hydrogen atom are **degenerate,** which means that they all have the same energy. This degeneracy is true only of the hydrogen atom and one-electron ions (such as He$^+$ and U^{91+})

The third quantum number required to specify an orbital is m_l, the **magnetic quantum number,** which distinguishes the individual orbitals within a subshell. This quantum number can take the values

$$m_l = l, l - 1, . . . , -l$$

There are $2l + 1$ different values of m_l for a given value of l and therefore $2l + 1$ orbitals in a subshell of quantum number l. For example, when $l = 1$, $m_l = +1$, 0, -1 (note that a + sign is always used for positive values of m_l); so there are three p-orbitals in a given shell. Alternatively, we can say that a subshell with $l = 1$ consists of three orbitals.

The magnetic quantum number tells us the *orientation* of the orbital motion of the electron. Specifically, it tells us that the orbital angular momentum around an arbitrary axis is equal to $m_l\hbar$, the rest of the orbital motion (to make up the full amount of $\{l(l + 1)\}^{1/2}\hbar$ being around other axes. For instance, if $m_l = +1$, then the orbital angular momentum of the electron around the arbitrary axis is $+\hbar$,
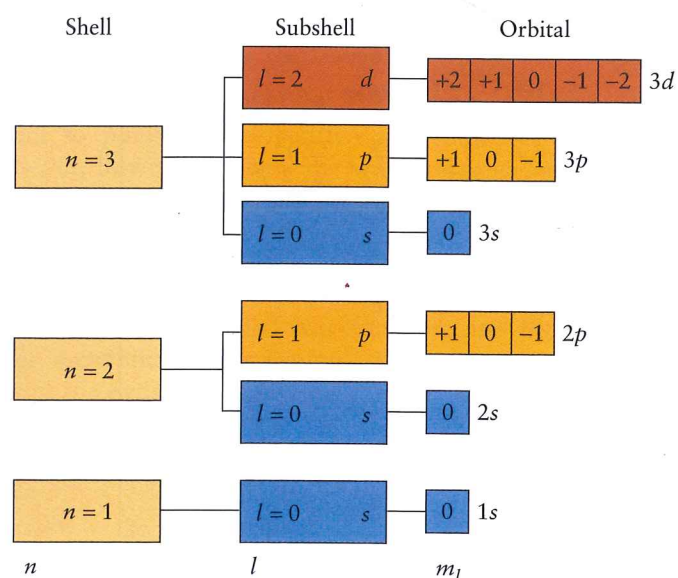
TABLE 1.3 Quantum Numbers for Electrons in Atoms

Name	Symbol	Values	Specifies	Indicates
principal	n	1, 2, . . .	shell	size
orbital angular momentum*	l	0, 1, . . . , $n - 1$	subshell: $l = 0, 1, 2, 3, 4, . . .$ s, p, d, f, g, . . .	shape
magnetic	m_l	$l, l - 1, . . . , -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

*Also called the *azimuthal quantum number.*

whereas, if $m_l = -1$, then the orbital angular momentum of the electron around the same arbitrary axis is $-\hbar$. If $m_l = 0$, then the electron is not circulating around the selected axis. The difference in sign simply means that the direction of motion is opposite, the electron in one state circulating clockwise and an electron in the other state circulating counterclockwise.

The hierarchy of shells, subshells, and orbitals is summarized in Fig. 1.25 and Table 1.3. Each possible combination of the three quantum numbers specifies an orbital. For example, an electron in the ground state of a hydrogen atom has the specification $n = 1$, $l = 0$, $m_l = 0$. Because $l = 0$, the ground-state wavefunction is an example of an s-orbital and is denoted 1s. Each shell has one s-orbital, and the s-orbital in the shell with quantum number n is called an ns-orbital.

All s-orbitals are independent of the angles θ and ϕ; so we say that they are **spherically symmetrical** (Fig. 1.26). The probability density of an electron at the point (r,θ,ϕ) when it is in a 1s-orbital is found from the wavefunction for the ground state of the hydrogen atom:

$$\psi^2(r,\theta,\phi) = \frac{e^{-2r/a_0}}{\pi a_0^3} \qquad (19)$$

In principle, the cloud never thins to exactly zero, no matter how large the value of r. So we could think of an atom as being bigger than the Earth! However, there is virtually no chance of finding an electron farther from the nucleus than about 250 pm, and so atoms are in fact very small. As we can see from the high density of the cloud at the nucleus, an electron in an s-orbital has a nonzero probability of being found right at the nucleus: because $l = 0$, there is no orbital angular momentum to fling the electron away from the nucleus.

FIGURE 1.26 The three-dimensional electron cloud corresponding to an electron in a 1s-orbital of hydrogen. The density of shading represents the probability of finding the electron at any point. The superimposed graph shows how the probability varies with the distance of the point from the nucleus along any radius.

FIGURE 1.25 A summary of the arrangement of shells, subshells, and orbitals in an atom and the corresponding quantum numbers. Note that the quantum number m_l is an alternative label for the individual orbitals: in chemistry, it is more common to use x, y, and z instead, as shown in Figs. 1.31 through 1.33.

EXAMPLE 1.8 Sample exercise: Calculating the probability of finding an electron at a certain location

What is the probability of finding the electron in a small region a distance a_0 from the nucleus relative to the probability of finding it in the same small region located right at the nucleus?

SOLUTION We calculate the following ratio of the squares of the wavefunction at the two points:

$$\frac{\text{Probability density at } r = a_0}{\text{Probability density at } r = 0} = \frac{\psi^2(a_0,\theta,\phi)}{\psi^2(0,\theta,\phi)} = \frac{e^{-2a_0/a_0}/\pi a_0^3}{1/\pi a_0^3}$$

$$= \frac{e^{-2}/\pi a_0^3}{1/\pi a_0^3} = e^{-2} = 0.14$$

That is, the probability of finding the electron in a small region at a distance a_0 from the nucleus is only 14% of that of findin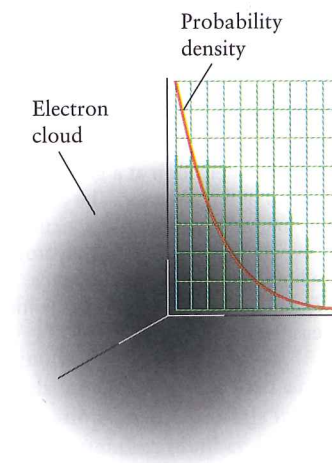g the electron in a similar region located at the nucleus.