

# More About Matter Waves

## 39.1 ENERGIES OF A TRAPPED ELECTRON

### Learning Objectives

*After reading this module, you should be able to . . .*

**39.1.1** Identify the confinement principle: Confinement of a wave (including a matter wave) leads to the quantization of wavelengths and energy values.

**39.1.2** Sketch a one-dimensional infinite potential well, indicating the length (or width) and the potential energy of the walls.

**39.1.3** For an electron, apply the relationship between the de Broglie wavelength  $\lambda$  and the kinetic energy.

**39.1.4** For an electron in a one-dimensional infinite potential well, apply the relationship between the de Broglie wavelength  $\lambda$ , the well's length  $L$ , and the quantum number  $n$ .

**39.1.5** For an electron in a one-dimensional infinite potential well, apply the relationship between the allowed energies  $E_n$ , the well length  $L$ , and the quantum number  $n$ .

**39.1.6** Sketch an energy-level diagram for an electron in a one-dimensional infinite potential well, indicating the ground state and several excited states.

**39.1.7** Identify that a trapped electron tends to be in its ground state, can be excited to a higher-energy state, and cannot exist between the allowed states.

**39.1.8** Calculate the energy change required for an electron to move between states: a quantum jump up or down an energy-level diagram.

**39.1.9** If a quantum jump involves light, identify that an upward jump requires the absorption of a photon (to increase the electron's energy) and a downward jump requires the emission of a photon (to reduce the electron's energy).

**39.1.10** If a quantum jump involves light, apply the relationships between the energy change and the frequency and wavelength associated with the photon.

**39.1.11** Identify the emission and absorption spectra of an electron in a one-dimensional infinite potential well.

### Key Ideas

- Confinement of waves (string waves, matter waves—any type of wave) leads to quantization—that is, discrete states with certain energies. States with intermediate energies are not allowed.

- Because it is a matter wave, an electron confined to an infinite potential well can exist in only certain discrete states. If the well is one-dimensional with length  $L$ , the energies associated with these quantum states are

$$E_n = \left( \frac{h^2}{8mL^2} \right) n^2, \quad \text{for } n = 1, 2, 3, \dots,$$

where  $m$  is the electron mass and  $n$  is a quantum number.

- The lowest energy is not zero but is given by  $n = 1$ .
- The electron can change (jump) from one quantum state to another only if its energy change is

$$\Delta E = E_{\text{high}} - E_{\text{low}},$$

where  $E_{\text{high}}$  is the higher energy and  $E_{\text{low}}$  is the lower energy.

- If the change is done by photon absorption or emission, the energy of the photon must be equal to the change in the electron's energy:

$$hf = \frac{hc}{\lambda} = \Delta E = E_{\text{high}} - E_{\text{low}},$$

where frequency  $f$  and wavelength  $\lambda$  are associated with the photon.

### What Is Physics?

One of the long-standing goals of physics has been to understand the nature of atoms. Early in the 20th century nobody knew how the electrons in an atom are arranged, what their motions are, how atoms emit or absorb light, or even

why atoms are stable. Without this knowledge it was not possible to understand how atoms combine to form molecules or stack up to form solids. As a consequence, the foundations of chemistry—including biochemistry, which underlies the nature of life itself—were more or less a mystery.

In 1926, all these questions and many others were answered with the development of quantum physics. Its basic premise is that moving electrons, protons, and particles of any kind are best viewed as matter waves, whose motions are governed by Schrödinger's equation. Although quantum theory also applies to larger objects, such as baseballs and planets, it yields the same results as Newtonian physics, which is easier to use and more intuitive.

Before we can apply quantum physics to the problem of atomic structure, we need to develop some insights by applying quantum ideas in a few simpler situations. Some of these situations may seem simplistic and unreal, but they allow us to discuss the basic principles of the quantum physics of atoms without having to deal with the often overwhelming complexity of atoms. Besides, with advances in nano-technology, situations that were previously found only in textbooks are now being produced in laboratories and put to use in modern electronics and materials science applications. We are on the threshold of being able to use nanometer-scale constructions called *quantum corrals* and *quantum dots* to create “designer atoms” whose properties can be manipulated in the laboratory. For both natural atoms and these artificial ones, the starting point in our discussion is the wave nature of an electron.

## String Waves and Matter Waves

In Chapter 16 we saw that waves of two kinds can be set up on a stretched string. If the string is so long that we can take it to be infinitely long, we can set up a *traveling wave* of essentially any frequency. However, if the stretched string has only a finite length, perhaps because it is rigidly clamped at both ends, we can set up only *standing waves* on it; further, these standing waves can have only discrete frequencies. In other words, confining the wave to a finite region of space leads to *quantization* of the motion—to the existence of discrete *states* for the wave, each state with a sharply defined frequency.

This observation applies to waves of all kinds, including matter waves. For matter waves, however, it is more convenient to deal with the energy  $E$  of the associated particle than with the frequency  $f$  of the wave. In all that follows we shall focus on the matter wave associated with an electron, but the results apply to any confined matter wave.

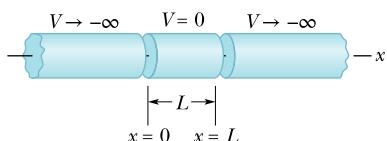
Consider the matter wave associated with an electron moving in the positive  $x$  direction and subject to no net force—a so-called *free particle*. The energy of such an electron can have any reasonable value, just as a wave traveling along a stretched string of infinite length can have any reasonable frequency.

Consider next the matter wave associated with an atomic electron, perhaps the *valence* (least tightly bound) electron. The electron—held within the atom by the attractive Coulomb force between it and the positively charged nucleus—is not a free particle. It can exist only in a set of discrete states, each having a discrete energy  $E$ . This sounds much like the discrete states and quantized frequencies that are available to a stretched string of finite length. For matter waves, then, as for all other kinds of waves, we may state a **confinement principle**:



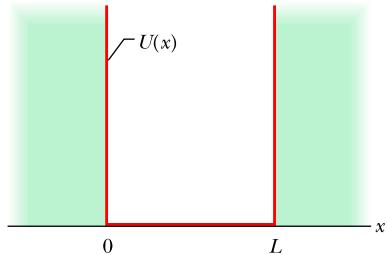
Confinement of a wave leads to quantization—that is, to the existence of discrete states with discrete energies.

An electron can be trapped in the  $V=0$  region.



**Figure 39.1.1** The elements of an idealized “trap” designed to confine an electron to the central cylinder. We take the semi-infinitely long end cylinders to be at an infinitely great negative potential and the central cylinder to be at zero potential.

An electron can be trapped in the  $U=0$  region.



**Figure 39.1.2** The electric potential energy  $U(x)$  of an electron confined to the central cylinder of the idealized trap of Fig. 39.1.1. We see that  $U=0$  for  $0 < x < L$ , and  $U \rightarrow \infty$  for  $x < 0$  and  $x > L$ .

## Energies of a Trapped Electron

### One-Dimensional Traps

Here we examine the matter wave associated with a nonrelativistic electron confined to a limited region of space. We do so by analogy with standing waves on a string of finite length, stretched along an  $x$  axis and confined between rigid supports. Because the supports are rigid, the two ends of the string are nodes, or points at which the string is always at rest. There may be other nodes along the string, but these two must always be present, as Fig. 16.7.5 shows.

The states, or discrete standing wave patterns in which the string can oscillate, are those for which the length  $L$  of the string is equal to an integer number of half-wavelengths. That is, the string can occupy only states for which

$$L = \frac{n\lambda}{2}, \quad \text{for } n = 1, 2, 3, \dots \quad (39.1.1)$$

Each value of  $n$  identifies a state of the oscillating string; using the language of quantum physics, we can call the integer  $n$  a **quantum number**.

For each state of the string permitted by Eq. 39.1.1, the transverse displacement of the string at any position  $x$  along the string is given by

$$y_n(x) = A \sin\left(\frac{n\pi}{L}x\right), \quad \text{for } n = 1, 2, 3, \dots \quad (39.1.2)$$

in which the quantum number  $n$  identifies the oscillation pattern and  $A$  depends on the time at which you inspect the string. (Equation 39.1.2 is a short version of Eq. 16.7.3.) We see that for all values of  $n$  and for all times, there is a point of zero displacement (a node) at  $x = 0$  and at  $x = L$ , as there must be. Figure 16.7.4 shows time exposures of such a stretched string for  $n = 2, 3$ , and 4.

Now let us turn our attention to matter waves. Our first problem is to physically confine an electron that is moving along the  $x$  axis so that it remains within a finite segment of that axis. Figure 39.1.1 shows a conceivable one-dimensional *electron trap*. It consists of two semi-infinitely long cylinders, each of which has an electric potential approaching  $-\infty$ ; between them is a hollow cylinder of length  $L$ , which has an electric potential of zero. We put a single electron into this central cylinder to trap it.

The trap of Fig. 39.1.1 is easy to analyze but is not very practical. Single electrons *can*, however, be trapped in the laboratory with traps that are more complex in design but similar in concept. At the University of Washington, for example, a single electron was held in a trap for months on end, permitting scientists to make extremely precise measurements of its properties.

### Finding the Quantized Energies

Figure 39.1.2 shows the potential energy of the electron as a function of its position along the  $x$  axis of the idealized trap of Fig. 39.1.1. When the electron is in the central cylinder, its potential energy  $U$  ( $= -eV$ ) is zero because there the potential  $V$  is zero. If the electron could get outside this region, its potential energy would be positive and of infinite magnitude because there  $V \rightarrow -\infty$ . We call the potential energy pattern of Fig. 39.1.2 an **infinitely deep potential energy well** or, for short, an *infinite potential well*. It is a “well” because an electron placed in the central cylinder of Fig. 39.1.1 cannot escape from it. As the electron approaches either end of the cylinder, a force of essentially infinite magnitude reverses the electron’s motion, thus trapping it. Because the electron can move along only a single axis, this trap can be called a *one-dimensional infinite potential well*.

Just like the standing wave in a length of stretched string, the matter wave describing the confined electron must have nodes at  $x = 0$  and  $x = L$ . Moreover, Eq. 39.1.1 applies to such a matter wave if we interpret  $\lambda$  in that equation as the de Broglie wavelength associated with the moving electron.

The de Broglie wavelength  $\lambda$  is defined in Eq. 38.5.1 as  $\lambda = h/p$ , where  $p$  is the magnitude of the electron's momentum. Because the electron is nonrelativistic, this momentum magnitude  $p$  is related to the kinetic energy  $K$  by  $p = \sqrt{2mK}$ , where  $m$  is the mass of the electron. For an electron moving within the central cylinder of Fig. 39.1.1, where  $U = 0$ , the total (mechanical) energy  $E$  is equal to the kinetic energy. Hence, we can write the de Broglie wavelength of this electron as

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}. \quad (39.1.3)$$

If we substitute Eq. 39.1.3 into Eq. 39.1.1 and solve for the energy  $E$ , we find that  $E$  depends on  $n$  according to

$$E_n = \left( \frac{h^2}{8mL^2} \right) n^2, \quad \text{for } n = 1, 2, 3, \dots \quad (39.1.4)$$

The positive integer  $n$  here is the quantum number of the electron's quantum state in the trap.

Equation 39.1.4 tells us something important: Because the electron is confined to the trap, it can have only the energies given by the equation. It *cannot* have an energy that is, say, halfway between the values for  $n = 1$  and  $n = 2$ . Why this restriction? Because an electron is a matter wave. Were it, instead, a particle as assumed in classical physics, it could have *any* value of energy while it is confined to the trap.

Figure 39.1.3 is a graph showing the lowest five allowed energy values for an electron in an infinite well with  $L = 100$  pm (about the size of a typical atom). The values are called *energy levels*, and they are drawn in Fig. 39.1.3 as levels, or steps, on a ladder, in an *energy-level diagram*. Energy is plotted vertically; nothing is plotted horizontally.

The quantum state with the lowest possible energy level  $E_1$  allowed by Eq. 39.1.4, with quantum number  $n = 1$ , is called the *ground state* of the electron. The electron tends to be in this lowest energy state. All the quantum states with greater energies (corresponding to quantum numbers  $n = 2$  or greater) are called *excited states* of the electron. The state with energy level  $E_2$ , for quantum number  $n = 2$ , is called the *first excited state* because it is the first of the excited states as we move up the energy-level diagram. The other states have similar names.

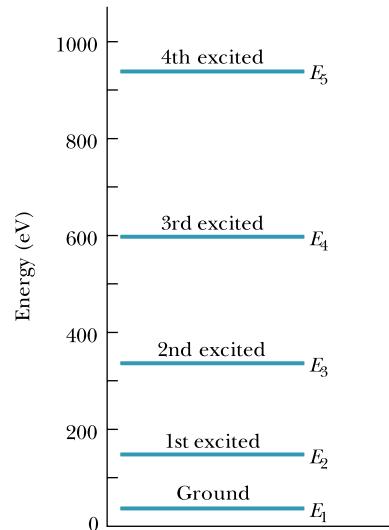
## Energy Changes

A trapped electron tends to have the lowest allowed energy and thus to be in its ground state. It can be changed to an excited state (in which it has greater energy) only if an external source provides the additional energy that is required for the change. Let  $E_{\text{low}}$  be the initial energy of the electron and  $E_{\text{high}}$  be the greater energy in a state that is higher on its energy-level diagram. Then the amount of energy that is required for the electron's change of state is

$$\Delta E = E_{\text{high}} - E_{\text{low}}. \quad (39.1.5)$$

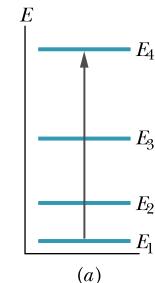
An electron that receives such energy is said to make a *quantum jump* (or *transition*), or to be *excited* from the lower-energy state to the higher-energy state. Figure 39.1.4a represents a quantum jump from the ground state (with energy level  $E_1$ ) to the third excited state (with energy level  $E_4$ ). As shown, the jump *must* be from one energy level to another, but it can bypass one or more intermediate energy levels.

These are the lowest five energy levels allowed the electron. (No intermediate levels are allowed.)



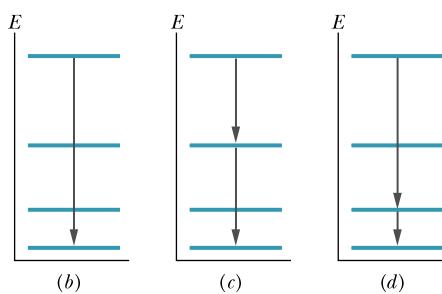
**Figure 39.1.3** Several of the allowed energies for an electron confined to the infinite well of Fig. 39.1.2, with width  $L = 100$  pm.

The electron is excited to a higher energy level.



(a)

It can de-excite to a lower level in several ways (set by chance).



**Figure 39.1.4** (a) Excitation of a trapped electron from the energy level of its ground state to the level of its third excited state. (b)–(d) Three of four possible ways the electron can de-excite to return to the energy level of its ground state. (Which way is not shown?)

**Photons.** One way an electron can gain energy to make a quantum jump up to a greater energy level is to absorb a photon. However, this absorption and quantum jump can occur only if the following condition is met:



If a confined electron is to absorb a photon, the energy  $hf$  of the photon must equal the energy difference  $\Delta E$  between the initial energy level of the electron and a higher level.

Thus, excitation by the absorption of light requires that

$$hf = \frac{hc}{\lambda} = \Delta E = E_{\text{high}} - E_{\text{low}}. \quad (39.1.6)$$

When an electron reaches an excited state, it does not stay there but quickly *de-excites* by decreasing its energy. Figures 39.1.4b to d represent some of the possible quantum jumps down from the energy level of the third excited state. The electron can reach its ground-state level either with one direct quantum jump (Fig. 39.1.4b) or with shorter jumps via intermediate levels (Figs. 39.1.4c and d).

An electron can decrease its energy by emitting a photon but only this way:



If a confined electron emits a photon, the energy  $hf$  of that photon must equal the energy difference  $\Delta E$  between the initial energy level of the electron and a lower level.

Thus, Eq. 39.1.6 applies to both the absorption and the emission of light by a confined electron. That is, the absorbed or emitted light can have only certain values of  $hf$  and thus only certain values of frequency  $f$  and wavelength  $\lambda$ .

*Aside:* Although Eq. 39.1.6 and what we have discussed about photon absorption and emission can be applied to physical (real) electron traps, they actually cannot be applied to one-dimensional (unreal) electron traps. The reason involves the need to conserve angular momentum in a photon absorption or emission process. In this book, we shall neglect that need and use Eq. 39.1.6 even for one-dimensional traps.

### Checkpoint 39.1.1

Rank the following pairs of quantum states for an electron confined to an infinite well according to the energy differences between the states, greatest first: (a)  $n = 3$  and  $n = 1$ , (b)  $n = 5$  and  $n = 4$ , (c)  $n = 4$  and  $n = 3$ .

### Sample Problem 39.1.1 Energy levels in a 1D infinite potential well

An electron is confined to a one-dimensional, infinitely deep potential energy well of width  $L = 100 \text{ pm}$ . (a) What is the smallest amount of energy the electron can have? (A trapped electron cannot have zero energy.)

#### KEY IDEA

Confinement of the electron (a matter wave) to the well leads to quantization of its energy. Because the well is infinitely deep, the allowed energies are given by Eq. 39.1.4 ( $E_n = (h^2/8mL^2)n^2$ ), with the quantum number  $n$  a positive integer.

**Lowest energy level:** Here, the collection of constants in front of  $n^2$  in Eq. 39.1.4 is evaluated as

$$\begin{aligned} \frac{h^2}{8mL^2} &= \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(8)(9.11 \times 10^{-31} \text{ kg})(100 \times 10^{-12} \text{ m})^2} \\ &= 6.031 \times 10^{-18} \text{ J}. \end{aligned} \quad (39.1.7)$$

The smallest amount of energy the electron can have corresponds to the lowest quantum number, which is  $n = 1$

for the ground state of the electron. Thus, Eqs. 39.1.4 and 39.1.7 give us

$$E_1 = \left( \frac{h^2}{8mL^2} \right) n^2 = (6.031 \times 10^{-18} \text{ J})(1^2)$$

$$\approx 6.03 \times 10^{-18} \text{ J} = 37.7 \text{ eV.} \quad (\text{Answer})$$

(b) How much energy must be transferred to the electron if it is to make a quantum jump from its ground state to its second excited state?

### KEY IDEA

*First a caution:* Note that, from Fig. 39.1.3, the second excited state corresponds to the third energy level, with quantum number  $n = 3$ . Then if the electron is to jump from the  $n = 1$  level to the  $n = 3$  level, the required change in its energy is, from Eq. 39.1.5,

$$\Delta E_{31} = E_3 - E_1. \quad (39.1.8)$$

**Upward jump:** The energies  $E_3$  and  $E_1$  depend on the quantum number  $n$ , according to Eq. 39.1.4. Therefore, substituting that equation into Eq. 39.1.8 for energies  $E_3$  and  $E_1$  and using Eq. 39.1.7 lead to

$$\begin{aligned} \Delta E_{31} &= \left( \frac{h^2}{8mL^2} \right) (3)^2 - \left( \frac{h^2}{8mL^2} \right) (1)^2 \\ &= \frac{h^2}{8mL^2} (3^2 - 1^2) \\ &= (6.031 \times 10^{-18} \text{ J})(8) \\ &= 4.83 \times 10^{-17} \text{ J} = 301 \text{ eV.} \quad (\text{Answer}) \end{aligned}$$

(c) If the electron gains the energy for the jump from energy level  $E_1$  to energy level  $E_3$  by absorbing light, what light wavelength is required?

### KEY IDEAS

(1) If light is to transfer energy to the electron, the transfer must be by photon absorption. (2) The photon's energy must equal the energy difference  $\Delta E$  between the initial energy level of the electron and a higher level, according to Eq. 39.1.6 ( $hf = \Delta E$ ). Otherwise, a photon *cannot* be absorbed.

**Wavelength:** Substituting  $c/\lambda$  for  $f$ , we can rewrite Eq. 39.1.6 as

$$\lambda = \frac{hc}{\Delta E} \quad (39.1.9)$$

For the energy difference  $\Delta E_{31}$  we found in (b), this equation gives us

$$\begin{aligned} \lambda &= \frac{hc}{\Delta E_{31}} \\ &= \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{4.83 \times 10^{-17} \text{ J}} \\ &= 4.12 \times 10^{-9} \text{ m.} \quad (\text{Answer}) \end{aligned}$$

(d) Once the electron has been excited to the second excited state, what wavelengths of light can it emit by de-excitation?

### KEY IDEAS

- The electron tends to de-excite, rather than remain in an excited state, until it reaches the ground state ( $n = 1$ ).
- If the electron is to de-excite, it must lose just enough energy to jump to a lower energy level.
- If it is to lose energy by emitting light, then the loss of energy must be by emission of a photon.

**Downward jumps:** Starting in the second excited state (at the  $n = 3$  level), the electron can reach the ground state ( $n = 1$ ) by *either* making a quantum jump directly to the ground-state energy level (Fig. 39.1.5a) or by making two *separate* jumps by way of the  $n = 2$  level (Figs. 39.1.5b and c).

The direct jump involves the same energy difference  $\Delta E_{31}$  we found in (c). Then the wavelength is the same as we calculated in (c)—except now the wavelength is for light that is emitted, not absorbed. Thus, the electron can jump directly to the ground state by emitting light of wavelength

$$\lambda = 4.12 \times 10^{-9} \text{ m.} \quad (\text{Answer})$$

Following the procedure of part (b), you can show that the energy differences for the jumps of Figs. 39.1.5b and c are

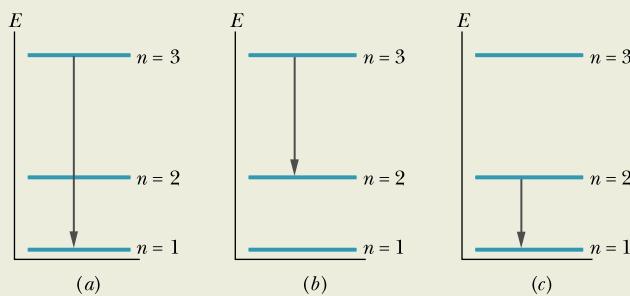
$$\Delta E_{32} = 3.016 \times 10^{-17} \text{ J} \quad \text{and} \quad \Delta E_{21} = 1.809 \times 10^{-17} \text{ J.}$$

From Eq. 39.1.9, we then find that the wavelength of the light emitted in the first of these jumps (from  $n = 3$  to  $n = 2$ ) is

$$\lambda = 6.60 \times 10^{-9} \text{ m,} \quad (\text{Answer})$$

and the wavelength of the light emitted in the second of these jumps (from  $n = 2$  to  $n = 1$ ) is

$$\lambda = 1.10 \times 10^{-8} \text{ m.} \quad (\text{Answer})$$



**Figure 39.1.5** De-excitation from the second excited state to the ground state either directly (a) or via the first excited state (b, c).

## 39.2 WAVE FUNCTIONS OF A TRAPPED ELECTRON

### Learning Objectives

After reading this module, you should be able to . . .

- 39.2.1 For an electron trapped in a one-dimensional, infinite potential well, write its wave function in terms of coordinates inside the well and in terms of the quantum number  $n$ .
- 39.2.2 Identify probability density.
- 39.2.3 For an electron trapped in a one-dimensional, infinite potential well in a given state, write the probability density as a function of position inside the

well, identify that the probability density is zero outside the well, and calculate the probability of detection between two given coordinates inside the well.

- 39.2.4 Identify the correspondence principle.
- 39.2.5 Normalize a given wave function and identify what that has to do with the probability of detection.
- 39.2.6 Identify that the lowest allowed energy (the zero-point energy) of a trapped electron is not zero.

### Key Ideas

- The wave functions for an electron in an infinite, one-dimensional potential well with length  $L$  along an  $x$  axis are given by

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right), \quad \text{for } n = 1, 2, 3, \dots,$$

where  $n$  is the quantum number.

- The product  $\psi_n^2(x) dx$  is the probability that the electron will be detected in the interval between coordinates  $x$  and  $x + dx$ .
- If the probability density of an electron is integrated over the entire  $x$  axis, the total probability must be 1:

$$\int_{-\infty}^{\infty} \psi_n^2(x) dx = 1.$$

### Wave Functions of a Trapped Electron

If we solve Schrödinger's equation for an electron trapped in a one-dimensional infinite potential well of width  $L$  and impose the boundary condition that the solutions be zero at the infinite walls, we find that the wave functions for the electron are given by

$$\psi_n(x) = A \sin\left(\frac{n\pi}{L}x\right), \quad \text{for } n = 1, 2, 3, \dots, \quad (39.2.1)$$

for  $0 \leq x \leq L$  (the wave function is zero outside that range). We shall soon evaluate the amplitude constant  $A$  in this equation.

Note that the wave functions  $\psi_n(x)$  have the same form as the displacement functions  $y_n(x)$  for a standing wave on a string stretched between rigid supports (see Eq. 39.1.2). We can picture an electron trapped in a one-dimensional well between infinite-potential walls as being a standing matter wave.

### Probability of Detection

The wave function  $\psi_n(x)$  cannot be detected or directly measured in any way—we cannot simply look inside the well to see the wave the way we can see, say, a wave in a bathtub of water. All we can do is insert a probe of some kind to try to detect the electron. At the instant of detection, the electron would materialize at the point of detection, at some position along the  $x$  axis within the well.

If we repeated this detection procedure at many positions throughout the well, we would find that the probability of detecting the electron is related to the probe's position  $x$  in the well. In fact, they are related by the *probability density*  $\psi_n^2(x)$ . Recall from Module 38.6 that in general the probability that a particle can be detected in a specified infinitesimal volume centered on a specified point is proportional to  $|\psi_n|^2$ . Here, with the electron trapped in a one-dimensional well, we are concerned only with detection of the electron along the  $x$  axis. Thus, the probability density  $\psi_n^2(x)$  here is a probability per unit length along the  $x$  axis.

(We can omit the absolute value sign here because  $\psi_n(x)$  in Eq. 39.2.1 is a real quantity, not a complex one.) The probability  $p(x)$  that an electron can be detected at position  $x$  within the well is

$$\begin{pmatrix} \text{probability } p(x) \\ \text{of detection in width } dx \\ \text{centered on position } x \end{pmatrix} = \begin{pmatrix} \text{probability density } \psi_n^2(x) \\ \text{at position } x \end{pmatrix} (\text{width } dx),$$

or

$$p(x) = \psi_n^2(x) dx. \quad (39.2.2)$$

From Eq. 39.2.1, we see that the probability density  $\psi_n^2(x)$  is

$$\psi_n^2(x) = A^2 \sin^2\left(\frac{n\pi}{L}x\right), \quad \text{for } n = 1, 2, 3, \dots, \quad (39.2.3)$$

for the range  $0 \leq x \leq L$  (the probability density is zero outside that range). Figure 39.2.1 shows  $\psi_n^2(x)$  for  $n = 1, 2, 3$ , and 15 for an electron in an infinite well whose width  $L$  is 100 pm.

To find the probability that the electron can be detected in any finite section of the well—say, between point  $x_1$  and point  $x_2$ —we must integrate  $p(x)$  between those points. Thus, from Eqs. 39.2.2 and 39.2.3,

$$\begin{aligned} \left( \text{probability of detection} \right) &= \int_{x_1}^{x_2} p(x) \\ &= \int_{x_1}^{x_2} A^2 \sin^2\left(\frac{n\pi}{L}x\right) dx. \end{aligned} \quad (39.2.4)$$

If the range  $\Delta x$  in which we search for the electron is much smaller than the well length  $L$ , then we can usually approximate the integral in Eq. 39.2.4 as being equal to the product  $p(x) \Delta x$ , with  $p(x)$  evaluated in the center of  $\Delta x$ .

If classical physics prevailed, we would expect the trapped electron to be detectable with equal probabilities in all parts of the well. From Fig. 39.2.1 we see that it is not. For example, inspection of that figure or of Eq. 39.2.3 shows that for the state with  $n = 2$ , the electron is most likely to be detected near  $x = 25$  pm and  $x = 75$  pm. It can be detected with near-zero probability near  $x = 0$ ,  $x = 50$  pm, and  $x = 100$  pm.

The case of  $n = 15$  in Fig. 39.2.1 suggests that as  $n$  increases, the probability of detection becomes more and more uniform across the well. This result is an instance of a general principle called the **correspondence principle**:

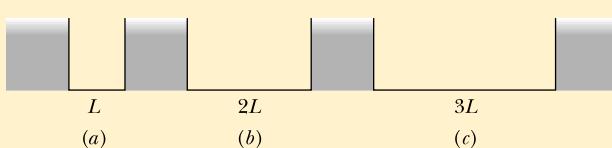


At large enough quantum numbers, the predictions of quantum physics merge smoothly with those of classical physics.

This principle, first advanced by Danish physicist Niels Bohr, holds for all quantum predictions.

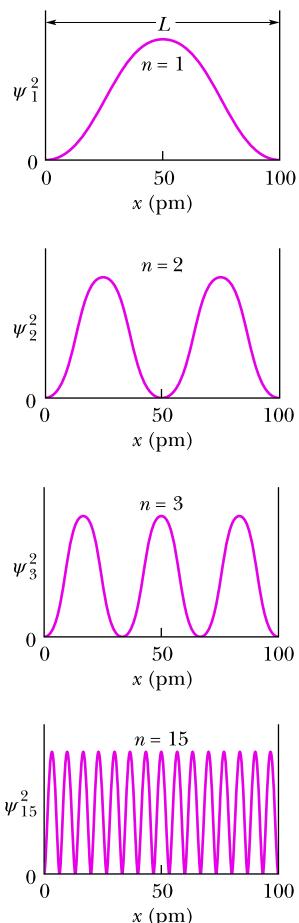
### Checkpoint 39.2.1

The figure shows three infinite potential wells of widths  $L$ ,  $2L$ , and  $3L$ ; each contains an elec-



tron in the state for which  $n = 10$ . Rank the wells according to (a) the number of maxima for the probability density of the electron and (b) the energy of the electron, greatest first.

The probability density must be zero at the infinite walls.



**Figure 39.2.1** The probability density  $\psi_n^2(x)$  for four states of an electron trapped in a one-dimensional infinite well; their quantum numbers are  $n = 1, 2, 3$ , and 15. The electron is most likely to be found where  $\psi_n^2(x)$  is greatest and least likely to be found where  $\psi_n^2(x)$  is least.

### Normalization

The product  $\psi_n^2(x) dx$  gives the probability that an electron in an infinite well can be detected in the interval of the  $x$  axis that lies between  $x$  and  $x + dx$ . We know that the electron must be *somewhere* in the infinite well; so it must be true that

$$\int_{-\infty}^{+\infty} \psi_n^2(x) dx = 1 \quad (\text{normalization equation}), \quad (39.2.5)$$

because the probability 1 corresponds to certainty. Although the integral is taken over the entire  $x$  axis, only the region from  $x = 0$  to  $x = L$  makes any contribution to the probability. Graphically, the integral in Eq. 39.2.5 represents the area under each of the plots of Fig. 39.2.1. If we substitute  $\psi_n^2(x)$  from Eq. 39.2.3 into Eq. 39.2.5, we find that  $A = \sqrt{2/L}$ . This process of using Eq. 39.2.5 to evaluate the amplitude of a wave function is called **normalizing** the wave function. The process applies to *all* one-dimensional wave functions.

### Zero-Point Energy

Substituting  $n = 1$  in Eq. 39.1.4 defines the state of lowest energy for an electron in an infinite potential well, the ground state. That is the state the confined electron will occupy unless energy is supplied to it to raise it to an excited state.

The question arises: Why can't we include  $n = 0$  among the possibilities listed for  $n$  in Eq. 39.1.4? Putting  $n = 0$  in this equation would indeed yield a ground-state energy of zero. However, putting  $n = 0$  in Eq. 39.2.3 would also yield  $\psi_n^2(x) = 0$  for all  $x$ , which we can interpret only to mean that there is no electron in the well. We know that there is; so  $n = 0$  is not a possible quantum number.

It is an important conclusion of quantum physics that confined systems cannot exist in states with zero energy. They must always have a certain minimum energy called the **zero-point energy**.

We can make the zero-point energy as small as we like by making the infinite well wider—that is, by increasing  $L$  in Eq. 39.1.4 for  $n = 1$ . In the limit as  $L \rightarrow \infty$ , the zero-point energy  $E_1 \rightarrow 0$ . However, the electron is then a free particle, no longer confined in the  $x$  direction. Also, because the energy of a free particle is not quantized, that energy can have any value, including zero. Only a confined particle must have a finite zero-point energy and can never be at rest.

### Checkpoint 39.2.2

Each of the following particles is confined to an infinite well, and all four wells have the same width: (a) an electron, (b) a proton, (c) a deuteron, and (d) an alpha particle. Rank their zero-point energies, greatest first. The particles are listed in order of increasing mass.

### Sample Problem 39.2.1 Detection probability in a 1D infinite potential well

A ground-state electron is trapped in the one-dimensional infinite potential well of Fig. 39.1.2, with width  $L = 100 \text{ pm}$ .

- (a) What is the probability that the electron can be detected in the left one-third of the well ( $x_1 = 0$  to  $x_2 = L/3$ )?

#### KEY IDEAS

- (1) If we probe the left one-third of the well, there is no guarantee that we will detect the electron. However, we can calculate the probability of detecting it with the integral

of Eq. 39.2.4. (2) The probability very much depends on which state the electron is in—that is, the value of quantum number  $n$ .

**Calculations:** Because here the electron is in the ground state, we set  $n = 1$  in Eq. 39.2.4. We also set the limits of integration as the positions  $x_1 = 0$  and  $x_2 = L/3$  and set the amplitude constant  $A$  as  $\sqrt{2/L}$  (so that the wave function is normalized). We then see that

$$\left( \text{probability of detection} \right)_{\text{in left one-third}} = \int_0^{L/3} \frac{2}{L} \sin^2\left(\frac{1\pi}{L}x\right) dx.$$

We could find this probability by substituting  $100 \times 10^{-12}$  m for  $L$  and then using a graphing calculator or a computer math package to evaluate the integral. Here, however, we shall evaluate the integral “by hand.” First we switch to a new integration variable  $y$ :

$$y = \frac{\pi}{L}x \quad \text{and} \quad dx = \frac{L}{\pi} dy.$$

From the first of these equations, we find the new limits of integration to be  $y_1 = 0$  for  $x_1 = 0$  and  $y_2 = \pi/3$  for  $x_2 = L/3$ . We then must evaluate

$$\text{probability} = \left(\frac{2}{L}\right)\left(\frac{L}{\pi}\right) \int_0^{\pi/3} (\sin^2 y) dy.$$

### Sample Problem 39.2.2 Normalizing wave functions in a 1D infinite potential well

Evaluate the amplitude constant  $A$  in Eq. 39.2.1 for an infinite potential well extending from  $x = 0$  to  $x = L$ .

#### KEY IDEA

The wave functions of Eq. 39.2.1 must satisfy the normalization requirement of Eq. 39.2.5, which states that the probability that the electron can be detected somewhere along the  $x$  axis is 1.

**Calculations:** Substituting Eq. 39.2.1 into Eq. 39.2.5 and taking the constant  $A$  outside the integral yield

$$A^2 \int_0^L \sin^2\left(\frac{n\pi}{L}x\right) dx = 1. \quad (39.2.6)$$

We have changed the limits of the integral from  $-\infty$  and  $+\infty$  to 0 and  $L$  because the “outside” wave function is zero.

We can simplify the indicated integration by changing the variable from  $x$  to the dimensionless variable  $y$ , where

$$y = \frac{n\pi}{L}x, \quad (39.2.7)$$

$$\text{hence} \quad dx = \frac{L}{n\pi} dy.$$

Using integral 11 in Appendix E, we then find

$$\text{probability} = \frac{2}{\pi} \left( \frac{y}{2} - \frac{\sin 2y}{4} \right)_0^{\pi/3} = 0.20.$$

Thus, we have

$$\left( \text{probability of detection} \right)_{\text{in left one-third}} = 0.20. \quad (\text{Answer})$$

That is, if we repeatedly probe the left one-third of the well, then on average we can detect the electron with 20% of the probes.

(b) What is the probability that the electron can be detected in the middle one-third of the well?

**Reasoning:** We now know that the probability of detection in the left one-third of the well is 0.20. By symmetry, the probability of detection in the right one-third of the well is also 0.20. Because the electron is certainly in the well, the probability of detection in the entire well is 1. Thus, the probability of detection in the middle one-third of the well is

$$\begin{aligned} \left( \text{probability of detection} \right)_{\text{in middle one-third}} &= 1 - 0.20 - 0.20 \\ &= 0.60. \quad (\text{Answer}) \end{aligned}$$

When we change the variable, we must also change the integration limits (again). Equation 39.2.7 tells us that  $y = 0$  when  $x = 0$  and that  $y = n\pi$  when  $x = L$ ; thus 0 and  $n\pi$  are our new limits. With all these substitutions, Eq. 39.2.6 becomes

$$A^2 \frac{L}{n\pi} \int_0^{n\pi} (\sin^2 y) dy = 1.$$

We can use integral 11 in Appendix E to evaluate the integral, obtaining the equation

$$\frac{A^2 L}{n\pi} \left[ \frac{y}{2} - \frac{\sin 2y}{4} \right]_0^{n\pi} = 1.$$

Evaluating at the limits yields

$$\frac{A^2 L}{n\pi} \frac{n\pi}{2} = 1;$$

thus

$$A = \sqrt{\frac{2}{L}}. \quad (\text{Answer}) \quad (39.2.8)$$

This result tells us that the dimension for  $A^2$ , and thus for  $\psi_n^2(x)$ , is an inverse length. This is appropriate because the probability density of Eq. 39.2.3 is a probability *per unit length*.

## 39.3 AN ELECTRON IN A FINITE WELL

### Learning Objectives

After reading this module, you should be able to . . .

- 39.3.1 Sketch a one-dimensional finite potential well, indicating the length and height.
- 39.3.2 For an electron trapped in a finite well with given energy levels, sketch the energy-level diagram, indicate the nonquantized region, and compare the energies and de Broglie wavelengths with those of an infinite well of the same length.
- 39.3.3 For an electron trapped in a finite well, explain (in principle) how the wave functions for the allowed states are determined.
- 39.3.4 For an electron trapped in a finite well with a given quantum number, sketch the probability density as a function of position across the well and into the walls.
- 39.3.5 Identify that a trapped electron can exist in only the allowed states and relate that energy of the state to the kinetic energy of the electron.

### Key Ideas

- The wave function for an electron in a finite, one-dimensional potential well extends into the walls, where the wave function decreases exponentially with depth.

- 39.3.6 Calculate the energy that an electron must absorb or emit to move between the allowed states or between an allowed state and any value in the nonquantized region.

- 39.3.7 If a quantum jump involves light, apply the relationship between the energy change and the frequency and wavelength associated with the photon.

- 39.3.8 From a given allowed state in a finite well, calculate the minimum energy required for the electron to escape and the kinetic energy of the escaped electron if provided more than that minimal energy.

- 39.3.9 Identify the emission and absorption spectra of an electron in a one-dimensional finite potential well, including escaping the trap and falling into the trap.

- Compared to the states in an infinite well of the same size, the states in a finite well have a limited number, longer de Broglie wavelengths, and lower energies.

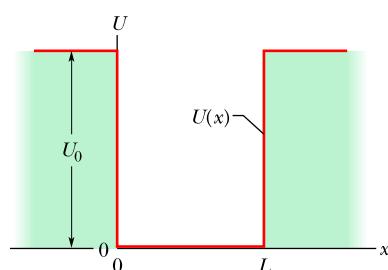
### An Electron in a Finite Well

A potential energy well of infinite depth is an idealization. Figure 39.3.1 shows a realizable potential energy well—one in which the potential energy of an electron outside the well is not infinitely great but has a finite positive value  $U_0$ , called the **well depth**. The analogy between waves on a stretched string and matter waves fails us for wells of finite depth because we can no longer be sure that matter wave nodes exist at  $x = 0$  and at  $x = L$ . (As we shall see, they don't.)

To find the wave functions describing the quantum states of an electron in the finite well of Fig. 39.3.1, we *must* resort to Schrödinger's equation, the basic equation of quantum physics. From Module 38.6 recall that, for motion in one dimension, we use Schrödinger's equation in the form of Eq. 38.6.2:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}[E - U(x)]\psi = 0. \quad (39.3.1)$$

Rather than attempting to solve this equation for the finite well, we simply state the results for particular numerical values of  $U_0$  and  $L$ . Figure 39.3.2 shows three results as graphs of  $\psi_n^2(x)$ , the probability density, for a well with  $U_0 = 450$  eV and  $L = 100$  pm.



**Figure 39.3.1** A *finite* potential energy well. The depth of the well is  $U_0$  and its width is  $L$ . As in the infinite potential well of Fig. 39.1.2, the motion of the trapped electron is restricted to the  $x$  direction.

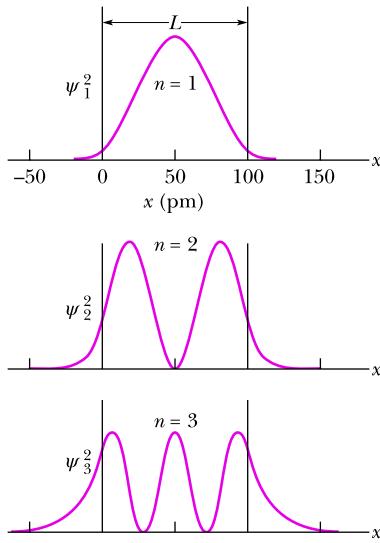
The probability density  $\psi_n^2(x)$  for each graph in Fig. 39.3.2 satisfies Eq. 39.2.5, the normalization equation; so we know that the areas under all three probability density plots are numerically equal to 1.

If you compare Fig. 39.3.2 for a finite well with Fig. 39.2.1 for an infinite well, you will see one striking difference: For a finite well, the electron matter wave penetrates the walls of the well—into a region in which Newtonian mechanics says the electron cannot exist. This penetration should not be surprising because we saw in Module 38.9 that an electron can tunnel through a potential energy barrier. “Leaking” into the walls of a finite potential energy well is a similar phenomenon. From the plots of density  $\psi^2$  for in Fig. 39.3.2, we see that the leakage is greater for greater values of quantum number  $n$ .

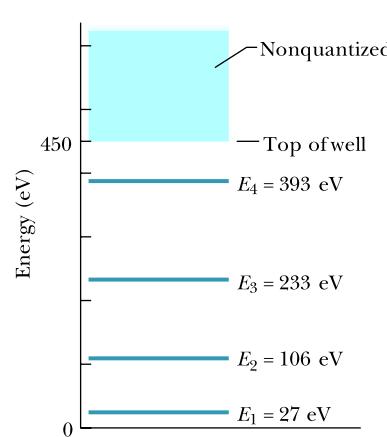
Because a matter wave *does* leak into the walls of a finite well, the wavelength  $\lambda$  for any given quantum state is greater when the electron is trapped in a finite well than when it is trapped in an infinite well of the same length  $L$ . Equation 39.1.3 ( $\lambda = h/\sqrt{2mE}$ ) then tells us that the energy  $E$  for an electron in any given state is less in the finite well than in the infinite well.

That fact allows us to approximate the energy-level diagram for an electron trapped in a finite well. As an example, we can approximate the diagram for the finite well of Fig. 39.3.2, which has width  $L = 100$  pm and depth  $U_0 = 450$  eV. The energy-level diagram for an *infinite* well of that width is shown in Fig. 39.1.3. First we remove the portion of Fig. 39.1.3 above 450 eV. Then we shift the remaining four energy levels down, shifting the level for  $n = 4$  the most because the wave leakage into the walls is greatest for  $n = 4$ . The result is approximately the energy-level diagram for the finite well. The actual diagram is Fig. 39.3.3.

In that figure, an electron with an energy greater than  $U_0$  ( $= 450$  eV) has too much energy to be trapped in the finite well. Thus, it is not confined, and its energy is not quantized; that is, its energy is not restricted to certain values. To reach this *nonquantized* portion of the energy-level diagram and thus to be free, a trapped electron must somehow obtain enough energy to have a mechanical energy of 450 eV or greater.



**Figure 39.3.2** The first three probability densities  $\psi_n^2(x)$  for an electron confined to a finite potential well of depth  $U_0 = 450$  eV and width  $L = 100$  pm. Only states  $n = 1, 2, 3$ , and 4 are allowed.



**Figure 39.3.3** The energy-level diagram corresponding to the probability densities of Fig. 39.3.2. If an electron is trapped in the finite potential well, it can have only the energies corresponding to  $n = 1, 2, 3$ , and 4. If it has an energy of 450 eV or greater, it is not trapped and its energy is not quantized.

### Sample Problem 39.3.1 Electron escaping from a finite potential well

Suppose a finite well with  $U_0 = 450 \text{ eV}$  and  $L = 100 \text{ pm}$  confines a single electron in its ground state.

- (a) What wavelength of light is needed to barely free it with a single photon absorption?

#### KEY IDEA

For the electron to escape, it must receive enough energy to jump to the nonquantized energy region of Fig. 39.3.3 and end up with an energy of at least  $U_0$  ( $= 450 \text{ eV}$ ).

**Barely escaping:** The electron is initially in its ground state, with an energy of  $E_1 = 27 \text{ eV}$ . So, to barely become free, it must receive an energy of

$$U_0 - E_1 = 450 \text{ eV} - 27 \text{ eV} = 423 \text{ eV}.$$

Thus the photon must have this much energy. From Eq. 39.1.6 ( $hf = E_{\text{high}} - E_{\text{low}}$ ), with  $c/\lambda$  substituted for  $f$ , we write

$$\frac{hc}{\lambda} = U_0 - E_1,$$

from which we find

$$\begin{aligned} \lambda &= \frac{hc}{U_0 - E_1} \\ &= \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(423 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})} \\ &= 2.94 \times 10^{-9} \text{ m} = 2.94 \text{ nm}. \quad (\text{Answer}) \end{aligned}$$

Thus, if  $\lambda = 2.94 \text{ nm}$ , the electron just barely escapes.

- (b) Can the ground-state electron absorb light with  $\lambda = 2.00 \text{ nm}$ ? If so, what then is the electron's energy?

#### KEY IDEAS

- In (a) we found that light of 2.94 nm will just barely free the electron from the potential well.
- We are now considering light with a shorter wavelength of 2.00 nm and thus a greater energy per photon ( $hf = hc/\lambda$ ).
- Hence, the electron *can* absorb a photon of this light. The energy transfer will not only free the electron but will also provide it with more kinetic energy. Further, because the electron is then no longer trapped, its energy is not quantized.

**More than escaping:** The energy transferred to the electron is the photon energy:

$$\begin{aligned} hf &= h \frac{c}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{2.00 \times 10^{-9} \text{ m}} \\ &= 9.95 \times 10^{-17} \text{ J} = 622 \text{ eV}. \end{aligned}$$

From (a), the energy required to just barely free the electron from the potential well is  $U_0 - E_1$  ( $= 423 \text{ eV}$ ). The remainder of the 622 eV goes to kinetic energy. Thus, the kinetic energy of the freed electron is

$$\begin{aligned} K &= hf - (U_0 - E_1) \\ &= 622 \text{ eV} - 423 \text{ eV} = 199 \text{ eV}. \quad (\text{Answer}) \end{aligned}$$

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## 39.4 TWO- AND THREE-DIMENSIONAL ELECTRON TRAPS

### Learning Objectives

After reading this module, you should be able to . . .

**39.4.1** Discuss nanocrystallites as being electron traps and explain how their threshold wavelength can determine their color.

**39.4.2** Identify quantum dots and quantum corrals.

**39.4.3** For a given state of an electron in an infinite potential well with two or three dimensions, write equations for the wave function and probability density and then calculate the probability of detection for a given range in the well.

**39.4.4** For a given state of an electron in an infinite potential well with two or three dimensions,

calculate the allowed energies and draw an energy-level diagram, complete with labels for the quantum numbers, the ground state, and several excited states.

**39.4.5** Identify degenerate states.

**39.4.6** Calculate the energy that an electron must absorb or emit to move between the allowed states in a 2D or 3D trap.

**39.4.7** If a quantum jump involves light, apply the relationships between the energy change and the frequency and wavelength associated with the photon.

## Key Ideas

- The quantized energies for an electron trapped in a two-dimensional infinite potential well that forms a rectangular corral are

$$E_{nx, ny} = \frac{h^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right),$$

where  $n_x$  is a quantum number for well width  $L_x$  and  $n_y$  is a quantum number for well width  $L_y$ .

- The wave functions for an electron in a two-dimensional well are given by

$$\psi_{nx, ny} = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y \pi}{L_y} y\right).$$

## More Electron Traps

Here we discuss three types of artificial electron traps.

### Nanocrystallites

Perhaps the most direct way to construct a potential energy well in the laboratory is to prepare a sample of a semiconducting material in the form of a powder whose granules are small—in the nanometer range—and of uniform size. Each such granule—each **nanocrystallite**—acts as a potential well for the electrons trapped within it.

Equation 39.1.4 ( $E = (h^2/8mL^2)n^2$ ) shows that we can increase the energy-level values of an electron trapped in an infinite well by reducing the width  $L$  of the well. This would also shift the photon energies that the well can absorb to higher values and thus shift the corresponding wavelengths to shorter values.

These general results are also true for a well formed by a nanocrystallite. A given nanocrystallite can absorb photons with an energy above a certain threshold energy  $E_t$  ( $= hf_t$ ) and thus wavelengths below a corresponding threshold wavelength

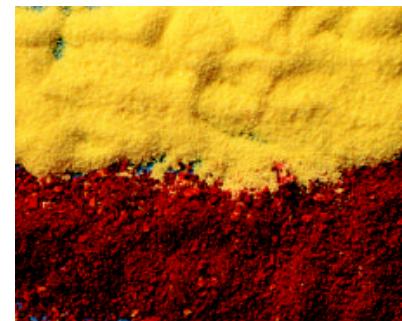
$$\lambda_t = \frac{c}{f_t} = \frac{ch}{E_t}.$$

Light with any wavelength longer than  $\lambda_t$  is scattered by the nanocrystallite instead of being absorbed. The color we attribute to the nanocrystallite is then determined by the wavelength composition of the scattered light we intercept.

If we reduce the size of the nanocrystallite, the value of  $E_t$  is increased, the value of  $\lambda_t$  is decreased, and the light that is scattered to us changes in its wavelength composition. Thus, the color we attribute to the nanocrystallite changes. As an example, Fig. 39.4.1 shows two samples of the semiconductor cadmium selenide, each consisting of a powder of nanocrystallites of uniform size. The lower sample scatters light at the red end of the spectrum. The upper sample differs from the lower sample *only* in that the upper sample is composed of smaller nanocrystallites. For this reason its threshold energy  $E_t$  is greater and, from above, its threshold wavelength  $\lambda_t$  is shorter, in the green range of visible light. Thus, the sample now scatters both red and yellow. Because the yellow component happens to be brighter, the sample's color is now dominated by the yellow. The striking contrast in color between the two samples is compelling evidence of the quantization of the energies of trapped electrons and the dependence of these energies on the size of the electron trap.

### Quantum Dots

The highly developed techniques used to fabricate computer chips can be used to construct, atom by atom, individual potential energy wells that behave, in many respects, like artificial atoms. These **quantum dots**, as they are usually called, have promising applications in electron optics and computer technology.



From *Scientific American*, January 1993, page 119. Reproduced with permission of Michael Steigerwald.

**Figure 39.4.1** Two samples of powdered cadmium selenide, a semiconductor, differing only in the size of their granules. Each granule serves as an electron trap. The lower sample has the larger granules and consequently the smaller spacing between energy levels and the lower photon energy threshold for the absorption of light. Light not absorbed is scattered, causing the sample to scatter light of greater wavelength and appear red. The upper sample, because of its smaller granules, and consequently its larger level spacing and its larger energy threshold for absorption, appears yellow.

In one such arrangement, a “sandwich” is fabricated in which a thin layer of a semiconducting material, shown in purple in Fig. 39.4.2a, is deposited between two insulating layers, one of which is much thinner than the other. Metal end caps with conducting leads are added at both ends. The materials are chosen to ensure that the potential energy of an electron in the central layer is less than it is in the two insulating layers, causing the central layer to act as a potential energy well. Figure 39.4.2b is a photograph of an actual quantum dot; the well in which individual electrons can be trapped is the purple region.

The lower (but not the upper) insulating layer in Fig. 39.4.2a is thin enough to permit electrons to tunnel through it if an appropriate potential difference is applied between the leads. In this way the number of electrons confined to the well can be controlled. The arrangement does indeed behave like an artificial atom with the property that the number of electrons it contains can be controlled. Quantum dots can be constructed in two-dimensional arrays that could well form the basis for computing systems of great speed and storage capacity.

### Quantum Corrals

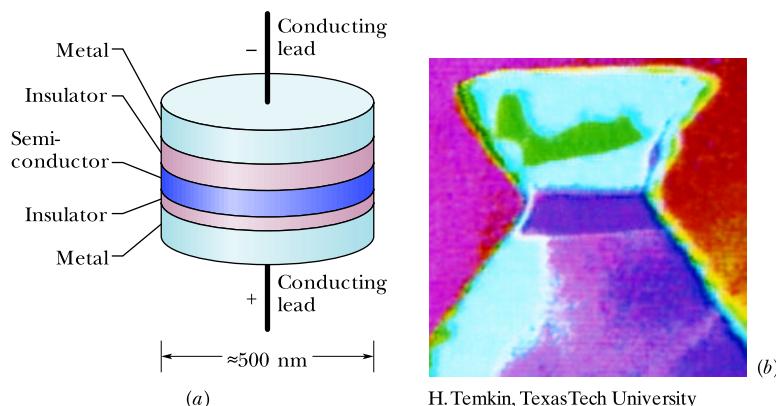
When a scanning tunneling microscope (described in Module 38.9) is in operation, its tip exerts a small force on isolated atoms that may be located on an otherwise smooth surface. By careful manipulation of the position of the tip, such isolated atoms can be “dragged” across the surface and deposited at another location. Using this technique, scientists at IBM’s Almaden Research Center moved iron atoms across a carefully prepared copper surface, forming the atoms into a circle (Fig. 39.4.3), which they named a **quantum corral**. Each iron atom in the circle is nestled in a hollow in the copper surface, equidistant from three nearest-neighbor copper atoms. The corral was fabricated at a low temperature (about 4 K) to minimize the tendency of the iron atoms to move randomly about on the surface because of their thermal energy.

The ripples within the corral are due to matter waves associated with electrons that can move over the copper surface but are largely trapped in the potential well of the corral. The dimensions of the ripples are in excellent agreement with the predictions of quantum theory.

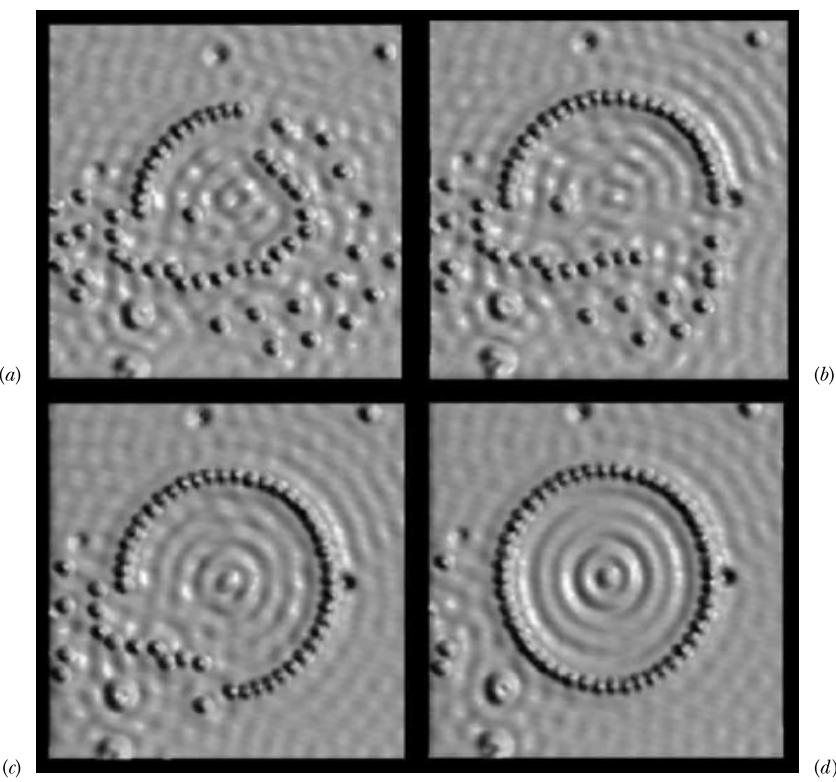
## Two- and Three-Dimensional Electron Traps

In the next module, we shall discuss the hydrogen atom as being a three-dimensional finite potential well. As a warm-up for the hydrogen atom, let us extend our discussion of infinite potential wells to two and three dimensions.

**Figure 39.4.2** A quantum dot, or “artificial atom.” (a) A central semiconducting layer forms a potential energy well in which electrons are trapped. The lower insulating layer is thin enough to allow electrons to be added to or removed from the central layer by barrier tunneling if an appropriate voltage is applied between the leads. (b) A photograph of an actual quantum dot. The central purple band is the electron confinement region.



H. Temkin, Texas Tech University



Source: Zotov Andrey & Saranin AlexanderA. Licensed under CC BY-SA 3.0.

**Figure 39.4.3** A quantum corral during four stages of construction. Note the appearance of ripples caused by electrons trapped in the corral when it is almost complete.

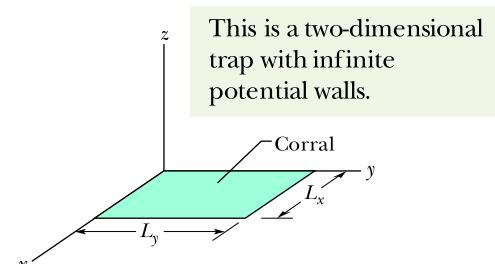
### Rectangular Corral

Figure 39.4.4 shows the rectangular area to which an electron can be confined by the two-dimensional version of Fig. 39.1.2—a two-dimensional infinite potential well of widths  $L_x$  and  $L_y$  that forms a rectangular corral. The corral might be on the surface of a body that somehow prevents the electron from moving parallel to the  $z$  axis and thus from leaving the surface. You have to imagine infinite potential energy functions (like  $U(x)$  in Fig. 39.1.2) along each side of the corral, keeping the electron within the corral.

Solution of Schrödinger's equation for the rectangular corral of Fig. 39.4.4 shows that, for the electron to be trapped, its matter wave must fit into each of the two widths separately, just as the matter wave of a trapped electron must fit into a one-dimensional infinite well. This means the wave is separately quantized in width  $L_x$  and in width  $L_y$ . Let  $n_x$  be the quantum number for which the matter wave fits into width  $L_x$ , and let  $n_y$  be the quantum number for which the matter wave fits into width  $L_y$ . As with a one-dimensional potential well, these quantum numbers can be only positive integers. We can extend Eqs. 39.2.1 and 39.2.8 to write the normalized wave function as

$$\psi_{n_x, n_y} = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y \pi}{L_y} y\right), \quad (39.4.1)$$

The energy of the electron depends on both quantum numbers and is the sum of the energy the electron would have if it were confined along the  $x$  axis alone

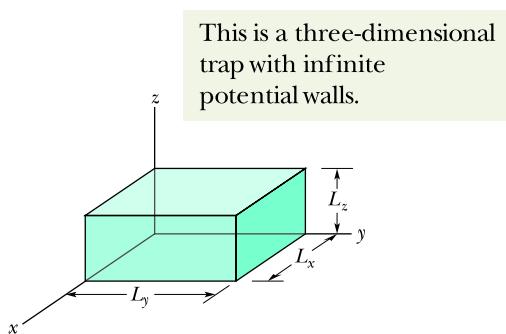


**Figure 39.4.4** A rectangular corral—a two-dimensional version of the infinite potential well of Fig. 39.1.2—with widths  $L_x$  and  $L_y$ .

and the energy it would have if it were confined along the  $y$  axis alone. From Eq. 39.1.4, we can write this sum as

$$E_{nx, ny} = \left(\frac{h^2}{8mL_x^2}\right)n_x^2 + \left(\frac{h^2}{8mL_y^2}\right)n_y^2 = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right). \quad (39.4.2)$$

Excitation of the electron by photon absorption and de-excitation of the electron by photon emission have the same requirements as for one-dimensional traps. Now, however, two quantum numbers ( $n_x$  and  $n_y$ ) are involved. Because of that, different states might have the same energy; such states and their energy levels are said to be *degenerate*.



**Figure 39.4.5** A rectangular box—a three-dimensional version of the infinite potential well of Fig. 39.1.2—with widths  $L_x$ ,  $L_y$ , and  $L_z$ .

### Rectangular Box

An electron can also be trapped in a three-dimensional infinite potential well—a *box*. If the box is rectangular as in Fig. 39.4.5, then Schrödinger's equation shows us that we can write the energy of the electron as

$$E_{nx, ny, nz} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right). \quad (39.4.3)$$

Here  $n_z$  is a third quantum number, for fitting the matter wave into width  $L_z$ .

### Checkpoint 39.4.1

In the notation of Eq. 39.4.2, is  $E_{0,0}$ ,  $E_{1,0}$ ,  $E_{0,1}$ , or  $E_{1,1}$  the ground-state energy of an electron in a (two-dimensional) rectangular corral?

### Sample Problem 39.4.1 Energy levels in a 2D infinite potential well

An electron is trapped in a square corral that is a two-dimensional infinite potential well (Fig. 39.4.4) with widths  $L_x = L_y$ .

(a) Find the energies of the lowest five possible energy levels for this trapped electron, and construct the corresponding energy-level diagram.

#### KEY IDEA

Because the electron is trapped in a two-dimensional well that is rectangular, the electron's energy depends on two quantum numbers,  $n_x$  and  $n_y$ , according to Eq. 39.4.2.

**Energy levels:** Because the well here is square, we can let the widths be  $L_x = L_y = L$ . Then Eq. 39.4.2 simplifies to

$$E_{nx, ny} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2). \quad (39.4.4)$$

The lowest energy states correspond to low values of the quantum numbers  $n_x$  and  $n_y$ , which are the positive integers  $1, 2, \dots, \infty$ . Substituting those integers for  $n_x$  and  $n_y$  in Eq. 39.4.4, starting with the lowest value 1, we can

obtain the energy values as listed in Table 39.4.1. There we can see that several of the pairs of quantum numbers ( $n_x$ ,  $n_y$ ) give the same energy. For example, the (1, 2) and (2, 1) states both have an energy of  $5(h^2/8mL^2)$ . Each such pair is associated with degenerate energy levels. Note also that, perhaps surprisingly, the (4, 1) and (1, 4) states have less energy than the (3, 3) state.

**Table 39.4.1 Energy Levels**

$n_x$	$n_y$	Energy <sup>a</sup>	$n_x$	$n_y$	Energy <sup>a</sup>
1	3	10	2	4	20
3	1	10	4	2	20
2	2	8	3	3	18
1	2	5	1	4	17
2	1	5	4	1	17
1	1	2	2	3	13
			3	2	13

<sup>a</sup>In multiples of  $h^2/8mL^2$ .

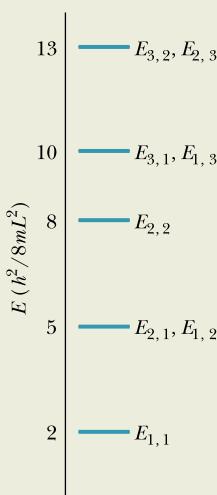
From Table 39.4.1 (carefully keeping track of degenerate levels), we can construct the energy-level diagram of Fig. 39.4.6.

(b) As a multiple of  $\hbar^2/8mL^2$ , what is the energy difference between the ground state and the third excited state?

**Energy difference:** From Fig. 39.4.6, we see that the ground state is the  $(1, 1)$  state, with an energy of  $2(\hbar^2/8mL^2)$ . We also see that the third excited state (the third state up from the ground state in the energy-level diagram) is the degenerate  $(1, 3)$  and  $(3, 1)$  states, with an energy of  $10(\hbar^2/8mL^2)$ . Thus, the difference  $\Delta E$  between these two states is

$$\Delta E = 10\left(\frac{\hbar^2}{8mL^2}\right) - 2\left(\frac{\hbar^2}{8mL^2}\right) = 8\left(\frac{\hbar^2}{8mL^2}\right). \quad (\text{Answer})$$

These are the lowest five energy levels allowed the electron. Different quantum states may have the same energy.



**Figure 39.4.6** Energy-level diagram for an electron trapped in a square corral.

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## 39.5 THE HYDROGEN ATOM

### Learning Objectives

After reading this module, you should be able to . . .

**39.5.1** Identify Bohr's model of the hydrogen atom and explain how he derived the quantized radii and energies.

**39.5.2** For a given quantum number  $n$  in the Bohr model, calculate the electron's orbital radius, kinetic energy, potential energy, total energy, orbital period, orbital frequency, momentum, and angular momentum.

**39.5.3** Distinguish the Bohr and Schrödinger descriptions of the hydrogen atom, including the discrepancy between the allowed angular momentum values.

**39.5.4** For a hydrogen atom, apply the relationship between the quantized energies  $E_n$  and the quantum number  $n$ .

**39.5.5** For a given jump in hydrogen, between quantized states or between a quantized state and a nonquantized state, calculate the change in energy and, if light is involved, the associated energy, frequency, wavelength, and momentum of the photon.

**39.5.6** Sketch an energy-level diagram for hydrogen, identifying the ground state, several of the excited

states, the nonquantized region, the Paschen series, the Balmer series, and the Lyman series (including the series limits).

**39.5.7** For each transition series, identify the jumps giving the longest wavelength, the shortest wavelength for downward jumps, the series limit, and ionization.

**39.5.8** List the quantum numbers for an atom and indicate the allowed values.

**39.5.9** Given a normalized wave function for a state, find the radial probability density  $P(r)$  and the probability of detecting the electron in a given range of radii.

**39.5.10** For ground-state hydrogen, sketch a graph of the radial probability density versus radial distance and locate one Bohr radius  $a$ .

**39.5.11** For a given normalized wave function for hydrogen, verify that it satisfies the Schrödinger equation.

**39.5.12** Distinguish shell from subshell.

**39.5.13** Explain a dot plot of a probability density.

### Key Ideas

- The Bohr model of the hydrogen atom successfully derived the energy levels for the atom, to explain the emission/absorption spectrum of the atom, but it is incorrect in almost every other aspect.

- The Bohr model is a planetary model in which the electron orbits the central proton with an angular momentum  $L$  that is limited to values given by

$$L = n\hbar, \quad \text{for } n = 1, 2, 3, \dots,$$

where  $n$  is a quantum number. The value  $L = 0$  is incorrectly disallowed.

- Application of the Schrödinger equation gives the correct values of  $L$  and the quantized energies:

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} = -\frac{13.60 \text{ eV}}{n^2}, \quad \text{for } n = 1, 2, 3, \dots$$

- The atom (or the electron in the atom) can change energy only by jumping between these allowed energies.

- If the jump is by photon absorption (the atom's energy increases) or photon emission (the atom's energy decreases), this restriction in energy changes leads to

$$\frac{1}{\lambda} = R \left( \frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right),$$

for the wavelength of the light, where  $R$  is the Rydberg constant,

$$R = \frac{me^4}{8\epsilon_0^2 h^3 c} = 1.097 373 \times 10^7 \text{ m}^{-1}.$$

- The radial probability density  $P(r)$  for a state of the hydrogen atom is defined so that  $P(r) dr$  is the probability that the electron will be detected in the space between two spherical shells of radii  $r$  and  $r + dr$  that are centered on the nucleus.

- Normalization requires that

$$\int_0^\infty P(r) dr = 1.$$

- The probability that the electron will be detected between any two given radii  $r_1$  and  $r_2$  is

$$(\text{probability of detection between } r_1 \text{ and } r_2) = \int_{r_1}^{r_2} P(r) dr.$$

## The Hydrogen Atom Is an Electron Trap

We now move from artificial or fictitious electron traps to natural ones—atoms. In this chapter we focus on the simplest example, a hydrogen atom, which contains an electron that is trapped by the Coulomb force it experiences from the proton, which is the nucleus of the atom. Because the proton's mass is much greater than the electron's mass, we shall assume that the proton is fixed in place. So, we think of the atom as a fixed potential trap with the electron moving around inside it.

We have now discussed at length that confinement of an electron means that the electron's energy  $E$  is quantized and thus so is any change  $\Delta E$  in its energy. In this module we want to calculate the quantized energies of the electron confined to a hydrogen atom. We shall, in principle at least, apply Schrödinger's equation to the trap, to find those energies and the associated wave functions. However, at the discretion of your instructor, let's take an historical aside to examine how the quantizing of atoms began, back when quantization was a revolutionary concept.

## The Bohr Model of Hydrogen, a Lucky Break

By the early 1900s, scientists understood that matter came in tiny pieces called atoms and that an atom of hydrogen contained positive charge  $+e$  at its center and negative charge  $-e$  (an electron) outside that center. However, no one understood why the electrical attraction between the electron and the positive charge did not simply cause the two to collapse together.

**Visible Wavelengths.** One clue lay in the experimental fact that a hydrogen atom can emit and absorb only four wavelengths in the visible spectrum (656 nm, 486 nm, 434 nm, and 410 nm). Why did it not emit all wavelengths as, say, a hot blackbody radiator? In 1913, Niels Bohr had a remarkable idea that simultaneously explained not only the four visible wavelengths but also why the atom did not simply collapse. However, as successful as his theory was on those two counts, it turned out to be quite wrong in almost every other aspect of the atom and led to very little success in explaining atoms more complicated than hydrogen. Nevertheless, the Bohr model is historically important because it ushered in the quantum physics of atoms.

**Assumptions.** To build his model, Bohr made two bold (completely unjustified) assumptions: (1) The electron in a hydrogen atom orbits the nucleus in a circle much like Earth orbits the Sun (Fig. 39.5.1a). (2) The magnitude of the angular momentum  $\vec{L}$  of the electron in its orbit is restricted (quantized) to the values

$$L = n\hbar, \quad \text{for } n = 1, 2, 3, \dots, \quad (39.5.1)$$

where  $\hbar$  (h-bar) is  $h/2\pi$  and  $n$  is a positive integer (a quantum number). We are going to follow Bohr's relatively simple arguments to get an equation for the quantized energies of the hydrogen atom, but let's be explicit here: The electron is *not* simply a particle in a planetary orbit and Eq. 39.5.1 does *not* correctly give the angular momentum values. (For example,  $L = 0$  is missing.)

**Newton's Second Law.** In the orbit picture of Fig. 39.5.1a, the electron is in uniform circular motion and thus experiences a centripetal force (Fig. 39.5.1b), which causes a centripetal acceleration. The force is the Coulomb force (Eq. 21.1.4) between the electron (with charge  $-e$ ) and the proton (with charge  $+e$ ), separated by the orbital radius  $r$ . The centripetal acceleration has the magnitude  $a = v^2/r$  (Eq. 4.5.1), where  $v$  is the electron's speed. So, we can write Newton's second law for a radial axis as

$$\begin{aligned} F &= ma \\ -\frac{1}{4\pi\epsilon_0} \frac{|-e||e|}{r^2} &= m\left(\frac{v^2}{r}\right), \end{aligned} \quad (39.5.2)$$

where  $m$  is the electron mass.

We next introduce quantization by using Bohr's assumption expressed in Eq. 39.5.1. From Eq. 11.5.2, the magnitude  $\ell$  of the angular momentum of a particle of mass  $m$  and speed  $v$  moving in a circle of radius  $r$  is  $\ell = rmv \sin \phi$ , where  $\phi$  (the angle between  $\vec{r}$  and  $\vec{v}$ ) is  $90^\circ$ . Replacing  $L$  in Eq. 39.5.1 with  $rmv \sin 90^\circ$  gives us

$$rmv = n\hbar,$$

or

$$v = \frac{n\hbar}{rm}. \quad (39.5.3)$$

Substituting this equation into Eq. 39.5.2, replacing  $\hbar$  with  $h/2\pi$ , and rearranging, we find

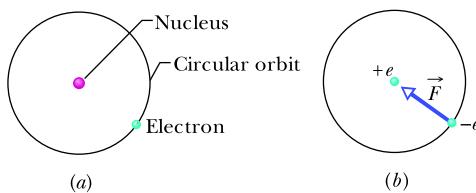
$$r = \frac{h^2\epsilon_0}{\pi me^2}n^2, \quad \text{for } n = 1, 2, 3, \dots \quad (39.5.4)$$

We can rewrite this as

$$r = an^2, \quad \text{for } n = 1, 2, 3, \dots, \quad (39.5.5)$$

$$\text{where } a = \frac{h^2\epsilon_0}{\pi me^2} = 5.291\ 772 \times 10^{-11} \text{ m} \approx 52.92 \text{ pm}. \quad (39.5.6)$$

These last three equations tell us that, in the *Bohr model of the hydrogen atom*, the electron's orbital radius  $r$  is quantized and the smallest possible orbital radius (for  $n = 1$ ) is  $a$ , which is called the *Bohr radius*. According to the Bohr model, the electron cannot get any closer to the nucleus than orbital radius  $a$ , and that is why the attraction between electron and nucleus does not simply collapse them together.



Bohr's model for hydrogen resembles the orbital model of a planet around a star.

**Figure 39.5.1** (a) Circular orbit of an electron in the Bohr model of the hydrogen atom. (b) The Coulomb force  $\vec{F}$  on the electron is directed radially inward toward the nucleus.

### Orbital Energy Is Quantized

Let's next find the energy of the hydrogen atom according to the Bohr model. The electron has kinetic energy  $K = \frac{1}{2}mv^2$ , and the electron–nucleus system has electric potential energy  $U = q_1q_2/4\pi\epsilon_0 r$  (Eq. 24.7.4). Again, let  $q_1$  be the electron's charge  $-e$  and  $q_2$  be the nuclear charge  $+e$ . Then the mechanical energy is

$$\begin{aligned} E &= K + U \\ &= \frac{1}{2}mv^2 + \left( -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \right). \end{aligned} \quad (39.5.7)$$

Solving Eq. 39.5.2 for  $mv^2$  and substituting the result in Eq. 39.5.7 lead to

$$E = -\frac{1}{8\pi\epsilon_0} \frac{e^2}{r}. \quad (39.5.8)$$

Next, replacing  $r$  with its equivalent from Eq. 39.5.4, we have

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2} \frac{1}{n^2}, \quad \text{for } n = 1, 2, 3, \dots, \quad (39.5.9)$$

where the subscript  $n$  on  $E$  signals that we have now quantized the energy.

From this equation, Bohr was able to calculate the visible wavelengths emitted and absorbed by hydrogen, but before we discuss how to go from the energy equation to the wavelengths, let's discuss the correct model of the hydrogen atom.

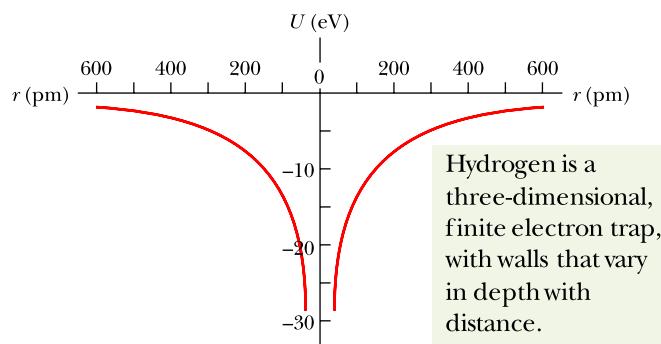
### Schrödinger's Equation and the Hydrogen Atom

In Schrödinger's model of the hydrogen atom, the electron (charge  $-e$ ) is in a potential energy trap due to its electrical attraction to the proton (charge  $+e$ ) at the center of the atom. From Eq. 24.7.4, we write the potential energy function as

$$U(r) = \frac{-e^2}{4\pi\epsilon_0 r}. \quad (39.5.10)$$

Because this well is three-dimensional, it is more complex than our previous one- and two-dimensional wells. Because this well is finite, it is more complex than the three-dimensional well of Fig. 39.4.5. Moreover, it does not have sharply defined walls. Rather, its walls vary in depth with radial distance  $r$ . Figure 39.5.2 is probably the best we can do in drawing the hydrogen potential well, but even that drawing takes much effort to interpret.

To find the allowed energies and wave functions for an electron trapped in the potential well given by Eq. 39.5.10, we need to apply Schrödinger's equation. With



**Figure 39.5.2** The potential energy  $U$  of a hydrogen atom as a function of the separation  $r$  between the electron and the central proton. The plot is shown twice (on the left and on the right) to suggest the three-dimensional spherically symmetric trap in which the electron is confined.

some manipulation, we would find that we could separate the equation into three separate differential equations, two depending on angles and one depending on radial distance  $r$ . The solution of the latter equation requires a quantum number  $n$  and produces the energy values  $E_n$  of the electron:

$$E_n = -\frac{me^4}{8e_0^2 h^2 n^2}, \quad \text{for } n = 1, 2, 3, \dots, \quad (39.5.11)$$

(This equation is exactly what Bohr found by using a very wrong planetary model of the atom.) Evaluating the constants in Eq. 39.5.11 gives us

$$E_n = -\frac{2.180 \times 10^{-18} \text{ J}}{n^2} = -\frac{13.61 \text{ eV}}{n^2}, \quad \text{for } n = 1, 2, 3, \dots \quad (39.5.12)$$

This equation tells us that the energy  $E_n$  of the hydrogen atom is quantized; that is,  $E_n$  is restricted by its dependence on the quantum number  $n$ . Because the nucleus is assumed to be fixed in place and only the electron has motion, we can assign the energy values of Eq. 39.5.12 either to the atom as a whole or to the electron alone.

### Energy Changes

The energy of a hydrogen atom (or, equivalently, of its electron) changes when the atom emits or absorbs light. As we have seen several times since Eq. 39.1.6, emission and absorption involve a quantum of light according to

$$hf = \Delta E = E_{\text{high}} - E_{\text{low}}. \quad (39.5.13)$$

Let's make three changes to Eq. 39.5.13. On the left side, we substitute  $c/\lambda$  for  $f$ . On the right side, we use Eq. 39.5.11 twice to replace the energy terms. Then, with a simple rearrangement, we have

$$\frac{1}{\lambda} = -\frac{me^4}{8e_0^2 h^3 c} \left( \frac{1}{n_{\text{high}}^2} - \frac{1}{n_{\text{low}}^2} \right). \quad (39.5.14)$$

We can rewrite this as

$$\frac{1}{\lambda} = R \left( \frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right), \quad (39.5.15)$$

in which  $R$  is the *Rydberg constant*:

$$R = \frac{me^4}{8e_0^2 h^3 c} = 1.097 373 \times 10^7 \text{ m}^{-1}. \quad (39.5.16)$$

For example, if we replace  $n_{\text{low}}$  with 2 in Eq. 39.5.14 and then restrict  $n_{\text{high}}$  to be 3, 4, 5, and 6, we generate the four visible wavelengths at which hydrogen can emit or absorb light: 656 nm, 486 nm, 434 nm, and 410 nm.

### The Hydrogen Spectrum

Figure 39.5.3a shows the energy levels corresponding to various values of  $n$  in Eq. 39.5.12. The lowest level, for  $n = 1$ , is the ground state of hydrogen. Higher levels correspond to excited states, just as we saw for our simpler potential traps. Note several differences, however. (1) The energy levels now have negative values rather than the positive values we previously chose in, for instance, Figs. 39.1.3 and 39.3.3. (2) The levels now become progressively closer as we move to higher levels. (3) The energy for the greatest value of  $n$ —namely,  $n = \infty$ —is now  $E_\infty = 0$ . For any energy greater than  $E_\infty = 0$ , the electron and proton are not bound together (there is no hydrogen atom), and the  $E > 0$  region in Fig. 39.5.3a is like the nonquantized region for the finite well of Fig. 39.3.3.

A hydrogen atom can jump between quantized energy levels by emitting or absorbing light at the wavelengths given by Eq. 39.5.14. Any such wavelength is often called a *line* because of the way it is detected with a spectroscope; thus, a hydrogen atom has *absorption lines* and *emission lines*. A collection of such lines, such as in those in the visible range, is called a **spectrum** of the hydrogen atom.

**Series.** The lines for hydrogen are said to be grouped into *series*, according to the level at which upward jumps start and downward jumps end. For example, the emission and absorption lines for all possible jumps up from the  $n = 1$  level and down to the  $n = 1$  level are said to be in the *Lyman series* (Fig. 39.5.3b), named after the person who first studied those lines. Further, we can say that the Lyman series has a *home-base level* of  $n = 1$ . Similarly, the *Balmer series* has a home-base level of  $n = 2$  (Fig. 39.5.3c), and the *Paschen series* has a home-base level of  $n = 3$  (Fig. 39.5.3d).

Some of the downward quantum jumps for these three series are shown in Fig. 39.5.3. Four lines in the Balmer series are in the visible range and are represented in Fig. 39.5.3c with arrows corresponding to their colors. The shortest of those arrows represents the shortest jump in the series, from the  $n = 3$  level to the  $n = 2$  level. Thus, that jump involves the smallest change in the electron's energy and the smallest amount of emitted photon energy for the series. The emitted light is red. The next jump in the series, from  $n = 4$  to  $n = 2$ , is longer, the photon energy is greater, the wavelength of the emitted light is shorter, and the light is green. The third, fourth, and fifth arrows represent longer jumps and shorter wavelengths. For the fifth jump, the emitted light is in the ultraviolet range and thus is not visible.

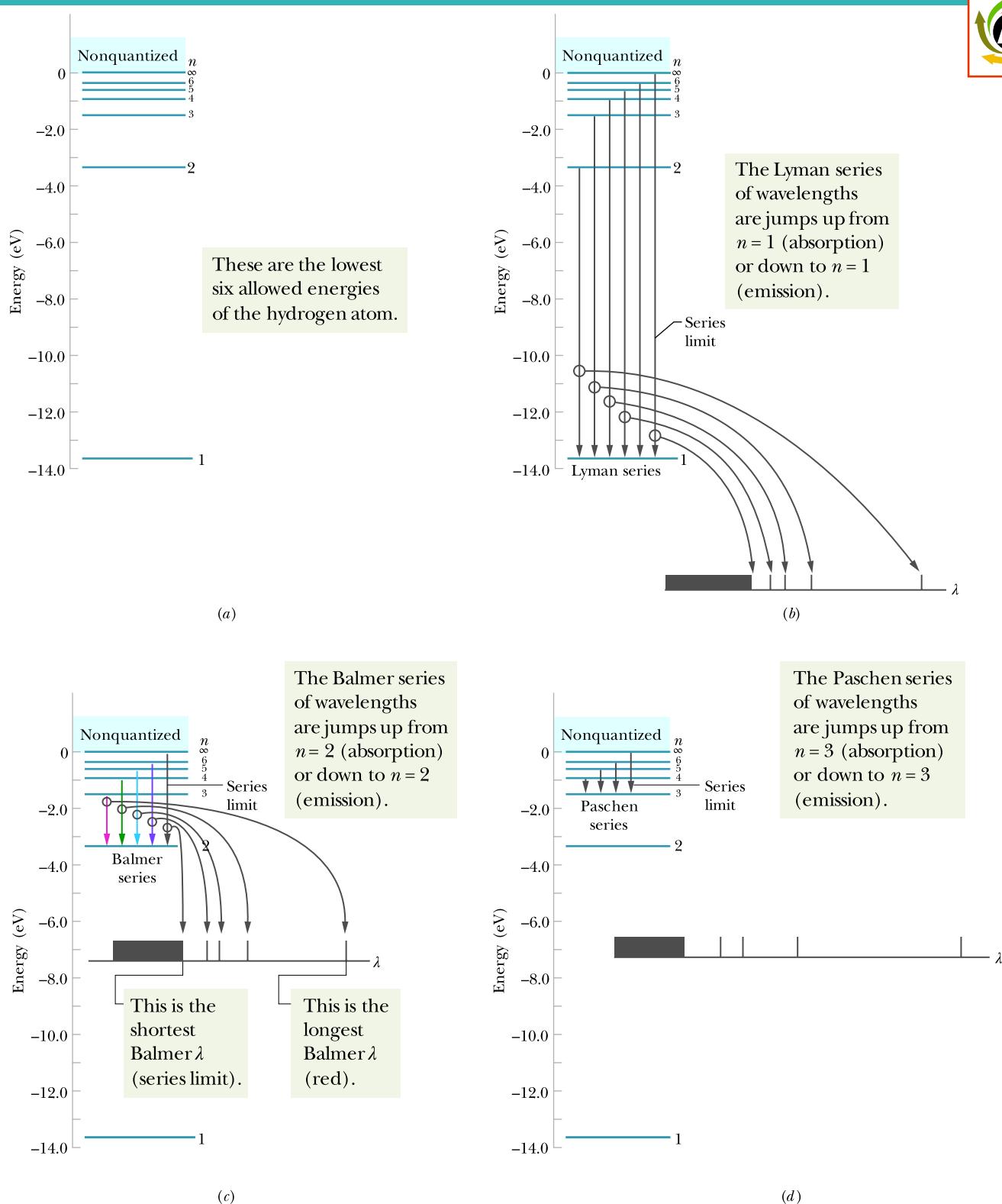
The *series limit* of a series is the line produced by the jump between the home-base level and the highest energy level, which is the level with the limiting quantum number  $n = \infty$ . Thus, the series limit corresponds to the shortest wavelength in the series.

If a jump is upward into the nonquantized portion of Fig. 39.5.3, the electron's energy is no longer given by Eq. 39.5.12 because the electron is no longer trapped in the atom. That is, the hydrogen atom has been *ionized*, meaning that the electron has been removed to a distance so great that the Coulomb force on it from the nucleus is negligible. The atom can be ionized if it absorbs any wavelength shorter than the series limit. The free electron then has only kinetic energy  $K (= \frac{1}{2}mv^2$ , assuming a nonrelativistic situation).

### Quantum Numbers for the Hydrogen Atom

Although the energies of the hydrogen atom states can be described by the single quantum number  $n$ , the wave functions describing these states require three quantum numbers, corresponding to the three dimensions in which the electron can move. The three quantum numbers, along with their names and the values that they may have, are shown in Table 39.5.1.

Each set of quantum numbers ( $n, \ell, m_\ell$ ) identifies the wave function of a particular quantum state. The quantum number  $n$ , called the **principal quantum number**, appears in Eq. 39.5.12 for the energy of the state. The **orbital quantum number**  $\ell$  is a measure of the magnitude of the angular momentum associated with the quantum state. The **orbital magnetic quantum number**  $m_\ell$  is related to the orientation in space of this angular momentum vector. The restrictions on the values of the quantum numbers for the hydrogen atom, as listed in Table 39.5.1, are not arbitrary but come out of the solution to Schrödinger's equation. Note that for the ground state ( $n = 1$ ), the restrictions require that  $\ell = 0$  and  $m_\ell = 0$ . That is, the hydrogen atom in its ground state has zero angular momentum, which is not predicted by Eq. 39.5.1 in the Bohr model.



**Figure 39.5.3** (a) An energy-level diagram for the hydrogen atom. Some of the transitions for (b) the Lyman series, (c) the Balmer series, and (d) the Paschen series. For each, the longest four wavelengths and the series-limit wavelength are plotted on a wavelength axis. Any wavelength shorter than the series-limit wavelength is allowed.

**Table 39.5.1** Quantum Numbers for the Hydrogen Atom

Symbol	Name	Allowed Values
$n$	Principal quantum number	1, 2, 3, ...
$\ell$	Orbital quantum number	0, 1, 2, ..., $n - 1$
$m_\ell$	Orbital magnetic quantum number	$-\ell, -( \ell - 1 ), \dots, +(\ell - 1), +\ell$

**Checkpoint 39.5.1**

(a) A group of quantum states of the hydrogen atom has  $n = 5$ . How many values of  $\ell$  are possible for states in this group? (b) A subgroup of hydrogen atom states in the  $n = 5$  group has  $\ell = 3$ . How many values of  $m_\ell$  are possible for states in this subgroup?

**The Wave Function of the Hydrogen Atom's Ground State**

The wave function for the ground state of the hydrogen atom, as obtained by solving the three-dimensional Schrödinger equation and normalizing the result, is

$$\psi(r) = \frac{1}{\sqrt{\pi}a^{3/2}}e^{-r/a} \quad (\text{ground state}), \quad (39.5.17)$$

where  $a (= 5.291772 \times 10^{-11} \text{ m})$  is the Bohr radius. This radius is loosely taken to be the effective radius of a hydrogen atom and turns out to be a convenient unit of length for other situations involving atomic dimensions.

As with other wave functions,  $\psi(r)$  in Eq. 39.5.17 does not have physical meaning but  $\psi^2(r)$  does, being the probability density—the probability per unit volume—that the electron can be detected. Specifically,  $\psi^2(r) dV$  is the probability that the electron can be detected in any given (infinitesimal) volume element  $dV$  located at radius  $r$  from the center of the atom:

$$\begin{pmatrix} \text{probability of detection} \\ \text{in volume } dV \\ \text{at radius } r \end{pmatrix} = \begin{pmatrix} \text{volume probability} \\ \text{density } \psi^2(r) \\ \text{at radius } r \end{pmatrix} (\text{volume } dV). \quad (39.5.18)$$

Because  $\psi^2(r)$  here depends only on  $r$ , it makes sense to choose, as a volume element  $dV$ , the volume between two concentric spherical shells whose radii are  $r$  and  $r + dr$ . That is, we take the volume element  $dV$  to be

$$dV = (4\pi r^2) dr, \quad (39.5.19)$$

in which  $4\pi r^2$  is the surface area of the inner shell and  $dr$  is the radial distance between the two shells. Then, combining Eqs. 39.5.17, 39.5.18, and 39.5.19 gives us

$$\begin{pmatrix} \text{probability of detection} \\ \text{in volume } dV \\ \text{at radius } r \end{pmatrix} = \psi^2(r) dV = \frac{4}{a^3} e^{-2r/a} r^2 dr. \quad (39.5.20)$$

Describing the probability of detecting an electron is easier if we work with a **radial probability density**  $P(r)$  instead of a volume probability density  $\psi^2(r)$ . This  $P(r)$  is a linear probability density such that

$$\begin{pmatrix} \text{radial probability} \\ \text{density } P(r) \\ \text{at radius } r \end{pmatrix} \left( \frac{\text{radial}}{\text{width } dr} \right) = \begin{pmatrix} \text{volume probability} \\ \text{density } \psi^2(r) \\ \text{at radius } r \end{pmatrix} (\text{volume } dV)$$

$$\text{or} \quad P(r) dr = \psi^2(r) dV. \quad (39.5.21)$$

Substituting for  $\psi^2(r) dV$  from Eq. 39.5.20, we obtain

$$P(r) = \frac{4}{a^3} r^2 e^{-2r/a} \quad (\text{radial probability density, hydrogen atom ground state}). \quad (39.5.22)$$

To find the probability of detecting the ground-state electron between any two radii  $r_1$  and  $r_2$  (that is, between a spherical shell of radius  $r_1$  and another of radius  $r_2$ ), we integrate Eq. 39.5.22 between those two radii:

$$\left( \begin{array}{c} \text{probability of detection} \\ \text{between } r_1 \text{ and } r_2 \end{array} \right) = \int_{r_1}^{r_2} P(r) dr. \quad (39.5.23)$$

If the radial range  $\Delta r (= r_2 - r_1)$  in which we search for the electron is small enough such that  $P(r)$  does not vary by much over the range, then we can usually approximate the integral in Eq. 39.5.23 as being equal to the product  $P(r) \Delta r$ , with  $P(r)$  evaluated in the center of  $\Delta r$ .

Figure 39.5.4 is a plot of Eq. 39.5.22. The area under the plot is unity; that is,

$$\int_0^\infty P(r) dr = 1. \quad (39.5.24)$$

This equation states that in a hydrogen atom, the electron must be *somewhere* in the space surrounding the nucleus.

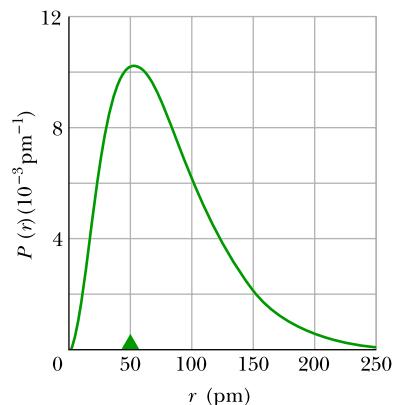
The triangular marker on the horizontal axis of Fig. 39.5.4 is located one Bohr radius from the origin. The graph tells us that in the ground state of the hydrogen atom, the electron is most likely to be found at about this distance from the center of the atom.

Figure 39.5.4 conflicts sharply with the popular view that electrons in atoms follow well-defined orbits like planets moving around the Sun. *This popular view, however familiar, is incorrect.* Figure 39.5.4 shows us all that we can ever know about the location of the electron in the ground state of the hydrogen atom. The appropriate question is not “When will the electron arrive at such-and-such a point?” but “What are the odds that the electron will be detected in a small volume centered on such-and-such a point?” Figure 39.5.5, which we call a dot plot, suggests the probabilistic nature of the wave function: The density of dots represents the probability density of detection of the electron with the hydrogen atom in its ground state. Think of the atom in this state as a fuzzy ball with no sharply defined boundary and no hint of orbits.

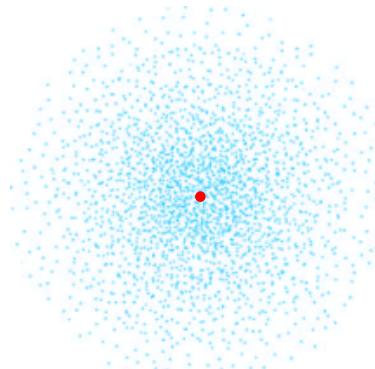
It is not easy for a beginner to envision subatomic particles in this probabilistic way. The difficulty is our natural impulse to regard an electron as something like a tiny jelly bean, located at certain places at certain times and following a well-defined path. Electrons and other subatomic particles simply do not behave in this way.

The energy of the ground state, found by putting  $n = 1$  in Eq. 39.5.12, is  $E_1 = -13.6\text{ eV}$ . The wave function of Eq. 39.5.17 results if you solve Schrödinger’s equation with this value of the energy. Actually, you can find a solution of Schrödinger’s equation for *any* value of the energy—say,  $E = -11.6\text{ eV}$  or  $-14.3\text{ eV}$ . This may suggest that the energies of the hydrogen atom states are not quantized—but we know that they are.

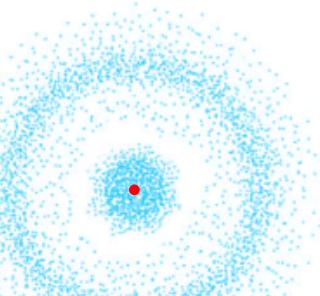
The puzzle was solved when physicists realized that such solutions of Schrödinger’s equation are not physically acceptable because they yield increasingly large values as  $r \rightarrow \infty$ . These “wave functions” tell us that the electron is more likely to be found very far from the nucleus rather than closer to it, which makes no sense. We discard such solutions and accept only solutions that meet the boundary condition  $\psi(r) \rightarrow 0$  as  $r \rightarrow \infty$ ; that is, we agree to deal only with *confined* electrons. With this restriction, the solutions of Schrödinger’s equation form a discrete set, with quantized energies given by Eq. 39.5.12.



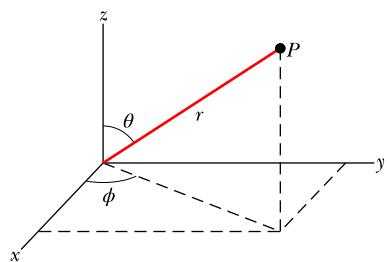
**Figure 39.5.4** A plot of the radial probability density  $P(r)$  for the ground state of the hydrogen atom. The triangular marker is located at one Bohr radius from the origin, and the origin represents the center of the atom.



**Figure 39.5.5** A “dot plot” showing the volume probability density  $\psi^2(r)$ —not the radial probability density  $P(r)$ —for the ground state of the hydrogen atom. The density of dots drops exponentially with increasing distance from the nucleus, which is represented here by a red spot.



**Figure 39.5.6** A dot plot showing the volume probability density  $\psi^2(r)$  for the hydrogen atom in the quantum state with  $n = 2$ ,  $\ell = 0$ , and  $m_\ell = 0$ . The plot has spherical symmetry about the central nucleus. The gap in the dot density pattern marks a spherical surface over which  $\psi^2(r) = 0$ .



**Figure 39.5.7** The relationship between the coordinates  $x$ ,  $y$ , and  $z$  of the rectangular coordinate system and the coordinates  $r$ ,  $\theta$ , and  $\phi$  of the spherical coordinate system. The latter are more appropriate for analyzing situations involving spherical symmetry, such as the hydrogen atom.

**Table 39.5.2** Quantum Numbers for Hydrogen Atom States with  $n = 2$

$n$	$\ell$	$m_\ell$
2	0	0
2	1	+1
2	1	0
2	1	-1

### Hydrogen Atom States with $n = 2$

According to the requirements of Table 39.5.1, there are four states of the hydrogen atom with  $n = 2$ ; their quantum numbers are listed in Table 39.5.2. Consider first the state with  $n = 2$  and  $\ell = m_\ell = 0$ ; its probability density is represented by the dot plot of Fig. 39.5.6. Note that this plot, like the plot for the ground state shown in Fig. 39.5.5, is spherically symmetric. That is, in a spherical coordinate system like that defined in Fig. 39.5.7, the probability density is a function of the radial coordinate  $r$  only and is independent of the angular coordinates  $\theta$  and  $\phi$ .

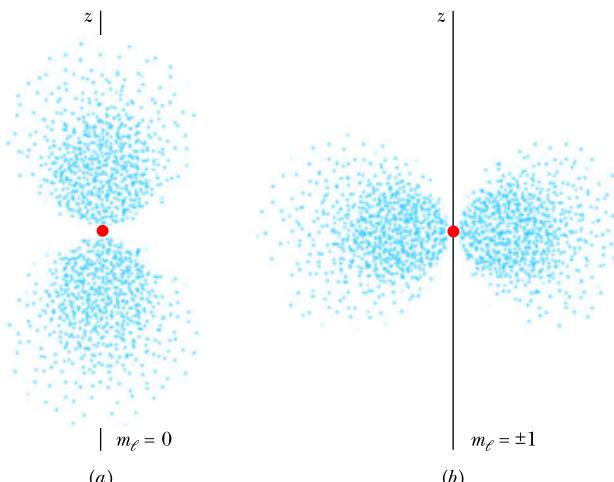
It turns out that all quantum states with  $\ell = 0$  have spherically symmetric wave functions. This is reasonable because the quantum number  $\ell$  is a measure of the angular momentum associated with a given state. If  $\ell = 0$ , the angular momentum is also zero, which requires that the probability density representing the state have no preferred axis of symmetry.

Dot plots of  $\psi^2$  for the three states with  $n = 2$  and  $\ell = 1$  are shown in Fig. 39.5.8. The probability densities for the states with  $m_\ell = +1$  and  $m_\ell = -1$  are identical. Although these plots are symmetric about the  $z$  axis, they are *not* spherically symmetric. That is, the probability densities for these three states are functions of both  $r$  and the angular coordinate  $\theta$ .

Here is a puzzle: What is there about the hydrogen atom that establishes the axis of symmetry that is so obvious in Fig. 39.5.8? The answer: *absolutely nothing*.

The solution to this puzzle comes about when we realize that all three states shown in Fig. 39.5.8 have the same energy. Recall that the energy of a state, given by Eq. 39.5.11, depends only on the principal quantum number  $n$  and is independent of  $\ell$  and  $m_\ell$ . In fact, for an *isolated* hydrogen atom there is no way to differentiate experimentally among the three states of Fig. 39.5.8.

If we add the volume probability densities for the three states for which  $n = 2$  and  $\ell = 1$ , the combined probability density turns out to be spherically symmetrical, with no unique axis. One can, then, think of the electron as spending



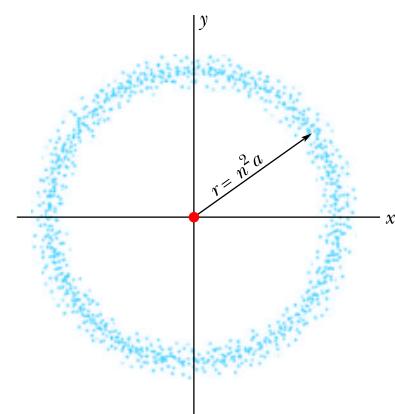
**Figure 39.5.8** Dot plots of the volume probability density  $\psi^2(r, \theta)$  for the hydrogen atom in states with  $n = 2$  and  $\ell = 1$ . (a) Plot for  $m_\ell = 0$ . (b) Plot for  $m_\ell = +1$  and  $m_\ell = -1$ . Both plots show that the probability density is symmetric about the  $z$  axis.

one-third of its time in each of the three states of Fig. 39.5.8, and one can think of the weighted sum of the three independent wave functions as defining a spherically symmetric **subshell** specified by the quantum numbers  $n = 2$ ,  $\ell = 1$ . The individual states will display their separate existence only if we place the hydrogen atom in an external electric or magnetic field. The three states of the  $n = 2$ ,  $\ell = 1$  subshell will then have different energies, and the field direction will establish the necessary symmetry axis.

The  $n = 2, \ell = 0$  state, whose volume probability density is shown in Fig. 39.5.6, also has the same energy as each of the three states of Fig. 39.5.8. We can view all four states whose quantum numbers are listed in Table 39.5.2 as forming a spherically symmetric **shell** specified by the single quantum number  $n$ . The importance of shells and subshells will become evident in Chapter 40, where we discuss atoms having more than one electron.

To round out our picture of the hydrogen atom, we display in Fig. 39.5.9 a dot plot of the *radial* probability density for a hydrogen atom state with a relatively high quantum number ( $n = 45$ ) and the highest orbital quantum number that the restrictions of Table 39.5.1 permit ( $\ell = n - 1 = 44$ ). The probability density forms a ring that is symmetrical about the  $z$  axis and lies very close to the  $xy$  plane. The mean radius of the ring is  $n^2a$ , where  $a$  is the Bohr radius. This mean radius is more than 2000 times the effective radius of the hydrogen atom in its ground state.

Figure 39.5.9 suggests the electron orbit of classical physics—it resembles the circular orbit of a planet around a star. Thus, we have another illustration of Bohr's correspondence principle—namely, that at large quantum numbers the predictions of quantum mechanics merge smoothly with those of classical physics. Imagine what a dot plot like that of Figure 39.5.9 would look like for *really* large values of  $n$  and  $\ell$ —say,  $n = 1000$  and  $\ell = 999$ .



**Figure 39.5.9** A dot plot of the radial probability density  $P(r)$  for the hydrogen atom in a quantum state with a relatively large principal quantum number—namely,  $n = 45$ —and angular momentum quantum number  $\ell = n - 1 = 44$ . The dots lie close to the  $xy$  plane, the ring of dots suggesting a classical electron orbit.

### Sample Problem 39.5.1 Radial probability density for the electron in a hydrogen atom

Show that the radial probability density for the ground state of the hydrogen atom has a maximum at  $r = a$ .

#### KEY IDEAS

- (1) The radial probability density for a ground-state hydrogen atom is given by Eq. 39.5.22,

$$P(r) = \frac{4}{a^3} r^2 e^{-2r/a}.$$

- (2) To find the maximum (or minimum) of any function, we must differentiate the function and set the result equal to zero.

**Calculation:** If we differentiate  $P(r)$  with respect to  $r$ , using derivative 7 of Appendix E and the chain rule for differentiating products, we get

$$\begin{aligned} \frac{dP}{dr} &= \frac{4}{a^3} r^2 \left( \frac{-2}{a} \right) e^{-2r/a} + \frac{4}{a^3} 2r e^{-2r/a} \\ &= \frac{8r}{a^3} e^{-2r/a} - \frac{8r^2}{a^4} e^{-2r/a} \\ &= \frac{8}{a^4} r(a - r) e^{-2r/a}. \end{aligned}$$

If we set the right side equal to zero, we obtain an equation that is true if  $r = a$ , so that the term  $(a - r)$  in the middle of the equation is zero. In other words,  $dP/dr$  is equal to zero when  $r = a$ . (Note that we also have  $dP/dr = 0$  at  $r = 0$  and at  $r = \infty$ . However, these conditions correspond to a *minimum* in  $P(r)$ , as you can see in Fig. 39.5.4.)

### Sample Problem 39.5.2 Probability of detection of the electron in a hydrogen atom

It can be shown that the probability  $p(r)$  that the electron in the ground state of the hydrogen atom will be detected inside a sphere of radius  $r$  is given by

$$p(r) = 1 - e^{-2x}(1 + 2x + 2x^2),$$

in which  $x$ , a dimensionless quantity, is equal to  $r/a$ . Find  $r$  for  $p(r) = 0.90$ .

#### KEY IDEA

There is no guarantee of detecting the electron at any particular radial distance  $r$  from the center of the hydrogen atom. However, with the given function, we can calculate the probability that the electron will be detected *somewhere* within a sphere of radius  $r$ .

**Calculation:** We seek the radius of a sphere for which  $p(r) = 0.90$ . Substituting that value in the expression for  $p(r)$ , we have

$$0.90 = 1 - e^{-2x}(1 + 2x + 2x^2)$$

$$\text{or} \quad 10e^{-2x}(1 + 2x + 2x^2) = 1.$$

We must find the value of  $x$  that satisfies this equality. It is not possible to solve explicitly for  $x$ , but an equation

solver on a calculator yields  $x = 2.66$ . This means that the radius of a sphere within which the electron will be detected 90% of the time is  $2.66a$ . Mark this position on the horizontal axis of Fig. 39.5.4. The area under the curve from  $r = 0$  to  $r = 2.66a$  gives the probability of detection in that range and is 90% of the total area under the curve.

### Sample Problem 39.5.3 Light emission from a hydrogen atom

(a) What is the wavelength of light for the least energetic photon emitted in the Lyman series of the hydrogen atom spectrum lines?

#### KEY IDEAS

(1) For any series, the transition that produces the least energetic photon is the transition between the home-base level that defines the series and the level immediately above it. (2) For the Lyman series, the home-base level is at  $n = 1$  (Fig. 39.5.3). Thus, the transition that produces the least energetic photon is the transition from the  $n = 2$  level to the  $n = 1$  level.

**Calculations:** From Eq. 39.5.12 the energy difference is

$$\Delta E = E_2 - E_1 = -(13.60 \text{ eV}) \left( \frac{1}{2^2} - \frac{1}{1^2} \right) = 10.20 \text{ eV.}$$

Then from Eq. 39.1.6 ( $\Delta E = hf$ ), with  $c/\lambda$  replacing  $f$ , we have

$$\begin{aligned} \lambda &= \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(10.20 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})} \\ &= 1.22 \times 10^{-7} \text{ m} = 122 \text{ nm.} \end{aligned} \quad (\text{Answer})$$

Light with this wavelength is in the ultraviolet range.

(b) What is the wavelength of the series limit for the Lyman series?

#### KEY IDEA

The series limit corresponds to a jump between the home-base level ( $n = 1$  for the Lyman series) and the level at the limit  $n = \infty$ .

**Calculations:** Now that we have identified the values of  $n$  for the transition, we could proceed as in (a) to find the corresponding wavelength  $\lambda$ . Instead, let's use a more direct procedure. From Eq. 39.5.15, we find

$$\begin{aligned} \frac{1}{\lambda} &= R \left( \frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right) \\ &= 1.097373 \times 10^7 \text{ m}^{-1} \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right), \end{aligned}$$

which yields

$$\lambda = 9.11 \times 10^{-8} \text{ m} = 91.1 \text{ nm.} \quad (\text{Answer})$$

Light with this wavelength is also in the ultraviolet range.

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## Review & Summary

**Confinement** Confinement of waves (string waves, matter waves—any type of wave) leads to quantization—that is, discrete states with certain energies. States with intermediate energies are not allowed.

**Electron in an Infinite Potential Well** Because it is a matter wave, an electron confined to an infinite potential well can exist in only certain discrete states. If the well is one-dimensional with length  $L$ , the energies associated with these quantum states are

$$E_n = \left( \frac{\hbar^2}{8mL^2} \right) n^2, \quad \text{for } n = 1, 2, 3, \dots, \quad (39.1.4)$$

where  $m$  is the electron mass and  $n$  is a *quantum number*. The lowest energy, said to be the *zero-point energy*, is not zero but is

given by  $n = 1$ . The electron can change (jump) from one state to another only if its energy change is

$$\Delta E = E_{\text{high}} - E_{\text{low}}, \quad (39.1.5)$$

where  $E_{\text{high}}$  is the higher energy and  $E_{\text{low}}$  is the lower energy. If the change is done by photon absorption or emission, the energy of the photon must be equal to the change in the electron's energy:

$$hf = \frac{hc}{\lambda} = \Delta E = E_{\text{high}} - E_{\text{low}}, \quad (39.1.6)$$

where frequency  $f$  and wavelength  $\lambda$  are associated with the photon.

The wave functions for an electron in an infinite, one-dimensional potential well with length  $L$  along an  $x$  axis are given by

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi}{L} x \right), \quad \text{for } n = 1, 2, 3, \dots, \quad (39.2.1)$$

where  $n$  is the quantum number and the factor  $\sqrt{2/L}$  comes from normalizing the wave function. The wave function  $\psi_n(x)$  does not have physical meaning, but the probability density  $\psi_n^2(x)$  does have physical meaning: The product  $\psi_n^2(x) dx$  is the probability that the electron will be detected in the interval between  $x$  and  $x + dx$ . If the probability density of an electron is integrated over the entire  $x$  axis, the total probability must be 1, which means that the electron will be detected somewhere along the  $x$  axis:

$$\int_{-\infty}^{\infty} \psi_n^2(x) dx = 1. \quad (39.2.5)$$

**Electron in a Finite Well** The wave function for an electron in a finite, one-dimensional potential well extends into the walls. Compared to the states in an infinite well of the same size, the states in a finite well have a limited number, longer de Broglie wavelengths, and lower energies.

**Two-Dimensional Electron Trap** The quantized energies for an electron trapped in a two-dimensional infinite potential well that forms a rectangular corral are

$$E_{nx, ny} = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right), \quad (39.4.2)$$

where  $n_x$  is a quantum number for which the electron's matter wave fits in well width  $L_x$  and  $n_y$  is a quantum number for which it fits in well width  $L_y$ . The wave functions for an electron in a two-dimensional well are given by

$$\psi_{nx, ny} = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y \pi}{L_y} y\right). \quad (39.4.1)$$

**The Hydrogen Atom** The Bohr model of the hydrogen atom successfully derived the energy levels for the atom, to explain the emission/absorption spectrum of the atom, but it is

incorrect in almost every other aspect. It is a planetary model in which the electron orbits the central proton with an angular momentum  $L$  that is limited to values given by

$$L = n\hbar, \quad \text{for } n = 1, 2, 3, \dots, \quad (39.5.1)$$

where  $n$  is a quantum number. The equation is, however, incorrect. Application of the Schrödinger equation gives the correct values of  $L$  and the quantized energies:

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2 n^2} = -\frac{13.60 \text{ eV}}{n^2}, \quad \text{for } n = 1, 2, 3, \dots. \quad (39.5.12)$$

The atom (or, the electron in the atom) can change energy only by jumping between these allowed energies. If the jump is by photon absorption (the atom's energy increases) or photon emission (the atom's energy decreases), this restriction in energy changes leads to

$$\frac{1}{\lambda} = R \left( \frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right), \quad (39.5.15)$$

for the wavelength of the light, where  $R$  is the Rydberg constant,

$$R = \frac{me^4}{8\epsilon_0^2 h^3 c} = 1.097373 \times 10^7 \text{ m}^{-1}. \quad (39.5.16)$$

The radial probability density  $P(r)$  for a state of the hydrogen atom is defined so that  $P(r) dr$  is the probability that the electron will be detected somewhere in the space between two spherical shells of radii  $r$  and  $r + dr$  that are centered on the nucleus. The probability that the electron will be detected between any two given radii  $r_1$  and  $r_2$  is

$$(\text{probability of detection}) = \int_{r_1}^{r_2} P(r) dr. \quad (39.5.23)$$

## Questions

- 1 Three electrons are trapped in three different one-dimensional infinite potential wells of widths (a) 50 pm, (b) 200 pm, and (c) 100 pm. Rank the electrons according to their ground-state energies, greatest first.
- 2 Is the ground-state energy of a proton trapped in a one-dimensional infinite potential well greater than, less than, or equal to that of an electron trapped in the same potential well?
- 3 An electron is trapped in a one-dimensional infinite potential well in a state with quantum number  $n = 17$ . How many points of (a) zero probability and (b) maximum probability does its matter wave have?
- 4 Figure 39.1 shows three infinite potential wells, each on an  $x$  axis. Without written calculation, determine the wave function  $\psi$  for a ground-state electron trapped in each well.

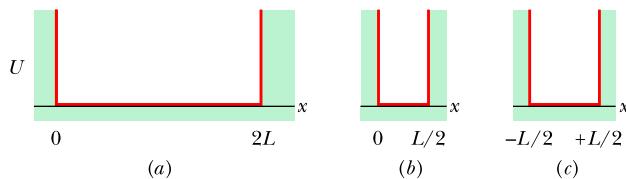


Figure 39.1 Question 4.

- 5 A proton and an electron are trapped in identical one-dimensional infinite potential wells; each particle is in its ground state. At the center of the wells, is the probability density for the proton greater than, less than, or equal to that of the electron?
- 6 If you double the width of a one-dimensional infinite potential well, (a) is the energy of the ground state of the trapped electron multiplied by 4, 2,  $\frac{1}{2}$ ,  $\frac{1}{4}$ , or some other number? (b) Are the energies of the higher energy states multiplied by this factor or by some other factor, depending on their quantum number?
- 7 If you wanted to use the idealized trap of Fig. 39.1.1 to trap a positron, would you need to change (a) the geometry of the trap, (b) the electric potential of the central cylinder, or (c) the electric potentials of the two semi-infinite end cylinders? (A positron has the same mass as an electron but is positively charged.)
- 8 An electron is trapped in a finite potential well that is deep enough to allow the electron to exist in a state with  $n = 4$ . How many points of (a) zero probability and (b) maximum probability does its matter wave have within the well?
- 9 An electron that is trapped in a one-dimensional infinite potential well of width  $L$  is excited from the ground state to

the first excited state. Does the excitation increase, decrease, or have no effect on the probability of detecting the electron in a small length of the  $x$  axis (a) at the center of the well and (b) near one of the well walls?

**10** An electron, trapped in a finite potential energy well such as that of Fig. 39.3.1, is in its state of lowest energy. Are (a) its de Broglie wavelength, (b) the magnitude of its momentum, and (c) its energy greater than, the same as, or less than they would be if the potential well were infinite, as in Fig. 39.1.2?

**11** From a visual inspection of Fig. 39.3.2, rank the quantum numbers of the three quantum states according to the de Broglie wavelength of the electron, greatest first.

**12** You want to modify the finite potential well of Fig. 39.3.1 to allow its trapped electron to exist in more than four quantum states. Could you do so by making the well (a) wider or narrower, (b) deeper or shallower?

**13** A hydrogen atom is in the third excited state. To what state (give the quantum number  $n$ ) should it jump to (a) emit light with the longest possible wavelength, (b) emit light with the shortest possible wavelength, and (c) absorb light with the longest possible wavelength?

**14** Figure 39.2 indicates the lowest energy levels (in electron-volts) for five situations in which an electron is trapped in a one-dimensional infinite potential well. In wells  $B$ ,  $C$ ,  $D$ , and  $E$ , the electron is in the ground state. We shall excite the electron in well  $A$  to the fourth excited state (at 25 eV). The electron can then de-excite to the ground state by emitting one or more photons, corresponding to one long jump or several

short jumps. Which photon *emission* energies of this de-excitation match a photon *absorption* energy (from the ground state) of the other four electrons? Give the  $n$  values.

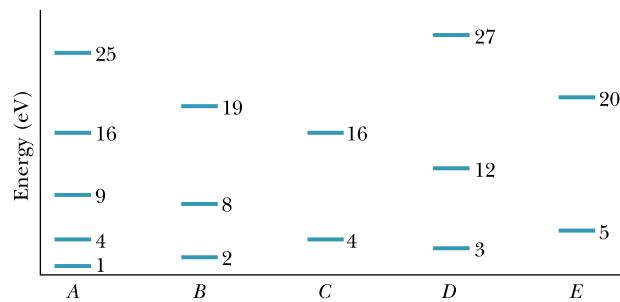


Figure 39.2 Question 14.

**15** Table 39.1 lists the quantum numbers for five proposed hydrogen atom states. Which of them are not possible?

Table 39.1

	$n$	$\ell$	$m_\ell$
(a)	3	2	0
(b)	2	3	1
(c)	4	3	-4
(d)	5	5	0
(e)	5	3	-2

## Problems

**GO** Tutoring problem available (at instructor's discretion) in WileyPLUS

**SSM** Worked-out solution available in Student Solutions Manual

**E** Easy **M** Medium **H** Hard

**FCP** Additional information available in *The Flying Circus of Physics* and at [flyingcircusofphysics.com](http://flyingcircusofphysics.com)

### Module 39.1 Energies of a Trapped Electron

**1 E** An electron in a one-dimensional infinite potential well of length  $L$  has ground-state energy  $E_1$ . The length is changed to  $L'$  so that the new ground-state energy is  $E'_1 = 0.500 E_1$ . What is the ratio  $L'/L$ ?

**2 E** What is the ground-state energy of (a) an electron and (b) a proton if each is trapped in a one-dimensional infinite potential well that is 200 pm wide?

**3 E** The ground-state energy of an electron trapped in a one-dimensional infinite potential well is 2.6 eV. What will this quantity be if the width of the potential well is doubled?

**4 E** An electron, trapped in a one-dimensional infinite potential well 250 pm wide, is in its ground state. How much energy must it absorb if it is to jump up to the state with  $n = 4$ ?

**5 E** What must be the width of a one-dimensional infinite potential well if an electron trapped in it in the  $n = 3$  state is to have an energy of 4.7 eV?

**6 E** A proton is confined to a one-dimensional infinite potential well 100 pm wide. What is its ground-state energy?

**7 E** Consider an atomic nucleus to be equivalent to a one-dimensional infinite potential well with  $L = 1.4 \times 10^{-14}$  m, a typical nuclear diameter. What would be the ground-state energy of an electron if it were trapped in such a potential well? (Note: Nuclei do not contain electrons.)

**8 M GO** An electron is trapped in a one-dimensional infinite well and is in its first excited state. Figure 39.3 indicates the five longest wavelengths of light that the electron could absorb in transitions from this initial state via a single photon absorption:  $\lambda_a = 80.78$  nm,  $\lambda_b = 33.66$  nm,  $\lambda_c = 19.23$  nm,  $\lambda_d = 12.62$  nm, and  $\lambda_e = 8.98$  nm. What is the width of the potential well?

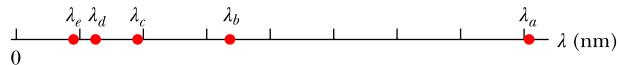


Figure 39.3 Problem 8.

**9 M** Suppose that an electron trapped in a one-dimensional infinite well of width 250 pm is excited from its first excited state to its third excited state. (a) What energy must be transferred to the electron for this quantum jump? The electron then de-excites

back to its ground state by emitting light. In the various possible ways it can do this, what are the (b) shortest, (c) second shortest, (d) longest, and (e) second longest wavelengths that can be emitted? (f) Show the various possible ways on an energy-level diagram. If light of wavelength 29.4 nm happens to be emitted, what are the (g) longest and (h) shortest wavelength that can be emitted afterwards?

**10 M** An electron is trapped in a one-dimensional infinite potential well. For what (a) higher quantum number and (b) lower quantum number is the corresponding energy difference equal to the energy difference  $\Delta E_{43}$  between the levels  $n = 4$  and  $n = 3$ ? (c) Show that no pair of adjacent levels has an energy difference equal to  $2\Delta E_{43}$ .

**11 M** An electron is trapped in a one-dimensional infinite potential well. For what (a) higher quantum number and (b) lower quantum number is the corresponding energy difference equal to the energy of the  $n = 5$  level? (c) Show that no pair of adjacent levels has an energy difference equal to the energy of the  $n = 6$  level.

**12 M GO** An electron is trapped in a one-dimensional infinite well of width 250 pm and is in its ground state. What are the (a) longest, (b) second longest, and (c) third longest wavelengths of light that can excite the electron from the ground state via a single photon absorption?

### Module 39.2 Wave Functions of a Trapped Electron

**13 M GO** A one-dimensional infinite well of length 200 pm contains an electron in its third excited state. We position an electron-detector probe of width 2.00 pm so that it is centered on a point of maximum probability density. (a) What is the probability of detection by the probe? (b) If we insert the probe as described 1000 times, how many times should we expect the electron to materialize on the end of the probe (and thus be detected)?

**14 M** An electron is in a certain energy state in a one-dimensional, infinite potential well from  $x = 0$  to  $x = L = 200$  pm. The electron's probability density is zero at  $x = 0.300L$  and  $x = 0.400L$ ; it is not zero at intermediate values of  $x$ . The electron then jumps to the next lower energy level by emitting light. What is the change in the electron's energy?

**15 M SSM** An electron is trapped in a one-dimensional infinite potential well that is 100 pm wide; the electron is in its ground state. What is the probability that you can detect the electron in an interval of width  $\Delta x = 5.0$  pm centered at  $x =$  (a) 25 pm, (b) 50 pm, and (c) 90 pm? (Hint: The interval  $\Delta x$  is so narrow that you can take the probability density to be constant within it.)

**16 M** A particle is confined to the one-dimensional infinite potential well of Fig. 39.1.2. If the particle is in its ground state, what is its probability of detection between (a)  $x = 0$  and  $x = 0.25L$ , (b)  $x = 0.75L$  and  $x = L$ , and (c)  $x = 0.25L$  and  $x = 0.75L$ ?

### Module 39.3 An Electron in a Finite Well

**17 E** An electron in the  $n = 2$  state in the finite potential well of Fig. 39.3.1 absorbs 400 eV of energy from an external source. Using the energy-level diagram of Fig. 39.3.3, determine the electron's kinetic energy after this absorption, assuming that the electron moves to a position for which  $x > L$ .

**18 E** Figure 39.3.3 gives the energy levels for an electron trapped in a finite potential energy well 450 eV deep. If the electron is in the  $n = 3$  state, what is its kinetic energy?

**19 M GO** Figure 39.4a shows the energy-level diagram for a finite, one-dimensional energy well that contains an electron. The nonquantized region begins at  $E_4 = 450.0$  eV. Figure 39.4b gives the absorption spectrum of the electron when it is in the ground state—it can absorb at the indicated wavelengths:  $\lambda_a = 14.588$  nm and  $\lambda_b = 4.8437$  nm and for any wavelength less than  $\lambda_c = 2.9108$  nm. What is the energy of the first excited state?

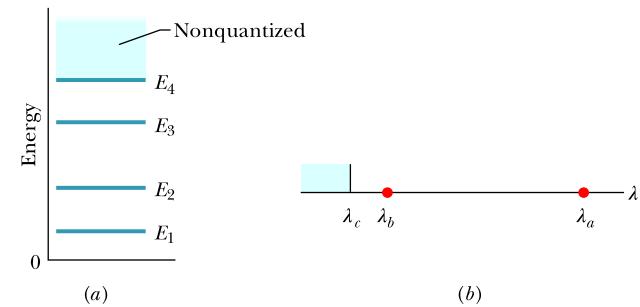


Figure 39.4 Problem 19.

**20 M GO** Figure 39.5a shows a thin tube in which a finite potential trap has been set up where  $V_2 = 0$  V. An electron is shown traveling rightward toward the trap, in a region with a voltage of  $V_1 = -9.00$  V, where it has a kinetic energy of 2.00 eV. When the electron enters the trap region, it can become trapped if it gets rid of enough energy by emitting a photon. The energy levels of the electron within the trap are  $E_1 = 1.0$ ,  $E_2 = 2.0$ , and  $E_3 = 4.0$  eV, and the nonquantized region begins at  $E_4 = 9.0$  eV as shown in the energy-level diagram of Fig. 39.5b. What is the smallest energy (eV) such a photon can have?

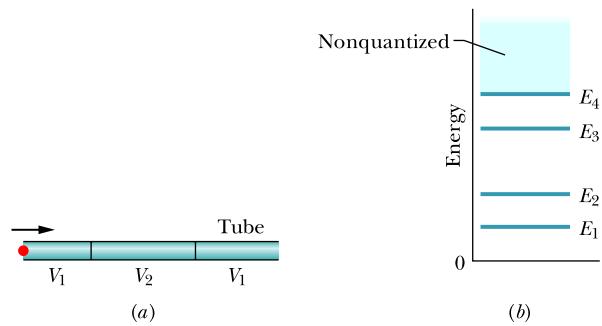


Figure 39.5 Problem 20.

**21 M** (a) Show that for the region  $x > L$  in the finite potential well of Fig. 39.3.1,  $\psi(x) = De^{2kx}$  is a solution of Schrödinger's equation in its one-dimensional form, where  $D$  is a constant and  $k$  is positive. (b) On what basis do we find this mathematically acceptable solution to be physically unacceptable?

### Module 39.4 Two- and Three-Dimensional Electron Traps

**22 E GO** An electron is contained in the rectangular corral of Fig. 39.4.4, with widths  $L_x = 800$  pm and  $L_y = 1600$  pm. What is the electron's ground-state energy?

**23 E** An electron is contained in the rectangular box of Fig. 39.4.5, with widths  $L_x = 800$  pm,  $L_y = 1600$  pm, and  $L_z = 390$  pm. What is the electron's ground-state energy?

**24 M** Figure 39.6 shows a two-dimensional, infinite-potential well lying in an  $xy$  plane that contains an electron. We probe for the electron along a line that bisects  $L_x$  and find three points at which the detection probability is maximum. Those points are separated by 2.00 nm. Then we probe along a line that bisects  $L_y$  and find five points at which the detection probability is maximum. Those points are separated by 3.00 nm. What is the energy of the electron?

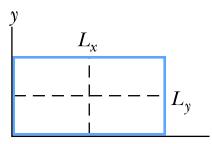


Figure 39.6 Problem 24.

**25 M GO** The two-dimensional, infinite corral of Fig. 39.7 is square, with edge length  $L = 150$  pm. A square probe is centered at  $xy$  coordinates  $(0.200L, 0.800L)$  and has an  $x$  width of 5.00 pm and a  $y$  width of 5.00 pm. What is the probability of detection if the electron is in the  $E_{1,3}$  energy state?

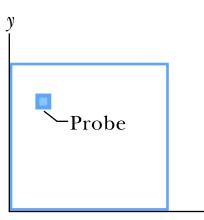


Figure 39.7 Problem 25.

**26 M** A rectangular corral of widths  $L_x = L$  and  $L_y = 2L$  holds an electron. What multiple of  $\hbar^2/8mL^2$ , where  $m$  is the electron mass, gives (a) the energy of the electron's ground state, (b) the energy of its first excited state, (c) the energy of its lowest degenerate states, and (d) the difference between the energies of its second and third excited states?

**27 M SSM** An electron (mass  $m$ ) is contained in a rectangular corral of widths  $L_x = L$  and  $L_y = 2L$ . (a) How many different frequencies of light could the electron emit or absorb if it makes a transition between a pair of the lowest five energy levels? What multiple of  $\hbar/8mL^2$  gives the (b) lowest, (c) second lowest, (d) third lowest, (e) highest, (f) second highest, and (g) third highest frequency?

**28 M GO** A cubical box of widths  $L_x = L_y = L_z = L$  contains an electron. What multiple of  $\hbar^2/8mL^2$ , where  $m$  is the electron mass, is (a) the energy of the electron's ground state, (b) the energy of its second excited state, and (c) the difference between the energies of its second and third excited states? How many degenerate states have the energy of (d) the first excited state and (e) the fifth excited state?

**29 M** An electron (mass  $m$ ) is contained in a cubical box of widths  $L_x = L_y = L_z$ . (a) How many different frequencies of light could the electron emit or absorb if it makes a transition between a pair of the lowest five energy levels? What multiple of  $\hbar/8mL^2$  gives the (b) lowest, (c) second lowest, (d) third lowest, (e) highest, (f) second highest, and (g) third highest frequency?

**30 H GO** An electron is in the ground state in a two-dimensional, square, infinite potential well with edge lengths  $L$ . We will probe for it in a square of area  $400 \text{ pm}^2$  that is centered at  $x = L/8$  and  $y = L/8$ . The probability of detection turns out to be  $4.5 \times 10^{-8}$ . What is edge length  $L$ ?

### Module 39.5 The Hydrogen Atom

**31 E SSM** What is the ratio of the shortest wavelength of the Balmer series to the shortest wavelength of the Lyman series?

**32 E** An atom (not a hydrogen atom) absorbs a photon whose associated wavelength is 375 nm and then immediately emits a

photon whose associated wavelength is 580 nm. How much net energy is absorbed by the atom in this process?

**33 E** What are the (a) energy, (b) magnitude of the momentum, and (c) wavelength of the photon emitted when a hydrogen atom undergoes a transition from a state with  $n = 3$  to a state with  $n = 1$ ?

**34 E** Calculate the radial probability density  $P(r)$  for the hydrogen atom in its ground state at (a)  $r = 0$ , (b)  $r = a$ , and (c)  $r = 2a$ , where  $a$  is the Bohr radius.

**35 E** For the hydrogen atom in its ground state, calculate (a) the probability density  $\psi^2(x)$  and (b) the radial probability density  $P(r)$  for  $r = a$ , where  $a$  is the Bohr radius.

**36 E** (a) What is the energy  $E$  of the hydrogen-atom electron whose probability density is represented by the dot plot of Fig. 39.5.6? (b) What minimum energy is needed to remove this electron from the atom?

**37 E SSM** A neutron with a kinetic energy of 6.0 eV collides with a stationary hydrogen atom in its ground state. Explain why the collision must be elastic—that is, why kinetic energy must be conserved. (*Hint:* Show that the hydrogen atom cannot be excited as a result of the collision.)

**38 E** An atom (not a hydrogen atom) absorbs a photon whose associated frequency is  $6.2 \times 10^{14}$  Hz. By what amount does the energy of the atom increase?

**39 M CALC SSM** Verify that Eq. 39.5.22, the radial probability density for the ground state of the hydrogen atom, is normalized. That is, verify that the following is true:

$$\int_0^\infty P(r) dr = 1.$$

**40 M** What are the (a) wavelength range and (b) frequency range of the Lyman series? What are the (c) wavelength range and (d) frequency range of the Balmer series?

**41 M** What is the probability that an electron in the ground state of the hydrogen atom will be found between two spherical shells whose radii are  $r$  and  $r + \Delta r$ , (a) if  $r = 0.500a$  and  $\Delta r = 0.010a$  and (b) if  $r = 1.00a$  and  $\Delta r = 0.01a$ , where  $a$  is the Bohr radius? (*Hint:*  $\Delta r$  is small enough to permit the radial probability density to be taken to be constant between  $r$  and  $r + \Delta r$ .)

**42 M** A hydrogen atom, initially at rest in the  $n = 4$  quantum state, undergoes a transition to the ground state, emitting a photon in the process. What is the speed of the recoiling hydrogen atom? (*Hint:* This is similar to the explosions of Chapter 9.)

**43 M** In the ground state of the hydrogen atom, the electron has a total energy of  $-13.6$  eV. What are (a) its kinetic energy and (b) its potential energy if the electron is one Bohr radius from the central nucleus?

**44 M** A hydrogen atom in a state having a *binding energy* (the energy required to remove an electron) of 0.85 eV makes a transition to a state with an *excitation energy* (the difference between the energy of the state and that of the ground state) of 10.2 eV. (a) What is the energy of the photon emitted as a result of the transition? What are the (b) higher quantum number and (c) lower quantum number of the transition producing this emission?

- 45 M SSM** The wave functions for the three states with the dot plots shown in Fig. 39.5.8, which have  $n = 2$ ,  $\ell = 1$ , and  $m_\ell = 0, +1$ , and  $-1$ , are

$$\begin{aligned}\psi_{210}(r, \theta) &= (1/4\sqrt{2\pi})(a^{-3/2})(r/a)^{-r/2a} \cos \theta, \\ \psi_{21+1}(r, \theta) &= (1/8\sqrt{\pi})(a^{-3/2})(r/a)e^{-r/2a}(\sin \theta)e^{+i\phi}, \\ \psi_{21-1}(r, \theta) &= (1/8\sqrt{\pi})(a^{-3/2})(r/a)e^{-r/2a}(\sin \theta)e^{-i\phi},\end{aligned}$$

in which the subscripts on  $\psi(r, \theta)$  give the values of the quantum numbers  $n$ ,  $\ell$ ,  $m_\ell$ , and the angles  $\theta$  and  $\phi$  are defined in Fig. 39.5.7. Note that the first wave function is real but the others, which involve the imaginary number  $i$ , are complex. Find the radial probability density  $P(r)$  for (a)  $\psi_{210}$  and (b)  $\psi_{21+1}$  (same as for  $\psi_{21-1}$ ). (c) Show that each  $P(r)$  is consistent with the corresponding dot plot in Fig. 39.5.8. (d) Add the radial probability densities for  $\psi_{210}$ ,  $\psi_{21+1}$ , and  $\psi_{21-1}$  and then show that the sum is spherically symmetric, depending only on  $r$ .

- 46 M** Calculate the probability that the electron in the hydrogen atom, in its ground state, will be found between spherical shells whose radii are  $a$  and  $2a$ , where  $a$  is the Bohr radius.

- 47 M** For what value of the principal quantum number  $n$  would the effective radius, as shown in a probability density dot plot for the hydrogen atom, be 1.0 mm? Assume that  $\ell$  has its maximum value of  $n - 1$ . (Hint: See Fig. 39.5.9.)

- 48 M** Light of wavelength 121.6 nm is emitted by a hydrogen atom. What are the (a) higher quantum number and (b) lower quantum number of the transition producing this emission? (c) What is the name of the series that includes the transition?

- 49 M** How much work must be done to pull apart the electron and the proton that make up the hydrogen atom if the atom is initially in (a) its ground state and (b) the state with  $n = 2$ ?

- 50 M** Light of wavelength 102.6 nm is emitted by a hydrogen atom. What are the (a) higher quantum number and (b) lower quantum number of the transition producing this emission? (c) What is the name of the series that includes the transition?

- 51 M** What is the probability that in the ground state of the hydrogen atom, the electron will be found at a radius greater than the Bohr radius?

- 52 M** A hydrogen atom is excited from its ground state to the state with  $n = 4$ . (a) How much energy must be absorbed by the atom? Consider the photon energies that can be emitted by the atom as it de-excites to the ground state in the several possible ways. (b) How many different energies are possible; what are the (c) highest, (d) second highest, (e) third highest, (f) lowest, (g) second lowest, and (h) third lowest energies?

- 53 M SSM** Schrödinger's equation for states of the hydrogen atom for which the orbital quantum number  $\ell$  is zero is

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) + \frac{8\pi^2 m}{h^2} [E - U(r)]\psi = 0.$$

Verify that Eq. 39.5.17, which describes the ground state of the hydrogen atom, is a solution of this equation.

- 54 H CALC** The wave function for the hydrogen-atom quantum state represented by the dot plot shown in Fig. 39.5.6, which has  $n = 2$  and  $\ell = m_\ell = 0$ , is

$$\psi_{200}(r) = \frac{1}{4\sqrt{2\pi}} a^{-3/2} \left( 2 - \frac{r}{a} \right) e^{-r/2a},$$

in which  $a$  is the Bohr radius and the subscript on  $\psi(r)$  gives the values of the quantum numbers  $n$ ,  $\ell$ ,  $m_\ell$ . (a) Plot  $\psi_{200}(r)$  and show that your plot is consistent with the dot plot of Fig. 39.5.6. (b) Show analytically that  $\psi_{200}(r)$  has a maximum at  $r = 4a$ . (c) Find the radial probability density  $P_{200}(r)$  for this state. (d) Show that

$$\int_0^\infty P_{200}(r) dr = 1$$

and thus that the expression above for the wave function  $\psi_{200}(r)$  has been properly normalized.

- 55 H CALC** The radial probability density for the ground state of the hydrogen atom is a maximum when  $r = a$ , where  $a$  is the Bohr radius. Show that the average value of  $r$ , defined as

$$r_{\text{avg}} = \int P(r) r dr,$$

has the value  $1.5a$ . In this expression for  $r_{\text{avg}}$ , each value of  $P(r)$  is weighted with the value of  $r$  at which it occurs. Note that the average value of  $r$  is greater than the value of  $r$  for which  $P(r)$  is a maximum.

#### Additional Problems

- 56** Let  $\Delta E_{\text{adj}}$  be the energy difference between two adjacent energy levels for an electron trapped in a one-dimensional infinite potential well. Let  $E$  be the energy of either of the two levels. (a) Show that the ratio  $\Delta E_{\text{adj}}/E$  approaches the value  $2/n$  at large values of the quantum number  $n$ . As  $n \rightarrow \infty$ , does (b)  $\Delta E_{\text{adj}}$  (c)  $E$ , or (d)  $\Delta E_{\text{adj}}/E$  approach zero? (e) What do these results mean in terms of the correspondence principle?

- 57** An electron is trapped in a one-dimensional infinite potential well. Show that the energy difference  $\Delta E$  between its quantum levels  $n$  and  $n + 2$  is  $(\hbar^2/2mL^2)(n + 1)$ .

- 58 CALC** As Fig. 39.3.2 suggests, the probability density for an electron in the region  $0 < x < L$  for the finite potential well of Fig. 39.3.1 is sinusoidal, being given by  $\psi^2(x) = B \sin^2 kx$ , in which  $B$  is a constant. (a) Show that the wave function  $\psi(x)$  that may be found from this equation is a solution of Schrödinger's equation in its one-dimensional form. (b) Find an expression for  $k$  that makes this true.

- 59 CALC SSM** As Fig. 39.3.2 suggests, the probability density for the region  $x > L$  in the finite potential well of Fig. 39.3.1 drops off exponentially according to  $\psi^2(x) = Ce^{-2kx}$ , where  $C$  is a constant. (a) Show that the wave function  $\psi(x)$  that may be found from this equation is a solution of Schrödinger's equation in its one-dimensional form. (b) Find an expression for  $k$  for this to be true.

- 60** An electron is confined to a narrow evacuated tube of length 3.0 m; the tube functions as a one-dimensional infinite potential well. (a) What is the energy difference between the electron's ground state and its first excited state? (b) At what quantum number  $n$  would the energy difference between adjacent energy levels be 1.0 eV—which is measurable, unlike the result of (a)? At that quantum number, (c) what multiple of the electron's rest energy would give the electron's total energy and (d) would the electron be relativistic?

- 61 CALC** (a) Show that the terms in Schrödinger's equation (Eq. 39.3.1) have the same dimensions. (b) What is the common SI unit for each of these terms?

**62** (a) What is the wavelength of light for the least energetic photon emitted in the Balmer series of the hydrogen atom spectrum lines? (b) What is the wavelength of the series limit?

**63** (a) For a given value of the principal quantum number  $n$  for a hydrogen atom, how many values of the orbital quantum number  $\ell$  are possible? (b) For a given value of  $\ell$ , how many values of the orbital magnetic quantum number  $m_\ell$  are possible? (c) For a given value of  $n$ , how many values of  $m_\ell$  are possible?

**64** Verify that the combined value of the constants appearing in Eq. 39.5.11 is 13.6 eV.

**65** A diatomic gas molecule consists of two atoms of mass  $m$  separated by a fixed distance  $d$  rotating about an axis as indicated in Fig. 39.8. Assuming that its angular momentum is quantized as in the Bohr model for the hydrogen atom, find (a) the possible angular velocities and (b) the possible quantized rotational energies.

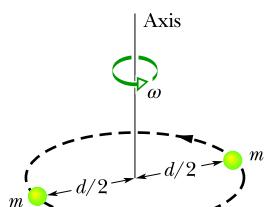


Figure 39.8 Problem 65.

**66** In atoms there is a finite, though very small, probability that, at some instant, an orbital electron will actually be found inside the nucleus. In fact, some unstable nuclei use this occasional appearance of the electron to decay by *electron capture*. Assuming that the proton itself is a sphere of radius  $1.1 \times 10^{-15}$  m and that the wave function of the hydrogen atom's electron holds all the way to the proton's center, use the ground-state wave function to calculate the probability that the hydrogen atom's electron is inside its nucleus.

**67** (a) What is the separation in energy between the lowest two energy levels for a container 20 cm on a side containing argon atoms? Assume, for simplicity, that the argon atoms are trapped in a one-dimensional well 20 cm wide. The molar mass of argon is 39.9 g/mol. (b) At 300 K, to the nearest power of ten, what is the ratio of the thermal energy of the atoms to this energy separation? (c) At what temperature does the thermal energy equal the energy separation?

**68** A muon of charge  $-e$  and mass  $m = 207m_e$  (where  $m_e$  is the mass of an electron) orbits the nucleus of a singly ionized helium atom ( $\text{He}^+$ ). Assuming that the Bohr model of the hydrogen

atom can be applied to this muon–helium system, verify that the energy levels of the system are given by

$$E = -\frac{11.3 \text{ keV}}{n^2}.$$

**69** From the energy-level diagram for hydrogen, explain the observation that the frequency of the second Lyman-series line is the sum of the frequencies of the first Lyman-series line and the first Balmer-series line. This is an example of the empirically discovered *Ritz combination principle*. Use the diagram to find some other valid combinations.

**70 [CALC]** A hydrogen atom can be considered as having a central point-like proton of positive charge  $e$  and an electron of negative charge  $-e$  that is distributed about the proton according to the volume charge density  $\rho = A \exp(-2r/a_0)$ . Here  $A$  is a constant,  $a_0 = 0.53 \times 10^{-10}$  m, and  $r$  is the distance from the center of the atom. (a) Using the fact that the hydrogen is electrically neutral, find  $A$ . Then find the (b) magnitude and (c) direction of the atom's electric field at  $a_0$ .

**71 [CALC]** An old model of a hydrogen atom has the charge  $+e$  of the proton uniformly distributed over a sphere of radius  $a_0$ , with the electron of charge  $-e$  and mass  $m$  at its center. (a) What would then be the force on the electron if it were displaced from the center by a distance  $r \leq a_0$ ? (b) What would be the angular frequency of oscillation of the electron about the center of the atom once the electron was released?

**72** In a simple model of a hydrogen atom, the single electron orbits the single proton (the nucleus) in a circular path. Calculate (a) the electric potential set up by the proton at the orbital radius of 52.9 pm, (b) the electric potential energy of the atom, and (c) the kinetic energy of the electron. (d) How much energy is required to ionize the atom (that is, to remove the electron to an infinite distance with no kinetic energy)? Give the energies in electron-volts.

**73** Consider a conduction electron in a cubical crystal of a conducting material. Such an electron is free to move throughout the volume of the crystal but cannot escape to the outside. It is trapped in a three-dimensional infinite well. The electron can move in three dimensions, so that its total energy is given by

$$E = \frac{\hbar^2}{8L^2m} (n_1^2 + n_2^2 + n_3^2),$$

in which  $n_1$ ,  $n_2$ , and  $n_3$  are positive integer values. Calculate the energies of the lowest five distinct states for a conduction electron moving in a cubical crystal of edge length  $L = 0.25 \mu\text{m}$ .