

13. Consider a quantum encryption scheme using photons. Assume that a photon can only exist in either state 1,  $\psi_1$ , having energy  $E_1$ , or state 2,  $\psi_2$ , having energy  $E_2$ , or in a superposition of the two states,  $\Psi = a\psi_1 + b\psi_2$ . Assume that the states are orthonormal.
- If a photon exists in the superposition state  $\Psi = a\psi_1 + b\psi_2$ , what is the relationship between  $a$  and  $b$ ?
  - If a photon exists in the superposition state  $\Psi = a\psi_1 + b\psi_2$ , determine the probability of measuring energy  $E_2$ . Show all work and/or explain your answer.
  - If the photon in a superposition state is sent over a network, explain how undetected eavesdropping would be impossible.
14. In Chapter 6, the reflection and transmission of a particle across a potential barrier will be considered. For now, assume that a potential energy discontinuity is present at  $x = a$ , and that to the left of the discontinuity, the wavefunction is given by

$$\Psi(x, t) = (e^{ikx} + Re^{-ikx})e^{-iEt/\hbar},$$

and to the right of the discontinuity

$$\Psi(x, t) = Te^{iqx}e^{-iEt/\hbar},$$

where  $R$  and  $T$  are reflection and transmission coefficients, respectively, which will depend on the properties of the different regions and on the discontinuity in potential at  $x = a$ . Determine the probability current density on either side of the discontinuity.

15. In the example of solving the one-dimensional Schrödinger's equation on page 65, we obtained the state functions

$$\Psi(x, t) = \psi(x)e^{-iE_n t/\hbar}$$

where

$$\begin{aligned} \psi(x) &= \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right), & n \text{ even,} \\ &= \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{n\pi}{L}x\right), & n \text{ odd,} \end{aligned}$$

and where

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2.$$

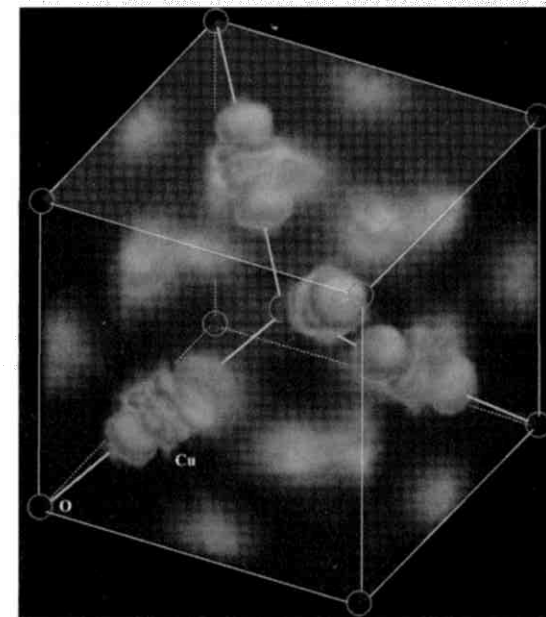
Determine the probability current density. Discuss your result.

16. Assume that the wave function

$$\psi(z, t) = 200e^{i(kz - \omega t)}$$

describes a beam of 2 eV electrons having only kinetic energy. Determine numerical values for  $k$  and  $\omega$ , and find the associated current density in A/m.

## FREE AND CONFINED ELECTRONS



Electron and X-ray diffraction image of dumbbell-shaped clouds of electrons shared by covalent bonds between copper and oxygen atoms in cuprite,  $\text{Cu}_2\text{O}$ . The nuclei of the copper atoms (not shown) are at the center of the dumbbells, and those of the oxygen atoms (also not shown) are at the center and corners of the superimposed cube. The fuzzy clouds are less defined electron clouds representing covalent bonds between the copper atoms. (From J.M. Zuo, M. Kim, M. O'Keeffe, and J.C.H. Spence, *Nature* 401, 49–52 (1999). Used by permission.)

In the last chapter, Schrödinger's equation was introduced, along with the basic ideas of quantum mechanics. In this chapter, some examples of solving Schrödinger's equation are presented relevant to understanding physical phenomena associated with electrons confined to nanoscale regions of space, including quantum dots, wires, and wells. The chapter begins, however, with a discussion of free (unconfined) electrons, in part to provide a comparison to the bounded space result.

## 4.1 FREE ELECTRONS

As a first application of solving Schrödinger's equation, consider a free electron in an infinite space. By "free electron," we mean that there is no potential energy variation to influence the particle, i.e.,  $V(\mathbf{r}) = V_0$  (where  $V_0$  can be zero; the important thing is that  $V$  is constant). For solid materials, the most common source of a potential is the atomic lattice, where the potential energy between an electron with charge  $q_e$  and an ionized atom of charge  $-q_e$  is

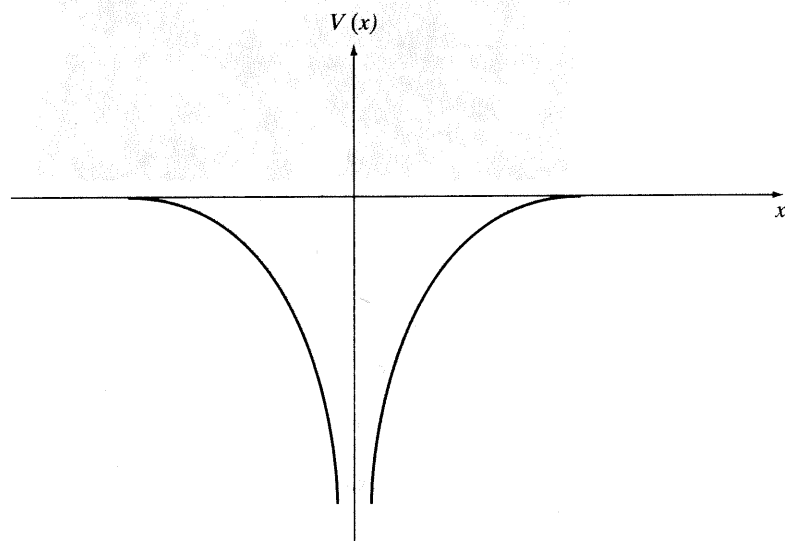
$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{(q_e)(-q_e)}{r} = -A \frac{1}{r}, \quad (4.1)$$

where  $r$  is the distance between the electron and the ion. In one dimension,

$$V(x) = \frac{1}{4\pi\epsilon_0} \frac{(q_e)(-q_e)}{|x|} = -A \frac{1}{|x|}, \quad (4.2)$$

as shown in Fig. 4.1.

Other sources of potential could be, for example, other electrons. Here it will be assumed that there is a single electron and no other particles. Therefore, there is obviously no boundary on the space since a material boundary would involve other electrons. Thus, the electron is totally unencumbered by interactions, and is considered free. It is worth noting that, although we will primarily discuss electrons since they are our main interest, most of the obtained results will apply generally to particles with mass.



**Figure 4.1** Potential  $V(x)$  given by (4.2) versus position  $x$ , as a one-dimensional model of the potential due to an atom.

## 4.1.1 One-Dimensional Space

Considering first a one-dimensional problem, Schrödinger's equation (3.140),

$$\left( -\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} + V_0 \right) \psi(x) = E\psi(x), \quad (4.3)$$

where  $m_e$  is the mass of the electron and  $E$  is the electron's energy, has the solution

$$\psi(x) = Ae^{ikx} + Be^{-ikx}. \quad (4.4)$$

In (4.4),

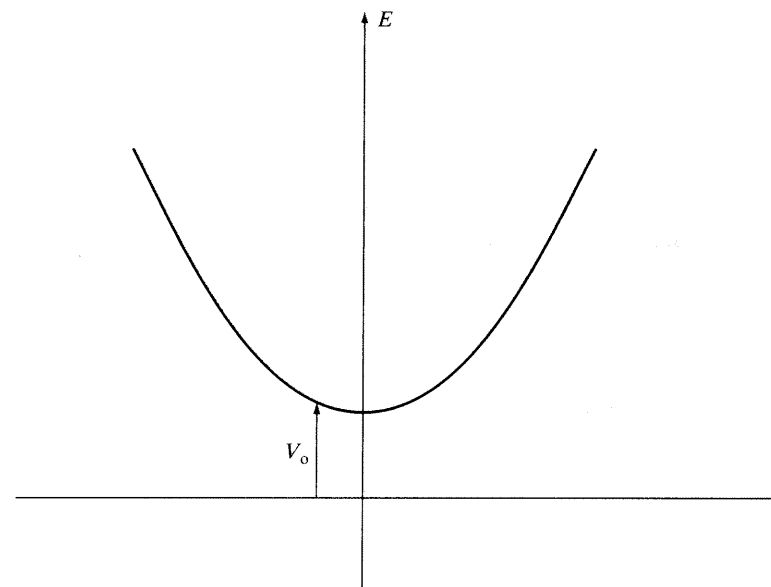
$$k^2 = \frac{2m_e(E - V_0)}{\hbar^2}, \quad (4.5)$$

where  $k$  is called the *wavevector* (in general), or wavenumber (for the scalar case), and where  $A$  and  $B$  are constants. The parabolic relationship between wavevector  $k$  and energy  $E$ , (4.5), is shown in Fig. 4.2; later this type of diagram will have great importance. Putting in the time variation (3.141), we have

$$\Psi(x, t) = (Ae^{ikx} + Be^{-ikx}) e^{-iEt/\hbar}, \quad (4.6)$$

from which we can see that the terms associated with  $A$  and  $B$  represent forward and backward traveling waves, respectively. A solution such as (4.6) is called a *plane wave solution* since the surfaces of constant amplitude and phase are plane surfaces.

Recall that two concepts of velocity for a wave were developed in Section 2.5, the phase velocity (2.30),  $v_p = \omega/k$ , and the group velocity (2.48),  $v_g = \partial\omega/\partial k$ . Although they



**Figure 4.2** Relationship between energy and wavenumber, (4.5), for a free electron.

were derived from a consideration of wavepackets, they can be taken as possible definitions of wave velocities. For the solutions of Schrödinger's equation presented previously, setting  $V_0 = 0$  for convenience and using  $E = \hbar\omega$ , we obtain

$$v_p = \frac{\omega}{k} = \frac{\hbar k}{2m_e} = \frac{p}{2m_e}. \quad (4.7)$$

Recalling that solutions of Schrödinger's equation should agree with classical physics in the classical limit, in order to see if the phase velocity agrees with our classical notion of velocity, we equate  $p = m_e v$  for a classical electron to obtain

$$v_p = \frac{v}{2}. \quad (4.8)$$

Therefore, the phase velocity does not yield a reasonable value for the electron's velocity. However, the group velocity is

$$v_g = \frac{\partial\omega}{\partial k} = \frac{\hbar k}{m_e} = \frac{p}{m_e}, \quad (4.9)$$

which, with  $p = m_e v$  for a classical electron, leads to

$$v_g = v, \quad (4.10)$$

the classical velocity. Therefore, as concepts of velocity, the group velocity is the more physically meaningful. For a classical electromagnetic plane wave in free space, where  $k = \omega/c$ ,  $v_p = v_g = c$ .

Because the electron does not interact with anything, it can be assumed that it will be moving either along the positive or negative  $x$  coordinate. Let's assume that the electron is moving along the positive  $x$  coordinate ( $B = 0$ ). Then, the probability of finding the electron in a range  $\Delta x$  centered at some  $x$  is

$$|\Psi(x, t)|^2 \Delta x = |A|^2 \Delta x, \quad (4.11)$$

which is independent of  $x$ . Therefore, the electron has equal probability to be found at any point in space. This is consistent with the uncertainty principle (2.39); since  $k$  is known exactly (i.e., it is assumed that we know the electron's energy), and, therefore, momentum is known by (2.15), the uncertainty in the electron's position must be infinite.

The probabilistic current density associated with the wave is, from (3.187),

$$\begin{aligned} \mathbf{J}(\mathbf{r}, t) &= \frac{-i\hbar}{2m_e} (\Psi^*(\mathbf{r}, t) \nabla \Psi(\mathbf{r}, t) - \Psi(\mathbf{r}, t) \nabla \Psi^*(\mathbf{r}, t)) \\ &= \mathbf{a}_x |A|^2 \frac{\hbar k}{m_e}. \end{aligned} \quad (4.12)$$

The probabilistic charge density is

$$\rho = \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) = |A|^2, \quad (4.13)$$

and, with  $\hbar k = p = m_e v$ ,

$$\mathbf{J}(\mathbf{r}, t) = \mathbf{a}_x |A|^2 v = \mathbf{a}_x \rho v, \quad (4.14)$$

which has the usual interpretation of current density being the product of charge density and velocity.

The amplitude  $A$  is usually determined by normalization (3.8), although in this case the normalization cannot be performed since we have a plane wave existing everywhere in an infinite space. A resolution of this difficulty, and a fact that should always be kept in mind, is that Schrödinger's equation is a homogeneous linear differential equation. Its solution merely details the possible allowed states of the system, not which states will actually be filled.<sup>†</sup> (You can think of a filled state as a state "containing" an electron. Filling of the states will be considered in Section 8.2.) Furthermore, a sum of homogeneous solutions to a linear differential equation is itself a homogeneous solution, and so an electron may not be in a single state, but in a superposition of states having the form (3.53). As considered in Section 2.5, a superposition of plane waves is a wavepacket, which is suitably localized in space and energy (and time). A more realistic wavepacket solution can be normalized by (3.8), although this topic will not be pursued here.

### 4.1.2 Three-Dimensional Space

Now, moving to a three-dimensional space, Schrödinger's equation (3.139) is

$$\left( -\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V_0 - E \right) \psi(x, y, z) = 0, \quad (4.15)$$

where the Laplacian term is explicitly written in rectangular coordinates. The preceding equation can be easily solved using separation of variables, which was used in Section 3.2 to separate the time and space dependence of Schrödinger's equation. Assume a product solution of the form

$$\psi(x, y, z) = \psi_x(x) \psi_y(y) \psi_z(z). \quad (4.16)$$

Inserting (4.16) into (4.15), we have

$$\left( \frac{1}{\psi_x} \frac{\partial^2}{\partial x^2} \psi_x + \frac{1}{\psi_y} \frac{\partial^2}{\partial y^2} \psi_y + \frac{1}{\psi_z} \frac{\partial^2}{\partial z^2} \psi_z + \frac{2m_e}{\hbar^2} (E - V_0) \right) = 0. \quad (4.17)$$

The first term can be, at most, a function of  $x$  (but not  $y$  or  $z$ ), the second term can be, at most, a function of  $y$  (but not  $x$  or  $z$ ), and third term can be, at most, a function of  $z$  (but not  $x$  or  $y$ ). These three terms then add to a constant to yield zero. The only way this can happen, for all possible values of  $x$ ,  $y$ , and  $z$ , is if each of the three terms is actually equal to a constant.

<sup>†</sup>This is analogous to solving the source-free Newton's equations for a mass-spring system (or for a guitar string, bridge span, etc.) The solutions are the possible resonances of the system, although without knowing the input force, one does not know which resonances will be implicated in a force-driven problem.

Let the constant associated with the first term be  $-k_x^2$ , and similarly for the other two terms. Then

$$\frac{1}{\psi_x} \frac{\partial^2}{\partial x^2} \psi_x = -k_x^2 \rightarrow \psi_x(x) = Ae^{ik_x x} + Be^{-ik_x x}, \quad (4.18)$$

$$\frac{1}{\psi_y} \frac{\partial^2}{\partial y^2} \psi_y = -k_y^2 \rightarrow \psi_y(y) = Ce^{ik_y y} + De^{-ik_y y},$$

$$\frac{1}{\psi_z} \frac{\partial^2}{\partial z^2} \psi_z = -k_z^2 \rightarrow \psi_z(z) = Fe^{ik_z z} + Ge^{-ik_z z},$$

where we must have, from (4.17),

$$k_x^2 + k_y^2 + k_z^2 = \frac{2m_e}{\hbar^2} (E - V_0). \quad (4.19)$$

Since the electron is unencumbered by electrical or mechanical influences, we can assume that the electron is moving in a certain direction in the three-dimensional space. Therefore, one constant in each pair of constants ( $A$  or  $B$ ,  $C$  or  $D$ ,  $F$  or  $G$ ) will be zero. For example, if the wave movement is along the positive  $x$  and  $y$  coordinates, but the negative  $z$  coordinate, then  $B = D = F = 0$ . The product solution can be written as

$$\psi(\mathbf{r}) = (A_0 e^{ik_x x} e^{ik_y y} e^{ik_z z}), \quad (4.20)$$

where the wavenumbers  $k_x$ ,  $k_y$ , and  $k_z$  can still be chosen as positive or negative to fix the electron's direction, and where  $A_0$  is the product of the three constants remaining in (4.18). We can write (4.20) compactly as

$$\psi(\mathbf{r}) = A_0 e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (4.21)$$

where

$$\mathbf{k} = \mathbf{a}_x k_x + \mathbf{a}_y k_y + \mathbf{a}_z k_z, \quad k = |\mathbf{k}|, \quad (4.22)$$

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \frac{2m_e (E - V_0)}{\hbar^2}$$

(hence the name *wavevector* for  $\mathbf{k}$ ). Putting in the time variation using (3.135), we have

$$\Psi(\mathbf{r}, t) = A_0 e^{i\mathbf{k} \cdot \mathbf{r}} e^{-iEt/\hbar}, \quad (4.23)$$

which is a plane wave moving in three-dimensional space. A more physically realistic solution would be a three-dimensional wavepacket, consisting of a superposition of waves having the form (4.23).

## 4.2 THE FREE ELECTRON GAS THEORY OF METALS

Assume now that we have, instead of a single electron,  $N$  electrons in an otherwise empty space (no lattice, etc.), where  $N$  is typically a very large number. For example, a copper atom

has 29 electrons, 28 of which are strongly bound to the atom. However, the 29th electron is bound very loosely to the atom, and can essentially freely move about the material. Thus, copper has a free electron density of  $N$  electrons per cubic meter, where  $N$  is also the number of atoms per cubic meter (for copper,  $N \sim 8.45 \times 10^{22}$  atoms/cm<sup>3</sup>).

As discussed in Section 3.5, for a system of  $N$  electrons, the Schrödinger equation is much more difficult to solve compared with the case of a single electron. Part of this difficulty lies in the fact that the interaction among electrons will result in a very complicated potential term  $V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ . However, if the interaction between electrons can be neglected, which is often a particularly appropriate approximation due in part to the Pauli exclusion principle, then each electron obeys the one-particle Schrödinger equation (3.139), where  $V$  will be a constant (since an otherwise empty space is considered).

The rationale behind ignoring electron–electron and electron–lattice interactions in a material was discussed in Section 3.5. The fact that in a metal the electron density is large actually implied being able to ignore electron–electron and electron–ion interactions, due to Coulomb screening and the exclusion principle. Therefore, to a first approximation, in many metals the  $N$  electrons tend to act freely, and, thus, these metals can be modeled as a collection of  $N$  non-interacting free electrons, often called a *free electron gas*. For many metals, this simple model is quite good at describing and predicting physically observed phenomena. The free electron gas model is discussed further in Chapter 10.

## 4.3 ELECTRONS CONFINED TO A BOUNDED REGION OF SPACE AND QUANTUM NUMBERS

The simplest solution of Schrödinger's equation has now been considered, i.e., the model of an electron, or some other particle, in an infinite space with no spatial energy variation. Of course, this is an unrealistic scenario, although it models a situation when an electron is relatively free. It also provides a comparison with the slightly more complicated, but more realistic case of an electron confined to a finite region of space. This confinement could be due to, for instance, an electron being bound to an atom, or to an electron being confined to a small nanoscopic material region such as a quantum dot. It turns out that this *particle-in-a-box* model is of the utmost importance in understanding nanoelectronic devices, since it is the simplest model that leads to the important topic of energy discretization.

Assume that the potential energy profile is constant (and, in fact, assume that  $V_0 = 0$ ), but that the region of space is now finite in size. In particular, we will consider a rectangular box having dimensions  $L_x \times L_y \times L_z$ , although first we'll look at the one-dimensional problem of a finite line segment having length  $L_x$ .

### 4.3.1 One-Dimensional Space

Consider an electron confined to an interval  $(0, L_x)$ . In one dimension, Schrödinger's equation (3.140) with  $V = 0$  is

$$-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi(x) = E\psi(x), \quad (4.24)$$

which has the solution<sup>†</sup>

$$\psi(x) = A \sin kx + B \cos kx, \quad (4.25)$$

which are obviously energy eigenfunctions (i.e., an eigenfunction of  $H = -(\hbar^2/2m_e) d^2/dx^2$ ) where

$$k^2 = \frac{2m_e E}{\hbar^2}. \quad (4.26)$$

Outside of the line segment, we'll assume that the probability of finding the electron is zero (i.e., the electron is confined to the line segment by some sort of barrier), and so outside of the line segment,  $\psi = 0$ . This structure is often called a *quantum well* or *quantum box*. Quantum wells are very important in nanoelectronics, since a nanoelectronic device would naturally confine electrons to nanoscopic regions of space.

Continuity of the wavefunction (3.144) requires that

$$\psi(0) = \psi(L_x) = 0, \quad (4.27)$$

and so we find

$$B = 0, \quad (4.28)$$

$$k = \frac{n\pi}{L_x}, \quad n = 1, 2, 3, \dots$$

The wavefunction is, therefore,

$$\psi_n(x) = A \sin \frac{n\pi}{L_x} x, \quad (4.29)$$

which is normalized according to (3.8),

$$\int_0^{L_x} |\psi_n(x)|^2 dx = 1, \quad (4.30)$$

resulting in

$$\psi_n(x) = \left(\frac{2}{L_x}\right)^{1/2} \sin \frac{n\pi}{L_x} x, \quad (4.31)$$

or<sup>‡</sup>

$$\Psi_n(x, t) = \left(\frac{2}{L_x}\right)^{1/2} \sin \left(\frac{n\pi}{L_x} x\right) e^{-iE_n t/\hbar}. \quad (4.34)$$

<sup>†</sup>An exponential solution of the form (4.4) could be used, alternatively, although the sine/cosine form is preferred here since we will obtain bound states.

<sup>‡</sup>The solutions (4.34) exhibit even symmetry about the center of the box for  $n$  odd, and odd symmetry about the center of the box for  $n$  even. It is sometimes more convenient to consider a symmetric box, extending

Since  $k$  is discrete,

$$E = \frac{\hbar^2 k^2}{2m_e} = \frac{\hbar^2}{2m_e} \left(\frac{n\pi}{L_x}\right)^2 = E_n, \quad (4.35)$$

which denote eigenvalues of the Hamiltonian  $H$ . From (3.113), the expectation value of the electron's position is

$$\langle x \rangle = \int_0^{L_x} \Psi_n^*(x, t) x \Psi_n(x, t) dx \quad (4.36)$$

$$= \frac{2}{L_x} \int_0^{L_x} x \sin^2 \left(\frac{n\pi}{L_x} x\right) dx \quad (4.37)$$

$$= \frac{L_x}{2}, \quad (4.38)$$

i.e., the average position of the electron is the center of the box. Furthermore, since the electron only has kinetic energy ( $V = 0$ ), the de Broglie wavelength is given by

$$\lambda_e = \frac{h}{\sqrt{2m_e E}}. \quad (4.39)$$

Using (4.35), we obtain

$$L_x = \frac{n\lambda_e}{2}, \quad (4.40)$$

so that an integral number of half de Broglie wavelengths fit inside the segment  $L_x$ . In addition, if we assume that the electron is in a superposition state,

$$\Psi(x, t) = \sum_n a_n \Psi_n(x, t), \quad (4.41)$$

then the probability of measuring energy  $E_m$  is

$$P(E_n) = \left| \int_0^L \Psi(\mathbf{r}, t) \Psi_n^*(\mathbf{r}) dx \right|^2 = |a_n|^2. \quad (4.42)$$

from  $x = -L_x/2$  to  $x = L_x/2$ , where we would obtain (see the example on page 65)

$$\Psi(x, t) = \left(\frac{2}{L_x}\right)^{1/2} \cos \left(\frac{n\pi}{L_x} x\right) e^{-iE_n t/\hbar}, \quad n \text{ odd}, \quad (4.32)$$

$$= \left(\frac{2}{L_x}\right)^{1/2} \sin \left(\frac{n\pi}{L_x} x\right) e^{-iE_n t/\hbar}, \quad n \text{ even}, \quad (4.33)$$

where  $n = 1, 2, 3, \dots$

At this point, it is important to appreciate two things.

- The size of the box *dictates* the possible energy levels of an electron confined to the box, via (4.35). That is, an electron confined to a box can only have energies given by the discrete values  $E_n$ , which depend only on the size of the box and on the electron's mass.
- Although the electron's wavefunctions (4.34) and energies (4.35) are the only possible solutions, since Schrödinger's equation is a homogeneous differential equation, the electron can be either in one of the discrete states  $\Psi_n$ , or in a superposition of states given by (3.142) (i.e., (4.41)).

We do not know the actual state that an electron will occupy; this will typically depend on temperature and other energy inputs. We have only obtained the *allowed, possible* states that the electron can occupy, and we have not discussed which states would actually be filled. We will get to the filling of states subsequently, at which point we will need to consider temperature.

Note that by simply confining the electron to a finite region of space, the solution obtained radically differs from the totally free electron case. In particular, for the free electron, the solution (4.4) represents a traveling wave (since it can be assumed that one of  $A$  or  $B$  is zero), and for the confined electron, the solution (4.29) represents a standing wave. The first several standing wave patterns are shown in Fig. 4.3.

Of equal, if not greater, importance, is the observation that the energy obtained for the particle without boundaries is continuous, whereas in a bounded region of space the particle's energy is discrete. The energy versus wavevector curve is parabolic, in a discrete sense, and is shown in Fig. 4.4, which should be compared to Fig. 4.2 on page 87 for the free electron.

For the spatially bounded particle,  $n$  in (4.31)–(4.35) is called the *quantum number*. Since we are dealing with electrons, to each state there is another quantum number,  $m_s$ , corresponding to spin, which does not affect the energy. Together, these two quantum numbers completely describe the state of the particle. The lowest state is the ground state, with  $n = 1$ .

One can gain an appreciation of the discreteness of energy by considering a numerical example. Let an electron be confined to an atomic-sized region of space,  $L_x = 2 \times 10^{-10}$  m. The first two energy levels,  $E_1$  and  $E_2$  from (4.35), are

$$E_1 = 1.5 \times 10^{-18} \text{ J} \Rightarrow \frac{1.5 \times 10^{-18} \text{ J}}{1.6021 \times 10^{-19} \text{ C}} = 9.4 \text{ eV}, \quad (4.43)$$

$$E_2 = 6.0 \times 10^{-18} \text{ J} = 37.6 \text{ eV}.$$

In particular, the spacing between any successive energy levels is

$$E_n - E_{n-1} = 9.4(2n - 1) \text{ eV}, \quad (4.44)$$

and, thus, the discrete nature of the allowed energy levels is clearly evident. (Energy levels on the order of electron volts are easily measured.) If, instead, we consider a macroscopic

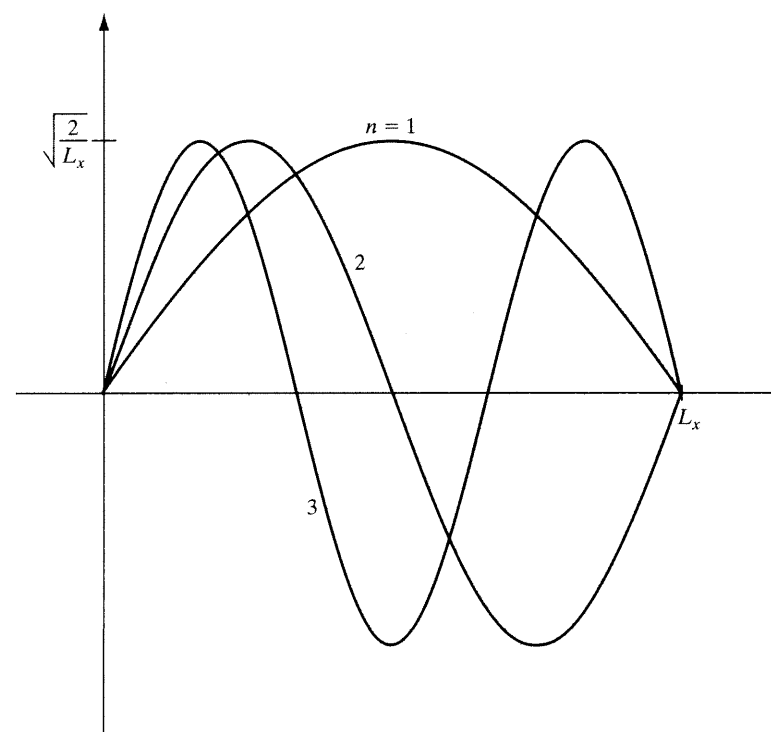


Figure 4.3 The first several standing wave patterns for (4.31).

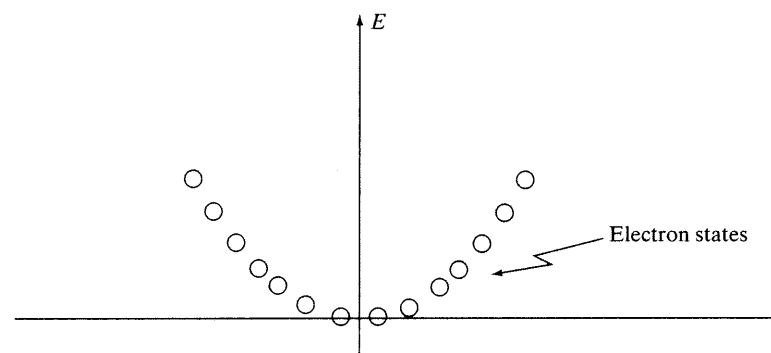


Figure 4.4 Energy versus wavenumber for discrete energy levels. Only values of energy and wavenumber represented by circles are allowed.

region of space,  $L_x = 1$  cm, then (4.35) results in

$$E_1 = 6.0 \times 10^{-34} \text{ J} = 3.8 \times 10^{-15} \text{ eV}, \quad (4.45)$$

and the spacing between any two energy levels is

$$E_n - E_{n-1} = 3.8 \times 10^{-15} (2n - 1) \text{ eV}, \quad (4.46)$$

which is too small to be measurable. Thus, in a macroscopic region of space, the energy spacings are so close they appear to be continuous. This is yet another example of the “classical limit,” where quantum mechanics provides the expected classical result known from experiments on macroscopic systems.

Viewing this from another perspective, let’s assume that electron energies on the order of  $10^{-3}$ – $10^3$  electron volts are of most interest, commensurate with typical energy levels encountered in electronics and optics. Then, assuming that the electron has only kinetic energy, from (4.39), we see that the electron’s de Broglie wavelength is in the range

$$\lambda_e = 10^{-8} - 10^{-11} \text{ nm}. \quad (4.47)$$

In what will become a familiar theme throughout this text, note that when a particle’s de Broglie wavelength is on the order of, or larger than, the size of a confining space, the particle “feels” the boundaries of the space and exhibits energy level discretization. When a particle’s de Broglie wavelength is much smaller than the size of a confining space, conversely, the particle does not “feel” the finiteness of the space, and it behaves as if it were a free particle, which was the case examined in Section 4.1. Relating this to (4.40), we find that an electron with an energy level in the specified range actually inhabits one of the discrete levels  $E_n$ , although if  $\lambda_e \ll L_x$ , the electron is in one of the higher energy states (i.e., corresponding to a large value of  $n$ ), and in this situation, the spacing between energy levels is so small we can model them as forming a continuum.

Note that  $E$  (the kinetic energy in this case, since  $V = 0$ ) is not zero in the ground state. The lowest energy of a particle would be zero, classically, corresponding to the particle being at rest ( $V = 0$ ,  $E = 0$ ), which would occur at the temperature absolute zero ( $T = 0$  K). Again, classically, at any nonzero temperature the electron would acquire thermal energy and start to vibrate.

Viewing this from the quantum mechanical picture, we can see a reason why the lowest energy, called the *ground state energy*, is nonzero. If the particle’s kinetic energy were zero, then  $p = 0$ , and, via the uncertainty principle (2.39), the uncertainty in position would be infinity. Since we have bounded the particle’s position to a finite range ( $x = 0$  to  $x = L_x$ ), then the particle’s momentum can’t be zero.<sup>†</sup> This ground state energy is also called *internal kinetic energy*, or *zero-point energy*.

**Quantum Versus Classical Physics – What is Quantized?** In classical physics, one has the concept of discrete resonant frequencies, but not the quantization of energy.

<sup>†</sup>We can view this phenomena as de Broglie waves reflected back and forth. For allowed  $E_n$ ’s, the interference is constructive; otherwise, the interference is destructive. However, this is a mathematical representation, and we shouldn’t take this to mean that the particle is literally bouncing back and forth.

For example, in an electrical inductor–capacitor circuit, a discrete resonant frequency exists that depends on the inductance and capacitance values. However, the energy associated with the resonance is a continuous quantity, associated with the amplitude of the current or voltage in the circuit. Stored energy changes from electrical (energy stored in the capacitor) to magnetic (energy stored in the inductor) over the course of the oscillation. In a similar manner, the energy of a swinging pendulum converts between potential energy (the height of the bob) and kinetic energy (the velocity of the bob) as the bob oscillates at the discrete resonant frequency of the pendulum, although the energy of the bob is continuous (e.g., the height of the bob, which is the amplitude of the oscillation, is a continuous quantity). Guitar strings obviously lead to discrete resonance frequencies, although, again, energy is associated with the amplitude of the string displacement, and not to the discrete frequency of the resonance. Therefore, in classical physics, energy is associated with amplitude, which is not quantized, although frequency can be quantized. In the quantum picture, energy is often quantized, and energy and frequency quantization are connected by  $E = \hbar\omega$ .

### 4.3.2 Three-Dimensional Space

The example of an electron confined to a three-dimensional region of space, such as a quantum dot, follows easily from the previous result. Assume that the space has dimensions  $L_x \times L_y \times L_z$ , and that within the space  $V = 0$ . Schrödinger’s equation (3.139) is

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi(\mathbf{r}) = E \psi(\mathbf{r}), \quad (4.48)$$

and, assuming that the wavefunction can be written in product form,

$$\psi(x, y, z) = \psi_x(x) \psi_y(y) \psi_z(z), \quad (4.49)$$

the boundary conditions<sup>†</sup>

$$\psi_x(0) = \psi_x(L_x) = 0, \quad (4.50)$$

$$\psi_y(0) = \psi_y(L_y) = 0,$$

$$\psi_z(0) = \psi_z(L_z) = 0,$$

lead to

$$\psi(x, y, z) = \left( \frac{8}{L_x L_y L_z} \right)^{1/2} \sin \frac{n_x \pi}{L_x} x \sin \frac{n_y \pi}{L_y} y \sin \frac{n_z \pi}{L_z} z. \quad (4.51)$$

We now have three quantum numbers,

$$n_x = 1, 2, 3, \dots, \quad (4.52)$$

$$n_y = 1, 2, 3, \dots,$$

$$n_z = 1, 2, 3, \dots,$$

<sup>†</sup>This is sometimes called the hard-wall case, i.e., the electron is confined to the box by infinite hard walls.



and a fourth quantum number  $m_s$  that accounts for spin. Together, these four quantum numbers describe the state of the particle,<sup>†</sup> where different combinations of the quantum numbers refer to different states of the system.

The allowed discrete values of energy are given by

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m_e} \left( \left( \frac{n_x}{L_x} \right)^2 + \left( \frac{n_y}{L_y} \right)^2 + \left( \frac{n_z}{L_z} \right)^2 \right). \quad (4.53)$$

Of course, if  $L_x = L_y = L_z = L$ , then we obtain the simpler result

$$E = \frac{\hbar^2 \pi^2}{2m_e L^2} (n_x^2 + n_y^2 + n_z^2) = E_n. \quad (4.54)$$

In this case, states with different quantum numbers but the same energy (e.g.,  $(n_x, n_y, n_z) = (1, 2, 3)$  and  $(n_x, n_y, n_z) = (3, 1, 2)$ ) are called *degenerate*, and the number of states having the same energy is called the *degeneracy*.

As an aside, if we think of a cube of material of side  $L$  and we compress (squeeze) the material, then  $L$  decreases and, by (4.54), the energy levels increase. Thus, electrons in the material must increase their energy, and this energy gain comes from the work done by squeezing the material. The resulting pressure is called *Pauli pressure*, since the Pauli exclusion principle keeps multiple electrons (more than two) from occupying the same energy level. This pressure partially accounts for the resistance to squeezing of materials with high electron concentrations. (This also explains partially the avoidance of gravitational collapse.) Metals have a high electron concentration, although repulsive forces between nuclei, etc., also contribute to the pressure. If the exclusion principle did not hold and all electrons could be in the lowest state, their energy would still increase upon squeezing since  $E_1$  would nevertheless increase as  $L$  decreased, although the effect would be much weaker.

Lastly, it is worth reiterating that we have solved the time-independent Schrödinger's equation to obtain the *possible* (i.e., allowed) electron states. What state an electron actually occupies will depend on other factors such as temperature, the presence of other electrons, and other energy sources.

### 4.3.3 Periodic Boundary Conditions

Rather than the boundary conditions (4.50), it is often convenient to consider periodic boundary conditions that result in traveling, rather than standing, wave solutions.<sup>‡</sup> Periodic

<sup>†</sup>Readers familiar with electromagnetic theory will recognize the connection between the results in this section and the allowed resonances in a three-dimensional cavity (except, in that case, there is no spin integer).

<sup>‡</sup>If the region of space is large compared with atomic dimensions, then the influence of the boundary conditions on the motion of the particle will be small.

boundary conditions emulate an infinite solid, rather than a finite region, and are given by

$$\psi(x, y, z) = \psi(x + L_x, y, z), \quad (4.55)$$

$$\psi(x, y, z) = \psi(x, y + L_y, z),$$

$$\psi(x, y, z) = \psi(x, y, z + L_z),$$

leading to the solution of (4.48) as

$$\psi(\mathbf{r}) = \left( \frac{1}{L_x L_y L_z} \right)^{1/2} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (4.56)$$

where

$$\mathbf{k} = \mathbf{a}_x k_x + \mathbf{a}_y k_y + \mathbf{a}_z k_z, \quad k = |\mathbf{k}|, \quad (4.57)$$

$$k^2 = (k_x^2 + k_y^2 + k_z^2) = \frac{2m_e E}{\hbar^2},$$

$$k_x = \frac{2n_x \pi}{L_x}, \quad k_y = \frac{2n_y \pi}{L_y}, \quad k_z = \frac{2n_z \pi}{L_z},$$

$n_{x,y,z} = 0, \pm 1, \pm 2, \dots$ . Note that now we have the index  $2n_{x,y,z}$ , instead of  $n_{x,y,z}$ , and that both positive and negative values of  $k$  are allowed to account for waves moving in opposite directions. Allowed energy levels are given by

$$E_n = \frac{2\hbar^2 \pi^2}{m_e} \left( \left( \frac{n_x}{L_x} \right)^2 + \left( \frac{n_y}{L_y} \right)^2 + \left( \frac{n_z}{L_z} \right)^2 \right), \quad (4.58)$$

and, for a box having equal sides  $L$ ,

$$E_n = \frac{2\hbar^2 \pi^2}{m_e L^2} (n_x^2 + n_y^2 + n_z^2). \quad (4.59)$$

Note that the equation

$$E_n = \alpha \frac{\hbar^2 \pi^2}{m_e L^2} (n_x^2 + n_y^2 + n_z^2) \quad (4.60)$$

represents either the hard-wall case for  $\alpha = 1/2$  or, for  $\alpha = 2$ , the periodic boundary condition case.

## 4.4 FERMI LEVEL AND CHEMICAL POTENTIAL

An important concept that will be used throughout this text is the *Fermi level*. A related concept, the *chemical potential*, which has the symbol  $\mu$  (not to be confused with permeability from electromagnetic theory, or magnetic moment), will first be introduced.



The precise definition of the chemical potential is complicated, and beyond what we need for the treatment described here (it involves the change in the Gibbs free energy with respect to a change in the number of particles in a system). However, we can think of the chemical potential as (approximately) the energy needed to add the  $N$ th electron to a system of  $N - 1$  electrons. For noninteracting electrons, this is simply the energy of the highest occupied state. To agree with the statistical definition utilized in Chapter 8 relating to Fermi level, we will define the chemical potential of a  $N$ -electron system by

$$[E_t(N + 1) - E_t(N - 1)]/2, \quad (4.61)$$

where  $E_t(N)$  is the total energy of an  $N$  particle system.

### Example

Consider a one-dimensional box of length  $L$ , as considered in Section 4.3.1, and assume that five noninteracting electrons are contained within the box. If we assume that electrons are in their lowest energy configuration, since two electrons can occupy each state (due to the Pauli exclusion principle), then the first two states are completely filled, and the third state is partially filled. The total energy of the  $N + 1$ -electron system is

$$E_t(6) = 2E_1 + 2E_2 + 2E_3,$$

where the energy levels  $E_n$  are defined by (4.35). The total energy of a four-electron system would be

$$E_t(4) = 2E_1 + 2E_2,$$

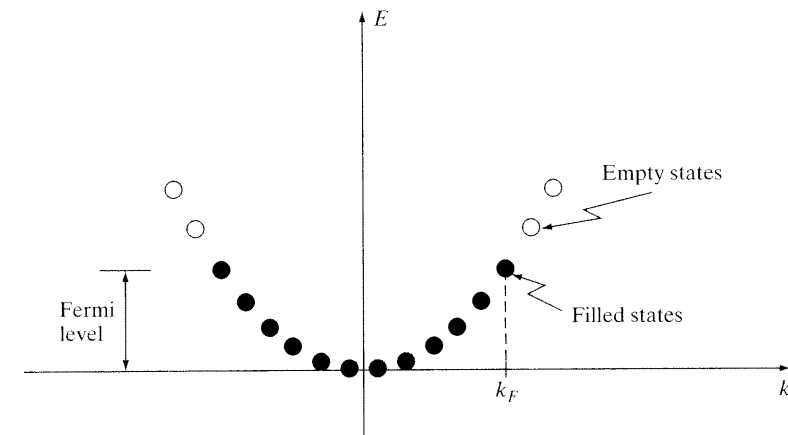
and, therefore, the chemical potential is

$$\mu(5) = [E_t(6) - E_t(4)]/2 = E_3 = \frac{\hbar^2}{2m_e} \left( \frac{3\pi}{L} \right)^2.$$

The *Fermi level* is defined as the value of the chemical potential at  $T = 0$ , i.e.,  $E_F = \mu(T = 0)$ , and so the Fermi level (Fermi energy) is (nearly) the maximum energy of a particle at  $T = 0$ . It is common in semiconductor physics to use the term Fermi level rather than chemical potential, regardless of temperature. The main idea is that at absolute zero, a collection of  $N$  electrons will arrange themselves into the lowest available energy states, and form what is called a *Fermi sea* of electrons. The Fermi level is the surface of that sea at absolute zero. The concept of the Fermi energy is of considerable importance in nanoelectronics, and will be discussed further in Sections 5.4 and 8.2.

The chemical potential is a weak function of temperature, given approximately as

$$\mu(T) = E_F \left( 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{E_F} \right)^2 + \dots \right) \quad (4.62)$$



**Figure 4.5** Energy versus wavenumber for discrete energy levels. Filled circles denote filled states, and empty circles denote empty states.

for a noninteracting Fermi gas (i.e., a collection of noninteracting fermions, which models many metals at low temperatures). In (4.62),  $k_B$  is *Boltzmann's constant*,

$$\begin{aligned} k_B &= 1.38 \times 10^{-23} \text{ J/K} \\ &= 8.62 \times 10^{-5} \text{ eV/K}, \end{aligned}$$

which can be thought of as a conversion factor between temperature and energy. As mentioned previously, with a slight abuse of notation, we usually denote  $\mu(T)$  as simply the Fermi level, and use  $E_F$  to denote the value of the chemical potential at a given temperature.

With the concept of the Fermi level established, Fig. 4.4 on page 95 can be modified to account for the fact that at absolute zero, states below the Fermi level will be filled, and those above the Fermi level will be empty, as depicted in Fig. 4.5. Of course, spin must be accounted for, such that two electrons can occupy each state.

## 4.5 PARTIALLY CONFINED ELECTRONS—FINITE POTENTIAL WELLS

In Section 4.3, when an electron confined to a finite region of space (the particle-in-a-box model) was considered, the electron had no possibility of escape. Although the potential energy profile  $V$  was not specifically indicated, the assumption that the electron must be inside the box ( $\psi = 0$  outside the box) is equivalent to the potential profile (in one dimension)

$$\begin{aligned} V &= 0, & 0 \leq x \leq L, \\ V &= \infty, & x < 0, x > L. \end{aligned} \quad (4.63)$$

The box can be thought of as an infinite quantum well, as shown in Fig. 4.6.

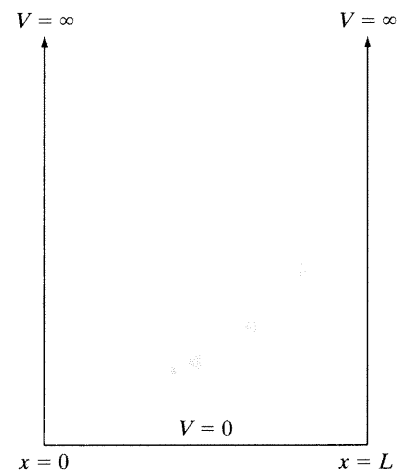


Figure 4.6 Potential profile for an infinite square well.

In the case of an infinite well, the particle has no chance of escaping the well. However, no jail is perfect, and we often want to allow for the possibility of the particle getting out of the well. Thus, we often need to model the walls as having finite height (finite potential), which is a more realistic model of what a particle such as an electron will “see” due to being confined in some way (say, by the potential of an atom).

#### 4.5.1 Finite Rectangular Well

In this section, the symmetric potential well having finite, rather than infinite, walls (potential barriers) will be considered,

$$\begin{aligned} V &= 0, & -L \leq x \leq L, \\ V &= V_0, & x < -L, x > L, \end{aligned} \quad (4.64)$$

as shown in Fig. 4.7.

Comparing this figure with Fig. 4.1 on page 86, which shows the potential energy between an electron and an ionized atom, we can see that the profile in Fig. 4.7. approximates the influence of an ionized atom on an electron.<sup>†</sup> As will be shown in Chapters 6 and 9, this will also model the confining potential of material interfaces.

We introduce an electron having total energy  $E < V_0$  into the potential energy well. The electron would be stuck in the well, classically. This is because outside the well, the electron's total energy would still be  $E$ , since there is no source of energy for the electron

<sup>†</sup>Of course, the electron has the same influence on the atom, although, since the mass of the atom is so much greater than that of the electron, we can assume the atom to be stationary.

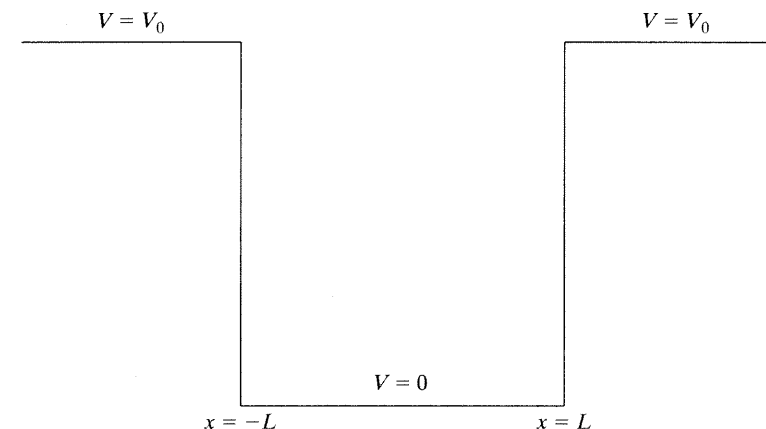


Figure 4.7 Finite square well potential.

(no incident radiation, nor collisions with other particles, etc.) Therefore, if the electron were outside the well, we would have

$$\begin{aligned} E &= E_{KE} + E_{PE} \\ &= E_{KE} + V_0 < V_0, \end{aligned} \quad (4.65)$$

where  $E_{KE}$  is kinetic energy and  $E_{PE}$  is potential energy. So

$$E_{KE} < 0,$$

which indicates that the electron's kinetic energy would be negative (i.e.,  $(1/2)mv^2 < 0$ )! According to classical physics, this cannot occur, and therefore, classically, the electron must be in the well.

However, quantum mechanically, there is some (perhaps small) probability that the particle will be found outside the well. To see this, we start with Schrödinger's equation

$$\left( -\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} + V(x) \right) \psi(x) = E\psi(x), \quad (4.66)$$

where  $V(x)$  corresponds to the profile given in (4.64). We solve this equation by considering separately the three regions (inside and outside of the well), solving Schrödinger's equation in each region, and applying boundary conditions at each interface between the regions to connect the three solutions together.

In the well region, which we'll call region II, we have

$$\left( \frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} + E \right) \psi_2(x) = 0 \quad (4.67)$$

since  $V = 0$  inside the well, leading to

$$\psi_2(x) = C \sin k_2 x + D \cos k_2 x, \quad (4.68)$$

with

$$k_2^2 = \frac{2m_e E}{\hbar^2}. \quad (4.69)$$

In the region  $x < -L$ , which we'll call region I, we have

$$\left( \frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} - (V_0 - E) \right) \psi_1(x) = 0, \quad (4.70)$$

leading to

$$\psi_1(x) = A e^{k_1 x} + B e^{-k_1 x}, \quad (4.71)$$

with

$$k_1^2 = \frac{2m_e (V_0 - E)}{\hbar^2}. \quad (4.72)$$

However, the wavefunction should be finite as  $x \rightarrow -\infty$  and, assuming that  $E < V_0$ , then

$$B = 0. \quad (4.73)$$

In the region  $x > L$ , region III, we have

$$\left( \frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} - (V_0 - E) \right) \psi_3(x) = 0 \quad (4.74)$$

leading to

$$\psi_3(x) = F e^{k_3 x} + G e^{-k_3 x}, \quad (4.75)$$

with

$$k_3^2 = \frac{2m_e (V_0 - E)}{\hbar^2} = k_1^2. \quad (4.76)$$

Finiteness of the wavefunction as  $x \rightarrow +\infty$  leads to

$$F = 0. \quad (4.77)$$

In summary, we have

$$\begin{aligned} \psi_1(x) &= A e^{k_1 x}, & x < -L, & \quad (4.78) \\ \psi_2(x) &= C \sin k_2 x + D \cos k_2 x, & -L \leq x \leq L, & \\ \psi_3(x) &= G e^{-k_3 x}, & x > L, & \end{aligned}$$

with

$$\begin{aligned} k_2^2 &= \frac{2m_e E}{\hbar^2}, & (4.79) \\ k_1^2 = k_3^2 &= \frac{2m_e (V_0 - E)}{\hbar^2}. \end{aligned}$$

It can be shown that symmetric potentials lead to either symmetric or antisymmetric solutions, and so either

$$\begin{aligned} C = 0, & \quad \text{symmetric solution, or} & (4.80) \\ D = 0, & \quad \text{antisymmetric solution.} \end{aligned}$$

Applying the four boundary conditions obtained from (3.143),

$$\begin{aligned} \psi_1(x = -L) &= \psi_2(x = -L), & (4.81) \\ \psi_2(x = L) &= \psi_3(x = L) \\ \psi_1'(x = -L) &= \psi_2'(x = -L), \\ \psi_2'(x = L) &= \psi_3'(x = L), \end{aligned}$$

to the symmetric case leads to the symmetric solution

$$\begin{aligned} \psi_1(x) &= D \cos(k_2 L) e^{k_1(x+L)}, & x < -L, & \quad (4.82) \\ \psi_2(x) &= D \cos k_2 x, & -L \leq x \leq L, & \\ \psi_3(x) &= D \cos(k_2 L) e^{-k_3(x-L)}, & x > L, & \end{aligned}$$

where  $k_1 = k_3$  and  $k_1, k_2$  must satisfy the *eigenvalue equation*

$$k_2 \tan(k_2 L) = k_1. \quad (4.83)$$

One can appreciate that, although the finite well is usually a much more realistic model of a quantum well, the infinite well is often used to get a rough approximation of energy states within quantum structures. That is, the assumption of an infinite well leads to a simple formula for the energy states  $E_n$  (e.g., (4.35)), whereas the finite well does not yield a nice

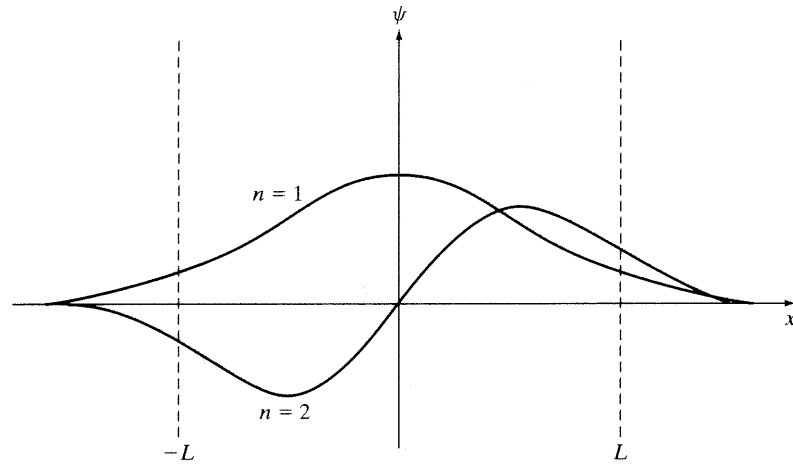


Figure 4.8 The two lowest states for the finite-height potential well.

formula, but only an eigenvalue equation that must be solved graphically or numerically for  $E$  (although discrete values  $E_n$  will still be obtained). Typical wavefunctions for the first two modes are shown in Fig. 4.8, from which it can be appreciated that the wavefunction is largest in the well region, but has nonzero “tails” extending outside the well. This is in contrast to the infinity-high wall case ( $V_0 = \infty$ ), where the electron is absolutely bound to the well, shown in Fig. 4.3 on page 95. Therefore, for the finite potential energy barrier, electrons are quasi-confined, or localized, to the well, although they can also be found outside the well.

Applying the four boundary conditions (4.81) to the antisymmetric form of (4.78) (i.e., setting  $D = 0$ ), we have

$$\begin{aligned}\psi_1(x) &= -C \sin(k_2 L) e^{k_1(x+L)}, & x < -L, \\ \psi_2(x) &= C \sin k_2 x, & -L \leq x \leq L, \\ \psi_3(x) &= C \sin(k_2 L) e^{-k_3(x-L)}, & x > L,\end{aligned}\quad (4.84)$$

where  $k_1 = k_3$  and  $k_1, k_2$  must satisfy the eigenvalue equation

$$-k_2 \cot(k_2 L) = k_1, \quad (4.85)$$

which can be solved graphically or numerically. As in the case of the symmetric solution, in general, no simple formula for the energy states can be found.

**Graphical Solution of the Eigenvalue Equation.** Although it is usually desirable to solve (4.83) and (4.85) numerically, a simple graphical procedure can be applied that leads to considerable insight into the nature of the solutions (and, in fact, shows that discrete

solutions do exist). In the following discussion, we will consider the eigenvalue equation for symmetric solutions, (4.83), although the same procedure works for the eigenvalue equation governing antisymmetric wavefunctions. In general, symmetric and antisymmetric solutions alternate (i.e., the lowest state is symmetric, and the next higher state is antisymmetric, etc.), just as was found for the infinite well case previously discussed.

First, note that

$$k_1^2 + k_2^2 = \frac{2m_e(V_0 - E)}{\hbar^2} - \frac{2m_e E}{\hbar^2} = \frac{2m_e V_0}{\hbar^2}, \quad (4.86)$$

such that

$$(k_1 L)^2 + (k_2 L)^2 = \frac{2m_e V_0 L^2}{\hbar^2}, \quad (4.87)$$

which is the equation of a circle in the  $k_1 L$ - $k_2 L$  plane. We can also plot

$$k_1 L = k_2 L \tan(k_2 L) \quad (4.88)$$

in the  $k_1 L$ - $k_2 L$  plane, and, obviously, the intersections will be the desired (discrete) solutions for energy  $E_n$ . A representative plot is shown in Fig. 4.9.

Only intersections in the upper-half plane are valid, since  $k_1 < 0$  would cause the wavefunctions  $\psi_1$  and  $\psi_3$  to become infinitely large as  $|x| \rightarrow \infty$  (far away from the well). We will label the  $N$  intersections in the upper-half plane by the index  $n = 1, 3, 5, \dots, N$  ( $N = 1$  shown in Fig. 4.9, for two different  $V_0$  values).

Several features of the solutions are evident from Fig. 4.9. From (4.87), the radius of the circle is

$$\sqrt{\frac{2m_e V_0 L^2}{\hbar^2}}, \quad (4.89)$$

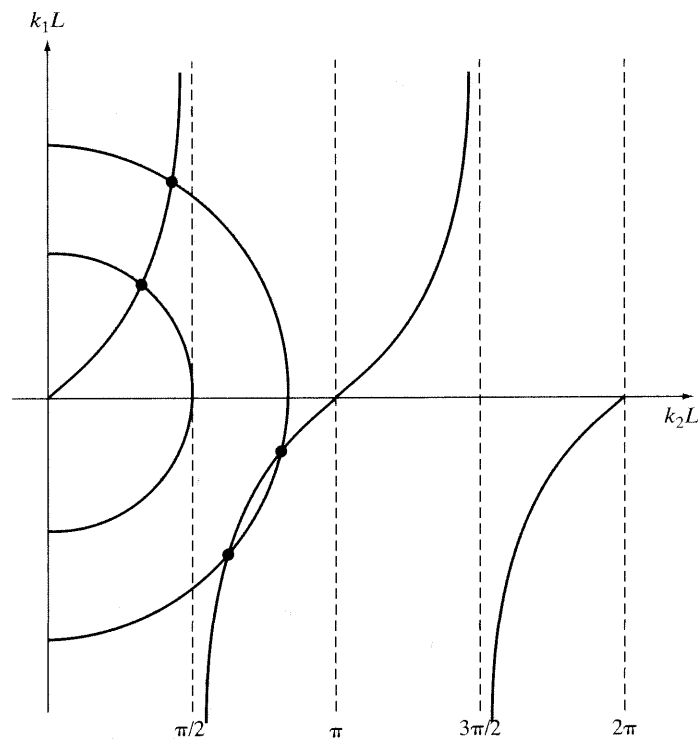
so that for very small  $V_0$  or  $L$  (small radius circle), there is only one solution. As  $V_0$  or  $L$  increase, the radius of the circle increases, and so more discrete states will exist, although for any finite  $V_0$  and  $L$  there will be a finite number ( $N$ ) of solutions. In the limit  $V_0 \rightarrow \infty$  or  $L \rightarrow \infty$ , a countable infinity of discrete solutions will exist,  $N \rightarrow \infty$ , in agreement with the infinite well discussed in Section 4.3.1.

In particular, we can determine at which point additional discrete states emerge. Increasing  $V_0$  (or  $L$ ) from low values, we see that when

$$\sqrt{\frac{2m_e V_0 L^2}{\hbar^2}} = m\pi, \quad (4.90)$$

and  $m = 1, 2, 3, \dots$ , new intersections occur. For instance, solving for  $V_0$  yields

$$V_0 = \frac{m}{2} \left( \frac{\hbar\pi}{L} \right)^2. \quad (4.91)$$



**Figure 4.9** Graphical technique for determining the solutions of the eigenvalue equation (4.88). The tan function repeats indefinitely, with period  $\pi$ . The two circles represent two different values of confining potential  $V_0$ . Only intersections in the upper-half plane indicate the desired solutions.

As  $V_0$  increases, the  $n$ th intersection moves along the upper parts of the tangent curve, approaching a value  $k_2L = n\pi/2$ , and the value  $k_1L \rightarrow \infty$ . Furthermore, in the limit  $V_0 \rightarrow \infty$  the infinite well case should be recovered. This can be seen by using (4.79) and setting  $k_2L = n\pi/2$ , such that

$$k_2L = \sqrt{\frac{2m_e E}{\hbar^2}} L = \frac{n\pi}{2} \rightarrow E = \frac{\hbar^2}{2m_e} \left(\frac{n\pi}{2L}\right)^2,$$

in agreement with (4.35). (Here the well has length  $2L$ , and in (4.35), the length of the well is  $L$ .) Examining the eigenfunctions (4.82), we see that in this limit

$$\lim_{V_0 \rightarrow \infty} \psi_1(x) = D \cos\left(\frac{n\pi}{2}\right) e^{\infty(x+L)} \rightarrow 0, \quad x < -L, \quad (4.92)$$

$$\lim_{V_0 \rightarrow \infty} \psi_2(x) = D \cos\left(\frac{n\pi}{2L}x\right), \quad -L \leq x \leq L,$$

$$\lim_{V_0 \rightarrow \infty} \psi_3(x) = D \cos\left(\frac{n\pi}{2}\right) e^{-\infty(x-L)} \rightarrow 0, \quad x > L,$$

which becomes simply the even modes of the infinite well, (4.32), as expected. The point is that as the potential increases, the wavefunction becomes bound more tightly to the well, reflecting the increasing probability that the particle will be found in the well, and, as  $V_0 \rightarrow \infty$ , we recover the infinite well result.

In arriving at the bound solutions, it was assumed that  $E < V_0$ , and discrete allowed energy values were obtained. The electron is most likely to be found in the well, although it can also be found outside the well, with decreasing probability as we move away from the well. Other solutions exist for  $E > V_0$ , corresponding to a continuum of allowed energy values. In this case, the presence of the well merely perturbs the electron's wavefunction. Far from the well, we expect the wavefunction to correspond to a plane wave, since in these locations the electron is essentially free. The details will not be included here, although the idea is that for  $E < V_0$ , the electron is (at least somewhat) bound to the well, although it can be found outside the well with decreasing probability, and as  $E \rightarrow V_0$ , the electron becomes less bound to the well. For  $E > V_0$ , the electron can occupy a continuum of states, the well merely serving to perturb the electron's wavefunction. The same scenario occurs in classical electromagnetic theory for the modes of a finite-thickness dielectric layer, which tends to confine, though not perfectly, electromagnetic energy within the layer. It should be emphasized once again that we have found only possible allowed states for an electron. Whether or not an electron is in a certain state depends on other factors, as will be discussed in Chapters 5 and 8.

#### 4.5.2 Parabolic Well—Harmonic Oscillator

Rather than the rectangular well considered in the previous section, here we briefly consider a parabolic potential profile, which has importance in modeling quantum heterostructures and split-gate devices. In this case, we assume the potential profile

$$V(x) = \frac{1}{2}Kx^2, \quad (4.93)$$

as shown in Fig. 4.10, which describes a classical harmonic oscillator. For example, a mass on a spring sees the force (4.93), where  $K$  is the spring constant and  $x$  is the displacement from equilibrium. This gives rise to harmonic motion  $x(t) = A \cos \omega_0 t$ , where the frequency of oscillation is  $\omega_0 = \sqrt{K/m}$ .

For the harmonic potential, Schrödinger's equation is

$$\left(-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} + \frac{1}{2}\omega_0^2 m_e x^2\right) \psi(x) = E\psi(x). \quad (4.94)$$

Although the details will be omitted here, the solution of (4.94) is

$$\psi(x) = C_n H_n \left[ \left(\frac{m_e \omega_0}{\hbar}\right)^{1/2} x \right] e^{-\frac{m_e \omega_0}{2\hbar} x^2}, \quad (4.95)$$

where  $C_n$  is a constant,

$$C_n = \left(\frac{1}{\sqrt{\pi} 2^n n!}\right)^{1/2} \left(\frac{m_e \omega_0}{\hbar}\right)^{1/4},$$

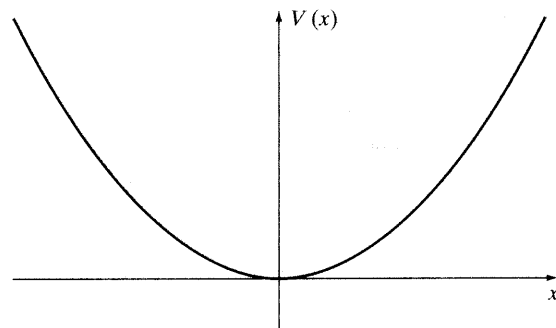


Figure 4.10 Harmonic oscillator (parabolic) potential.

and where  $H_n$  are Hermite polynomials, the first several of which are

$$H_0(x) = 1, \quad (4.96)$$

$$H_1(x) = 2x,$$

$$H_2(x) = 4x^2 - 2,$$

$$H_3(x) = 8x^3 - 12x, \dots \quad (4.97)$$

Despite the difference in the form of the solutions, the first several wavefunctions for the parabolic potential resemble those for the square well potential.

Energy levels are found to be

$$E_n = \left(n - \frac{1}{2}\right) \hbar\omega_0, \quad n = 1, 2, 3, \dots, \quad (4.98)$$

and are equally spaced according to the index  $n$ .

### 4.5.3 Triangular Well

As a final example, we consider the case of the triangular well, shown in Fig. 4.11. As discussed in Section 6.3.1, triangular wells are often used to model the junction between two materials.

The potential profile is

$$V(x) = \begin{cases} \infty, & x < 0, \\ Cx, & x > 0, \end{cases} \quad (4.99)$$

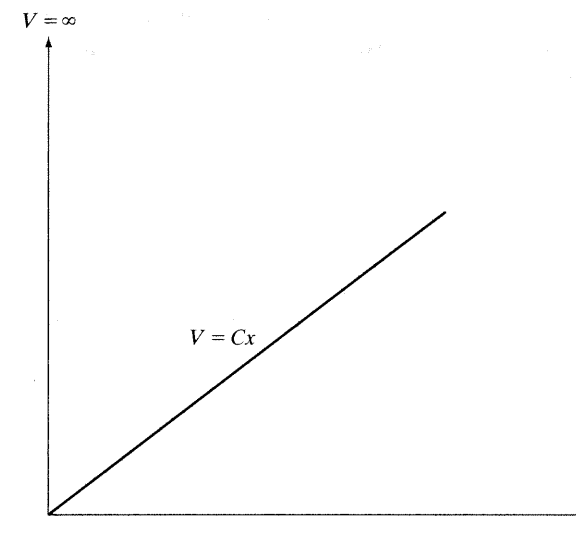


Figure 4.11 Triangular well potential.

where  $C$  is a constant. The solution of Schrödinger's equation with the triangular potential is fairly complicated, and the resulting wavefunctions are expressed in terms of *Airy functions*. The details will be omitted here, although the energy levels are given in a simple form,

$$E_n = \left(\frac{\hbar}{2m_e}\right)^{1/3} \left(\frac{3}{2}\pi C\right)^{2/3} \left(n - \frac{1}{4}\right)^{2/3}, \quad (4.100)$$

$n = 1, 2, 3, \dots$

It can be appreciated that for a rectangular well,  $E_n \propto n^2$ , for the parabolic well,  $E_n \propto n$ , and for the triangular well,  $E_n \propto n^{2/3}$ .

## 4.6 ELECTRONS CONFINED TO ATOMS—THE HYDROGEN ATOM AND THE PERIODIC TABLE

In Sections 4.3 and 4.5, we obtained discrete allowed energy states for an electron confined to a finite region of space, and we introduced the notion of quantum numbers. As a next step up in complexity, it is worthwhile to consider individual atoms, which confine electrons to atomic regions. Perhaps not surprisingly, it turns out that for atoms, electronic states are also quantized. By considering the simplest atom, hydrogen, we can introduce other quantum numbers that represent important physics not encountered in the simple quantum box

previously considered. The hydrogen atom is one of the few realistic quantum mechanics problems that can be solved exactly, since problems with more electrons can usually only be solved numerically.

#### 4.6.1 The Hydrogen Atom and Quantum Numbers

The hydrogen atom consists of one proton and one electron, interacting via the Coulomb force. Let the electron's position be denoted by  $(x_e, y_e, z_e)$  and the proton's position by  $(x_p, y_p, z_p)$ . Thus, we have a two-particle Schrödinger's equation,

$$\left( -\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) - \frac{\hbar^2}{2m_p} \left( \frac{\partial^2}{\partial x_p^2} + \frac{\partial^2}{\partial y_p^2} + \frac{\partial^2}{\partial z_p^2} \right) + V(\mathbf{r}_e, \mathbf{r}_p) \right) \psi(\mathbf{r}_e, \mathbf{r}_p) = E \psi(\mathbf{r}_e, \mathbf{r}_p), \quad (4.101)$$

where  $m_e$  and  $m_p$  are the electron and proton mass, respectively.

As is well known, the Coulomb potential energy depends only on the separation between the charges,  $\mathbf{r}_e - \mathbf{r}_p$ . It can be shown that in this case the problem can be separated into two, one-body problems,

$$\left( -\frac{\hbar^2}{2\mu_m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(\mathbf{r}) \right) \psi(\mathbf{r}) = E \psi(\mathbf{r}), \quad (4.102)$$

$$-\frac{\hbar^2}{2M} \left( \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) U(\mathbf{R}) = E' U(\mathbf{R}), \quad (4.103)$$

with

$$\mu_m = \frac{m_e m_p}{m_e + m_p}, \quad M = m_e + m_p, \quad (4.104)$$

$$MX = m_e x_e + m_p x_p, \quad (4.105)$$

$$MY = m_e y_e + m_p y_p, \quad (4.105)$$

$$MZ = m_e z_e + m_p z_p, \quad (4.106)$$

where  $\mu_m$  is known as the *reduced mass*,<sup>†</sup> and where the total energy is

$$E_{tot} = E + E'. \quad (4.108)$$

<sup>†</sup>The reduced mass can also be written as

$$\frac{1}{\mu_m} = \frac{1}{m_e} + \frac{1}{m_p}. \quad (4.107)$$

Equation (4.103) is Schrödinger's equation for a particle of mass  $M$  in free space, and so, by the results of Section 4.1.2, we obtain plane wave solutions

$$U(\mathbf{R}) = A_0 e^{i\mathbf{k}\cdot\mathbf{R}}, \quad (4.109)$$

with

$$E' = \frac{\hbar^2 k^2}{2M}, \quad k = |\mathbf{k}|. \quad (4.110)$$

Turning to (4.102), since  $m_e = 9.1095 \times 10^{-31}$  kg and  $m_p = 1.6726 \times 10^{-27}$  kg, we can make the approximation

$$\mu_m = \frac{m_e m_p}{m_e + m_p} \simeq m_e. \quad (4.111)$$

The potential  $V(r)$  is the well-known Coulomb potential,

$$V(r) = -\frac{q_e^2}{4\pi\epsilon_0 r}, \quad (4.112)$$

and the Schrödinger equation (4.102) can be cast into spherical coordinates and solved via separation of variables. The details will be omitted here, although the result can be expressed as

$$\psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r) Y_l^{m_l}(\theta, \phi), \quad (4.113)$$

where

$n = 1, 2, 3, \dots$ , is called the *principle quantum number*,

$l = 0, 1, 2, \dots, n-1$ , is called the *angular momentum quantum number*, and

$m_l = 0, \pm 1, \pm 2, \dots, \pm l$ , is called the *magnetic quantum number*.

The principle quantum number  $n$  plays the role of the quantum number  $n$  found in the electron box (quantum well) examples considered in Sections 4.3 and 4.5. The angular momentum quantum number is so named because it relates to the (quantized) orbital angular momentum of the electron and the magnetic quantum number relates to the projection of the angular momentum vector. Note that the indices are interconnected. For example, for  $n = 2$ , we have

$$n = 2, \quad l = 0, \quad m_l = 0, \quad (4.114)$$

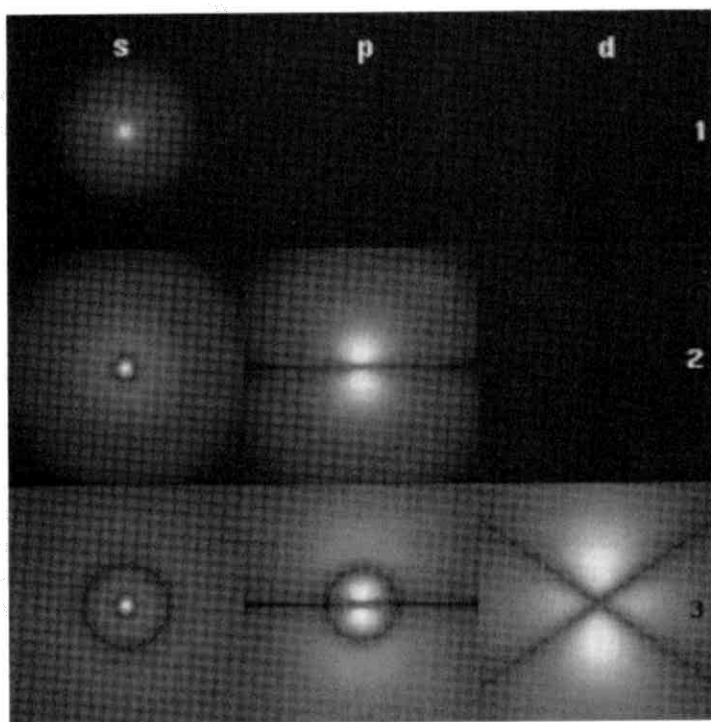
$$n = 2, \quad l = 1, \quad m_l = \pm 1.$$

Although we won't consider in detail the wavefunctions (4.113), Table 4.1 summarizes some of the functions that make up the wavefunction for low orders, and Fig. 4.12 shows a few of the low-order wavefunctions  $\psi_{n,l,0}$ . Recall that the probability of finding an electron is high where  $|\psi_{n,l,m_l}|^2$  is relatively large, and that it is less likely to find an electron where  $|\psi_{n,l,m_l}|$  is small.



**TABLE 4.1** COMPONENTS OF THE HYDROGEN WAVEFUNCTIONS FOR LOW-PRINCIPLE QUANTUM NUMBERS.

$n$	$l$	$m$	$R_{n,l}(r)$	$Y_l^{m_l}(\theta, \phi)$
1	0	0	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{4\pi}}$
2	0	0	$\frac{1}{(2a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{\sqrt{4\pi}}$
2	1	0	$\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\sqrt{\frac{3}{4\pi}} \cos \theta$
2	1	$\pm 1$	$\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi}$



**Figure 4.12** Several low-order hydrogen atom orbitals (plots of the probability density). The designations s,p,d refer to the quantum numbers  $l = 0,1,2$ , and the right-side designation is the principal quantum number  $n$ . In all cases  $m = 0$ . (Courtesy Wikipedia, The Free Encyclopedia.)

In Table 4.1, the constant  $a_0$  is called the *Bohr radius*, and is given by

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e q_e^2} = 0.53 \text{ \AA}. \quad (4.115)$$

This quantity, which comes about as a constant in the process of solving for the eigenfunctions  $\psi$ , does have important physical meaning. The Bohr radius is taken as the approximate “size” of the hydrogen atom, since for  $r > a_0$ , the wavefunction decreases rapidly, as can be seen from the function  $R_{1,0}$  in Table 4.1. Somewhat more precisely, since the Coulomb potential varies as  $r^{-1}$ , the expectation value of  $r^{-1}$  gives the reciprocal of the approximate “size” of the hydrogen atom,

$$\begin{aligned} \left\langle \frac{1}{r} \right\rangle &= \int \psi_{100}^*(r) \frac{1}{r} \psi_{100}(r) d^3r \\ &= \int_0^{2\pi} \int_0^\pi \int_0^\infty \frac{2}{a_0^{3/2}} e^{-r/a_0} \frac{1}{\sqrt{4\pi}} \left( \frac{1}{r} \right) \frac{2}{a_0^{3/2}} e^{-r/a_0} \frac{1}{\sqrt{4\pi}} r^2 \sin \theta dr d\theta d\phi \\ &= \left( \frac{2}{a_0^{3/2}} \right)^2 \int_0^\infty e^{-2r/a_0} r dr \\ &= \frac{1}{a_0}. \end{aligned} \quad (4.116)$$

It can be shown that energy is only dependent on the principle quantum number  $n$ , and its value is

$$E_n = -\frac{\mu_m q_e^4}{8\epsilon_0^2 h^2 n^2}. \quad (4.117)$$

Therefore, for  $n = 1$  (called the *ground state*) the corresponding energy is, replacing  $\mu_m$  by  $m_e$ ,

$$E_1 = -\frac{m_e q_e^4}{8\epsilon_0^2 h^2} = -2.18 \times 10^{-18} \text{ J} = -13.6 \text{ eV}, \quad (4.118)$$

and, thus,<sup>†</sup>

$$E_n = -13.6 \frac{1}{n^2} \text{ eV}. \quad (4.119)$$

In general, and not only for the hydrogen atom, the principle quantum number  $n$  is called the *shell* number, and the states

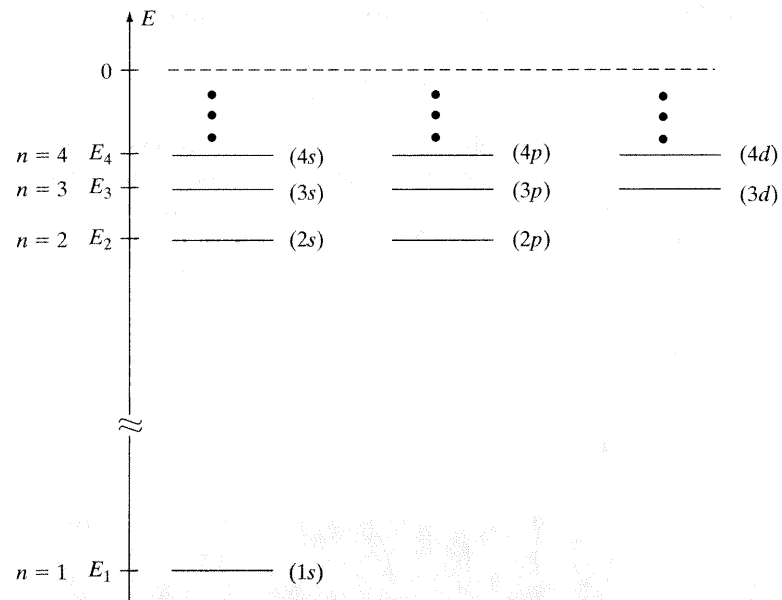
$$l = 0, 1, 2, 3, 4, 5, 6, 7, \dots \quad (4.120)$$

are called the *s, p, d, f, g, h, i, k, ...* states, i.e.,

$$l = 0, 1, 2, 3, 4, 5, 6, 7 \quad (4.121)$$

$$= s, p, d, f, g, h, i, k.$$

<sup>†</sup>  $R_Y = m_e q_e^4 / (8\epsilon_0^2 h^2) = -13.6 \text{ eV}$  is known as the *Rydberg energy*.



**Figure 4.13** Schematic depiction of the energy levels of hydrogen. For  $E > 0$ , discrete energy levels cease to exist, although a continuum of states is present.

Thus,  $n = 3, l = 1$  is the  $3p$  state (third shell, second state ( $l = 1$ )). Energy levels for hydrogen are schematically depicted in Fig. 4.13.

The quantum numbers  $n, l$ , and  $m_l$  need to be augmented by a spin number,  $s = \pm 1/2$ . Together, the four quantum numbers  $(n, l, m_l, s)$  characterize the quantum state of the hydrogen atom.

Note that as an electron moves about a nucleus, it doesn't maintain constant radius or follow a set path. Unless some energy is supplied or extracted from the atom, the electron maintains constant total energy. Since its potential energy varies with distance away from the nucleus, an electron will change its kinetic energy (i.e., either speeding up or slowing down) to compensate for changes in radius as it moves about the nucleus.

The relatively simple two-particle hydrogen model is very important for modeling more complicated multiparticle configurations. In the next section, we will apply the hydrogen model to other atoms, leading to an approximate construction of the electronic configuration of many elements. In Chapter 5, the two-particle hydrogen model will be used to analyze semiconductor doping, and the creation of bound electron-hole pairs known as excitons.

#### 4.6.2 Beyond Hydrogen—Multiple Electron Atoms and the Periodic Table

The hydrogen atom consists of one electron and one proton, and, for this system, Schrödinger's equation can be solved exactly. However, even for the next simplest atom—helium—which consists of two protons and two electrons, Schrödinger's equation cannot be solved in closed form. However, the usual procedure to gain some understanding of atoms beyond

hydrogen is to invoke the Pauli exclusion principle. Recall that this principle dictates that two or more identical fermions (electrons are fermions) cannot occupy the same allowed state. We do the following for atoms consisting of multiple electrons:

1. Using the hydrogen model, start with the lowest energy level and count the number of states to be filled, dictated by the number of electrons associated with the atom in question.
2. Fill the states up one by one with electrons.
3. Once an energy level is full, proceed to the next higher energy level, and so on.

For example, for the first shell,  $n = 1$ , we have  $l = m = 0$ . There are two possible states,  $(n, l, m_l, s) = (1, 0, 0, \pm 1/2)$ , i.e.,

$$\text{state 1 : } n = 1, \quad l = 0, \quad m_l = 0, \quad s = \frac{1}{2},$$

$$\text{state 2 : } n = 1, \quad l = 0, \quad m_l = 0, \quad s = -\frac{1}{2}.$$

Therefore, hydrogen has one “ $1s$ ” electron, and helium has two “ $1s$ ” electrons, denoted as  $1s^2$ . Since helium has two electrons that fill the two  $1s$  states and “close” the  $n = 1$  shell, helium is chemically inert. In fact, the number of outer shell electrons is the single most important quantity in characterizing how an element will react with its environment. Elements with partially filled outer shells will tend to react with other elements, whereas elements with full (closed) outer shells will tend to be nonreactive. The number of outer shell electrons is so important that elements in the periodic table are grouped together (in columns) by the number of outer shell electrons.

Continuing in this fashion, we fill up the shells  $n = 2, 3, 4, \dots$  with available electrons. Note that, for example, the  $n = 2$  shell has eight states,

$$\text{state 1 : } n = 2, \quad l = 0, \quad m_l = 0, \quad s = \frac{1}{2},$$

$$\text{state 2 : } n = 2, \quad l = 0, \quad m_l = 0, \quad s = -\frac{1}{2},$$

$$\text{state 3 : } n = 2, \quad l = 1, \quad m_l = 0, \quad s = \frac{1}{2},$$

$$\text{state 4 : } n = 2, \quad l = 1, \quad m_l = 0, \quad s = -\frac{1}{2},$$

$$\text{state 5 : } n = 2, \quad l = 1, \quad m_l = 1, \quad s = \frac{1}{2},$$

$$\text{state 6 : } n = 2, \quad l = 1, \quad m_l = 1, \quad s = -\frac{1}{2},$$

$$\text{state 7 : } n = 2, \quad l = 1, \quad m_l = -1, \quad s = \frac{1}{2},$$

$$\text{state 8 : } n = 2, \quad l = 1, \quad m_l = -1, \quad s = -\frac{1}{2}.$$

so that, together, the  $n = 1$  and  $n = 2$  shells can accommodate 10 electrons. For example, neon has 10 electrons, thus filling the  $n = 1$  and  $n = 2$  shells, but not going into the  $n = 3$  shell. Neon's electronic configuration is denoted by

$$1s^2 2s^2 2p^6,$$

since it has 2 "1s" electrons, 2 "2s" electrons, and 6 "2p" electrons. The next element, sodium, with 11 electrons, breaks into the 3s shell; its configuration is  $1s^2 2s^2 2p^6 3s^1$ .

Thus, it would seem that to determine the electronic configuration of any atom, one only has to know how many electrons it possesses. This procedure works surprisingly well in many cases; however, we need to remember that it is based on the simple hydrogen result. Most atoms are considerably more complicated than hydrogen, obviously. In particular, the hydrogen model applied to multi-electron atoms implicitly assumes that there is no interaction between electrons, which is not really true. Also, for elements other than hydrogen, it turns out that energy is not constant within a shell. Therefore, although the preceding procedure can be used as a starting point, it does not provide an exact description of the electronic configuration of other atoms. In particular, starting with potassium, some modifications to the described procedure must be made. In Table 4.2, the electronic configuration of the first 32 elements of the periodic table is provided, and, for convenience, the periodic table of the elements is shown in Fig. 4.14.

At this point, one comment should be made concerning spin and the filling of states. It turns out that spin interactions favor filling same-spin states first, before beginning to fill the other spin state. This is called *Hund's rule*. For example, carbon has the configuration  $1s^2 2s^2 2p^2$ . The 2p shell is partially filled, having two electrons, but in the ground state, both have the same spin. The same can be said of nitrogen, with three same-spin electrons. In the next element, oxygen, the addition of a fourth (out of six) 2p electron finally results in a spin down electron. This is shown in Table 4.3. The filling of spin states has particular importance in considering the magnetic properties of materials, since filled shells will have no net magnetic moment.

#### 4.7 QUANTUM DOTS, WIRES, AND WELLS

So far in this chapter, we have studied electrons confined to finite regions of space via infinite potential energy barriers (Section 4.3), electrons localized to a region of space by finite potential energy barriers (Section 4.5), and electrons confined to (or associated with) atoms (Section 4.6). In all cases, we have found that the energy of the electron will be discrete, given by  $E_n$ . Furthermore, if we confine a particle to a region of space on the order of, or smaller than, the particle's de Broglie wavelength, the discreteness of possible energy states that the particle can occupy will be evident. Chapters previous to this one were intended to provide the necessary machinery to study electrons in various situations, and, in previous sections of this chapter, we examined the effects of confining electrons to finite regions of space. At this point, we can begin to consider the important topics of quantum dots, quantum wires, and quantum wells. Since these structures are often made from semiconductors, we will also revisit this topic in Chapter 9, after, among other things, considering some basic semiconductor physics in the next chapter.

**TABLE 4.2** ELECTRON CONFIGURATION OF THE FIRST 32 ELEMENTS (OBTAINED BY SELF-CONSISTENT METHODS). Z IS THE ATOMIC NUMBER, I.E., THE NUMBER OF ELECTRONS.

Z	Element	1s	2s	2p	3s	3p	3d	4s	4p	4d
1	H, hydrogen	1								
2	He, helium	2								
3	Li, lithium	2	1							
4	Be, beryllium	2	2							
5	B, boron	2	2	1						
6	C, carbon	2	2	2						
7	N, nitrogen	2	2	3						
8	O, oxygen	2	2	4						
9	F, fluorine	2	2	5						
10	Ne, neon	2	2	6						
11	Na, sodium	2	2	6	1					
12	Mg, magnesium	2	2	6	2					
13	Al, aluminium	2	2	6	2	1				
14	Si, silicon	2	2	6	2	2				
15	P, phosphorus	2	2	6	2	3				
16	S, sulfur	2	2	6	2	4				
17	Cl, chlorine	2	2	6	2	5				
18	Ar, argon	2	2	6	2	6				
19	K, potassium	2	2	6	2	6		1		
20	Ca, calcium	2	2	6	2	6		2		
21	Sc, scandium	2	2	6	2	6	1	2		
22	Ti, titanium	2	2	6	2	6	2	2		
23	V, vanadium	2	2	6	2	6	3	2		
24	Cr, chromium	2	2	6	2	6	5	1		
25	Mn, manganese	2	2	6	2	6	5	2		
26	Fe, iron	2	2	6	2	6	6	2		
27	Co, cobalt	2	2	6	2	6	7	2		
28	Ni, nickel	2	2	6	2	6	8	2		
29	Cu, copper	2	2	6	2	6	10	1		
30	Zn, zinc	2	2	6	2	6	10	2		
31	Ga, gallium	2	2	6	2	6	10	2	1	
32	Ge, germanium	2	2	6	2	6	10	2	2	

We first need to specify what we mean by a quantum dot, a quantum wire, and a quantum well. Assume that electrons reside in a three-dimensional region of space, as shown in Fig. 4.15. From previous sections, we know that if  $\lambda_e \ll L_x, L_y, L_z$ , then the electrons will be free in all directions (i.e., they will act like free particles), and we have an effectively three-dimensional system. That is, the system in all directions is large compared with the size scale of the electrons. Even though the space is finite, and therefore the possible energy levels of the electron are discrete, because the space is relatively large, the discrete energy levels form, essentially, a continuum. For example, if we

## Periodic Table of the Elements

Figure 4.14 Periodic table of the elements. (Courtesy Carol and Mike Werner/Phototake NYC.)

TABLE 4.3 SPIN CONFIGURATION OF THE FIRST 10 ELEMENTS ACCORDING TO HUND'S RULE. NOTE THE DIFFERENCE BETWEEN CARBON, NITROGEN, AND OXYGEN.

Z	Element	1s	2s	2p
1	H, hydrogen	↑		
2	He, helium	↑↓		
3	Li, lithium	↑↓	↑	
4	Be, beryllium	↑↓	↑↓	
5	B, boron	↑↓	↑↓	↑
6	C, carbon	↑↓	↑↓	↑↑
7	N, nitrogen	↑↓	↑↓	↑↑↑
8	O, oxygen	↑↓	↑↓	↑↓↑↑
9	F, fluorine	↑↓	↑↓	↑↓↑↓↑
10	Ne, neon	↑↓	↑↓	↑↓↑↓↑↓

assume that the boundaries of the space have hard walls, then the energy levels are given by (4.53),

$$E = \frac{\hbar^2 \pi^2}{2m_e} \left[ \left( \frac{n_x}{L_x} \right)^2 + \left( \frac{n_y}{L_y} \right)^2 + \left( \frac{n_z}{L_z} \right)^2 \right]. \quad (4.122)$$

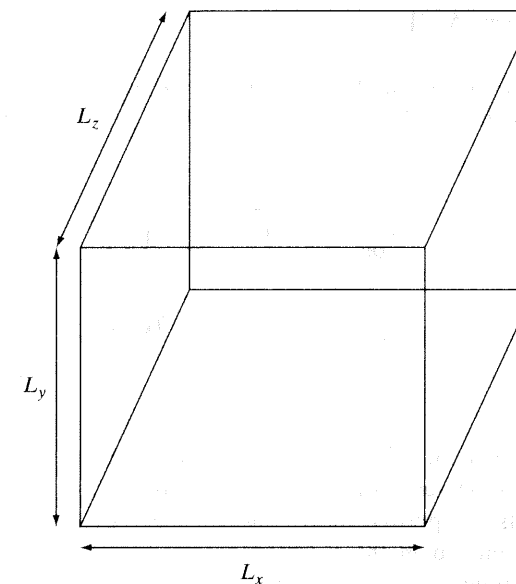


Figure 4.15 An effectively three-dimensional region of space;  $L_{x,y,z} \gg \lambda_e$ .

Since  $L_{xyz}$  are very large, and  $n_{xyz}$  are integers, the ratios  $n_x/L_x$ ,  $n_y/L_y$ , and  $n_z/L_z$  vary almost continuously from very small values to very large values. Making the replacements

$$\frac{\pi n_x}{L_x} \rightarrow k_x, \quad \frac{\pi n_y}{L_y} \rightarrow k_y, \quad \frac{\pi n_z}{L_z} \rightarrow k_z, \quad (4.123)$$

where  $k_x$ ,  $k_y$ , and  $k_z$  are continuous variables, we have

$$E = \frac{\hbar^2}{2m_e} (k_x^2 + k_y^2 + k_z^2) \quad (4.124)$$

$$= E_{\text{cont}}(k_x, k_y, k_z). \quad (4.125)$$

If  $L_{xyz}$  are large yet finite,  $E_{\text{cont}}(k_x, k_y, k_z)$  is an approximately continuous energy profile, and, as  $L_{xyz} \rightarrow \infty$ ,  $E_{\text{cont}}(k_x, k_y, k_z)$  becomes the purely continuous energy for an electron in an infinite space, as derived in Section 4.1.2. (See, e.g., (4.19).)

In the preceding discussion, we used the de Broglie wavelength as the important "size" of the electron; that is, a region of space having length  $L$  is "large" if  $L \gg \lambda_e$ , and "small" if  $L \leq \lambda_e$ . While this is true, the de Broglie wavelength depends on the energy of the electron and, as discussed further in later chapters, the most important energy is the Fermi energy, introduced in Section 4.4. The de Broglie wavelength at the Fermi energy is called the *Fermi wavelength*, and is denoted by the symbol  $\lambda_F$ . Therefore, for a space to be sufficiently "large" so that the energy levels of the electron form an approximately continuous set, we usually require  $L_x, L_y, L_z \gg \lambda_F$ .

## 4.7.1 Quantum Wells

Now, assume that we make the space narrow in one direction, as depicted in Fig. 4.16.

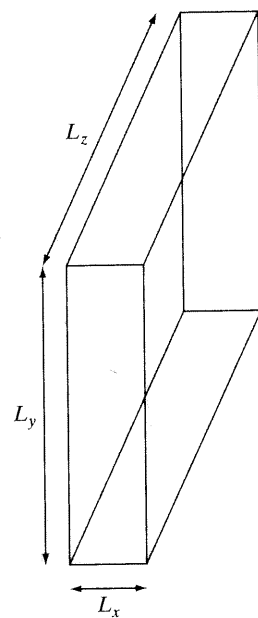
By narrow in one direction, we mean,  $L_x \leq \lambda_F \ll L_y, L_z$ . In this case, we can write (4.122) as

$$E = \frac{\hbar^2 \pi^2}{2m_e} \left( \frac{n_x}{L_x} \right)^2 + \frac{\hbar^2 \pi^2}{2m_e} \left( \left( \frac{n_y}{L_y} \right)^2 + \left( \frac{n_z}{L_z} \right)^2 \right) \quad (4.126)$$

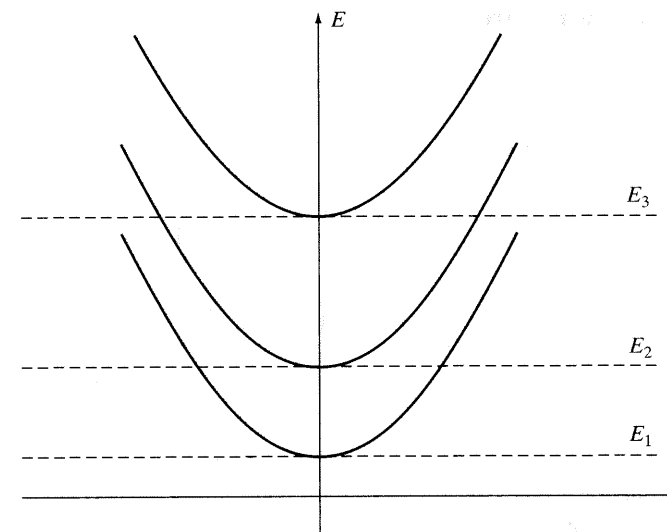
$$= \frac{\hbar^2 \pi^2}{2m_e} \left( \frac{n_x}{L_x} \right)^2 + \frac{\hbar^2}{2m_e} (k_y^2 + k_z^2) \quad (4.127)$$

$$= E_{n_x} + E_{\text{cont}}(k_y, k_z), \quad (4.128)$$

where, since  $L_x$  is relatively small,  $E_{n_x}$  represents discrete, one-dimensional energies. Since  $L_y$  and  $L_z$  are relatively large, two of the substitutions in (4.123) lead to  $E_{\text{cont}}(k_y, k_z)$ , which represents an approximately continuous energy profile. In this case, electron movement will be confined in the  $x$ -direction (i.e., electrons will “feel” the boundary in the  $x$ -direction), exhibiting energy quantization in that direction, and will be free in the two other directions. This makes for an effectively two-dimensional system, called a *two-dimensional electron gas*, also called a *quantum well*. The discrete energy levels given by  $n_x$  form what are called *subbands*. The idea is that an electron is in a certain discrete energy level  $n_x$ ; that is, it is in a certain subband, but it is otherwise free in the



**Figure 4.16** A quantum well, an effectively two-dimensional region of space, where  $L_x \leq \lambda_F$ ,  $L_{y,z} \gg \lambda_F$ .



**Figure 4.17** Energy versus continuous wavevector  $k = \sqrt{k_x^2 + k_y^2}$ , showing three subbands.

$y$ - $z$  plane. A depiction of the energy-wavenumber relationship is shown in Fig. 4.17. As previously mentioned, note that we have only found the allowed energy states; it remains to be seen how electrons “fill up” the various subbands, which will also be considered in Chapters 8 and 9.

To obtain the wavefunction we can consider the electron to be totally free in the  $y$ - $z$  plane, but constrained in the  $x$ -direction by hard walls at  $x = 0$ , and  $x = L_x$ . Schrödinger’s equation with  $V = 0$  is

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi(\mathbf{r}) = E \psi(\mathbf{r}), \quad (4.129)$$

and, given the longitudinal invariance of the problem and our experience with free electrons, we write the wavefunction in the product form

$$\psi(x, y, z) = \psi_x(x) e^{ik_y y} e^{ik_z z}, \quad (4.130)$$

where the plane-wave factor contains the continuous wavevectors  $k_y$  and  $k_z$ . The boundary conditions

$$\psi_x(0) = \psi_x(L_x) = 0$$

lead to

$$\psi(x, y, z) = \left( \frac{2}{L_x} \right)^{1/2} \sin \frac{n_x \pi}{L_x} x e^{ik_y y} e^{ik_z z}, \quad (4.131)$$

where  $n_x = 1, 2, 3, \dots$  and where the allowed energy is given by (4.127).

### 4.7.2 Quantum Wires

Continuing in the same fashion, now assume that we make the original space depicted in Fig. 4.15 narrow in two directions,  $L_x, L_y \leq \lambda_F \ll L_z$ , as depicted in Fig. 4.18. In this case, we can reorganize (4.122) as

$$E = \frac{\hbar^2 \pi^2}{2m_e} \left( \left( \frac{n_x}{L_x} \right)^2 + \left( \frac{n_y}{L_y} \right)^2 \right) + \frac{\hbar^2 \pi^2}{2m_e} \left( \frac{n_z}{L_z} \right)^2 \quad (4.132)$$

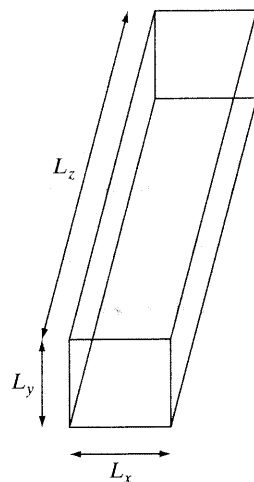
$$= \frac{\hbar^2 \pi^2}{2m_e} \left( \left( \frac{n_x}{L_x} \right)^2 + \left( \frac{n_y}{L_y} \right)^2 \right) + \frac{\hbar^2}{2m_e} k_z^2 \quad (4.133)$$

$$= E_{n_x, n_y} + E_{\text{cont}}(k_z), \quad (4.134)$$

where, since  $L_x$  and  $L_y$  are both relatively small,  $E_{n_x, n_y}$  represents discrete, two-dimensional subband energies, and, since  $L_z$  is relatively large,  $E_{\text{cont}}(k_z)$  represents an approximately continuous energy profile. In this case, electron movement will be confined in the  $x$ - $y$  plane (i.e., electrons will “feel” the boundaries in the  $x$ - and  $y$ -directions), exhibiting energy quantization in that plane, and will be free in the  $z$ -direction. This makes for an effectively one-dimensional system called a *quantum wire*.<sup>†</sup>

Regarding the electron as being totally free in one direction, but constrained by hard walls at  $x = 0, L_x$  and  $y = 0, L_y$ , Schrödinger's equation with  $V = 0$ ,

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi(\mathbf{r}) = E \psi(\mathbf{r}), \quad (4.135)$$



**Figure 4.18** A quantum wire, an effectively one-dimensional space;  $L_{x,y} \leq \lambda_F$ ,  $L_z \gg \lambda_F$ .

<sup>†</sup>Circular cross-section wires are also of interest, but won't be discussed here to avoid mathematical complications associated with the circular geometry.

will have solutions in the product form

$$\psi(x, y, z) = \psi_x(x) \psi_y(y) e^{ik_z z}. \quad (4.136)$$

Imposing the boundary conditions

$$\psi_x(0) = \psi_x(L_x) = 0, \quad (4.137)$$

$$\psi_y(0) = \psi_y(L_y) = 0,$$

we obtain

$$\psi(x, y, z) = \left( \frac{4}{L_x L_y} \right)^{1/2} \sin \frac{n_x \pi}{L_x} x \sin \frac{n_y \pi}{L_y} y e^{ik_z z}, \quad (4.138)$$

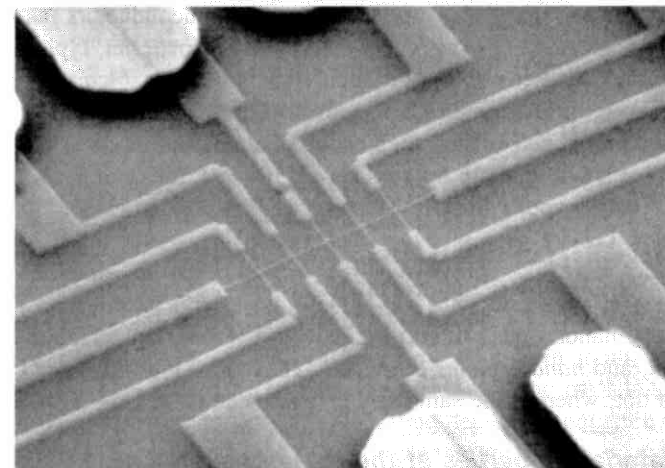
where  $n_{x,y} = 1, 2, 3, \dots$ , and where energy is given by (4.133). An early quantum wire fabricated by electron beam lithography and etching is shown in Fig. 4.19.

### 4.7.3 Quantum Dots

Now assume that we make the space small in all three directions,  $L_x, L_y, L_z \leq \lambda_F$ , as depicted in Fig. 4.20. In this case, we can write (4.122) as

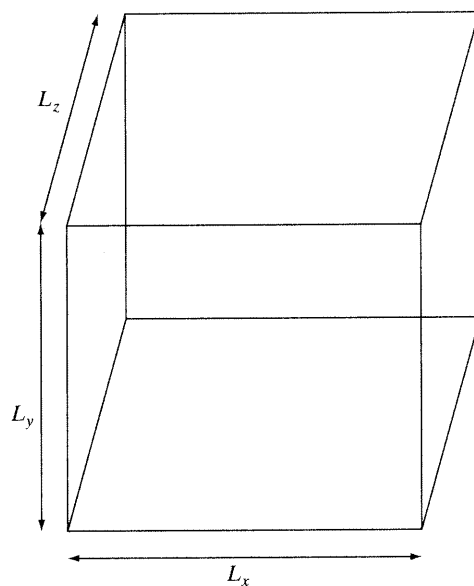
$$E = \frac{\hbar^2 \pi^2}{2m_e} \left( \left( \frac{n_x}{L_x} \right)^2 + \left( \frac{n_y}{L_y} \right)^2 + \left( \frac{n_z}{L_z} \right)^2 \right) \quad (4.139)$$

$$= E_{n_x, n_y, n_z} \quad (4.140)$$



**Figure 4.19** 75-nm-wide etched quantum wire, (Reprinted with permission from Roukes, M. L. et al., “Quenching of the Hall Effect in a One-Dimensional Wire,” *Phys. Rev. Lett.* 59 (1987): 3011. Copyright 1987, American Physical Society.)





**Figure 4.20** A quantum dot, an effectively zero-dimensional space;  $L_{x,y,z} \leq \lambda_F$ .

where, since  $L_x$ ,  $L_y$ , and  $L_z$  are all relatively small,  $E_{n_x, n_y, n_z}$  represents discrete energies. Electron movement will be confined in all three directions (i.e., electrons will “feel” the boundaries in the  $x$ -,  $y$ -, and  $z$ -directions), exhibiting energy quantization in three dimensions, and will not be free in any direction. This makes for an effectively zero-dimensional system called a *quantum dot*.

Since the typical electron of interest has a Fermi wavelength on the order of a nanometer in metals, and many tens of nanometers in semiconductors (as further considered later in the text), quantum dots are nanoscale pieces of material, typically ranging in size from several nm to hundreds of nm. As such, quantum dots can contain from several hundred to several hundred thousand atoms. For example, as a rough estimate, assuming that the size of an atom is 0.1 nm ( $= 1 \text{ \AA}$ ), then about 10 atoms can fit along a 1 nm line. A cube having sides of 1 nm will contain approximately  $10^3 = 1,000$  atoms. A cube having sides of 10 nm will contain approximately  $10^6$  atoms. Thus, quantum dots are typically much larger than atoms, but are generally too small to act like a bulk solid. An electron in a quantum dot will act more like an electron in a molecule than an electron in a bulk solid, and for this reason, quantum dots are sometimes called *artificial molecules*. In general, one would tend to call nanoscopic material regions *quantum dots* if quantum confinement effects are important, and *nanoparticles* otherwise. Thus, a 10-nm-radius sphere of GaAs would be a quantum dot, whereas the same size sphere made from copper would be a nanoparticle.

**Material Properties at the Nanoscale.** Of particular importance for quantum dots is that material properties change dramatically at the nanoscale. One reason for this is the previously mentioned confinement effect of electrons in regions of space that are not large compared to the de Broglie or Fermi wavelength. Another reason for nanoscale

materials to behave differently is that a large percentage of their atoms are located on the surface of the material, and the relatively large surface-to-volume ratio leads to material behavior different than the bulk specimen. As an example, consider again a  $1 \text{ nm}^3$  cube, consisting of 1,000 atoms. Counting the six surfaces of the cube, we find that roughly  $6 \times 10^2 = 600$  atoms, or more than half of the atoms, are on the surface of the cube, where they can easily interact with the outside environment (via unsatisfied chemical bonds, etc.) In general, the smaller the dot, the higher the percentage of atoms at the surface. Thus, one would then expect that quantum dots have higher chemical reactivity than bulk materials, which is generally found to be the case.

#### 4.8 MAIN POINTS

This chapter presented the main ideas of what happens to particles, in particular, electrons, when they are confined to different-sized regions of space. After studying this chapter, you should know

- the difference between free and bound particles, and, in particular, the important idea that the possible energy states of a particle confined to a finite spatial region are quantized;
- the free electron gas model of conductors, and the assumptions behind this model;
- the role that the de Broglie and Fermi wavelength plays in determining what is a “small” region of space;
- the role of the Pauli exclusion principle in filling quantum states;
- the idea of the Fermi level and chemical potential, and how to compute these quantities for low electron density systems;
- the difference between an infinite (hard-wall) and finite confining potential, and, in the latter case, how to determine the allowed particle states;
- the general concept of where the periodic table comes from, and why elements are grouped as they are;
- the concepts of quantum wells, quantum wires, and quantum dots.

#### 4.9 PROBLEMS

1. Write down the wavefunction  $\psi(z, t)$  for a 3 eV electron in an infinite space, traveling along the positive  $z$  axis. Assume that the electron has only kinetic energy. Plug your answer into Schrödinger’s time-dependent equation to verify that it is a solution.
2. Determine the wavefunction  $\psi(z, t)$  for a 3 eV electron in an infinite space, traveling along the  $z$  axis at a velocity of  $10^5 \text{ m/s}$ . Determine the particle’s potential energy, and plug your answer into Schrödinger’s time-dependent equation to verify that it is a solution.
3. For classical light, the expression

$$c = \lambda f \quad (4.141)$$



holds, where  $c$  is the speed of light,  $f$  is the frequency, and  $\lambda$  is the wavelength. This expression also holds for quantized light (i.e., photons), where the classical wavelength  $\lambda$  is the same as the de Broglie wavelength. Does the expression

$$v = \lambda f, \quad (4.142)$$

where  $v$  is velocity, hold for electrons if  $\lambda$  is the de Broglie wavelength and  $f = \omega/2\pi$  is the frequency, such that  $E = \hbar\omega$ ? Assume that the electrons have only kinetic energy.

4. Consider an electron in a room of size  $10 \times 10 \times 10 \text{ m}^3$ . Assume that within the room, potential energy is zero, and that the walls and ceilings of the room are perfect (so that the electron cannot escape from the room). If the electron's energy is approximately 5 eV, what is the state index  $n^2 = n_x^2 + n_y^2 + n_z^2$ ? What is the approximate energy difference  $E_{2,1,1} - E_{1,1,1}$ ?
5. Repeat problem 4.4 for an electron confined to a nanoscale space,  $10^{-9} \times 10^{-9} \times 10^{-9} \text{ m}^3$ .
6. Consider an electron having kinetic energy 2.5 eV. What size space does the electron need to be confined to in order to observe clear energy discretization? Repeat for a proton having the same kinetic energy.
7. Consider a 44 kg object (perhaps a desk) in a typical room with dimensions  $10 \times 10 \times 10 \text{ m}^3$ . Assume that within the room, potential energy is zero, and that the walls of the room are perfect (so that the room can be modeled as an infinitely deep potential well).
  - (a) If the desk is in the ground state, what is the velocity of the desk?
  - (b) If the desk is moving at 0.01 m/s, what is the desk's quantum state (i.e., what is the state index  $n$ )?
8. Consider the one-dimensional, infinite square well existing from  $0 \leq x \leq L$ . The wavefunction for a particle confined to the well is (4.34),

$$\psi(x, t) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right) e^{-iE_n t/\hbar}. \quad (4.143)$$

If the particle is in the ground state, determine the probability, as a function of time, that the particle will be in the right half of the well (i.e., from  $L/2 \leq x \leq L$ ).

9. Consider an electron in the first excited state ( $n = 2$ ) of an infinitely high square well of length 2.3 nm. Assuming zero potential energy in the well, determine the electron's velocity.
10. Consider an electron confined to an infinite potential well having length 2 nm. What wavelength photons will be emitted from transitions between the lowest three energy levels?
11. Consider the one-dimensional, infinite square well existing from  $0 \leq x \leq L$ . Recall that the energy eigenfunctions for a particle confined to the well are (4.31),

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right), \quad (4.144)$$

$n = 1, 2, 3, \dots$ . Now, assume that the particle state is

$$\Psi(x) = A(x(L-x)), \quad (4.145)$$

such that  $\Psi(0) = \Psi(L) = 0$ .

- (a) Determine  $A$  such that the particle's state function is suitably normalized.
- (b) Expand  $\Psi(x)$  in the energy eigenfunctions, i.e., use orthogonality to find  $c_n$  such that

$$\Psi(x) = A(x(L-x)) = \sum_{n=1}^{\infty} c_n \psi_n(x). \quad (4.146)$$

- (c) Determine the probability of measuring energy  $E_n$ , and use this result to determine the probability of measuring energy  $E_1$  through  $E_6$ .
12. Repeat problem 4.11 if the particle state is

$$\Psi(x) = A\sqrt{x(L-x)}. \quad (4.147)$$

13. Consider the one-dimensional, infinite square well existing from  $0 \leq x \leq L$ . If nine electrons are in the well, what is the ground state energy of the system?
14. Consider a one-dimensional quantum well of length  $L = 10 \text{ nm}$  containing 11 non-interacting ground state electrons. Determine the chemical potential of the system.
15. Apply boundary conditions (4.81) to the symmetric form of (4.78) (i.e., set  $C = 0$  in (4.78)) for the finite rectangular potential energy well considered in Section 4.5.1 to show that the wavefunction (4.82) results, where (4.83) must be satisfied.
16. Repeat problem 4.15 for the antisymmetric form of (4.78) (i.e., with  $D = 0$ ), showing that (4.84) results, where the wavenumbers must obey (4.85).
17. Comparing energy levels in one-dimensional quantum wells, for an infinite-height well of width  $2L$ , energy states are given by (4.35) with  $L$  replaced by  $2L$ ,

$$E_n = \frac{\hbar^2}{2m_e} \left(\frac{n\pi}{2L}\right)^2, \quad (4.148)$$

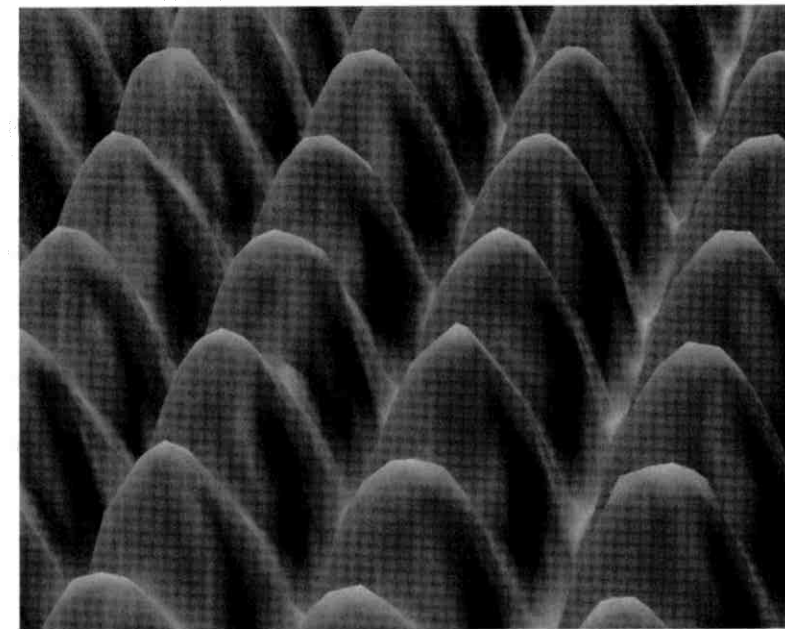
and for a finite-height well of width  $2L$  the symmetric states are given by a numerical solution of (4.83),

$$k_2 \tan(k_2 L) = k_1. \quad (4.149)$$

Assume that  $L = 2 \text{ nm}$ , and compute  $E_1$  and  $E_3$  (the second symmetric state) for the infinite-height well. Then compare it with the corresponding values obtained from the numerical solution of (4.149) for the finite-height well. (You will need to use a numerical root solver.) For the finite-height well, assume barrier heights  $V_0 = 1,000, 100, 10, 1, 0.5, \text{ and } 0.2 \text{ eV}$ . Make a table comparing the infinite-height and finite-height results (with percent errors), and comment on the appropriateness, at least for low energy states, of the much simpler infinite well model for reasonable barrier heights, such as  $V_0 = 0.5 \text{ eV}$ .

18. For a  $1s$  electron in the ground state of hydrogen, determine the expectation value of energy.
19. For an electron in the  $(n, l, m) = (2, 0, 0)$  state of hydrogen, determine the expectation value of position.
20. Repeat problem 4.19 for an electron in the  $(n, l, m) = (2, 1, 0)$  state of hydrogen.
21. For an electron in the  $(n_x, n_y) = (1, 1)$  subband of a metallic quantum wire having  $L_x = L_y = 1$  nm, if the total energy is 1 eV, what is the electron's longitudinal (i.e.,  $z$ -directed) group velocity?
22. A 3 eV electron is to be confined in a square quantum dot of side  $L$ . What should  $L$  be in order for the electron's energy levels to be well quantized?

## ELECTRONS SUBJECT TO A PERIODIC POTENTIAL — BAND THEORY OF SOLIDS



STM image of a nickel surface. (Image reproduced by permission of IBM Research, Almaden Research Center. Unauthorized use not permitted.)

In the previous chapter, we considered several different environments, including infinite and finite spatial regions, and we solved Schrödinger's equation to determine the possible allowed states for a particle in these environments. In this chapter we continue to use these ideas, but here we consider an electron in a crystalline material, leading to the important *band theory of solids*. It is hard to overestimate the importance of band theory. It turns out