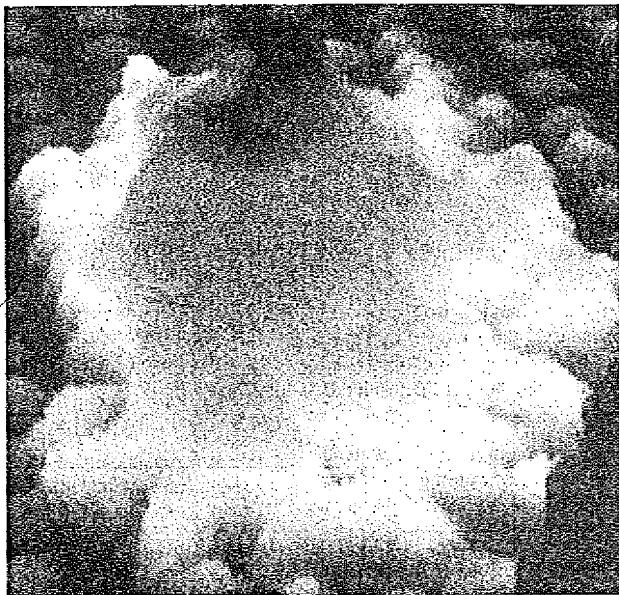


CHAPTER 5

Quantum Mechanics



Scanning tunneling micrograph of gold atoms on a carbon (graphite) substrate.
The cluster of gold atoms is about 1.5 nm across and three atoms high.

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APPENDIX: THE TUNNEL EFFECT

Although the Bohr theory of the atom, which can be extended further than was done in Chap. 4, is able to account for many aspects of atomic phenomena, it has a number of severe limitations as well. First of all, it applies only to hydrogen and one-electron ions such as He^+ and Li^{2+} —it does not even work for ordinary helium. The Bohr theory cannot explain why certain spectral lines are more intense than others (that is, why certain transitions between energy levels have greater probabilities of occurrence than others). It cannot account for the observation that many spectral lines actually consist of several separate lines whose wavelengths differ slightly. And perhaps most important, it does not permit us to obtain what a really successful theory of the atom should make possible: an understanding of how individual atoms interact with one another to endow macroscopic aggregates of matter with the physical and chemical properties we observe.

The preceding objections to the Bohr theory are not put forward in an unfriendly way, for the theory was one of those seminal achievements that transform scientific thought, but rather to emphasize that a more general approach to atomic phenomena is required. Such an approach was developed in 1925 and 1926 by Erwin Schrödinger, Werner Heisenberg, Max Born, Paul Dirac, and others under the apt name of quantum mechanics. "The discovery of quantum mechanics was nearly a total surprise. It described the physical world in a way that was fundamentally new. It seemed to many of us a miracle," noted Eugene Wigner, one of the early workers in the field. By the early 1930s the application of quantum mechanics to problems involving nuclei, atoms, molecules, and matter in the solid state made it possible to understand a vast body of data ("a large part of physics and the whole of chemistry," according to Dirac) and—vital for any theory—led to predictions of remarkable accuracy. Quantum mechanics has survived every experimental test thus far of even its most unexpected conclusions.

5.1 QUANTUM MECHANICS

Classical mechanics is an approximation of quantum mechanics

The fundamental difference between classical (or Newtonian) mechanics and quantum mechanics lies in what they describe. In classical mechanics, the future history of a particle is completely determined by its initial position and momentum together with the forces that act upon it. In the everyday world these quantities can all be determined well enough for the predictions of Newtonian mechanics to agree with what we find.

Quantum mechanics also arrives at relationships between observable quantities, but the uncertainty principle suggests that the nature of an observable quantity is different in the atomic realm. Cause and effect are still related in quantum mechanics, but what they concern needs careful interpretation. In quantum mechanics the kind of certainty about the future characteristic of classical mechanics is impossible because the initial state of a particle cannot be established with sufficient accuracy. As we saw in Sec. 3.7, the more we know about the position of a particle now, the less we know about its momentum and hence about its position later.

The quantities whose relationships quantum mechanics explores are *probabilities*. Instead of asserting, for example, that the radius of the electron's orbit in a ground-state hydrogen atom is always exactly 5.3×10^{-11} m, as the Bohr theory does, quantum mechanics states that this is the *most probable* radius. In a suitable experiment most trials will yield a different value, either larger or smaller, but the value most likely to be found will be 5.3×10^{-11} m.

Quantum mechanics might seem a poor substitute for classical mechanics. However, classical mechanics turns out to be just an approximate version of quantum mechanics. The certainties of classical mechanics are illusory, and their apparent agreement with experiment occurs because ordinary objects consist of so many individual atoms that departures from average behavior are unnoticeable. Instead of two sets of physical principles, one for the macroworld and one for the microworld, there is only the single set included in quantum mechanics.

Wave Function

As mentioned in Chap. 3, the quantity with which quantum mechanics is concerned is the wave function Ψ of a body. While Ψ itself has no physical interpretation, the square of its absolute magnitude $|\Psi|^2$ evaluated at a particular place at a particular time is proportional to the probability of finding the body there at that time. The linear momentum, angular momentum, and energy of the body are other quantities that can be established from Ψ . The problem of quantum mechanics is to determine Ψ for a body when its freedom of motion is limited by the action of external forces.

Wave functions are usually complex with both real and imaginary parts. A probability, however, must be a positive real quantity. The probability density $|\Psi|^2$ for a complex Ψ is therefore taken as the product $\Psi^*\Psi$ of Ψ and its complex conjugate Ψ^* . The complex conjugate of any function is obtained by replacing $i(\sqrt{-1})$ by $-i$ wherever it appears in the function. Every complex function Ψ can be written in the form

$$\text{Wave function} \quad \Psi = A + iB$$

where A and B are real functions. The complex conjugate Ψ^* of Ψ is

$$\text{Complex conjugate} \quad \Psi^* = A - iB$$

$$\text{and so} \quad |\Psi|^2 = \Psi^*\Psi = A^2 - i^2B^2 = A^2 + B^2$$

since $i^2 = -1$. Hence $|\Psi|^2 = \Psi^*\Psi$ is always a positive real quantity, as required.

Normalization

Even before we consider the actual calculation of Ψ , we can establish certain requirements it must always fulfill. For one thing, since $|\Psi|^2$ is proportional to the probability density P of finding the body described by Ψ , the integral of $|\Psi|^2$ over all space must be finite—the body is somewhere, after all. If

$$\int_{-\infty}^{\infty} |\Psi|^2 dV \neq 0$$

the particle does not exist, and the integral obviously cannot be ∞ and still mean anything. Furthermore, $|\Psi|^2$ cannot be negative or complex because of the way it is defined. The only possibility left is that the integral be a finite quantity if Ψ is to describe properly a real body.

It is usually convenient to have $|\Psi|^2$ be equal to the probability density P of finding the particle described by Ψ , rather than merely be proportional to P . If $|\Psi|^2$ is to

equal P , then it must be true that

$$\text{Normalization} \quad \int_{-\infty}^{\infty} |\Psi|^2 dV = 1 \quad (5.1)$$

since if the particle exists somewhere at all times,

$$\int_{-\infty}^{\infty} P dV = 1$$

A wave function that obeys Eq. (5.1) is said to be **normalized**. Every acceptable wave function can be normalized by multiplying it by an appropriate constant; we shall shortly see how this is done.

Well-Behaved Wave Functions

Besides being normalizable, Ψ must be single-valued, since P can have only one value at a particular place and time, and continuous. Momentum considerations (see Sec. 5.6) require that the partial derivatives $\partial\Psi/\partial x$, $\partial\Psi/\partial y$, $\partial\Psi/\partial z$ be finite, continuous, and single-valued. Only wave functions with all these properties can yield physically meaningful results when used in calculations, so only such "well-behaved" wave functions are admissible as mathematical representations of real bodies. To summarize:

- 1 Ψ must be continuous and single-valued everywhere.
- 2 $\partial\Psi/\partial x$, $\partial\Psi/\partial y$, $\partial\Psi/\partial z$ must be continuous and single-valued everywhere.
- 3 Ψ must be normalizable, which means that Ψ must go to 0 as $x \rightarrow \pm\infty$, $y \rightarrow \pm\infty$, $z \rightarrow \pm\infty$ in order that $\int |\Psi|^2 dV$ over all space be a finite constant.

These rules are not always obeyed by the wave functions of particles in model situations that only approximate actual ones. For instance, the wave functions of a particle in a box with infinitely hard walls do not have continuous derivatives at the walls, since $\Psi = 0$ outside the box (see Fig. 5.4). But in the real world, where walls are never infinitely hard, there is no sharp change in Ψ at the walls (see Fig. 5.7) and the derivatives are continuous. Exercise 7 gives another example of a wave function that is not well-behaved.

Given a normalized and otherwise acceptable wave function Ψ , the probability that the particle it describes will be found in a certain region is simply the integral of the probability density $|\Psi|^2$ over that region. Thus for a particle restricted to motion in the x direction, the probability of finding it between x_1 and x_2 is given by

$$\text{Probability} \quad P_{x_1 x_2} = \int_{x_1}^{x_2} |\Psi|^2 dx \quad (5.2)$$

We will see examples of such calculations later in this chapter and in Chap. 6.

5.2 THE WAVE EQUATION

It can have a variety of solutions, including complex ones

Schrödinger's equation, which is the fundamental equation of quantum mechanics in the same sense that the second law of motion is the fundamental equation of Newtonian mechanics, is a wave equation in the variable Ψ .

Before we tackle Schrödinger's equation, let us review the wave equation

$$\text{Wave equation} \quad \frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2} \quad (5.3)$$

which governs a wave whose variable quantity is y that propagates in the x direction with the speed v . In the case of a wave in a stretched string, y is the displacement of the string from the x axis; in the case of a sound wave, y is the pressure difference; in the case of a light wave, y is either the electric or the magnetic field magnitude. Equation (5.3) can be derived from the second law of motion for mechanical waves and from Maxwell's equations for electromagnetic waves.

Partial Derivatives

Suppose we have a function $f(x, y)$ of two variables, x and y , and we want to know how f varies with only one of them, say x . To find out, we differentiate f with respect to x while treating the other variable y as a constant. The result is the partial derivative of f with respect to x , which is written $\partial f / \partial x$.

$$\frac{\partial f}{\partial x} = \left(\frac{df}{dx} \right)_{y=\text{constant}}$$

The rules for ordinary differentiation hold for partial differentiation as well. For instance, if $f = cx^2$,

$$\frac{df}{dx} = 2cx$$

and so, if $f = yx^2$,

$$\frac{\partial f}{\partial x} = \left(\frac{df}{dx} \right)_{y=\text{constant}} = 2yx$$

The partial derivative of $f = yx^2$ with respect to the other variable, y , is

$$\frac{\partial f}{\partial y} = \left(\frac{df}{dy} \right)_{x=\text{constant}} = x^2$$

Second order partial derivatives occur often in physics, as in the wave equation. To find $\partial^2 f / \partial x^2$, we first calculate $\partial f / \partial x$ and then differentiate again, still keeping y constant:

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial x} \right)$$

For $f = yx^2$,

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x} (2yx) = 2y$$

Similarly

$$\frac{\partial^2 f}{\partial y^2} = \frac{\partial}{\partial y} (x^2) = 0$$

Solutions of the wave equation may be of many kinds, reflecting the variety of waves that can occur—a single traveling pulse, a train of waves of constant amplitude and wavelength, a train of superposed waves of the same amplitudes and wavelengths, a train of superposed waves of different amplitudes and wavelengths,

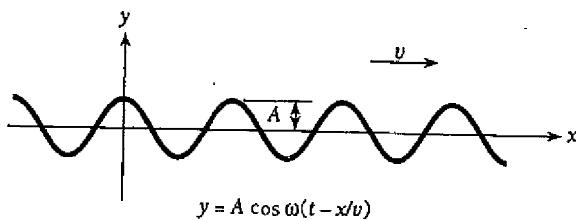


Figure 5.1 Waves in the xy plane traveling in the $+x$ direction along a stretched string lying on the x axis.

a standing wave in a string fastened at both ends, and so on. All solutions must be of the form

$$y = F\left(t \pm \frac{x}{v}\right) \quad (5.4)$$

where F is any function that can be differentiated. The solutions $F(t - x/v)$ represent waves traveling in the $+x$ direction, and the solutions $F(t + x/v)$ represent waves traveling in the $-x$ direction.

Let us consider the wave equivalent of a "free particle," which is a particle that is not under the influence of any forces and therefore pursues a straight path at constant speed. This wave is described by the general solution of Eq. (5.3) for undamped (that is, constant amplitude A), monochromatic (constant angular frequency ω) harmonic waves in the $+x$ direction, namely

$$y = Ae^{-i\omega(t-x/v)} \quad (5.5)$$

In this formula y is a complex quantity, with both real and imaginary parts.

Because

$$e^{-i\theta} = \cos \theta - i \sin \theta$$

Eq. (5.5) can be written in the form

$$y = A \cos \omega \left(t - \frac{x}{v}\right) - iA \sin \omega \left(t - \frac{x}{v}\right) \quad (5.6)$$

Only the real part of Eq. (5.6) [which is the same as Eq. (3.5)] has significance in the case of waves in a stretched string. There y represents the displacement of the string from its normal position (Fig. 5.1), and the imaginary part of Eq. (5.6) is discarded as irrelevant.

Example 5.1

Verify that Eq. (5.5) is a solution of the wave equation.

Solution

The derivative of an exponential function e^u is

$$\frac{d}{dx}(e^u) = e^u \frac{du}{dx}$$

The partial derivative of y with respect to x (which means t is treated as a constant) from Eq. (5.5) is therefore

$$\frac{\partial y}{\partial x} = \frac{i\omega}{v} y$$

and the second partial derivative is

$$\frac{\partial^2 y}{\partial x^2} = \frac{i^2 \omega^2}{v^2} y = -\frac{\omega^2}{v^2} y$$

since $i^2 = -1$. The partial derivative of y with respect to t (now holding x constant) is

$$\frac{\partial y}{\partial t} = -i\omega y$$

and the second partial derivative is

$$\frac{\partial^2 y}{\partial t^2} = i^2 \omega^2 y = -\omega^2 y$$

Combining these results gives

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2}$$

which is Eq. (5.3). Hence Eq. (5.5) is a solution of the wave equation.

5.3 SCHRÖDINGER'S EQUATION: TIME-DEPENDENT FORM

A basic physical principle that cannot be derived from anything else

In quantum mechanics the wave function Ψ corresponds to the wave variable y of wave motion in general. However, Ψ , unlike y , is not itself a measurable quantity and may therefore be complex. For this reason we assume that Ψ for a particle moving freely in the $+x$ direction is specified by

$$\Psi = A e^{-i\omega(t-x/v)} \quad (5.7)$$

Replacing ω in the above formula by $2\pi\nu$ and v by $\lambda\nu$ gives

$$\Psi = A e^{-2\pi i(\nu t - x/\lambda)} \quad (5.8)$$

This is convenient since we already know what ν and λ are in terms of the total energy E and momentum p of the particle being described by Ψ . Because

$$E = \hbar\nu = 2\pi\hbar\nu \quad \text{and} \quad \lambda = \frac{\hbar}{p} = \frac{2\pi\hbar}{p}$$

we have

$$\text{Free particle} \quad \Psi = A e^{-i(\hbar/E)(Et - px)} \quad (5.9)$$

Equation (5.9) describes the wave equivalent of an unrestricted particle of total energy E and momentum p moving in the $+x$ direction, just as Eq. (5.5) describes, for example, a harmonic displacement wave moving freely along a stretched string.

The expression for the wave function Ψ given by Eq. (5.9) is correct only for freely moving particles. However, we are most interested in situations where the motion of a particle is subject to various restrictions. An important concern, for example, is an electron bound to an atom by the electric field of its nucleus. What we must now do is obtain the fundamental differential equation for Ψ , which we can then solve for Ψ in a specific situation. This equation, which is Schrödinger's equation, can be arrived at in various ways, but it *cannot* be rigorously derived from existing physical principles:

the equation represents something new. What will be done here is to show one route to the wave equation for Ψ and then to discuss the significance of the result.

We begin by differentiating Eq. (5.9) for Ψ twice with respect to x , which gives

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{p^2}{\hbar^2} \Psi$$

$$p^2 \Psi = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \quad (5.10)$$

Differentiating Eq. (5.9) once with respect to t gives

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar} \Psi$$

$$E\Psi = -\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} \quad (5.11)$$

At speeds small compared with that of light, the total energy E of a particle is the sum of its kinetic energy $p^2/2m$ and its potential energy U , where U is in general a function of position x and time t :

$$E = \frac{p^2}{2m} + U(x, t) \quad (5.12)$$

The function U represents the influence of the rest of the universe on the particle. Of course, only a small part of the universe interacts with the particle to any extent; for



Erwin Schrödinger (1887–1961) was born in Vienna to an Austrian father and a half-English mother and received his doctorate at the university there. After World War I, during which he served as an artillery officer, Schrödinger had appointments at several German universities before becoming professor of physics in Zurich, Switzerland. Late in November, 1925, Schrödinger gave a talk on de Broglie's notion that a moving particle has a wave character. A colleague remarked to him afterward that to deal properly with a wave, one needs a wave equation. Schrödinger took this to heart, and a few weeks later he was "struggling with a new atomic theory. If only I knew more mathematics! I am very optimistic about this thing and expect that if I can only . . . solve it, it will be very beautiful." (Schrödinger was not the only physicist to find the mathematics he needed difficult; the eminent mathematician David Hilbert said at about this time, "Physics is much too hard for physicists.")

The struggle was successful, and in January 1926 the first of four papers on "Quantization as an Eigenvalue Problem" was completed. In this epochal paper Schrödinger introduced the equation that bears his name and solved it for the hydrogen atom,

thereby opening wide the door to the modern view of the atom which others had only pushed ajar. By June Schrödinger had applied wave mechanics to the harmonic oscillator, the diatomic molecule, the hydrogen atom in an electric field, the absorption and emission of radiation, and the scattering of radiation by atoms and molecules. He had also shown that his wave mechanics was mathematically equivalent to the more abstract Heisenberg-Born-Jordan matrix mechanics.

The significance of Schrödinger's work was at once realized. In 1927 he succeeded Planck at the University of Berlin but left Germany in 1933, the year he received the Nobel Prize, when the Nazis came to power. He was at Dublin's Institute for Advanced Study from 1939 until his return to Austria in 1956. In Dublin, Schrödinger became interested in biology, in particular the mechanism of heredity. He seems to have been the first to make definite the idea of a genetic code and to identify genes as long molecules that carry the code in the form of variations in how their atoms are arranged. Schrödinger's 1944 book *What Is Life?* was enormously influential, not only by what it said but also by introducing biologists to a new way of thinking—that of the physicist—about their subject. *What Is Life?* started James Watson on his search for "the secret of the gene," which he and Francis Crick (a physicist) discovered in 1953 to be the structure of the DNA molecule.

instance, in the case of the electron in a hydrogen atom, only the electric field of the nucleus must be taken into account.

Multiplying both sides of Eq. (5.12) by the wave function Ψ gives

$$E\Psi = \frac{p^2\Psi}{2m} + U\Psi \quad (5.13)$$

Now we substitute for $E\Psi$ and $p^2\Psi$ from Eqs. (5.10) and (5.11) to obtain the time-dependent form of Schrödinger's equation:

Time-dependent
Schrödinger
equation in one
dimension

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi \quad (5.14)$$

In three dimensions the time-dependent form of Schrödinger's equation is

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + U\Psi \quad (5.15)$$

where the particle's potential energy U is some function of x, y, z , and t .

Any restrictions that may be present on the particle's motion will affect the potential-energy function U . Once U is known, Schrödinger's equation may be solved for the wave function Ψ of the particle, from which its probability density $|\Psi|^2$ may be determined for a specified x, y, z, t .

Validity of Schrödinger's Equation

Schrödinger's equation was obtained here using the wave function of a freely moving particle (potential energy $U = \text{constant}$). How can we be sure it applies to the general case of a particle subject to arbitrary forces that vary in space and time [$U = U(x, y, z, t)$]? Substituting Eqs. (5.10) and (5.11) into Eq. (5.13) is really a wild leap with no formal justification; this is true for all other ways in which Schrödinger's equation can be arrived at, including Schrödinger's own approach.

What we must do is postulate Schrödinger's equation, solve it for a variety of physical situations, and compare the results of the calculations with the results of experiments. If both sets of results agree, the postulate embodied in Schrödinger's equation is valid. If they disagree, the postulate must be discarded and some other approach would then have to be explored. In other words,

Schrödinger's equation cannot be derived from other basic principles of physics; it is a basic principle in itself.

What has happened is that Schrödinger's equation has turned out to be remarkably accurate in predicting the results of experiments. To be sure, Eq. (5.15) can be used only for nonrelativistic problems, and a more elaborate formulation is needed when particle speeds near that of light are involved. But because it is in accord with experience within its range of applicability, we must consider Schrödinger's equation as a valid statement concerning certain aspects of the physical world.

It is worth noting that Schrödinger's equation does not increase the number of principles needed to describe the workings of the physical world. Newton's second law

of motion $F = ma$, the basic principle of classical mechanics, can be derived from Schrödinger's equation provided the quantities it relates are understood to be averages rather than precise values. (Newton's laws of motion were also not derived from any other principles. Like Schrödinger's equation, these laws are considered valid in their range of applicability because of their agreement with experiment.)

5.4 LINEARITY AND SUPERPOSITION

Wave functions add, not probabilities

An important property of Schrödinger's equation is that it is linear in the wave function Ψ . By this is meant that the equation has terms that contain Ψ and its derivatives but no terms independent of Ψ or that involve higher powers of Ψ or its derivatives. As a result, a linear combination of solutions of Schrödinger's equation for a given system is also itself a solution. If Ψ_1 and Ψ_2 are two solutions (that is, two wave functions that satisfy the equation), then

$$\Psi = a_1\Psi_1 + a_2\Psi_2$$

is also a solution, where a_1 and a_2 are constants (see Exercise 8). Thus the wave functions Ψ_1 and Ψ_2 obey the superposition principle that other waves do (see Sec. 2.1) and we conclude that interference effects can occur for wave functions just as they can for light, sound, water, and electromagnetic waves. In fact, the discussions of Secs. 3.4 and 3.7 assumed that de Broglie waves are subject to the superposition principle.

Let us apply the superposition principle to the diffraction of an electron beam. Figure 5.2a shows a pair of slits through which a parallel beam of monoenergetic electrons pass on their way to a viewing screen. If slit 1 only is open, the result is the intensity variation shown in Fig. 5.2b that corresponds to the probability density

$$P_1 = |\Psi_1|^2 = \Psi_1^* \Psi_1$$

If slit 2 only is open, as in Fig. 5.2c, the corresponding probability density is

$$P_2 = |\Psi_2|^2 = \Psi_2^* \Psi_2$$

We might suppose that opening both slits would give an electron intensity variation described by $P_1 + P_2$, as in Fig. 5.2d. However, this is not the case because in quantum

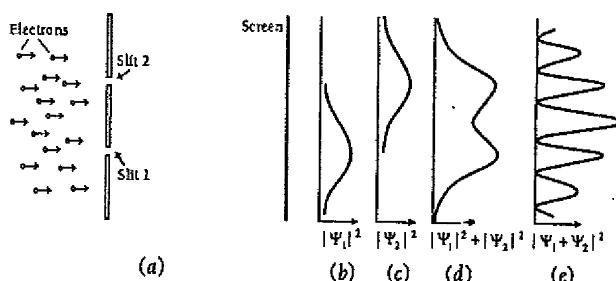


Figure 5.2 (a) Arrangement of double-slit experiment. (b) The electron intensity at the screen with only slit 1 open. (c) The electron intensity at the screen with only slit 2 open. (d) The sum of the intensities of (b) and (c). (e) The actual intensity at the screen with slits 1 and 2 both open. The wave functions Ψ_1 and Ψ_2 add to produce the intensity at the screen, not the probability densities $|\Psi_1|^2$ and $|\Psi_2|^2$.

mechanics wave functions add, *not* probabilities. Instead the result with both slits open is as shown in Fig. 5.2e, the same pattern of alternating maxima and minima that occurs when a beam of monochromatic light passes through the double slit of Fig. 2.4.

The diffraction pattern of Fig. 5.2e arises from the superposition Ψ of the wave functions Ψ_1 and Ψ_2 of the electrons that have passed through slits 1 and 2:

$$\Psi = \Psi_1 + \Psi_2$$

The probability density at the screen is therefore

$$\begin{aligned} P &= |\Psi|^2 = |\Psi_1 + \Psi_2|^2 = (\Psi_1^* + \Psi_2^*)(\Psi_1 + \Psi_2) \\ &= \Psi_1^*\Psi_1 + \Psi_2^*\Psi_2 + \Psi_1^*\Psi_2 + \Psi_2^*\Psi_1 \\ &= P_1 + P_2 + \Psi_1^*\Psi_2 + \Psi_2^*\Psi_1 \end{aligned}$$

The two terms at the right of this equation represent the difference between Fig. 5.2d and e and are responsible for the oscillations of the electron intensity at the screen. In Sec. 6.8 a similar calculation will be used to investigate why a hydrogen atom emits radiation when it undergoes a transition from one quantum state to another of lower energy.

5.5 EXPECTATION VALUES

How to extract information from a wave function

Once Schrödinger's equation has been solved for a particle in a given physical situation, the resulting wave function $\Psi(x, y, z, t)$ contains all the information about the particle that is permitted by the uncertainty principle. Except for those variables that are quantized this information is in the form of probabilities and not specific numbers.

As an example, let us calculate the expectation value $\langle x \rangle$ of the position of a particle confined to the x axis that is described by the wave function $\Psi(x, t)$. This is the value of x we would obtain if we measured the positions of a great many particles described by the same wave function at some instant t and then averaged the results.

To make the procedure clear, we first answer a slightly different question: What is the average position \bar{x} of a number of identical particles distributed along the x axis in such a way that there are N_1 particles at x_1 , N_2 particles at x_2 , and so on? The average position in this case is the same as the center of mass of the distribution, and so

$$\bar{x} = \frac{N_1x_1 + N_2x_2 + N_3x_3 + \dots}{N_1 + N_2 + N_3 + \dots} = \frac{\sum N_i x_i}{\sum N_i} \quad (5.16)$$

When we are dealing with a single particle, we must replace the number N_i of particles at x_i by the probability P_i that the particle be found in an interval dx at x_i . This probability is

$$P_i = |\Psi_i|^2 dx \quad (5.17)$$

where Ψ_i is the particle wave function evaluated at $x = x_i$. Making this substitution and changing the summations to integrals, we see that the expectation value of the

position of the single particle is

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x |\Psi|^2 dx}{\int_{-\infty}^{\infty} |\Psi|^2 dx} \quad (5.18)$$

If Ψ is a normalized wave function, the denominator of Eq. (5.18) equals the probability that the particle exists somewhere between $x = -\infty$ and $x = \infty$ and therefore has the value 1. In this case

Expectation value
for position

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi|^2 dx \quad (5.19)$$

Example 5.2

A particle limited to the x axis has the wave function $\Psi = ax$ between $x = 0$ and $x = 1$; $\Psi = 0$ elsewhere. (a) Find the probability that the particle can be found between $x = 0.45$ and $x = 0.55$. (b) Find the expectation value $\langle x \rangle$ of the particle's position.

Solution

(a) The probability is

$$\int_{x_1}^{x_2} |\Psi|^2 dx = a^2 \int_{0.45}^{0.55} x^2 dx = a^2 \left[\frac{x^3}{3} \right]_{0.45}^{0.55} = 0.0251a^2$$

(b) The expectation value is

$$\langle x \rangle = \int_0^1 x |\Psi|^2 dx = a^2 \int_0^1 x^3 dx = a^2 \left[\frac{x^4}{4} \right]_0^1 = \frac{a^2}{4}$$

The same procedure as that followed above can be used to obtain the expectation value $\langle G(x) \rangle$ of any quantity—for instance, potential energy $U(x)$ —that is a function of the position x of a particle described by a wave function Ψ . The result is

$$\text{Expectation value} \quad \langle G(x) \rangle = \int_{-\infty}^{\infty} G(x) |\Psi|^2 dx \quad (5.20)$$

The expectation value $\langle p \rangle$ for momentum cannot be calculated this way because, according to the uncertainty principle, no such function as $p(x)$ can exist. If we specify x , so that $\Delta x = 0$, we cannot specify a corresponding p since $\Delta x \Delta p \geq \hbar/2$. The same problem occurs for the expectation value $\langle E \rangle$ for energy because $\Delta E \Delta t \geq \hbar/2$ means that, if we specify t , the function $E(t)$ is impossible. In Sec. 5.6 we will see how $\langle p \rangle$ and $\langle E \rangle$ can be determined.

In classical physics no such limitation occurs, because the uncertainty principle can be neglected in the macroworld. When we apply the second law of motion to the motion of a body subject to various forces, we expect to get $p(x, t)$ and $E(x, t)$ from the solution as well as $x(t)$. Solving a problem in classical mechanics gives us the entire future course of the body's motion. In quantum physics, on the other hand, all we get directly by applying Schrödinger's equation to the motion of a particle is the wave function Ψ , and the future course of the particle's motion—like its initial state—is a matter of probabilities instead of certainties.

5.6 OPERATORS

Another way to find expectation values

A hint as to the proper way to evaluate $\langle p \rangle$ and $\langle E \rangle$ comes from differentiating the free-particle wave function $\Psi = Ae^{-i(\hbar XEt - px)}$ with respect to x and to t . We find that

$$\frac{\partial \Psi}{\partial x} = \frac{i}{\hbar} p\Psi$$

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} E\Psi$$

which can be written in the suggestive forms

$$p\Psi = \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi \quad (5.21)$$

$$E\Psi = i\hbar \frac{\partial}{\partial t} \Psi \quad (5.22)$$

Evidently the dynamical quantity p in some sense corresponds to the differential operator $(\hbar/i) \partial/\partial x$ and the dynamical quantity E similarly corresponds to the differential operator $i\hbar \partial/\partial t$.

An operator tells us what operation to carry out on the quantity that follows it. Thus the operator $i\hbar \partial/\partial t$ instructs us to take the partial derivative of what comes after it with respect to t and multiply the result by $i\hbar$. Equation (5.22) was on the postmark used to cancel the Austrian postage stamp issued to commemorate the 100th anniversary of Schrödinger's birth.

It is customary to denote operators by using a caret, so that \hat{p} is the operator that corresponds to momentum p and \hat{E} is the operator that corresponds to total energy E . From Eqs. (5.21) and (5.22) these operators are

$$\text{Momentum operator} \quad \hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x} \quad (5.23)$$

$$\text{Total-energy operator} \quad \hat{E} = i\hbar \frac{\partial}{\partial t} \quad (5.24)$$

Though we have only shown that the correspondences expressed in Eqs. (5.23) and (5.24) hold for free particles, they are entirely general results whose validity is the same as that of Schrödinger's equation. To support this statement, we can replace the equation $E = KE + U$ for the total energy of a particle with the operator equation

$$\hat{E} = \hat{K}\hat{E} + \hat{U} \quad (5.25)$$

The operator \hat{U} is just $U(\Psi)$. The kinetic energy KE is given in terms of momentum p by

$$KE = \frac{p^2}{2m}$$

and so we have

$$\text{Kinetic-energy operator } \hat{K}E = \frac{\hat{p}^2}{2m} = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (5.26)$$

Equation (5.25) therefore reads

$$i\hbar \frac{\partial}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U \quad (5.27)$$

Now we multiply the identity $\Psi = \Psi$ by Eq. (5.27) and obtain

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi$$

which is Schrödinger's equation. Postulating Eqs. (5.23) and (5.24) is equivalent to postulating Schrödinger's equation.

Operators and Expectation Values

Because p and E can be replaced by their corresponding operators in an equation, we can use these operators to obtain expectation values for p and E . Thus the expectation value for p is

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{p} \Psi \, dx = \int_{-\infty}^{\infty} \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi \, dx = \frac{\hbar}{i} \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} \, dx \quad (5.28)$$

and the expectation value for E is

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{E} \Psi \, dx = \int_{-\infty}^{\infty} \Psi^* \left(i\hbar \frac{\partial}{\partial t} \right) \Psi \, dx = i\hbar \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial t} \, dx \quad (5.29)$$

Both Eqs. (5.28) and (5.29) can be evaluated for any acceptable wave function $\Psi(x, t)$.

Let us see why expectation values involving operators have to be expressed in the form

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{p} \Psi \, dx$$

The other alternatives are

$$\int_{-\infty}^{\infty} \hat{p} \Psi^* \Psi \, dx = \frac{\hbar}{i} \int_{-\infty}^{\infty} \frac{\partial}{\partial x} (\Psi^* \Psi) \, dx = \frac{\hbar}{i} \left[\Psi^* \Psi \right]_{-\infty}^{\infty} = 0$$

since Ψ^* and Ψ must be 0 at $x = \pm\infty$, and

$$\int_{-\infty}^{\infty} \Psi^* \Psi \hat{p} \, dx = \frac{\hbar}{i} \int_{-\infty}^{\infty} \Psi^* \Psi \frac{\partial}{\partial x} \, dx$$

which makes no sense. In the case of algebraic quantities such as x and $V(x)$, the order of factors in the integrand is unimportant, but when differential operators are involved, the correct order of factors must be observed.

Every observable quantity G characteristic of a physical system may be represented by a suitable quantum-mechanical operator \hat{G} . To obtain this operator, we express G in terms of x and p and then replace p by $(\hbar/i) \partial/\partial x$. If the wave function Ψ of the system is known, the expectation value of $G(x, p)$ is

$$\begin{array}{ll} \text{Expectation value} & \langle G(x, p) \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{G} \Psi \, dx \\ \text{of an operator} & \end{array} \quad (5.30)$$

In this way all the information about a system that is permitted by the uncertainty principle can be obtained from its wave function Ψ .

5.7 SCHRÖDINGER'S EQUATION: STEADY-STATE FORM

Eigenvalues and eigenfunctions

In a great many situations the potential energy of a particle does not depend on time explicitly; the forces that act on it, and hence U , vary with the position of the particle only. When this is true, Schrödinger's equation may be simplified by removing all reference to t .

We begin by noting that the one-dimensional wave function Ψ of an unrestricted particle may be written

$$\Psi = A e^{-(i/\hbar)(Et - px)} = A e^{-(iE/\hbar)t} e^{(ip/\hbar)x} = \psi e^{-(iE/\hbar)t} \quad (5.31)$$

Evidently Ψ is the product of a time-dependent function $e^{-(iE/\hbar)t}$ and a position-dependent function ψ . As it happens, the time variations of all wave functions of particles acted on by forces independent of time have the same form as that of an unrestricted particle. Substituting the Ψ of Eq. (5.31) into the time-dependent form of Schrödinger's equation, we find that

$$E\psi e^{-(iE/\hbar)t} = -\frac{\hbar^2}{2m} e^{-(iE/\hbar)t} \frac{\partial^2 \psi}{\partial x^2} + U\psi e^{-(iE/\hbar)t}$$

Dividing through by the common exponential factor gives

$$\begin{array}{ll} \text{Steady-state} & \\ \text{Schrödinger equation} & \frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - U)\psi = 0 \\ \text{in one dimension} & \end{array} \quad (5.32)$$

Equation (5.32) is the steady-state form of Schrödinger's equation. In three dimensions it is

$$\begin{array}{ll} \text{Steady-state} & \\ \text{Schrödinger} & \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - U)\psi = 0 \\ \text{equation in three} & \\ \text{dimensions} & \end{array} \quad (5.33)$$

An important property of Schrödinger's steady-state equation is that, if it has one or more solutions for a given system, each of these wave functions corresponds to a specific value of the energy E . Thus energy quantization appears in wave mechanics as a natural element of the theory, and energy quantization in the physical world is revealed as a universal phenomenon characteristic of all stable systems.

A familiar and quite close analogy to the manner in which energy quantization occurs in solutions of Schrödinger's equation is with standing waves in a stretched string of length L that is fixed at both ends. Here, instead of a single wave propagating indefinitely in one direction, waves are traveling in both the $+x$ and $-x$ directions simultaneously. These waves are subject to the condition (called a boundary condition) that the displacement y always be zero at both ends of the string. An acceptable function $y(x, t)$ for the displacement must, with its derivatives (except at the ends), be as well-behaved as ψ and its derivatives—that is, be continuous, finite, and single-valued. In this case y must be real, not complex, as it represents a directly measurable quantity. The only solutions of the wave equation, Eq. (5.3), that are in accord with these various limitations are those in which the wavelengths are given by

$$\lambda_n = \frac{2L}{n+1} \quad n = 0, 1, 2, 3, \dots$$

as shown in Fig. 5.3. It is the combination of the wave equation and the restrictions placed on the nature of its solution that leads us to conclude that $y(x, t)$ can exist only for certain wavelengths λ_n .

Eigenvalues and Eigenfunctions

The values of energy E_n for which Schrödinger's steady-state equation can be solved are called **eigenvalues** and the corresponding wave functions ψ_n are called **eigenfunctions**. (These terms come from the German *Eigenwert*, meaning "proper or characteristic value," and *Eigenfunktion*, "proper or characteristic function.") The discrete energy levels of the hydrogen atom

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \left(\frac{1}{n^2} \right) \quad n = 1, 2, 3, \dots$$

are an example of a set of eigenvalues. We shall see in Chap. 6 why these particular values of E are the only ones that yield acceptable wave functions for the electron in the hydrogen atom.

An important example of a dynamical variable other than total energy that is found to be quantized in stable systems is angular momentum L . In the case of the hydrogen atom, we shall find that the eigenvalues of the magnitude of the total angular momentum are specified by

$$L = \sqrt{l(l+1)} \hbar \quad l = 0, 1, 2, \dots, (n-1)$$

Of course, a dynamical variable G may not be quantized. In this case measurements of G made on a number of identical systems will not yield a unique result but instead a spread of values whose average is the expectation value

$$\langle G \rangle = \int_{-\infty}^{\infty} G|\psi|^2 dx$$

In the hydrogen atom, the electron's position is not quantized, for instance, so that we must think of the electron as being present in the vicinity of the nucleus with a certain probability $|\psi|^2$ per unit volume but with no predictable position or even orbit in the classical sense. This probabilistic statement does not conflict with the fact that

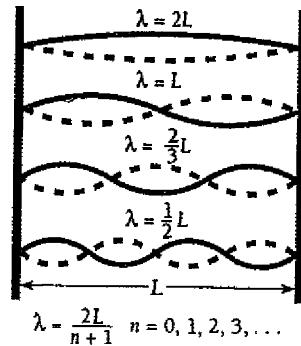


Figure 5.3 Standing waves in a stretched string fastened at both ends.

experiments performed on hydrogen atoms always show that each one contains a whole electron, not 27 percent of an electron in a certain region and 73 percent elsewhere. The probability is one of finding the electron, and although this probability is smeared out in space, the electron itself is not.

Operators and Eigenvalues

The condition that a certain dynamical variable G be restricted to the discrete values G_n —in other words, that G be quantized—is that the wave functions ψ_n of the system be such that

$$\text{Eigenvalue equation} \quad \hat{G}\psi_n = G_n\psi_n \quad (5.34)$$

where \hat{G} is the operator that corresponds to G and each G_n is a real number. When Eq. (5.34) holds for the wave functions of a system, it is a fundamental postulate of quantum mechanics that any measurement of G can only yield one of the values G_n . If measurements of G are made on a number of identical systems all in states described by the particular eigenfunction ψ_k , each measurement will yield the single value G_k .

Example 5.3

An eigenfunction of the operator d^2/dx^2 is $\psi = e^{2x}$. Find the corresponding eigenvalue.

Solution

Here $\hat{G} = d^2/dx^2$, so

$$\hat{G}\psi = \frac{d^2}{dx^2}(e^{2x}) = \frac{d}{dx} \left[\frac{d}{dx}(e^{2x}) \right] = \frac{d}{dx}(2e^{2x}) = 4e^{2x}$$

But $e^{2x} = \psi$, so

$$\hat{G}\psi = 4\psi$$

From Eq. (5.34) we see that the eigenvalue G here is just $G = 4$.

In view of Eqs. (5.25) and (5.26) the total-energy operator \hat{E} of Eq. (5.24) can also be written as

$$\begin{array}{ll} \text{Hamiltonian} & \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U \\ \text{operator} & \end{array} \quad (5.35)$$

and is called the **Hamiltonian operator** because it is reminiscent of the Hamiltonian function in advanced classical mechanics, which is an expression for the total energy of a system in terms of coordinates and momenta only. Evidently the steady-state Schrödinger equation can be written simply as

$$\begin{array}{ll} \text{Schrödinger's} & \hat{H}\psi_n = E_n\psi_n \\ \text{equation} & \end{array} \quad (5.36)$$

Table 5.1 Operators Associated with Various Observable Quantities

Quantity	Operator
Position, x	x
Linear momentum, p	$i \frac{\partial}{\partial x}$
Potential energy, $U(x)$	$U(x)$
Kinetic energy, $KE = \frac{p^2}{2m}$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
Total energy, E	$i\hbar \frac{\partial}{\partial t}$
Total energy (Hamiltonian form), H	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x)$

so we can say that the various E_n are the eigenvalues of the Hamiltonian operator \hat{H} . This kind of association between eigenvalues and quantum-mechanical operators is quite general. Table 5.1 lists the operators that correspond to various observable quantities.

5.8 PARTICLE IN A BOX

How boundary conditions and normalization determine wave functions

To solve Schrödinger's equation, even in its simpler steady-state form, usually requires elaborate mathematical techniques. For this reason the study of quantum mechanics has traditionally been reserved for advanced students who have the required proficiency in mathematics. However, since quantum mechanics is the theoretical structure whose results are closest to experimental reality, we must explore its methods and applications to understand modern physics. As we shall see, even a modest mathematical background is enough for us to follow the trains of thought that have led quantum mechanics to its greatest achievements.

The simplest quantum-mechanical problem is that of a particle trapped in a box with infinitely hard walls. In Sec. 3.6 we saw how a quite simple argument yields the energy levels of the system. Let us now tackle the same problem in a more formal way, which will give us the wave function ψ_n that corresponds to each energy level.

We may specify the particle's motion by saying that it is restricted to traveling along the x axis between $x = 0$ and $x = L$ by infinitely hard walls. A particle does not lose energy when it collides with such walls, so that its total energy stays constant. From a formal point of view the potential energy U of the particle is infinite on both sides of the box, while U is a constant—say 0 for convenience—on the inside (Fig. 5.4). Because the particle cannot have an infinite amount of energy, it cannot exist outside the box, and so its wave function ψ is 0 for $x \leq 0$ and $x \geq L$. Our task is to find what ψ is within the box, namely, between $x = 0$ and $x = L$.

Within the box Schrödinger's equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad (5.37)$$

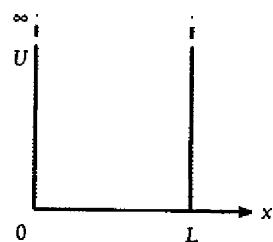


Figure 5.4 A square potential well with infinitely high barriers at each end corresponds to a box with infinitely hard walls.

since $U = 0$ there. (The total derivative $d^2\psi/dx^2$ is the same as the partial derivative $\partial^2\psi/\partial x^2$ because ψ is a function only of x in this problem.) Equation (5.37) has the solution

$$\psi = A \sin \frac{\sqrt{2mE}}{\hbar} x + B \cos \frac{\sqrt{2mE}}{\hbar} x \quad (5.38)$$

which we can verify by substitution back into Eq. (5.37). A and B are constants to be evaluated.

This solution is subject to the boundary conditions that $\psi = 0$ for $x = 0$ and for $x = L$. Since $\cos 0 = 1$, the second term cannot describe the particle because it does not vanish at $x = 0$. Hence we conclude that $B = 0$. Since $\sin 0 = 0$, the sine term always yields $\psi = 0$ at $x = 0$, as required, but ψ will be 0 at $x = L$ only when

$$\frac{\sqrt{2mE}}{\hbar} L = n\pi \quad n = 1, 2, 3, \dots \quad (5.39)$$

This result comes about because the sines of the angles $\pi, 2\pi, 3\pi, \dots$ are all 0.

From Eq. (5.39) it is clear that the energy of the particle can have only certain values, which are the eigenvalues mentioned in the previous section. These eigenvalues, constituting the energy levels of the system, are found by solving Eq. (5.39) for E_n , which gives

$$\text{Particle in a box} \quad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad n = 1, 2, 3, \dots \quad (5.40)$$

Equation (5.40) is the same as Eq. (3.18) and has the same interpretation [see the discussion that follows Eq. (3.18) in Sec. 3.6].

Wave Functions

The wave functions of a particle in a box whose energies are E_n are, from Eq. (5.38) with $B = 0$,

$$\psi_n = A \sin \frac{\sqrt{2mE_n}}{\hbar} x \quad (5.41)$$

Substituting Eq. (5.40) for E_n gives

$$\psi_n = A \sin \frac{n\pi x}{L} \quad (5.42)$$

for the eigenfunctions corresponding to the energy eigenvalues E_n .

It is easy to verify that these eigenfunctions meet all the requirements discussed in Sec. 5.1: for each quantum number n , ψ_n is a finite, single-valued function of x , and ψ_n and $\partial\psi_n/\partial x$ are continuous (except at the ends of the box). Furthermore, the integral

of $|\psi_n|^2$ over all space is finite, as we can see by integrating $|\psi_n|^2 dx$ from $x = 0$ to $x = L$ (since the particle is confined within these limits). With the help of the trigonometric identity $\sin^2 \theta = \frac{1}{2}(1 - \cos 2\theta)$ we find that

$$\begin{aligned} \int_{-\infty}^{\infty} |\psi_n|^2 dx &= \int_0^L |\psi_n|^2 dx = A^2 \int_0^L \sin^2 \left(\frac{n\pi x}{L} \right) dx \\ &= \frac{A^2}{2} \left[\int_0^L dx - \int_0^L \cos \left(\frac{2n\pi x}{L} \right) dx \right] \\ &= \frac{A^2}{2} \left[x - \left(\frac{L}{2n\pi} \right) \sin \frac{2n\pi x}{L} \right]_0^L = A^2 \left(\frac{L}{2} \right) \end{aligned} \quad (5.43)$$

To normalize ψ we must assign a value to A such that $|\psi_n|^2 dx$ is equal to the probability $P dx$ of finding the particle between x and $x + dx$, rather than merely proportional to $P dx$. If $|\psi_n|^2 dx$ is to equal $P dx$, then it must be true that

$$\int_{-\infty}^{\infty} |\psi_n|^2 dx = 1 \quad (5.44)$$

Comparing Eqs. (5.43) and (5.44), we see that the wave functions of a particle in a box are normalized if

$$A = \sqrt{\frac{2}{L}} \quad (5.45)$$

The normalized wave functions of the particle are therefore

$$\text{Particle in a box} \quad \psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad n = 1, 2, 3, \dots \quad (5.46)$$

The normalized wave functions ψ_1 , ψ_2 , and ψ_3 together with the probability densities $|\psi_1|^2$, $|\psi_2|^2$, and $|\psi_3|^2$ are plotted in Fig. 5.5. Although ψ_n may be negative as well as positive, $|\psi_n|^2$ is never negative and, since ψ_n is normalized, its value at a given x is equal to the probability density of finding the particle there. In every case $|\psi_n|^2 = 0$ at $x = 0$ and $x = L$, the boundaries of the box.

At a particular place in the box the probability of the particle being present may be very different for different quantum numbers. For instance, $|\psi_1|^2$ has its maximum value of $2/L$ in the middle of the box, while $|\psi_2|^2 = 0$ there. A particle in the lowest energy level of $n = 1$ is most likely to be in the middle of the box, while a particle in the next higher state of $n = 2$ is never there! Classical physics, of course, suggests the same probability for the particle being anywhere in the box.

The wave functions shown in Fig. 5.5 resemble the possible vibrations of a string fixed at both ends, such as those of the stretched string of Fig. 5.2. This follows from the fact that waves in a stretched string and the wave representing a moving particle are described by equations of the same form, so that when identical restrictions are placed upon each kind of wave, the formal results are identical.

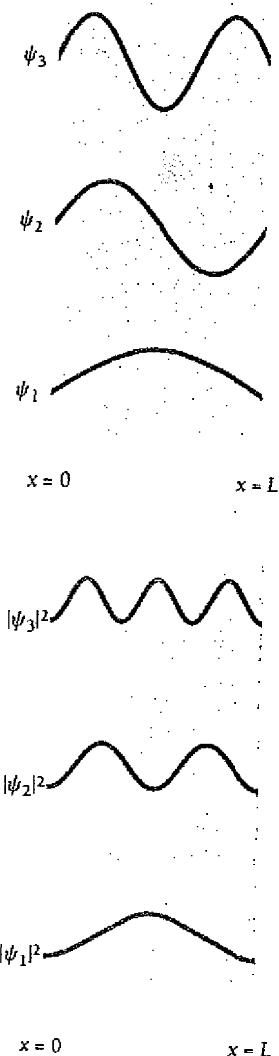


Figure 5.5 Wave functions and probability densities of a particle confined to a box with rigid walls.

Example 5.4

Find the probability that a particle trapped in a box L wide can be found between $0.45L$ and $0.55L$ for the ground and first excited states.

Solution

This part of the box is one-tenth of the box's width and is centered on the middle of the box (Fig. 5.6). Classically we would expect the particle to be in this region 10 percent of the time. Quantum mechanics gives quite different predictions that depend on the quantum number of the particle's state. From Eqs. (5.2) and (5.46) the probability of finding the particle between x_1 and x_2 when it is in the n th state is

$$\begin{aligned} P_{x_1, x_2} &= \int_{x_1}^{x_2} |\psi_n|^2 dx = \frac{2}{L} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L} dx \\ &= \left[\frac{x}{L} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{L} \right]_{x_1}^{x_2} \end{aligned}$$

Here $x_1 = 0.45L$ and $x_2 = 0.55L$. For the ground state, which corresponds to $n = 1$, we have

$$P_{x_1, x_2} = 0.198 = 19.8 \text{ percent}$$

This is about twice the classical probability. For the first excited state, which corresponds to $n = 2$, we have

$$P_{x_1, x_2} = 0.0065 = 0.65 \text{ percent}$$

This low figure is consistent with the probability density of $|\psi_n|^2 = 0$ at $x = 0.5L$.

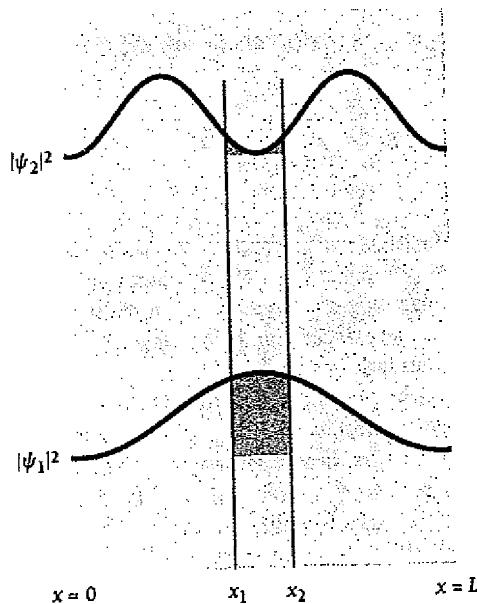


Figure 5.6 The probability P_{x_1, x_2} of finding a particle in the box of Fig. 5.5 between $x_1 = 0.45L$ and $x_2 = 0.55L$ is equal to the area under the $|\psi|^2$ curves between these limits.

Example 5.5

Find the expectation value $\langle x \rangle$ of the position of a particle trapped in a box L wide.

Solution

From Eqs. (5.19) and (5.46) we have

$$\begin{aligned}\langle x \rangle &= \int_{-\infty}^{\infty} x |\psi|^2 dx = \frac{2}{L} \int_0^L x \sin^2 \frac{n\pi x}{L} dx \\ &= \frac{2}{L} \left[\frac{x^2}{4} - \frac{x \sin(2n\pi x/L)}{4n\pi/L} - \frac{\cos(2n\pi x/L)}{8(n\pi/L)^2} \right]_0^L\end{aligned}$$

Since $\sin n\pi = 0$, $\cos 2n\pi = 1$, and $\cos 0 = 1$, for all the values of n the expectation value of x is

$$\langle x \rangle = \frac{2}{L} \left(\frac{L^2}{4} \right) = \frac{L}{2}$$

This result means that the average position of the particle is the middle of the box in all quantum states. There is no conflict with the fact that $|\psi|^2 = 0$ at $L/2$ in the $n = 2, 4, 6, \dots$ states because $\langle x \rangle$ is an *average*, not a probability, and it reflects the symmetry of $|\psi|^2$ about the middle of the box.

Momentum

Finding the momentum of a particle trapped in a one-dimensional box is not as straightforward as finding $\langle x \rangle$. Here

$$\begin{aligned}\psi^* &= \psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \\ \frac{d\psi}{dx} &= \sqrt{\frac{2}{L}} \frac{n\pi}{L} \cos \frac{n\pi x}{L}\end{aligned}$$

and so, from Eq. (5.30),

$$\begin{aligned}\langle p \rangle &= \int_{-\infty}^{\infty} \psi^* \hat{p} \psi dx = \int_{-\infty}^{\infty} \psi^* \left(\frac{\hbar}{i} \frac{d}{dx} \right) \psi dx \\ &= \frac{\hbar}{i} \frac{2}{L} \frac{n\pi}{L} \int_0^L \sin \frac{n\pi x}{L} \cos \frac{n\pi x}{L} dx\end{aligned}$$

We note that

$$\int \sin ax \cos ax dx = \frac{1}{2a} \sin^2 ax$$

With $a = n\pi/L$ we have

$$\langle p \rangle = \frac{\hbar}{iL} \left[\sin^2 \frac{n\pi x}{L} \right]_0^L = 0$$

since $\sin^2 0 = \sin^2 n\pi = 0 \quad n = 1, 2, 3, \dots$

The expectation value $\langle p \rangle$ of the particle's momentum is 0.

At first glance this conclusion seems strange. After all, $E = p^2/2m$, and so we would anticipate that

Momentum eigenvalues for trapped particle $p_n = \pm \sqrt{2mE_n} = \pm \frac{n\pi\hbar}{L}$ (5.47)

The \pm sign provides the explanation: The particle is moving back and forth, and so its average momentum for any value of n is

$$p_{av} = \frac{(+n\pi\hbar/L) + (-n\pi\hbar/L)}{2} = 0$$

which is the expectation value.

According to Eq. (5.47) there should be two momentum eigenfunctions for every energy eigenfunction, corresponding to the two possible directions of motion. The general procedure for finding the eigenvalues of a quantum-mechanical operator, here \hat{p} , is to start from the eigenvalue equation

$$\hat{p}\psi_n = p_n\psi_n \quad (5.48)$$

where each p_n is a real number. This equation holds only when the wave functions ψ_n are eigenfunctions of the momentum operator \hat{p} , which here is

$$\hat{p} = \frac{\hbar}{i} \frac{d}{dx}$$

We can see at once that the energy eigenfunctions

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

are not also momentum eigenfunctions, because

$$\frac{\hbar}{i} \frac{d}{dx} \left(\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \right) = \frac{\hbar}{i} \frac{n\pi}{L} \sqrt{\frac{2}{L}} \cos \frac{n\pi x}{L} \neq p_n \psi_n$$

To find the correct momentum eigenfunctions, we note that

$$\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i} = \frac{1}{2i} e^{i\theta} - \frac{1}{2i} e^{-i\theta}$$

Hence each energy eigenfunction can be expressed as a linear combination of the two wave functions

Momentum eigenfunctions for trapped particle

$$\psi_n^+ = \frac{1}{2i} \sqrt{\frac{2}{L}} e^{in\pi x/L} \quad (5.49)$$

$$\psi_n^- = \frac{1}{2i} \sqrt{\frac{2}{L}} e^{-in\pi x/L} \quad (5.50)$$

Inserting the first of these wave functions in the eigenvalue equation, Eq. (5.48), we have

$$\hat{p}\psi_n^+ = p_n^+ \psi_n^+$$

$$\frac{\hbar}{i} \frac{d}{dx} \psi_n^+ = \frac{\hbar}{i} \frac{1}{2i} \sqrt{\frac{2}{L}} \frac{in\pi}{L} e^{in\pi x/L} = \frac{n\pi\hbar}{L} \psi_n^+ = p_n^+ \psi_n^+$$

so that

$$p_n^+ = +\frac{n\pi\hbar}{L} \quad (5.51)$$

Similarly the wave function ψ_n^- leads to the momentum eigenvalues

$$p_n^- = -\frac{n\pi\hbar}{L} \quad (5.52)$$

We conclude that ψ_n^+ and ψ_n^- are indeed the momentum eigenfunctions for a particle in a box, and that Eq. (5.47) correctly states the corresponding momentum eigenvalues.

5.9 FINITE POTENTIAL WELL

The wave function penetrates the walls, which lowers the energy levels

Potential energies are never infinite in the real world, and the box with infinitely hard walls of the previous section has no physical counterpart. However, potential wells with barriers of finite height certainly do exist. Let us see what the wave functions and energy levels of a particle in such a well are.

Figure 5.7 shows a potential well with square corners that is U high and L wide and contains a particle whose energy E is less than U . According to classical mechanics, when the particle strikes the sides of the well, it bounces off without entering regions I and III. In quantum mechanics, the particle also bounces back and forth, but now it has a certain probability of penetrating into regions I and III even though $E < U$.

In regions I and III Schrödinger's steady-state equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - U)\psi = 0$$

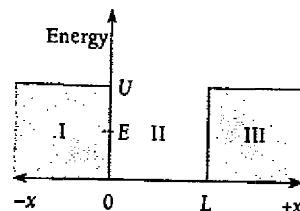


Figure 5.7 A square potential well with finite barriers. The energy E of the trapped particle is less than the height U of the barriers.

which we can rewrite in the more convenient form

$$\frac{d^2\psi}{dx^2} - a^2\psi = 0 \quad \begin{cases} x < 0 \\ x > L \end{cases} \quad (5.53)$$

where

$$a = \frac{\sqrt{2m(U - E)}}{\hbar} \quad (5.54)$$

The solutions to Eq. (5.53) are real exponentials:

$$\psi_1 = Ce^{ax} + De^{-ax} \quad (5.55)$$

$$\psi_{II} = Fe^{ax} + Ge^{-ax} \quad (5.56)$$

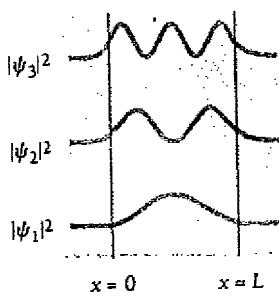
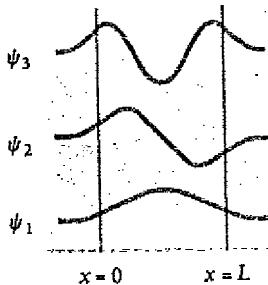


Figure 5.8 Wave functions and probability densities of a particle in a finite potential well. The particle has a certain probability of being found outside the wall.

Both ψ_1 and ψ_{II} must be finite everywhere. Since $e^{-ax} \rightarrow \infty$ as $x \rightarrow -\infty$ and $e^{ax} \rightarrow \infty$ as $x \rightarrow \infty$, the coefficients D and F must therefore be 0. Hence we have

$$\psi_1 = Ce^{ax} \quad (5.57)$$

$$\psi_{II} = Ge^{-ax} \quad (5.58)$$

These wave functions decrease exponentially inside the barriers at the sides of the well.

Within the well Schrödinger's equation is the same as Eq. (5.37) and its solution is again

$$\psi_{II} = A \sin \frac{\sqrt{2mE}}{\hbar} x + B \cos \frac{\sqrt{2mE}}{\hbar} x \quad (5.59)$$

In the case of a well with infinitely high barriers, we found that $B = 0$ in order that $\psi = 0$ at $x = 0$ and $x = L$. Here, however, $\psi_{II} = C$ at $x = 0$ and $\psi_{II} = G$ at $x = L$, so both the sine and cosine solutions of Eq. (5.59) are possible.

For either solution, both ψ and $d\psi/dx$ must be continuous at $x = 0$ and $x = L$: the wave functions inside and outside each side of the well must not only have the same value where they join but also the same slopes, so they match up perfectly. When these boundary conditions are taken into account, the result is that exact matching only occurs for certain specific values E_n of the particle energy. The complete wave functions and their probability densities are shown in Fig. 5.8.

Because the wavelengths that fit into the well are longer than for an infinite well of the same width (see Fig. 5.5), the corresponding particle momenta are lower (we recall that $\lambda = h/p$). Hence the energy levels E_n are lower for each n than they are for a particle in an infinite well.

5.10 TUNNEL EFFECT

A particle without the energy to pass over a potential barrier may still tunnel through it

Although the walls of the potential well of Fig. 5.7 were of finite height, they were assumed to be infinitely thick. As a result the particle was trapped forever even though it could penetrate the walls. We next look at the situation of a particle that strikes a potential barrier of height U , again with $E < U$, but here the barrier has a finite width (Fig. 5.9). What we will find is that the particle has a certain probability—not

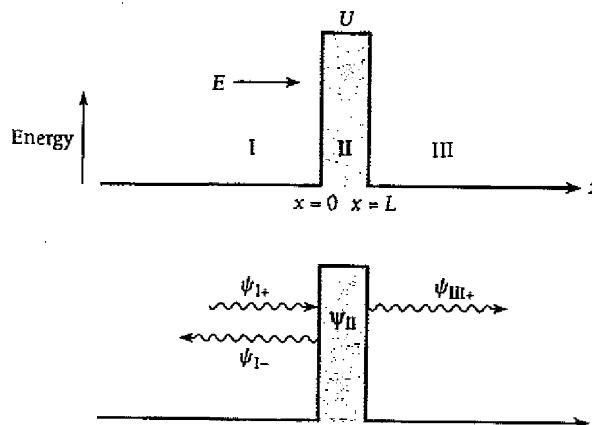


Figure 5.9 When a particle of energy $E < U$ approaches a potential barrier, according to classical mechanics the particle must be reflected. In quantum mechanics, the de Broglie waves that correspond to the particle are partly reflected and partly transmitted, which means that the particle has a finite chance of penetrating the barrier.

necessarily great, but not zero either—of passing through the barrier and emerging on the other side. The particle lacks the energy to go over the top of the barrier, but it can nevertheless tunnel through it, so to speak. Not surprisingly, the higher the barrier and the wider it is, the less the chance that the particle can get through.

The tunnel effect actually occurs, notably in the case of the alpha particles emitted by certain radioactive nuclei. As we shall learn in Chap. 12, an alpha particle whose kinetic energy is only a few MeV is able to escape from a nucleus whose potential wall is perhaps 25 MeV high. The probability of escape is so small that the alpha particle might have to strike the wall 10^{38} or more times before it emerges, but sooner or later it does get out. Tunneling also occurs in the operation of certain semiconductor diodes (Sec. 10.7) in which electrons pass through potential barriers even though their kinetic energies are smaller than the barrier heights.

Let us consider a beam of identical particles all of which have the kinetic energy E . The beam is incident from the left on a potential barrier of height U and width L , as in Fig. 5.9. On both sides of the barrier $U = 0$, which means that no forces act on the particles there. The wave function ψ_{I+} represents the incoming particles moving to the right and ψ_{I-} represents the reflected particles moving to the left; ψ_{III+} represents the transmitted particles moving to the right. The wave function ψ_{II} represents the particles inside the barrier, some of which end up in region III while the others return to region I. The transmission probability T for a particle to pass through the barrier is equal to the fraction of the incident beam that gets through the barrier. This probability is calculated in the Appendix to this chapter. Its approximate value is given by

Approximate
transmission
probability

$$T = e^{-2k_2 L} \quad (5.60)$$

where

$$k_2 = \frac{\sqrt{2m(U - E)}}{\hbar} \quad (5.61)$$

and L is the width of the barrier.

Example 5.6

Electrons with energies of 1.0 eV and 2.0 eV are incident on a barrier 10.0 eV high and 0.50 nm wide. (a) Find their respective transmission probabilities. (b) How are these affected if the barrier is doubled in width?

Solution

(a) For the 1.0-eV electrons

$$\begin{aligned} k_2 &= \frac{\sqrt{2m(U - E)}}{\hbar} \\ &= \frac{\sqrt{(2)(9.1 \times 10^{-31} \text{ kg})[(10.0 - 1.0) \text{ eV}](1.6 \times 10^{-19} \text{ J/eV})}}{1.054 \times 10^{-34} \text{ J} \cdot \text{s}} \\ &= 1.6 \times 10^{10} \text{ m}^{-1} \end{aligned}$$

Since $L = 0.50 \text{ nm} = 5.0 \times 10^{-10} \text{ m}$, $2k_2 L = (2)(1.6 \times 10^{10} \text{ m}^{-1})(5.0 \times 10^{-10} \text{ m}) = 16$, and the approximate transmission probability is

$$T_1 = e^{-2k_2 L} = e^{-16} = 1.1 \times 10^{-7}$$

One 1.0-eV electron out of 8.9 million can tunnel through the 10-eV barrier on the average. For the 2.0-eV electrons a similar calculation gives $T_2 = 2.4 \times 10^{-7}$. These electrons are over twice as likely to tunnel through the barrier.

(b) If the barrier is doubled in width to 1.0 nm, the transmission probabilities become

$$T'_1 = 1.3 \times 10^{-14} \quad T'_2 = 5.1 \times 10^{-14}$$

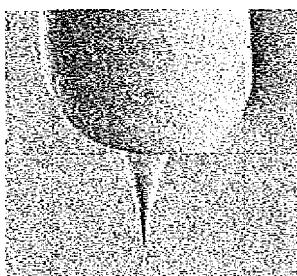
Evidently T is more sensitive to the width of the barrier than to the particle energy here.

Scanning Tunneling Microscope

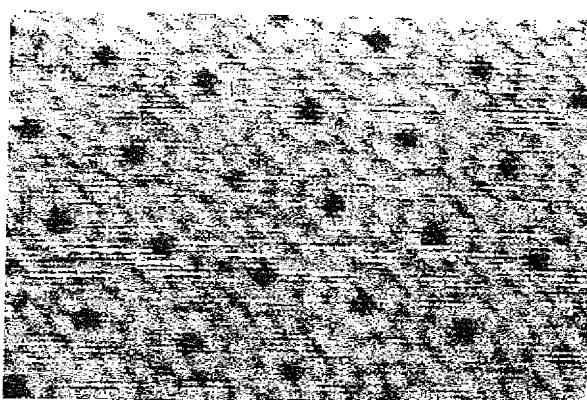
The ability of electrons to tunnel through a potential barrier is used in an ingenious way in the scanning tunneling microscope (STM) to study surfaces on an atomic scale of size. The STM was invented in 1981 by Gert Binnig and Heinrich Rohrer, who shared the 1986 Nobel Prize in physics with Ernst Ruska, the inventor of the electron microscope. In an STM, a metal probe with a point so fine that its tip is a single atom is brought close to the surface of a conducting or semiconducting material. Normally even the most loosely bound electrons in an atom on a surface need several electron-volts of energy to escape—this is the work function discussed in Chap. 2 in connection with the photoelectric effect. However, when a voltage of only 10 mV or so is applied between the probe and the surface, electrons can tunnel across the gap between them if the gap is small enough, a nanometer or two.

According to Eq. (5.60) the electron transmission probability is proportional to e^{-L} , where L is the gap width, so even a small change in L (as little as 0.01 nm, less than a twentieth the diameter of most atoms) means a detectable change in the tunneling current. What is done is to move the probe across the surface in a series of closely spaced back-and-forth scans in about the same way an electron beam traces out an image on the screen of a television picture tube. The height of the probe is continually adjusted to give a constant tunneling current, and the adjustments are recorded so that a map of surface height versus position is built up. Such a map is able to resolve individual atoms on a surface.

How can the position of the probe be controlled precisely enough to reveal the outlines of individual atoms? The thickness of certain ceramics changes when a voltage is applied across them, a property called piezoelectricity. The changes might be several tenths of a nanometer per volt. In an STM, piezoelectric controls move the probe in x and y directions across a surface and in the z direction perpendicular to the surface.



The tungsten probe of a scanning tunneling microscope.



Silicon atoms on the surface of a silicon crystal form a regular, repeated pattern in this image produced by an STM.

Actually, the result of an STM scan is not a true topographical map of surface height but a contour map of constant electron density on the surface. This means that atoms of different elements appear differently, which greatly increases the value of the STM as a research tool.

Although many biological materials conduct electricity, they do so by the flow of ions rather than of electrons and so cannot be studied with STMs. A more recent development, the atomic force microscope (AFM) can be used on any surface, although with somewhat less resolution than an STM. In an AFM, the sharp tip of a fractured diamond presses gently against the atoms on a surface. A spring keeps the pressure of the tip constant, and a record is made of the deflections of the tip as it moves across the surface. The result is a map showing contours of constant repulsive force between the electrons of the probe and the electrons of the surface atoms. Even relatively soft biological materials can be examined with an AFM and changes in them monitored. For example, the linking together of molecules of the blood protein fibrin, which occurs when blood clots, has been watched with an AFM.

5.11 HARMONIC OSCILLATOR

Its energy levels are evenly spaced

Harmonic motion takes place when a system of some kind vibrates about an equilibrium configuration. The system may be an object supported by a spring or floating in a liquid, a diatomic molecule, an atom in a crystal lattice—there are countless examples on all scales of size. The condition for harmonic motion is the presence of a restoring force that acts to return the system to its equilibrium configuration when it is disturbed. The inertia of the masses involved causes them to overshoot equilibrium, and the system oscillates indefinitely if no energy is lost.

In the special case of simple harmonic motion, the restoring force F on a particle of mass m is linear; that is, F is proportional to the particle's displacement x from its equilibrium position and in the opposite direction. Thus

Hooke's law

$$F = -kx$$

This relationship is customarily called Hooke's law. From the second law of motion, $F = ma$, we have

$$-kx = m \frac{d^2x}{dt^2}$$

Harmonic oscillator $\frac{d^2x}{dt^2} + \frac{k}{m}x = 0$ (5.62)

There are various ways to write the solution to Eq. (5.62). A common one is

$$x = A \cos(2\pi\nu t + \phi) \quad (5.63)$$

where

Frequency of harmonic oscillator $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$ (5.64)

is the frequency of the oscillations and A is their amplitude. The value of ϕ , the phase angle, depends upon what x is at the time $t = 0$ and on the direction of motion then.

The importance of the simple harmonic oscillator in both classical and modern physics lies not in the strict adherence of actual restoring forces to Hooke's law, which is seldom true, but in the fact that these restoring forces reduce to Hooke's law for small displacements x . As a result, any system in which something executes small vibrations about an equilibrium position behaves very much like a simple harmonic oscillator.

To verify this important point, we note that any restoring force which is a function of x can be expressed in a Maclaurin's series about the equilibrium position $x = 0$ as

$$F(x) = F_{x=0} + \left(\frac{dF}{dx}\right)_{x=0} x + \frac{1}{2}\left(\frac{d^2F}{dx^2}\right)_{x=0} x^2 + \frac{1}{6}\left(\frac{d^3F}{dx^3}\right)_{x=0} x^3 + \dots$$

Since $x = 0$ is the equilibrium position, $F_{x=0} = 0$. For small x the values of x^2, x^3, \dots are very small compared with x , so the third and higher terms of the series can be neglected. The only term of significance when x is small is therefore the second one. Hence

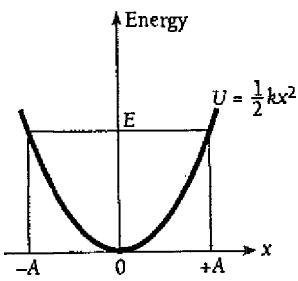


Figure 5.10 The potential energy of a harmonic oscillator is proportional to x^2 , where x is the displacement from the equilibrium position. The amplitude A of the motion is determined by the total energy E of the oscillator, which classically can have any value.

$$F(x) = \left(\frac{dF}{dx}\right)_{x=0} x$$

which is Hooke's law when $(dF/dx)_{x=0}$ is negative, as of course it is for any restoring force. The conclusion, then, is that all oscillations are simple harmonic in character when their amplitudes are sufficiently small.

The potential-energy function $U(x)$ that corresponds to a Hooke's law force may be found by calculating the work needed to bring a particle from $x = 0$ to $x = x$ against such a force. The result is

$$U(x) = - \int_0^x F(x) dx = k \int_0^x x dx = \frac{1}{2} kx^2 \quad (5.65)$$

which is plotted in Fig. 5.10. The curve of $U(x)$ versus x is a parabola. If the energy of the oscillator is E , the particle vibrates back and forth between $x = -A$ and $x = +A$, where E and A are related by $E = \frac{1}{2}kA^2$. Figure 8.18 shows how a nonparabolic potential energy curve can be approximated by a parabola for small displacements.

Even before we make a detailed calculation we can anticipate three quantum-mechanical modifications to this classical picture:

- 1 The allowed energies will not form a continuous spectrum but instead a discrete spectrum of certain specific values only.
- 2 The lowest allowed energy will not be $E = 0$ but will be some definite minimum $E = E_0$.
- 3 There will be a certain probability that the particle can penetrate the potential well it is in and go beyond the limits of $-A$ and $+A$.

Energy Levels

Schrödinger's equation for the harmonic oscillator is, with $U = \frac{1}{2}kx^2$,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2}kx^2 \right) \psi = 0 \quad (5.66)$$

It is convenient to simplify Eq. (5.75) by introducing the dimensionless quantities

$$y = \left(\frac{1}{\hbar} \sqrt{km} \right)^{1/2} x = \sqrt{\frac{2\pi m\nu}{\hbar}} x \quad (5.67)$$

and

$$\alpha = \frac{2E}{\hbar} \sqrt{\frac{m}{k}} = \frac{2E}{\hbar\nu} \quad (5.68)$$

where ν is the classical frequency of the oscillation given by Eq. (5.64). In making these substitutions, what we have done is change the units in which x and E are expressed from meters and joules, respectively, to dimensionless units.

In terms of y and α Schrödinger's equation becomes

$$\frac{d^2\psi}{dy^2} + (\alpha - y^2)\psi = 0 \quad (5.69)$$

The solutions to this equation that are acceptable here are limited by the condition that $\psi \rightarrow 0$ as $y \rightarrow \infty$ in order that

$$\int_{-\infty}^{\infty} |\psi|^2 dy = 1$$

Otherwise the wave function cannot represent an actual particle. The mathematical properties of Eq. (5.69) are such that this condition will be fulfilled only when

$$\alpha = 2n + 1 \quad n = 0, 1, 2, 3, \dots$$

Since $\alpha = 2E/\hbar\nu$ according to Eq. (5.68), the energy levels of a harmonic oscillator whose classical frequency of oscillation is ν are given by the formula

Energy levels of
harmonic oscillator $E_n = (n + \frac{1}{2})\hbar\nu \quad n = 0, 1, 2, 3, \dots \quad (5.70)$

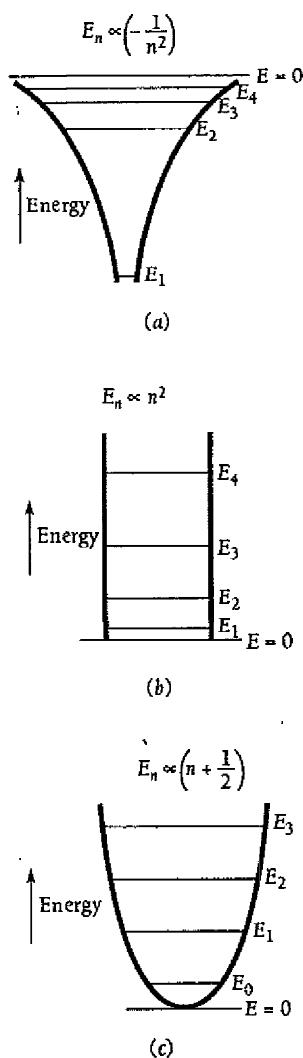


Figure 5.11 Potential wells and energy levels of (a) a hydrogen atom, (b) a particle in a box, and (c) a harmonic oscillator. In each case the energy levels depend in a different way on the quantum number n . Only for the harmonic oscillator are the levels equally spaced. The symbol \propto means "is proportional to."

The energy of a harmonic oscillator is thus quantized in steps of $\hbar\nu$.

We note that when $n = 0$,

Zero-point energy

$$E_0 = \frac{1}{2}\hbar\nu \quad (5.71)$$

which is the lowest value the energy of the oscillator can have. This value is called the **zero-point energy** because a harmonic oscillator in equilibrium with its surroundings would approach an energy of $E = E_0$ and not $E = 0$ as the temperature approaches 0 K.

Figure 5.11 is a comparison of the energy levels of a harmonic oscillator with those of a hydrogen atom and of a particle in a box with infinitely hard walls. The shapes of the respective potential-energy curves are also shown. The spacing of the energy levels is constant only for the harmonic oscillator.

Wave Functions

For each choice of the parameter α , there is a different wave function ψ_n . Each function consists of a polynomial $H_n(y)$ (called a **Hermite polynomial**) in either odd or even powers of y , the exponential factor $e^{-y^2/2}$, and a numerical coefficient which is needed for ψ_n to meet the normalization condition

$$\int_{-\infty}^{\infty} |\psi_n|^2 dy = 1 \quad n = 0, 1, 2 \dots$$

The general formula for the n th wave function is

$$\text{Harmonic oscillator} \quad \psi_n = \left(\frac{2m\nu}{\hbar} \right)^{1/4} (2^n n!)^{-1/2} H_n(y) e^{-y^2/2} \quad (5.72)$$

The first six Hermite polynomials $H_n(y)$ are listed in Table 5.2.

The wave functions that correspond to the first six energy levels of a harmonic oscillator are shown in Fig. 5.12. In each case the range to which a particle oscillating classically with the same total energy E_n would be confined is indicated. Evidently the particle is able to penetrate into classically forbidden regions—in other words, to exceed the amplitude A determined by the energy—with an exponentially decreasing probability, just as in the case of a particle in a finite square potential well.

It is interesting and instructive to compare the probability densities of a classical harmonic oscillator and a quantum-mechanical harmonic oscillator of the same energy. The upper curves in Fig. 5.13 show this density for the classical oscillator. The probability P of finding the particle at a given position is greatest at the endpoints of its motion,

Table 5.2 Some Hermite Polynomials

n	$H_n(y)$	α_n	E_n
0	1	1	$\frac{1}{2}\hbar\nu$
1	$2y$	3	$\frac{3}{2}\hbar\nu$
2	$4y^2 - 2$	5	$\frac{5}{2}\hbar\nu$
3	$8y^3 - 12y$	7	$\frac{7}{2}\hbar\nu$
4	$16y^4 - 48y^2 + 12$	9	$\frac{9}{2}\hbar\nu$
5	$32y^5 - 160y^3 + 120y$	11	$\frac{11}{2}\hbar\nu$

where it moves slowly, and least near the equilibrium position ($x = 0$), where it moves rapidly.

Exactly the opposite behavior occurs when a quantum-mechanical oscillator is in its lowest energy state of $n = 0$. As shown, the probability density $|\psi_0|^2$ has its maximum value at $x = 0$ and drops off on either side of this position. However, this disagreement becomes less and less marked with increasing n . The lower graph of Fig. 5.13 corresponds to $n = 10$, and it is clear that $|\psi_{10}|^2$ when averaged over x has approximately the general character of the classical probability P . This is another example of the correspondence principle mentioned in Chap. 4: In the limit of large quantum numbers, quantum physics yields the same results as classical physics.

It might be objected that although $|\psi_{10}|^2$ does indeed approach P when smoothed out, nevertheless $|\psi_{10}|^2$ fluctuates rapidly with x whereas P does not. However, this objection has meaning only if the fluctuations are observable, and the smaller the spacing of the peaks and hollows, the more difficult it is to detect them experimentally. The exponential "tails" of $|\psi_{10}|^2$ beyond $x = \pm A$ also decrease in magnitude with increasing n . Thus the classical and quantum pictures begin to resemble each other more and more the larger the value of n , in agreement with the correspondence principle, although they are very different for small n .

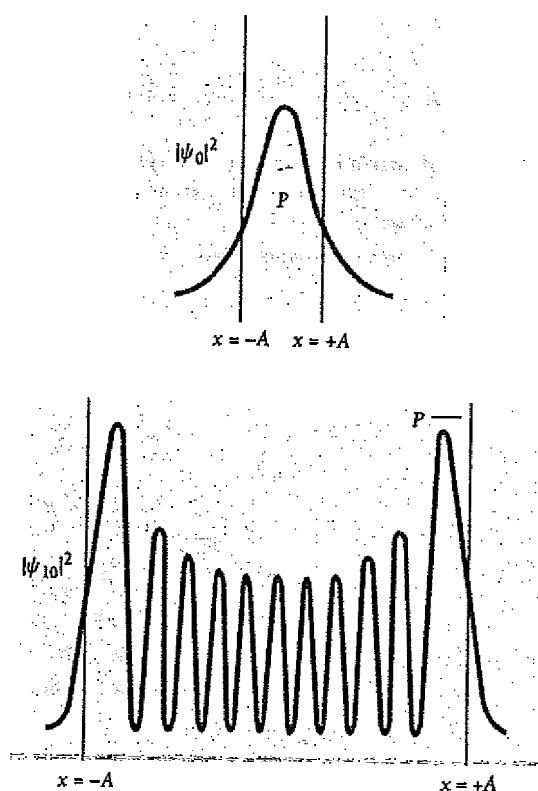


Figure 5.13 Probability densities for the $n = 0$ and $n = 10$ states of a quantum-mechanical harmonic oscillator. The probability densities for classical harmonic oscillators with the same energies are shown in white. In the $n = 10$ state, the wavelength is shortest at $x = 0$ and longest at $x = -A$.

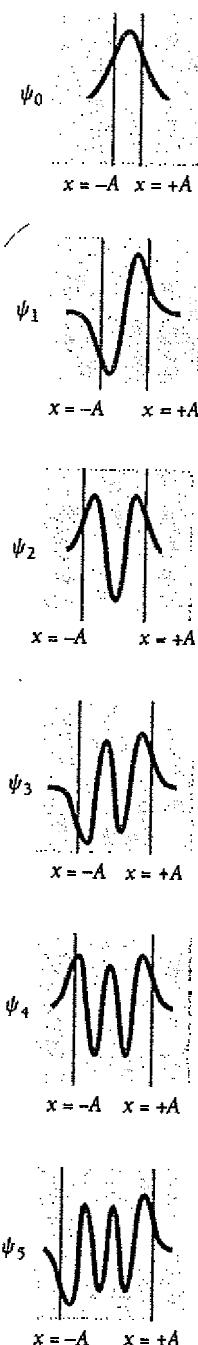


Figure 5.12 The first six harmonic-oscillator wave functions. The vertical lines show the limits $-A$ and $+A$ between which a classical oscillator with the same energy would vibrate.

Example 5.7

Find the expectation value $\langle x \rangle$ for the first two states of a harmonic oscillator.

Solution

The general formula for $\langle x \rangle$ is

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi|^2 dx$$

In calculations such as this it is easier to begin with y in place of x and afterward use Eq. (5.67) to change to x . From Eq. (5.72) and Table 5.2,

$$\psi_0 = \left(\frac{2m\nu}{\hbar} \right)^{1/4} e^{-y^2/2}$$

$$\psi_1 = \left(\frac{2m\nu}{\hbar} \right)^{1/4} \left(\frac{1}{2} \right)^{1/2} (2y) e^{-y^2/2}$$

The values of $\langle x \rangle$ for $n = 0$ and $n = 1$ will respectively be proportional to the integrals

$$n = 0: \int_{-\infty}^{\infty} y |\psi_0|^2 dy = \int_{-\infty}^{\infty} y e^{-y^2} dy = - \left[\frac{1}{2} e^{-y^2} \right]_{-\infty}^{\infty} = 0$$

$$n = 1: \int_{-\infty}^{\infty} y |\psi_1|^2 dy = \int_{-\infty}^{\infty} y^3 e^{-y^2} dy = - \left[\left(\frac{1}{4} + \frac{y^2}{2} \right) e^{-y^2} \right]_{-\infty}^{\infty} = 0$$

The expectation value $\langle x \rangle$ is therefore 0 in both cases. In fact, $\langle x \rangle = 0$ for all states of a harmonic oscillator, which could be predicted since $x = 0$ is the equilibrium position of the oscillator where its potential energy is a minimum.

Appendix to Chapter 5

The Tunnel Effect

We consider the situation that was shown in Fig. 5.9 of a particle of energy $E < U$ that approaches a potential barrier U high and L wide. Outside the barrier in regions I and III Schrödinger's equation for the particle takes the forms

$$\frac{d^2\psi_I}{dx^2} + \frac{2m}{\hbar^2} E \psi_I = 0 \quad (5.73)$$

$$\frac{d^2\psi_{III}}{dx^2} + \frac{2m}{\hbar^2} E \psi_{III} = 0 \quad (5.74)$$

The solutions to these equations that are appropriate here are

$$\psi_I = A e^{ik_1 x} + B e^{-ik_1 x} \quad (5.75)$$

$$\psi_{III} = F e^{ik_1 x} + G e^{-ik_1 x} \quad (5.76)$$

where

$$\begin{array}{ll} \text{Wave number} & k_1 = \frac{\sqrt{2mE}}{\hbar} = \frac{p}{\hbar} = \frac{2\pi}{\lambda} \\ \text{outside barrier} & \end{array} \quad (5.77)$$

is the wave number of the de Broglie waves that represent the particles outside the barrier.

Because

$$e^{i\theta} = \cos \theta + i \sin \theta$$

$$e^{-i\theta} = \cos \theta - i \sin \theta$$

these solutions are equivalent to Eq. (5.38)—the values of the coefficients are different in each case, of course—but are in a more suitable form to describe particles that are not trapped.

The various terms in Eqs. (5.75) and (5.76) are not hard to interpret. As was shown schematically in Fig. 5.9, $A e^{ik_1 x}$ is a wave of amplitude A incident from the left on the barrier. Hence we can write

$$\text{Incoming wave} \quad \psi_{I+} = A e^{ik_1 x} \quad (5.78)$$

This wave corresponds to the incident beam of particles in the sense that $|\psi_{I+}|^2$ is their probability density. If v_{I+} is the group velocity of the incoming wave, which equals the velocity of the particles, then

$$S = |\psi_{I+}|^2 v_{I+}$$

is the flux of particles that arrive at the barrier. That is, S is the number of particles per second that arrive there.

At $x = 0$ the incident wave strikes the barrier and is partially reflected, with

$$\text{Reflected wave} \quad \psi_{l-} = Be^{-ik_l x} \quad (5.79)$$

representing the reflected wave. Hence

$$\psi_l = \psi_{l+} + \psi_{l-} \quad (5.80)$$

On the far side of the barrier ($x > L$) there can only be a wave

$$\text{Transmitted wave} \quad \psi_{III+} = Fe^{ik_l x} \quad (5.81)$$

traveling in the $+x$ direction at the velocity v_{III+} since region III contains nothing that could reflect the wave. Hence $G = 0$ and

$$\psi_{III} = \psi_{III+} = Fe^{ik_l x} \quad (5.82)$$

The transmission probability T for a particle to pass through the barrier is the ratio

$$\text{Transmission probability} \quad T = \frac{|\psi_{III+}|^2 v_{III+}}{|\psi_{l+}|^2 v_{l+}} = \frac{FF^* v_{III+}}{AA^* v_{l+}} \quad (5.83)$$

between the flux of particles that emerges from the barrier and the flux that arrives at it. In other words, T is the fraction of incident particles that succeed in tunneling through the barrier. Classically $T = 0$ because a particle with $E < U$ cannot exist inside the barrier; let us see what the quantum-mechanical result is.

In region II Schrödinger's equation for the particles is

$$\frac{d^2\psi_{II}}{dx^2} + \frac{2m}{\hbar^2} (E - U) \psi_{II} = \frac{d^2\psi_{II}}{dx^2} - \frac{2m}{\hbar^2} (U - E) \psi_{II} = 0 \quad (5.84)$$

Since $U > E$ the solution is

$$\text{Wave function inside barrier} \quad \psi_{II} = Ce^{-k_2 x} + De^{k_2 x} \quad (5.85)$$

where the wave number inside the barrier is

$$\text{Wave number inside barrier} \quad k_2 = \frac{\sqrt{2m(U - E)}}{\hbar} \quad (5.86)$$

Since the exponents are real quantities, ψ_{II} does not oscillate and therefore does not represent a moving particle. However, the probability density $|\psi_{II}|^2$ is not zero, so there is a finite probability of finding a particle within the barrier. Such a particle may emerge into region III or it may return to region I.

Applying the Boundary Conditions

In order to calculate the transmission probability T we have to apply the appropriate boundary conditions to ψ_1 , ψ_{1l} , and ψ_{1r} . Fig. 5.14 shows the wave functions in regions I, II, and III. As discussed earlier, both ψ and its derivative $\partial\psi/\partial x$ must be continuous everywhere. With reference to Fig. 5.14, these conditions mean that for a perfect fit at each side of the barrier, the wave functions inside and outside must have the same value and the same slope. Hence at the left-hand side of the barrier

$$\text{Boundary conditions} \quad \left. \begin{array}{l} \psi_1 = \psi_{1l} \\ \frac{d\psi_1}{dx} = \frac{d\psi_{1l}}{dx} \end{array} \right\} x = 0 \quad (5.87)$$

$$\text{at } x = 0 \quad \left. \begin{array}{l} \psi_{1l} = \psi_{1r} \\ \frac{d\psi_{1l}}{dx} = \frac{d\psi_{1r}}{dx} \end{array} \right\} x = 0 \quad (5.88)$$

and at the right-hand side

$$\text{Boundary conditions} \quad \left. \begin{array}{l} \psi_{1l} = \psi_{1r} \\ \frac{d\psi_{1l}}{dx} = \frac{d\psi_{1r}}{dx} \end{array} \right\} x = L \quad (5.89)$$

$$\text{at } x = L \quad \left. \begin{array}{l} \psi_{1l} = \psi_{1r} \\ \frac{d\psi_{1l}}{dx} = \frac{d\psi_{1r}}{dx} \end{array} \right\} x = L \quad (5.90)$$

Now we substitute ψ_1 , ψ_{1l} , and ψ_{1r} from Eqs. (5.75), (5.81), and (5.85) into the above equations. This yields in the same order

$$A + B = C + D \quad (5.91)$$

$$ik_1 A - ik_1 B = -k_2 C + k_2 D \quad (5.92)$$

$$Ce^{-k_2 L} + De^{k_2 L} = Fe^{ik_1 L} \quad (5.93)$$

$$-k_2 Ce^{-k_2 L} + k_2 De^{k_2 L} = ik_1 F e^{ik_1 L} \quad (5.94)$$

Equations (5.91) to (5.94) may be solved for (A/F) to give

$$\left(\frac{A}{F} \right) = \left[\frac{1}{2} + \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1 + k_2)L} + \left[\frac{1}{2} - \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1 - k_2)L} \quad (5.95)$$

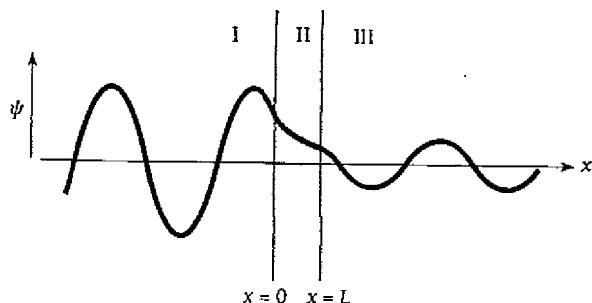


Figure 5.14 At each wall of the barrier, the wave functions inside and outside it must match up perfectly, which means that they must have the same values and slopes there.

Let us assume that the potential barrier U is high relative to the energy E of the incident particles. If this is the case, then $k_2/k_1 > k_1/k_2$ and

$$\frac{k_2}{k_1} - \frac{k_1}{k_2} \approx \frac{k_2}{k_1} \quad (5.96)$$

Let us also assume that the barrier is wide enough for ψ_{II} to be severely weakened between $x = 0$ and $x = L$. This means that $k_2 L \gg 1$ and

$$e^{k_2 L} \gg e^{-k_2 L}$$

Hence Eq. (5.95) can be approximated by

$$\left(\frac{A}{F} \right) = \left(\frac{1}{2} + \frac{ik_2}{4k_1} \right) e^{(ik_1+k_2)L} \quad (5.97)$$

The complex conjugate of (A/F) , which we need to compute the transmission probability T , is found by replacing i by $-i$ wherever it occurs in (A/F) :

$$\left(\frac{A}{F} \right)^* = \left(\frac{1}{2} - \frac{ik_2}{4k_1} \right) e^{(-ik_1+k_2)L} \quad (5.98)$$

Now we multiply (A/F) and $(A/F)^*$ to give

$$\frac{AA^*}{FF^*} = \left(\frac{1}{4} + \frac{k_2^2}{16k_1^2} \right) e^{2k_2 L}$$

Here $v_{III+} = v_{I+}$ so $v_{III+}/v_{I+} = 1$ in Eq. (5.83), which means that the transmission probability is

$$\text{Transmission probability } T = \frac{FF^*v_{III+}}{AA^*v_{I+}} = \left(\frac{AA^*}{FF^*} \right)^{-1} = \left[\frac{16}{4 + (k_2/k_1)^2} \right] e^{-2k_2 L} \quad (5.99)$$

From the definitions of k_1 , Eq. (5.77), and of k_2 , Eq. (5.86), we see that

$$\left(\frac{k_2}{k_1} \right)^2 = \frac{2m(U-E)/\hbar^2}{2mE/\hbar^2} = \frac{U}{E} - 1 \quad (5.100)$$

This formula means that the quantity in brackets in Eq. (5.99) varies much less with E and U than does the exponential. The bracketed quantity, furthermore, always is of the order of magnitude of 1 in value. A reasonable approximation of the transmission probability is therefore

Approximate transmission probability	$T = e^{-2k_2 L} \quad (5.101)$
--	---------------------------------

as stated in Sec. 5.10.

EXERCISES

Press on, and faith will catch up with you. —Jean D'Alembert

5.1 Quantum Mechanics

1. Which of the wave functions in Fig. 5.15 cannot have physical significance in the interval shown? Why not?
2. Which of the wave functions in Fig. 5.16 cannot have physical significance in the interval shown? Why not?

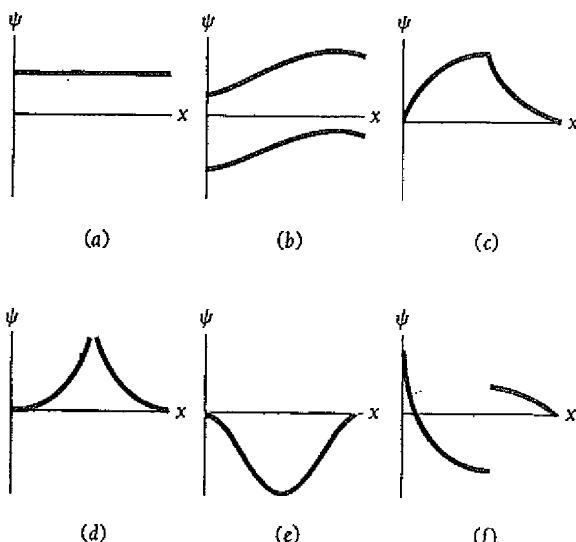


Figure 5.15

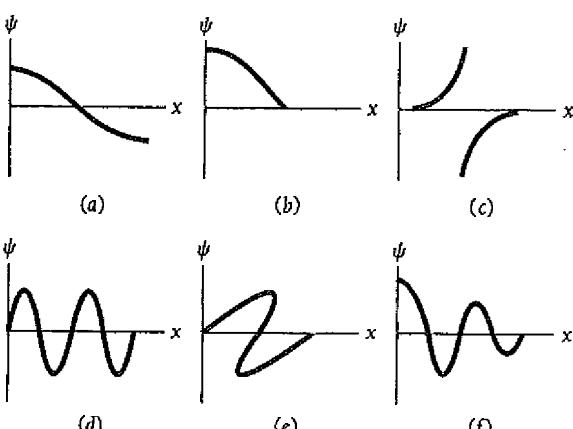


Figure 5.16

3. Which of the following wave functions cannot be solutions of Schrödinger's equation for all values of x ? Why not? (a) $\psi = A \sec x$; (b) $\psi = A \tan x$; (c) $\psi = Ae^x$; (d) $\psi = Ae^{-x^2}$.
4. Find the value of the normalization constant A for the wave function $\psi = Axe^{-x^2/2}$.
5. The wave function of a certain particle is $\psi = A \cos^2 x$ for $-\pi/2 < x < \pi/2$. (a) Find the value of A . (b) Find the probability that the particle be found between $x = 0$ and $x = \pi/4$.

5.2 The Wave Equation

6. The formula $y = A \cos \omega(t - x/v)$, as we saw in Sec. 3.3, describes a wave that moves in the $+x$ direction along a stretched string. Show that this formula is a solution of the wave equation, Eq. (5.3).
7. As mentioned in Sec. 5.1, in order to give physically meaningful results in calculations a wave function and its partial derivatives must be finite, continuous, and single-valued, and in addition must be normalizable. Equation (5.9) gives the wave function of a particle moving freely (that is, with no forces acting on it) in the $+x$ direction as

$$\Psi = Ae^{-(i/\hbar)(Et - px)}$$

where E is the particle's total energy and p is its momentum. Does this wave function meet all the above requirements? If not, could a linear superposition of such wave functions meet these requirements? What is the significance of such a superposition of wave functions?

5.4 Linearity and Superposition

8. Prove that Schrödinger's equation is linear by showing that

$$\Psi = a_1\Psi_1(x, t) + a_2\Psi_2(x, t)$$

is also a solution of Eq. (5.14) if Ψ_1 and Ψ_2 are themselves solutions.

5.6 Operators

9. Show that the expectation values $\langle px \rangle$ and $\langle xp \rangle$ are related by

$$\langle px \rangle - \langle xp \rangle = \frac{\hbar}{i}$$

This result is described by saying that p and x do not commute and it is intimately related to the uncertainty principle.

10. An eigenfunction of the operator d^2/dx^2 is $\sin nx$, where $n = 1, 2, 3, \dots$. Find the corresponding eigenvalues.

5.7 Schrödinger's Equation: Steady-State Form

11. Obtain Schrödinger's steady-state equation from Eq. (3.5) with the help of de Broglie's relationship $\lambda = h/mv$ by letting $y = \psi$ and finding $\partial^2\psi/\partial x^2$.

5.8 Particle in a Box

12. According to the correspondence principle, quantum theory should give the same results as classical physics in the limit of large quantum numbers. Show that as $n \rightarrow \infty$, the probability of finding the trapped particle of Sec. 5.8 between x and $x + \Delta x$ is $\Delta x/L$ and so is independent of x , which is the classical expectation.
13. One of the possible wave functions of a particle in the potential well of Fig. 5.17 is sketched there. Explain why the wavelength and amplitude of ψ vary as they do.

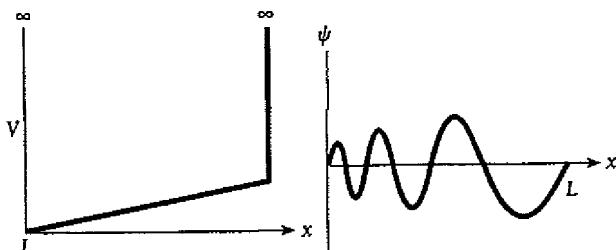


Figure 5.17

14. In Sec. 5.8 a box was considered that extends from $x = 0$ to $x = L$. Suppose the box instead extends from $x = x_0$ to $x = x_0 + L$, where $x_0 \neq 0$. Would the expression for the wave functions of a particle in this box be any different from those in the box that extends from $x = 0$ to $x = L$? Would the energy levels be different?
15. An important property of the eigenfunctions of a system is that they are orthogonal to one another, which means that

$$\int_{-\infty}^{\infty} \psi_n \psi_m dV = 0 \quad n \neq m$$

Verify this relationship for the eigenfunctions of a particle in a one-dimensional box given by Eq. (5.46).

16. A rigid-walled box that extends from $-L$ to L is divided into three sections by rigid interior walls at $-x$ and x , where $x < L$. Each section contains one particle in its ground state. (a) What is the total energy of the system as a function of x ? (b) Sketch $E(x)$ versus x . (c) At what value of x is $E(x)$ a minimum?
17. As shown in the text, the expectation value $\langle x \rangle$ of a particle trapped in a box L wide is $L/2$, which means that its average position is the middle of the box. Find the expectation value $\langle x^2 \rangle$.
18. As noted in Exercise 8, a linear combination of two wave functions for the same system is also a valid wave function. Find the normalization constant B for the combination

$$\psi = B \left(\sin \frac{\pi x}{L} + \sin \frac{2\pi x}{L} \right)$$

of the wave functions for the $n = 1$ and $n = 2$ states of a particle in a box L wide.

19. Find the probability that a particle in a box L wide can be found between $x = 0$ and $x = L/n$ when it is in the n th state.
20. In Sec. 3.7 the standard deviation σ of a set of N measurements of some quantity x was defined as

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - x_0)^2}$$

- (a) Show that, in terms of expectation values, this formula can be written as

$$\sigma = \sqrt{\langle (x - \langle x \rangle)^2 \rangle} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

- (b) If the uncertainty in position of a particle in a box is taken as the standard deviation, find the uncertainty in the expectation value $\langle x \rangle = L/2$ for $n = 1$. (c) What is the limit of Δx as n increases?

21. A particle is in a cubic box with infinitely hard walls whose edges are L long (Fig. 5.18). The wave functions of the particle are given by

$$\psi = A \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L} \quad \begin{matrix} n_x = 1, 2, 3, \dots \\ n_y = 1, 2, 3, \dots \\ n_z = 1, 2, 3, \dots \end{matrix}$$

Find the value of the normalization constant A .

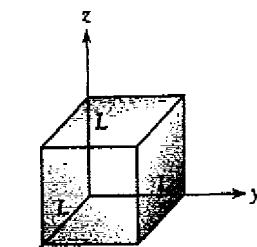


Figure 5.18 A cubic box.

22. The particle in the box of Exercise 21 is in its ground state of $n_x = n_y = n_z = 1$. (a) Find the probability that the particle will be found in the volume defined by $0 \leq x \leq L/4$, $0 \leq y \leq L/4$, $0 \leq z \leq L/4$. (b) Do the same for $L/2$ instead of $L/4$.
23. (a) Find the possible energies of the particle in the box of Exercise 21 by substituting its wave function ψ in Schrödinger's equation and solving for E . (Hint: Inside the box $U = 0$.) (b) Compare the ground-state energy of a particle in a one-dimensional box of length L with that of a particle in the three-dimensional box.

5.10 Tunnel Effect

24. Electrons with energies of 0.400 eV are incident on a barrier 3.00 eV high and 0.100 nm wide. Find the approximate probability for these electrons to penetrate the barrier.

25. A beam of electrons is incident on a barrier 6.00 eV high and 0.200 nm wide. Use Eq. (5.60) to find the energy they should have if 1.00 percent of them are to get through the barrier.

5.11 Harmonic Oscillator

26. Show that the energy-level spacing of a harmonic oscillator is in accord with the correspondence principle by finding the ratio $\Delta E_n/E_n$ between adjacent energy levels and seeing what happens to this ratio as $n \rightarrow \infty$.
27. What bearing would you think the uncertainty principle has on the existence of the zero-point energy of a harmonic oscillator?
28. In a harmonic oscillator, the particle varies in position from $-A$ to $+A$ and in momentum from $-p_0$ to $+p_0$. In such an oscillator, the standard deviations of x and p are $\Delta x = A/\sqrt{2}$ and $\Delta p = p_0/\sqrt{2}$. Use this observation to show that the minimum energy of a harmonic oscillator is $\frac{1}{2}\hbar\nu$.
29. Show that for the $n = 0$ state of a harmonic oscillator whose classical amplitude of motion is A , $y = 1$ at $x = A$, where y is the quantity defined by Eq. (5.67).
30. Find the probability density $|\psi_0|^2 dx$ at $x = 0$ and at $x = \pm A$ of a harmonic oscillator in its $n = 0$ state (see Fig. 5.13).
31. Find the expectation values $\langle x \rangle$ and $\langle x^2 \rangle$ for the first two states of a harmonic oscillator.
32. The potential energy of a harmonic oscillator is $U = \frac{1}{2}kx^2$. Show that the expectation value $\langle U \rangle$ of U is $E_0/2$ when the oscillator is in the $n = 0$ state. (This is true of all states of the harmonic oscillator, in fact.) What is the expectation value of the oscillator's kinetic energy? How do these results compare with the classical values of \bar{U} and \bar{K} ?
33. A pendulum with a 1.00-g bob has a massless string 250 mm long. The period of the pendulum is 1.00 s. (a) What is its zero-point energy? Would you expect the zero-point oscillations to be detectable? (b) The pendulum swings with a very small

amplitude such that its bob rises a maximum of 1.00 mm above its equilibrium position. What is the corresponding quantum number?

34. Show that the harmonic-oscillator wave function ψ_1 is a solution of Schrödinger's equation.
35. Repeat Exercise 34 for ψ_2 .
36. Repeat Exercise 34 for ψ_3 .
- Appendix: The Tunnel Effect**
37. Consider a beam of particles of kinetic energy E incident on a potential step at $x = 0$ that is U high, where $E > U$ (Fig. 5.19). (a) Explain why the solution $D e^{-ik_1 x}$ (in the notation of appendix) has no physical meaning in this situation, so that $D = 0$. (b) Show that the transmission probability here is $T = CC^*v'/AA^*v_1 = 4k_1^2/(k_1 + k')^2$. (c) A 1.00-mA beam of electrons moving at 2.00×10^6 m/s enters a region with a sharply defined boundary in which the electron speeds are reduced to 1.00×10^6 m/s by a difference in potential. Find the transmitted and reflected currents.
38. An electron and a proton with the same energy E approach a potential barrier whose height U is greater than E . Do they have the same probability of getting through? If not, which has the greater probability?

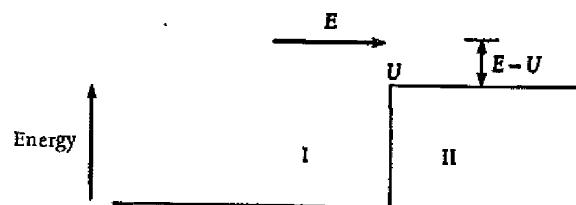


Figure 5.19