

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  $\text{He}^+$  and  $\text{Li}^{2+}$ —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  $5.3 \times 10^{-11}$  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  $5.3 \times 10^{-11}$  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**  $\Psi$  of a body. While  $\Psi$  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  $\Psi$ . The problem of quantum mechanics is to determine  $\Psi$  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  $\Psi$  is therefore taken as the product  $\Psi^*\Psi$  of  $\Psi$  and its **complex conjugate**  $\Psi^*$ . The complex conjugate of any function is obtained by replacing  $i(=\sqrt{-1})$  by  $-i$  wherever it appears in the function. Every complex function  $\Psi$  can be written in the form

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

where  $A$  and  $B$  are real functions. The complex conjugate  $\Psi^*$  of  $\Psi$  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  $\Psi$ , 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  $\Psi$ , the integral of  $|\Psi|^2$  over all space must be finite—the body is *somewhere*, after all. If

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

the particle does not exist, and the integral obviously cannot be  $\infty$  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  $\Psi$  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  $\Psi$ , 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,  $\Psi$  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  $\Psi$  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  $\Psi$  must be normalizable, which means that  $\Psi$  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  $\Psi$  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  $\Psi$ , 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  $\Psi$ .

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,

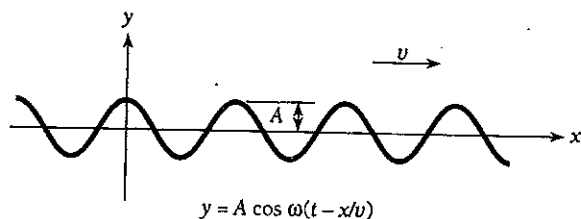


Figure 5.1 Waves in the  $xy$  plane traveling in the  $+x$  direction along a stretched string lying on the  $x$  axis.

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

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

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

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

This is convenient since we already know what  $\nu$  and  $\lambda$  are in terms of the total energy  $E$  and momentum  $p$  of the particle being described by  $\Psi$ . Because

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

we have

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

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  $\Psi$  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  $\Psi$ , which we can then solve for  $\Psi$  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  $\Psi$  and then to discuss the significance of the result.

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

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

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

$$\begin{aligned}\frac{\partial \Psi}{\partial t} &= -\frac{iE}{\hbar} \Psi \\ E\Psi &= -\frac{\hbar}{i} \frac{\partial \Psi}{\partial t}\end{aligned}\quad (5.11)$$

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  $\Psi$  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  $\Psi$  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  $\Psi$ . By this is meant that the equation has terms that contain  $\Psi$  and its derivatives but no terms independent of  $\Psi$  or that involve higher powers of  $\Psi$  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  $\Psi_1$  and  $\Psi_2$  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  $\Psi_1$  and  $\Psi_2$  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

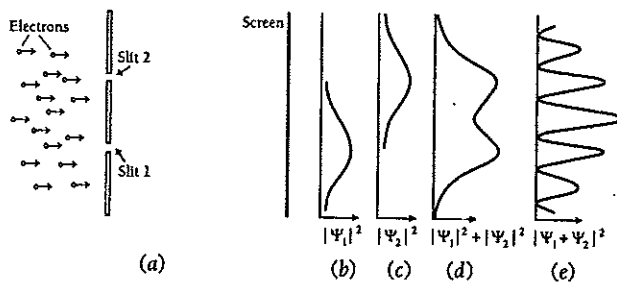


Figure 5.2 (a) Arrangement of double-slit experiment. (b) The electron intensity at the screen with only slit 1 open. (c) The electron intensity at the screen with only slit 2 open. (d) The sum of the intensities of (b) and (c). (e) The actual intensity at the screen with slits 1 and 2 both open. The wave functions  $\Psi_1$  and  $\Psi_2$  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  $\Psi$  of the wave functions  $\Psi_1$  and  $\Psi_2$  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

$$\bar{x} = \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + \cdots}{N_1 + N_2 + N_3 + \cdots} = \frac{\sum N_i x_i}{\sum N_i} \quad (5.16)$$

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  $\Psi_i$  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  $\Psi$  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  $\Psi$ . The result is

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

The expectation value  $\langle p \rangle$  for momentum cannot be calculated this way because, according to the uncertainty principles, 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  $\Psi$ , 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  $\Psi = Ae^{-(i/\hbar)(Et - px)}$  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

$$\begin{array}{ll} \text{Momentum} & \hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x} \\ \text{operator} & \end{array} \quad (5.23)$$

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

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

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

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

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

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  $\Psi^*$  and  $\Psi$  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  $\Psi$  of the system is known, the expectation value of  $G(x, p)$  is

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

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

## 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  $\Psi$  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  $\Psi$  is the product of a time-dependent function  $e^{-(iE/\hbar)t}$  and a position-dependent function  $\psi$ . 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  $\Psi$  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

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

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

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

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.