15

The Principles of Quantum Mechanics. II. The Postulates of Quantum Mechanics

OBJECTIVES

After studying this chapter, the student should:

1. understand the use of postulates as the foundation of quantum mechanics;
2. be able to solve a variety of problems involving mathematical operators;
3. be able to construct a quantum-mechanical operator from the classical expression for the corresponding operator;
4. be able to calculate expectation values for mechanical variables and determine whether the variable has a unique value for the state in question;
5. understand the determination of the state of a system by a set of measurements.

PRINCIPAL FACTS AND IDEAS

1. Quantum mechanics is based on a set of postulates.
2. The first two postulates establish the role of the wave function in quantum mechanics.
3. The third postulate of quantum mechanics establishes a connection between each mechanical variable and a mathematical operator.
4. The fourth postulate provides the means to obtain information about the values of mechanical variables.
5. The fifth postulate concerns the determination of the state of a system by experimental measurements.

15.1 The First Two Postulates of Quantum Mechanics

Werner Karl Heisenberg, 1901–1976, was a German physicist who invented matrix mechanics, a form of quantum mechanics equivalent to the Schrödinger formulation, and who discovered the uncertainty principle, for which he received the 1932 Nobel prize in physics.

Schrödinger did not derive his equation from other principles, and it is not based on experimental fact. We take the time-dependent Schrödinger equation as a **postulate**. A postulate is a fundamental assumption on which a theory is based, and the consequences of any postulates must be compared with experiment to validate the theory. Schrödinger, Heisenberg and others devised several postulates that form a consistent logical foundation for quantum mechanics. We will state five postulates in a form similar to that of Mandl[1] and Levine.[2] The first two postulates were introduced in Chapter 14, without calling them postulates. They are:

Postulate 1. *All information that can be obtained about the state of a mechanical system is contained in a wave function* Ψ, *which is a continuous, finite, and single-valued function of time and of the coordinates of the particles of the system.*

Postulate 2. *The wave function* Ψ *obeys the time-dependent Schrödinger equation*

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{15.1-1}$$

where $\hat{H}$ *is the Hamiltonian operator.*

Since the available information about the state is contained in the wave function, we can specify the state by specifying which wave function applies to the system at a given instant. There is a **one-to-one relationship** between the state of the system and its wave function. That is, to each state there corresponds one wave function, and to each wave function there corresponds one state. The terms "state" and "wave function" are often used interchangeably, and the wave function is sometimes referred to as the **state function**. Information about values of energy, momentum, etc., must be obtained from this wave function, instead of from values of coordinates and velocities as in classical mechanics. Specification of the state in quantum mechanics usually gives less information about the mechanical variables of the system than it does in classical mechanics, where specification of the state allows precise calculation of the values of all mechanical variables. In some cases we will be able to predict with certainty from a known wave function what result an error-free measurement of a mechanical variable will give. In other cases only statistical predictions can be made, even in the absence of experimental error. We will discuss this strange situation when we reach the fourth postulate.

There is no need to have a separate postulate for the time-independent Schrödinger equation. It can be derived from the time-dependent equation, as was shown in Chapter 14, by assuming that the wave function is a product of two factors,

$$\Psi(q, t) = \psi(q)\zeta(t) \tag{15.1-2}$$

where q stands for all of the coordinates of the particles in the system. With this assumption, the coordinate wave function ψ is an energy eigenfunction, and satisfies the time-independent Schrödinger equation. There are solutions to the time-dependent Schrödinger equation that are not of this form, but wave functions of the form of Eq. (15.1-2) are the most important wave functions in chemistry.

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[1] F. Mandl, *Quantum Mechanics*, Butterworths Scientific Publications, London, 1957, pp. 60ff.

[2] I. N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, N.J., 1991, pp. 173ff.

15.2

Mathematical Operators

The third postulate will assert that there is a mathematical operator that corresponds to each mechanical variable. A **mathematical operator** is a symbol standing for carrying out one or more mathematical operations. The Hamiltonian operator $\hat{H}$ in the Schrödinger equation is an important example of a quantum-mechanical operator. When the symbol for an operator is written to the left of the symbol for a function, the operation is to be applied to that function. For example, d/dx is a derivative operator, standing for differentiation of the function with respect to x; $h(z)$ is a multiplication operator, standing for multiplication of a function by the function $h(z)$; and c is also a multiplication operator, standing for multiplication of the function by the constant c. We will usually denote an operator by putting a letter with a caret (ˆ) over it.

The result of operating on a function with an operator is another function. If $f(x)$ is the function on which we operate and $g(x)$ is the resulting function, in most cases $g(x)$ is a different function from $f(x)$. Figure 15.1 shows an example of a function, $f(x) = \ln(x)$, and $g(x) = 1/x$, the result of operating on f with the derivative operator, d/dx.

Operator Algebra

There is an **operator algebra** in which we symbolically operate on operators themselves without specifying the functions on which the operators operate. For example, an operator can be set equal to another operator in an **operator equation**. The operator that always produces the same function as the one on which it operates is called the **identity operator** and is denoted by $\hat{E}$. It is equivalent to multiplying by unity:

$$\hat{E}f(q) = f(q) \tag{15.2-2}$$

where q is an abbreviation for the independent variables of the function f. Equation (15.2-1) can be written as an operator equation:

$$\hat{E} = 1 \tag{15.2-2}$$

An **operator equation** means that the operators on the two sides of the equation always produce the same result when applied to any well-behaved function, which is not written explicitly in the equation. It is not an operator equation if it must be applied to a certain function or set of functions in order to give an equality.

The **product of two operators** is defined as successive application of the operators, and is denoted by writing the two operator symbols adjacent to each other:

$$\hat{C}f(q) = \hat{A}\hat{B}f(q) = \hat{A}(\hat{B}f(q)) = \hat{A}g(q) \tag{15.2-3}$$

where $g(q)$ is the function produced when $\hat{B}$ operates on $f(q)$. The operator written on the right operates first. That is, the operator closest to the function operates first. The first equality in Eq. (15.2-3) is equivalent to the operator equation:

$$\hat{C} = \hat{A}\hat{B} \tag{15.2-4}$$

Operator multiplication is **associative**, which means that

$$\hat{A}\hat{B}\hat{C} = (\hat{A}\hat{B})\hat{C} = \hat{A}(\hat{B}\hat{C}) \tag{15.2-5}$$

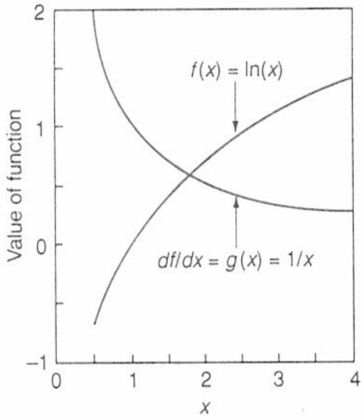

Figure 15.1. A Function and Its Derivative. This figure illustrates the fact that operating on a function generally yields a different function.

Operator multiplication is not necessarily **commutative**. It can happen that

$$\hat{A}\hat{B} \neq \hat{B}\hat{A} \quad \text{(in some cases)} \tag{15.2-6}$$

If $\hat{A}\hat{B} = \hat{B}\hat{A}$, the operators $\hat{A}$ and $\hat{B}$ are said to **commute**.

The **commutator** of two operators $\hat{A}$ and $\hat{B}$ is denoted by $[\hat{A}, \hat{B}]$ and is equal to the two-term operator

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad \text{(definition of commutator)} \tag{15.2-7}$$

If two operators commute, their commutator vanishes.

EXAMPLE 15.1

Find the commutator $\left[x, \dfrac{d}{dx}\right]$.

Solution

We let the commutator act an arbitrary function, $f(x)$:

$$\left[x, \frac{d}{dx}\right] f(x) = x\frac{df}{dx} - \frac{d(xf)}{dx} = x\frac{df}{dx} - x\frac{df}{dx} - f(x) = -f(x)$$

As an operator equation,

$$\left[x, \frac{d}{dx}\right] = -\hat{E} = -1$$

*Exercise 15.1

Find the commutator $\left[x^2, \dfrac{d}{dx}\right]$.

The following facts are useful:

1. Every operator commutes with itself.
2. Multiplication operators commute with each other.
3. A constant multiplication operator commutes with all other operators.
4. Operators that act on different variables commute with each other.
5. A derivative operator almost never commutes with a multiplication operator containing the same independent variable.

EXAMPLE 15.2

Find the operator $\hat{C} = (\hat{\mathscr{H}} + \hat{\mathscr{V}})^2$ if $\hat{\mathscr{H}}$ and $\hat{\mathscr{V}}$ are two operators that do not commute.

Solution

$$\hat{C} = (\hat{\mathscr{H}} + \hat{\mathscr{V}})^2 = (\hat{\mathscr{H}} + \hat{\mathscr{V}})(\hat{\mathscr{H}} + \hat{\mathscr{V}}) = (\hat{\mathscr{H}}^2 + \hat{\mathscr{H}}\hat{\mathscr{V}} + \hat{\mathscr{V}}\hat{\mathscr{H}} + \hat{\mathscr{V}}^2)$$

Terms like $\hat{\mathscr{H}}\hat{\mathscr{V}}$ and $\hat{\mathscr{V}}\hat{\mathscr{H}}$ are different from each other if the two operators do not commute.

***Exercise 15.2**

a. Find the operator $(\hat{\mathscr{H}} + \hat{\mathscr{V}})^3$ if $\hat{\mathscr{H}}$ and $\hat{\mathscr{V}}$ do not commute.
b. Find the operator $(\hat{A} + \hat{B})^3$ if $\hat{A}$ and $\hat{B}$ do commute.

The operators that are used in quantum mechanics have two important properties: they are linear and hermitian. We discuss these two properties before establishing the operators that correspond to specific mechanical variables.

Linear Operators

An operator $\hat{A}$ is **linear** if

$$\hat{A}[f(q) + g(q)] = \hat{A}f(q) + \hat{A}g(q) \quad \text{(linear operator)} \tag{15.2-8}$$

and if

$$\hat{A}[cf(q)] = c\hat{A}f(q) \quad \text{(linear operator)} \tag{15.2-9}$$

where c is an arbitrary constant and where f and g are arbitrary functions. That is, Eq. (15.2-8) and (15.2-9) must hold no matter what the functions f and g are, so long as the functions are well-behaved (for example, if $\hat{A}$ is a derivative operator, they must be differentiable).

Hermitian Operators

An operator $\hat{A}$ is **hermitian** if it obeys the relation

$$\int f^*\hat{A}g\,dq = \int (\hat{A}f)^*g\,dq = \int (\hat{A}^*f^*)g\,dq \quad \text{(hermitian operator)} \tag{15.2-10}$$

The functions f and g must obey boundary conditions such that the integral converges. All independent variables must be integrated over their entire ranges of values. For example, if q represents the cartesian coordinates of two particles that can move in three dimensions, the integral in this equation is a sixfold integral, and dq stands for $dx_1\,dy_1\,dz_1\,dx_2\,dy_2\,dz_2$. If the particles can move in all of space, the integration limits are $-\infty$ to ∞ for each cartesian coordinate. In Eq. (15.2-10), f^* denotes the complex conjugate of the function f and $\hat{A}^*$ denotes the complex conjugate of the operator $\hat{A}$. The complex conjugate of an operator is taken in the same way as is that of a complex number, by changing the sign of its imaginary part. A real quantity or a real operator is equal to its complex conjugate, and an imaginary quantity or an imaginary operator is the negative of its complex conjugate. Complex quantities are surveyed briefly in Appendix B.

Hermitian operators have several important properties:

1. Hermitian operators are linear.
2. Two hermitian operators are not required to commute with each other.
3. A hermitian operator has a set of eigenfunctions.
4. The eigenvalues of a hermitian operator are real.
5. Two eigenfunctions of a hermitian operator with different eigenvalues are orthogonal to each other.

6. Two commuting hermitian operators can have a set of common eigenfunctions.
7. The set of eigenfunctions of a hermitian operator form a complete set for expansion of functions obeying the same boundary conditions.

The proofs for Properties 4 and 5 are in Appendix B.

EXAMPLE 15.3

Show

a. the operator d/dx is linear;

b. it is not hermitian.

Solution

a. Linearity:

$$\frac{d}{dx}(f+g)=\frac{df}{dx}+\frac{dg}{dx}$$

$$\frac{d(cf)}{dx}=c\frac{df}{dx}$$

b. Integrating by parts, we obtain

$$\int_{-\infty}^{\infty} f(x)^*\frac{dg}{dx}\,dx=f(x)^*g(x)\Big|_{-\infty}^{\infty}-\int_{-\infty}^{\infty} g(x)\frac{df^*}{dx}\,dx$$

If f and g obey the same boundary conditions as wave functions, they will vanish at the limits of integration, and we have

$$\int_{-\infty}^{\infty} f(x)^*\frac{dg}{dx}\,dx=-\int_{-\infty}^{\infty}\frac{df^*}{dx}g(x)\,dx$$

which is the negative of what we would require for a hermitian operator.

Exercise 15.3

a. Show that the multiplication operator x is linear and hermitian.

b. Show that the operator $i(d/dx)$ is linear and hermitian.

c. Show that any hermitian operator is linear.

*Exercise 15.4

Show that the two hermitian operators x and $i(d/dx)$ do not commute and find their commutator.

Two functions f and g are **orthogonal** to each other if

$$\int f^*g\,dq=\int g^*f\,dq=0\quad\begin{pmatrix}\text{definition of}\\ \text{orthogonality}\end{pmatrix}\qquad(15.2\text{-}11)$$

where f^* is the complex conjugate of f and g^* is the complex conjugate of g. The two integrals in Eq. (15.2-11) are the complex conjugates of each other, so that if one vanishes, so does the other.

EXAMPLE 15.4

Show that the first two eigenfunctions of the Hamiltonian operator for the particle in a hard one-dimensional box are orthogonal to each other.

Solution

Since the wave function vanishes outside of the region $0 \leq x \leq a$, we can change the limits of the integral to 0 and a. In general, quantum-mechanical integrals are taken over all values of the coordinates. When we integrate wave functions between finite limits instead of between infinite limits, it is because for the particular system the wave functions vanish outside of the finite limits.

$$\int_{-\infty}^{\infty} \psi_1(x)\psi_2(x)\,dx = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)dx = \frac{2}{\pi}\int_0^{\pi} \sin(y)\sin(2y)\,dy = 0$$

where we have looked the integral up in Appendix C. One can also make a graph of the integrand and argue that the positive and negative contributions to the integral cancel each other.

Exercise 15.5

Show that the first two energy eigenfunctions of the harmonic oscillator are orthogonal to each other.

Property 6, that two commuting hermitian operators can have a set of common eigenfunctions, means that a set of functions $f_{jk}(q)$ can be found such that

$$\hat{A}f_{jk}(q) = a_j f_{jk}(q) \qquad (15.2\text{-}12a)$$

$$\hat{B}f_{jk}(q) = b_k f_{jk}(q) \qquad (15.2\text{-}12b)$$

where $\hat{A}$ and $\hat{B}$ are two hermitian operators that commute and where a_j and b_k are eigenvalues. Two indices are needed to enumerate all of the functions in the set, because several functions can have the same eigenvalue for $\hat{A}$ but have different eigenvalues for $\hat{B}$. An example of simultaneous eigenfunctions is found in the electronic wave functions of the hydrogen atom, which are simultaneous eigenfunctions of the Hamiltonian operator and two angular momentum operators.

The completeness specified in Property 7 means we can accurately represent any wave function as a **linear combination** (sum of functions multiplied by constant coefficients) of all of the eigenfunctions of a hermitian operator if the function obeys the same boundary conditions as the eigenfunctions:

$$\psi = \sum_{j=1}^{\infty} c_j f_j \qquad (15.2\text{-}13)$$

where $f_1, f_2, f_3, \ldots$ are the set of eigenfunctions of some hermitian operator $\hat{A}$, having eigenvalues $a_1, a_2, a_3, \ldots$. The wave function ψ is said to be **expanded** in terms of the set of functions $f_1, f_2, f_3, \ldots$. This set of functions $f_1, f_2, f_3, \ldots$ is called the **basis set**. Sometimes the notation $\{f\}$ or $\{f_j\}$ is used to represent the entire set of functions. The coefficients $c_1, c_2, c_3, \ldots$ are called the **expansion coefficients**, and must have values chosen to represent the specific function ψ. Equation (15.2-13) corresponds to the principle of superposition, already mentioned in Chapter 14 in connection with waves in a flexible string. The sine and cosine functions in a Fourier series are an example of a complete set of functions for representing periodic functions. Although a general proof of this property for eigenfunctions of hermitian operators is lacking, it is generally accepted.

It is possible to represent a time-dependent wave function in terms of time-independent basis functions if the expansion coefficients are time-dependent. For example, we choose the energy eigenfunctions of a system as our basis functions and write

$$\Psi = \sum_{j=1}^{\infty} c_j(t)\psi_j \tag{15.2-14}$$

where $\psi_1, \psi_2, \ldots$ are the energy eigenfunctions (which are time-independent). This function can satisfy the time-dependent Schrödinger equation if the set of expansion coefficients have the proper time dependence.

Exercise 15.6

Show that the function Ψ in Eq. (15.2-14) satisfies the time-dependent Schrödinger equation if

$$c_j(t) = c_j(0)e^{-iE_jt/\hbar} \tag{15.2-15}$$

The result of this exercise shows that the wave function of a system at a given instant can be any function of the proper coordinates that satisfies the boundary conditions required of a wave function (continuity and finiteness). It will then evolve according to the time dependence of the expansion coefficients given in Eq. (15.2-15).

15.3

Postulate 3. Mathematical Operators Corresponding to Mechanical Variables in Quantum Mechanics

This postulate asserts that every mechanical variable has its own hermitian operator.

> **Postulate 3.** *There is a hermitian mathematical operator in one-to-one correspondence with every mechanical variable.*

Finding the Operator to Correspond with a Particular Variable

We begin by asserting that the Hamiltonian operator is the mathematical operator that is in one-to-one correspondence with the energy of a system. This is plausible because the operator $\hat{H}$ occurs on one side of the time-independent Schrödinger equation and the eigenvalue E occurs on the other side of the equation. There is a **one-to-one correspondence** between $\hat{H}$ and E in this equation, which means that the variable E has a unique connection with the operator $\hat{H}$ and vice versa.

We next write the classical Hamiltonian (the classical expression for the energy), which is written as a function of momenta and coordinates (see Appendix D), and associate it with the Hamiltonian operator. For one particle moving in the direction of the x axis,

$$\frac{p_x^2}{2m} + \mathscr{V}(x) \leftrightarrow -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \mathscr{V}(x) \tag{15.3-1}$$

where p_x stands for the x component of the momentum, equal to mv_x. The symbol $\leftrightarrow$ means "is in one-to-one correspondence with." The potential energy function $\mathscr{V}(x)$ occurs on both sides of this equation in the same way, so we postulate that the operator for the potential energy is the operator for multiplication by the potential energy function.

$$\hat{\mathscr{V}} \leftrightarrow \mathscr{V}(x) \tag{15.3-2}$$

We extend this assumption, and postulate that *any function of coordinates corresponds to the operator for multiplication by that function.*

If the potential energy is canceled from the two sides of Eq. (15.3-1), the remaining terms indicate that the operator for the kinetic energy $\mathscr{K}$ is

$$\mathscr{K} \leftrightarrow \frac{1}{2m}\hat{p}_x^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{15.3-3}$$

The operator for the square of the x component of the momentum is therefore

$$\hat{p}_x^2 = -\hbar^2\frac{d^2}{dx^2} \tag{15.3-4}$$

The operator for the square of a momentum component must be the square of the operator for that momentum component. The square of an operator means operating twice with the operator. Therefore, the operator for p_x is

$$p_x \leftrightarrow \hat{p}_x = -i\hbar\frac{d}{dx} = \frac{\hbar}{i}\frac{d}{dx} \tag{15.3-5}$$

If more than one coordinate is involved, we replace the derivative in Eq. (15.3-5) by a partial derivative. Since any quantity has two square roots, the opposite sign could also have been taken. The sign in Eq. (15.3-5) gives the momentum the correct sign when a particle is moving in a known direction (see Problem 15.37).

We complete the third postulate by the additional assumption that the pattern of Eq. (15.3-5) holds for all cartesian momentum components and all functions of momentum components: *The quantum-mechanical operator for any mechanical variable is obtained by (1) expressing the quantity classically in terms of cartesian coordinates and cartesian momentum components and (2) replacing the momentum components by $\hbar/i$ times the derivative with respect to the corresponding coordinate.* If the use of a coordinate system other than cartesian coordinates is required in a particular problem, the expression for an operator is constructed in cartesian coordinates and then transformed to the other coordinate system. The operator must be hermitian, and it must be verified by comparison of its action with experimental fact.

We can now obtain the Hamiltonian operator for motion in three dimensions, Eq. (14.4-24). For one particle moving in three dimensions

$$\mathscr{K} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \tag{15.3-6a}$$

and

$$\hat{\mathscr{K}} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{15.3-6b}$$

EXAMPLE 15.5

Construct the operator for the z component of the angular momentum of one particle about the origin of a cartesian coordinate system.

Solution

The angular momentum is defined in Appendix D as the vector product (cross product)

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{15.3-7}$$

The expression for the z component is

$$L_z = xp_y - yp_x \tag{15.3-8}$$

The operator for this component is

$$\hat{L}_z = \frac{\hbar}{i}\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right] \tag{15.3-9}$$

The expressions for $\hat{L}_x$ and $\hat{L}_y$ can be obtained similarly.

*Exercise 15.7

a. Construct the operator for $\hat{L}_x$.
b. Construct the operator for $\hat{L}_y$.
c. Construct the operator for $\hat{L}_z^2$.

EXAMPLE 15.6

For motion in the x–y plane, transform the expression for $\hat{L}_z$ to plane polar coordinates.

Solution

The necessary relations are

$$\phi = \arctan(y/x) \qquad \rho^2 = (x^2 + y^2)$$

If f is an arbitrary function of x and y and is also expressible as a function of ρ and ϕ, then

$$x\frac{\partial f}{\partial y} = x\frac{\partial f}{\partial \phi}\frac{\partial \phi}{\partial y} + x\frac{\partial f}{\partial \rho}\frac{\partial \rho}{\partial y} = x\frac{\partial f}{\partial \phi}\frac{x}{x^2+y^2} + x\frac{\partial f}{\partial \rho}\frac{y}{(x^2+y^2)^{1/2}}$$

$$y\frac{\partial f}{\partial x} = y\frac{\partial f}{\partial \phi}\frac{\partial \phi}{\partial x} + y\frac{\partial f}{\partial \rho}\frac{\partial \rho}{\partial x} = y\frac{\partial f}{\partial \phi}\frac{-y}{x^2+y^2} - y\frac{\partial f}{\partial \rho}\frac{x}{(x^2+y^2)^{1/2}}$$

Since the second terms cancel,

$$\hat{L}_z f = \frac{\hbar}{i}\left(\frac{\partial f}{\partial \phi}\frac{x^2}{x^2+y^2} - \frac{\partial f}{\partial \phi}\frac{-y^2}{x^2+y^2}\right) = \frac{\hbar}{i}\frac{\partial f}{\partial \phi}$$

so that

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi} \tag{15.3-10}$$

This operator equation also holds for spherical polar coordinates and for cylindrical polar coordinates in three dimensions.

Example 15.6 illustrates the procedure that must be used if an operator is needed in other than cartesian coordinates. The operator is first written in cartesian coordinates and then transformed to another coordinate system. The expression for the operator $\hat{L}_z$ in Eq. (15.3-10) will be important in our later discussions of atomic and molecular wave functions. We will also use the expression for $\hat{L}^2$ in spherical polar coordinates, which we present without derivation:

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta} + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right] \tag{15.3-11}$$

Equation (15.3-11) can also be written

$$\hat{L}^2 = -\hbar^2\left[\frac{\partial^2}{\partial^2\theta} + \cot(\theta)\frac{\partial}{\partial\theta} + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right] \tag{15.3-12}$$

EXAMPLE 15.7

Find the commutator $[\hat{x}, \hat{p}_x]$.

Solution

Operate on an arbitrary function $f(x)$:

$$[\hat{x}, \hat{p}_x]f = \frac{\hbar}{i}\left[x\frac{\partial f}{\partial x} - \frac{\partial(xf)}{\partial x}\right] = -\frac{\hbar}{i}f$$

so that

$$[\hat{x}, \hat{p}_x] = -\frac{\hbar}{i} = i\hbar \tag{15.3-13}$$

This example was solved by operating on an arbitrary function. The result does not depend on what this function is.

The commutation relations between operators are important. Some authors find the form of $\hat{p}_x$ by postulating that the commutation relation of Eq. (15.3-13) and its analogues must hold, instead of deducing the form of $\hat{p}_x$ by inspecting the Hamiltonian operator.

Exercise 15.8

*a. Find the commutator $[\hat{p}_x, \hat{p}_y]$.
b. Show that $[\hat{L}_x, \hat{p}_y] = i\hbar\hat{p}_z$.

15.4 Postulate 4. Expectation Values

The first postulate of quantum mechanics asserts that the wave function of a system determines its state. Any information about the values of mechanical variables must therefore be obtained from the wave function. The fourth postulate provides the methods for obtaining this information:

Postulate 4: (a) *If a mechanical variable A is measured without experimental error, the only possible measured values of a variable A are eigenvalues of the operator* $\hat{A}$ *that corresponds to A.*

(b) *The expectation value of the error-free measurement of a mechanical variable A can be calculated from the formula*

$$\langle A\rangle = \frac{\int \Psi^* \hat{A} \Psi \, dq}{\int \Psi^* \Psi \, dq} \tag{15.4-1}$$

where $\hat{A}$ is the operator corresponding to the variable A, and where $\Psi = \Psi(q, t)$ is the wave function corresponding to the state of the system immediately prior to the measurement.

As is the case with all quantum-mechanical integrations, the integrals in Eq. (15.4-1) extend over all values of all of the coordinates, which are abbreviated by q. The **expectation value** is defined to be the predicted mean of a set of many measurements of the variable, given that the system is in the state corresponding to the wave function Ψ immediately prior to each measurement. It is therefore a statistical piece of information unless it can be shown that every measurement will give the same result.

If the wave function Ψ is a product of a coordinate wave function and a time-dependent factor as in Eq. (14.4-22), the expectation value can be calculated from the coordinate wave function. We substitute the product wave function into Eq. (15.4-1) and use the fact that the complex conjugate of any complex function can be obtained by changing the sign in front of every i symbol that occurs (see Appendix B):

$$(e^{iEt/\hbar})^* = e^{-iEt/\hbar}$$

Therefore,

$$\langle A\rangle = \frac{\int \psi^* e^{iEt/\hbar} \hat{A} \psi e^{-iEt/\hbar} \, dq}{\int \psi^* e^{iEt/\hbar} \psi e^{-iEt/\hbar} \, dq} \tag{15.4-2}$$

The two time-dependent factors in the denominator cancel. If the operator $\hat{A}$ is the operator for an ordinary mechanical variable, it does not depend on time. The time-dependent factor to its right can be factored through it, and cancels with the other time-dependent factor as in the denominator. Therefore,

$$\langle A\rangle = \frac{\int \psi^* \hat{A} \psi \, dq}{\int \psi^* \psi \, dq} \tag{15.4-3}$$

The expectation value in Eq. (15.4-3) is time-independent. This behavior occurs with any expectation value if the operator is independent of the time and if the wave function is the product of an energy eigenfunction and a time factor. A state corresponding to such a wave function is called a **stationary state**. For stationary states, coordinate wave functions can be used to calculate expectation values.

Normalization

There is a conventional way to simplify the formula for the expectation value. The denominator in Eq. (15.4-1) is the same whether we are calculating the expectation value of the angular momentum, the energy, or any other variable. We use the following fact: **If any wave function that satisfies the Schrödinger equation is multiplied by an arbitrary constant it will still satisfy the Schrödinger equation and will still give the same value for any expectation value.**

Exercise 15.9

a. Show that if a wave function Ψ satisfies the time-dependent Schrödinger equation

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

then the function $C\Psi$ also satisfies it, where C is any constant.

b. Show that if a wave function ψ satisfies the time-independent Schrödinger equation

$$\hat{H}\psi = E\psi$$

then the function $C\psi$ also satisfies it, where C is any constant.

c. Show that the formula in Eq. (15.4-1) for the expectation value is unchanged if Ψ is replaced by $C\Psi$, where C is any constant.

If we choose a value of a constant multiplying a wave function such that

$$\int \Psi^*\Psi\, dq = 1 \quad \text{(definition of normalization)} \tag{15.4-4}$$

the wave function Ψ is then said to be **normalized**. If a normalized wave function is used in Eq. (15.4-1), the expectation value is unchanged and the denominator in the equation equals unity.

$$\langle A\rangle = \int \Psi^*\hat{A}\Psi\, dq \quad (\Psi \text{ is a normalized wave function}) \tag{15.4-5}$$

If the time-dependent wave function in Eq. (15.4-4) is the product of a coordinate factor and a time-dependent factor, the coordinate factor is normalized if the full wave function is normalized.

Exercise 15.10

a. Show that if

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

and if

$$\int \Psi^*\Psi\, dq = 1$$

then

$$\int \psi^*\psi\, dq = 1$$

b. Carry out the integration to show that the harmonic oscillator coordinate wave function in Eq. (14.6-8) is normalized.

The Use of Postulate 4 to Obtain Information about Variables

Part (a) of the fourth postulate allows us to determine the list of possible values for any variable by solving the eigenvalue equation for that variable. If there is a discrete spectrum of eigenvalues, the variable is quantized (can take on values from a discrete list). This part of the postulate is not related to a particular state. Part (b) of the postulate provides the means to extract all possible information about mechanical variables from knowledge of the state of the system, but sometimes provides only statistical information about the values of state variables. We distinguish between two different cases. For certain systems, certain states, and certain variables, it is possible to make a precise prediction of the outcome of a measurement from knowledge of the wave function. We will refer to this case as case 1. For some states and some variables, the outcomes of individual measurements will be distributed over various values (all of which must be eigenvalues of the operator). Only statistical predictions can be made. We will refer to this case as case 2.

Position Measurements

Position measurements provide an important example of case 2. Consider the position of a particle that moves parallel to the x axis. Assume that we make a set of position measurements with the state of the system corresponding to the same wave function, $\Psi(x, t)$, just before each measurement. The expectation value of x is

$$\langle x \rangle = \int \Psi(x, t)^* x \Psi(x, t)\, dx \qquad (15.4\text{-}6)$$

where we assume that the wave function Ψ is normalized. We will not discuss the eigenfunctions of the position operator in detail, but all values of x can be eigenvalues and are thus possible outcomes of the position measurement. See Problem 15.33 for some information about these eigenfunctions and eigenvalues.

Since the multiplication operator x commutes with multiplication by Ψ^*, we can write

$$\langle x \rangle = \int \Psi(x, t)^* x \Psi(x, t)\, dx = \int x \Psi(x, t)^* \Psi(x, t)\, dx = \int x |\Psi(x, t)|^2\, dx \qquad (15.4\text{-}7)$$

where we use the fact that any quantity times its complex conjugate is equal to the square of the magnitude of the quantity (see Appendix B). If the wave function is a product of an energy eigenfunction and a time factor, the time factor cancels against its complex conjugate, as in Eq. (15.4-3):

$$\langle x \rangle = \int x \psi(x, t)^* \psi(x, t)\, dx = \int x |\psi(x, t)|^2\, dx \qquad (15.4\text{-}8)$$

EXAMPLE 15.8

Find the expectation value for the position of a particle in a one-dimensional hard box of length a if the coordinate wave function is the energy eigenfunction with $n = 1$.

Solution

The normalized particle-in-a-box energy eigenfunction is

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \qquad (15.4\text{-}9)$$

Since this wave function is normalized and since we are dealing with a stationary state, the expectation value for $n = 1$ can be written as in Eq. (15.4-8):

$$\langle x \rangle = \frac{2}{a} \int_0^a \sin\left(\frac{\pi x}{a}\right) x \sin\left(\frac{\pi x}{a}\right) dx = \frac{2}{a} \int_0^a x \sin^2\left(\frac{\pi x}{a}\right) dx \qquad (15.4\text{-}10)$$

Integrations like the one in this example are to be taken over all values of the coordinates. The wave function vanishes except in the region between $x = 0$ and $x = a$, so we omit the rest of the region of integration. We change variables and write

$$\langle x\rangle = \frac{2}{a}\left(\frac{a}{\pi}\right)^2 \int_0^{\pi} y \sin^2(y)\, dy = \frac{a}{2} \qquad (15.4\text{-}11)$$

The predicted mean position of the particle is the middle of the box. This is a reasonable result, since the two halves of the box are like mirror images of each other.

Exercise 15.11

a. Show that the particle-in-a-box energy eigenfunction given in Eq. (15.4-9) is normalized.
b. Verify the value of the integral used in Example 15.8 without using a table.

*Exercise 15.12

Find $\langle x\rangle$ for a particle in a hard one-dimensional box of length a for the $n = 2$ state.

Probability Densities

We have asserted that position measurements belong to case 2 for almost any kind of wave function. The mean of a set of many repeated measurements of the position of a particle is well defined, but individual members of the set can have different values. We now want to study the probabilities of different outcomes of the position measurement. In Chapter 10, we defined a probability density for a variable denoted by u:

$$\begin{pmatrix} \text{Probability that } u \text{ lies} \\ \text{between } u' \text{ and } u' + du \end{pmatrix} = f(u')\, du$$

The function $f(u)$ is a probability per unit length on the u axis. The mean value of u is given by

$$\langle u\rangle = \int u f(u)\, du \qquad (15.4\text{-}12)$$

Comparison of Eq. (15.4-7) with Eq. (15.4-12) shows that the probability of finding the particle between x and $x + dx$ is equal to

$$(\text{Probability}) = |\Psi(x, t)|^2\, dx \qquad (15.4\text{-}13)$$

or

$$(\text{Probability density}) = |\Psi(x, t)|^2 \qquad (15.4\text{-}14)$$

This is an important result, which we will generalize to three dimensions and to more than one particle. *The square of the magnitude of the wave function is the probability density for finding the particle or particles.* For a single cartesian coordinate, the probability density is a probability per unit length. At any location where the square of the wave function is nonzero, there is some probability of finding the particle. Where the wave function vanishes there is no probability of finding the particle. This corresponds to our earlier assertion that a wave function equal to zero corresponds to the absence of a particle.

For the motion of one particle in three dimensions, the probability that the particle lies between x and $x + dx$ in the x direction, between y and $y + dy$ in the y direction, and between z and $z + dz$ in the z direction is analogous to that in Eq. (15.4-13):

$$(\text{Probability}) = |\Psi(x, y, z, t)|^2\, dx\, dy\, dz \qquad (15.4\text{-}15)$$

The probability density in this case is a probability per unit volume in three dimensions.

$$(\text{Probability density}) = |\Psi(x, y, z, t)|^2 \qquad (15.4\text{-}16)$$

To obtain the probability that a particle is to be found in a finite region, we integrate $|\Psi(x, y, z, t)|^2$ over the region of interest.

17

*Exercise 15.13

For a particle in a three-dimensional hard box, the eigenfunction of the Hamiltonian operator is given by Eq. (14.5-39). For the $n_x = 1$, $n_y = 1$, $n_z = 1$ state, find the probability that the particle is in a small rectangular region in the center of the box such that the length of the region in each direction is equal to 1.000% of the length of the box in that direction. Avoid an integration by proceeding as though the wave function were constant in the region so that the probability is the product of the wave function squared times the volume of the region.

For the motion of two particles in three dimensions, the probability that the first particle is between x_1 and $x_1 + dx_1$ and between y_1 and $y_1 + dy_1$ and between z_1 and $z_1 + dz_1$ and that simultaneously the second particle is between x_2 and $x_2 + dx_2$ and between y_2 and $y_2 + dy_2$ and between z_2 and $z_2 + dz_2$ is

$$\begin{aligned}(\text{Probability}) &= |\Psi(x_1, y_1, z_1, x_2, y_2, z_2, t)|^2\, dx_1\, dy_1\, dz_1\, dx_2\, dy_2\, dz_2 \\ &= |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2 \qquad (15.4\text{-}17)\end{aligned}$$

$$(\text{Probability density}) = |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 \qquad (15.4\text{-}18)$$

That is, $|\Psi|^2$ is a probability per unit six-dimensional volume. For a system with n particles the square of the magnitude of the wave function is a probability density in a space with $3n$ dimensions (a probability per unit $3n$-dimensional volume).

If a wave function is normalized, its probability density is also normalized. The total probability of all positions is equal to the integral of the square of the magnitude of the wave function over all values of the coordinates, which equals unity for a normalized wave function. For a stationary state, in which the wave function is a product of a coordinate wave function and time factor, the probability density is time-independent:

$$|\Psi(x, t)|^2 = \psi(x)^* e^{iEt/\hbar} \psi(x) e^{-iEt/\hbar} = \psi^*(x)\psi(x) = |\psi(x)|^2 \qquad (15.4\text{-}19)$$

The analogue of Eq. (15.4-19) can be written for a wave function that depends on more than one coordinate.

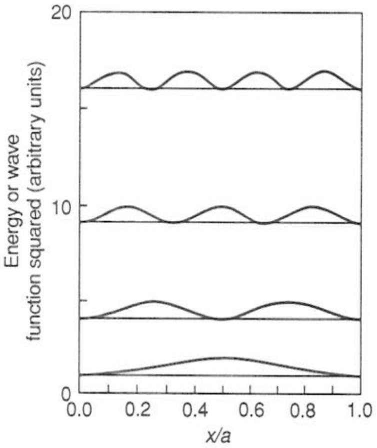

Figure 15.2. The Probability Density for Positions of a Particle in a One-Dimensional Hard Box. This diagram shows the squares of the energy eigenfunctions (probability densities) for the first four states of a particle in a one-dimensional hard box.

Figure 15.2 shows the probability density (square of the magnitude of the wave function) for four energy eigenfunctions of a particle in the box. These four graphs are placed at heights proportional to the energy eigenvalue corresponding to each wave function. These probability densities are very different from the predictions of classical mechanics. If the state of a classical particle in a box is known, the probability at a given time will be nonzero at only one point, as in Figure 15.3a. The classical

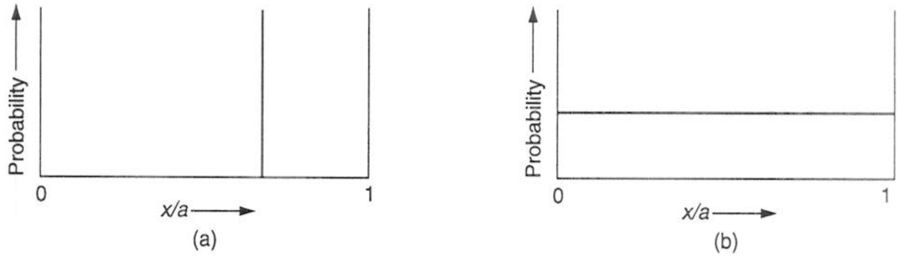

Figure 15.3. The Probability Density for Positions of a Particle in a One-Dimensional Hard Box according to Classical Mechanics. (a) **The instantaneous probability.** At a given time, there is no uncertainty about the position of the particle. (b) **The probability averaged over a long time.** The average probability density is uniform, with all parts of the box equally probable.

probability density averaged over a long time would be uniform, with all parts of the box being equally probable, as shown in Figure 15.3b.

The quantum-mechanical probability density for a stationary state of a particle in a box is time-independent, and is best compared with the time-average classical probability distribution. The probability is distributed over the entire box but is not uniform, and there are points at which the probability density vanishes. However, if a very large value of n is taken, these points become closer and closer together, as schematically shown in Figure 15.4, which is drawn for $n = 10$. For very large values of n, the probability density resembles that of the classical case, since the width of the oscillations in the curve become smaller than the experimental uncertainty of a real measurement. This behavior conforms to the **correspondence principle**, which states that for sufficiently large energies and masses, the behavior predicted by quantum mechanics approaches the behavior predicted by classical mechanics.

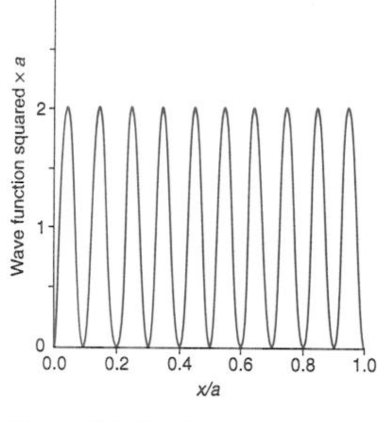

Figure 15.4. The Probability Density for Positions of a Particle in a One-Dimensional Hard Box for $n = 10$. This probability density resembles the time-averaged classical probability density more closely than does that of the lower-energy states.

EXAMPLE 15.9

For a particle in a one-dimensional box with $n = 2$, find the probability that the particle will be found in each of the regions making up thirds of the box.

Solution

For $0 < x < a/3$,

$$(\text{Probability}) = \int_0^{a/3} \psi(x)^2\,dx = \frac{2}{a}\int_0^{a/3} \sin^2\left(\frac{2\pi x}{a}\right)dx$$

$$= \frac{2}{a}\frac{a}{2\pi}\int_0^{2\pi/3} \sin^2(y)\,dy = \frac{1}{\pi}\left[\frac{y}{2} - \frac{1}{4}\sin(2y)\right]_0^{2\pi/3}$$

$$= \frac{1}{\pi}\left[\frac{\pi}{3} - \frac{1}{4}\sin(4\pi/3)\right] = 0.402249$$

The right one-third of the box will have the same probability as the left one-third. The probability of finding the particle in the center region will be

$$(\text{Probability}) = 1 - 2(0.402249) = 0.195501$$

Near a node, the probability density is relatively small. The node in the wave function at $x = a/2$ results in a smaller probability for the middle third of the box than for the left third or right third of the box.

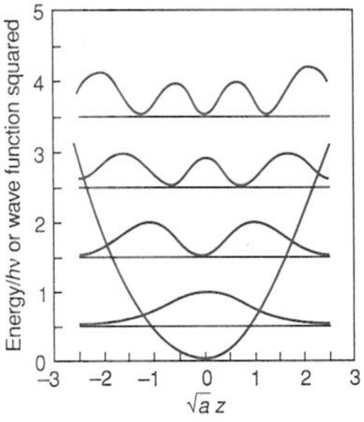

Figure 15.5. The Probability Density for the First Few Energy Eigenstates of the Harmonic Oscillator. Each wave function graph is placed at the height corresponding to its energy eigenvalue, and the potential energy is also plotted The point where the potential energy curve crosses the energy level line is the classical turning point.

*Exercise 15.14

From inspection of Figure 15.2, estimate the probability of finding the particle in the left one-third of the box for the $n = 1$ state. After making this estimate, make an accurate calculation of the probability.

Figure 15.5 shows the probability densities for the first few energy eigenfunctions of a harmonic oscillator. Each graph is placed at a height in the figure proportional to its energy eigenvalue, and the potential energy is also plotted in the figure. The classical turning point for each state is located where the axis for that state crosses the potential energy curve, since that is the point where the energy is all potential energy. The vertical axis is used for two different variables, as in Figure 15.2. The behavior of the harmonic oscillator probability density is qualitatively like that of the particle in a box, and the numbers of nodes follows the same pattern. However, for the harmonic oscillator the probability density does not vanish outside of the classically permitted region, but extends beyond the classical turning points. Penetration into a classically forbidden region is called **tunneling**. The name was chosen because a tunnel into a hillside allows access to a location under an inaccessible location of high gravitational potential energy.

Distinguishing Case 1 from Case 2

A common measure of the "spread" of a probability distribution is the **standard deviation**, which we have already defined in Eq. (10.2-38). The standard deviation for the measurement of a variable A is denoted by σ_A and defined by

$$\sigma_A = (\langle A^2\rangle - \langle A\rangle^2)^{1/2} \quad \text{(definition)} \tag{15.4-20}$$

The square of the standard deviation is called the **variance**.

Exercise 15.15

Show that application of the definition of the standard deviation in Eq. (15.4-20) to the gaussian probability distribution in Eq. (10.2-37) gives the same standard deviation as specified in that equation.

Calculation of the standard deviation provides a general way to distinguish case 1 from case 2. In case 1, all outcomes for repetition of a measurement will be equal, so that the standard deviation will equal zero. In case 2, the outcomes will be distributed statistically and the standard deviation will be nonzero.

EXAMPLE 15.10

Find the standard deviation for the position of a particle in a hard one-dimensional box of length a for the $n = 1$ state.

Solution

$$\begin{aligned}\langle x^2\rangle &= \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)x^2 \sin\left(\frac{\pi x}{a}\right)dx\\ &= \frac{2}{a}\left(\frac{a}{\pi}\right)^3\int_0^\pi y^2\sin(y)\,dy = a^2\left[\frac{1}{3}-\frac{1}{2\pi^2}\right] = 0.282673a^2\end{aligned}$$

From Example 15.8 we have $\langle x\rangle = a/2$, so that

$$\sigma_x = [0.282673a^2 - (a/2)^2]^{1/2} = 0.180756a$$

The fact that the standard deviation is nonzero shows that for this system and this wave function, case 2 applies to the position of the particle, as can be deduced from inspection of the probability distribution.

EXAMPLE 15.11

Calculate the probability that a particle in a one-dimensional hard box of length a will be found within one standard deviation of its mean position if the wave function is the $n = 1$ energy eigenfunction.

Solution

The probability is given by integrating the probability density:

$$(\text{Probability}) = \frac{2}{a}\int_{0.319244a}^{0.6807566a} \sin^2\left(\frac{\pi x}{a}\right) dx = \frac{2}{\pi}\int_{1.00293}^{2.13866} \sin^2(y)\, dy$$

$$= \frac{2}{\pi}\left[\frac{y}{2} - \frac{\sin(2y)}{4}\right]\Bigg|_{1.00293}^{2.13866} = 0.65017$$

This value is reasonably close to 0.683, which is the probability for a gaussian distribution that the variable will lie within one standard deviation of the mean. For most probability distributions, approximately two-thirds of a statistical population lie within one standard deviation of the mean.

*Exercise 15.16

a. Calculate the probability that a particle in a one-dimensional hard box will be found within one standard deviation of its mean position for the $n = 2$ state. Comment on the comparison with the fact that with a gaussian distribution the probability would be 0.683.

b. Calculate the probability that a particle in a one-dimensional hard box will be found within one standard deviation of its mean position for the $n = 3$ state.

Uncertainty in the Measurement of a Variable

If case 2 applies, we will use the standard deviation, which we can evaluate from Eq. (15.4-20), as a measure of the width of the probability distribution, or of the **uncertainty** of the measurements of the variable. In general, a single measurement will have roughly a two-thirds probability of lying within one standard deviation of the expectation value.

EXAMPLE 15.12

Calculate the probability that the harmonic oscillator will be found in the classically forbidden region for the $v = 0$ state.

Solution

For a classical energy equal to the quantum-mechanical energy for $v = 0$, the turning point is given by

$$z_t^2 = \frac{h\nu}{k} = \frac{h}{k}\frac{1}{2\pi}\sqrt{\frac{k}{m}} = \frac{\hbar}{\sqrt{km}} = \frac{1}{a}$$

$$|z_t| = \sqrt{\frac{1}{a}}$$

The probability that the harmonic oscillator is in the classically permitted region is

$$(\text{Probability}) = \left(\frac{a}{\pi}\right)^{1/2}\int_{-\sqrt{1/a}}^{\sqrt{1/a}} e^{-az^2}\, dz = 2\left(\frac{a}{\pi}\right)^{1/2}\int_{0}^{\sqrt{1/a}} e^{-az^2}\, dz$$

where we have used the fact that since the integrand is an even function, the integral over half of the interval is equal to half of the integral over the entire interval. This integral is related to the error function, which was introduced in Chapter 10 and for which tables of values are available.[3] The error function is defined by

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-y^2}\,dy \quad \text{(definition)} \tag{15.4-21}$$

If we make the substitution $y = \sqrt{a}\,z$, we have, from the table of values of the error function in Appendix C:

$$(\text{Probability}) = \frac{2}{\sqrt{\pi}}\int_0^1 e^{-y^2}\,dy = \mathrm{erf}(1) = 0.8427$$

The probability that the oscillating particle is farther away from its equilibrium position than the classical turning point is thus $1.0000 - 0.8427 = 0.1573$, or 15.73% (7.86% being past each end of the classically permitted region). This probability is represented by the two shaded areas in Figure 15.6, which shows the probability density superimposed on a graph of the potential energy function.

*Exercise 15.17

Calculate the value of the following ratio for the harmonic oscillator:

$$\text{Ratio} = \frac{|\psi_0(z_t)|^2}{|\psi_0(0)|^2}$$

Explain in words what this ratio represents.

We have used the position of a particle as an example of a mechanical variable. We must consider other variables, such as the momentum, the energy, and the angular momentum.

EXAMPLE 15.13

For a particle in a one-dimensional box, find $\langle p_x\rangle$, $\langle p_x^2\rangle$ and σ_{p_x} for the $n = 1$ state.

Solution

$$\langle p_x\rangle = \frac{2}{\pi}\int_0^a \sin\left(\frac{\pi x}{a}\right)\frac{\hbar}{i}\frac{d}{dx}\sin\left(\frac{\pi x}{a}\right)dx = \frac{2\hbar}{\pi i}\int_0^a \sin\left(\frac{\pi x}{a}\right)\cos\left(\frac{\pi x}{a}\right)dx = 0$$

$$\langle p_x^2\rangle = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)(-\hbar^2)\frac{d^2}{dx^2}\sin\left(\frac{\pi x}{a}\right)dx = \frac{2}{a}\hbar^2\left(\frac{\pi}{a}\right)^2\int_0^a \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi x}{a}\right)dx$$

$$= \frac{2}{a}\hbar^2\left(\frac{\pi}{a}\right)^2\frac{a}{2} = \frac{\hbar^2\pi^2}{a^2}$$

$$\sigma_{p_x} = [\langle p_x^2\rangle - \langle p_x\rangle^2]^{1/2} = \langle p_x^2\rangle^{1/2} = \frac{\hbar\pi}{a} = \frac{h}{2a}$$

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[3] M. Abramowitz and I. A. Stegun, eds. *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, U.S. Government Printing Office, Washington, D.C., 1964. See Appendix 8 for a table of values.

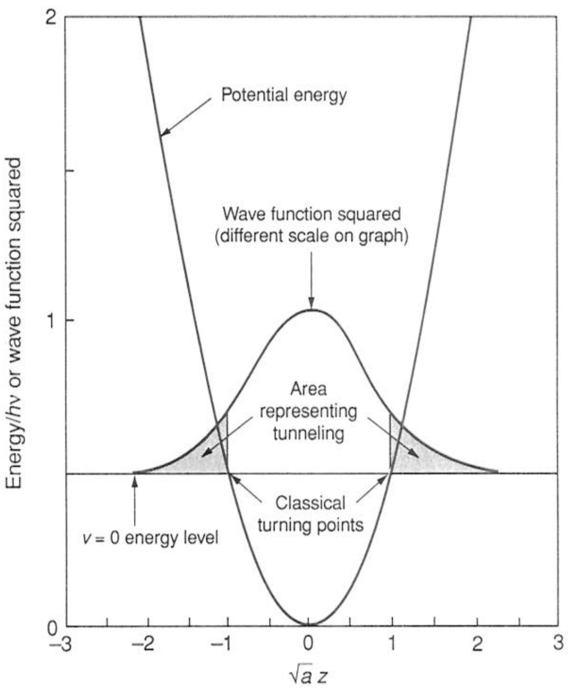

Figure 15.6. The Probability Density of a Harmonic Oscillator in Its Ground State, Showing Tunneling. The shaded areas represent the probability that the oscillator will be in classically forbidden regions.

Exercise 15.18

Show that the uncertainty in the energy of a particle in a box is equal to zero if it is known that the particle is in the $n = 1$ state or any other state corresponding to an energy eigenfunction.

The nonzero value of the standard deviation shows that for this system and this state, case 2 applies to the momentum, while the zero value for the standard deviation of the energy in Exercise 15.18 shows that the energy belongs to case 1 for this system and this state.

Heisenberg's Uncertainty Principle

We use σ_x and σ_{p_x} as measures of the uncertainty in predictions of position and momentum. Their product is a measure of the combined uncertainty of the two variables, and is called an **uncertainty product**. From Examples 15.10 and 15.13, the value of the uncertainty product of x and p_x for the $n = 1$ state of the particle in a one-dimensional hard box is

$$\sigma_x \sigma_{p_x} = (0.180756a)\frac{\hbar\pi}{a} = 0.56786\hbar = 0.09038h \qquad (15.4\text{-}22)$$

Table 15.1 gives some values of σ_x and p_{p_x} for a particle in a box. The coordinate x and the momentum component p_x are **conjugate variables** in the sense of Eq. (D-19) of Appendix D. The **Heisenberg uncertainty principle** is a general statement of the combined uncertainties of two conjugate variables: *The product of the uncertainties of*

Table 15.1. Values of the Uncertainty Product for a Particle in a One-Dimensional Box

n	σ_x	σ_{p_x}	$\sigma_x\sigma_{p_x}$
1	$0.18076a$	$h/2a$	$0.09038h = 0.56786\hbar$
2	$0.26258a$	h/a	$0.26583h = 1.67029\hbar$
3	$0.27876a$	$3h/2a$	$0.41813h = 2.62720\hbar$
...	...	...	...
∞	$0.28868a$	∞	∞

Numerical Values for a Box of Length 10.0×10^{-10} m (Model for π Electrons in 1,3,5-Hexatriene)

n	σ_x/m	$\sigma_{p_x}/\mathrm{kg\,m\,s^{-1}}$	$\sigma_x\sigma_{p_x}/\mathrm{kg\,m^2\,s^{-1}}$
1	1.808×10^{-10}	3.313×10^{-25}	5.909×10^{-35}
2	2.626×10^{-10}	6.626×10^{-25}	1.761×10^{-34}
3	2.788×10^{-10}	9.939×10^{-25}	2.771×10^{-34}
...	...	...	...
∞	2.887×10^{-10}	∞	∞

two conjugate variables is equal to or larger than $h/4\pi$, where h is Planck's constant. If we use the symbols Δx and Δp_x for the uncertainties of a coordinate and its conjugate momentum, then the uncertainty principle is

$$\Delta x\,\Delta p_x \geq \frac{h}{4\pi} = \frac{\hbar}{2} \tag{15.4-23}$$

Equation (15.4-23) corresponds to the use of the standard deviation as the measure of uncertainty. There are other measures of the uncertainty of a statistical prediction besides the standard deviation. For a gaussian probability distribution, the uncertainty in a prediction at the 95% probability level is equal to 1.96 times the standard deviation. At this level of probability the right-hand side of Eq. (15.4-23) would be replaced by a larger value. The actual value of the uncertainty product depends on the nature of the system and on the state considered. The uncertainty product for the $n = 1$ state of the particle in a box, $0.09038h$, is slightly larger than $h/(4\pi)$, which equals $0.079577h$. The uncertainty product for the $v = 0$ state of the harmonic oscillator is exactly equal to $h/(4\pi)$.

Coordinates and momenta are not the only variables that have nonzero uncertainty products. The commutator of the operators of two conjugate variables is nonzero, as we have already seen for the commutator $[x, p_x]$. Any two variables whose operators do not commute must have a nonzero uncertainty product. There is a general relation

$$\Delta A\,\Delta B \geq \left|\frac{1}{2}\int \psi^*[\hat{A}, \hat{B}]\psi\,dq\right| \tag{15.4-24}$$

where $[\hat{A}, \hat{B}]$ is the commutator of $\hat{A}$ and $\hat{B}$.[4] From the commutator of two angular momentum components, we can see that two components of the angular momentum

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[4] Levine (*Quantum Chemistry*, 4th ed, Prentice-Hall, Engelwood Cliffs, N.J., 1991 pp. 82, 188) assigns the proof as a homework problem. A lot of hints are included, but it is a fairly long proof.

obey an uncertainty relation, at least for states for which the eigenvalue of the third component is not equal to zero. See Problem 15.36.

Exercise 15.19

Use Eqs. (15.4-24) and (15.3-13) to obtain the uncertainty relation for x and p_x.

The uncertainty principle is a rather subtle concept, and deserves more discussion than we give it in this book. However, the main idea is that it requires that case 2 applies to at least one of a conjugate pair of variables, and if case 1 applies to one of the variables, the other variable has an infinite uncertainty.

EXAMPLE 15.14

Find $\langle p_x \rangle$ and σ_{p_x} for a free particle in a state corresponding to the wave function of Eq. (14.5-25).

Solution

We cancel the time-dependent factors to obtain

$$\langle p_x \rangle = \frac{\frac{\hbar}{i} D^*D \int e^{-i\kappa x} \frac{d}{dx} e^{i\kappa x}\, dx}{D^*D \int e^{-i\kappa x} e^{i\kappa x}\, dx} = \hbar\kappa \frac{D^*D \int e^{-i\kappa x} e^{i\kappa x}\, dx}{D^*D \int e^{-i\kappa x} e^{i\kappa x}\, dx} = \hbar\kappa \frac{D^*D \int dx}{D^*D \int dx}$$

We have not written the limits on the integrals, which are $-\infty$ and ∞. We specify that the limits are $-L$ and L, with the intention of taking the limit that $L \to \infty$. We cancel the integrals in the last quotient of integrals prior to taking the limit, and obtain

$$\langle p_x \rangle = \hbar\kappa$$

To calculate σ_{p_x}, we require $\langle p_x^2 \rangle$, which is given by a similar quotient of integrals except that the second derivative is taken:

$$\langle p_x^2 \rangle = \hbar^2\kappa^2$$

The square of the standard deviation is

$$\sigma_{p_x}^2 = \langle p_x^2 \rangle - \langle p_x \rangle^2 = \hbar^2\kappa^2 - \hbar^2\kappa^2 = 0$$

The uncertainty in one of a pair of conjugate variables can vanish only if the uncertainty in the other variable is infinite, so in this case the uncertainty in x is infinite.

Exercise 15.20

Write the integral to calculate σ_x for the free particle of Example 15.14 and argue that its value is infinite.

From the expectation value of the momentum of a free particle we can now justify the apparently arbitrary choice of sign that we made in Eq. (15.3-5). It appeared at that time that either $i\hbar\, d/dx$ or $-i\hbar\, d/dx$ could have been chosen as the operator for p_x. The free-particle wave function $De^{i\kappa x}$ corresponds to a positive value of $\langle p_x \rangle$, as shown in Example 15.14. If we combine this coordinate wave function with the appropriate time factor, $\exp(-iEt/\hbar)$, we obtain the time-dependent wave function

$$\Psi = D \exp^{i(\kappa x - Et/\hbar)}$$

which represents a traveling wave moving to the right (with positive value of p_x). If $i\hbar\, d/dx$ had been chosen for the p_x operator, a negative value for $\langle p_x \rangle$ would have resulted, indicating motion in the wrong direction.

Exercise 15.21

Show that taking the opposite sign for the momentum operator leads to a negative value of $\langle p_x \rangle$.

The Time–Energy Uncertainty Relation

Like position and momentum, energy and time also obey an uncertainty relation:

$$\Delta E\, \Delta t \geq \frac{h}{4\pi} \tag{15.4-25}$$

The time–energy uncertainty relation is different from that of position and momentum, since time is not a mechanical variable that can be expressed in terms of coordinates and momenta and does not correspond to any quantum-mechanical operator. Although the time-dependent Schrödinger equation has the Hamiltonian operator on one side and the time derivative operator on the other, this does not imply that $i\hbar\, \partial/\partial t$ can be used as an operator for the energy, although such an operator relationship would lead to a commutator that would establish Eq. (15.4-25).[5] The Hamiltonian operator is the operator corresponding to the energy, and a single variable cannot correspond to two different operators.

The standard interpretation of the time–energy uncertainty relation is that if Δt is the time during which the system is known to be in a given state (the "lifetime" of the state) then there is a minimum uncertainty ΔE in the energy of the state as given by Eq. (15.4-25). This is a different interpretation from the interpretation of the uncertainties in position and momentum, which can be expressed as standard deviations. Even if the state being considered corresponds to an energy eigenfunction, which has a zero value of σ_E, the fact that it is known to be in this state for only a finite length of time imposes an uncertainty on the energy, which we understand to be an actual uncertainty in the value of the energy eigenvalue. It is as though when a system makes a transition into a new state, the energy of the system gradually settles toward the fixed value corresponding to having been in the state forever. This uncertainty can be observed experimentally. It imposes a broadening on spectral lines that is larger if the system spends a shorter time in a given state. This phenomenon is known as "uncertainty broadening." It is important only if a system is observed very shortly after it makes a transition to a given state.

EXAMPLE 15.15

The lowest energy eigenvalue for a hydrogen atom is −13.6 eV. Calculate the uncertainty in this energy if the atom has been in the state corresponding to this energy for 1.0 nanosecond.

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[5] Y. Aharanov and D. Bohm, *Phys. Rev.*, **122**, 1649 (1961).

Solution

$$\Delta E \geq \frac{\hbar}{2}\frac{1}{\Delta t} = \frac{6.6261 \times 10^{-34}\,\mathrm{J\,s}}{4\pi}\frac{1}{1.0 \times 10^{-9}\,\mathrm{s}} = 5.3 \times 10^{-26}\,\mathrm{J}$$
$$= 3.3 \times 10^{-7}\,\mathrm{eV}$$

This uncertainty is smaller than the energy eigenvalue by a factor of 2.4×10^{-8}.

*Exercise 15.22

If the energy of a system is to be measured to an uncertainty of 1.0×10^{-21} J, find the minimum time during which the system must be in the state at the measured energy.

We have stated that case 1 applies when the state of the system just prior to a measurement corresponds to an eigenfunction of the operator for the variable. The time–energy uncertainty principle means that it must be known that the system has been in this state for an infinite length of time for case 1 to apply with absolute accuracy.

EXAMPLE 15.16

For a particle in a one-dimensional hard box, find $\langle E\rangle$ and σ_E for the state corresponding to the $n = 1$ energy eigenfunction.

Solution

$$\sigma_E = [\langle E^2\rangle - \langle E\rangle^2]^{1/2} \tag{15.4-26}$$

Using the normalized wave function,

$$\langle E\rangle = \int \psi_1^* \hat{H}\psi\, dx = \int \psi_1^* E_1 \psi_1\, dx = E\int \psi_1^*\psi_1\, dx = E_1 = \frac{h^2}{8ma^2}$$

since the wave function is an eigenfunction of $\hat{H}$. Also

$$\langle E^2\rangle = \int \psi_1^* \hat{H}^2 \psi_1\, dx = \int \psi_1^* E_1^2 \psi_1\, dx = E_1^2 \int \psi_1^*\psi_1\, dx = E_1^2$$

where we have used the fact that $\hat{H}^2$ means operation twice with $\hat{H}$. The standard deviation vanishes:

$$\sigma_E = (E_1^2 - E_1^2)^{1/2} = 0$$

However, it must be known that the system has been in this state for an infinite length of time for this result to apply exactly.

The result of Example 15.16 illustrates the important general fact: *If the wave function is an eigenfunction of the operator corresponding to the variable being measured, the outcome of an error-free measurement is completely predictable (the measurement belongs to case 1).* The only value that will occur is the eigenvalue corresponding to the given eigenfunction.

Exercise 15.23

a. For a general system whose wave function ψ_j is an eigenfunction of the operator $\hat{A}$ with eigenvalue a_j, show that $\langle A\rangle = a_j$ and that the standard deviation, σ_A, vanishes.

***b.** For a one-dimensional harmonic oscillator, find $\langle E\rangle$ and σ_E for the state corresponding to the $v = 1$ energy eigenfunction.

Although we have discussed energy eigenfunctions to the exclusion of other kinds of wave functions, there is no requirement that the wave function actually corresponding to the state of a system be an energy eigenfunction.

EXAMPLE 15.17

For a one-dimensional harmonic oscillator, find $\langle E\rangle$ and σ_E if the state just prior to the measurements corresponds to the normalized wave function

$$\psi = \sqrt{\frac{1}{2}}(\psi_0 + \psi_1)$$

where ψ_0 and ψ_1 are the first two energy eigenfunctions, given in Eqs. (14.6-8) and (14.6-9).

Solution

Since ψ is normalized, we can omit the denominator in the formula for the expectation value:

$$\begin{aligned}\langle E\rangle &= \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)\hat{H}(\psi_0 + \psi_1)\,dx = \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)(E_0\psi_0 + E_1\psi_1)\,dx \\ &= \frac{1}{2}\left[E_0\int_{-\infty}^{\infty}\psi_0^*\psi_0\,dx + E_1\int_{-\infty}^{\infty}\psi_0^*\psi_1\,dx + E_0\int_{-\infty}^{\infty}\psi_1^*\psi_0\,dx + E_1\int_{-\infty}^{\infty}\psi_1^*\psi_1\,dx\right] \\ &= \frac{1}{2}(E_0 + 0 + 0 + E_1) = \frac{1}{2}(E_0 + E_1) = h\nu\end{aligned}$$

We have used the normalization of the energy eigenfunctions, the fact that the two energy eigenfunctions are orthogonal to each other, and the expression for the energy eigenvalues.

$$\begin{aligned}\langle E^2\rangle &= \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)\hat{H}^2(\psi_0 + \psi_1)\,dx \\ &= \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)(E_0^2\psi_0 + E_1^2\psi_1)\,dx = \frac{1}{2}(E_0^2 + E_1^2) = \frac{5}{4}(h\nu)^2\end{aligned}$$

We have omitted some steps. We now have

$$\sigma_E = [\langle E^2\rangle - \langle E\rangle^2]^{1/2} = \left[\frac{5}{4}(h\nu)^2 - (h\nu)^2\right]^{1/2} = \frac{h\nu}{2}$$

For the state corresponding to this wave function, case 2 applies to the energy.

*Exercise 15.24

For a particle in a one-dimensional hard box, find $\langle E\rangle$ and σ_E for the coordinate wave function

$$\psi = \sqrt{\frac{1}{3}}\psi_1 + \sqrt{\frac{2}{3}}\psi_2$$

where ψ_1 and ψ_2 are the first two energy eigenfunctions.

We now obtain a general formula for the expectation value of $\hat{A}$ when the wave function is expressed as a linear combination of basis functions as in Eq. (15.2-13). If the set of functions $f_1, f_2, f_3, \ldots,$ are eigenfunctions of a hermitian operator $\hat{A}$ they form a complete set and we can write

$$\psi = \sum_{k=1}^{\infty} c_k f_k^* \qquad (15.4\text{-}27)$$

If a complete set consists of normalized functions that are orthogonal to each other, we call it a **complete orthonormal set**. We substitute the expansion of Eq. (15.4-27) into the expression for the expectation value, Eq. (15.4-1), assuming that ψ is normalized:

$$\langle A\rangle = \int \psi^* \hat{A}\psi\, dq = \sum_{j=1}^{\infty}\sum_{k=1}^{\infty} c_j^* c_k a_k \int f_j^* f_k\, dq \tag{15.4-28}$$

We have used the eigenfunction property, have factored the constants out of the integrals, and have exchanged the order of integrating and summing. In order for it to be possible to exchange the order of summing and integrating, the sums and integrals must be uniformly convergent

Since the functions $f_1, f_2, \ldots$ are an orthonormal set, those integrals in which $j \neq k$ will vanish, and the integrals with $j = k$ will equal unity. We write

$$\int f_j^* f_k\, dq = \delta_{jk} = \begin{cases} 1 & \text{if } j = k \\ 0 & \text{if } j \neq k \end{cases} \tag{15.4-29}$$

This equation defines the quantity δ_{jk}, which equals unity when its two indices are equal and equals zero otherwise. It is called the **Kronecker delta**. When the sum over k is performed, only the $j = k$ term will be nonzero, and the sum over k collapses to a single term and the double sum collapses to a single sum.

$$\langle A\rangle = \sum_{j=1}^{\infty}\sum_{k=1}^{\infty} c_j^* c_k a_k \delta_{jk} = \sum_{j=1}^{\infty} c_j^* c_j a_j = \sum_{j=1}^{\infty} |c_j|^2 a_j \tag{15.4-30}$$

Comparison of Eq. (15.4-30) with Eq. (1.5-4) shows that $\langle A\rangle$ is given in the same way as a mean value is given from individual values and their probabilities. We have already asserted in Postulate 4 that individual measurements of A can give as a result only one or another of the eigenvalues of the operator $\hat{A}$, and we now assert that the probability that the eigenvalue a_j will occur is

$$p_j = |c_j|^2 \tag{15.4-31}$$

***Exercise 15.25**

Find the probability of each of the eigenvalues in Exercise 15.24.

15.5 Postulate 5. The Determination of the State of a System

The fifth and final postulate gives the rule for determining the mechanical state of a quantum-mechanical system:

> **Postulate 5.** *Immediately after an error-free measurement of the mechanical variable A in which the outcome was the eigenvalue a_j, the state of the system corresponds to a wave function that is an eigenfunction of $\hat{A}$ with eigenvalue equal to a_j.*

This postulate says nothing about the state of the system prior to the measurement, because the act of measurement can change the state of the system. If the energy of a particle in a box is measured and the result equals E_2, then the system is definitely in the state corresponding to the energy eigenfunction ψ_2 immediately after the measurement. It could have been in any state prior to the measurement so long as the wave function for that state if represented as a linear combination of energy eigenfunctions included a term for ψ_2.

The measurement of a variable belonging to case 2 is more complicated. Consider the determination of the position of a particle by allowing it to scatter electromagnetic radiation, much as an airplane reflects radar waves. When a macroscopic object such as an airplane reflects an electromagnetic wave, the effect on the object is negligible. When an object of small mass such as an electron scatters light, the effect is not negligible. If the position of an electron is to be determined to an accuracy of 0.1 nm, radiation with a wavelength of no more than 0.1 nm is needed.

EXAMPLE 15.18

Assume that we want to find the location of an electron in a box of length 1.0 nm to the nearest 0.1 nm. Compare the energy of a photon of wavelength 0.10 nm with the lowest kinetic energy of an electron in a one-dimensional box of length 1.0 nm.

Solution

$$E(\text{photon}) = h\nu = \frac{hc}{\lambda} = \frac{(6.6261\times 10^{-34}\,\text{J s})(3.00\times 10^{8}\,\text{m s}^{-1})}{1.00\times 10^{-10}\,\text{m}}$$

$$= 1.99\times 10^{-15}\,\text{J}$$

From the result of Example 14.6,

$$E(\text{electron}) = 6.0\times 10^{-20}\,\text{J}$$

The photon energy is about 30,000 times as large as the kinetic energy of the electron, so that the energy transferred to the electron in a measurement can be much larger than the original kinetic energy of the electron.

There is another argument. Assume that a particle in a box of length a is in a state corresponding to one of the energy eigenfunctions. The square of the wave function is the probability density for finding the particle, and this quantity is nonzero over the entire box except for the locations of nodes in the wave function. However, a single position measurement will give a single well-defined outcome, such as the location of a flash of light at a screen. An immediate repetition of the measurement would have to give a position very near the first position, since there would be no time for the particle to move appreciably. The wave function immediately after the first measurement must be a function that is nonzero only in the immediate vicinity of the measured position, since the square of the magnitude of the wave function is the probability density for finding the particle. The act of measurement must have changed the wave function. Figure 15.7a shows a possible wave function just before the measurement of position. Figure 15.7b shows the wave function schematically immediately after the position measurement. Figure 15.7c shows the wave function after a fairly short time has elapsed. The wave function has begun to evolve back into a delocalized wave function. We could follow this evolution by solving the time-dependent Schrödinger equation.

The fifth postulate asserts that the wave function immediately after the measurement of an observable A is an eigenfunction of $\hat{A}$ with eigenvalue a_i equal to the outcome of the measurement. If the eigenvalue is nondegenerate, the act of measurement has put the system into a known state. If several eigenfunctions of $\hat{A}$ have the same eigenvalue, the act of measurement has not put the system into a known state. Let g_i be the number

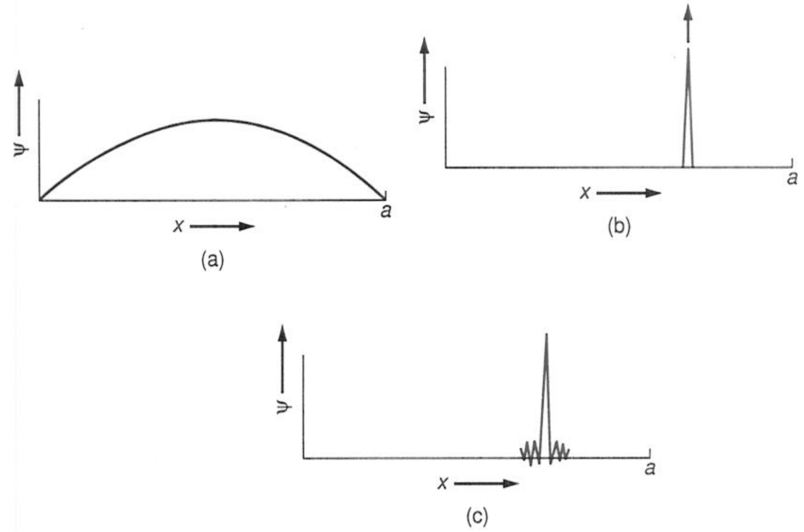

Figure 15.7. The Wave Function of a Particle in a Box. (a) **Before a position measurement (schematic).** The probability density is nonzero over the entire box (except for the endpoints). (b) **Immediately after the position measurement (schematic).** In a very short time, the particle cannot have moved far from the position given by the measurement, and the probability density must be a sharply peaked function. (c) **Shortly after a position measurement (schematic).** After a short time, the probability density can be nonzero over a larger region.

of different eigenfunctions whose eigenvalues equal a_i. If these are numbered from 1 to g, the wave function immediately after the measurement is

$$\psi(\text{after}) = \sum_{j=1}^{g_i} c_j(\text{after}) f_j \tag{15.5-1}$$

where $f_1, f_2, \ldots,$ are the eigenfunctions whose eigenvalues equal a_i. Only the functions with the same value for the eigenvalue are included in the sum, but we do not know what the coefficients $c_1, c_2, c_3, \ldots, c_{g_i}$ are. However, if there are other variables whose operators commute with $\hat{A}$, measurement of enough of these variables can put the system into a known state. We say that such a set of variables form a **complete set of commuting observables**. For example, a complete set of commuting observables for the electron in a hydrogen atom has four variables. We will discuss this in the next chapter.

Information about the State Prior to a Measurement

A single measurement gives us information about the state after the measurement. Some information about the original wave function of a quantum-mechanical system can be obtained by repeated measurements if we have a procedure to put the system back into the original state before each measurement.

Consider the nondegenerate case, that each eigenfunction of the operator $\hat{A}$ corresponding to a variable A has a distinct eigenvalue. Since the set of eigenfunctions is assumed to be a complete set, the wave function prior to the measurement can be represented as a linear combination of eigenfunctions of $\hat{A}$, as in Eq. (15.2-13):

$$\psi(\text{prior}) = \sum_{j=1}^{\infty} c_j(\text{prior}) f_j \tag{15.5-2}$$

We now make a set of many measurements of A, ensuring somehow that the system is in the same state prior to each measurement. (If this cannot be done, we cannot determine anything about the state prior to the measurements.) Each outcome will be an eigenvalue of $\hat{A}$, and we can determine the fraction of measurements corresponding to each eigenvalue. Let the fraction that results in the value a_j be equal to p_j. By Eq. (15.4-31),

$$|c_j(\text{prior})| = \sqrt{p_j} \tag{15.5-3}$$

If all of the measurements give the same result, say a_i, and if the state corresponding to f_i is nondegenerate, then p_i equals unity and we can assert that the state prior to the measurement must have been the state corresponding to f_i. If more than one eigenvalue has a nonzero probability, we can determine the magnitudes of the c_j(prior) coefficients. We cannot know the real and imaginary parts of each expansion coefficient, so we cannot know exactly what the wave function was prior to the measurement unless case 1 applies.

Summary of the Chapter

In this chapter we have presented postulates that are the theoretical basis of quantum mechanics. The first two postulates establish a one-to-one correspondence between the mechanical state of a system and a wave function and establish the Schrödinger equation, which governs the wave functions.

The third postulate was that there is a hermitian mathematical operator in one-to-one correspondence to each mechanical variable for a given system. The recipe for writing the operator for a given variable is: (1) write the classical expression for the variable in terms of cartesian coordinates and momentum component, (2) replace each momentum component by the relation

$$p_{x_j} \leftrightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}$$

and its analogues.

The fourth postulate provides the means for predicting values of mechanical variables from operators and the wave function of the system. The first part of the postulate is that the only possible outcomes of a measurement of a variable are the eigenvalues of the operator corresponding to that variable, and the second part is that the expectation value of the variable A is given by

$$\langle A\rangle = \frac{\int \Psi^* \hat{A}\Psi \, dq}{\int \Psi^*\Psi \, dq}$$

By study of the standard deviation of A, given by

$$\sigma_A = [\langle A^2\rangle - \langle A\rangle^2]^{1/2}$$

it was established that if the state just before a measurement of A corresponds to an eigenfunction of $\hat{A}$, the only possible outcome of the measurement is the eigenvalue corresponding to that eigenfunction. In this case, a measurement is completely predictable, similar to the case in classical mechanics. If the wave function is not an eigenfunction of $\hat{A}$, the standard deviation gives a measure of the spread of the distribution of results.

The fifth postulate states that in a measurement of A, if the result is a_j, one of the eigenvalues of $\hat{A}$, then the state of the system immediately after the measurement corresponds to a wave function that is a linear combination only of those eigenfunctions whose eigenvalues equal a_j.

The measurement on the same system of a complete set of commuting observables suffices to put the system into a state that is completely known, even though only partial information is available about the state of the system prior to the measurements.

PROBLEMS

Problems for Section 15.2

15.26. Determine whether each of the following operators is linear and whether it is hermitian.

a. $\dfrac{d^2}{dx^2}$

b. $\dfrac{d^3}{dx^3}$

c. $\sin(\ldots)$

*15.27. Determine whether each of the following operators is linear and whether it is hermitian.

a. $\ln(\ldots)$

b. $\dfrac{c}{x}+i\dfrac{d}{dx}$, where c is a constant and $i=\sqrt{-1}$.

c. $ix\dfrac{d}{dx}$, where $i=\sqrt{-1}$.

15.28. Find an expression for the commutator $\left[x,\dfrac{d^2}{dx^2}\right]$.

*15.29. Find a simplified expression for the operator $\left[\dfrac{1}{x}+\dfrac{d}{dx}\right]^2$

15.30. A **function of an operator** is defined through the Taylor series representing the function. For example, the exponential of an operator is defined as the series

$$e^{\hat{A}}=1+\hat{A}+\frac{1}{2!}\hat{A}^2+\frac{1}{3!}\hat{A}^3+\cdots$$

where the operator products are defined in the usual way, as successive operations of the operator.

a. Write the formula for the result when $e^{\hat{A}}$ operates on an eigenfunction of $\hat{A}$.

b. Write the expression for the first three terms of $e^{(\hat{A}+\hat{B})}$, where $\hat{A}$ and $\hat{B}$ are two operators that do not necessarily commute.

15.31. **a.** Find the expression for $\sin(\hat{A})$.

b. Find the expression for $\cos(\hat{A})$.

c. Find the expression for $\ln(\hat{A})$.

c. Write the expression for the first two terms of $\sin(\hat{A}+\hat{B})$, where $\hat{A}$ and $\hat{B}$ are two operators that do not necessarily commute.

15.32. Find the complex conjugate of each of the following. Do it once by replacing i by $-i$, and once by separating the real and imaginary parts. In each case $z=x+iy$, where x and y are real.

a. $\sinh(z)$

b. $\cos(z)$

c. $\tan(z)$

Problems for Section 15.3

15.33. The eigenfunctions of coordinate operators are **Dirac delta functions**, defined such that $\delta(x-a)\to\infty$ if $x=a$ and $\delta(x-a)=0$ if $x\neq a$, and such that

$$\int_b^c \delta(x-a)\,dx=1$$

if $b<a<c$.

a. Show that $\delta(x-a)$ is an eigenfunction of x.

***b.** What is the eigenvalue of $\delta(x-a)$?

15.34. **a.** Show that the operator x is linear and hermitian.

b. Show that the operator for multiplication by a function, $h(x)$, is linear and hermitian.

*15.35. **a.** Find the eigenfunctions and eigenvalues of $\hat{p}_x=-i\hbar(\partial/\partial x)$.

b. Are the energy eigenfunctions for a particle in a hard one-dimensional box eigenfunctions of this operator? If so, find the eigenvalues.

c. Are the energy eigenfunctions for a free particle eigenfunctions of this operator? If so, find the eigenvalues.