CHAPTER 3

THE POSTULATES OF QUANTUM MECHANICS. OPERATORS, EIGENFUNCTIONS, AND EIGENVALUES

In this chapter we consider four basic postulates of quantum mechanics, which when taken with the Born postulate described in Section 2.8, serve to formalize the rules of quantum mechanics. Mathematical concepts material to these postulates are developed along with the physics. The postulates are applied over and over again throughout the text. We choose the simplest problems first to exhibit their significance and method of application—that is, problems in one dimension.

3.1 OBSERVABLES AND OPERATORS

Postulate I

This postulate states the following: To any self-consistently and well-defined observable in physics (call it A), such as linear momentum, energy, mass, angular momentum, or number of particles, there corresponds an operator (call it $\hat{A}$) such that measurement of A yields values (call these measured values a) which are eigenvalues of $\hat{A}$. That is, the values, a, are those values for which the equation

$$\hat{A}\varphi = a\varphi \qquad \boxed{\text{an eigenvalue equation}} \tag{3.1}$$

3.2 MEASUREMENT IN QUANTUM MECHANICS

Postulate II

The second postulate[1] of quantum mechanics is: measurement of the observable A that yields the value a leaves the system in the state φ_a, where φ_a is the eigenfunction of $\hat{A}$ that corresponds to the eigenvalue a.

As an example, suppose that a free particle is moving in one dimension. We do not know which state the particle is in. At a given instant we measure the particle's momentum and find the value $p = \hbar k$ (with k a specific value, say $1.3 \times 10^{10}\ \text{cm}^{-1}$). This measurement[2] leaves the particle in the state φ_k, so immediate subsequent measurement of p is certain to yield $\hbar k$.

Suppose that one measures the position of a free particle and the position $x = x'$ is measured. The first two postulates tell us the following. (1) There is an operator corresponding to the measurement of position, call it $\hat{x}$. (2) Measurement of x that yields the value x' leaves the particle in the eigenfunction of $\hat{x}$ corresponding to the eigenvalue x'.

The operator equation appears as

$$\hat{x}\delta(x - x') = x'\delta(x - x') \tag{3.26}$$

Dirac Delta Function

The eigenfunction of $\hat{x}$ has been written[3] $\delta(x - x')$ and is called the *Dirac delta function*. It is defined in terms of the following two properties. The first are the integral properties

$$\begin{aligned} \int_{-\infty}^{\infty} f(x')\delta(x - x')\,dx' &= f(x) \\ \int_{-\infty}^{\infty} \delta(x - x')\,dx' &= 1 \end{aligned} \tag{3.27}$$

[1] This postulate has been the source of some discussion among physicists. For further reference, see B. S. DeWitt, *Phys. Today* **23**, 30 (September 1970).

[2] Measurement is taken in the idealized sense. More formal discussions on the theory of measurement may be found in K. Gottfried, *Quantum Mechanics*, W. A. Benjamin, New York, 1966; J. Jauch, *Foundations of Quantum Mechanics*, Addison-Wesley, Reading, Mass., 1968, and E. C. Kemble, *The Fundamental Principles of Quantum Mechanics with Elementary Applications*, Dover, New York, 1958.

[3] More accurately one says that $\delta(x - x')$ is an eigenfunction of $\hat{x}$ in the coordinate representation. This topic is returned to in Section 7.4 and in Appendix A.

3.3 THE STATE FUNCTION AND EXPECTATION VALUES

Postulate III

The third postulate of quantum mechanics establishes the existence of the state function and its relevance to the properties of a system: The state of a system at any instant of time may be represented by a state or wave function ψ which is continuous and differentiable. All information regarding the state of the system is contained in the wavefunction. Specifically, if a system is in the state $\psi(\mathbf{r}, t)$, the average of any physical observable C relevant to that system at time t is

$$\langle C \rangle = \int \psi^* \hat{C} \psi \, d\mathbf{r} \tag{3.32}$$

(The differential of volume is written $d\mathbf{r}$.) The average, $\langle C \rangle$, is called the *expectation value* of C.

The physical meaning of the average of an observable C involves the following type of (conceptual) measurements. The observable C is measured in a specific experiment, X. One prepares a very large number (N) of identical replicas of X. The initial states $\psi(\mathbf{r}, 0)$ in each such replica are all identical. At the time t, one measures C in all these replica experiments and obtains the set of values $C_1, C_2, \ldots, C_N$. The average of C is then given by the rule

$$\langle C \rangle = \frac{1}{N} \sum_{i=1}^{N} C_i \qquad (N \gg 1) \tag{3.33}$$

The postulate stated above claims that this experimentally calculated average (3.33) is the same as that given by the integral in (3.32). Another way of defining $\langle C \rangle$ is in terms of the probability $P(C_i)$. This function gives the probability that measurement of C finds the value C_i. For $\langle C \rangle$, we then have

$$\langle C \rangle = \sum_{\text{all } C} C_i P(C_i) \tag{3.34}$$

This is a consistent formula if all the values C may assume comprise a discrete set (e.g., the number of marbles in a box). In the event that the values that C may assume comprise a continuous set (e.g., the values of momentum of a free particle), $\langle C \rangle$ becomes

$$\langle C \rangle = \int C P(C) \, dC \tag{3.35}$$

The integration is over all values of C. Here $P(C)$ is the probability of finding C in the interval $C, C + dC$.

The quantity $\langle C \rangle$ is also called the *expectation value* of C because it is representative of the value one expects to obtain in any given measurement of C. This will

3.4 TIME DEVELOPMENT OF THE STATE FUNCTION

Postulate IV

The fourth postulate of quantum mechanics specifies the time development of the state function $\psi(\mathbf{r}, t)$: the state function for a system (e.g., a single particle) develops in time according to the equation

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \hat{H}\psi(\mathbf{r}, t) \tag{3.45}$$

This equation is called the *time-dependent Schrödinger* equation.[1] The operator $\hat{H}$ is the Hamiltonian operator. For a single particle of mass m, in a potential field $V(\mathbf{r})$, it is given by (3.12). If $\hat{H}$ is assumed to be independent of time, we may write

$$\hat{H} = \hat{H}(\mathbf{r}) \tag{3.46}$$

Under these circumstances, one is able to construct a solution to the time-dependent Schrödinger equation through the technique of separation of variables. We assume a solution of the form

$$\psi(\mathbf{r}, t) = \varphi(\mathbf{r})T(t) \tag{3.47}$$

Substitution into (3.45) gives

$$i\hbar \frac{T_t}{T} = \frac{\hat{H}\varphi}{\varphi} \tag{3.48}$$

The subscript t denotes differentiation with respect to t. Equation (3.48) is such that the left-hand side is a function of t only, while the right-hand side is a function of $\mathbf{r}$ only. Such an equation can be satisfied only if both sides are equal to the same constant, call it E (we do not yet know that E is the energy).

$$\hat{H}\varphi(\mathbf{r}) = E\varphi(\mathbf{r}) \tag{3.49}$$

$$\left(\frac{\partial}{\partial t} + \frac{iE}{\hbar}\right)T(t) = 0 \tag{3.50}$$

The first of these equations is the time-independent Schrödinger equation (3.13). This identification serves to label E, in (3.49), the energy of the system. That is, E, as it appears in this equation, is an eigenvalue of $\hat{H}$. But the eigenvalues of $\hat{H}$ are the allowed energies a system may assume, and we again conclude that E is the energy of the system.

[1] A formulation of the Schrödinger equation that has its origin in the classical principle of least action has been offered by R. P. Feynman, *Rev. Mod. Phys.* **60**, 367 (1948). An elementary description of this derivation may be found in S. Borowitz, *Quantum Mechanics*, W. A. Benjamin, New York, 1967.

PROBLEMS

4.3 For the one-dimensional box problem, show that $P = |\varphi_n|^2$ is maximum at the values $x = x_j$ given by

$$x_j = \frac{2j+1}{2n} L, \qquad j = 0, 1, 2, \ldots, n-1$$

4.3 DIRAC NOTATION

In this section we introduce a notation that proves to be an invaluable tool in calculation, called the *Dirac notation.* It gives a monogram to the integral of the product of two state functions, $\psi(x)$ and $\varphi(x)$, which appears as

$$\langle \psi | \varphi \rangle = \int_{-\infty}^{\infty} \psi^*(x)\varphi(x)\, dx \tag{4.19}$$

In Dirac notation, the integral on the right is written in the form shown on the left.

More generally, the integral operation $\langle \psi | \varphi \rangle$ denotes: (1) take the complex conjugate of the object in the first slot ($\psi \to \psi^*$) and then, (2) integrate the product ($\psi^*\varphi$). This operation has the following simple properties. If a is any complex number and the functions ψ and φ are such that

$$\int_{-\infty}^{\infty} \psi^*\varphi\, dx < \infty \tag{4.20}$$

the following rules hold:

$$\langle \psi | a\varphi \rangle = a\langle \psi | \varphi \rangle \tag{4.21}$$

$$\langle a\psi | \varphi \rangle = a^*\langle \psi | \varphi \rangle \tag{4.22}$$

$$\langle \psi | \varphi \rangle^* = \langle \varphi | \psi \rangle \tag{4.23}$$

$$\langle \varphi + \psi | = \langle \psi | + \langle \varphi | \tag{4.24}$$

$$\begin{aligned} &\int (\psi_1 + \psi_2)^*(\varphi_1 + \varphi_2)\, dx \\ &= \langle \psi_1 + \psi_2 | \varphi_1 + \varphi_2 \rangle = (\langle \psi_1 | + \langle \psi_2 |)(|\varphi_1\rangle + |\varphi_2\rangle) \\ &= \langle \psi_1 | \varphi_1 \rangle + \langle \psi_1 | \varphi_2 \rangle + \langle \psi_2 | \varphi_1 \rangle + \langle \psi_2 | \varphi_2 \rangle \end{aligned} \tag{4.25}$$

The object $\langle \psi |$ (called a "bra vector") has an inevitable fate. Eventually, it is integrated in a product form with a ("ket vector") $|\varphi\rangle$, to form the "bra-ket," $\langle \psi | \varphi \rangle$.

Dirac notation is not complicated. The properties above tell the whole story. We move next to function spaces, where $\langle \varphi | \psi \rangle$ assumes a geometrical quality.

PROBLEMS

4.4 Write the following equations for the state vectors f, g, and so on, in Dirac notation.

(a) $f(x) = g(x)$.

(b) $c = \int g^*(x')h(x')\,dx'$.

(c) $f(x) = \sum_n \varphi_n(x) \int \varphi_n^*(x')f(x')\,dx'$.

(d) $\hat{O} \equiv \psi(x) \int dx'\varphi^*(x')$.

(e) $\frac{\partial}{\partial x} f(x) = h(x) \int h^*(x')g(x')\,dx'$.

4.5 Consider the operator $\hat{O} = |\varphi\rangle\langle\psi|$ and the arbitrary state function $f(x)$. Describe the following forms.

(a) $\langle f|\hat{O}$.
(b) $\hat{O}|f\rangle$.
(c) $\langle f|\hat{O}|f\rangle$.
(d) $\langle f|\hat{O}|\varphi\rangle$.

Answer (partial)

(a) $\langle f|\hat{O}$ is the bra vector $C\langle\psi|$, where the constant $C \equiv \langle f|\varphi\rangle = \int_{-\infty}^{\infty} f^*\varphi\,dx$.

4.4 HILBERT SPACE

In this section we introduce the concept of a space of functions. Specifically we will deal with a Hilbert space. This serves the purpose of giving a geometrical quality to some of the abstract concepts of quantum mechanics.

We recall that in Cartesian 3-space a vector **V** is a set of three numbers, called components (V_x, V_y, V_z). Any vector in this space can be expanded in terms of the three unit vectors $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$ (Fig. 4.5). Under such conditions one terms the triad $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$, a *basis*.

$$\mathbf{V} = \mathbf{e}_x V_x + \mathbf{e}_y V_y + \mathbf{e}_z V_z \tag{4.26}$$

The vectors $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$ are said to *span* the vector space.

The inner ("dot") product of two vectors (**U** and **V**) in the space is defined as

$$\mathbf{V}\cdot\mathbf{U} = V_x U_x + V_y U_y + V_z U_z \tag{4.27}$$

The length of the vector **V** is $\sqrt{\mathbf{V}\cdot\mathbf{V}}$.

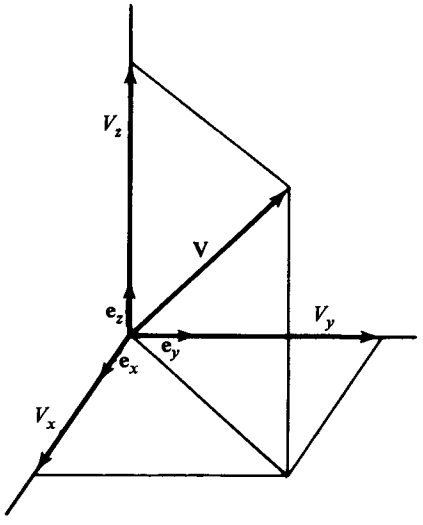

FIGURE 4.5 Vector V in Cartesian 3-space and its components (V_x, V_y, V_z). The orthogonal triad (e_x, e_y, e_z) spans the space.

A Hilbert space is much the same type of object. Its elements are functions instead of three-dimensional vectors. The similarity is so close that the functions are sometimes called vectors. A Hilbert space $\mathfrak{H}$ has the following properties.

1. The space is linear. A function space is linear under the following two conditions: (a) If a is a constant and φ is any element of the space, then $a\varphi$ is also an element of the space. (b) If φ and ψ are any two elements of the space, then $\varphi + \psi$ is also an element of the space.
2. There is an *inner product*, $\langle\psi|\varphi\rangle$, for any two elements in the space. For functions defined in the interval $a \leq x \leq b$ (in one dimension), we may take

$$\langle\varphi|\psi\rangle = \int_a^b \varphi^*\psi\, dx \tag{4.28}$$

3. Any element of $\mathfrak{H}$ has a norm ("length") that is related to the inner product as follows:

$$(\text{norm of } \varphi)^2 = \|\varphi\|^2 = \langle\varphi|\varphi\rangle \tag{4.29}$$

4. $\mathfrak{H}$ is complete. Every Cauchy sequence of functions in $\mathfrak{H}$ converges to an element of $\mathfrak{H}$. A Cauchy sequence $\{\varphi_n\}$ is such that $\|\varphi_n - \varphi_l\| \to 0$ as n and l approach infinity. (See Problem 4.24.) Loosely speaking, a Hilbert space contains all its limit points.

An example of a Hilbert space is given by the set of functions defined on the interval ($0 \leq x \leq L$) with finite norm

$$\boxed{\|\varphi\|^2 = \int_0^L \varphi^* \varphi \, dx < \infty \qquad \mathfrak{H}_1} \tag{4.30}$$

Another example is the space of functions commonly referred to by mathematicians as "L^2 space." This is the set of square-integrable functions defined on the whole x interval.

$$\boxed{\|\varphi\|^2 = \int_{-\infty}^{\infty} \varphi^* \varphi \, dx < \infty \qquad \mathfrak{H}_2} \tag{4.31}$$

Let us see how the preceding concept of inner product (4.28) is similar to the definition of the inner product between two finite-dimensional vectors (4.27). To see this we interpret the function $\varphi(x)$ as a vector with infinitely many components. These components are the values that φ assumes at each distinct value of its independent variable x. Just as the inner product between **U** and **V** is a sum over the products of parallel components, so is the inner product between φ and ψ a sum over parallel components. This sum is nothing but the integral of the product of φ and ψ. The reason we complex-conjugate the first "vector" is to ensure that the "length" (square root of the inner product between a "vector" φ and itself) of a vector φ is real.

Thus we see that Hilbert space is closely akin to a vector space. Mathematicians[1] call it that—an infinite-dimensional vector space (also: a complete, normed, linear vector space). Elements of this space have length and one can form an inner product between any two elements. The vector quality of Hilbert space can be pushed a bit further. We recall that if two vectors **U** and **V** in three-dimensional vector space are orthogonal to each other, their inner product vanishes. In a similar vein two vectors in Hilbert space, φ and ψ, are said to be orthogonal if

$$\langle \varphi | \psi \rangle = 0 \tag{4.32}$$

Furthermore, we recall that the three unit vectors $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ "span" 3-space. Similarly, there is a set of vectors that "spans" Hilbert space. For instance, the Hilbert space whose elements all have the property given by (4.30) is spanned by the sequence of functions $\{\varphi_n\}$, which are the eigenfunctions of the Hamiltonian relevant

[1] A more mathematically accurate presentation of function spaces may be found in C. Goffman and G. Pedrick, *First Course in Functional Analysis*, Prentice-Hall, Englewood Cliffs, N.J., 1965. Another book in this area, but more directly related to quantum mechanics, is T. F. Jordan, *Linear Operators for Quantum Mechanics*, Wiley, New York, 1969.

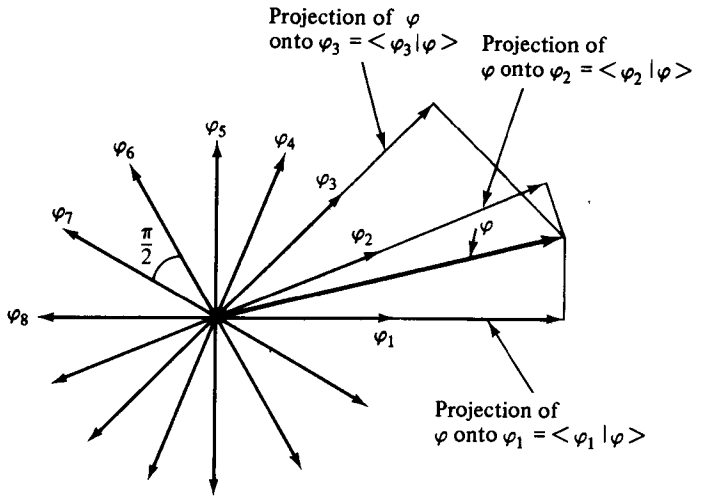

FIGURE 4.6 Projection of φ onto an orthonormal set of eigenfunctions in Hilbert space.

to the one-dimensional box Problem (4.15). This means that any function φ in this Hilbert space may be expanded in a series of the sequence $\{\varphi_n\}$.

$$\varphi(x) = \sum_{n=1}^{\infty} a_n \varphi_n(x) \tag{4.33}$$

The geometrical interpretation of this relation is depicted in Fig. 4.6. The coefficient a_n is the projection of φ onto the vector φ_n. To see this, first we state a fact to be illustrated in the next section. The *basis* vectors $\{\varphi_n\}$ comprise an orthogonal set. That is,

$$\langle \varphi_n | \varphi_{n'} \rangle = 0 \qquad (n \neq n') \tag{4.34}$$

Furthermore, φ_n is a unit vector; that is, it has unit "length"

$$\langle \varphi_n | \varphi_n \rangle = \|\varphi_n\|^2 = 1 \tag{4.35}$$

These latter two statements may be combined into the single equation

$$\langle \varphi_n | \varphi_{n'} \rangle = \delta_{n,n'} \tag{4.36}$$

The symbol $\delta_{n,n'}$ is called the *Kronecker delta* and is defined by

$$\delta_{n,n'} = 0 \quad \text{for } n \neq n', \qquad \delta_{n,n'} = 1 \quad \text{for } n = n' \tag{4.37}$$

Any sequence of functions that obeys (4.36) is called an *orthonormal set*.

To show that a_n is the projection of φ into φ_n, we first rewrite (4.33) in Dirac notation.

$$|\varphi\rangle = \sum_n |a_n \varphi_n\rangle \tag{4.38}$$

Then we multiply from the left by $\langle\varphi_{n'}|$ and use the relation (4.36).

$$\begin{aligned} \langle\varphi_{n'}|\varphi\rangle &= \sum_n \langle\varphi_{n'}|a_n\varphi_n\rangle \\ &= \sum_n a_n\langle\varphi_{n'}|\varphi_n\rangle = \sum_n a_n\delta_{n,n'} = a_{n'} \\ a_{n'} &= \langle\varphi_{n'}|\varphi\rangle \end{aligned} \tag{4.39}$$

The coefficient $a_{n'}$ is the inner product between the basis vector $\varphi_{n'}$ and the vector φ. Since $\varphi_{n'}$ is a "unit" vector, $a_{n'}$ is the projection of φ onto $\varphi_{n'}$ (Fig. 4.6). The student should recognize (4.33) to be a discrete Fourier series representation of φ, in terms of the trigonometric sequence (4.15).

Delta-Function Orthogonality

We will continue with the use of the labels $\mathfrak{H}_1$ and $\mathfrak{H}_2$ to denote the two Hilbert spaces defined by (4.30) and (4.31), respectively. As stated previously, the sequence $\{\varphi_n\}$ given by (4.15) "spans" $\mathfrak{H}_1$. The sequence $\{\varphi_n\}$ is a basis of $\mathfrak{H}_1$. What are the vectors which span $\mathfrak{H}_2$? The answer is: the eigenfunctions of the momentum operator $\hat{p}$,

$$\varphi_k(x) = \frac{1}{\sqrt{2\pi}} e^{ikx} \tag{4.40}$$

Let us see if this (continuous) set of functions is an orthogonal set. Toward these ends we form the inner product

$$\langle\varphi_k|\varphi_{k'}\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ix(k'-k)}\,dx = \delta(k'-k) \tag{4.41}$$

It follows that the inner product between any two distinct eigenvectors of the operator $\hat{p}$ vanishes.

Any function in $\mathfrak{H}_2$ may be expanded in terms of the eigenvectors $\{\varphi_k\}$. Since this sequence comprises a continuous set, the expansion is not a discrete sum as in (4.33), but an integral. If $\varphi(x)$ is any element of $\mathfrak{H}_2$, then since $\{\varphi_k\}$ spans this space, one may write

$$\varphi(x) = \int_{-\infty}^{\infty} b(k)\varphi_k(x)\,dk \tag{4.42}$$

This is the Fourier integral representation of $\varphi(x)$. Again, the coefficient of expansion $b(k)$ is the projection of $\varphi(x)$ onto φ_k. To exhibit this fact, we first rewrite the last integral in the form

$$|\varphi\rangle = \int_{-\infty}^{\infty} dk\, |b(k)\varphi_k\rangle \tag{4.43}$$

Again, if this equation is compared to (4.38), we see how the sum over discrete a_n values is replaced by an integration over the continuum of $b(k)$ values. If we now multiply (4.43) from the left with $\langle\varphi_{k'}|$, there results

$$\begin{aligned}\langle\varphi_{k'}|\varphi\rangle &= \int_{-\infty}^{\infty} dk\langle\varphi_{k'}|b(k)\varphi_k\rangle = \int_{-\infty}^{\infty} dk b(k)\langle\varphi_{k'}|\varphi_k\rangle \\ &= \int_{-\infty}^{\infty} dk b(k)\delta(k' - k) = b(k')\end{aligned} \tag{4.44}$$

The coefficient of expansion $b(k')$ is the inner product between $\varphi_{k'}$ and φ, hence it may be termed a projection of φ onto $\varphi_{k'}$. But $\varphi_{k'}$ does not appear to be a "unit" vector. Indeed, the vector φ_k is infinitely long.

$$\|\varphi_k\|^2 = \langle\varphi_k|\varphi_k\rangle = \delta(0) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dx = \infty \tag{4.45}$$

Although this disqualifies the set $\{\varphi_k\}$ for membership in $\mathfrak{H}_2$, they nevertheless span the space. They comprise a valid set of basis vectors and the projection of any function in $\mathfrak{H}_2$ onto any member of the basis $\{\varphi_k\}$ gives a finite result. If φ is any function in $\mathfrak{H}_2$, then

$$\langle\varphi_k|\varphi\rangle < \infty \tag{4.46}$$

The functions $\{\varphi_k\}$ may, through proper renormalization, be cast in a form which allows them to be members of $\mathfrak{H}_2$. (See Problem 4.6.)

PROBLEMS

4.6 Consider the functions

$$\varphi_k = \frac{1}{\sqrt{L}} e^{ikx}$$

defined over the interval $(-L/2, +L/2)$.

(a) Show that these functions are all normalized to unity and maintain this normalization in the limit $L \to \infty$.

(b) Show that these functions comprise an orthogonal set in the limit $L \to \infty$.

4.7 State to which space each of the functions listed belongs, $\mathfrak{H}_1$ or $\mathfrak{H}_2$.

(a) $f_1 = (x^5 - x^4 - Lx^4 + Lx^3)/(x - 2L)$

(b) $f_2 = (\sin x)e^{-x^2}$

(c) $f_3 = \sqrt{\ln[x(x - L) + 1]}$

(d) $f_4 = \sin 2n\pi[x(x - L) + 1], \quad n = 0, 1, 2, \ldots$

(e) $f_5 = e^{iax}(x^2 + a^2)^{-1}$

(f) $f_6 = x^{10}e^{-x^2}$

(g) $f_7 = 1/\sin kx$

4.8 The function

$$g(x) = x(x - L)e^{ikx}$$

is in $\mathfrak{H}_1$. Calculate the coefficients of expansion, a_n, of this function, in the series representation (4.33), in terms of the constants L and k. Use the basis functions (4.15).

4.9 Two vectors ψ and φ in a Hilbert space are orthogonal. Show that their lengths obey the Pythagorean theorem,

$$\|\psi + \varphi\|^2 = \|\psi\|^2 + \|\varphi\|^2$$

4.10 Consider a free particle moving in one dimension. The state functions for this particle are all elements of $\mathfrak{H}_2$. Show that the expectation of the momentum $\langle p_x \rangle$ vanishes in any state that is purely real ($\psi^* = \psi$). Does this property hold for $\langle H \rangle$? Does it hold for $\langle x \rangle$?

4.5 HERMITIAN OPERATORS

The average of an observable A for a system in the state $\psi(x, t)$ is given by (3.32). In Dirac notation this equation appears as (in one dimension)

$$\langle A \rangle = \int \psi^*(x, t)\hat{A}\psi(x, t)\, dx = \langle \psi | \hat{A}\psi \rangle \tag{4.47}$$

Since t is a fixed parameter in this equation, we may conclude that the formula gives the expectation of A at the time t. Now one may ask: What are the possible state functions for a particle moving in one dimension at a given instant of time? The answer is: any function in $\mathfrak{H}_2$. For example, the particle could be in any of the following states at some specified time:

$$\psi_1 = Be^{-x/a^2}, \qquad \psi_2 = \frac{Ce^{ikx}}{x}, \qquad \psi_3 = \frac{iD}{\sqrt{x^2 + a^2}} \tag{4.48}$$

where B, C, and D are normalization constants. Again consider the observable A. If the average of this observable is calculated in any of these states (that is, any

member of $\mathfrak{H}_2$), the result must be a real number. This is a property that we demand an operator have if it is to qualify as the operator corresponding to a physical observable. The object $\langle\psi|\hat{A}\psi\rangle$ must be real for all ψ in $\mathfrak{H}_2$. When working with the one-dimensional box problem, $\langle\psi|\hat{A}\psi\rangle$ must be real for all ψ in $\mathfrak{H}_1$. For example, if $\hat{H}$ is the operator corresponding to energy, then

$$\langle E\rangle = \langle\psi|\hat{H}\psi\rangle = -\int_0^L \frac{\psi^*\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi\, dx \tag{4.49}$$

must be real for any state function ψ in $\mathfrak{H}_1$.

These observations give rise to the following rule: In quantum mechanics one requires that the eigenvalues of an operator corresponding to a physical observable be real numbers. In this section we discuss the class of operators that have this property. They are called *Hermitian operators* and are a cornerstone in the theory of quantum mechanics.

The Hermitian Adjoint

To understand what a Hermitian operator is, we must first understand what the *Hermitian adjoint* of an operator is. Consider the operator $\hat{A}$. The Hermitian adjoint of $\hat{A}$ is written $\hat{A}^\dagger$. Under most circumstances, it is an entirely different operator from $\hat{A}$. For instance, the Hermitian adjoint of the complex number c is the complex conjugate of c. That is,

$$c^\dagger = c^* \tag{4.50}$$

How is the Hermitian adjoint defined? First, let us agree that an operator is defined over a specific Hilbert space, $\mathfrak{H}$. Also if $\hat{A}$ is the operator and ψ is any element of $\mathfrak{H}$, then $\hat{A}\psi$ is also in $\mathfrak{H}$. For any two elements of this space, say ψ_l and ψ_n, we can form the inner product

$$\langle\psi_l|\hat{A}\psi_n\rangle \tag{4.51}$$

Suppose there is another operator, $\hat{A}^\dagger$, also defined over $\mathfrak{H}$, for which

$$\langle\hat{A}^\dagger\psi_l|\psi_n\rangle = \langle\psi_l|\hat{A}\psi_n\rangle \tag{4.52}$$

Suppose further that this equality holds for *all* ψ_l and ψ_n in $\mathfrak{H}$. Then $\hat{A}^\dagger$ is called the *Hermitian adjoint* of $\hat{A}$. To find the Hermitian adjoint of an operator $\hat{A}$, we have to find the object $\hat{A}^\dagger$ that fits (4.52) for all ψ_l and ψ_n. Consider $\hat{A} = a$, a complex number. Then

$$\langle a^\dagger\psi_l|\psi_n\rangle = \langle\psi_l|a\psi_n\rangle = a\langle\psi_l|\psi_n\rangle = \langle a^*\psi_l|\psi_n\rangle \tag{4.53}$$

Equating the first and the last terms, we see that $a^\dagger = a^*$. As a second example, consider the operator

$$\hat{D} = \frac{\partial}{\partial x} \tag{4.54}$$

defined in $\mathfrak{H}_2$. Then

$$\begin{aligned} \langle \psi_l | \hat{D}\psi_n \rangle &= \int_{-\infty}^{\infty} dx \psi_l^* \frac{\partial}{\partial x}\psi_n = [\psi_l^* \psi_n]_{-\infty}^{+\infty} - \int_{-\infty}^{\infty} dx \left(\frac{\partial}{\partial x}\psi_l^*\right)\psi_n \\ &= \langle -\hat{D}\psi_l | \psi_n \rangle \end{aligned} \tag{4.55}$$

The "surface" term is zero since ψ_l and ψ_n are elements of $\mathfrak{H}_2$. Thus we find

$$\hat{D}^\dagger = -\hat{D} \tag{4.56}$$

For some cases we will find that the Hermitian adjoint of an operator is the operator itself. For such an operator $\hat{A}$, we may write

$$\hat{A}^\dagger = \hat{A} \tag{4.57}$$

In terms of the defining equation (4.52), this implies that for all ψ_l and ψ_n in $\mathfrak{H}$ (over which $\hat{A}$ is defined),

$$\langle \psi_l | \hat{A}\psi_n \rangle = \langle \hat{A}\psi_l | \psi_n \rangle \tag{4.58}$$

Operators that have this property are called *Hermitian operators.* The simplest example of a Hermitian operator is any real number a, since

$$\langle \psi_l | a\psi_n \rangle = \langle a\psi_l | \psi_n \rangle \tag{4.59}$$

If $\hat{A}$ and $\hat{B}$ are two Hermitian operators, is the product operator $\hat{A}\hat{B}$ Hermitian? This is most simply answered with the aid of Problem 4.11(b), according to which

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger \tag{4.60}$$

If $\hat{A}$ and $\hat{B}$ are Hermitian, then

$$(\hat{A}\hat{B})^\dagger = \hat{B}\hat{A} \tag{4.61}$$

and $\hat{A}\hat{B}$ is not (necessarily) Hermitian. What about $\hat{A}\hat{B} + \hat{B}\hat{A}$?

$$\begin{aligned} (\hat{A}\hat{B} + \hat{B}\hat{A})^\dagger &= \hat{B}^\dagger \hat{A}^\dagger + \hat{A}^\dagger \hat{B}^\dagger = \hat{B}\hat{A} + \hat{A}\hat{B} \\ &= \hat{A}\hat{B} + \hat{B}\hat{A} \end{aligned} \tag{4.62}$$

It follows that if $\hat{A}$ and $\hat{B}$ are both Hermitian, so is the bilinear form $(\hat{A}\hat{B} + \hat{B}\hat{A})$.

Is the square of a Hermitian operator Hermitian?

$$(\hat{A}^2)^\dagger = (\hat{A}\hat{A})^\dagger = \hat{A}^\dagger \hat{A}^\dagger = \hat{A}\hat{A} = (\hat{A})^2 \tag{4.63}$$

The answer is yes. Another way of doing this problem is as follows. Look at the inner product,

$$\langle \psi_l | \hat{A}\hat{A}\psi_n \rangle = \langle \hat{A}\psi_l | \hat{A}\psi_n \rangle = \langle \hat{A}\hat{A}\psi_l | \psi_n \rangle \tag{4.64}$$

The first equality follows because $\hat{A}\psi_n$ is in $\mathfrak{H}$ and $\hat{A}$ is Hermitian, while the second equality follows simply because $\hat{A}$ is Hermitian. Comparing the first and third terms shows that $\hat{A}^2$ is Hermitian.

The Momentum and Energy Operators

Let us test the momentum operator $\hat{p}$ and see if it is Hermitian. For the free-particle case, $\hat{p}$ is Hermitian if for all ψ_l and ψ_n in $\mathfrak{H}_2$,

$$\langle \psi_l | \hat{p}\psi_n \rangle = \langle \hat{p}\psi_l | \psi_n \rangle \tag{4.65}$$

Developing the left-hand side, we have

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_l^* \left(-i\hbar \frac{\partial}{\partial x} \psi_n \right) dx &= -i\hbar [\psi_l^* \psi_n]_{-\infty}^{\infty} + i\hbar \int_{-\infty}^{\infty} \left(\frac{\partial}{\partial x} \psi_l^* \right) \psi_n \, dx \\ &= \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial}{\partial x} \psi_l \right)^* \psi_n \, dx = \langle \hat{p}\psi_l | \psi_n \rangle \end{aligned} \tag{4.66}$$

This technique is, by and large, the principal method by which a specific operator is shown to be Hermitian.

Having shown that $\hat{p}$ is Hermitian, it follows that the free-particle Hamiltonian, $\hat{H}$, is Hermitian.

$$\hat{H} = \frac{\hat{p}^2}{2m} \tag{4.67}$$

$$\hat{H}^\dagger = \left(\frac{\hat{p}^2}{2m} \right)^\dagger = \frac{\hat{p}^2}{2m} = \hat{H} \tag{4.68}$$

[Recall (4.63).] For a particle in a potential field $V(x)$,

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) \tag{4.69}$$

Since $V(x)$ is a real function that merely multiplies (say in $\mathfrak{H}_2$), it is Hermitian.

$$\begin{aligned} \langle \psi_l | V\psi_n \rangle &= \int_{-\infty}^{\infty} \psi_l^* V \psi_n \, dx = \int_{-\infty}^{\infty} V \psi_l^* \psi_n \, dx \\ &= \int (V\psi_l)^* \psi_n \, dx = \langle V\psi_l | \psi_n \rangle \end{aligned} \tag{4.70}$$

It follows that $\hat{H}$ as given by (4.69) is Hermitian.

PROBLEMS

4.11 (a) Show that $(a\hat{A} + b\hat{B})^\dagger = a^*\hat{A}^\dagger + b^*\hat{B}^\dagger$.
(b) Show that $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$.
(c) What is the Hermitian adjoint of the real number a?
(d) What is the Hermitian adjoint of $\hat{D}^2$? [See (4.54).]
(e) What is the Hermitian adjoint of $(\hat{A}\hat{B} - \hat{B}\hat{A})$?
(f) What is the Hermitian adjoint of $(\hat{A}\hat{B} + \hat{B}\hat{A})$?
(g) What is the Hermitian ajoint of $i(\hat{A}\hat{B} - \hat{B}\hat{A})$?
(h) What is $(\hat{A}^\dagger)^\dagger$?
(i) What is $(\hat{A}^\dagger\hat{A})^\dagger$?

4.12 If $\hat{A}$ and $\hat{B}$ are both Hermitian, which of the following three operators are Hermitian?
(a) $i(\hat{A}\hat{B} - \hat{B}\hat{A})$.
(b) $(\hat{A}\hat{B} - \hat{B}\hat{A})$.
(c) $\left(\dfrac{\hat{A}\hat{B} + \hat{B}\hat{A}}{2}\right)$.
(d) If $\hat{A}$ is not Hermitian, is the product $\hat{A}^\dagger\hat{A}$ Hermitian?
(e) If $\hat{A}$ corresponds to the observable A, and $\hat{B}$ corresponds to B, what is a "good" (i.e., Hermitian) operator that corresponds to the physically observable product AB?

4.13 If $\hat{A}$ is Hermitian, show that

$$\langle \hat{A}^2 \rangle \geq 0$$

Answer (in $\mathfrak{H}_2$)

$$\langle \hat{A}^2 \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A}^2 \psi \, dx = \int_{-\infty}^{\infty} (\hat{A}\psi)^* \hat{A}\psi \, dx$$

$$= \int_{-\infty}^{\infty} |\hat{A}\psi|^2 \, dx \geq 0$$

4.14 If $\hat{A}$ is Hermitian, show that $\langle A \rangle$ is real; that is, show that $\langle A \rangle^* = \langle A \rangle$.

4.15 For a particle moving in one dimension, show that the operator $\hat{x}\hat{p}$ is not Hermitian. Construct an operator which corresponds to this physically observable product that is Hermitian.

4.6 PROPERTIES OF HERMITIAN OPERATORS

The first property of Hermitian operators we wish to establish is that their eigenvalues are real. Let $\hat{A}$ be a Hermitian operator. Let $\{\varphi_n\}$ and $\{a_n\}$ represent, respectively, the eigenfunctions and eigenvalues of the operator $\hat{A}$.

$$\hat{A}\varphi_n = a_n\varphi_n \tag{4.71}$$

In Dirac notation

$$|\hat{A}\varphi_n\rangle = |a_n\varphi_n\rangle \quad \text{or equivalently} \quad \hat{A}|\varphi_n\rangle = a_n|\varphi_n\rangle \tag{4.72}$$

Multiplying from the left with $\langle\varphi_n|$ gives

$$\langle\varphi_n|\hat{A}\varphi_n\rangle = \langle\varphi_n|a_n\varphi_n\rangle = a_n\langle\varphi_n|\varphi_n\rangle \tag{4.73}$$

Since $\hat{A}$ is Hermitian, we can write the left-hand side as

$$\langle\hat{A}\varphi_n|\varphi_n\rangle = \langle a_n\varphi_n|\varphi_n\rangle = a_n^*\langle\varphi_n|\varphi_n\rangle \tag{4.74}$$

Equating the last terms in the latter two equations gives

$$a_n^* = a_n \tag{4.75}$$

and a_n is real.

The second property of Hermitian operators we wish to establish is that *their eigenfunctions are orthogonal.* Again consider (4.72). Now multiply from the left with another eigenvector of $\hat{A}$, $\langle\varphi_l|$. There results

$$\langle\varphi_l|\hat{A}\varphi_n\rangle = a_n\langle\varphi_l|\varphi_n\rangle \tag{4.76}$$

Since $\hat{A}$ is Hermitian, the left-hand side of this equation can be rewritten

$$\langle\hat{A}\varphi_l|\varphi_n\rangle = a_l^*\langle\varphi_l|\varphi_n\rangle = a_l\langle\varphi_l|\varphi_n\rangle \tag{4.77}$$

The eigenvalue a_l is real because it is an eigenvalue of a Hermitian operator (i.e., $\hat{A}$). Subtracting the two equations above gives

$$(a_l - a_n)\langle\varphi_l|\varphi_n\rangle = 0 \tag{4.78}$$

If $a_l \neq a_n$, this equation says that

$$\langle\varphi_l|\varphi_n\rangle = 0 \tag{4.79}$$

which is the expression of the orthogonality of the set of functions $\{\varphi_n\}$. If these functions are all normalized, then (4.79) may be generalized to read

$$\langle\varphi_l|\varphi_n\rangle = \delta_{ln} \tag{4.80}$$

Thus, the eigenvalues of a Hermitian operator are real, and its eigenfunctions are orthogonal.

PROBLEMS

4.16 Show that if an operator $\hat{B}$ has an eigenvalue $b_1 \neq b_1^*$, then $\hat{B}$ is not Hermitian.

4.17 Consider the operator $\hat{C}$,

$$\hat{C}\varphi(x) = \varphi^*(x)$$

(a) Is $\hat{C}$ Hermitian?
(b) What are the eigenfunctions of $\hat{C}$?
(c) What are the eigenvalues of $\hat{C}$?

4.18 Given that the operator $\hat{O}$ annihilates the ket vector $|f\rangle$, that is, $\hat{O}|f\rangle = 0$, what is the value of the bra vector $\langle f|\hat{O}^\dagger$? Interpret the meaning of your answer.

4.19 The parallelogram law of geometry states that: the sum of the squares of the diagonals of a parallelogram equals twice the sum of the squares of the sides. Show that this is also true in Hilbert space; that is, if ψ and φ are any two elements of a Hilbert space, then

$$\|\psi + \varphi\|^2 + \|\psi - \varphi\|^2 = 2\|\psi\|^2 + 2\|\varphi\|^2$$

4.20 Show that the standard properties of $\cos\theta$, together with the definition of the inner product between two vectors φ and ψ, in $\mathfrak{H}$, with respective lengths, $\|\varphi\|$ and $\|\psi\|$, imply the Cauchy–Schwartz inequality

$$|\langle\varphi|\psi\rangle| \leq \|\varphi\|\,\|\psi\|$$

4.21 Use the Cauchy–Schwartz inequality to prove the triangle inequality

$$\|\varphi + \psi\|^2 \leq (\|\varphi\| + \|\psi\|)^2$$

4.22 Construct the squared length of $(\psi - \varphi)$ to show that

$$\|\psi\|^2 + \|\varphi\|^2 \geq 2\,\mathrm{Re}\,\langle\psi|\varphi\rangle$$

4.23 Let the sequence $\{\varphi_n\}$ be an orthonormal basis in $\mathfrak{H}$. Let the sequence $\{\cos\theta_n\}$ represent the angles between the vectors $\{\varphi_n\}$ and an arbitrary element ψ in $\mathfrak{H}$. Using Bessel's inequality,

$$\sum_{n=1}^{\infty} |\langle\varphi_n|\psi\rangle|^2 \leq \|\psi\|^2$$

show that

$$\sum_{n=1}^{\infty} \cos^2\theta_n \leq 1$$

Under what circumstances does the equality hold?

4.24 Every convergent sequence is also a *Cauchy sequence*. A sequence $\{\varphi_n(x)\}$ is a Cauchy sequence if

$$\lim_{\substack{n\to\infty \\ l\to\infty}} \|\varphi_n - \varphi_l\| = 0$$

A function space $\mathfrak{H}$ is a *complete space* if every Cauchy sequence in $\mathfrak{H}$ converges to an element of $\mathfrak{H}$. This is a requirement that a function space must satisfy in order that it be termed a Hilbert space. (See property 4 after Eq. 4.27.) Show that the space of functions on the unit interval with the property $\varphi(0) = \varphi(1) = 0$ is not a Hilbert space.

4.25 In addition to a complete space, one also defines a *complete sequence*. An orthonormal sequence $\{\varphi_n\}$ is complete in $\mathfrak{H}$ if there is no vector ψ, in $\mathfrak{H}$ of nonzero length ($\|\psi\| > 0$), which is perpendicular to all the elements in the sequence $\{\varphi_n\}$. Show that if $\{\varphi_n\}$ is an orthonormal basis of $\mathfrak{H}$, it is complete in $\mathfrak{H}$.

Answer

Let $\{\varphi_n\}$ be an orthonormal basis of $\mathfrak{H}$. Let ψ be an element of $\mathfrak{H}$ with nonzero length, which is normal to all the elements of $\{\varphi_n\}$. If $\{\varphi_n\}$ is a basis, then we may expand ψ,

$$\psi = \sum a_n \varphi_n = \sum \langle \varphi_n | \psi \rangle \varphi_n$$

But ψ is normal to all φ_n. Therefore, $\langle \varphi_n | \psi \rangle = 0$, which gives $\psi = 0$, so the hypothesis leads to a contradiction, hence the hypothesis is an incorrect statement and there is no such ψ in $\mathfrak{H}$.

4.26 Show that any operator $\hat{A}$ may be expressed as the linear combination of a Hermitian and an anti-Hermitian ($\hat{B}^\dagger = -\hat{B}$) operator.

Answer

$$\hat{A} = \left(\frac{\hat{A} + \hat{A}^\dagger}{2}\right) + i\left(\frac{\hat{A} - \hat{A}^\dagger}{2i}\right)$$

[*Note:* $\hat{A} + \hat{A}^\dagger$ and $i(\hat{A} - \hat{A}^\dagger)$ are both Hermitian.]

4.27 Show that the wavefunctions for a particle in a one-dimensional box with walls at $x = 0$ and L satisfy the equality

$$\int_0^L \psi^* \psi_{xx}\, dx = -\int_0^L |\psi_x|^2\, dx$$

The subscript x denotes differentiation.

4.28 Use the equality proved in Problem 4.27 to establish the following *variational principle.* If the expectation $\int \psi^* \hat{H} \psi\, dx$ is minimum, the normalized wavefunction ψ is the ground state. Specifically, establish the theorem for a particle in a one-dimensional box, assuming real wavefunctions.

Answer

Apart from a constant factor and with the results of Problem 4.27, we may write

$$\langle H \rangle = -\int_0^L \psi^* \psi_{xx}\, dx = \int_0^L \psi_x{}^2\, dx$$

Let ψ minimize $\langle H \rangle$. Then infinitesimal variation of ψ causes no change in $\langle H \rangle$. Let $\psi \to \psi + \delta\psi$. The variation $\delta\psi$ is an arbitrary infinitesimal function of x that vanishes at $x = 0$ and L. Then

$$\langle H \rangle = \int \psi_x{}^2\, dx \to \int (\psi_x + \delta\psi_x)^2\, dx = \langle H \rangle + \delta\langle H \rangle$$

$$\delta\langle H \rangle = 2\int \psi_x\, \delta\psi_x\, dx = 2\int \psi_x \frac{d}{dx}\, \delta\psi\, dx = 0$$

Integrating the last term by parts and dropping the "surface" terms gives

$$\int \psi_{xx}\, \delta\psi\, dx = 0$$

Variation of the normalization statement (both ψ and $\psi + \delta\psi$ are normalized) gives

$$\lambda \int \psi \delta\psi \, dx = 0$$

where λ is an arbitrary undetermined multiplier. Combining the last two equations yields

$$\int_0^L \delta\psi(\psi_{xx} - \lambda\psi) \, dx = 0$$

If this equation is to be satisfied for arbitrary variation of ψ about the minimizing value, we may conclude

$$\psi_{xx} = \lambda\psi$$

It follows that ψ is an eigenstate of $\hat{H}$, in which case $\langle H \rangle$ is an energy eigenvalue which has minimum value for the ground state.