

Theorems of Quantum Mechanics

.1 Introduction

The Schroedinger equation for the one-electron atom (Chapter 6) and the electronic Schroedinger equation for the one-electron diatomic molecule (Section 13.3) are exactly soluble; however, because of the inter-electronic repulsion terms in the Hamiltonian, the Schroedinger equation for many-electron atoms and molecules is not separable in any coordinate system, and cannot be solved exactly. Hence, we must seek approximate methods of solution. The two main approximation methods, the variation method and perturbation theory, will be developed in Chapters 8 and 9; to derive these methods, we must develop further the theory of quantum mechanics, which is what we will do in this chapter. Although much of the work will be of an abstract nature, and perhaps not so easy to master, the theorems we will derive are basic to an understanding of quantum mechanics.

We will conclude this chapter with a summary of the postulates of quantum mechanics.

.2 Notation

Before getting started, we introduce some notations for the integrals with which we will be dealing. These notations are in widespread use, and it is helpful to be familiar with them.

The definite integral over all space of an operator sandwiched between two functions is of frequent occurrence, and various abbreviations are used:

$$\int \varphi_m^* \hat{A} \varphi_n d\tau \equiv \langle \varphi_m | \hat{A} | \varphi_n \rangle \equiv (\varphi_m | \hat{A} | \varphi_n) \quad (7.1)$$

where φ_m and φ_n are two functions. If it is clear what functions are meant, we can use just the indices:

$$\int \varphi_m^* \hat{A} \varphi_n d\tau \equiv \langle m | \hat{A} | n \rangle \quad (7.2)$$

The above notation, introduced by Dirac, is called *bracket notation*. Another notation is:

$$\int \varphi_m^* \hat{A} \varphi_n d\tau \equiv A_{mn} \quad (7.3)$$

The notations A_{mn} and $\langle m | \hat{A} | n \rangle$ imply that we use the complex conjugate of the function whose letter appears first. (An integral like $\int \varphi_m^* \hat{A} \varphi_n d\tau$ is called a *matrix element* of the operator \hat{A} . Matrices are rectangular arrays of numbers, and obey certain rules of combination. We will discuss matrices in Volume II, Chapter 7; until then we will not use them. As a historical note, just prior to Schrodinger's discovery of his equation, the German physicist Werner Heisenberg discovered an equally valid form of quantum mechanics, which uses matrices instead of differential equations. Heisenberg's matrix mechanics and Schrodinger's wave mechanics are fully equivalent to each other.)

For the integral between two functions, we write

$$\int \varphi_m^* \varphi_n d\tau \equiv \langle \varphi_m | \varphi_n \rangle \equiv \langle m | n \rangle \quad (7.4)$$

Another notation is:

$$\int \varphi_m^* \varphi_n d\tau \equiv (\varphi_m, \varphi_n) \quad (7.5)$$

Since

$$\left[\int \varphi_m^* \varphi_n d\tau \right]^* = \int \varphi_n^* \varphi_m d\tau \quad (7.6)$$

we have the identity

$$\langle m | n \rangle^* = \langle n | m \rangle \quad (7.7)$$

In particular

$$\langle m | m \rangle^* = \langle m | m \rangle \quad (7.8)$$

In general

$$(1) \quad \langle i | \hat{A} | j \rangle^* = \langle j | \hat{A}^\dagger | i \rangle \quad A^\dagger \text{ is adjoint operator}$$

$$\begin{aligned} \left(\int dx \varphi_i^*(x) \hat{A} \varphi_j(x) \right)^* &= \int dx \varphi_i(x) (\hat{A} \varphi_j(x))^* \\ &= \int dx (\varphi_i \overleftarrow{A^\dagger}) \varphi_j^*(x) = \int dx \varphi_j^*(x) (A^\dagger \varphi_i(x)) \end{aligned}$$

If A is Hermitian, so $A^\dagger = A$, then

$$= \int dx \varphi_j^*(x) A \varphi_i(x) = \langle j | A | i \rangle$$

(or $\langle i | \hat{A} | j \rangle = \langle j | A | i \rangle^*$ what we claimed before for Hermitian operator).

In terms of "matrix" notation (1) is

$$A_{ij}^* = A_{ji}^\dagger \Rightarrow A_{ij} = (A_{ji}^\dagger)^*$$

For a matrix the transpose means interchange elements and take their complex conjugates

i.e. For matrix \underline{B} w elements b_{ij} ,

$$\underline{B}^\dagger = b_{ji}^*$$

More on notation

$$\int dx \varphi_m^*(x) A(x) \varphi_n(x) = \langle m|A|n \rangle$$

$$\int dx dx' \langle m|x \rangle \langle x|A|x' \rangle \langle x'|n \rangle$$

$$\begin{aligned} \mathbb{1} &= \int dx |x \rangle \langle x| && \text{Completeness (abstract)} \\ \langle x'|x \rangle &= \int dx'' \langle x'|x'' \rangle \langle x''|x \rangle && \text{"} \\ \delta(x-x') &= \int dx'' \delta(x'-x'') \delta(x''-x) && \text{pos. rep.} \end{aligned}$$
$$= \int dx \int dx' \varphi_m(x) A(x, x') \varphi_n(x')$$

$$\text{sg } A = V \quad A(x, x') = V(x) \delta(x-x')$$

$$\int dx \varphi_m^*(x) V(x) \varphi_n(x)$$

$$A = \frac{d}{dx}$$

$$A(x, x') = \frac{d}{dx} \delta(x-x')$$

$$\int dx \int dx' \varphi_m^*(x) \frac{d}{dx} \delta(x-x') \varphi_n(x') \quad \text{uv/parts (on } x' \text{ integral)}$$

$$= + \int dx \int dx' \varphi_m^*(x) \delta(x-x') \frac{d}{dx'} \varphi_n(x') = \int dx \varphi_m^*(x) \frac{d}{dx} \varphi_n(x)$$

7.3 Hermitian Operators

We stated in Section 3.1 that the operators representing physical quantities are linear. There is another requirement such operators must meet, which we now discuss.

Let \hat{A} be the linear operator representing the physical property A . For the average value of A , Eq. (3.117) gives

for the total wavefunction $\langle A \rangle = \int \Psi^* \hat{A} \Psi d\tau$ (7.9)

where Ψ is the state function of the system. The average value of a physical quantity must be a real number; therefore we demand that

$$\langle A \rangle = \langle A \rangle^* \quad (7.10)$$

$$\int \Psi^* \hat{A} \Psi d\tau = \int \Psi (\hat{A} \Psi)^* d\tau \quad (7.11)$$

Equation (7.11) must hold for any function Ψ that can represent a possible state of the system; i.e., it must hold for all well-behaved functions Ψ . An operator that satisfies (7.11) for all well-behaved functions is called a *Hermitian operator*.

Many texts define a Hermitian operator as one that satisfies

$$\int f^* \hat{A} g d\tau = \int g (\hat{A} f)^* d\tau \quad (7.12)$$

for all well-behaved functions f and g . [Note especially that on the left side of (7.12) \hat{A} operates on g , but on the right side \hat{A} operates on f .] For the special case $f = g$, (7.12) reduces to (7.11). Equation (7.12) is apparently a more stringent requirement than (7.11), but we will prove that (7.12) is a consequence of (7.11), so that the two definitions of a Hermitian operator are equivalent.

We begin the proof by setting $\Psi = f + cg$ in (7.11), where c is an arbitrary parameter; this gives

$$\begin{aligned} \int (f + cg)^* \hat{A} (f + cg) d\tau &= \int (f + cg) [\hat{A} (f + cg)]^* d\tau \\ \int (f^* + c^* g^*) \hat{A} f d\tau + \int (f^* + c^* g^*) \hat{A} c g d\tau &= \int (f + cg) (\hat{A} f)^* d\tau + \int (f + cg) (\hat{A} c g)^* d\tau \\ \int f^* \hat{A} f d\tau + c^* \int g^* \hat{A} f d\tau + c \int f^* \hat{A} g d\tau + c c^* \int g^* \hat{A} g d\tau &= \int f (\hat{A} f)^* d\tau + c \int g (\hat{A} f)^* d\tau + c^* \int f (\hat{A} g)^* d\tau + c^* c \int g (\hat{A} g)^* d\tau \end{aligned}$$

Just state
- don't prove
a problem
PS -
Say use
 $c=1$
and $c=i$

By virtue of (7.11), the first terms on each side of this last equation are equal to each other; likewise the last terms on each side are equal. Hence

$$c^* \int g^* \hat{A} f d\tau + c \int f^* \hat{A} g d\tau = c \int g(\hat{A} f)^* d\tau + c^* \int f(\hat{A} g)^* d\tau \quad (7.13)$$

Setting $c = 1$ in (7.13), we have

$$\int g^* \hat{A} f d\tau + \int f^* \hat{A} g d\tau = \int g(\hat{A} f)^* d\tau + \int f(\hat{A} g)^* d\tau \quad (7.14)$$

Setting $c = i$ in (7.13), we have, after dividing by i ,

$$- \int g^* \hat{A} f d\tau + \int f^* \hat{A} g d\tau = \int g(\hat{A} f)^* d\tau - \int f(\hat{A} g)^* d\tau \quad (7.15)$$

We now add (7.14) and (7.15) to get

$$\int f^* \hat{A} g d\tau = \int g(\hat{A} f)^* d\tau \quad (7.16)$$

Q.E.D.

Therefore, a Hermitian operator \hat{A} possesses the property that

$$\int \varphi_i^* \hat{A} \varphi_j d\tau = \int \varphi_j(\hat{A} \varphi_i)^* d\tau \quad (7.17)$$

where φ_i and φ_j are arbitrary well-behaved functions. Using the bracket and matrix-element notations, we write

$$\langle \varphi_i | \hat{A} | \varphi_j \rangle = \langle \varphi_j | \hat{A} | \varphi_i \rangle^* \quad (7.18)$$

$$\langle i | \hat{A} | j \rangle = \langle j | \hat{A} | i \rangle^* \quad (7.18)$$

$$A_{ij} = A_{ji}^* \quad (7.19)$$

By A_{ji}^* we mean $(A_{ji})^*$.

Let us show that some of the operators we have been using are indeed Hermitian. For simplicity we will work in one dimension. To prove that an operator is Hermitian, it suffices to show that it satisfies (7.11) for all well-behaved functions; however, we will make things a bit tougher on ourselves by proving that (7.17) is satisfied.

First consider the potential-energy operator. The right side of (7.17) is

$$\int_{-\infty}^{\infty} \varphi_j(x) [V(x) \varphi_i(x)]^* dx \quad \text{Prob. 1} \quad (7.20)$$

We have $V^* = V$, since the potential energy is a real function. Moreover, the order of the factors in (7.20) is immaterial. Hence

$$\int \varphi_j [V \varphi_i]^* dx = \int \varphi_j V^* \varphi_i^* dx = \int \varphi_i^* V \varphi_j dx$$

which proves V is Hermitian.

prob. 2 The operator for the x component of linear momentum is given by Eq. (3.28). For this operator, the left side of (7.17) is

$$-i\hbar \int_{-\infty}^{\infty} \varphi_i^*(x) \frac{d\varphi_j(x)}{dx} dx \quad (7.21)$$

Now we use the formula for integration by parts:

$$\int_a^b f(x) \frac{dg(x)}{dx} dx = f(x)g(x) \Big|_a^b - \int_a^b g(x) \frac{df(x)}{dx} dx \quad (7.22)$$

$$f(x) = -i\hbar\varphi_i^*(x) \quad g(x) = \varphi_j(x)$$

$$-i\hbar \int_{-\infty}^{\infty} \varphi_i^* \frac{d\varphi_j}{dx} dx = -i\hbar\varphi_i^*\varphi_j \Big|_{-\infty}^{\infty} + i\hbar \int_{-\infty}^{\infty} \varphi_j(x) \frac{d\varphi_i^*(x)}{dx} dx \quad (7.23)$$

Now φ_i and φ_j are well-behaved functions; hence they vanish at $x = \pm\infty$. Therefore, (7.23) becomes

$$\int_{-\infty}^{\infty} \varphi_i^* \left(-i\hbar \frac{d\varphi_j}{dx} \right) dx = \int_{-\infty}^{\infty} \varphi_j \left(-i\hbar \frac{d\varphi_i}{dx} \right)^* dx \quad (7.24)$$

which is the same as (7.17), and proves that \hat{p}_x is Hermitian. The proof that the kinetic-energy operator is Hermitian is left to the reader. The sum of two Hermitian operators can be shown to be Hermitian; hence the Hamiltonian operator $\hat{H} = \hat{T} + \hat{V}$ is Hermitian.

7.4 Properties of Hermitian Operators

In this section, we prove some theorems about the eigenvalues and eigenfunctions of Hermitian operators.

Since the eigenvalues of the operator \hat{A} corresponding to the physical quantity A are the possible results of a measurement of A , these eigenvalues should all be real numbers. We now prove this, using the Hermitian property of \hat{A} . We start by setting $\varphi_j = \varphi_i$ in (7.17):

$$\int \varphi_i^* \hat{A} \varphi_i d\tau = \int \varphi_i (\hat{A} \varphi_i)^* d\tau \quad (7.25)$$

Now let us suppose that φ_i is an eigenfunction of \hat{A} with eigenvalue b :

$$\hat{A} \varphi_i = b \varphi_i \quad (7.26)$$

Equation (7.25) becomes

$$b \int \varphi_i^* \varphi_i d\tau = \int \varphi_i (b \varphi_i)^* d\tau = b^* \int \varphi_i \varphi_i^* d\tau \quad (7.27)$$

$$(b - b^*) \int |\varphi_i|^2 d\tau = 0 \quad (7.28)$$

Since the integrand $|\varphi_t|^2$ is never negative, the only way the integral in (7.28) could be zero would be if φ_t were zero for all values of the coordinates. However, we always reject zero as an eigenfunction on physical grounds; hence, the integral in (7.28) cannot be zero. Therefore, $(b - b^*) = 0$, or $b = b^*$, which completes the proof.

To develop a familiarity with bracket notation, we will repeat the proof that eigenvalues of Hermitian operators are real, using bracket notation. We begin by setting $i = j$ in (7.18):

$$\langle i|\hat{A}|i\rangle = \langle i|\hat{A}|i\rangle^* \quad (7.29)$$

Using (7.26), we have

$$\langle i|b|i\rangle = \langle i|b|i\rangle^* \quad (7.30)$$

$$b\langle i|i\rangle = b^*\langle i|i\rangle^* = b^*\langle i|i\rangle$$

$$(b - b^*)\langle i|i\rangle = 0$$

$$b = b^* \quad (7.31)$$

where (7.8) was used.

We showed that the particle-in-a-box wave functions are mutually orthogonal. We now prove the general theorem that *the eigenfunctions of a Hermitian operator are, or can be chosen to be, mutually orthogonal*. Given that

$$\hat{B}F = sF \quad \hat{B}G = tG \quad \text{prb. 4. Don't do it! - refer to Merz.} \quad (7.32)$$

where F and G are two independent eigenfunctions of \hat{B} , we want to prove that

$$\int F^*G \, d\tau \equiv \langle F|G\rangle = 0 \quad (7.33)$$

We begin with Eq. (7.18), which expresses the Hermitian nature of \hat{B} :

$$\langle F|\hat{B}|G\rangle = \langle G|\hat{B}|F\rangle^* \quad (7.34)$$

Using (7.32), we have

$$\begin{aligned} \langle F|t|G\rangle &= \langle G|s|F\rangle^* \\ t\langle F|G\rangle &= s^*\langle G|F\rangle^* \end{aligned} \quad (7.35)$$

Since eigenvalues of Hermitian operators are real, we have $s^* = s$. Using (7.7), we have

$$\begin{aligned} t\langle F|G\rangle &= s\langle F|G\rangle \\ (t - s)\langle F|G\rangle &= 0 \end{aligned} \quad (7.36)$$

If $s \neq t$, then

$$\langle F|G\rangle = 0 \quad (7.37)$$

We have proved that two eigenfunctions of a Hermitian operator that correspond to *different* eigenvalues are orthogonal. The question now is: Can we have two independent eigenfunctions that have the *same* eigenvalue? The answer is yes. In the case of *degeneracy*, we have the same eigenvalue for more than one independent eigenfunction. Therefore, we can only be certain that two independent eigenfunctions of a Hermitian operator are orthogonal to each other, if they do not correspond to a degenerate eigenvalue. We now show that in the case of degeneracy, we may *construct* eigenfunctions that will be orthogonal to one another. We shall use the theorem proved in Section 3.6, that any linear combination of eigenfunctions corresponding to a degenerate eigenvalue is an eigenfunction with the same eigenvalue. Let us therefore suppose that F and G are independent eigenfunctions that have the same eigenvalue:

$$\hat{B}F = sF \quad \hat{B}G = sG \quad (7.38)$$

We take linear combinations of F and G , to form two new eigenfunctions φ_1 and φ_2 that will be orthogonal to each other. We choose φ_1 equal to F , and for φ_2 we write

$$\varphi_2 = G + cF \quad \varphi_1 = F \quad (7.39)$$

The constant c will be chosen to insure orthogonality. We want

$$\int \varphi_1^* \varphi_2 \, d\tau = 0 \quad (7.40)$$

$$\int F^*(G + cF) \, d\tau = \int F^*G \, d\tau + c \int F^*F \, d\tau = 0 \quad (7.41)$$

Hence, choosing

$$c = - \int F^*G \, d\tau / \int F^*F \, d\tau \quad (7.42)$$

we have two orthogonal eigenfunctions φ_1 and φ_2 , corresponding to the degenerate eigenvalue. This procedure (called the Schmidt orthogonalization method) can be extended to the case of n -fold degeneracy, to give n linearly independent orthogonal eigenfunctions corresponding to the degenerate eigenvalue.

Thus, although there is no guarantee that the eigenfunctions of a degenerate eigenvalue are orthogonal, we can always *choose* them to be orthogonal, if we desire, by using the Schmidt (or some other) orthogonalization method. In fact, unless stated otherwise, we will always assume that we have chosen the eigenfunctions to be orthogonal:

$$\int \varphi_i^* \varphi_j \, d\tau = 0 \quad i \neq j \quad (7.43)$$

where φ_i and φ_j are two independent eigenfunctions of a Hermitian operator.

We can usually multiply an eigenfunction by a suitable constant to normalize it, and we shall assume, unless stated otherwise, that all eigenfunctions are normalized:

$$\int \varphi_i^* \varphi_i d\tau = 1 \quad (7.44)$$

The exception is where the eigenvalues form a continuum, rather than a discrete set of values; in this case, the eigenfunctions are not quadratically integrable. Examples are the linear-momentum eigenfunctions, the free-particle energy eigenfunctions, and the hydrogen-atom continuum energy eigenfunctions.

Using the Kronecker delta, we can combine (7.43) and (7.44) into one equation:

$$\int \varphi_i^* \varphi_j d\tau = \delta_{ij} \quad (7.45)$$

$$\langle i | j \rangle = \delta_{ij} \quad (7.46)$$

where φ_i and φ_j are eigenfunctions of some Hermitian operator.

As an example, consider the spherical harmonics. We ask for the value of the integral

$$\int_0^{2\pi} \int_0^\pi [Y_l^m(\theta, \varphi)]^* Y_{l'}^{m'}(\theta, \varphi) \sin \theta d\theta d\varphi \quad (7.47)$$

where the $\sin \theta$ factor comes from the volume element in spherical polar coordinates, (5.127). The spherical harmonics are eigenfunctions of the Hermitian operator L^2 [Eq. (5.173)]. Since eigenfunctions of a Hermitian operator belonging to different eigenvalues are orthogonal, we conclude that the integral (7.47) is zero unless $l = l'$. Similarly, Eq. (5.174) allows us to conclude that (7.47) is zero unless $m = m'$. Also, the multiplicative constant in (5.172) has been chosen so that the spherical harmonics are normalized [Eq. (6.139)]. Therefore

$$\int_0^{2\pi} \int_0^\pi [Y_l^m(\theta, \varphi)]^* Y_{l'}^{m'}(\theta, \varphi) \sin \theta d\theta d\varphi = \delta_{l,l'} \delta_{m,m'} \quad (7.48)$$

7.5 Expansion in Terms of Eigenfunctions

In the previous section, we proved the orthogonality of the eigenfunctions of a Hermitian operator. We now discuss another important property of these functions; this property allows us to expand an arbitrary well-behaved function in terms of these eigenfunctions.

function of the hydrogen atom, and $\psi_{Elm}(r, \theta, \varphi)$ is a continuum eigenfunction, then (7.73) becomes

$$f(r, \theta, \varphi) = \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^l a_{nlm} \psi_{nlm}(r, \theta, \varphi) + \sum_{l=0}^{\infty} \sum_{m=-l}^l \int_0^{\infty} a_{lm}(E) \psi_{Elm}(r, \theta, \varphi) dE$$

As another example, consider the eigenfunctions of \hat{p}_x , which are [Eq. (3.43)]

$$\varphi_k = e^{ikx/\hbar} \quad -\infty < k < \infty \quad (7.75)$$

Here the eigenvalues are all continuous, and the eigenfunction expansion (7.73) of an arbitrary function f becomes

$$f(x) = \int_{-\infty}^{\infty} a(k) e^{ikx/\hbar} dk \quad (7.76)$$

For the reader with a good mathematical background, we note that the integral in (7.76) is very nearly the Fourier transform of $a(k)$.

Let us evaluate the expansion coefficients in (7.73). The work is identical to that involved in deriving (7.57). We multiply (7.73) by φ_j^* and integrate over all space to get

$$\int \varphi_j^* f d\tau = \sum_i a_i \int \varphi_j^* \varphi_i d\tau = \sum_i a_i \delta_{ij} \quad (7.77)$$

$$a_j = \int \varphi_j^* f d\tau \quad (7.78)$$

where the orthonormality of the eigenfunctions, Eq. (7.45), was used. The expansion (7.73) becomes

$$f = \sum_i \left[\int \varphi_i^* f d\tau \right] \varphi_i \quad (7.79)$$

$$f = \sum_i \langle \varphi_i | f \rangle \varphi_i \quad (7.80)$$

If we introduce the notation

$$|f\rangle \equiv f \quad |\varphi_i\rangle \equiv \varphi_i \quad (7.81)$$

then we can write (7.80) as

$$|f\rangle = \sum_i |\varphi_i\rangle \langle \varphi_i | f \rangle \quad (7.82)$$

$$|f\rangle = \sum_i |i\rangle \langle i | f \rangle \quad (7.83)$$

write out a_i using $\delta(x-x') =$

$$f(x) = \langle x | f \rangle = \int dx' \langle x | i \rangle \langle i | x' \rangle \langle x' | f \rangle = \int dx' \int \varphi_i^*(x) \varphi_i(x') f(x')$$

possibility 4

and any function in
reduces out by orthonormality

This last equation is easy to remember, if we remember the operator equation

$$\sum_i |i\rangle\langle i| = \hat{1} \quad (7.84)$$

plane wave
or
glow wave

If we start with the identity

$$|f\rangle = |f\rangle \quad (7.85)$$

and operate on one side of (7.85) with the unit operator, and on the other side with the operator

$$\sum_i |i\rangle\langle i| \quad (7.86)$$

which is equal to the unit operator, we get (7.83).

The contents of Sections 7.4 and 7.5 can be summarized by the statement that *the eigenfunctions of a linear, Hermitian operator form a complete, orthonormal set.*

7.6 Eigenfunctions of Commuting Operators

In Section 5.1 we made some statements about simultaneous eigenfunctions of two different operators. We now prove these statements.

First we show that if there exists a common *complete set* of eigenfunctions for two linear operators, then the operators commute. Let \hat{A} and \hat{B} denote two linear operators that possess a common complete set of eigenfunctions, φ_i . We have

$$\hat{A}\varphi_i = s_i\varphi_i \quad \hat{B}\varphi_i = t_i\varphi_i \quad (7.87)$$

where s_i and t_i are the eigenvalues. We must prove that

$$[\hat{A}, \hat{B}] = \hat{0} \quad (7.88)$$

Equation (7.88) is an operator equation; for two operators to be equal, the result of operating with either of them on an arbitrary function f must be the same; we must therefore show that

$$(\hat{A}\hat{B} - \hat{B}\hat{A})f = \hat{0}f = 0 \quad (7.89)$$

where f is an arbitrary function. We begin the proof by expanding f (assuming that it obeys the proper boundary conditions) in terms of the complete set of eigenfunctions φ_i :

$$f = \sum_i c_i \varphi_i \quad (7.90)$$

$$\langle x|f\rangle = \sum_i \langle x|\varphi_i\rangle \langle \varphi_i|f\rangle = \int_{-\infty}^{\infty} dk \langle x|k\rangle \langle k|f\rangle$$

$$\text{ex. } \psi(x) = \int dk c(k) e^{ikx}$$

Operating on each side of (7.90) with $\hat{A}\hat{B} - \hat{B}\hat{A}$, we have

$$(\hat{A}\hat{B} - \hat{B}\hat{A})f = (\hat{A}\hat{B} - \hat{B}\hat{A}) \sum_{\mathfrak{I}} c_{\mathfrak{I}} \varphi_{\mathfrak{I}} \quad (7.91)$$

Since $\hat{A}\hat{B}$ and $\hat{B}\hat{A}$ are linear operators (Problem 3.7); we have

$$(\hat{A}\hat{B} - \hat{B}\hat{A})f = \sum_{\mathfrak{I}} c_{\mathfrak{I}} (\hat{A}\hat{B} - \hat{B}\hat{A})\varphi_{\mathfrak{I}} \quad (7.92)$$

$$(\hat{A}\hat{B} - \hat{B}\hat{A})f = \sum_{\mathfrak{I}} c_{\mathfrak{I}} [\hat{A}(\hat{B}\varphi_{\mathfrak{I}}) - \hat{B}(\hat{A}\varphi_{\mathfrak{I}})] \quad (7.93)$$

where we have used the definitions of the sum and the product of operators. Use of (7.87) yields

$$(\hat{A}\hat{B} - \hat{B}\hat{A})f = \sum_{\mathfrak{I}} c_{\mathfrak{I}} [\hat{A}t_{\mathfrak{I}}\varphi_{\mathfrak{I}} - \hat{B}s_{\mathfrak{I}}\varphi_{\mathfrak{I}}] \quad (7.94)$$

$$(\hat{A}\hat{B} - \hat{B}\hat{A})f = \sum_{\mathfrak{I}} c_{\mathfrak{I}} (s_{\mathfrak{I}}t_{\mathfrak{I}}\varphi_{\mathfrak{I}} - t_{\mathfrak{I}}s_{\mathfrak{I}}\varphi_{\mathfrak{I}}) = 0 \quad (7.95)$$

which completes the proof that \hat{A} and \hat{B} commute if they have a common complete set of eigenfunctions.

It is sometimes erroneously stated that if there exists a common eigenfunction of \hat{A} and \hat{B} , then they commute. We have already seen an example that shows this statement to be false; in Section 5.3 we saw that the spherical harmonic Y_0^0 is an eigenfunction of both \hat{L}_z and \hat{L}_x even though these two operators do not commute. It is instructive to examine the "proof" that is often given of this erroneous statement. Let φ be the common eigenfunction:

$$\hat{A}\varphi = s\varphi \quad (7.96)$$

$$\hat{B}\varphi = t\varphi \quad (7.97)$$

We have

$$\hat{A}\hat{B}\varphi = \hat{A}t\varphi = st\varphi \quad (7.98)$$

$$\hat{B}\hat{A}\varphi = \hat{B}s\varphi = ts\varphi = st\varphi \quad (7.99)$$

$$\hat{A}\hat{B}\varphi = \hat{B}\hat{A}\varphi \quad (7.100)$$

The "proof" is completed by canceling φ from each side of (7.100) to get

$$\hat{A}\hat{B} = \hat{B}\hat{A} \quad (?) \quad (7.101)$$

It is in going from (7.100) to (7.101) that the error lies. Just because the two operators $\hat{A}\hat{B}$ and $\hat{B}\hat{A}$ give the same result when acting on the single function φ is no reason to conclude that $\hat{A}\hat{B} = \hat{B}\hat{A}$. (For example, d/dx and d^2/dx^2 give the same result when operating on e^x , but d/dx is certainly not equal to d^2/dx^2 .) The two operators must give the same result when acting on *every* (well-behaved) function in order to conclude that they are equal. Thus, even though \hat{A} and \hat{B} do not commute, there might exist one or more common eigenfunctions of \hat{A} and \hat{B} . However, we cannot have a common *complete* set of

eigenfunctions of two noncommuting operators, as we proved earlier in this section.

We have shown that *if there exists a common complete set of eigenfunctions of \hat{A} and \hat{B} , then they commute*. We now prove the converse theorem: *if \hat{A} and \hat{B} commute, we can select a common complete set of eigenfunctions for them*. Let φ_i and t_i be the eigenfunctions and eigenvalues of \hat{B} :

$$\hat{B}\varphi_i = t_i\varphi_i \quad (7.102)$$

Operating on both sides of this equation with \hat{A} , we have

$$\hat{A}\hat{B}\varphi_i = \hat{A}t_i\varphi_i \quad (7.103)$$

Since \hat{A} and \hat{B} commute, and \hat{A} is linear, we have

$$\hat{B}(\hat{A}\varphi_i) = t_i(\hat{A}\varphi_i) \quad (7.104)$$

This equation states that the function $\hat{A}\varphi_i$ is also an eigenfunction of the operator \hat{B} with the same eigenvalue t_i as the eigenfunction φ_i . Let us for the moment assume that the eigenvalues of \hat{B} are nondegenerate, i.e., that for any given eigenvalue t_i there corresponds one and only one linearly independent eigenfunction. If this is so, then the two eigenfunctions φ_i and $\hat{A}\varphi_i$, which correspond to the same eigenvalue t_i , must be linearly dependent, i.e., one must simply be a multiple of the other:

$$\hat{A}\varphi_i = c_i\varphi_i \quad (7.105)$$

where c_i is some constant. This equation states that the functions φ_i are eigenfunctions of \hat{A} , which is what we wanted to prove. In Section 7.5, we postulated that the eigenfunctions of any operator that represents a physical quantity form a complete set; hence, the φ_i form a complete set.

We have just proved the desired theorem for the nondegenerate case, but what about the degenerate case? Let the level with eigenvalue t_i be n -fold degenerate. We know from Eq. (7.104) that $\hat{A}\varphi_i$ is an eigenfunction of \hat{B} with eigenvalue t_i . Hence, it must be some linear combination of the n linearly independent eigenfunctions corresponding to the eigenvalue t_i . From this statement, we cannot conclude that φ_i is an eigenfunction of \hat{A} . However, by taking suitable linear combinations of the n linearly independent eigenfunctions, we can construct a new set of n linearly independent eigenfunctions of \hat{B} that will also be eigenfunctions of \hat{A} . We omit the proof¹ that this can be done.

Thus, when \hat{A} and \hat{B} commute it is always possible to *select* a common set of eigenfunctions for them. As an example, consider the hydrogen atom, where the operators \hat{L}_z and \hat{H} were shown to commute. If we

¹ See Merzbacher, Section 8.5.

So solve the easy one first

prob
do not
prove
this way

write both ways

desired, we could take the ϕ factor in the eigenfunctions of \hat{H} as $\sin m\phi$ and $\cos m\phi$. In this case, we will not have eigenfunctions of \hat{L}_z , except for $m = 0$. However, the linear combinations

$$R(r)S(\theta)[\cos m\phi + i \sin m\phi] = RSe^{im\phi} \quad m = -l, \dots, +l$$

give us eigenfunctions of \hat{L}_z that are still eigenfunctions of \hat{H} by virtue of the theorem in Section 3.6.

We conclude this section by proving a useful theorem about matrix elements. Let \hat{A} be a Hermitian operator with eigenfunctions φ_i :

$$\hat{A}\varphi_i = s_i\varphi_i \quad \Rightarrow \quad \hat{A} \int \varphi_j^* \varphi_i \, d\tau = s_i \int \varphi_j^* \varphi_i \, d\tau \quad (7.106)$$

Let \hat{B} be an operator that commutes with \hat{A} . We assert that the matrix element

$$B_{ij} = \int \varphi_i^* \hat{B}\varphi_j \, d\tau \quad (7.107)$$

is zero unless $s_i = s_j$. We have

$$\int \varphi_i^* \hat{B}\varphi_j \, d\tau = \frac{1}{s_j} \int \varphi_i^* \hat{B}s_j\varphi_j \, d\tau$$

$$B_{ij} = \frac{1}{s_j} \int \varphi_i^* \hat{B}\hat{A}\varphi_j \, d\tau \quad (7.108)$$

$$B_{ij} = \frac{1}{s_j} \int \varphi_i^* \hat{A}\hat{B}\varphi_j \, d\tau \quad (7.109)$$

$$s_j B_{ij} = \langle \varphi_i | \hat{A} | \hat{B}\varphi_j \rangle \quad (7.110)$$

Using the Hermitian property of \hat{A} [Eq. (7.18)], we have

$$s_j B_{ij} = \langle \hat{B}\varphi_j | \hat{A} | \varphi_i \rangle^* = \left(\int \varphi_j \hat{B} \varphi_i^* \, d\tau \right)^* = \left(\int \varphi_j \hat{B} \varphi_i^* \, d\tau \right)^*$$

Using (7.106) and the fact that the eigenvalues of \hat{A} are real, we have

$$\begin{aligned} s_j B_{ij} &= s_i^* \langle \hat{B}\varphi_j | \varphi_i \rangle^* \\ s_j B_{ij} &= s_i \langle \varphi_i | \hat{B}\varphi_j \rangle = s_i B_{ij} \\ B_{ij}(s_j - s_i) &= 0 \end{aligned} \quad (7.111)$$

Since we assumed $s_i \neq s_j$, we conclude that

$$B_{ij} = 0 \quad (7.112)$$

7.7 Parity

Up to now, each quantum-mechanical operator we have used has corresponded to some macroscopic classical physical property. However, there are certain quantum-mechanical operators that have no classical

$\langle \varphi_i | A | \varphi_j \rangle$
 $= \langle \varphi_j | A | \varphi_i \rangle^*$
 $\int dx \varphi_i^*(x) A \varphi_j(x)$
 $= \left(\int dx \varphi_j^*(x) (A \varphi_i) \right)^*$
 lets examine
 $\langle \varphi_i | A | B \varphi_j \rangle$
 $= \int dx \varphi_i^* A (B \varphi_j)$
 $= \left(\int (B \varphi_j)^* (A \varphi_i) \right)^*$
 $= \langle B \varphi_j | A | \varphi_i \rangle^*$

$\langle \varphi_j | A | \varphi_i \rangle$
 $= s_i \langle \varphi_j | \varphi_i \rangle$
 $= s_i \delta_{ij}$
 $A_{ij} = s_i \delta_{ij}$

definite parity when V is an even function. For example, the one-dimensional harmonic oscillator has $V = \frac{1}{2}kx^2$, which is an even function, and we found the wave functions to be of definite parity.

For the degenerate case, we have an element of choice in the wave functions, since an arbitrary linear combination of the functions corresponding to the degenerate level is an eigenfunction of \hat{H} . For a degenerate energy level, by taking appropriate linear combinations we can choose wave functions that are of definite parity, but there is no necessity that they be of definite parity.

Parity is important in evaluating integrals. In Chapter 4, we showed that

$$\int_{-\infty}^{\infty} f(x) dx = 0 \quad (7.129)$$

when $f(x)$ is an odd function. Let us extend this result to the $3n$ -dimensional case. An odd function of $3n$ variables satisfies

$$g(-x_1, -y_1, -z_1, \dots, -x_n, -y_n, -z_n) = -g(x_1, y_1, z_1, \dots, x_n, y_n, z_n) \quad (7.130)$$

If g is an odd function of the $3n$ variables, then

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} g(x_1, \dots, z_n) dx_1 \cdots dz_n = 0 \quad (7.131)$$

where the integration is over the $3n$ coordinates. This equation holds because the contribution to the integral from the value of g at $(x_1, y_1, z_1, \dots, x_n, y_n, z_n)$ is cancelled by the contribution from $(-x_1, -y_1, -z_1, \dots, -x_n, -y_n, -z_n)$.

A more general case than (7.130) and (7.131) is where the integrand is an odd function of some (but not necessarily all) of the variables. Let f be a function such that

$$f(-q_1, -q_2, \dots, -q_k, q_{k+1}, q_{k+2}, \dots, q_m) = -f(q_1, q_2, \dots, q_k, q_{k+1}, q_{k+2}, \dots, q_m) \quad (7.132)$$

where $1 \leq k \leq m$. Equation (7.130) is a special case of (7.132) with $k = m = 3n$. We assert that if f obeys (7.132), then

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} f(q_1, \dots, q_m) dq_1 \cdots dq_m = 0 \quad (7.133)$$

The proof of (7.133) is simple. We have

$$\begin{aligned} & \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} f(q_1, \dots, q_m) dq_1 \cdots dq_m \\ &= \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left[\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} f(q_1, \dots, q_k, q_{k+1}, \dots, q_m) dq_1 \cdots dq_k \right] \\ & \quad \times dq_{k+1} \cdots dq_m \quad (7.134) \end{aligned}$$

As far as the multiple integral in brackets is concerned, q_{k+1} through q_m are constants. By virtue of (7.132), the contributions from

$$f(-q_1, \dots, -q_k, q_{k+1}, \dots, q_m) \quad \text{and} \quad f(q_1, \dots, q_k, q_{k+1}, \dots, q_m)$$

cancel, so that

$$\left[\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} f(q_1, \dots, q_k, q_{k+1}, \dots, q_m) dq_1 \dots dq_k \right] = 0 \quad (7.135)$$

and (7.133) follows.

7.8 Measurement and the Superposition of States

Quantum mechanics can be regarded as a scheme for calculating the probabilities of the various possible outcomes of a measurement. For example, if we know the state function $\Psi(x, t)$, then the probability that a measurement at time t of the particle's position yields a value between x and $x + dx$ is given by $|\Psi(x, t)|^2 dx$. We now consider measurement of the general property G ; our aim is to find out how to use Ψ to calculate the probabilities for each possible result of a measurement of G . The results of this section lie at the very heart of quantum mechanics.

We will deal with an n -particle system, and will use q to symbolize the $3n$ coordinates. We have postulated that the eigenvalues g_i of the operator \hat{G} are the only possible results of a measurement of the property G . Using φ_i for the eigenfunctions of \hat{G} , we have

$$\hat{G}\varphi_i(q) = g_i\varphi_i(q) \quad (7.136)$$

ex: energy levels in $L-\infty/1-\text{atom}$

We postulated in Section 7.5 that the eigenfunctions of any linear Hermitian operator which represents a physical observable form a complete set. Since the φ_i form a complete set, we can expand any well-behaved function in terms of them; in particular, we can expand the state function Ψ in terms of the φ_i :

$$\Psi(q, t) = \sum_i c_i(t)\varphi_i(q) \quad (7.137)$$

To allow for the change of Ψ with time, the expansion coefficients c_i vary with time.

Now $|\Psi|^2$ is a probability density, so that we require

$$\int \Psi^*\Psi d\tau = 1 \quad (7.138)$$

Substituting (7.137) into the normalization condition, we get

$$1 = \int \sum_i c_i^* \varphi_i^* \sum_j c_j \varphi_j d\tau = \int \sum_i c_i^* \varphi_i^* \sum_j c_j \varphi_j d\tau$$

$$1 = \int \sum_i \sum_j c_i^* c_j \varphi_i^* \varphi_j d\tau \quad (7.139)$$

[It is important to use different symbols for the two dummy summation indices in (7.139). For example, consider the following product of two sums:

$$\sum_{i=1}^2 a_i \sum_{i=1}^2 b_i = (a_1 + a_2)(b_1 + b_2) = a_1 b_1 + a_1 b_2 + a_2 b_1 + a_2 b_2$$

If we carelessly write

$$\sum_{i=1}^2 a_i \sum_{i=1}^2 b_i \stackrel{\text{(wrong)}}{=} \sum_{i=1}^2 \sum_{i=1}^2 a_i b_i = \sum_{i=1}^2 (a_i b_1 + a_i b_2) = 2(a_1 b_1 + a_2 b_2)$$

we get the wrong answer. The correct way to write the product is

$$\sum_{i=1}^2 a_i \sum_{i=1}^2 b_i = \sum_{i=1}^2 a_i \sum_{j=1}^2 b_j = \sum_{i=1}^2 \sum_{j=1}^2 a_i b_j$$

$$= \sum_{i=1}^2 (a_i b_1 + a_i b_2) = a_1 b_1 + a_1 b_2 + a_2 b_1 + a_2 b_2$$

which gives the right answer.] Assuming the validity of interchanging the infinite summation and integration in (7.139), we have

$$\sum_i \sum_j c_i^* c_j \int \varphi_i^* \varphi_j d\tau = 1$$

Since \hat{G} is Hermitian, the eigenfunctions φ_i are orthonormal [Eq. (7.45)]; hence

$$\sum_i \sum_j c_i^* c_j \delta_{ij} = 1$$

$$\rightarrow \sum_i |c_i|^2 = 1 \quad (7.140)$$

We will point out the significance of (7.140) shortly.

Recall the postulate (Section 3.7) that if Ψ is the normalized state function of a system, then the average value of the property G is

$$\langle G \rangle = \int \Psi^*(q, t) \hat{G} \Psi(q, t) d\tau$$

Using the expansion (7.137) in the average-value expression, we have

$$\langle G \rangle = \int \sum_i c_i^* \varphi_i^* \hat{G} \sum_j c_j \varphi_j d\tau = \sum_i \sum_j c_i^* c_j \int \varphi_i^* \hat{G} \varphi_j d\tau \quad (7.141)$$

Applying (7.136), we get

$$\begin{aligned}\langle G \rangle &= \sum_i \sum_j c_i^* c_j g_j \int \varphi_i^* \varphi_j d\tau = \sum_i \sum_j c_i^* c_j g_j \delta_{ij} \\ \langle G \rangle &= \sum_i |c_i|^2 g_i\end{aligned}\quad (7.142)$$

How do we interpret (7.142)? We postulated (Section 3.3) that the eigenvalues of an operator are the only possible numbers we can get when we measure the property that the operator represents. In any measurement of G we will get one of the values g_i . Now recall Eq. (3.108):

$$\langle G \rangle = \sum_i P_{g_i} g_i \quad \begin{array}{l} \text{"Ordinary" average} \\ \text{(av. height) of} \\ \text{students} \end{array} \quad (7.143) \quad \leftarrow$$

where P_{g_i} is the probability of getting g_i in a measurement of G . Comparing (7.142) and (7.143), we conclude that $|c_i|^2$ is the probability² of getting the value g_i in a measurement of the property G ; the quantity c_i is the coefficient of the eigenfunction φ_i in the expansion (7.137). The $|c_i|^2$ sum to 1, as probabilities should [Eq. (7.140)].

When can we predict the result of a measurement of G with certainty? We can do this if all the coefficients c_i are zero, except one: $c_i = 0, i \neq k$; $c_k \neq 0$. For this case, Eq. (7.140) gives $|c_k|^2 = 1$, so that we are certain to find the result g_k . In this case, the state function (7.137) reduces to

$$\Psi = \varphi_k$$

We may thus view the expansion (7.137) as expressing the general state Ψ as a *superposition* of the eigenstates φ_i of the operator \hat{G} ; each eigenstate φ_i corresponds to the value g_i for the property G . The degree to which any function φ_i occurs in the expansion of Ψ , as measured by $|c_i|^2$, determines the probability of getting the value g_i in a measurement of G .

How do we calculate the expansion coefficients c_i , so that we can get the probabilities $|c_i|^2$? We multiply (7.137) by φ_j^* and integrate over all space to get

$$\begin{aligned}\int \varphi_j^* \Psi d\tau &= \sum_i c_i \int \varphi_j^* \varphi_i d\tau = \sum_i c_i \delta_{ij} \\ c_j &= \int \varphi_j^* \Psi d\tau = \langle \varphi_j | \Psi \rangle\end{aligned}\quad (7.144)$$

The probability of finding the value g_j in a measurement of G is

$$|c_j|^2 = \left| \int \varphi_j^* \Psi d\tau \right|^2 = |\langle \varphi_j | \Psi \rangle|^2 \quad (7.145)$$

² However, if g_i is a degenerate eigenvalue, we must add together the probabilities for all the states with eigenvalue g_i .

The quantity

$$\langle \varphi_j | \Psi \rangle \quad (7.146)$$

is called a *probability amplitude*.

Thus, if we know the state of the system, as determined by the state function Ψ , we can use (7.145) to predict the probabilities for the various possible outcomes of a measurement of any property G . (Determination of the eigenfunctions φ_j and eigenvalues g_j is a mathematical problem.)

(To determine experimentally the probability of finding g_j on measurement, we take a large number of identical, noninteracting systems, each in the same state Ψ , and carry out a measurement of G on each system. If n_j of the measurements yield g_j , then

$$\frac{n_j}{n} = |\langle \varphi_j | \Psi \rangle|^2 \quad (7.147)$$

where n is the total number of measurements made.)

We illustrate our conclusions with an example. Let the property G be the linear momentum p_x . The eigenfunctions and eigenvalues in (7.136) are [see Eqs. (3.43) and (3.44)]

$$\varphi_i = e^{ik_i x/\hbar} \quad g_i = k_i \quad (7.148)$$

where k_i is any real number. Now consider a free particle moving in one dimension and having energy E ; its state function is, according to (2.30) and (3.39),

$$\Psi = a_1 e^{-iEt/\hbar} e^{i(2mE)^{1/2}x/\hbar} + a_2 e^{-iEt/\hbar} e^{-i(2mE)^{1/2}x/\hbar} \quad (7.149)$$

Letting

$$\begin{aligned} c_1 &= a_1 e^{-iEt/\hbar} & c_2 &= a_2 e^{-iEt/\hbar} \\ k_1 &= (2mE)^{1/2} & k_2 &= -(2mE)^{1/2} \end{aligned}$$

we write Ψ as

$$\Psi = c_1 e^{ik_1 x/\hbar} + c_2 e^{ik_2 x/\hbar} \quad (7.150)$$

Comparing this equation with (7.137), we see that the free-particle state function is a superposition of two of the eigenfunctions of \hat{p}_x ; the probability that a measurement of p_x yields the value $k_1 = (2mE)^{1/2}$ is, according to the italicized statement following (7.143),

$$|c_1|^2 = |a_1 e^{-iEt/\hbar}|^2 = |a_1|^2$$

while the probability that a measurement of p_x yields $-(2mE)^{1/2}$ is

$$|c_2|^2 = |a_2|^2$$

Free-particle

$\Psi = \sum_i c_i(t) \varphi_i(x)$

The probability of getting any other value in a measurement of p_x is zero, since eigenfunctions corresponding to eigenvalues other than k_1 and k_2 do not occur in the expansion (7.150).

If G is a property that takes on a continuous range of eigenvalues (e.g., position), the summation in the expansion (7.137) is replaced by an integration over the values of g :

$$\Psi = \int c_g \varphi_g(q) dg \quad (7.151)$$

and the quantity

$$|\langle \varphi_g(q) | \Psi \rangle|^2 = \int dx \varphi^* x \Psi$$

use wave packets
ex: φ is prob

is interpreted as a probability density; i.e., the probability of finding a value of G between g and $g + dg$ for a system in the state Ψ is

$$|\langle \varphi_g(q) | \Psi(q, t) \rangle|^2 dg \quad (7.152)$$

We now consider the superposition of energy eigenstates. When the Hamiltonian is independent of time, we have shown that there are solutions of the time-dependent Schroedinger equation of the form

$$\Psi_n(q, t) = e^{-iE_n t/\hbar} \psi_n(q) \quad (7.153)$$

where the $\psi_n(q)$ are eigenfunctions of \hat{H} :

$$\hat{H} \psi_n(q) = E_n \psi_n(q) \quad (7.154)$$

Let the function Ψ be a superposition of the stationary states Ψ_n :

$$\Psi = \sum_n c_n \Psi_n = \sum_n c_n e^{-iE_n t/\hbar} \psi_n \quad (7.155)$$

The linear combination (7.155) is, of course, not an eigenfunction of \hat{H} (unless all the stationary states in the sum belong to the same degenerate energy level), but it is a solution of the time-dependent Schroedinger equation. The time-dependent Schroedinger equation (3.51) is

$$\left[\frac{\hbar}{i} \frac{\partial}{\partial t} + \hat{H} \right] \Psi = 0 \quad (7.156)$$

Since the operator in brackets in (7.156) is linear, it follows that a linear combination [such as (7.155)] of solutions of (7.156) is a solution of (7.156). Also, a linear combination of well-behaved functions is a well-behaved function. Hence, the superposition (7.155) of energy eigenstates is a possible (nonstationary) state of the system. Because of the completeness of the eigenfunctions of \hat{H} , any state function can be written in the form (7.155). The state function (7.155) represents a state that does not

of finding optm in $x, x+dx$.

have a definite energy; rather, when we make an energy measurement, the probability of getting E_n is, according to the results of this section,

$$|c_n e^{-iE_n t/\hbar}|^2 = |c_n|^2$$

What determines whether a system is in a stationary state such as (7.153) or a nonstationary state such as (7.155)? The answer is that the past history of the system determines its present state. For example, if we take a system that is in a stationary state and expose it to radiation, the time-dependent Schroedinger equation shows that the radiation causes the state to change to a nonstationary state. We will show this in Volume II, Chapter 2, where we deal with transitions between states.

7.9 Position Eigenfunctions

We have derived the eigenfunctions of the linear-momentum and angular-momentum operators. We now ask: What are the eigenfunctions of the position operator?

We have

$$\hat{x} = x \cdot$$

Denoting the position eigenfunctions by $\varphi_a(x)$, we write

$$x\varphi_a(x) = a\varphi_a(x) \quad (7.157)$$

where a symbolizes the possible eigenvalues. It follows that

$$(x - a)\varphi_a(x) = 0 \quad (7.158)$$

We conclude from (7.158) that

$$\varphi_a(x) = 0 \quad \text{for } x \neq a \quad (7.159)$$

Moreover, since an eigenfunction that is zero everywhere is unacceptable, we have

$$\varphi_a(x) \neq 0 \quad \text{for } x = a \quad (7.160)$$

These conclusions make sense. If the state function is an eigenfunction of x with eigenvalue a , $\Psi = \varphi_a(x)$, we know (Section 7.8) that a measurement of x is certain to give the value a ; this can only be true if the probability density $|\Psi|^2$ is zero for $x \neq a$, in agreement with (7.159).

Before considering further properties of $\varphi_a(x)$, we define the *Heaviside step function* $H(x)$ by (see Fig. 7.2):

$$\begin{aligned} H(x) &= 1 & \text{for } x > 0 \\ H(x) &= 0 & \text{for } x < 0 \\ H(x) &= \frac{1}{2} & \text{for } x = 0 \end{aligned} \quad (7.161)$$

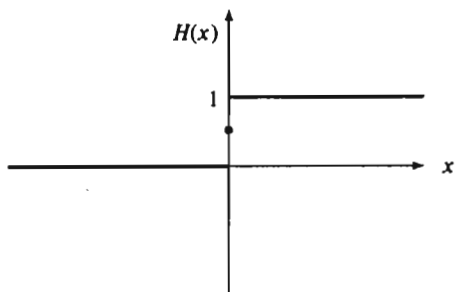


FIGURE 7.2 The Heaviside step function.

We next define the *Dirac delta function* $\delta(x)$ as the derivative of the Heaviside step function:

$$\delta(x) \equiv \frac{dH(x)}{dx} \quad (7.162)$$

From (7.161) and (7.162) we have at once (see also Fig. 7.2):

$$\delta(x) = 0 \quad \text{for } x \neq 0 \quad (7.163)$$

Since $H(x)$ makes a sudden jump at $x = 0$, its derivative is infinite at the origin:

$$\delta(x) = \infty \quad \text{for } x = 0 \quad (7.164)$$

We can generalize these equations slightly by setting $x = t - a$, and then changing the symbol t to x ; Eqs. (7.161)–(7.164) become

$$H(x - a) = 1 \quad x > a \quad (7.165)$$

$$H(x - a) = 0 \quad x < a \quad (7.166)$$

$$H(x - a) = \frac{1}{2} \quad x = a \quad (7.167)$$

$$\delta(x - a) = \frac{d}{dx} H(x - a) \quad (7.168)$$

$$\delta(x - a) = 0 \quad x \neq a \quad (7.169)$$

$$\delta(x - a) = \infty \quad x = a \quad (7.170)$$

Now consider the following integral:

$$\int_{-\infty}^{\infty} f(x)\delta(x - a) dx$$

We evaluate it using integration by parts:

$$\int u dv = uv - \int v du$$

$$u = f(x) \quad dv = \delta(x - a) dx$$

We have, using (7.168),

$$du = f'(x) dx \quad v = H(x - a)$$

$$\begin{aligned} \int_{-\infty}^{\infty} f(x)\delta(x - a) dx &= f(x)H(x - a) \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} H(x - a)f'(x) dx \\ \int_{-\infty}^{\infty} f(x)\delta(x - a) dx &= f(\infty) - \int_{-\infty}^{\infty} H(x - a)f'(x) dx \end{aligned} \quad (7.171)$$

where (7.165) and (7.166) have been used. Since $H(x - a)$ vanishes for $x < a$, Eq. (7.171) becomes

$$\begin{aligned} \int_{-\infty}^{\infty} f(x)\delta(x - a) dx &= f(\infty) - \int_a^{\infty} H(x - a)f'(x) dx \\ &= f(\infty) - \int_a^{\infty} f'(x) dx = f(\infty) - f(x) \Big|_a^{\infty} \\ \int_{-\infty}^{\infty} f(x)\delta(x - a) dx &= f(a) \end{aligned} \quad (7.172)$$

Comparing (7.172) with the equation

$$\sum_j c_j \delta_{ij} = c_i \quad (7.173)$$

we see that the Dirac delta function plays the same role in an integral that the Kronecker delta plays in a sum. The special case of (7.172) with $f(x) = 1$ is worth noting:

$$\int_{-\infty}^{\infty} \delta(x - a) dx = 1$$

The properties (7.169) and (7.170) of the Dirac' delta function are in accord with the properties (7.159) and (7.160) for the position eigenfunctions. Let us therefore tentatively set

$$\varphi_a(x) = \delta(x - a) \quad (7.174)$$

To verify (7.174), we now show it to be in accord with the Born postulate that $|\Psi(a, t)|^2 da$ is the probability of observing a value of x between a and $a + da$. According to (7.152), this probability is given by

$$|\langle \varphi_a(x) | \Psi(x, t) \rangle|^2 da = \left| \int_{-\infty}^{\infty} \varphi_a^*(x) \Psi(x, t) dx \right|^2 da \quad (7.175)$$

Using (7.174) and then (7.172), we have for (7.175)

$$\left| \int_{-\infty}^{\infty} \delta(x - a) \Psi(x, t) dx \right|^2 da = |\Psi(a, t)|^2 da \quad (7.176)$$

Q.E.D.

Since the quantity a in $\delta(x - a)$ can have any real value, the eigenvalues of x form a continuum: $-\infty < a < \infty$. As usual for continuum eigenfunctions, $\delta(x - a)$ is not quadratically integrable; we have, using (7.172),

$$\int_{-\infty}^{\infty} |\delta(x - a)|^2 dx = \int_{-\infty}^{\infty} \delta(x - a) \delta(x - a) dx = \delta(a - a) = \delta(0) = \infty$$

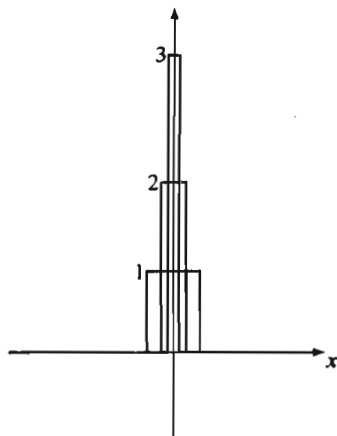


FIGURE 7.3 Functions that approximate $\delta(x)$ with successively increasing accuracy. The area under each curve is 1.

Summarizing, the eigenfunctions and eigenvalues of position are

$$\hat{x}\delta(x - a) = a\delta(x - a) \quad (7.177)$$

where a is any real number.

(The delta function is rather badly behaved and, as a consequence, the various manipulations we performed are lacking in rigor, and would make a mathematician shudder. However, use of the delta function can be put on a rigorous basis by considering it to be the limiting case of a function that becomes successively more peaked at the origin; see Fig. 7.3.)

7.10 The Postulates of Quantum Mechanics

We have introduced the postulates of quantum mechanics as we went along. In this section we summarize them. There is no unique set of postulates; we will simply use a convenient set.

Postulate 1. *The state of a system is described by a function Ψ of the coordinates and the time. This function, called the state function (or wave function) contains all the information that can be determined about the system. We further postulate that Ψ is single-valued, continuous, and quadratically integrable. (For continuum states, the quadratic integrability requirement is omitted.)*

The designation “wave function” for Ψ is perhaps not the best choice. A physical wave moving in three-dimensional space is a function

of the three spatial coordinates and the time; however, for an n -particle system, the function Ψ is a function of $3n$ spatial coordinates and the time. Hence, for a many-particle system, we cannot interpret Ψ as any sort of physical wave. The state function is best thought of as a function from which we can calculate various properties of the system; the nature of the information that Ψ contains is the subject of Postulate 5 and its consequences.

Postulate 2. *To every physical observable there corresponds a linear Hermitian operator. To find this operator, write down the classical-mechanical expression for the observable in terms of Cartesian coordinates³ and corresponding linear-momentum components, and then replace each coordinate x by the operator $x \cdot$ and each momentum component p_x by the operator $-i\hbar\partial/\partial x$.*

We saw in Section 7.3 that the restriction to Hermitian operators arises naturally from the requirement that average values of physical quantities be real numbers. The requirement of linearity is closely connected to the superposition of states discussed in Section 7.8. In deriving (7.142) for the average value of a property G for a state that was expanded as a superposition of the eigenfunctions of \hat{G} , the linearity of \hat{G} played a key role. In (7.141) we had to use the linearity condition:

$$\hat{G}(c_1\varphi_1 + c_2\varphi_2 + \dots) = c_1\hat{G}\varphi_1 + c_2\hat{G}\varphi_2 + \dots$$

Postulate 3. *The only possible values that can result from measurements of the physical observable G are the eigenvalues g_i of the equation*

$$\hat{G}\varphi_i = g_i\varphi_i$$

where \hat{G} is the operator corresponding to the property G . The eigenfunctions φ_i are required to be well-behaved.

Our main concern is with the energy levels of atoms and molecules. These are given by the eigenvalues of the energy operator, the Hamiltonian \hat{H} . The eigenvalue equation for \hat{H} , $\hat{H}\psi = E\psi$, is the time-independent Schroedinger equation. However, finding the possible values of any property involves solving an eigenvalue equation.

Postulate 4. *If \hat{G} is any linear Hermitian operator that represents a physical observable, then the eigenfunctions φ_i of the eigenvalue equation*

$$\hat{G}\varphi_i = g_i\varphi_i$$

form a complete set.

³ The process of finding the quantum-mechanical operators in coordinates other than Cartesian involves complications. For a discussion see K. Simon, *Am. J. Phys.*, **33**, 60 (1965).

This postulate is more a mathematical than a physical postulate. Since there is no mathematical proof (except in various special cases) of the completeness of the eigenfunctions of a linear Hermitian operator, we must assume completeness. Postulate 4 allows us to expand the wave function for any state as a superposition of the eigenfunctions of any quantum-mechanical operator:

$$\Psi = \sum_i c_i \varphi_i = \sum_i |\varphi_i\rangle \langle \varphi_i | \Psi \rangle \quad (7.178)$$

Postulate 5. If $\Psi(q, t)$ is the normalized state function of a system at time t , then the average value of a physical observable G at time t is

$$\langle G \rangle = \int \Psi^* \hat{G} \Psi \, d\tau$$

The definition of the quantum-mechanical average value is given in Section 3.7, and should not be confused with the time average used in classical mechanics.

From Postulates 4 and 5, we showed in Section 7.8 that the probability of observing the value g_i in a measurement of G at time t is given by

$$P_{g_i} = \left| \int \varphi_i^* \Psi \, d\tau \right|^2 = |\langle \varphi_i | \Psi \rangle|^2 \quad (7.179)$$

where $\hat{G}\varphi_i = g_i\varphi_i$. If the state function Ψ happens to be one of the eigenfunctions of \hat{G} , $\Psi = \varphi_k$, then (7.179) becomes

$$P_{g_i} = \left| \int \varphi_i^* \varphi_k \, d\tau \right|^2 = |\delta_{ik}|^2 = \delta_{ik} \quad (7.180)$$

where we have used the orthonormality of the eigenfunctions of a Hermitian operator. Equation (7.180) says that we are certain to observe the value g_k when $\Psi = \varphi_k$.

Postulate 6. The time development of the state of an undisturbed system is given by the Schrodinger time-dependent equation

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad (7.181)$$

where \hat{H} is the Hamiltonian (i.e., energy) operator of the system.

The time-dependent Schrodinger equation is a first-order differential equation in the time, so that, just as in classical mechanics, the present state of an undisturbed system determines the future state. However, unlike classical mechanics, knowledge of the state in quantum mechanics involves only a knowledge of the probabilities for various possible outcomes of a measurement. Thus, suppose we have several identical non-interacting systems, each having the same state function $\Psi(t_0)$ at time t_0 .

If we leave each system to itself, then the state function for each system will change in accord with (7.181); since each system has the same Hamiltonian, each system will have the same state function $\Psi(t_1)$ at any future time t_1 . However, suppose that at time t_2 we make a measurement of property G in each system; although each system has the same state function $\Psi(t_2)$ at the instant the measurement begins, we will not get the same result for each system. Rather, we will get a spread of possible values g_i , where g_i are the eigenvalues of \hat{G} . The relative number of times we get each g_i can be calculated from the quantities $|c_i|^2$ where

$$\Psi(t_2) = \sum_i c_i \varphi_i$$

with φ_i being the eigenfunctions of \hat{G} .

In quantum mechanics, the state function of a system changes in two ways.⁴ First, there is the continuous, causal change with time given by the time-dependent Schroedinger equation. Second, there is the sudden, discontinuous, probabilistic change that occurs when a measurement is made on the system; this kind of change cannot be predicted with certainty, since the result of a measurement cannot be predicted with certainty. The sudden change in Ψ caused by a measurement is called "the reduction of the wave function." A measurement of property G that yields the result g_k changes the state function to φ_k , the eigenfunction of \hat{G} with eigenvalue g_k . Let us give an example. Suppose that at time t we carry out a measurement of the particle's position. Let $\Psi(x, t_-)$ be the state function of the particle the instant before the measurement is made (Fig. 7.4a). We further suppose that the result of the measurement is that the particle is found to be in the small region of space:

$$a < x < a + da \quad \text{at } t\text{-instant of measurement.} \quad (7.182)$$

We ask, what is the state function $\Psi(x, t_+)$ the instant after the measurement? To answer this question, suppose we were to make a second measurement of position at time t_+ . Since t_+ differs from the time t of the first measurement by an infinitesimal amount, we must still find that the particle is confined to the region (7.182). (If the particle moved a finite distance in an infinitesimal amount of time, it would have infinite velocity, which is unacceptable.) Since $|\Psi(x, t_+)|^2$ is the probability density for finding various values of x , we conclude that $\Psi(x, t_+)$ must be zero outside the region (7.182) and must look something like Fig. 7.4b. Thus, the position measurement at time t has reduced Ψ from a function that is spread out over all space to one that is localized in the region (7.182). The change in state function from $\Psi(x, t_-)$ to $\Psi(x, t_+)$ is a probabilistic change.

⁴ For a discussion, see E. P. Wigner, *Am. J. Phys.*, 31, 6 (1963).

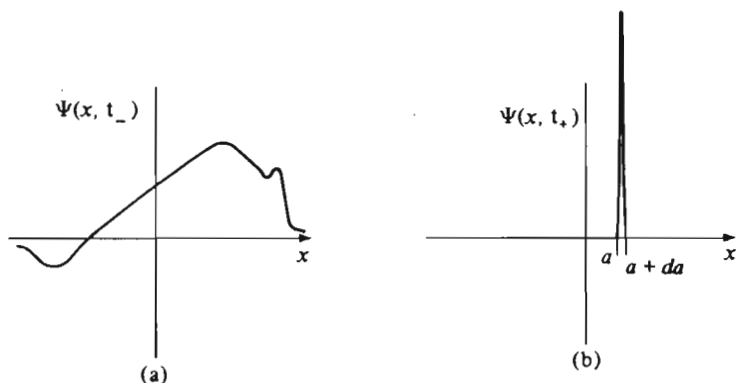


FIGURE 7.4 Reduction of the wave function caused by a measurement of position.

The probabilistic nature of quantum mechanics has disturbed many eminent physicists, such as Einstein, de Broglie, and Schroedinger. These physicists and others have suggested that quantum mechanics may not furnish a complete description of physical reality; they propose that the probabilistic laws of quantum mechanics might simply be a reflection of deterministic laws that operate at a subquantum-mechanical level, and involve "hidden variables." An analogy given by the physicist Bohm is the Brownian motion of a dust particle in air. The particle undergoes random fluctuations of position, and its motion is not completely determined by its position and velocity. Of course, Brownian motion is a result of collisions with the gas molecules, and is determined by variables existing on the level of molecular motion. Analogously, the motions of electrons might be determined by hidden variables existing on a subquantum-mechanical level. The orthodox interpretation (often called the Copenhagen interpretation) of quantum mechanics, which was developed by Heisenberg and Bohr, denies the existence of hidden variables and asserts that the laws of quantum mechanics provide a complete description of physical reality. The views⁵ of the proponents of hidden variables have not gained much acceptance among physicists.

If the Hamiltonian is independent of time, we have the possibility of states of definite energy E . For such states, the state function must satisfy

$$\hat{H}\Psi = E\Psi \quad (7.183)$$

⁵ See L. de Broglie, *Non-Linear Wave Mechanics*, Elsevier, Amsterdam, 1960; D. Bohm, *Causality and Chance in Modern Physics*, Van Nostrand, New York, 1957; D. Bohm, "Hidden Variables in the Quantum Theory," in Volume III of *Bates*; D. Bohm and J. Bub, *Rev. Mod. Phys.*, **38**, 453, 470 (1966).

and the time-dependent Schroedinger equation becomes

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

which integrates to

$$\Psi = B e^{-iEt/\hbar}$$

where B , the integration "constant," is independent of time. The function Ψ depends on the coordinates and the time, so that B is some function of the coordinates, which we designate as $\psi(q)$. We have

$$\Psi(q, t) = e^{-iEt/\hbar} \psi(q) \quad (7.184)$$

for a state of constant energy. The function $\psi(q)$ satisfies the time-independent Schroedinger equation

$$\hat{H}\psi(q) = E\psi(q) \quad (7.185)$$

which follows from (7.182) and (7.184). The factor $\exp(-iEt/\hbar)$ simply indicates a change in the phase of the wave function $\Psi(q, t)$ with time, and has no direct physical significance; hence, we generally refer to $\psi(q)$ as "the wave function." The Hamiltonian operator plays a unique role in quantum mechanics in that it occurs in the fundamental dynamical equation, the time-dependent Schroedinger equation; the eigenstates of \hat{H} (known as stationary states) have the special property that the probability density $|\Psi|^2$ is independent of time.

(You might be wondering about the absence from our list of the Born postulate that $|\Psi(x, t)|^2 dx$ is the probability at time t for finding the particle between x and $x + dx$; this postulate is actually a consequence of Postulate 5, as we now demonstrate. From the definition of average value in Section 3.7, we derived Eq. (3.108):

$$\langle G \rangle = \sum_g P_g g$$

where P_g is the probability of observing the value g in a measurement of the property G . This equation is for a variable that takes on discrete values; the corresponding equation for a continuous variable is

$$\langle G \rangle = \int P(g) g dg \quad (7.186)$$

where $P(g)$ is the probability density for observing various values of G . For the average value of the x coordinate, Eq. (7.186) reads

$$\langle x \rangle = \int P(x) x dx$$

According to Postulate 5, we have

$$\langle x \rangle = \int \Psi^* x \Psi dx = \int |\Psi|^2 x dx$$

Comparing these last two equations, we conclude that $|\Psi|^2$ is the probability density for the x coordinate of a one-dimensional system.)

In Chapter 10, we will introduce two further postulates, dealing with spin and the Pauli principle.

PROBLEMS

7.1 True or false: (a) The state function is always equal to a function of time multiplied by a function of the coordinates. (b) In both classical and quantum mechanics, knowledge of the present state of an isolated system allows its future state to be calculated. (c) The state function is always an eigenfunction of the Hamiltonian. (d) Any linear combination of eigenfunctions of the Hamiltonian is an eigenfunction of the Hamiltonian. (e) If the state function is not an eigenfunction of the operator \hat{A} , then a measurement of the property A might give a value that is not one of the eigenvalues of \hat{A} . (f) The probability density is independent of time for a stationary state. (g) If two operators do not commute, then they cannot possess any common eigenfunctions. (h) If two operators commute, then every eigenfunction of one must be an eigenfunction of the other.

7.2 Let \hat{A} and \hat{B} be Hermitian operators and let c be a real constant. Show that $c\hat{A}$ and $\hat{A} + \hat{B}$ are Hermitian.

7.3 Show that d^2/dx^2 is Hermitian.

7.4 Which of the following operators are Hermitian: d/dx , $i(d/dx)$, $4d^2/dx^2$, $i(d^2/dx^2)$?

7.5 Let \hat{A} be a Hermitian operator. Show that $\langle A^2 \rangle = \int |\hat{A}\psi|^2 d\tau$ and therefore $\langle A^2 \rangle \geq 0$. [This result can be used to derive Eq. (5.204) more rigorously than in the text. Thus, since $\hat{M}^2 - \hat{M}_z^2 = \hat{M}_x^2 + \hat{M}_y^2$, we have $\langle M^2 \rangle - \langle M_z^2 \rangle = \langle M_x^2 \rangle + \langle M_y^2 \rangle$. Now $\langle M^2 \rangle = c$, $\langle M_z^2 \rangle = b_k^2$ and by the theorem of this exercise $\langle M_x^2 \rangle \geq 0$, $\langle M_y^2 \rangle \geq 0$. Hence $c - b_k^2 \geq 0$.]

7.6 Verify that \hat{L}_z is Hermitian using: (a) spherical polar coordinates; (b) Cartesian coordinates.

7.7 Extend the Schmidt orthogonalization procedure to the case of threefold degeneracy.

7.8 Evaluate the coefficients in the sine-series expansion (7.51) for the parabolic function $f(x) = x(l-x)$. What is the result at $x = \frac{1}{2}l$? Use the first five terms of the result to approximate π^3 .

7.9 What operator is shown to be Hermitian by the identity $\langle m|n \rangle = \langle n|m \rangle^*$?

7.10 For the hydrogenlike atom, we have $V = -Ze^2(x^2 + y^2 + z^2)^{-1/2}$ so that the potential energy is an even function of the coordinates. (a) What is the parity of ψ_{2s} ? (b) What is the parity of ψ_{2p_x} ? (c) Consider $\psi_{2s} + \psi_{2p_x}$. Is it an eigenfunction of \hat{H} ? Does it have definite parity?

TABLE 4.1 Dirac's Bracket Notation

	Operator		
	H	x_{op}	p_{op}
Eigenvector	$ E_n\rangle$	$ x\rangle$	$ p\rangle$
Component of arbitrary $ \psi\rangle$ w.r.t. eigenvector	$\langle E_n \psi\rangle \equiv A_n$	$\langle x \psi\rangle \equiv \psi(x)$	$\langle p \psi\rangle \equiv \phi(p)$
Component of eigenvector w.r.t.			
$ E_m\rangle$	$\langle E_m E_n\rangle = \delta_{mn}$	$\langle E_n x\rangle = \psi_{E_n}^*(x)$	$\langle E_n p\rangle = \phi_{E_n}^*(p)$
$ x'\rangle$	$\langle x' E_n\rangle = \psi_{E_n}(x')$	$\langle x' x\rangle = \delta(x' - x)$	$\langle x' p\rangle = \frac{e^{ipx'/\hbar}}{\sqrt{2\pi\hbar}}$
$ p'\rangle$	$\langle p' E_n\rangle = \phi_{E_n}(p')$	$\langle p' x\rangle = \frac{e^{-ip'x/\hbar}}{\sqrt{2\pi\hbar}}$	$\langle p' p\rangle = \delta(p' - p)$
Completeness of eigenvectors	$I = \sum_n E_n\rangle\langle E_n $	$I = \int dx x\rangle\langle x $	$I = \int dp p\rangle\langle p $
Completeness in position representation	$\langle x' x\rangle = \sum_n \langle x' E_n\rangle\langle E_n x\rangle$ i.e., $\delta(x' - x) = \sum_n \psi_{E_n}(x')\psi_{E_n}^*(x)$	$\langle x' x\rangle = \int dx''\langle x' x''\rangle\langle x'' x\rangle$ $\delta(x' - x) = \int dx''\delta(x' - x'')\delta(x'' - x)$	$\langle x' x\rangle = \int dp\langle x' p\rangle\langle p x\rangle$ $\delta(x' - x) = \frac{1}{2\pi\hbar} \int dp e^{ip(x'-x)/\hbar}$
Expansion of arbitrary $ \psi\rangle$	$ \psi\rangle = \sum_n E_n\rangle\langle E_n \psi\rangle$	$ \psi\rangle = \int dx' x'\rangle\langle x' \psi\rangle$	$ \psi\rangle = \int dp p\rangle\langle p \psi\rangle$
Expansion in position representation	$\langle x \psi\rangle = \sum_n \langle x E_n\rangle\langle E_n \psi\rangle$ i.e., $\psi(x) = \sum_n \psi_{E_n}(x)A_n$	$\langle x \psi\rangle = \int dx'\langle x x'\rangle\langle x' \psi\rangle$ $\psi(x) = \int dx'\delta(x - x')\psi(x')$	$\langle x \psi\rangle = \int dp\langle x p\rangle\langle p \psi\rangle$ $\psi(x) = \int dp \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}} \phi(p)$