Chapter 5
Postulates and Basic Elements of Quantum Mechanics: Properties of Operators

In this chapter I present a somewhat more formal introduction to the theory that underlies quantum mechanics. Although the discussion is limited mainly to single particles, many of the results apply equally well to many-particle systems. Some of the postulates of the theory depend on the properties of *Hermitian* operators, operators that play a central role in quantum mechanics. First I state the postulates, then discuss Hermitian operators, and finally explore some results that follow directly from Schrödinger's equation.

The postulates are:

1. The absolute square of the wave function $|\psi(\mathbf{r},t)|^2$ that characterizes a particle corresponds to the probability density of finding the particle at position $\mathbf{r}$ at time t.
2. To each dynamic physical observable in classical mechanics (such as position, momentum, energy), there corresponds a Hermitian operator in quantum mechanics.
3. The time dependence of $\psi(\mathbf{r},t)$ is governed by the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t}=\hat{H}\psi(\mathbf{r},t) \tag{5.1}$$

   where $\hat{H}$ is the energy operator of the system.
4. The only possible outcome of a measurement on a *single* quantum system of a physical observable associated with a given Hermitian operator is one of the eigenvalues of the operator.
5. I must add one additional postulate. This postulate can take different forms. The one I use at this juncture is that the wave functions in coordinate space, $\psi(\mathbf{r},t)$, and in momentum space, $\Phi(\mathbf{p},t)$, are Fourier transforms of one another, namely

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$$\psi(\mathbf{r},t) = \frac{1}{(2\pi\hbar)^{3/2}} \int d\mathbf{p}\, \Phi(\mathbf{p},t) e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}; \tag{5.2}$$

$$\Phi(\mathbf{p},t) = \frac{1}{(2\pi\hbar)^{3/2}} \int d\mathbf{r}\, \psi(\mathbf{r},t)\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}. \tag{5.3}$$

The function $|\Phi(\mathbf{p},t)|^2$ is the probability density in momentum space for the particle to have momentum $\mathbf{p}$ at time t.

You cannot measure $|\psi(\mathbf{r},t)|^2$ or $|\Phi(\mathbf{p},t)|^2$ directly. The only way you can build up information on the wave function is to make a series of measurements on *identically* prepared quantum systems, since each measurement generally modifies the system in some way. Quantum mechanics does not contain a prescription for carrying out the measurements. In fact, in the model I have adopted, the measuring apparatus is *external* to the quantum system. Moreover, it is often not trivial to construct experiments that *directly* measure physical observables such as energy, angular momentum, position, and momentum.

For the moment I associate quantum-mechanical operators with the coordinate, momentum, kinetic energy and potential energy functions of classical mechanics. For the coordinate and potential energy *operators*, $\hat{\mathbf{r}}$ and $\hat{V}$, corresponding to the classical variables $\mathbf{r}$ and $V(\mathbf{r})$, I define their operations in *coordinate space* by

$$\hat{\mathbf{r}}f(\mathbf{r}) = \mathbf{r}f(\mathbf{r}) \tag{5.4a}$$

$$\hat{V}f(\mathbf{r}) = V(\mathbf{r})f(\mathbf{r}) \tag{5.4b}$$

for any function $f(\mathbf{r})$. Similarly for the momentum and kinetic energy operators, $\hat{\mathbf{p}}$ and $\hat{p}^2/2m$, corresponding to the classical variables $\mathbf{p}$ and $p^2/2m$, I define their operations in *momentum space* by

$$\hat{\mathbf{p}}g(\mathbf{p}) = \mathbf{p}g(\mathbf{p}) \tag{5.5a}$$

$$\frac{\hat{p}^2}{2m}g(\mathbf{p}) = \frac{p^2}{2m}g(\mathbf{p}) \tag{5.5b}$$

for any function $g(\mathbf{p})$. It will turn out that postulate 5 will allow me to determine how $\hat{\mathbf{r}}$ and $\hat{V}$ act on functions of momentum, as well as how $\hat{\mathbf{p}}$ and $\hat{p}^2$ act on functions of position. We have already seen in Chap. 4 that $\hat{p}^2 f(\mathbf{r}) = -\hbar^2\nabla^2 f(\mathbf{r})$, but this relationship will be rederived using the postulates.

5.1 Hermitian Operators: Eigenvalues and Eigenfunctions

The time-independent Schrödinger equation,

$$\hat{H}\psi_E(\mathbf{r}) = E\psi_E(\mathbf{r}), \tag{5.6}$$

represents an *eigenvalue equation* in which E is the *eigenvalue* and $\psi_E(\mathbf{r})$ is the corresponding *eigenfunction*. It turns out that there are always solutions of equations of this type, provided the operators are Hermitian. To define what I mean by a Hermitian operator, I need to introduce the concept of the expectation value of an operator.

The *expectation value* of an operator $\hat{A}$ for a quantum system described by wave functions in coordinate and momentum space, $\psi(\mathbf{r},t)$ or $\Phi(\mathbf{p},t)$, respectively, is defined as

$$\begin{aligned}\left\langle\hat{A}\right\rangle &= \int d\mathbf{r}\, \psi^*(\mathbf{r},t)\hat{A}\psi(\mathbf{r},t)\\ &= \int d\mathbf{p}\, \Phi^*(\mathbf{p},t)\hat{A}\Phi(\mathbf{p},t).\end{aligned} \tag{5.7}$$

The symbols $d\mathbf{r}$ and $d\mathbf{p}$ correspond to volume elements in coordinate and momentum space, respectively, and the integrals in Eq. (5.7) are over all coordinate or momentum space. The expectation value is independent of whether the coordinate or momentum representation for the wave function is used. The operator $\hat{A}$ is assumed to be time-independent, but $\left\langle\hat{A}\right\rangle$ is a function of t, in general, owing to the time-dependence of the wave function. In writing Eq. (5.7), I assumed that the wave functions were normalized probability distributions; that is

$$\int d\mathbf{r}\ |\psi(\mathbf{r},t)|^2 = \int d\mathbf{p}\ |\Phi(\mathbf{p},t)|^2 = 1. \tag{5.8}$$

If the distributions are not normalized, then

$$\begin{aligned}\left\langle\hat{A}\right\rangle &= \frac{\int d\mathbf{r}\, \psi^*(\mathbf{r},t)\hat{A}\psi(\mathbf{r},t)}{\int d\mathbf{r}\ |\psi(\mathbf{r},t)|^2}\\ &= \frac{\int d\mathbf{p}\, \Phi^*(\mathbf{p},t)\hat{A}\Phi(\mathbf{p},t)}{\int d\mathbf{p}\ |\Phi(\mathbf{p},t)|^2}.\end{aligned} \tag{5.9}$$

Let us work in coordinate space and use a shorthand notation in which

$$\left\langle\hat{A}\right\rangle = \int d\mathbf{r}\, \psi^*(\mathbf{r},t)\hat{A}\psi(\mathbf{r},t) = \left(\psi,\hat{A}\psi\right). \tag{5.10}$$

Suppose that we demand that $\left\langle\hat{A}\right\rangle$ is *real* for an *arbitrary* $\psi(\mathbf{r},t)$. Then

$$\left\langle\hat{A}\right\rangle^* = \int d\mathbf{r}\, \psi(\mathbf{r},t)\left[\hat{A}\psi(\mathbf{r},t)\right]^* = \left(\hat{A}\psi,\psi\right) = \left\langle\hat{A}\right\rangle = \left(\psi,\hat{A}\psi\right) \tag{5.11}$$

or

$$\left(\hat{A}\psi, \psi\right) = \left(\psi, \hat{A}\psi\right). \tag{5.12}$$

Equation (5.12) can be used as the definition of a *Hermitian* operator. I will *assume* that all the operators we encounter in quantum mechanics are Hermitian operators. This is not unreasonable, since the expectation value of any physical dynamic variable must be real.

It turns out that the properties of Hermitian operators have been well-established by mathematicians. One of the most important properties is that there *exists* a *complete set* of *eigenfunctions* $\psi_a(\mathbf{r})$ associated with a time-independent Hermitian operator $\hat{A}$ for which

$$\hat{A}\psi_a(\mathbf{r}) = a\psi_a(\mathbf{r}) \tag{5.13}$$

where a is the eigenvalue associated with the eigenfunction $\psi_a(\mathbf{r})$. The proof of existence and completeness is not trivial and is not given here. For the problems we encounter in quantum mechanics, there are certain boundary conditions that apply. The Hermitian nature of the operators and the completeness of the eigenfunctions depend implicitly on the appropriate boundary conditions. Examples are given as we go along.

At this point you might be getting frustrated and confused. What relationship do the eigenfunctions and eigenvalues have to physical systems? If we solve for these quantities, what have we gained? It turns out that the eigenfunctions and eigenvalues give us a *complete* picture of what is going on in quantum mechanics. The reason for this is that we can associate a Hermitian operator with every dynamic physical observable that can be measured. The outcome of a physical measurement of the operator associated with a *single* quantum system *must* be *one and only one* of the eigenvalues associated with that operator. Thus, if we measure the energy of a particle, we get one possible eigenvalue of the energy operator for that particle. If we measure the angular momentum of a particle, we get one eigenvalue of the angular momentum operator. Moreover, if we find the eigenfunctions and eigenvalues of the energy operator, we completely determine the wave function for the quantum system, given the initial conditions. The wave function allows you to calculate all properties of the quantum system. Many of these ideas will become clear with the examples that are given after I establish some properties of Hermitian operators.

5.1.1 Eigenvalues Real

I start from the eigenvalue equation (5.13),

$$\hat{A}\psi_a(\mathbf{r}) = a\psi_a(\mathbf{r}), \tag{5.14}$$

and take the *inner product* (or integral) of both sides with $\psi_a^*(\mathbf{r})$,

$$\left(\psi_a, \hat{A}\psi_a\right) = (\psi_a, a\psi_a) = a\,(\psi_a, \psi_a)\,, \tag{5.15}$$

where (ϕ, ψ) is a shorthand notation for

$$(\phi, \psi) = \int d\mathbf{r}\,\phi^*(\mathbf{r}, t)\psi(\mathbf{r}, t) = (\psi, \phi)^*\,. \tag{5.16}$$

Next, I take the complex conjugate of Eq. (5.13),

$$\left[\hat{A}\psi_a(\mathbf{r})\right]^* = [a\psi_a(\mathbf{r})]^*\,, \tag{5.17}$$

and take the *inner product* (or integral) of both sides with $\psi_a(\mathbf{r})$,

$$\left(\hat{A}\psi_a, \psi_a\right) = (a\psi_a, \psi_a) = a^*\,(\psi_a, \psi_a)\,. \tag{5.18}$$

Subtracting Eq. (5.18) from Eq. (5.15), using Eq. (5.12), I find

$$\left(\psi_a, \hat{A}\psi_a\right) - \left(\hat{A}\psi_a, \psi_a\right) = 0 = \left(a - a^*\right)(\psi_a, \psi_a)\,. \tag{5.19}$$

But since $(\psi_a, \psi_a) > 0$, it follows that $a = a^*$. The eigenvalues of a Hermitian operator are real.

5.1.2 Orthogonality

You are familiar with the concept of two vectors being orthogonal. The concept of orthogonality can be extended to *functions* by defining two functions $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$ to be orthogonal if

$$(\phi_1, \phi_2) = \int d\mathbf{r}\phi_1^*(\mathbf{r})\,\phi_2(\mathbf{r}) = 0. \tag{5.20}$$

I will now show that the eigenfunctions of a Hermitian operator are either automatically orthogonal or can be chosen to be orthogonal. First, I prove a useful lemma (for some unknown reason, I love the word "lemma").

Lemma: If ϕ_1 and ϕ_2 are two *arbitrary* functions and if $\hat{A}$ is a Hermitian operator, then

$$\left(\phi_1, \hat{A}\phi_2\right) = \left(\hat{A}\phi_1, \phi_2\right). \tag{5.21}$$

The proof is straightforward. I use the definition given in Eq. (5.12), but replace ψ by

$$\psi\left(\mathbf{r}\right) = b_1\phi_1\left(\mathbf{r}\right) + b_2\phi_2\left(\mathbf{r}\right) \tag{5.22}$$

where b_1 and b_2 are *arbitrary* complex numbers. Then, for any b_1 and b_2

$$\left(b_1\phi_1 + b_2\phi_2, \hat{A}\left[b_1\phi_1 + b_2\phi_2\right]\right) = \left(\hat{A}\left[b_1\phi_1 + b_2\phi_2\right], b_1\phi_1 + b_2\phi_2\right) \tag{5.23}$$

or

$$\begin{aligned} &\left|b_1\right|^2\left(\phi_1, \hat{A}\phi_1\right) + \left|b_2\right|^2\left(\phi_2, \hat{A}\phi_2\right) + b_1^*b_2\left(\phi_1, \hat{A}\phi_2\right) + b_1b_2^*\left(\phi_2, \hat{A}\phi_1\right) \\ &\quad = \left|b_1\right|^2\left(\hat{A}\phi_1, \phi_1\right) + \left|b_2\right|^2\left(\hat{A}\phi_2, \phi_2\right) + b_1^*b_2\left(\hat{A}\phi_1, \phi_2\right) + b_1b_2^*\left(\hat{A}\phi_2, \phi_1\right). \end{aligned} \tag{5.24}$$

Since $\left(\phi_j, \hat{A}\phi_j\right) = \left(\hat{A}\phi_j, \phi_j\right)$ $(j = 1, 2)$ as a consequence of Eq. (5.12), Eq. (5.24) reduces to

$$b_1^*b_2\left(\phi_1, \hat{A}\phi_2\right) + b_1b_2^*\left(\phi_2, \hat{A}\phi_1\right) = b_1^*b_2\left(\hat{A}\phi_1, \phi_2\right) + b_1b_2^*\left(\hat{A}\phi_2, \phi_1\right). \tag{5.25}$$

The only way this can be satisfied for *arbitrary* complex b_1 and b_2 is if

$$\begin{aligned} \left(\phi_1, \hat{A}\phi_2\right) &= \left(\hat{A}\phi_1, \phi_2\right); \\ \left(\phi_2, \hat{A}\phi_1\right) &= \left(\hat{A}\phi_2, \phi_1\right). \end{aligned} \tag{5.26}$$

This is an alternative way to define a Hermitian operator.

5.1.2.1 Nondegenerate Eigenvalues

I first consider two eigenfunctions ψ_{a_1}, ψ_{a_2}whose eigenvalues are unequal or *nondegenerate*. I start from

$$\begin{aligned} \hat{A}\psi_{a_1}(\mathbf{r}) &= a_1\psi_{a_1}(\mathbf{r}); \\ \left[\hat{A}\psi_{a_2}(\mathbf{r})\right]^* &= \left[a_2\psi_{a_2}(\mathbf{r})\right]^* = a_2\left[\psi_{a_2}(\mathbf{r})\right]^*, \end{aligned} \tag{5.27}$$

having used the fact that a_2 is real, take the inner product of the first equation with ψ_{a_2} and the second equation with ψ_{a_1}, namely

$$\begin{aligned}\left(\psi_{a_2},\hat{A}\psi_{a_1}\right) &= a_1\left(\psi_{a_2},\psi_{a_1}\right);\\ \left(\hat{A}\psi_{a_2},\psi_{a_1}\right) &= a_2\left(\psi_{a_2},\psi_{a_1}\right),\end{aligned} \tag{5.28}$$

subtract these equations, and use Eq. (5.21) to obtain

$$\left(\psi_{a_2},\hat{A}\psi_{a_1}\right)-\left(\hat{A}\psi_{a_2},\psi_{a_1}\right)=0=(a_1-a_2)\left(\psi_{a_2},\psi_{a_1}\right). \tag{5.29}$$

But since $a_1 \neq a_2$, it follows that

$$\left(\psi_{a_2},\psi_{a_1}\right)=\int d\mathbf{r}\psi_{a_2}^{*}(\mathbf{r})\,\psi_{a_1}(\mathbf{r})=0; \tag{5.30}$$

eigenfunctions of a Hermitian operator corresponding to nondegenerate eigenvalues are *automatically* orthogonal. Moreover, I can *normalize* the eigenfunctions by setting

$$\left(\psi_{a_n},\psi_{a_{n'}}\right)=\delta_{n,n'}, \tag{5.31}$$

where $\delta_{n,n'}$ is the Kronecker delta function that is equal to 1 if $n = n'$ and zero otherwise.

5.1.2.2 Degenerate Eigenvalues

The above proof fails if $a_1 = a_2$, but it still is possible to construct orthogonal eigenfunctions using a method called Schmidt orthogonalization. You know that in three-dimensional space, any three non-collinear unit vectors can serve as basis vectors. It is just convenient to choose orthogonal unit vectors. The same ideas apply here. Suppose that there are N eigenfunctions having the same eigenvalue a_n. I label these eigenfunctions by $\psi_{a_n}^{(m)}$ with m going from 1 to N. It is clear that any linear combination of these eigenfunctions also has eigenvalue a_n, since

$$\hat{A}\sum_{m=1}^{N}b_m\psi_{a_n}^{(m)}=\sum_{m=1}^{N}b_m\hat{A}\psi_{a_n}^{(m)}=a_n\sum_{m=1}^{N}b_m\psi_{a_n}^{(m)}. \tag{5.32}$$

The point is that it is always possible to choose N linear combinations of the eigenfunctions

$$\tilde{\psi}_{a_n}^{(q)}=\sum_{m=1}^{N}b_{qm}\psi_{a_n}^{(m)}; \qquad q=1,2,\ldots,N \tag{5.33}$$

which have eigenvalue a_n and are orthogonal to each other. Often the choice is easy to make by inspection; for example, symmetric and anti-symmetric combinations of two functions. In fact it is rare to actually have to use the Schmidt orthogonalization procedure.

If you *must* use it, you could proceed as follows: Suppose $\left(\psi_{a_n}^{(1)}, \psi_{a_n}^{(2)}\right) = c_{12} \neq 0$. If the $\psi_{a_n}^{(j)}$ are normalized, as is assumed, then $|c_{12}| < 1$.[1] Take $\tilde{\psi}_{a_n}^{(1)} = \psi_{a_n}^{(1)}$ and

$$\tilde{\psi}_{a_n}^{(2)} = b_{21}\psi_{a_n}^{(1)} + b_{22}\psi_{a_n}^{(2)}. \tag{5.34}$$

For $\tilde{\psi}_{a_n}^{(1)}$ and $\tilde{\psi}_{a_n}^{(2)}$ to be orthogonal, I must require that

$$\left(\tilde{\psi}_{a_n}^{(1)}, \tilde{\psi}_{a_n}^{(2)}\right) = b_{21} + b_{22}c_{12} = 0 \tag{5.35}$$

or

$$b_{21} = -c_{12}b_{22}. \tag{5.36}$$

The values of b_{21} and b_{22} can be determined if I normalize $\tilde{\psi}_{a_n}^{(2)}$,

$$\begin{aligned}\left(\tilde{\psi}_{a_n}^{(2)}, \tilde{\psi}_{a_n}^{(2)}\right) &= \left(b_{21}\psi_{a_n}^{(1)} + b_{22}\psi_{a_n}^{(2)}, b_{21}\psi_{a_n}^{(1)} + b_{22}\psi_{a_n}^{(2)}\right)\\ &= |b_{22}|^2\left(-c_{12}\psi_{a_n}^{(1)} + \psi_{a_n}^{(2)}, -c_{12}\psi_{a_n}^{(1)} + \psi_{a_n}^{(2)}\right)\\ &= |b_{22}|^2\left(|c_{12}|^2 - |c_{12}|^2 - |c_{12}|^2 + 1\right)\\ &= |b_{22}|^2\left(1 - |c_{12}|^2\right) = 1,\end{aligned} \tag{5.37}$$

having used Eq. (5.36) and the fact that

$$\left(\psi_{a_n}^{(1)}, \psi_{a_n}^{(2)}\right) = \left(\psi_{a_n}^{(2)}, \psi_{a_n}^{(1)}\right)^* = c_{12}. \tag{5.38}$$

Thus, if

$$b_{22} = \left(1 - |c_{12}|^2\right)^{-1/2}; \quad b_{21} = -c_{12}b_{22} = -c_{12}\left(1 - |c_{12}|^2\right)^{-1/2}, \tag{5.39}$$

then $\tilde{\psi}_{a_n}^{(1)}$ and $\tilde{\psi}_{a_n}^{(2)}$ are orthonormal wave functions.

Now suppose $\left(\tilde{\psi}_{a_n}^{(1)}, \psi_{a_n}^{(3)}\right) = c_{13} \neq 0$ and $\left(\tilde{\psi}_{a_n}^{(2)}, \psi_{a_n}^{(3)}\right) = c_{23} \neq 0$. I set

$$\tilde{\psi}_{a_n}^{(3)} = g_{31}\tilde{\psi}_{a_n}^{(1)} + g_{32}\tilde{\psi}_{a_n}^{(2)} + g_{33}\psi_{a_n}^{(3)}, \tag{5.40}$$

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[1] The fact that $|c_{12}| < 1$ follows from the Schwarz inequality, $\left|\left(\psi_{a_n}^{(1)}, \psi_{a_n}^{(2)}\right)\right|^2 \leq \left(\psi_{a_n}^{(1)}, \psi_{a_n}^{(1)}\right)\left(\psi_{a_n}^{(2)}, \psi_{a_n}^{(2)}\right) = 1$.

(the g's differ from the b's in Eq. (5.33) since I expand in terms of the *new* first two eigenfunctions) and demand that

$$\left(\tilde{\psi}_{a_n}^{(1)}, \tilde{\psi}_{a_n}^{(3)}\right) = 0, \tag{5.41a}$$

$$\left(\tilde{\psi}_{a_n}^{(2)}, \tilde{\psi}_{a_n}^{(3)}\right) = 0, \tag{5.41b}$$

$$\left(\tilde{\psi}_{a_n}^{(3)}, \tilde{\psi}_{a_n}^{(3)}\right) = 1. \tag{5.41c}$$

These constitute three complex equations that allow you to solve for the complex numbers g_{31}, g_{32}, g_{33}. And so on, for the remaining of the N degenerate eigenfunctions. In the end you have an orthonormal basis for these degenerate eigenfunctions. Thus the eigenfunctions corresponding to degenerate eigenvalues are not *automatically* orthogonal, but can be chosen to be so.

5.1.3 Completeness

Although the proof of the completeness of the eigenvalues is not trivial, a statement of the completeness *condition* is not difficult to obtain. If the eigenfunctions are complete, any function $\psi(\mathbf{r})$ can be expanded as

$$\psi(\mathbf{r}) = \sum_m b_m \psi_{a_m}(\mathbf{r}). \tag{5.42}$$

If I take the inner product of this equation with ψ_{a_n}, I find

$$\left(\psi_{a_n}, \psi\right) = \sum_m b_m \left(\psi_{a_n}, \psi_{a_m}\right) = \sum_m b_m \delta_{m,n} = b_n. \tag{5.43}$$

Note that Eq.(5.43) can be used to calculate the expansion coefficients b_n. Substituting Eq. (5.43) into Eq. (5.42), I obtain

$$\psi(\mathbf{r}) = \sum_m \left(\psi_{a_m}, \psi\right) \psi_{a_m}(\mathbf{r}) = \int_{-\infty}^{\infty} d\mathbf{r}' \left[\sum_m \psi_{a_m}^*(\mathbf{r}')\psi_{a_m}(\mathbf{r})\right] \psi(\mathbf{r}'). \tag{5.44}$$

For the equality to hold, the term in square brackets must equal $\delta(\mathbf{r}-\mathbf{r}')$, implying that

$$\sum_m \psi_{a_m}^*(\mathbf{r}')\psi_{a_m}(\mathbf{r}) = \delta\left(\mathbf{r}-\mathbf{r}'\right). \tag{5.45}$$

Equation (5.45) is a condition that must be satisfied if the eigenfunctions are complete.

Equation (5.42) is analogous to the expansion of a vector in terms of unit vectors, except that the unit vectors are now replaced by orthonormal *functions*. The dot product of vectors is replaced by an integral of the form given in Eq. (5.16). Moreover, Eq. (5.43) is equivalent to projecting out the component of a vector. The analogue with vector spaces will become exact when I consider Dirac notation in Chap. 11.

5.1.4 Continuous Eigenvalues

So far it has been assumed implicitly that the eigenvalues are discrete. As you shall see, this is always the case if the particles are confined to a finite volume. However unbound particles have *continuous* eigenvalues. For example, consider a free particle having mass m. The time-independent Schrödinger equation for this particle is

$$\hat{H}\psi_E(\mathbf{r}) = \frac{\hat{p}^2}{2m}\psi_E(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi_E(\mathbf{r}). \tag{5.46}$$

Clearly the momentum of a free particle can take on any value. Moreover, for a given positive energy, there is an *infinite* number of momenta corresponding to a given energy—there is infinite degeneracy. To label each of the degenerate eigenfunctions, I can use the momentum and take as eigenfunctions

$$\psi_{\mathbf{p}}(\mathbf{r}) = e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}, \tag{5.47}$$

which are solutions of Eq. (5.46), provided

$$E = \frac{p^2}{2m}. \tag{5.48}$$

The question arises as to how to normalize these eigenfunctions. Clearly $\int d\mathbf{r}\left|\psi_{\mathbf{p}}(\mathbf{r})\right|^2 = \infty$, so I cannot normalize as I did in the case of discrete eigenvalues. However, from the definition of the Dirac delta function, we know that

$$\int d\mathbf{r}\, e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}/\hbar} = (2\pi\hbar)^3\,\delta\left(\mathbf{p}-\mathbf{p}'\right). \tag{5.49}$$

By convention, I use this result and take as free-particle eigenfunctions,

$$\psi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{(2\pi\hbar)^{3/2}}e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \tag{5.50}$$

or, in $\mathbf{k}$ space ($\mathbf{p} = \hbar\mathbf{k}$),

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{5.51}$$

With this choice, the normalization conditions for the free particle eigenfunctions are

$$\int d\mathbf{r}\, \psi^*_{\mathbf{p}}(\mathbf{r})\psi_{\mathbf{p}'}(\mathbf{r}) = \delta\left(\mathbf{p} - \mathbf{p}'\right); \tag{5.52a}$$

$$\int d\mathbf{r}\, \psi^*_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}'}(\mathbf{r}) = \delta\left(\mathbf{k} - \mathbf{k}'\right). \tag{5.52b}$$

Equations (5.52) can still be used as the normalization condition in the more general case of unbound motion in the presence of a potential; however, the eigenfunctions are no longer given by Eqs. (5.50) and (5.51).

In going from discrete to continuous eigenvalues, the units for the wave functions and the expansion coefficients change. For discrete eigenenergies, the eigenfunctions in coordinate space have units of $1/\sqrt{\text{volume}}$. For continuous eigenvalues, $\psi_{\mathbf{p}}(\mathbf{r})$ has units of $(\hbar)^{-3/2}$ while $\psi_{\mathbf{k}}(\mathbf{r})$ is dimensionless. Similar differences arise for the expansion coefficients. In the case of continuous eigenvalues, an arbitrary function can be expanded as

$$\psi(\mathbf{r}) = \int d\mathbf{p}\, b(\mathbf{p})\psi_{\mathbf{p}}(\mathbf{r}); \tag{5.53a}$$

$$\psi(\mathbf{r}) = \int d\mathbf{k}\, \tilde{b}(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r}). \tag{5.53b}$$

In contrast to the case of discrete eigenenergies for which the expansion coefficients of the wave function are dimensionless, the expansion coefficients $b(\mathbf{p})$ have units of (momentum)$^{-3/2}$,while the expansion coefficients $\tilde{b}(\mathbf{k})$ have units of (volume)$^{3/2}$.

For continuous variables, the completeness conditions are

$$\int d\mathbf{p}\, \psi^*_{\mathbf{p}}(\mathbf{r})\psi_{\mathbf{p}}(\mathbf{r}') = \delta\left(\mathbf{r} - \mathbf{r}'\right); \tag{5.54}$$

$$\int d\mathbf{k}\, \psi^*_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}') = \delta\left(\mathbf{r} - \mathbf{r}'\right). \tag{5.55}$$

A formal method for going from discrete to continuous variables is given in the Appendix.

5.1.5 Relationship Between Operators

I have already derived an expression for the square of the momentum operator in coordinate space in Chap. 4. I now want to rederive this result from the postulates. To do so, I calculate the momentum operator in the coordinate representation. The expectation value of any operator is the same in both the coordinate and momentum representations. Let's see how this works for the momentum operator. I start from

$$\begin{aligned}\int d\mathbf{r}\,[\psi(\mathbf{r},t)]^*\,\hat{p}_x\psi(\mathbf{r},t) &= \int d\mathbf{p}\,[\Phi(\mathbf{p},t)]^*\,\hat{p}_x\Phi(\mathbf{p},t)\\ &= \int d\mathbf{p}\,[\Phi(\mathbf{p},t)]^*\,p_x\Phi(\mathbf{p},t),\end{aligned} \tag{5.56}$$

where I made use of Eq. (5.5a). I substitute the expression $\Phi(\mathbf{p},t)$ given in Eq. (5.3) into the right-hand side of this equation (being careful to use different dummy variables for the integrals) and obtain

$$\begin{aligned}\int d\mathbf{p}\,[\Phi(\mathbf{p},t)]^*\,p_x\Phi(\mathbf{p},t) = \frac{1}{(2\pi\hbar)^3}\int d\mathbf{r}\int d\mathbf{r}'\,[\psi(\mathbf{r},t)]^*\,\psi(\mathbf{r}',t)\\ \times\int d\mathbf{p}\,p_x e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar}.\end{aligned} \tag{5.57}$$

Since

$$\frac{\hbar}{i}\frac{\partial}{\partial x'}e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar} = -p_x e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar}, \tag{5.58}$$

I find that

$$\begin{aligned}\int d\mathbf{p}\,[\Phi(\mathbf{p},t)]^*\,p_x\Phi(\mathbf{p},t) = -\frac{1}{(2\pi\hbar)^3}\int d\mathbf{r}\int d\mathbf{r}'\,[\psi(\mathbf{r},t)]^*\,\psi(\mathbf{r}',t)\\ \times\frac{\hbar}{i}\frac{\partial}{\partial x'}\int d\mathbf{p}\,e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar}.\end{aligned} \tag{5.59}$$

The integral over $\mathbf{p}$ yields $(2\pi\hbar)^3\,\delta(\mathbf{r}-\mathbf{r}')$, such that, with the help of the chain rule,

$$\begin{aligned}&\int d\mathbf{p}\,[\Phi(\mathbf{p},t)]^*\,p_x\Phi(\mathbf{p},t)\\ &= -\int d\mathbf{r}\int d\mathbf{r}'\,[\psi(\mathbf{r},t)]^*\,\psi(\mathbf{r}',t)\frac{\hbar}{i}\frac{\partial}{\partial x'}\delta\left(\mathbf{r}-\mathbf{r}'\right)\\ &= -\frac{\hbar}{i}\int d\mathbf{r}\,[\psi(\mathbf{r},t)]^*\int d\mathbf{r}'\frac{\partial}{\partial x'}\left[\psi(\mathbf{r}',t)\delta\left(\mathbf{r}-\mathbf{r}'\right)\right]\\ &\quad+\frac{\hbar}{i}\int d\mathbf{r}\,[\psi(\mathbf{r},t)]^*\int d\mathbf{r}'\delta\left(\mathbf{r}-\mathbf{r}'\right)\frac{\partial}{\partial x'}\psi(\mathbf{r}',t).\end{aligned} \tag{5.60}$$

The second integral in the first term involves an exact differential whose integral vanishes for a wave function having finite extent. I am left with

$$\int d\mathbf{p}\,[\Phi(\mathbf{p},t)]^{*}\,p_x\Phi(\mathbf{p},t)=\int d\mathbf{r}\,[\psi(\mathbf{r},t)]^{*}\,\frac{\hbar}{i}\frac{\partial}{\partial x}\psi(\mathbf{r},t), \tag{5.61}$$

which, according to Eq. (5.56), implies that

$$\hat{p}_x=\frac{\hbar}{i}\frac{\partial}{\partial x}. \tag{5.62}$$

In three dimensions the analogous equation is

$$\hat{\mathbf{p}}=\frac{\hbar}{i}\boldsymbol{\nabla}_r, \tag{5.63}$$

which is consistent with $\hat{p}^2=-\hbar^2\nabla^2$.

The same technique can be used for *any* operator, except that the functions corresponding to the operators must be Fourier transformed as well. For example, suppose that $B(\mathbf{p})$ is a function of momentum only. I associate a quantum-mechanical operator $\hat{B}(\hat{\mathbf{p}})$ with this function and *assume* that

$$\hat{B}(\hat{\mathbf{p}})\Phi(\mathbf{p})=B(\mathbf{p})\Phi(\mathbf{p}) \tag{5.64}$$

for any function $\Phi(\mathbf{p})$ having a Fourier transform $\psi(\mathbf{r})$. Next I consider

$$\begin{aligned}
&\frac{1}{(2\pi\hbar)^{3/2}}\int d\mathbf{p}\,e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}B(\mathbf{p})\Phi(\mathbf{p})\\
&=\frac{1}{(2\pi\hbar)^{3/2}}\frac{1}{(2\pi\hbar)^{3}}\int d\mathbf{r}\int d\mathbf{r}'\int d\mathbf{p}\,e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}'-\mathbf{r}'')/\hbar}\tilde{B}(\mathbf{r}'')\psi(\mathbf{r}')\\
&=\frac{1}{(2\pi\hbar)^{3/2}}\int d\mathbf{r}\int d\mathbf{r}'\,\delta(\mathbf{r}-\mathbf{r}'-\mathbf{r}'')\tilde{B}(\mathbf{r}'')\psi(\mathbf{r}')\\
&=\frac{1}{(2\pi\hbar)^{3/2}}\int d\mathbf{r}'\,\tilde{B}(\mathbf{r}-\mathbf{r}')\psi(\mathbf{r}'),
\end{aligned} \tag{5.65}$$

where $\tilde{B}(\mathbf{r})$ is the Fourier transform of $B(\mathbf{p})$. I interpret this result to imply that an operator $\hat{B}(\hat{\mathbf{p}})$ acting on a function $\psi(\mathbf{r})$ produces the *integral* operation,

$$\hat{B}(\hat{\mathbf{p}})\psi(\mathbf{r})=\frac{1}{(2\pi\hbar)^{3/2}}\int d\mathbf{r}'\,\tilde{B}(\mathbf{r}-\mathbf{r}')\psi(\mathbf{r}'). \tag{5.66}$$

Similarly, for an operator $\hat{C}(\hat{\mathbf{r}})$ that is associated with a function $C(\mathbf{r})$ that is a function of coordinates only and for which it is assumed that

$$\hat{C}(\hat{\mathbf{r}})\psi(\mathbf{r}) = C(\mathbf{r})\psi(\mathbf{r}), \tag{5.67}$$

the action of the operator $\hat{C}(\hat{\mathbf{r}})$ acting on a function $\Phi(\mathbf{p})$ produces the integral operation,

$$\hat{C}(\hat{\mathbf{r}})\Phi(\mathbf{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int d\mathbf{p}' \, \tilde{C}(\mathbf{p}-\mathbf{p}')\Phi(\mathbf{p}'), \tag{5.68}$$

where $\tilde{C}(\mathbf{p})$ is the Fourier transform of $C(\mathbf{r})$ and $\Phi(\mathbf{p})$ is the Fourier transform of $\psi(\mathbf{r})$. We now know how operators act on the wave function in both coordinate and momentum space. In fact, Eq. (5.68) implies that Schrödinger's equation in momentum space is

$$i\hbar\frac{\partial\Phi(\mathbf{p},t)}{\partial t} = \frac{p^2}{2m}\Phi(\mathbf{p},t) + \frac{1}{(2\pi\hbar)^{3/2}}\int_{-\infty}^{\infty} d\mathbf{p}' \, \tilde{V}(\mathbf{p}-\mathbf{p}')\Phi(\mathbf{p}',t), \tag{5.69}$$

where $\tilde{V}(\mathbf{p})$ is the Fourier transform of $V(\mathbf{r})$. I will derive the time-independent Schrödinger equation in momentum space in Chap. 11 using Dirac notation.

5.1.6 Commutator of Operators

I now look at some additional properties of operators. The *commutator* $\hat{C}$ of two operators $\hat{A}$ and $\hat{B}$ is defined as

$$\hat{C} = \left[\hat{A},\hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} = -\left[\hat{B},\hat{A}\right]. \tag{5.70}$$

For example, the operators $\hat{x}$ and $\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$ do not commute since

$$\begin{aligned}
[\hat{x},\hat{p}_x]\,\psi(x) &= \frac{\hbar}{i}\left(x\frac{d}{dx} - \frac{d}{dx}x\right)\psi \\
&= \frac{\hbar}{i}\left(x\frac{d\psi}{dx} - \frac{d}{dx}(x\psi)\right) = -\frac{\hbar}{i}\psi(x),
\end{aligned} \tag{5.71}$$

which can be satisfied for *arbitrary* $\psi(x)$ only if

$$[\hat{x},\hat{p}_x] = i\hbar. \tag{5.72}$$

Similarly,

$$\left[\hat{y},\hat{p}_y\right] = [\hat{z},\hat{p}_z] = i\hbar. \tag{5.73}$$

As you can see, the commutator of two operators can be calculated by looking at its action on functions. Using this method, it is easy to show that any two components of the position operator commute and any two components of the momentum operator commute,

$$[\hat{x},\hat{y}] = [\hat{x},\hat{z}] = [\hat{y},\hat{z}] = [\hat{p}_x,\hat{p}_z] = \left[\hat{p}_x,\hat{p}_y\right] = \left[\hat{p}_y,\hat{p}_z\right] = 0. \tag{5.74}$$

Moreover, *different* components of the position and momentum operators commute as well,

$$\left[\hat{x},\hat{p}_y\right] = [\hat{x},\hat{p}_z] = [\hat{y},\hat{p}_x] = [\hat{y},\hat{p}_z] = [\hat{z},\hat{p}_x] = \left[\hat{z},\hat{p}_y\right] = 0. \tag{5.75}$$

Equations (5.72)–(5.75) are the fundamental commutator relations. Remember them at all times!

Commuting operators play a central role in quantum mechanics. I first prove that two Hermitian operators commute *if and only if* they possess simultaneous eigenfunctions. There are two parts to the proof. First suppose that Hermitian operators $\hat{A}$ and $\hat{B}$ possess simultaneous eigenfunctions ψ_{ab},

$$\hat{A}\psi_{ab} = a\psi_{ab}; \quad \hat{B}\psi_{ab} = b\psi_{ab}\,. \tag{5.76}$$

Then

$$\left[\hat{A},\hat{B}\right]\psi_{ab} = \left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)\psi_{ab} = (ba - ab)\,\psi_{ab} = 0 \tag{5.77}$$

and the operators commute. Conversely, suppose that ψ_a is an eigenfunction of $\hat{A}$ and that $\left[\hat{A},\hat{B}\right]\psi_a = 0$. Then

$$\begin{aligned} \left[\hat{A},\hat{B}\right]\psi_a &= \left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)\psi_a = 0; \\ \hat{A}\left(\hat{B}\psi_a\right) &= a\left(\hat{B}\psi_a\right). \end{aligned} \tag{5.78}$$

Equation (5.78) is nothing but a statement of the fact that $\left(\hat{B}\psi_a\right)$ is an eigenfunction of $\hat{A}$ with eigenvalue a, having the most general form

$$\hat{B}\psi_a = b\psi_a, \tag{5.79}$$

where b is some constant. Therefore, ψ_a is a simultaneous eigenfunction of $\hat{B}$ with eigenvalue b. Actually the proof is valid only if the eigenfunctions ψ_a are nondegenerate. If there are N degenerate eigenfunctions $\psi_a^{(m)}$ associated with eigenvalue a, Eq. (5.78) implies only that

$$\hat{B}\psi_a^{(n)} = \sum_{m=1}^{N} b_{nm}\psi_a^{(m)}. \tag{5.80}$$

However, as in the Schmidt orthogonalization procedure, it is always possible to find linear combinations of the degenerate eigenfunctions that are simultaneous eigenfunctions of $\hat{B}$.

Thus if two Hermitian operators commute and one of these operators has nondegenerate eigenvalues, then its eigenfunctions are *automatically* eigenfunctions of the other operator. On the other hand, if two Hermitian operators commute and one of these operators has degenerate eigenvalues, then a degenerate eigenfunction of one of the operators is not *automatically* an eigenfunction of the other operator, but some linear combinations of the degenerate eigenfunctions can be chosen that *is* an eigenfunction of the other operator. Examples are given later in this chapter.

The central problem in quantum mechanics is to solve the time-independent Schrödinger equation. As long as there is no energy degeneracy, for discrete energy eigenvalues, you can always label the energy by a quantum number n with the lowest value of n corresponding to the lowest energy, the second value to the next highest energy, etc. For example, if $V(x) = ax^4 + bx^2 + cx$ with $a > 0$, it is not possible to find analytic expressions for the eigenenergies and eigenfunctions, but you can still label the lowest energy state and eigenfunction by $n = 0$, the next by $n = 1$, etc. When there is *energy degeneracy*, however, we need additional labels to distinguish states having the same energy; that is we need additional quantum numbers. Where can we get these quantum numbers? There may be a number of ways to specify the quantum numbers, but the most systematic way is to identify additional operators that commute with the Hamiltonian. You can then label the states by the eigenvalues of the simultaneous eigenfunctions of the commuting operators. It turns out, whenever there is energy degeneracy, it is usually possible to identify an operator that commutes with the Hamiltonian that is in some way associated with the degeneracy.

We have already seen one example of energy degeneracy and will see many more throughout this book. For the free particle in one dimension, the eigenfunctions are two-fold degenerate for each positive energy, $\psi_E(x) = e^{\pm i\sqrt{2mE}x/\hbar}$. That is, given the energy, you cannot uniquely label the eigenfunction. However the momentum and energy operators commute. Moreover, the momentum state eigenfunctions, given by $e^{ip_x x/\hbar}$, are *nondegenerate* (each momentum eigenfunction is associated with a different momentum). As a consequence the momentum state eigenfunctions *must* be simultaneous eigenfunctions of the energy operator. If we label the eigenfunctions by p_x alone, we completely specify the energy eigenfunctions as well. In other words, the eigenfunctions

$$\psi_{p_x}(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ip_x x/\hbar} \tag{5.81}$$

are simultaneous eigenfunctions of the energy operator if $E = p_x^2/2m$. Similarly in three dimensions, where there is infinite degeneracy for each positive energy,

$$\psi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \tag{5.82}$$

uniquely labels the eigenfunctions, provided $E = p^2/2m$. We shall see later that the fact that the momentum operator commutes with the Hamiltonian is linked to the translational symmetry of the Hamiltonian.

5.1.6.1 Commutator Algebra Relationships

It is very easy to prove the following relationships for commutators:

$$\left[\hat{A}\hat{B}, \hat{C}\right] = \hat{A}\left[\hat{B}, \hat{C}\right] + \left[\hat{A}, \hat{C}\right]\hat{B}; \tag{5.83}$$

$$\left[\hat{A}, \hat{B}\hat{C}\right] = \hat{B}\left[\hat{A}, \hat{C}\right] + \left[\hat{A}, \hat{B}\right]\hat{C}. \tag{5.84}$$

Also, if $\hat{C} = \left[\hat{A}, \hat{B}\right]$, and if $\left[\hat{A}, \hat{C}\right] = 0$ and $\left[\hat{B}, \hat{C}\right] = 0$, then

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}e^{-\hat{C}/2}. \tag{5.85}$$

Another useful identity is

$$e^{\hat{A}}\hat{B}e^{-\hat{A}} = \hat{B} + \left[\hat{A}, \hat{B}\right] + \frac{1}{2!}\left[\hat{A}, \left[\hat{A}, \hat{B}\right]\right] + \cdots \tag{5.86}$$

which is known as the Baker-Campbell-Hausdorff theorem. Moreover, if $\hat{A}$ and $\hat{B}$ are Hermitian operators, then $\hat{A}\hat{B} + \hat{B}\hat{A}$ and $i\left[\hat{A}, \hat{B}\right]$ are Hermitian, but $\hat{A}\hat{B}$ is Hermitian only if $\left[\hat{A}, \hat{B}\right] = 0$ (see problems).

The basic commutation relations for coordinate and momentum space operators, obtained in a manner similar to the one used to arrive at Eq. (5.72) are

$$\left[\hat{\mathbf{r}}, \hat{B}(\hat{\mathbf{p}})\right] = i\hbar\nabla_p B(\mathbf{p}); \tag{5.87a}$$

$$\left[\hat{\mathbf{p}}, \hat{C}(\hat{\mathbf{r}})\right] = -i\hbar\nabla_r C(\mathbf{r}); \tag{5.87b}$$

$$\left[\hat{\mathbf{r}}, \hat{C}(\hat{\mathbf{r}})\right] = 0; \tag{5.87c}$$

$$\left[\hat{\mathbf{p}}, \hat{B}(\hat{\mathbf{p}})\right] = 0. \tag{5.87d}$$

For commutators involving higher powers of r and p, such as r^2 and p^2, one usually uses a combination of Eqs. (5.83), (5.84), and (5.87), rather than calculate the effect of the commutator on functions as I did in deriving Eq. (5.72). For example,

$$\left[\hat{x}, \hat{p}_x^2\right] = [\hat{x}, \hat{p}_x\hat{p}_x] = \hat{p}_x [\hat{x}, \hat{p}_x] + [\hat{x}, \hat{p}_x] \hat{p}_x = 2i\hbar\hat{p}_x. \tag{5.88}$$

5.1.7 Uncertainty Principle

Many people have heard about *Heisenberg's Uncertainty Relation*, even if they do not understand it. Actually, it is possible to derive an uncertainty relation for the product $\Delta A^2 \Delta B^2$ for any two non-commuting Hermitian operators $\hat{A}$ and $\hat{B}$. To do so I start from the inequality

$$\int d\mathbf{r} \left[\left(\hat{A} + i\lambda\hat{B}\right)\psi(\mathbf{r})\right]^* \left(\hat{A} + i\lambda\hat{B}\right)\psi(\mathbf{r}) \geq 0, \tag{5.89}$$

where λ is a constant taken to be real (a somewhat more general uncertainty relation can be derived if λ is taken to be complex). Without loss of generality, I take $\left\langle \hat{A} \right\rangle = 0$ and $\left\langle \hat{B} \right\rangle = 0$. If this were not the case, I would replace $\hat{A}$ by $\hat{A} - \left\langle \hat{A} \right\rangle$ and $\hat{B}$ by $\hat{B} - \left\langle \hat{B} \right\rangle$ in Eq. (5.89). Since $\hat{A}$ and $\hat{B}$ are Hermitian, Eq. (5.89) can be rewritten as

$$\begin{aligned} &\int d\mathbf{r}\,[\psi(\mathbf{r})]^* \left(\hat{A} - i\lambda\hat{B}\right)\left(\hat{A} + i\lambda\hat{B}\right)\psi(\mathbf{r}) \\ &\quad = \int d\mathbf{r}\,[\psi(\mathbf{r})]^* \left(\hat{A}^2 + i\lambda\hat{A}\hat{B} - i\lambda\hat{B}\hat{A} + \lambda^2\hat{B}^2\right)\psi(\mathbf{r}) \geq 0, \end{aligned} \tag{5.90}$$

or

$$\lambda^2 \Delta B^2 + i\lambda \left\langle \hat{C} \right\rangle + \Delta A^2 \geq 0, \tag{5.91}$$

where

$$\hat{C} = \left[\hat{A}, \hat{B}\right]. \tag{5.92}$$

The minimum occurs for

$$\lambda = \frac{-i\left\langle \hat{C} \right\rangle}{2\Delta B^2} \tag{5.93}$$

and, when this result is substituted into Eq. (5.91), I find

$$\Delta A^2 \Delta B^2 \geq -\frac{\left\langle \hat{C} \right\rangle^2}{4}, \tag{5.94}$$

which implies that the expectation value of the commutator of two Hermitian operators either vanishes or is purely imaginary (this is not surprising since one prescription for quantization is to obtain the commutator as $i\hbar$ times the Poisson bracket of the classical variables associated with the operators). For $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}_x$, $\hat{C} = i\hbar$ and

$$\Delta x^2 \Delta p_x^2 \geq \frac{\hbar^2}{4}, \tag{5.95}$$

which is known as the Heisenberg Uncertainty Relation.

From Eq. (5.89), it follows that the equality in Eq. (5.94) holds only if

$$\left(\hat{A} + i\lambda\hat{B}\right) \psi (x) = 0. \tag{5.96}$$

For $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}_x$, $\lambda = \hbar / \left(2\Delta p_x^2\right)$ [see Eq. (5.93)] and the *minimum uncertainty wave function* $\psi_{\min}(x)$ must satisfy the differential equation

$$\begin{aligned} (\hat{x} + i\lambda\hat{p}_x)\, \psi_{\min}(x) &= \left[x + i\left(\frac{\hbar}{2\Delta p_x^2}\right)\frac{\hbar}{i}\frac{d}{dx}\right]\psi_{\min}(x) \\ &= \frac{\hbar^2}{2\Delta p_x^2}\frac{d\psi_{\min}(x)}{dx} + x\psi_{\min}(x) = 0. \end{aligned} \tag{5.97}$$

The solution of this equation is

$$\psi_{\min}(x) = N \exp\left(-\frac{x^2 \Delta p_x^2}{\hbar^2}\right) = N \exp\left(-\frac{x^2}{4\Delta x^2}\right), \tag{5.98}$$

where N is a normalization constant. The minimum uncertainty wave packet is a Gaussian and *only* a Gaussian! For example, we will see that the lowest energy state wave function for a particle confined to an infinite potential well is not a Gaussian—consequently $\Delta x^2 \Delta p_x^2$ *must* be greater than $\hbar^2/4$ for this wave function.

The uncertainty principle is often illustrated by examples in which you show that by measuring the position of a particle to a given precision, you necessarily introduce an uncertainty in the momentum that satisfies the uncertainty principle. You will note that my derivation has nothing to do with measurement, *per se*. In effect, the position-momentum uncertainty relation is related directly to the fact that the corresponding operators do not commute. Equivalently, it is linked to the fact that matter is described by a wave theory in which the wave functions in coordinate and momentum space are Fourier transforms of one another. Any measurements must be consistent with the theory, but the measurements themselves are not directly related to the uncertainty principle.

5.1.8 *Examples of Operators*

In most of the examples below, I consider one-dimensional motion only, with p standing for the x component of the momentum. Moreover, I work in the coordinate representation only. The generalization to two and three dimensions is often obvious. The Hamiltonian is assumed to be of the form

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}. \tag{5.99}$$

5.1.8.1 Position Operator $\hat{x}$

The position operator is not often discussed in textbooks. I have assumed that, in coordinate space,

$$\hat{x}\psi(x') = x'\psi(x'). \tag{5.100}$$

Clearly $\hat{x}$ is Hermitian since

$$\begin{aligned}\int dx\, \psi^*(x)\,[\hat{x}\psi(x)] &= \int dx\, \psi^*(x) x\psi(x)\\ &= \int dx\, [x\psi(x)]^*\, \psi(x) = \int dx\, [\hat{x}\psi(x)]^*\, \psi(x)\end{aligned} \tag{5.101}$$

for real x.

The operator $\hat{x}$ does not commute with the momentum operator $\hat{p}$, nor with the Hamiltonian operator $\hat{H}$. As a consequence, it is impossible to find simultaneous eigenfunctions of $\hat{x}$ and $\hat{p}$ and it is also impossible to find simultaneous eigenfunctions of $\hat{x}$ and $\hat{H}$. But what *are* the eigenfunctions of $\hat{x}$? The eigenvalue equation in coordinate space is

$$\hat{x}\psi_a(x) = a\psi_a(x), \tag{5.102}$$

where the eigenvalue is designated by a to avoid confusion. From Eq. (5.100), we know that

$$\hat{x}\psi_a(x) = x\psi_a(x) \tag{5.103}$$

which, together with Eq. (5.102), implies that

$$x\psi_a(x) = a\psi_a(x) \tag{5.104}$$

for all x. The only way this can be true is if

$$\psi_a(x) = \delta\,(x-a)\,. \tag{5.105}$$

This has the proper normalization for continuous eigenvalues,

$$\int_{-\infty}^{\infty} dx\,\psi_a^*(x)\psi_{a'}(x) = \int_{-\infty}^{\infty} dx\,\delta\,(x-a)\,\delta\left(x-a'\right) = \delta\left(a-a'\right). \tag{5.106}$$

Thus the eigenfunctions of the position operator are Dirac delta functions.

5.1.8.2 Momentum Operator $\hat{p}$

The momentum operator in coordinate space is

$$\hat{p} = \frac{\hbar}{i}\frac{d}{dx}. \tag{5.107}$$

This operator is Hermitian since

$$\begin{aligned}\int_{-\infty}^{\infty} dx\,\psi^*(x)\hat{p}\psi(x) &= \int_{-\infty}^{\infty} dx\,\psi^*(x)\frac{\hbar}{i}\frac{d}{dx}\psi(x)\\ &= \frac{\hbar}{i}\left[\left|\psi(x)\right|^2\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} dx\,\frac{d\psi^*(x)}{dx}\psi(x)\right]\\ &= -\frac{\hbar}{i}\int_{-\infty}^{\infty} dx\,\frac{d\psi^*(x)}{dx}\psi(x) = \int_{-\infty}^{\infty} dx\,\left[\hat{p}\psi(x)\right]^*\psi(x),\end{aligned} \tag{5.108}$$

where it is assumed that the boundary conditions are such that the endpoint term, $\left|\psi(x)\right|^2\Big|_{-\infty}^{\infty}$, vanishes. This is true for any localized wave function. It would also be true for periodic boundary conditions in which $\psi(L/2) = \psi(-L/2)$. This example shows how the Hermiticity of an operator depends on boundary conditions.

The momentum operator does not commute with the Hamiltonian, except in the case where $V(x)$ is a constant C, independent of x, which can be taken equal to zero without loss of generality (all energies in the problem are simply shifted by C). Thus, it is only for the free particle that it is possible to find simultaneous eigenfunctions of $\hat{p}$ and $\hat{H}$, which are

$$\psi_{p,E}(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}, \tag{5.109}$$

with $E = p^2/2m$. In this equation, p can be positive or negative. The two independent, degenerate energy eigenfunctions are

$$\psi_E(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{\pm i\sqrt{2mE}x/\hbar} \tag{5.110}$$

with $E > 0$.[2]

5.1.8.3 Parity Operator $\hat{P}$

An important operator in quantum mechanics is the *parity operator* that simply inverts the signs of coordinates. In other words

$$\hat{P}\psi(x) = \psi(-x). \tag{5.111}$$

You can prove easily that $\hat{P}$ is a Hermitian operator. Therefore, it has real eigenvalues. To find these eigenvalues, I note that

$$\hat{P}^2\psi(x) = \hat{P}\psi(-x) = \psi(x), \tag{5.112}$$

implying that the eigenvalue of $\hat{P}^2$ is one, which can be realized only if the (real) eigenvalues of $\hat{P}$ are ± 1. That is, there are only two eigenvalues. For the eigenvalue $+1$,

$$\hat{P}\psi_+(x) = \psi_+(-x) = \psi_+(x), \tag{5.113}$$

which implies that *any* even function is an eigenfunction of $\hat{P}$ having eigenvalue $+1$. Similarly,

$$\hat{P}\psi_-(x) = \psi_-(-x) = -\psi_-(x); \tag{5.114}$$

any odd function is an eigenfunction of $\hat{P}$ having eigenvalue -1. For example, $\cos(ax)$ has even parity and is an eigenfunction of $\hat{P}$ having eigenvalue $+1$, $\sin(ax)$ has odd parity and is an eigenfunction of $\hat{P}$ having eigenvalue -1, while $\exp(iax)$ does not have well-defined parity and is not an eigenfunction of the parity operator. The eigenfunctions of the parity operator are *infinitely* degenerate; any even function has eigenvalue $+1$ and any odd function has eigenvalue -1.

Since $\hat{P}$ does not commute with $\hat{x}$ and does not commute with $\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$, it is not possible to find simultaneous eigenfunctions of $\hat{P}$ and $\hat{x}$ nor of $\hat{P}$ and $\hat{p}$. On

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[2] Note that, in the *momentum* representation, the eigenfunctions of $\hat{p}$ are $\Phi_q(p) = \delta(p - q)$ and the eigenfunctions of $\hat{x}$ are $\Phi_x(p) = e^{-ipx/\hbar}/\sqrt{2\pi\hbar}$.

the other hand, $\left[\hat{P},\hat{p}^2\right]=0$ and, as a consequence $\left[\hat{P},\hat{H}\right]=0$ if $V(x)$ is an even function of x. This is an important result, that will become even more important when generalized to problems in three dimensions. For any Hamiltonian that is invariant under an inversion of coordinates, the eigenfunctions can be written as simultaneous eigenfunctions of the energy and the parity operator. That is, the eigenfunctions can be written as either even or odd functions of the coordinates. In an introductory quantum mechanics course, students often forget this very important result, nor do they appreciate the importance of the parity operator.

You might argue that the eigenfunctions for the free particle given in Eq. (5.109) are not eigenfunctions of the parity operator and you would be right. Those eigenfunctions are simultaneous eigenfunctions of the momentum and energy operators and cannot be simultaneous eigenfunctions of the parity operator since it is not possible to find simultaneous eigenfunctions of $\hat{P}$ and $\hat{p}$. On the other hand, we could have equally well taken our (unnormalized) *energy* eigenfunctions as

$$\psi_{p,E}(x)=\begin{cases}\cos\left(px/\hbar\right)\\ \sin\left(px/\hbar\right)\end{cases}, \tag{5.115}$$

which *are* simultaneous eigenfunctions of the parity operator, but no longer eigenfunctions of the momentum operator. This is an example where there is a two-fold energy degeneracy; for each value of the energy (other than zero), there are two independent eigenfunctions. These eigenfunctions can be taken as simultaneous eigenfunctions of the momentum operator *or* the parity operator, but not *both* (since the momentum and parity operators do not commute). With either choice, however, we have a unique way to label all the eigenfunctions. Recall that, if operators $\hat{A}$ and $\hat{B}$ commute, and if the eigenfunctions of operator $\hat{A}$ are degenerate, they are not *automatically* eigenfunctions of operator $\hat{B}$, but that some linear combination of the degenerate eigenfunctions of operator $\hat{A}$ can be chosen to be an eigenfunction of operator $\hat{B}$

5.2 Back to the Schrödinger Equation

5.2.1 How to Solve the Time-Dependent Schrödinger Equation

With our knowledge of the properties of Hermitian operators, it is a simple matter to construct a solution of the time-dependent Schrödinger equation if we know the eigenfunctions and eigenvalues of the Hamiltonian, as well as the initial condition for the wave function. The general solution of the time-dependent Schrödinger equation is

$$\psi(\mathbf{r},t)=\sum_E a_E e^{-iEt/\hbar}\psi_E(\mathbf{r}). \tag{5.116}$$

It is important to recognize that the summation index E appearing in this equation is a *dummy* index; any other letter works equally well. As a good general practice, when you have a product of two summations such as

$$\left(\sum_E a_E e^{-iEt/\hbar}\psi_E(\mathbf{r})\right)\left(\sum_E a_E e^{-iEt/\hbar}\psi_E(\mathbf{r})\right)^*,$$

you should use *different* summation indices to avoid getting into trouble. That is, write

$$\begin{aligned}
&\left(\sum_E a_E e^{-iEt/\hbar}\psi_E(\mathbf{r})\right)\left(\sum_E a_E e^{-iEt/\hbar}\psi_E(\mathbf{r})\right)^* \\
&= \left(\sum_E a_E e^{-iEt/\hbar}\psi_E(\mathbf{r})\right)\left(\sum_{E'} a_{E'} e^{-iE't/\hbar}\psi_{E'}(\mathbf{r})\right)^* \\
&= \sum_{E,E'} a_E a_{E'}^* e^{-i(E-E')t/\hbar}\psi_E(\mathbf{r})\psi_{E'}^*(\mathbf{r}). \qquad (5.117)
\end{aligned}$$

If you use the same summation index, you cannot obtain the correct form in the double summation.

I assume that the initial condition is

$$\psi(\mathbf{r},0) = \psi_0(\mathbf{r}), \qquad (5.118)$$

allowing me to solve for the expansion coefficients a_E by taking the inner product of Eq. (5.116) with $\psi_{E'}$, namely

$$(\psi_{E'},\psi_0) = \sum_E a_E\,(\psi_{E'},\psi_E) = \sum_E a_E\delta_{E,E'} = a_{E'}. \qquad (5.119)$$

Therefore, $a_E = (\psi_E,\psi_0)$ and

$$\psi(\mathbf{r},t) = \sum_E (\psi_E,\psi_0)\,e^{-iEt/\hbar}\psi_E(\mathbf{r}). \qquad (5.120)$$

For continuous variables in **k**-space for a particle having mass m moving in a potential for which the eigenfunctions are denoted by $\psi_{\mathbf{k}}(\mathbf{r})$ and the eigenenergies by E_k, the corresponding equation is

$$\psi(\mathbf{r},t) = \int d\mathbf{k}\;(\psi_{\mathbf{k}},\psi_0)\,e^{-iE_kt/\hbar}\psi_{\mathbf{k}}(\mathbf{r}), \qquad (5.121)$$

where

$$(\psi_{\mathbf{k}}, \psi_0) = a(\mathbf{k}) = \int d\mathbf{r}\, \psi_0(\mathbf{r})\psi_{\mathbf{k}}^*(\mathbf{r}). \tag{5.122}$$

Although I concentrate on solutions of the time-independent Schrödinger equation in the next several chapters, you should not forget Eqs. (5.120) and (5.121). They are *central* to an understanding of quantum dynamics. In effect, there is a *three-step program* for solving any problem in quantum mechanics, given an initial condition for the wave function. The first step, and the most difficult, is to solve the time-independent Schrödinger equation for the eigenfunctions and eigenenergies. The second step is to obtain the expansion coefficients, a_E or $a(\mathbf{k})$ in terms of the initial wave function and the final step is to use Eq. (5.120) or (5.121) to obtain the time-dependent wave function. Often one is content just to find the eigenenergies and eigenfunctions.

Equation (5.116) can be written as

$$\psi(\mathbf{r}, t) = \sum_E a_E(t)\psi_E(\mathbf{r}), \tag{5.123}$$

where

$$a_E(t) = a_E e^{-iEt/\hbar} \tag{5.124}$$

is the *probability amplitude* for the particle to be in state E at time t. Although the probability to be in a specific state

$$|a_E(t)|^2 = \left|a_E e^{-iEt/\hbar}\right|^2 = |a_E|^2, \tag{5.125}$$

is *constant* in time, the probability density

$$\begin{aligned}|\psi(\mathbf{r}, t)|^2 &= \left|\sum_E a_E e^{-iEt/\hbar}\psi_E(\mathbf{r})\right|^2 \\ &= \sum_{E,E'} a_E a_{E'}^* e^{-i(E-E')t/\hbar}\psi_E(\mathbf{r})\psi_{E'}^*(\mathbf{r})\end{aligned} \tag{5.126}$$

is a function of time if any two state amplitudes corresponding to nondegenerate eigenenergies are non-vanishing. Equation (5.126) contains all the dynamics.

One final point to engrave in your memory bank. *Each potential energy function gives rise to its own set of eigenfunctions and eigenenergies.* Some (or even all) of the eigenenergies may be the same for different potentials, but the eigenfunctions will *always* differ. For example, for the step potential to be considered in the next chapter, the eigenenergies take on all non-negative values, just as for a free particle, but the eigenfunctions differ.

5.2.2 Quantum-Mechanical Probability Current Density

The total probability is conserved for a single-particle quantum system. That is, if I consider a finite volume, the time rate of change of the probability to find the particle in the volume must equal the rate at which probability flows *into* the volume. In other words,

$$\frac{\partial}{\partial t}\int_V |\psi(\mathbf{r},t)|^2 \, d\mathbf{r} = -\oint_S \mathbf{J}(\mathbf{r},\mathbf{t})\cdot \mathbf{n}da, \tag{5.127}$$

where S is the surface enclosing the volume V and $\mathbf{n}$ is a unit vector pointing normally *outwards* from the volume. The quantity $\mathbf{J}$ is called the *probability current density*. By using the divergence theorem, I find

$$\int_V \left[\frac{\partial}{\partial t}\rho(\mathbf{r},t) + \nabla\cdot\mathbf{J}(\mathbf{r},t)\right] d\mathbf{r} = 0, \tag{5.128}$$

where

$$\rho(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2 \tag{5.129}$$

is the *probability density*. Since Eq. (5.128) must hold for an arbitrary volume, it can be satisfied only if

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) + \nabla\cdot\mathbf{J}(\mathbf{r},t) = 0, \tag{5.130}$$

an equation known as the *equation of continuity*.

To get an expression for $\mathbf{J}$, I use Schrödinger's equation with

$$\hat{H}\psi(\mathbf{r},t) = \frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r})\,\psi(\mathbf{r},t)$$

to write

$$\begin{aligned}
\frac{\partial}{\partial t}\rho(\mathbf{r},t) &= \frac{\partial}{\partial t}|\psi(\mathbf{r},t)|^2 = \frac{\partial}{\partial t}\left[\psi^*(\mathbf{r},t)\,\psi(\mathbf{r},t)\right] \\
&= -\frac{1}{i\hbar}\left[\hat{H}\psi(\mathbf{r},t)\right]^*\psi(\mathbf{r},t) + \left(\frac{1}{i\hbar}\right)\psi^*(\mathbf{r},t)\left[\hat{H}\psi(\mathbf{r},t)\right] \\
&= \frac{\hbar}{2mi}\psi(\mathbf{r},t)\,\nabla^2\psi^*(\mathbf{r},t) - \frac{\hbar}{2mi\hbar}\psi^*(\mathbf{r},t)\,\nabla^2\psi(\mathbf{r},t) \\
&= \frac{\hbar}{2mi}\boldsymbol{\nabla}\cdot\left[\psi(\mathbf{r},t)\,\boldsymbol{\nabla}\psi^*(\mathbf{r},t) - \psi^*(\mathbf{r},t)\,\boldsymbol{\nabla}\psi(\mathbf{r},t)\right].
\end{aligned} \tag{5.131}$$

By comparing this equation with Eq. (5.130), I obtain the probability current density

$$\mathbf{J}(\mathbf{r},t) = \frac{i\hbar}{2m}\left[\psi(\mathbf{r},t)\,\nabla\psi^*(\mathbf{r},t) - \psi^*(\mathbf{r},t)\,\nabla\psi(\mathbf{r},t)\right]. \tag{5.132}$$

For a plane wave,

$$\psi(\mathbf{r},t) = \frac{1}{(2\pi\hbar)^{3/2}}e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}e^{-ip^2t/(2m)}, \tag{5.133}$$

$$\begin{aligned}\mathbf{J}(\mathbf{r},t) &= \frac{1}{(2\pi\hbar)^3}\frac{i\hbar}{2m}\left[-\frac{i\mathbf{p}}{\hbar} - \frac{i\mathbf{p}}{\hbar}\right] \\ &= \frac{1}{(2\pi\hbar)^3}\frac{\mathbf{p}}{m} = |\psi(\mathbf{r},t)|^2\,\frac{\mathbf{p}}{m} = \rho(\mathbf{r},t)\,\mathbf{v},\end{aligned} \tag{5.134}$$

where $\mathbf{v} = \mathbf{p}/m$. The probability current has the general form of a spatial density times a velocity, as expected. For real wave functions, the probability current density vanishes.

In general, it is easy to show that, for an arbitrary $\psi(\mathbf{r},t)$,

$$\langle\hat{\mathbf{p}}(t)\rangle/m = \int d\mathbf{r}\,\mathbf{J}(\mathbf{r},t). \tag{5.135}$$

Equation (5.135) follows from the fact that $\hat{\mathbf{p}}$ is Hermitian,

$$\begin{aligned}\langle\hat{\mathbf{p}}(t)\rangle &= \frac{\hbar}{i}\int d\mathbf{r}\,\psi^*(\mathbf{r},t)\,\nabla\psi(\mathbf{r},t) \\ &= \langle\hat{\mathbf{p}}(t)\rangle^* = -\frac{\hbar}{i}\int d\mathbf{r}\,\psi(\mathbf{r},\mathbf{t})\,\nabla\psi^*(\mathbf{r},t),\end{aligned} \tag{5.136}$$

since this equation implies that

$$\frac{\langle\hat{\mathbf{p}}(t)\rangle}{m} = \frac{i\hbar}{2m}\int d\mathbf{r}\left[\psi(\mathbf{r},t)\,\nabla\psi^*(\mathbf{r},t) - \psi^*(\mathbf{r},t)\,\nabla\psi(\mathbf{r},t)\right] = \int d\mathbf{r}\,\mathbf{J}(\mathbf{r},t). \tag{5.137}$$

In one dimension, the equation of continuity is

$$\frac{\partial}{\partial t}\rho(x,t) + \frac{\partial J_x(x,t)}{\partial x} = \frac{\partial}{\partial t}|\psi(x,t)|^2 + \frac{\partial J_x(x,t)}{\partial x} = 0, \tag{5.138}$$

where

$$J_x(x,t) = \frac{i\hbar}{2m}\left[\psi(x,t)\,\frac{\partial\psi^*(x,t)}{\partial x} - \psi^*(x,t)\,\frac{\partial\psi(x,t)}{\partial x}\right]. \tag{5.139}$$

The probability current must be conserved in problems where there is no loss. I will use the probability current density to get reflection and transmission coefficients in problems involving wells or barriers.

5.2.3 *Operator Dynamics*

The operators I consider are time-independent, but the expectation value of an operator for a quantum system characterized by the wave function $\psi(\mathbf{r},t)$ is time-dependent, in general. To see this I write

$$\begin{aligned}
i\hbar\frac{d\left\langle\hat{A}\right\rangle}{dt} &= i\hbar\frac{d}{dt}\int d\mathbf{r}\,\psi^*(\mathbf{r},t)\hat{A}\psi(\mathbf{r},t)\\
&= i\hbar\int d\mathbf{r}\,\frac{\partial\psi^*(\mathbf{r},t)}{\partial t}\hat{A}\psi(\mathbf{r},t)+i\hbar\int d\mathbf{r}\psi^*(\mathbf{r},t)\,\hat{A}\frac{\partial\psi(\mathbf{r},t)}{\partial t}\\
&= -\int d\mathbf{r}\,\left[\hat{H}\psi(\mathbf{r},t)\right]^*\hat{A}\psi(\mathbf{r},t)+\int d\mathbf{r}\psi^*(\mathbf{r},t)\,\hat{A}\hat{H}\psi(\mathbf{r},t)\\
&= -\int d\mathbf{r}\,\psi^*(\mathbf{r},t)\hat{H}\hat{A}\psi(\mathbf{r},t)+\int d\mathbf{r}\psi^*(\mathbf{r},t)\,\hat{A}\hat{H}\psi(\mathbf{r},t);
\end{aligned}$$

$$i\hbar\frac{d\left\langle\hat{A}\right\rangle}{dt} = \left\langle\left[\hat{A},\hat{H}\right]\right\rangle, \tag{5.140}$$

where the fact that $\hat{H}$ is Hermitian has been used. The expectation value of any operator that commutes with the Hamiltonian is constant in time. Another way of saying this is that the dynamic variable associated with any Hermitian operator that commutes with the Hamiltonian is a constant of the motion. For the free particle, momentum is conserved, consistent with the fact that the momentum operator commutes with the Hamiltonian. In problems with spherically symmetric potentials, the angular momentum is conserved classically, implying that the angular momentum operator commutes with the Hamiltonian. If you know that a classical variable is a constant of the motion for a given potential, then the eigenvalues of the associated quantum operator can sometimes be used to distinguish between degenerate eigenfunctions of the Hamiltonian.

Although Eq. (5.140) appears to provide a simple prescription for obtaining the expectation value of an operator, it is deceiving. In calculating the commutator $\left[\hat{A},\hat{H}\right]$, one normally introduces new operators. As such one is often led to a never-ending set of coupled equations for the expectation values of different operators. It is only for potentials such as those for the free particle and simple harmonic oscillator that Eq. (5.140) can be used to obtain a *closed* set of equations for the expectation values of the position and momentum operators.

An alternative method for obtaining $\left\langle \hat{A} \right\rangle$ is to calculate the expectation value of any operator directly from the wave function. For example, if

$$\psi(\mathbf{r},t) = \sum_{E} a_E e^{-iEt/\hbar} \psi_E(\mathbf{r}), \tag{5.141}$$

then

$$\begin{aligned}\left\langle \hat{A} \right\rangle &= \int d\mathbf{r}\, \psi^*(\mathbf{r},t) \hat{A} \psi(\mathbf{r},t) \\ &= \sum_{E,E'} a_E a_{E'}^* e^{-i(E-E')t/\hbar} \int d\mathbf{r}\, \psi_{E'}^*(\mathbf{r}) \hat{A} \psi_E(\mathbf{r}).\end{aligned} \tag{5.142}$$

In general there is time dependence in $\left\langle \hat{A} \right\rangle$ resulting from the exponential factors. For operators that commute with $\hat{H}$ the time dependence must disappear since $\left\langle \hat{A} \right\rangle$ is constant in this limit.

Since $\hat{H}$ commutes with itself, the average energy is time-independent. Explicitly,

$$\begin{aligned}\left\langle \hat{H} \right\rangle &= \sum_{E,E'} a_E a_{E'}^* e^{-i(E-E')t/\hbar} \int d\mathbf{r}\, \psi_{E'}^*(\mathbf{r}) E \psi_E(\mathbf{r}) \\ &= \sum_{E,E'} a_E a_{E'}^* e^{-i(E-E')t/\hbar} E \delta_{E,E'} \\ &= \sum_{E} \left| a_E \right|^2 E,\end{aligned} \tag{5.143}$$

simply a weighted sum of the energy E with the probability to be in the state corresponding to energy E. In fact, for any operator $\hat{G}(E)$ that correspond to a classical dynamic variable $G(E)$, it is not difficult to prove that

$$\left\langle \hat{G}(E) \right\rangle = \sum_{E} \left| a_E \right|^2 G(E). \tag{5.144}$$

5.2.4 Sum of Two Independent Quantum Systems

Finally I consider two *independent* quantum systems characterized by Hamiltonians $\hat{H}_1$ and $\hat{H}_2$, where

$$\begin{aligned}\hat{H}_1 \psi_{E_1} &= E_1 \psi_{E_1}, \\ \hat{H}_2 \psi_{E_2} &= E_2 \psi_{E_2},\end{aligned} \tag{5.145}$$

and the total Hamiltonian is

$$\hat{H} = \hat{H}_1 + \hat{H}_2. \tag{5.146}$$

Since the Hamiltonians correspond to independent quantum systems, they must satisfy $\left[\hat{H}_1, \hat{H}_2\right] = 0$; consequently, the operators can possess simultaneous eigenfunctions. I can guess a solution in which the eigenfunctions for the composite system are simply the *product* of the eigenfunctions of the individual systems, while the eigenenergies are the *sums* of the individual energies. This guess works since

$$\begin{aligned}
\hat{H}\psi_{E_1}\psi_{E_2} &= \left(\hat{H}_1 + \hat{H}_2\right)\psi_{E_1}\psi_{E_2} = \hat{H}_1\psi_{E_1}\psi_{E_2} + \hat{H}_2\psi_{E_1}\psi_{E_2} \\
&= E_1\psi_{E_1}\psi_{E_2} + \psi_{E_1}\hat{H}_2\psi_{E_2} = E_1\psi_{E_1}\psi_{E_2} + E_2\psi_{E_1}\psi_{E_2} \\
&= (E_1 + E_2)\psi_{E_1}\psi_{E_2}.
\end{aligned} \tag{5.147}$$

Although this result is extremely simple, students often have trouble accepting or remembering it. For two independent systems, the eigenfunctions are products of the individual system eigenfunctions and the eigenenergies are the sum of the individual system eigenenergies.

5.3 Measurements in Quantum Mechanics: "Collapse" of the Wave Function

It has already been stated that a measurement on a single quantum system of a dynamic variable yields one and only one eigenvalue of the Hermitian operator associated with that dynamic variable. The wave function can be expanded in terms of the eigenfunctions of any Hermitian operator, provided the appropriate boundary conditions are met. For discrete eigenvalues, this implies that

$$\psi(\mathbf{r}, t) = \sum_n b_{a_n}(t)\psi_{a_n}(\mathbf{r}) \tag{5.148}$$

where a_n is an eigenvalue of some operator $\hat{A}$ and $\psi_{a_n}(\mathbf{r})$ is the corresponding eigenfunction. If this operator corresponds to a physical observable, then $|b_{a_n}(t)|^2$ corresponds to the probability that a measurement on a single quantum system at time t of the classical variable associated with $\hat{A}$ will yield the value a_n. For continuous eigenvalues a, this equation is replaced by

$$\psi(\mathbf{r}, t) = \int da\, b(a, t)\psi_a(\mathbf{r}), \tag{5.149}$$

where $|b(a,t)|^2\,da$ is the probability that a measurement with on a single quantum system at time t of the classical variable associated with $\hat{A}$ will yield a value between a and $a + da$.

Often it is stated in quantum mechanics texts that the wave function *collapses* into the eigenfunction associated with the eigenvalue that was measured. I have never been a big fan of this terminology. I have already noted that any *direct* measurement of a physical variable associated with a quantum system generally modifies the system, implying that the state of the system following the measurement is no longer the eigenfunction associated with that eigenvalue.

For example, in the two-slit experiment involving a single particle, the wave function before detection on a screen is spread out over an interference pattern associated with two-slit interference. One detector on the screen fires, localizing the particle, but the state of the particle is altered by the measurement. You can say that the measurement has collapsed the wave function, but I do not think this is a particularly useful image. Collapse tends to imply a physical collapse of the wave function, but quantum mechanics say nothing about the collapse process itself. As long as you deal with the probabilistic predictions of quantum mechanics you will not run into any problems. However if you try to associate a physical mechanism with the collapse process, you will be led down a path that seems to lead nowhere.

Although direct measurement of a physical variable that leaves a quantum system in an eigenfunction of the Hermitian operator associated with that variable is not possible, *indirect* measurements of the variable can be made that leave the quantum state of the system unchanged. Such measurements fall into two general classes: *quantum nondemolition measurements* on a single quantum system or measurements on a *correlated* or *entangled* state of a two-particle quantum system.

In a quantum nondemolition (QND) experiment,[3] one measures one of two noncommuting operators associated with a quantum system without introducing any noise (modification) of the dynamics associated with this operator. All the noise that is introduced goes into the dynamics associated with the other operator, but that operator is assumed *not* to appear in the Hamiltonian. In this *back-evading noise* scheme, the operator of interest can be measured with absolute accuracy, at least in principle. Such schemes were proposed as a means for measuring the small displacements produced on mechanical systems by gravitational waves. Note that such a scheme does not work if we measure the position of a free particle to arbitrary accuracy. Such a measurement would introduce an uncertainty in the momentum that acts back on the particle to modify its subsequent position. On the other hand, we could, in principle, measure the momentum of a free particle to arbitrary accuracy. Although the measurement would affect the position of the particle, the position does not appear in the Hamiltonian. To measure the momentum we would have to couple the particle of interest to another quantum system and make a measurement of the second quantum system that determines the momentum of the

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[3] See, for example, M. O. Scully and M. S. Zubairy, *Quantum Optics* (Cambridge University Press, Cambridge, U.K., 1997), Chapter 19.

system of interest, using a method similar to that described in the next paragraph. To make QND work, the probe must provide a measure of the quantum variable being probed, without affecting its value. For example, when atoms are sent through a microwave cavity, they can acquire a phase shift that depends on the microwave intensity in the cavity; measuring this phase shift is an indirect way of measuring the microwave intensity, without altering its value.[4]

In an entangled state measurement, one measures properties of one particle or system and infers the properties of the other particle or system. The most famous example of this type of measurement is related to the so-called Einstein-Podolsky-Rosen (EPR) paradox. We shall see that a particle such as an electron has an intrinsic angular momentum and that a measure of the z-component of this intrinsic angular momentum can be either $\hbar/2$ (spin $\uparrow$) or $-\hbar/2$ (spin $\downarrow$). The electron is said to have a spin of $1/2$. If a spinless particle decays into two identical spin 1/2 particles, then the quantum state of the combined system is

$$\psi_{1,2} = \frac{1}{\sqrt{2}} \left[\psi_{1\uparrow}\psi_{2\downarrow} - \psi_{2\uparrow}\psi_{1\downarrow} \right], \tag{5.150}$$

since we don't know which particle is in either of the spin states. This is an *entangled* wave function since it cannot be written as the product of individual wave functions for each particle. However, if we measure the spin of one of the particles as "up" along some direction we are guaranteed that the other particle is in its spin "down" state along the same direction. In several quantum computation schemes one entangles the internal state of an atom with the polarization of the radiation emitted from the atom. In this way, a measurement of the polarization of the emitted radiation can be correlated with a given superposition of the internal states of the atom.

5.4 Summary

In this chapter, the basic postulates of quantum mechanics were stated. A detailed catalogue was constructed giving various properties of Hermitian operators and their eigenfunctions and eigenvalues. The central problem in quantum mechanics is reduced to finding the eigenfunctions and eigenvalues of the Hamiltonian operator, from which all properties of quantum systems can be derived.

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[4] Experiments of this type were pioneered in the group of Serge Haroche, who was awarded the Nobel prize in recognition of these and other experiments.

5.5 Appendix: From Discrete to Continuous Eigenvalues

One way of going over to continuous from discrete eigenvalues is to use *periodic boundary conditions*. In one dimension a model to accomplish this goal involves a mapping of the one-dimensional problem onto a circular path having length L. The free-particle wave functions in this case are of the form

$$\psi_E(x) = \sqrt{1/L}e^{ikx}, \tag{5.151}$$

where $E = \hbar^2 k^2/2m$. The boundary condition that must be imposed is $\psi_E(0) = \psi_E(L)$. As a consequence of this requirement, it is necessary that

$$\begin{aligned} \sqrt{1/L}e^0 &= \sqrt{1/L}e^{ik_nL}; \\ e^{ik_nL} &= 1; \\ k_n &= \frac{2\pi n}{L}, \end{aligned} \tag{5.152}$$

where n is an integer, positive, negative, or zero. The eigenfunctions are

$$\psi_n(x) = \sqrt{1/L}e^{2\pi inx/L} \tag{5.153}$$

and they form an orthonormal basis since

$$\int_0^L dx\psi_n^*(x)\psi_m(x) = \frac{1}{L}\int_0^L dxe^{2\pi i(m-n)x/L} = \delta_{m,n}. \tag{5.154}$$

An arbitrary wave function can be written as

$$\psi(x,t) = \sum_n a_{k_n}(t)\psi_{k_n}(x), \tag{5.155}$$

where the k_ns take on discrete values. To take the limit that $L \to \infty$ you must do two things. First, the sum over n must be converted to an integral over a continuous variable k. Second, $a_{k_n}(t)$ must be replaced by a continuous amplitude $a(k,t)$ that has units of $1/\sqrt{k}$. To go over to a continuum, I set

$$\begin{aligned} \psi(x,t) &= \sum_n a_{k_n}(t)\psi_{k_n}(x) \\ &= \sqrt{1/L}\sum_{k_n} a_{k_n}(t)e^{ik_nx} \\ &= \sqrt{1/L}\frac{1}{\Delta k}\sum_{k_n} a_{k_n}(t)e^{ik_nx}\Delta k_n. \end{aligned} \tag{5.156}$$

where $\Delta k_n = 2\pi\left[(n+1-n)\right]/L = 2\pi/L = \Delta k$. To achieve the final result I now make the replacements

$$\sum_{k_n} \Delta k_n \rightarrow \frac{L}{2\pi}\int_{-\infty}^{\infty} dk \tag{5.157}$$

and

$$a_{k_n}(t) \rightarrow \sqrt{2\pi/L}a(k,t). \tag{5.158}$$

to arrive at

$$\psi(x,t) = \sqrt{\frac{1}{2\pi}}\int_{-\infty}^{\infty} dk\, a(k,t)e^{ikx}. \tag{5.159}$$

This method can be generalized to three dimensions by adopting periodic boundary conditions in all three directions, namely

$$(k_x)_n = \frac{2\pi n_x}{L};\quad \left(k_y\right)_n = \frac{2\pi n_y}{L}\quad (k_z)_n = \frac{2\pi n_z}{L}. \tag{5.160}$$

The sum over n is converted to an integral over $\mathbf{k}$ using the prescription

$$\sum_{n_x,n_y,n_z} \rightarrow \left(\frac{L}{2\pi}\right)^3 \int d\mathbf{k} \tag{5.161}$$

and Eq. (5.158) is replaced by

$$a\left[(k_x)_{n_x}, \left(k_y\right)_{n_y}, (k_z)_{n_z}; t\right] \rightarrow \left(\frac{2\pi}{L}\right)^{3/2} a(\mathbf{k},t). \tag{5.162}$$

5.6 Problems

Note: You can always assume that the eigenfunctions have been chosen to be orthonormal unless specifically told otherwise.

1. Why are Hermitian operators important in quantum mechanics? What is the possible outcome of a single measurement on a single quantum system of the physical observable associated with a Hermitian operator? Why does the energy operator play such an important role in quantum mechanics? If the eigenvalues of the Hamiltonian are nondegenerate, what do you know about the eigenfunctions of that Hamiltonian? If the eigenvalues of the Hamiltonian are degenerate, are the eigenfunctions of that Hamiltonian necessarily orthogonal? Explain.

2. Suppose a Hermitian operator $\hat{A}$ has eigenfunctions $\psi_{a_n}(\mathbf{r})$ and eigenvalues a_n. At a given time, the (normalized) state of a single quantum system is equal to

$$\psi(\mathbf{r}) = \sum_n b_n \psi_{a_n}(\mathbf{r}) .$$

Prove that

$$\left\langle \hat{A}^m \right\rangle = \sum_n (a_n)^m |b_n|^2 .$$

If

$$\psi(\mathbf{r}) = \sum_E b_E \psi_E(\mathbf{r}) ,$$

where the $\psi_E(\mathbf{r})$ are (normalized) eigenfunctions of the Hamiltonian, derive an expression the variance of the energy (assume that $\psi(\mathbf{r})$ is normalized) in terms of the b_E's and the energy eigenvalues.

3. Consider a Hermitian operator $\hat{A}$ having eigenfunctions $\psi_{a_n}(\mathbf{r})$ and eigenvalues a_n. At a given time, the state of a single quantum system is equal to

$$\psi(\mathbf{r}) = N\left[\psi_{a_1}(\mathbf{r}) + 2\psi_{a_2}(\mathbf{r}) + 3\psi_{a_3}(\mathbf{r})\right]$$

with $a_1 = 1$, $a_2 = 3$, $a_3 = 5$ in some appropriate units.

(a) Find N such that $\psi(\mathbf{r})$ is normalized.
(b) For this state, what are the only possible values of the dynamic variable associated with the operator $\hat{A}$ that could be obtained in a single measurement?
(c) Find $\left\langle \hat{A} \right\rangle$ in this state.
(d) Find the variance of $\hat{A}$ in this state.

[Hint: This is an easy problem and doesn't require any complicated expressions. Use the results of Problem 5.2.]

4. Use the fact that

$$\langle \hat{x} \rangle = \int \psi^*(\mathbf{r},t)\, \hat{x}\psi(\mathbf{r},t)\, d\mathbf{r} = \int \Phi^*(\mathbf{p},t)\, \hat{x}\phi(\mathbf{p},t)\, d\mathbf{p}$$

to prove that

$$\hat{x} = i\hbar \frac{\partial}{\partial p_x}$$

when operating on functions of momentum.

5. (a) Prove

$$\left[\hat{A}\hat{B},\hat{C}\right]=\hat{A}\left[\hat{B},\hat{C}\right]+\left[\hat{A},\hat{C}\right]\hat{B}$$

and

$$\left[\hat{A},\hat{B}\hat{C}\right]=\hat{B}\left[\hat{A},\hat{C}\right]+\left[\hat{A},\hat{B}\right]\hat{C}.$$

(b) Prove that if $\hat{A}$ and $\hat{B}$ are Hermitian, then $\hat{A}\hat{B}+\hat{B}\hat{A}$ and $i\left[\hat{A},\hat{B}\right]$ are Hermitian, but $\hat{A}\hat{B}$ is Hermitian only if $\left[\hat{A},\hat{B}\right]=0$.

6. Evaluate $[\hat{p}_x, V(x)]$, $\left[\hat{p}_x^2, x\right]$, and $\left[\hat{p}_x, \frac{\hat{p}_x^2}{2m}+\frac{kx^2}{2}\right]$. If $\hat{p}_x$ does not commute with the Hamiltonian, how do you know that $e^{ip_x/\hbar}$ is not an eigenfunction of the Hamiltonian?

7. Show that, to second order in the operators,

$$e^{\hat{A}+\hat{B}}=e^{\hat{A}}e^{\hat{B}}e^{-\hat{C}/2}$$

where $\hat{C}=\left[\hat{A},\hat{B}\right]$. Note that this equation is true to higher order only if both $\hat{A}$ and $\hat{B}$ commute with $\hat{C}$. Also prove that to second order in the operator $\hat{A}$,

$$e^{\hat{A}}\hat{B}e^{-\hat{A}}=\hat{B}+\left[\hat{A},\hat{B}\right]+\frac{1}{2!}\left[\hat{A},\left[\hat{A},\hat{B}\right]\right]+\cdots$$

8. (a) Prove by a counterexample that $\left[\hat{A},\hat{B}\right]=0$ and $\left[\hat{B},\hat{C}\right]=0$ does not imply $\left[\hat{A},\hat{C}\right]=0$.

(b) The *projection operator* $\hat{P}_a$ is defined by

$$\hat{P}_a\psi_{a'}=\delta_{a,a'}\psi_{a'}$$

where a is an eigenvalue of the Hermitian operator $\hat{A}$. Prove that $\hat{P}_a$ is Hermitian, that $\hat{P}_a^2=\hat{P}_a$, $\sum_a\hat{P}_a=\hat{1}$, and that $\hat{A}\hat{P}_a=a\hat{P}_a$.

9. Suppose you are given a Hamiltonian

$$\hat{H}=\frac{\hat{p}^2}{2m}+\hat{V},$$

having eigenfunctions $\psi_E(x)$. At $t=0$ the wave function can be written as

$$\psi(x,0)=\sum_E a_E\psi_E(x).$$

(a) Write the solution valid for any $t > 0$.
(b) Obtain an integral expression for $\langle \hat{p} \rangle$ and show that, in general, $\langle \hat{p} \rangle$ is a function of time. Why is this so?

10. How do you know that eigenfunctions of the momentum operator must be eigenfunctions of the free particle Hamiltonian? Why is it that eigenfunctions of the free particle Hamiltonian are not necessarily eigenfunctions of the momentum operator even though the two operators commute? For problems in one dimension, why is the maximum energy degeneracy equal to 2?

11. Prove that $[\hat{P}, \hat{p}_x] \neq 0$, $[\hat{P}, \hat{p}_x^2] = 0$, and that $[\hat{P}, \hat{H}] = 0$ only if $V(x) = V(-x)$, where $\hat{H} = \frac{\hat{p}_x^2}{2m} + \hat{V}$ and $\hat{P}$ is the parity operator. Under what condition are you guaranteed that the energy eigenfunctions are either even or odd functions of x?

12. Consider that we have two *independent* quantum Hamiltonians, $\hat{H}_1$ and $\hat{H}_2$ and the total Hamiltonian is

$$\hat{H} = \hat{H}_1 + \hat{H}_2.$$

The eigenfunctions and eigenenergies of $\hat{H}_1$ and $\hat{H}_2$ are

$$\hat{H}_1 \psi_{E_{1n}}(\mathbf{r}_1) = E_{1n} \psi_{E_{1n}}(\mathbf{r}_1);$$
$$\hat{H}_2 \psi_{E_{2m}}(\mathbf{r}_2) = E_{2m} \psi_{E_{2m}}(\mathbf{r}_2).$$

Since the Hamiltonians correspond to independent quantum systems,

$$\left[\hat{H}_1, \hat{H}_2\right] = 0$$

and the operators can possess simultaneous eigenfunctions. Prove that the eigenfunctions for the composite system are simply the *product* of the eigenfunctions of the individual systems, while the eigenenergies are the *sums* of the individual energies.

13. (a) Prove that the current density $J_x(x)$ vanishes at all points in space only if $\psi(x)$ is purely real or purely imaginary.
(b) As a consequence show that $\langle \hat{p}_x \rangle = 0$ if $J_x(x) = 0$.
(c) Prove that the converse is not true. In other words, there are wave functions such as eigenfunctions of the parity operator for which $\langle \hat{p}_x \rangle = 0$, but for which $J_x(x)$ is not necessarily equal to zero.

14–15. For a particle of mass m having an initial normalized square integrable wave function of the form

$$\psi(x, 0) = f(x) e^{ikx},$$

where $f(x)$ is real, prove that

$$\langle \hat{x}\hat{p} + \hat{p}\hat{x} \rangle = 2\hbar k \int_{-\infty}^{\infty} dx f^2(x) x = 2\hbar k \langle x(0) \rangle .$$

Use this result to prove that, for such an initial wave function,

$$\Delta x(t)^2 = \Delta x(0)^2 + (\Delta v)^2 t^2,$$

where $\Delta v = \Delta p/m$.

16. For a free particle wave packet, prove that

$$\frac{d\left\langle \hat{x}^2(t) \right\rangle}{dt} = \langle \hat{x}\hat{p} + \hat{p}\hat{x} \rangle /m,$$

where m is the mass of the particle. Specifically, for the free particle wave packet whose wave function is given by Eq. (3.36) with $k_0 = 0$, prove *explicitly* that

$$\frac{d\int_{-\infty}^{\infty} dx \psi(x,t)^* \hat{x}^2 \psi(x,t)}{dt} = \frac{1}{m} \int_{-\infty}^{\infty} dx \psi(x,t)^* (\hat{x}\hat{p} + \hat{p}\hat{x}) \psi(x,t)$$

by evaluating both sides of the equation.