(d) What can you conclude about observing "quantum effects" using 1 kg balls? What kind of objects would you need to use to see quantum effects on these length scales?

13. If we know that the velocity of an electron is 40.23 ± 0.01 m/s, what is the minimum uncertainty in its position? Repeat for a 150 g baseball traveling at the same velocity.

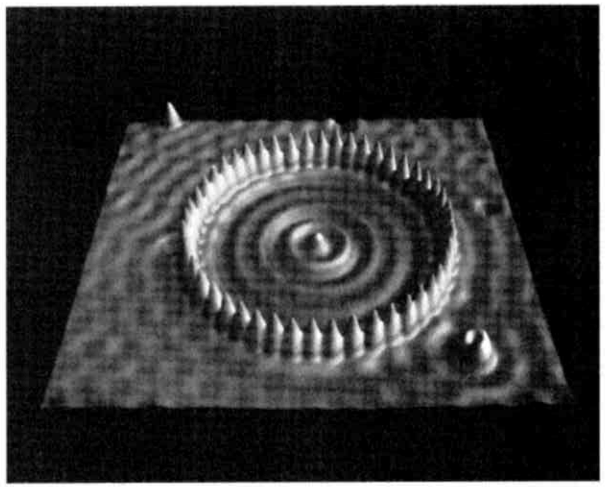
14. If a molecule having mass 2.3×10^{-26} kg is confined to a region 200 nm in length, what is the minimum uncertainty in the molecule's velocity?

15. Determine the minimum uncertainty in the velocity of an electron that has its position specified to within 10 nm.

16. Explain the difference between a fermion and a boson, and give two examples of each.

Chapter 3

QUANTUM MECHANICS OF ELECTRONS



STM image of atoms forming a "quantum corral," resulting in standing electron waves. The diameter of the ring is approximately 14 nm. (Courtesy Almaden Research Center/Research Division/NASA/Media Services.)

As described in the previous chapter, in the early 1900s, it became clear that classical Newtonian mechanics was unable to explain a considerable amount of experimentally observed phenomena. Light was recognized to have a discrete nature, and both light and matter were found to exhibit properties of classical waves and classical particles, and, in addition, to exhibit behavior that was completely unknown to classical physics. In the following discussion, when particles (usually electrons, but perhaps atoms, paper clips, billiard balls, etc.) are referred to, it should be recognized that all such objects, irrespective of size, are really quantum particles. The mathematical description of such particles is given by solutions of Schrödinger's equation.[†]

[†] Schrödinger's equation describes quantum particles having mass. Photons, which do not have mass, obey a quantized version of Maxwell's equations, although we will not consider that development here.

Schrödinger's equation cannot be derived from fundamental principles (the same can be said for Newton's equations), although before presenting Schrödinger's equation formally, a plausible development will be outlined.

From the wave standpoint, a one-dimensional plane wave has the form[†]

$$\psi(x,t) = Ae^{i(kx-\omega t)}, \tag{3.1}$$

where k is the wavenumber and $\omega = \omega(k)$ is the radian frequency. From (3.1), note that

$$\omega = \frac{i}{\psi(x,t)}\frac{\partial \psi(x,t)}{\partial t}, \quad k^2 = -\frac{1}{\psi(x,t)}\frac{\partial^2 \psi(x,t)}{\partial x^2}. \tag{3.2}$$

From the particle perspective, the total energy E of a particle is the sum of kinetic and potential energies,

$$E = \frac{1}{2}mv^2 + V = \frac{p^2}{2m} + V,$$

where p is the particle's momentum, m is the particle's mass, and V is the potential energy seen by the particle. So far, these are classical relations. The quantum nature of the problem is incorporated into the energy expression using quantization of energy, (2.12), and the de Broglie relation, (2.15), leading to

$$\begin{aligned} E = \hbar\omega = \hbar\left(\frac{i}{\psi(x,t)}\frac{\partial \psi(x,t)}{\partial t}\right) &= \frac{(\hbar k)^2}{2m} + V, \\ &= \frac{\hbar^2}{2m}\left(-\frac{1}{\psi(x,t)}\frac{\partial^2 \psi(x,t)}{\partial x^2}\right) + V, \end{aligned} \tag{3.3}$$

such that

$$i\hbar\frac{\partial \psi(x,t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right)\psi(x,t). \tag{3.4}$$

This is Schrödinger's equation in one dimension, although not the most general form. As will be seen, this is the fundamental equation for describing quantum particles with mass, of which, throughout the text, primary consideration will be given to electrons. In the next section, the general postulates of quantum mechanics will be presented, one of which refers to Schrödinger's equation, followed by a discussion of each postulate. In the field of nanoelectronics this constitutes the most difficult material to comprehend; however, it is extremely important.

[†] To obtain the time-domain wave classically, we would take the real part of a time-harmonic phasor,

$$\psi(x,t) = \mathrm{Re}\left\{Ae^{i(kx-\omega t)}\right\} = A\cos(kx-\omega t),$$

assuming the amplitude A is real valued. Here, it is more useful to consider a complex exponential form.

3.1 GENERAL POSTULATES OF QUANTUM MECHANICS

Postulate 1. To every quantum system there is a state function, $\Psi(\mathbf{r},t)$, that contains everything that can be known about the system.[†]

In the following discussion, a quantum system will be either a single particle, typically an electron, and its environment, or a system of particles. The state function, or *wavefunction*, is complex valued and mathematically well behaved (i.e., it is a finite, single valued, and continuous function), and probabilistic in nature. This latter fact makes the wavefunction fundamentally different from quantities obtained from Newtonian dynamics, such as the trajectory of a particle, or the motion of a wave. In particular, $\rho(\mathbf{r},t) = |\Psi(\mathbf{r},t)|^2$ *is the probability density of finding the particle at a particular point in space* $\mathbf{r}$ *at time* t.

That is, the probability of finding the particle in a region of space Ω is

$$P = \int_\Omega |\Psi(\mathbf{r},t)|^2\, d^3r = \int_\Omega \Psi^*(\mathbf{r},t)\,\Psi(\mathbf{r},t)\, d^3r. \tag{3.5}$$

In particular, in one dimension, the probability of finding the particle between points $x = a$ and $x = b$ is

$$P = \int_a^b \Psi^*(x,t)\,\Psi(x,t)\, dx. \tag{3.6}$$

By continuity of the wavefunction, the probability of finding the particle in a small volume element $d\Omega$ centered at $\mathbf{r}$ is

$$P = \int_{d\Omega} |\Psi(\mathbf{r},t)|^2\, d^3r = |\Psi(\mathbf{r},t)|^2\, d\Omega. \tag{3.7}$$

Furthermore, since the particle must be somewhere in space at any time t,

$$\int_{\text{all space}} \Psi^*(\mathbf{r},t)\,\Psi(\mathbf{r},t)\, d^3r = 1. \tag{3.8}$$

We frequently use (3.8) to normalize solutions of Schrödinger's equation.

It is worthwhile to reiterate that quantum systems are true probabilistic systems.[‡] As mentioned previously, most classical systems we think of as probabilistic, e.g., rolling a die or flipping a coin, are not really probabilistic at a fundamental level.[§] Probabilities are

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[†] The vector $\mathbf{r}$ is called the *position vector*, and represents the vector from the origin to some point in space. In rectangular coordinates,

$$\mathbf{r} = \mathbf{a}_x x + \mathbf{a}_y x + \mathbf{a}_z z,$$

where $\mathbf{a}_x$, $\mathbf{a}_y$, and $\mathbf{a}_z$ are unit vectors. The use of the position vector leads to notational convenience, since $\Psi(\mathbf{r},t)$ simply means $\Psi(x,y,z,t)$.

[‡] Here we take the view of what is called the *Copenhagen Interpretation* (or *Born interpretation)* of quantum mechanics, which is a mainstream view, although not the only view, in physics.

[§] Although, if you want to be a stickler, quantum mechanics governs the behavior of the die, too, and so we are back to a probabilistic description. However, the quantum nature of the die is obscured due to its large mass (resulting in a minuscule de Broglie wavelength). Newtonian dynamics, however complicated to apply in this case, models the trajectory of the die very well.

merely assigned to provide a convenient model of the system. Some scientists interpret the probabilistic nature of quantum mechanics to reflect the base probabilistic nature of, well, nature, although others argue that quantum mechanics is simply a probabilistic model of nature, and not the true description of physical reality. However, there is no argument about the accuracy of quantum mechanics—it is considered to be one of the most successful physical models ever developed.

Example

The following chapters will present methods to find the state function for electrons in several relatively simple structures. However, at this point, it is worthwhile to give a concrete example of a state function, since it is a relatively abstract concept (although the mathematical functions involved are usually quite ordinary).

Consider an electron that is confined to a line segment of length L, where the line segment extends from $x = -L/2$ to $x = L/2$ and where, on the line segment, potential energy is zero. As will be seen in the example on page 65 and in the next chapter, it turns out that the electron can be in one of an infinite number of possible states, where each state can be signified by an index[†] n. The possible states are given by wavefunctions $\Psi_n(x,t)$, where

$$\Psi_n(x,t) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right) e^{-iE_n t/\hbar}, \tag{3.9}$$

for n even, and

$$\Psi_n(x,t) = \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{n\pi}{L}x\right) e^{-iE_n t/\hbar}, \tag{3.10}$$

for n odd, where

$$E_n = \frac{\hbar^2}{2m_e}\left(\frac{n\pi}{L}\right)^2 \tag{3.11}$$

is the energy of the electron in the nth state, $n = 1, 2, 3, \ldots$. If the electron is in a state given by an even value of n, then the probability of finding the electron somewhere along the line segment is, from (3.6),

$$P = \int_{-L/2}^{L/2} \Psi_n^*(x,t)\,\Psi_n(x,t)\,dx = \frac{2}{L}\int_{-L/2}^{L/2} \sin^2\left(\frac{n\pi}{L}x\right) dx = 1. \tag{3.12}$$

That is, as expected, the probability of finding the electron somewhere along the line segment is 100 percent. The same result holds if the electron is in a state given by an odd value of n. Furthermore, the probability of finding the electron, say, on the left half of the line segment is

$$P = \frac{2}{L}\int_{-L/2}^{0} \sin^2\left(\frac{n\pi}{L}x\right) dx = \frac{1}{2},$$

or 50 percent, and is similar for odd values of n. Note that in a classical model, one would be able to say exactly where the electron is at all times. In the quantum model, one can only talk about probabilities of finding the electron at a certain position at a certain time. For a given state, at time t that probability is high where $|\Psi_n(x,t)|^2$ is large.

Postulate 2.[†]

(a) Every physical observable $\mathcal{O}$ (position, momentum, energy, etc.) is associated with a linear Hermitian operator $\widehat{o}$.

(b) Associated with the operator $\widehat{o}$ is the eigenvalue problem,

$$\widehat{o}\psi_n = \lambda_n \psi_n, \tag{3.13}$$

such that the result of a measurement of an observable is one of the eigenvalues λ_n of the operator $\widehat{o}$.

(c) If a system is in the initial state Ψ, measurement of $\mathcal{O}$ will yield one of the eigenvalues λ_n of $\widehat{o}$ with probability[‡]

$$P(\lambda_n) = \left|\int \Psi(\mathbf{r},t)\,\psi_n^*(\mathbf{r})\,d^3r\right|^2, \tag{3.14}$$

and the state of the system will change from Ψ to ψ_n.

This is a fairly long postulate, and each item will be discussed in some detail.

3.1.1 Operators

First, let us discuss briefly what is meant by an operator. An operator is a mapping from one quantity to another, loosely speaking. For instance, a 3×2 matrix maps 2×1 matrices to 3×1 matrices,

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \\ a_{31} & a_{32} \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix}. \tag{3.15}$$

[†] In addition, the electron can be in some combination of states, i.e., a sum over n, although this will be discussed later.

[†] Postulate 2 is quite complicated, and its explanation is rather long and involves difficult concepts. For the specific purpose of understanding the remainder of the text, it is also the least directly useful of the four postulates (beyond this chapter, with the exception of a few examples, we really only need Postulates 1 and 4, although Postulates 2 and 3 are included for completeness). Therefore, if desired the reader may choose to skip this postulate and move on to postulate 4.

[‡] Here we assume spatial eigenvectors (i.e., those associated with time-independent operators), and it is assumed that the eigenvectors are appropriately normalized to form an orthonormal set. This will be discussed later.

If one considers a set S_1 consisting of all 2×1 matrices, and a set S_2 consisting of all 3×1 matrices, the mapping $M : S_1 \rightarrow S_2$ can be accomplished via 3×2 matrices.

For our purposes, we will often need operators that map one function to another. For instance, when we take the derivative of the sine function, we obtain the cosine function. One can think of the mapping between these two functions as the derivative operator, $\widehat{o} = d/dx : \{\text{sine}\} \rightarrow \{\text{cosine}\}$. That is, apply the derivative operator to the sine function, and obtain the cosine function,

$$\frac{d}{dx} \sin(x) = \cos(x). \tag{3.16}$$

3.1.2 Eigenvalues and Eigenfunctions

Now, with the idea of an operator established, the concepts of eigenvalues and eigenfunctions can be discussed. An *eigenfunction* of a certain operator is a nonzero function such that, when we apply the operator to the eigenfunction, we obtain a multiple of the eigenfunction back again. That is,

$$\widehat{o}\psi_n = \lambda_n \psi_n, \tag{3.17}$$

where $\widehat{o}$ is an operator, ψ_n is an eigenfunction of the operator, and λ_n is called an *eigenvalue* (not to be confused with wavelength). In general, there are many (perhaps infinitely many) eigenfunctions and eigenvalues. For example, consider the operator

$$\widehat{o} = \frac{d^2}{dx^2}, \tag{3.18}$$

the second derivative operator, acting on functions defined over $0 \leq x \leq L$. Every function $\psi_n(x) = \sin(n\pi x/L)$ is an eigenfunction with eigenvalue $\lambda_n = -(n\pi/L)^2$, since

$$\frac{d^2}{dx^2}\left(\sin\frac{n\pi}{L}x\right) = -\left(\frac{n\pi}{L}\right)^2\left(\sin\frac{n\pi}{L}x\right). \tag{3.19}$$

As an example of a matrix operator,[†] simple matrix multiplication shows that the operator

$$\widehat{o} = \begin{bmatrix} 1 & 1 \\ 2 & -1 \end{bmatrix} \tag{3.20}$$

has eigenvalues and eigenvectors

$$\lambda_1 = \sqrt{3}, \qquad \psi_1 = \begin{bmatrix} \alpha \\ \left(\sqrt{3}-1\right)\alpha \end{bmatrix}, \tag{3.21}$$

$$\lambda_2 = -\sqrt{3}, \qquad \psi_2 = \begin{bmatrix} \beta \\ \left(-\sqrt{3}-1\right)\beta \end{bmatrix},$$

[†] Finding the eigenvalues and eigenvectors of a matrix operator is obviously more involved, and will be omitted here, although this topic is discussed in textbooks on linear algebra and applied mathematics.

where $\alpha, \beta \neq 0$. That is,

$$\begin{bmatrix} 1 & 1 \\ 2 & -1 \end{bmatrix}\begin{bmatrix} \alpha \\ \left(\sqrt{3}-1\right)\alpha \end{bmatrix} = \sqrt{3}\begin{bmatrix} \alpha \\ \left(\sqrt{3}-1\right)\alpha \end{bmatrix}, \tag{3.22}$$

and

$$\begin{bmatrix} 1 & 1 \\ 2 & -1 \end{bmatrix}\begin{bmatrix} \beta \\ \left(-\sqrt{3}-1\right)\beta \end{bmatrix} = -\sqrt{3}\begin{bmatrix} \beta \\ \left(-\sqrt{3}-1\right)\beta \end{bmatrix}. \tag{3.23}$$

3.1.3 Hermitian Operators

Hermitian operators form an important special class of operators. Hermitian operators have real eigenvalues, and their eigenfunctions form an *orthogonal*, *complete* set of functions. Orthogonal means that

$$\int \psi_i^*(\mathbf{r})\,\psi_j(\mathbf{r})\,d^3r = 0 \tag{3.24}$$

for all $i \neq j$, which is called an *orthogonality* condition. The subscript indicates a certain eigenfunction. That is, if ψ_1 and ψ_2 are two different eigenfunctions, i.e.,

$$\widehat{o}\psi_1 = \lambda_1\psi_1, \tag{3.25}$$

$$\widehat{o}\psi_2 = \lambda_2\psi_2, \tag{3.26}$$

and $\psi_1 \neq \psi_2$, then

$$\int \psi_1^*(\mathbf{r})\,\psi_2(\mathbf{r})\,d^3r = 0. \tag{3.27}$$

If the wavefunctions have been normalized such that

$$\int \psi_i^*(\mathbf{r})\,\psi_i(\mathbf{r})\,d^3r = 1, \tag{3.28}$$

then the wavefunctions are said to form an *orthonormal set*, i.e.,

$$\int \psi_i^*(\mathbf{r})\,\psi_j(\mathbf{r})\,d^3r = \begin{cases} 1, & i = j \\ 0, & i \neq j. \end{cases} \tag{3.29}$$

When one says that the eigenfunctions of a Hermitian operator form a *complete set* of functions, it means that any function can be represented as a sum of eigenfunctions,

$$\Psi(\mathbf{r}) = \sum_n a_n \psi_n(\mathbf{r}). \tag{3.30}$$

The expansion coefficients a_n can be obtained using orthonormality. That is, start with (3.30), multiply both sides by ψ_m^*, and integrate.

$$\int \psi_m^*(\mathbf{r})\,\Psi(\mathbf{r})\,d^3r = \sum_n a_n \int \psi_m^*(\mathbf{r})\,\psi_n(\mathbf{r})\,d^3r \tag{3.31}$$

$$= a_m. \tag{3.32}$$

Example

As a familiar example, any periodic function with period 2π can be written as the Fourier series

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{\infty} a_n e^{inx}, \tag{3.33}$$

where $\psi_n(x) = e^{inx}/\sqrt{2\pi}$ are normalized eigenfunctions of d^2/dx^2 subject to periodic boundary conditions,

$$\psi_n(-\pi) = \psi_n(\pi), \qquad \psi_n'(-\pi) = \psi_n'(\pi), \tag{3.34}$$

with eigenvalues $\lambda_n = -n^2$, i.e.,

$$\frac{d^2}{dx^2} e^{inx} = -n^2 e^{inx}. \tag{3.35}$$

Note that the same function Ψ has, in general, many different representations, associated with different operators. That is,

$$\Psi(\mathbf{r}) = \sum_n a_n \psi_n(\mathbf{r}) \tag{3.36}$$

$$= \sum_n b_n \phi_n(\mathbf{r}), \tag{3.37}$$

where $\{\psi_n\}$ and $\{\phi_n\}$ are sets of eigenfunctions associated with different operators (say, $\widehat{o}$ and $\widehat{s}$),

$$\widehat{o}\psi_n = \lambda_n \psi_n, \tag{3.38}$$

$$\widehat{s}\phi_n = \upsilon_n \phi_n. \tag{3.39}$$

However, as long as both operators $\widehat{o}$ and $\widehat{s}$ are Hermitian, the expansions (3.36) and (3.37) will be valid.

Example

It is easy to see that the differential operator d^2/dx^2, $\psi_n(0) = \psi_n(L) = 0$, on the segment from $x = 0$ to $x = L$ leads to eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \tag{3.40}$$

with corresponding eigenvalues $\lambda_n = (n\pi/L)^2$, $n = 1, 2, 3, \ldots$. Functions on this interval can be expanded as

$$\Psi(x) = \sum_{n=1}^{\infty} a_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \tag{3.41}$$

For the differential operator d^2/dx^2, $\psi'(0) = \psi'(L) = 0$, the eigenfunctions are found to be

$$\psi_n(x) = \sqrt{\frac{\varepsilon_n}{L}} \cos\left(\frac{n\pi x}{L}\right) \tag{3.42}$$

with corresponding eigenvalues $\lambda_n = (n\pi/L)^2$, $n = 0, 1, 2, \ldots$, where, for notational convenience, we use Neumann's number ε_n, defined as

$$\varepsilon_n \equiv \begin{cases} 1, & n = 0 \\ 2, & n \neq 0. \end{cases} \tag{3.43}$$

Functions on this interval can be expanded as

$$\Psi(x) = \sum_{n=0}^{\infty} b_n \sqrt{\frac{\varepsilon_n}{L}} \cos\left(\frac{n\pi x}{L}\right). \tag{3.44}$$

Since both sets of eigenfunctions form a complete set of functions on the interval $(0, L)$, either representation can be used. For example, the function $\Psi(x)$ that is equal to 0 from $x = 0$ to $x = L/2$, and equal to 1 from $x = L/2$ to $x = L$, can be expressed as (3.41) with

$$a_n = \int_0^L \psi_n^*(x)\, \Psi(x)\, dx \tag{3.45}$$

$$= \sqrt{\frac{2}{L}} \int_0^{L/2} \sin\left(\frac{n\pi x}{L}\right)(0)\, dx + \sqrt{\frac{2}{L}} \int_{L/2}^{L} \sin\left(\frac{n\pi x}{L}\right)(1)\, dx$$

$$= -\frac{\sqrt{2L}}{n\pi}\left(\cos(n\pi) - \cos\left(\frac{n\pi}{2}\right)\right), \tag{3.46}$$

or as (3.44) with

$$b_n = \int_0^L \psi_n^*(x)\, \Psi(x)\, dx \tag{3.47}$$

$$= \int_0^{L/2} \sqrt{\frac{\varepsilon_n}{L}} \cos\left(\frac{n\pi x}{L}\right)(0)\, dx + \int_{L/2}^{L} \sqrt{\frac{\varepsilon_n}{L}} \cos\left(\frac{n\pi x}{L}\right)(1)\, dx$$

$$= \begin{cases} \sqrt{\dfrac{1}{L}}\dfrac{L}{2}, & n = 0, \\ -\sqrt{\dfrac{\varepsilon_n}{L}}\dfrac{L}{n\pi}\sin\left(\dfrac{n\pi}{2}\right), & n > 0. \end{cases} \tag{3.48}$$

The only significant difference between the two expansions is the interpretation of the equality at the boundary points $x = 0, L$.

Of course, when one says that *any function* can be expanded as an eigenfunction series, the class or group of functions of interest needs to be specified (e.g., functions that go to zero at $x = a$ and $x = b$, or functions that possess derivatives, etc.) In this text, *any function* means any quantum mechanical state function Ψ, and if we consider the operators encountered in quantum mechanics (as discussed next), we will be able to form the expansion (3.30).

The eigenvalues could alternatively form a continuous, rather than a discrete, set.[†] In this case, the eigenvalue problem will be denoted as

$$\widehat{o}\psi(\mathbf{r}, \lambda) = \lambda\psi(\mathbf{r}, \lambda), \tag{3.49}$$

and the representation has the form of a continuous summation (integration), rather than a discrete summation,

$$\Psi(\mathbf{r}) = \int c(\lambda)\,\psi(\mathbf{r}, \lambda)\,d\lambda. \tag{3.50}$$

Example

The operator

$$\widehat{o} = -i\frac{\partial}{\partial x} \tag{3.51}$$

on $-\infty < x < \infty$ (i.e., with no "boundary conditions") has $\psi(x, \lambda) = e^{i\lambda x}$ as eigenfunctions,

$$-i\frac{\partial}{\partial x}e^{i\lambda x} = \lambda e^{i\lambda x}, \tag{3.52}$$

where any value of λ is allowed. In one dimension, functions can be represented as the continuous sum of eigenfunctions

$$\Psi(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} a(\lambda)\,e^{i\lambda x}d\lambda, \tag{3.53}$$

which is merely the familiar Fourier transform representation. The expansion coefficient is the Fourier transform itself,

$$a(\lambda) = \int_{-\infty}^{\infty} \Psi(x)\,e^{-i\lambda x}dx. \tag{3.54}$$

3.1.4 Operators for Quantum Mechanics

Typical operators encountered in quantum mechanics will now be discussed. It is useful to start by examining a plane–wave function of the form

$$\psi(x, t) = Ae^{i(kx - Et/\hbar)}, \tag{3.55}$$

which happens to be a solution to Schrödinger's equation in one dimension if $V = 0$ and

$$E = \frac{\hbar^2k^2}{2m}. \tag{3.56}$$

Momentum Operator. Considering first the spatial part of the function (3.55),

$$\psi(x) = Ae^{ikx}, \tag{3.57}$$

and applying the operator

$$\widehat{o} = -i\hbar\frac{\partial}{\partial x} \tag{3.58}$$

to the function $\psi(x)$ leads to

$$-i\hbar\frac{\partial}{\partial x}\psi(x) = -i\hbar\frac{\partial}{\partial x}Ae^{ikx} = \hbar k\psi(x) = p\psi(x), \tag{3.59}$$

where $p = \hbar k$ is the momentum. Therefore, (3.57) is an eigenfunction of the operator (3.58) with momentum as an eigenvalue. Hence, (3.58) is called the *momentum operator*, written as

$$\widehat{p} = -i\hbar\frac{\partial}{\partial x}. \tag{3.60}$$

Of course, there is nothing special about the coordinate x, and therefore we have momentum operators in rectangular coordinates as

$$\widehat{p}_x = -i\hbar\frac{\partial}{\partial x}, \quad \widehat{p}_y = -i\hbar\frac{\partial}{\partial y}, \quad \widehat{p}_z = -i\hbar\frac{\partial}{\partial z}. \tag{3.61}$$

In three dimensions, the vector momentum operator is

$$\mathbf{p} = \mathbf{a}_x\,\widehat{p}_x + \mathbf{a}_y\,\widehat{p}_y + \mathbf{a}_z\,\widehat{p}_z = -i\hbar\nabla, \tag{3.62}$$

where in rectangular coordinates $\nabla = \mathbf{a}_x\,(\partial/\partial x) + \mathbf{a}_y\,(\partial/\partial y) + \mathbf{a}_z\,(\partial/\partial z)$.

Energy Operator. In the same manner, the operator

$$\widehat{E} = i\hbar\frac{\partial}{\partial t} \tag{3.63}$$

[†] Such eigenfunctions are sometimes called *improper eigenfunctions*.

is the *energy operator*. Considering the temporal dependence of (3.55),

$$g(t) = e^{-iEt/\hbar}, \tag{3.64}$$

leads to

$$\widehat{E} g(t) = i\hbar \frac{\partial}{\partial t} g(t) = i\hbar \frac{\partial}{\partial t} e^{-iEt/\hbar} = \hbar \frac{E}{\hbar} g(t) = E g(t), \tag{3.65}$$

and so (3.64) are eigenfunctions of the energy operator (3.63) with energy as eigenvalues. As will be seen in Postulate 4, the energy operator (3.63) can be related to the Hamiltonian.

Position Operator. Now consider the position operator, $\widehat{x} = x$. Assume that a particle is at position x_α, and denote the position operator by $\widehat{x}$. Then

$$\widehat{x}\psi_\alpha(x) = x_\alpha \psi_\alpha(x) \tag{3.66}$$

must be true, such that

$$x\psi_\alpha(x) = x_\alpha \psi_\alpha(x). \tag{3.67}$$

This should be true for all x, which means that $\psi_\alpha(x) = 0$ for all $x \neq x_\alpha$. The eigenfunction is taken to be the delta function,

$$\psi_\alpha(x) = \psi(x, \alpha) = \delta(x - x_\alpha), \tag{3.68}$$

which, technically, is not a true function, but a distribution. That is, the eigenvalue equation is

$$x\delta(x - x_\alpha) = x_\alpha \delta(x - x_\alpha). \tag{3.69}$$

The delta function has the useful properties

$$\int_a^b \delta(x - x_\alpha) f(x)\, dx = \begin{cases} f(x_\alpha), & a \leq x_\alpha \leq b, \\ 0, & \text{otherwise}, \end{cases} \tag{3.70}$$

$$\int_a^b \delta(x - x_\alpha)\, dx = 1, \quad a < x_\alpha < b, \tag{3.71}$$

$$\int_{-\infty}^{\infty} e^{ikx} dx = 2\pi\delta(x). \tag{3.72}$$

Using these properties, we can see that, upon integrating both sides, the eigenvalue equation (3.69) holds.

The position operator $\widehat{x} = x$ is Hermitian, and so its eigenfunctions form a complete (continuous) set. Manipulating (3.70) gives the representation for any good function as

$$\Psi(x) = \int \Psi(x')\, \delta(x - x')\, dx', \tag{3.73}$$

using $x' = x_\alpha$.

Commutation and the Uncertainty Principle. Recall that the Heisenberg uncertainty principle in one dimension,

$$\Delta p \Delta x \geq \hbar/2, \tag{3.74}$$

places a constraint on the product of the uncertainties in momentum and position. On page 38, the generalization to three dimensions was given as

$$\Delta p_x \Delta x \geq \hbar/2, \tag{3.75}$$

$$\Delta p_y \Delta y \geq \hbar/2, \tag{3.76}$$

$$\Delta p_z \Delta z \geq \hbar/2, \tag{3.77}$$

so that, for example, there is no problem with measuring momentum in one direction and position in another. The question then arises as to when it is possible to have simultaneous knowledge of two quantities, and the answer is obtained by considering operators.

Consider two observables, α and β, associated with two operators, $\widehat{\alpha}$ and $\widehat{\beta}$, respectively, and assume that we would like to measure α and β for a given system Ψ. If we are to be able to measure α and β with arbitrary precision, then the measurement of α cannot influence β, and vice versa. Therefore, if this is to be true, the order of the measurements will not be important. Thus,

$$\widehat{\alpha}\widehat{\beta}\Psi = \widehat{\beta}\widehat{\alpha}\Psi, \tag{3.78}$$

and so

$$\left(\widehat{\alpha}\widehat{\beta} - \widehat{\beta}\widehat{\alpha}\right)\Psi = 0. \tag{3.79}$$

The difference operator in (3.79) is called the *commutator*,

$$\left[\widehat{\alpha}, \widehat{\beta}\right] = \left(\widehat{\alpha}\widehat{\beta} - \widehat{\beta}\widehat{\alpha}\right), \tag{3.80}$$

such that when the commutator of two operators is zero (the two operators are then said to *commute*), the corresponding observables can be measured to arbitrary precision.

As an example, consider the position and momentum operators. For $\widehat{x}$ and $\widehat{p}_x$,

$$\begin{aligned} \left(\widehat{x}\left(-i\hbar\frac{\partial}{\partial x}\right) - \left(-i\hbar\frac{\partial}{\partial x}\right)\widehat{x}\right)\Psi &= x\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi - \left(-i\hbar\frac{\partial}{\partial x}\right)x\Psi && (3.81) \\ &= -i\hbar\left(x\frac{\partial}{\partial x}\Psi - \left(x\frac{\partial}{\partial x}\Psi + \Psi\right)\right) && (3.82) \\ &= i\hbar\Psi, && (3.83) \end{aligned}$$

and, therefore,

$$\left[\widehat{x}, \widehat{p}_x\right] = i\hbar \neq 0. \tag{3.84}$$

So one cannot measure position and momentum along the x-axis with arbitrary precision. However, for the operators $\widehat{x}$ and $\widehat{p}_y$, one obtains

$$\left(\widehat{x}\left(-i\hbar\frac{\partial}{\partial y}\right)-\left(-i\hbar\frac{\partial}{\partial y}\right)\widehat{x}\right)\Psi = x\left(-i\hbar\frac{\partial}{\partial y}\right)\Psi-\left(-i\hbar\frac{\partial}{\partial y}\right)x\Psi \tag{3.85}$$

$$= -i\hbar\left(x\frac{\partial}{\partial y}\Psi-\left(x\frac{\partial}{\partial y}\Psi+0\right)\right) \tag{3.86}$$

$$= 0, \tag{3.87}$$

and so

$$\left[\widehat{x},\widehat{p}_y\right]=0, \tag{3.88}$$

allowing the possibility of measuring position along the x-axis and momentum along the y-axis with arbitrary precision. It can be easily seen that

$$\left[\widehat{\alpha},\widehat{p}_\beta\right]=\left[\widehat{p}_\alpha,\widehat{p}_\beta\right]=\left[\widehat{\alpha},\widehat{\beta}\right]=0 \tag{3.89}$$

for $\alpha, \beta = x, y, z$ with $\alpha \neq \beta$.

3.1.5 Measurement Probability

The last part of Postulate 2 gives the probability of obtaining a certain measurement result (a certain eigenvalue). From (3.14), if the system is already in state ψ_n before measurement ($\Psi = \psi_n$), where ψ_n is an eigenfunction of the measurement operator $\widehat{o}$ (i.e., $\widehat{o}\psi_n = \lambda_n\psi_n$), then (3.14) tells us that, with 100 percent certainty, the result of the measurement will be λ_n, since

$$P(\lambda_n)=\left|\int \Psi(\mathbf{r},t)\,\psi_n^*(\mathbf{r},t)\,d^3r\right|^2 \tag{3.90}$$

$$=\left|\int \psi_n(\mathbf{r},t)\,\psi_n^*(\mathbf{r},t)\,d^3r\right|^2=1. \tag{3.91}$$

However, if the initial state of the system is not ψ_n, then the best that can be done is to obtain the probability that the result of a measurement will be a certain λ_n, given by (3.14). For example, assume that the initial state of the particle is

$$\Psi(\mathbf{r},t)=a_1\psi_1(\mathbf{r},t)+a_2\psi_2(\mathbf{r},t). \tag{3.92}$$

Then

$$P(\lambda_1)=\left|\int \Psi(\mathbf{r},t)\,\psi_1^*(\mathbf{r},t)\,d^3r\right|^2 \tag{3.93}$$

$$=\left|\int \left[a_1\psi_1(\mathbf{r},t)+a_2\psi_2(\mathbf{r},t)\right]\psi_1^*(\mathbf{r},t)\,d^3r\right|^2,$$

which, using orthonormality, results in

$$P(\lambda_1)=|a_1|^2. \tag{3.94}$$

It it obvious that $P(\lambda_2)=|a_2|^2$, and $P(\lambda_n)=0$ for $n>2$ (thus, $|a_1|^2+|a_2|^2=1$ must be true).

However, regardless of the initial state, we do know with 100 percent certainty that after a measurement, the system will be in the state ψ_n (the eigenfunction of $\widehat{o}$). So, if we want to obtain a system in a certain state, we can "prepare" this state by doing a measurement.

Example

Coming back to the example of an electron confined to a line segment between $x=-L/2$ and $x=L/2$, we assume that an electron is in the $n=2$ state. The state function is (3.9),

$$\Psi(x,t)=\Psi_2(x,t)=\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{2\pi}{L}x\right)e^{-iE_2t/\hbar}, \tag{3.95}$$

and the probability that the electron is located at some position x_α is

$$P(x_\alpha)=\frac{2}{L}\left|\int_{-L/2}^{L/2}\sin\left(\frac{2\pi}{L}x\right)e^{-iE_2t/\hbar}\delta(x-x_\alpha)\,dx\right|^2 \tag{3.96}$$

$$=\frac{2}{L}\left|\sin\left(\frac{2\pi}{L}x_\alpha\right)\right|^2=|\Psi(x,t)|^2, \tag{3.97}$$

consistent with Postulate 1.

Collapse of the State Function—the Measurement Problem. Postulate 2 states that every physically measurable property of a system (any so-called observable) is associated with a linear Hermitian operator, and that the result of every measurement is one of the eigenvalues of the operator associated with that observable. That is, before measurement, the state of the system may not be known, but after measurement (i.e., observation), the system's state will be an eigenstate ψ_n of the operator $\widehat{o}$ associated with the measurement, and that an eigenvalue λ_n must be obtained as the measurement result.

In classical physics, the idea of a measurement is that one is measuring something about the system the instant before the measurement is performed. For example, if the velocity of a car is measured to be 80 km/h, it can be inferred that the instants before and after the measurement was performed, the car was going 80 km/h. Thus, in classical physics, when a measurement is performed, one is "taking a peek" into the system, and it is assumed that the act of measurement does not perturb the system (at least not too much).

The view in the Copenhagen Interpretation of quantum mechanics is quite different. All that we know about the system is its state *after* the measurement is performed. The instant before the measurement, the system is, most generally, in a superposition of states. The act of measuring (observing), no matter how carefully and unobtrusively done, collapses the superposition of states into a single eigenstate. This is called *collapse of the state function*, or the *measurement problem*. This collapse is an instantaneous process. The wave function will stay in the collapsed state until it is perturbed by the outside world, after which, depending on the type of perturbation, it may revert back to a superposition state.

To further consider the collapse of the state function, let's consider consecutive measurements of position and momentum. Let $\delta(x - x_\alpha)$ denote a position eigenfunction, and $e^{ipx/\hbar}$ denote a momentum eigenfunction. Further, note that any momentum eigenfunction can be written as a (continuous) sum of position eigenfunctions,

$$e^{ipx/\hbar} = \int_{-\infty}^{\infty} c(x_\alpha)\,\delta(x - x_\alpha)\,dx_\alpha, \tag{3.98}$$

where $c(x_\alpha) = e^{ipx_\alpha/\hbar}$, and that any position eigenfunction can be written as a (continuous) sum of momentum eigenfunctions,

$$\delta(x - x_\alpha) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} d(p)\,e^{ip(x - x_\alpha)/\hbar}dp, \tag{3.99}$$

where $d(p) = 1$. Therefore, if the system is in a certain momentum state, it is, equivalently, in a superposition of position states, by (3.98). In a similar manner, if the system is in a certain position state, it is, equivalently, in a superposition of momentum states, by (3.99).

Now say that the position of a particle is measured. Before the measurement, assume that the particle wavefunction is a superposition of several position eigenfunctions, as in (3.30), such that

$$\Psi(x) = \int_{-\infty}^{\infty} \Psi(x_\alpha)\,\delta(x - x_\alpha)\,dx_\alpha. \tag{3.100}$$

When the measurement is made, the wavefunction collapses into one of these eigenfunctions, say, $\delta(x - x_\beta)$, the one corresponding to the measured position x_β. That is,

$$\Psi(x) = \int_{-\infty}^{\infty} \Psi(x_\alpha)\,\delta(x - x_\alpha)\,dx_\alpha \xrightarrow{\text{measure position}} \delta(x - x_\beta). \tag{3.101}$$

In fact, position x_β is measured with probability

$$P(x_\beta) = \left|\int \Psi(x)\,\delta(x - x_\beta)\,dx\right|^2 = \left|\Psi(x_\beta)\right|^2. \tag{3.102}$$

If a further position measurement is made immediately afterwards, the wavefunction will still be in the collapsed state, $\delta(x - x_\beta)$, and so the same position (x_β) will be measured. That is,

$$\Psi(x) = \delta(x - x_\beta) \xrightarrow{\text{measure position}} \delta(x - x_\beta). \tag{3.103}$$

However, if immediately after this the momentum of the particle is measured, the wavefunction will collapse to one of the momentum eigenfunctions (recall that the specific position eigenfunction can be written as a continuous sum of momentum eigenfunctions), corresponding to the measured momentum p. That is,

$$\Psi(x) = \delta(x - x_\beta) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{ip(x - x_\beta)/\hbar}dp \xrightarrow{\text{measure momentum}} e^{ipx/\hbar} \tag{3.104}$$

with probability

$$P(p) = \left|\int_{-\infty}^{\infty} \Psi(x)\,e^{-ipx/\hbar}dx\right|^2 = \left|\int_{-\infty}^{\infty} \delta(x - x_\beta)\,e^{-ipx/\hbar}dx\right|^2 = \left|e^{ipx_\beta/\hbar}\right|^2 = 1. \tag{3.105}$$

All values of momentum are equally likely, since the position is known exactly. That is, the uncertainty in position is zero, and so the uncertainty in momentum must be infinite; recall the uncertainty principle (2.39).

Further measurements of momentum will, with 100 percent probability, yield the same value of momentum, and so the system would stay in the momentum state $e^{ipx/\hbar}$,

$$\Psi(x) = e^{ipx/\hbar} \xrightarrow{\text{measure momentum}} e^{ipx/\hbar}, \tag{3.106}$$

until disturbed by an interaction with the "outside world." If a still later measurement of the position is made, because the particle is in a specific momentum state (a superposition of position eigenfunctions), the position recorded by the measurement will once again come down to probability, as the state function collapses to a certain position eigenfunction.

The preceding description follows from the Copenhagen Interpretation, which, obviously, engenders some philosophical problems. Other theories exist, each with their own potential philosophical problems, although the details will not be presented here. However, experiments have shown quantum systems existing in a superposition of states, and so this is not merely a philosophical issue. As an interesting practical application, in quantum cryptography, the collapse of the state function can be used to insure that data is securely delivered to its destination over a network. This is because any detection of information, no matter by what means, constitutes a measurement. This would cause the state function to collapse, indicating that the data had been compromised. Such systems have already been demonstrated in laboratory settings.

As another example, consider the two-slit experiment performed with electrons. Common sense would indicate that the electron passes through one slit or the other to arrive at the detector. However, quantum mechanically, before reaching the detector the electron exists in a superposition of states, and only upon detection does this state function collapse to a single state and a particle-like existence. If one were to try to measure which slit the electron passes through, however carefully the measurement is performed, the double-slit interference pattern would not be observed, since by performing this observation (i.e., measurement), the state function collapses, and the electron acts like a particle.

Postulate 3. The mean value of an observable is the expectation value of the corresponding operator.

In classical probability theory, the mean (mathematical expectation) of a function f of a random variable x, $\mu = \langle f \rangle$, is calculated from

$$\langle f \rangle = \int_{-\infty}^{\infty} f(x)\,\rho(x)\,dx, \tag{3.107}$$

where $\rho(x)$ is called the *probability density function* (pdf), such that

$$\int_{-\infty}^{\infty} \rho(x)\,dx = 1. \tag{3.108}$$

Speaking loosely, the state function Ψ is the square root of the probability density function for a particle, and so it might be expected that Ψ^2 will play a role in determining expectation values of quantities. Since the wavefunction is, in general, complex-valued, rather than the square of the function, we actually need the modulus squared,

$$\rho(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 = \Psi^*(\mathbf{r}, t)\,\Psi(\mathbf{r}, t). \tag{3.109}$$

In general, for any physical observable $\mathcal{O}$, the mean of $\mathcal{O}$ (i.e., the average, taken over many individual measurements under identical conditions, and with the same initial state) is given by

$$\langle \mathcal{O} \rangle = \int \widehat{o}\rho(\mathbf{r}, t)\,d^3r \tag{3.110}$$

$$= \int \Psi^*(\mathbf{r}, t)\,\widehat{o}\,\Psi(\mathbf{r}, t)\,d^3r, \tag{3.111}$$

where $\widehat{o}$ is the operator corresponding to that observable. For example, the expectation value of position ($\mathcal{O} = \mathbf{r}$, $\widehat{o} = \mathbf{r}$) is

$$\langle \mathbf{r} \rangle = \int \Psi^*(\mathbf{r}, t)\,\mathbf{r}\,\Psi(\mathbf{r}, t)\,d^3r, \tag{3.112}$$

and in one dimension,

$$\langle x \rangle = \int \Psi^*(x, t)\,x\,\Psi(x, t)\,dx. \tag{3.113}$$

The expectation value for momentum is

$$\langle p_x \rangle = \int \Psi^*(\mathbf{r}, t)\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi(\mathbf{r}, t)\,d^3r, \tag{3.114}$$

and similarly for p_y and p_z, such that the three-dimensional momentum is obtained from

$$\langle p \rangle = \int \Psi^*(\mathbf{r}, t)\,(-i\hbar\nabla)\,\Psi(\mathbf{r}, t)\,d^3r. \tag{3.115}$$

From (3.63), the expectation value of energy is obtained as

$$\langle E \rangle = \int \Psi^*(\mathbf{r}, t)\left(i\hbar\frac{\partial}{\partial t}\right)\Psi(\mathbf{r}, t)\,d^3r. \tag{3.116}$$

In all cases, the wavefunction used in (3.110)–(3.116) is normalized according to (3.8).

Example

Considering again the example of an electron confined to a line segment between $x = -L/2$ and $x = L/2$, with the state function given by (3.9), we find that

$$\Psi(x, t) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right) e^{-iE_n t/\hbar}. \tag{3.117}$$

The expectation value of the particle is

$$\langle x \rangle = \int_{-L/2}^{L/2} \Psi^*(x, t)\,x\,\Psi(x, t)\,dx \tag{3.118}$$

$$= \frac{2}{L}\int_{-L/2}^{L/2} x \sin^2\left(\frac{n\pi}{L}x\right) dx \tag{3.119}$$

$$= 0. \tag{3.120}$$

That is, the average position of the electron is in the middle of the line segment. Note that this is not necessarily the most likely location to find the electron. For example, for the $n = 2$ state $|\Psi|$ peaks at $x = \pm L/4$, which is the most likely place to find the electron, although the average position is still zero.

Postulate 4. The state function $\Psi(\mathbf{r}, t)$ obeys the Schrödinger equation

$$i\hbar\frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = H\Psi(\mathbf{r}, t), \tag{3.121}$$

where H is the system Hamiltonian (total energy operator).

The Hamiltonian is comprised of kinetic and potential energy terms (and terms corresponding to applied electric or magnetic fields if such fields are present). For a particle with mass[†] m in the absence of applied electric and magnetic fields,

$$H = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)\right), \tag{3.122}$$

where the first term corresponds to momentum and the second term is potential energy. It should be noted that the environment that a particle resides in enters Schrödinger's equation via the potential energy term $V(\mathbf{r}, t)$, and by the boundary conditions enforced on Ψ, which will be discussed shortly.

Example

The state function for an electron confined to a line segment between $x = -L/2$ and $x = L/2$ has been given as (3.9),

$$\Psi(x, t) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right) e^{-iE_n t/\hbar}, \tag{3.123}$$

for n even, with zero potential energy on the line segment. In this case, in one dimension

$$H = -\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2}, \tag{3.124}$$

and so it is easy to see that (3.121) is satisfied as long as E_n is defined as in (3.11). That is, plugging (3.123) into (3.121) leads to

$$i\hbar\frac{\partial}{\partial t}\left(\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right) e^{-iE_n t/\hbar}\right) = -\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2}\left(\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right) e^{-iE_n t/\hbar}\right), \tag{3.125}$$

or

$$E_n = \frac{\hbar^2}{2m_e}\left(\frac{n\pi}{L}\right)^2.$$

3.2 TIME-INDEPENDENT SCHRÖDINGER'S EQUATION

Equipped with Schrödinger's equation, and some understanding of the wavefunction, some simple problems involving quantum particles with mass can be formulated and solved. For a particle of mass m in a potential $V(\mathbf{r}, t)$, Schrödinger's equation is

$$i\hbar\frac{\partial\Psi(\mathbf{r}, t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)\right)\Psi(\mathbf{r}, t). \tag{3.126}$$

[†] Photons, which are quantum particles without mass, can be represented as electromagnetic wave oscillators whose states obey (3.121) as well, although with a Hamiltonian different from (3.122). However, in light–material interactions, it is often sufficient to treat the electrons quantum mechanically and the photons as classical electromagnetic fields. We will follow this procedure here.

However, a considerable simplification occurs if the potential energy does not depend on time, which will be the case considered throughout this text. Assuming a product form for the wavefunction,

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\, g(t), \tag{3.127}$$

and substituting into Schrödinger's equation results in

$$\left(-\frac{\hbar^2}{2m}\frac{1}{\psi(\mathbf{r})}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\right) = i\hbar\frac{1}{g(t)}\frac{\partial g(t)}{\partial t}. \tag{3.128}$$

The left side of (3.128) is clearly, at most, a function of position $\mathbf{r}$ (but not time), and the right side is, at most, a function of time (but not position). How can a function of position but not time be equal to a function of time but not position, for all times and positions? They clearly cannot be equal unless each side is equal to the same constant, which will be called E (because, although it is not proven here, this constant will represent energy). Therefore,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{3.129}$$

$$i\hbar\frac{dg(t)}{dt} = Eg(t). \tag{3.130}$$

The method of separating the time and space dependence in (3.126) is called *separation of variables*. Note that (3.129) is really an eigenvalue problem, $\widehat{H}\psi = \lambda\psi$, where the operator is the Hamiltonian (total energy operator),

$$\widehat{H} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right), \tag{3.131}$$

and where the eigenvalue is the (usually unknown) energy E. For constant potentials, solutions of the time-independent Schrödinger's equation are eigenfunctions of the Laplacian operator, ∇^2, which for one dimension is d^2/dx^2.

The time-dependent equation (3.130) is easy to solve, leading to

$$g(t) = g_0 e^{-iEt/\hbar}. \tag{3.132}$$

Notice that if (3.132) is compared with a general oscillatory form

$$g(t) = g_0 e^{-i\omega t}, \tag{3.133}$$

then it can be seen that

$$E = \hbar\omega \tag{3.134}$$

makes sense, which is nothing more than the previously stated energy–frequency relation (2.12). Of course, this is not a proof that the constant E in (3.129) is the total energy, but it turns out to be true.

From (3.127), a general time-dependent wavefunction for a particle in a time-independent potential is

$$\Psi(\mathbf{r},t)=\psi(\mathbf{r})\,e^{-iEt/\hbar}. \tag{3.135}$$

For the time-independent wavefunctions, the orthogonality condition is

$$\int \psi_i^*(\mathbf{r})\,\psi_j(\mathbf{r})\,d^3r=0 \tag{3.136}$$

for $i\neq j$, where i and j denote different energy eigenvalues,

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right)\psi_i(\mathbf{r})=E_i\psi(\mathbf{r}), \tag{3.137}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right)\psi_j(\mathbf{r})=E_j\psi(\mathbf{r}). \tag{3.138}$$

In summary, the time-independent Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right)\psi(\mathbf{r})=E\psi(\mathbf{r}), \tag{3.139}$$

where E is the total energy of the particle, which has mass m. The time-dependent wavefunction is obtained from the time-independent wavefunction as (3.135). In one dimension, the time-independent Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right)\psi(x)=E\psi(x), \tag{3.140}$$

where

$$\psi(x,t)=\psi(x)\,e^{-iEt/\hbar}. \tag{3.141}$$

For time-independent potentials, the evolution of the state function is determined uniquely in time upon specification of the initial state $\psi(x,0)$.

It should be noted that Schrödinger's equation (time dependent, or time independent) is a linear homogeneous equation. As such, a superposition of homogeneous solutions ψ_n is itself a solution. Therefore, the most general state function for the separable case can be written as

$$\Psi(\mathbf{r},t)=\sum_n a_n\psi_n(\mathbf{r})\,e^{-iE_nt/\hbar}, \tag{3.142}$$

i.e., as an eigenfunction expansion, where ψ_n are eigenfunctions of the Hamiltonian operator and a_n are weighting constants.

For example, a wavepacket can be constructed from a superposition of plane waves, where each plane wave is a solution to Schrödinger's equation having a different wavenumber k. The wavepacket is not associated with a specific energy, but with a range of energies. This is a general situation—one often cannot say that a particle has a definite energy, only that the particle may have any of the possible energies occurring in the superposition, with a probability proportional to the wavepacket probability, which is related to the amplitude a_n of a particular plane wave having that energy.

3.2.1 Boundary Conditions on the Wavefunction

Before treating some simple problems, notice that Schrödinger's equation is a second-order differential equation, and so boundary conditions need to be imposed on the wavefunction Ψ. The boundary or connection conditions will be obtained in one dimension for simplicity. A typical situation involves considering two adjacent regions, region 1 for $x<a$, where the particle has mass m_1 and "sees" a potential V_1, and region 2 for $x>a$, in which the particle has mass m_2 and "sees" a potential V_2. It will be assumed that the quantity V_1-V_2 is finite.

While it may seem that the particle should have the same mass in both regions, there are many situations (especially for semiconductors, as discussed in Chapter 5) where the particle has an effective mass that is different in different regions of space. By assuming that the transition between regions occurs not abruptly at $x=a$, but over a small range of x values, and then taking the limit that the transition becomes abrupt, it can be shown that

$$\begin{aligned}\Psi\left(x=a^-\right)&=\Psi\left(x=a^+\right),\\ \frac{1}{m_1}\Psi'\left(x=a^-\right)&=\frac{1}{m_2}\Psi'\left(x=a^+\right),\end{aligned} \tag{3.143}$$

where $\Psi\left(x=a^-\right)$ and $\Psi\left(x=a^+\right)$ are the wavefunctions in regions 1 and 2, respectively, infinitesimally close to the transition point $x=a$, and where Ψ' denotes the derivative of Ψ with respect to x.

However, if V has an infinite step discontinuity, say, V_1 is finite and V_2 is infinite, then only the wavefunction, and not its derivative, will be continuous at $x=a$,

$$\Psi\left(x=a^-\right)=\Psi\left(x=a^+\right). \tag{3.144}$$

Example

In previous examples, a one-dimensional space was considered, wherein an electron was constrained to be in the range $-L/2\leq x\leq L/2$, with $V=0$. Here we collect the various results concerning this example, and show the derivation of the state function.[†]

Since $V=0$, Schrödinger's equation (3.140) is

$$-\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2}\psi(x)=E\psi(x), \tag{3.145}$$

[†] The confined region of space considered in this example is often called a *quantum well* or *quantum box*.

which has the solution

$$\psi(x) = \begin{cases} A \sin kx + B \cos kx, & -\frac{L}{2} \le x \le \frac{L}{2}, \\ 0, & |x| > \frac{L}{2}, \end{cases} \tag{3.146}$$

where

$$k^2 = \frac{2m_e E}{\hbar^2}. \tag{3.147}$$

It is easy to verify this solution by inserting (3.146) into (3.145). Continuity of the wavefunction at $x = \pm L/2$, i.e., applying (3.144) at $x = \pm L/2$, leads to

$$\psi\left(-\frac{L}{2}\right) = \psi\left(\frac{L}{2}\right) = 0, \tag{3.148}$$

and so it is obvious that either

$$B = 0, \quad \frac{kL}{2} = n\pi, \quad n = 0, \pm1, \pm2, \ldots, \tag{3.149}$$

or

$$A = 0, \quad \frac{kL}{2} = \left(n + \frac{1}{2}\right)\pi, \quad n = 0, \pm1, \pm2, \ldots. \tag{3.150}$$

The wavefunction for $-L/2 \le x \le L/2$ is, therefore,

$$\begin{aligned} \psi_n(x) &= A \sin \frac{n\pi}{L} x, \quad n \text{ even} \\ &= B \cos \frac{n\pi}{L} x, \quad n \text{ odd}, \end{aligned} \tag{3.151}$$

which represents odd and even solutions with respect to the center of the space ($x = 0$). Furthermore, note that (3.145) has the form of an eigenvalue equation $H\psi = E\psi$, and therefore (3.151) are energy eigenfunctions. These wavefunctions clearly exhibit orthogonality,

$$\int \psi_n^*(x)\, \psi_m(x)\, dx = A^* A \int_{-L/2}^{L/2} \left(\sin \frac{n\pi}{L} x\right)\left(\sin \frac{m\pi}{L} x\right) dx = 0 \tag{3.152}$$

$$= B^* B \int_{-L/2}^{L/2} \left(\cos \frac{n\pi}{L} x\right)\left(\cos \frac{m\pi}{L} x\right) dx = 0 \tag{3.153}$$

$$= A^* B \int_{-L/2}^{L/2} \left(\sin \frac{n\pi}{L} x\right)\left(\cos \frac{m\pi}{L} x\right) dx = 0 \tag{3.154}$$

for $m \neq n$ in the first two expressions, and for all m, n in (3.154). The solutions can be normalized according to (3.8),

$$1 = \int_{-L/2}^{L/2} |\psi_n(x)|^2\, dx = \int_{-L/2}^{L/2} A^2 \sin^2 \frac{n\pi}{L} x\, dx, \tag{3.155}$$

resulting in

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin \frac{n\pi}{L} x, \tag{3.156}$$

or

$$\Psi_n(x, t) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L} x\right) e^{-iEt/\hbar}, \tag{3.157}$$

for the odd solution (n even). The even solution is

$$\Psi_n(x, t) = \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{n\pi}{L} x\right) e^{-iEt/\hbar}, \tag{3.158}$$

for n odd. These are the functions provided in the original example on page 46.

Since k is discrete, the energy of the particle (in this case, the energy eigenvalue) is found to be discrete,

$$E = \frac{\hbar^2 k^2}{2m_e} = \frac{\hbar^2}{2m_e}\left(\frac{n\pi}{L}\right)^2 = E_n. \tag{3.159}$$

The momentum associated with any given state is

$$p = \frac{h}{\lambda} = \frac{hk}{2\pi} = \frac{n\pi\hbar}{L} = p_n, \tag{3.160}$$

where the relation $k = 2\pi/\lambda$ was used.

From (3.113), the expectation values of the particle's position and momentum are, by Postulate 3,

$$\langle x \rangle = \int_{-L/2}^{L/2} \psi^*(x, t)\, x\, \psi(x, t)\, dx \tag{3.161}$$

$$= \frac{2}{L} \int_{-L/2}^{L/2} x \sin^2\left(\frac{n\pi}{L} x\right) dx = 0, \tag{3.162}$$

$$\langle p_x \rangle = \int \Psi^*(x, t)\left(-i\hbar \frac{\partial}{\partial x}\right) \Psi(x, t)\, dx \tag{3.163}$$

$$= -i\hbar \frac{2}{L}\frac{n\pi}{L} \int_{-L/2}^{L/2} \sin\left(\frac{n\pi}{L} x\right) \cos\left(\frac{n\pi}{L} x\right) dx = 0. \tag{3.164}$$

Furthermore, for example, the odd eigenfunction (sine) can be written as

$$\begin{aligned} \psi_n(x) &= \frac{1}{\sqrt{2}}\left[\frac{1}{i\sqrt{L}} e^{i\frac{p_n}{\hbar}x} - \frac{1}{i\sqrt{L}} e^{-i\frac{p_n}{\hbar}x}\right] \\ &= \psi_n^+ - \psi_n^-. \end{aligned} \tag{3.165}$$

(See problem 3.8.) The term ψ_n^+ (ψ_n^-) is a plane wave propagating with positive (negative) momentum. Thus, any particular state described by the sine function (eigenfunctions of the Hamilton) can be thought of as representing a superposition of positive and negative momentum states (eigenfunctions of the momentum operator). See the comment about different representations of the state function on page 50. The same comment naturally applies to the cosine eigenfunction.

The previous example is one of the simplest quantum mechanical problems that can be solved. This problem will be revisited in considerable detail in the next chapter. It shows that if a particle is confined to a finite region of space, its wavefunction forms standing waves and the possible energy levels that it can occupy are discrete. In a two-dimensional space, one can consider an analogous situation of a circular boundary at $r = a$ and solve Schrödinger's equation in a circular region $r < a$, subject to $\psi = 0$ for $r \geq a$. The solution involves Bessel functions and will not be discussed here, although the result is a standing wave pattern in the radial direction. Assuming that the particle in question is an electron, we can consider these to be standing electron waves, which have been experimentally observed in a structure called a *quantum corral*. The corral is formed by moving atoms on the surface of a material to form a boundary, setting up an electron standing wave pattern, as shown in the figure at the beginning of this chapter. In Fig. 3.1, the various panels depict assembling the corral from iron atoms on a copper surface, and the resulting electron standing waves are obtained by radial interference. Imaging is done using STM. In Fig. 3.2, a similar structure called a *stadium corral* is shown, and other shapes are possible.

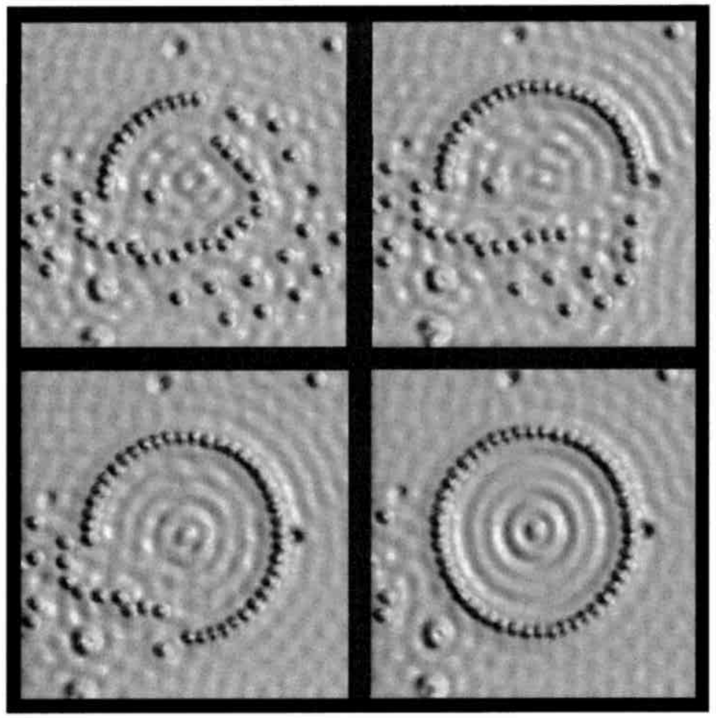

Figure 3.1 Evidence for the existence of electron waves—electron waves on the surface of copper, imaged by STM. The waves are trapped by a ring of iron atoms, which were manipulated into place using an atomic force microscope. (Reprinted with permission from Crommie, M. F., C. P. Lutz, and D. M. Eigler, "Confinement of Electrons to Quantum Corrals on a Metal Surface," *Science* 262 (1993): 218–220. Courtesy IBM Research, Almaden Research Center. Unauthorized use not permitted.)

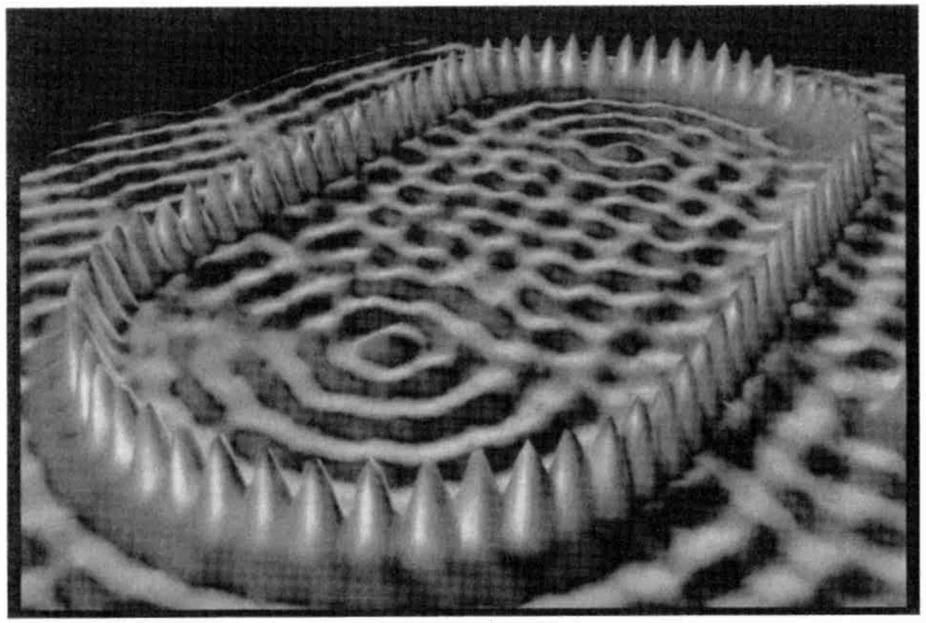

Figure 3.2 Stadium corral made from iron atoms on a copper surface. Ripples are due to the standing wave patterns of the electron density distribution of quantum states. (Courtesy IBM Research, Almaden Research Center. Unauthorized use not permitted.)

3.3 ANALOGIES BETWEEN QUANTUM MECHANICS AND CLASSICAL ELECTROMAGNETICS

For students already familiar with classical electromagnetic theory, it is worthwhile to point out briefly some analogies between Schrödinger's equation and the equations describing electromagnetic waves.

Maxwell's equations describe classical electromagnetics waves, and for a vacuum, Maxwell's equations are

$$\begin{aligned} \nabla \cdot \mathbf{E}(\mathbf{r}, t) &= \rho_e(\mathbf{r}, t)/\varepsilon_0, \\ \nabla \cdot \mathbf{B}(\mathbf{r}, t) &= 0, \\ \nabla \times \mathbf{E}(\mathbf{r}, t) &= -\frac{\partial}{\partial t}\mathbf{B}(\mathbf{r}, t), \\ \nabla \times \mathbf{B}(\mathbf{r}, t) &= \mu_0 \varepsilon_0 \frac{\partial}{\partial t}\mathbf{E}(\mathbf{r}, t) + \mu_0 \mathbf{J}_e(\mathbf{r}, t), \end{aligned} \tag{3.166}$$

where $\mathbf{E}$ is the electric field intensity (V/m), $\mathbf{B}$ is the magnetic flux density (Wb/m^2), ρ_e is the electric charge density (C/m^3), $\mathbf{J}_e$ is the electric current density (A/m^2), ϵ_0 is the permittivity of vacuum ($\varepsilon_0 \simeq 8.85 \times 10^{-12}$ F/m), and μ_0 is the permeability of vacuum ($\mu_0 \simeq 4\pi \times 10^{-7}$ H/m), and where V stands for volts, C for coulombs, Wb for webers, A for amperes, F for farads, H for henrys, and m for meters. For dimensional analysis, C = A · s = F · V and Wb = V · s = H · A, where s stands for seconds. The equations are known, respectively, as *Gauss's law*, the *magnetic Gauss's law*, *Faraday's law*, and *Ampère's law*.

Wave phenomena are predicted from Maxwell's equations by suitable manipulation. For example, taking the curl of Faraday's law, and using Ampère's law, we have

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}, t) = -\left(\mu_0\varepsilon_0 \frac{\partial^2}{\partial t^2}\mathbf{E}(\mathbf{r}, t) + \mu_0 \frac{\partial}{\partial t}\mathbf{J}_e(\mathbf{r}, t)\right). \tag{3.167}$$

If we assume that for any position and time of interest the electric and magnetic currents and charges (the sources of the field) are not present, then

$$\frac{\partial^2}{\partial t^2}\mathbf{E}(\mathbf{r}, t) = \frac{1}{\mu_0\varepsilon_0}\nabla^2\mathbf{E}(\mathbf{r}, t), \tag{3.168}$$

where the vector identity $\nabla \times \nabla \times \mathbf{A} = \nabla(\nabla \cdot \mathbf{A}) - \nabla^2\mathbf{A}$, for $\mathbf{A}$, a general vector, was used.

There is obviously some similarity between (3.168) and Schrödinger's equation for a particle of mass m in the absence of a potential,

$$i\hbar\frac{\partial\Psi(\mathbf{r}, t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}, t), \tag{3.169}$$

although the presence of the second time derivative in (3.168) is actually quite an important distinction. However, if an oscillatory time variation $e^{-i\omega t}$ is assumed for the electric field (corresponding to a radian frequency ω) and for the wavefunction (corresponding to the form (3.135) with $E = \hbar\omega$), then

$$\nabla^2\mathbf{E}(\mathbf{r}, t) = -k_{ME}^2\mathbf{E}(\mathbf{r}, t) \tag{3.170}$$

for the electromagnetic field. Also,

$$\nabla^2\Psi(\mathbf{r}, t) = -k_{SE}^2\Psi(\mathbf{r}, t), \tag{3.171}$$

for Schrödinger's equation, where

$$k_{ME}^2 = \omega^2\mu\varepsilon, \quad k_{SE}^2 = \frac{2mE}{\hbar^2}, \tag{3.172}$$

are in each case simply constants. (E on the right side of the equation for k_{SE} is energy, not electric field.) In this case, the equations governing the electric field and the Schrödinger wavefunction have the same form.

If a particle is bound to a certain region of space Ω, then outside of Ω, the wavefunction will be zero, and at the boundary S of the region $\Psi(S) = 0$. Thus, one would solve (3.171) subject to $\Psi(S) = 0$, leading to discrete values of k_{SE}, and, hence, discrete energy levels E_n, as obtained in the example of page 65. In an analogous manner, if a perfectly conducting electromagnetic cavity were considered, then $\mathbf{E}_{\tan}(S) = 0$, where $\mathbf{E}_{\tan}$ is the tangential electric field. Solving (3.170) subject to $\mathbf{E}_{\tan}(S) = 0$ leads to discrete values of k_{ME}, and, hence, discrete resonant frequencies[†] ω_n. Aside from the difference arising from the vector nature of $\mathbf{E}$ and the scalar nature of Ψ, the mathematical solutions for Ψ and for $\mathbf{E}$ will be the same.

Furthermore, in quantum mechanics $|\Psi|^2$ is a probability density, and provides the likelihood of finding a particle in a certain location at a certain time. If $|\Psi(\mathbf{r}, t)|^2$ is large at a certain $(\mathbf{r}, t)$, then it is more likely to find the particle there. In electromagnetics, $|\mathbf{E}(\mathbf{r}, t)|^2$ is related to the intensity of the field, and, viewed from a photon standpoint, where $|\mathbf{E}(\mathbf{r}, t)|^2$ is large, there are a large number of photons present at $(\mathbf{r}, t)$. Viewed quantum mechanically, there is *likely* to be a large number of photons present at $(\mathbf{r}, t)$ when $|\mathbf{E}(\mathbf{r}, t)|^2$ is large.

Many more analogies are possible, although these will not be discussed in detail here. For example, one analogous situation will arise later when quantum wires are considered. These structures lead to discrete modal solutions of Schrödinger's equation, similar to electromagnetic modes of a conducting or dielectric waveguide in classical electromagnetics. In fact, these structures are often called *electron waveguides*.

3.4 PROBABILISTIC CURRENT DENSITY

In electromagnetic theory, $\mathbf{J}_e$ in Maxwell's equations (3.166) represents electric current density. Current I flowing through a conductor is classically obtained from the current density as

$$I = \int_S \mathbf{J}_e \cdot \widehat{\mathbf{n}}\, dS, \tag{3.173}$$

where S is the cross-sectional surface through which we want to determine the current (charge movement), and $\widehat{\mathbf{n}}$ is a unit amplitude vector normal to the surface (such that $\mathbf{J}_e \cdot \widehat{\mathbf{n}}$ is the component of current crossing the surface, as depicted in Fig. 3.3.)

Recall also that electrical current is the flow of electrical charge q (often, but not necessarily, electrons),

$$I = \frac{\partial q(t)}{\partial t}. \tag{3.174}$$

An important equation that demonstrates that charge conservation is embedded in (3.166) is known as the *continuity equation*. Taking the divergence of Ampère's law, we have

$$0 = \nabla \cdot \nabla \times \mathbf{H} = \nabla \cdot \mathbf{J}_e + \nabla \cdot \frac{\partial \mathbf{D}}{\partial t}, \tag{3.175}$$

noting the vector identity $\nabla \cdot \nabla \times \mathbf{A} = 0$ for any vector $\mathbf{A}$. Upon interchanging the spatial and temporal derivatives, and invoking Gauss's law, we obtain the continuity equation

$$\nabla \cdot \mathbf{J}_e(\mathbf{r}, t) = -\frac{\partial \rho_e(\mathbf{r}, t)}{\partial t}. \tag{3.176}$$

[†] In fact, this really relates to photons having discrete energy via $E_n = \hbar\omega_n$.

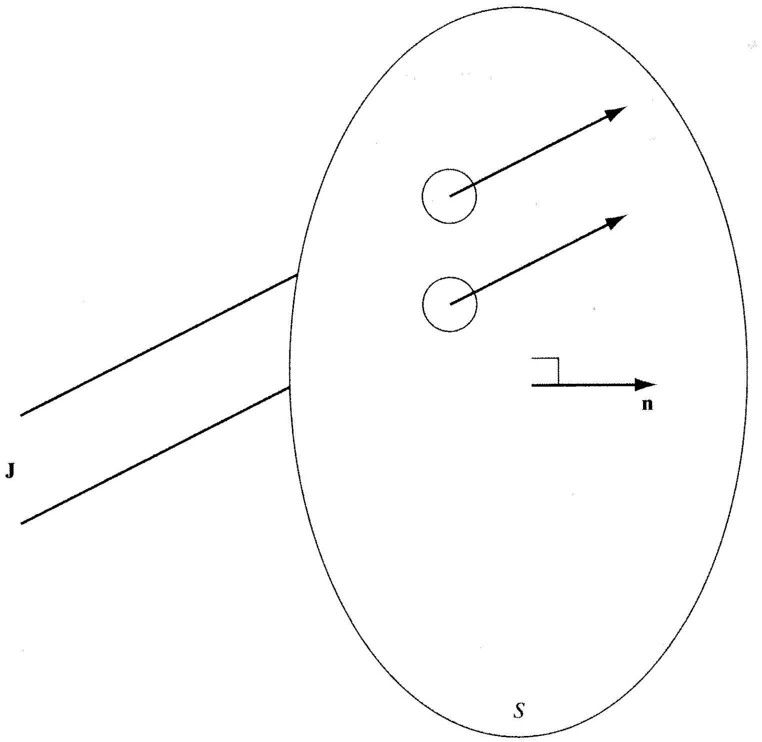

Figure 3.3 Current density incident on a surface S.

Often it is useful to take the volume integral of (3.176), leading to

$$\int_{\Omega} \nabla \cdot \mathbf{J}_e(\mathbf{r}, t)\, d^3r = \oint_S \mathbf{J}_e \cdot \widehat{\mathbf{n}}\, d^2r = -\int_{\Omega} \frac{\partial \rho_e(\mathbf{r}, t)}{\partial t} d^3r = -\frac{d}{dt} Q(t), \tag{3.177}$$

where the divergence theorem was used,

$$\int_{\Omega} \nabla \cdot \mathbf{A}\, d^3r = \oint_S \widehat{\mathbf{n}} \cdot \mathbf{A}\, d^2r, \tag{3.178}$$

where S is the surface of Ω and $\widehat{\mathbf{n}}$ is a unit vector normal to the surface. The physical interpretation of (3.177) is that the net outward flux of current from a volume Ω bounded by a closed surface S must equal the time rate of decrease of charge Q within the surface.

In quantum mechanics, we are often concerned with the location and movement of particles, which are described by the wavefunction. The flow of quantum particles can be considered using the following development, which will result in a relationship analogous to (3.176).

It is easy to see that

$$\frac{\partial}{\partial t}\left(\Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t)\right) = \Psi^*(\mathbf{r}, t) \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) + \Psi(\mathbf{r}, t) \frac{\partial}{\partial t} \Psi^*(\mathbf{r}, t). \tag{3.179}$$

From (3.126),

$$\frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)\right)\Psi(\mathbf{r}, t), \tag{3.180}$$

$$\frac{\partial \Psi^*(\mathbf{r}, t)}{\partial t} = \frac{1}{-i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)\right)\Psi^*(\mathbf{r}, t), \tag{3.181}$$

assuming the potential V is real valued. Substituting into (3.179), we have

$$\frac{\partial}{\partial t}\left(\Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t)\right) = i\frac{\hbar}{2m}\left(\Psi^*(\mathbf{r}, t)\, \nabla^2\Psi(\mathbf{r}, t) - \Psi(\mathbf{r}, t)\, \nabla^2\Psi^*(\mathbf{r}, t)\right). \tag{3.182}$$

Using the vector identities

$$\begin{aligned} \nabla \cdot (\alpha\mathbf{A}) &= \mathbf{A} \cdot \nabla\alpha + \alpha\nabla \cdot \mathbf{A}, \\ \nabla \cdot \nabla\alpha &= \nabla^2\alpha, \end{aligned} \tag{3.183}$$

where α is a scalar and $\mathbf{A}$ is a vector,

$$\frac{\partial}{\partial t}\left(\Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t)\right) = \nabla \cdot \frac{i\hbar}{2m}\left(\Psi^*(\mathbf{r}, t)\, \nabla\Psi(\mathbf{r}, t) - \Psi(\mathbf{r}, t)\, \nabla\Psi^*(\mathbf{r}, t)\right). \tag{3.184}$$

Comparing (3.184) with (3.176), and recalling that

$$\rho(\mathbf{r}, t) = \Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t) \tag{3.185}$$

is a probability density, we can recognize (3.184) as a conservation equation,

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{J}(\mathbf{r}, t), \tag{3.186}$$

where

$$\mathbf{J}(\mathbf{r}, t) = \frac{-i\hbar}{2m}\left(\Psi^*(\mathbf{r}, t)\, \nabla\Psi(\mathbf{r}, t) - \Psi(\mathbf{r}, t)\, \nabla\Psi^*(\mathbf{r}, t)\right) \tag{3.187}$$

is called the *probability current density*. Multiplying by the charge q, we interpret $q\rho$ and $q\mathbf{J}$ as the probabilistic charge density and probabilistic current density, respectively, associated with the charge[†] q. The unit of probability current density is probability/m^2s.

[†] The normalization condition (3.8) leads to

$$\int_{\text{all space}} q\psi^*(\mathbf{r}, t)\, \psi(\mathbf{r}, t)\, d^3r = q,$$

in agreement with $q\psi^*\psi$ being a charge density, the integral of which provides the total charge.

From (3.187), we can appreciate that Ψ is often complex valued—if Ψ is real valued, there is no net current. In contradistinction, in classical time-harmonic (sinusoidal steady state) electromagnetics,

$$\mathbf{J}_e(\mathbf{r},t) = \text{Re}\left\{\mathbf{J}_e(\mathbf{r})\, e^{i\omega t}\right\}, \tag{3.188}$$

resulting in a real-valued quantity. In classical electromagnetics, as in sinusoidal steady-state circuit analysis, the use of complex phasors and the complex time-variation $e^{i\omega t}$ is merely for convenience. In quantum mechanics, the use of complex quantities is a necessity.

To aid in the interpretation of (3.187), it is useful to refer again to the electromagnetic case. Consider the flow of classical electrons in the x direction, crossing the y–z plane, where we assume that the current density is independent of x, $\mathbf{J}_e = \mathbf{J}_e(y,z,t)$. Then, the current at time t crossing the y–z plane is

$$I(t) = \int_y \int_z \mathbf{J}_e(y,z,t)\cdot \mathbf{a}_x\, dydz. \tag{3.189}$$

In a similar manner, in the quantum mechanical case

$$I(t) = \int_y \int_z q\mathbf{J}(y,z,t)\cdot \mathbf{a}_x\, dydz \tag{3.190}$$

is the probability current at time t crossing the y–z plane. This expression will be used later in describing electron transport through materials. (See, e.g., Section 10.2.3.)

Example

Assume a plane-wave wavefunction

$$\Psi(x,t) = Ae^{i(kx-Et/\hbar)}. \tag{3.191}$$

The probability current density is

$$\mathbf{J}(\mathbf{r},t) = \frac{-i\hbar}{2m}\left(\Psi^*(\mathbf{r},t)\nabla\Psi(\mathbf{r},t) - \Psi(\mathbf{r},t)\nabla\Psi^*(\mathbf{r},t)\right) \tag{3.192}$$

$$= \frac{-i\hbar}{2m}\mathbf{a}_x |A|^2\left(e^{-i(kx-Et/\hbar)}\frac{\partial}{\partial x}\left(e^{i(kx-Et/\hbar)}\right) - e^{i(kx-Et/\hbar)}\frac{\partial}{\partial x}\left(e^{-i(kx-Et/\hbar)}\right)\right) \tag{3.193}$$

$$= \mathbf{a}_x |A|^2\frac{\hbar k}{m} = |A|^2\frac{\mathbf{a}_x p}{m} = |A|^2\frac{\mathbf{p}}{m} = |A|^2\mathbf{v}, \tag{3.194}$$

where (2.15) was used. Therefore, in this case, the quantum current density is merely the product of the particle's probability density and the particle velocity.

3.5 MULTIPLE PARTICLE SYSTEMS

For much of this book, we will need to consider only the single particle Schrödinger equation, as presented in previous sections. With typically on the order of 10^{22} electrons per cubic centimeter for many materials, this should seem like a rather coarse approximation! To understand why the Schrödinger equation for a single particle is often adequate, we need to first examine how to model a system containing multiple particles.

Consider the case of two particles, particle 1 and particle 2. Recall that the state function describes the state of the system, which in this case is comprised of both particles. Therefore, the state function must depend on both particles,

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,t), \tag{3.195}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the "positions" of particles 1 and 2, respectively, in the following sense,

$$|\Psi(\mathbf{r}_1,\mathbf{r}_2,t)|^2\, d^3r_1 d^3r_2 \tag{3.196}$$

is the joint probability of finding particle 1 in the vicinity d^3r_1 of point $\mathbf{r}_1$, and simultaneously finding particle 2 in the vicinity d^3r_2 of point $\mathbf{r}_2$.

The state function obeys (3.121),

$$i\hbar\frac{\partial\Psi(\mathbf{r}_1,\mathbf{r}_2,t)}{\partial t} = H\Psi(\mathbf{r}_1,\mathbf{r}_2,t), \tag{3.197}$$

where H is the system Hamiltonian that has the form

$$H = H_1 + H_2 + H_{12}. \tag{3.198}$$

In (3.198), H_1 is the Hamiltonian for particle 1 by itself, H_2 is the Hamiltonian for particle 2 by itself, and H_{12} represents the interaction between the two particles.

As an example, consider two charged particles in an otherwise empty space. Then, from (3.122),

$$H_1 = -\frac{\hbar^2}{2m_1}\nabla_1^2, \quad H_2 = -\frac{\hbar^2}{2m_2}\nabla_2^2, \tag{3.199}$$

$$H_{12} = \frac{q_1 q_2}{4\pi\varepsilon_0}\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

where $\nabla_{1,2}^2$ indicates the Laplacian in terms of each particle's coordinates,

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \tag{3.200}$$

for particle i, and where $\mathbf{r}_i = (x_i, y_i, z_i)$, $i = 1, 2$. In (3.199), H_{12} is merely the electrostatic Coulomb interaction between the charged particles, i.e., the classical term for particle interaction.

The two-particle wavefunction, $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$, is said to exist in a six-dimensional *configuration space*. That is, particle 1 is described by three coordinates, and likewise for particle 2 (plus a time coordinate). For N interacting particles, one must consider a $3N$ dimensional configuration space. It is easy to see that the complexity grows rapidly with increasing the number of particles.

However, a vast simplification occurs if N particles are present, but if the particles do not interact with each other. Returning to the two-particle system, in the limit of noninteracting particles ($H_{12} = 0$), Schrödinger's equation becomes

$$i\hbar\frac{\partial\Psi(\mathbf{r}_1, \mathbf{r}_2, t)}{\partial t} = (H_1 + H_2)\,\Psi(\mathbf{r}_1, \mathbf{r}_2, t). \tag{3.201}$$

By setting

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \Psi_1(\mathbf{r}_1, t)\,\Psi_2(\mathbf{r}_2, t), \tag{3.202}$$

we obtain two independent single-particle equations,

$$i\hbar\frac{\partial\psi_1(\mathbf{r}_1, t)}{\partial t} = H_1\Psi(\mathbf{r}_1, t), \tag{3.203}$$

$$i\hbar\frac{\partial\psi_2(\mathbf{r}_2, t)}{\partial t} = H_2\Psi(\mathbf{r}_2, t), \tag{3.204}$$

both of which can be solved independently of the other. Thus, for a system of N noninteracting particles one need "only" solve N single-particle equations. However, often the particles in question are identical (say, the 10^{22} particles in each cubic centimeter are all electrons), and indistinguishable (as explained in the following discussion). In this case, all 10^{22} equations are identical, and we only need to solve one single-particle equation. It is for this reason that often we only need to consider the single-particle Schrödinger equation. The simplicity gained by a one-particle approach, compared to a multiparticle approach, cannot be overestimated.

Of course, the validity of the single-particle Schrödinger equation relies on some assumptions that may appear questionable. First, it was assumed that the electrons don't interact with each other. One reason why electron-electron interactions may be ignored, as a first approximation, could be that the electrons are initially very distant from one another. Then, although the "system" really consists of all of the electrons, it is reasonable to assume, since the electrons are very far apart, and since the Coulomb potential between electrons varies as the reciprocal of distance, that the electrons don't influence each other. Then the single-particle Schrödinger equation can be solved for each particle (N independent equations for N different particles, or merely one equation if all of the particles are identical), obtaining the wavefunction. Often, in this case, the individually obtained wavefunctions are called *orbitals*, to distinguish them from the exact quantum state of the system. Each orbital will be a wavepacket concentrated where the likelihood of finding the electron is high. If electrons are brought closer together, at some point the individual orbitals will begin to overlap significantly. At this point the electrons will interact, and we may need to account for this interaction.

However, what about solid materials, where the electron density is on the order of 10^{22} electrons per cubic centimeter? In this case, the assumption of electrons being distant from each other clearly will not hold. In solids, one would expect that, with so many electrons present, they would be frequently bumping into each other. Amazingly, in many materials the assumption of noninteracting electrons is quite good. In general, this is a consequence of what is known as the *screening effect*: the electrons screen, or shield themselves, from each other. This is, in turn, related to the Pauli exclusion principle. Each electron repels the other electrons due to (1) the classical electrostatic repulsion (Coulomb interaction) between like charges, and (2) the exclusion principle, which says that electrons with the same spins tend to avoid each other. Because no two electrons can be in the same state, electrons with the same spin will not have a high probability of being located near each other. Thus, electrons tend to move through a material somewhat independently of the other electrons.

If we are truly talking about a collection of electrons in an otherwise empty space, then the electron–electron noninteracting assumption is all that is needed. However, we are often interested in solids, and so you might ask, what about the other atomic particles (the protons, neutrons, etc.), that make up atoms, which, in turn, make up the solid? They are, after all, quantum particles themselves, and therefore the system in question contains nonidentical particles, and we seem to be back to the multiparticle equation. It turns out that in crystalline materials, the so-called background lattice, which is everything associated with the regular array of atoms in a crystal except certain (outer shell) electrons that have been ionized, *does* have an important effect on the electrons. To be more specific, if the lattice is perfectly periodic, waves can pass freely through the structure at certain energies, whereas waves at other energies will not propagate. This leads to the concept of band theory and effective mass, which will be discussed in detail in Chapter 5. However, we can state at this point that band theory allows us to account for the lattice in a simple manner, via an effective mass in Schrödinger's equation, with the end result that we can solve the single-particle Schrödinger's equation in this case without treating the quantum particles that make up the background lattice individually. Again, the simplification provided by this approach cannot be overestimated. However, any disruption of perfect periodicity in the lattice, due to imperfections, thermal vibrations, etc., tends to scatter electrons, and must be accounted for separately.

Pauli Exclusion Principle. The consideration of multiple indistinguishable particles also provides some insight into the Pauli exclusion principle. Note that classical particles that may be identical are, nevertheless, distinguishable. Consider, for instance, identical bowling balls. One could mark each ball with a number or paint spot, thus making the balls distinguishable, without altering their properties. Systems consisting of large numbers of distinguishable particles follow Boltzmann statistics (page 268).

However, electrons are both identical and indistinguishable. Systems consisting of large numbers of indistinguishable particles follow either Fermi–Dirac or Bose–Einstein statistics (pages 268–269). Large numbers of indistinguishable particles that obey the Pauli exclusion principle follow Fermi–Dirac statistics, whereas indistinguishable particles that aren't bound to the exclusion principle follow Bose–Einstein statistics. In the following discussion a somewhat casual development of the Pauli exclusion principle for two particles is provided.

If two particles are indistinguishable, although perhaps interacting, then

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2\, d^3r_1 d^3r_2 \tag{3.205}$$

is the probability of finding one particle in d^3r_1 centered at $\mathbf{r}_1$ and one particle in d^3r_2 centered at $\mathbf{r}_2$. Since the particles are indistinguishable, the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ are used simply because there are two particles—it is impossible to say which particle is which. This means that we must have

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 = |\Psi(\mathbf{r}_2, \mathbf{r}_1, t)|^2 . \tag{3.206}$$

Wavefunctions that satisfy (3.206) include the symmetric case

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \Psi(\mathbf{r}_2, \mathbf{r}_1, t), \tag{3.207}$$

and the antisymmetric case

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, t). \tag{3.208}$$

The antisymmetric case (3.208) admits an interesting interpretation relevant to electrons. Consider the special case $\mathbf{r}_1 = \mathbf{r}_2$. Then, to satisfy (3.208), we must have

$$\Psi(\mathbf{r}_1, \mathbf{r}_1, t) = 0, \tag{3.209}$$

such that the probability of finding two such particles within the same small volume d^3r_1 is zero. It turns out that electrons obey this constraint, such that only one electron can occupy a certain state. This rule, which applies to fermions, is the Pauli exclusion principle.

More generally, the Pauli exclusion principle states that particles with half-integral spin quantum numbers (fermions; electrons, protons, neutrons) must have antisymmetric state functions, in the sense that a pairwise interchange of particles merely changes the sign of the state function, as in (3.208). Particles with integral spin quantum numbers (bosons; photons) must have symmetric state functions, (3.207).

If two fermions are considered, each of which satisfies a single particle state ψ_1 and ψ_2, respectively, then the composite wavefunction

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left(\psi_1(\mathbf{r}_1)\, \psi_2(\mathbf{r}_2) - \psi_1(\mathbf{r}_2)\, \psi_2(\mathbf{r}_1) \right) \tag{3.210}$$

will satisfy the antisymmetric condition (3.208). In a similar manner, for bosons, the wavefunction

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left(\psi_1(\mathbf{r}_1)\, \psi_2(\mathbf{r}_2) + \psi_1(\mathbf{r}_2)\, \psi_2(\mathbf{r}_1) \right) \tag{3.211}$$

will satisfy the symmetric condition (3.207).

3.6 SPIN AND ANGULAR MOMENTUM

As described previously, quantum particles have an intrinsic property called spin that has no classical counterpart. The name actually derives from early interpretations of experiments where electrons acted as though they were, in addition to orbiting the nucleus in an atom, spinning about their own axis. However, it was quickly understood that this was not the case. Spin is a purely quantum phenomenon that cannot be understood by appealing to everyday experiences—it should be regarded as just another property of quantum particles.

The Stern–Gerlach experiment in the early 1920s demonstrated the existence of spin, although spin was not known at the time and the experiment was performed for other reasons. Recall from classical electromagnetic theory that the force on a particle having charge q moving with velocity $\mathbf{v}$ in the presence of an electric field $\mathbf{E}$ and magnetic field $\mathbf{B}$ is given by the Lorentz force law,

$$\mathbf{F}_L = q\,(\mathbf{E} + \mathbf{v} \times \mathbf{B}). \tag{3.212}$$

Now assume that the electric field is not present, and consider passing a particle through a magnetic field. If the particle in question is charge neutral ($q = 0$), such as a nonionized atom, then it should suffer no Lorentz force deflection. However, another force may influence the particle. If the particle has a net magnetic moment[†] μ, then in passing through a magnetic field $\mathbf{B}$, it will experience a force

$$\mathbf{F}_\mu = \nabla\,(\mu \cdot \mathbf{B}). \tag{3.213}$$

Assume that the particles are moving along the y coordinate, the magnetic moment is constant, $\mu = \pm \mathbf{a}_z \mu_z$, and that the magnetic field is $\mathbf{B} = \mathbf{a}_z B_z(y)$. Then,

$$\mathbf{F}_\mu = \pm \mathbf{a}_y \mu_z \frac{\partial B_z(y)}{\partial y}, \tag{3.214}$$

so that the particles will be deflected in the $\pm y$ direction if the magnetic field is a function of y (i.e., not constant along y). The sign is chosen according to the direction of the magnetic moment vector.

In the Stern–Gerlach experiment, the atoms (i.e., charge-neutral quantum particles) are in the lowest energy state (as discussed further in Section 4.6), such that the electrons do not have any net angular momentum associated with electrons orbiting the nucleus. Thus, the magnetic moment of the atom should be zero. Since neutral atoms in the lowest energy state are used, $\mathbf{F}_L = \mathbf{F}_\mu = 0$, and, thus, the trajectory of the atoms should not be changed in passing through an inhomogeneous magnetic field. However, in the Stern–Gerlach experiment, it is found that the original beam of atoms splits into two components. One part of the beam is deflected in a certain direction (say, $+\mathbf{a}_y$), and the other part of the beam is deflected in the opposite direction ($-\mathbf{a}_y$). Thus, the atoms act in a manner that would be consistent with having a magnetic moment. Thus, the idea arose that electrons have an intrinsic magnetic moment, positive or negative but equal in magnitude, called spin. It can

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[†] Magnetic moment shouldn't be confused with magnetic permeability, also denoted by μ. The magnetic moment of a current loop, i.e., a circulating charge, is $\mu = \hat{a} I A$, where I is the current in the loop, A is the cross-sectional area of the loop, and $\hat{a}$ is a unit vector normal to the loop's cross section, chosen to be in the direction given by the right-hand rule. The total magnetic moment of an atom is due to angular momentum (orbiting electrons forming small current loops) and spin.

be shown that the nuclei also have spin, which results in fine structure in the experimental results, but that the main effect is due to the electrons. Also, although the results could seemingly be explained classically if the electrons were spinning about their own axes, it can be shown that this is not the case.

Spin is quantized, taking either integral or half-integral values of $\hbar$. As mentioned in Section 2.4.3, particles with integral (in units of $\hbar$) spin are called bosons, and particles with half-integral (in units of $\hbar$) spin are called fermions.

Although not related to spin per se, recall that classical particles can possess angular momentum,

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \tag{3.215}$$

where $\mathbf{r}$ is the particle's position vector and $\mathbf{p}$ is the particle's linear momentum. A good example is a particle in a circular orbit, such that

$$\mathbf{L} = \mathbf{a}_z mvr, \tag{3.216}$$

where $\mathbf{a}_z$ is a unit vector normal to the plane formed by $\mathbf{r}$ and $\mathbf{p}$ (following the right-hand rule), m is the mass of the particle, v is the particle's linear velocity, and r is the radius of the orbit. Recall that, in the absence of external forces, angular momentum is conserved, which explains why an ice skater spins faster as the skater's arms are lowered: r is reduced so that v must increase to maintain a constant angular momentum.

Whereas classical objects do not have any intrinsic spin, they do have angular momentum, although, perhaps not unexpectedly, in the quantum theory, angular momentum is quantized in integral units of $\hbar$, including 0 (i.e., 0, $\hbar$, $2\hbar$, $3\hbar$, ...). Therefore, a quantum particle in general has both quantized spin and quantized angular momentum. Electronics based on the transport of spin, rather than the transport of charge, will be discussed in Section 10.4. Spin is also important in magnetic resonance imaging (MRI) technologies.

3.7 MAIN POINTS

In this chapter, the fundamental principles of quantum mechanics have been presented in simplified form. After studying this chapter, you should understand the four postulates of quantum mechanics, and related ideas. In particular, you should know

- the meaning of the state function;
- how to calculate the probability of finding a particle in a given region of space;
- how to determine the probability of measuring a certain observable, λ_n;
- the concepts of operators, eigenvalues, and eigenfunctions, and how to solve eigenvalue problems based on differential operators;
- the important quantum mechanical operators associated with momentum and energy;
- how to determine the expectation value (mean) of an observable;

- the general time-dependent and time-independent Schrödinger equations, and how to solve these equations in simple regions of space;
- the concept of the probability current density;
- the analysis of multiple particle systems, screening, the Pauli exclusion principle, and the concepts of spin and angular momentum.

3.8 PROBLEMS

1. For the matrix operator $L = \begin{bmatrix} -5 & 0 \\ 1 & 2 \end{bmatrix}$, show that eigenvalues and eigenvectors are

$$\lambda = 2, \qquad x = \begin{bmatrix} 0 \\ \alpha \end{bmatrix},$$

$$\lambda = -5, \qquad x = \begin{bmatrix} -7\beta \\ \beta \end{bmatrix},$$

where $\alpha, \beta \neq 0$. That is, show that the preceding quantities satisfy the eigenvalue problem $Lx = \lambda x$.

2. Consider the set of functions $\left\{\frac{1}{\sqrt{2\pi}}e^{inx},\ n = 0, \pm 1, \pm 2, \ldots\right\}$.

(a) Show that this is an orthonormal set on the interval $(-\pi, \pi)$.

(b) On the interval $(-\pi/2, \pi/2)$, is the set an orthogonal set, an orthonormal set, or neither?

3. Consider the set of functions $\left\{\sqrt{\frac{2}{\pi}}\sin(nx),\ n = 1, 2, \ldots\right\}$ on the interval $(0, \pi)$.

(a) Show that this is an orthonormal set.

(b) Determine an operator (including boundary conditions) for which the preceding set are eigenfunctions. What are the eigenvalues?

4. For the differential operator $L = -d^2/dx^2$, $u(0) = u(a) = 0$, determine eigenvalues λ and eigenfunctions u. That is, solve

$$Lu = \lambda u,$$

where $u(x)$ is a nonzero function subject to the given boundary conditions. Normalize the eigenfunctions, and show that the eigenfunctions are orthonormal.

5. Repeat problem 3.4, but for boundary conditions $u'(0) = u'(a) = 0$, where $u' = du/dx$.

6. Assume that some observable of a certain system is measured and found to be λ_n for some integer n. By Postulate 2, we know that immediately after the measurement, the system is in state ψ_n, which is an eigenstate of the measurement operator $\widehat{o}$ (i.e., where $\widehat{o}\psi_n = \lambda_n\psi_n$).

(a) What can we conclude about the system's state immediately before the measurement?

(b) Assume that the identical measurement is then performed on 100,000 identical systems, and each time the measurement result is the same, λ_n. What can we infer about the system's state immediately before the measurement?

7. Assume that an electronic state has a lifetime of 10^{-8} s. What is the minimum uncertainty in the energy of an electron in this state?

8. In the example of solving the one-dimensional Schrödinger equation on page 65, we obtained the state functions

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

where

$$\begin{aligned} \psi(x) &= \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right), \quad n \text{ even}, \qquad (3.217) \\ &= \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{n\pi}{L}x\right), \quad n \text{ odd}, \end{aligned}$$

are eigenfunctions of the second derivative operator d^2/dx^2, and where energy eigenvalues were found to be

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2. \qquad (3.218)$$

(a) Show that the odd eigenfunction (sine) can be written as

$$\begin{aligned} \psi(x) &= \frac{1}{\sqrt{2}}\left[\frac{1}{i\sqrt{L}}e^{i\frac{p_n}{\hbar}x} - \frac{1}{i\sqrt{L}}e^{-i\frac{p_n}{\hbar}x}\right] \qquad (3.219) \\ &= \psi_+ - \psi_-, \end{aligned}$$

and determine a similar relation expression for the even eigenfunction. The term ψ_+ (ψ_-) represents a wave propagating with positive (negative) momentum. Thus, any state described by sine and cosine can be thought of as representing a superposition of positive and negative momentum states.

(b) Although the decomposition of a standing wave into two counterpropagating waves, as in part (a), is useful, it can be misinterpreted. Since the probability density $\psi(x,t)\,\psi^*(x,t)$ is independent of time, the expectation value of position, $\langle x \rangle$, is independent of time, and so, really, we should not think of the particle as "bouncing" back and forth in the confined space (otherwise, $\langle x \rangle$ would be a function of t). Determine the expectation value of momentum, using either (3.217) or (3.219), and discuss your answer in light of the preceding comment.

(c) Assume that the particle is in a state composed of the first two eigenfunctions,

$$\psi(x,t) = \frac{1}{\sqrt{2}}\left(\left(\frac{2}{L}\right)^{1/2}\cos\left(\frac{\pi}{L}x\right)e^{-i\frac{E_1 t}{\hbar}} + \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{2\pi}{L}x\right)e^{-i\frac{E_2 t}{\hbar}}\right).$$

Show that the expectation value of position as a function of time is

$$\langle x \rangle = \frac{16}{9}\frac{L}{\pi^2}\cos\left(\frac{3}{2}\frac{\hbar}{m}\frac{\pi^2}{L^2}t\right).$$

Interpret this solution, compared with the expectation value of position for a single stationary state ψ_n, which is time independent.

9. Since Schrödinger's equation is a homogeneous equation, the most general solution for the state function is a sum of homogeneous solutions (3.142),

$$\Psi(\mathbf{r},t) = \sum_n a_n \psi_n(\mathbf{r})\, e^{-iE_n t/\hbar}. \qquad (3.220)$$

Show that if $\Psi(\mathbf{r},0)$ is known, then an expression for the weighting amplitudes a_n can be determined. Assume that the eigenfunction ψ_n forms an orthonormal set. Hint: Multiply

$$\Psi(\mathbf{r},0) = \sum_n a_n \psi_n(\mathbf{r}) \qquad (3.221)$$

by $\psi_m^*(\mathbf{r})$ and integrate. What is the interpretation of $|a_n|^2$?

10. Consider a particle with time-independent potential energy, and assume that the initial state of the particle is

$$\Psi(\mathbf{r},t) = a_1\psi_1(\mathbf{r},t) + a_2\psi_2(\mathbf{r},t),$$

such that $P(\lambda_1) = |a_1|^2 = P_1$, $P(\lambda_2) = |a_2|^2 = P_2$, and $|a_1|^2 + |a_2|^2 = 1$. Show that

$$\langle E \rangle = P_1\langle E_1 \rangle + P_2\langle E_2 \rangle.$$

11. For the example of solving the one-dimensional Schrödinger's equation on page 65, determine the probability of observing the particle very near the boundary wall, $x = \pm L/2$. If the particle is in the $n = 2$ state, where is the particle most likely to be found?

12. For the example of solving the one-dimensional Schrödinger's equation on page 65, assume that the particle is in the $n = 2$ state. What is the probability that a measurement of energy will yield

$$E_2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2?$$

What is the probability that a measurement of energy will yield

$$E_3 = \frac{\hbar^2}{2m}\left(\frac{3\pi}{L}\right)^2?$$

13. Consider a quantum encryption scheme using photons. Assume that a photon can only exist in either state 1, ψ_1, having energy E_1, or state 2, ψ_2, having energy E_2, or in a superposition of the two states, $\Psi = a\psi_1 + b\psi_2$. Assume that the states are orthonormal.

(a) If a photon exists in the superposition state $\Psi = a\psi_1 + b\psi_2$, what is the relationship between a and b?

(b) If a photon exists in the superposition state $\Psi = a\psi_1 + b\psi_2$, determine the probability of measuring energy E_2. Show all work and/or explain your answer.

(c) If the photon in a superposition state is sent over a network, explain how undetected eavesdropping would be impossible.

14. In Chapter 6, the reflection and transmission of a particle across a potential barrier will be considered. For now, assume that a potential energy discontinuity is present at $x = a$, and that to the left of the discontinuity, the wavefunction is given by

$$\Psi(x,t) = \left(e^{ikx} + Re^{-ikx}\right) e^{-iEt/\hbar},$$

and to the right of the discontinuity

$$\Psi(x,t) = Te^{iqx} e^{-iEt/\hbar},$$

where R and T are reflection and transmission coefficients, respectively, which will depend on the properties of the different regions and on the discontinuity in potential at $x = a$. Determine the probability current density on either side of the discontinuity.

15. In the example of solving the one-dimensional Schrödinger's equation on page 65, we obtained the state functions

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

where

$$\begin{aligned}\psi(x) &= \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right), \quad && n \text{ even,} \\ &= \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{n\pi}{L}x\right), \quad && n \text{ odd,}\end{aligned}$$

and where

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2.$$

Determine the probability current density. Discuss your result.

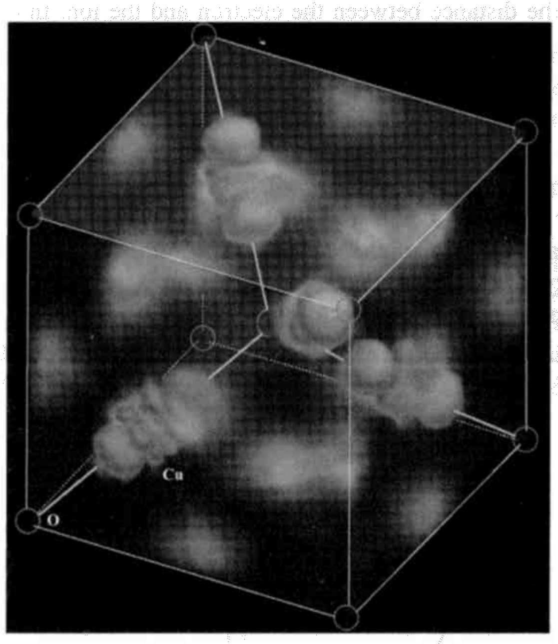
16. Assume that the wave function

$$\psi(z,t) = 200e^{i(kz-\omega t)}$$

describes a beam of 2 eV electrons having only kinetic energy. Determine numerical values for k and ω, and find the associated current density in A/m.

Chapter
4

FREE AND CONFINED ELECTRONS



Electron and X-ray diffraction image of dumbbell-shaped clouds of electrons shared by covalent bonds between copper and oxygen atoms in cuprite, C_2O. The nuclei of the copper atoms (not shown) are at the center of the dumbbells, and those of the oxygen atoms (also not shown) are at the center and corners of the superimposed cube. The fuzzy clouds are less defined electron clouds representing covalent bonds between the copper atoms. (From J.M. Zuo, M. Kim, M. O'Keeffe, and J.C.H. Spence, *Nature* 401, 49–52 (1999). Used by permission.)

In the last chapter, Schrödinger's equation was introduced, along with the basic ideas of quantum mechanics. In this chapter, some examples of solving Schrödinger's equation are presented relevant to understanding physical phenomena associated with electrons confined to nanoscale regions of space, including quantum dots, wires, and wells. The chapter begins, however, with a discussion of free (unconfined) electrons, in part to provide a comparison to the bounded space result.