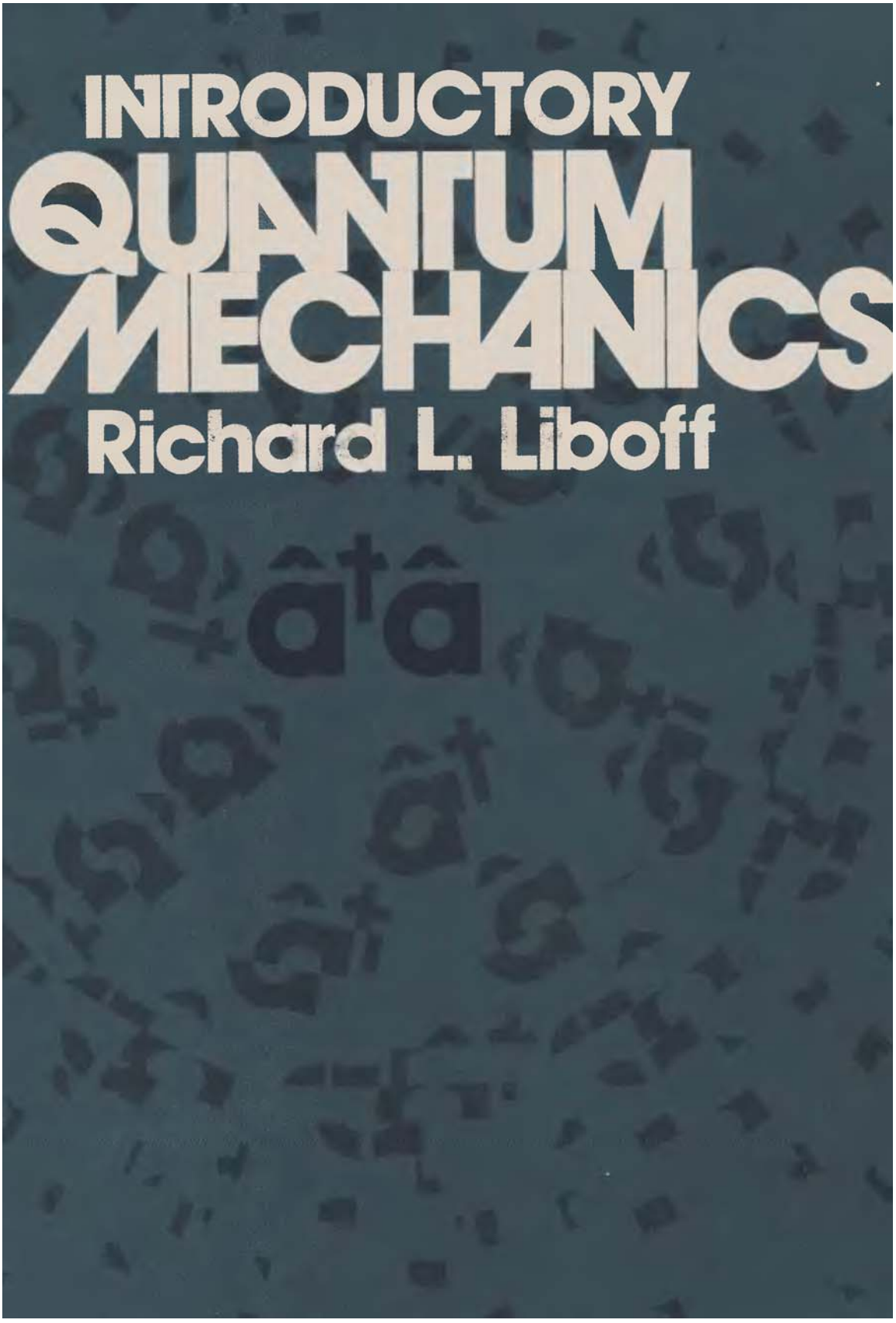
INTRODUCTORY QUANTUM MECHANICS

Richard L. Liboff



CONTENTS

CHAPTER 1
REVIEW OF CONCEPTS OF CLASSICAL MECHANICS

This is a preparatory chapter in which we review fundamental concepts of classical mechanics important to the development and understanding of quantum mechanics. Hamilton's equations are introduced and the relevance of cyclic coordinates and constants of the motion is noted. In discussing the state of a system, we briefly encounter our first distinction between classical and quantum descriptions. The notions of forbidden domains and turning points relevant to classical motion, which find application in quantum mechanics as well, are also described. The experimental motivation and historical background of quantum mechanics are described in Chapter 2.

1.1 GENERALIZED OR "GOOD" COORDINATES

Our discussion begins with the concept of *generalized* or *good* coordinates.

A bead (idealized to a point particle) constrained to move on a straight rigid wire has *one degree of freedom* (Fig. 1.1). This means that only one variable (or parameter) is needed to uniquely specify the location of the bead in space. For the problem under discussion, the variable may be displacement from an arbitrary but specified origin along the wire.

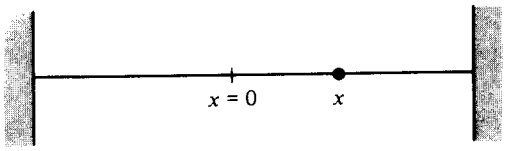


FIGURE 1.1 A bead constrained to move on a straight wire has one degree of freedom.

A particle constrained to move on a flat plane has two degrees of freedom. Two independent variables suffice to uniquely determine the location of the particle in space. With respect to an arbitrary, but specified origin in the plane, such variables might be the Cartesian coordinates (x, y) or the polar coordinates (r, θ) of the particle (Fig. 1.2).

Two beads constrained to move on the same straight rigid wire have two degrees of freedom. A set of appropriate coordinates are the displacements of the individual particles (x_1, x_2) (Fig. 1.3).

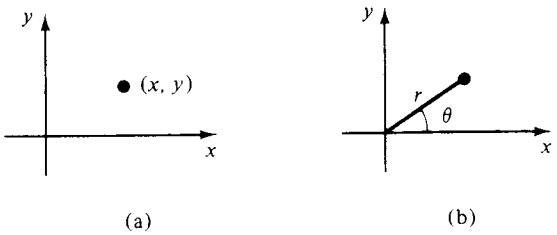


FIGURE 1.2 A particle constrained to move in a plane has two degrees of freedom. Examples of coordinates are (x, y) or (r, θ).

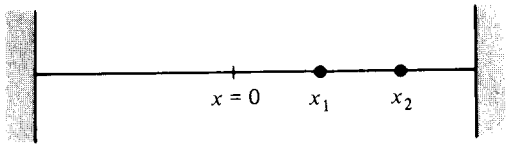


FIGURE 1.3 Two beads on a wire have two degrees of freedom. The coordinates x_1 and x_2 denote displacements of particles 1 and 2, respectively.

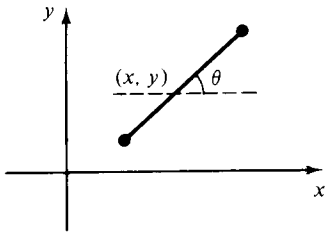


FIGURE 1.4 A rigid dumbbell in a plane has three degrees of freedom. A good set of coordinates are: (x, y), the location of the center, and θ, the inclination of the rod with the horizontal.

A rigid rod (or dumbbell) constrained to move in a plane has three degrees of freedom. Appropriate coordinates are: the location of its center (x, y) and the angular displacement of the rod from the horizontal, θ (Fig. 1.4).

Independent coordinates that serve to uniquely determine the orientation and location of a system in physical space are called *generalized* or *canonical* or *good* coordinates. *A system with N generalized coordinates has N degrees of freedom.* The orientation and location of a system with, say, three degrees of freedom are not specified until all three generalized coordinates are specified. The fact that *good* coordinates may be specified independently of one another means that given the values of all but one of the coordinates, the last coordinate remains arbitrary. Having specified (x, y) for a point particle in 3-space, one is still free to choose z independently of the assigned values of x and y.

PROBLEMS

1.1 For each of the following systems, specify the number of degrees of freedom and a set of good coordinates.

(a) A bead constrained to move on a closed circular hoop that is fixed in space.
(b) A bead constrained to move on a helix of constant pitch and constant radius.
(c) A particle on a right circular cylinder.
(d) A pair of scissors on a plane.
(e) A rigid rod in 3-space.
(f) A rigid cross in 3-space.
(g) A linear spring in 3-space.
(h) Any rigid body with one point fixed.
(i) A hydrogen atom.
(j) A lithium atom.
(k) A compound pendulum (two pendulums attached end to end).

1.2 Show that a particle constrained to move on a curve of any shape has one degree of freedom.

Answer

A curve is a one-dimensional locus and may be generated by the parameterized equations

$$x = x(\eta), \qquad y = y(\eta), \qquad z = z(\eta)$$

Once the independent variable η (e.g., length along the curve) is given, x, y, and z are specified.

1.3 Show that a particle constrained to move on a surface of arbitrary shape has two degrees of freedom.

Answer

A surface is a two-dimensional locus. It is generated by the equation

$$u(x, y, z) = 0$$

Any two of the three variables x, y, z determine the third. For instance, we may solve for z in the equation above to obtain the more familiar equation for a surface (height z at the point x, y),

$$z = z(x, y)$$

In this case, x and y may serve as generalized coordinates.

1.4 How many degrees of freedom does a classical gas composed of 10^{23} point particles have?

1.2 ENERGY, THE HAMILTONIAN, AND ANGULAR MOMENTUM

These three elements of classical mechanics have been singled out because they have direct counterparts in quantum mechanics. Furthermore, as in classical mechanics, their role in quantum mechanics is very important.

Consider that a particle of mass m in the potential field $V(x, y, z)$ moves on the trajectory

$$\begin{aligned} x &= x(t) \\ y &= y(t) \\ z &= z(t) \end{aligned} \tag{1.1}$$

At any instant t, the energy of the particle is

$$E = \tfrac{1}{2}mv^2 + V(x, y, z) = \tfrac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + V(x, y, z) \tag{1.2}$$

The velocity of the particle is $\mathbf{v}$. Dots denote time derivatives. The force on the particle $\mathbf{F}$ is the negative gradient of the potential.

$$\mathbf{F} = -\nabla V = -\left(\mathbf{e}_x \frac{\partial}{\partial x} V + \mathbf{e}_y \frac{\partial}{\partial y} V + \mathbf{e}_z \frac{\partial}{\partial z} V\right) \tag{1.3}$$

The three unit vectors $(\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z)$ lie along the three Cartesian axes.

Here are two examples of potential. The energy of a particle in the gravitational force field,

$$\mathbf{F} = -\mathbf{e}_z mg = -\nabla mgz$$

is

$$E = \tfrac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + mgz \tag{1.4}$$

The particle is at the height z above sea level. For this example,

$$V = mgz$$

An electron of charge q and mass m, between capacitor plates that are maintained at the potential difference Φ_0 and separated by the distance d (Fig. 1.5), has potential

$$V = \frac{q\Phi_0}{d} z$$

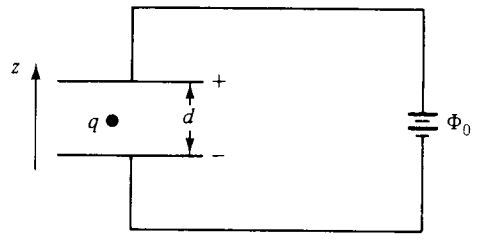


FIGURE 1.5 Electron in a uniform capacitor field.

The displacement of the electron from the bottom plate is z. The electron's energy is

$$E = \tfrac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \frac{q\Phi_0}{d}z \tag{1.5}$$

In both examples above, the system (particle) has three degrees of freedom. The Cartesian coordinates (x, y, z) of the particle are by no means the only "good" coordinates for these cases. For instance, in the last example, we may express the energy of the electron in spherical coordinates (Fig. 1.6):

$$E = \tfrac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\dot{\phi}^2 \sin^2\theta) + \frac{q\Phi_0}{d}r\cos\theta \tag{1.6}$$

In cylindrical coordinates (Fig. 1.7) the energy is

$$E = \tfrac{1}{2}m(\dot{\rho}^2 + \rho^2\dot{\phi}^2 + \dot{z}^2) + \frac{q\Phi_0}{d}z \tag{1.7}$$

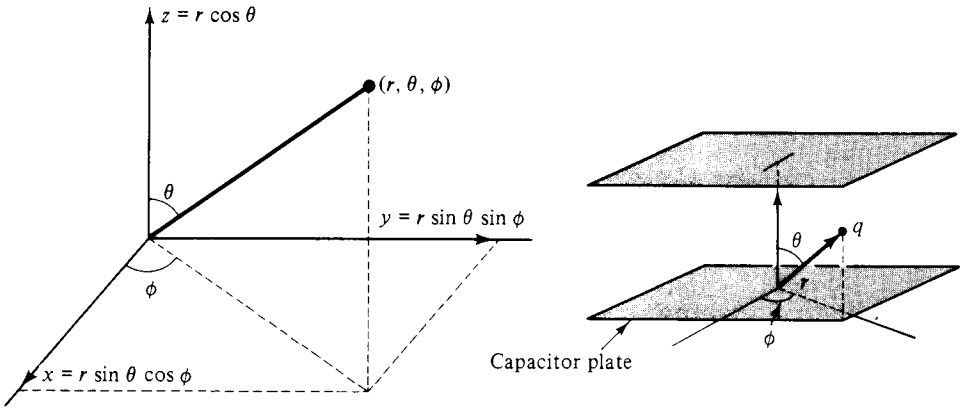


FIGURE 1.6 Spherical coordinates.

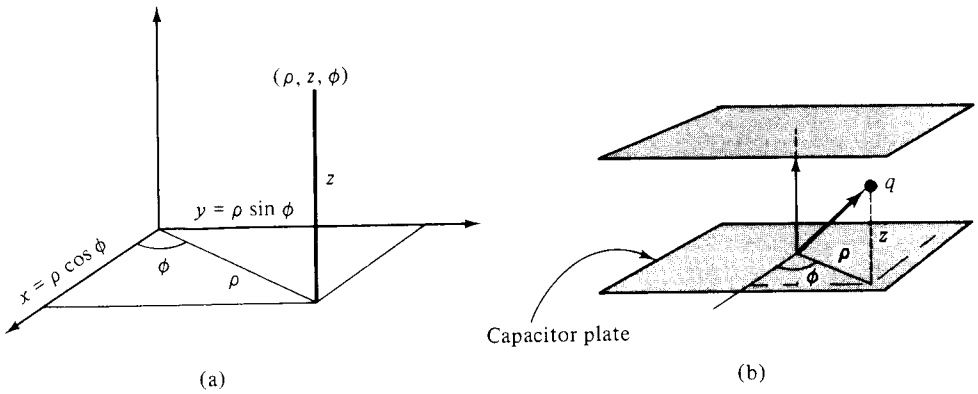


FIGURE 1.7 Cylindrical coordinates.

The hydrogen atom has six degrees of freedom. If (x_1, y_1, z_1) are the coordinates of the proton and (x_2, y_2, z_2) are the coordinates of the electron, the energy of the hydrogen atom appears as

$$E = \tfrac{1}{2}M(\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2) + \tfrac{1}{2}m(\dot{x}_2^2 + \dot{y}_2^2 + \dot{z}_2^2) - \frac{q^2}{\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}} \tag{1.8}$$

(Fig. 1.8). The mass of the proton is M and that of the electron is m. In all the cases above, the energy is a *constant of the motion.* A constant of the motion is a dynamical function that is constant as the system unfolds in time. For each of these cases,

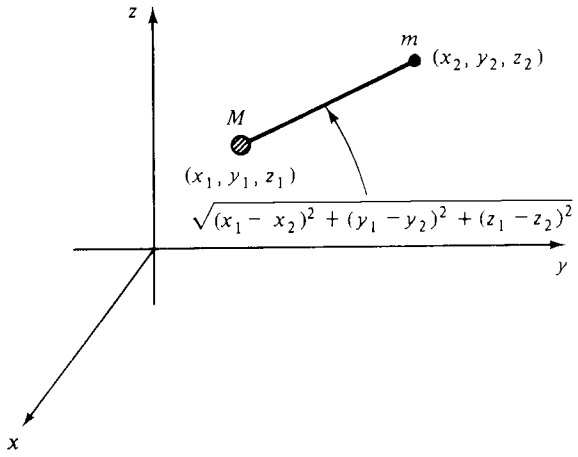


FIGURE 1.8 The hydrogen atom has six degrees of freedom. The Cartesian coordinates of the proton and electron serve as good generalized coordinates.

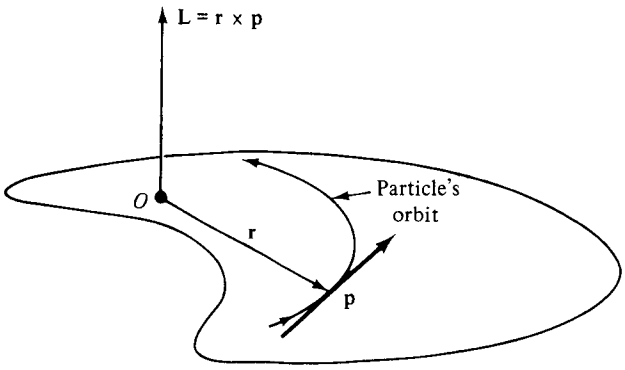


FIGURE 1.9 Angular momentum of a particle with momentum p about the origin O.

whatever E is initially, it maintains that value, no matter how complicated the subsequent motion is. Constants of the motion are extremely useful in classical mechanics and often serve to facilitate calculation of the trajectory.

A system that in no way interacts with any other object in the universe is called an *isolated system*. The total energy, linear momentum, and angular momentum of an isolated system are constant. Let us recall the definition of linear and angular momentum for a particle. A particle of mass m moving with velocity $\mathbf{v}$ has linear momentum

$$\mathbf{p} = m\mathbf{v} \tag{1.9}$$

The angular momentum of this particle, measured about a specific origin, is

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{1.10}$$

where $\mathbf{r}$ is the radius vector from the origin to the particle (Fig. 1.9).

If there is no component of force on a particle in a given (constant) direction, the component of momentum in that direction is constant. For example, for a particle in a gravitational field that is in the z direction, p_x and p_y are constant.

If there is no component of torque $\mathbf{N}$ in a given direction, the component of angular momentum in that direction is constant. This follows directly from Newton's second law for angular momentum,

$$\mathbf{N} = \frac{d\mathbf{L}}{dt} \tag{1.11}$$

For a particle in a gravitational field that is in the minus z direction, the torque on the particle is

$$\mathbf{N} = \mathbf{r} \times \mathbf{F} = -\mathbf{r} \times \mathbf{e}_z mg$$

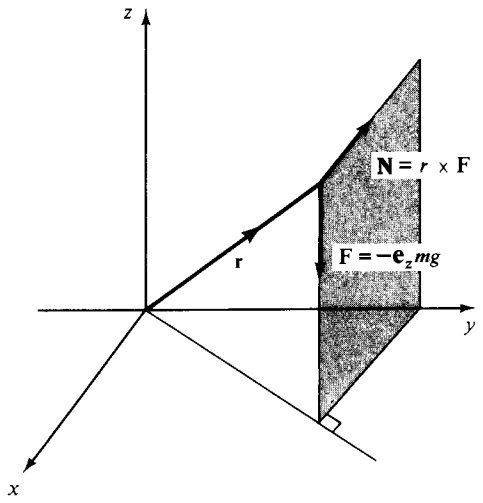


FIGURE 1.10 The torque $\mathbf{r} \times \mathbf{F}$ has no component in the z direction.

The radius vector from the origin to the particle is $\mathbf{r}$ (Fig. 1.10). Since $\mathbf{e}_z \times \mathbf{r}$ has no component in the z direction ($\mathbf{e}_z \cdot \mathbf{e}_z \times \mathbf{r} = 0$), it follows that

$$L_z = xp_y - yp_x = \text{constant} \tag{1.12}$$

Since p_x and p_y are also constants, this equation tells us that the projected orbit in the xy plane is a straight line (Fig. 1.11).

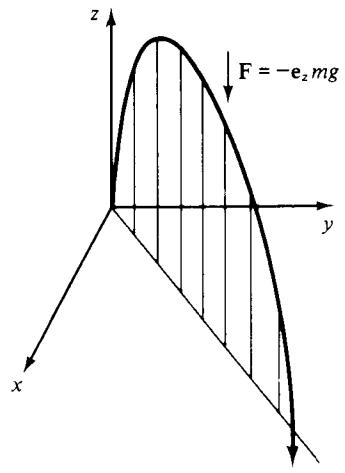


FIGURE 1.11 The projected motion in the xy plane is a straight line. Its equation is given by the constant z component of angular momentum: $L_z = xp_y - yp_x$.

Hamilton's Equations

The constants of motion for more complicated systems are not so easily found. However, there is a formalism that treats this problem directly. It is Hamiltonian mechanics. Consider the energy expression for an electron between capacitor plates (1.5). Rewriting this expression in terms of the linear momentum **p** (as opposed to velocity) gives

$$(1.13)\quad E(x, y, z, \dot{x}, \dot{y}, \dot{z}) \rightarrow H(x, y, z, p_x, p_y, p_z) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{q\Phi_0}{d} z$$

The energy, written in this manner, as a function of coordinates and momenta is called the *Hamiltonian*, H. One speaks of p_x as being the momentum *conjugate* to x; p_y is the momentum conjugate to y; and so on.

The equations of motion (i.e., the equations that replace Newton's second law) in Hamiltonian theory are (for a point particle moving in three-dimensional space)

$$(1.14)\quad \begin{aligned} \frac{\partial H}{\partial x} &= -\dot{p}_x & \frac{\partial H}{\partial p_x} &= \dot{x} \\ \frac{\partial H}{\partial y} &= -\dot{p}_y & \frac{\partial H}{\partial p_y} &= \dot{y} \\ \frac{\partial H}{\partial z} &= -\dot{p}_z & \frac{\partial H}{\partial p_z} &= \dot{z} \end{aligned}$$

Cyclic Coordinates

For the Hamiltonian (1.13) corresponding to an electron between capacitor plates, one obtains

$$(1.15)\quad \frac{\partial H}{\partial x} = \frac{\partial H}{\partial y} = 0$$

The Hamiltonian does not contain x or y. When coordinates are missing from the Hamiltonian, they are called *cyclic* or *ignorable*. The momentum conjugate to a cyclic coordinate is a constant of the motion. This important property follows directly from Hamilton's equations, (1.14). For example, for the case at hand, we see that $\partial H/\partial x = 0$ implies that $\dot{p}_x = 0$, so p_x is constant; similarly for p_y. (Note that there is no component of force in the x or y directions.) The remaining four Hamilton's equations give

$$(1.16)\quad \dot{p}_z = -\frac{q\Phi_0}{d}, \qquad p_x = m\dot{x}, \qquad p_y = m\dot{y}, \qquad p_z = m\dot{z}$$

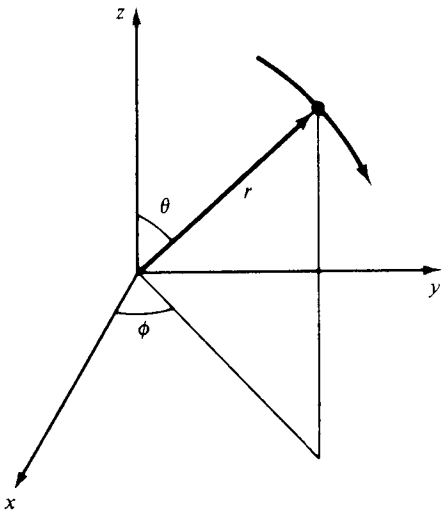


FIGURE 1.12 Motion of a particle in spherical coordinates with r and ϕ fixed: $v_\theta = r\dot{\theta}$, $p_\theta = rmv_\theta = mr^2\dot{\theta}$. The moment arm is r.

The last three equations return the definitions of momenta in terms of velocities. The first equation is the z component of Newton's second law. (For an electron, $q = -|q|$. It is attracted to the positive plate.)

Consider next the Hamiltonian for this same electron but expressed in terms of spherical coordinates. We must transform E as given by (1.5) to an expression involving r, θ, ϕ, and the momenta conjugate to these coordinates. The momentum conjugate to r is the component of linear momentum in the direction of $\mathbf{r}$. If $\mathbf{e}_r$ is a unit vector in the $\mathbf{r}$ direction, then

$$p_r = \frac{\mathbf{r} \cdot \mathbf{p}}{r} = \mathbf{e}_r \cdot \mathbf{p} = m\mathbf{e}_r \cdot \mathbf{v} = m\dot{r} \tag{1.17}$$

The momentum conjugate to the angular displacement θ is the component of angular momentum corresponding to a displacement in θ (with r and ϕ fixed). The moment arm for this motion is r. The velocity is $r\dot{\theta}$. It follows that

$$p_\theta = mr(r\dot{\theta}) = mr^2\dot{\theta} \tag{1.18}$$

(Fig. 1.12).

The momentum conjugate to ϕ is the angular momentum corresponding to a displacement in ϕ (with r and θ fixed). The moment arm for this motion is $r \sin \theta$. The velocity is $r\dot{\phi} \sin \theta$ (Fig. 1.13). The angular momentum of this motion is

$$p_\phi = mr^2\dot{\phi} \sin^2 \theta \tag{1.19}$$

Since such motion is confined to a plane normal to the z axis, p_ϕ is the z component of angular momentum. This was previously denoted as L_z in (1.12).

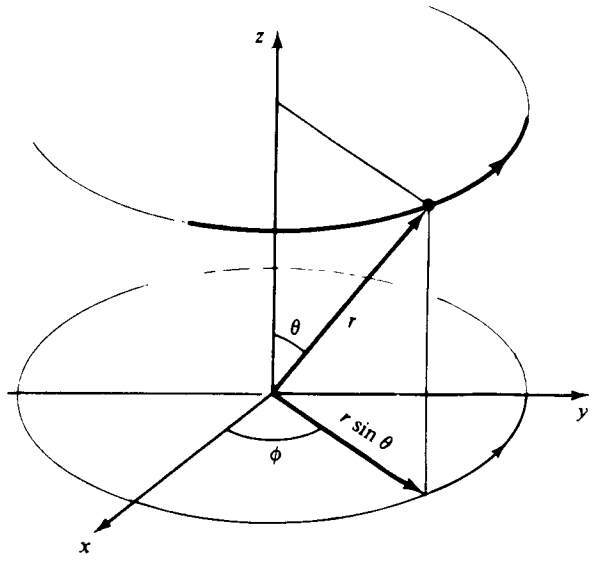


FIGURE 1.13 Motion of a particle with r and θ fixed: $v_\phi = r \sin\theta\, \dot{\phi}$. The moment arm is $r \sin\theta$, $p_\phi = (r \sin\theta) m v_\phi = m r^2 \dot{\phi} \sin^2\theta$.

In terms of these coordinates and momenta, the energy expression (1.6) becomes

$$H(r, \theta, \phi, p_r, p_\theta, p_\phi) = \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} + \frac{p_\phi^2}{2mr^2 \sin^2\theta} + \frac{q\Phi_0}{d} r \cos\theta \tag{1.20}$$

Hamilton's equations for a point particle, in spherical coordinates, become

$$\begin{aligned} \frac{\partial H}{\partial \theta} &= -\dot{p}_\theta & \frac{\partial H}{\partial p_\theta} &= \dot{\theta} \\ \frac{\partial H}{\partial \phi} &= -\dot{p}_\phi & \frac{\partial H}{\partial p_\phi} &= \dot{\phi} \\ \frac{\partial H}{\partial r} &= -\dot{p}_r & \frac{\partial H}{\partial p_r} &= \dot{r} \end{aligned} \tag{1.21}$$

From the form of the Hamiltonian (1.20) we see that ϕ is a cyclic coordinate. That is,

$$\frac{\partial H}{\partial \phi} = 0 = -\dot{p}_\phi \tag{1.22}$$

It follows that p_ϕ, as given by (1.19), is constant. Thus, the component of angular momentum in the z direction is conserved. The torque on the particle has no component in this direction.

Again the momentum derivatives of H in (1.20) return the definitions of momenta in terms of velocities. For example, from (1.20),

$$\frac{\partial H}{\partial p_\theta} = \dot{\theta} = \frac{p_\theta}{mr^2} \tag{1.23}$$

which is (1.18). Hamilton's equation for $\dot{p}_r$ is

$$-\frac{\partial H}{\partial r} = \dot{p}_r = \frac{{p_\theta}^2}{mr^3} + \frac{{p_\phi}^2}{mr^3 \sin^2 \theta} - \frac{q\Phi_0}{d} \cos \theta \tag{1.24}$$

The first two terms on the right-hand side of this equation are the components of centripetal force in the radial direction, due to θ and ϕ displacements, respectively. The last term is the component of electric force $-\mathbf{e}_z q\Phi_0/d$ in the radial direction. Hamilton's equation for $\dot{p}_\theta$ is

$$-\frac{\partial H}{\partial \theta} = \dot{p}_\theta = \frac{{p_\phi}^2 \cos \theta}{mr^2 \sin^3 \theta} + \frac{q\Phi_0}{d} r \sin \theta \tag{1.25}$$

The right-hand side is a component of torque. It contains the centripetal force factor due to the ϕ motion $({p_\phi}^2/mr^3 \sin^3 \theta)$ and a moment arm factor, $r \cos \theta$. At any instant of time this component of torque is normal to the plane swept out by r due to θ motion alone.

A very instructive example concerns the motion of a free particle. A free particle is one that does not interact with any other particle or field. It is free of all interactions and is an isolated system. A particle moving by itself in an otherwise empty universe is a free particle. In Cartesian coordinates the Hamiltonian for a free particle is

$$H = \frac{1}{2m} p^2 = \frac{1}{2m} ({p_x}^2 + {p_y}^2 + {p_z}^2) \tag{1.26}$$

All coordinates (x, y, z) are cyclic. Therefore, the three components of momenta are constant and may be equated to their respective initial values at time $t = 0$.

$$\begin{aligned} p_x &= p_x(0) \\ p_y &= p_y(0) \\ p_z &= p_z(0) \end{aligned} \tag{1.27}$$

Combining these with the remaining three Hamilton's equations gives

$$\begin{aligned} m\dot{x} &= p_x(0) \\ m\dot{y} &= p_y(0) \\ m\dot{z} &= p_z(0) \end{aligned} \tag{1.28}$$

These are simply integrated to obtain

$$x(t) = \frac{p_x(0)}{m} t + x(0)$$

$$y(t) = \frac{p_y(0)}{m} t + y(0) \tag{1.29}$$

$$z(t) = \frac{p_z(0)}{m} t + z(0)$$

which are parametric equations for a straight line.

Let us calculate the y component of angular momentum of the (free) particle.

$$L_y = zp_x - xp_z = \left[z(0) + \frac{p_z(0)}{m} t\right] p_x(0) - \left[x(0) + \frac{p_x(0)}{m} t\right] p_z(0) \tag{1.30}$$

Canceling terms, we obtain

$$L_y = z(0)p_x(0) - x(0)p_z(0) = L_y(0) \tag{1.31}$$

and similarly for L_x and L_z. It follows that

$$\mathbf{L} = (L_x, L_y, L_z) = \text{constant} \tag{1.32}$$

for a free particle.

Investigating the dynamics of a free particle in Cartesian coordinates has given us immediate and extensive results. We know that $\mathbf{p}$ and $\mathbf{L}$ are both constant. The orbit is rectilinear.

We may also consider the dynamics of a free particle in spherical coordinates. The Hamiltonian is

$$H = \frac{{p_r}^2}{2m} + \frac{{p_\theta}^2}{2mr^2} + \frac{{p_\phi}^2}{2mr^2 \sin^2 \theta} \tag{1.33}$$

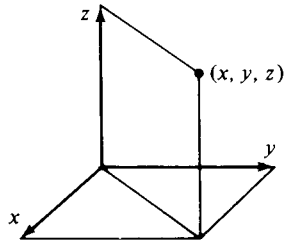
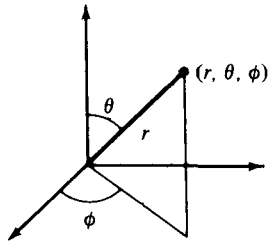
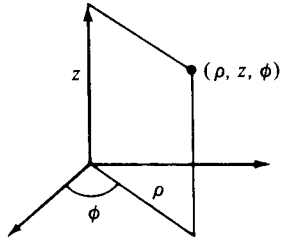
Only ϕ is cyclic, and we immediately conclude that p_ϕ (or equivalently, L_z) is constant. However, p_r and p_θ are not constant. From Hamilton's equations, we obtain

$$\dot{p}_r = \frac{{p_\theta}^2}{mr^3} + \frac{{p_\phi}^2}{mr^3 \sin^2 \theta}$$

$$\dot{p}_\theta = \frac{{p_\phi}^2 \cos \theta}{mr^2 \sin^3 \theta} \tag{1.34}$$

These centripetal terms were interpreted above. In this manner we find that the rectilinear, constant-velocity motion of a free particle, when cast in a spherical coordinate frame, involves accelerations in the r and θ components of motion. These accelerations

TABLE 1.1 Hamiltonian of a free particle in three coordinate frames

	Cartesian Coordinates	Spherical Coordinates	Cylindrical Coordinates
Frames			
Hamiltonian	$H(x, y, z, p_x, p_y, p_z)$ $= \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$	$H(r, \theta, \phi, p_r, p_\theta, p_\phi)$ $= \frac{1}{2m}\left[p_r^2 + \frac{1}{r^2}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right)\right]$ $= \frac{1}{2m}\left(p_r^2 + \frac{L^2}{r^2}\right)$	$H(\rho, z, \phi, p_\rho, p_z, p_\phi)$ $= \frac{1}{2m}\left(p_\rho^2 + p_z^2 + \frac{p_\phi^2}{\rho^2}\right)$
Momenta	$p_x = m\dot{x}$ $p_y = m\dot{y}$ $p_z = m\dot{z}$	$p_r = m\dot{r}$ $p_\theta = mr^2\dot{\theta}$ $p_\phi = mr^2\dot{\phi}\sin^2\theta$	$p_\rho = m\dot{\rho}$ $p_z = m\dot{z}$ $p_\phi = m\rho^2\dot{\phi}$
Cyclic coordinates	x, y, z	ϕ	z, ϕ
Constant momenta	p_x, p_y, p_z	$p_\phi = L_z$	p_z, p_ϕ

arise from an inappropriate choice of coordinates. In simple language: Fitting a straight line to spherical coordinates gives peculiar results.

A comparison of the Hamiltonian for a free particle in Cartesian, spherical, and cylindrical coordinates is shown in Table 1.1.

Canonical Coordinates and Momenta

While the reader may feel some familiarity with the components of linear momentum (p_x, p_y, p_z) and angular momentum (p_θ, p_ϕ), it is clear that these intuitive notions are exhausted for a system with, say, 17 degrees of freedom. If we call the seventeenth coordinate q_{17}, what is the momentum p_{17} conjugate to q_{17}? There is a formal procedure for determining the momentum conjugate to a given generalized coordinate. For example, it gives $p_\theta = mr^2\dot{\theta}$ as the momentum conjugate to θ for a particle in spherical coordinates. This procedure is described in any book in graduate mechanics.[1]

The coordinates of a system with N degrees of freedom, $(q_1, q_2, q_3, \ldots, q_N)$, and conjugate momenta $(p_1, p_2, p_3, \ldots, p_N)$ are also called *canonical* coordinates and momenta. A set of coordinates and momenta are canonical if with the Hamiltonian, $H(q_1, \ldots, q_N, p_1, \ldots, p_N, t)$, Hamilton's equations

$$\frac{\partial H}{\partial q_l} = -\dot{p}_l, \qquad \frac{\partial H}{\partial p_l} = \dot{q}_l \qquad (l = 1, \ldots, N) \tag{1.35}$$

are entirely consistent with Newton's laws of motion. We have seen this to be the case for all the problems considered above. (Time-dependent Hamiltonians are considered in Chapter 13.)

PROBLEMS

1.5 Show that the z component of angular momentum for a point particle

$$L_z = xp_y - yp_x$$

when expressed in spherical coordinates, becomes

$$L_z = p_\phi = mr^2\dot{\phi}\sin^2\theta$$

(*Hint*: Recall the transformation equations

$$z = r\cos\theta$$
$$y = r\sin\theta\sin\phi$$
$$x = r\sin\theta\cos\phi.)$$

[1] See, for example, H. Goldstein, *Classical Mechanics*, Addison-Wesley, Reading, Mass., 1951.

1.6 (a) Calculate $\dot{p}_r$, $\dot{p}_\theta$, and $\dot{p}_\phi$ as explicit functions of time for the following motion of a particle.

$$y = y_0, \qquad z = z_0, \qquad x = v_0 t$$

(b) For what type of free-particle orbit are the following conditions obeyed?

(1) $\dot{p}_r = 0$
(2) $\dot{p}_\theta = 0$
(3) $\dot{p}_\phi = 0$
(4) $\dot{p}_r = \dot{p}_\theta = \dot{p}_\phi = 0$

(c) Describe an experiment to measure p_r, at a given instant, for the motion of part (a).

1.7 Show that the energy of a free particle may be written

$$H = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2}$$

where $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. [*Hint:* Use the vector relation

$$L^2 = (\mathbf{r} \times \mathbf{p})^2 = r^2 p^2 - (\mathbf{r} \cdot \mathbf{p})^2$$

together with the definition $p_r = (\mathbf{r} \cdot \mathbf{p})/r$.]

1.8 Show that angular momentum of a free particle obeys the relation

$$L^2 = L_x^2 + L_y^2 + L_z^2 = p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta}$$

(*Hint:* Employ the results of Problem 1.7.)

1.9 A particle of mass m is in the environment of a force field with components

$$F_z = -\mathrm{K}z, \qquad F_x = 0, \qquad F_y = 0$$

with K constant.

(a) Write down the Hamiltonian of the particle in Cartesian coordinates. What are the constants of motion?
(b) Use the fact that the Hamiltonian itself is also constant to obtain the orbit.
(c) What is the Hamiltonian in cylindrical coordinates? What are the constants of motion?

1.10 Suppose that one calculates the Hamiltonian for a given system and finds a coordinate missing. What can be said about the symmetry of the system?

1.11 A particle of mass m is attracted to the origin by the force

$$\mathbf{F} = -\mathrm{K}\mathbf{r}$$

Write the Hamiltonian for this system in spherical and Cartesian coordinates. What are the cyclic coordinates in each of these frames? [*Hint:* The potential for this force, $V(r)$, is given by $\mathbf{F} = -\mathrm{K}\mathbf{r} = -\nabla V(r)$.]

1.12 A "spherical pendulum" consists of a particle of mass m attached to one end of a weightless rod of length a. The other end of the rod is fixed in space (the origin). The rod is free to rotate

about this point. If at any instant the angular velocity of the particle about the origin is ω, its energy

$$E = \tfrac{1}{2}ma^2\omega^2 = \tfrac{1}{2}I\omega^2$$

The moment of inertia is I. What is the Hamiltonian of this system in spherical coordinates? (*Hint:* Recall the relation $L = I\omega$.)

1.3 THE STATE OF A SYSTEM

To know the values of the generalized coordinates of a system at a given instant is to know the location and orientation of the system at that instant. In classical physics we can ask for more information about the system at any given instant. We may ask for its motion as well. The location, orientation, and motion of the system at a given instant specify the state of the system at that instant. For a point particle in 3-space, the classical state Γ is given by the six quantities (Fig. 1.14)

$$\Gamma = (x, y, z, \dot{x}, \dot{y}, \dot{z}) \tag{1.36}$$

In terms of momenta,

$$\Gamma = (x, y, z, p_x, p_y, p_z) \tag{1.37}$$

More generally, the state of a system is a minimal aggregate of information about the system which is maximally informative. A set of good coordinates and their corresponding time derivatives (generalized velocities) or corresponding momenta (canonical momenta) always serves as such a minimal aggregate which is maximally informative and serves to specify the state of a system in classical physics.

The state of the system composed of two point particles moving in a plane is given by the eight parameters

$$\Gamma = (x_1, y_1, x_2, y_2, p_{x_1}, p_{y_1}, p_{x_2}, p_{y_2}) \tag{1.38}$$

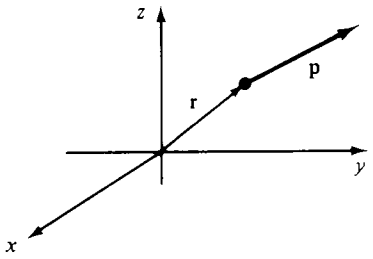


FIGURE 1.14 The classical state of a free particle is given by six scalar quantities (x, y, z, p_x, p_y, p_z).

Just as the set of generalized coordinates one assigns to a given system is not unique, neither is the description of the state Γ. For instance, the state of a point particle moving in a plane in Cartesian representation is

$$\Gamma = (x, y, p_x, p_y) \tag{1.39}$$

In polar representation it is

$$\Gamma = (r, \theta, p_r, p_\theta) \tag{1.40}$$

All representations of the state of a given system in classical mechanics contain an equal number of variables. If we think of Γ as a vector, then for a system with N degrees of freedom, Γ is $2N$-dimensional. In classical mechanics change of representation is effected by a change from one set of canonical coordinates and momenta (q, p) to another valid set of canonical coordinates and momenta (q', p').

$$\Gamma(q_1, \ldots, q_N, p_1, \ldots, p_N) \rightarrow \Gamma(q_1', \ldots, q_N', p_1', \ldots, p_N')$$

One form of canonical transformation results simply from a change in coordinates. For example, the transformation from Cartesian to polar coordinates for a particle moving in a plane effects the following change in representation:

$$\Gamma(x, y, p_x, p_y) \rightarrow \Gamma(r, \theta, p_r, p_\theta)$$

Representations in Quantum Mechanics

Next, we turn briefly to the form these concepts take in quantum mechanics. The specification of parameters that determines the state of a system in quantum mechanics is more subtle than in classical mechanics. As will emerge in the course of development of this text, in quantum mechanics one is not free to simultaneously specify certain sets of variables relating to a system. For example, while the classical state of a free particle moving in the x direction is given by the values of its position x, and momentum p_x, in quantum mechanics such simultaneous specification cannot be made. Thus, if the position x of the particle is measured at a given instant, the particle is left in a state wherein the particle's momentum is maximally uncertain. If on the other hand the momentum p_x is measured, the particle is left in a state in which its position is maximally uncertain. Suppose it is known that the particle has a specific value of momentum. One may then ask if there are any other variables whose values may be ascertained without destroying the established value of momentum. For a free particle one may further specify the energy E; that is, in quantum mechanics it is possible for the particle to be in a state such that measurement of momentum definitely finds the value p_x and measurement of energy definitely finds the value E. Suppose there are no further observable properties of the free particle that may be specified

simultaneously with those two variables. Consequently, values of p_x and E comprise the most informative statement one can make about the particle and these values may be taken to comprise the state of the system of the particle

$$\Gamma = \Gamma(p_x, E)$$

As remarked above, if the particle is in this state, it is certain that measurement of momentum finds p_x and measurement of energy finds E. Such values of p_x and E are sometimes called *good quantum numbers*. As with their classical counterpart, good quantum numbers are an independent set of parameters which may be simultaneously specified and which are maximally informative.

For some problems in quantum mechanics it will prove convenient to give the state in terms of the Cartesian components of angular momentum: L_x, L_y, and L_z. We will find that specifying the value of L_z, say, induces an uncertainty in the accompanying components of L_x and L_y, so that, for example, it is impossible to simultaneously specify L_z and L_x for a given system. One may, however, simultaneously specify L_z together with the square of the magnitude of the total momentum, L^2. For a particle moving in a spherically symmetric environment, one may also simultaneously specify the energy of the particle. This is the most informative[1] statement one can make about such a particle, and the values of energy, L^2 and L_z, comprise a quantum state of the system.

$$\Gamma = (E, L^2, L_z) \tag{1.41}$$

The values of E, L^2, and L_z are then good quantum numbers. That is, they are an independent set of parameters which may be simultaneously specified and which are maximally informative.

Just as change in representation, as discussed above, plays an important role in classical physics, so does its counterpart in quantum mechanics. A representation in quantum mechanics relates to the observables that one can precisely specify in a given state. In transforming to a new representation, new observables are specified in the state. For a free point particle moving in 3-space, in one representation the three components of linear momentum p_x, p_y, and p_z are specified while in another representation the energy $p^2/2m$, the square of the angular momentum L^2, and any component of angular momentum, say L_z, are specified. In this change of representation,

$$\Gamma(p_x, p_y, p_z) \rightarrow \Gamma(E, L^2, L_z) \tag{1.42}$$

When treating the problem of the angular momentum of two particles ($\mathbf{L}_1$ and $\mathbf{L}_2$, respectively) in one representation, $(L_1^2, L_2^2, L_{z_1}, L_{z_2})$ are specified while in another representation, (L_1^2, L_2^2, L^2, L_z) are specified. Here we are writing $\mathbf{L}$ for

[1] More precisely, Γ includes the *parity* of the system. This is a purely quantum mechanical notion and will be discussed more fully in Chapter 6

the *total angular momentum of the system* $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$. In this change of representation,

$$\Gamma(L_1^2, L_2^2, L_{z_1}, L_{z_2}) \rightarrow \Gamma(L_1^2, L_2^2, L^2, L_z^2) \tag{1.43}$$

Finally, in this very brief introductory description, we turn to the concept of the change of the quantum state in time. In classical mechanics, Newton's laws of motion determine the change of the state of the system in time. In quantum mechanics, the evolution in time of the state of the system is incorporated in the *wave (or state) function* and its equation of motion, the *Schrödinger equation*. Through the wavefunction, one may calculate (expected) values of observable properties of the system, including the time development of the state of the system.

These concepts of the quantum state—its evolution in time and change in representation—comprise principal themes in quantum mechanics. Their understanding and application are important and are fully developed later in the text.

PROBLEMS

1.13 Write down a set of variables that may be used to prescribe the classical state for each of the 11 systems listed in Problem 1.1.

Answer (partial)

(e) A rigid rod in 3-space: Since the system has five degrees of freedom, the classical state of the system is given by 10 parameters. For example,

$$\Gamma = \{x, y, z, \theta, \phi, \dot{x}, \dot{y}, \dot{z}, \dot{\theta}, \dot{\phi}\}$$

[*Note:* The quantum state is less informative. For example, such a state is prescribed by five variables (x, y, z, θ, ϕ). Another specification of the quantum state is given by five momenta $(p_x, p_y, p_z, p_\theta, p_\phi)$. However, simultaneous specification of, say, x and p_x is not possible in quantum mechanics.]

1.14 (a) Use Hamilton's equations for a system with N degrees of freedom to show that H is constant in time if H does not contain the time explicitly. [*Hint:* Write

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} + \sum_{l=1}^{N} \left(\frac{\partial H}{\partial q_l} \dot{q}_l + \frac{\partial H}{\partial p_l} \dot{p}_l \right).]$$

(b) Construct a simple system for which H is an explicit function of the time.

1.15 For a system with N degrees of freedom, the Poisson bracket of two dynamical functions A and B is defined as

$$\{A, B\} \equiv \sum_{l=1}^{N} \left(\frac{\partial A}{\partial q_l} \frac{\partial B}{\partial p_l} - \frac{\partial B}{\partial q_l} \frac{\partial A}{\partial p_l} \right)$$

(a) Use Hamilton's equations to show that the total time rate of change of a dynamical function A may be written

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \{A, H\}$$

where H is the Hamiltonian of the system.

(b) Prove the following: (1) If $A(q, p)$ does not contain the time explicitly and $\{A, H\} = 0$, then A is a constant of the motion. (2) If A does contain the time explicitly, it is constant if $\partial A/\partial t = \{H, A\}$.

(c) For a free particle moving in one dimension, show that

$$A = x - \frac{pt}{m}$$

satisfies the equation

$$\frac{\partial A}{\partial t} = -\{A, H\}$$

so that it is a constant of the motion. What does this constant correspond to physically?

1.16 How many degrees of freedom does the compound pendulum depicted in Fig. 1.15 have? Choose a set of generalized coordinates (be certain they are independent). What is the Hamiltonian for this system in terms of the coordinates you have chosen? What are the immediate constants of motion?

1.17 How many constants of the motion does a system with N degrees of freedom have?

Answer

Each of the coordinates $\{q_l\}$ and momenta $\{p_l\}$ satisfies a first-order differential equation in time (i.e., Hamilton's equations). Every such equation has one constant of integration. These comprise $2N$ constants of the motion.

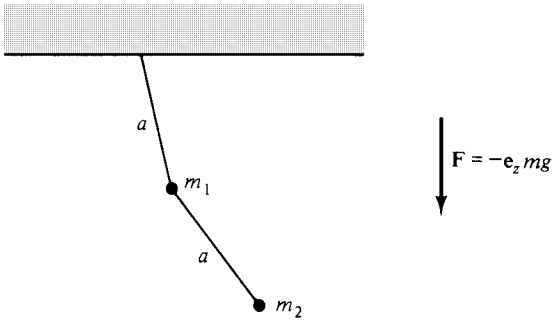


FIGURE 1.15 Compound pendulum composed of two masses connected by weightless rods of length a. The motion is in the plane of the paper. (See Problem 1.16.)

1.4 PROPERTIES OF THE ONE-DIMENSIONAL POTENTIAL FUNCTION

Consider a particle that is constrained to move in one dimension, x. The particle is in the potential field $V(x)$ depicted in Fig. 1.16. What is the direction of force at the point $x = A$? We can calculate the gradient (in the x direction) and conclude that the direction of force at A is in the $+x$ direction. There is a simpler technique. Imagine that the curve drawn is the contour of a range of mountain peaks. If a ball is placed at A, it rolls down the hill. The force is in the $+x$ direction. If placed at B (or C), it remains there. If placed at D, it rolls back toward the origin; the force is in the $-x$ direction. This technique always works (even for three-dimensional potential surfaces) because the gravity potential is proportional to height z, so the potential surface for a particle constrained to move on the surface of a mountain is that same surface.

The one-dimensional spring potential, $V = Kx^2/2$, is depicted in Fig. 1.17. If the particle is started from rest at $x = A$, it oscillates back and forth in the potential well between $x = +A$ and $x = -A$.

Motion described by a potential function is said to be *conservative*. For such motion, the energy

$$E = T + V \tag{1.44}$$

is constant. In terms of the kinetic energy T,

$$T = \frac{mv^2}{2} = E - V \tag{1.45}$$

Forbidden Domains

From (1.45) we see that if $V > E$, then $T < 0$ and the velocity becomes imaginary. In classical physics, particles are excluded from such domains. They are called *forbidden regions*. Again consider a one-dimensional problem with potential $V(x)$ shown in Fig. 1.18. The constant energy E is superimposed on this diagram. Segments AB and

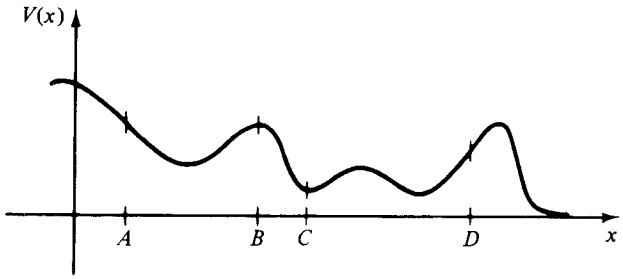


FIGURE 1.16 Arbitrary potential function.

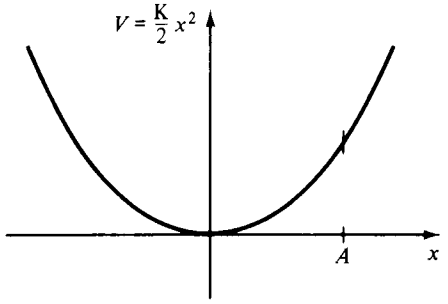


FIGURE 1.17 Spring potential.

CD are forbidden regions. Points A, B, C, and D are *stationary* or *turning* points. Since $E = V$ at these points, $T = 0$ and $\dot{x} = 0$. Suppose that a particle is started from rest from the point C. What is the subsequent motion? The particle is trapped in the potential well between B and C. It accelerates down the hill, slows down in climbing the middle peak, then slows down further in climbing to B, where it comes to rest and turns around. This periodic motion continues without end.

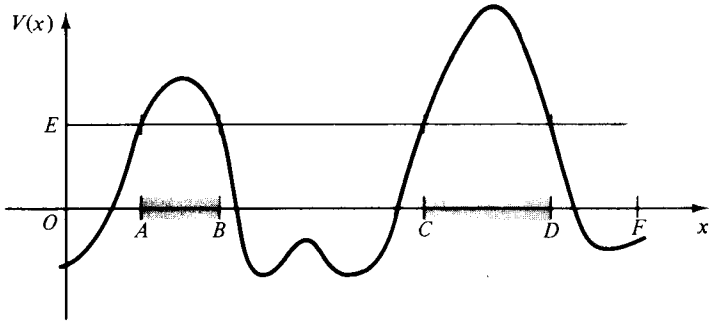


FIGURE 1.18 Forbidden domains at energy E.

The one-dimensional potential depicted in Fig. 1.18 can be effected by appropriately charging and spacing a linear array of plates with holes bored along the axis. The potential depicted in Fig. 1.18 is seen by an electron constrained to move along this (x) axis.

PROBLEMS

1.18 A particle constrained to move in one dimension (x) is in the potential field

$$V(x) = \frac{V_0(x - a)(x - b)}{(x - c)^2} \qquad (0 < a < b < c < \infty)$$

(a) Make a sketch of V.

(b) Discuss the possible motions, forbidden domains, and turning points. Specifically, if the particle is known to be at $x = -\infty$ with

$$E = \frac{3V_0}{c - b}(b - 4a + 3c)$$

at which value of x does it reflect?

1.19 A particle of mass m moves in a "central potential," $V(r)$, where r denotes the radial displacement of the particle from a fixed origin.

(a) What is the (vector) force on the particle? Recall here the components of the ∇ operator in spherical coordinates.

(b) Show that the angular momentum $\mathbf{L}$ of the particle about the origin is constant. (*Hint:* Calculate the time derivative of $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ and recall that $\mathbf{p} = m\dot{\mathbf{r}}$.)

(c) Show that the energy of the particle may be written

$$E = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + V(r)$$

(d) From Hamilton's equations obtain a "one-dimensional" equation for $\dot{p}_r$, in the form

$$\dot{p}_r = -\frac{\partial}{\partial r} V_{\text{eff}}(r)$$

where V_{eff} denotes an "effective" potential that is a function of r only.

(e) For the case of gravitational attraction between two masses (M, m), $V = -GmM/r$, where G is the gravitational constant. Make a sketch of V_{eff} versus r for this case. Use this sketch to establish the conditions for circular motion (assume that M is fixed in space) for a given value of L^2.

1.20 Complex variables play an important role in quantum mechanics. The following two problems are intended as a short review.

If

$$\psi = |\psi| \exp(i\alpha_1)$$
$$\chi = |\chi| \exp(i\alpha_2)$$

show that

$$|\psi + \chi|^2 = |\psi|^2 + |\chi|^2 + 2|\psi\chi| \cos(\alpha_1 - \alpha_2)$$

1.21 Use the expansion

$$e^{i\theta} = \cos\theta + i \sin\theta$$

to derive the following relations.

(a) $\cos(\theta_1 + \theta_2) = \cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2$

(b) $\sin(\theta_1 + \theta_2) = \cos\theta_1 \sin\theta_2 + \sin\theta_1 \cos\theta_2$

(c) $2\sin\theta_1 \cos\theta_2 = \sin(\theta_1 - \theta_2) + \sin(\theta_1 + \theta_2)$

(d) $2\cos\theta_1 \cos\theta_2 = \cos(\theta_1 + \theta_2) + \cos(\theta_1 - \theta_2)$

(e) $2\cos^2\theta = 1 + \cos 2\theta$

(f) $2\sin^2\theta = 1 - \cos 2\theta$

(g) $e^{i\theta} - 1 = 2ie^{i\theta/2}\sin(\theta/2)$

(h) $\frac{1}{2}|e^{i\theta_1} + e^{i\theta_2}|^2 = \frac{1}{2}(e^{i\theta_1} + e^{i\theta_2})(e^{i\theta_1} + e^{i\theta_2})^* = 1 + \cos(\theta_1 - \theta_2)$

CHAPTER 3

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

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

3.1 OBSERVABLES AND OPERATORS

Postulate I

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

$$\hat{A}\varphi = a\varphi \tag{3.1}$$

an eigenvalue equation

TABLE 3.1 Examples of operators

$\hat{D} = \partial/\partial x$	$\hat{D}\varphi(x) = \partial\varphi(x)/\partial x$
$\hat{\Delta} = -\partial^2/\partial x^2 = -\hat{D}^2$	$\hat{\Delta}\varphi(x) = -\partial^2\varphi(x)/\partial x^2$
$\hat{M} = \partial^2/\partial x\,\partial y$	$\hat{M}\varphi(x, y) = \partial^2\varphi(x, y)/\partial x\,\partial y$
$\hat{I}$ = operation that leaves φ unchanged	$\hat{I}\varphi = \varphi$
$\hat{Q} = \int_0^1 dx'$	$\hat{Q}\varphi(x) = \int_0^1 dx'\varphi(x')$
$\hat{F}$ = multiplication by $F(x)$	$\hat{F}\varphi(x) = F(x)\varphi(x)$
$\hat{B}$ = division by the number 3	$\hat{B}\varphi(x) = \frac{1}{3}\varphi(x)$
$\hat{\Theta}$ = operator that annihilates φ	$\hat{\Theta}\varphi = 0$
$\hat{P}$ = operator that changes φ to a specific polynomial of φ	$\hat{P}\varphi = \varphi^3 - 3\varphi^2 - 4$
$\hat{G}$ = operator that changes φ to the number 8	$\hat{G}\varphi = 8$

has a solution φ. The function φ is called the *eigenfunction* of $\hat{A}$ corresponding to the eigenvalue a.

Examples of mathematical operators, which are not necessarily connected to physics, are offered in Table 3.1. (Labels such as D, G, and M are of no special significance.) An operator operates on a function and makes it something else (except for the identity operator $\hat{I}$).

Let us now turn to operators that correspond to physical observables. Two very important such observables are the momentum and the energy.

The Momentum Operator $\hat{\mathbf{p}}$

The operator that corresponds to the observable linear momentum is

$$\hat{\mathbf{p}} = -i\hbar\nabla \tag{3.2}$$

What are the eigenfunctions and eigenvalues of the momentum operator? Consider that the particle (whose momentum is in question) is constrained to move in one dimension (x). Then the momentum has only one nonvanishing component, p_x. The corresponding operator is

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.3}$$

The eigenvalue equation for this operator is

$$-i\hbar\frac{\partial}{\partial x}\varphi = p_x\varphi \tag{3.4}$$

The values p_x represent the *only* possible values that measurement of the x component of momentum will yield. The eigenfunction $\varphi(x)$ corresponding to a specific value of

momentum (p_x) is such that $|\varphi|^2\,dx$ is the probability of finding the particle (with momentum p_x) in the interval x, $x + dx$. Suppose we stipulate that the particle is a *free* particle. It is unconfined (along the x axis). For this case there is no boundary condition on φ and the solution to (3.4) is

$$\varphi = A \exp\left(\frac{ip_x x}{\hbar}\right) = Ae^{ikx} \tag{3.5}$$

where we have labeled the wavenumber k and have deleted the subscript x.

$$k = \frac{p}{\hbar} \tag{3.6}$$

The eigenfunction given by (3.5) is a periodic function (in x). To find its wavelength λ, we set

$$e^{ikx} = e^{ik(x+\lambda)} \tag{3.7}$$

$$1 = e^{ik\lambda} = \cos k\lambda + i \sin k\lambda$$

which is satisfied if

$$\cos k\lambda = 1 \tag{3.8}$$

$$\sin k\lambda = 0$$

The first nonvanishing solution to these equations is

$$k\lambda = 2\pi \tag{3.9}$$

which (with 3.6) is equivalent to the de Broglie relation

$$p = \frac{h}{\lambda} \tag{3.10}$$

We conclude that the eigenfunction of the momentum operator corresponding to the eigenvalue p has a wavelength that is the de Broglie wavelength h/p.

In quantum mechanics it is convenient to speak in terms of wavenumber k instead of momentum p. In this notation one says that the eigenfunctions and eigenvalues of the momentum operator are

$$\varphi_k = Ae^{ikx}, \qquad p = \hbar k \tag{3.11}$$

The subscript k on φ_k denotes that there is a continuum of eigenfunctions and eigenvalues, $\hbar k$, which yield nontrivial solutions to the eigenvalue equation, (3.4).

The Energy Operator $\hat{H}$

The operator corresponding to the energy is the Hamiltonian $\hat{H}$, with momentum $\mathbf{p}$ replaced by its operator counterpart, $\hat{\mathbf{p}}$. For a single particle of mass m, in a potential field $V(\mathbf{r})$,

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \tag{3.12}$$

The eigenvalue equation for $\hat{H}$,

$$\hat{H}\varphi(\mathbf{r}) = E\varphi(\mathbf{r}) \tag{3.13}$$

is called the *time-independent Schrödinger equation*. It yields the possible energies E which the particle may have. Again consider the free particle. The energy of a free particle is purely kinetic, so

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \tag{3.14}$$

Constraining the particle to move in one dimension, the time-independent Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\varphi = E\varphi \tag{3.15}$$

In terms of the wave vector

$$k^2 = \frac{2mE}{\hbar^2} \tag{3.16}$$

(3.15) appears as

$$\varphi_{xx} + k^2\varphi = 0 \tag{3.17}$$

The subscript x denotes differentiation. For a free particle there are no boundary conditions and we obtain[1]

$$\varphi = Ae^{ikx} + Be^{-ikx} \tag{3.18}$$

This is the eigenfunction of $\hat{H}$ which corresponds to the energy eigenvalue

$$E = \frac{\hbar^2 k^2}{2m} \tag{3.19}$$

We have found above (3.11) that the momentum of a free particle is $\hbar k$. This is clearly the same $\hbar k$ that appears in (3.19), since for a free particle

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \tag{3.20}$$

[1] The solution to (3.17) with boundary conditions imposed is discussed in Section 4.1.

Note also that the eigenfunction of $\hat{H}$ (3.18), with $B = 0$, is also an eigenfunction of $\hat{p}$ (3.11). That $\hat{H}$ and $\hat{p}$ for a free particle have common eigenfunctions is a special case of a more general theorem to be discussed later.[1] The following simple argument demonstrates this fact. Let

$$\hat{p}\varphi = \hbar k\varphi \tag{3.21}$$

Let us see if φ is also an eigenfunction of $\hat{H}$ (for a free particle).

$$\hat{H}\varphi = \frac{\hat{p}}{2m}(\hat{p}\varphi) = \frac{\hat{p}(\hbar k\varphi)}{2m} = \frac{\hbar k}{2m}\hat{p}\varphi \tag{3.22}$$

$$= \frac{(\hbar k)^2}{2m}\varphi$$

It follows that φ is also an eigenfunction of $\hat{H}$.

Both the energy and momentum eigenvalues for the free particle comprise a continuum of values:

$$\boxed{E = \frac{\hbar^2 k^2}{2m} \qquad p = \hbar k} \tag{3.23}$$

That is, these are valid eigenvalues for *any* wavenumber k. The eigenfunction (of both $\hat{H}$ and $\hat{p}$) corresponding to these eigenvalues is

$$\varphi_k = Ae^{ikx} \tag{3.24}$$

If the free particle is in this state, measurement of its momentum will definitely yield $\hbar k$, and measurement of its energy will definitely yield $(\hbar^2 k^2/2m)$.

Suppose that we measure its position x; what do we find? Well, where is the particle most likely to be? Again we call on the Born postulate. If the particle is in the state φ_k, the probability density relating to the probability of finding the particle in the interval x, $x + dx$, is

$$|\varphi_k|^2 = |A|^2 = \text{constant} \tag{3.25}$$

The probability density is the same constant value for all x. That means we would be equally likely to find the particle at any point from $x = -\infty$ to $x = +\infty$. This is a statement of maximum uncertainty which is in agreement with the Heisenberg uncertainty principle. In the state φ_k, it is known with absolute certainty that measurement of momentum yields $\hbar k$. Therefore, for the state φ_k, $\Delta p = 0$, whence $\Delta x = \infty$.

We mentioned in Section 2.7 that E and t are complementary variables; that is, they obey the relation $\Delta E\, \Delta t \geq \hbar$. Specifically, this means that if the energy is uncertain by amount ΔE, *the time it takes to measure* E is uncertain by $\Delta t \geq \hbar/\Delta E$. Now for the problem at hand, in the state φ_k, it is certain that measurement of E yields $\hbar^2 k^2/2m$.

[1] The commutator theorem, Chapter 5.

Therefore, $\Delta E = 0$. To measure E we have to let the particle interact with some sort of energy-measuring apparatus, say a plate with a spring attached to measure the momentum imparted to the plate when the particle hits it head on. Well, if the plate with attached spring is placed in the path of the particle, how long must we wait before we detect something? We can wait 10^{-8} s—or we can wait 10^{10} yr. The uncertainty Δt is infinite in the present case, since there is an infinite uncertainty in Δx.

PROBLEMS

3.1 For each of the operators listed in Table 3.1 ($\hat{D}$, $\hat{\Delta}$, $\hat{M}$, etc.), construct the square, that is, $\hat{D}^2$, $\hat{\Delta}^2$, ...

Answer (partial)

$$\hat{I}^2\varphi = \hat{I}\varphi = \varphi$$

$$\hat{Q}^2\varphi = \hat{Q}\int_0^1 dx'\varphi(x') = \int_0^1 dx'' \int_0^1 dx'\varphi(x')$$

$$\hat{F}^2\varphi = F^2\varphi$$

$$\hat{B}^2\varphi = \tfrac{1}{9}\varphi$$

$$\hat{P}^2\varphi = \hat{P}(\hat{P}\varphi) = (\varphi^3 - 3\varphi^2 - 4)^3 - 3(\varphi^3 - 3\varphi^2 - 4)^2 - 4$$

3.2 The inverse of an operator $\hat{A}$ is written $\hat{A}^{-1}$. It is such that

$$\hat{A}^{-1}\hat{A}\varphi = \hat{I}\varphi = \varphi$$

Construct the inverses of $\hat{D}$, $\hat{I}$, $\hat{F}$, $\hat{B}$, $\hat{\Theta}$, $\hat{G}$, provided that such inverses exist.

3.3 An operator $\hat{O}$ is *linear* if

$$\hat{O}(a\varphi_1 + b\varphi_2) = a\hat{O}\varphi_1 + b\hat{O}\varphi_2$$

where a and b are arbitrary constants. Which of the operators in Table 3.1 are linear and which are nonlinear?

3.4 The displacement operator $\hat{\mathscr{D}}$ is defined by the equation

$$\hat{\mathscr{D}}f(x) = f(x + \zeta)$$

Show that the eigenfunctions of $\hat{\mathscr{D}}$ are of the form

$$\varphi_\beta = e^{\beta x}g(x)$$

where

$$g(x + \zeta) = g(x)$$

and β is any complex number. What is the eigenvalue corresponding to φ_β?

3.5 An electron moves in the x direction with de Broglie wavelength 10^{-8} cm.

(a) What is the energy of the electron (in eV)?

(b) What is the time-independent wavefunction of the electron?

3.2 MEASUREMENT IN QUANTUM MECHANICS

Postulate II

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

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

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

The operator equation appears as

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

Dirac Delta Function

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

$$\int_{-\infty}^{\infty} f(x')\delta(x - x')\,dx' = f(x)$$

$$\int_{-\infty}^{\infty} \delta(x - x')\,dx' = 1 \tag{3.27}$$

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

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

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

or equivalently, in terms of the single variable y

$$\int_{-\infty}^{\infty} f(y)\delta(y)\,dy = f(0)$$
$$\int_{-\infty}^{\infty} \delta(y)\,dy = 1 \tag{3.28}$$

The second defining property is the value

$$\delta(y) = 0 \qquad (\text{for } y \neq 0) \tag{3.29}$$

A sketch of $\delta(y)$ is given in Fig. 3.1. Properties of $\delta(y)$ are usually proved with the aid of the defining integral (3.27). For instance, consider the relation

$$y\delta'(y) = -\delta(y) \tag{3.30}$$

To establish this relation we employ a *test function* $f(y)$ and perform the following integration by parts.

$$\begin{aligned}\int_{-\infty}^{\infty} f(y)y\delta'(y)\,dy &= \int_{-\infty}^{\infty} \frac{d}{dy}(fy\delta)\,dy - \int_{-\infty}^{\infty} \delta\frac{d}{dy}(yf)\,dy \\ &= -\int_{-\infty}^{\infty} \delta(y)\left(y\frac{df}{dy} + f\right)dy = -\int_{-\infty}^{\infty} \delta(y)f(y)\,dy\end{aligned} \tag{3.31}$$

which establishes (3.30).

The student should not lose sight of the fact that $\hat{x}$, when operating on a function $f(x)$, merely represents multiplication by x. For example, $\hat{x}f(x) = xf(x)$. It is only with regard to its own eigenvalue problem that $\hat{x}$ assumes a somewhat more abstract quality. These topics will be returned to in Chapter 11 and discussed further in Appendix A.

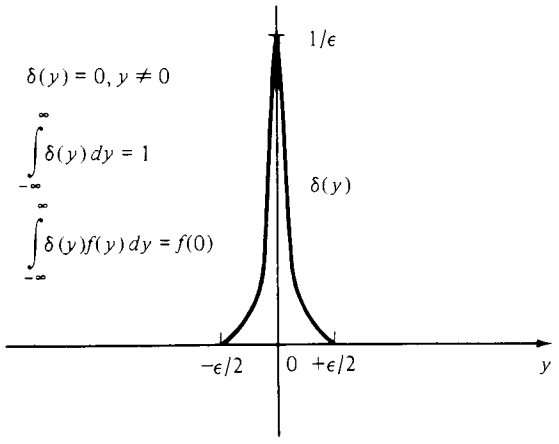


FIGURE 3.1 Dirac delta function $\delta(y)$. The curve is distorted to bring out essential features. A more accurate picture is obtained in the limit $\epsilon \to 0$.

PROBLEMS

3.6 Establish the following properties of $\delta(y)$.

(a) $\delta(y) = \delta(-y)$

(b) $\delta'(y) = -\delta'(-y)$

(c) $y\delta(y) = 0$

(d) $\delta(ay) = a^{-1}\,\delta(y)$

(e) $\delta(y^2 - a^2) = (2a)^{-1}[\delta(y - a) + \delta(y + a)]$

(f) $\displaystyle\int_{-\infty}^{\infty} \delta(a - y)\,\delta(y - b)\,dy = \delta(a - b)$

(g) $f(y)\,\delta(y - a) = f(a)\,\delta(y - a)$

(h) $y\,\delta'(y) = -\delta(y)$

(i) $\displaystyle\int g(y)\,\delta[f(y) - a]\,dy = \left.\frac{g(y)}{df/dy}\right|_{\substack{y = y_0 \\ f(y_0) = a}}$

3.7 Show that the following are valid representations of $\delta(y)$:

(a) $\displaystyle 2\pi\delta(y) = \int_{-\infty}^{\infty} e^{iky}\,dk$

(b) $\displaystyle \pi\delta(y) = \lim_{\eta \to \infty} \frac{\sin \eta y}{y}$

Note: In mathematics, an object such as $\delta(y)$; which is defined in terms of its integral properties, is called a *distribution*. Consider all $\chi(y)$ defined on the interval $(-\infty, \infty)$ for which

$$\int_{-\infty}^{\infty} |\chi(y)|^2\,dy < \infty$$

Then two distributions, δ_1 and δ_2, are *equivalent* if for all $\chi(y)$,

$$\int_{-\infty}^{\infty} \chi\,\delta_1\,dy = \int_{-\infty}^{\infty} \chi\,\delta_2\,dy$$

When one establishes that a mathematical form such as $\int_{-\infty}^{\infty} \exp(iky)\,dy$ is a representation of $\delta(y)$, one is in effect demonstrating that these two objects are *equivalent as distributions.*

3.8 Show that the continuous set of eigenfunctions $\{\delta(x - x')\}$ obeys the "orthonormality" condition

$$\int_{-\infty}^{\infty} \delta(x - x')\,\delta(x - x'')\,dx = \delta(x' - x'')$$

3.9 (a) Show that $\delta(\sqrt{x}) = 0$.

(b) Evaluate $\delta(\sqrt{x^2 - a^2})$.

3.3 THE STATE FUNCTION AND EXPECTATION VALUES

Postulate III

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

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

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

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

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

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

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

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

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

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

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

be especially true if the deviation of values of C from the mean value $\langle C \rangle$ is not large. As discussed in Section 2.7, a measure of this spread of values about the value $\langle C \rangle$ is given by the mean-square deviation ΔC, defined through

$$(\Delta C)^2 = \langle (C - \langle C \rangle)^2 \rangle = \langle C^2 \rangle - \langle C \rangle^2 \tag{3.36}$$

In order to become familiar with the operational use of postulate III, we work out the following one-dimensional problem. A particle is known to be in the state

$$\psi(x, t) = A \exp\left[\frac{-(x - x_0)^2}{4a^2}\right] \exp\left(\frac{ip_0 x}{\hbar}\right) \exp(i\omega_0 t) \tag{3.37}$$

The lengths x_0 and a are constants, as are the momentum p_0 and frequency ω_0. The (real) constant A is determined through normalization. This then ensures that $\psi^*\psi$ is a numerically correct probability density.

$$\begin{aligned} \int_{-\infty}^{\infty} |\psi|^2 \, dx &= A^2 a \int_{-\infty}^{\infty} e^{-\eta^2/2} \, d\eta = \sqrt{2\pi} \, A^2 a = 1 \\ A^2 &= \frac{1}{a\sqrt{2\pi}} \end{aligned} \tag{3.38}$$

The nondimensional "dummy" variable η and constant η_0 are such that

$$\begin{aligned} \eta &= \frac{x - x_0}{a} \\ x &= a(\eta + \eta_0) \\ \eta_0 &= \frac{x_0}{a} \end{aligned} \tag{3.39}$$

Having obtained A, we may now calculate the expectation of x:

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} \psi^* \hat{x} \psi \, dx = \int_{-\infty}^{\infty} \psi^* x \psi \, dx \\ &= A^2 a^2 \int_{-\infty}^{\infty} e^{-\eta^2/2} (\eta + \eta_0) \, d\eta = a\eta_0 \left(aA^2 \int_{-\infty}^{\infty} e^{-\eta^2/2} \, d\eta \right) \end{aligned} \tag{3.40}$$

which, with the normalization condition (3.38), gives

$$\langle x \rangle = a\eta_0 = x_0 \tag{3.41}$$

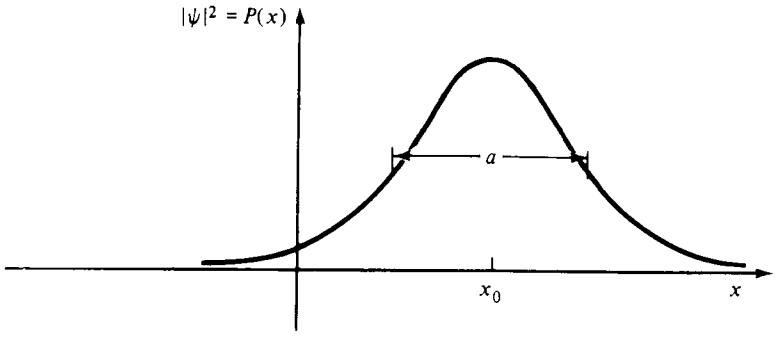


FIGURE 3.2 Gaussian probability density with variance a^2. The variance measures the spread of $P(x)$ about the mean, $\langle x \rangle = x_0$. In quantum mechanics the square root of variance a is called the uncertainty in x and is denoted as Δx, so for the case under discussion,

$$a = \Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

[Note that integration of the odd integrand $\eta \exp(-\eta^2)$ in (3.40) vanishes.] That x_0 is the proper value for $\langle x \rangle$ is evident from the sketch of $|\psi|^2$ shown in Fig. 3.2.

If we call

$$|\psi|^2 \, dx = P(x) \, dx \tag{3.42}$$

the probability of finding the particle in the interval x, $x + dx$, then

$$\langle x \rangle = \int_{-\infty}^{\infty} xP(x) \, dx \tag{3.43}$$

This is consistent with definition (3.35).

The probability density

$$P(x) = \frac{1}{a\sqrt{2\pi}} \exp\left[\frac{-(x - x_0)^2}{2a^2}\right]$$

is called the *Gaussian* or *normal distribution*, and a^2 is called the *variance* of x. It is a measure of the spread of $P(x)$ about the mean value

$$\langle x \rangle = x_0$$

As shown in Problem 3.10, the variance of x is the same as the mean-square deviation, $(\Delta x)^2$.

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2 = a^2 + x_0{}^2 - x_0{}^2 = a^2$$

If it is known that a particle is in the state $\psi(x)$ at a given instant of time, and that in this state, $\langle x \rangle = x_0$, one may then ask: With what certainty will measurement of x find the value x_0? A measure of the relative *uncertainty* is given by the square root of the variance, Δx. If this value is large (compared to $\langle x \rangle$), one may say with little certainty that measurement will find the particle at x_0. If, on the other hand, Δx is small, one is more certain that measurement will find the particle at $x = x_0$. In quantum mechanics Δx is called the *uncertainty in x*, introduced previously in Section 2.7.

Next, we calculate the expectation of the momentum for a particle in the state ψ, (3.37).

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p} \psi \, dx = \int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi \, dx \tag{3.44}$$

$$= A^2 a \int_{-\infty}^{\infty} \left(p_0 + \frac{i\hbar}{2a} \eta \right) e^{-\eta^2/2} \, d\eta = p_0 \left(A^2 a \int_{-\infty}^{\infty} e^{-\eta^2/2} \, d\eta \right)$$

$$= p_0$$

It follows that the parameter p_0 which appears in the state function ψ is the average value of p. In any given measurement of p, any of a continuum of values can be obtained. Only in the event that ψ is an eigenfunction of $\hat{p}$ would measurement of p yield one definite value (i.e., the eigenvalue corresponding to the said eigenfunction).

PROBLEMS

3.10 For the state ψ, given by (3.37), show that

$$(\Delta x)^2 = a^2$$

Argue the consistency of this conclusion with the change in shape that $|\psi|^2$ suffers with a change in the parameter a.

3.11 Calculate the uncertainty Δp for a particle in the state ψ given by (3.37). Do you find your answer to be consistent with the uncertainty principle? (In this problem one must calculate $\langle \hat{p}^2 \rangle$. The operator $\hat{p}^2 = -\hbar^2 \, \partial^2/\partial x^2$.)

3.12 Let s be the number of spots shown by a die thrown at random.

(a) Calculate $\langle s \rangle$.

(b) Calculate Δs.

3.13 The number of hairs (N_l) on a certain rare species can only be the number 2^l ($l = 0, 1, 2, \ldots$). The probability of finding such an animal with 2^l hairs is $e^{-1}/l!$ What is the expectation, $\langle N \rangle$? What is ΔN?

3.4 TIME DEVELOPMENT OF THE STATE FUNCTION

Postulate IV

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

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

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

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

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

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

Substitution into (3.45) gives

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

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

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

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

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

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

The second equation (3.50) is simply solved to give the oscillating form

$$T(t) = A \exp\left(-\frac{iEt}{\hbar}\right) \tag{3.51}$$

Suppose that we solve the time-independent Schrödinger equation and obtain the eigenfunctions and eigenvalues

$$\hat{H}\varphi_n = E_n\varphi_n \tag{3.52}$$

For each such eigensolution, there is a corresponding eigensolution to the time-dependent Schrödinger equation

$$\psi_n(\mathbf{r}, t) = A\varphi_n(\mathbf{r}) \exp\left(-\frac{iE_n t}{\hbar}\right) \tag{3.53}$$

In equations (3.52) and (3.53) the index n denotes the set of integers $n = 1, 2, \ldots$. This notation is appropriate to the case where solution to the time-independent Schrödinger equation gives a discrete set of eigenfunctions, $\{\varphi_n\}$. Such is the case for problems that pertain to a finite system, such as a particle confined to a finite domain of space. We will encounter this property in Chapter 4 when we solve the problem of a bead constrained to move on a straight wire strung between two impenetrable walls.

In the one-dimensional free-particle case treated in Section 3.2, one obtains a continuum of eigenfunctions $\varphi_k(x)$ and, correspondingly, a continuum of eigenvalues. E_k. To repeat, these values are

$$\hat{H}\varphi_k = E_k\varphi_k \tag{3.54}$$

$$\varphi_k = A \exp(ikx), \qquad E_k = \frac{\hbar^2 k^2}{2m} \tag{3.55}$$

For each such time-independent solution, there is a solution to the time-dependent Schrödinger equation

$$\psi_k(x, t) = Ae^{i(kx - \omega t)} \tag{3.56}$$

where we have labeled

$$\hbar\omega = E_k \tag{3.57}$$

The structure of the solution (3.56) is characteristic of a propagating wave. More generally, any function of x and t of the form

$$f(x, t) = f(x - vt) \tag{3.58}$$

represents a wave propagating in the positive x direction with velocity v. To see this, we note the following property of f:

$$f(x + v\,\Delta t, t + \Delta t) = f(x, t) \tag{3.59}$$

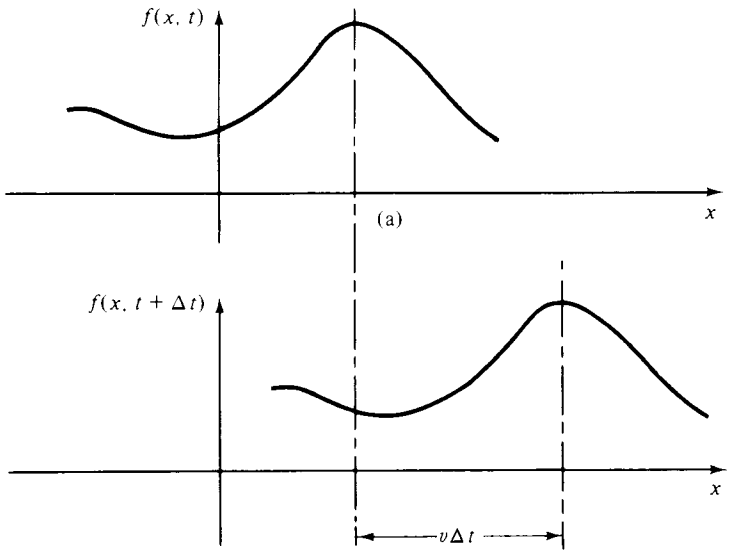


FIGURE 3.3 Propagating wave, $f(x, t) = f(x - vt)$: (a) at time t; (b) at time $t + \Delta t$.

At any given instant t, one may plot the x dependence of f (Fig. 3.3). If t increases to $t + \Delta t$, this curve is displaced to the right (as a rigid body) by the amount $v\,\Delta t$. We conclude from these arguments that the disturbance f (3.58) propagates with the wave speed v.

Now let us return to the free-particle eigenstate, (3.56), and rewrite it in the form

$$\psi_k(x, t) = A \exp\left[ik\left(x - \frac{\omega}{k}t\right)\right] \tag{3.60}$$

Comparison with the waveform (3.58) indicates that (1) ψ_k is a propagating wave (moving to the right), and (2) the speed of this wave is

$$v = \frac{\omega}{k} = \frac{\hbar\omega}{\hbar k} = \frac{p^2/2m}{p} = \frac{p}{2m} = \frac{v_{CL}}{2} \tag{3.61}$$

The velocity v_{CL} represents the classical velocity of a particle of mass m and momentum p. Thus we find that the wave speed of the state function of a particle with well-defined momentum, $p = \hbar k$, is half the classical speed, $v_{CL} = p/m$.

This discrepancy is due to the following fact. Suppose that we calculate the probability density corresponding to the state given in (3.56). We obtain the result that it is uniformly probable to find the particle anywhere along the x axis. This is not a

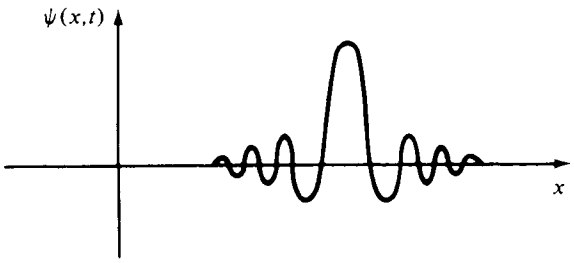


FIGURE 3.4 Wave packet at a given instant of time t.

typical classical property of a particle. The state function that better represents a classical (localized) particle is a wave packet. The shape of such a function is sketched in Fig. 3.4. Such a state may be constructed as a sum of eigenstates of the form given in (3.56) (a Fourier series). The velocity with which the packet moves is called the *group velocity*,[1]

$$v_g = \frac{\partial \omega}{\partial k} \tag{3.62}$$

For a wave packet composed of free-particle eigenstates, v_g takes the value

$$v_g = \frac{\partial \hbar\omega}{\hbar\, \partial k} = \frac{\partial(\hbar^2 k^2/2m)}{\hbar\, \partial k} = \frac{\hbar k}{m} = \frac{p}{m} \tag{3.63}$$

$$= v_{CL}$$

The value of k that enters the formula for v_g is the value about which there is a superabundance of ψ_k component waves. These topics will be more fully developed in Chapter 4. For the moment we are concerned only with the identification given in (3.63).

PROBLEMS

3.14 Describe the evolution in time of the following wavefunctions:

$$\psi_1 = A \sin \omega t \cos k(x + ct)$$
$$\psi_2 = A \sin (10^{-5}\, kx) \cos k(x - ct)$$
$$\psi_3 = A \cos k(x - ct) \sin [10^{-5} k(x - ct)]$$

3.15 What is the expectation of momentum $\langle p \rangle$ for a particle in the state

$$\psi(x, t) = Ae^{-(x/a)^2} e^{-i\omega t} \sin kx?$$

[1] The concepts of phase and group velocities are returned to in Section 6.1.

3.5 SOLUTION TO THE INITIAL-VALUE PROBLEM IN QUANTUM MECHANICS

Functions of Operators

The time-dependent Schrödinger equation permits solution of the initial-value problem: given the initial value of the state function $\psi(\mathbf{r}, 0)$, determine $\psi(\mathbf{r}, t)$. We will formulate the solution to the problem for a time-independent Hamiltonian. The more general case is given as an exercise (Problem 3.18).

First we rewrite (3.45) in the form

$$\frac{\partial}{\partial t}\psi(\mathbf{r}, t) + \frac{i\hat{H}}{\hbar}\psi(\mathbf{r}, t) = 0 \tag{3.64}$$

Next, we multiply this equation (from the left) by the integrating factor $\hat{U}^{-1}$

$$\hat{U}^{-1} = \exp\left(\frac{it\hat{H}}{\hbar}\right) \tag{3.65}$$

which is the inverse of

$$\hat{U} \equiv \exp\left(-\frac{it\hat{H}}{\hbar}\right) \tag{3.66}$$

This function of the operator, $\hat{H}$, is itself an operator. It is defined in terms of its Taylor series expansion.

$$\hat{U}^{-1} = \exp\left(\frac{it\hat{H}}{\hbar}\right) = 1 + \frac{it\hat{H}}{\hbar} + \frac{1}{2!}\left(\frac{it\hat{H}}{\hbar}\right)^2 + \cdots \tag{3.67}$$

More generally for any operator $\hat{A}$, the function operator $f(\hat{A})$ is defined in terms of a series in powers of $\hat{A}$. A few examples are provided in the problems.

Let us return to the problem under discussion. Multiplying the time-dependent Schrödinger equation through by the integrating factor (3.65), one obtains the equation

$$\frac{\partial}{\partial t}\left[\exp\left(\frac{it\hat{H}}{\hbar}\right)\psi(\mathbf{r}, t)\right] = 0 \tag{3.68}$$

Integrating over the time interval $(0, t)$ gives

$$\exp\left(\frac{it\hat{H}}{\hbar}\right)\psi(\mathbf{r}, t) - \psi(\mathbf{r}, 0) = 0 \tag{3.69}$$

Multiplying this equation through by $\hat{U}$ gives the desired result:

$$\boxed{\psi(\mathbf{r}, t) = \exp\left(-\frac{it\hat{H}}{\hbar}\right)\psi(\mathbf{r}, 0) = \hat{U}\psi(\mathbf{r}, 0)} \tag{3.70}$$

Here we have used the fact that

$$\hat{U}\hat{U}^{-1} = \exp\left(-\frac{it\hat{H}}{\hbar}\right)\exp\left(\frac{it\hat{H}}{\hbar}\right) = \hat{I} \tag{3.71}$$

where $\hat{I}$ is the identity operator.

Suppose that in solution (3.70) we choose the initial state to be an eigenstate of $\hat{H}$. Call it φ_n, so that

$$\begin{aligned} \psi_n(\mathbf{r}, 0) &= \varphi_n(\mathbf{r}) \\ \hat{H}\varphi_n &= E_n\varphi_n \end{aligned} \tag{3.72}$$

By virtue of the theorem presented in Problem 3.16,

$$\begin{aligned} \psi_n(\mathbf{r}, t) &= \exp\left(-\frac{it\hat{H}}{\hbar}\right)\varphi_n = \exp\left(-\frac{iE_nt}{\hbar}\right)\varphi_n \\ &= e^{-i\omega_n t}\varphi_n(\mathbf{r}) \\ \hbar\omega_n &= E_n \end{aligned} \tag{3.73}$$

This is the solution of the time-dependent Schrödinger equation, derived in Section 3.4 by the technique of separation of variables. The solution given in (3.70) is more general. It exhibits the development of an arbitrary initial state $\psi(\mathbf{r}, 0)$ in time. It will be used extensively in the chapters to follow, where the student will gain a more workable understanding of the equation.

As a final topic of discussion in this chapter we note the following. Suppose that a system is in an eigenstate of the Hamiltonian at $t = 0$, described by (3.72). At this (initial) time the expectation of an observable A is

$$\langle A\rangle_{t=0} = \int \psi^*(\mathbf{r}, 0)\hat{A}\psi(\mathbf{r}, 0)\, d\mathbf{r} = \int \varphi_n^*\hat{A}\varphi_n\, d\mathbf{r} \tag{3.74}$$

What is $\langle A\rangle$ at a later time, $t > 0$? The state of the system at $t > 0$ is given by (3.73):

$$\psi_n(\mathbf{r}, t) = e^{i\omega_n t}\varphi_n(\mathbf{r}) \tag{3.75}$$

so that at $t > 0$ (assuming that $\partial \hat{A}/\partial t = 0$),

$$\langle A \rangle_t = \int \psi^*(\mathbf{r}, t) \hat{A} \psi(\mathbf{r}, t)\, d\mathbf{r} = e^{+i\omega_n t} e^{-i\omega_n t} \int \varphi_n^* \hat{A} \varphi_n\, d\mathbf{r}$$

$$= \int \varphi_n^* \hat{A} \varphi_n\, d\mathbf{r} = \langle A \rangle_{t=0} \tag{3.76}$$

$$\boxed{\langle A \rangle_{t>0} = \langle A \rangle_{t=0} \qquad \text{in a stationary state}}$$

The expectation of *any* observable is constant in time, if at any instant in time the system is in an eigenstate of the Hamiltonian. For this reason eigenstates of the Hamiltonian are called *stationary states.*

$$\boxed{\psi_n(\mathbf{r}, t) = e^{-i\omega_n t} \varphi_n(\mathbf{r}) \qquad \text{a stationary state}} \tag{3.77}$$

In the first three sections of this chapter we encountered functions relevant to a system which are eigenfunctions of operators corresponding to observable properties of that same system. In what sense are these eigenfunctions related to the *state function* of the system? From postulate II we know that ideal measurement of A leaves the system in the eigenstate of $\hat{A}$ corresponding to the value of A that was found in measurement. Thus, the state function of the system immediately after measurement is this same eigenstate of $\hat{A}$. The state function then evolves in time according to (3.70).

PROBLEMS

3.16 Let the eigenfunctions and eigenvalues of an operator $\hat{A}$ be $\{\varphi_n\}$ and $\{a_n\}$, respectively, so that

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

Let the function $f(x)$ have the expansion

$$f(x) = \sum_{l=0}^{\infty} b_l x^l$$

Show that φ_n is an eigenfunction of $f(\hat{A})$ with eigenvalue $f(a_n)$. That is,

$$f(\hat{A})\varphi_n = f(a_n)\varphi_n$$

3.17 If $\hat{p}$ is the momentum operator in the x direction, and $f(x)$ is an arbitrary "well-behaved" function, show that

$$\exp\left(\frac{i\zeta\hat{p}}{\hbar}\right)f(x) = f(x + \zeta)$$

The constant ζ represents a small displacement. In this problem the student must demonstrate that the left-hand side of the equation above is the Taylor series expansion of the right-hand side about $\zeta = 0$.

3.18 If $\hat{H}$ is an explicit function of time, show that the solution to the initial-value problem (by direct differentiation) is

$$\psi(\mathbf{r}, t) = \exp\left[-\frac{i}{\hbar}\int_0^t dt'\hat{H}(t')\right]\psi(\mathbf{r}, 0)$$

You may assume that $\hat{H}(t)\hat{H}(t') = \hat{H}(t')\hat{H}(t)$.

3.19. What is the effect of operating on an arbitrary function $f(x)$ with the following two operators?

(a) $\hat{O}_1 \equiv (\partial^2/\partial x^2) - 1 + \sin^2(\partial^3/\partial x^3) + \cos^2(\partial^3/\partial x^3)$.

(b) $\hat{O}_2 \equiv \cos(2\partial/\partial x) + 2\sin^2(\partial/\partial x) + \int_a^b dx$.

3.20 (a) The time-dependent Schrödinger equation is of the form

$$a\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

Consider that a is an unspecified constant. Show that this equation has the following property. Let $\hat{H}$ be the Hamiltonian of a system composed of two independent parts, so that

$$\hat{H}(x_1, x_2) = \hat{H}_1(x_1) + \hat{H}_2(x_2)$$

and let the stationary states of system 1 be $\psi_1(x_1, t)$ and those of system 2 be $\psi_2(x_2, t)$. Then the stationary states of the composite system are

$$\psi(x_1, x_2) = \psi_1(x_1, t)\psi_2(x_2, t)$$

That is, show that this product form is a solution to the preceding equation for the given composite Hamiltonian.

Such a system might be two beads that are invisible to each other and move on the same straight wire. The coordinate of bead 1 is x_1 and the coordinate of bead 2 is x_2.

(b) Show that this property is not obeyed by a wave equation that is second order in time, such as

$$a^2\frac{\partial^2\psi}{\partial t^2} = \hat{H}\psi$$

(c) Arguing from the Born postulate, show that the wavefunction for a system composed of two independent components must be in the preceding product form, thereby disqualifying the wave equation in part (b) as a valid equation of motion for the wavefunction ψ.

Answer (partial)

(c) If the two components are independent of each other, the joint probability density describing the state of the system is given by

$$P_{12} = P_1 P_2$$

This, in turn, guarantees that the probability density associated with component 1,

$$P_1(x_1) = \int P_{12}(x_1, x_2)\, dx_2$$

is independent of the form of $P_2(x_2)$ (and vice versa). The product form for P_{12} is guaranteed by the product structure for the wavefunction $\psi(x_1, x_2)$.

3.21 It is established in Problem 3.20 that for the joint probability for two independent systems to be consistently described by the time-dependent Schrödinger equation, this equation must be of the form

$$a\frac{\partial \psi}{\partial t} = \hat{H}\psi$$

where a is some number. Show that for this equation to imply wave motion, a must be complex. You may assume that $\hat{H}$ has only real eigenvalues.

Answer

Following development of the general solution (3.70), we find that the given equation implies the solution

$$\psi(\mathbf{r}, t) = \exp\left(\frac{t\hat{H}}{a}\right)\psi(\mathbf{r}, 0)$$

Since $\hat{H}$ has only real eigenvalues, the time dependence of $\psi(\mathbf{r}, t)$ is nonoscillating. It modulates $\psi(\mathbf{r}, 0)$ in time and does not give propagation. Thus, if a is real, ψ cannot represent a propagating wave. (*Note*: The fact that a is complex implies that ψ is complex. These last two problems illustrate the necessity of complex wavefunctions in quantum mechanics.)