Chapter 1

MATHEMATICAL PRELIMINARIES

PHYSICAL CHEMISTRY is a science requiring the application of mathematics and mathematical reasoning to chemical problems. Emphasis on the use of mathematics is especially pronounced in the branch of physical chemistry dealing with quantum mechanics and molecular structure, and the purpose of this chapter is to outline briefly some of the mathematical tools needed by the student to understand the material that follows. Other mathematical procedures are introduced later as needed. The student interested in advanced work in physical chemistry should make his mathematical background as extensive as possible, and it is recommended that such students supplement the material in this chapter with additional study [1–4].

1-1 COORDINATE SYSTEMS

The purpose of a coordinate system is to make it convenient to describe a point, a curve, or a surface in space. There are many different kinds of coordinate systems, and four will be used in this text: (1) rectangular or Cartesian coordinates, (2) spherical polar coordinates, (3) cylindrical coordinates, and (4) confocal ellipsoidal coordinates. The choice of the kind of coordinates to use depends on the problem one is trying to solve. The coordinate system is always chosen to make the mathematical equations that describe the problem as simple as possible. Of course, any numerical result which one calculates must be independent of the choice of a coordinate system.

Cartesian coordinates are the most familiar. A point P in "Cartesian space" is represented by distances along three mutually perpendicular axes called X, Y, and Z (Figure 1-1). A rectangular coordinate system should always make use of the "right-hand rule." This rule states that, when the fingers of the *right* hand are curled so that they point from the X to the Y axis, the thumb points along Z.

The other kinds of coordinates are most conveniently expressed in terms of Cartesian coordinates. In spherical polar coordinates (Figure 1-2), a point $P(r, \theta, \phi)$ is represented by one distance r and two angles θ and ϕ. The coordinate r is the length of the line OP drawn from the origin to point P. The angle θ is called the polar angle, and is the angle between the Z axis and line OP. The angle ϕ is called the azimuthal angle and is the angle between the X axis and the projection of line OP in the XY plane. It is left for the student to show that the Cartesian coordinates of point P are related to the spherical polar coordinates by the relations

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned} \tag{1-1}$$

EXERCISE 1-1 Using Eq. 1-1 show that $(x^2 + y^2 + z^2) = r^2$.

Cylindrical coordinates are shown in Figure 1-3. The location of point P is given by two distances and one angle. The two distances are z and the

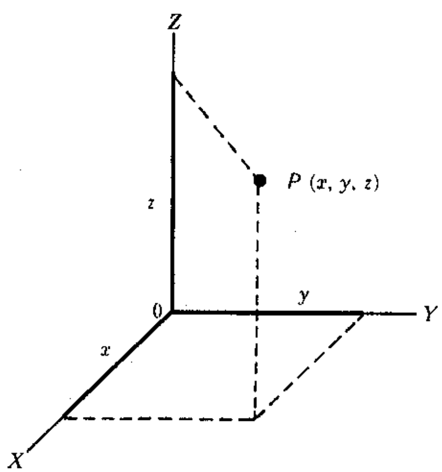

FIGURE 1-1 *Cartesian or rectangular coordinates. A point P(x, y, z) is defined by three distances along three mutually perpendicular axes.*

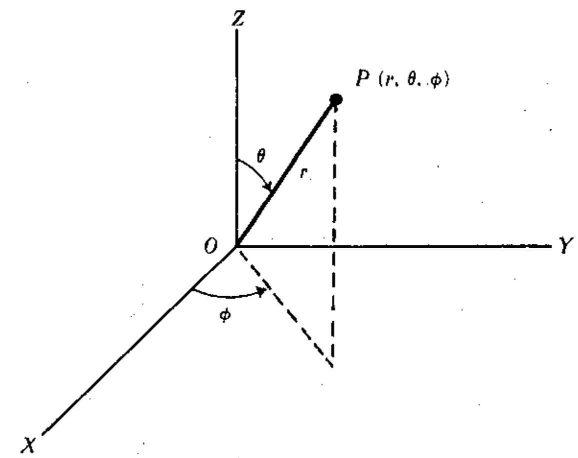

FIGURE 1-2 *Spherical polar coordinates. A point P(r, θ, φ,) is defined by two angles and one distance.*

length of the projection of line OP in the XY plane, ρ. The angle ϕ is the same as in spherical polar coordinates. The student may easily verify the relations

$$\begin{aligned} x &= \rho \cos \phi \\ y &= \rho \sin \phi \\ z &= z \end{aligned} \tag{1-2}$$

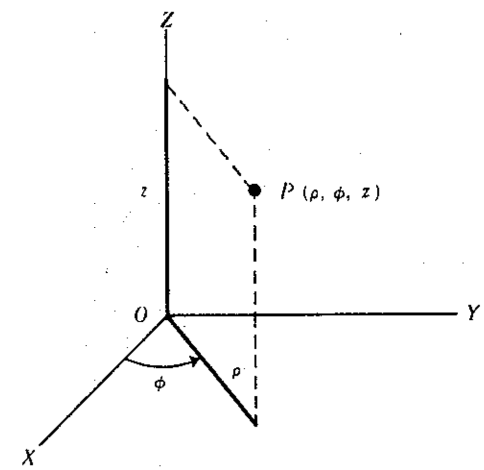

FIGURE 1-3 *Cylindrical coordinates. A point P(ρ, φ, z) is defined by two distances and one angle.*

Confocal ellipsoidal coordinates, sometimes just called elliptical coordinates, are shown in Figure 1-4. These coordinates are used for problems involving two centers, A and B, a fixed distance R apart. The lines AP and BP define a plane and the line formed by the intersection of this plane with the XY plane defines the angle ϕ. The point $P(\mu, \nu, \phi)$ can be defined by specifying the distances r_A and r_B along lines AP and BP, respectively, and the angle ϕ. Elliptical coordinates μ and ν are then defined as

$$\mu = \frac{r_A + r_B}{R} \qquad \nu = \frac{r_A - r_B}{R} R \tag{1-3}$$

The third coordinate is the angle ϕ described above. Keeping μ constant defines an ellipsoid of revolution with the points A and B as foci. Surfaces of constant ν are paraboloids of revolution about the z axis. These surfaces are shown in Figure 1-4, and some of their properties are illustrated in Exercises 1-7 and 1-8. The equations that express x, y, and z in terms of μ, ν, and ϕ are

$$x = \frac{R}{2}(\mu^2 - 1)^{\frac{1}{2}}(1 - \nu^2)^{\frac{1}{2}} \cos \phi$$

$$y = \frac{R}{2}(\mu^2 - 1)^{\frac{1}{2}}(1 - \nu^2)^{\frac{1}{2}} \sin \phi \tag{1-4}$$

$$z = \frac{R}{2}\mu\nu$$

In problems of quantum mechanics, one will often be required to evaluate integrals over all space. To do this, the differential volume element, called $d\tau$, must be known for each kind of coordinate system. These volume elements for the various coordinate systems, and the limits of integration that include all space, are

Cartesian

$d\tau = dx\,dy\,dz \qquad -\infty \le x \le +\infty$
$\qquad -\infty \le y \le +\infty$
$\qquad -\infty \le z \le +\infty$

Spherical polar

$d\tau = r^2 \sin\theta\,dr\,d\theta\,d\phi \qquad 0 \le r \le +\infty$
$\qquad 0 \le \theta \le \pi$
$\qquad 0 \le \phi \le 2\pi$

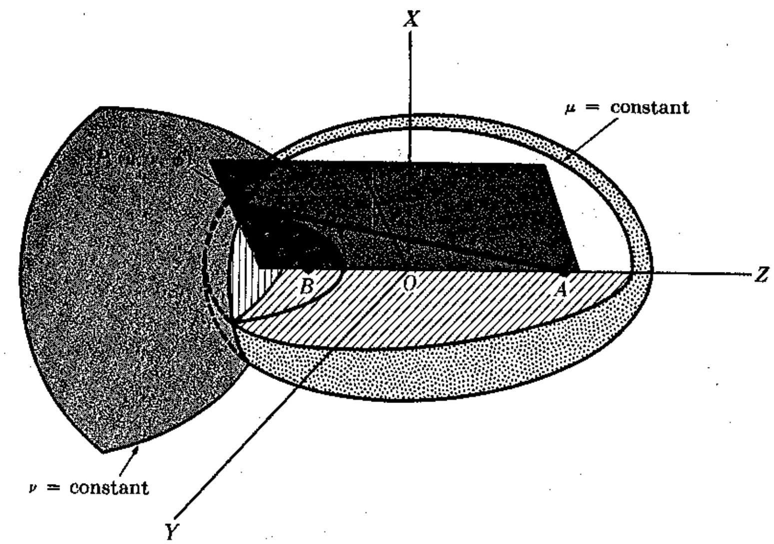

FIGURE 1-4 *Confocal ellipsoidal coordinates. Surfaces of constant μ are ellipsoids of revolution about the Z axis. Surfaces of constant ν are paraboloids of revolution. The intersection of these two surfaces defines a circle. The final coordinate ϕ specifies a point $P(\mu, \nu, \phi)$ on the circle.*

Cylindrical

$d\tau = \rho\,d\rho\,d\phi\,dz \qquad 0 \le \rho \le \infty$
$\qquad 0 \le \phi \le 2\pi$
$\qquad -\infty \le z \le +\infty$

Elliptical

$d\tau = \frac{R^3}{8}(\mu^2 - \nu^2)\,d\mu\,d\nu\,d\phi \qquad 1 \le \mu \le \infty$
$\qquad -1 \le \nu \le +1$
$\qquad 0 \le \phi \le 2\pi$

The interested student may find a discussion of the derivation of these volume elements in [1, 5].

1-2 *DETERMINANTS*

There are many physical problems of interest that are most conveniently described by writing down an array of mathematical quantities. These arrays are then dealt with according to a set of predetermined rules. Two types of arrays commonly used in quantum chemistry are determinants and matrices. Matrices, although not difficult to handle, are not used in this book even though some problems are more conveniently formulated using matrix notation. It is necessary for us to use determinants, however, and some of their properties will be briefly discussed.

A determinant is an arrangement of N^2 quantities into a square array with N rows and N columns. The number N of rows or columns is called the order of the determinant. Thus the arrays

$$\begin{vmatrix} x - E & B \\ B & 2x - E \end{vmatrix} \tag{1-5a}$$

$$\begin{vmatrix} 8 & 5 & 3 \\ 3 & 5 & 8 \\ 5 & 3 & 8 \end{vmatrix} \tag{1-5b}$$

are determinants, the first of order 2 and the second of order 3. For a determinant, designated by a symbol enclosed between vertical lines, for example $|A|$, each element will have two subscripts. The first subscript defines the row; the second defines the column in which the element appears. Thus the quantity a_{ij} is the element from the ith row and the jth column of $|A|$.

Every determinant has a numerical value although in some cases the value of a determinant may be expressed in terms of unspecified quantities, such as in array 1-5a. The most convenient way to evaluate a determinant is to make use of the method of *signed minors* or *cofactors*. The minor of an element A_{ij} is the $(N-1)$th order determinant remaining when the row i and column j of the original determinant are struck out. To form the cofactor, the minor is given a sign according to the position of the element A_{ij} in the original determinant. This sign is $(-1)^{i+j}$. A determinant is evaluated by picking either a row or a column, forming the product of each element in the row (or column) with its cofactor, and summing the products.

Example: Evaluate the determinant 1-5b by the method of cofactors.

$$\begin{vmatrix} 8 & 5 & 3 \\ 3 & 5 & 8 \\ 5 & 3 & 8 \end{vmatrix} = 8\begin{vmatrix} 5 & 8 \\ 3 & 8 \end{vmatrix} - 5\begin{vmatrix} 3 & 8 \\ 5 & 8 \end{vmatrix} + 3\begin{vmatrix} 3 & 5 \\ 5 & 3 \end{vmatrix}$$

$$= 8(40 - 24) - 5(24 - 40) + 3(9 - 25)$$

$$= 128 + 80 - 48 = 160$$

Two useful properties of determinants that will be used in this text are the following.

1. The value of a determinant changes sign when two rows or two columns are interchanged.

2. If two rows are identical, or if two columns are identical, the determinant is zero.

For proof of these properties and other characteristics of determinants, see [1–4].

EXERCISE 1-2 Evaluate the determinant

$$\begin{vmatrix} 4 & 1 & 2 & 3 \\ 1 & 2 & 3 & 4 \\ 2 & 3 & 4 & 1 \\ 3 & 4 & 1 & 2 \end{vmatrix}$$

by the method of cofactors.

1-3 *SUMMATION AND PRODUCT NOTATION*

In physical chemistry one often encounters equations of the form

$$y = a_1 + a_2 + \cdots a_i + \cdots a_n \tag{1-6a}$$

$$z = a_1 a_2 \cdots a_i \cdots a_m \tag{1-6b}$$

In order to simplify notation, sums of the type shown in Eq. 1-6a are designated by a capital sigma ($\sum$) with the limits of summation shown by index numbers placed below and above the $\sum$. A similar procedure is followed for products except that a capital pi ($\prod$) replaces the sigma. Using this notation, Eqs. 1-6 become

$$y = \sum_{i=1}^{n} a_i \tag{1-7a}$$

$$z = \prod_{i=1}^{m} a_i \tag{1-7b}$$

EXERCISE 1-3 Let the a_i be the series of even integers beginning with $a_1 = 2$. Evaluate

$$y = \sum_{i=1}^{4} a_i \qquad z = \prod_{i=1}^{4} a_i$$

1-4 *VECTORS*

Most numerical and algebraic quantities that the student is familiar with have been scalar quantities. These are quantities such as 106 and $x^2 + 3x + 2$, which have magnitude only. A vector is used to represent a physical quantity which has *both* magnitude and direction. Quantities such as force, an electric field, or an acceleration are all vector quantities. A vector will be represented in this book by **boldface type.** It can also be represented by a symbol with an arrow above or below it, that is, $\vec{r}$ or $\underset{\rightarrow}{E}$. The length of a vector is called its magnitude and is a scalar quantity. A vector that has a length of one unit is called a unit vector. A vector often used is the radius vector **r.** I Figure 1-2, this is the vector whose length or magnitude is r and whose direction is from the origin to the point P.

It is usually most convenient to work with vectors in terms of thier components. To do this, three mutually perpendicular unit vectors called **i, j,** and **k** are defined that point along the X, Y, and Z axes, respectively. Any vector can then be written in terms of its components (projections) along these three axes. The radius vector becomes simply

$$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k} \tag{1-8}$$

Just as multiplication and division of numbers follow certain rules, so there are rules which define the combination of vectors. These rules are summarized as follows.

1. *Addition.* Addition of vectors can either be done graphically or analytically. Consider the vector sum

$$\mathbf{A} + \mathbf{B} = \mathbf{C} \tag{1-9}$$

In the graphical method, the tail of **B** is placed at the head of **A**. The sum **C** is the vector which starts at the tail of **A** and ends at the head of **B** (Figure 1-5a). The magnitude and direction of a vector are independent of the coordinate system used to describe the vector and, therefore, the origin of a vector can be taken at any point in space.

If the vectors **A** and **B** can be written in terms of their components, then the addition can be done analytically. Thus if

$$\mathbf{A} = A_x\mathbf{i} + A_y\mathbf{j} + A_z\mathbf{k} \tag{1-10a}$$

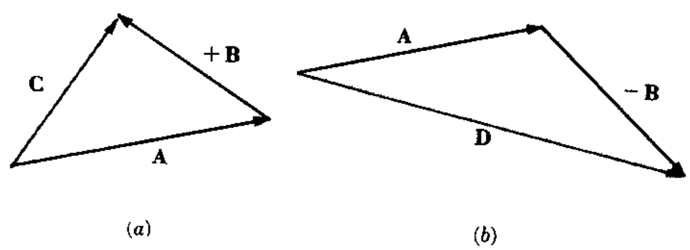

FIGURE 1-5 *Illustration of the graphical addition (a) and subtraction (b) of two vectors* **A** *and* **B**.

and

$$\mathbf{B} = B_x\mathbf{i} + B_y\mathbf{j} + B_z\mathbf{k} \tag{1-10b}$$

then

$$\mathbf{C} = (A_x + B_x)\mathbf{i} + (A_y + B_y)\mathbf{j} + (A_z + B_z)\mathbf{k} \tag{1-10c}$$

2. *Subtraction.* Vectors are subtracted by adding the negative of the appropriate vector. Thus **A** − **B** = **D** is illustrated in Figure 1-5b. Analytically,

$$\mathbf{D} = (A_x - B_x)\mathbf{i} + (A_y - B_y)\mathbf{j} + (A_z - B_z)\mathbf{k} \tag{1-11}$$

3. *Magnitude.* Frequently one needs to express the magnitude of a vector in terms of its components. By elementary trigonometry, the student may verify that the length of the radius vector **r** in Figure 1-3 is (see Exercise 1-1)

$$r = (x^2 + y^2 + z^2)^{\frac{1}{2}} \tag{1-12}$$

Similarly, the magnitude of any vector $\mathbf{A} = A_x\mathbf{i} + A_y\mathbf{j} + A_z\mathbf{k}$ is $|A| = (A_x^2 + A_y^2 + A_z^2)^{\frac{1}{2}}$.

4. *Multiplication.* Two different kinds of vector multiplication have been defined. The first kind, symbolized **A · B**, is called the dot or scalar product and results in a scalar. The second kind, symbolized **A × B**, is called the vector or cross product and results in a vector.

The scalar product **A · B** is defined as

$$\mathbf{A} \cdot \mathbf{B} \equiv AB\cos\theta \tag{1-13}$$

where A and B are the magnitudes of **A** and **B**, respectively, and where θ is the angle between **A** and **B**. The angle θ is always taken to be less than 180°. The student should note that there is a simple geometrical interpretation to the dot product. It is equal to the length **A** times the length of the projection of **B** on **A** *or vice versa.* If two vectors are perpendicular,

$$\cos\theta = \cos 90° = 0 \tag{1-14}$$

and **A · B** = 0. Conversely, it is also true that if **A · B** = 0, then **A** and **B** are perpendicular. When this is the case, the two vectors are said to be *orthogonal.* For two vectors written in terms of their components, we can show that

$$\mathbf{A} \cdot \mathbf{B} = A_xB_x + A_yB_y + A_zB_z \tag{1-15}$$

EXERCISE 1-4 Prove Eq. 1-15 making use of the definitions of **A · B** and of the unit vectors **i, j,** and **k.**

The cross product **A × B** is defined as

$$\mathbf{A} \times \mathbf{B} = \mathbf{n}AB \sin\theta \tag{1-16}$$

where A, B, and θ have the same meaning as above. The vector **n** is a unit vector perpendicular to *both* **A** and **B**. If **A** and **B** are parallel, $\sin\theta = 0$ and $\mathbf{A} \times \mathbf{B} = 0$. Conversely, if $\mathbf{A} \times \mathbf{B} = 0$, the two vectors are parallel.

The "right-hand rule" must be used in evaluating the cross product. To use this rule, one places the bottom edge of the right palm along **A** and curls the fingers toward **B**. The thumb will then point in the direction of **n** as shown in Figure 1-6. As a result of this rule, it should be clear that

$$\mathbf{A} \times \mathbf{B} \neq \mathbf{B} \times \mathbf{A} \tag{1-17}$$

In fact,

$$\mathbf{A} \times \mathbf{B} = -(\mathbf{B} \times \mathbf{A})$$

When an equation such as Eq. 1-17 is true, it is said that the vectors **A** and **B** do not *commute*, or that they are not commutative. The multiplication of scalar quantities is always commutative; that is, the result does not depend

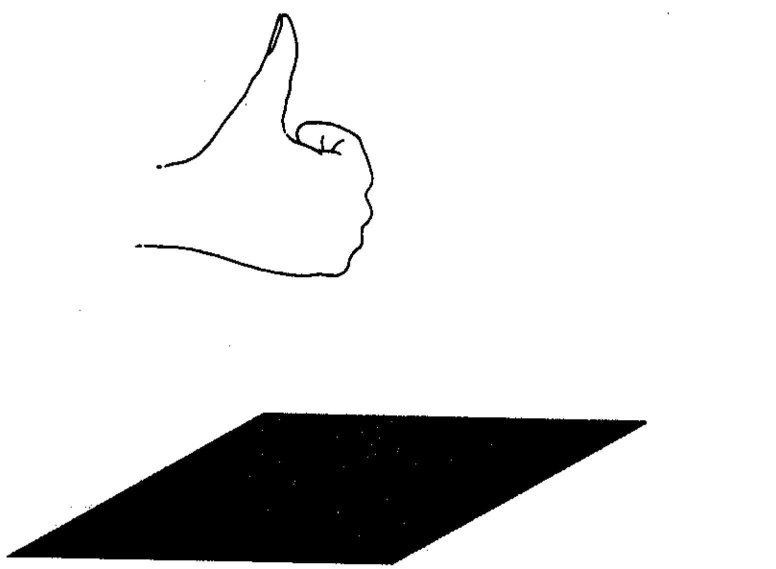

FIGURE 1-6 *The use of the right-hand rule to determine the direction of the vector* **A × B**. *In using the right-hand rule, the angle between* **A** *and* **B** *is always chosen to be less than* 180°.

on the order in which the multiplication is carried out. The commutative property does not hold, in general, for vector or matrix multiplication.

The geometrical interpretation of the cross product **A × B** is that of a vector perpendicular to both **A** and **B** whose length is equal to the area of the parallelogram defined by **A** and **B**. A consideration of Figure 1-7 may help clarify this point. In terms of components, **A × B** is most conveniently written in the form of a determinant. Thus

$$\mathbf{A} \times \mathbf{B} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{vmatrix} = \mathbf{i}(A_y B_z - A_z B_y) - \mathbf{j}(A_x B_z - B_x A_z) + \mathbf{k}(A_x B_y - B_x A_y) \tag{1-18}$$

For proof of Eq. 1-15, the reader is referred to [1–4] or to any standard work on vector analysis.

EXERCISE 1-5 Let $\mathbf{A} = 4\mathbf{i} + \mathbf{j} + 3\mathbf{k}$, $\mathbf{B} = \mathbf{i} - 3\mathbf{j} - \mathbf{k}$. Evaluate $\mathbf{A} + \mathbf{B}$, $\mathbf{A} - \mathbf{B}$, $\mathbf{A} \cdot \mathbf{B}$, and $\mathbf{A} \times \mathbf{B}$.

5. *Division* of vectors is not defined.
6. *Differentiation of vectors.* A vector is differentiated simply by differentiating its components. Thus

$$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$$

$$\frac{d\mathbf{r}}{dt} = \frac{dx}{dt}\mathbf{i} + \frac{dy}{dt}\mathbf{j} + \frac{dz}{dt}\mathbf{k} = v_x\mathbf{i} + v_y\mathbf{j} + v_z\mathbf{k} = \mathbf{v} \tag{1-19}$$

where **v** is the velocity vector.

7. *Vector equations.* It should be noted that a vector equation is actually a summary of three scalar equations because, for two vectors to be equal, the

FIGURE 1-7 *The geometrical significance of* **A × B**. *The quantity AB sin θ is the area of the parallelogram. The vector* **n** *is one unit in length.*

appropriate components on both sides of the equal sign must be equal. This point is illustrated in Exercise 1-6.

EXERCISE 1-6 In physics, the angular momentum **L** about a point is defined as

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

when **p** is the linear momentum at a point **r**. The origin of the vector **r** is taken at the point about which the angular momentum is to be calculated. Write the equation for each component of angular momentum L_x, L_y, and L_z in terms of x, y, and z and the components of linear momentum p_x, p_y, and p_z.

EXERCISE 1-7 Referring to Figure 1-4 and using the additive property of vectors, derive an expression for r_A and r_B in terms of x, y, and z and R, the distance between the two foci of the ellipse.

EXERCISE 1-8 Using the results of Exercise 1-7, set μ equal to a constant in Eq. 1-3 and plot the intersection of the resulting surface with the XZ plane. This can be done by setting $y = 0$ and plotting z for different values of x. This procedure should result in an ellipse, as pointed out in Section 1-1. Repeat this procedure setting $\nu = \text{const.}$

1-5 COMPLEX NUMBERS

A complex number is one which contains $\sqrt{-1}$, or i as it is usually symbolized. Thus $A + iB$ is a complex number. We speak of the real (A) and the imaginary (B) part of a complex number. If

$$C = A + iB \tag{1-20}$$

then the complex conjugate of C, called C^*, is formed by replacing i wherever it appears by $-i$. Thus

$$C^* = A - iB \tag{1-21}$$

The magnitude or absolute value of a complex number is defined as

$$|C| \equiv (CC^*)^{\frac{1}{2}} = (A^2 + B^2)^{\frac{1}{2}} \tag{1-22}$$

Note that the magnitude of a complex number is always real. Two complex numbers are equal only if *both* their real and imaginary parts are equal. Addition and subtraction follow the same rules as for vectors. That is, the real and imaginary parts are added independently. Thus if $z_1 = x_1 + iy_1$ and $z_2 = x_2 + iy_2$, then $z_1 + z_2 = (x_1 + x_2) + i(y_1 + y_2)$.

An equation which will often be used in dealing with complex numbers is Euler's formula

$$e^{i\alpha} = \cos\alpha + i\sin\alpha \tag{1-23}$$

Euler's formula can be derived by expanding each of the quantities $e^{i\alpha}$, $\cos\alpha$, and $\sin\alpha$ in a Maclaurin series. By equating the power series expansions, it can easily be shown that Eq. 1-23 leads to an identity.

EXERCISE 1-9 Express the following quantities in the form $A + iB$:

(a) $(1 + i)^3$ (b) $(x + iy)(u + iv)$ (c) $e^{\pi i/2}$

What is the complex conjugate and magnitude of part (b)?

1-6 OPERATORS

In a study of quantum mechanics, it is necessary to utilize mathematical *operators*. An operator is nothing more than a symbol that tells one to do something to what follows the symbol. Thus in the expression $\sqrt{2}$, the $\sqrt{\ }$ is an operator telling one to take the square root of what follows, in this case 2. Likewise, in the expression

$$\frac{d}{dx}(x^2 + 5x + 1) \tag{1-24}$$

d/dx is an operator telling one to take the derivative with respect to x of what follows, that is, $x^2 + 5x + 1$. General operators will be indicated by a symbol with a caret over it, that is, $\hat{P}$ or $\hat{Q}$.

The algebra of operators follows definite mathematical procedures which the student is familiar with, although perhaps not consciously. Thus if

$$\hat{P} = \left(\frac{\partial}{\partial x}\right)_{yz} \qquad \hat{Q} = \left(\frac{\partial}{\partial y}\right)_{xz}$$

then (1-25)

$$\hat{P}\hat{Q} = \left|\frac{\partial}{\partial x}\left(\frac{\partial}{\partial y}\right)_{xz}\right|_{yz} = \frac{\partial^2}{\partial x\,\partial y}$$

When dealing with operators one must be careful of the order of operations because operations like vector multiplication are not necessarily commutative. By convention, one always begins with the operator on the right and works toward the left. In Eq. 1-25, it turns out that $\hat{P}$ and $\hat{Q}$ do commute. That is,

$$\hat{P}\hat{Q} = \hat{Q}\hat{P} \quad \text{since} \quad \frac{\partial^2}{\partial x\, \partial y} = \frac{\partial^2}{\partial y\, \partial x} \tag{1-26}$$

but this, in general, will not be the case (see Exercise 1-10).

EXERCISE 1-10 Consider the function $f(x, y) = x^2 + y^2 + 2xy$. Let $\hat{P}$ and $\hat{Q}$ be the operators given in Eq. 1-25 and operate first on $f(x, y)$ with $\hat{P}\hat{Q}$, then with $\hat{Q}\hat{P}$. Note that the result is the same. What would be the result of operating on $f(x, y)$ with $\hat{P}\hat{Q} - \hat{Q}\hat{P}$?

EXERCISE 1-11 Let $\hat{P} = d/dx$, $\hat{O} = x$ (multiply by x), and $f(x) = x^2 + 2x + 1$. Show that $\hat{O}\hat{P}f(x) \neq \hat{P}\hat{O}f(x)$. For these two operators, can you derive a general expression for $\hat{P}\hat{O} - \hat{O}\hat{P}$?

The quantity $\hat{P}\hat{Q} - \hat{Q}\hat{P}$ (see Exercises 1-10 and 1-11) is called the commutator of $\hat{P}$ and $\hat{Q}$, and is often symbolized $[\hat{P}, \hat{Q}]$. If $\hat{P}$ and $\hat{Q}$ commute, then the value of the commutator is zero. Conversely, if the value of the commutator is zero, the operators $\hat{P}$ and $\hat{Q}$ commute.

An operator can be a vector or a complex quantity. If an operator is a vector, one usually works with it in terms of its components. An example of a vector operator is "del."

$$\nabla = \frac{\partial}{\partial x}\mathbf{i} + \frac{\partial}{\partial y}\mathbf{j} + \frac{\partial}{\partial z}\mathbf{k} \tag{1-27}$$

The quantity ∇f, where f is some scalar function, is called the gradient of f. For example, suppose $f = x^2 + y^2 + z^2$; then the gradient of f is the vector

$$\nabla f = 2x\mathbf{i} + 2y\mathbf{j} + 2z\mathbf{k} \tag{1-28}$$

The gradient will be used in Chapter 2 in the discussion of classical mechanics. Since for a scalar function f, the quantities $\partial f/\partial x$, $\partial f/\partial y$, and $\partial f/\partial z$ are the rates of change of f with respect to distance in the x, y, and z directions, the gradient of f provides a means of evaluating the rate of change of f with distance in any direction.

If an operator $\hat{P}$ is complex, the complex conjugate $\hat{P}^*$ is formed by replacing i by $-i$ wherever it occurs. Thus, if $\hat{P} = i\, d/dx$, $\hat{P}^* = -i\, d/dx$.

In quantum mechanics, only linear operators are used. An operator is linear if it is true that

$$\hat{P}(f + g) = \hat{P}f + \hat{P}g$$

or

$$\hat{P}af = a\hat{P}f \tag{1-29}$$

where a is a constant. The student may easily verify that d/dx is a linear operator whereas $\sqrt{\ }$ is not.

EXERCISE 1-12 It is true in algebra that

$$(P + Q)(P - Q) = P^2 - Q^2$$

What is the value of $(P + Q)(P - Q)$ if P and Q are operators? Under what conditions will the first relation be true for operators?

An operator that will be used frequently in quantum mechanics is $\nabla^2 \equiv \nabla \cdot \nabla$. It will be shown in Chapter 3 that this operator is related to the kinetic energy. In Cartesian coordinates it can be seen using Eq. 1-15 and 1-27 that

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{1-30}$$

For many quantum chemical problems, spherical polar coordinates will be more appropriate than Cartesian coordinates and it will be necessary to express ∇^2 as a function of r, θ, and ϕ. This relation is given by

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2} \tag{1-31}$$

The derivation of the expression for ∇^2 in a general system of orthogonal coordinates as well as the derivation of Eq. 1-31 is given in [1].

1-7 *EIGENVALUE EQUATIONS*

An equation of the type

$$\hat{P}(q_i)G(q_i) = pG(q_i) \tag{1-32}$$

where $\hat{P}(q_i)$ is an operator, $G(q_i)$ is a function, both involving variable q_i, and p is a constant, is called an *eigenvalue equation*. When such an equation holds, $G(q_i)$ is called an eigenfunction of the operator $\hat{P}(q_i)$ and p is called the eigenvalue.

Eigenvalue equations play a major role in the mathematical formalism of quantum mechanics. In quantum mechanics, $\hat{P}$ is usually a differential operator and, therefore, the eigenvalue equation is a differential equation. The principal mathematical problem of quantum mechanics is to find the solution G and the eigenvalues p to these eigenvalue equations. The student must keep in mind that the mathematics of these equations were known long before quantum mechanics was developed. The mathematical properties of these equations should not be confused with the physical interpretation to be placed upon them in the discussion of quantum mechanics in Chapter 3.

To give an example of an eigenvalue equation, suppose that the operator of interest is $\hat{P} = d^2/dx^2$. We seek to find functions $G(x)$ such that when $\hat{P}$ operates on $G(x)$, $G(x)$ again results, multiplied by a constant. Looking at the specific form of the operator, it can be seen that what is required is a function which when differentiated twice results in the original function. There are a number of functions which have this property, for example, $\sin ax$, $\cos ax$, $e^{\pm ax}$. Let us choose $G(x) = \sin ax$ and evaluate

$$\hat{P}(x)G(x) = \frac{d^2}{dx}G(x) = \frac{d}{dx}\left(\frac{d}{dx}\sin ax\right) = \frac{d}{dx}(a\cos ax)$$

$$= -a^2 \sin ax \tag{1-33}$$

Thus if a is a constant, the function $G(x) = \sin ax$ is an eigenfunction of the operator d/dx^2 and the eigenvalue is $-a^2$.

EXERCISE 1-13 Show that the function Ae^{-ax} is an eigenfunction of the operator d^2/dx^2. What is the eigenvalue?

EXERCISE 1-14 Show that the function $\cos ax \cos by \cos cz$ is an eigenfunction of the operator ∇^2. What is the eigenvalue?

EXERCISE 1-15 Under what conditions is the function e^{-aq^2} an eigenfunction of the operator

$$\frac{d^2}{dq^2} - kq^2$$

where k is a constant. What is the eigenvalue under these conditions? *Hint*: the quantity a must be adjusted to eliminate terms involving q in the result.

1-8 SUMMARY

1. Some of the properties of coordinate systems, determinants, vectors, and complex numbers were reviewed.
2. Mathematical operators were introduced and some of their properties were discussed.
3. Several terms were introduced which will be important throughout the book. The student should be especially familiar with the meaning of the following terms: orthogonal, commute and commutator, complex conjugate, eigenvalue, and eigenfunction.

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Chapter 2

CLASSICAL MECHANICS

THE SCIENCE of mechanics, which dealt with the motions of bodies and with the forces that affected these motions, provided before 1900 a powerful example of the ability of a mathematical, scientific theory to predict, correlate, and interpret observations on the nature of the physical world. For systems where the particles involved are considerably larger than atoms or molecules, this science still retains its power and usefulness. Mechanics, or classical mechanics as it is now called, was first based upon Newton's laws of motion. More general and powerful formulations were developed later by Lagrange and by Hamilton.

Since quantum mechanics developed out of classical mechanics, some of the ideas and nomenclature of the earlier science were retained. In fact one of the guideposts in the development of quantum mechanics was that in the limit of classical sized systems the quantum mechanical result had to go over into the classical mechanical one. This idea is referred to now as the "correspondence principle." It is for this reason that the student approaching quantum mechanics for the first time needs to have some knowledge about classical mechanics. This chapter provides a brief introduction to some of the necessary classical mechanical concepts. Students interested in a more complete study should see [1]. Good short introductions are provided in [2–4].

The fundamental problem of classical mechanics is to describe the motion of systems of particles under various kinds of forces and initial conditions. More practically, the problem is to solve the differential equations resulting

from Newton's second law

$$\mathbf{F}_i = m\mathbf{a}_i \tag{2-1}$$

where $\mathbf{F}_i$ is the force acting on the ith particle in the system, and $\mathbf{a}_i$ is its acceleration.

2-1 *CONSERVATIVE SYSTEMS*

Before going into more detail concerning the solutions to Eq. 2-1, it is necessary to distinguish between two types of systems—conservative and nonconservative. For our purposes, it will be sufficient to define a conservative system as one in which the sum of the kinetic and potential energies of the system remains constant with time. A conservative system is, therefore, an isolated system and is not acted upon by external forces. Also, it cannot have any internal dissipative forces such as friction.

An equivalent definition of a conservative system is that it is a system in which the forces can be represented as the negative gradient (see Section 1-4) of some potential function V. That is,

$$\mathbf{F}_i = -\nabla_i V \tag{2-2}$$

To show that these two definitions are equivalent, consider the case of a single particle constrained to move in one dimension, say, the x direction. Newton's second law for this case is

$$F_x = m\frac{d^2x}{dt^2} \tag{2-3}$$

and, if Eq. 2-2 holds,

$$F_x = -\frac{dV(x)}{dx} \tag{2-4}$$

Substituting Eq. 2-4 into 2-3 gives

$$-\frac{dV(x)}{dx} = m\ddot{x} = m\frac{d\dot{x}}{dt} \tag{2-5}$$

which upon integrating over x yields

$$-\int \frac{dV(x)}{dx}\,dx = -\int dV = m \int \frac{d\dot{x}}{dt}\,dx = m \int d\dot{x}\,\frac{dx}{dt} = m \int \dot{x}\,d\dot{x}$$

$$-V(x) + C = \tfrac{1}{2}m\dot{x}^2 \qquad (2\text{-}6)$$

$$\tfrac{1}{2}m\dot{x}^2 + V(x) = C = E$$

where C is an arbitrary constant of integration. Thus if Eq. 2-2 is assumed, the sum of the potential and kinetic energies ($\tfrac{1}{2}m\dot{x}^2$) of the particle is independent of the time t. The two definitions of a conservative system are thus seen to be equivalent.

Any property of a mechanical system independent of time is called a constant of motion of the system. In this particular case, the constant of motion is the total energy of the particle, E. In what follows, the symbol T will be used for kinetic energy. Equation 2-6 then becomes $C = T + V$, and it becomes clear that the constant of integration in Eq. 2-6 is the total energy of the system.

2-2 *AN EXAMPLE OF NEWTONIAN MECHANICS*

The motion of a particle in which there is a restoring force proportional to the displacement of the particle from some point is called simple harmonic motion. This situation is applicable to the case of the stretching of an ideal spring (one which obeys Hooke's law) and, as will be seen in Chapter 5, is used as the lowest level of approximation in treating the vibration of diatomic molecules.

For motion in one dimension, say, the x direction, the force is

$$F_x = -kx \qquad (2\text{-}7)$$

where k is usually referred to as the force constant and Newton's second law of motion becomes

$$-kx(t) = m\,\frac{d^2x(t)}{dt^2} \qquad (2\text{-}8)$$

The classical mechanical problem is to find x as a function of t.

Rearranging Eq. 2-8 slightly, we obtain

$$\ddot{x} \equiv \frac{d^2x(t)}{dt^2} = -\frac{k}{m}\,x(t) \qquad (2\text{-}9)$$

It is seen from Eq. 2-9 that what is required is a function $x(t)$ which when differentiated twice gives the same function back again multiplied by a constant. This is the same situation that was encountered in Section 1-7, and the solutions discussed there are also appropriate here. Remembering that general solutions to a second order differential equation have two undetermined constants, we try to find a solution to Eq. 2-9 of the form

$$x(t) = A \sin \alpha t \qquad (2\text{-}10)$$

where A and α are the undetermined constants. Differentiating twice gives

$$\ddot{x}(t) = -\alpha^2 A \sin \alpha t \qquad (2\text{-}11)$$

and we see that Eq. 2-10 is a solution to Eq. 2-8 if we make the identification

$$\alpha = \left(\frac{k}{m}\right)^{\frac{1}{2}} \qquad (2\text{-}12)$$

The solution to the problem of one-dimensional simple harmonic motion then becomes

$$x(t) = A \sin \left(\frac{k}{m}\right)^{\frac{1}{2}} t \qquad (2\text{-}13)$$

Since the sine function oscillates between -1 and $+1$, it can be seen that the constant A represents the maximum amplitude of displacement in the x direction.

This problem again illustrates the equivalence of the two definitions of a conservative system discussed in the previous section. Equation 2-2 holds, and therefore

$$-\frac{dV(x)}{dx} = -kx$$

$$\int dV(x) = \int kx\,dx \qquad (2\text{-}14)$$

$$V(x) = \tfrac{1}{2}kx^2 + C$$

By choosing the initial conditions such that at $x = 0$, $V = 0$ we can set $C = 0$. Using Eq. 2-13 we see that the potential energy as a function of time is

$$V(t) = \frac{1}{2}kA^2 \sin^2\left(\frac{k}{m}\right)^{\frac{1}{2}} t \qquad (2\text{-}15)$$

The kinetic energy of the particle is

$$T = \frac{1}{2} mv^2 = \frac{1}{2} m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2} m\left(\frac{k}{m}\right)A^2 \cos^2\left(\frac{k}{m}\right)^{\frac{1}{2}} t$$
$$= \frac{1}{2} kA^2 \cos^2\left(\frac{k}{m}\right)^{\frac{1}{2}} t \tag{2-16}$$

The total energy of the particle is then

$$E = T + V = \frac{1}{2} kA^2\left[\sin^2\left(\frac{k}{m}\right)^{\frac{1}{2}} t + \cos^2\left(\frac{k}{m}\right)^{\frac{1}{2}} t\right]$$
$$= \frac{1}{2} kA^2 \tag{2-17}$$

a quantity independent of time.

EXERCISE 2-1 Consider the case of a particle of mass m moving in a gravitational field $V = mgz$. Write and solve the laws of motion starting with Newton's second law.

2-3 THE LAGRANGIAN AND HAMILTONIAN FORMS OF THE EQUATIONS OF MOTION

The equations of motion in Newtonian form are usually most convenient to solve if the physical problem is such as to make Cartesian coordinates appropriate. For problems in other coordinate systems it is often difficult even to write down the equations of motion. For this reason it would be more convenient if equations of motion could be derived whose form is independent of a coordinate system. Such general equations of motion were derived by two mathematicians, Joseph Lagrange and William Hamilton, and are called the Lagrangian and Hamiltonian forms of the equations of motion. The Hamiltonian form is especially important because it is directly used in the transformation from classical to quantum mechanics.

Before discussing these two forms of the equations of motion, it is necessary to introduce the idea of generalized coordinates, velocities, and momenta.

Suppose a conservative system containing three particles is considered. In order to specify completely the state of the system at a given time t, one would have to specify the positions and velocities of the three particles. To do this, one would have to specify nine coordinates, that is, $(x_1, y_1, z_1, \ldots, x_3, y_3, z_3)$ and nine velocities, that is, $(\dot{x}_1, \dot{y}_1, \dot{z}_1, \ldots, \dot{x}_3, \dot{y}_3, \dot{z}_3)$. In general, for a system containing N particles, one would have to specify $3N$ coordinates and $3N$ velocities. Such a system would have $6N$ degrees of freedom. [This statement is true only if there are no constraints inherent in the system which make some of the $6N$ variables dependent. For instance, if the three particles were required to move on the spherical surface $x^2 + y^2 + z^2 = R^2$, then only 12 degrees of freedom (six coordinates and six velocities) would exist rather than 18. We will always assume that the coordinates have been chosen so that the restraints have already been accounted for.] To formulate classical mechanics in a general way we introduce for a system containing N particles $3N$ generalized coordinates q_i and $3N$ generalized velocities $\dot{q}_i \equiv dq_i/dt$. We then derive the Lagrangian and Hamiltonian forms of the equations of motion in terms of these generalized coordinates and velocities. When working problems, these generalized quantities are given a specific form.

The Lagrangian function $L(\dot{q}, q)$ is defined as

$$L(\dot{q}, q, t) = T(\dot{q}, q) - V(q, t) \tag{2-18}$$

where T is the kinetic energy expressed as a function of the generalized velocities and coordinates, and V is the potential energy expressed as a function of the generalized coordinates and the time t. For conservative systems, the Lagrangian function L and the potential energy V will not depend explicitly on the time. For these systems, L is a function only of the $6N$ q_i and $\dot{q}_i$. Going through considerable algebra, one can show that the equations of motion in Lagrangian form are [2–4]

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right)_{q_j, \dot{q}_{j \neq i}} = \left(\frac{\partial L}{\partial q_i}\right)_{q_{j \neq i}, \dot{q}_j} \tag{2-19}$$

These equations, since they are in generalized coordinates, hold for any system of coordinates. It should be pointed out that in the partial derivatives in Eq. 2-19, the other $6N - 1$ variables are held constant. From this point on, the constancy of these variables will be understood and the subscripts will not be used.

To illustrate the use of Eq. 2-18 and 2-19 let us return to the problem of simple harmonic motion discussed in the previous section. We first write down the appropriate quantities for this problem.

$$\begin{aligned} q_i &= x \\ \dot{q}_i &= \dot{x} \\ T(q_i, \dot{q}_i) &= \tfrac{1}{2} m\dot{x}^2 \\ V(q_i) &= \tfrac{1}{2} kx^2 \end{aligned} \tag{2-20}$$

The Lagrangian function $L(\dot{q}, q)$ is then

$$L(x, \dot{x}) = \tfrac{1}{2}m\dot{x}^2 - \tfrac{1}{2}kx^2 \tag{2-21}$$

To write the equations of motion we calculate

$$\left(\frac{\partial L}{\partial \dot{x}}\right) = m\dot{x} \qquad \left(\frac{\partial L}{\partial x}\right) = -kx$$

and substitute these quantities into Eq. 2-19 to obtain

$$\frac{d}{dt}(m\dot{x}) = m\ddot{x} = -kx \tag{2-22}$$

which is the same result as that obtained from Newton's second law.

The student can see that Lagrangian equations of motion are a set of $3N$ second order differential equations. To derive the equations of motion in Hamiltonian form, we transform these to a set of $6N$ first order equations. To do this, we first define the generalized momenta p_k as

$$p_k = \left(\frac{\partial L}{\partial \dot{q}_k}\right) \tag{2-23}$$

Applying Eq. 2-23 to the case of a free single particle whose motion is described by Cartesian coordinates gives the usual components of linear momentum $m\dot{x}$, $m\dot{y}$, and $m\dot{z}$. Note that with the definition 2-23 the equations of motion in Lagrangian form become simply

$$\dot{p}_i = \frac{\partial L}{\partial q_i} \tag{2-24}$$

EXERCISE 2-2 Write the Lagrangian function for a free (potential equal to a constant) particle moving in a three-dimensional space. Show that $p_x = m\dot{x}$, $p_y = m\dot{y}$, and $p_z = m\dot{z}$. Use Eq. 2-19 to write down the equations of motion. Solve them.

EXERCISE 2-3 Write the Lagrangian function for the particle of mass m moving in a gravitational field $V = mgz$. Derive the equations of motion from Eq. 2-7. Show that the equations obtained by this method are the same as those obtained from Newton's second law.

We next define a new function

$$\mathscr{H} = \sum_{i=1}^{3N} p_i \dot{q}_i - L \tag{2-25}$$

from which we can show that for a conservative system [2–4]

$$\begin{cases} \dfrac{\partial \mathscr{H}}{\partial p_i} = \dot{q}_i \\[2ex] \dfrac{\partial \mathscr{H}}{\partial q_i} = -\dfrac{\partial L}{\partial q_i} = -\dot{p}_i \end{cases} \tag{2-26}$$

EXERCISE 2-4 Show that Eq. 2-26 follows from Eq. 2-25. *Hint*: Write down the total differential for $\mathscr{H}$ using Eq. 2-25. Then compare it with the general expression for the total differential of $\mathscr{H}$ regarding $\mathscr{H}$ as a function of p_i and q_i. Use Eqs. 2-23 and 2-24 to prove the final result.

These are the equations of motion in Hamiltonian form. The quantity $\mathscr{H}$ is expressed as a function of the coordinates and the *momenta*, and is called the Hamiltonian function for the system. The Hamiltonian function for a conservative system has the property that it is equivalent to the total energy of the system. To show this, we substitute Eq. 2-18 into Eq. 2-25 to obtain

$$\mathscr{H} = \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - T + V \tag{2-27a}$$

$$= \sum_i \dot{q}_i \frac{\partial T}{\partial \dot{q}_i} - T + V \tag{2-27b}$$

Equation 2-27b follows from Eq. 2-27a because, for conservative systems, all of the dependence of L on $\dot{q}_i$ is in the T term. The first term in Eq. 2-27, however, is equal to $2T$. Rather than prove this general result, an example will be given. For more details, see [1–4]. Consider the example of a system in which one particle is constrained to move in one dimension. The kinetic energy for Cartesian coordinates is

$$T = \tfrac{1}{2}m\dot{q}_i^2$$

It is easily seen, then, that

$$\frac{\partial T}{\partial \dot{q}_i} = m\dot{q}_i$$

and

$$\dot{q}_i \frac{\partial T}{\partial \dot{q}_i} = m\dot{q}_i^2 = 2T$$

For the many-particle, many-dimensional system, using Cartesian coordinates $T = \frac{1}{2}\sum m_i \dot{q}_i$, and, following an argument similar to the above, we can show that

$$\sum_i \dot{q}_i \frac{\partial T}{\partial \dot{q}_i} = 2T \tag{2-28}$$

Using this result in Eq. 2-27b, it follows that

$$\mathscr{H} = 2T - T + V = T + V \tag{2-29}$$

Thus we see that Hamilton's function is identical with the total energy.

We now return to our one-dimensional harmonic oscillator problem to write it in the Hamiltonian formalism. The first step is to use L, Eq. 2-21, to define the appropriate momenta. Thus

$$p_x = \frac{\partial L}{\partial \dot{x}} = m\dot{x} \tag{2-30}$$

Then, in terms of *momenta*, T becomes

$$T = \frac{1}{2} m\dot{x}^2 = \frac{1}{2} m\left(\frac{p_x}{m}\right)^2 = \frac{1}{2m} p_x{}^2 \tag{2-31}$$

and the Hamiltonian is

$$\mathscr{H} = T + V = \frac{1}{2m} p_x{}^2 + \frac{1}{2} kx^2 \tag{2-32}$$

The student may easily show that applying Eqs. 2-26 through 2-32 gives the same equations of motion that were obtained previously.

EXERCISE 2-5 Write Hamilton's function for the case of a particle of mass m in a gravitational field. Write the equations of motion and show that they are identical with Newton's equation.

EXERCISE 2-6 A particle is constrained to move in the XY plane ($\theta = 90°$) under the potential $V = \frac{1}{2} k(x^2 + y^2)$.

1. Using Cartesian coordinates, write the equations of motion in Newtonian form.
2. Write the Lagrangian function L in Cartesian and polar coordinates.
3. Write the equations of motion in polar coordinates using the Lagrangian form.
4. Find the momenta p_r and p_ϕ.
5. Write the Hamiltonian function in both systems of coordinates.
6. What famous conservation law is obvious from the results of 3 above?

2-4 *INTERNAL COORDINATES AND THE MOTION OF THE CENTER OF MASS*

A specific problem that will be of great importance in quantum mechanics is that of two interacting particles of masses m_1 and m_2, where the potential is only a function of their distance apart, or, in other words, of their *relative* coordinates. The following treatment of this problem is essentially that of [3].

If the Cartesian coordinates of the two particles are x_1, y_1, z_1, and x_2, y_2, z_2, respectively, the square of their distance apart is

$$r_{12}^2 = (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2 \tag{2-33}$$

The problem discussed above can be greatly simplified by transforming to new coordinates which involve the coordinates of the center of mass X, Y, Z and the "internal" or relative coordinates x, y, z. Thus we define

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \qquad Y = \frac{m_1 y_1 + m_2 y_2}{m_1 + m_2} \qquad Z = \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$$
$$x = x_2 - x_1 \qquad y = y_2 - y_1 \qquad z = z_2 - z_1 \tag{2-34}$$

EXERCISE 2-7 Write an expression for the kinetic energy of a system containing two particles of masses m_1 and m_2 moving in only two dimensions. Let the coordinates be x_1, y_1, x_2, y_2. Transform this expression to the new coordinate system X, Y, x, y making use of the relations 2-34. Show that the final expression is

$$T = \frac{1}{2}(m_1 + m_2)(\dot{X}^2 + \dot{Y}^2) + \frac{1}{2}\frac{m_1 m_2}{m_1 + m_2}(\dot{x}^2 + \dot{y}^2)$$

Write the corresponding equation for a system of two particles moving in three dimensions by analogy.

Making use of the results of Exercise 2-7, we can write

$$L = \frac{1}{2}(m_1 + m_2)(\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2) + \frac{\mu}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) - V(x, y, z) \tag{2-35}$$

where $\mu = m_1 m_2/(m_1 + m_2)$ and is called the reduced mass, and where V is a function only of x, y, z since, by hypothesis, the potential energy depends only on the internal or relative coordinates.

From the Lagrangian function in Eq. 2-35, the equations of motion for the six coordinates can be calculated using Eq. 2-19. These six equations of motion are

$$(m_1 + m_2)\ddot{X} = (m_1 + m_2)\ddot{Y} = (m_1 + m_2)\ddot{Z} = 0 \quad (2\text{-}36)$$

$$\mu\ddot{x} = -\frac{\partial V}{\partial x} \qquad \mu\ddot{y} = -\frac{\partial V}{\partial y} \qquad \mu\ddot{z} = -\frac{\partial V}{\partial z} \quad (2\text{-}37)$$

Equations 2-36 are identical to the equations of motion that are obtained if the problem of the motion of a free particle (see Exercise 2-2) of mass M is solved. Thus the motion of the center of mass of our two-particle system is the same as the motion of a free particle with mass equal to the total mass of the system. Equations 2-36 can be integrated to give

$$M\dot{q}_i = C \quad (2\text{-}38)$$

where $M = (m_1 + m_2)$, $\dot{q}_i$ can be $\dot{X}$, $\dot{Y}$, or $\dot{Z}$, and C is a constant. Equation 2-38 shows that the three components of the velocity of the center of mass are constants. The kinetic energy due to the motion of the center of mass, therefore, must also be a constant.

Equations 2-37 are identical to those that are obtained in solving the problem of the motion of a particle with mass μ subject to the potential function $V(x, y, z)$. The total energy of the system is the sum of the energies due to the motion of the center of mass and to the internal motion of the system. Since the translational energy of the center of mass adds only a constant to the total energy, it is usual to neglect its contribution and solve only the problem of the internal motion of the system. This example points up the power of expressing the laws of motion in generalized coordinates. In this case, we let $q_1 = X$, $q_2 = Y, \ldots, q_6 = z$, and so on, and we can immediately write down the equations of motion from the Lagrangian function.

The above example is an extremely important one that should be thoroughly understood. In general terms, its significance is that, as long as the potential energy depends only on the internal coordinates of the system, *the motion of the center of mass can always be separated from the internal motion of the system*, and the two problems can be solved independently.

2-5 THE BASIC ASSUMPTIONS OF CLASSICAL MECHANICS

At this point, it is good to think about the philosophical implications inherent in classical mechanics. First, it is implied that an experimentalist can precisely measure the positions and velocities of all of the particles in a system at some time t in order to describe the state of the system. Second, once this initial state is specified, the laws of mechanics and a knowledge of the forces acting on the system enable the system to be characterized at any later time. In principle, then, an experimentalist could measure the position, velocity, energy, momentum, and so on, of any particle at any time and compare it with the theoretical prediction. The following three statements summarize the assumptions inherent in this view.

1. There is no limit to the accuracy with which one or more of the dynamical variables of a classical system can be simultaneously measured *except* the limit imposed by the precision of the measuring instruments.
2. There is no restriction on the number of dynamical variables that can be accurately measured simultaneously.
3. Since the expressions for velocity are continuously varying functions of time, the velocity, and hence the kinetic energy, can vary continuously. That is, there are no restrictions on the values that a dynamical variable can have.

We shall see that when very small particles are involved, all three of these assumptions must be abandoned. For these systems, classical mechanics fails completely to describe their behavior. The new mechanics that was developed for these systems is called quantum mechanics.

2-6 SUMMARY

1. A conservative system was defined as a system in which the sum of the kinetic and potential energies remains constant with time, or one in which the forces are equal to the negative gradient of some potential function.
2. Newton's second law of motion was applied to the case of simple harmonic motion.
3. The Lagrangian and Hamiltonian forms of the equations of motion were introduced and shown to give the same results for a specific problem as Newton's second law. These equations are more general than Newton's because the forms of the equations are independent of the coordinate system.
4. For systems containing many particles, the motion of the center of mass was shown to be separable from the internal motion of the system as long as the potential energy depended only on the relative coordinates of the particles.
5. The basic assumptions of classical mechanics were discussed.
6. Terms which the student should understand are the following: conservative system, Lagrangian function, Hamiltonian function, internal coordinates, and reduced mass.

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Chapter 3

QUANTUM MECHANICS

BY THE end of the nineteenth century three types of observations made it apparent that classical mechanics could not give correct results when it was applied to molecular and atomic phenomena. These observations involved studies of atomic spectra, blackbody radiation, and the photoelectric effect. In the section that follows, each of these experiments is discussed, and it is shown how the basic assumptions of classical mechanics had to be abandoned. Following this, quantum mechanics is introduced by a series of postulates and these postulates are then applied to calculations on some simple systems.

3-1 ATOMIC SPECTRA, BLACKBODY RADIATION, AND THE PHOTOELECTRIC EFFECT

The discipline of spectroscopy began in the early part of the nineteenth century with the observation of the sunlight spectrum by Josef Fraunhofer. The study of the spectra of atoms was begun in 1861 by Kirchoff and by Bunsen, who extensively studied the spectrum of the alkali metals. In 1885, Balmer discovered the series of lines in the spectrum of atomic hydrogen that now bears his name, and found that he could write an empirical relationship that gave the positions of all the lines. This relationship was

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n_2^{\,2}}\right) \qquad n_2 = 3, 4, 5 \cdots \tag{3-1}$$