Definition 1: *An operator $\hat{O}$ is a mathematical entity that transforms a function $f(x)$ into another function $g(x)$ as follows,* **R4(96)**

$$\hat{O}f(x) = g(x),$$

where f and g are functions of x.

Definition 2: *An operator $\hat{O}$ that represents an observable O is obtained by first writing the classical expression of such observable in Cartesian coordinates (e.g., $O = O(x, p)$) and then substituting the coordinate x in such expression by the* coordinate operator $\hat{x}$ *as well as the momentum p by the* momentum operator $\hat{p} = -i\hbar\partial/\partial x$.

Definition 3: *An operator $\hat{O}$ is* linear *if and only if (iff),*

$$\hat{O}(af(x) + bg(x)) = a\hat{O}f(x) + b\hat{O}g(x),$$

where a and b are constants.
Definition 4: *An operator $\hat{O}$ is* hermitian *iff,*

$$\int dx\phi_n^*(x)\hat{O}\psi_m(x) = \left[\int dx\psi_m^*(x)\hat{O}\phi_n(x)\right]^*,$$

where the asterisk represents the complex conjugate.

Definition 5: *A function $\phi_n(x)$ is an* eigenfunction *of $\hat{O}$ iff,*

$$\hat{O}\phi_n(x) = O_n\phi_n(x),$$

where O_n is a number called eigenvalue.

Property 1: The eigenvalues of a hermitian operator are real.
Proof: Using Definition 4, we obtain

$$\int dx\phi_n^*(x)\hat{O}\phi_n(x) - \left[\int dx\phi_n^*(x)\hat{O}\phi_n(x)\right]^* = 0,$$

therefore,

$$[O_n - O_n^*]\int dx\phi_n(x)^*\phi_n(x) = 0.$$

Since $\phi_n(x)$ are square integrable functions, then,

$$O_n = O_n^*.$$

Property 2: Different eigenfunctions of a hermitian operator (i.e., eigenfunctions with different eigenvalues) are orthogonal (i.e., the *scalar product* of two different eigenfunctions is equal to zero). Mathematically, if $\hat{O}\phi_n = O_n\phi_n$, and $\hat{O}\phi_m = O_m\phi_m$, with $O_n \neq O_m$, then $\int dx\phi_n^*\phi_m = 0$.
Proof:

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The ***square*** of an operator is defined as the product of the operator with itself: $\hat{A}^2 = \hat{A}\hat{A}$. Let us find the square of the differentiation operator:

$$\hat{D}^2 f(x) = \hat{D}(\hat{D}f) = \hat{D}f' = f''$$
$$\hat{D}^2 = d^2/dx^2$$

As another example, the square of the operator that takes the complex conjugate of a function is equal to the unit operator, since taking the complex conjugate twice gives the original function. The nth power of an operator ($n = 1, 2, 3, \ldots$) is defined to mean applying the operator n times in succession.

It turns out that the operators occurring in quantum mechanics are linear. $\hat{A}$ is a ***linear operator*** if and only if it has the following two properties:

$$\hat{A}[f(x) + g(x)] = \hat{A}f(x) + \hat{A}g(x) \tag{3.9*}$$
$$\hat{A}[cf(x)] = c\hat{A}f(x) \tag{3.10*}$$

where f and g are arbitrary functions and c is an arbitrary constant (not necessarily real). Examples of linear operators include $\hat{x}^2$, d/dx, and d^2/dx^2. Some nonlinear operators are cos and $(\ \ )^2$, where $(\ \ )^2$ squares the function it acts on.

EXAMPLE Is d/dx a linear operator? Is $\sqrt{\ \ }$ a linear operator?

We have

$$(d/dx)[f(x) + g(x)] = df/dx + dg/dx = (d/dx)f(x) + (d/dx)g(x)$$
$$(d/dx)[cf(x)] = c\, df(x)/dx$$

so d/dx obeys (3.9) and (3.10) and is a linear operator. However,

$$\sqrt{f(x) + g(x)} \neq \sqrt{f(x)} + \sqrt{g(x)}$$

so $\sqrt{\ \ }$ does not obey (3.9) and is nonlinear.

A major difference between operator algebra and ordinary algebra is that numbers obey the commutative law of multiplication, but operators do not necessarily do so; $ab = ba$ if a and b are numbers, but $\hat{A}\hat{B}$ and $\hat{B}\hat{A}$ are not necessarily equal operators. We define the ***commutator*** $[\hat{A}, \hat{B}]$ of the operators $\hat{A}$ and $\hat{B}$ as the operator $\hat{A}\hat{B} - \hat{B}\hat{A}$:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \tag{3.7*}$$

If $\hat{A}\hat{B} = \hat{B}\hat{A}$, then $[\hat{A}, \hat{B}] = 0$, and we say that $\hat{A}$ and $\hat{B}$ ***commute.*** If $\hat{A}\hat{B} \neq \hat{B}\hat{A}$, then $\hat{A}$ and $\hat{B}$ do not commute. Note that $[\hat{A}, \hat{B}]f = \hat{A}\hat{B}f - \hat{B}\hat{A}f$. Since the order in which we apply the operators 3 and d/dx makes no difference, we have

$$\left[\hat{3}, \frac{d}{dx}\right] = \hat{3}\frac{d}{dx} - \frac{d}{dx}\hat{3} = 0$$

From Eq. (3.5) we have

$$\left[\frac{d}{dx}, \hat{x}\right] = \hat{D}\hat{x} - \hat{x}\hat{D} = 1 \tag{3.8}$$

The operators d/dx and $\hat{x}$ do not commute.

3.2 EIGENFUNCTIONS AND EIGENVALUES

Suppose that the effect of operating on some function $f(x)$ with the operator $\hat{A}$ is simply to multiply $f(x)$ by a certain constant k. We then say that $f(x)$ is an ***eigenfunction*** of $\hat{A}$ with ***eigenvalue*** k. As part of the definition, we shall require that the eigenfunction $f(x)$ is not identically zero. By this we mean that, although $f(x)$ may vanish at various points, it is not everywhere zero. We have

$$\hat{A}f(x) = kf(x) \qquad \textbf{(3.14)*}$$

(*Eigen* is a German word meaning *characteristic*. "Eigenvalue" is a hybrid word; it has been suggested that "characteristicwert" would be just as suitable.) As an example of (3.14), e^{2x} is an eigenfunction of the operator d/dx with eigenvalue 2:

$$(d/dx)e^{2x} = 2e^{2x}$$

However, sin $2x$ is not an eigenfunction of d/dx, since $(d/dx)(\sin 2x) = 2\cos 2x$, which is not a constant times sin $2x$.

EXAMPLE (a) Find the eigenfunctions and eigenvalues of the operator d/dx. (b) If we impose the boundary condition that the eigenfunctions remain finite as $x \rightarrow \pm\infty$, find the eigenvalues.

(a) Equation (3.14) with $\hat{A} = d/dx$ becomes

$$df(x)/dx = kf(x) \qquad (3.17)$$

$$df/f = k\,dx$$

Integration gives

$$\ln f = kx + \text{constant}$$

$$f = e^{\text{constant}}e^{kx}$$

$$f = ce^{kx} \qquad (3.18)$$

The eigenfunctions of d/dx are given by (3.18). The eigenvalues are k, which can be any number whatever and (3.17) will still be satisfied. The eigenfunctions contain an arbitrary multiplicative constant c. This is true for the eigenfunctions of any linear operator, as was proved in the previous example. Each different value of k in (3.18) gives a different eigenfunction. However, eigenfunctions with the same value of k but different values of c are not independent of each other.

(b) Since k can be complex, we write it as $k = a + ib$, where a and b are real numbers. We then have $f(x) = ce^{ax}e^{ibx}$. The factor e^{ax} goes to infinity as x goes to infinity if a is positive; it goes to infinity as x goes to minus infinity if a is negative. Hence the boundary conditions require that $a = 0$, and the eigenvalues are $k = ib$.

$$\hat{q} = q \cdot$$

Each Cartesian component of linear momentum p_q is replaced by the operator

$$\hat{p}_q = \frac{\hbar}{i}\frac{\partial}{\partial q} = -i\hbar\frac{\partial}{\partial q}$$

where $i = \sqrt{-1}$ and $\partial/\partial q$ is the operator for the partial derivative with respect to the coordinate q. Note that $1/i = i/i^2 = i/(-1) = -i$.

Consider some examples. The operator corresponding to the x coordinate is multiplication by x:

$$\hat{x} = x \cdot \quad \textbf{(3.21)*}$$

Also,

$$\hat{y} = y \cdot \quad \text{and} \quad \hat{z} = z \cdot \quad \textbf{(3.22)*}$$

The operators for the components of linear momentum are

$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}, \qquad \hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y}, \qquad \hat{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z} \quad \textbf{(3.23)*}$$

The operator corresponding to p_x^2 is

$$\hat{p}_x^2 = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 = \frac{\hbar}{i}\frac{\partial}{\partial x}\frac{\hbar}{i}\frac{\partial}{\partial x} = -\hbar^2\frac{\partial^2}{\partial x^2} \quad (3.24)$$

with similar expressions for $\hat{p}_y^2$ and $\hat{p}_z^2$.

$$\mathbf{v} \equiv \frac{d\mathbf{r}}{dt} = \mathbf{i}\frac{dx}{dt} + \mathbf{j}\frac{dy}{dt} + \mathbf{k}\frac{dz}{dt} \tag{5.34}$$

$$v_x = dx/dt\,, \qquad v_y = dy/dt\,, \qquad v_z = dz/dt$$

We define the particle's ***linear momentum*** vector $\mathbf{p}$ by

$$\mathbf{p} \equiv m\mathbf{v} \qquad \textbf{(5.35)*}$$

$$p_x = mv_x\,, \qquad p_y = mv_y\,, \qquad p_z = mv_z \tag{5.36}$$

The particle's ***angular momentum*** $\mathbf{L}$ with respect to the coordinate origin is defined in classical mechanics as

$$\mathbf{L} \equiv \mathbf{r} \times \mathbf{p} \qquad \textbf{(5.37)*}$$

$$\mathbf{L} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \tag{5.38}$$

$$L_x = yp_z - zp_y\,, \qquad L_y = zp_x - xp_z\,, \qquad L_z = xp_y - yp_x \tag{5.39}$$

where (5.29) was used. L_x, L_y, and L_z are the components of $\mathbf{L}$ along the x, y, and z axes. The angular-momentum vector $\mathbf{L}$ is perpendicular to the plane defined by the particle's position vector $\mathbf{r}$ and its velocity $\mathbf{v}$ (Fig. 5.4).

The *torque* $\boldsymbol{\tau}$ acting on a particle is defined as the cross product of $\mathbf{r}$ and the force $\mathbf{F}$ acting on the particle: $\boldsymbol{\tau} \equiv \mathbf{r} \times \mathbf{F}$. It is readily shown that (*Halliday and Resnick,* Section 12-3) $\boldsymbol{\tau} = d\mathbf{L}/dt$. When there is no torque acting on the particle, the rate of change of its angular momentum is zero; that is, its angular momentum is constant (or conserved). For a planet orbiting the sun, the gravitational force is radially directed. Since the cross product of two parallel vectors is zero, there is no torque on the planet and its angular momentum is conserved.

One-Particle Orbital-Angular-Momentum Operators. Now for the quantum-mechanical treatment. In quantum mechanics, there are two kinds of angular momenta: ***orbital angular momentum*** results from the motion of a particle through space, and is the analog of the classical-mechanical quantity **L**; ***spin angular momentum*** (Chapter 10) is an intrinsic property of many microscopic particles and has no classical-mechanical analog. We are now considering only orbital angular momentum.

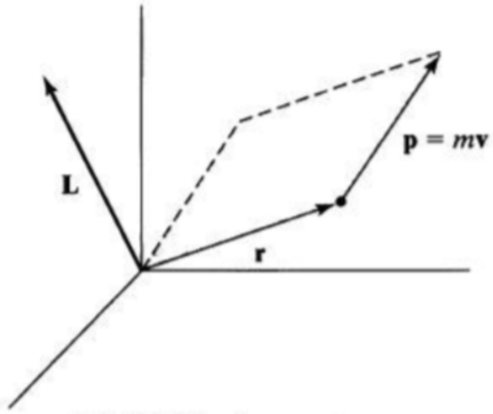

FIGURE 5.4 $\mathbf{L} = \mathbf{r} \times \mathbf{p}$

We get the quantum-mechanical operators for the components of orbital angular momentum of a particle by replacing the coordinates and momenta in the classical equations (5.39) by their corresponding operators [Eqs. (3.21)–(3.23)]. We find

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{5.40}$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{5.41}$$

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{5.42}$$

(Since $\hat{y}\hat{p}_z = \hat{p}_z\hat{y}$, and so on, we do not run into any problems of noncommutativity in constructing these operators.) Using

$$\hat{L}^2 = |\hat{\mathbf{L}}|^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{5.43}$$

we can construct the operator for the square of the angular-momentum magnitude from the operators in (5.40)–(5.42).

At last, we are ready to express the angular-momentum components in spherical coordinates. Substituting (5.51), (5.63), and (5.64) into (5.40), we have

$$\hat{L}_x = -i\hbar\left[r\sin\theta\sin\phi\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)\right.$$
$$\left. - r\cos\theta\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\right]$$

$$\hat{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \tag{5.65}$$

Now consider the potential-energy and kinetic-energy operators in one dimension. Suppose we had a system with the potential-energy function $V(x) = ax^2$, where a is a constant. Replacing x with $x\cdot$, we see that the potential-energy operator is simply multiplication by ax^2:

$$\hat{V}(x) = ax^2 \cdot$$

In general, we have for any potential-energy function

$$\hat{V}(x) = V(x)\cdot \qquad \textbf{(3.25)*}$$

The classical-mechanical expression for the kinetic energy T in (3.20) is

$$T = p_x^2/2m \qquad \textbf{(3.26)*}$$

Replacing p_x by the corresponding operator (3.23), we have

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \qquad (3.27)$$

where (3.24) has been used, and the partial derivative becomes an ordinary derivative in one dimension. The classical-mechanical Hamiltonian (3.20) is

$$H = T + V = p_x^2/2m + V(x) \qquad (3.28)$$

The corresponding quantum-mechanical Hamiltonian (or energy) operator is

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \qquad \textbf{(3.29)*}$$

which agrees with the operator in the Schrödinger equation (3.1). Note that all these operators are linear.

One-Particle Orbital-Angular-Momentum Eigenfunctions and Eigenvalues. We now find the common eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$, which we denote by Y. Since these operators involve only θ and ϕ, Y is a function of these two coordinates: $Y = Y(\theta, \phi)$. (Of course, since the operators are linear, we can multiply Y by an arbitrary function of r and still have an eigenfunction of $\hat{L}^2$ and $\hat{L}_z$.) We must solve

$$\hat{L}_z Y(\theta, \phi) = bY(\theta, \phi) \qquad (5.69)$$

$$\hat{L}^2 Y(\theta, \phi) = cY(\theta, \phi) \qquad (5.70)$$

where b and c are the eigenvalues of $\hat{L}_z$ and $\hat{L}^2$.

Using the $\hat{L}_z$ operator, we have

$$-i\hbar\frac{\partial}{\partial\phi}Y(\theta, \phi) = bY(\theta, \phi) \qquad (5.71)$$

Since the operator in (5.71) does not involve θ, we try a separation of variables, writing

$$Y(\theta, \phi) = S(\theta)T(\phi) \qquad (5.72)$$

In summary, the one-particle orbital angular-momentum eigenfunctions and eigenvalues are [Eqs. (5.69), (5.70), (5.75), and (5.94)]

$$\hat{L}^2 Y_l^m(\theta, \phi) = l(l+1)\hbar^2 Y_l^m(\theta, \phi), \quad l = 0, 1, 2, \ldots \qquad \textbf{(5.108)*}$$

$$\hat{L}_z Y_l^m(\theta, \phi) = m\hbar Y_l^m(\theta, \phi), \quad m = -l, -l+1, \ldots, l-1, l \qquad \textbf{(5.109)*}$$

where the eigenfunctions are given by (5.107). Often the symbol m_l is used instead of m for the L_z quantum number.

Notación de Dirac:

Notación funcional		Notación de Dirac
$\Psi(q,t)$	$\longrightarrow$	**ket:** $\|\Psi\rangle$
$\Psi(q,t)^*$	$\longrightarrow$	**bra:** $\langle\Psi\|$
$\int_{\mathbb{R}^n} \Psi_i^* \Psi_j dq$	$\longrightarrow$	**bracket:** $\langle\Psi_i\|\Psi_j\rangle = \langle i\|j\rangle$
$\hat{\alpha}\Psi$	$\longrightarrow$	$\hat{\alpha}\,\|\Psi\rangle$
$(\hat{\alpha}\Psi)^*$	$\longrightarrow$	$\langle\Psi\|\,\hat{\alpha}^\dagger$
$\int_{\mathbb{R}^n} \Psi_i^* \hat{\alpha}\Psi_j dq$	$\longrightarrow$	$\langle\Psi_i\|\hat{\alpha}\|\Psi_j\rangle = \langle i\|\hat{\alpha}\|j\rangle$
$\hat{\alpha}\Psi = a\Psi$	$\longrightarrow$	$\hat{\alpha}\,\|a\rangle = a\,\|a\rangle$

- La unión de bra y ket, en ese orden, genera una integral a todo el espacio.
- $\hat{\alpha}^\dagger$ es el operador **adjunto** de $\hat{\alpha}$. El adjunto actúa sobre los bra del mismo modo que el operador actúa sobre los ket. Se cumple: $(\hat{\alpha}^\dagger)^\dagger \equiv \hat{\alpha}$.
- Un operador es **hermítico** sí y sólo si $\hat{\alpha}^\dagger = \hat{\alpha}$.
- Para un producto de operadores $(\hat{\alpha}\hat{\beta})^\dagger = \hat{\beta}^\dagger\hat{\alpha}^\dagger$, de modo que $(\hat{\alpha}\hat{\beta}\Psi)^* \longrightarrow \langle\Psi|\,\hat{\beta}^\dagger\hat{\alpha}^\dagger$
- Para una combinación lineal de operadores $(c_1\hat{\alpha} \pm c_2\hat{\beta})^\dagger = c_1^*\hat{\alpha}^\dagger \pm c_2^*\hat{\beta}^\dagger$.

Suma de operadores: Definimos la suma de operadores de modo que, para cualquier función Ψ

$$\hat{C} = \hat{A} + \hat{B} \quad \Longrightarrow \quad \hat{C}\Psi = \hat{A}\Psi + \hat{B}\Psi. \tag{6}$$

De este modo, la suma de operadores hereda las propiedades de la suma de funciones: conmutativa y asociativa.

El operador nulo, $\hat{0}\Psi = 0$ para cualquier función Ψ, es el *elemento neutro* de la suma: $\forall_{\hat{A}} : \hat{A}+\hat{0} = \hat{A}$.

Producto de operadores: Definimos el producto de dos operadores como la aplicación sucesiva de ambos, siendo el más cercano a la función el primero que actúa:

$$\hat{C} = \hat{A}\hat{B} \quad \Longrightarrow \quad \hat{C}\Psi = \hat{A}(\hat{B}\Psi). \tag{7}$$

Este producto es asociativo, y distributivo respecto de la suma. Sin embargo, en general, el producto de dos operadores cualesquiera no conmuta.

El operador unidad o identidad, $\hat{1}\Psi = \Psi$ para toda función Ψ, es el *elemento neutro* del producto: $\forall_{\hat{A}} : \hat{A}\hat{1} = \hat{1}\hat{A}$.

Dado un operador $\hat{A}$ su *inverso*, $\hat{A}^{-1}$, es tal que $\hat{A}\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = \hat{1}$.

El conjunto de operadores lineales y hermíticos, con la adición y producto definidos, constituye un *álgebra* no conmutativa.

Se define el *conmutador* de dos operadores como: $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. El conmutador es, en general, un operador, y será nulo sí y sólo si los operadores conmutan.

Operador de posición de una partícula: En un problema unidimensional (1D), el operador posición es $\hat{x} = x\hat{1}$ y tiene carácter multiplicativo. Generalizándo a 3D, podemos definir el operador *vectorial* de posición:

$$\hat{\vec{r}} = \hat{x}\vec{u}_x + \hat{y}\vec{u}_y + \hat{z}\vec{u}_z, \tag{8}$$

donde los $\vec{u}_\xi$ son los vectores unidad cartesianos.

Operador momento lineal de una partícula: Su forma en 1D y en 3D es:

$$\text{(1D): } \hat{p}_x = -i\hbar\frac{\partial}{\partial x}, \quad \text{(3D): } \hat{\vec{p}} = -i\hbar\left\{\vec{u}_x\frac{\partial}{\partial x} + \vec{u}_y\frac{\partial}{\partial y} + \vec{u}_z\frac{\partial}{\partial z}\right\} = -i\hbar\hat{\vec{\nabla}}, \tag{9}$$

donde $i = \sqrt{-1}$ es el número imaginario, y $\hbar = h/2\pi$. La presencia de i permite que el operador sea hermítico. Veámoslo en 1D:

$$\int_{-\infty}^{\infty}\left[-i\hbar\frac{d}{dx}\Psi(x)\right]^*\Psi(x)dx = +i\hbar\int_{-\infty}^{\infty}\frac{d\Psi^*}{dx}\Psi(x)dx = \left\{\begin{array}{c}\text{Por partes:}\\ U = \Psi \Longrightarrow dU = \frac{d\Psi}{dx}dx\\ dV = \frac{d\Psi^*}{dx}dx \Longrightarrow V = \Psi^*\end{array}\right\}$$

$$= i\hbar\,[\Psi^*\Psi]_{-\infty}^{\infty} + \int_{-\infty}^{\infty}\Psi^*[-i\hbar\frac{d}{dx}]\Psi dx, \tag{10}$$

de modo que $\hat{p}_x$ es hermítico sí y sólo si $\lim_{x\to\pm\infty}|\Psi|^2 = 0$, pero este comportamiento está garantizado por la condición de cuadrado integrable que debe cumplir la función de onda.