Part 3
Quantum Mechanics

6 Mathematical Techniques

This chapter, and the following one, contain a brief review of mathematical techniques and the basic results of quantum mechanics. Other texts should be consulted for a fuller discussion (see *Further Reading*). A more 'physical' presentation is given in the following chapters.

It is impossible to provide the necessary background without employing some rather technical mathematics, which some readers may find difficult. It should be possible to skip these chapters on a first reading.

6.1 Functions

6.1.1 Continuous functions

Spinless quantum mechanics makes extensive use of *continuous functions*. An example of a continuous function of the coordinate x is the sine function $\sin(x)$. The term 'continuous' indicates that the function never makes a sudden jump when x changes by small amounts.

The discussion below uses the following set of continuous functions:

$$\psi_n(x) = \begin{cases} 0 & \text{if } x < 0 \\ 2^{1/2}\sin(\pi n x) & \text{if } 0 \le x \le 1 \\ 0 & \text{if } 1 < x \end{cases} \tag{6.1}$$

If n is an integer, each function $\psi_n(x)$ is continuous, since there are no sudden jumps at the points $x = 0$ and $x = 1$:

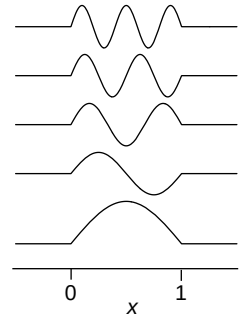


Figure 6.1
Some continuous functions.

The function $\psi_n(x)$ is *localized* to the interval $0 \le x \le 1$.

Spin Dynamics: Basics of Nuclear Magnetic Resonance, Second Edition Malcolm H. Levitt

Functions of importance to quantum mechanics are often complex. The complex conjugate is denoted by an asterisk:

$$f(x) = \text{Re}\{f(x)\} + \text{i Im}\{f(x)\}$$
$$f(x)^* = \text{Re}\{f(x)\} - \text{i Im}\{f(x)\}$$

6.1.2 Normalization

A function $f(x)$ of one variable x is said to be *normalized* if the following condition holds:

$$\int_{-\infty}^{\infty} \mathrm{d}x\ f(x)^* f(x) = 1 \qquad \text{(normalization)} \tag{6.2}$$

Functions may be normalized by multiplication with a suitable scaling factor, chosen to satisfy Equation 6.2.

6.1.3 Orthogonal and orthonormal functions

Two functions $f(x)$ and $g(x)$ are said to be *orthogonal* if the following condition holds:

$$\int_{-\infty}^{\infty} \mathrm{d}x\ f(x)^* g(x) = 0 \qquad \text{(orthogonality)} \tag{6.3}$$

The set of functions $\psi_n(x)$, with $n = 1, 2, 3 \ldots$ are all orthogonal to each other:

$$\int_{-\infty}^{\infty} \mathrm{d}x\ \psi_m(x)^* \psi_n(x) = \delta_{mn} \tag{6.4}$$

In this expression, the *Kronecker delta function* δ_{mn} is used. This symbol has the following meaning:

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{otherwise} \end{cases} \tag{6.5}$$

A set of orthogonal, normalized functions are said to be *orthonormal*.

6.1.4 Dirac notation

The functions $\psi_n(x)$ are distinguished by the value of the integer n. Dirac introduced the following elegant notation for orthonormal functions, indexed by the integer n:

$$\psi_n(x) \equiv |n\rangle \qquad \psi_n(x)^* \equiv \langle n|$$

The symbol $|n\rangle$ is pronounced 'ket-n'. The symbol $\langle n|$ is pronounced 'bra-n'.

The 'bra-ket' $\langle m|n\rangle$ implies integration, as follows:

$$\langle m|n\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\ \psi_m(x)^* \psi_n(x)$$

The orthonormalization condition (Equation 6.4) may therefore be written very concisely:

$$\langle m|n\rangle = \delta_{mn} \qquad \text{(orthonormality)} \tag{6.6}$$

In general, the Dirac 'bra' and the 'ket' are related to each other by an operation known as the *adjoint*, denoted by a dagger (†):

$$\langle n| = \{|n\rangle\}^\dagger \qquad |n\rangle = \{\langle n|\}^\dagger$$

For functions, the adjoint is equivalent to taking the complex conjugate. A more general definition of the adjoint, which applies to operators as well as to functions, is given in Section 6.2.6.

6.1.5 Vector representation of functions

Suppose that a function $f(x)$ is expressed as a sum of the orthonormal functions $|n\rangle$, multiplied by numbers, called *coefficients*:

$$f(x) = f_1\psi_1(x) + f_2\psi_2(x) + f_3\psi_3(x) + \ldots$$

In the above example, this is possible only if the function $f(x)$ vanishes in the regions $x < 0$ and $x > 1$, since all of the functions $\psi_n(x)$ also vanish there.

Using the Dirac notation, the above expression reads

$$|f\rangle = f_1|1\rangle + f_2|2\rangle + f_3|3\rangle + \ldots$$

(The Dirac notation $|f\rangle$ for the function $f(x)$ is a little loose, but is convenient.)

By multiplying both sides from the left by $\langle n|$, and using orthonormality, we get

$$\langle n|f\rangle = f_n$$

which shows that the coefficents in the expansion may be evaluated from the integral

$$f_n = \int_{-\infty}^{\infty} \mathrm{d}x\ \psi_n(x)^* f(x)$$

For example, consider the following normalized function:

$$f(x) = \begin{cases} 0 & \text{if } x < 0 \\ \frac{16}{3\sqrt{7}} \sin^5(\pi x) & \text{if } 0 \le x \le 1 \\ 0 & \text{if } 1 < x \end{cases} \tag{6.7}$$

which has the following appearance:

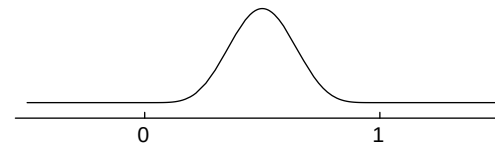


Figure 6.2
The function given in Equation 6.7.

The expansion coefficients in terms of the basis functions in Equation 6.1 may be evaluated as follows:

$$\begin{aligned} f_1 &= \frac{5}{3}\sqrt{\frac{2}{7}} \qquad & f_2 &= 0 \\ f_3 &= -\frac{5}{3\sqrt{14}} \qquad & f_4 &= 0 \\ f_5 &= \frac{1}{3\sqrt{14}} \\ &\vdots \end{aligned} \tag{6.8}$$

All higher terms f_6, $f_7 \ldots$ are equal to zero in this case.

It is convenient to list the coefficients f_1, $f_2 \ldots$ as a *column vector*, which is conveniently written as $|f\rangle$:

$$|f\rangle = \begin{pmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \\ \vdots \end{pmatrix}$$

This is called the *vector representation* of the function $f(x)$ in the *basis* $\{\psi_1(x), \psi_2(x), \ldots\}$.

For example, the function in Equation 6.7 could be written as

$$|f\rangle = \begin{pmatrix} \frac{5}{3}\sqrt{\frac{2}{7}} \\ 0 \\ -\frac{5}{3\sqrt{14}} \\ 0 \\ \frac{1}{3\sqrt{14}} \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

The 'bra' representation of f is a *row vector*, generated by exchanging rows and columns, and taking the complex conjugate:

$$\langle f| = \{|f\rangle\}^\dagger = \left({f_1}^*,\ {f_2}^*,\ {f_3}^*,\ {f_4}^*,\ {f_5}^* \cdots \right)$$

(Note that the adjoint turns a column vector into a row vector, as well as taking the complex conjugate.) For example, the bra vector for the function given above is

$$\langle f| = \{|f\rangle\}^\dagger = \left(\tfrac{5}{3}\sqrt{\tfrac{2}{7}},\ 0,\ -\tfrac{5}{3\sqrt{14}},\ 0,\ \tfrac{1}{3\sqrt{14}}\ 0,\ 0\cdots\right)$$

(The complex conjugate does not do anything in this case, since the coefficients are real.)

By definition, the vector representation of a basis ket contains only zeros, except in one place, where the number one appears, for example:

$$|2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

and

$$\langle 2| = (0\,,\quad 1\,,\quad 0\,,\quad 0\,,\quad \ldots)$$

Using this representation, the orthonormality of the basis states appears as a straightforward application of matrix multiplication; for example:

$$\langle 1|2\rangle = (1\,,\quad 0\,,\quad 0\,,\quad 0\,,\quad \ldots)\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} = 0$$

6.2 Operators

Quantum mechanics makes extensive use of *operators*, denoted in this book by a hat (ˆ). Two examples are the first and second derivative operators $\widehat{D}_x$ and $\widehat{D}_x^2$, which have the following effect on operand functions $f(x)$:

$$\widehat{D}_x f(x) = \frac{\mathrm{d}f(x)}{\mathrm{d}x}$$

$$\widehat{D}_x^2 f(x) = \widehat{D}_x\left\{\widehat{D}_x f(x)\right\} = \frac{\mathrm{d}^2 f(x)}{\mathrm{d}x^2}$$

Another example is the operator $\hat{x}$, which has the effect of multiplying the operand by the coordinate value:

$$\hat{x} f(x) = x f(x)$$

For example, the operator $\widehat{D}_x$ applied to the function $\psi_n(x)$ yields

$$\widehat{D}_x \psi_n(x) = \sqrt{2}\, n\pi \cos(n\pi x)$$

in the range $0 < x < 1$.

A trivial example of an operator is the *unity operator* $\widehat{1}$, which simply leaves any operand unchanged:

$$\widehat{1} f(x) = f(x)$$

Another trivial example is the *null operator* $\widehat{0}$, which always generates the result zero, whatever the operand:

$$\widehat{0} f(x) = 0$$

6.2.1 Commutation

In everyday life, the effect of consecutive operations depends on their order. For example, the effect of driving straight for 100 m, then turning left, and driving straight for 50 m, is different from the effect of driving straight for 50 m, turning left, and driving straight for 100 m.

The effect of mathematical operators is also dependent on their order. The effect of applying an operator $\widehat{A}$ and then applying the operator $\widehat{B}$ is notated $\widehat{B}\widehat{A}$, which implies

$$\widehat{B}\widehat{A} f(x) = \widehat{B}\left\{\widehat{A} f(x)\right\}$$

Similarly, the effect of applying an operator $\widehat{B}$ and then applying the operator $\widehat{A}$ is notated $\widehat{A}\widehat{B}$. Note that operators are written in order from *right to left*.

The *commutator* of two operators is defined thus:

$$\left[\widehat{A}, \widehat{B}\right] = \widehat{A}\widehat{B} - \widehat{B}\widehat{A} \tag{6.9}$$

For example, the commutator of the operators $\hat{x}$ and $\widehat{D}_x$ is given by

$$\left[\hat{x}, \widehat{D}_x\right] = -\widehat{1}$$

which may be seen by applying the operators to a function $f(x)$:

$$\begin{aligned}
\left[\hat{x}, \widehat{D}_x\right] f(x) &= \hat{x}\left\{\widehat{D}_x f(x)\right\} - \widehat{D}_x\left\{\hat{x} f(x)\right\} \\
&= \hat{x}\left\{\frac{\mathrm{d} f(x)}{\mathrm{d}x}\right\} - \frac{\mathrm{d}}{\mathrm{d}x}\left\{x f(x)\right\} \\
&= x\frac{\mathrm{d} f(x)}{\mathrm{d}x} - \left\{x\frac{\mathrm{d} f(x)}{\mathrm{d}x} + f(x)\frac{\mathrm{d}x}{\mathrm{d}x}\right\} \\
&= -f(x)
\end{aligned} \tag{6.10}$$

Two operators are said to *commute* if their commutator is zero. The result of applying two commuting operators does not depend on the order in which they are applied. For example, the unity operator $\widehat{1}$ commutes with all other operators.

Any operator commutes with any number. The symbols $a\widehat{A}$ and $\widehat{A}a$ have the same meaning.

6.2.2 Matrix representations

The *matrix element* of an operator $\widehat{Q}$ is defined as follows:

$$\langle m|\widehat{Q}|n\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\ {\psi_m}^*\widehat{Q}\psi_n \tag{6.11}$$

The matrix element depends on the basis states.

Here are some examples of matrix elements, using the operators discussed above and the basis set defined in Equation 6.1:

$$\begin{aligned}
&\langle 1|\widehat{D}_x|3\rangle = 0 && \langle 1|\hat{x}|4\rangle = -\frac{32}{225\pi^2}\\
&\langle 1|\widehat{D}_x^2|1\rangle = -\pi^2 && \langle 1|\hat{x}\widehat{D}_x|3\rangle = \frac{3}{4}\\
&\langle 2|\widehat{D}_x^2|2\rangle = -4\pi^2 && \langle 1|\widehat{D}_x\hat{x}|3\rangle = \frac{3}{4}\\
&\langle 1|\hat{x}|2\rangle = -\frac{16}{9\pi^2} && \langle 1|\hat{x}\widehat{D}_x|1\rangle = -\frac{1}{2}\\
&\langle 1|\hat{x}|3\rangle = 0 && \langle 1|\widehat{D}_x\hat{x}|1\rangle = \frac{1}{2}
\end{aligned} \tag{6.12}$$

The *matrix representation* of an operator is an array of all possible matrix elements:

$$\widehat{Q} = \begin{pmatrix} \langle 1|\widehat{Q}|1\rangle & \langle 1|\widehat{Q}|2\rangle & \dots \\ \langle 2|\widehat{Q}|1\rangle & \langle 2|\widehat{Q}|2\rangle & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \tag{6.13}$$

The matrix representation of an operator depends on the choice of basis.

For example, the operator $\hat{x}$ has the following matrix representation in the basis set of Equation 6.1:

$$\hat{x} = \begin{pmatrix} \frac{1}{2} & -\frac{16}{9\pi^2} & 0 & -\frac{32}{225\pi^2} & \dots \\ -\frac{16}{9\pi^2} & \frac{1}{2} & -\frac{48}{25\pi^2} & 0 & \dots \\ 0 & -\frac{48}{25\pi^2} & \frac{1}{2} & -\frac{96}{49\pi^2} & \dots \\ -\frac{32}{225\pi^2} & 0 & -\frac{96}{49\pi^2} & \frac{1}{2} & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{6.14}$$

The operators $\widehat{0}$ and $\widehat{1}$ have the following matrix representations:

$$\widehat{0} = \begin{pmatrix} 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

$$\widehat{1} = \begin{pmatrix} 1 & 0 & 0 & 0 & \dots \\ 0 & 1 & 0 & 0 & \dots \\ 0 & 0 & 1 & 0 & \dots \\ 0 & 0 & 0 & 1 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{6.15}$$

In this book, I use the same symbol for an operator and its matrix representation. There are occasional pitfalls in this practice, which will be pointed out when they occur.

The *matrix representation of the product of two operators* is given by the usual law for matrix multiplication, i.e.

$$\langle m|\widehat{B}\widehat{A}|n\rangle = \sum_p \langle m|\widehat{B}|p\rangle\langle p|\widehat{A}|n\rangle \tag{6.16}$$

where the sum runs over all basis states $|p\rangle$.

For example, the matrix representations of $\hat{x}\widehat{D}_x$ and $\widehat{D}_x\hat{x}$ in the basis set of Equation 6.1 are given by

$$\hat{x}\widehat{D}_x = \begin{pmatrix} -\frac{1}{2} & -\frac{4}{3} & \frac{3}{4} & -\frac{8}{15} & \cdots \\ \frac{4}{3} & -\frac{1}{2} & -\frac{12}{5} & \frac{4}{3} & \cdots \\ -\frac{3}{4} & \frac{12}{5} & -\frac{1}{2} & -\frac{24}{7} & \cdots \\ \frac{8}{15} & -\frac{4}{3} & \frac{24}{7} & -\frac{1}{2} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

$$\widehat{D}_x\hat{x} = \begin{pmatrix} \frac{1}{2} & -\frac{4}{3} & \frac{3}{4} & -\frac{8}{15} & \cdots \\ \frac{4}{3} & \frac{1}{2} & -\frac{12}{5} & \frac{4}{3} & \cdots \\ -\frac{3}{4} & \frac{12}{5} & \frac{1}{2} & -\frac{24}{7} & \cdots \\ \frac{8}{15} & -\frac{4}{3} & \frac{24}{7} & \frac{1}{2} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{6.17}$$

Note that the matrix representations of $\hat{x}\widehat{D}_x$ and $\widehat{D}_x\hat{x}$ are different, since the operators $\hat{x}$ and $\widehat{D}_x$ do not commute. The matrix representations obey the equation $\left[\hat{x}, \widehat{D}_x\right] = \hat{x}\widehat{D}_x - \widehat{D}_x\hat{x} = -\widehat{1}$, as they should according to Equation 6.10.

6.2.3 Diagonal matrices

The matrix representation of an operator is said to be *diagonal* if it has the following type of structure:

$$\begin{pmatrix} \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & \bullet & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 0 & \bullet & 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 0 & 0 & \bullet & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & 0 & \cdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{6.18}$$

where the symbol $\bullet$ represents any number. The matrix representation of $\widehat{1}$, given in Equation 6.15, is diagonal.

6.2.4 Block diagonal matrices

A matrix representation is said to be *block-diagonal* if it has the following type of structure:

$$\begin{pmatrix} \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & \bullet & \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & \bullet & \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & \bullet & \cdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & \bullet & \cdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & \bullet & \cdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & \bullet & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{6.19}$$

where the symbol $\bullet$ represents any number.

6.2.5 Inverse

If two operators $\widehat{A}$ and $\widehat{B}$ satisfy the two relationships

$$\widehat{B}\widehat{A} = \widehat{A}\widehat{B} = \widehat{1}$$

then the operators are said to be *inverses* of each other. This relationship may be written

$$\widehat{A} = \widehat{B}^{-1}$$
$$\widehat{B} = \widehat{A}^{-1}$$

The inverse of a product of two operators is equal to the product of the inverses, taken in opposite order, i.e.

$$\left\{\widehat{D}\widehat{C}\right\}^{-1} = \widehat{C}^{-1}\widehat{D}^{-1}$$

6.2.6 Adjoint

Two operators $\widehat{A}$ and $\widehat{B}$ are said to be *adjoints* of each other if their matrix elements are related as follows:

$$\langle m|\widehat{A}|n\rangle = \langle n|\widehat{B}|m\rangle^*$$

for all (m, n). The adjoint relationship between these operators is written

$$\widehat{A} = \widehat{B}^{\dagger}$$
$$\widehat{B} = \widehat{A}^{\dagger}$$

The matrix representations of adjoint operators are related by (i) taking the *complex conjugate* of all elements and (ii) *exchanging rows and columns* (equal to transposing the matrix). For example, the adjoint of the operator $\hat{x}\widehat{D}_x$ has the following matrix representation in the basis set of Equation 6.1:

$$\left(\hat{x}\widehat{D}_x\right)^{\dagger} = \begin{pmatrix} -\frac{1}{2} & \frac{4}{3} & -\frac{3}{4} & \frac{8}{15} & \cdots \\ -\frac{4}{3} & -\frac{1}{2} & \frac{12}{5} & -\frac{4}{3} & \cdots \\ \frac{3}{4} & -\frac{12}{5} & -\frac{1}{2} & \frac{24}{7} & \cdots \\ -\frac{8}{15} & \frac{4}{3} & -\frac{24}{7} & -\frac{1}{2} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{6.20}$$

The adjoint of a product of two operators is equal to the product of the adjoints, taken in opposite order, i.e.

$$\left\{\widehat{D}\widehat{C}\right\}^{\dagger} = \widehat{C}^{\dagger}\widehat{D}^{\dagger}$$

The adjoint of an operator multiplied by a number is given by the adjoint of the operator, multiplied by the complex conjugate of the number, as follows:

$$\left\{a\widehat{C}\right\}^{\dagger} = a^*\widehat{C}^{\dagger}$$

6.2.7 Hermitian operators

An operator that is equal to its own adjoint is said to be *hermitian*:

$$\widehat{A} = \widehat{A}^\dagger \qquad \text{(hermitian)} \tag{6.21}$$

The operators $\hat{x}$ and $\widehat{D}_x^2$ are hermitian (the proofs are left as an exercise). The operator $\hat{x}\widehat{D}_x$, on the other hand, is not hermitian, as may be seen by comparing Equations 6.17 and 6.20.

In quantum mechanics, all experimental observations are associated with hermitian operators.

6.2.8 Unitary operators

If the adjoint of an operator is equal to the inverse, then the operator is said to be *unitary*:

$$\widehat{A}^{-1} = \widehat{A}^\dagger \qquad \text{(unitary)} \tag{6.22}$$

6.3 Eigenfunctions, Eigenvalues and Eigenvectors

6.3.1 Eigenequations

When an operator $\widehat{Q}$ is applied to a function $f(x)$, the result is in general a completely new function. For example, the application of $\widehat{D}_x$ to $\sin(x)$ leads to the function $\cos(x)$. However, in some cases, the result is simply proportional to the original function. An example of this is when the double derivative operator $\widehat{D}_x^2$ is applied to the function $\sin(x)$:

$$\widehat{D}_x^2 \sin(x) = \widehat{D}_x \cos(x) = -\sin(x)$$

The original function $\sin(x)$ is regenerated, but with a negative sign. This is an example of an *eigenequation*.[1] The function $\sin(x)$ is said to be an *eigenfunction* of the operator $\widehat{D}_x^2$, with *eigenvalue* -1.

In general, an eigenequation has the form

$$\widehat{Q}|f\rangle = q|f\rangle \tag{6.23}$$

where $|f\rangle$ is an *eigenfunction* of $\widehat{Q}$, and q is a number (possibly complex), called the *eigenvalue*.

An operator may have many possible eigenfunctions, each with its own eigenvalue. For example, the functions $|n\rangle = \psi_n(x)$, defined in Equation 6.1, are all eigenfunctions of $\widehat{D}_x^2$, with eigenvalues $-\pi^2 n^2$:

$$\widehat{D}_x^2|n\rangle = -\pi^2 n^2 |n\rangle$$

6.3.2 Degeneracy

In some cases, several eigenvalues of an operator are identical, even though the corresponding eigenfunctions are different. This is called *degeneracy*, and the identical eigenvalues are said to be *degenerate*. If all the eigenvalues of an operator are different, then that operator is said to be *non-degenerate*.

6.3.3 Eigenfunctions and eigenvalues of hermitian operators

The eigenfunctions and eigenvalues of *hermitian operators* have some useful properties: (i) the eigenvalues are real and (ii) the eigenfunctions associated with non-degenerate eigenvalues are orthogonal. It is always possible to choose the normalized eigenfunctions of a hermitian operator so as to form an orthonormal basis set, called the *eigenbasis* of that operator. For example, the set of functions $\psi_n(x)$ defined in Equation 6.1 is an eigenbasis of the hermitian operator $\widehat{D}_x^2$.

By definition, the matrix representation of a hermitian operator is *diagonal* in its own eigenbasis. For example, the matrix representation of $\widehat{D}_x^2$, in its own eigenbasis, is given by the following:

$$\widehat{D}_x^2 = \begin{pmatrix} -\pi^2 & 0 & 0 & 0 & \dots \\ 0 & -4\pi^2 & 0 & 0 & \dots \\ 0 & 0 & -9\pi^2 & 0 & \dots \\ 0 & 0 & 0 & -16\pi^2 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{6.24}$$

6.3.4 Eigenfunctions of commuting operators: non-degenerate case

Suppose that two operators $\widehat{A}$ and $\widehat{B}$ commute and that all the eigenvalues of the operator $\widehat{A}$ are different. Then *the eigenbasis of $\widehat{A}$ is also the eigenbasis of $\widehat{B}$*.

This property may be stated a little more narrowly: if $\widehat{A}$ has an eigenfunction $|f\rangle$ with a non-degenerate eigenvalue a:

$$\widehat{A}|f\rangle = a|f\rangle$$

then $|f\rangle$ must also be an eigenfunction of $\widehat{B}$:

$$\widehat{B}|f\rangle = b|f\rangle$$

The same property may be stated using the matrix representations of operators: *if $\widehat{A}$ has non-degenerate eigenvalues and if $\widehat{A}$ commutes with $\widehat{B}$, then the matrix representation of an operator $\widehat{B}$ in the eigenbasis of $\widehat{A}$ is diagonal*.

6.3.5 Eigenfunctions of commuting operators: degenerate case

What happens if $\widehat{A}$ does have degenerate eigenvalues? Suppose, for example, that the matrix representation of $\widehat{A}$ in its own eigenbasis has the following form:

$$\begin{pmatrix}
a_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & a_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & a_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & a_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & a_4 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & a_4 & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & 0 & a_4 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & a_5 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & a_5 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & a_5 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & a_5 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix}$$

where $a_1, a_2 \ldots$ are all different, but the second and third eigenfunctions are degenerate, as are the fifth, sixth and seventh. If $\widehat{A}$ and $\widehat{B}$ commute, then the matrix representation of $\widehat{B}$ is block diagonal in the eigenbasis of $\widehat{A}$:

$$\widehat{B} = \begin{pmatrix}
\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & \bullet & \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & \bullet & \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & \bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & \bullet & \cdots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & \bullet & \cdots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & \bullet & \cdots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \bullet & \bullet & \bullet & \bullet & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix}$$

Note how the blocks follow the pattern of degeneracy in the eigenvalues of $\widehat{A}$.

6.3.6 Eigenfunctions of commuting operators: summary

The interplay of degeneracy and the form of matrix representations is therefore quite tricky. The key results, for two commuting operators $\widehat{A}$ and $\widehat{B}$, are as follows:

1. If the eigenvalues of $\widehat{A}$ are all different, then the matrix represention of $\widehat{B}$ in the eigenbasis of $\widehat{A}$ is always *diagonal*.

2. If some of the eigenvalues of $\widehat{A}$ are degenerate, then the matrix represention of $\widehat{B}$ in the eigenbasis of $\widehat{A}$ is *block diagonal*, but not necessarily diagonal.

3. In *all* cases, a basis may be *found* in which the matrix representations of two commuting operators $\widehat{A}$ and $\widehat{B}$ are *both* diagonal. However, one may have to look for such a basis.

6.3.7 Eigenvectors

The vector representation of an operator eigenfunction is called an *eigenvector*. The eigenvectors of a matrix are the vector representations of the eigenfunctions of the corresponding operator.

For example, suppose that an operator $\widehat{A}$ has the following eigenequation:

$$\widehat{A}|f\rangle = a|f\rangle$$

where a is the eigenvalue and $|f\rangle$ is the eigenfunction.

The following matrix-vector equation then applies:

$$\mathbf{Af} = a\mathbf{f}$$

where $\mathbf{A}$ is the matrix representation of the operator $\widehat{A}$ and $\mathbf{f}$ is the vector representation of the function $|f\rangle$. This equation implies that when the vector $\mathbf{f}$ is multiplied from the left by the matrix $\mathbf{A}$, the result is the same as the starting vector $\mathbf{f}$, but multiplied by a number a.

Eigenfunctions and eigenvectors are so closely related that the terms are often used interchangeably.

6.4 Diagonalization

A square matrix $\mathbf{A}$ may always be written in the following form:

$$\mathbf{A} = \mathbf{XDX}^{-1} \tag{6.25}$$

where the matrix $\mathbf{D}$ is diagonal. The expression Equation 6.25 is called the *diagonal form* of $\mathbf{A}$, and the procedure for finding the matrices $\mathbf{X}$ and $\mathbf{D}$ is called the *diagonalization* of $\mathbf{A}$.

Diagonalization is closely related to finding the eigenvalues and eigenvectors of a matrix:

1. The elements of the diagonal matrix $\mathbf{D}$ are the *eigenvalues* of $\mathbf{A}$.

2. The *columns* of the matrix $\mathbf{X}$ are *eigenvectors* of $\mathbf{A}$.

Suppose, for example, that a matrix $\mathbf{A}$ has a set of eigenvalues $\{a_1, a_2 \ldots\}$, each with a corresponding eigenvector $\{\mathbf{f}_1, \mathbf{f}_2 \ldots\}$:

$$\mathbf{Af}_1 = a_1\mathbf{f}_1$$

$$\mathbf{Af}_2 = a_2\mathbf{f}_2$$

The diagonal elements of $\mathbf{D}$ are the eigenvalues of $\mathbf{A}$:

$$\mathbf{D} = \begin{pmatrix} a_1 & 0 & 0 & \ldots \\ 0 & a_2 & 0 & \ldots \\ 0 & 0 & a_3 & \ldots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

The columns of the matrix $\mathbf{X}$ are the eigenvectors of $\mathbf{A}$:

$$\mathbf{X} = \begin{pmatrix} \vdots & \vdots & \vdots & \\ \mathbf{f}_1\ , & \mathbf{f}_2\ , & \mathbf{f}_3\ , & \ldots \\ \vdots & \vdots & \vdots & \end{pmatrix}$$

6.4.1 Diagonalization of hermitian or unitary matrices

In general, the matrix $\mathbf{X}^{-1}$ must be determined by a full matrix inversion of $\mathbf{X}$. However, in the common case that $\mathbf{A}$ is *hermitian* or *unitary*, a shortcut is available. Suppose that the eigenvectors are *normalized*, so that

$$\mathbf{f}_1{}^\dagger \cdot \mathbf{f}_1 = 1$$
$$\mathbf{f}_2{}^\dagger \cdot \mathbf{f}_2 = 1$$

and so on, where the adjoint (†) implies transforming a column vector into a row vector, followed by taking the complex conjugate. If the eigenvectors are normalized, then the matrix $\mathbf{X}^{-1}$ is simply the adjoint of $\mathbf{X}$:

$$\mathbf{X}^{-1} = \mathbf{X}^\dagger$$

In this case, the diagonalization Equation 6.25 reads

$$\mathbf{A} = \mathbf{X}\mathbf{D}\mathbf{X}^\dagger \tag{6.26}$$

The adjoint is much easier to calculate than the inverse, so this form is very useful.

⚠ Equation 6.26 may only be used if $\mathbf{A}$ is hermitian or unitary, and the eigenvectors are *normalized*.

6.5 Exponential Operators

6.5.1 Powers of operators

The symbol $\widehat{A}^N$, where N is an integer, should be understood in the following way:

$$\widehat{A}^0 = \widehat{1}$$
$$\widehat{A}^1 = \widehat{A}$$
$$\widehat{A}^2 = \widehat{A}\widehat{A}$$
$$\widehat{A}^3 = \widehat{A}\widehat{A}\widehat{A} \tag{6.27}$$

and so on.

All powers of an operator commute with each other, which implies that they have the same eigenfunctions; i.e. if

$$\widehat{Q}|f\rangle = q|f\rangle$$

then

$$\widehat{Q}^N|f\rangle = q^N|f\rangle \tag{6.28}$$

The powers of the null and unity operators are given by

$$\begin{aligned}\widehat{0}^N &= \widehat{0}\\ \widehat{1}^N &= \widehat{1}\end{aligned} \tag{6.29}$$

6.5.2 Exponentials of operators

The exponential of an ordinary number q is given by the following series:

$$\exp\{q\} = 1 + q + \frac{1}{2!}q^2 + \frac{1}{3!}q^3 + \dots$$

Similarly, the exponential of an operator has the following meaning:

$$\exp\{\widehat{Q}\} = \widehat{1} + \widehat{Q} + \frac{1}{2!}\widehat{Q}^2 + \frac{1}{3!}\widehat{Q}^3 + \dots \tag{6.30}$$

The exponential of an operator commutes with the original operator and, therefore, has the same eigenfunctions. The eigenvalues of $\exp\{\widehat{Q}\}$ are given by the exponentials of the eigenvalues of $\widehat{Q}$, i.e.

$$\mathrm{e}^{\widehat{Q}}|f\rangle = \mathrm{e}^{q}|f\rangle \tag{6.31}$$

The matrix representation of an exponential operator $\exp\{\widehat{Q}\}$ is diagonal in the eigenbase of $\widehat{Q}$. For example, the matrix representation of the operator $\exp\{\widehat{D}_x^2\}$, in the eigenbasis $|n\rangle$, is given from Equation 6.24 by

$$\exp\{\widehat{D}_x^2\} = \begin{pmatrix} \mathrm{e}^{-\pi^2} & 0 & 0 & 0 & \dots \\ 0 & \mathrm{e}^{-4\pi^2} & 0 & 0 & \dots \\ 0 & 0 & \mathrm{e}^{-9\pi^2} & 0 & \dots \\ 0 & 0 & 0 & \mathrm{e}^{-16\pi^2} & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

6.5.3 Exponentials of unity and null operators

From Equations 6.29 and 6.30, the exponential of the unity operator is given by

$$\exp\{\widehat{1}\} = \mathrm{e} \times \widehat{1}$$

and the exponential of the null operator is equal to the unity operator:

$$\exp\{\widehat{0}\} = \widehat{1}$$

6.5.4 Products of exponential operators

In the mathematics of ordinary numbers, the following equation is always valid: $\exp\{a+b\} = \exp\{a\}\exp\{b\} = \exp\{b\}\exp\{a\}$. The analogous property is true for *commuting operators*:

$$\exp\{\widehat{A}+\widehat{B}\} = \exp\{\widehat{A}\}\exp\{\widehat{B}\} = \exp\{\widehat{B}\}\exp\{\widehat{A}\} \quad \text{if} \quad \left[\widehat{A},\widehat{B}\right] = 0 \tag{6.32}$$

If the operators $\widehat{A}$ and $\widehat{B}$ do not commute, then there is no general result for $\exp\{\widehat{A}+\widehat{B}\}$. However, if the non-commuting operators are both *small*, then an *approximate* formula for the exponential of their sum does exist (see Equation 6.35).

6.5.5 Inverses of exponential operators

The inverse of an exponential operator is produced simply by changing the sign of the exponent:

$$\exp\{\widehat{A}\}^{-1} = \exp\{-\widehat{A}\}$$

This is easily proved by using Equation 6.32 and the fact that any operator commutes with itself:

$$\exp\{\widehat{A}\}\exp\{-\widehat{A}\} = \exp\{\widehat{A}-\widehat{A}\} = \exp\{\widehat{0}\} = \widehat{1}$$

6.5.6 Complex exponentials of operators

The *complex exponential* of an operator has a straightforward meaning:

$$\exp\{\mathrm{i}\widehat{Q}\} = \widehat{1} + \mathrm{i}\widehat{Q} + \frac{\mathrm{i}^2}{2!}\widehat{Q}^2 + \frac{\mathrm{i}^3}{3!}\widehat{Q}^3 + \ldots \tag{6.33}$$

The complex exponential of a hermitian operator is unitary:

$$\exp\{\mathrm{i}\widehat{Q}\}^\dagger = \exp\{(\mathrm{i}\widehat{Q})^\dagger\} = \exp\{(\mathrm{i}^*)(\widehat{Q}^\dagger)\} = \exp\{(-\mathrm{i})\widehat{Q}\} = \exp\{\mathrm{i}\widehat{Q}\}^{-1}$$

6.5.7 Exponentials of small operators

If an operator $\widehat{A}$ is *small*,[2] then the exponential may be approximated thus:

$$\exp\{\widehat{A}\} \cong \widehat{1} + \widehat{A} \tag{6.34}$$

It follows that the product of exponentials of two *small* operators may be written as

$$\exp\{\widehat{A}\}\exp\{\widehat{B}\} \cong \exp\{\widehat{B}\}\exp\{\widehat{A}\} \cong \exp\{\widehat{B}+\widehat{A}\} \tag{6.35}$$

Note that this property only applies to *general* operators if the operators commute (see Section 6.5.4).

6.5.8 Matrix representations of exponential operators

Suppose that an operator $\widehat{A}$ has a matrix representation $\mathbf{A}$. What is the matrix representation of $\exp\{\widehat{A}\}$?

If $\mathbf{A}$ is diagonal, then the result is very simple. The matrix representation of $\widehat{A}$ is also diagonal and the diagonal elements are simply the exponentials of the original matrix elements. For example, if

$$\mathbf{A} = \begin{pmatrix} a_1 & 0 & 0 & \dots \\ 0 & a_2 & 0 & \dots \\ 0 & 0 & a_3 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

then

$$\exp\{\mathbf{A}\} = \begin{pmatrix} \exp\{a_1\} & 0 & 0 & \dots \\ 0 & \exp\{a_2\} & 0 & \dots \\ 0 & 0 & \exp\{a_3\} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{6.36}$$

⚠ Note that one cannot derive $\exp\{\mathbf{A}\}$ from $\mathbf{A}$ by taking the exponentials of *each* element (remember that $\exp\{0\} = 1$!).

If $\mathbf{A}$ is *not* diagonal, then the route to the matrix $\exp\{\mathbf{A}\}$ leads through *diagonalization* (see Section 6.4): suppose that matrix $\mathbf{A}$ is diagonalized, so that the matrices $\mathbf{X}$ and $\mathbf{D}$ solving the following equation are known:

$$\mathbf{A} = \mathbf{X}\mathbf{D}\mathbf{X}^{-1}$$

The matrix representation of the exponential operator may be calculated through the following equation:

$$\exp\{\mathbf{A}\} = \mathbf{X}\exp\{\mathbf{D}\}\mathbf{X}^{-1} \tag{6.37}$$

Since $\mathbf{D}$ is diagonal, the matrix $\exp\{\mathbf{D}\}$ is readily calculated through Equation 6.36.

6.6 Cyclic Commutation

6.6.1 Definition of cyclic commutation

Consider the three operators $\widehat{A}$, $\widehat{B}$ and $\widehat{C}$, which obey the following three commutation relationships:

$$\begin{aligned} \left[\widehat{A}, \widehat{B}\right] &= \mathrm{i}\widehat{C} \\ \left[\widehat{C}, \widehat{A}\right] &= \mathrm{i}\widehat{B} \\ \left[\widehat{B}, \widehat{C}\right] &= \mathrm{i}\widehat{A} \end{aligned} \tag{6.38}$$

This is called a *cyclic commutation* relationship, since the three relationships may be generated from each other by permuting the operators in a cyclic fashion, i.e.

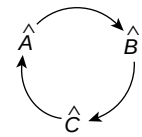


Figure 6.3
Cyclic permutation of three operators.

Cyclic commutation is very important in the theory of NMR, and a special symbol $\circlearrowleft$ is now introduced for it. The following single expression implies *all three* relationships in Equation 6.38:

$$\left[\widehat{A}, \widehat{B}\right] = \mathrm{i}\widehat{C} \qquad \circlearrowleft \tag{6.39}$$

6.6.2 Sandwich formula

If the three operators $\widehat{A}$, $\widehat{B}$ and $\widehat{C}$ cyclically commute, then the following *sandwich formula* applies:

$$\exp\{-\mathrm{i}\theta\widehat{A}\}\widehat{B}\exp\{+\mathrm{i}\theta\widehat{A}\} = \widehat{B}\cos\theta + \widehat{C}\sin\theta \qquad \circlearrowleft \tag{6.40}$$

Geometrically, this result may be depicted as the 'rotation' of an operator $\widehat{B}$ 'by' an operator $\widehat{A}$, through an angle θ:

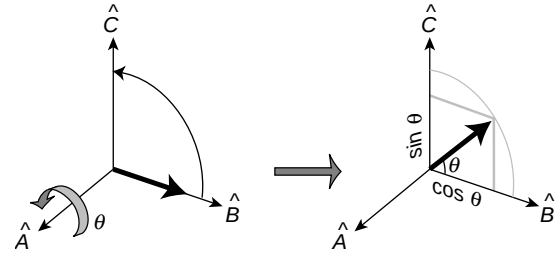


Figure 6.4
Geometrical representation of the sandwich formula (Equation 6.40).

This relationship provides a fundamental link between cyclic commutation and the geometry of rotations. It is of fundamental importance to the geometrical description of nuclear spin dynamics. A proof is given in Appendix A.2.

The symbol $\circlearrowleft$ in Equation 6.40 indicates that the operators may be cyclically permuted $\widehat{A} \rightarrow \widehat{B} \rightarrow \widehat{C} \rightarrow \widehat{A} \ldots$. By doing this one gets two more relationships:

$$\exp\{-\mathrm{i}\theta\widehat{B}\}\widehat{C}\exp\{+\mathrm{i}\theta\widehat{B}\} = \widehat{C}\cos\theta + \widehat{A}\sin\theta \tag{6.41}$$

and

$$\exp\{-\mathrm{i}\theta\widehat{C}\}\widehat{A}\exp\{+\mathrm{i}\theta\widehat{C}\} = \widehat{A}\cos\theta + \widehat{B}\sin\theta \tag{6.42}$$

which have the following geometrical interpretation:

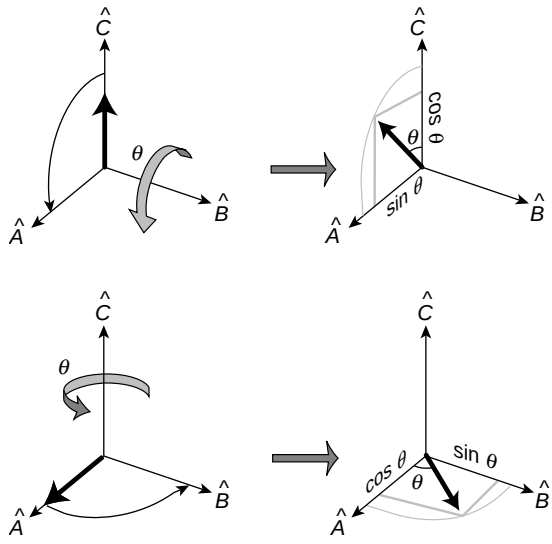


Figure 6.5
Geometrical representation of Equations 6.41 and 6.42.

What happens if the operator $\widehat{A}$ is rotated by $\widehat{B}$? One can figure this out by rearranging the cyclic commutation relationship as follows:

$$\begin{aligned} \left[\widehat{A}, \widehat{B}\right] &= \mathrm{i}\widehat{C} \qquad \circlearrowleft \\ -\left[\widehat{B}, \widehat{A}\right] &= \mathrm{i}\widehat{C} \qquad \circlearrowleft \\ \left[(-\widehat{B}), \widehat{A}\right] &= \mathrm{i}\widehat{C} \qquad \circlearrowleft \end{aligned} \tag{6.43}$$

This implies that

$$\begin{aligned} \exp\{-\mathrm{i}\theta\widehat{B}\}\widehat{A}\exp\{+\mathrm{i}\theta\widehat{B}\} &= \exp\{-\mathrm{i}(-\theta)(-\widehat{B})\}\widehat{A}\exp\{+\mathrm{i}(-\theta)(-\widehat{B})\} \\ &= \widehat{A}\cos(-\theta) + \widehat{C}\sin(-\theta) \\ &= \widehat{A}\cos\theta - \widehat{C}\sin\theta \qquad \circlearrowleft \end{aligned} \tag{6.44}$$

which has the following geometric interpretation:

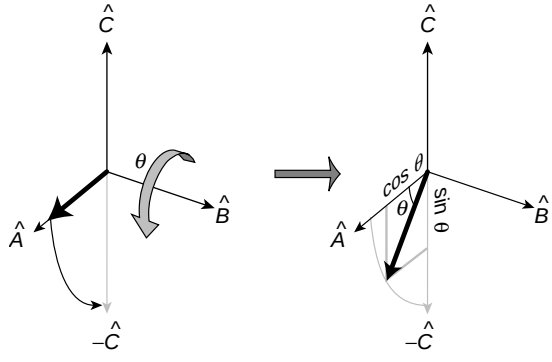


Figure 6.6
Geometrical representation of Equation 6.44.

Note that the rotation goes towards the negative axis this time.

By cyclically permuting Equation 6.44, one gets two more sandwich relationships:

$$\exp\{-\mathrm{i}\theta\widehat{C}\}\widehat{B}\exp\{+\mathrm{i}\theta\widehat{C}\} = \widehat{B}\cos\theta - \widehat{A}\sin\theta$$

$$\exp\{-\mathrm{i}\theta\widehat{A}\}\widehat{C}\exp\{+\mathrm{i}\theta\widehat{A}\} = \widehat{C}\cos\theta - \widehat{B}\sin\theta$$

Notes

1. The term 'eigen' is a German word meaning 'own' or 'characteristic'.

2. An operator is 'small' if the largest and the smallest eigenvalues differ by much less than 1.

Further Reading

- For a good introduction to the mathematics of complex numbers and matrices, see E. Steiner, *The Chemistry Maths Book*, Oxford University Press, Oxford, 1996.
- For a good textbook on matrices and linear algebra, see G. Strang, *Linear Algebra and its Applications*, 3rd edition, Harcourt Brace Jovanovich, San Diego, 1988.

Exercises

6.1 (i) Prove that the functions $\psi_n(x)$ in Equation 6.1 are normalized.
(ii) Prove that the function $f(x)$ in Equation 6.7 is normalized.
(iii) What value of N normalizes the following function?

$$g(x) = \begin{cases} 0 & \text{if } x < 0 \\ N\sin^3(\pi x) & \text{if } 0 \le x \le 1 \\ 0 & \text{if } 1 < x \end{cases}$$

6.2 Prove that the functions $\psi_n(x)$ in Equation 6.1 are orthogonal.

6.3 Evaluate the commutator $\left[\hat{x}, \widehat{D}_x^2\right]$, by using the same technique as in Equation 6.10.

6.4 Derive the matrix elements listed in Equation 6.12.

6.5 Derive the first row of the matrix representation in Equation 6.14.

6.6 (i) Prove that the eigenvalues of Hermitian operators are real.
(ii) Prove that non-degenerate eigenvectors of Hermitian operators are orthogonal.

7 Review of Quantum Mechanics

Quantum mechanics provides three major theoretical tools: (1) a mathematical tool for describing the *state* of the particle, at any moment of time; (2) a mathematical tool for predicting how the state of the particle changes in time and space (the *equation of motion*); (3) a set of rules for predicting the results of experimental *observations*.

These rules are essentially postulates that are justified by comparing predictions with experimental results. In 2007, there were no verified discrepancies between quantum theory and experimental results.

7.1 Spinless Quantum Mechanics

Consider a single quantum particle, able to move in one spatial direction, specified by the coordinate x. For now, we assume that the particle has no spin.

7.1.1 The state of the particle

In spinless quantum mechanics, the state of the particle is described by a continuous function of space, denoted $\psi(x, t)$ in the case of a single spatial coordinate x. This *wavefunction* (or *state function*) is, in general, complex, i.e. $\psi(x, t) \neq \psi(x, t)^*$.

The wavefunction is indexed with the parameter t to emphasize the fact that the wavefunction is, in general, time dependent. The wavefunction may be visualized as a wave, moving through time and space:

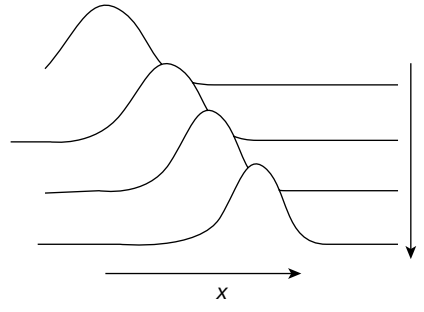


Figure 7.1 A moving wavefunction.

The wavefunction of the particle is *normalized*:

$$\int_{-\infty}^{\infty} \mathrm{d}x\ \psi(x, t)^* \psi(x, t) = 1 \qquad \text{(normalization)} \tag{7.1}$$

Spin Dynamics: Basics of Nuclear Magnetic Resonance, Second Edition Malcolm H. Levitt

7.1.2 The equation of motion

The equation of motion of the wavefunction is given by the following:

$$\frac{\mathrm{d}}{\mathrm{d}t}\psi(x,t) = -\mathrm{i}\hbar^{-1}\widehat{\mathrm{H}}\psi(x,t) \tag{7.2}$$

which is known as the *time-dependent Schrödinger equation*. The constant $\hbar$ (pronounced "h-bar") is given by

$$\hbar = \frac{h}{2\pi} \tag{7.3}$$

where h is Planck's constant. The numerical value is $\hbar = 1.054 \times 10^{-34}\,\mathrm{J\,s}$.

The symbol $\widehat{\mathrm{H}}$ signifies a special operator, known as the *Hamiltonian*. The Hamiltonian is a hermitian operator, given by

$$\widehat{\mathrm{H}} = \widehat{\mathrm{V}} + \widehat{\mathrm{K}} \tag{7.4}$$

where $\widehat{\mathrm{V}}$ is the *potential energy operator* and $\widehat{\mathrm{K}}$ is the *kinetic energy operator*.

The potential energy operator $\widehat{\mathrm{V}}$ depends on the forces acting on the particle. For the case of a particle confined to an infinitely deep square 'potential well', with edges at $x = 0$ and $x = 1$, the potential energy operator is given by

$$\widehat{\mathrm{V}} = \begin{cases} \infty & \text{if } x < 0 \\ 0 & \text{if } 0 \le x \le 1 \\ \infty & \text{if } 1 < x \end{cases}$$

The infinite potential energy outside the box has the effect of confining the particle completely to the interior of the box. Situations involving more realistic potential energy operators are treated in many texts (see *Further Reading*) and are not discussed further here.

In one-dimensional quantum mechanics, the kinetic energy operator is proportional to the second derivative operator, divided by the mass of the particle m:

$$\widehat{\mathrm{K}} = -(\hbar^2/2m)\widehat{D}_x^2 \tag{7.5}$$

In the case of the one-dimensional square well, there is no potential energy inside the box, so the Hamiltonian $\widehat{\mathrm{H}}$ is equal to the kinetic energy operator.

Knowledge of the Hamiltonian allows one to specify the equation of motion (Equation 7.2). In principle, this equation of motion may be solved to predict all future quantum states of the particle, if the initial state is known.

7.1.3 Experimental observations

Quantum mechanics provides a procedure for predicting the results of experimental observations – or, more precisely, for predicting the *probabilities* of obtaining particular results. This distinction is important. Quantum mechanics states that, in some circumstances, it is *fundamentally impossible* to predict the result of even highly controlled experiments. Only the *probabilities* may be predicted. This is one of the most counter-

intuitive and controversial aspects of quantum mechanics, which is nevertheless in full agreement with all known experimental results.

In quantum mechanics, each experimental observation is associated with a hermitian operator. For example, the measurement of the position of a particle along the x-axis is associated with the operator $\hat{x}$.

According to quantum mechanics, there are several *possible* results of any experimental observation, which correspond to the *eigenvalues of the observable operator*. For example, an observation of the position of a particle can only lead to a result that is an eigenvalue of the observable $\hat{x}$. In general, there are many such eigenvalues and, hence, many possible results of a given observation.

Can one specify the answer more precisely? Which of the many possible eigenvalues is actually chosen when an observation is made? Remarkably, quantum mechanics does not make any definite commitment about this. It only gives a formula for the *probability* of getting a particular eigenvalue. If the quantum state is $|\psi\rangle$ and the observable operator is $\widehat{Q}$, then the probability of obtaining the result q_n is given by

$$\mathrm{P}(q_n) = |\langle n|\psi\rangle|^2 \tag{7.6}$$

where $|n\rangle$ is the eigenstate of $\widehat{Q}$ with eigenvalue q_n, i.e.

$$\widehat{Q}|n\rangle = q_n|n\rangle$$

The probability of getting a particular result q_n is equal to 1 only if the system is in the corresponding eigenstate, i.e. $|\psi\rangle = |n\rangle$. In this case, the result is certain: the same experiment always gives the same result, namely q_n. In all other cases, the results of observations only follow statistical laws and the result of an individual experiment is fundamentally unpredictable.

Although quantum mechanics is non-committal about the result of *single* observations, it does give a definite formula for the *average* result of *very many* observations. This is called the *expectation value*, equal to the matrix element

$$\langle\widehat{Q}\rangle = \langle\psi|\widehat{Q}|\psi\rangle \tag{7.7}$$

where $\widehat{Q}$ is the observable operator. The implications for nuclear spins are explored in Chapter 10.

7.2 Energy Levels

Since the Hamiltonian is hermitian, its eigenstates are orthogonal and its eigenvalues are real. The Hamiltonian eigenstates and eigenvalues play a very important role in the behaviour of quantum systems and have special names. The Hamiltonian eigenvalues are called the *energy levels* of the quantum system, and the Hamiltonian eigenstates are called the *stationary states* of the system or, equivalently, the *energy eigenstates*.

It is customary to draw an energy level diagram of the system, in which the Hamiltonian eigenvalues are represented by horizontal lines. For example, a 'particle in a one-dimensional box' has a set of Hamiltonian eigenstates that are equal to the functions $|n\rangle = \psi_n(x)$ defined in Equation 6.1:

$$\widehat{\mathrm{H}}|n\rangle = E_n|n\rangle \tag{7.8}$$

Here, E_n is the energy of the state $|n\rangle$, given by

$$E_n = \frac{\pi^2 n^2 \hbar^2}{2mL^2}$$

where L is the length of the box ($L = 1$ in the current case).

Equation 7.8 is known as the *time-independent Schrödinger equation*. The diagram below shows the first few energy levels E_n, and the corresponding stationary wavefunctions $|n\rangle$, for the particle in a box:

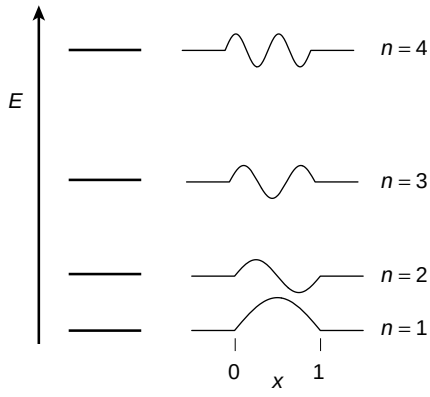


Figure 7.2
Energy levels for a particle in a box and the corresponding wavefunctions.

7.3 Natural Units

The factor $\hbar^{-1}$ in Equation 7.2 is inconvenient. It may be removed by defining a 'Hamiltonian in natural units' $\widehat{\mathcal{H}}$ as follows:

$$\widehat{\mathcal{H}} = \hbar^{-1}\widehat{\mathrm{H}} \tag{7.9}$$

The Schrödinger equation then reads

$$\frac{\mathrm{d}}{\mathrm{d}t}\psi(x,t) = -\mathrm{i}\widehat{\mathcal{H}}\psi(x,t) \tag{7.10}$$

which proves to be more convenient to handle.

The Hamiltonians $\widehat{\mathcal{H}}$ and $\widehat{\mathrm{H}}$ have the same eigenfunctions:

$$\widehat{\mathcal{H}}|n\rangle = \omega_n|n\rangle$$

The eigenvalues of $\widehat{\mathcal{H}}$ are denoted ω_n, and are given by

$$\omega_n = \hbar^{-1}E_n$$

The eigenvalues ω_n, therefore, are the energies of the states $|n\rangle$, in units of $\hbar$. For the particle in a one-dimensional box, the energies ω_n are given by

$$\omega_n = \frac{\pi^2 n^2 \hbar}{2m}$$

From now on, natural units are used consistently. Energies in natural units are denoted by the symbol ω, to emphasize that they have the dimensions of frequency (s^{-1}). The energies may be converted into SI units (joules) by multiplication with the factor $\hbar$.

7.4 Superposition States and Stationary States

It is sometimes stated that the only 'allowed' states of a quantum system are the energy eigenstates, and that the system moves between these allowed states by discontinuous transitions ('quantum jumps'). These statements are incorrect. In fact, *any* state of the form

$$|f\rangle = f_1|1\rangle + f_2|2\rangle + f_3|3\rangle + \ldots$$

is a valid quantum state, providing that all of $\{|1\rangle, |2\rangle \ldots\}$ are energy eigenstates and that the total state $|f\rangle$ is normalized (Equation 6.2).

Superposition states are of fundamental importance in the theory of NMR, and they are discussed at length in the following chapters.

What is the significance of the energy eigenstates $|n\rangle$, given that they are not the only 'allowed' states?

The answer is that the energy eigenstates are the only states that are *stationary*. This means that if the system is prepared in an energy eigenstate, then it remains in that eigenstate and does not change into some other state, as long as the Hamiltonian does not change.

This may be seen as follows. Suppose that the state of the system is described at some time t by the state vector $|\psi\rangle(t)$. The Schrödinger equation for the system is

$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi\rangle(t) = -\mathrm{i}\widehat{\mathcal{H}}|\psi\rangle(t)$$

If the Hamiltonian $\widehat{\mathcal{H}}$ is time independent, then this is a first-order differential equation and is easily solved. The solution is

$$|\psi\rangle(t) = \exp\{-\mathrm{i}\widehat{\mathcal{H}}t\}|\psi\rangle(0) \tag{7.11}$$

where the exponential operator should be interpreted as in Section 6.5 and where $|\psi\rangle(0)$ is the state of the system at time $t = 0$. Now suppose that the system is in an energy eigenstate at time $t = 0$:

$$|\psi\rangle(0) = |n\rangle$$

From Section 6.5, this state is an eigenstate of the exponential operator $\exp\{-\mathrm{i}\widehat{\mathcal{H}}t\}$:

$$\exp\{-\mathrm{i}\widehat{\mathcal{H}}t\}|n\rangle = \exp\{-\mathrm{i}\omega_n t\}|n\rangle$$

It follows that the state of the system at time t is given by

$$|\psi\rangle(t) = \exp\{-\mathrm{i}\omega_n t\}|\psi\rangle(0)$$

The system, therefore, remains in the same state, multiplied by a complex time-dependent number, called a *phase factor*. As discussed in Chapter 10, this phase factor may often be ignored, for most purposes. The important thing is that the state $|n\rangle$ does not evolve into a mixture of states with different quantum numbers.

This simple relationship between the initial and final states only applies if the system is initially in an energy eigenstate. For this reason, the energy eigenstates are said to be *stationary*. As time goes on, each stationary state $|n\rangle$ acquires a complex phase factor $\exp\{-\mathrm{i}\omega_n t\}$, but does not mix with the other states.

The stationary states of a quantum system have a clear relationship with the 'normal modes' of a vibrating molecule, or the 'standing wave patterns' in a guitar string or an organ pipe. They represent conserved patterns of motion, which persist over a substantial length of time.

7.5 Conservation Laws

The following general theorem is important:

> If an operator $\widehat{Q}$ commutes with the Hamiltonian $\widehat{\mathcal{H}}$, and the Hamiltonian is independent of time, then the expectation value of $\widehat{Q}$ is also independent of time. The expectation value $\langle\widehat{Q}\rangle$ is said to be *conserved*.

This theorem is easily proved from the formula for the expectation value:

$$\langle\widehat{Q}\rangle(t) = \langle\psi|(t)\ \widehat{Q}\ |\psi\rangle(t)$$

The wavefunction evolves in time as given in Equation 7.11:

$$|\psi\rangle(t) = \exp\{-\mathrm{i}\widehat{\mathcal{H}}t\}|\psi\rangle(0)$$

The adjoint of this equation may be taken as follows:

$$\langle\psi|(t) = \{|\psi\rangle(t)\}^\dagger = \left\{\exp\{-\mathrm{i}\widehat{\mathcal{H}}t\}|\psi\rangle(0)\right\}^\dagger = \langle\psi|(0)\left\{\exp\{-\mathrm{i}\widehat{\mathcal{H}}t\}\right\}^\dagger$$
$$= \langle\psi|(0)\exp\{+\mathrm{i}\widehat{\mathcal{H}}^\dagger t\} = \langle\psi|(0)\exp\{+\mathrm{i}\widehat{\mathcal{H}}t\}$$

Note that the adjoint involves taking complex conjugates as well as reversing the order of multiplication. The last identity exploits the fact that the Hamiltonian is hermitian.

The expectation value is therefore given by

$$\langle\widehat{Q}\rangle(t) = \langle\psi|(0)\exp\{+\mathrm{i}\widehat{\mathcal{H}}t\}\widehat{Q}\exp\{-\mathrm{i}\widehat{\mathcal{H}}t\}|\psi\rangle(0)$$

If $\widehat{\mathcal{H}}$ and $\widehat{Q}$ commute, then $\widehat{\mathcal{H}}\widehat{Q} = \widehat{Q}\widehat{\mathcal{H}}$, and it is easily shown that

$$\exp\{+\mathrm{i}\widehat{\mathcal{H}}t\}\widehat{Q}\exp\{-\mathrm{i}\widehat{\mathcal{H}}t\} = \widehat{Q}$$

and hence

$$\langle\widehat{Q}\rangle(t) = \langle\psi|(0)\ \widehat{Q}\ |\psi\rangle(0) = \langle\widehat{Q}\rangle(0)$$

It follows that the expectation value of $\widehat{Q}$ is *conserved*.

A trivial example of this theorem is when the operator $\widehat{Q}$ is equal to the Hamiltonian $\widehat{\mathcal{H}}$. Since the expectation value of $\widehat{\mathcal{H}}$ is the energy of the system, the above theorem states that the energy of the system is conserved (first law of thermodynamics).

7.6 Angular Momentum

Consider now the quantum mechanics of systems that are free to *rotate* in three-dimensional space, e.g. a molecule floating freely in a vacuum, or an electron circling around a positive central charge, as in the hydrogen atom:

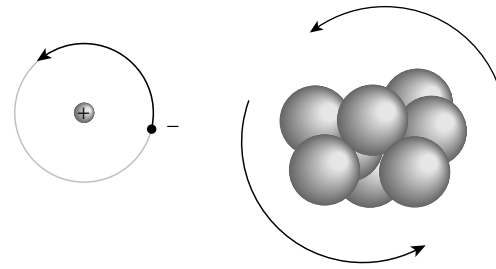


Figure 7.3
Two rotating objects.

The quantum state of a particle moving in three-dimensional space is a function of all three spatial coordinates, as well as the time coordinate, i.e. $\psi = \psi(x, y, z, t)$.

7.6.1 Angular momentum operators

Quantum mechanical theory attaches great importance to the *angular momentum operators* of a rotating object. There are three such operators, representing the angular momentum components along the three Cartesian axes, as follows:

$$\begin{aligned}\hat{l}_x &= -\mathrm{i}(\hat{y}\hat{D}_z - \hat{z}\hat{D}_y)\\ \hat{l}_y &= -\mathrm{i}(\hat{z}\widehat{D}_x - \hat{x}\hat{D}_z)\\ \hat{l}_z &= -\mathrm{i}(\hat{x}\hat{D}_y - \hat{y}\widehat{D}_x)\end{aligned} \tag{7.12}$$

The operators $\hat{x}$, $\hat{y}$ and $\hat{z}$ multiply the operand by the spatial coordinate, e.g.

$$\hat{x}\psi(x, y, z, t) = x\psi(x, y, z, t)$$

The operators $\widehat{D}_x$, $\hat{D}_y$ and $\hat{D}_z$ take the partial derivative with respect to one of the spatial coordinates, keeping the other coordinates fixed; for example:

$$\widehat{D}_x\psi(x, y, z, t) = \frac{\partial}{\partial x}\psi(x, y, z, t)$$

The definitions in Equation 7.12 provide the angular momentum operators in 'natural units' of $\hbar$: the right-hand sides should be multiplied by $\hbar$ to obtain the expressions in SI units.

The angular momentum operators are hermitian.

It may be shown (see *Further Reading*) that the three angular momentum operators obey the cyclic commutation relationships, defined in Equation 6.38:

$$\left[\hat{l}_x, \hat{l}_y\right] = \mathrm{i}\hat{l}_z \qquad \circlearrowleft \tag{7.13}$$

7.6.2 Rotation operators

The complex exponentials of angular momentum operators are called *rotation operators*. The rotation operators around the three Cartesian axes are denoted as follows:

$$\begin{aligned}\widehat{R}_x(\beta) &= \exp\{-\mathrm{i}\beta\hat{l}_x\}\\ \widehat{R}_y(\beta) &= \exp\{-\mathrm{i}\beta\hat{l}_y\}\\ \widehat{R}_z(\beta) &= \exp\{-\mathrm{i}\beta\hat{l}_z\}\end{aligned} \tag{7.14}$$

Here, β denotes the rotation angle. For example, the operator $\widehat{R}_x(\pi/2)$ performs a rotation through the angle $\pi/2$ about the x-axis:

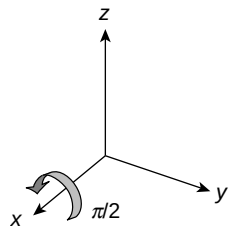


Figure 7.4
A rotation by $\pi/2$ about the x-axis.

The operator $\widehat{R}_y(\pi)$ performs a rotation through the angle π about the y-axis:

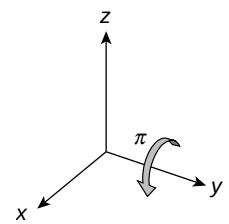


Figure 7.5
A rotation by π about the y-axis.

Note that the formulae for the rotation operators in Equation 7.14 involve a negative sign. The operator for a *positive* rotation about the x-axis through the angle β is equal to $\exp\{-\mathrm{i}\beta\hat{l}_x\}$.

The inverse of a rotation through the angle β is a rotation through the angle $-\beta$, about the same axis; for example:

$$\widehat{R}_x(\beta)\widehat{R}_x(-\beta) = \widehat{R}_x(-\beta)\widehat{R}_x(\beta) = \widehat{1}$$

Since the angular momentum operators are hermitian, the rotation operators are *unitary*:

$$\widehat{R}_x(\beta)^\dagger = \widehat{R}_x(\beta)^{-1} = \widehat{R}_x(-\beta)$$

A rotation operator commutes with the angular momentum operator about the same axis; for example:

$$\widehat{R}_x(\beta)\hat{l}_x = \hat{l}_x\widehat{R}_x(\beta)$$

This implies the following sandwich relationship:

$$\widehat{R}_x(\beta)\hat{l}_x\widehat{R}_x(-\beta) = \hat{l}_x$$

Geometrically, this corresponds to the fact that a rotation of a vector about its own axis does nothing:

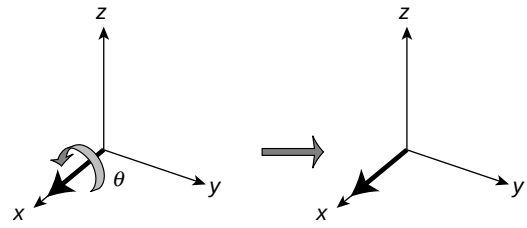


Figure 7.6
Rotation of a vector along the x-axis about the x-axis.

When a rotation operator is applied to the angular momentum about a different axis, the sandwich relationship reads

$$\widehat{R}_x(\beta)\hat{l}_y\widehat{R}_x(-\beta) = \hat{l}_y\cos\beta + \hat{l}_z\sin\beta$$

which follows from the cyclic commutation of the angular momentum operators. The equation above has the following geometric interpretation:

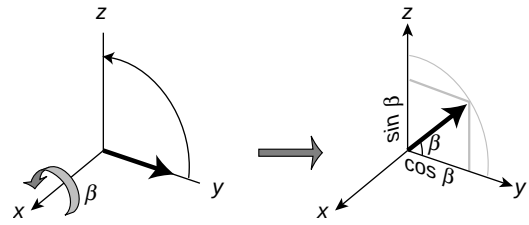


Figure 7.7
Rotation of a vector along the y-axis about the x-axis.

7.6.3 Rotation sandwiches

As shown in Appendix A.3, the sandwich relationship for angular momentum operators

$$\widehat{R}_x(\theta)\hat{l}_y\widehat{R}_x(-\theta) = \hat{l}_y\cos\theta + \hat{l}_z\sin\theta \qquad \circlearrowleft$$

implies a corresponding sandwich relationship for rotation operators:

$$\widehat{R}_x(\theta)\widehat{R}_y(\beta)\widehat{R}_x(-\theta) = \exp\{-\mathrm{i}\beta(\hat{l}_y\cos\theta + \hat{l}_z\sin\theta)\} \qquad \circlearrowleft \tag{7.15}$$

where the operator on the right-hand side implies a rotation through the angle β about the axis $\mathbf{e}_y\cos\theta + \mathbf{e}_z\sin\theta$, i.e. an axis in the yz-plane, subtending an angle θ with respect to the y-axis:

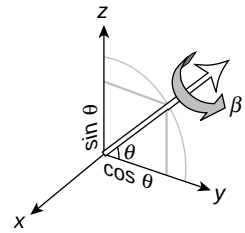


Figure 7.8
Rotation around an axis in the yz-plane.

A specific example of Equation 7.15 is as follows:

$$\widehat{R}_x(\pi/2)\widehat{R}_y(\beta)\widehat{R}_x(-\pi/2) = \widehat{R}_z(\beta)$$

This states that a $-\pi/2$ rotation about the x-axis, followed by a rotation through β about the y-axis, followed by a $+\pi/2$ rotation about the x-axis is the same as a rotation through β about the z-axis (Note carefully that the order of the rotations should be read from right to left.) This may be seen physically by rotating any three-dimensional shape through the sequence of rotations given on the left-hand side of the equation:

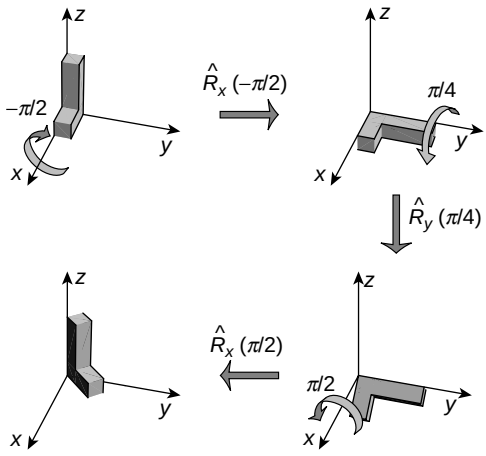


Figure 7.9
An L-shaped object undergoes a sequence of three rotations.

(This is shown for the case $\beta = \pi/4$.) The result is the same as a single rotation by $\pi/4$ around the z-axis:

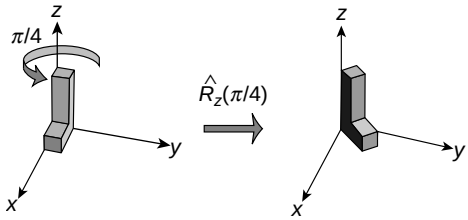


Figure 7.10
The same result is obtained by a single rotation.

Some further examples are

$$\widehat{R}_x(\pi)\widehat{R}_y(\beta)\widehat{R}_x(-\pi) = \widehat{R}_y(-\beta)$$
$$\widehat{R}_z(\pi/2)\widehat{R}_x(\beta)\widehat{R}_z(-\pi/2) = \widehat{R}_y(\beta)$$

These equations all have the form of two equal and opposite rotations bracketing another rotation about a different axis. This common motif is called a *rotation sandwich*.

7.6.4 Angular momentum eigenstates and eigenvalues

Consider now the eigenstates and eigenvalues of one of the angular momentum operators. The traditional choice is $\hat{l}_z$, although, in principle, any one of the three operators could be considered. In many textbooks

(see *Further Reading*) it is shown that the eigenstates of $\hat{l}_z$ may be specified by two quantum numbers, called here ℓ and m, which take the following values:

$$\ell = 0, 1, 2, \ldots$$
$$m = -\ell,\ -\ell+1,\ -\ell+2\ \ldots\ +\ell \tag{7.16}$$

The eigenstates of $\hat{l}_z$ may, therefore, be written $|\ell, m\rangle$ and obey the following eigenequation:

$$\hat{l}_z|\ell, m\rangle = m|\ell, m\rangle \tag{7.17}$$

The eigenvalue of angular momentum along the z-axis is therefore given by an integer m called the *azimuthal quantum number* or *projection quantum number*.

The permitted values of m depend on the quantum number ℓ. If $\ell = 0$, then only the value $m = 0$ is allowed. If $\ell = 1$, then there are three possible values: $m = -1$, 0 or 1. If $\ell = 2$, then there are five possible values: $m = -2, -1, 0, 1$ or 2, and so on.

The quantum number ℓ does not appear in Equation 7.17. The role of ℓ is revealed if an operator $\hat{l}^2$ is defined as follows:

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 \tag{7.18}$$

This is called the *total square angular momentum operator*. It is shown in standard texts (see *Further Reading*) that $\hat{l}^2$ commutes with $\hat{l}_z$, and that the eigenequation for $\hat{l}^2$ is

$$\hat{l}^2|\ell, m\rangle = \ell(\ell+1)|\ell, m\rangle \tag{7.19}$$

The quantum number ℓ defines the total square angular momentum, and the quantum number m defines the angular momentum along the z-axis.

Since the operators $\hat{l}_z$ and $\hat{l}^2$ are hermitian, the set of eigenfunctions $|\ell, m\rangle$ is orthogonal. The set of functions $|\ell, m\rangle$ may, therefore, be used as a basis for matrix representations, and is called here the *Zeeman eigenbasis*.

If the eigenstates are arranged in the order $|\ell, m\rangle = |0, 0\rangle, |1, 1\rangle, |1, 0\rangle, |1, -1\rangle, |2, 2\rangle, |2, 1\rangle, |2, 0\rangle, |2, -1\rangle, |2, -2\rangle \ldots$, then the matrix representations of $\hat{l}_z$ and $\hat{l}^2$ in the Zeeman eigenbasis are

$$\hat{l}_z = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & \ldots \\ 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & \ldots \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & \ldots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & \ldots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2 & \ldots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

and

$$\hat{l}^2 = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 6 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 6 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 6 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Note that both of these matrices are diagonal and that the diagonal elements reflect the eigenequations in Equations 7.17 and 7.19.

7.6.5 The angular momentum eigenstates

The eigenstates $|\ell, m\rangle$ are functions of space, called *spherical harmonics*. They may be familiar to the reader as the angular parts of the hydrogen atom orbitals. The function $|0, 0\rangle$ has a spherical symmetry and resembles the s-orbital of a hydrogen atom. The three functions $|1, 1\rangle$, $|1, 0\rangle$ and $|1, -1\rangle$ have the symmetry of the three p-orbitals. The five functions $|2, 2\rangle$, $|2, 1\rangle$, $|2, 0\rangle$, $|2, -1\rangle$ and $|2, -2\rangle$ have the symmetry of the five d-orbitals, and so on. Figure 7.11 shows a physical representation of these functions:[1]

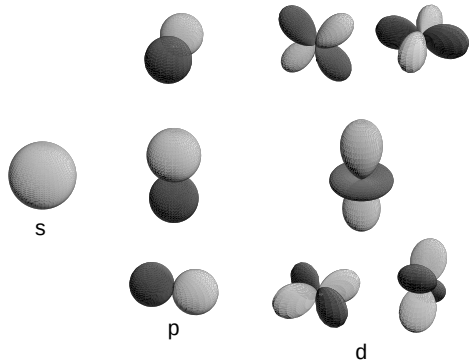


Figure 7.11
The spatial form of the angular momentum eigenfunctions. In some cases, linear combinations of the eigenfunctions have been taken, in order to remove imaginary factors (see Note 1). A negative sign is indicated by a darker colour.

The explicit forms of the angular momentum eigenfunctions are given in many quantum mechanics texts (see *Further Reading*).

7.6.6 Shift operators

The angular momentum operators $\hat{l}_x$ and $\hat{l}_y$ do not commute with $\hat{l}_z$, so their matrix representations are not diagonal in the $\hat{l}_z$ eigenbasis. In order to investigate the matrix representations of $\hat{l}_x$ and $\hat{l}_y$, it is convenient to define the *shift operators* $\hat{l}^+$ and $\hat{l}^-$ as follows:

$$\hat{l}^+ = \hat{l}_x + \mathrm{i}\hat{l}_y$$
$$\hat{l}^- = \hat{l}_x - \mathrm{i}\hat{l}_y \tag{7.20}$$

The shift operators have the following effect on the eigenstates of $\hat{l}_z$:

$$\hat{l}^+|\ell, m\rangle = \left\{\ell(\ell+1) - m(m+1)\right\}^{1/2} |\ell, m+1\rangle$$
$$\hat{l}^-|\ell, m\rangle = \left\{\ell(\ell+1) - m(m-1)\right\}^{1/2} |\ell, m-1\rangle \tag{7.21}$$

The shift operator $\hat{l}^+$ increases the quantum number m by one, while leaving ℓ unchanged; the shift operator $\hat{l}^-$ decreases the quantum number m by one, while leaving ℓ unchanged. In both cases, the shift in quantum number m is accompanied by scaling of the quantum state by one of the fearsome-looking factors given in Equation 7.21. These factors are called *shift operator matrix elements*.

The matrix representations of the shift operators in the Zeeman eigenbasis are therefore

$$\hat{l}^+ = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

and

$$\hat{l}^- = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

The shift operators are not hermitian. Note that the matrix elements are zero except on a line next to the diagonal.

7.6.7 Matrix representations of the angular momentum operators

The operators $\hat{l}_x$ and $\hat{l}_y$ are related to the shift operators as follows:

$$\hat{l}_x = \frac{1}{2}(\hat{l}^+ + \hat{l}^-)$$
$$\hat{l}_y = \frac{1}{2\mathrm{i}}(\hat{l}^+ - \hat{l}^-) \tag{7.22}$$

The matrix representations of the angular momentum operators along the x and y-axes, in the Zeeman eigenbasis, are as follows:

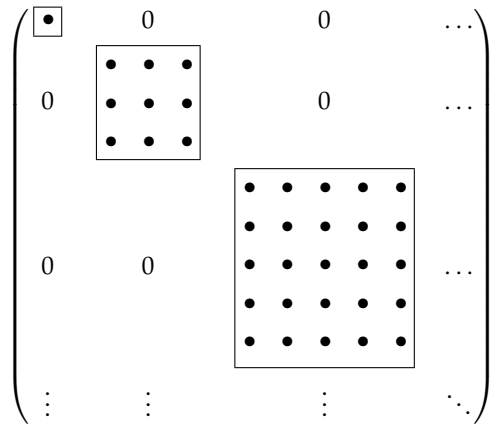
$$\hat{l}_x = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 2 & 0 & \sqrt{6} & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & \sqrt{6} & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & 2 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{7.23}$$

and

$$\hat{l}_y = \frac{1}{2\mathrm{i}}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & -\sqrt{2} & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & -\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & -2 & 0 & \sqrt{6} & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & -\sqrt{6} & 0 & \sqrt{6} & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & -\sqrt{6} & 0 & 2 & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2 & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{7.24}$$

Since $\hat{l}^2$ has degenerate eigenvalues and commutes with both $\hat{l}_x$ and $\hat{l}_y$, the matrix representations given in Equations 7.23 and 7.24 are *block diagonal*, as described in Section 6.3.6. The matrix representations of $\hat{l}_x$ and $\hat{l}_y$ contain only zeros except for within the one-dimensional, three-dimensional, and five-dimensional

blocks corresponding to the quantum numbers $\ell = 0, 1, 2 \ldots$:



(7.25)

7.7 Spin

Long before the experimental demonstration of particles with spin, mathematicians had noticed the *abstract* possibility of ℓ taking *half-integer* values $1/2, 3/2 \ldots$, as well as the integer values $0, 1, 2 \ldots$ that arise from angular momentum physics, as discussed above.

For example, if ℓ is equal to $3/2$, then Equation 7.16 shows that m may take the values $m = +3/2, +1/2, -1/2$ and $-3/2$. The four states $|\ell, m\rangle = |3/2, +3/2\rangle$, $|3/2, +1/2\rangle$, $|3/2, -1/2\rangle$ and $|3/2, -3/2\rangle$ define a four-dimensional 'block', in the sense of Equation 7.25. The same cyclic commutation relationships apply as before, and the shift operators have matrix elements that conform to the standard equation, Equation 7.21.

However, there is a catch. Although half-integer spin is a fully consistent 'mathematical' possibility, it long appeared to have absolutely no relationship with the real world.[2] The 'physical' angular momentum operators defined in Equation 7.12 can *never* generate half-integer values of ℓ.

Nevertheless, there is a wealth of experimental evidence for the *existence*, and even the *prevalence*, of half-integer spin in the world of fundamental particles. The existence of half-integer spin has been forced upon scientists by the weight of experimental evidence, although it is now understood on a deeper level using relativistic quantum mechanics.

Spin is now interpreted as *intrinsic* angular momentum of the particle, completely distinct from the rotational motion described by the angular momentum operators given in Equation 7.12. Remarkably, the mathematics of spin has taken on a life of its own, released from any 'physical' framework. As long as the mathematics is consistent, there is no need to ask 'where does the angular momentum come from'.

Most of this book concerns the spin of atomic nuclei. The symbol I is used for the nuclear spin angular momentum.

7.7.1 Spin angular momentum operators

The operators for the three components of the spin angular momentum are denoted $\hat{I}_x$, $\hat{I}_y$ and $\hat{I}_z$, and have the cyclic commutation relationships

$$\left[\hat{I}_x, \hat{I}_y\right] = \mathrm{i}\hat{I}_z \qquad \circlearrowleft \tag{7.26}$$

If the nuclear spin quantum number is I, then the operator $\hat{I}_z$ has $2I+1$ eigenstates $|M\rangle$:

$$\hat{I}_z|I, M\rangle = M|I, M\rangle \tag{7.27}$$

The azimuthal quantum number M takes one of the $2I+1$ values:

$$M = -I,\ -I+1,\ -I+2\ \ldots\ +I \tag{7.28}$$

The shift operators $\hat{I}^+$ and $\hat{I}^-$ are defined as

$$\begin{aligned}\hat{I}^+ &= \hat{I}_x + \mathrm{i}\hat{I}_y \\ \hat{I}^- &= \hat{I}_x - \mathrm{i}\hat{I}_y\end{aligned} \tag{7.29}$$

and have the following effect on the spin states:

$$\begin{aligned}\hat{I}^+|I, M\rangle &= \left\{I(I+1) - M(M+1)\right\}^{1/2}|I, M+1\rangle \\ \hat{I}^-|I, M\rangle &= \left\{I(I+1) - M(M-1)\right\}^{1/2}|I, M-1\rangle\end{aligned} \tag{7.30}$$

7.7.2 Spin rotation operators

The spin rotation operators are given by

$$\begin{aligned}\widehat{R}_x(\beta) &= \exp\{-\mathrm{i}\beta\hat{I}_x\} \\ \widehat{R}_y(\beta) &= \exp\{-\mathrm{i}\beta\hat{I}_y\} \\ \widehat{R}_z(\beta) &= \exp\{-\mathrm{i}\beta\hat{I}_z\}\end{aligned} \tag{7.31}$$

just as in Equation 7.14.

The same sandwich relationships apply as for 'ordinary' angular momentum; for example:

$$\widehat{R}_x(\beta)\hat{I}_y\widehat{R}_x(-\beta) = \hat{I}_y\cos\beta + \hat{I}_z\sin\beta$$

and

$$\widehat{R}_x(\pi/2)\widehat{R}_y(\beta)\widehat{R}_x(-\pi/2) = \widehat{R}_z(\beta)$$

7.7.3 Spin Zeeman basis

Any spin state of a nucleus with quantum number I may be represented as a superposition of the $2I+1$ Zeeman eigenstates $|M\rangle$. One says that the Zeeman eigenstates $|M\rangle$ form a *finite basis* for the representation of the spin operators, with *dimension* $2I+1$.

The spin operators of a nucleus with quantum number I may, therefore, be represented as matrices with dimension $(2I+1)\times(2I+1)$. For example, the matrix representation of the operator $\hat{I}_x$ for a spin-3/2 nucleus, in the Zeeman eigenbasis $\{|3/2, +3/2\rangle, |3/2, +1/2\rangle, |3/2, -1/2\rangle, |3/2, -3/2\rangle\}$ is given by

$$\hat{I}_x = \frac{1}{2}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix} \tag{7.32}$$

For 'conventional' angular momentum, it is possible to visualize the angular momentum eigenstates as spherical harmonics, spreading out in a symmetrical way in three-dimensional space. No such construction is possible for spin. The question 'apart from the mathematics, what *is* the spin state $|3/2, +1/2\rangle$?' appears to have no meaningful answer. Certainly, the spin state $|3/2, +1/2\rangle$ does not correspond to any function of spatial coordinates $\{x, y, z\}$. Remarkably, it appears to be possible to exploit and manipulate these spin states, without ever acquiring a deeper understanding of what these states 'actually are'. Maybe the spin states *are* their mathematical properties – nothing more, and nothing less.

7.7.4 Trace

The sum of diagonal matrix elements is called the *trace* of an operator:

$$\mathrm{Tr}\{\widehat{A}\} = \sum_m \langle m|\widehat{A}|m\rangle \tag{7.33}$$

The trace of an operator may only be defined for a *finite* basis.

For example, the trace of the operator $\hat{I}_x$ is equal to zero, since all diagonal elements in Equation 7.32 are equal to zero. An operator with zero trace is said to be *traceless*.

The traces of spin operators have several important properties, which will be used extensively in later sections:

1. The trace of an operator is independent of the basis, as long as the basis is orthonormal.

2. The trace of the product of two operators is independent of the order of the operators:[3]

$$\mathrm{Tr}\{\widehat{A}\widehat{B}\} = \sum_{m,n} \langle m|\widehat{A}|n\rangle\langle n|\widehat{B}|m\rangle = \sum_{m,n} \langle n|\widehat{B}|m\rangle\langle m|\widehat{A}|n\rangle = \mathrm{Tr}\{\widehat{B}\widehat{A}\}$$

3. The trace of a product of three or more operators is unchanged by a cyclic permutation of the operators:

$$\mathrm{Tr}\{\widehat{A}\widehat{B}\widehat{C}\} = \mathrm{Tr}\{\widehat{C}\widehat{A}\widehat{B}\} = \mathrm{Tr}\{\widehat{B}\widehat{C}\widehat{A}\}$$

A further useful property of the trace is as follows:

$$\mathrm{Tr}\{\widehat{A}|r\rangle\langle s|\} = \langle s|\widehat{A}|r\rangle \tag{7.34}$$

This may be seen from

$$\mathrm{Tr}\{\widehat{A}|r\rangle\langle s|\} = \sum_m \langle m|\widehat{A}|r\rangle\langle s|m\rangle = \sum_m \langle m|\widehat{A}|r\rangle\delta_{sm} = \langle s|\widehat{A}|r\rangle$$

in which δ_{sm} is the Kronecker delta (see Section 6.1.3) and $|r\rangle$, $|s\rangle$ and $|m\rangle$ are orthonormal basis functions.

7.8 Spin-1/2

Nuclei with $I = 1/2$ are particularly important in NMR, and some special notation has been developed for the eigenstates and spin operators of these nuclei.

7.8.1 Zeeman eigenstates

Spin-1/2 nuclei have two Zeeman eigenstates, for which the following special symbols are used:

$$\begin{aligned} |\alpha\rangle &= |\tfrac{1}{2},+\tfrac{1}{2}\rangle \\ |\beta\rangle &= |\tfrac{1}{2},-\tfrac{1}{2}\rangle \end{aligned} \tag{7.35}$$

The symbol β is used here to denote a spin state. Sometimes, β is used to denote an angle instead. The meaning should be clear from the context.

The result of applying the spin operators to these states is as follows:

$$\begin{aligned} \hat{I}_z|\alpha\rangle &= +\tfrac{1}{2}|\alpha\rangle & \hat{I}_z|\beta\rangle &= -\tfrac{1}{2}|\beta\rangle \\ \hat{I}^+|\alpha\rangle &= 0 & \hat{I}^+|\beta\rangle &= |\alpha\rangle \\ \hat{I}^-|\alpha\rangle &= |\beta\rangle & \hat{I}^-|\beta\rangle &= 0 \end{aligned}$$

7.8.2 Angular momentum operators

The matrix representations of the three angular momentum operators in the Zeeman eigenbasis $\{|\alpha\rangle, |\beta\rangle\}$ are

$$\hat{I}_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \hat{I}_y = \frac{1}{2\mathrm{i}}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad \hat{I}_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{7.36}$$

The reader should verify the cyclic commutation relationships for these matrices (Equation 6.38).

7.8.3 Spin-1/2 rotation operators

As shown in Appendix A.4, the spin-1/2 matrix representations of the rotation operators are

$$\begin{aligned} \widehat{R}_x(\beta) &= \begin{pmatrix} \cos\tfrac{1}{2}\beta & -\mathrm{i}\sin\tfrac{1}{2}\beta \\ -\mathrm{i}\sin\tfrac{1}{2}\beta & \cos\tfrac{1}{2}\beta \end{pmatrix} \\ \widehat{R}_y(\beta) &= \begin{pmatrix} \cos\tfrac{1}{2}\beta & -\sin\tfrac{1}{2}\beta \\ \sin\tfrac{1}{2}\beta & \cos\tfrac{1}{2}\beta \end{pmatrix} \\ \widehat{R}_z(\beta) &= \begin{pmatrix} \exp\{-\mathrm{i}\tfrac{1}{2}\beta\} & 0 \\ 0 & \exp\{+\mathrm{i}\tfrac{1}{2}\beta\} \end{pmatrix} \end{aligned} \tag{7.37}$$

One should verify that these matrices obey the relevant sandwich relationships; for example:

$$\widehat{R}_x(\beta)\hat{I}_y\widehat{R}_x(-\beta) = \hat{I}_y\cos\beta + \hat{I}_z\sin\beta$$

and

$$\widehat{R}_x(\pi/2)\widehat{R}_y(\beta)\widehat{R}_x(-\pi/2) = \widehat{R}_z(\beta)$$

7.8.4 Unity operator

The unity operator for spin-1/2 has the following matrix representation:

$$\widehat{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

It is convenient to multiply the unity operator by a factor 1/2 in order to give it the same 'size' as the three angular momentum operators:

$$\frac{1}{2}\widehat{1} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{7.38}$$

7.8.5 Shift operators

The matrix representations of the shift operators have a very simple form for spins-1/2. Consider, for example, the following matrix element:

$$\langle\alpha|\hat{I}^+|\beta\rangle = \langle\frac{1}{2}, +\frac{1}{2}|\hat{I}^+|\frac{1}{2}, -\frac{1}{2}\rangle$$

Direct application of Equation 7.30 leads to a simple result:

$$\left\{\frac{1}{2}\left(\frac{1}{2}+1\right) - \left(-\frac{1}{2}\right)\left(-\frac{1}{2}+1\right)\right\}^{1/2} = \left\{\frac{3}{4}+\frac{1}{4}\right\}^{1/2} = 1$$

Repetition for all elements provides the following matrix representations of the shift operators:

$$\hat{I}^+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \hat{I}^- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{7.39}$$

In the case of spins-1/2, all of the matrix elements are either 0 or 1.

7.8.6 Projection operators

The unity operator may be combined with $\hat{I}_z$ to give two new operators, denoted $\hat{I}^\alpha$ and $\hat{I}^\beta$:

$$\hat{I}^\alpha = \frac{1}{2}\widehat{1} + \hat{I}_z$$
$$\hat{I}^\beta = \frac{1}{2}\widehat{1} - \hat{I}_z \tag{7.40}$$

These operators have the properties

$$\hat{I}^{\alpha}|\alpha\rangle = |\alpha\rangle \quad \hat{I}^{\beta}|\alpha\rangle = 0$$
$$\hat{I}^{\alpha}|\beta\rangle = 0 \quad \hat{I}^{\beta}|\beta\rangle = |\beta\rangle$$

Their matrix representations are as follows:

$$\hat{I}^{\alpha} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \hat{I}^{\beta} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \tag{7.41}$$

The operators $\hat{I}^{\alpha}$ and $\hat{I}^{\beta}$ are called *projection operators* in this book.[4] The term *polarization operator* is also used.[5] The polarization operator matrices (Equation 7.41) and shift operator matrices (Equation 7.39) complement each other nicely.

7.8.7 Ket-bra notation

Sometimes it is convenient to notate the operators in terms of 'ket-bra' products. For spin-1/2, the shift and projection operators may be written as follows:

$$\begin{aligned} \hat{I}^{\alpha} &= |\alpha\rangle\langle\alpha| & \hat{I}^{+} &= |\alpha\rangle\langle\beta| \\ \hat{I}^{\beta} &= |\beta\rangle\langle\beta| & \hat{I}^{-} &= |\beta\rangle\langle\alpha| \end{aligned} \tag{7.42}$$

One can see how this works by applying an operator to a particular state and using the orthonormality of the states (Equation 6.6). For example, we have

$$\hat{I}^{+}|\beta\rangle = |\alpha\rangle\langle\beta|\beta\rangle = |\alpha\rangle \times 1 = |\alpha\rangle$$

and similarly for the other states and other operators.

The 'ket-bra' product $|\alpha\rangle\langle\beta|$ must be distinguished from the 'bra-ket' product $\langle\alpha|\beta\rangle$, which evaluates to zero in this case.

Using this notation, the three angular momentum operators and the half-unity operator may be written as follows:

$$\begin{aligned} \hat{I}_x &= \tfrac{1}{2}(\hat{I}^{+} + \hat{I}^{-}) &&= \tfrac{1}{2}(|\alpha\rangle\langle\beta| + |\beta\rangle\langle\alpha|) \\ \hat{I}_y &= \tfrac{1}{2\mathrm{i}}(\hat{I}^{+} - \hat{I}^{-}) &&= \tfrac{1}{2\mathrm{i}}(|\alpha\rangle\langle\beta| - |\beta\rangle\langle\alpha|) \\ \hat{I}_z &= \tfrac{1}{2}(\hat{I}^{\alpha} - \hat{I}^{\beta}) &&= \tfrac{1}{2}(|\alpha\rangle\langle\alpha| - |\beta\rangle\langle\beta|) \\ \tfrac{1}{2}\widehat{1} &= \tfrac{1}{2}(\hat{I}^{\alpha} + \hat{I}^{\beta}) &&= \tfrac{1}{2}(|\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|) \end{aligned} \tag{7.43}$$

7.9 Higher Spin

The matrix representations of the angular momentum and rotation operators for spin $> 1/2$ may be calculated using the general equations in Sections 7.7.1 and 7.7.2. These matrices are now given explicitly for a few important cases.

7.9.1 Spin $I = 1$

In the case of spin $I = 1$, the matrix elements of the shift operators are either 0 or $\sqrt{2}$. For example, consider the matrix element $\langle 1, +1|\hat{I}^+|1, 0\rangle$, which may be evaluated by using Equation 7.30 as follows:

$$\langle 1, +1|\hat{I}^+|1, 0\rangle = \left\{1 \times (1+1) - 0 \times (0+1)\right\}^{1/2} = 2^{1/2}$$

Repetition for all relevant elements leads to the following matrices for angular momentum along the x- and y-axes:

$$\hat{I}_x = \frac{1}{2}\begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{pmatrix} \quad \text{for } I = 1 \tag{7.44}$$

and

$$\hat{I}_y = \frac{1}{2\mathrm{i}}\begin{pmatrix} 0 & \sqrt{2} & 0 \\ -\sqrt{2} & 0 & \sqrt{2} \\ 0 & -\sqrt{2} & 0 \end{pmatrix} \quad \text{for } I = 1 \tag{7.45}$$

As usual, the matrix representation of the operator $\hat{I}_z$ is diagonal in the Zeeman basis, with the quantum numbers $M = \{1, 0, -1\}$ on the diagonal:

$$\hat{I}_z = \begin{pmatrix} +1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{for } I = 1 \tag{7.46}$$

The reader should verify the cyclic commutation relationships in Equation 6.38 by calculating the matrix products.

The spin-1 matrix representations for the rotation operators may be derived by using the techniques described in Section 6.5.8. The results are

$$\widehat{R}_x(\beta) = \exp\{-\mathrm{i}\beta\hat{I}_x\} = \begin{pmatrix} \cos^2(\beta/2) & -\mathrm{i}2^{-1/2}\sin\beta & -\sin^2(\beta/2) \\ -\mathrm{i}2^{-1/2}\sin\beta & \cos\beta & -\mathrm{i}2^{-1/2}\sin\beta \\ -\sin^2(\beta/2) & -\mathrm{i}2^{-1/2}\sin\beta & \cos^2(\beta/2) \end{pmatrix} \quad \text{for } I = 1 \tag{7.47}$$

$$\widehat{R}_y(\beta) = \exp\{-\mathrm{i}\beta\hat{I}_y\} = \begin{pmatrix} \cos^2(\beta/2) & -2^{-1/2}\sin\beta & \sin^2(\beta/2) \\ 2^{-1/2}\sin\beta & \cos\beta & -2^{-1/2}\sin\beta \\ \sin^2(\beta/2) & 2^{-1/2}\sin\beta & \cos^2(\beta/2) \end{pmatrix} \quad \text{for } I = 1 \tag{7.48}$$

$$\widehat{R}_z(\phi) = \exp\{-\mathrm{i}\phi\hat{I}_z\} = \begin{pmatrix} \exp\{-\mathrm{i}\phi\} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \exp\{+\mathrm{i}\phi\} \end{pmatrix} \quad \text{for } I = 1 \tag{7.49}$$

7.9.2 Spin $I = 3/2$

In the case $I = 3/2$, the non-zero matrix elements of the shift operators are equal to either 2 or $\sqrt{3}$; for example:

$$\langle 3/2, +3/2|\hat{I}^{+}|3/2, +1/2\rangle = \left\{\frac{3}{2} \times \left(\frac{3}{2}+1\right) - \frac{1}{2} \times \left(\frac{1}{2}+1\right)\right\}^{1/2} = \sqrt{3}$$

$$\langle 3/2, +1/2|\hat{I}^{+}|3/2, -1/2\rangle = \left\{\frac{3}{2} \times \left(\frac{3}{2}+1\right) - \left(-\frac{1}{2}\right) \times \left(-\frac{1}{2}+1\right)\right\}^{1/2} = 2$$

The transverse angular momentum matrices are therefore given by

$$\hat{I}_x = \frac{1}{2}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix} \quad \text{for } I = 3/2 \tag{7.50}$$

and

$$\hat{I}_y = \frac{1}{2\mathrm{i}}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix} \quad \text{for } I = 3/2 \tag{7.51}$$

The longitudinal angular momentum matrix has the eigenvalues $\{+3/2, +1/2, -1/2, -3/2\}$ along the diagonal:

$$\hat{I}_z = \frac{1}{2}\begin{pmatrix} +3 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix} \quad \text{for } I = 3/2 \tag{7.52}$$

The expressions for the spin-3/2 rotation matrices are complicated and are not given here.

7.9.3 Higher spins

The angular momentum matrices for higher spins are readily derived using the same formalism. For example, the matrix $\hat{I}_x$ for spin-5/2 is given by

$$\hat{I}_x = \frac{1}{2}\begin{pmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & 2\sqrt{2} & 0 & 3 & 0 & 0 \\ 0 & 0 & 3 & 0 & 2\sqrt{2} & 0 \\ 0 & 0 & 0 & 2\sqrt{2} & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{pmatrix} \quad \text{for } I = 5/2 \tag{7.53}$$

This concludes our brief review of quantum mechanics. Further theoretical results will be introduced as they are needed.

Notes

1. The 'balloon' pictures in Figure 7.11 are used in many texts to represent the angular momentum eigenfunctions, and hence the angular parts of the atomic orbitals. However, it should be noted that, although they are angular momentum eigenfunctions, they do not all represent eigenfunctions of the *same* angular momentum operator. For example, the angular part of the p_z orbital (second column, centre row in Figure 7.11) is an eigenfunction of the $\hat{l}_z$ operator, with eigenvalue 0, and is the same as the ket $|1, 0\rangle$. The angular part of the p_x orbital (second column, top row in Figure 7.11), on the other hand, is an eigenfunction of the $\hat{l}_x$ operator, also with eigenvalue 0. It is a superposition of two eigenfunctions of the $\hat{l}_z$ operator, namely $|1, +1\rangle$ and $|1, -1\rangle$. The angular part of the p_y orbital (second column, lowest row in Figure 7.11) is an eigenfunction of the $\hat{l}_y$ operator, with eigenvalue 0, and is also a superposition of the $|1, +1\rangle$ and $|1, -1\rangle$ functions. The three p-orbitals sketched in Figure 7.11, therefore, are all eigenfunctions of *different* angular momentum operators. It would be difficult to draw the $\hat{l}_z$ eigenfunctions $|1, +1\rangle$ and $|1, -1\rangle$ directly, since they are complex. Similar considerations apply to the d-orbitals.

2. One of the more bizarre mathematical properties of half-integer spins is called *spinor* behaviour. Spinors have the property that they do not return to their initial state after a full 2π rotation, but instead change sign. They only return to their initial state after a 4π rotation, i.e. *two* full revolutions.

3. The matrix representations of $\hat{x}\widehat{D}_x$ and $\widehat{D}_x\hat{x}$ given in Equation 6.17 appear to contradict this. In the former case, all the diagonal elements are $-\frac{1}{2}$, whereas in the latter case all the diagonal elements are $+\frac{1}{2}$. So how can the sum of the diagonal elements be the same in both cases? This paradox may be resolved by noting that the trace is only defined for a *finite* basis. The matrix representations in Equation 6.17 are *infinite*, and do not allow a definition of the trace.

4. The justification for the term *projection operator* is as follows. Consider a spin-1/2 in an arbitrary superposition state, of the form

$$|\psi\rangle = c_\alpha|\alpha\rangle + c_\beta|\beta\rangle$$

where c_α and c_β are complex numbers. This spin state may be written as a two-dimensional vector:

$$|\psi\rangle = \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}$$

Application of the operator $\hat{I}^\alpha$ to this state has the following effect:

$$\hat{I}^\alpha|\psi\rangle = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix} = c_\alpha \begin{pmatrix} 1 \\ 0 \end{pmatrix} = c_\alpha|\alpha\rangle$$

The operator $\hat{I}^\alpha$ removes the '$|\beta\rangle$ part' of the state $|\psi\rangle$, and leaves only the '$|\alpha\rangle$ part'. Mathematically, this corresponds to a *projection* of the state $|\psi\rangle$ onto the state $|\alpha\rangle$.

5. The operators $\hat{I}^\alpha$ and $\hat{I}^\beta$ are often referred to as *polarization operators*, but this is rather misleading. The polarization of the spin along a particular axis is associated with the *angular momentum operator* along that axis, not with the $\hat{I}^\alpha$ or $\hat{I}^\beta$ operators.

Further Reading

- Some recommended quantum mechanics textbooks include the following: J. J. Sakurai, *Modern Quantum Mechanics*, Addison-Wesley, 1994; P. W. Atkins, *Molecular Quantum Mechanics*, Oxford University Press, Oxford, 1983; C. Cohen-Tannoudji, B. Diu and F. Laloë, *Quantum Mechanics*, Wiley, London, 1977; E. Merzbacher, *Quantum Mechanics*, 3rd edition, Wiley, New York, 1998.
- For the quantum theory of angular momentum, see the textbooks above and also W. J. Thompson, *Angular Momentum*, Wiley, New York, 1994.
- For an accessible article describing the origin of spin-1/2, see N. Zumbulyadis, *Concepts Magn. Reson.* **3**, 89 (1991).
- The following book is recommended to the more advanced reader as a useful compilation of formulae relating to the quantum mechanics of angular momentum: D. A. Varshalovich, A. N. Moskalev and V. K. Kheronskii, *Quantum Theory of Angular Momentum*, World Scientific, Singapore, 1988.

Exercises

7.1 The following three operators have a cyclic commutation relationship (in the case of spins-1/2):

$$\left[2\hat{I}_{1x}\hat{I}_{2y}, 2\hat{I}_{1x}\hat{I}_{2z}\right] = \mathrm{i}\hat{I}_{2x} \qquad \circlearrowleft \tag{7.54}$$

(i) Write down explicitly the three commutation relationships implied by Equation 7.54.
(ii) Evaluate the following expression:

$$\exp\{-\mathrm{i}\theta 2\hat{I}_{1x}\hat{I}_{2y}\}2\hat{I}_{1x}\hat{I}_{2z}\exp\{+\mathrm{i}\theta 2\hat{I}_{1x}\hat{I}_{2y}\}$$

(iii) Evaluate the following expression:

$$\exp\{-\mathrm{i}\theta 2\hat{I}_{1x}\hat{I}_{2y}\}\hat{I}_{2x}\exp\{+\mathrm{i}\theta 2\hat{I}_{1x}\hat{I}_{2y}\}$$

7.2 Suppose that a particle is confined to a one-dimensional box between $x = 0$ and $x = 1$ and has a quantum wave function given by Equation 6.7. An observation is performed that is associated with the operator $\widehat{Q} = \widehat{D}_x^2$.

(i) What is the probability of obtaining the result $-\pi^2$?
(ii) What is the probability of obtaining the result $-9\pi^2$?
(iii) What is the probability of obtaining the result 2?
(iv) Suppose that a large number of measurements are made, on particles all in the same state given by Equation 6.7. The results of all the measurements are averaged. To what value does the average tend, as the number of measurements becomes very large?

7.3 Prove that the result of three consecutive rotations $\widehat{R}_x(\pi/2)\widehat{R}_y(\pi)\widehat{R}_x(\pi/2)$ is the same as that given by a single rotation $\widehat{R}_y(\pi)$. Verify the identity by rotating your shoe.

7.4 Write down the matrix representations of $\hat{I}^+$, $\hat{I}^-$, $\hat{I}_y$ and $\hat{I}_z$ for a spin-5/2 particle.