

The foundations of quantum mechanics

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The whole of quantum mechanics can be expressed in terms of a small set of postulates. When their consequences are developed, they embrace the behaviour of all known forms of matter, including the molecules, atoms, and electrons that will be at the centre of our attention in this book. This chapter introduces the postulates and illustrates how they are used. The remaining chapters build on them, and show how to apply them to problems of chemical interest, such as atomic and molecular structure and the properties of molecules. We assume that you have already met the concepts of 'hamiltonian' and 'wavefunction' in an elementary introduction, and have seen the Schrödinger equation written in the form

$$H\psi = E\psi$$

This chapter establishes the full significance of this equation and provides a foundation for its application in the following chapters. It will also be helpful to bear in mind the solutions of the Schrödinger equation for a particle in a box, which we also presume to be generally familiar. In brief, for a particle of mass m in a one-dimensional box of length L :

- The energies are quantized, with $E_n = n^2 h^2 / 8mL^2$, $n = 1, 2, \dots$
- The normalized wavefunctions are $\psi_n(x) = (2/L)^{1/2} \sin(n\pi x/L)$

We use these solutions to illustrate some of the points made in this chapter (they are developed formally in Chapter 2). A final preparatory point is that quantum mechanics makes extensive use of complex numbers: they are reviewed in *Mathematical background 1* following this chapter.

Operators in quantum mechanics

An **observable** is any dynamical variable that can be measured. The principal mathematical difference between classical mechanics and quantum mechanics is that whereas in the former physical observables are represented by functions (such as position as a function of time), in quantum mechanics they are represented by mathematical operators. An **operator** is a symbol for an instruction to carry out some action, an operation, on a function. In most of the examples we shall meet, the action will be nothing more complicated than multiplication or differentiation. Thus, one typical operation might be multiplication by x , which is represented by the operator $x \times$. Another operation might be differentiation with respect to x , represented by the operator d/dx . We shall represent operators by the symbol Ω (uppercase omega) in general, but use A, B, \dots when we want to refer to a series of operators. We shall not in general distinguish between the observable and the operator that represents that observable; so the position of a particle along the x -axis will be denoted x and the corresponding operator will also be denoted x (with multiplication implied). We shall always make it clear whether we are referring to the observable or the operator.

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We shall need a number of concepts related to operators and functions on which they operate, and this first section introduces some of the more important features.

1.1 Linear operators

The operators we shall meet in quantum mechanics are all linear. A **linear operator** is one for which

$$\Omega(af) = a\Omega f \quad (1.1)$$

where a is a constant and f is a function. Multiplication is a linear operation; so are differentiation and integration. An example of a non-linear operation is that of taking the logarithm of a function, because it is not true, for example, that $\log 2x = 2 \log x$ for all x . The operation of taking a square is also non-linear, because it is not true, for example, that $(2x)^2 = 2x^2$ for all x .

1.2 Eigenfunctions and eigenvalues

In general, when an operator operates on a function, the outcome is another function. Differentiation of $\sin x$, for instance, gives $\cos x$. However, in certain cases, the outcome of an operation is the same function multiplied by a constant. Functions of this kind are called ‘eigenfunctions’ of the operator. More formally, a function f (which may be complex) is an **eigenfunction** of an operator Ω if it satisfies an equation of the form

$$\Omega f = \omega f \quad (1.2)$$

where ω is a constant. Such an equation is called an **eigenvalue equation**. The function e^{ax} is an eigenfunction of the operator d/dx because $(d/dx)e^{ax} = ae^{ax}$, which is a constant (a) multiplying the original function. In contrast, e^{ax^2} is not an eigenfunction of d/dx , because $(d/dx)e^{ax^2} = 2axe^{ax^2}$, which is a constant ($2a$) times a *different* function of x (the function xe^{ax^2}). The constant ω in an eigenvalue equation is called the **eigenvalue** of the operator Ω .



Example 1.1 Determining if a function is an eigenfunction

Is the wavefunction $\psi_1(x) = (2/L)^{1/2} \sin(\pi x/L)$ of a particle in a box an eigenfunction of the operator d^2/dx^2 and, if so, what is the corresponding eigenvalue?

Method Perform the indicated operation on the given function and see if the function satisfies an eigenvalue equation. Use $(d/dx)\sin ax = a \cos ax$ and $(d/dx)\cos ax = -a \sin ax$.

Answer The operation on the function yields

$$\begin{aligned} \frac{d^2\psi_1(x)}{dx^2} &= \left(\frac{2}{L}\right)^{1/2} \frac{d^2\sin(\pi x/L)}{dx^2} = \left(\frac{2}{L}\right)^{1/2} \left(\frac{\pi}{L}\right) \frac{d\cos(\pi x/L)}{dx} \\ &= -\left(\frac{2}{L}\right)^{1/2} \left(\frac{\pi}{L}\right)^2 \sin(\pi x/L) = -\left(\frac{\pi}{L}\right)^2 \psi_1(x) \end{aligned}$$

and we see that the original function reappears multiplied by a constant, so $\psi_1(x)$ is an eigenfunction of d^2/dx^2 , and its eigenvalue is $-(\pi/L)^2$.

Self-test 1.1 Is the function e^{3x+5} an eigenfunction of the operator d^2/dx^2 and, if so, what is the corresponding eigenvalue?

[Yes; 9]

An important point is that a general function can be expanded in terms of all the eigenfunctions of an operator, a so-called **complete set** of functions. The functions used to construct a general function are called **basis functions**. That is, if f_n is an eigenfunction of an operator Ω with eigenvalue ω_n (so $\Omega f_n = \omega_n f_n$), then a general function g can be expressed as the **linear combination**

$$g = \sum_n c_n f_n \quad (1.3)$$

where the c_n are coefficients and the sum is over a complete set of basis functions f_n . For instance, the straight line $g = ax$ can be recreated over a certain range ($-L/2 \leq x \leq L/2$) by superimposing an infinite number of sine functions, each of which is an eigenfunction of the operator d^2/dx^2 :

$$g(x) = \left(\frac{aL}{\pi}\right) \sum_{n=1}^{\infty} \{(-1)^{n+1}/n\} \sin(2n\pi x/L)$$

(The formulation and illustration of expressions like this are described in *Mathematical background 5* following Chapter 10.) The same function may also be constructed from an infinite number of exponential functions, which are eigenfunctions of d/dx .

The advantage of expressing a general function as a linear combination of a set of eigenfunctions is that it allows us to deduce the effect of an operator on a function that is not one of its own eigenfunctions. Thus, the effect of Ω on g in eqn 1.3, using the property of linearity, is simply

$$\Omega g = \Omega \sum_n c_n f_n = \sum_n c_n \Omega f_n = \sum_n c_n \omega_n f_n \quad (1.4)$$

A special case of these linear combinations is when we have a set of **degenerate** eigenfunctions, a set of functions with the same eigenvalue. Thus, suppose that f_1, f_2, \dots, f_k are all eigenfunctions of the operator Ω , and that they all correspond to the same eigenvalue ω :

$$\Omega f_n = \omega f_n \quad \text{with } n = 1, 2, \dots, k \quad (1.5)$$

Then it is quite easy to show that *any* linear combination of the functions f_n is also an eigenfunction of Ω with the same eigenvalue ω . The proof is as follows. For an arbitrary linear combination g of the degenerate set of functions, we can write

$$\Omega g = \Omega \sum_{n=1}^k c_n f_n = \sum_{n=1}^k c_n \Omega f_n = \sum_{n=1}^k c_n \omega f_n = \omega \sum_{n=1}^k c_n f_n = \omega g \quad (1.6)$$

This expression has the form of an eigenvalue equation ($\Omega g = \omega g$).

Example 1.2 Demonstrating that a linear combination of degenerate eigenfunctions is also an eigenfunction

Show that any linear combination of the complex functions e^{2ix} and e^{-2ix} is an eigenfunction of the operator d^2/dx^2 , where $i = (-1)^{1/2}$.

Method Consider an arbitrary linear combination $ae^{2ix} + be^{-2ix}$ and see if the function satisfies an eigenvalue equation.

Answer First we demonstrate that e^{2ix} and e^{-2ix} are degenerate eigenfunctions:

$$\frac{d^2}{dx^2} e^{\pm 2ix} = \frac{d}{dx} (\pm 2ie^{\pm 2ix}) = -4e^{\pm 2ix} \quad \gg$$

where we have used $i^2 = -1$. Both functions correspond to the same eigenvalue, -4 . Then we operate on a linear combination of the functions:

$$\frac{d^2}{dx^2}(ae^{2ix} + be^{-2ix}) = -4(ae^{2ix} + be^{-2ix})$$

The linear combination satisfies the eigenvalue equation and has the same eigenvalue (-4) as do the two exponential functions.

Self-test 1.2 Show that any linear combination of the functions $\sin(3x)$ and $\cos(3x)$ is an eigenfunction of the operator d^2/dx^2 .

[Eigenvalue is -9]

A further technical point is that from N basis functions it is possible to construct N linearly independent combinations. A set of functions g_1, g_2, \dots, g_N is said to be **linearly independent** if we cannot find a set of constants c_1, c_2, \dots, c_N (other than the trivial set $c_1 = c_2 = \dots = 0$) for which

$$\sum_i c_i g_i = 0 \quad (1.7)$$

A set of functions that are not linearly independent are said to be **linearly dependent**. From a set of N linearly independent functions, it is possible to construct an infinite number of sets of linearly independent combinations, but each set can have no more than N members.

A brief illustration

Consider an $1s$ orbital on each hydrogen atom in NH_3 , and denote them s_A, s_B , and s_C . The three linear combinations

$$2s_A - s_B - s_C \quad 2s_B - s_C - s_A \quad 2s_C - s_A - s_B$$

are not linearly independent (their sum is zero). Put another way: the third can be expressed as the sum of the first two. On the other hand, the linear combinations

$$2s_A - s_B - s_C \quad s_A + s_B + s_C \quad s_B - s_C$$

are linearly independent, and any one cannot be expressed as a sum or difference of the other two. The three p orbitals (p_x, p_y, p_z) of a shell of an atom are linearly independent. It is possible to form any number of sets of linearly independent combinations of them, but each set has no more than three members. One such set (which will be discussed further in Section 3.15) is

$$p_{+1} = -\frac{1}{2^{1/2}}(p_x + ip_y) \quad p_{-1} = \frac{1}{2^{1/2}}(p_x - ip_y) \quad p_0 = p_z$$

1.3 Representations

The remaining work of this section is to put forward some explicit forms of the operators we shall meet. Much of quantum mechanics can be developed in terms of an abstract set of operators, as we shall see later. However, it is often fruitful to adopt an explicit form for particular operators and to express them in terms of the mathematical operations of multiplication, differentiation, and so on. Different choices of the operators that correspond to a particular observable give rise to the different **representations** of quantum mechanics, because the explicit

forms of the operators represent the abstract structure of the theory in terms of actual manipulations.

One of the most common representations is the **position representation**, in which the position operator is represented by multiplication by x (or whatever coordinate is specified) and the linear momentum parallel to x is represented by differentiation with respect to x . Explicitly:

$$\text{Position representation: } x \rightarrow x \times \quad p_x \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x} \quad (1.8)$$

where $\hbar = h/2\pi$. We replace the partial derivative, $\partial/\partial x$, by an ordinary derivative, d/dx , when considering one-dimensional systems in which x is the only variable. Why the linear momentum should be represented in precisely this manner is explained in the following section. For the time being, it may be taken to be a basic postulate of quantum mechanics. An alternative choice of operators is the **momentum representation**, in which the linear momentum parallel to x is represented by the operation of multiplication by p_x and the position operator is represented by differentiation with respect to p_x . Explicitly:

$$\text{Momentum representation: } x \rightarrow -\frac{\hbar}{i} \frac{\partial}{\partial p_x} \quad p_x \rightarrow p_x \times \quad (1.9)$$

There are other representations. We shall normally use the position representation when the adoption of a representation is appropriate, but we shall also see that many of the calculations in quantum mechanics can be done independently of a representation.

1.4 Commutation and non-commutation

An important feature of operators is that in general the outcome of successive operations (A followed by B , which is denoted BA , or B followed by A , denoted AB) depends on the order in which the operations are carried out. That is, in general $BA \neq AB$. We say that, in general, operators do not **commute**.

A brief illustration

Consider the operators x and p_x and a specific function x^2 . In the position representation,

$$(xp_x)x^2 = x \times \frac{\hbar}{i} \frac{d}{dx} x^2 = -2i\hbar x^2$$

whereas

$$(p_x x)x^2 = \frac{\hbar}{i} \frac{d}{dx} x \times x^2 = -3i\hbar x^2$$

We see that because the outcomes are different, the operators x and p_x do not commute.

The quantity $AB - BA$ is called the **commutator** of A and B and is denoted $[A, B]$:

$$[A, B] = AB - BA \quad (1.10)$$

It is instructive to evaluate the commutator of the position and linear momentum operators in the two representations shown above; the procedure is illustrated in the following example.

Example 1.3 Evaluating a commutator

Evaluate the commutator $[x, p_x]$ in the position representation.

Method To evaluate the commutator $[A, B]$ we need to remember that the operators operate on some function, which we shall write f . So, evaluate $[A, B]f$ for an arbitrary function f , and then cancel f at the end of the calculation.

Answer Substitution of the explicit expressions for the operators into $[x, p_x]$ proceeds as follows:

$$\begin{aligned} [x, p_x]f &= (xp_x - p_x x)f = x \times \frac{\hbar}{i} \frac{\partial f}{\partial x} - \frac{\hbar}{i} \frac{\partial (xf)}{\partial x} \\ &= x \times \frac{\hbar}{i} \frac{\partial f}{\partial x} - \frac{\hbar}{i} f - x \times \frac{\hbar}{i} \frac{\partial f}{\partial x} = i\hbar f \end{aligned}$$

where we have used $(1/i) = -i$. This derivation is true for any function f , so in terms of the operators themselves, $[x, p_x] = i\hbar$. The right-hand side of this expression should be interpreted as the operator ‘multiply by the constant $i\hbar$ ’.

Self-test 1.3 Evaluate the same commutator in the momentum representation.

[Same]

The non-commutation of operators is highly reminiscent of the non-commutation of matrix multiplication. Indeed, Heisenberg formulated his version of quantum mechanics, which is called **matrix mechanics**, by representing position and linear momentum by the matrices x and p_x , and requiring that $xp_x - p_x x = i\hbar \mathbf{1}$ where $\mathbf{1}$ is the **unit matrix**, a square matrix with all diagonal elements equal to 1 and all others 0. (Matrices are discussed in *Mathematical background 4* following Chapter 5.)

1.5 The construction of operators

Operators for other observables of interest can be constructed from the operators for position and momentum. For example, the kinetic energy operator T can be constructed by noting that kinetic energy is related to linear momentum by $T = p^2/2m$, where m is the mass of the particle and p^2 (in general Ω^2) means that the operator is applied twice in succession. It follows that in one dimension and in the position representation

$$T = \frac{p_x^2}{2m} = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{d}{dx} \right)^2 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad (1.11a)$$

In three dimensions the operator in the position representation is

$$T = -\frac{\hbar^2}{2m} \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right\} = -\frac{\hbar^2}{2m} \nabla^2 \quad (1.11b)$$

The operator ∇^2 , which is read ‘del squared’ and called the **laplacian**, is the sum of the three second derivatives.

Because the potential energy depends only on position coordinates, the operator for potential energy of a particle in one dimension, $V(x)$, is multiplication by the function $V(x)$ in the position representation. The same is true of the potential energy operator in three dimensions. For example, in the position representation the operator for the Coulomb potential energy of an electron (charge $-e$) in the field of a nucleus of atomic number Z and charge Ze is the multiplicative operator

A brief comment

Although eqn 1.11b has explicitly used Cartesian coordinates, the relation between the kinetic energy operator and the laplacian is true in any coordinate system; for example, spherical polar coordinates. These alternative versions of the laplacian are given in *Mathematical background 3* following Chapter 4.

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad (1.12)$$

where r is the distance from the nucleus to the electron. As here, it is usual to omit the multiplication sign from multiplicative operators, but it should not be forgotten that such expressions imply multiplications of whatever stands on their right.

The operator for the total energy of a system is called the **hamiltonian operator** and is denoted H :

$$H = T + V \quad (1.13)$$

The name commemorates W.R. Hamilton's contribution to the formulation of classical mechanics in terms of what became known as a hamiltonian *function*. To write the explicit form of this operator we simply substitute the appropriate expressions for the kinetic and potential energy operators in the chosen representation. For example, the hamiltonian operator for a particle of mass m moving in one dimension is

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad (1.14)$$

where $V(x)$ is the operator for the potential energy. Similarly, the hamiltonian operator (from now on, just 'the hamiltonian') for an electron of mass m_e in a hydrogen atom is

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad (1.15)$$

The general prescription for constructing operators in the position representation should be clear from these examples. In short:

1. Write the classical expression for the observable in terms of position coordinates and the linear momentum.
2. Replace x by multiplication by x , and replace p_x by $(\hbar/i)\partial/\partial x$ (and likewise for the other coordinates).

1.6 Integrals over operators

When we want to make contact between a calculation done using operators and the actual outcome of an experiment, it will turn out that we shall need to evaluate certain integrals. These integrals all have the form

$$I = \int f_m^* \Omega f_n d\tau \quad (1.16)$$

where f_m^* is the complex conjugate (*Mathematical background 1*) of f_m . In this integral $d\tau$ is the **volume element**. In one dimension, $d\tau$ can be identified as dx ; in three dimensions it is $dx dy dz$. The integral is taken over the entire space available to the system, which is typically from $x = -\infty$ to $x = +\infty$ (and similarly for the other coordinates). A glance at the later pages of this book will show that many molecular properties are expressed as combinations of integrals of this form (often in a notation which will be explained later). Certain special cases of this type of integral have special names, and we shall introduce them here.

When the operator Ω in eqn 1.16 is simply multiplication by 1, the integral is called an **overlap integral** and commonly denoted S :

$$S = \int f_m^* f_n d\tau \quad (1.17)$$

It is helpful to regard S as a measure of the similarity of two functions: when $S = 0$, the functions are classified as **orthogonal**, rather like two perpendicular vectors. When S is close to 1, the two functions are almost identical. The recognition of mutually orthogonal functions often helps to reduce the amount of calculation considerably, and rules will emerge in later sections and chapters.

The **normalization integral** is the special case of eqn 1.17 for $m = n$. A function f_m is said to be **normalized** (strictly, normalized to 1) if

$$\int f_m^* f_m d\tau = 1 \quad (1.18)$$

The integration here, as (by convention) it always is when $d\tau$ is used to denote the volume element, is over all space. It is almost always easy to ensure that a function is normalized by multiplying it by an appropriate numerical factor, which is called a **normalization factor**, typically denoted N and taken to be real so that $N^* = N$. We could take N to have any complex phase, but because all observables are proportional to N^*N , the phase cancels and it is simply convenient to make N real. The procedure is illustrated in the following example.

Example 1.4 Normalizing a function

The ground state wavefunction of a particle in a box is $\psi_1(x) = N \sin(\pi x/L)$ between $x = 0$ and $x = L$ and is zero elsewhere. Confirm that $N = (2/L)^{1/2}$.

Method To find N we substitute this expression into eqn 1.18, evaluate the integral, and select N to ensure normalization. Note that ‘all space’ in effect extends from $x = 0$ to $x = L$ because the function is identically zero outside this region.

Answer The necessary integration is

$$\int f^* f d\tau = \int_0^L N^2 \sin^2(\pi x/L) dx = \frac{1}{2}LN^2$$

where we have used $\int \sin^2 ax dx = (x/2) - (\sin 2ax)/4a + \text{constant}$. For this integral to be equal to 1, we require $N = (2/L)^{1/2}$.

Self-test 1.4 Normalize the function $f = e^{i\varphi}$, where φ ranges from 0 to 2π .

$$[N = 1/(2\pi)^{1/2}]$$

A set of functions f_n that are (a) normalized and (b) mutually orthogonal are said to satisfy the **orthonormality condition**:

$$\int f_m^* f_n d\tau = \delta_{mn} \quad (1.19)$$

In this expression, δ_{mn} denotes the **Kronecker delta**, which is 1 when $m = n$ and 0 otherwise.

1.7 Dirac bracket and matrix notation

The appearance of many quantum mechanical expressions is greatly simplified by adopting a simplified notation.

(a) Dirac brackets

In the **Dirac bracket notation** integrals are written as follows:

$$\langle m | \Omega | n \rangle = \int f_m^* \Omega f_n d\tau \quad (1.20)$$

The symbol $|n\rangle$ is called a **ket**, and denotes the state described by the function f_n . Similarly, the symbol $\langle n|$ is called a **bra**, and denotes the complex conjugate of the function, f_n^* . When a bra and ket are strung together with an operator between them, as in the **bracket** $\langle m|\Omega|n\rangle$, the integral in eqn 1.20 is to be understood. When the operator is simply multiplication by 1, the 1 is omitted and we use the convention

$$\langle m|n\rangle = \int f_m^* f_n d\tau \quad (1.21)$$

This notation is very elegant. For example, the normalization integral becomes $\langle n|n\rangle = 1$ and the orthogonality condition becomes $\langle m|n\rangle = 0$ for $m \neq n$. The combined orthonormality condition (eqn 1.19) is then

$$\langle m|n\rangle = \delta_{mn} \quad (1.22)$$

A further point is that, as can readily be deduced from the definition of a Dirac bracket,

$$\langle m|n\rangle = \langle n|m\rangle^* \quad (1.23)$$

(b) Matrix notation

A **matrix**, M , is an array of numbers (which may be complex), called **matrix elements**. Each element is specified by quoting the row (r) and column (c) that it occupies, and denoting the matrix element as M_{rc} . The rules of matrix algebra are set out in *Mathematical background 4* following Chapter 5, where they are centre stage. Dirac brackets are commonly abbreviated to Ω_{mn} , which immediately suggests that they are elements of a matrix. For this reason, the Dirac bracket $\langle m|\Omega|n\rangle$ is often called a **matrix element** of the operator Ω . A **diagonal matrix element** Ω_{nn} is then a bracket of the form $\langle n|\Omega|n\rangle$ with the bra and the ket referring to the same state.

We shall often encounter sums over products of Dirac brackets that have the form

$$\sum_s \langle r|A|s\rangle \langle s|B|c\rangle$$

If the brackets that appear in this expression are interpreted as matrix elements, then we see that it has the form of a matrix multiplication, and we may write

$$\sum_s \langle r|A|s\rangle \langle s|B|c\rangle = \sum_s A_{rs} B_{sc} = (AB)_{rc} = \langle r|AB|c\rangle \quad (1.24)$$

That is, the sum is equal to the single matrix element (bracket) of the product of operators AB . Comparison of the first and last terms in this line of equations also allows us to write the symbolic relation

$$\sum_s |s\rangle \langle s| = 1 \quad (1.25)$$

This **completeness relation** (or *closure relation*) is exceptionally useful for developing quantum mechanical equations. It is often used in reverse: the matrix element $\langle r|AB|c\rangle$ can always be split into a sum of two factors by regarding it as $\langle r|A1B|c\rangle$ and then replacing the 1 by a sum over a complete set of states of the form in eqn 1.25.

1.8 Hermitian operators

'Hermitian operators' are central to the development of quantum theory. Here we define what it means to be Hermitian and then unfold the consequences of that property.

(a) The definition of hermiticity

An operator is **Hermitian** if it satisfies the following relation:

$$\int f_m^* \Omega f_n \, d\tau = \left\{ \int f_n^* \Omega f_m \, d\tau \right\}^* \quad (1.26a)$$

for any two functions f_m and f_n . An alternative version of this definition is

$$\int f_m^* \Omega f_n \, d\tau = \int (\Omega f_m)^* f_n \, d\tau \quad (1.26b)$$

This expression is obtained by taking the complex conjugate of each term on the right-hand side of eqn 1.26a. In terms of the Dirac notation, the definition of hermiticity is

$$\langle m | \Omega | n \rangle = \langle n | \Omega | m \rangle^* \quad (1.26c)$$

Example 1.5 Confirming the hermiticity of operators

Show that the position and momentum operators in the position representation are Hermitian.

Method We need to show that the operators satisfy eqn 1.26a. In some cases (the position operator, for instance), the hermiticity is obvious as soon as the integral is written down. When a differential operator is used, it may be necessary to use integration by parts at some stage in the argument to transfer the differentiation from one function to another:

$$\int u \, dv = uv - \int v \, du$$

Answer That the position operator is Hermitian is obvious from inspection:

$$\int f_m^* x f_n \, d\tau = \int f_n^* x f_m \, d\tau = \left\{ \int f_n^* x f_m \, d\tau \right\}^*$$

We have used the facts that $(f^*)^* = f$ and x is real. The demonstration of the hermiticity of p_x , a differential operator in the position representation, involves an integration by parts and we consider the definite integral over all space to show the disappearance of one of the terms:

$$\begin{aligned} \int_{-\infty}^{\infty} f_m^* p_x f_n \, dx &= \int_{-\infty}^{\infty} f_m^* \frac{\hbar}{i} \frac{df_n}{dx} \, dx = \frac{\hbar}{i} \int_{-\infty}^{\infty} f_m^* df_n \\ &= \frac{\hbar}{i} \left\{ f_m^* f_n - \int_{-\infty}^{\infty} f_n df_m^* \right\} = \frac{\hbar}{i} \left\{ f_m^* f_n \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f_n \frac{df_m^*}{dx} \, dx \right\} \end{aligned}$$

The first term on the right is zero (because when $|x|$ is infinite, a normalizable function must be vanishingly small; see Section 1.12). Therefore, reverting for notational simplicity to indefinite integrals:

$$\int f_m^* p_x f_n \, dx = -\frac{\hbar}{i} \int f_n \frac{d}{dx} f_m^* \, dx = \left\{ \int f_n^* \frac{\hbar}{i} \frac{d}{dx} f_m \, dx \right\}^* = \left\{ \int f_n^* p_x f_m \, dx \right\}^*$$

Hence, the operator is Hermitian.

Self-test 1.5 Show that the two operators are Hermitian in the momentum representation.

(b) The consequences of hermiticity

As we shall now see, the property of hermiticity has far-reaching implications. First, we shall establish the following property:

Property 1. The eigenvalues of Hermitian operators are real.

Proof 1.1 The reality of eigenvalues

Consider the eigenvalue equation

$$\Omega|\omega\rangle = \omega|\omega\rangle$$

The ket $|\omega\rangle$ denotes an **eigenstate** of the operator Ω in the sense that the corresponding function f_ω is an eigenfunction of the operator Ω and we are labelling the eigenstates with the eigenvalue ω of the operator Ω . It is often convenient to use the eigenvalues as labels in this way. Multiplication from the left by $\langle\omega|$ results in the equation

$$\langle\omega|\Omega|\omega\rangle = \omega\langle\omega|\omega\rangle = \omega$$

taking $|\omega\rangle$ to be normalized. Now take the complex conjugate of both sides:

$$\langle\omega|\Omega|\omega\rangle^* = \omega^*$$

However, by hermiticity, $\langle\omega|\Omega|\omega\rangle^* = \langle\omega|\Omega|\omega\rangle$. Therefore, it follows that $\omega = \omega^*$, which implies that the eigenvalue ω is real.

The second property we shall prove is as follows:

Property 2. Eigenfunctions corresponding to different eigenvalues of an Hermitian operator are orthogonal.

That is, if we have two eigenfunctions of an Hermitian operator Ω with eigenvalues ω and ω' , with $\omega \neq \omega'$, then $\langle\omega|\omega'\rangle = 0$. For example, it follows at once that all the eigenfunctions of a particle in a box are mutually orthogonal, for as we shall see each one corresponds to a different energy (the eigenvalue of the hamiltonian, an Hermitian operator).

A brief illustration

The (real) wavefunctions $\psi_1(x) = (2/L)^{1/2} \sin(\pi x/L)$ and $\psi_2(x) = (2/L)^{1/2} \sin(2\pi x/L)$ of a particle in a box correspond to different energies ($b^2/8mL^2$ and $b^2/2mL^2$, respectively). That they are mutually orthogonal is verified by writing

$$\int_0^L \psi_1(x)\psi_2(x)dx = \frac{2}{L} \int_0^L \sin(\pi x/L)\sin(2\pi x/L)dx = 0$$

We have made use of a standard result to evaluate the integral; alternatively, note that $\sin(\pi x/L)$ is an even function with respect to reflection in $x = 1/2L$ whereas $\sin(2\pi x/L)$ is odd.

Proof 1.2 The orthogonality of eigenstates

Suppose we have two eigenstates $|\omega\rangle$ and $|\omega'\rangle$ that satisfy the following relations:

$$\Omega|\omega\rangle = \omega|\omega\rangle \quad \text{and} \quad \Omega|\omega'\rangle = \omega'|\omega'\rangle$$

»

Then multiplication of the first relation by $\langle \omega' |$ and the second by $\langle \omega |$ gives

$$\langle \omega' | \Omega | \omega \rangle = \omega \langle \omega' | \omega \rangle \quad \text{and} \quad \langle \omega | \Omega | \omega' \rangle = \omega' \langle \omega | \omega' \rangle$$

Now take the complex conjugate of the second relation and subtract it from the first while using Property 1 ($\omega'^* = \omega'$):

$$\langle \omega' | \Omega | \omega \rangle - \langle \omega | \Omega | \omega' \rangle^* = \omega \langle \omega' | \omega \rangle - \omega' \langle \omega | \omega' \rangle^*$$

Because Ω is Hermitian, the left-hand side of this expression is zero; so (noting that ω' is real and using $\langle \omega | \omega' \rangle^* = \langle \omega' | \omega \rangle$ as explained earlier) we arrive at

$$(\omega - \omega') \langle \omega' | \omega \rangle = 0$$

However, because the two eigenvalues are different, the only way of satisfying this relation is for $\langle \omega' | \omega \rangle = 0$, as was to be proved.



Example 1.6 Making use of the completeness relation

Use the completeness relation to prove that the eigenvalues of the square of an Hermitian operator are non-negative.

Method We have to prove, for $\Omega^2 | \omega \rangle = a(\omega) | \omega \rangle$, that $a(\omega) \geq 0$ if Ω is Hermitian. If both sides of the eigenvalue equation are multiplied by $\langle \omega |$, converting it to $\langle \omega | \Omega^2 | \omega \rangle = a(\omega)$, we see that the proof requires us to show that the expectation value on the left is non-negative. As it has the form $\langle \omega | \Omega \Omega | \omega \rangle$, it suggests that the completeness relation might provide a way forward. The hermiticity of Ω implies that it will be appropriate to use the property $\langle m | \Omega | n \rangle = \langle n | \Omega | m \rangle^*$ at some stage in the argument.

Answer The diagonal matrix element $\langle \omega | \Omega^2 | \omega \rangle$ can be developed as follows:

$$\begin{aligned} \langle \omega | \Omega^2 | \omega \rangle &= \langle \omega | \Omega \Omega | \omega \rangle = \sum_s \langle \omega | \Omega | s \rangle \langle s | \Omega | \omega \rangle \\ &= \sum_s \langle \omega | \Omega | s \rangle \langle \omega | \Omega | s \rangle^* = \sum_s |\langle \omega | \Omega | s \rangle|^2 \geq 0 \end{aligned}$$

The final inequality follows from the fact that all the terms in the sum are non-negative.

Self-test 1.6 Show that if $(\Omega f)^* = -\Omega f^*$, then $\langle \Omega \rangle = 0$ for any real function f .

The postulates of quantum mechanics

Now we turn to an application of the preceding material, and move into the foundations of quantum mechanics. The postulates we use as a basis for quantum mechanics are by no means the most subtle that have been devised, but they are strong enough for what we have to do.

1.9 States and wavefunctions

The first postulate concerns the information we can know about a state:

Postulate 1. The state of a system is fully described by a function $\Psi(r_1, r_2, \dots, t)$.

In this statement, r_1, r_2, \dots are the spatial coordinates of particles 1, 2, \dots that constitute the system and t is the time, a variable parameter common to the entire system. The function Ψ (uppercase psi) plays a central role in quantum mechanics, and is called the **wavefunction** of the system (more specifically, the time-dependent wavefunction). When we are not interested in how the system changes in time we shall denote the wavefunction by a lowercase psi as $\psi(r_1, r_2, \dots)$ and refer to it as the **time-independent wavefunction**. The state of the system may also depend on some internal variable of the particles (their spin states); we ignore that for now and return to it later. By ‘describe’ we mean that the wavefunction contains information about all the properties of the system that are open to experimental determination.

The wavefunction must also behave in a certain way (specifically, change sign or not change sign) when the labels of identical particles are interchanged. This is the realm of the ‘Pauli principle’. The principle is properly considered to be an additional postulate of quantum mechanics, but as it requires concepts that are beyond the scope of this chapter (specifically, the classification of particles according to their spin, their intrinsic angular momentum), we delay its introduction until Section 7.11, where it first plays a role.

We shall see that the wavefunction of a system will be specified by a set of labels called **quantum numbers**, and may then be written $\psi_{a,b,\dots}$, where a, b, \dots are the quantum numbers. For a particle in a one-dimensional box, the single quantum number is $n = 1, 2, \dots$. The values of these quantum numbers specify the wavefunction and thus allow the values of various physical observables to be calculated (for instance, from $E_n = n^2 h^2 / 8mL^2$). It is often convenient to refer to the **state** of the system without referring to the corresponding wavefunction; the state is specified by listing the values of the quantum numbers that define it.

1.10 The fundamental prescription

The next postulate concerns the selection of operators:

Postulate 2. Observables are represented by Hermitian operators chosen to satisfy the commutation relations

$$[q, p_{q'}] = i\hbar \delta_{qq'} \quad [q, q'] = 0 \quad [p_q, p_{q'}] = 0 \quad (1.27)$$

where q and q' each denote one of the coordinates x, y, z and p_q and $p_{q'}$ the corresponding linear momenta.

The requirement that the operators are Hermitian ensures that the observables have real values (see below). Each commutation relation can be regarded as a basic, unprovable, and underivable postulate. This postulate is the basis of the selection of the form of the operators in the position and momentum representations for all observables that depend on the position and the momentum.¹

A brief illustration

If we choose the operator for position along the coordinate q as $q \times$, then (as we saw in Example 1.3), the appropriate operator for p_q is $(\hbar/i)\partial/\partial q$, for these two operators satisfy the first of the three commutation relations in eqn 1.27. The second of the commutation relations implies, trivially, $xy = yx$ and the third implies $p_x p_y = p_y p_x$, which also follows from the properties of partial differentials, $\partial^2/\partial x \partial y = \partial^2/\partial y \partial x$. Similarly, if the linear momentum is represented by multiplication, then the form of the position operator is fixed as a derivative with respect to the linear momentum.

¹ This prescription excludes intrinsic observables, such as spin (Section 4.8).

1.11 The outcome of measurements

The next postulate brings together the wavefunction and the operators and establishes the link between formal calculations and experimental observations:

Postulate 3. When a system is described by a wavefunction ψ , the mean value of the observable Ω in a series of measurements is equal to the expectation value of the corresponding operator.

The **expectation value** of an operator Ω for an arbitrary state ψ is denoted $\langle \Omega \rangle$ and defined as

$$\langle \Omega \rangle = \frac{\int \psi^* \Omega \psi \, d\tau}{\int \psi^* \psi \, d\tau} = \frac{\langle \psi | \Omega | \psi \rangle}{\langle \psi | \psi \rangle} \quad (1.28a)$$

If the wavefunction is chosen to be normalized to 1, then the expectation value is simply

$$\langle \Omega \rangle = \int \psi^* \Omega \psi \, d\tau = \langle \psi | \Omega | \psi \rangle \quad (1.28b)$$

Unless we state otherwise, from now on we shall assume that the wavefunction is normalized to 1.

A brief illustration

The average value of the position of a particle in the ground state of a one-dimensional box is

$$\langle x \rangle = \int_0^L \left\{ \left(\frac{2}{L} \right)^{1/2} \sin(\pi x/L) \right\} x \left\{ \left(\frac{2}{L} \right)^{1/2} \sin(\pi x/L) \right\} dx = \frac{2}{L} \int_0^L x \sin^2(\pi x/L) dx$$

The integral evaluates to $L^2/4$ (use mathematical software), so $\langle x \rangle = 1/2L$: the average value of x is half the length of the box. Similarly, the average value of the linear momentum along the x -axis is

$$\langle p_x \rangle = \frac{2}{L} \int_0^L \sin(\pi x/L) \frac{\hbar}{i} \frac{d}{dx} \sin(\pi x/L) dx = \frac{2\pi\hbar}{L^2 i} \int_0^L \sin(\pi x/L) \cos(\pi x/L) dx$$

The integral on the right is zero (use software, or note that the sine function is symmetric and the cosine function is antisymmetric around the centre of the range), so we conclude that the average linear momentum is zero: in the classical picture, the particle travels to the right as often as it travels to the left.

The meaning of Postulate 3 can be unravelled as follows. First, suppose that ψ is an eigenfunction of Ω with eigenvalue ω ; then

$$\langle \Omega \rangle = \int \psi^* \Omega \psi \, d\tau = \int \psi^* \omega \psi \, d\tau = \omega \int \psi^* \psi \, d\tau = \omega \quad (1.29)$$

That is, for an ensemble of identically prepared systems all in the state ψ (an eigenstate of the operator Ω), each measurement of the property Ω will give the same outcome ω (a real quantity, because Ω is Hermitian), and that outcome will therefore also be the average value of the observations. Now suppose that although the system is in an eigenstate of the hamiltonian it is not in an eigenstate of Ω . In this case the wavefunction can be expressed as a linear combination of eigenfunctions of Ω :

$$\psi = \sum_n c_n \psi_n \quad \text{where} \quad \Omega \psi_n = \omega_n \psi_n \quad (1.30)$$

In this case, the expectation value is

$$\langle \Omega \rangle = \int \left(\sum_m c_m \psi_m \right)^* \Omega \left(\sum_n c_n \psi_n \right) d\tau = \sum_{m,n} c_m^* c_n \int \psi_m^* \Omega \psi_n d\tau = \sum_{m,n} c_m^* c_n \omega_n \int \psi_m^* \psi_n d\tau$$

Because the eigenfunctions form an orthonormal set, the integral in the last expression is zero if $n \neq m$, is 1 if $n = m$, and the double sum reduces to a single sum:

$$\langle \Omega \rangle = \sum_n c_n^* c_n \omega_n \int \psi_n^* \psi_n d\tau = \sum_n c_n^* c_n \omega_n = \sum_n |c_n|^2 \omega_n \quad (1.31)$$

That is, the expectation value is a weighted sum of the eigenvalues of Ω , the contribution of a particular eigenvalue to the sum being determined by the square modulus of the corresponding coefficient in the expansion of the wavefunction.

We can now interpret the difference between eqns 1.29 and 1.31 in the form of a subsidiary postulate:

Postulate 3'. When ψ is an eigenfunction of the operator Ω , the determination of the property Ω always yields one result, namely the corresponding eigenvalue ω . The expectation value will simply be the eigenvalue ω . When ψ is not an eigenfunction of Ω , a single measurement of the property yields a single outcome which is one of the eigenvalues of Ω , and the probability that a particular eigenvalue ω_n is measured is equal to $|c_n|^2$, where c_n is the coefficient of the eigenfunction ψ_n in the expansion of the wavefunction. Moreover, immediately after that measurement, the state of the system will be ψ_n .

That the measurement of the property Ω forces a general wavefunction to become an eigenfunction of the operator Ω , and specifically that the observation of the eigenvalue ω_n forces the wavefunction to become ψ_n , is called the **collapse of the wavefunction**.

One measurement can give only one result: a pointer can indicate only one value on a dial at any instant. In an ensemble of systems all identically prepared in some particular state ψ , a series of determinations will result in a series of values. The subsidiary postulate asserts that a measurement of the observable Ω in each case results in the pointer indicating one of the eigenvalues of the corresponding operator. If the function that describes the state of the system is an eigenfunction of Ω , then every pointer reading is precisely ω and the mean value is also ω . If the systems have been prepared in a state that is not an eigenfunction of Ω , then different measurements give different values, but each individual measurement is one of the eigenvalues of Ω , and the probability that a particular outcome ω_n is obtained is determined by the value of $|c_n|^2$. In this case, the mean value of all the observations is the weighted average of the eigenvalues. Note that in either case, the hermiticity of the operator guarantees that the observables are real.

A brief illustration

The wavefunction for the ground state of a particle in a box is not an eigenfunction of the linear momentum operator $p_x = (\hbar/i)d/dx$. However, by using Euler's relation, $e^{ix} = \cos x + i \sin x$ we note that $\sin(\pi x/L) = (e^{i\pi x/L} - e^{-i\pi x/L})/2i$; therefore, we recognize that the wavefunction is the linear combination, with equal weights, of two functions that are eigenfunctions of p_x with eigenvalues $+\hbar\pi/L$ and $-\hbar\pi/L$, respectively. Therefore in a series of measurements of the linear momentum along x , we obtain one of these two values in each measurement with equal probability. (The average, as we saw in the preceding *brief illustration*, is zero.)

1.12 The interpretation of the wavefunction

The next postulate concerns the interpretation of the wavefunction itself, and is commonly called the **Born interpretation**:

Postulate 4. The probability that a particle will be found in the volume element $d\tau$ at the point r is proportional to $|\psi(r)|^2 d\tau$.

As we have already remarked, in one dimension the volume element is dx . In three dimensions the volume element is $dx dy dz$. It follows from this postulate that $|\psi(r)|^2$ is a **probability density**, in the sense that it yields a probability when multiplied by the volume $d\tau$ of an infinitesimal region (just as a mass density gives a mass when multiplied by a volume element). The wavefunction itself is a **probability amplitude**, and has no direct physical meaning. Note that whereas the probability density is real and non-negative, the wavefunction may be complex and negative. It is usually convenient to use a normalized wavefunction; then the Born interpretation becomes an equality rather than a proportionality.

A brief illustration

We continue to use the ground-state wavefunction of the particle in a box, $\psi_1(x) = (2/L)^{1/2} \sin(\pi x/L)$. We can infer that the probability of finding the particle in the range x to $x + dx$ is $(2/L) \sin^2(\pi x/L) dx$. At the centre of the box, $x = 1/2L$, and at that point the probability density is $(2/L) \sin^2(\pi/2) = 2/L$ and the probability itself is $2 dx/L$. At $x = 1/4L$, the probability density has fallen to $(2/L) \sin^2(\pi/4) = 1/L$ and the probability itself is dx/L . If we approximate the infinitesimal quantity dx by $10^{-3}L$ (so, in a box of length 1 m, we are interested in a region of length 1 mm), then the two probabilities are 0.002 (that is, in an ensemble of 500 identically prepared systems all in the state $\psi_1(x)$, in only one of these systems the particle will be found in the region inspected) and 0.001 (1 in 1000 inspections), respectively.

The implication of the Born interpretation is that the wavefunction should be square-integrable; that is

$$\int |\psi|^2 d\tau < \infty \quad (1.32)$$

because there must be a finite probability of finding the particle somewhere in the whole of space (and that probability is 1 for a normalized wavefunction). This postulate in turn implies that $\psi \rightarrow 0$ as $x \rightarrow \pm\infty$, for otherwise the integral of $|\psi|^2$ would be infinite. We shall make frequent use of this implication throughout the text.

1.13 The equation for the wavefunction

The final postulate concerns the dynamical evolution of the wavefunction with time:

Postulate 5. The wavefunction $\Psi(r_1, r_2, \dots, t)$ evolves in time according to the equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (1.33)$$

This partial differential equation is the celebrated **Schrödinger equation** introduced by Erwin Schrödinger in 1926. The operator H in the Schrödinger

equation is the hamiltonian operator for the system, the operator corresponding to the total energy.

A brief illustration

The hamiltonian for the motion of a particle of mass m free to move in one dimension in a region where its potential energy varies with position but not time is specified in eqn 1.14. The corresponding time-dependent Schrödinger equation is therefore

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi \quad (1.34)$$

If the potential energy is that of a particle in a box, then V is infinite outside the box and zero within the box (between 0 and L).

Needless to say, we shall have a great deal to say about the Schrödinger equation and its solutions in the rest of the text.

1.14 The separation of the Schrödinger equation

The Schrödinger equation can often be separated into equations for the time and space variation of the wavefunction. The separation is possible when the potential energy is independent of time.

In one dimension the equation has the form

$$H\Psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Equations of this form can be solved by the technique of **separation of variables**, in which a trial solution takes the form

$$\Psi(x,t) = \psi(x)\theta(t) \quad (1.35)$$

When this substitution is made, we obtain

$$-\frac{\hbar^2}{2m} \theta \frac{d^2 \psi}{dx^2} + V(x)\psi\theta = i\hbar \psi \frac{d\theta}{dt}$$

Division of both sides of this equation by $\psi\theta$ gives

$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2 \psi}{dx^2} + V(x) = i\hbar \frac{1}{\theta} \frac{d\theta}{dt}$$

Only the left-hand side of this equation is a function of x , so when x changes, only the left-hand side can change. But as the left-hand side is equal to the right-hand side, and the latter does not change, the left-hand side must be equal to a constant. Because the dimensions of the constant are those of an energy (the same as those of V), we shall write it E . It follows that the time-dependent equation separates into the following two differential equations:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x)\psi = E\psi \quad (1.36a)$$

$$i\hbar \frac{d\theta}{dt} = E\theta \quad (1.36b)$$

The second of these equations has the solution

$$\theta \propto e^{-iEt/\hbar} \quad (1.37)$$

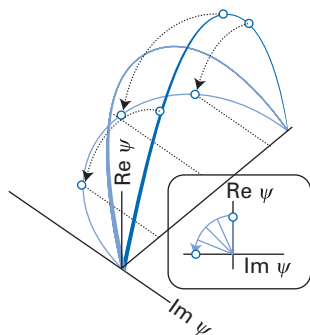


Fig. 1.1 A wavefunction corresponding to an energy E rotates in the complex plane from real to imaginary and back to real at a frequency E/\hbar (and circular frequency E/\hbar).

Therefore, the complete wavefunction ($\Psi = \psi\theta$) has the form

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \quad (1.38)$$

The constant of proportionality in eqn 1.37 has been absorbed into the normalization constant for ψ . The time-independent wavefunction satisfies eqn 1.36a, which may be written in the form

$$H\psi = E\psi \quad (1.39)$$

This expression is the **time-independent Schrödinger equation**, on which much of the following development will be based.

This analysis stimulates several remarks. First, eqn 1.36a has the form of a standing-wave equation. Therefore, as long as we are interested only in the spatial dependence of the wavefunction, it is legitimate to regard the time-independent Schrödinger equation as a wave equation. Second, when the potential energy of the system does not depend on the time, and the system is in a state of energy E , it is a very simple matter to construct the time-dependent wavefunction from the time-independent wavefunction simply by multiplying the latter by $e^{-iEt/\hbar}$. The time dependence of such a wavefunction is simply a modulation of its phase, because we can use Euler's relation, $e^{ix} = \cos x + i \sin x$ to write

$$e^{-iEt/\hbar} = \cos(Et/\hbar) - i \sin(Et/\hbar) \quad (1.40)$$

It follows that the time-dependent factor oscillates periodically from 1 to $-i$ to -1 to i and back to 1 with a frequency E/\hbar and period \hbar/E . This behaviour is depicted in Fig. 1.1. Therefore, to imagine the time variation of a wavefunction of a definite energy, think of it as rotating from positive through imaginary to negative amplitudes with a frequency proportional to the energy.

A brief illustration

The time-independent ground-state wavefunction of a particle in a box is $\psi(x) = (2/L)^{1/2} \sin(\pi x/L)$ and its energy is $\hbar^2/8mL^2$. The time-dependent wavefunction for the same state is $\Psi(x,t) = (2/L)^{1/2} \sin(\pi x/L)e^{-i\hbar\pi^2/4mL^2 t}$. As well as containing all the dynamical information about the particle in this state, it also shows how the wavefunction evolves with time.

Although the phase of a wavefunction Ψ with definite energy E oscillates in time, the product $\Psi^*\Psi$ (or $|\Psi|^2$) remains constant:

$$\Psi^*\Psi = (\psi^* e^{iEt/\hbar})(\psi e^{-iEt/\hbar}) = \psi^*\psi \quad (1.41)$$

States of this kind are called **stationary states**. From what we have seen so far, it follows that systems with a specific, precise energy and in which the potential energy does not vary with time are in stationary states. Although their wavefunctions oscillate from real to imaginary with frequency E/\hbar , the value of $\Psi^*\Psi$ remains constant in time.

The specification and evolution of states

Let us suppose for the moment that the state of a system can be specified as $|a, b, \dots\rangle$, where each of the eigenvalues a, b, \dots corresponds to the operators representing different observables A, B, \dots of the system. If the system is in the

state $|a, b, \dots\rangle$, then when we measure the property A we shall get exactly a as an outcome, and likewise for the other properties. But can a state be specified *arbitrarily* fully? That is, can it be *simultaneously* an eigenstate of all possible observables A, B, \dots without restriction? With this question we are moving into the domain of the uncertainty principle.

1.15 Simultaneous observables

As a first step, we establish the conditions under which two observables may be specified simultaneously with arbitrary precision. That is, we establish the conditions for a state $|\psi\rangle$ corresponding to the wavefunction ψ to be simultaneously an eigenstate of two operators A and B . In fact, we shall prove the following:

Property 3. If two observables are to have simultaneously precisely defined values, then their corresponding operators must commute.

That is, AB must equal BA , or equivalently, $[A, B] = 0$.

Proof 1.3 Simultaneous eigenstates

Assume that $|\psi\rangle$ is an eigenstate of both operators: $A|\psi\rangle = a|\psi\rangle$ and $B|\psi\rangle = b|\psi\rangle$. That being so, we can write the following chain of relations:

$$AB|\psi\rangle = Ab|\psi\rangle = bA|\psi\rangle = ba|\psi\rangle = ab|\psi\rangle = aB|\psi\rangle = Ba|\psi\rangle = BA|\psi\rangle$$

Therefore, if $|\psi\rangle$ is an eigenstate of both A and B , and if the same is true for all functions ψ of a complete set, then it is certainly necessary that $[A, B] = 0$. However, does the condition $[A, B] = 0$ actually guarantee that A and B have simultaneous eigenvalues? In other words, if $A|\psi\rangle = a|\psi\rangle$ and $[A, B] = 0$, can we be confident that $|\psi\rangle$ is also an eigenstate of B ? We confirm this as follows for non-degenerate eigenstates. Because $A|\psi\rangle = a|\psi\rangle$, we can write

$$BA|\psi\rangle = Ba|\psi\rangle = aB|\psi\rangle$$

Because A and B commute, the first term on the left is equal to $AB|\psi\rangle$. Therefore, this relation has the form

$$A(B|\psi\rangle) = a(B|\psi\rangle)$$

However, on comparison of this eigenvalue equation with $A|\psi\rangle = a|\psi\rangle$, we can conclude that, for non-degenerate eigenstates $|\psi\rangle$, $B|\psi\rangle \propto |\psi\rangle$, or $B|\psi\rangle = b|\psi\rangle$, where b is a coefficient of proportionality. That is, $|\psi\rangle$ is an eigenstate of B , as was to be proved.

It follows from this discussion that we are now in a position to determine which observables may be specified simultaneously. All we need do is to inspect the commutator $[A, B]$: if it is zero, then A and B may be specified simultaneously.

A brief illustration

All three position operators x , y , and z commute with one another, so there is no constraint on the complete specification of position. The same is true of the three operators for the components of linear momentum, so all three components can be determined simultaneously. However, x and p_x do not commute, so these two observables cannot be specified simultaneously, and likewise for (y, p_y) and (z, p_z) . »

Self-test 1.7 Can the kinetic energy and the linear momentum be specified simultaneously?

[Yes]

Pairs of observables that *cannot* be determined simultaneously are said to be **complementary**. Thus, position along the x -axis and linear momentum parallel to that axis are complementary observables. Classical physics (in the absence of any evidence to the contrary) made the mistake of presuming that there was no restriction on the simultaneous determination of observables, that there was no complementarity. Quantum mechanics forces us to choose a selection of all possible observables if we seek to specify a state fully.

1.16 The uncertainty principle

Although we cannot specify the eigenvalues of two non-commuting operators simultaneously, it is possible to give up precision in the specification of one property in order to acquire greater precision in the specification of a complementary property. For example, if we know the location of a particle to within a range Δx , then we can specify the linear momentum parallel to x to within a range Δp_x subject to the constraint

$$\Delta x \Delta p_x \geq \frac{1}{2} \hbar \quad (1.42)$$

Thus, as Δx increases (an increased uncertainty in x), the uncertainty in p_x can decrease, and vice versa. This relation between the uncertainties in the specification of two complementary observables is a special case of the **uncertainty principle** proposed by Werner Heisenberg in 1927. A very general form of the uncertainty principle was developed by H.P. Robertson in 1929 for two observables A and B :

$$\Delta A \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle| \quad (1.43a)$$

where the **root mean square deviation** of A is defined as

$$\Delta A = \{\langle A^2 \rangle - \langle A \rangle^2\}^{1/2} \quad (1.43b)$$

Equation 1.43 is an exact and precise form of the uncertainty principle: the precise form of the ‘uncertainties’ ΔA and ΔB are given (they are root mean square deviations) and the right-hand side of eqn 1.43a gives a precise lower bound on the value of the product of uncertainties.

Proof 1.4 The uncertainty principle

Suppose that the observables A and B obey the commutation relation $[A, B] = iC$. (The imaginary i is included for future convenience. For $A = x$ and $B = p_x$ it follows from the fundamental commutation relation that $C = \hbar$.) We shall suppose that the system is prepared in a normalized but otherwise arbitrary state $|\psi\rangle$, which is not necessarily an eigenstate of either operator A or B . The mean values of the observables A and B are expressed by the expectation values

$$\langle A \rangle = \langle \psi | A | \psi \rangle \quad \text{and} \quad \langle B \rangle = \langle \psi | B | \psi \rangle$$

The operators for the spread of individual determinations of A and B around their mean values are

$$\delta A = A - \langle A \rangle \quad \text{and} \quad \delta B = B - \langle B \rangle$$

»

It is easy to verify that the commutation relation for these deviation operators is

$$[\delta A, \delta B] = [A - \langle A \rangle, B - \langle B \rangle] = [A, B] = iC$$

because the expectation values $\langle A \rangle$ and $\langle B \rangle$ are simple numbers and commute with operators.

To evaluate the constraints on the joint values of δA and δB it turns out to be fruitful to consider the properties of the following integral, where α is a real but otherwise arbitrary number:

$$I = \int |(\alpha\delta A - i\delta B)\psi|^2 d\tau$$

The integral I is clearly non-negative as the integrand is positive everywhere. This integral can be developed as follows:

$$\begin{aligned} I &= \int \{(\alpha\delta A - i\delta B)\psi\}^* \{(\alpha\delta A - i\delta B)\psi\} d\tau \\ &= \int \{[(\alpha\delta A)\psi]^* + i[(\delta B)\psi]^*\} \{(\alpha\delta A - i\delta B)\psi\} d\tau \\ &= \int \psi^* (\alpha\delta A + i\delta B) (\alpha\delta A - i\delta B) \psi d\tau \end{aligned}$$

In the third step we have used the Hermitian character of the two operators (as expressed in eqn 1.26b). At this point it is convenient to recognize that the final expression is an expectation value, and to write it in the form

$$I = \langle (\alpha\delta A + i\delta B)(\alpha\delta A - i\delta B) \rangle$$

This expression expands to

$$I = \alpha^2 \langle (\delta A)^2 \rangle + \langle (\delta B)^2 \rangle - i\alpha \langle \delta A \delta B - \delta B \delta A \rangle = \alpha^2 \langle (\delta A)^2 \rangle + \langle (\delta B)^2 \rangle + \alpha \langle C \rangle$$

In the second step we have recognized the presence of the commutator. The integral is still non-negative, even though that is no longer obvious. At this point we recognize that I has the general form of a quadratic expression in α , and so express it as a square:

$$I = \langle (\delta A)^2 \rangle \left(\alpha + \frac{\langle C \rangle}{2\langle (\delta A)^2 \rangle} \right)^2 + \langle (\delta B)^2 \rangle - \frac{\langle C \rangle^2}{4\langle (\delta A)^2 \rangle}$$

(We have ‘completed the square’ for the first term.) This expression is still non-negative whatever the value of α , and remains non-negative even if we choose a value for α that corresponds to the minimum value of I . That value of α is the value that ensures that the first term on the right is zero (because that term always supplies a positive contribution to I). Therefore, with that choice of α , we obtain

$$I = \langle (\delta B)^2 \rangle - \frac{\langle C \rangle^2}{4\langle (\delta A)^2 \rangle} \geq 0$$

The inequality rearranges to

$$\langle (\delta A)^2 \rangle \langle (\delta B)^2 \rangle \geq \frac{1}{4} \langle C \rangle^2$$

The expectation values on the left can be put into a simpler form by writing them as follows:

$$\begin{aligned} \langle (\delta A)^2 \rangle &= \langle (A - \langle A \rangle)^2 \rangle \\ &= \langle A^2 - 2A\langle A \rangle + \langle A \rangle^2 \rangle = \langle A^2 \rangle - 2\langle A \rangle \langle A \rangle + \langle A \rangle^2 \\ &= \langle A^2 \rangle - \langle A \rangle^2 \end{aligned}$$

»

We see that $\langle(\delta A)^2\rangle$ is the mean square deviation of A from its mean value (and likewise for B). Then the inequality becomes

$$\Delta A \Delta B \geq \frac{1}{2} |\langle C \rangle|$$

Finally, because $[A, B] = iC$, we obtain the final form of the uncertainty principle in eqn 1.43a.

1.17 Consequences of the uncertainty principle

The first point to note is that the uncertainty principle is consistent with Property 3, for if A and B commute, then C is zero and there is no constraint on the uncertainties: there is no inconsistency in having both $\Delta A = 0$ and $\Delta B = 0$. On the other hand, when A and B do not commute, the values of ΔA and ΔB are related. For instance, while it may be possible to prepare a system in a state in which $\Delta A = 0$, the uncertainty principle then implies that ΔB must be infinite in order to ensure that $\Delta A \Delta B$ is not less than $\frac{1}{2} |\langle [A, B] \rangle|$. In the particular case of the simultaneous specification of x and p_x , as we have seen, $[x, p_x] = i\hbar$, so the lower bound on the simultaneous specification of these two complementary observables is $\frac{1}{2}\hbar$.

Example 1.7 Calculating the joint uncertainty in two observables

Calculate the value of $\Delta x \Delta p_x$ for the ground state of a particle of mass m in a box of length L .

Method The wavefunction is $\psi_1(x) = (2/L)^{1/2} \sin(\pi x/L)$. We must evaluate the expectation values $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p_x \rangle$, and $\langle p_x^2 \rangle$ by integration and then combine their values to obtain Δx and Δp_x . There are two short cuts. For $\langle x \rangle$, we note that ψ is symmetrical around $x = 1/2L$, and so $\langle x \rangle = 1/2L$. We have already seen (in the *brief illustration* in Section 1.11) that $\langle p_x \rangle = 0$. For the remaining integrals it is best to use mathematical software.

Answer The following integrals are obtained:

$$\langle x^2 \rangle = \frac{2}{L} \int_0^L x^2 \sin^2(\pi x/L) dx = \frac{L^2}{6\pi^2} (2\pi^2 - 3)$$

$$\langle p_x^2 \rangle = \frac{2}{L} \int_0^L \sin(\pi x/L) \left(-\hbar^2 \frac{d^2}{dx^2} \right) \sin(\pi x/L) dx = \frac{2\pi^2 \hbar^2}{L^3} \int_0^L \sin^2(\pi x/L) dx = \frac{\pi^2 \hbar^2}{L^2}$$

It follows that (because $\langle x \rangle = L/2$ and $\langle p_x \rangle = 0$)

$$\Delta x \Delta p_x = \left\{ \left[\frac{L^2}{6\pi^2} (2\pi^2 - 3) - \frac{L^2}{4} \right] \frac{\pi^2 \hbar^2}{L^2} \right\}^{1/2} = \left\{ \frac{1}{12} (\pi^2 - 6) \right\}^{1/2} \hbar \approx 0.568 \hbar$$

The product of uncertainties is greater than $1/2\hbar$, in accord with the uncertainty principle.

Self-test 1.8 A particle was prepared in a state with wavefunction $\psi = N \exp(-x^2/2\Gamma)$, where $N = (1/\pi\Gamma)^{1/4}$. Evaluate Δx and Δp_x , and confirm that the uncertainty principle is satisfied. *Hint:* use mathematical software to evaluate the integrals.

$$[\Delta x \Delta p_x = \frac{1}{2}\hbar]$$

The uncertainty principle in the form given in eqn 1.43a can be applied to all pairs of complementary observables. We shall see additional examples in later chapters.

1.18 The uncertainty in energy and time

It is appropriate at this point to make a few remarks about the so-called **energy–time uncertainty relation**, which is often expressed in the form $\Delta E \Delta t \geq \hbar$ and interpreted as implying a complementarity between energy and time. As we have seen, for this relation to be a true uncertainty relation, it would be necessary for there to be a non-zero commutator for energy and time. However, although the energy operator is well defined (it is the hamiltonian for the system), *there is no operator for time in quantum mechanics*. Time is a *parameter*, not an observable. Therefore, strictly speaking, there is no uncertainty relation between energy and time. In Section 6.11 we shall see the true significance of the energy–time ‘uncertainty principle’ is that it is a relation between the uncertainty in the energy of a system that has a finite lifetime τ (tau), and is of the form $\delta E \approx \hbar/\tau$.

1.19 Time-evolution and conservation laws

As well as determining which operators are complementary, the commutator of two operators also plays a role in determining the time-evolution of systems and in particular the time-evolution of the expectation values of observables. The precise relation for operators that do not have an intrinsic dependence on the time (in the sense that $\partial\Omega/\partial t = 0$) is

$$\frac{d\langle\Omega\rangle}{dt} = \frac{i}{\hbar}\langle[H,\Omega]\rangle \quad (1.44)$$

We see that if the operator for the observable commutes with the hamiltonian, then the expectation value of the operator does not change with time. An observable that commutes with the hamiltonian for the system, and which therefore has an expectation value that does not change with time, is called a **constant of the motion**, and its expectation value is said to be **conserved**.

Proof 1.5 Time-evolution

Differentiation of $\langle\Omega\rangle$ with respect to time gives

$$\frac{d\langle\Omega\rangle}{dt} = \frac{d}{dt}\langle\Psi|\Omega|\Psi\rangle = \int\left(\frac{\partial\Psi^*}{\partial t}\right)\Omega\Psi\,d\tau + \int\Psi^*\Omega\left(\frac{\partial\Psi}{\partial t}\right)d\tau$$

because only the state Ψ (not the operator Ω) depends on the time. The Schrödinger equation lets us write

$$\begin{aligned} \int\Psi^*\Omega\left(\frac{\partial\Psi}{\partial t}\right)d\tau &= \int\Psi^*\Omega\left(\frac{1}{i\hbar}\right)H\Psi\,d\tau = \frac{1}{i\hbar}\int\Psi^*\Omega H\Psi\,d\tau \\ \int\left(\frac{\partial\Psi^*}{\partial t}\right)\Omega\Psi\,d\tau &= -\int\left(\frac{1}{i\hbar}\right)(H\Psi)^*\Omega\Psi\,d\tau = -\left(\frac{1}{i\hbar}\right)\int\Psi^*H\Omega\Psi\,d\tau \end{aligned}$$

In the second line we have used the hermiticity of the hamiltonian (in the form of eqn 1.26b). It then follows, by combining these two expressions, that

$$\frac{d\langle\Omega\rangle}{dt} = -\left(\frac{1}{i\hbar}\right)(\langle H\Omega\rangle - \langle\Omega H\rangle) = \frac{i}{\hbar}\langle[H,\Omega]\rangle$$

as was to be proved.

As an important example, consider the rate of change of the expectation value of the linear momentum of a particle in a one-dimensional system. The commutator of H and p_x is

$$[H, p_x] = \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V, \frac{\hbar}{i} \frac{d}{dx} \right] = \frac{\hbar}{i} \left[V, \frac{d}{dx} \right]$$

because the derivatives commute. The remaining commutator can be evaluated by remembering that there is an unwritten function on the right on which the operators operate, and writing

$$[H, p_x]\psi = \frac{\hbar}{i} \left\{ V \frac{d\psi}{dx} - \frac{d(V\psi)}{dx} \right\} = \frac{\hbar}{i} \left\{ V \frac{d\psi}{dx} - V \frac{d\psi}{dx} - \frac{dV}{dx} \psi \right\} = -\frac{\hbar}{i} \frac{dV}{dx} \psi$$

This relation is true for all functions ψ ; therefore the commutator itself is

$$[H, p_x] = -\frac{\hbar}{i} \frac{dV}{dx} \quad (1.45)$$

It follows that the linear momentum is a constant of the motion if the potential energy does not vary with position, that is when $dV/dx = 0$. Specifically, we can conclude that the rate of change of the expectation value of linear momentum is

$$\frac{d}{dt} \langle p_x \rangle = \frac{i}{\hbar} \langle [H, p_x] \rangle = -\left\langle \frac{dV}{dx} \right\rangle \quad (1.46a)$$

Then, because the negative slope of the potential energy is by definition the force that is acting ($F = -dV/dx$), the rate of change of the expectation value of linear momentum is given by

$$\frac{d}{dt} \langle p_x \rangle = \langle F \rangle \quad (1.46b)$$

That is, the rate of change of the expectation value of the linear momentum is equal to the expectation value of the force. It is also quite easy to prove in the same way (see Problem 1.28) that

$$\frac{d}{dt} \langle x \rangle = \frac{\langle p_x \rangle}{m} \quad (1.47)$$

which shows that the rate of change of the mean position can be identified with the mean velocity along the x -axis. These two relations (eqns 1.46b and 1.47) jointly constitute **Ehrenfest's theorem**. Ehrenfest's theorem clarifies the relation between classical and quantum mechanics: classical mechanics deals with average values (expectation values); quantum mechanics deals with the underlying details.

Exercises

- *1.1** Which of the following operations are linear and which are non-linear: (a) integration, (b) extraction of a square root, (c) translation (replacement of x by $x + a$, where a is a constant), (d) inversion (replacement of x by $-x$)?
- *1.2** Which of the following functions are eigenfunctions of (a) d/dx , (b) d^2/dx^2 : (i) e^{ax} , (ii) e^{ax^2} , (iii) x , (iv) x^2 , (v) $ax + b$, (vi) $\sin x$? If it is an eigenfunction, identify the eigenvalue.
- *1.3** Demonstrate that the linear combinations $A + iB$ and $A - iB$ are not Hermitian if A and B are Hermitian operators.
- *1.4** An electron is confined to a linear box of length 0.10 nm. What are the minimum uncertainties in (a) its velocity and (b) its kinetic energy?
- *1.5** Calculate the value of $\Delta x \Delta p_x$ for the first excited state ($n = 2$) of a particle of mass m in a box of length L . Can you infer a general trend for the uncertainty product as n increases?
- *1.6** A particle is confined to the region $0 \leq x \leq \infty$ and its state is described by the unnormalized wavefunction $\psi(x) = e^{-2x}$. What is the probability of finding the particle at a distance $x \geq 1$?
- *1.7** Confirm that the z -component of angular momentum, $l_z = (\hbar/i) d/d\phi$, is a constant of the motion for a particle on a ring with uniform potential energy $V(\phi) = V$.
- *1.8** A state of a system is described by the wavefunction $\psi(x) = Nx e^{-x^2/2r^2}$. Where is the most probable location of the particle?
- *1.9** On the basis of the information in Problem 1.7, calculate the probability density of finding the electron (a) at the nucleus, (b) at a point in space at a distance a_0 from the nucleus. Calculate the probabilities of finding the electron inside a region of volume 1.0 pm^3 located at these points assuming that the probability density is constant inside the small volume region.

Problems

- *1.1** Evaluate the expectation values of the operators p_x and p_x^2 for a particle with wavefunction $(2/L)^{1/2} \sin(\pi x/L)$ in the range 0 to L .
- 1.2** Are the linear combinations $2x - y - z$, $2y - x - z$, $2z - x - y$ linearly independent?
- 1.3** Evaluate the commutators (a) $[x, y]$, (b) $[p_x, p_y]$, (c) $[x, p_x]$, (d) $[x^2, p_x]$, (e) $[x^n, p_x]$.
- *1.4** Show that (a) $[A, B] = -[B, A]$, (b) $[A^m, A^n] = 0$ for all m, n , (c) $[A^2, B] = A[A, B] + [A, B]A$, (d) $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$.
- 1.5** Evaluate the commutator $[l_y, [l_y, l_z]]$ given that $[l_x, l_y] = i\hbar l_z$, $[l_y, l_z] = i\hbar l_x$, and $[l_z, l_x] = i\hbar l_y$.
- 1.6** A particle in an infinite one-dimensional system was described by the wavefunction $\psi(x) = Ne^{-x^2/2r^2}$. Normalize this function. Calculate the probability of finding the particle in the range $-r \leq x \leq r$. *Hint.* The integral encountered in the second part is the error function. It is available in mathematical software.
- *1.7** The ground-state wavefunction of a hydrogen atom has the form $\psi(r) = Ne^{-br}$, b being a collection of fundamental constants with the magnitude $1/a_0$, with $a_0 = 53 \text{ pm}$. Normalize this spherically symmetrical function. *Hint.* The volume element is $d\tau = \sin\theta d\theta d\phi r^2 dr$, with $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$, and $0 \leq r < \infty$. 'Normalize' always means 'normalize to 1' in this text.
- 1.8** Confirm that the operators (a) $T = -(\hbar^2/2m)(d^2/dx^2)$ and (b) $l_z = (\hbar/i)(d/d\phi)$ are Hermitian. *Hint.* Consider the integrals $\int_0^L \psi_a^* T \psi_b dx$ and $\int_0^{2\pi} \psi_a^* l_z \psi_b d\phi$ and integrate by parts.
- 1.9** Find the operator for position x if the operator for momentum p is taken to be $(\hbar/2m)^{1/2}(A + B)$, with $[A, B] = 1$ and all other commutators zero. *Hint.* Write $x = aA + bB$ and find one set of solutions for a and b .
- *1.10** Evaluate the commutators (a) $[(1/x), p_x]$, (b) $[(1/x), p_x^2]$, (c) $[xp_y - yp_x, yp_z - zp_y]$, (d) $[x^2(\partial^2/\partial y^2), y(\partial/\partial x)]$.
- 1.11** Evaluate the commutators (a) $[H, p_x]$ and (b) $[H, x]$, where $H = p_x^2/2m + V(x)$. Choose (i) $V(x) = V$, a constant, (ii) $V(x) = \frac{1}{2}kx^2$, (iii) $V(x) \rightarrow V(r) = e^2/4\pi\epsilon_0 r$. *Hint.* For part (b), case (iii), use $(\partial r^{-1}/\partial x) = -x/r^3$.
- 1.12** Use the momentum representation and a general function $f(p_x)$ of the linear momentum to confirm that the position and momentum operators in this representation do not commute, and find the value of their commutator.
- *1.13** Construct quantum mechanical operators in the position representation for the following observables: (a) kinetic energy in one and in three dimensions, (b) the inverse separation, $1/x$, (c) electric dipole moment ($\sum_i Q_i r_i$ where r_i is the position of a charge Q_i), (d) z -component of angular momentum ($xp_y - yp_x$), (e) the mean square deviations of the position and momentum of a particle from the mean values.
- 1.14** Repeat Problem 1.13, but find operators in the momentum representation. *Hint.* The observable $1/x$ should be regarded as x^{-1} ; hence the operator required is the inverse of the operator for x .

* Indicates that the solution can be found in the *Student's solution manual*, which is available in the Online Resource Centre accompanying this book. Go to www.oxfordtextbooks.co.uk/orc/mqm5e/

1.15 In relativistic mechanics, energy and momentum are related by the expression $E^2 = p^2c^2 + m^2c^4$. (a) Show that when $p^2c^2 \ll m^2c^4$ this expression reduces to $E = p^2/2m + mc^2$. (b) Construct the relativistic analogue of the Schrödinger equation from the relativistic expression. (c) What can be said about the conservation of probability? *Hint:* For part (b), use $i\hbar(\partial/\partial t)$ for the energy operator. For part (c), see Problem 1.16.

***1.16** Show that if the Schrödinger equation had the form of a true wave equation, then the integrated probability would be time dependent. *Hint.* A wave equation has $\kappa\partial^2/\partial t^2$ in place of $i\hbar\partial/\partial t$, where κ is a constant with the appropriate dimensions (what are they?). Solve the time component of the separable equation and investigate the behaviour of $\int\psi^*\psi d\tau$.

1.17 The operator e^A has a meaning if it is expanded as a power series: $e^A = \sum_n (1/n!)A^n$. Show that if $|a\rangle$ is an eigenstate of A with eigenvalue a , then it is also an eigenstate of e^A . Find the latter's eigenvalue.

1.18 Evaluate the expectation value of e^{iLp_x} for a particle in a square well of length L and described by the wavefunction $(2/L)^{1/2} \sin(\pi x/L)$ in the range 0 to L . *Hint:* $e^{iA} = \cos A + i \sin A$, $\cos \theta = 1 - (1/2!)\theta^2 + (1/4!)\theta^4 - \dots$, $\sin \theta = \theta - (1/3!)\theta^3 + (1/5!)\theta^5 - \dots$.

***1.19** (a) Show that $e^A e^B = e^{A+B}$ only if $[A, B] = 0$. (b) If $[A, B] \neq 0$ but $[A, [A, B]] = [B, [A, B]] = 0$, show that $e^A e^B = e^{A+B} e^f$, where f is a simple function of $[A, B]$. *Hint.* This is another example of the differences between operators (q -numbers) and ordinary numbers (c -numbers). The simplest approach is to expand the exponentials and to collect and compare terms on both sides of the equality. Note that $e^A e^B$ will give terms like $2AB$ while e^{A+B} will give $AB + BA$. Be careful with order.

1.20 Evaluate (by considering eqn 1.43a) the limitation on the simultaneous specification of the following observables: (a) the position and momentum of a particle, (b) the three components of linear momentum of a particle, (c) the kinetic energy and potential energy of a particle, (d) the electric dipole moment ($-ex$) and the total energy of a one-dimensional system, (e) the kinetic energy and the position of a particle in one dimension.

1.21 Evaluate the quantity $\Delta_4 x \Delta_4 p_x$ for the ground state ($n = 1$) of a particle of mass m in a box of length L , where $\Delta_4 \Omega = \langle (\Omega - \langle \Omega \rangle)^4 \rangle^{1/4}$.

***1.22** Use eqn 1.44 to find expressions for the rate of change of the expectation values of position and momentum of a harmonic oscillator; solve the pair of differential equations, and show that the expectation values change in time in the same way as for a classical oscillator. *Hint.* Use the results of Problem 1.11 part (ii).

1.23 The only non-zero matrix elements of x and p_x for a harmonic oscillator are

$$\langle \nu + 1 | x | \nu \rangle = \left(\frac{\hbar}{2m\omega} \right)^{1/2} (\nu + 1)^{1/2}$$

$$\langle \nu - 1 | x | \nu \rangle = \left(\frac{\hbar}{2m\omega} \right)^{1/2} \nu^{1/2}$$

$$\langle \nu + 1 | p_x | \nu \rangle = i \left(\frac{\hbar m \omega}{2} \right)^{1/2} (\nu + 1)^{1/2}$$

$$\langle \nu - 1 | p_x | \nu \rangle = -i \left(\frac{\hbar m \omega}{2} \right)^{1/2} \nu^{1/2}$$

See Section 2.15. Use the completeness relation, eqn 1.25, to deduce the value of the matrix element $\langle \nu | x p_x^2 x | \nu \rangle$.

1.24 Write the time-independent Schrödinger equations for (a) the hydrogen atom, (b) the helium atom, (c) the hydrogen molecule, (d) a free particle, (e) a particle subjected to a constant, uniform force. *Hint.* Identify the appropriate potential energy terms and express them as operators in the position representation.

***1.25** The time-dependent Schrödinger equation is separable when V is independent of time. (a) Show that it is also separable when V is a function only of time and is uniform in space. (b) Solve the pair of equations. Let $V(t) = V \cos \omega t$; find an expression for $\Psi(x, t)$ in terms of $\Psi(x, 0)$. (c) Is $\Psi(x, t)$ stationary in the sense specified in Section 1.14?

1.26 (a) Calculate the probability of the electron being found anywhere within a sphere of radius a_0 for the atom defined in Problem 1.7. (b) If the radius of the atom is defined as the radius of the sphere inside which there is a 90 per cent probability of finding the electron, what is the atom's radius? *Hint.* For part (b), find the solution numerically (e.g. by successive approximation, using software, or graphically).

1.27 A particle is moving in a circle in the xy plane. The only coordinate of importance is the angle ϕ which can vary from 0 to 2π as the particle goes around the circle. We are interested in measurements of the angular momentum L_z of the particle. The angular momentum operator for such a system is given by $(\hbar/i)d/d\phi$. (a) Suppose that the state of the particle is described by the wavefunction $\psi(\phi) = N e^{-i\phi}$ where N is the normalization constant. What values will we find when we measure the angular momentum of the particle? If more than one value is possible, what is the probability of obtaining each result? What is the expectation value of the angular momentum? (b) Now suppose that the state of the particle is described by the normalized wavefunction $\psi(\phi) = N \{ (3/4)^{1/2} e^{-i\phi} - (i/2) e^{2i\phi} \}$. When we measure the angular momentum of the particle, what values will we find? If more than one value is possible, what is the probability of obtaining each result? What is the expectation value of the angular momentum?

***1.28** Provide a proof of eqn 1.47; eqns 1.47 and 1.46b jointly form *Ehrenfest's theorem*.

* Indicates that the solution can be found in the *Student's solution manual*, which is available in the Online Resource Centre accompanying this book. Go to www.oxfordtextbooks.co.uk/orc/mqm5e/

Mathematical background 1 Complex numbers

MB1.1 Definitions	35
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MB1.3 Operations	36

We describe here general properties of complex numbers and functions, which are mathematical constructs frequently encountered in quantum mechanics.

MB1.1 Definitions

Complex numbers have the general form

$$z = x + iy \quad (\text{MB1.1})$$

where $i = (-1)^{1/2}$. The real numbers x and y are, respectively, the real and imaginary parts of z , denoted $\text{Re}(z)$ and $\text{Im}(z)$. When $y = 0$, $z = x$ is a real number; when $x = 0$, $z = iy$ is a pure imaginary number. Two complex numbers $z_1 = x_1 + iy_1$ and $z_2 = x_2 + iy_2$ are equal when $x_1 = x_2$ and $y_1 = y_2$. Although the general form of the imaginary part of a complex number is written iy , a specific numerical value is typically written in the reverse order; for instance, as $3i$.

The **complex conjugate** of z , denoted z^* , is formed by replacing i by $-i$:

$$z^* = x - iy \quad (\text{MB1.2})$$

The product of z^* and z is denoted $|z|^2$ and is called the **square modulus** of z . From eqn MB1.1,

$$|z|^2 = (x + iy)(x - iy) = x^2 + y^2 \quad (\text{MB1.3})$$

since $i^2 = -1$. The square modulus is a real number. The **absolute value** or **modulus** is itself denoted $|z|$ and is given by:

$$|z| = (z^*z)^{1/2} = (x^2 + y^2)^{1/2} \quad (\text{MB1.4})$$

Since $zz^* = |z|^2$ it follows that $z \times (z^*/|z|^2) = 1$, from which we can identify the (multiplicative) inverse of z (which exists for all non-zero complex numbers):

$$z^{-1} = \frac{z^*}{|z|^2} \quad (\text{MB1.5})$$

A brief illustration

Consider the complex number $z = 8 - 3i$. Its square modulus is

$$|z|^2 = z^*z = (8 - 3i)^*(8 - 3i) = (8 + 3i)(8 - 3i) = 64 + 9 = 73$$



The modulus is therefore $|z| = 73^{1/2}$. From eqn MB1.5, the inverse of z is

$$z^{-1} = \frac{8 + 3i}{73} = \frac{8}{73} + \frac{3}{73}i$$

MB1.2 Polar representation

The complex number $z = x + iy$ can be represented as a point in a plane, the **complex plane**, with $\text{Re}(z)$ along the x -axis and $\text{Im}(z)$ along the y -axis (Fig. MB1.1). If, as shown in the figure, r and θ denote the polar coordinates of the point, then since $x = r \cos \theta$ and $y = r \sin \theta$, we can express the complex number in **polar form** as

$$z = r(\cos \theta + i \sin \theta) \quad (\text{MB1.6})$$

The angle θ , called the **argument** of z , is the angle that z makes with the x -axis. Because $y/x = \tan \theta$, it follows that the polar form can be constructed from

$$r = (x^2 + y^2)^{1/2} = |z| \quad \theta = \arctan \frac{y}{x} \quad (\text{MB1.7a})$$

To convert from polar to Cartesian form, use

$$x = r \cos \theta \quad \text{and} \quad y = r \sin \theta \quad \text{to form } z = x + iy \quad (\text{MB1.7b})$$

One of the most useful relations involving complex numbers is **Euler's formula**:

$$e^{i\theta} = \cos \theta + i \sin \theta \quad (\text{MB1.8a})$$

The simplest proof of this relation is to expand the exponential function as a power series and to collect real and imaginary terms. It follows that

$$\cos \theta = 1/2(e^{i\theta} + e^{-i\theta}) \quad \sin \theta = -1/2i(e^{i\theta} - e^{-i\theta}) \quad (\text{MB1.8b})$$

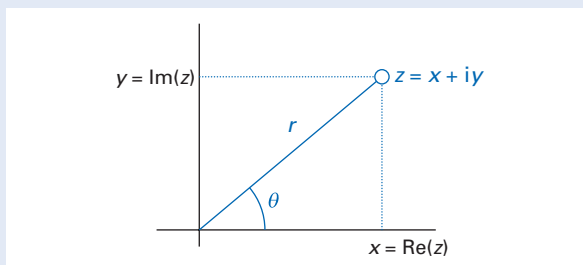


Fig. MB1.1 The representation of a complex number z as a point in the complex plane using Cartesian coordinates (x, y) or polar coordinates (r, θ) .

The polar form in eqn MB1.6 then becomes

$$z = re^{i\theta} \quad (\text{MB1.9})$$

A brief illustration

Consider the complex number $z = 8 - 3i$. From the previous *brief illustration*, $r = |z| = 73^{1/2}$. The argument of z is

$$\theta = \arctan \frac{-3}{8} = -0.359 \text{ rad or } -20.6^\circ$$

The polar form of the number is therefore

$$z = 73^{1/2} e^{-0.359i}$$

MB1.3 Operations

The following rules apply for arithmetic operations for the complex numbers $z_1 = x_1 + iy_1$ and $z_2 = x_2 + iy_2$.

1. Addition: $z_1 + z_2 = (x_1 + x_2) + i(y_1 + y_2)$ (MB1.10a)

2. Subtraction: $z_1 - z_2 = (x_1 - x_2) + i(y_1 - y_2)$ (MB1.10b)

3. Multiplication: $z_1 z_2 = (x_1 + iy_1)(x_2 + iy_2) = (x_1 x_2 - y_1 y_2) + i(x_1 y_2 + y_1 x_2)$ (MB1.10c)

4. Division: We interpret z_1/z_2 as $z_1 z_2^{-1}$ and use eqn MB1.5 for the inverse:

$$\frac{z_1}{z_2} = z_1 z_2^{-1} = \frac{z_1 z_2^*}{|z_2|^2} \quad (\text{MB1.10d})$$

A brief illustration

Consider the complex numbers $z_1 = 6 + 2i$ and $z_2 = -4 - 3i$. Then

$$z_1 + z_2 = (6 - 4) + (2 - 3)i = 2 - i$$

$$z_1 - z_2 = 10 + 5i$$

$$z_1 z_2 = \{6(-4) - 2(-3)\} + \{6(-3) + 2(-4)\}i = -18 - 26i$$

$$\frac{z_1}{z_2} = (6 + 2i) \left(\frac{-4 + 3i}{25} \right) = -\frac{6}{5} + \frac{2}{5}i$$

The polar form of a complex number is commonly used to perform arithmetical operations. For instance the product of two complex numbers in polar form is

$$z_1 z_2 = (r_1 e^{i\theta_1})(r_2 e^{i\theta_2}) = r_1 r_2 e^{i(\theta_1 + \theta_2)} \quad (\text{MB1.11})$$

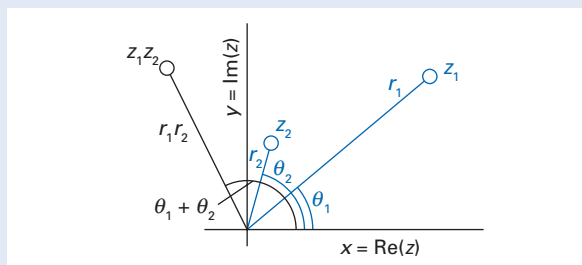


Fig. MB1.2 The multiplication of two complex numbers depicted in the complex plane.

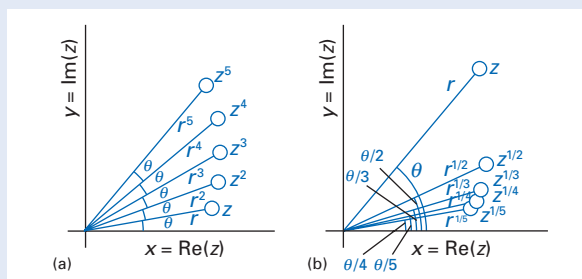


Fig. MB1.3 (a) The n th powers and (b) the n th roots ($n = 1, 2, 3, 4, 5$) of a complex number depicted in the complex plane.

This multiplication is depicted in the complex plane as shown in Fig. MB1.2. The n th power and the n th root of a complex number are

$$z^n = (re^{i\theta})^n = r^n e^{in\theta} \quad z^{1/n} = (re^{i\theta})^{1/n} = r^{1/n} e^{i\theta/n} \quad (\text{MB1.12})$$

The depictions in the complex plane are shown in Fig. MB1.3.

A brief illustration

To determine the 5th root of $z = 8 - 3i$, we note that from the second *brief illustration* its polar form is

$$z = 73^{1/2} e^{-0.359i} = 8.544 e^{-0.359i}$$

The 5th root is therefore

$$\begin{aligned} z^{1/5} &= (8.544 e^{-0.359i})^{1/5} = 8.544^{1/5} e^{-0.359i/5} \\ &= 1.536 e^{-0.0718i} \end{aligned}$$

It follows that $x = 1.536 \cos(-0.0718) = 1.532$ and $y = 1.536 \sin(-0.0718) = -0.110$ (note that we work in radians), so

$$(8 - 3i)^{1/5} = 1.532 - 0.110i$$