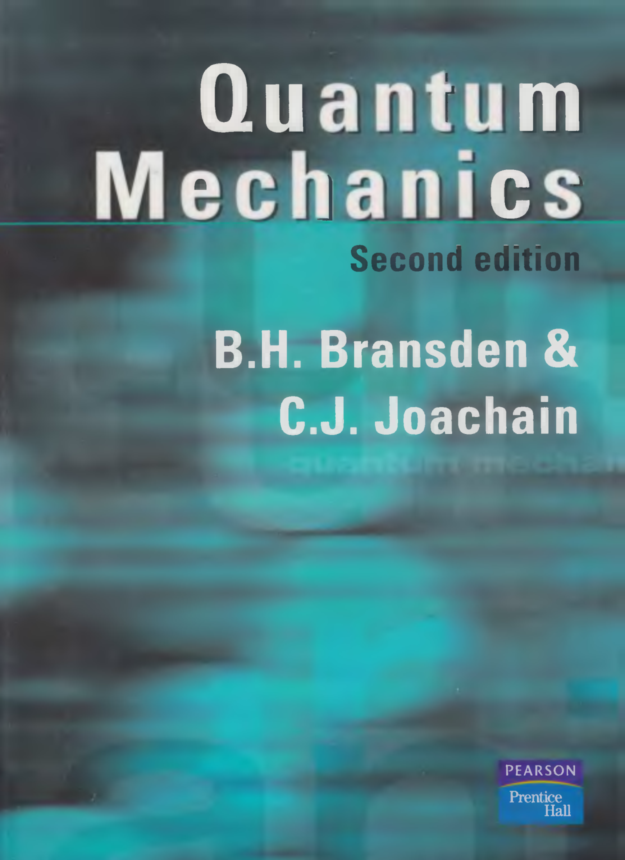
Quantum Mechanics

Second edition

B.H. Bransden &
C.J. Joachain



PEARSON
Prentice Hall

Quantum Mechanics

2nd edition

Quantum Mechanics

2nd edition

B. H. Bransden and C. J. Joachain

PEARSON
Prentice Hall

Harlow, England • London • New York • Boston • San Francisco • Toronto • Sydney • Singapore • Hong Kong
Tokyo • Seoul • Taipei • New Delhi • Cape Town • Madrid • Mexico City • Amsterdam • Munich • Paris • Milan

Pearson Education Limited
Edinburgh Gate
Harlow
Essex CM20 2JE
England

and Associated Companies throughout the world

Visit us on the World Wide Web at:
www.pearsoned.co.uk

First published under the Longman Scientific & Technical imprint 1989
Second edition 2000

ISBN-10: 0-582-35691-1
ISBN-13: 978-0-582-35691-7

British Library Cataloguing-in-Publication Data
A catalogue record for this book can be obtained from the British Library

Library of Congress Cataloging-in-Publication Data
Bransden, B. H., 1926-
Quantum mechanics / B.H. Bransden and C.J. Joachain.– 2nd ed.
p. cm.
Rev. ed. of: Introduction to quantum mechanics. 1989.
Includes bibliographical references and index.
ISBN 0-582-35691-1
1. Quantum theory. I. Joachain, C.J. (Charles Jean) II. Bransden, B. H., 1926- Introduction to quantum mechanics. III. Title.
QC174.12.B74 2000
530.12–dc21 99-055742

10 9 8 7 6
07 06

Typeset in Times at 10pt by 56.

Produced by Pearson Education Asia Pte Ltd.,
Printed in Great Britain by Henry Ling Limited, at the Dorset Press, Dorchester, DT1 1HD.

Contents

Preface to the Second Edition

The purpose of this book remains as outlined in the preface to the first edition: to provide a core text in quantum mechanics for students in physics at undergraduate level. It has not been found necessary to make major alterations to the contents of the book. However, we have taken advantage of the opportunity provided by the preparation of a new edition to make a number of minor improvements throughout the text, to introduce some new topics and to include a new chapter on relativistic quantum mechanics. This inclusion stems from a reconsideration of our earlier decision to exclude this material. We believe that a significant number of core courses now include an introduction to relativistic quantum mechanics; this is the subject of the new chapter (Chapter 15). Among the other important changes are the inclusion of the Feynman path integral approach to quantum mechanics (Chapter 5), a discussion of the Berry phase (Chapter 9) with applications (Chapters 10 and 12), an account of the Aharonov–Bohm effect (Chapter 12) and a discussion of quantum jumps (Chapter 17). We have also included the integral equation of potential scattering in our treatment of quantum collision theory (Chapter 13) and have given a more extended discussion of Bose–Einstein condensation in Chapter 14.

It is a pleasure to acknowledge the many helpful comments made to us by colleagues who have used the first edition of this book. Their remarks have been of great benefit to us in preparing this new edition. One of us (CJJ) would like to thank Professor H. Walther for his hospitality at the Max-Planck-Institut für Quantenoptik in Garching, where part of this work was carried out. We also wish to thank Mrs R. Lareppe for her expert and careful typing of the manuscript.

B. H. Bransden, Durham
C. J. Joachain, Brussels
August 1999

Preface to the First Edition

The study of quantum mechanics and its applications pervades much of the modern undergraduate course in physics. Virtually all undergraduates are expected to become familiar with the principles of non-relativistic quantum mechanics, with a variety of approximation methods and with the application of these methods to simple systems occurring in atomic, nuclear and solid state physics. This core material is the subject of this book. We have firmly in mind students of physics, rather than of mathematics, whose mathematical equipment is limited, particularly at the beginning of their studies. Relativistic quantum theory, the application of group theoretical methods and many-body techniques are usually taught in the form of optional courses and we have made no attempt to cover more advanced material of this nature. Although a fairly large number of examples drawn from atomic, nuclear and solid state physics are given in the text, we assume that the reader will be following separate systematic courses on those subjects, and only as much detail as necessary to illustrate the theory is given here.

Following an introductory chapter in which the evidence that led to the development of quantum theory is reviewed, we develop the concept of a wave function and its interpretation, and discuss Heisenberg's uncertainty relations. Chapter 3 is devoted to the Schrödinger equation and in the next chapter a variety of applications to one-dimensional problems is discussed. The next three chapters deal with the formal development of the theory, the properties of angular momenta and the application of Schrödinger's wave mechanics to simple three-dimensional systems.

Chapters 8 and 9 deal with approximation methods for time-independent and time-dependent problems, respectively, and these are followed by six chapters in which the theory is illustrated through application to a range of specific systems of fundamental importance. These include atoms, molecules, nuclei and their interaction with static and radiative electromagnetic fields, the elements of collision theory and quantum statistics. Finally, in Chapter 17, we discuss briefly some of the difficulties that arise in the interpretation of quantum theory. Problem sets are provided covering all the most important topics, which will help the student monitor his understanding of the theory.

We wish to thank our colleagues and students for numerous helpful discussions and suggestions. Particular thanks are due to Professor A. Aspect, Dr P. Francken, Dr R. M. Potvliege, Dr P. Castoldi and Dr J. M. Frère. It is also a pleasure to thank Miss P. Carse, Mrs E. Péan and Mrs M. Leclercq for their patient and careful typing of the manuscript, and Mrs H. Joachain-Bukowinski and Mr C. Depraetere for preparing a large number of the diagrams.

B. H. Bransden, Durham
C. J. Joachain, Brussels
November 1988

Acknowledgements

We are indebted to the following for permission to reproduce copyright material: Oxford University Press for figs. 17.1, 17.2 & 17.3 adapted from figs. 1.4, 1.1 & 1.8, pp. 2–12, from an article by A. Aspect and P. Grangier in *Quantum Concepts in Space and Time* edited by Penrose and Isham (1986), the *American Journal of Physics* and A. Tonomura *et al.* for fig. 2.3, *Physics World* and L. Kouwenhoven and C. Marcus for fig. 16.7 and the *Journal of Optical Communications* and Th. Sauter *et al.* for fig. 17.5.

1 The origins of quantum theory

Until the end of the nineteenth century, classical physics appeared to be sufficient to explain all physical phenomena. The universe was conceived as containing matter, consisting of particles obeying Newton's laws of motion and radiation (waves) following Maxwell's equations of electromagnetism. The theory of special relativity, formulated by A. Einstein in 1905 on the basis of a critical analysis of the notions of space and time, generalised classical physics to include the region of high velocities. In the theory of special relativity the velocity c of light plays a fundamental role: it is the upper limit of the velocity of any material particle. Newtonian mechanics is an accurate approximation to relativistic mechanics only in the 'non-relativistic' regime, that is when all relevant particle velocities are small with respect to c. It should be noted that Einstein's theory of relativity does not modify the clear distinction between matter and radiation which is at the root of classical physics. Indeed, all pre-quantum physics, non-relativistic or relativistic, is now often referred to as classical physics.

During the late nineteenth century and the first quarter of the twentieth, however, experimental evidence accumulated which required new concepts radically different from those of classical physics. In this chapter we shall discuss some of the key experiments which prompted the introduction of these new concepts: *the quantisation of physical quantities* such as energy and angular momentum, *the particle properties of radiation* and *the wave properties of matter*. We shall see that they are directly related to the existence of a universal constant, called *Planck's constant h*. Thus, just as the velocity c of light plays a central role in relativity, so does Planck's constant in *quantum physics*. Because Planck's constant is very small when measured in 'macroscopic' units (such as SI units), quantum physics essentially deals with phenomena at the atomic and subatomic levels. As we shall see in this chapter, the new ideas were first introduced in a more or less *ad hoc* fashion. They evolved later to become part of a new theory, *quantum mechanics*, which we will begin to study in Chapter 2.

1.1 Black body radiation

We start by considering the problem which led to the birth of quantum physics, namely the formulation of the *black body radiation law*. It is a matter of common experience that the surface of a hot body emits energy in the form of electromagnetic radiation. In fact, this emission occurs at any temperature greater than absolute zero, the emitted radiation being continuously distributed over all wavelengths. The distribution in wavelength, or *spectral distribution* depends on temperature. At low temperature (below about 500 °C), most of the emitted energy is concentrated at relatively long wavelengths, such as those corresponding to infrared radiation. As the temperature increases, a larger fraction of the energy is radiated at lower wavelengths. For example, at temperatures between 500 and 600 °C, a large enough fraction of the emitted energy has wavelengths within the visible spectrum, so that the body 'glows', and at 3000 °C the spectral distribution has shifted sufficiently to the lower wavelengths for the body to appear 'white hot'. Not only does the spectral distribution change with temperature, but the total power (energy per unit time) radiated increases as the body becomes hotter.

When radiation falls on the surface of a body some is reflected and some is absorbed. For example, dark bodies absorb most of the radiation falling on them, while light-coloured bodies reflect most of it. The *absorption coefficient* of a material surface at a given wavelength is defined as the fraction of the radiant energy, incident on the surface, which is absorbed at that wavelength. Now, if a body is in thermal equilibrium with its surroundings, and therefore is at constant temperature, it must emit and absorb the same amount of radiant energy per unit time, for otherwise its temperature would rise or fall. The radiation emitted or absorbed under these circumstances is known as *thermal radiation*.

A *black body* is defined as a body which absorbs all the radiant energy falling upon it. In other words its absorption coefficient is equal to unity at all wavelengths. Thermal radiation absorbed or emitted by a black body is called *black body radiation* and is of special importance. Indeed, G. R. Kirchhoff proved in 1859 by using general thermodynamical arguments that, for any wavelength, the ratio of the *emissive power* or spectral emittance (defined as the power emitted per unit area at a given wavelength) to the absorption coefficient is the same for all bodies at the same temperature, and is equal to the emissive power of a black body at that temperature. This relation is known as *Kirchhoff's law*. Since the maximum value of the absorption coefficient is unity and corresponds to a black body, it follows from Kirchhoff's law that the black body is not only the most efficient absorber, but is also the most efficient emitter of electromagnetic energy. Moreover, it is clear from Kirchhoff's law that the emissive power of a black body does not depend on the nature of the body. Hence black body radiation has 'universal' properties and is therefore of particular interest.

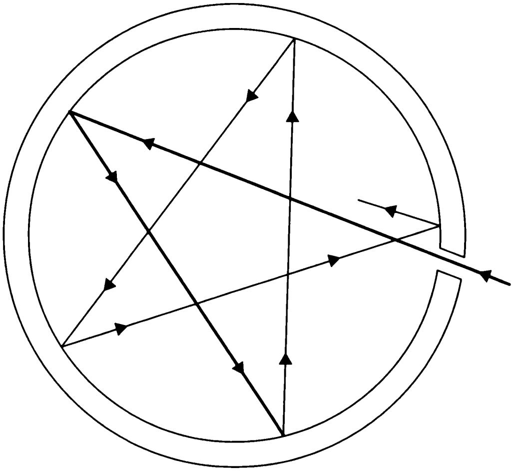


Figure 1.1 A good approximation to a black body. A cavity kept at a constant temperature and having blackened interior walls is connected to the outside by a small hole. To an outside observer, this small hole appears like a black body surface because any radiation incident from the outside on the hole will be almost completely absorbed after multiple reflections on the interior surface of the cavity. Because the cavity is in thermal equilibrium, the radiation inside it can be closely identified with black body radiation, and the hole also emits like a black body.

A perfect black body is of course an idealisation, but it can be very closely approximated in the following way. Consider a cavity kept at a constant temperature, whose interior walls are blackened (see Fig. 1.1). To an outside observer, a small hole made in the wall of such a cavity behaves like a black body surface. The reason is that any radiation incident from the outside upon the hole will pass through it and will almost completely be absorbed in multiple reflections inside the cavity, so that the hole has an effective absorption coefficient close to unity. Since the cavity is in thermal equilibrium, the radiation within it and that escaping from the small opening can thus be closely identified with the thermal radiation from a black body. It should be noted that the hole appears black only at low temperatures, where most of the energy is emitted at wavelengths longer than those corresponding to visible light.

Let us denote by R the *total emissive power* (or *total emittance*) of a black body, that is the total power emitted per unit area of the black body. In 1879 J. Stefan found an empirical relation between the quantity R and the absolute temperature T of a black body

$$R(T) = \sigma T^4 \tag{1.1}$$

where $\sigma = 5.67 \times 10^{-8}$ W m^{-2} K^{-4} is a constant known as Stefan's constant. (Throughout this book we use SI units; the symbol W denotes a watt and K refers to a degree Kelvin). In 1884, L. Boltzmann deduced the relation (1.1) from thermodynamics; it is now called the *Stefan–Boltzmann law*.

We now consider the spectral distribution of black body radiation. We denote by

$R(\lambda, T)$ the emissive power or spectral emittance of a black body, so that $R(\lambda, T)\mathrm{d}\lambda$ is the power emitted per unit area from a black body at the absolute temperature T, corresponding to radiation with wavelengths between λ and $\lambda + \mathrm{d}\lambda$. The total emissive power $R(T)$ is of course the integral of $R(\lambda, T)$ over all wavelengths,

$$R(T) = \int_0^\infty R(\lambda, T)\mathrm{d}\lambda \tag{1.2}$$

and by the Stefan–Boltzmann law $R(T) = \sigma T^4$. Since R depends only on the temperature, it follows that the spectral emittance $R(\lambda, T)$ is a 'universal' function, in agreement with the conclusions drawn previously from Kirchhoff's law.

The first accurate measurements of $R(\lambda, T)$ were made by O. Lummer and E. Pringsheim in 1899. The observed spectral emittance $R(\lambda, T)$ is shown plotted against λ, for a number of different temperatures, in Fig. 1.2. We see that, for fixed λ, $R(\lambda, T)$ increases with increasing T. At each temperature, there is a wavelength λ_{max} for which $R(\lambda, T)$ has its maximum value; this wavelength varies inversely with the temperature:

$$\lambda_{\text{max}} T = b \tag{1.3}$$

a result which is known as Wien's displacement law. The constant b which appears in (1.3) is called the *Wien displacement constant* and has the value $b = 2.898 \times 10^{-3}$ m K.

We have seen above that if a small hole is made in a cavity whose walls are uniformly heated to a given temperature, this hole will emit black body radiation, and that the radiation inside the cavity is also that of a black body. Using the second law of thermodynamics, Kirchhoff proved that the flux of radiation in the cavity is the same in all directions, so that the radiation is isotropic. He also showed that the radiation is homogeneous, namely the same at every point inside the cavity, and that it is identical in all cavities at the same temperature. Furthermore, all these statements hold at each wavelength.

Instead of using the spectral emittance $R(\lambda, T)$, it is convenient to specify the spectrum of black body radiation inside the cavity in terms of a quantity $\rho(\lambda, T)$ which is called the (wavelength) *spectral distribution function* or (wavelength) *monochromatic energy density*. It is defined so that $\rho(\lambda, T)\mathrm{d}\lambda$ is the energy density (that is, the energy per unit volume) of the radiation in the wavelength interval $(\lambda, \lambda + \mathrm{d}\lambda)$, at the absolute temperature T. As we expect on physical grounds, $\rho(\lambda, T)$ is proportional to $R(\lambda, T)$, and it can be shown[1] that the proportionality constant is $4/c$, where c is the velocity of light *in vacuo*

$$\rho(\lambda, T) = \frac{4}{c} R(\lambda, T). \tag{1.4}$$

Hence, measurements of the spectral emittance $R(\lambda, T)$ also determine the spectral distribution function $\rho(\lambda, T)$.

---

[1] See, for example, Richtmyer *et al.* (1969).

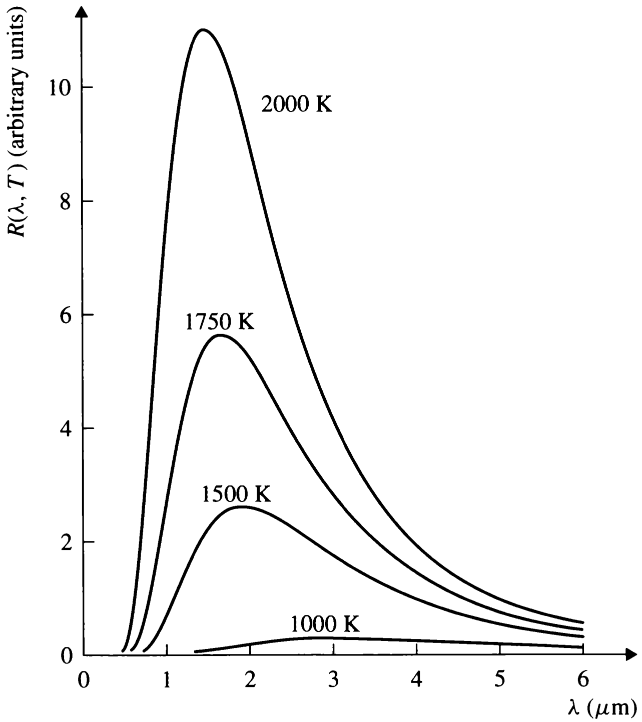


Figure 1.2 Spectral distribution of black body radiation. The spectral emittance $R(\lambda, T)$ is plotted as a function of the wavelength λ for different absolute temperatures.

Using general thermodynamical arguments, W. Wien showed in 1893 that the function $\rho(\lambda, T)$ had to be of the form

$$\rho(\lambda, T) = \lambda^{-5} f(\lambda T) \tag{1.5}$$

where $f(\lambda T)$ is a function of the single variable λT, which cannot be determined from thermodynamics. It is a simple matter to show (Problem 1.3) that Wien's law (1.5) includes the Stefan–Boltzmann law (1.1) as well as Wien's displacement law (1.3). Of course, the values of the Stefan constant σ and of the Wien displacement constant b cannot be obtained until the function $f(\lambda T)$ is known.

In order to determine the function $f(\lambda T)$ – and hence $\rho(\lambda, T)$ – one must go beyond thermodynamical reasoning and use a more detailed theoretical model. After some attempts by Wien, Lord Rayleigh and J. Jeans derived a spectral distribution function $\rho(\lambda, T)$ from the laws of classical physics in the following way. First, from electromagnetic theory, it follows that the thermal radiation within a cavity must exist in the form of standing electromagnetic waves. The number of such waves – or in other words the number of modes of oscillation of the electromagnetic field in the cavity – per unit volume, with wavelengths within the interval λ to $\lambda + d\lambda$, can be shown[1] to be $(8\pi/\lambda^4)\mathrm{d}\lambda$, so that $n(\lambda) = 8\pi/\lambda^4$ is the number of modes per unit volume and per unit wavelength range. This number is independent of the size and shape of a sufficiently large cavity. Now, if $\bar{\varepsilon}$ denotes the average energy in the mode with wavelength λ, the spectral distribution function $\rho(\lambda, T)$ is simply the product of $n(\lambda)$ and $\bar{\varepsilon}$, and hence may be written as

$$\rho(\lambda, T) = \frac{8\pi}{\lambda^4}\bar{\varepsilon} \tag{1.6}$$

Rayleigh and Jeans then suggested that the standing waves of electromagnetic radiation are caused by the constant absorption and emission of radiation by atoms in the wall of the cavity, these atoms acting as electric dipoles, that is linear harmonic oscillators of frequency $\nu = c/\lambda$. The energy, ε, of each of these classical oscillators can take any value between 0 and ∞. However, since the system is in thermal equilibrium, the average energy $\bar{\varepsilon}$ of an assemblage of these oscillators can be obtained from classical statistical mechanics by weighting each value of ε with the Boltzmann probability distribution factor $\exp(-\varepsilon/kT)$, where k is Boltzmann's constant. Setting $\beta = 1/kT$, we have

$$\begin{aligned}\bar{\varepsilon} &= \frac{\int_0^\infty \varepsilon \exp(-\beta\varepsilon)\mathrm{d}\varepsilon}{\int_0^\infty \exp(-\beta\varepsilon)\mathrm{d}\varepsilon} \\ &= -\frac{\mathrm{d}}{\mathrm{d}\beta}\log\left[\int_0^\infty \exp(-\beta\varepsilon)\mathrm{d}\varepsilon\right] = \frac{1}{\beta} = kT.\end{aligned} \tag{1.7}$$

This result is in agreement with the classical law of *equipartition of energy*, according to which the average energy per degree of freedom of a dynamical system in equilibrium is equal to $kT/2$. In the present case the linear harmonic oscillators must be assigned $kT/2$ for the contribution to the average energy coming from their kinetic energy, plus another contribution $kT/2$ arising from their potential energy.

Inserting the value (1.7) of $\bar{\varepsilon}$ into (1.6) gives the Rayleigh–Jeans spectral distribution law

$$\rho(\lambda, T) = \frac{8\pi}{\lambda^4}kT \tag{1.8}$$

from which, using (1.5), we see that $f(\lambda T) = 8\pi k(\lambda T)$.

In the limit of long wavelengths, the Rayleigh–Jeans result (1.8) approaches the experimental values, as shown in Fig. 1.3. However, as can be seen from this figure, $\rho(\lambda, T)$ does not exhibit the observed maximum, and diverges as $\lambda \to 0$. This behaviour at short wavelengths is known as the 'ultraviolet catastrophe'. As a consequence, the total energy per unit volume

$$\rho_{\text{tot}}(T) = \int_0^\infty \rho(\lambda, T)\mathrm{d}\lambda \tag{1.9}$$

is seen to be infinite, which is clearly incorrect.

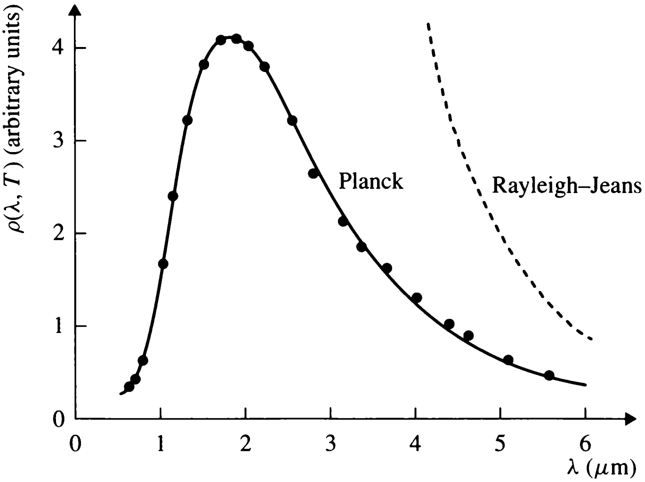


Figure 1.3 Comparison of the Rayleigh–Jeans and Planck spectral distribution laws with experiment at 1600 K. The dots represent experimental points.

Planck's quantum theory

No solution to these difficulties can be found using classical physics. However, in December 1900, M. Planck presented a new form of the black body radiation spectral distribution, based on a revolutionary hypothesis. He postulated that the energy of an oscillator of a given frequency ν cannot take arbitrary values between zero and infinity, but can only take on the discrete values $n\varepsilon_0$, where n is a positive integer or zero, and ε_0 is a finite amount, or *quantum*, of energy, which may depend on the frequency ν. In this case the average energy of an assemblage of oscillators of frequency ν, in thermal equilibrium, is given by

$$\begin{aligned}\bar{\varepsilon} &= \frac{\sum_{n=0}^{\infty} n\varepsilon_0 \exp(-\beta n\varepsilon_0)}{\sum_{n=0}^{\infty} \exp(-\beta n\varepsilon_0)} = -\frac{\mathrm{d}}{\mathrm{d}\beta}\left[\log \sum_{n=0}^{\infty} \exp(-\beta n\varepsilon_0)\right] \\ &= -\frac{\mathrm{d}}{\mathrm{d}\beta}\left[\log\left(\frac{1}{1-\exp(-\beta\varepsilon_0)}\right)\right] = \frac{\varepsilon_0}{\exp(\beta\varepsilon_0)-1} \qquad \textbf{(1.10)}\end{aligned}$$

where we have assumed, as did Planck, that the Boltzmann probability distribution factor can still be used. Substituting the new value (1.10) of $\bar{\varepsilon}$ into (1.6), we find that

$$\rho(\lambda, T) = \frac{8\pi}{\lambda^4} \frac{\varepsilon_0}{\exp(\varepsilon_0/kT) - 1}. \qquad \textbf{(1.11)}$$

In order to satisfy Wien's law (1.5), ε_0 must be taken to be proportional to the frequency ν

$$\varepsilon_0 = h\nu = hc/\lambda \qquad \textbf{(1.12)}$$

where h is a fundamental physical constant, called *Planck's constant.* The *Planck spectral distribution law* for $\rho(\lambda, T)$ is thus given by

$$\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp(hc/\lambda kT) - 1} \tag{1.13}$$

and we see from (1.5) that in Planck's theory the function $f(\lambda T)$ is given by $f(\lambda T) = 8\pi hc[\exp(hc/\lambda kT) - 1]^{-1}$.

By expanding the denominator in the Planck expression (1.13), it is easy to show (Problem 1.4) that at long wavelengths $\rho(\lambda, T) \rightarrow 8\pi kT/\lambda^4$, in agreement with the Rayleigh–Jeans formula (1.8). On the other hand, for short wavelengths, the presence of $\exp(hc/\lambda kT)$ in the denominator of the Planck radiation law (1.13) ensures that $\rho \rightarrow 0$ as $\lambda \rightarrow 0$. The physical reason for this behaviour is clear. At long wavelengths the quantity $\varepsilon_0 = hc/\lambda$ is small with respect to kT or, in other words, the quantum steps are small with respect to thermal energies; as a result the quantum states are almost continuously distributed, and the classical equipartition law is essentially unaffected. On the contrary, at short wavelengths, the available quantum states are widely separated in energy in comparison to thermal energies, and can be reached only by the absorption of high-energy quanta, a relatively rare phenomenon.

The value of λ for which the Planck spectral distribution (1.13) is a maximum can be evaluated (Problem 1.5), and it is found that

$$\lambda_{\text{max}} T = \frac{hc}{4.965k} = b \tag{1.14}$$

where b is Wien's displacement constant. Moreover, in Planck's theory the total energy density is finite and we find from (1.9) and (1.13) that (Problem 1.6)

$$\rho_{\text{tot}} = aT^4, \qquad a = \frac{8\pi^5}{15} \frac{k^4}{h^3 c^3}. \tag{1.15}$$

Since ρ_{tot} is related to the total emissive power R by $\rho_{\text{tot}} = 4R/c$, where R is given by the Stefan–Boltzmann law (1.1), we see that Stefan's constant σ is given by

$$\sigma = \frac{2\pi^5}{15} \frac{k^4}{h^3 c^2}. \tag{1.16}$$

Equations (1.14) and (1.16) relate b and σ to the three fundamental constants c, k and h. In 1900, the velocity of light, c, was known accurately, and the experimental values of σ and b were also known. Using this data, Planck calculated both the values of k and h, which he found to be $k = 1.346 \times 10^{-23}$ J K^{-1} and $h = 6.55 \times 10^{-34}$ J s. (The symbol J denotes a joule and s a second.) This was not only the most accurate value of Boltzmann's constant k available at the time, but also, most importantly, the first calculation of Planck's constant h. Using his values of k and h, Planck obtained very good agreement with the experimental data for the spectral distribution of black body radiation over the entire range of wavelengths (see Fig. 1.3). The modern value of k is given by[2] $k = 1.38066 \times 10^{-23}$ J K^{-1} and that of h is

$$h = 6.62618 \times 10^{-34} \text{ J s.} \tag{1.17}$$

We remark that the physical dimensions of h are those of [energy] × [time] = [length] × [momentum]. These dimensions are those of a physical quantity called *action*, and consequently Planck's constant h is also known as the *fundamental quantum of action*. As seen from (1.17), the numerical value of h, when expressed in 'macroscopic units', such as SI units, is very small, which is in agreement with the statement made at the beginning of this chapter. We therefore expect that if, for a physical system, every variable having the dimension of action is very large when measured in units of h, then quantum effects will be negligible and the laws of classical physics will be sufficiently accurate.

As an illustration, let us consider a *macroscopic* linear harmonic oscillator of mass 10^{-2} kg, maximum velocity $v_{\text{max}} = 10^{-1}$ m s^{-1} and maximum amplitude $x_0 = 10^{-2}$ m. The frequency of this oscillator is $\nu = v_{\text{max}}/(2\pi x_0) \simeq 1.6$ Hz, its period is $T = \nu^{-1} \simeq 0.63$ s and its energy is given by $E = mv_{\text{max}}^2/2 = 5 \times 10^{-5}$ J. The product of the energy times the period has the dimensions of an action, with the value 3.14×10^{-5} J s, which is about 5×10^{28} times larger than h! We also see that at the frequency $\nu = 1.6$ Hz of this oscillator, the quantum of energy $\varepsilon_0 = h\nu \simeq 10^{-33}$ J. Hence the ratio $\varepsilon_0/E \simeq 2 \times 10^{-29}$ is utterly negligible, and quantum effects can be neglected in this case. On the contrary, for high-frequency electromagnetic waves in black body radiation quantum effects are very important, as we have seen above. In the remaining sections of this chapter we shall discuss several examples of physical phenomena occurring in microphysics, where quantum effects are also of crucial importance.

The idea of quantisation of energy, in which the energy of a system can only take certain discrete values, was totally at variance with classical physics, and Planck's theory was not accepted readily. It should be noted in this respect that some aspects of Planck's derivation of the black body radiation law (1.13) are not completely sound. A revised proof of Planck's black body radiation law, based on modern quantum theory, will be given in Chapter 14. However, Planck's fundamental postulate about the quantisation of energy is correct, and it was not long before the quantum concept was used to explain other phenomena. In particular, as we shall see in Section 1.2, A. Einstein in 1905 was able to understand the photoelectric effect by extending Planck's idea of the quantisation of energy. In Planck's theory, the oscillators representing the source of the electromagnetic field could only vibrate with energies given by $n\varepsilon_0 = nh\nu (n = 0, 1, 2, \dots)$. In contrast, Einstein assumed that the electromagnetic field itself was quantised and that light consists of corpuscles, called *light quanta* or *photons*, each photon travelling with the velocity c of light and having an energy

$$E = h\nu = hc/\lambda. \tag{1.18}$$

---

[2] See the Table of Fundamental Constants at the end of the book, p. 789.

According to Einstein, black body radiation may thus be considered as a photon gas in thermal equilibrium with the atoms in the walls of the cavity; it is this idea which will be developed in Chapter 14 to re-derive Planck's radiation law (1.13) from quantum statistical mechanics. We remark that since each photon has an energy hc/λ, the number $\mathrm{d}N$ of black body radiation photons per unit volume, with wavelengths between λ and $\lambda + \mathrm{d}\lambda$, at absolute temperature T, is

$$\mathrm{d}N = \frac{\rho(\lambda, T)\mathrm{d}\lambda}{hc/\lambda} = \frac{8\pi}{\lambda^4}\frac{\mathrm{d}\lambda}{\exp(hc/\lambda kT) - 1}. \qquad \textbf{(1.19)}$$

The total number of black body photons per unit volume, at absolute temperature T, can be obtained by integrating (1.19) over all wavelengths. The result is (Problem 1.9)

$$N = 2.029 \times 10^7 T^3 \text{ photons m}^{-3}. \qquad \textbf{(1.20)}$$

The average energy $\bar{E}$ of a black body photon at absolute temperature T is then readily deduced by dividing the total energy density ρ_{tot}, given by (1.15), by the total number N of photons per unit volume. We find in this way that

$$\bar{E} = 3.73 \times 10^{-23} T \text{ J}. \qquad \textbf{(1.21)}$$

In quantum physics it is particularly convenient to specify energies in units of *electronvolts* (eV) or multiples of them. The electronvolt is defined to be the energy acquired by an electron passing through a potential difference of one volt. Since the charge of the electron has the absolute value $e = 1.60 \times 10^{-19}$ C, we see that[3]

$$\begin{aligned} 1 \text{ eV} &= 1.60 \times 10^{-19} \text{ C V} \\ &= 1.60 \times 10^{-19} \text{ J}. \end{aligned} \qquad \textbf{(1.22)}$$

Hence the average energy of a black body photon is given in eV by

$$\bar{E} = \frac{3.73 \times 10^{-23}}{1.60 \times 10^{-19}} T \text{ eV} = 2.33 \times 10^{-4} T \text{ eV}. \qquad \textbf{(1.23)}$$

The 3 K cosmic black body radiation

Before leaving the subject of black body radiation, we briefly discuss a particularly fascinating example of it. In 1964 A. A. Penzias and R. W. Wilson, using a radio-telescope, detected at a wavelength $\lambda = 7.35$ cm an isotropic radio 'noise' of cosmic origin, whose intensity corresponded to an effective temperature of about 3 K. This 'noise' was soon interpreted as due to black body radiation at an absolute temperature of approximately 3 K, which fills the universe uniformly and hence is incident on the Earth with equal intensity from all directions. Measurements of the intensity of this radiation at other wavelengths confirmed that its spectral distribution is given by Planck's radiation law (1.13), for a temperature of about 3 K.

The presence of this cosmic radiation provides strong evidence for the *big bang* theory of the origin of the universe, according to which the expansion of the universe

---

[3] Conversion factors between various units are given in a table at the end of this volume (p. 791).

began from a state of enormous density and temperature, that is an extremely hot fireball of particles and radiation. To see why this is the case, let us analyse black body radiation in an expanding universe. Assuming that the size of the universe has grown by a factor S, the wavelengths will be increased by the same factor because of the Doppler shift, so that the new values of the wavelengths are given by $\lambda' = S\lambda$. Now, after this expansion, the energy density $\rho(\lambda', T)\mathrm{d}\lambda'$ in the wavelength interval $(\lambda', \lambda' + \mathrm{d}\lambda')$ at absolute temperature T is smaller than the former energy density $\rho(\lambda, T)\mathrm{d}\lambda$ by a factor S^{-4}. Indeed, the volume of the universe having increased by a factor S^3, the number of photons per unit volume has dropped by this factor (we assume that no photons are created or destroyed). Moreover, since $\lambda' = S\lambda$, the energy hc/λ' of a photon at the wavelength λ' is smaller than that of a photon at wavelength λ by a factor S. Hence

$$\rho(\lambda', T)\mathrm{d}\lambda' = S^{-4}\rho(\lambda, T)\mathrm{d}\lambda = \frac{8\pi hc}{S^4\lambda^5}\frac{\mathrm{d}\lambda}{\exp(hc/\lambda kT) - 1} \tag{1.24}$$

and therefore, since $\mathrm{d}\lambda' = S\mathrm{d}\lambda$, we have

$$\rho(\lambda', T) = \frac{8\pi hc}{(\lambda')^5}\frac{1}{\exp(hcS/\lambda' kT) - 1}. \tag{1.25}$$

Upon comparison with (1.13) we see that if we replace T by a new temperature

$$T' = \frac{T}{S} \tag{1.26}$$

the expression (1.25) is identical with the Planck radiation law for the energy density $\rho(\lambda', T')$. Thus black body radiation in an expanding universe can still be described by the Planck formula, in which the temperature T' decreases according to (1.26) as the universe expands. The cosmic radiation at $T' = 3$ K which is now observed is therefore 'fossil' radiation, cooled by expansion, originating from an epoch when the universe was smaller and hotter than at the present time. It is estimated[4] that this radiation comes from an epoch when the universe was about 1 million years old and was flooded with radiation at a temperature $T \simeq 3000$ K. Using (1.26) we see that since that time the universe has expanded by a factor $S \simeq 1000$.

Further applications of Planck's quantisation postulate

We have seen above that the quantisation postulate introduced in 1900 by Planck was successful in explaining the black body radiation problem. We have also mentioned that the quantum idea was used by Einstein in 1905 to understand the photoelectric effect in terms of light quanta or photons; we shall return to this subject in Section 1.2. In 1907, Einstein also used the Planck formula (1.10) for the average energy of an oscillator to study the variation of the specific heats of solids with temperature, a problem which could not be solved by using classical physics. Einstein's results were improved in 1912 by P. Debye, and the excellent agreement between the Debye theory

---

[4] For an excellent account of this subject, see Weinberg (1977).

and experiment provided additional support for the existence of energy quanta. As we shall see in the last four sections of this chapter, the quantum concept also proved to be essential in understanding the Compton effect, the existence of atomic line spectra and the Stern–Gerlach experiment, and it played a central role in predicting the wave properties of matter, thereby giving birth to the new quantum mechanics.

1.2 The photoelectric effect

In 1887 H. Hertz performed the celebrated experiments in which he produced and detected electromagnetic waves, thus confirming Maxwell's theory. Ironically enough, in the course of the same experiments he also discovered a phenomenon which ultimately led to the description of light in terms of corpuscles: the *photons*. Specifically, Hertz observed that ultraviolet light falling on metallic electrodes facilitates the passage of a spark. Further work by W. Hallwachs, M. Stoletov, P. Lenard and others showed that charged particles are ejected from metallic surfaces irradiated by high-frequency electromagnetic waves. This phenomenon is called the *photoelectric effect*. In 1900, Lenard measured the charge-to-mass ratio of the charged particles by performing experiments similar to those which had led J. J. Thomson to discover the electron[5], and in this way he was able to identify the charged particles as electrons.

In his experiments to establish the mechanism of the photoelectric effect. Lenard used an apparatus shown in schematic form in Fig. 1.4. In an evacuated glass tube, ultraviolet light incident on a polished metal cathode C (called a photocathode) liberates electrons. If some of these electrons strike the anode A, there is a current I in the external circuit. Lenard studied this current as a function of the potential difference V between the surface and the anode. The variation of the photoelectric current I with V is shown in Fig. 1.5. When V is positive, the electrons are attracted towards the anode. As V is increased the current I increases until it saturates when V is large enough so that all the emitted electrons reach the anode. Lenard also observed that if V is reversed, so that the cathode becomes positive with respect to the anode, there is a definite negative voltage $-V_0$ at which the photoelectric current ceases, implying that the emission of electrons from the cathode stops (see Fig. 1.5). From this result it follows that the photoelectrons are emitted with velocities up to a maximum v_{max} and that the voltage $-V_0$ is just sufficient to repel the fastest photoelectrons (having the maximum kinetic energy $T_{\text{max}} = mv_{\text{max}}^2/2$) so that

$$eV_0 = \frac{1}{2}mv_{\text{max}}^2. \tag{1.27}$$

The potential V_0 is called the *stopping potential*. The fact that not all the photoelectrons have the same kinetic energy is readily explained: the electrons having the maximum kinetic energy T_{max} are emitted from the surface of the photocathode, while those having a lower energy originate from inside the photocathode, and thus lose energy in reaching the surface.

---

[5] See Bransden and Joachain (1983).

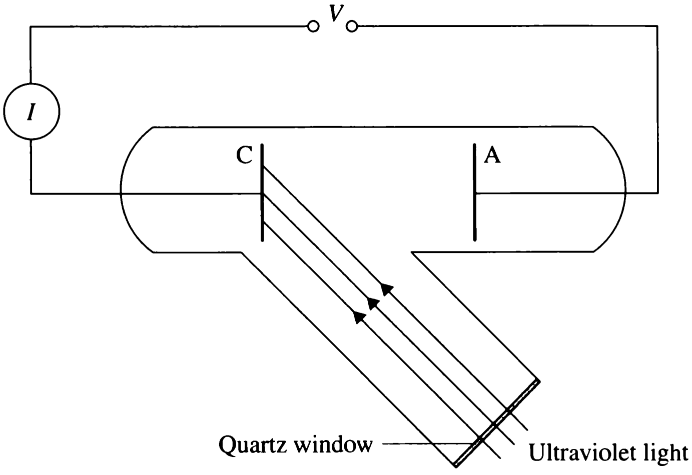


Figure 1.4 Schematic drawing of Lenard's apparatus for investigating the photoelectric effect.

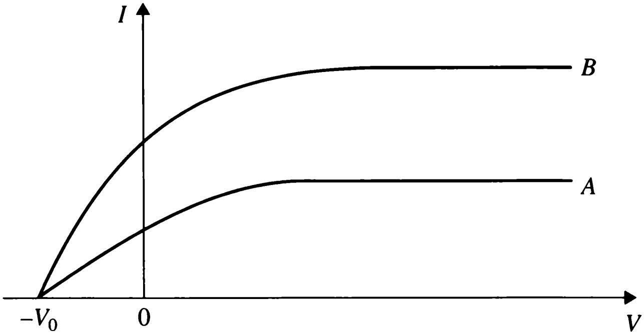


Figure 1.5 Variation of the photoelectric current I with the potential difference V between the cathode and the anode, for two values $A < B$ of the intensity of the light incident on the cathode. No current is observed when V is less than $-V_0$; the stopping potential V_0 is found to be independent of the light intensity.

Lenard found that the photoelectric current I is proportional to the intensity of the incident light (see Fig. 1.5). This result can be understood by using classical electromagnetic theory, which predicts that the number of electrons emitted per unit time should be proportional to the intensity of the incident light. However, the following important features exhibited by the experimental data cannot be explained in terms of the classical electromagnetic theory:

(1) There is a minimum, or *threshold* frequency ν_t of the radiation, characteristic of the surface, below which no emission of electrons takes place, no matter what the intensity of the incident radiation, or for how long it falls on the surface.

According to the classical wave theory, the photoelectric effect should occur for any frequency of the incident radiation, provided that the radiation intensity is large enough to give the energy required for ejecting the photoelectrons.

(2) The stopping potential V_0 and, hence, the maximum kinetic energy $T_{\text{max}} = mv_{\text{max}}^2/2$ of the photoelectrons are found to depend *linearly* on the frequency of the radiation and to be independent of its intensity. According to classical electromagnetic theory, the maximum kinetic energy of the emitted electrons should increase with the energy density (or intensity) of the incident radiation, independently of the frequency.

(3) Electron emission takes place immediately the light shines on the surface, with *no detectable time delay*. Now, in the classical wave theory of light, the light energy is spread uniformly over the wave front. To eject an electron from an atom described by classical mechanics, enough energy would have to be concentrated over an area of atomic dimensions, and to achieve such a concentration would require a certain time delay. Experiments can be arranged for which the predicted time delay is minutes, or even hours, and yet no detectable time lag is actually observed.

In 1905, Einstein offered an explanation of these seemingly strange aspects of the photoelectric effect, based on a generalisation of Planck's postulate of the quantisation of energy. In order to explain the spectral distribution of black body radiation, Planck had assumed that the processes of absorption and emission of radiation by matter do not take place continuously, but in finite quanta of energy $h\nu$. Einstein went further and advanced the idea that these quantum properties were inherent in the nature of electromagnetic radiation itself, so that light consists of quanta (corpuscles) called *photons*[6], each photon having an energy $E = h\nu = hc/\lambda$ (see (1.18)). The photons are sufficiently localised so that the whole quantum of energy can be absorbed by a single atom of the cathode at one time. Thus, when a photon falls on a metallic surface, its entire energy $h\nu$ is used to eject an electron from an atom. However, since electrons do not normally escape from surfaces, a certain minimum energy W is required for the ejected electron to leave the surface. This minimum energy, which depends on the metal, is called the *work function*. It follows that the maximum kinetic energy of a photoelectron is given in terms of the frequency ν by the linear relation

$$\tfrac{1}{2}mv_{\text{max}}^2 = h\nu - W \tag{1.28}$$

which is called Einstein's equation. The threshold frequency ν_t is determined by the work function since in this case $v_{\text{max}} = 0$, so that

$$h\nu_t = W. \tag{1.29}$$

The number of electrons emerging from the metal surface per unit time is proportional to the number of photons striking the surface per unit time, but the intensity of the

---

[6] In his 1905 paper entitled 'On a heuristic point of view concerning the creation and conversion of light', Einstein used the word *quantum of light*. The word *photon* was introduced by G. N. Lewis in 1926.

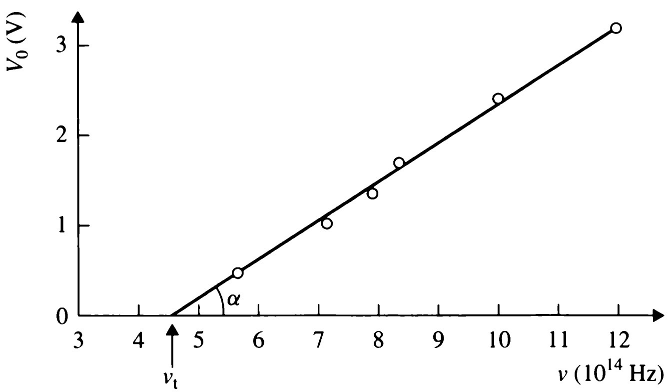


Figure 1.6 Millikan's results (circles) for the stopping potential V_0 as a function of the frequency ν. The data fall on a straight line, of slope $\tan\alpha = h/e$.

radiation is also proportional to the number of photons falling on a certain area per unit time, since each photon carries a fixed energy $h\nu$. It follows that the photoelectric current is proportional to the intensity of the radiation and that all the experimental observations are explained by Einstein's theory.

A series of very accurate measurements carried out between 1914 and 1916 by R. A. Millikan provided further confirmation of Einstein's theory. Combining (1.27) and (1.28), we see that the stopping potential V_0 satisfies the equation

$$V_0 = \frac{h}{e}\nu - \frac{W}{e}. \tag{1.30}$$

Millikan measured, for a given surface, V_0 as a function of ν. As seen from Fig. 1.6, his results indeed fell on a straight line, of slope h/e. Knowing the absolute charge e of the electron from his earlier 'oil-drop' experiments, Millikan obtained for h the value 6.56×10^{-34} J s, which agreed very well with Planck's result $h = 6.55 \times 10^{-34}$ J s determined from the black body spectral distribution. It is interesting that Millikan was able to use visible, rather than ultraviolet light for his photoelectric experiments using surfaces of lithium, sodium and potassium which have small values of the work function W.

Although the photoelectric effect provides compelling evidence for a *corpuscular* theory of light, it must not be forgotten that the existence of diffraction and interference phenomena demonstrate that light also exhibits a *wave* behaviour. This dual aspect of electromagnetic radiation is incompatible with classical physics. As we shall see below, the wave–particle duality is a general characteristic of all physical quantities, and the paradoxes resulting from this situation can only be resolved by using the new concepts embodied in quantum theory.

1.3 The Compton effect

The corpuscular nature of electromagnetic radiation was exhibited in a spectacular way in a quite different experiment performed in 1923 by A. H. Compton, in which a beam of X-rays was scattered through a block of material. X-rays had been discovered by W. K. Röntgen in 1895 and were known to be electromagnetic radiation of high frequency. The scattering of X-rays by various substances was first studied by C. G. Barkla in 1909, who interpreted his results with the help of J. J. Thomson's classical theory, developed around 1900. According to this theory, the oscillating electric field of the radiation acts on the electrons contained in the atoms of the target material. This interaction forces the atomic electrons to vibrate with the same frequency as the incident radiation. The oscillating electrons, in turn, radiate electromagnetic waves of the same frequency. The net effect is that the incident radiation is scattered with no change in wavelength, and this is called *Thomson scattering*. In general, Barkla found that the scattered intensity predicted by Thomson's theory agreed well with his experimental data. However, he found that some of his results were anomalous, particularly in the region of 'hard' X-rays, which correspond to shorter wavelengths. At the time of Barkla's work, it was not possible to measure the wavelengths of X-rays, and a further advance could not be made until M. von Laue in 1912, and later W. L. Bragg had shown that the wavelengths could be determined by studying the diffraction of X-rays by crystals. The experiment of Compton, which we shall now describe, was only possible because a precise determination of X-ray wavelengths could be made using a crystal spectrometer.

The experimental arrangement used by Compton is sketched in Fig. 1.7. He irradiated a graphite target with a nearly monochromatic beam of X-rays, of wavelength λ_0. He then measured the intensity of the scattered radiation as a function of wavelength. His results, illustrated in Fig. 1.8, showed that although part of the scattered radiation had the same wavelength λ_0 as the incident radiation, there was also a second component of wavelength λ_1, where $\lambda_1 > \lambda_0$. This phenomenon, called the *Compton effect*, could not be explained by the classical Thomson model. The shift in wavelength between the incident and scattered radiation, the *Compton shift* $\Delta\lambda = \lambda_1 - \lambda_0$, was found to vary with the angle of scattering (see Fig. 1.8) and to be proportional to $\sin^2(\theta/2)$, where θ is the angle between the incident and scattered beams. Further investigation showed $\Delta\lambda$ to be independent of both λ_0 and of the material used as the scatterer, and that the value of the constant of proportionality was 0.048×10^{-10} m.

In order to understand the origin of the wavelength shift $\Delta\lambda$, Compton suggested that the modified line at wavelength λ_1 could be attributed to X-ray photons scattered by loosely bound electrons in the atoms of the target. In fact, it is a good approximation to treat such electrons as *free*, since their binding energies are small compared with the energy of an X-ray photon; this explains why the results are independent of the nature of the material used for the target.

Let us then consider the scattering of an X-ray photon by a free electron, which can

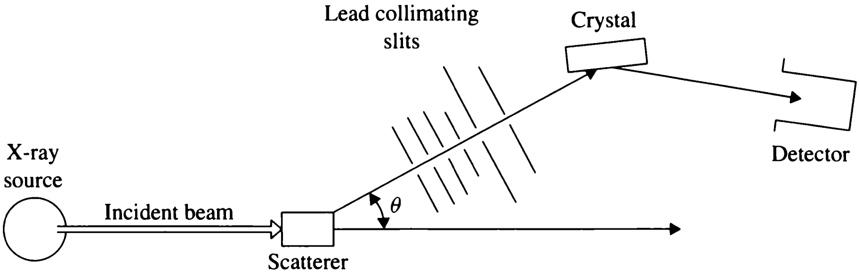


Figure 1.7 Schematic diagram of Compton's apparatus.

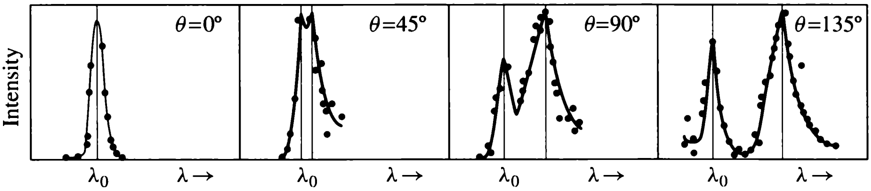


Figure 1.8 Compton's data for the scattering of X-rays by graphite.

be taken to be initially at rest. After the collision, the electron recoils (see Fig. 1.9) and since its velocity is not always small compared with the velocity of light, c, it is necessary to use *relativistic kinematics*. The relevant formulae will be quoted without derivation[7]. In particular, the total energy, E, of a particle having a rest mass m and moving with a velocity $\mathbf{v}$ is given by

$$E = \frac{mc^2}{(1 - v^2/c^2)^{1/2}}. \tag{1.31}$$

The kinetic energy T of the particle is defined as the difference between its total energy E and its rest mass energy mc^2, so that

$$T = E - mc^2. \tag{1.32}$$

The corresponding momentum of the particle is

$$\mathbf{p} = \frac{m\mathbf{v}}{(1 - v^2/c^2)^{1/2}} \tag{1.33}$$

and from (1.31) and (1.33) we see that the energy and momentum are related by

$$E^2 = m^2c^4 + p^2c^2. \tag{1.34}$$

---

[7] For a discussion of the theory of special relativity, see for example the text by Taylor and Wheeler (1966).

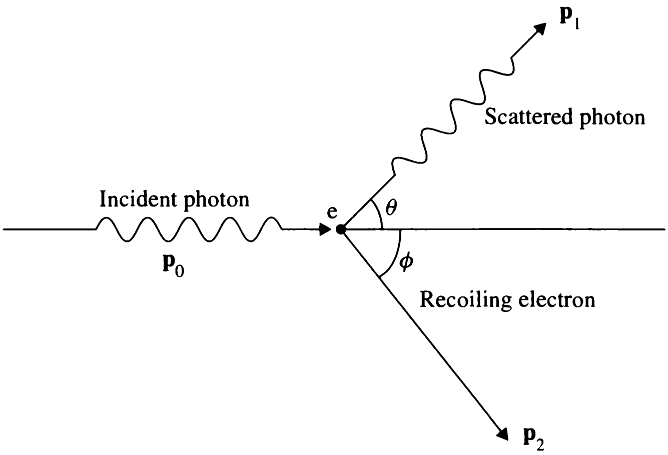


Figure 1.9 A photon of momentum $\mathbf{p}_0$ is incident on a free electron e at rest. After the collision, the photon has a momentum $\mathbf{p}_1$ while the electron recoils with a momentum $\mathbf{p}_2$.

Since the velocity of a photon is c and its energy $E = h\nu = hc/\lambda$ is finite, we see from (1.31) that we must take the mass of a photon to be zero, in which case we observe from (1.34) that the magnitude of its momentum is

$$p = E/c = h/\lambda. \tag{1.35}$$

Let us now apply these formulae to the situation depicted in Fig. 1.9, where a photon of energy $E_0 = hc/\lambda_0$ and momentum $\mathbf{p}_0$ (with $p_0 = E_0/c = h/\lambda_0$) collides with an electron of rest mass m initially at rest. After the collision, the photon has an energy $E_1 = hc/\lambda_1$ and a momentum $\mathbf{p}_1$ (with $p_1 = E_1/c = h/\lambda_1$) in a direction making an angle θ with the direction of incidence, while the electron recoils with a momentum $\mathbf{p}_2$ making an angle ϕ with the incident direction. Conservation of momentum yields $\mathbf{p}_0 = \mathbf{p}_1 + \mathbf{p}_2$ or, in other words

$$\begin{aligned} p_0 &= p_1 \cos\theta + p_2 \cos\phi & \text{(1.36a)} \\ 0 &= p_1 \sin\theta - p_2 \sin\phi & \text{(1.36b)} \end{aligned}$$

from which we find that

$$p_2^2 = p_0^2 + p_1^2 - 2p_0 p_1 \cos\theta. \tag{1.37}$$

Conservation of energy yields the relation

$$E_0 + mc^2 = E_1 + (m^2c^4 + p_2^2c^2)^{1/2} \tag{1.38}$$

and therefore, if we denote by T_2 the kinetic energy of the electron after the collision, we have

$$\begin{aligned} T_2 &= (m^2c^4 + p_2^2c^2)^{1/2} - mc^2 \\ &= E_0 - E_1 = c(p_0 - p_1) \end{aligned} \tag{1.39}$$

so that

$$p_2^2 = (p_0 - p_1)^2 + 2mc(p_0 - p_1). \tag{1.40}$$

Combining (1.40) with (1.37) we then find that

$$\begin{aligned} mc(p_0 - p_1) &= p_0 p_1(1 - \cos\theta) \\ &= 2p_0 p_1 \sin^2(\theta/2). \end{aligned} \tag{1.41}$$

Multiplying both sides of (1.41) by $h/(mcp_0p_1)$ and using the fact that $\lambda_0 = h/p_0$ and $\lambda_1 = h/p_1$, we finally obtain

$$\Delta\lambda = \lambda_1 - \lambda_0 = 2\lambda_C \sin^2(\theta/2) \tag{1.42}$$

where the constant λ_C is given by

$$\lambda_C = \frac{h}{mc} \tag{1.43}$$

and is called the *Compton wavelength* of the electron. Equation (1.42) is known as the *Compton equation*. The calculated value of $(2\lambda_C)$ is 0.048 52 Å[8], and this agrees very well with the experimental value which is 0.048 Å.

The existence of the unmodified component of the scattered radiation, which has the same wavelength λ_0 as the incident radiation, can be explained by assuming that it results from scattering by electrons so tightly bound that the entire atom recoils. In this case, the mass to be used in (1.43) is M, the mass of the entire atom, and since $M \gg m$, the Compton shift $\Delta\lambda$ is negligible. For the same reason, there is no Compton shift for light in the visible region because the photon energy in this case is not large compared with the binding energy of even the loosely bound electrons. In contrast, for very energetic γ-rays only the shifted line is observed, since the photon energies are large compared with the binding energies of even the tightly bound electrons.

The recoil electrons predicted by Compton's theory were observed in 1923 by W. Bothe and also by C. T. R. Wilson. A little later, in 1925, W. Bothe and H. Geiger demonstrated that the scattered photon and the recoiling electron appear simultaneously. Finally, in 1927, A. A. Bless measured the energy of the ejected electrons, which he found to be in agreement with the prediction of Compton's theory.

1.4 Atomic spectra and the Bohr model of the hydrogen atom

Isaac Newton was the first to resolve white light into separate colours by dispersion with a prism. However, it was not until 1752 that T. Melvill showed that light from

---

[8] The Ångström unit of length, abbreviated as Å, is such that 1 Å $= 10^{-10}$ m.

an incandescent gas is composed of a number of *discrete* wavelengths[9], now called *emission lines* because of the corresponding lines appearing on a photographic plate. Such *emission line spectra* are produced in particular when an electric discharge passes through a gas, or when a volatile salt is put into a flame, and the emitted light is dispersed by a prism. It was subsequently discovered that atoms also exhibit *absorption line spectra* when they are exposed to light having a continuous spectrum. For example, if white light is passed through an absorbing layer of an element and is then analysed with a spectrograph, it is found that the photographic plate is darkened everywhere, except for a number of unexposed lines. These lines must therefore correspond to certain *discrete* wavelengths missing from the continuous background, which have been absorbed by the atoms of the layer. In a crucial experiment performed in 1859, G. R. Kirchhoff showed that for a given element the wavelengths of the absorption lines coincide with those of the corresponding emission lines. He also understood that each element has its own *characteristic* line spectrum. This fact is of great importance, since it is the basis of chemical analysis by spectroscopic methods; it is also used in astrophysics to determine the presence of particular elements in the Sun, in the stars and in interstellar space.

A major discovery in the search for *regularities* in the line spectra of atoms was made in 1885 by J. Balmer, who studied the spectrum of atomic hydrogen. As seen from Fig. 1.10, in the visible and near ultraviolet regions this spectrum consists of a series of lines (denoted by H_α, H_β, H_γ, ...), now called the *Balmer series*; these lines come closer together as the wavelength decreases, and reach a limit at a wavelength $\lambda = 3646$ Å. There is an apparent regularity in this spectrum, and Balmer observed that the wavelengths of the nine lines known at the time satisfied the simple formula

$$\lambda = C\frac{n^2}{n^2-4} \tag{1.44}$$

where C is a constant equal to 3646 Å, and n is an integer taking on the values $3, 4, 5, \ldots$, for the lines H_α, H_β, H_γ, ... respectively. In 1889, J. R. Rydberg found that the lines of the Balmer series could be described in a more useful way in terms of the *wave number* $\tilde{\nu} = 1/\lambda = \nu/c$. According to Rydberg, the wave numbers of the Balmer lines are given by

$$\tilde{\nu} = R_{\mathrm{H}}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{1.45}$$

where $n = 3, 4, 5, \ldots$, and R_{H} is a constant, called the *Rydberg constant* for atomic hydrogen. Its value determined from spectroscopic measurements is

$$R_{\mathrm{H}} = 109\,677.58\ \mathrm{cm}^{-1}. \tag{1.46}$$

---

[9] This is in contrast to the continuous spectrum of electromagnetic radiation emitted from the surface of a hot solid, which we discussed in Section 1.1. Indeed, line spectra are emitted by atoms in rarefied gases, while in a solid there is a very large number of densely packed vibrating atoms, so that neighbouring spectral lines overlap, and as a result a continuous spectrum is emitted.

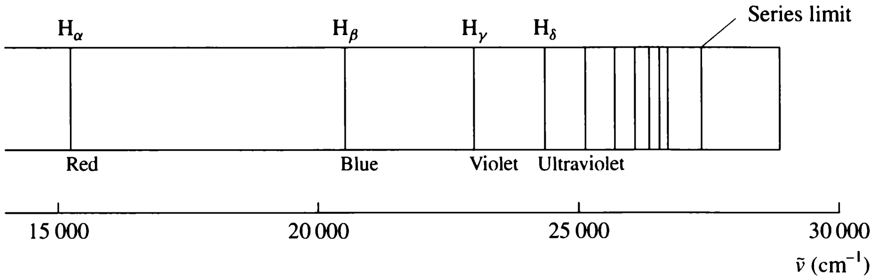


Figure 1.10 The Balmer series of atomic hydrogen.

Once it was written in the form (1.45), the Balmer–Rydberg formula could be easily generalised and applied to other series of atomic hydrogen spectral lines discovered subsequently in the ultraviolet and infrared regions. The generalised Balmer–Rydberg formula reads

$$\tilde{\nu}_{ab} = R_{\mathrm{H}}\left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right); \qquad \begin{aligned} n_a &= 1, 2, \ldots \\ n_b &= 2, 3, \ldots \end{aligned} \tag{1.47}$$

where $\tilde{\nu}_{ab}$ is the wave number of either an emission or an absorption line, and n_a and n_b are positive integers with $n_b > n_a$. A particular series of lines is obtained by setting n_a to be a fixed positive integer and letting n_b take on the values $n_a + 1, n_a + 2, \ldots$. The series are given different names after their discoverers. In particular, the series with $n_a = 1$ is known as the Lyman series and lies in the ultraviolet part of the spectrum; that with $n_a = 2$ is the Balmer series discussed above; the series with $n_a = 3, 4$ and 5 lie in the infrared region and are called, respectively, the Paschen, Brackett and Pfund series. Within each series the lines are labelled $\alpha, \beta, \gamma, \ldots$, in order of increasing wave number, as illustrated in Fig. 1.10 for the case of the Balmer series.

As seen from (1.47), the wave number $\tilde{\nu}_{ab}$ of a line in the atomic hydrogen spectrum can be expressed in the form

$$\tilde{\nu}_{ab} = T_a - T_b \tag{1.48}$$

that is as the difference of two *spectral terms*

$$T_a = R_{\mathrm{H}}/n_a^2, \qquad T_b = R_{\mathrm{H}}/n_b^2. \tag{1.49}$$

For other atoms than hydrogen the formula (1.48) can still be applied, although the spectral terms T_a and T_b usually have a more complicated form than (1.49). Thus, the wave number $\tilde{\nu}_{ab}$ of *any* line emitted or absorbed by an atom can be expressed as a difference of two spectral terms T_a and T_b. An atomic spectrum is therefore characterised by a *set* of spectral terms, called the *term system* of the atom. This generalisation of the Balmer–Rydberg formula was obtained in 1908 by W. Ritz. As a consequence, if the wave numbers of three spectral lines are associated with three terms as

$$\tilde{\nu}_{ij} = T_i - T_j, \qquad \tilde{\nu}_{jk} = T_j - T_k, \qquad \tilde{\nu}_{ik} = T_i - T_k \tag{1.50}$$

we have

$$\tilde{\nu}_{ik} = (T_i - T_j) + (T_j - T_k) = \tilde{\nu}_{ij} + \tilde{\nu}_{jk} \tag{1.51}$$

which is an example of the *Ritz combination principle.*

The existence of atomic line spectra, which exhibit the regularities discussed above, cannot be explained by models of atomic structure based on classical physics. As we shall shortly see, N. Bohr was able in 1913 to explain the spectrum of the hydrogen atom by introducing the quantum concept into the physics of atoms. In formulating his new theory, Bohr used a picture of the atom evolved from the work of E. Rutherford, H. W. Geiger and E. Marsden, which we now discuss briefly.

The nuclear atom

In a series of experiments Rutherford, Geiger and Marsden studied the scattering of alpha particles (doubly ionised helium atoms) by atoms of thin metallic foils[10]. To interpret the results of these experiments, Rutherford postulated in 1911 that all the positive charge and almost all the mass of an atom is concentrated in a positively charged *nucleus* of very small dimension ($\simeq 10^{-14}$ m) compared with the dimension of the atom as a whole ($\simeq 10^{-10}$ m). The predictions of Rutherford's theory of alpha-particle scattering, based on this *nuclear atom* model, were fully confirmed in 1913 by further experiments performed by Geiger and Marsden.

The excellent agreement between the experimental results and the conclusions reached by Rutherford was interpreted as establishing the correctness of the concept of the nuclear atom. However, there were still important difficulties with the nuclear atom model, due to the fact that there exists no stable arrangement of positive and negative point charges at rest. Therefore, one must consider a *planetary model* of the atom, in which the negatively charged electrons move in orbits in the Coulomb field of the positively charged nucleus. Now, a particle moving on a curved trajectory is accelerating, and an accelerated charged particle can be shown from electromagnetic theory to radiate, thus losing energy. In fact, the laws of classical physics, applied to the Rutherford planetary atom, imply that in a time of the order of 10^{-10} s all the energy of the revolving electrons would be radiated away and the electrons would collapse into the nucleus. This is clearly contrary to experiment and is another piece of evidence that the classical laws of motion must be modified on the atomic scale.

---

[10] A discussion of Rutherford scattering may be found in Bransden and Joachain (1983). See also Section 13.6.

Bohr's model of the hydrogen atom

A major step forward was taken by N. Bohr in 1913. Combining the concepts of Rutherford's nuclear atom, Planck's quanta and Einstein's photons, he was able to explain the observed spectrum of atomic hydrogen.

Bohr assumed, as in the Rutherford model, that an electron in an atom moves in an orbit about the nucleus under the influence of the electrostatic attraction of the nucleus. Circular or elliptical orbits are allowed by classical mechanics, and Bohr elected to consider circular orbits for simplicity. He then postulated that instead of the infinity of orbits which are possible in classical mechanics, only a certain set of stable orbits, which he called *stationary states* are allowed. As a result, atoms can only exist in certain allowed energy levels, with internal energies E_a, E_b, E_c, ... Bohr further postulated that an electron in a stable orbit does not radiate electromagnetic energy, and that radiation can only take place when a transition is made between the allowed energy levels. To obtain the frequency of the radiation, he made use of the idea that the energy of electromagnetic radiation is quantised and is carried by photons, each photon associated with the frequency ν carrying an energy $h\nu$. Thus, if a photon of frequency ν is absorbed by an atom, conservation of energy requires that[11]

$$h\nu = E_b - E_a \tag{1.52}$$

where E_a and E_b are the internal energies of the atom in the initial and final states, with $E_b > E_a$. Similarly, if the atom passes from a state of energy E_b to another state of lower energy E_a, the frequency of the emitted photon must be given by the *Bohr frequency relation* (1.52).

We note that because of the existence of an energy–frequency relationship, we can use frequency (or wave number) units of energy where convenient. For example, using (1.52) and the fact that the frequency ν corresponds to a wave number $\tilde{\nu} = \nu/c$, we find that one electronvolt of energy can be converted in hertz or in inverse centimetres as

$$\begin{aligned} 1\ \mathrm{eV} &\equiv 2.417\,97 \times 10^{14}\ \mathrm{Hz} \\ &\equiv 8065.48\ \mathrm{cm}^{-1}. \end{aligned} \tag{1.53}$$

Other conversions of units are given in the table at the end of the book. We also remark that the Bohr frequency relation (1.52) implies that the *terms* of spectroscopy can be interpreted as being the energies of the various allowed energy levels of the atom.

For the case of one-electron (also called hydrogenic) atoms[12], Bohr was able to modify the classical planetary model to obtain the quantisation of energy levels. To achieve this aim, he made the additional assumption that the magnitude of the orbital angular momentum of the electron moving in a circular orbit around the nucleus can

---

[11] We neglect here small recoil effects, which will be considered below.

[12] The word 'atom' denotes here a neutral atom (such as the hydrogen atom H) as well as an ion (such as He^+, Li^{2+} and so on).

only take one of the values $L = nh/2\pi = n\hbar$, where the *quantum number* n is a positive integer, $n = 1, 2, 3, \ldots$, and the commonly occurring quantity $h/2\pi$ is conventionally denoted by $\hbar$. The allowed energy levels of the bound system made up of a nucleus and an electron can then be determined in the following way.

Let us consider an electron moving with a non-relativistic velocity v in a circular orbit of radius r around the nucleus. We shall make the approximation (which we shall remove later) that the nucleus is infinitely heavy compared with the electron, and is therefore at rest. The Coulomb attractive force acting on the electron, due to its electrostatic interaction with the nucleus of charge Ze, can be equated with the electron mass m times the centripetal acceleration (v^2/r), giving

$$\frac{Ze^2}{(4\pi\varepsilon_0)r^2} = \frac{mv^2}{r}, \tag{1.54}$$

where ε_0 is the permittivity of free space. A second equation is obtained from Bohr's postulate that the magnitude of the orbital angular momentum of the electron is quantised:

$$L = mvr = n\hbar, \qquad n = 1, 2, 3, \ldots . \tag{1.55}$$

From (1.54) and (1.55), we obtain the allowed values of v and r

$$v = \frac{Ze^2}{(4\pi\varepsilon_0)\hbar n} \tag{1.56}$$

and

$$r = \frac{(4\pi\varepsilon_0)\hbar^2 n^2}{Zme^2}. \tag{1.57}$$

The total energy of the electron is the sum of its kinetic energy and its potential energy. The kinetic energy, T, is given by

$$T = \frac{1}{2}mv^2 = \frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2} \tag{1.58}$$

where we have used the result (1.56). Choosing the zero of the energy scale in such a way that the electron has a total energy $E = 0$ when it is at rest and completely separated from the nucleus ($r = \infty$), the potential energy of the electron is given by $V = -Ze^2/(4\pi\varepsilon_0)r$. Hence, using (1.57) we have

$$V = -\frac{Ze^2}{(4\pi\varepsilon_0)r} = -\frac{m}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2}. \tag{1.59}$$

The allowed values obtained by Bohr for the total energy $T + V$ of the bound electron are thus given by

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2}, \qquad n = 1, 2, 3, \ldots . \tag{1.60}$$

Since n may take on all integral values from 1 to $+\infty$, the *energy spectrum* corresponding to the bound states of the one-electron atom contains an infinite number of *discrete* energy levels. The subscript n in E_n reminds us that this *quantisation of the energy levels* is due to the presence of the quantum number n, is called the *principal quantum number* to distinguish it from other quantum numbers we shall meet later. The state with the lowest energy is known as the *ground state*; we see from (1.60) that it corresponds to the value $n = 1$. The states corresponding to the values $n = 2, 3, \dots,$ are called *excited states* of the atom, since their energies are greater that the energy of the ground state; the energies of the excited states are seen to converge to the value zero as $n \to \infty$. A commonly used notation is one in which an electron in an energy level with $n = 1, 2, 3, \dots,$ is said to be in the K, L, M, ..., shell, respectively.

It is convenient to represent graphically the energy spectrum of an atom by means of an *energy level diagram*, in which the ordinate gives the energy, and the energy levels or terms are drawn as horizontal lines. Fig. 1.11 shows the energy level diagram of atomic hydrogen, drawn according to the prediction (1.60) of the Bohr model. The energy scale on the right is in electronvolts; on the left another scale, increasing from top to bottom, gives the wave number $\tilde{\nu}$ in cm^{-1}.

Using the Bohr frequency relation (1.52), the frequencies of the spectral lines corresponding to transitions between two energy levels E_a and E_b are

$$\nu_{ab} = \frac{m}{4\pi\hbar^3}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right) \tag{1.61}$$

where n_a and n_b are positive integers and $n_b > n_a$; the corresponding wave numbers are given by $\tilde{\nu}_{ab} = \nu_{ab}/c$. For the case of atomic hydrogen, where $Z = 1$, we have therefore

$$\tilde{\nu}_{ab} = R(\infty)\left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right) \tag{1.62}$$

where the constant $R(\infty)$ is given by

$$R(\infty) = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \tag{1.63}$$

and we have written $R(\infty)$ to recall that we are using the infinite nuclear mass approximation. The theoretical result (1.62) is seen to have exactly the same form as the empirical Balmer–Rydberg formula (1.47). Moreover, Bohr's theory also gives the value of $R(\infty)$ in terms of fundamental constants, and this value can be compared with the experimental Rydberg constant R_{H} appearing in (1.47). Evaluating $R(\infty)$ from (1.63) one finds that $R(\infty) = 109\,737$ cm^{-1}, in good (but not perfect) agreement with the experimental value of R_{H} given by (1.46).

Returning to equation (1.60), we see that the Bohr energy levels of a one-electron atom may be written as

$$E_n = -I_{\text{P}}/n^2, \qquad n = 1, 2, 3, \dots \tag{1.64}$$

where

$$I_{\text{P}} = \frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 = hcR(\infty)Z^2 = 13.6\ Z^2\ \text{eV}. \tag{1.65}$$

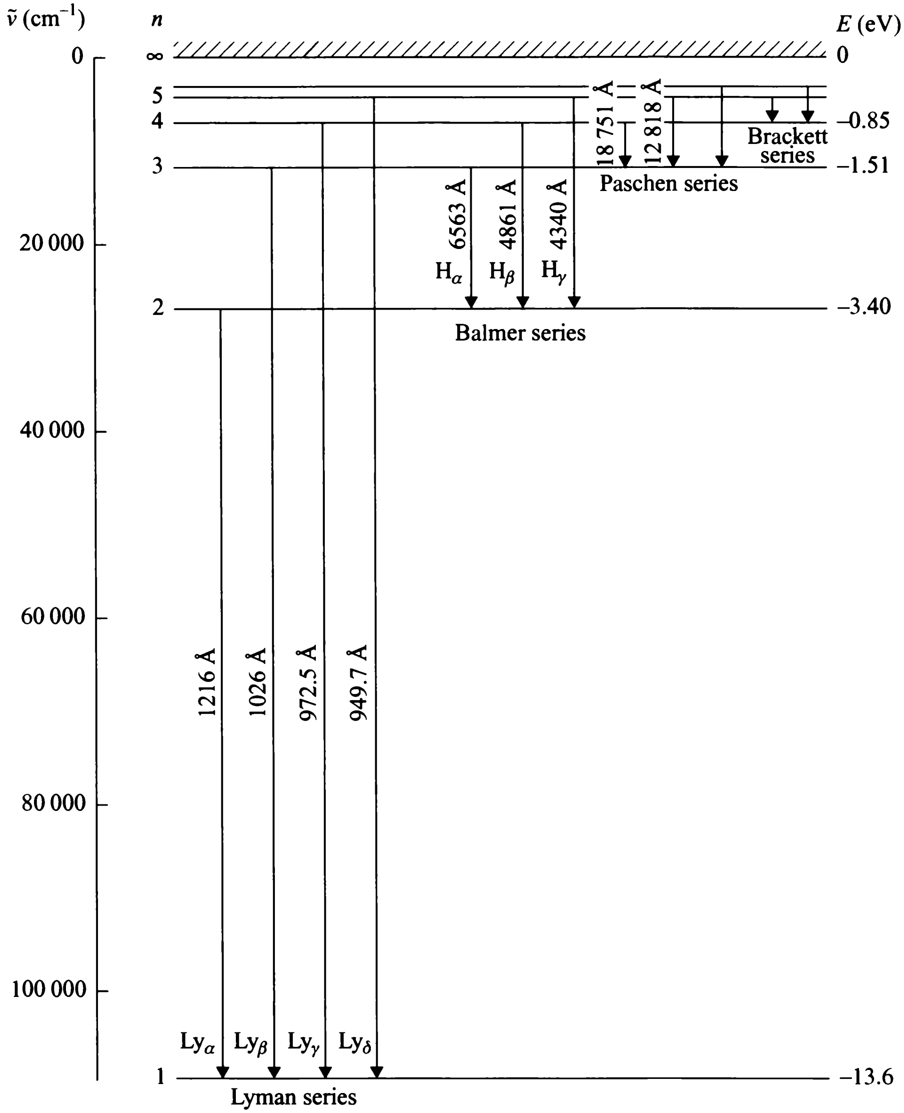


Figure 1.11 Energy level diagram of the hydrogen atom. The energy scale on the right is in electronvolts; on the left another scale, increasing from top to bottom, gives the wave number $\tilde{\nu}$ in cm^{-1}. The principal quantum number n corresponding to each energy level is also indicated. A spectral line, resulting from the transition of the atom from one energy level to another is represented by a vertical line joining the two energy levels. The numbers against the lines indicate the corresponding wavelengths in ångströms (1 Å = 10^{-10} m). For clarity, only transitions between lower-lying levels are shown.

Because the zero of the energy scale has been chosen so that it corresponds to an electron at rest, infinitely far from the nucleus, the (positive) amount of work required to remove the electron from its nth orbit to infinity (that is, to *ionise* the atom) is just $-E_n = I_P/n^2$. The energy needed to remove one electron from an atom in its ground state is called the *ionisation potential* of the atom. Since the ground state of one-electron atoms corresponds to the value $n = 1$, we see that the quantity I_P given by (1.65) is the value of the ionisation potential of hydrogenic atoms predicted by the Bohr theory (in the infinite nuclear mass approximation). The ionisation of atoms may occur in several ways, for example in collision processes or when a photon of sufficiently high frequency is absorbed by the atom. The latter phenomenon is known as *photoionisation* and is the process responsible for the photoelectric effect.

It is interesting to note that if the atom is initially in a bound state of (negative) energy E_n, and then absorbs an energy greater than the *binding energy* $|E_n|$, it will be ionised and the ejected electron will have a *positive energy*. States of positive energy therefore correspond to the situation in which the nucleus–electron system is *unbound*. It is clear that these states are relevant in *collision* processes between electrons and nuclei. In such a collision event, an electron having a given initial kinetic energy and coming from a very large distance is scattered by a nucleus and after being deflected recedes to an infinite separation without forming a bound system with the nucleus. Since the initial kinetic energy of the electron may be chosen arbitrarily, it is obvious that unbound states of the nucleus–electron system may have any positive energy value. Therefore, joining the bound state spectrum of one-electron atoms at the value $E = 0$, there is a *continuous* energy spectrum extending from $E = 0$ to $E = +\infty$, which is indicated in Fig. 1.11 by hatchings. Transitions may thus occur not only between two bound states of the discrete energy spectrum (bound–bound transitions), but also between a state of the discrete spectrum and one of the continuous spectrum (bound–free transitions), or between two states of the continuous spectrum (free–free transitions).

Let us now evaluate a few key quantities which appear in Bohr's theory. The radius of the orbit of the electron in the ground state of the hydrogen atom is known as the (first) Bohr radius of hydrogen and is denoted by a_0. It is obtained by setting $Z = n = 1$ in (1.57) so that

$$a_0 = \frac{(4\pi\varepsilon_0)\hbar^2}{me^2} = 5.29 \times 10^{-11}\ \text{m}. \tag{1.66}$$

The velocity v_0 of the electron in the first Bohr orbit of the hydrogen atom is seen from (1.56) to be given by

$$v_0 = \frac{e^2}{(4\pi\varepsilon_0)\hbar} = \alpha c \tag{1.67}$$

where we have introduced the dimensionless constant

$$\alpha = \frac{e^2}{(4\pi\varepsilon_0)\hbar c} \tag{1.68}$$

which is known as the *fine-structure constant* and has the value $\alpha \simeq 1/137$. Thus $v_0 \simeq c/137$ and it is reasonable to treat the electron of an hydrogen atom in a non-relativistic way, as done by Bohr. We also remark in this context that the bound-state energies (1.60) of one-electron atoms may be rewritten as

$$E_n = -\frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2}. \tag{1.69}$$

Thus, provided Z is not too large, the binding energies $|E_n|$ are small with respect to mc^2, the rest energy of the electron; this again indicates that a non-relativistic treatment of the problem is a sensible approximation.

Finite nuclear mass

Although the approximation in which the nucleus is assumed to be infinitely heavy is good enough for many purposes, an improvement can be made by taking into account the fact that the mass of the nucleus is finite. If we consider a bound state of the nucleus–electron system in the Bohr model, then both the electron of mass m and the nucleus of mass M rotate about the centre of mass of the system. Since no forces external to the atom are present, the centre of mass will either be at rest or in uniform motion. As we are not interested in the motion of the atom as a whole, we shall take the centre of mass to be at rest and to be the origin of our coordinate system.

The magnitude of the total orbital angular momentum of the system is readily shown to be[13]

$$L = \mu v r \tag{1.70}$$

where r is the distance between the nucleus and the electron, v is the velocity of the electron with respect to the nucleus and

$$\mu = \frac{mM}{m + M} \tag{1.71}$$

is the *reduced mass*. Bohr's quantisation condition for the orbital angular momentum thus becomes

$$L = \mu v r = n\hbar, \qquad n = 1, 2, 3, \dots \tag{1.72}$$

which is the same as (1.55), but with μ replacing m.

Since the centre of mass is at rest in our coordinate system, the kinetic energy of the system is given by $T = \mu v^2/2$. The potential energy V, due to the electrostatic attraction between the nucleus and the electron, is of course still given by $V = -Ze^2/(4\pi\varepsilon_0)r$, since it does not depend on the masses of the particles. A

---

[13] See, for example, Bransden and Joachain (1983).

reasoning entirely similar to that made above in the infinite nuclear mass case then yields for the allowed energy levels of the bound nucleus–electron system

$$E_n = -\frac{\mu}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2} \tag{1.73}$$

which is the result (1.60) with m replaced by μ. Similarly, the allowed values of r are given by (1.57) with again μ replacing m,

$$r = \frac{(4\pi\varepsilon_0)\hbar^2 n^2}{Z\mu e^2} = \frac{n^2}{Z}\frac{m}{\mu}a_0 = \frac{n^2}{Z}a_\mu \tag{1.74}$$

where $a_\mu = (m/\mu)a_0$ is the *modified Bohr radius.*

As a consequence of the finite mass correction, the calculated value of the Rydberg constant becomes

$$R(M) = \frac{\mu}{m}R(\infty) = \frac{1}{1+(m/M)}R(\infty). \tag{1.75}$$

For atomic hydrogen the nuclear mass M is equal to M_P, the proton mass, and the corresponding theoretical value of $R(M_\mathrm{P})$ is 109 681 cm^{-1}, which agrees with the experimental value (1.46) to better than four parts in 10^5.

Because of the nuclear mass effect all the frequencies of the spectral lines of one-electron atoms are reduced by the factor $\mu/m = (1 + m/M)^{-1}$ with respect to their values calculated in the infinite nuclear mass approximation. As a result, there is an *isotopic shift* between the spectral lines of different isotopes[14]. For example, there is such a shift between the spectral lines of ordinary hydrogen (proton + electron) and those of its heavy isotope, deuterium. The nucleus of the deuterium atom, called the *deuteron*, contains a proton and a neutron, and hence has $Z = 1$ and a mass $M \simeq 2M_\mathrm{P}$. The ratio of frequencies of corresponding lines in deuterium and 'ordinary' hydrogen is 1.000 27, which is easily detectable. In fact, it is through this isotopic shift that deuterium was discovered.

Another consequence of the fact that the mass of the nucleus is finite is that the *recoil* of the atom must be taken into account when using the Bohr frequency relation (1.52). This is readily done by using momentum and energy conservation. Let us consider the emission or absorption of a photon of energy $h\nu$ by an atom initially at rest. After the transition, the atom recoils with a momentum $\mathbf{P}$ whose magnitude P is equal to the magnitude $h\nu/c$ of the photon momentum, and with a kinetic energy $P^2/2M = (h\nu)^2/2Mc^2$, where M is the mass of the atom (which is essentially equal to the mass of the nucleus). If ν_0 denotes the frequency of the transition uncorrected for the recoil effect, conservation of energy yields for the fractional change in the frequency due to recoil (Problem 1.21)

$$\frac{\Delta\nu_\mathrm{R}}{\nu} = \pm\frac{h\nu}{2Mc^2} \tag{1.76}$$

---

[14] We recall that isotopes are atoms of the same chemical element having different atomic masses. The nuclei of different isotopes contain the same number Z of protons, and hence have the same atomic number Z; they differ by their number of neutrons, N, so that they have different mass numbers $A = N + Z$.

where $\Delta\nu_R = \nu - \nu_0$, the plus sign corresponding to the absorption and the minus sign to the emission of a photon. Now, $2Mc^2$ is at least of the order of 10^9 eV (for a proton, $M_P c^2 \simeq 9.4 \times 10^8$ eV), so that for atomic transitions involving photons having energies $h\nu$ of a few electronvolts we find that $\Delta\nu_R/\nu \simeq 10^{-9}$, which is extremely small. Nevertheless, equation (1.76) does seem to imply that the atomic absorption spectrum of an atom is not completely identical to its emission spectrum, so that photons emitted by an atom could not be absorbed by another atom of the same kind, in contradiction with experiment. This apparent paradox will be resolved in Chapter 2, when we discuss the Heisenberg uncertainty relation for time and energy.

Limitation of the Bohr model

Although the Bohr model is successful in predicting the energy levels of one-electron atoms, and the idea of energy quantisation in atoms is correct, the model is unsatisfactory in many respects. Indeed, Bohr's theory is a hybrid one combining principles taken over from classical theory with new postulates breaking sharply with classical physics. For example, the stability problem is bypassed by postulating that an electron in one of the allowed stationary orbits does not radiate electromagnetic energy, and the quantisation of angular momentum is introduced in an *ad hoc* way. The hypothesis that only circular orbits are allowed is also arbitrary. Moreover, despite the fact that it provided an explanation of the regularities in X-ray spectra observed by Moseley in 1913[15], the Bohr model cannot be generalised to deal with atomic systems containing two or more electrons. Among other objections are the lack of a reliable method to calculate the rate of transitions between the different energy levels when radiation is emitted or absorbed, and the inability to handle unbound systems. In later work, W. Wilson and A. Sommerfeld showed how to remove the restriction to circular orbits, and Sommerfeld also obtained relativistic corrections to the Bohr model. However, the other objections still persisted and the theory – now called the *old quantum theory* – was eventually superseded by the quantum mechanics developed by E. Schrödinger, W. Heisenberg, P. A. M. Dirac and others, following the ideas of L. de Broglie.

The Bohr correspondence principle

In 1923, Bohr formulated a heuristic principle which had already inspired the development of the old quantum theory, and which proved to be of great help in the early development of quantum mechanics. This principle, known as the *correspondence principle*, states that *quantum theory results must tend asymptotically to those obtained from classical physics in the limit of large quantum numbers.* In other words, classical physics results are 'macroscopically correct' and may be considered as limiting cases of quantum mechanical results when the quantum discontinuities may be neglected.

As an illustration of the correspondence principle, let us consider the Bohr model for one-electron atoms, and compute the frequency of the radiation emitted in a

---

[15] See Bransden and Joachain (1983).

transition from the energy level E_n to that immediately below, E_{n-1}, when n is large. Assuming for simplicity that the nuclear mass is infinite, we find from (1.61) that this frequency is given by

$$\nu = \frac{m}{4\pi\hbar^3}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\left[\frac{1}{(n-1)^2} - \frac{1}{n^2}\right]. \qquad \textbf{(1.77)}$$

Now, when $n \gg 1$, one has $(n-1)^{-2} - n^{-2} \simeq 2n^{-3}$ and therefore, for large n,

$$\nu \simeq \frac{m}{2\pi\hbar^3}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{1}{n^3}. \qquad \textbf{(1.78)}$$

On the other hand, in classical physics, an electron moving in a circular orbit of radius r with a velocity v would be expected to radiate with the frequency of its rotational motion, namely $\nu_{\mathrm{cl}} = v/(2\pi r)$. Using the expressions (1.56) and (1.57) for v and r, we find that

$$\nu_{\mathrm{cl}} = \frac{v}{2\pi r} = \frac{m}{2\pi\hbar^3}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{1}{n^3} \qquad \textbf{(1.79)}$$

in agreement with (1.78).

The Franck and Hertz experiment

As we have seen above, the bound-state energies of atoms are quantised, so that only certain discrete energy values are allowed. This *energy quantisation of atoms* was confirmed directly by an experiment performed in 1914 by J. Franck and G. Hertz. A schematic diagram of the apparatus is shown in Fig. 1.12. In an evacuated tube, electrons are ejected from a heated cathode C and accelerated toward a wire grid G, maintained at a positive potential V_1 with respect to the cathode. The electrons accelerated by the potential V_1 attain a kinetic energy $mv^2/2 = eV_1$. Some of them pass through the grid and are collected by a plate P, thus causing a current I to flow in the collector circuit. The collector P is at a slightly lower potential V_2 than the grid, $V_2 = V_1 - \Delta V$, where $\Delta V \ll V_1$. The small retarding potential ΔV between the grid G and the collector P has the effect of reducing the kinetic energy of the electrons slightly, but not enough to stop them being collected.

The tube is now filled with mercury vapour. The electrons collide with the atoms of mercury, and if the collisions are elastic, so that there is no transfer of energy from the electrons to the internal structure of the atoms, the current I will be unaffected by the introduction of the gas. This follows because mercury atoms are too heavy to gain appreciable kinetic energy when struck by electrons. The electrons are deflected but retain the same kinetic energy. In contrast, if an electron makes an inelastic collision with a mercury atom in which it loses an energy E, exciting the mercury atom to a level of greater internal energy, then its final kinetic energy will be $mv_{\mathrm{f}}^2/2 = (eV_1 - E)$. If eV_1 is equal to E, or is only a little larger, the retarding potential ΔV will be sufficient to prevent this electron from reaching the collecting plate, and hence from contributing to the current I.

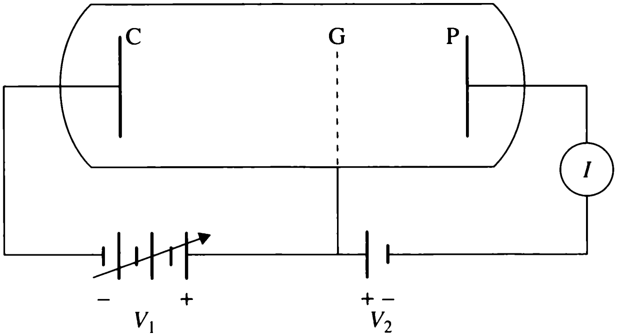


Figure 1.12 Schematic diagram of the Franck and Hertz experiment.

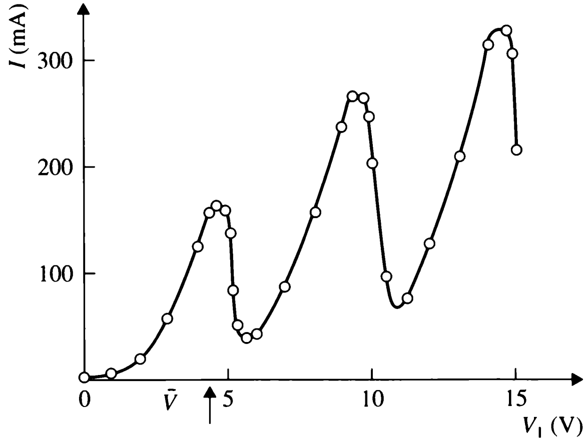


Figure 1.13 The variation of the current I as a function of the accelerating voltage V_1 in the Franck and Hertz experiment.

The experiment is carried out by gradually increasing V_1 from zero and measuring the current I as a function of V_1. The result obtained is illustrated in Fig. 1.13. The current I is seen to fall sharply at a potential $\bar{V}$, which for mercury is equal to 4.9 V. The results can be interpreted by supposing that the first excited level of the mercury atom has an energy about 4.9 eV higher than the ground state level. Thus, when the colliding electrons have an energy $eV_1 < 4.9$ eV, they cannot excite the mercury atoms to a level of higher internal energy, so that the collisions are elastic. On the contrary, when eV_1 reaches the value 4.9 eV, a large number of the colliding electrons excite mercury atoms to this level, losing their energy in the process; as a result the current I is sharply reduced.

If the voltage V_1 is further increased, the observed current I is seen to exhibit additional increases followed by sharp dips. Some of these dips are due to the excitation of higher discrete levels of the mercury atoms. Other dips arise from the fact that some colliding electrons have sufficient energy to excite two or more atoms to the first excited state, so that they lose 4.9 eV of energy more than once; such dips corresponding to multiple excitations of the first excited level are seen every 4.9 eV.

We have noted before (see (1.53)) that an energy of 1 eV corresponds to a wave number of 8065 cm^{-1}, so that if the above interpretation of the Franck and Hertz experiment is correct, a line would be expected in the mercury spectrum corresponding to a transition from the first excited state at 4.9 eV to the ground state, with a wave number of $4.9 \times 8065\ \text{cm}^{-1} \simeq 39\,500\ \text{cm}^{-1}$. Franck and Hertz were indeed able to verify the existence of such a line, and to show that radiation of this wave number was only emitted from the mercury vapour when V_1 exceeded 4.9 eV.

The Franck–Hertz experiment, and corresponding experiments using other gases and vapours, provide excellent confirmation of the discrete nature of bound-state energy levels of atoms. It can also be verified that when sufficient energy is available to ionise an atom, the energy of the ejected electron can take any positive value. Therefore, *the energy level spectrum of an atom consists of two parts: discrete negative energies corresponding to bound states and a continuum of positive energies corresponding to unbound (ionised) states.*

1.5 The Stern–Gerlach experiment. Angular momentum and spin

We shall now discuss another experiment of fundamental importance, carried out by O. Stern and W. Gerlach in 1922, to measure the magnetic dipole moments of atoms. The results demonstrated, once more, the inability of classical mechanics to describe atomic phenomena and confirmed the necessity of a quantum theory of angular momentum, which had been suggested by Bohr's model.

Let us first understand how an atom comes to possess a magnetic moment. In the Bohr model of a hydrogenic atom, an electron occupies a circular orbit, rotating with an orbital angular momentum **L**. A moving charge is equivalent to an electric current, so that an electron moving in a closed orbit forms a current loop, and this in turn creates a magnetic dipole[16]. In fact, whatever model of atomic structure we make, the electrons can be expected to possess angular momentum and accordingly atoms possess magnetic moments.

A circulating current of magnitude I enclosing a small plane area dA gives rise to a magnetic dipole moment

$$\boldsymbol{\mathcal{M}} = I\,\mathrm{d}\mathbf{A} \tag{1.80}$$

where the direction of $\boldsymbol{\mathcal{M}}$ is along the normal to the plane of the current loop, as shown in Fig. 1.14. When the current I is due to an electron moving with a velocity v in a circle of radius r, it is given by

$$I = \frac{ev}{2\pi r}. \tag{1.81}$$

---

[16] See, for example, Duffin (1968).

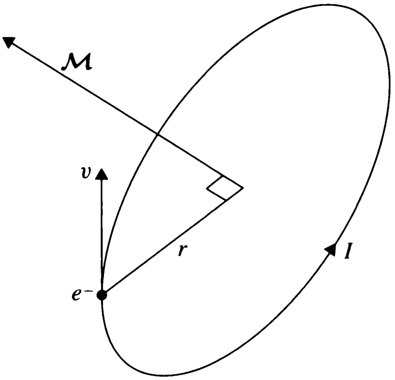


Figure 1.14 The magnetic dipole moment due to a current loop.

Since the area enclosed is πr^2, we have $\mathcal{M} = evr/2 = eL/2m$, and as the direction of the current is opposite to the direction of rotation of the electron,

$$\boldsymbol{\mathcal{M}} = -\frac{e}{2m}\mathbf{L} \tag{1.82}$$

where $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is the orbital angular momentum of the electron, $\mathbf{p} = m\mathbf{v}$ being its (linear) momentum. The Bohr quantisation rule (1.55) suggests that $\hbar$ is a natural unit of angular momentum, so that we shall rewrite equation (1.82) as

$$\boldsymbol{\mathcal{M}} = -\mu_{\mathrm{B}}(\mathbf{L}/\hbar) \tag{1.83}$$

where

$$\mu_{\mathrm{B}} = \frac{e\hbar}{2m}. \tag{1.84}$$

Because $(L/\hbar)$ is dimensionless, μ_{B} has the dimensions of a magnetic moment. It is known as the *Bohr magneton* and has the numerical value

$$\mu_{\mathrm{B}} = 9.27 \times 10^{-24}\ \mathrm{J\,T^{-1}} \tag{1.85}$$

where J denotes a joule and T a tesla.

Interaction with a magnetic field

If an atom with a magnetic moment $\boldsymbol{\mathcal{M}}$ is placed in a magnetic field $\boldsymbol{\mathcal{B}}$, the (potential) energy of interaction is (see Duffin, 1968)

$$W = -\boldsymbol{\mathcal{M}} \cdot \boldsymbol{\mathcal{B}}. \tag{1.86}$$

The system experiences a torque $\boldsymbol{\Gamma}$, where

$$\boldsymbol{\Gamma} = \boldsymbol{\mathcal{M}} \times \boldsymbol{\mathcal{B}} \tag{1.87}$$

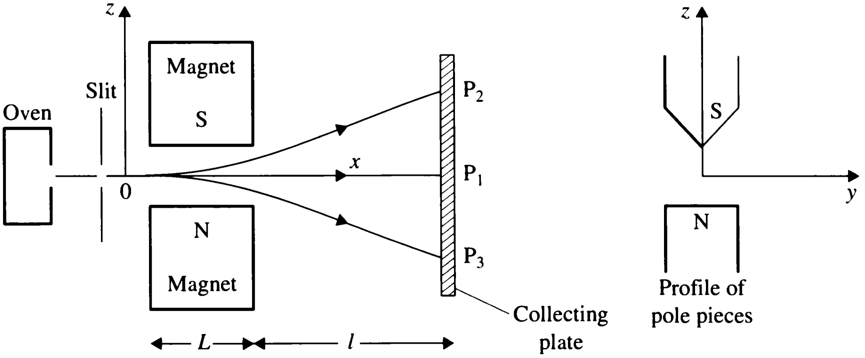


Figure 1.15 The Stern–Gerlach apparatus.

and a net force **F**, where

$$\mathbf{F} = -\nabla W. \tag{1.88}$$

Combining (1.86) with (1.88), we see that the components of **F** are

$$F_x = \mathcal{M}\cdot\frac{\partial \mathcal{B}}{\partial x}, \qquad F_y = \mathcal{M}\cdot\frac{\partial \mathcal{B}}{\partial y}, \qquad F_z = \mathcal{M}\cdot\frac{\partial \mathcal{B}}{\partial z}. \tag{1.89}$$

If the magnetic field is uniform, no net force is experienced by a magnetic dipole, which precesses with a constant angular frequency. For an orbiting electron this angular frequency is

$$\omega_{\mathrm{L}} = \frac{\mu_{\mathrm{B}}}{\hbar}\mathcal{B}. \tag{1.90}$$

It is called the *Larmor angular frequency*. On the other hand, in an inhomogeneous magnetic field, an atom experiences a net force proportional to the magnitude of the magnetic moment.

The Stern–Gerlach experiment

In 1921, Stern suggested that magnetic moments of atoms could be measured by detecting the deflection of an atomic beam by such an inhomogeneous field. The experiment was carried out a year later by Stern and Gerlach. The apparatus is shown in schematic form in Fig. 1.15.

The first experiments were made using atoms of silver. A sample of silver metal is vaporised in an oven and a fraction of the atoms, emerging from a small hole, is collimated by a system of slits so that it enters the magnetic field region as a narrow and nearly parallel atomic beam. This beam is then passed between the poles of a magnet shaped to produce an inhomogeneous field, as shown in Fig. 1.15. Finally, the beam is detected by allowing it to fall on a cool plate. The density of the deposit is proportional to the intensity of the beam and to the length of time for which the

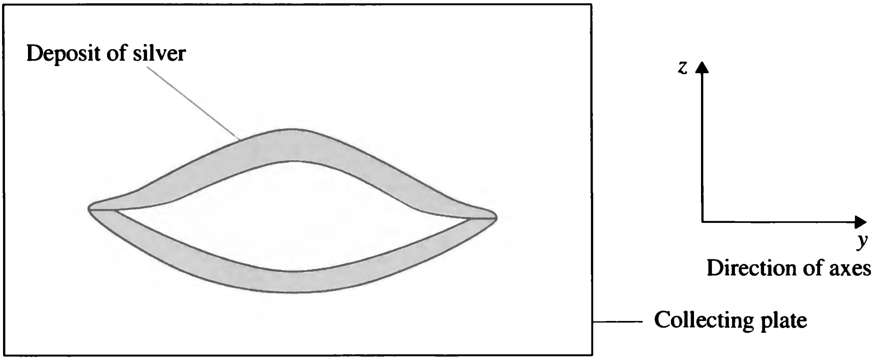


Figure 1.16 Results of the Stern–Gerlach experiment for silver. The atomic beam is split into two components having nearly equal and opposite deflections along the *z*-axis. Only in the centre is the field gradient sufficient to cause the splitting. The pattern is smeared because of the range of velocities of atoms in the beam. The shape of the upper line results from the greater inhomogeneity of the magnetic field near the upper-pole face.

beam falls on the plate. An important requirement for performing such an atomic beam experiment is a good vacuum, which allows the atoms of the beam to travel through the apparatus with a negligible probability of colliding with a molecule of the residual gas.

Taking the shape of the magnets as shown in Fig. 1.15, the force on each atom is given from (1.89) by

$$F_x = \mathcal{M}_z \frac{\partial \mathcal{B}_z}{\partial x}, \qquad F_y = \mathcal{M}_z \frac{\partial \mathcal{B}_z}{\partial y}, \qquad F_z = \mathcal{M}_z \frac{\partial \mathcal{B}_z}{\partial z}. \tag{1.91}$$

The magnet is symmetrical about the xz plane, and the beam is confined to this plane. It follows that $\partial \mathcal{B}_z/\partial y = 0$. Also, apart from edge effects, $\partial \mathcal{B}_z/\partial x = 0$, so that the only force on the atoms in the beam is in the z direction.

In the incident beam, the direction of the magnetic moment $\boldsymbol{\mathcal{M}}$ of the atoms is completely at random, and in the z direction it would be expected that every value of $\mathcal{M}_z$ such that $-\mathcal{M} \leqslant \mathcal{M}_z \leqslant \mathcal{M}$ would occur, with the consequence that the deposit on the collecting plate would be spread continuously over a region symmetrically disposed about the point of no deflection. The surprising result that Stern and Gerlach obtained in their experiments with silver atoms was that *two distinct* and *separate* lines of spots were formed on the plate (see Fig. 1.16), symmetrically about the point of no deflection. Similar results were found for atoms of copper and gold, and in later work for sodium, potassium, caesium and hydrogen.

The quantisation of the component of the magnetic moment along the direction defined by the magnetic field is termed *space quantisation*. This implies that the component of the angular momentum in a certain direction is quantised so that it can only take certain values. In general, for each type of atom, the values of $\mathcal{M}_z$ will range from $(\mathcal{M}_z)_{\text{max}}$ to $-(\mathcal{M}_z)_{\text{max}}$ and, correspondingly, L_z will range from $-(L_z)_{\text{max}}$ to $(L_z)_{\text{max}}$. If we denote the observed multiplicity of values of $\mathcal{M}_z$ (and hence L_z) by α, we can try to interpret α and to deduce the allowed values of L by using the Bohr model. Indeed, the Bohr quantisation of angular momentum suggests that orbital angular momentum only occurs in integral units of $\hbar$. We may postulate that the magnitude of orbital angular momentum can only take values $L = l\hbar$, where l is a positive integer or zero. Thus the maximum value of L_z is $+l\hbar$, and its minimum value is $-l\hbar$. If L_z is also quantised in the form

$$L_z = m\hbar \tag{1.92}$$

where m is a positive or negative integer or zero, then m must take on the values $-l, -l+1, \dots, l-1, l$, and the multiplicity α must be equal to $(2l+1)$. The number m is known as a *magnetic quantum number*. In fact, as we shall see in Chapter 6, the result (1.92) turns out to be correct in quantum mechanics, but the possible values of the total orbital angular momentum will be shown to be of the form $L = \sqrt{l(l+1)}\hbar$ with $l = 0, 1, 2, \dots$, rather than of the form $L = l\hbar$ suggested by the Bohr model. However the results of Stern and Gerlach for silver do not fit with this scheme, since the multiplicity of values of the z component of the angular momentum for silver is $\alpha = 2$. This implies that $(2l+1) = 2$, giving $l = \frac{1}{2}$, which is a non-integral value.

Electron spin

The explanation of this result for silver came in 1925, when S. Goudsmit and G. E. Uhlenbeck analysed the splitting of spectral lines occurring when atoms are placed in a magnetic field (the Zeeman effect). They showed that this splitting could be explained if electrons, in addition to the magnetic moment produced by orbital motion, were assumed to possess an *intrinsic magnetic moment* $\boldsymbol{\mathcal{M}}_s$, where the component of $\boldsymbol{\mathcal{M}}_s$ in a given direction can take only the two values $\pm\mathcal{M}_s$. One can postulate that this intrinsic magnetic moment is due to an *intrinsic angular momentum*, or *spin* of the electron, which we denote by $\mathbf{S}$. By analogy with (1.83), we then have

$$\boldsymbol{\mathcal{M}}_s = -g_s\mu_B(\mathbf{S}/\hbar) \tag{1.93}$$

where g_s is the *spin gyromagnetic ratio*. If we introduce a *spin quantum number s*, analogous to l, so that the multiplicity of the spin component in a given direction is $(2s+1)$, then for an electron we must have $s = \frac{1}{2}$, and the possible values of the component S_z of the electron spin $\mathbf{S}$ in the z direction are $\pm\hbar/2$; the magnitude S of the electron spin will be shown in Chapter 6 to be given by $S = \sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$.

Since the magnetic moment of an electron is due partly to its orbital angular momentum and partly to its spin angular momentum, we can use equations (1.83) and (1.93) to write this (total) magnetic moment as

$$\boldsymbol{\mathcal{M}} = -\mu_B(\mathbf{L} + g_s\mathbf{S})/\hbar. \tag{1.94}$$

Accurate measurements have shown that the electron spin gyromagnetic ratio g_s is very nearly equal to 2.

The discovery of the spin of the electron is of fundamental importance. In fact, it is now known that all particles can be assigned an intrinsic angular momentum (spin), and therefore a spin quantum number s. In some cases, such as the pion (π-meson), $s = 0$, but in others, such as the electron, the proton and the neutron one has $s = 1/2$, and for other 'elementary particles' the spin quantum number may be $s = 1, s = \frac{3}{2}, \ldots$. The theory of the spin angular momentum will be discussed in Chapter 6.

Total angular momentum

The total angular momentum of an atom is obtained by adding vectorially all angular momenta of the particles it contains. Because the mass of the nucleus is much larger than the electron mass, the angular momentum of the nucleus leads to very small hyperfine effects which we shall neglect here. We therefore consider only the angular momenta of the electrons in the atom. By adding vectorially all the orbital and spin angular momenta of these electrons, we obtain the total electronic angular momentum, which we denote by $\mathbf{J}$. A measurement of the component of $\mathbf{J}$ in a given direction (which we call the z direction) can only yield $(2j + 1)$ possible values, given by $m_j \hbar$, where the *magnetic quantum number* m_j can only take the values $-j, -j+1, \ldots, j-1, j$. Thus j is the maximum possible value of a component of $\mathbf{J}$, measured in units of $\hbar$, in any given direction. It is found that j can take integral or half-odd-integral values only; $j = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$. For an angular momentum whose component in a given direction has the multiplicity $(2j + 1)$, a measurement of the magnitude of the angular momentum produces the value $\sqrt{j(j+1)}\hbar$. Thus, in a Stern–Gerlach experiment, a beam of atoms with angular momentum of magnitude $\sqrt{j(j+1)}\hbar$ will produce $(2j+1)$ lines of spots on the detecting screen, symmetrically disposed about the point of zero deflection. The Stern–Gerlach results for silver atoms can then be explained if we assume that the orbital angular momentum of a silver atom is zero, but its spin angular momentum is equal to the spin of an electron, so that in this case $j = s = \frac{1}{2}$ and *two* lines of spots will appear on the screen. Similar experiments carried out with other atoms have confirmed the central features which emerge from the Stern–Gerlach experiment: *the quantisation of the z component of angular momentum* and *the existence of the electron spin*[17].

1.6 De Broglie's hypothesis. Wave properties of matter and the genesis of quantum mechanics

We have seen before that in addition to its classical wave properties, electromagnetic radiation also exhibits particle characteristics, as in the photoelectric effect and in the Compton effect. This dual nature of electromagnetic radiation, which is one of

---

[17] It should be noted that experiments of the Stern–Gerlach type cannot be performed directly on beams of electrons because of the deflection of the beam due to the Lorentz force.

the most striking features due to the appearance of quanta in physics, was generally recognised, although not understood, around 1923. On the other hand, at that time matter was believed to be purely of a corpuscular nature.

In 1923–24, L. de Broglie made a great unifying, bold hypothesis that *material particles might also possess wave-like properties*, so that, like radiation, they would exhibit a dual nature. In this way the wave–particle duality would be a universal characteristic of nature. The energy of a photon is given by $E = h\nu$, where ν is the frequency of the radiation; the magnitude of the photon momentum is $p = h\nu/c = h/\lambda$, where λ is the wavelength. For free material particles, de Broglie, using arguments based on the properties of wave packets[18], proposed that the associated matter waves also have a frequency ν and a wavelength λ, related respectively to the energy E and to the magnitude p of the momentum of the particle by

$$\nu = \frac{E}{h} \tag{1.95}$$

and

$$\lambda = \frac{h}{p}. \tag{1.96}$$

The wavelength $\lambda = h/p$ is known as the *de Broglie wavelength of a particle.* We remark that since $\lambda\nu = c$ for a photon, only one of the two relations (1.95)–(1.96) is required to obtain both its wavelength and frequency from its particle properties of energy and momentum. In contrast, for a material (massive) particle, one needs both relations (1.95) and (1.96) to obtain the associated frequency ν and wavelength λ.

The de Broglie idea immediately gives a *qualitative* explanation of the quantum condition (1.55) used in the Bohr model of one-electron atoms. Indeed, let us suppose that an electron in a hydrogenic atom moves in a circular orbit of radius r, with velocity v. If this is to be a stable stationary state, the wave associated with the electron must be a standing wave, and a whole number of wavelengths must fit into the circumference $2\pi r$. Thus

$$n\lambda = 2\pi r \qquad n = 1, 2, 3, \dots . \tag{1.97}$$

Since $\lambda = h/p$ and $L = rp$, we immediately find the condition

$$L = nh/2\pi = n\hbar \tag{1.98}$$

which is identical with (1.55). Later, in 1925 and 1926, these qualitative ideas were incorporated into the systematic theory of quantum mechanics developed by E. Schrödinger, which will be discussed in the next chapter.

De Broglie wrote the relations (1.95) and (1.96) for the general case of a relativistic particle. For a free particle of mass m moving at a non-relativistic speed v, one has $E \simeq mc^2 + mv^2/2$. Now, in the non-relativistic approximation, the energy $mv^2/2$ of a free particle is defined so that it does not contain the rest energy mc^2. This amounts to a modification of the zero of the energy scale, which has the effect of adding a

---

[18] Wave packets will be discussed in Chapter 2.

constant frequency $\nu_0 = mc^2/h$ to the right of (1.95). We shall see in Chapter 2 that this addition has no observable effect. Since $p = mv$ for a non-relativistic particle, we also remark that the de Broglie wavelength is given in the non-relativistic approximation by

$$\lambda = \frac{h}{mv}. \tag{1.99}$$

We now turn to the question of the experimental confirmation of de Broglie's hypothesis. We first recall that in order to observe the interference and diffraction effects which are characteristic of the wave properties of light, some geometric parameters of the instrument (such as apertures or slits) must have dimensions comparable to the wavelength of the light. If, on the contrary, this wavelength is much smaller than all the relevant dimensions of the optical instruments, we are in the domain of geometrical optics, where interference and diffraction effects are negligible. By analogy, we expect that in order to detect the presence of matter waves, an appropriate 'grating' having dimensions comparable to the de Broglie wavelength $\lambda = h/p$ of the particle is required.

Let us estimate the value of the de Broglie wavelength associated with a particle. For a macroscopic particle of mass $m = 10^{-3}$ kg, moving at a speed $v = 1 \text{ m s}^{-1}$, we find from (1.99) that the associated de Broglie wavelength $\lambda \simeq 6.6 \times 10^{-31}$ m = 6.6×10^{-21} Å, which is orders of magnitude smaller than any existing aperture. On the other hand, let us consider a non-relativistic electron, of mass $m = 9.1 \times 10^{-31}$ kg, which has been accelerated by a potential difference V_0, so that it has a kinetic energy $mv^2/2 = eV_0$. Using (1.99), we obtain for the associated de Broglie wavelength

$$\lambda = \frac{h}{(2meV_0)^{1/2}} = \frac{12.3}{[V_0(\text{Volts})]^{1/2}} \text{Å} \tag{1.100}$$

where we have used the fact that 1 eV = 1.6×10^{-19} J. Thus, the de Broglie wavelengths associated with electrons of energy 1, 10, 100 and 1000 eV are, respectively, 12.3, 3.89, 1.23 and 0.39 Å, comparable to the wavelength of X-rays. Hence, in macroscopic situations, such as in J. J. Thomson's experiments, where beams of electrons move under the influence of electric and magnetic fields, the de Broglie electron wavelengths are exceedingly small compared with the dimensions of any obstacles or slits in the apparatus, so that no interference or diffraction effects can be observed. However, the spacing of atoms in a crystal lattice is of the order of an ångström and therefore, just as in the case of X-rays, a crystal can be used as a grating to observe the diffraction and interference effects due to the electron matter waves. Experiments of this type were performed in 1927 by C. J. Davisson and L. H. Germer, and independently by G. P. Thomson.

In the Davisson–Germer experiment, the *reflection* of electrons from the face of a crystal was investigated. Electrons from a heated filament were accelerated through a potential difference V_0 and emerged from the 'electron gun' with kinetic energy eV_0. This beam of monoenergetic electrons was directed to strike at normal incidence the surface of a single nickel crystal, and the number $N(\theta)$ of electrons scattered at an

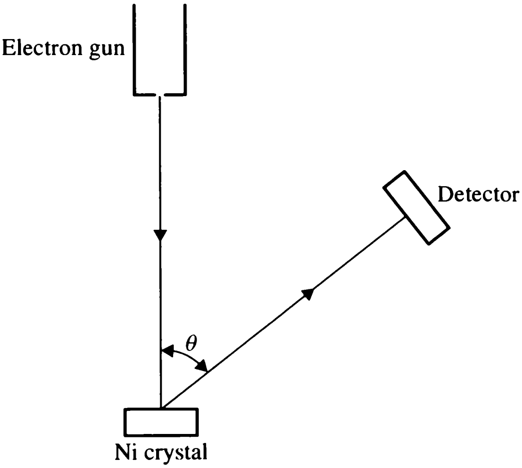


Figure 1.17 Schematic diagram of the Davisson–Germer experiment. Electrons strike at normal incidence the surface of a single nickel crystal. The number of electrons scattered at an angle θ to the incident direction is measured by means of a detector.

angle θ to the incident direction was measured by means of a detector (see Fig. 1.17). The data obtained by Davisson and Germer for 54 eV electrons are shown in Fig. 1.18. The scattered intensity is seen to fall from a maximum at $\theta = 0°$ to a minimum near 35°, and then to rise to a peak near 50°. The strong scattering at $\theta = 0°$ is expected from either a particle or a wave theory, but the peak at 50° can only be explained by constructive interference of the waves scattered by the regular crystal lattice.

Referring to Fig. 1.19, the Bragg condition for constructive interference is

$$n\lambda = 2d \sin\theta_{\mathrm{B}} \tag{1.101}$$

where d is the spacing of the Bragg planes and n is an integer. If D denotes the spacing of the atoms in the crystal, we see from Fig. 1.19 that $d = D \sin\alpha$, with $\alpha = \pi/2 - \theta_{\mathrm{B}}$. Moreover, the scattering angle $\theta = 2\alpha$, so that the Bragg condition (1.101) becomes

$$n\lambda = D \sin\theta. \tag{1.102}$$

Experiments in which X-rays were diffracted established that for a nickel crystal the atomic spacing is $D = 2.15$ Å. Assuming that the peak at $\theta = 50°$ corresponds to first-order diffraction ($n = 1$) we see from (1.102) that the experimental electron wavelength is given by $\lambda = (2.15 \sin 50°)$ Å $= 1.65$ Å. On the other hand, the de Broglie wavelength of a 54 eV electron is 1.67 Å, which agrees with the value of 1.65 Å, within the experimental error. By varying the voltage V_0, measurements were also performed at other incident electron energies, which confirmed the variation of λ with momentum as predicted by the formula (1.100), derived from the de Broglie relation (1.96). Higher-order maxima, corresponding to $n > 1$ in (1.102), were also observed and found to be in agreement with the theoretical predictions.

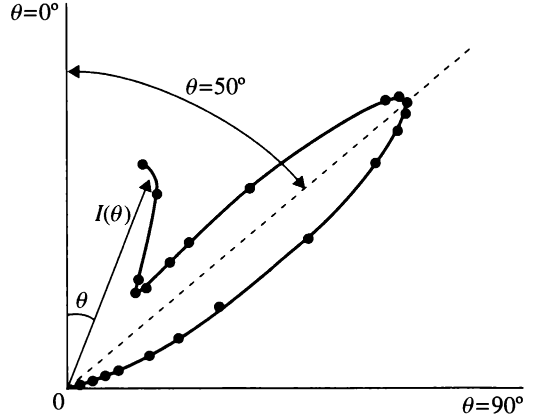


Figure 1.18 Polar plot of the scattered intensity as a function of the scattering angle θ for 54 eV electrons in the Davisson–Germer experiment. At each angle the intensity $I(\theta)$ is given by the distance of the point from the origin. A maximum is observed at $\theta = 50°$, which can only be explained by constructive interference of the waves scattered by the crystal lattice.

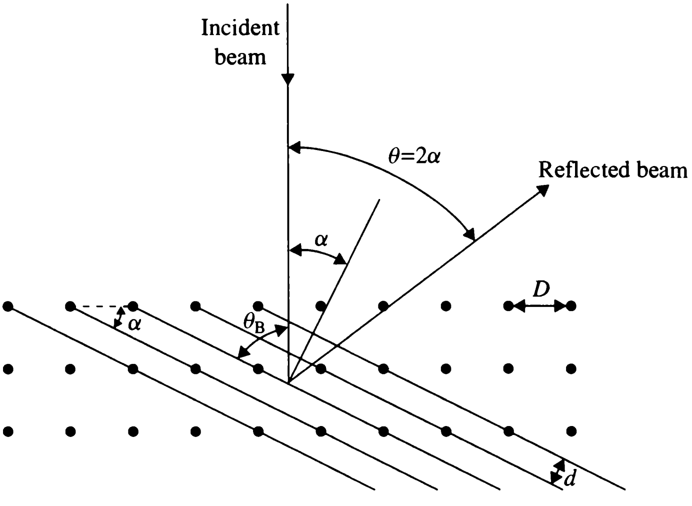


Figure 1.19 The scattering of electron waves by a crystal. Constructive interference occurs when the Bragg condition $n\lambda = 2d\sin\theta_B$ is satisfied.

In the experiment of G. P. Thomson, the *transmission* of electrons through a thin foil of polycrystalline material was analysed. A beam of monoenergetic electrons was directed towards the foil, and after passing through it the scattered electrons struck a photographic plate (see Fig. 1.20). This method is analogous to the Debye–Scherrer method used in the study of X-ray diffraction. Because the foil consists of many small randomly oriented microcrystals, 'classical' electrons behaving only as particles would yield a blurred image. However, the result obtained by G. P. Thomson

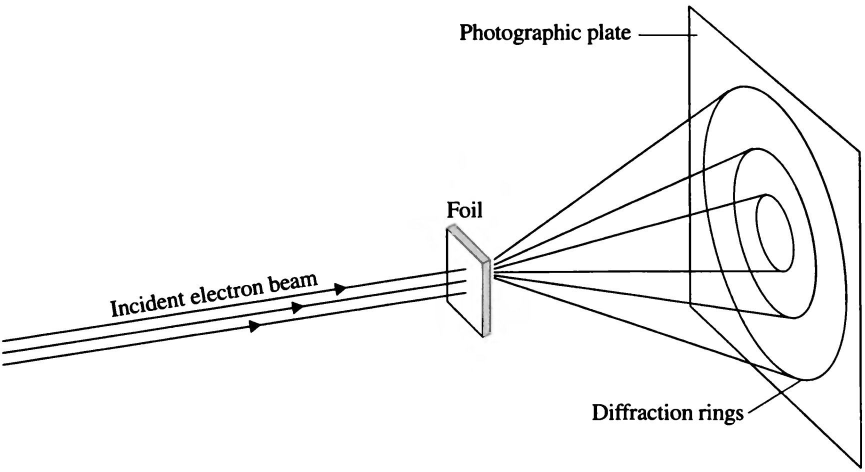


Figure 1.20 The experimental arrangement of G. P. Thomson for observing electron diffraction through a thin film of polycrystalline material.

was similar to the X-ray Debye–Scherrer diffraction pattern, which consists of a series of concentric rings. In the same way, when an electron beam passes through a single crystal, Laue spot patterns are observed, as in the case of the diffraction of X-rays.

The wave behaviour of electrons has also been demonstrated by observing the diffraction of electrons from edges and slits. For example, in 1961 C. Jönsson performed an electron diffraction experiment analogous to T. Young's famous double slit experiment, which in 1803 gave conclusive evidence of the wave properties of light. The principle of the experiment is illustrated in Fig. 1.21. Jönsson used 40 keV electrons, having a de Broglie wavelength $\lambda = 5 \times 10^{-2}$ Å. The slits, formed in copper foil, were very small (about 0.5×10^{-6} m wide), the slit separation being typically $d \simeq 2 \times 10^{-6}$ m. The interference fringes were observed on a screen at a distance $D = 0.35$ m from the slits. The spacing s of adjacent fringes is given by $s \simeq D\lambda/d \simeq 10^{-6}$ m. Because this spacing is very small, the fringes were magnified by placing electrostatic lenses between the slits and the screen.

According to de Broglie, not only electrons but *all material particles* possess wave-like characteristics. This universality of matter waves has been confirmed by a number of experiments. In all cases the measured wavelength was found to agree with the de Broglie formula (1.96). For example, in 1931 I. Esterman, R. Frisch and O. Stern observed the diffraction of helium atoms and hydrogen molecules by a crystal. Later, the diffraction of neutrons by crystals was also shown to occur. More recently, an atomic interferometer based on a Young double-slit arrangement has been demonstrated in 1991 by O. Carnal and J. Mlynek. In this apparatus, a beam of helium atoms from a gas reservoir G was passed through a source slit of width 2×10^{-6} m in a thin gold foil (see Fig. 1.22). The beam impinged on a screen S_1 having two slits, each of width 10^{-6} m, separated by a distance $d = 8 \times 10^{-6}$ m.

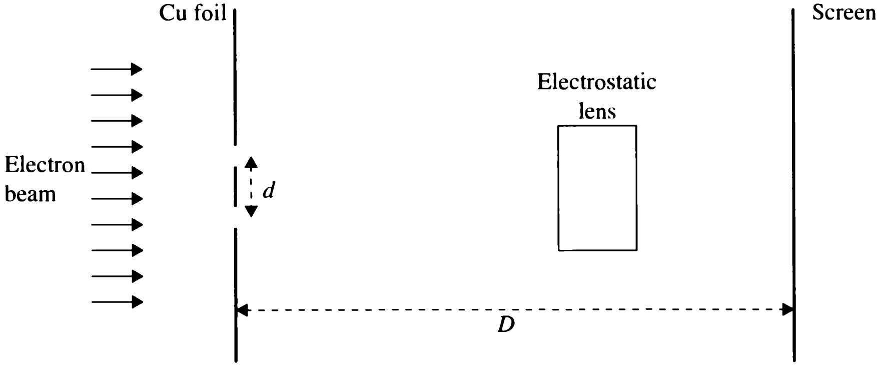


Figure 1.21 Schematic diagram illustrating the Jönsson double slit electron diffraction experiment.

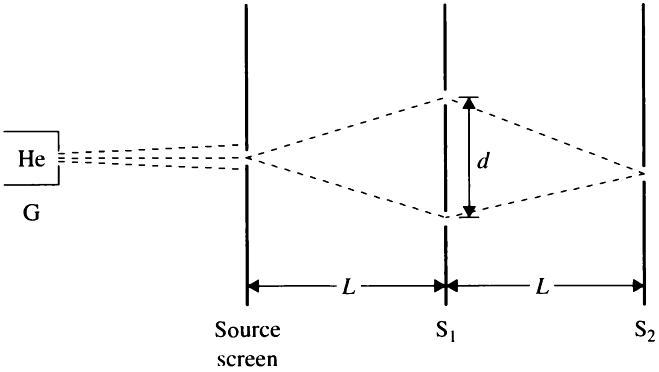


Figure 1.22 Schematic diagram of the atomic interferometer of Carnal and Mlynek.

The interference pattern was then observed on a detector screen S_2. The distance L between screens was fixed to be 64 cm. The mean velocity of the atoms, and hence their mean de Broglie wavelength, could be adjusted by changing the temperature of the gas reservoir. The experiments were performed with atoms with mean de Broglie wavelengths of $\lambda = 0.56$ Å and $\lambda = 1.03$ Å, corresponding to reservoir temperatures $T = 295$ K and $T = 83$ K, respectively.

It is worth stressing that the wave nature of matter is directly related to the finiteness of the Planck constant h. If h were zero, then the de Broglie wavelength $\lambda = h/p$ of a material particle would also vanish, and the particle would obey the laws of classical mechanics. It is precisely because Planck's constant is 'small' (when measured in units appropriate for the description of macroscopic phenomena) that the wave behaviour of matter is not apparent on the macroscopic scale. Thus, just as *geometrical optics is the short-wavelength limit of wave optics, classical mechanics can be considered as the short-wavelength limit of wave* (or *quantum*) *mechanics.*

The requirement that classical mechanics is contained in quantum mechanics in the limiting case $\lambda \to 0$ (i.e. $h \to 0$) is in accordance with the *correspondence principle*, which we discussed in Section 1.4.

Problems

1.1 Calculate the total emissive power of a black body at the following temperatures: (a) 1 K; (b) 300 K (room temperature); (c) 2000 K; (d) 4000 K. Find in each case the wavelength $\lambda_{\max}$ at which the spectral emittance $R(\lambda, T)$ has its maximum value.

1.2 (a) Calculate the surface temperature T of the Sun (in K) by assuming that it is a spherical black body with a radius of 7×10^8 m. The intensity of the solar radiation at the surface of the Earth is 1.4×10^3 W m^{-2} and the distance between the Sun and the Earth is 1.5×10^{11} m.

(b) Using the value of T obtained in (a), determine the wavelength $\lambda_{\max}$ at which the spectral emittance $R(\lambda, T)$ of the Sun (considered as a perfect black body) has its maximum value.

1.3 Using Wien's law (1.5), show the following:

(a) If the spectral distribution function of black body radiation, $\rho(\lambda, T)$, is known at one temperature, then it can be obtained at any temperature (so that a single curve can be used to represent black body radiation at all temperatures).

(b) The total emissive power is given by $R = \sigma T^4$ (the Stefan–Boltzmann law), where σ is a constant.

(c) The wavelength $\lambda_{\max}$ at which $\rho(\lambda, T)$ – or $R(\lambda, T)$ – has its maximum is such that $\lambda_{\max} T = b$ (Wien's displacement law), where b is a constant.

1.4 Obtain the Rayleigh–Jeans spectral distribution law (1.8) as the long-wavelength limit of the Planck spectral distribution law (1.13).

1.5 Using Planck's spectral distribution law (1.13) for $\rho(\lambda, T)$, prove that

$$\lambda_{\max} T = \frac{hc}{4.965k}$$

where $\lambda_{\max}$ is the wavelength at which $\rho(\lambda, T)$ has its maximum value for a given absolute temperature T. From this result and the values of h, c and k given in the table of fundamental constants at the end of the book (p. 789), obtain the constant b which occurs in Wien's displacement law (1.3).

(*Hint*: To solve the equation $\mathrm{d}\rho/\mathrm{d}\lambda = 0$, set $x = hc/\lambda kT$ and show that x must satisfy the equation $x = 5(1 - \mathrm{e}^{-x})$. Then, upon writing $x = 5 - \varepsilon$ show that $\varepsilon \simeq 0.035$ so that $x = 4.965$ is an approximate solution.)

1.6 Using Planck's spectral distribution law (1.13) for $\rho(\lambda, T)$, prove that the total energy density ρ_{tot} is given by $\rho_{\text{tot}} = aT^4$, where $a = 8\pi^5 k^4/15h^3c^3$.

$$\left(\textit{Hint}: \int_0^\infty \frac{x^3}{\mathrm{e}^x - 1}\mathrm{d}x = \frac{\pi^4}{15}.\right)$$

1.7 Consider the following three stars:

(1) a red star (such as Barnard's star) having a surface temperature of 3000 K;
(2) a yellow star (such as the Sun) having a surface temperature of 6000 K; and
(3) a blue-white star (such as Vega) having a surface temperature of 10 000 K.

Assuming that these stars radiate like black bodies, obtain for each of them:

(a) the total emissive power;
(b) the wavelength λ_{max} at which their spectral emittance $R(\lambda, T)$ peaks;
(c) the fraction of their energy which is radiated in the visible range of the electromagnetic spectrum (4000 Å $\leq \lambda \leq$ 7000 Å, where 1 Å $= 10^{-10}$ m).

(*Hint*: Use the integral given in Problem 1.6 and integrate Planck's spectral distribution numerically between the wavelengths $\lambda_1 = 4000$ Å and $\lambda_2 = 7000$ Å.)

1.8 What is the energy of:

(a) a γ-ray photon of wavelength $\lambda = 10^{-13}$ m?
(b) a photon of visible light, of wavelength $\lambda = 5 \times 10^{-7}$ m?
(c) a radio-wave photon of wavelength $\lambda = 10$ m?

1.9 Consider black body radiation at absolute temperature T. Show that:

(a) The number of photons per unit volume is $N = 2.029 \times 10^7\ T^3$ photons m^{-3}.

$$\left(\textit{Hint}: \int_0^\infty \frac{x^2}{e^x - 1} dx = 2.4041.\right)$$

(b) The average energy per photon is $\bar{E} = 3.73 \times 10^{-23}\ T$ J.

1.10 Consider an aluminium plate placed at a distance of 1 m from an ultraviolet source which radiates uniformly in all directions and has a power of 10^{-2} W. Suppose that an ejected photoelectron collects its energy from a classical atom modelled as a circular area of the plate whose radius is a typical atomic radius, $r \simeq 1$ Å. Assuming, as in classical physics that the energy is uniformly distributed over spherical wave fronts spreading out from the source, estimate the time required for a photoelectron to absorb the minimum amount of energy necessary to escape from the plate. The work function of aluminium is $W = 4.2$ eV.

1.11 The photoelectric work function W for lithium is 2.3 eV.

(a) Find the threshold frequency ν_t and the corresponding threshold wavelength λ_t.
(b) If ultraviolet light of wavelength $\lambda = 3000$ Å is incident on a lithium surface, calculate the maximum kinetic energy of the photoelectrons and the value of the stopping potential V_0.

1.12 A homogeneous light beam of wavelength $\lambda = 3000$ Å and intensity 5×10^{-2} W m^{-2} falls on a sodium surface. The photoelectric work function W for sodium is 2.3 eV. Calculate:

(a) the average number of electrons emitted per m^2 and per second; (you may assume that each photon striking the surface ejects an electron); and
(b) the maximum kinetic energy of the photoelectrons.

1.13 In a photoelectric experiment in which monochromatic light of wavelength λ falls on a potassium surface, it is found that the stopping potential is 1.91 V for $\lambda = 3000$ Å and 0.88 V for $\lambda = 4000$ Å. From these data, calculate:

(a) a value for Planck's constant, knowing that $e = 1.60 \times 10^{-19}$ C;
(b) the work function W for potassium; and
(c) the threshold frequency ν_t for potassium.

1.14 Consider the scattering of a photon by a free electron initially at rest. Referring to Fig. 1.9:

(a) prove that the angle ϕ at which the electron recoils is related to the angle θ of the scattered photon by

$$\tan\phi = \frac{\cot(\theta/2)}{1 + \lambda_C/\lambda_0} = \frac{\cot(\theta/2)}{1 + E_0/mc^2},$$

where $E_0 = hc/\lambda_0$ is the energy of the initial photon, m is the rest mass of the electron and $\lambda_C = h/mc$ is the Compton wavelength of the electron; and
(b) prove that the kinetic energy of the recoiling electron is given by

$$T_2 = E_0 \frac{(2\lambda_C/\lambda_0)\sin^2(\theta/2)}{1 + (2\lambda_C/\lambda_0)\sin^2(\theta/2)} = E_0 \frac{(2E_0/mc^2)\sin^2(\theta/2)}{1 + (2E_0/mc^2)\sin^2(\theta/2)}.$$

1.15 An X-ray photon of wavelength $\lambda_0 = 1$ Å is incident on a free electron which is initially at rest. The photon is scattered at an angle $\theta = 30°$ from the incident direction.

(a) Calculate the Compton shift $\Delta\lambda$.
(b) What is the angle ϕ (measured from the incident photon direction) at which the electron recoils?
(c) What is the kinetic energy T_2 of the recoiling electron?
(d) What fraction of its original energy does the photon lose?

1.16 Consider the Compton scattering of a photon of wavelength λ_0 by a free electron moving with a momentum of magnitude P in the same direction as that of the incident photon.

(a) Show that in this case the Compton equation (1.42) becomes

$$\Delta\lambda = 2\lambda_0 \frac{(p_0 + P)c}{E - Pc} \sin^2\left(\frac{\theta}{2}\right)$$

where $p_0 = h/\lambda_0$ is the magnitude of the incident photon momentum, θ is the photon scattering angle and $E = (m^2c^4 + P^2c^2)^{1/2}$ is the initial electron energy.

(b) What is the maximum value of the electron momentum after the collision? Compare with the case $P = 0$ considered in the text.

(c) Show that if the free electron initially moves with a momentum of magnitude P in a direction opposite to that of the incident photon, the Compton shift becomes

$$\Delta\lambda = 2\lambda_0 \frac{(p_0 - P)c}{E + Pc} \sin^2\left(\frac{\theta}{2}\right).$$

1.17 Consider a photon of energy $E_0 = 2$ eV which is scattered through an angle $\theta = \pi$ from an electron having a kinetic energy $T = 10$ GeV (1 GeV $= 10^9$ eV) and moving initially in a direction opposite to that of the photon. What is the energy E_1 of the scattered photon?

(*Hint*: Use the result (c) of Problem 1.16.)

1.18 Using the infinite nuclear mass approximation in the Bohr model, calculate:

(a) the ionisation potential (in eV), and
(b) the wavelengths of the first three lines of the Lyman, Balmer and Paschen series,

for H, He^+ $(Z = 2)$, Li^{2+} $(Z = 3)$ and C^{5+} $(Z = 6)$.

1.19 Consider a one-electron atom (or ion), the nucleus of which contains A nucleons (Z protons and $N = A - Z$ neutrons). The mass of that nucleus is given approximately by $M \simeq AM_\text{p}$, where $M_\text{p} \simeq 1.67 \times 10^{-27}$ kg is the proton mass. Using this value of M, obtain the relative correction $\Delta E/E$ to the Bohr energy levels due to the finite nuclear mass for the case of atomic hydrogen $(A = 1, Z = 1)$, deuterium $(A = 2, Z = 1)$, tritium $(A = 3, Z = 1)$ and $^4\text{He}^+ (A = 4, Z = 2)$.

1.20 Calculate the difference in wavelengths $\Delta\lambda$ between the Balmer H_α lines in atomic hydrogen and deuterium.

1.21 Show that the fractional change in the frequency of a photon absorbed or emitted by an atom initially at rest is

$$\frac{\nu - \nu_0}{\nu} = \pm\frac{h\nu}{2Mc^2}$$

where M is the mass of the atom and ν_0 is the frequency of the transition uncorrected for the recoil of the atom. In the above equation the plus sign corresponds to the absorption and the minus sign to the emission of a photon.

1.22 In an experiment of the Franck–Hertz type, atomic hydrogen is bombarded by electrons. It is found that the current I is sharply reduced when the potential V_1 has the values 10.2 V and 12.1 V, and three different spectral lines are observed.

(a) To which spectral series do these lines belong? What are the quantum numbers of the initial and final states in the transition corresponding to each spectral line?
(b) What is the wavelength of each of these spectral lines?

1.23 A beam of silver atoms, for which $\mathcal{M}_z = \pm\mu_B$, passes through an inhomogeneous magnetic field, as in the Stern–Gerlach apparatus shown schematically in Fig. 1.15. The field gradient is $\partial\mathcal{B}_z/\partial z = 10^3$ T m^{-1}, the length of the pole piece is $L = 0.1$ m, the distance to the screen is $l = 1$ m and the temperature of the oven is $T = 600$ K. Assuming that the velocity of the silver atoms is equal to the root-mean-square velocity of $(3kT/M)^{1/2}$ (where k is the Boltzmann constant and M is the mass of a silver atom) calculate the maximum separation (P_2P_3 in Fig. 1.15) of the two beams on the screen.

1.24 At what energy (in eV) will the non-relativistic expression (1.99) for the de Broglie wavelength lead to a 1% relative error for (a) an electron and (b) a proton?

1.25 Calculate the de Broglie wavelength of

(a) a mass of 1 g moving at a velocity of 1 m s^{-1},
(b) a free electron having a kinetic energy of 200 eV,
(c) a free electron having a kinetic energy of 50 GeV (1 GeV = 10^9 eV), and
(d) a free proton having a kinetic energy of 200 eV.

(*Hint*: Use the relativistic formula in (c).)

1.26 What is the kinetic energy of

(a) an electron,
(b) an alpha particle (doubly ionised helium atom), and
(c) a neutron,

having a de Broglie wavelength of 1 Å?

1.27 Thermal neutrons are neutrons in thermal equilibrium with matter at a given temperature; they have a kinetic energy of $3kT/2$, where k is the Boltzmann constant and T is the absolute temperature. What is the energy (in eV) and the de Broglie wavelength (in Å) of a thermal neutron at room temperature ($T = 300$ K)?

1.28 Consider electrons striking at normal incidence the surface of a nickel crystal, and undergoing first-order Bragg diffraction at a Bragg angle $\theta_B = 30°$. Knowing that the atomic separation in a nickel crystal is $D = 2.15$ Å calculate

(a) the de Broglie wavelength of the electrons, and
(b) the kinetic energy of the electrons.

1.29 The spacing of the Bragg planes in a NaCl crystal is $d = 2.82$ Å. Calculate the angular positions of the first- and second-order diffraction maximum for 100 eV electrons incident on the crystal surface at the Bragg angle θ_B.

1.30 A crystal has a set of Bragg planes separated by a distance $d = 1.1$ Å. What is the highest-order Bragg diffraction (i.e. the highest value of n in equation (1.101)) for incident neutrons having a kinetic energy of 0.5 eV?

(*Hint*: The maximum Bragg angle that can be attained is 90°.)

2 The wave function and the uncertainty principle

In the previous chapter we discussed a number of phenomena which cannot be explained within the framework of classical physics. As a result of this experimental evidence, revolutionary concepts had to be introduced such as those of *quantisation* and of *wave–particle duality.*

Attempts to construct a theoretical structure which incorporates these concepts in a satisfactory way met first with great difficulties, until a new theory, called *quantum mechanics*, was elaborated between the years 1925 and 1930. Quantum mechanics provides a consistent description of matter on the microscopic scale, and can be considered as one of the greatest intellectual achievements of the twentieth century. Two equivalent formulations of the theory were proposed at nearly the same time. The first, known as *matrix mechanics*, was developed in the years 1925 and 1926 by W. Heisenberg, M. Born and P. Jordan. In this approach, only physically observable quantities appear, and to each physical quantity the theory associates a matrix. These matrices obey a non-commutative algebra, which is the essential difference between matrix mechanics and classical mechanics. The second form of quantum mechanics, called *wave mechanics*, was proposed in 1925 by E. Schrödinger, following the ideas put forward in 1923 by L. de Broglie about matter waves. The equivalence of matrix mechanics and wave mechanics was proved in 1926 by Schrödinger. In fact, both matrix mechanics and wave mechanics are particular forms of a general formulation of quantum mechanics, which was developed by P. A. M. Dirac in 1930.

The general formulation of quantum mechanics, as well as matrix mechanics, requires a certain amount of abstract mathematics, and hence we shall defer discussion of it until Chapter 5. Wave mechanics, on the other hand, is more suitable for a first contact with quantum theory, and this is the approach which we shall use in most of this book. In this chapter we shall discuss the fundamental ideas underlying quantum mechanics in their simplest form. We begin with an analysis of wave–particle duality, introducing the notion of a wave function and its probabilistic interpretation. We then go on to construct wave functions corresponding to particles having a well-defined momentum, and to obtain localised wave functions by superposing plane waves into wave packets. Following this, we discuss the Heisenberg uncertainty relations which impose limits on the accuracy of simultaneous measurements of pairs of 'complementary' variables, such as position and momentum, or time and energy.

2.1 Wave–particle duality

In Chapter 1 we discussed several experiments which demonstrate conclusively that material particles possess wave-like properties, exhibiting interference and diffraction effects. On the other hand, we saw that electromagnetic radiation, which had been known for a long time to exhibit wave properties, can also show a particle-like behaviour. We shall now analyse this wave–particle duality in more detail.

Let us consider an idealised experiment in which monoenergetic particles, for example electrons, emitted by a source are directed on to a screen S_1 containing two slits A and B (see Fig. 2.1). At some distance beyond this screen a second screen S_2 is placed, incorporating detectors which can record each electron striking the screen S_2 at a given point. On detection, every electron exhibits purely particle-like properties, that is its mass and charge are localised, being never spread over more than one detector at a given time. In contrast, if after some time the total number of electrons arriving at the screen S_2 is plotted as a function of position, a diffraction pattern is found, which is characteristic of waves (see Fig. 2.2(a)). Thus, in a single experiment, both the particle and wave aspects of the electron are exhibited. A realisation of this ideal experiment by Jönsson has been described in Chapter 1. A similar experiment

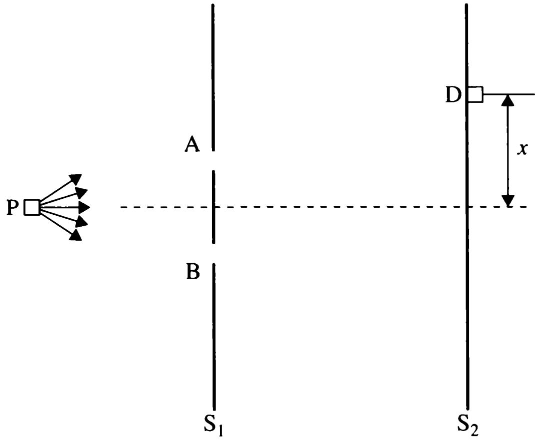


Figure 2.1 The two-slit experiment. Monoenergetic particles from a source at P fall on a screen S_1 containing slits at A and B. Detectors are placed on a second screen S_2 to record the number of particles arriving at each point. A particle detector D is indicated at a position x.

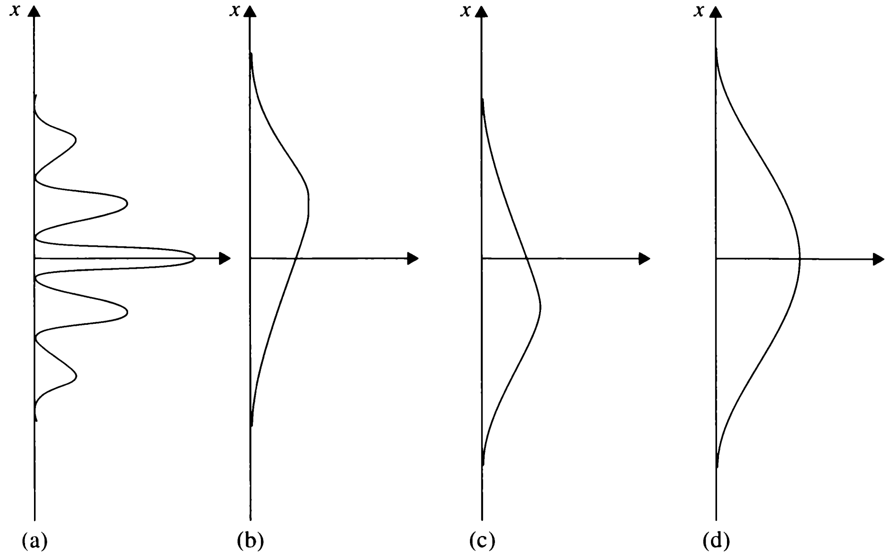


Figure 2.2 The intensity at a position x on the screen S_2 (see Fig. 2.1).
(a) A diffraction pattern characteristic of waves.
(b) The intensity with slit A open and B closed.
(c) The intensity with slit B open and A closed.
(d) An intensity distribution characteristic of classical particles when A and B are both open.

can be carried out with light. In this case the light can be detected by the photoelectric effect, showing its particle (photon) aspect, while the recorded intensity displays the diffraction pattern characteristic of the wave theory of light.

It might at first be supposed that the diffraction pattern is in some way due to interference between electrons (or photons) passing through the two slits. However, if the incident intensity is reduced until at any instant there is no more than one particle between the source and the detecting screen, the interference pattern is still accumulated. This was demonstrated originally in 1909 by G. I. Taylor, who photographed the diffraction pattern formed by the shadow of a needle, using a very weak source such that the exposures lasted for months. It can be concluded that interference does not occur between photons, but is a property of a single photon. This was confirmed in more recent experiments performed in 1989 by A. Aspect, P. Grangier and G. Roger. Material particles such as electrons exhibit a similar behaviour, as was demonstrated directly in 1989 by A. Tonomura, J. Endo, T. Matsuda, T. Kawasaki and H. Ezawa in two-slit experiments in which the accumulation of the interference pattern due to incoming single electrons was observed (see Fig. 2.3). It should be noted that if one slit is closed in a two-slit experiment, the diffraction pattern does not appear, so we may infer that when both slits are open the particle is not localised before it is detected, and hence must be considered as having passed through both slits!

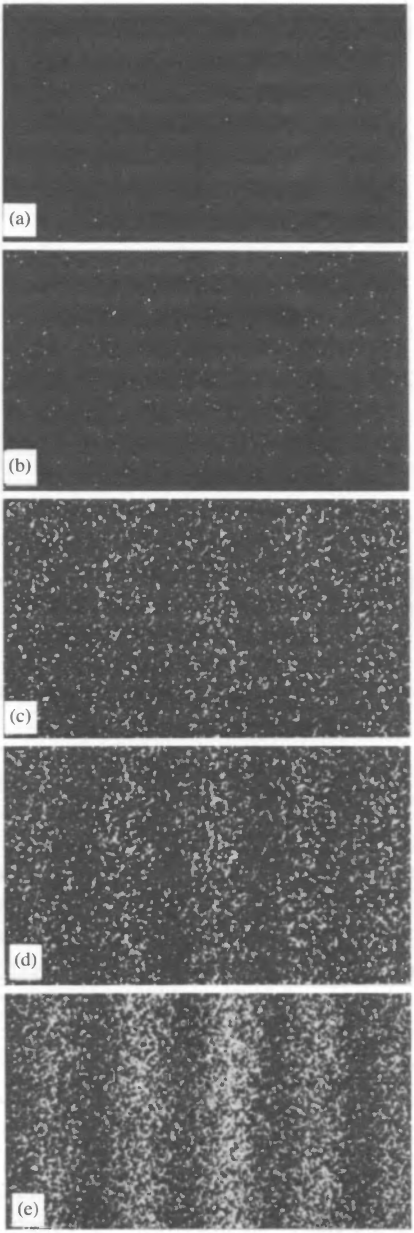


Figure 2.3 Buildup of an interference pattern by accumulating single electrons in the two-slit experiment of Tonomura *et al.*
(a) Number of electrons = 10; (b) number of electrons = 100;
(c) number of electrons = 3000; (d) number of electrons = 20 000; and
(e) number of electrons = 70 000.
(By courtesy of A. Tonomura.)

Another way of expressing these facts is to say that while in transit the electron or photon behaves like a wave, manifesting its particle-like property only on detection. This is of course in complete contradiction to the classical viewpoint, which would lead us to suppose that each particle being indivisible must pass either through one slit or the other. Let us put this to the test by detecting the particles as they pass through the slits. We can now record the particles which have passed through slit A and entered the detectors on screen S_2. Since all these particles passed through slit A, slit B might as well have been closed, in which case the intensity distribution will not show diffraction but will be as illustrated in Fig. 2.2(b). Similarly, if slit B is open and A is closed, the intensity distribution is that shown in Fig. 2.2(c). If we add the intensity distributions of Figs. 2.2(b) and 2.2(c) we obtain the intensity pattern shown in Fig. 2.2(d), which is very different from the diffraction pattern obtained in the absence of any knowledge about which slit the particles passed through (see Fig. 2.2(a)). Hence, if the particle nature of an electron, a photon, etc., is established by monitoring its trajectory, it cannot simultaneously behave like a wave. The wave and particle aspects of electrons, photons, etc., are *complementary*.

Let us now return to the case in which there is only one particle at a time transiting the apparatus and both slits are open. The place on the screen S_2 at which a given particle will be detected cannot be predicted, because if it could be predicted this would be equivalent to determining the trajectory, which we have seen would eliminate the diffraction pattern. What is predictable is the intensity distribution which builds up after a large number of individual events have occured. This suggests that for an individual particle the process is of a *statistical* nature, so that one can only determine the probability P that a particle will hit the screen S_2 at a certain point. By probability in this context we mean the number of times that an event occurs divided by the total number of events. The intensity of the pattern formed on the screen S_2, in the present case, is then proportional to the probability P.

In the classical theory of light, the intensity of light at each point is determined by the square of the amplitude of a wave. For example, in Young's two-slit experiment, the light intensity on the recording screen is given by the square of the amplitude of the wave formed by the *superposition* of the secondary waves arising from each slit. This classical wave theory cannot of course be used as it stands because it does not account for the particle aspect of light. However, it suggests, by analogy, that in quantum mechanics a *wave function* or *state function* $\Psi(x, y, z, t)$ can be introduced, which plays the role of a *probability amplitude*. We shall see later that in general the wave function Ψ is a *complex* quantity. We then expect that the probability $P(x, y, z, t)$ of finding the particle at a particular point within a volume V about the point with coordinates (x, y, z) at time t is proportional to $|\Psi|^2$:

$$P(x, y, z, t) \propto |\Psi(x, y, z, t)|^2. \tag{2.1}$$

Since probabilities are *real positive* numbers, we have associated in (2.1) the probability P with the square of the modulus of the wave function Ψ.

Let Ψ_A be the wave function at a particular point on the screen S_2 corresponding to waves spreading from the slit A. Similarly, let Ψ_B be the wave function at the same point corresponding to waves spreading from the slit B. The two intensity distributions of Fig. 2.2(b) and (c) corresponding to experiments performed with only one open slit are determined respectively by the probability distributions

$$P_A \propto |\Psi_A|^2, \qquad P_B \propto |\Psi_B|^2. \tag{2.2}$$

On the other hand, when both slits are open, the wave function Ψ is taken to be the sum of the two contributions Ψ_A and Ψ_B,

$$\Psi = \Psi_A + \Psi_B. \tag{2.3}$$

The corresponding probability distribution

$$P \propto |\Psi_A + \Psi_B|^2 \tag{2.4}$$

then determines the intensity pattern illustrated in Fig. 2.2(a). It is important to notice that in (2.4) the probability amplitudes Ψ_A and Ψ_B have been added and not the probabilities P_A and P_B. If the latter were the case there would be no possibility of obtaining interference patterns characteristic of a wave theory.

2.2 The interpretation of the wave function

In analysing the two-slit experiment, we introduced the concept that the probability of finding a particle at a given location is proportional to the square of the modulus of the wave function associated with the particle. This concept may be restated more precisely in the form of a fundamental assumption made by M. Born in 1926, which can be formulated in the following way. Let us imagine a very large number of identical, independent systems, each of them consisting of a single particle moving under the influence of some given external force. All these systems are identically prepared, and this ensemble is assumed to be described by a single wave function $\Psi(x, y, z, t)$ which contains all the information that can be known about them. It is then postulated that if measurements of the position of the particle are made on each of the systems, the probability (that is the statistical frequency) of finding the particle within the volume element $\mathrm{d}\mathbf{r} \equiv \mathrm{d}x\mathrm{d}y\mathrm{d}z$ about the point $\mathbf{r} \equiv (x, y, z)$ at the time t is

$$P(\mathbf{r}, t)\mathrm{d}\mathbf{r} = |\Psi(\mathbf{r}, t)|^2\mathrm{d}\mathbf{r} \tag{2.5}$$

so that

$$P(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 = \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t) \tag{2.6}$$

is the *position probability density*. Thus we see that the interpretation of the wave function introduced by Born is a statistical one. For convenience, we shall often speak of the wave function associated with a particular system, but it must always be understood that this is shorthand for the wave function associated with an ensemble of identical and identically prepared systems, as required by the statistical nature of the theory.

Since the probability of finding the particle somewhere must be unity, we deduce from (2.5) that the wave function $\Psi(\mathbf{r}, t)$ should be *normalised to unity*, so that

$$\int |\Psi(\mathbf{r}, t)|^2 \mathrm{d}\mathbf{r} = 1 \qquad \textbf{(2.7)}$$

where the integral extends over all space. A wave function for which the integral on the left of (2.7) is finite is said to be *square integrable*: such a wave function can always be normalised to unity by multiplying it by an appropriate complex constant.

It is important to notice that since $|\Psi(\mathbf{r}, t)|^2$ is the physically significant quantity, two wave functions which differ from each other by a constant multiplicative factor of modulus one (that is, a constant phase factor of the form $\exp(\mathrm{i}\alpha)$, where α is a real number) are equivalent, and satisfy the same normalisation condition.

The superposition principle

As we have seen in the previous section, in order to account for interference effects, it must be possible to *superpose* wave functions. This means that if one possible state of an ensemble of identical systems is described by a wave function Ψ_1 and another state of this ensemble by a wave function Ψ_2, then any *linear combination*

$$\Psi = c_1\Psi_1 + c_2\Psi_2 \qquad \textbf{(2.8)}$$

where c_1 and c_2 are complex constants, is also a wave function describing a possible state of the ensemble.

Let us write the (complex) wave functions Ψ_1 and Ψ_2 in the form

$$\Psi_1 = |\Psi_1|\mathrm{e}^{\mathrm{i}\alpha_1}, \qquad \Psi_2 = |\Psi_2|\mathrm{e}^{\mathrm{i}\alpha_2}. \qquad \textbf{(2.9)}$$

Using (2.8), we find that the square of the modulus of Ψ is given by

$$|\Psi|^2 = |c_1\Psi_1|^2 + |c_2\Psi_2|^2 + 2\mathrm{Re}\{c_1c_2^*|\Psi_1||\Psi_2|\exp[\mathrm{i}(\alpha_1 - \alpha_2)]\} \qquad \textbf{(2.10)}$$

so that, in general, $|\Psi|^2 \neq |c_1\Psi_1|^2 + |c_2\Psi_2|^2$, in keeping with the discussion of Section 2.1. It is worth stressing that although the quantity $|\Psi|^2$ is unaffected if Ψ is multiplied by an *overall* phase factor $\exp(\mathrm{i}\alpha)$ (where α is a real constant) it does depend on the *relative* phase $(\alpha_1 - \alpha_2)$ of Ψ_1 and Ψ_2 through the third term on the right of (2.10), which is an *interference* term.

Finally, we emphasise that unlike classical waves (such as sound waves or water waves) the wave function $\Psi(\mathbf{r}, t)$ is an *abstract* quantity, the interpretation of which is of a *statistical* nature. This wave function is assumed to provide a *complete* description of the dynamical state of an ensemble. Indeed, we shall see later that the knowledge of the wave function enables one to predict for each dynamical variable (position, momentum, energy and so on) a *statistical distribution* of values obtained in measurements.

2.3 Wave functions for particles having a definite momentum

In this section we begin to investigate how wave functions can be found, considering the simple case of *free* particles. The experiments exhibiting the corpuscular nature of the electromagnetic radiation, which we discussed in Chapter 1, require that with the electromagnetic field one associates a particle, the photon, whose energy E and magnitude p of momentum are related to the frequency ν and wavelength λ of the electromagnetic radiation by

$$E = h\nu, \qquad p = \frac{h}{\lambda}. \tag{2.11}$$

On the other hand, we have seen in Section 1.6 that de Broglie was led to associate matter waves with particles in such a way that the frequency ν and the wavelength λ of the wave were linked with the particle energy E and the magnitude p of its momentum by the same relations (2.11). The de Broglie relation $\lambda = h/p$ was confirmed by the results of a number of experiments exhibiting the wave nature of matter. Following de Broglie, we shall assume that the relations (2.11) hold for all types of particles and field quanta. Introducing the angular frequency $\omega = 2\pi\nu$, the wave number $k = 2\pi/\lambda$ and the reduced Planck constant $\hbar = h/2\pi$, we may write the relations (2.11) in the more symmetric form

$$E = \hbar\omega, \qquad p = \hbar k. \tag{2.12}$$

Let us consider a *free* particle of mass m, moving along the x-axis with a definite momentum $\mathbf{p} = p_x\hat{\mathbf{x}}$, where $\hat{\mathbf{x}}$ is a unit vector along the x-axis, and a corresponding energy E. Assuming that $p_x > 0$, so that the particle moves in the positive x-direction, we associate with this particle a wave travelling in the same direction with a fixed wave number k. Such a wave is a *plane wave* and can be written as

$$\Psi(x, t) = A\exp\{\mathrm{i}[kx - \omega(k)t]\} \tag{2.13a}$$

where A is a constant. This plane wave has a wavelength $\lambda = 2\pi/k$ and an angular frequency ω. Since from (2.12) $k = p/\hbar$ (with $p = p_x$) and $\omega = E/\hbar$, the wave function (2.13a) can be expressed as

$$\Psi(x, t) = A\exp\{\mathrm{i}[p_x x - E(p_x)t]/\hbar\}, \tag{2.13b}$$

In writing (2.13a,b) we have taken $\omega(k)$ and $E(p_x)$ as functions to be specified later. We note that the wave function (2.13) satisfies the two relations

$$-\mathrm{i}\hbar\frac{\partial}{\partial x}\Psi = p_x\Psi \tag{2.14}$$

and

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi = E\Psi \tag{2.15}$$

the significance of which will emerge shortly.

This one-dimensional treatment is easily extended to three dimensions. To a free particle of mass m, having a well-defined momentum $\mathbf{p}$ and an energy E, we now associate a plane wave

$$\begin{aligned}\Psi(\mathbf{r}, t) &= A\exp\{\mathrm{i}[\mathbf{k}.\mathbf{r} - \omega(k)t]\} \\ &= A\exp\{\mathrm{i}[\mathbf{p}.\mathbf{r} - E(p)t]/\hbar\}\end{aligned} \tag{2.16}$$

where the propagation vector (or wave vector) $\mathbf{k}$ is related to the momentum $\mathbf{p}$ by

$$\mathbf{p} = \hbar\mathbf{k} \tag{2.17}$$

with

$$k = |\mathbf{k}| = \frac{|\mathbf{p}|}{\hbar} = \frac{2\pi}{\lambda} \tag{2.18}$$

and the angular frequency ω is related to the energy by $\omega = E/\hbar$. Again, the functions $\omega(k)$ and $E(p)$ will be specified later. The equation (2.15) remains unchanged for the plane wave (2.16), while (2.14) is now replaced by its obvious generalisation

$$-\mathrm{i}\hbar\nabla\Psi = \mathbf{p}\Psi \tag{2.19}$$

where ∇ is the gradient operator, having Cartesian components $(\partial/\partial x, \partial/\partial y, \partial/\partial z)$. The relations (2.15) and (2.19) show that for a free particle the energy and momentum can be represented by the differential operators

$$E_{\mathrm{op}} = \mathrm{i}\hbar\frac{\partial}{\partial t}, \qquad \mathbf{p}_{\mathrm{op}} = -\mathrm{i}\hbar\nabla \tag{2.20}$$

acting on the wave function Ψ. It is a *postulate* of wave mechanics that when the particle is not free the dynamical variables E and $\mathbf{p}$ are still represented by these differential operators.

According to the discussion of Section 2.2, wave functions should be normalised to unity if the probability interpretation is to be maintained. For one-dimensional systems, the normalisation condition (2.7) reduces to

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 \mathrm{d}x = 1. \tag{2.21}$$

However, the plane wave (2.13) does not satisfy this requirement, since the integral on the left of (2.21) is given in this case by

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 \mathrm{d}x = |A|^2 \int_{-\infty}^{+\infty} \mathrm{d}x \tag{2.22}$$

and hence does not exist. Similarly, the three-dimensional plane wave (2.16) cannot be normalised according to (2.7). There are two ways out of this difficulty. The first is to give up the concept of *absolute* probabilities when dealing with wave functions such as (2.13) or (2.16) which are not square integrable. Instead, $|\Psi(\mathbf{r}, t)|^2\mathrm{d}\mathbf{r}$ is then interpreted as the *relative* probability of finding the particle at time t in a volume element $\mathrm{d}\mathbf{r}$ centred about $\mathbf{r}$, so that the ratio $|\Psi(\mathbf{r}_1, t)|^2/|\Psi(\mathbf{r}_2, t)|^2$ gives the probability of finding the particle within a volume element centred around $\mathbf{r} = \mathbf{r}_1$, compared with that of finding it within the same volume element at $\mathbf{r} = \mathbf{r}_2$. For the particular case of the plane wave (2.16), we see that $|\Psi|^2 = |A|^2$, so that there is an equal chance of finding the particle at any point. The plane wave (2.16) therefore describes the *idealised* situation of a free particle having a perfectly well-defined momentum, but which is completely '*delocalised*'. This suggests a second way out of the difficulty, which is to give up the requirement that the free particle should have a precisely defined momentum, and to superpose plane waves corresponding to different momenta to form a localised *wave packet*, which can be normalised to unity. It is to this question that we now turn our attention.

2.4 Wave packets

We have seen in the preceding section that plane waves such as (2.13) or (2.16) associated with free particles having a definite momentum are completely delocalised. To describe a particle which is confined to a certain spatial region, a *wave packet* can be formed by superposing plane waves of different wave numbers. Of course, in this case the momentum no longer has a precise value, but we shall construct a wave packet which 'represents' a particle having fairly precise values of both momentum and position.

Let us begin by considering the one-dimensional case. In order to describe a free particle confined to a region of the x-axis, we superpose plane waves of the form (2.13), where we now allow $p_x = \hbar k$ to be either positive or negative. The most general superposition of this kind is then given by the integral

$$\Psi(x, t) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} e^{i[p_x x - E(p_x)t]/\hbar} \phi(p_x) dp_x \tag{2.23}$$

where the factor $(2\pi\hbar)^{-1/2}$ in front of the integral has been chosen for future convenience. The function $\phi(p_x)$ is the amplitude of the plane wave corresponding to the momentum p_x. In general it is a complex function, but it is sufficient for our present purposes to discuss only the case for which $\phi(p_x)$ is real.

Let us assume that $\phi(p_x)$ is sharply peaked about some value $p_x = p_0$, falling rapidly to zero outside an interval $(p_0 - \Delta p_x, p_0 + \Delta p_x)$. Writing (2.23) in the form

$$\Psi(x, t) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} e^{i\beta(p_x)/\hbar} \phi(p_x) dp_x \tag{2.24}$$

where

$$\beta(p_x) = p_x x - E(p_x)t \tag{2.25}$$

we see that $|\Psi(x, t)|$ is largest when $\beta(p_x)$ is nearly constant in the vicinity of $p_x = p_0$. Indeed, if $\beta(p_x)$ were varying significantly over the interval $(p_0 - \Delta p_x, p_0 + \Delta p_x)$, the factor $\exp[i\beta(p_x)/\hbar]$ would oscillate rapidly, so that the value of the integral on the right of (2.24) would be small. Thus $|\Psi(x,t)|$ will only be significant in a limited region, its maximum value occurring when the *stationary phase condition*

$$\left[\frac{\mathrm{d}\beta(p_x)}{\mathrm{d}p_x}\right]_{p_x=p_0}=0 \tag{2.26}$$

is satisfied. This condition determines the *centre of the wave packet*, which upon using (2.25) is seen to travel according to the law

$$x=v_{\mathrm{g}}t \tag{2.27}$$

where

$$v_{\mathrm{g}}=\left[\frac{\mathrm{d}E(p_x)}{\mathrm{d}p_x}\right]_{p_x=p_0}. \tag{2.28}$$

It follows from (2.27) that the centre of the wave packet moves with the constant velocity v_{g}, which is known as the *group velocity* of the packet. From (2.28) and the fact that $E=\hbar\omega$, and $p_x=\hbar k$, we see that the group velocity can also be written as

$$v_{\mathrm{g}}=\left[\frac{\mathrm{d}\omega(k)}{\mathrm{d}k}\right]_{k=k_0} \tag{2.29}$$

with $k_0=p_0/\hbar$. We remark that this velocity is, in general, different from the *phase velocity* v_{ph}, which is the velocity of propagation of the individual plane waves (2.13) and is given for a particular plane wave $A\exp[\mathrm{i}(k_0x-\omega(k_0)t)]$ by

$$v_{\mathrm{ph}}=\frac{\omega(k_0)}{k_0}=\frac{E(p_0)}{p_0}. \tag{2.30}$$

In the macroscopic limit the motion of a particle must be governed by the laws of classical mechanics, in accordance with the correspondence principle (see Section 1.4). In this limit the extension of the wave packet is negligible so that the group velocity v_{g} can be identified with the classical velocity $v=p_0/m$ of the particle

$$v_{\mathrm{g}}=v=\frac{p_0}{m}. \tag{2.31}$$

Combining this result with (2.28) allows us to determine the functional dependence of $E(p_x)$ on p_x. We have

$$\frac{\mathrm{d}E(p_x)}{\mathrm{d}p_x}=\frac{p_x}{m} \tag{2.32}$$

so that $E(p_x)=p_x^2/2m+\text{constant}$. We may set the constant of integration equal to zero because the zero of energy can be chosen arbitarily, only *energy differences* being of physical interest. Hence we have

$$E(p_x)=\frac{p_x^2}{2m}. \tag{2.33}$$

It should be noted that since $E=h\nu$, the absolute value of the frequency has no physical significance in quantum mechanics, in contrast with classical wave theory (e.g. sound waves). We remark that since in our case $E(p_0) = p_0^2/2m$, the phase velocity (2.30) is given by

$$v_{\text{ph}} = \frac{p_0^2/2m}{p_0} = \frac{p_0}{2m} = \frac{v_g}{2}. \tag{2.34}$$

Let us return to the expression (2.23) of the wave packet and express $E(p_x) = p_x^2/2m$ in the form

$$\begin{aligned} E(p_x) &= \frac{p_0^2}{2m} + \frac{p_0}{m}(p_x - p_0) + \frac{(p_x - p_0)^2}{2m} \\ &= E(p_0) + v_g(p_x - p_0) + \frac{(p_x - p_0)^2}{2m}. \end{aligned} \tag{2.35}$$

Since the function $\phi(p_x)$ in (2.23) is negligible except in the interval $(p_0 - \Delta p_x, p_0 + \Delta p_x)$ we can neglect the third term on the right of (2.35), provided t is small enough so that

$$\frac{1}{2m\hbar}(\Delta p_x)^2 t \ll 1. \tag{2.36}$$

Indeed, if the condition (2.36) is satisfied, the quantity $\exp[-\mathrm{i}(p_x - p_0)^2 t/2m\hbar]$ which occurs in the integrand on the right of (2.23) is approximately equal to unity. Making this approximation, equation (2.23) reduces to

$$\Psi(x, t) = \mathrm{e}^{\mathrm{i}[p_0 x - E(p_0)t]/\hbar} F(x, t) \tag{2.37}$$

where

$$F(x, t) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} \mathrm{e}^{\mathrm{i}(p_x - p_0)(x - v_g t)/\hbar} \phi(p_x) \mathrm{d}p_x. \tag{2.38}$$

The wave packet (2.37) is the product of a plane wave of wavelength $\lambda_0 = h/|p_0|$ and angular frequency $\omega_0 = E(p_0)/\hbar$ times a *modulating* amplitude or *envelope* function $F(x, t)$ such that $|\Psi(x, t)|^2 = |F(x, t)|^2$. Since

$$F(x, t = 0) = F(x + v_g t, t) \tag{2.39}$$

this envelope function propagates *without change of shape* with the group velocity v_g (see Fig. 2.4). It should be borne in mind that this is only true for times t satisfying the condition (2.36); at later times the shape of the wave packet will change as it propagates.

Fourier transforms and momentum space wave function

Looking back at the wave packet (2.23), defining $\psi(x) \equiv \Psi(x, t = 0)$ and using the results of Appendix A, we see that the functions

$$\psi(x) = (2\pi\hbar)^{-1/2} \int \mathrm{e}^{\mathrm{i}p_x x/\hbar} \phi(p_x) \mathrm{d}p_x \tag{2.40}$$

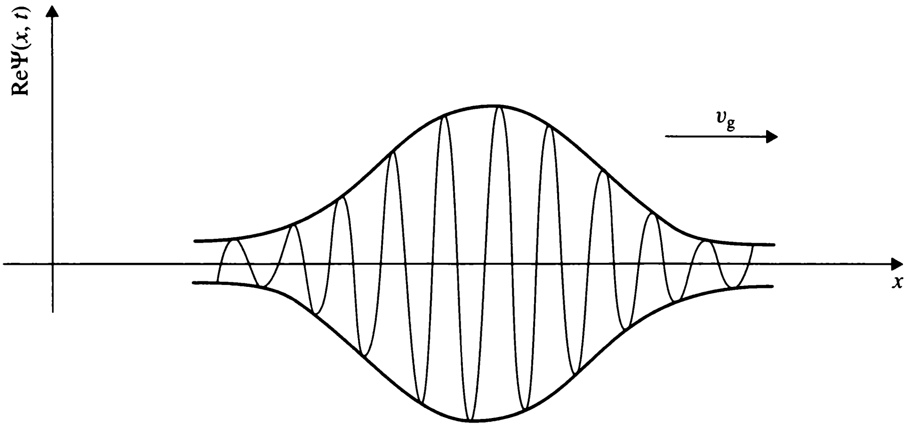


Figure 2.4 The function $\text{Re}\Psi(x, t)$ for a wave packet propagating along the x-axis, with a group velocity v_g.

and

$$\phi(p_x) = (2\pi\hbar)^{-1/2} \int e^{-ip_x x/\hbar} \psi(x) dx \tag{2.41}$$

are *Fourier transforms* of each other. More generally, at time t, we can introduce a function $\Phi(p_x, t)$ such that

$$\Psi(x, t) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} e^{ip_x x/\hbar} \Phi(p_x, t) dp_x \tag{2.42}$$

and

$$\Phi(p_x, t) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} e^{-ip_x x/\hbar} \Psi(x, t) dx \tag{2.43}$$

are also mutual Fourier transforms. The function $\Phi(p_x, t)$ is called the *wave function in momentum space*, and we see that $\phi(p_x) = \Phi(p_x, t = 0)$. The definition of the momentum space wave function given by (2.43) is completely general and holds for all types of wave function $\Psi(x, t)$, including the free particle wave packets which we have been considering.

From Parseval's theorem (see equation (A.43) of Appendix A), we infer that if the wave function $\phi(p_x)$ is normalised to unity in the sense that

$$\int_{-\infty}^{+\infty} |\phi(p_x)|^2 dp_x = 1 \tag{2.44}$$

then the wave function $\psi(x) \equiv \Psi(x, t = 0)$ given by (2.40) is also normalised to unity. Moreover, once $\Psi(x, t)$ is normalised to unity at $t = 0$, it remains normalised to unity at all times. Indeed,

$$\begin{aligned}\int_{-\infty}^{+\infty}\Psi^*(x,t)\Psi(x,t)\mathrm{d}x &= (2\pi\hbar)^{-1}\int_{-\infty}^{+\infty}\mathrm{d}x\int_{-\infty}^{+\infty}\mathrm{d}p_x\int_{-\infty}^{+\infty}\mathrm{d}p'_x\mathrm{e}^{\mathrm{i}[(p_x-p'_x)x]/\hbar}\\ &\quad\times\mathrm{e}^{-\mathrm{i}[E(p_x)-E(p'_x)]t/\hbar}\phi^*(p'_x)\phi(p_x)\\ &= \int_{-\infty}^{+\infty}\mathrm{d}p_x\int_{-\infty}^{+\infty}\mathrm{d}p'_x\delta(p_x-p'_x)\mathrm{e}^{-\mathrm{i}[E(p_x)-E(p'_x)]t/\hbar}\phi^*(p'_x)\phi(p_x)\\ &= \int_{-\infty}^{+\infty}\phi^*(p_x)\phi(p_x)\mathrm{d}p_x\\ &= 1 \end{aligned}\tag{2.45}$$

where in the second line we have introduced the Dirac delta function $\delta(p_x - p'_x)$ such that (see (A.18))

$$\begin{aligned}(2\pi\hbar)^{-1}\int_{-\infty}^{+\infty}\mathrm{e}^{\mathrm{i}[(p_x-p'_x)x]/\hbar}\mathrm{d}x &= (2\pi)^{-1}\int_{-\infty}^{+\infty}\mathrm{e}^{\mathrm{i}[(p_x-p'_x)x']}\mathrm{d}x'\\ &= \delta(p_x-p'_x)\end{aligned}\tag{2.46}$$

and used the property (A.26) in the third line. The result (2.45) expresses the *conservation of probability*, which is clearly a requirement of the theory. We note that if $\Psi(x,t)$ is normalised to unity, so is also the momentum space wave function $\Phi(p_x,t)$.

Gaussian wave packet

As an example, we shall now study the particular case in which the function $\phi(p_x)$ is a Gaussian function peaked about the value p_0

$$\phi(p_x) = C\exp\left[-\frac{(p_x-p_0)^2}{2(\Delta p_x)^2}\right]\tag{2.47}$$

where Δp_x, which we call the width of the distribution in p_x, is a constant such that $|\phi(p_x)|^2$ drops to $1/\mathrm{e}$ of its maximum value at $p_x = p_0 \pm \Delta p_x$ (see Fig. 2.5(a)). The constant C in (2.47) is a *normalisation constant* which we shall choose in such a way that the normalisation condition (2.44) is satisfied. Using the known result

$$\int_{-\infty}^{+\infty}\mathrm{e}^{-\alpha u^2}\mathrm{e}^{-\beta u}\mathrm{d}u = \left(\frac{\pi}{\alpha}\right)^{1/2}\mathrm{e}^{\beta^2/4\alpha}\tag{2.48}$$

with $u = p_x - p_0$, $\alpha = (\Delta p_x)^{-2}$ and $\beta = 0$, we have

$$\int_{-\infty}^{+\infty}|\phi(p_x)|^2\mathrm{d}p_x = |C|^2\pi^{1/2}\Delta p_x.\tag{2.49}$$

The normalisation condition (2.44) is therefore fulfilled by taking

$$|C|^2 = \pi^{-1/2}(\Delta p_x)^{-1}.\tag{2.50}$$

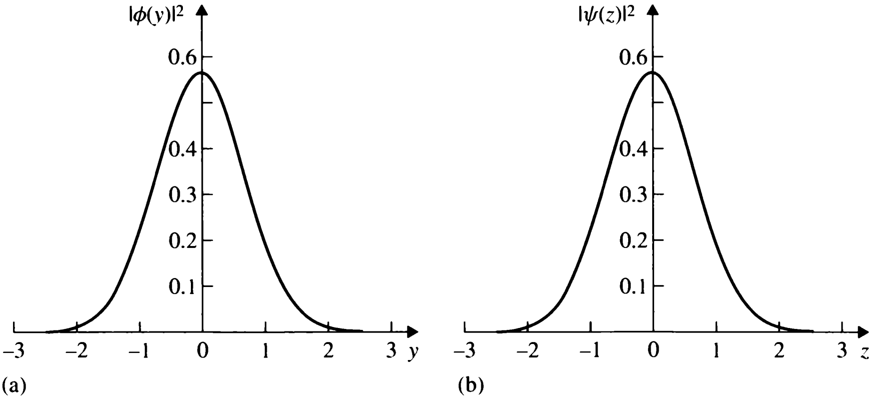


Figure 2.5 (a) The function $|\phi(y)|^2 = \pi^{-1/2}\exp(-y^2)$, where $y = (p_x - p_0)/\Delta p_x$. (b) The function $|\psi(z)|^2 = \pi^{-1/2}\exp(-z^2)$, where $z = (\Delta p_x/\hbar)x$.

The constant C is determined by (2.50) apart from a phase factor of unit modulus, which can be set equal to one, so that we can take C to be given by

$$C = \pi^{-1/4}(\Delta p_x)^{-1/2}. \tag{2.51}$$

Substituting $\phi(p_x)$ given by (2.47) into (2.40) and using (2.48) and (2.51), we find that

$$\psi(x) \equiv \Psi(x, t = 0) = \pi^{-1/4}\hbar^{-1/2}(\Delta p_x)^{1/2}\mathrm{e}^{\mathrm{i}p_0x/\hbar}\mathrm{e}^{-(\Delta p_x)^2x^2/2\hbar^2}. \tag{2.52}$$

Apart from the phase factor $\exp(ip_0x/\hbar)$, this function is again a Gaussian. We remark that $|\psi(x)|^2$ has a maximum at $x = 0$ and falls to $1/\mathrm{e}$ of its maximum value at $x = \pm\Delta x$, where $\Delta x = \hbar/\Delta p_x$ is the width of the distribution in the x variable (see Fig. 2.5(b)). Given the above definitions of the 'widths' Δx and Δp_x, we see that for a Gaussian wave packet $\Delta x \Delta p_x = \hbar$. Thus if we decrease Δp_x so that the wave function in momentum space, $\phi(p_x)$, is more sharply peaked about $p_x = p_0$, then Δx will increase and $\psi(x)$ becomes increasingly 'delocalised'. Conversely, if Δp_x is increased, so that $\phi(p_x)$ is 'delocalised' in momentum space, then $\psi(x)$ will become more strongly localised about $x = 0$. We shall return shortly to this important property, which is of a general nature. We note from (2.40) and (A.26) that in the limit in which $\phi(p_x)$ is the delta function $\delta(p_x - p_0)$, the wave function $\psi(x)$ becomes the plane wave $(2\pi\hbar)^{-1/2}\exp(\mathrm{i}p_0x/\hbar)$, which is completely delocalised.

Let us now examine how the Gaussian wave packet evolves in time. Using (2.23), (2.33), (2.47), (2.51) and (2.48) we find that

$$\Psi(x, t) = \pi^{-1/4}\left[\frac{\Delta p_x/\hbar}{1 + \mathrm{i}(\Delta p_x)^2t/m\hbar}\right]^{1/2} \times \exp\left[\frac{\mathrm{i}p_0x/\hbar - (\Delta p_x/\hbar)^2x^2/2 - \mathrm{i}p_0^2t/2m\hbar}{1 + \mathrm{i}(\Delta p_x)^2t/m\hbar}\right] \tag{2.53}$$

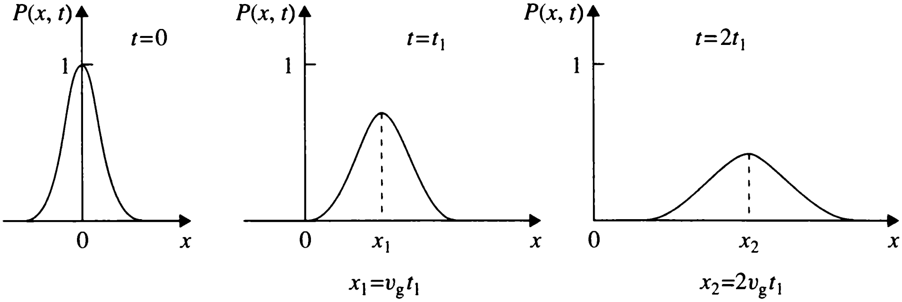


Figure 2.6 The position probability density $P(x, t) = |\Psi(x, t)|^2$ for a Gaussian wave packet at times $t = 0$, $t = t_1$ and $t = 2t_1$, plotted in arbitrary units.

and the corresponding position probability density is

$$P(x,t) = |\Psi(x,t)|^2 = \pi^{-1/2} \frac{\Delta p_x/\hbar}{[1 + (\Delta p_x)^4 t^2/m^2\hbar^2]^{1/2}} \times \exp\left[-\frac{(\Delta p_x/\hbar)^2 (x - v_g t)^2}{1 + (\Delta p_x)^4 t^2/m^2\hbar^2}\right] \tag{2.54}$$

where we recall that $v_g = p_0/m$ is the group velocity of the packet. It is clear from (2.54) that the centre of the wave packet moves uniformly with the velocity v_g. The width of the packet, defined so that $P(x, t)$ falls to 1/e of its maximum value at the points $x - v_g t = \pm\Delta x$, is given by

$$\Delta x(t) = \frac{\hbar}{\Delta p_x}\left[1 + \frac{(\Delta p_x)^4}{m^2\hbar^2} t^2\right]^{1/2} \tag{2.55}$$

and hence increases with time. However, if the time is sufficiently small so that

$$t \ll t_1 = \frac{m\hbar}{(\Delta p_x)^2} \tag{2.56}$$

the second term in brackets in (2.55) is very small and the wave packet propagates without changing its width appreciably. This is in accordance with our general discussion (see (2.36)–(2.39)). The spreading of the probability density (2.54) is illustrated in Fig. 2.6, where $P(x, t)$ is shown for times $t = 0$, $t = t_1$ and $t = 2t_1$.

To take a particular case, consider a Gaussian wave packet associated with an electron which at time $t = 0$ is localised to within a distance 10^{-10} m characteristic of atomic dimensions, so that $\Delta p_x = \hbar/\Delta x \simeq 10^{-24}$ kg m s^{-1}. According to (2.55) the wave packet will have spread to twice its size at time $t = \sqrt{3}t_1 \simeq 10^{-16}$ s (see Problem 2.7). On the other hand, for a macroscopic object having a mass of 1 g, whose position is initially defined within an accuracy $\Delta x \simeq 10^{-6}$ m, we find that the width of the packet doubles after a time $t \simeq 10^{19}$ s, which is larger than the estimated age of the universe.

A word of caution should be said about the interpretation of these results. Let us suppose that we have a wave packet representing an electron, which is spread so that the width of the packet is, for example, $\Delta x = 1$ km at a given time. If an electron detector is placed at a particular position at that time, it will record the presence or absence of the 'complete' electron, since when the electron manifests itself in the detection process it is indivisible. Before the electron is detected the wave function determines the *probability* that the electron will be found at a certain place, at a given time. As soon as the electron has been detected, its location is of course known to within a precision $\Delta x' \ll \Delta x$, so that a new wave function must describe the situation. This change of the wave function upon measurement is called the '*collapse of the wave packet*'. A more careful analysis of this measurement problem can be based on the study of the combined wave function of the measured system and the measuring apparatus. Using this approach, it will be shown in Chapter 17 that the idea of an instantaneous 'collapse' of 'reduction' of the wave function on measurement can be avoided.

Wave packets in three dimensions

Our discussions of one-dimensional free-particle wave packets can easily be extended to three dimensions. By superposing plane waves of the form (2.16) we obtain the wave packet

$$\begin{aligned}\Psi(\mathbf{r}, t) &= (2\pi\hbar)^{-3/2}\int_{-\infty}^{+\infty} \mathrm{d}p_x \int_{-\infty}^{+\infty} \mathrm{d}p_y \int_{-\infty}^{+\infty} \mathrm{d}p_z \mathrm{e}^{\mathrm{i}[\mathbf{p}.\mathbf{r}-E(p)t]/\hbar}\phi(\mathbf{p}) \\ &= (2\pi\hbar)^{-3/2}\int \mathrm{e}^{\mathrm{i}[\mathbf{p}.\mathbf{r}-E(p)t]/\hbar}\phi(\mathbf{p})\mathrm{d}\mathbf{p} \qquad \textbf{(2.57)}\end{aligned}$$

where $\mathrm{d}\mathbf{p} = \mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$ is the volume element in momentum space. Writing $\psi(\mathbf{r}) \equiv \Psi(\mathbf{r}, t = 0)$ we see from Appendix A that

$$\psi(\mathbf{r}) = (2\pi\hbar)^{-3/2}\int \mathrm{e}^{\mathrm{i}\mathbf{p}.\mathbf{r}/\hbar}\phi(\mathbf{p})\mathrm{d}\mathbf{p} \qquad \textbf{(2.58)}$$

and

$$\phi(\mathbf{p}) = (2\pi\hbar)^{-3/2}\int \mathrm{e}^{-\mathrm{i}\mathbf{p}.\mathbf{r}/\hbar}\psi(\mathbf{r})\mathrm{d}\mathbf{r} \qquad \textbf{(2.59)}$$

are three-dimensional *Fourier transforms* of each other. Paralleling our discussion of the one-dimensional case, a *momentum space wave function* $\Phi(\mathbf{p}, t)$ can be introduced as the Fourier transform of the wave function $\Psi(\mathbf{r}, t)$, so that

$$\Psi(\mathbf{r}, t) = (2\pi\hbar)^{-3/2}\int \mathrm{e}^{\mathrm{i}\mathbf{p}.\mathbf{r}/\hbar}\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p} \qquad \textbf{(2.60)}$$

and

$$\Phi(\mathbf{p}, t) = (2\pi\hbar)^{-3/2}\int \mathrm{e}^{-\mathrm{i}\mathbf{p}.\mathbf{r}/\hbar}\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} \qquad \textbf{(2.61)}$$

and we note that $\phi(\mathbf{p}) = \Phi(\mathbf{p}, t = 0)$. As in the one-dimensional case (see (2.43)) this definition of the momentum space wave function is completely general, and holds for all types of wave functions $\Psi(\mathbf{r}, t)$. If $\phi(\mathbf{p})$ is normalised to unity, then $\Psi(\mathbf{r}, t)$ is also normalised to unity at all times, i.e. satisfies (2.7). The momentum space wave function $\Phi(\mathbf{p}, t)$ will then also be normalised to unity, satisfying

$$\int |\Phi(\mathbf{p}, t)|^2 \mathrm{d}\mathbf{p} = 1. \tag{2.62}$$

As a result, the quantity

$$\Pi(\mathbf{p}, t)\mathrm{d}\mathbf{p} = |\Phi(\mathbf{p}, t)|^2 \mathrm{d}\mathbf{p} = \Phi^*(\mathbf{p}, t)\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p} \tag{2.63}$$

is the probability at time t that the momentum of the particle lies within the momentum space volume element $\mathrm{d}\mathbf{p} \equiv \mathrm{d}p_x \mathrm{d}p_y \mathrm{d}p_z$ about the point $\mathbf{p} \equiv (p_x, p_y, p_z)$.

A three-dimensional wave packet associated with a free particle having fairly well determined values of both position coordinates (x, y, z) and momentum coordinates (p_x, p_y, p_z) can be constructed analogously to the one-dimensional case. Assuming that the function $\phi(\mathbf{p})$ in (2.57) is peaked about $\mathbf{p} = \mathbf{p}_0$, and setting

$$\beta(\mathbf{p}) = \mathbf{p}.\mathbf{r} - E(p)t \tag{2.64}$$

one finds (Problem 2.8) that the centre of the wave packet, defined by the condition[1]

$$[\nabla_{\mathbf{p}}\beta(\mathbf{p})]_{\mathbf{p}=\mathbf{p}_0} = 0 \tag{2.65}$$

travels with a uniform motion according to the law

$$\mathbf{r} = \mathbf{v}_g t \tag{2.66}$$

where

$$\mathbf{v}_g = [\nabla_{\mathbf{p}} E(p)]_{\mathbf{p}=\mathbf{p}_0} \tag{2.67}$$

is the *group velocity* of the wave packet. Equations (2.66) and (2.67) are the generalisations of equations (2.27) and (2.28), respectively. In the classical limit the group velocity $\mathbf{v}_g$ must be equal to the velocity $\mathbf{v} = \mathbf{p}_0/m$ of the particle, from which we find that the functional relation between E and p is given by

$$E(p) = \frac{p^2}{2m} \tag{2.68}$$

apart from an additive constant which can be chosen to be zero.

---

[1] In equation (2.65), $\nabla_{\mathbf{p}}\beta(\mathbf{p})$ is a vector having Cartesian components $\partial\beta(p_x, p_y, p_z)/\partial p_x$, $\partial\beta(p_x, p_y, p_z)/\partial p_y$ and $\partial\beta(p_x, p_y, p_z)/\partial p_z$.

Wave packets in a slowly varying potential

The general idea we have developed for the motion of a free-particle wave packet in the classical limit can be extended to describe the motion of a particle in a potential $V(\mathbf{r})$ provided that the potential does not vary appreciably over a distance comparable to the de Broglie wavelength of the particle. In this case the centre of the wave packet travels along the trajectory followed by a classical particle moving in the potential $V(\mathbf{r})$. As the centre of the wave packet moves along this trajectory, the de Broglie wavelength changes slowly, being determined by the relation

$$\lambda = \frac{h}{p} = \frac{h}{[2m(E - V(\mathbf{r}))]^{1/2}} \tag{2.69}$$

where $p = [2m(E - V(\mathbf{r}))]^{1/2}$ is the classical local momentum of the particle.

2.5 The Heisenberg uncertainty principle

We have shown in the case of a one-dimensional Gaussian wave packet that the 'width' Δx of the distribution in the position variable x is linked with the 'width' Δp_x of the distribution in the momentum p_x by the relation $\Delta x \Delta p_x \geqslant \hbar$. In fact, it is a general property of Fourier transforms that 'widths' in position and momentum satisfy the relation

$$\Delta x \Delta p_x \gtrsim \hbar \tag{2.70}$$

where the sign $\gtrsim$ means 'greater than or of the order of'. In the context of quantum mechanics this is called the *Heisenberg uncertainty relation for position and momentum*, according to which a state cannot be prepared in which both the position and momentum of a particle can be defined simultaneously to arbitrary accuracy. In fact, the product of the uncertainty Δx in the precision with which the position can be defined with the uncertainty Δp_x in the precision with which the momentum can be defined, cannot be made smaller than a quantity of order $\hbar$. At this point we have not given a precise definition of the uncertainties Δx and Δp_x, but this will be done later, in Chapter 5.

The relation (2.70) is easily generalised to three dimensions by using the properties of three-dimensional Fourier transforms. The three-dimensional form of the Heisenberg uncertainty relations for position and momentum is

$$\Delta x \Delta p_x \gtrsim \hbar, \qquad \Delta y \Delta p_y \gtrsim \hbar, \qquad \Delta z \Delta p_z \gtrsim \hbar. \tag{2.71}$$

It should be noted that there is no relation between the uncertainty in one Cartesian component of the position vector of a particle, for example Δx, and the uncertainty in a *different* Cartesian component of the momentum, for example Δp_y. The only restrictions are on the 'complementary' pairs: Δx, Δp_x; Δy, Δp_y; and Δz, Δp_z.

It is worth stressing that the Heisenberg uncertainty relations do not place any restriction on the precision with which a position measurement of a particle can be made. However, once such a measurement has been made and the particle is known to be confined to some region of extent Δa, the ensemble of such particles is subsequently described by a wave function also of extent Δa. Subsequent measurements of the momentum on each of the identical systems composing the ensemble will then produce a range of values with a spread of order $\hbar/\Delta a$.

Suppose now that before the position measurement was made the particle was in a state of definite momentum. We see then that the act of measuring the position forces the system into a state in which the momentum is no longer known exactly but has become uncertain by an amount $\Delta p \gtrsim \hbar/\Delta a$. Thus the Heisenberg uncertainty relations do not refer to the period before the state was prepared, but only to the current situation.

Similarly, it can be seen that the Heisenberg relations do not restrict the precision with which a momentum measurement can be made, but once the system is known to have a momentum defined to within a precision Δp, subsequent measurements of the position must produce results spread over a range $\gtrsim \hbar/\Delta p$. The uncertainty Δp can be made arbitrarily small, but the more precisely the momentum of the system is known the greater the range of results that will be obtained in a series of position measurements on an ensemble of such systems.

Finally, it is hardly necessary to point out that the inherent limitations on measurement imposed by the Heisenberg relations have nothing to do with the 'experimental errors' that occur in actual measurements.

The γ-ray microscope

As a first illustration of the Heisenberg uncertainty relations, let us consider a conceptual ('*gedanken*') experiment first discussed by Heisenberg, which attempts to measure the position of a particle as accurately as possible. This experiment consists of illuminating the particle and observing the image through a microscope (see Fig. 2.7). If λ is the wavelength of the incident radiation, then the x component of the particle position can be determined to a precision Δx given by the resolving power of the microscope, namely

$$\Delta x = \frac{\lambda}{\sin\theta} \tag{2.72}$$

where θ is the half-angle subtended at the particle P by the lens L. This resolving power can be made very small by using radiation of short wavelength, such as γ rays. Now, for any measurement to be possible at least one photon must enter the microscope after scattering from the particle. This Compton scattering imparts to the particle a recoil momentum of the order of magnitude of the photon momentum $p_\gamma = h/\lambda$. However, this recoil momentum cannot be exactly known, since the direction of the scattered photon is only determined to within the angle θ. Thus there is an uncertainty in the recoil momentum of the particle in the x direction by an amount

$$\Delta p_x \simeq \frac{h}{\lambda}\sin\theta \tag{2.73}$$

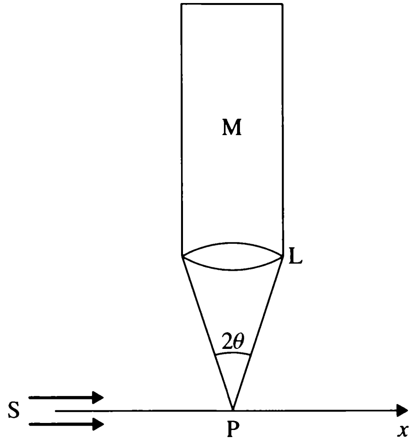


Figure 2.7 The Heisenberg γ-ray microscope. Photons from a source S are scattered into a microscope M from a particle located at P. The resolving power of the microscope is $\lambda/\sin\theta$, where λ is the photon wavelength and 2θ is the angle subtended by the lens L at the particle.

and upon combining (2.73) with (2.72) we see that after the observation one always has

$$\Delta x \Delta p_x \simeq h \tag{2.74}$$

which is consistent with the Heisenberg uncertainty relation (2.70).

The two-slit experiment

As a second example, let us return to the two-slit experiment discussed in Section 2.1, and analyse it in the light of the uncertainty principle. Suppose we attempt to discover which slit a particle (for example an electron) goes through. This might be done by placing a microscope behind one of the slits (see Fig. 2.8). In order to discriminate between particles which have passed through slit A or slit B the resolving power of the microscope must be less than the distance d between the slits. From (2.72) we see that the wavelength of the light illuminating the particle must be smaller than d. The corresponding photon momentum $p_\gamma = h/\lambda$ must therefore be larger than h/d. The interaction of a photon having this momentum with the electron will make the electron momentum p uncertain by an amount Δp which is of the order of p_γ, and hence will be such that

$$d\Delta p \gtrsim h \tag{2.75}$$

in agreement with the uncertainty relations. Consequently, the direction of motion of the particle also becomes uncertain by an amount $\Delta\theta$, where (see Fig. 2.8)

$$\Delta\theta \simeq \frac{\Delta p}{p} \simeq \frac{h}{pd} \simeq \frac{\lambda_e}{d} \tag{2.76}$$

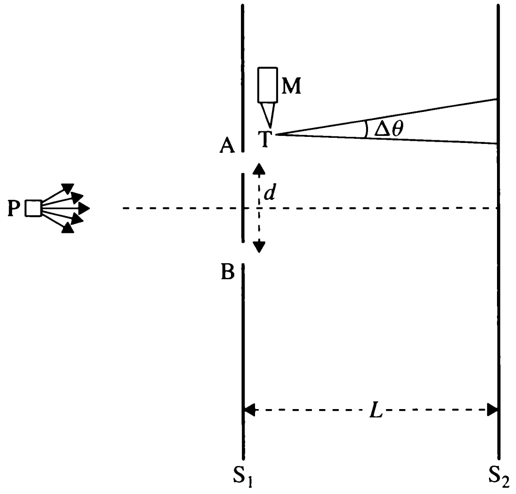


Figure 2.8 In the two-slit experiment of Fig. 2.1 a microscope M is placed behind the slit A and the area behind the slit is illuminated. A particle is located at the point T, but as a result of the photon–particle interaction the direction of motion of the particle becomes uncertain by $\Delta\theta$.

where $\lambda_e = h/p$ is the de Broglie wavelength of the electron. This in turn produces an uncertainty $\lambda_e L/d$ in the position of the particle on the screen, which is comparable to the distance between successive maxima of the interference pattern. Thus, if an attempt is made to determine through which slit the particles pass, the interference pattern is destroyed.

Stability of atoms

The position–momentum uncertainty relations (2.71) can be used to obtain an estimate of the binding energy of the hydrogen atom in its ground state. To this end, let us write the total classical energy of the electron in the field of the proton (assumed to be infinitely heavy) as

$$E = \frac{p^2}{2m} - \frac{e^2}{(4\pi\varepsilon_0)r}. \tag{2.77}$$

The first term on the right-hand side is the kinetic energy, which is positive, while the second term represents the negative potential energy. Classically, there is no lower limit to the value of the total energy E because r, the radius of the electronic orbit, can be made as small as one pleases. This is not the case in quantum mechanics. If p is interpreted as the average momentum of the electron in a given state, it follows that the momentum is determined within a range Δp of the order of p. From the uncertainty relations (2.71), this in turn implies that the smallest value of the uncertainty Δr of the position of the electron is of the order of $\hbar/p$. Assuming that the average value of the radius r is of the order of Δr, we then have $rp \simeq \hbar$, from which

$$E \simeq \frac{\hbar^2}{2mr^2} - \frac{e^2}{(4\pi\varepsilon_0)r}. \tag{2.78}$$

As a result, there is a *minimum* value of the total energy E at $r \simeq r_0$ such that $\mathrm{d}E/\mathrm{d}r = 0$, namely

$$r_0 \simeq \frac{(4\pi\varepsilon_0)\hbar^2}{me^2} = a_0 \tag{2.79}$$

where a_0 is the first Bohr radius (1.66). Substituting $r = a_0$ in (2.78) we find that the ground-state energy E_0 is given approximately by

$$E_0 \simeq -\frac{e^2}{(4\pi\varepsilon_0)2a_0}. \tag{2.80}$$

The fact that this estimate of E_0 coincides with the actual ground-state energy of atomic hydrogen must not be taken too seriously, as the argument is clearly qualitative. However, the important point is that this reasoning shows that there is a *minimum* value of the total energy E of an atom, which is *the lowest value of E compatible with the uncertainty principle.* We can therefore understand in this way why atoms are stable.

The uncertainty relation for time and energy

A time–energy uncertainty relation analogous to the position–momentum uncertainty relations (2.71) can be obtained in the following way. Let $\Psi(t) \equiv \Psi(\mathbf{r}_0, t)$ be a wave function, at a fixed point $\mathbf{r} = \mathbf{r}_0$, associated with a single particle state. We consider the case such that $\Psi(t)$ is a pulse or 'time packet', which is negligible except in a time interval Δt. This time packet can be expressed as a superposition of monochromatic waves of angular frequency ω by the Fourier integral (see Appendix A)

$$\Psi(t) = (2\pi)^{-1/2} \int_{-\infty}^{+\infty} G(\omega) \mathrm{e}^{-\mathrm{i}\omega t} \mathrm{d}\omega \tag{2.81}$$

where the function $G(\omega)$ is given by

$$G(\omega) = (2\pi)^{-1/2} \int_{-\infty}^{+\infty} \Psi(t) \mathrm{e}^{\mathrm{i}\omega t} \mathrm{d}t. \tag{2.82}$$

As $\Psi(t)$ takes only significant values for a duration Δt, it follows from the general properties of Fourier transforms that $G(\omega)$ is only significant for a range of angular frequencies such that

$$\Delta\omega\Delta t \gtrsim 1. \tag{2.83}$$

Since $E = \hbar\omega$, the width of the distribution in energy, ΔE, satisfies the time–energy uncertainty relation

$$\Delta E \Delta t \gtrsim \hbar. \tag{2.84}$$

The interpretation of this relationship is somewhat different from that of the position–momentum uncertainty relations (2.71) because the time t is a parameter, and not a dynamical variable like x or p_x. The relation (2.84) implies that if the dynamical state exists only for a time of order Δt, then the energy of the state cannot be defined to a precision better than $\hbar/\Delta t$. In other words, if we consider an ensemble of identically prepared systems described by the wave function Ψ, then the measurement of the energy on each member of the ensemble will produce a range of values spread over an interval ΔE of extent greater than or of the order of $\hbar/\Delta t$.

Energy width and natural lifetime of excited states of atoms

As an example, let us consider an atomic transition from an excited state of energy E_b, in which a photon is emitted (see Fig. 2.9(a)). The time of emission of the photon from a particular atom cannot be predicted. However, as we shall see in Chapter 11, quantum mechanics does predict the *probability* that the transition takes place at a given time. This in turn determines the *average duration* (over a large number of atoms) of the excited state b, called the *lifetime* τ_b of that state. Clearly, the wave function Ψ describing the atomic system in the state b must be negligible outside a time interval Δt of the order of τ_b. From the uncertainty relation (2.84) it follows that the energy of the excited state b is not sharply defined, but is uncertain at least by an amount

$$\Delta E_b = \frac{\hbar}{\tau_b} \tag{2.85}$$

known as the *natural energy width* of the state b. We see from (2.85) that the shorter the lifetime of an excited state, the larger the natural energy width of that state. On the other hand, the ground state a is stable, since in this state the system cannot make a transition to a state of lower energy. The lifetime of the ground state is therefore infinite ($\tau_a = \infty$) and the ground state energy E_a is perfectly sharp ($\Delta E_a = 0$).

Because of the natural energy width ΔE_b of the excited state b, the energy emitted (or absorbed) in a transition between the atomic states a and b is not sharply defined. Instead, the photons emitted (or absorbed) in transitions between the states a and b have an energy distribution of natural width ΔE_b about the value $E_b - E_a$. As a result, the spectral line associated with this transition does not have the sharply defined frequency $\nu_{ab} = (E_b - E_a)/h$, but has a distribution of frequencies of width at least as great as $\Delta\nu = \Delta E_b/h$ about the value ν_{ab}. The quantity $\Delta\nu$ is called the *natural linewidth* of that spectral line. If the transition occurs between two excited states a and b (see Fig. 2.9(b)), the photons emitted or absorbed in the transition will have an energy distribution of natural width

$$\Delta E_{ab} = \hbar\left(\frac{1}{\tau_a} + \frac{1}{\tau_b}\right) \tag{2.86}$$

where τ_a is the lifetime of the lower state a. The natural linewidth of the spectral line is then $\Delta\nu_{ab} = \Delta E_{ab}/h$.

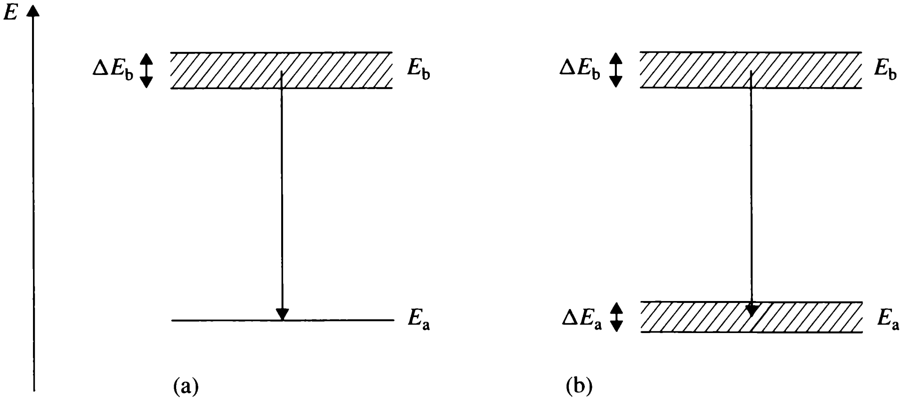


Figure 2.9 Widths of energy levels. In (a) the lower state is the ground state. In (b) both states are excited states.

The preceding discussion concerning the relation between the lifetime and the natural energy width of excited states is not confined to atomic states, but is equally applicable to other quantum systems such as molecules or nuclei.

Natural energy width and resonance absorption of radiation

In Chapter 1, we showed that because of the *recoil* of the atom the wavelength of an emission line is slightly different from that of the corresponding absorption line, with the consequence that radiation emitted by one atom could not be absorbed by another atom of the same kind (see (1.76)). This is contrary to what is observed. The paradox can be resolved by recognising that the energy levels of excited states have a finite width, so that an atom can emit or absorb photons within a range of energies determined by the natural energy widths of the levels concerned. Thus, if the change in frequency due to the recoil is smaller than the natural linewidth associated with the transition, an atom will be able to absorb radiation emitted by another atom of the same kind. Now, as seen from (1.76), the largest change of frequency due to recoil occurs for atoms of the smallest mass–hydrogen atoms. For a typical atomic transition involving photons having an energy $h\nu \simeq 2$ eV the change of frequency due to recoil is therefore of the order of or less than

$$|\Delta\nu_R| = \frac{(h\nu)^2}{2hM_pc^2} \simeq 5 \times 10^5 \text{ Hz.} \tag{2.87}$$

On the other hand, a typical atomic lifetime is about 10^{-8} s, corresponding to a natural linewidth of 1.5×10^7 Hz. Since this value is considerably larger than $|\Delta\nu_R|$ resonance absorption can indeed occur.

In contrast, for transitions occurring between energy levels of nuclei the change of frequency $|\Delta\nu_R|$ due to recoil often exceeds the natural linewidth, with the consequence that the γ-ray photons emitted by one nucleus cannot in general be absorbed by another nucleus of the same kind. An exception occurs when the nuclei are bound in a crystal lattice. Then, in a fraction of the transitions, the crystal recoils as a whole, so that the mass M to be used in (1.76) is extremely large. The corresponding frequency change $|\Delta\nu_R|$ is therefore negligible and resonance absorption can take place. This phenomenon is known as the *Mössbauer effect*; it is enhanced at low temperatures when the lattice becomes 'stiffer'.

The uncertainty principle and complementarity

The uncertainty relations for position and momentum and for energy and time are particular examples of the *uncertainty principle*, formulated by W. Heisenberg in 1927[2]. According to this principle, it is impossible to prepare states in which both members of certain pairs of variables, called *complementary variables*, have values determined with arbitrary precision. If one of the variables of a complementary pair is measured, information is inevitably lost about the other. We have studied in some detail the complementary pairs (x, p_x) and (E, t), but as we shall see in Chapter 5 other pairs of complementary variables exist which satisfy uncertainty relations.

The Heisenberg uncertainty principle is clearly a consequence of wave–particle duality, and reflects the fact that quantum mechanics, although a complete theory, provides a less detailed description of a physical system than does classical physics. In his *complementarity principle*, introduced in 1928, Bohr described this situation by stating that the wave and particle aspects of physical systems are complementary, both aspects being needed for a complete description of nature.

Problems

2.1 Consider the wave packet $\psi(x) \equiv \Psi(x, t = 0)$ given by

$$\psi(x) = C e^{\mathrm{i}p_0 x/\hbar} e^{-|x|/(2\Delta x)}$$

where C is a normalisation constant.

(a) Normalise $\psi(x)$ to unity.
(b) Obtain the corresponding momentum space wave function $\phi(p_x)$ and verify that it is normalised to unity according to (2.44).
(c) Suggest a reasonable definition of the width Δp_x of the momentum distribution and show that $\Delta x \Delta p_x \gtrsim \hbar$.

2.2 Consider the momentum space wave function

$$\phi(p_x) = \begin{cases} 0, & |p_x - p_0| > \gamma \\ C, & |p_x - p_0| \leqslant \gamma \end{cases}$$

where C and γ are constants.

---

[2] A detailed discussion of the uncertainty principle can be found in Heisenberg's book *The Physical Principles of the Quantum Theory* (1949).

(a) Normalise $\phi(p_x)$ to unity according to (2.44).

(b) Find the corresponding wave function $\psi(x)$ in configuration space, and verify that $\psi(x)$ is normalised to unity.

$$\left(\textit{Hint}\text{: Use the result } \int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2} \mathrm{d}x = \pi.\right)$$

(c) Using reasonable definitions of the widths Δx and Δp_x, show that

$$\Delta x \Delta p_x \gtrsim \hbar.$$

2.3 The family of functions $\delta_L(x)$ is defined by

$$\delta_L(x) = (2\pi)^{-1} \int_{-L}^{+L} \mathrm{e}^{\mathrm{i}kx} \mathrm{d}k.$$

Evaluate the integral and show that $\delta_L(x)$ behaves like the Dirac delta function $\delta(x)$ as $L \to \infty$.

2.4 Let $\delta_\varepsilon(x)$ be a family of functions defined by

$$\delta_\varepsilon(x) = (2\pi)^{-1} \int_{-\infty}^{+\infty} \mathrm{e}^{\mathrm{i}kx} \mathrm{e}^{-\varepsilon k^2} \mathrm{d}k, \qquad \varepsilon > 0.$$

Evaluate the integral and show that $\delta_\varepsilon(x)$ has the properties of the Dirac delta function $\delta(x)$ as $\varepsilon \to 0$.

2.5 Verify that the Dirac delta function can be represented in the following ways

$$\delta(x) = \lim_{\varepsilon \to 0^+} \frac{\varepsilon/\pi}{x^2 + \varepsilon^2} \tag{1}$$

$$= \lim_{\varepsilon \to 0^+} \frac{\sin(x/\varepsilon)}{\pi x} \tag{2}$$

$$= \lim_{\varepsilon \to 0^+} \frac{\varepsilon}{\pi x^2}[1 - \cos(x/\varepsilon)] \tag{3}$$

$$= \lim_{\varepsilon \to 0} \frac{\theta(x + \varepsilon) - \theta(x)}{\varepsilon} \tag{4}$$

where in equation (4) $\theta(x)$ is the step function

$$\theta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0. \end{cases}$$

2.6 (a) By multiplying both sides of the following equations by a differentiable function $f(x)$, and integrating over x, verify the following equations:

$$\begin{aligned}
\delta(x) &= \delta(-x) \\
\delta'(x) &= -\delta'(-x), \qquad \delta'(x) = \frac{\mathrm{d}}{\mathrm{d}x}\delta(x) \\
x\delta(x) &= 0 \\
x\delta'(x) &= -\delta(x) \\
\delta(ax) &= \frac{1}{|a|}\delta(x), \qquad a \neq 0 \\
\delta(x^2 - a^2) &= \frac{1}{2|a|}[\delta(x-a) + \delta(x+a)].
\end{aligned}$$

(b) Prove the following relations

$$\int \delta(a-x)\delta(x-b)\mathrm{d}x = \delta(a-b)$$

$$f(x)\delta(x-a) = f(a)\delta(x-a).$$

2.7 (a) A Gaussian wave packet is associated with an electron localised at time $t = 0$ to within a distance of 10^{-10} m. Show that this wave packet will have spread to twice its size after a time $t \simeq 10^{-16}$ s.

(b) Consider now a Gaussian wave packet associated with a proton localised at time $t = 0$ to within a distance of 10^{-14} m. Find the time after which this wave packet will have doubled in size.

2.8 Let $\Psi(\mathbf{r}, t)$ be a three-dimensional wave packet defined by (2.57). Show that if the function $\phi(\mathbf{p})$ is peaked about $\mathbf{p} = \mathbf{p}_0$, the centre of the wave packet, defined by the condition (2.65), travels uniformly according to the law $\mathbf{r} = \mathbf{v}_g t$, where the group velocity $\mathbf{v}_g$ is given by (2.67).

2.9 A monoenergetic beam of electrons falls on a screen containing a slit of width d. The coordinates of the electrons in the x direction (taken along the screen) are therefore known at the moment after passing the slit with the accuracy $\Delta x = d$. Now, because of the wave nature of the electron, diffraction phenomena are produced by the slit. The emergent beam has a finite angle of divergence θ which, according to diffraction theory is such that

$$\sin\theta = \frac{\lambda}{d}$$

where λ is the de Broglie wavelength of the electrons. Show that after the electrons have passed through the slit the component of their momentum along the x-axis becomes uncertain by an amount $\Delta p_x \gtrsim \hbar/d$.

2.10 An electron is confined within a region of atomic dimensions, of the order of 10^{-10} m. Find the uncertainty in its momentum. Repeat the calculation for a proton confined to a region of nuclear dimensions, of the order of 10^{-14} m.

2.11 Using the uncertainty principle, find the minimum value (in MeV) of the kinetic energy of a nucleon confined within a nucleus of radius $R = 5 \times 10^{-15}$ m.

2.12 Calculate the relative frequency spread $\Delta\nu/\nu$ for a nanosecond (10^{-9} s) pulse from a CO_2 laser, in which the nominal photon energy is $h\nu = 0.112$ eV.

2.13 A beam of monoenergetic electrons is used to raise atoms to an excited state in a Franck–Hertz experiment. If this excited state has a lifetime of 10^{-9} s, calculate the spread in energy of the inelastically scattered electrons.

3 The Schrödinger equation

In Chapter 2 we introduced the concept of the wave function to describe the properties of a physical system, and we saw that in the position representation the wave function Ψ of a particle is a function of its space coordinates $\mathbf{r}$ and of the time t. Clearly, in order to make progress we need a method of determining wave functions systematically. In this chapter we shall show that the wave function $\Psi(\mathbf{r}, t)$ can be calculated from a partial differential equation called the *Schrödinger wave equation.* We shall discuss some general properties of its solutions, examine how expectation values of physical quantities can be calculated from the knowledge of $\Psi(\mathbf{r}, t)$, and analyse the transition from quantum mechanics to classical mechanics. We shall also see how the Schrödinger theory accounts for the quantisation of energy levels, and we shall conclude the chapter with a brief discussion of the Schrödinger equation in momentum space.

In searching for an equation to be satisfied by the wave function Ψ, we shall be guided by the following principles. First, the equation should be *linear* and *homogeneous* so that the *superposition principle* holds. That is, if Ψ_1 and Ψ_2 are solutions of the wave equation for a given system, any linear combination $c_1\Psi_1 + c_2\Psi_2$ (where c_1 and c_2 are constants) must also be a solution. Secondly, the results obtained by using the equation should agree with those of classical mechanics in macroscopic situations, in accord with the *correspondence principle.* Finally, in order to satisfy the hypothesis that the evolution of the system is entirely determined once the wave function is known at a particular time, the equation should be of first order in the time derivative $\partial/\partial t$. If the equation contained the second derivative $\partial^2\Psi/\partial t^2$, it would be necessary to specify both Ψ and $\partial\Psi/\partial t$ at a certain time to obtain a unique solution, in contradiction to the hypothesis that only a knowledge of Ψ is required.

3.1 The time-dependent Schrödinger equation

Let us begin by considering the one-dimensional, non-relativistic motion of a free particle of mass m, having a well-defined momentum $\mathbf{p} = p_x\hat{\mathbf{x}}$ (where $\hat{\mathbf{x}}$ is the unit vector along the x-axis) of magnitude $p = |p_x|$ and an energy E. Assuming that the particle is travelling in the positive x direction (so that $p_x = p$) we have seen in Chapter 2 that this particle is described by a monochromatic plane wave of wave number $k = p_x/\hbar$ and angular frequency $\omega = E/\hbar$, namely

$$\begin{aligned}\Psi(x,t) &= A\mathrm{e}^{\mathrm{i}(kx-\omega t)}\\ &= A\mathrm{e}^{\mathrm{i}(p_x x-Et)/\hbar}\end{aligned} \tag{3.1}$$

where A is a constant. The angular frequency ω is connected with the wave number by the relation $\omega = \hbar k^2/2m$, which is equivalent to the classical relation

$$E = \frac{p_x^2}{2m} \tag{3.2}$$

connecting the momentum and energy of the particle. Now, if we differentiate (3.1) with respect to time, we have

$$\frac{\partial\Psi}{\partial t} = -\frac{\mathrm{i}E}{\hbar}\Psi. \tag{3.3}$$

On the other hand, differentiating (3.1) twice with respect to x, we find that

$$\frac{\partial^2\Psi}{\partial x^2} = -\frac{p_x^2}{\hbar^2}\Psi. \tag{3.4}$$

Hence, using (3.2), we see that the plane wave (3.1) satisfies the partial differential equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t). \tag{3.5}$$

More generally, since the equation (3.5) is *linear* and *homogeneous*, it will be satisfied by a linear superposition of plane waves (3.1). For example, the wave packet (2.23)

$$\Psi(x,t) = (2\pi\hbar)^{-1/2}\int_{-\infty}^{+\infty} \mathrm{e}^{\mathrm{i}[p_x x-E(p_x)t]/\hbar}\phi(p_x)\mathrm{d}p_x \tag{3.6}$$

associated with a 'localised' free particle moving in one dimension, is also a solution of the equation (3.5), since

$$\begin{aligned} \mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(x,t) &= (2\pi\hbar)^{-1/2}\int_{-\infty}^{+\infty} E(p_x)\mathrm{e}^{\mathrm{i}[p_x x - E(p_x)t]/\hbar}\phi(p_x)\mathrm{d}p_x \\ &= (2\pi\hbar)^{-1/2}\int_{-\infty}^{+\infty} \frac{p_x^2}{2m}\mathrm{e}^{\mathrm{i}[p_x x - E(p_x)t]/\hbar}\phi(p_x)\mathrm{d}p_x \\ &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t). \end{aligned} \tag{3.7}$$

The wave equation (3.5) is known as the *time-dependent Schrödinger equation* for the motion of a *free* particle in *one dimension*. We remark that this equation satisfies the requirements that we formulated at the beginning of this chapter. Indeed, we have already seen that it is a *linear* and *homogeneous* equation for the wave function Ψ. Furthermore, remembering that in wave mechanics the total energy E is represented by the operator $E_{\mathrm{op}} = \mathrm{i}\hbar\partial/\partial t$, and the component p_x of the momentum by the operator $(p_x)_{\mathrm{op}} = -\mathrm{i}\hbar\partial/\partial x$ (see (2.20)), we note that equation (3.5) may be written in the form

$$E_{\mathrm{op}}\Psi(x,t) = \frac{1}{2m}[(p_x)_{\mathrm{op}}]^2\Psi(x,t) \tag{3.8}$$

which is the quantum-mechanical 'translation' of the classical relation (3.2). This analogy with classical mechanics is in agreement with the *correspondence principle.* We also remark that the Schrödinger wave equation (3.5) is of *first order* in the time derivative $\partial/\partial t$. Hence, if the wave function $\Psi(x,t)$ is given at a certain time t_0, it is determined at all other times by this equation.

The generalisation of these considerations to free-particle motion in three dimensions is straightforward. A free particle of mass m having a well-defined momentum $\mathbf{p}$ and an energy E is now described by a plane wave

$$\begin{aligned} \Psi(\mathbf{r},t) &= A\mathrm{e}^{\mathrm{i}(\mathbf{k}.\mathbf{r}-\omega t)} \\ &= A\mathrm{e}^{\mathrm{i}(\mathbf{p}.\mathbf{r}-Et)/\hbar} \end{aligned} \tag{3.9}$$

characterised by the wave vector $\mathbf{k} = \mathbf{p}/\hbar$ and the angular frequency $\omega = E/\hbar$. Again we have $\omega = \hbar k^2/2m$, which is equivalent to the classical relation

$$E = \frac{\mathbf{p}^2}{2m} \tag{3.10}$$

between the momentum and energy of the particle. It is then readily verified that the plane wave (3.9) satisfies the partial differential equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t) \tag{3.11}$$

where

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{3.12}$$

is the Laplacian operator. The wave equation (3.11), which is the direct generalisation of (3.5), is the *three-dimensional time-dependent Schrödinger equation for a free particle*. As in the one-dimensional case, it is a *linear* and *homogeneous* equation which is therefore satisfied by arbitrary linear superpositions of plane waves (3.9), in particular by wave packets of the form (2.57) associated with 'localised' free particles. Equation (3.11) is also clearly of first order in the time derivative $\partial/\partial t$. Finally, using the fact that in wave mechanics the total energy E and the momentum $\mathbf{p}$ are represented by the differential operators (see (2.20))

$$E_{\text{op}} = i\hbar\frac{\partial}{\partial t}, \qquad \mathbf{p}_{\text{op}} = -i\hbar\boldsymbol{\nabla} \tag{3.13}$$

we observe that the free-particle Schrödinger equation (3.11) may also be written in the form

$$E_{\text{op}}\Psi(\mathbf{r},t) = \frac{1}{2m}(\mathbf{p}_{\text{op}})^2\Psi(\mathbf{r},t) \tag{3.14}$$

in formal analogy with the classical equation (3.10). Note that the quantity $\mathbf{p}^2/2m$ is represented by the operator[1]

$$T = \frac{1}{2m}(\mathbf{p}_{\text{op}})^2 = -\frac{\hbar^2}{2m}\nabla^2 \tag{3.15}$$

which is called the kinetic energy operator of the particle.

Let us now try to generalise the free-particle Schrödinger equation (3.11) to the case of a particle moving in a field of force. We shall assume that the force $F(\mathbf{r},t)$ acting on the particle is derivable from a potential

$$\mathbf{F}(\mathbf{r},t) = -\boldsymbol{\nabla}V(\mathbf{r},t) \tag{3.16}$$

so that, for a classical particle, the total energy E is given by the sum of its kinetic energy $\mathbf{p}^2/2m$ and its potential energy $V(\mathbf{r},t)$

$$E = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r},t). \tag{3.17}$$

Since the potential energy V does not depend on $\mathbf{p}$ or E, the above discussion of the free-particle case suggests using (3.13) to write

$$E_{\text{op}}\Psi(\mathbf{r},t) = \left[\frac{1}{2m}(\mathbf{p}_{\text{op}})^2 + V(\mathbf{r},t)\right]\Psi(\mathbf{r},t) \tag{3.18}$$

so that the generalisation of the free-particle Schrödinger equation (3.11) reads

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t)\right]\Psi(\mathbf{r},t). \tag{3.19}$$

This is the celebrated *time-dependent Schrödinger wave equation* for a particle moving in a potential, which was proposed by E. Schrödinger in 1926. It is the

---

[1] In what follows we shall drop the subscript 'op' which denotes operators, unless there is a possibility of confusion with a quantity (number, vector, etc.) denoted by the same symbol.

basic equation of non-relativistic quantum mechanics. We want to emphasise that we have not formally *derived* this equation, but have only made it appear plausible. The Schrödinger equation, like Newton's laws, cannot be proved to be true. Its best possible justification comes from an exhaustive comparison of the predictions based on this equation with experiment. It is the successful application of the Schrödinger equation to many problems which demonstrated its correctness in non-relativistic quantum mechanics.

The operator appearing inside the brackets on the right of the Schrödinger equation (3.19) will be seen shortly to play a very important role. It is called the Hamiltonian operator of the particle and is denoted by H. Using (3.15), we have

$$\begin{aligned} H &= -\frac{\hbar^2}{2m}\nabla^2 + V \\ &= \frac{1}{2m}(\mathbf{p}_{\text{op}})^2 + V = T + V \end{aligned} \tag{3.20}$$

and the time-dependent Schrödinger equation (3.19) may therefore be rewritten in the form

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = H\Psi(\mathbf{r}, t). \tag{3.21}$$

Now, in classical mechanics the total energy E of a system, when expressed in terms of the coordinates of the system, of their respective momenta and of the time, is called the (classical) Hamiltonian H_{cl} of this system. In particular, for the case of a classical particle moving in a potential, we have from (3.17)

$$E = H_{\text{cl}}(\mathbf{r}, \mathbf{p}, t) \tag{3.22}$$

where

$$H_{\text{cl}}(\mathbf{r}, \mathbf{p}, t) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, t). \tag{3.23}$$

Upon comparison of (3.20) and (3.23), we see that the quantum mechanical Hamiltonian operator H is obtained from the classical Hamiltonian H_{cl} by performing the substitution $\mathbf{p} \to \mathbf{p}_{\text{op}} = -\mathrm{i}\hbar\nabla$, namely

$$H \equiv H_{\text{cl}}(\mathbf{r}, -\mathrm{i}\hbar\nabla, t). \tag{3.24}$$

As a result, the time-dependent Schrödinger equation (3.21) may be obtained by starting from the classical equation (3.22), making the substitutions

$$E \to E_{\text{op}} = \mathrm{i}\hbar\frac{\partial}{\partial t}, \qquad \mathbf{p} \to \mathbf{p}_{\text{op}} = -\mathrm{i}\hbar\nabla \tag{3.25}$$

and applying the operators E_{op} and $H \equiv H_{\text{cl}}(\mathbf{r}, -\mathrm{i}\hbar\nabla, t)$ on both sides of the equation to the wave function $\Psi(\mathbf{r}, t)$. This makes even more apparent the analogy with classical mechanics required by the correspondence principle. Later in this chapter we shall discuss in more detail the classical limit of the Schrödinger equation.

As in the case of the free particle, the time-dependent Schrödinger equation (3.19) for a particle moving in a potential is *linear* and *homogeneous*. Therefore, if $\Psi_1(\mathbf{r}, t)$ and $\Psi_2(\mathbf{r}, t)$ are distinct solutions of (3.19)

$$\Psi(\mathbf{r}, t) = c_1\Psi_1(\mathbf{r}, t) + c_2\Psi_2(\mathbf{r}, t) \tag{3.26}$$

is also a solution, where c_1 and c_2 are complex constants. More generally, an arbitrary linear superposition of solutions of the time-dependent Schrödinger equation (3.19) is also a solution of the equation, in agreement with the superposition principle. We also emphasise that the time-dependent Schrödinger equation (3.19) is of *first order in the time derivative* $\partial/\partial t$, so that once the initial value of the wave function is given at some time t_0, namely $\Psi(\mathbf{r}, t_0)$, its value at all other times can be found by solving the equation. The basic mathematical problem is therefore to obtain a solution $\Psi(\mathbf{r}, t)$ of the Schrödinger equation (3.19) which satisfies given initial conditions.

Continuity conditions

Provided the potential $V(\mathbf{r}, t)$ is a continuous function of each of the Cartesian coordinates x, y and z, it is clear from the Schrödinger equation (3.19) that each of $\Psi(\mathbf{r}, t)$, $\partial\Psi/\partial t$ and $\boldsymbol{\nabla}\Psi$ is also a continuous function of x, y and z. If $V(\mathbf{r}, t)$ exhibits finite discontinuities (jumps) as a function of x, y and z, then from the Schrödinger equation we see that $\nabla^2\Psi$ exhibits corresponding finite jumps as a function of x, y and z. From this it follows that $\boldsymbol{\nabla}\Psi$ must be continuous as a function of x, y and z, for otherwise $\nabla^2\Psi$ would become infinite at the points where $\boldsymbol{\nabla}\Psi$ changed discontinuously. In turn, since $\boldsymbol{\nabla}\Psi$ is continuous, Ψ and $\partial\Psi/\partial t$ must also be continuous as functions of x, y and z.

Turning now to the time dependence, we see from (3.19) that if $V(\mathbf{r}, t)$ is a continuous function of t, so will be $\Psi(\mathbf{r}, t)$ and $\partial\Psi/\partial t$. However, if $V(\mathbf{r}, t)$ exhibits finite discontinuities as a function of t, so will $\partial\Psi/\partial t$, while $\Psi(\mathbf{r}, t)$ remains a continuous function of t.

3.2 Conservation of probability

As we have explained in Chapter 2, the wave function associated with a particle in quantum mechanics has a *statistical interpretation*. According to Born's postulate (see Section 2.2), if a particle is described by a wave function $\Psi(\mathbf{r}, t)$ normalised to unity the probability of finding the particle at time t within the volume element $\mathrm{d}\mathbf{r} \equiv \mathrm{d}x\mathrm{d}y\mathrm{d}z$ about the point $\mathbf{r} \equiv (x, y, z)$ is

$$P(\mathbf{r}, t)\mathrm{d}\mathbf{r} = |\Psi(\mathbf{r}, t)|^2\mathrm{d}\mathbf{r} \tag{3.27}$$

so that $P(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 = \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)$ is the *position probability density*. Assuming that the particle is confined within a given volume V_0 (for example, a room), we have seen in Chapter 2 that *at any arbitrary time* t the wave function $\Psi(\mathbf{r}, t)$ can be chosen to satisfy the *normalisation condition*

$$\int |\Psi(\mathbf{r}, t)|^2 \mathrm{d}\mathbf{r} = 1 \tag{3.28}$$

where the integral extends over all space. This condition simply expresses the fact that the probability of finding the particle somewhere at time t is unity. We noted in Chapter 2 that wave functions for which the integral on the left of (3.28) exists are said to be *square integrable*, and that some wave functions cannot be normalised in this way. For example, in the case of plane waves such as (3.9) the normalisation integral on the left of (3.28) diverges. However, we recognised that this difficulty is due to the fact that a plane wave represents the idealised physical situation of a free particle which has a perfectly well-defined momentum and hence is totally 'delocalised'. If the requirement that the particle should have a completely well-defined momentum is given up, we have seen in Chapter 2 that localised wave packets can be constructed, which can be normalised to unity. For the time being we shall only consider square integrable wave functions Ψ which satisfy the normalisation condition (3.28).

Let us now ask what happens as time changes. The interpretation of $|\Psi(\mathbf{r}, t)|^2$ as a position probability density clearly requires that the probability of finding the particle somewhere must remain unity as time varies, which is to say that *probability is conserved.* In other words, once $\Psi(\mathbf{r}, t)$ is normalised according to (3.28) at a given time t, it must remain so at all times. The normalisation integral on the left of (3.28) must therefore be independent of time, namely

$$\frac{\partial}{\partial t} \int P(\mathbf{r}, t) \mathrm{d}\mathbf{r} = 0 \tag{3.29}$$

where $P(\mathbf{r}, t)$ is given by (3.27) and we recall that the integral extends over all space.

In order to verify that this relation is indeed satisfied in Schrödinger's theory, let us start by considering the probability of finding the particle at time t within a finite volume V, namely

$$\int_V P(\mathbf{r}, t) \mathrm{d}\mathbf{r} = \int_V |\Psi(\mathbf{r}, t)|^2 \mathrm{d}\mathbf{r} \tag{3.30}$$

where the integrals extend over the volume V. The rate of change of this probability is

$$\frac{\partial}{\partial t} \int_V P(\mathbf{r}, t) \mathrm{d}\mathbf{r} = \int_V \left[\Psi^* \left(\frac{\partial \Psi}{\partial t} \right) + \left(\frac{\partial \Psi^*}{\partial t} \right) \Psi \right] \mathrm{d}\mathbf{r}. \tag{3.31}$$

Now, the time dependence of the wave function $\Psi(\mathbf{r}, t)$ is not arbitrary but is governed by the time-dependent Schrödinger equation (3.19). Using this equation and its complex conjugate

$$-\mathrm{i}\hbar \frac{\partial}{\partial t} \Psi^*(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right] \Psi^*(\mathbf{r}, t) \tag{3.32}$$

where we have used the fact that $V(\mathbf{r}, t)$ is a *real* quantity, we find that

$$\begin{aligned}\frac{\partial}{\partial t}\int_V P(\mathbf{r}, t)\mathrm{d}\mathbf{r} &= \frac{\mathrm{i}\hbar}{2m}\int_V [\Psi^*(\nabla^2\Psi) - (\nabla^2\Psi^*)\Psi]\mathrm{d}\mathbf{r}\\ &= \frac{\mathrm{i}\hbar}{2m}\int_V \boldsymbol{\nabla}.[\Psi^*(\boldsymbol{\nabla}\Psi) - (\boldsymbol{\nabla}\Psi^*)\Psi]\mathrm{d}\mathbf{r}\\ &= -\int_V \boldsymbol{\nabla}.\mathbf{j}\,\mathrm{d}\mathbf{r}. \end{aligned} \tag{3.33}$$

In the last line we have introduced the vector

$$\mathbf{j}(\mathbf{r}, t) = \frac{\hbar}{2m\mathrm{i}}[\Psi^*(\boldsymbol{\nabla}\Psi) - (\boldsymbol{\nabla}\Psi^*)\Psi] \tag{3.34}$$

whose physical significance will be discussed shortly. Using Green's theorem[2], we can convert the volume integral on the right of (3.33) into an integral over the surface S bounding the volume V

$$\frac{\partial}{\partial t}\int_V P(\mathbf{r}, t)\mathrm{d}\mathbf{r} = -\int_S \mathbf{j}.\mathrm{d}\mathbf{S} \tag{3.35}$$

where $\mathrm{d}\mathbf{S}$ is a vector whose magnitude is equal to an element $\mathrm{d}S$ of the surface S, and whose direction is that of the outward normal to $\mathrm{d}S$.

The above relations are valid for any finite volume V. In order to study the time rate of change of the normalisation integral (3.28), we must extend the volume to the entire space. The surface S in (3.35) then recedes to infinity. Since Ψ is square integrable it vanishes at large distances[3] so that the surface integral in (3.35) is equal to zero, and the condition (3.29) is satisfied. It is worth noting that the proof of (3.29) depends on the facts that the Schrödinger equation (3.19) is of first order in the time derivative $\partial/\partial t$ (this allowed us to eliminate the time derivatives on the right of (3.31)) and that the potential energy $V(\mathbf{r}, t)$ is *real*.

Probability conservation and the Hermiticity of the Hamiltonian

The condition (3.29) expressing the conservation in time of the normalisation of the wave function can also be formulated in terms of the Hamiltonian operator H. Indeed,

---

[2] Green's theorem (also called the divergence theorem of Gauss) states that the surface integral of the component of a vector **A** along the outward normal taken over a closed surface S is equal to the integral of the divergence of **A** taken over the volume V enclosed by the surface. That is

$$\int_V \boldsymbol{\nabla}.\mathbf{A}\mathrm{d}\mathbf{r} = \int_S \mathbf{A}.\mathrm{d}\mathbf{S}$$

where $\mathrm{d}\mathbf{S} = \hat{\mathbf{n}}\mathrm{d}S$, $\hat{\mathbf{n}}$ being the unit vector along the outward normal and $\mathrm{d}S$ being an element of the surface S.

[3] If the particle is confined within a volume V_0, then Ψ vanishes outside that volume, and hence over a surface bounding any volume that contains V_0.

using the form (3.21) of the time-dependent Schrödinger equation, and its complex conjugate

$$-i\hbar\frac{\partial}{\partial t}\Psi^*(\mathbf{r},t) = [H\Psi(\mathbf{r},t)]^* \tag{3.36}$$

we can write the left-hand side of (3.29) as

$$\begin{aligned}\frac{\partial}{\partial t}\int P(\mathbf{r},t)\mathrm{d}\mathbf{r} &= \frac{\partial}{\partial t}\int |\Psi(\mathbf{r},t)|^2\mathrm{d}\mathbf{r}\\ &= \int\left[\Psi^*\left(\frac{\partial\Psi}{\partial t}\right)+\left(\frac{\partial\Psi^*}{\partial t}\right)\Psi\right]\mathrm{d}\mathbf{r}\\ &= (i\hbar)^{-1}\int[\Psi^*(H\Psi)-(H\Psi)^*\Psi]\mathrm{d}\mathbf{r}\end{aligned} \tag{3.37}$$

so that the condition (3.29) becomes

$$\int \Psi^*(H\Psi)\mathrm{d}\mathbf{r} = \int (H\Psi)^*\Psi\mathrm{d}\mathbf{r}. \tag{3.38}$$

This condition must hold for all square integrable wave functions $\Psi(\mathbf{r},t)$, and hence is a restriction on the Hamiltonian operator H. Operators which satisfy the condition (3.38) for all functions Ψ of the function space in which they act are called *Hermitian operators*. We have thus shown that the requirement of probability conservation implies that the Hamiltonian operator H which appears in the Schrödinger equation (3.21) must be Hermitian when acting on square integrable wave functions. Of course, since the condition (3.29) expressing the conservation in time of the normalisation of $\Psi(\mathbf{r},t)$ has been shown above to follow from the Schrödinger equation (3.19), it follows that the Hamiltonian (3.20) of a particle in a real potential $V(\mathbf{r},t)$ is a Hermitian operator.

Probability current density

Let us now return to equation (3.35). Since the rate of change of the probability of finding the particle in the volume V is equal to the probability flux passing through the surface S bounding V, the vector $\mathbf{j}$ given by (3.34) can be interpreted as a *probability current density*. The equation

$$\frac{\partial}{\partial t}P(\mathbf{r},t) + \boldsymbol{\nabla}.\mathbf{j}(\mathbf{r},t) = 0 \tag{3.39}$$

which follows from (3.33) is analogous to the *continuity equation* expressing charge conservation in electrodynamics or the conservation of matter in hydrodynamics. It has the familiar form associated with the conservation law for a classical fluid of density P and current density $\mathbf{j}$ in a medium where there are no sources or sinks. Note that the probability current density (3.34) may also be written as

$$\mathbf{j}(\mathbf{r},t) = \mathrm{Re}\left\{\Psi^*\frac{\hbar}{im}\boldsymbol{\nabla}\Psi\right\}. \tag{3.40}$$

Since the operator $(\hbar/im)\nabla$ represents the quantity $\mathbf{p}/m$ (that is, the velocity $\mathbf{v}$ of the particle) we see that $\mathbf{j}$ corresponds to the product of the velocity and the density. Thus it is reasonable to interpret $\mathbf{j}$ as a probability current density. We also remark from (3.40) that $\mathbf{j}$ vanishes if the wave function Ψ is real. In order to describe situations in which the probability current is non-zero it is therefore necessary to use complex wave functions. Finally, we remark that since the wave function Ψ and its gradient $\nabla\Psi$ are continuous functions of $\mathbf{r}$, the probability current density $\mathbf{j}(\mathbf{r}, t)$ as well as the probability density $P(\mathbf{r}, t)$ have no discontinuous changes as $\mathbf{r}$ varies.

3.3 Expectation values and operators

Let $\Psi(\mathbf{r}, t)$ be the wave function of a particle, normalised to unity. Given the probabilistic interpretation attached to Ψ, we shall now show how information concerning the behaviour of the particle can be extracted from the knowledge of Ψ. First of all, since $P(\mathbf{r}, t)\mathrm{d}\mathbf{r} = \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}$ is the probability of finding the particle in the volume element $\mathrm{d}\mathbf{r}$ about the point $\mathbf{r}$ at the time t, the *expectation* value (or average value) of the position vector $\mathbf{r}$ of the particle, which we shall write $\langle\mathbf{r}\rangle$, is given by

$$\begin{aligned}\langle\mathbf{r}\rangle &= \int \mathbf{r}P(\mathbf{r}, t)\mathrm{d}\mathbf{r}\\ &= \int \Psi^*(\mathbf{r}, t)\mathbf{r}\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}.\end{aligned} \tag{3.41}$$

The order of the factors in the integrand is obviously immaterial; the one we have adopted in the second line of (3.41) has been chosen for future convenience.

As a result of the interpretation of $P(\mathbf{r}, t)$ as the position probability density, the physical meaning to be attributed to the expectation value $\langle\mathbf{r}\rangle$ is the following: it is the average value of the measurements of $\mathbf{r}$ performed on a very large number of equivalent, identically prepared independent systems represented by the wave function Ψ. We remark that equation (3.41) is equivalent to the three equations

$$\langle x\rangle = \int \Psi^*(\mathbf{r}, t)x\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} \tag{3.42a}$$

$$\langle y\rangle = \int \Psi^*(\mathbf{r}, t)y\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} \tag{3.42b}$$

$$\langle z\rangle = \int \Psi^*(\mathbf{r}, t)z\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}. \tag{3.42c}$$

It should be noted that the expectation values are functions only of the time, since the space coordinates have been integrated out. We also remark that the quantities $\langle x\rangle$, $\langle y\rangle$ and $\langle z\rangle$ are obviously real, so that the three components x, y and z, considered as operators acting on the wave function $\Psi(\mathbf{r}, t)$ on the right of equations (3.42) are Hermitian (see (3.38)).

More generally, the expectation value of an arbitrary function $f(\mathbf{r}, t) \equiv f(x, y, z, t)$ of the coordinates of the particle and of the time is given by

$$\begin{aligned} \langle f(\mathbf{r}, t)\rangle &= \int f(\mathbf{r}, t)P(\mathbf{r}, t)\mathrm{d}\mathbf{r} \\ &= \int \Psi^*(\mathbf{r}, t)f(\mathbf{r}, t)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} \end{aligned} \tag{3.43}$$

provided, of course, that the integral exists. The order of the factors in the integrand has again been chosen for future convenience. Note that $f(\mathbf{r}, t)$, considered as an operator acting on $\Psi(\mathbf{r}, t)$, is Hermitian if the function f is real. As an example, the expectation value of the potential energy is

$$\langle V(\mathbf{r}, t)\rangle = \int \Psi^*(\mathbf{r}, t)V(\mathbf{r}, t)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}. \tag{3.44}$$

In order to calculate the expectation value of the momentum $\mathbf{p}$ of the particle, we recall that if $\Phi(\mathbf{p}, t)$ is the wave function of the particle in momentum space, normalised to unity, then $\Pi(\mathbf{p}, t)\mathrm{d}\mathbf{p} = \Phi^*(\mathbf{p}, t)\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p}$ is the probability of finding at time t the momentum of the particle within the volume element $\mathrm{d}\mathbf{p} \equiv \mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$ about the point $\mathbf{p} \equiv (p_x, p_y, p_z)$ in momentum space (see (2.63)). The expectation value of $\mathbf{p}$ is therefore given by

$$\begin{aligned} \langle \mathbf{p}\rangle &= \int \mathbf{p}\Pi(\mathbf{p}, t)\mathrm{d}\mathbf{p} \\ &= \int \Phi^*(\mathbf{p}, t)\mathbf{p}\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p} \end{aligned} \tag{3.45}$$

an equation which is equivalent to the three equations

$$\langle p_x\rangle = \int \Phi^*(\mathbf{p}, t)p_x\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p} \tag{3.46a}$$

$$\langle p_y\rangle = \int \Phi^*(\mathbf{p}, t)p_y\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p} \tag{3.46b}$$

$$\langle p_z\rangle = \int \Phi^*(\mathbf{p}, t)p_z\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p}. \tag{3.46c}$$

More generally, the expectation value of an arbitrary function $g(\mathbf{p}, t) \equiv g(p_x, p_y, p_z, t)$ is

$$\begin{aligned} \langle g(\mathbf{p}, t)\rangle &= \int g(\mathbf{p}, t)\Pi(\mathbf{p}, t)\mathrm{d}\mathbf{p} \\ &= \int \Phi^*(\mathbf{p}, t)g(\mathbf{p}, t)\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p}. \end{aligned} \tag{3.47}$$

For example, the expectation value of the kinetic energy is

$$\left\langle \frac{\mathbf{p}^2}{2m}\right\rangle = \int \Phi^*(\mathbf{p}, t)\frac{\mathbf{p}^2}{2m}\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p} \tag{3.48}$$

We shall now obtain another form of the expectation value of **p** which involves the wave function in configuration space, $\Psi(\mathbf{r}, t)$, rather than the wave function in momentum space, $\Phi(\mathbf{p}, t)$. To this end, we consider first the expectation value of p_x, given by (3.46a). Using (2.61) to express $\Phi(\mathbf{p}, t)$ in terms of $\Psi(\mathbf{r}, t)$ and writing in a similar way

$$\Phi^*(\mathbf{p}, t) = (2\pi\hbar)^{-3/2} \int e^{i\mathbf{p}.\mathbf{r}'/\hbar} \Psi^*(\mathbf{r}', t) d\mathbf{r}' \tag{3.49}$$

we obtain upon substitution in (3.46a)

$$\langle p_x \rangle = (2\pi\hbar)^{-3} \int d\mathbf{p} \int d\mathbf{r} \int d\mathbf{r}' e^{i\mathbf{p}.\mathbf{r}'/\hbar} \Psi^*(\mathbf{r}', t) p_x e^{-i\mathbf{p}.\mathbf{r}/\hbar} \Psi(\mathbf{r}, t). \tag{3.50}$$

Now we observe that

$$\begin{aligned} p_x e^{-i\mathbf{p}.\mathbf{r}/\hbar} &= p_x e^{-i(p_x x + p_y y + p_z z)/\hbar} \\ &= i\hbar \frac{\partial}{\partial x} e^{-i\mathbf{p}.\mathbf{r}/\hbar} \end{aligned} \tag{3.51}$$

so that we may write (3.50) in the form

$$\langle p_x \rangle = (2\pi\hbar)^{-3} \int d\mathbf{p} \int d\mathbf{r} \int d\mathbf{r}' e^{i\mathbf{p}.\mathbf{r}'/\hbar} \Psi^*(\mathbf{r}', t) \left(i\hbar \frac{\partial}{\partial x} e^{-i\mathbf{p}.\mathbf{r}/\hbar} \right) \Psi(\mathbf{r}, t). \tag{3.52}$$

Let us now integrate by parts with respect to x. The integrated part, which is proportional to the value of the wave function $\Psi(\mathbf{r}, t)$ at $|x| = \infty$, vanishes since $\Psi(\mathbf{r}, t)$ is a normalisable wave function which is equal to zero in the limit $|x| \to \infty$. We therefore have

$$\langle p_x \rangle = (2\pi\hbar)^{-3} \int d\mathbf{p} \int d\mathbf{r} \int d\mathbf{r}' \Psi^*(\mathbf{r}', t) e^{i\mathbf{p}.(\mathbf{r}'-\mathbf{r})/\hbar} \left[-i\hbar \frac{\partial}{\partial x} \Psi(\mathbf{r}, t) \right]. \tag{3.53}$$

Now, from equation (A.50) of Appendix A we have

$$\delta(\mathbf{r}' - \mathbf{r}) = (2\pi\hbar)^{-3} \int e^{i\mathbf{p}.(\mathbf{r}'-\mathbf{r})/\hbar} d\mathbf{p} \tag{3.54}$$

where δ is the Dirac delta function. The **p** integration in (3.53) is thus readily performed to yield

$$\langle p_x \rangle = \int d\mathbf{r} \int d\mathbf{r}' \Psi^*(\mathbf{r}', t) \delta(\mathbf{r}' - \mathbf{r}) \left[-i\hbar \frac{\partial}{\partial x} \Psi(\mathbf{r}, t) \right] \tag{3.55}$$

and from equation (A.51) of Appendix A, we can perform the $\mathbf{r}'$ integration to obtain

$$\langle p_x \rangle = \int \Psi^*(\mathbf{r}, t) \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(\mathbf{r}, t) d\mathbf{r}. \tag{3.56a}$$

Proceeding in a similar way with $\langle p_y \rangle$ and $\langle p_z \rangle$, we find that

$$\langle p_y \rangle = \int \Psi^*(\mathbf{r}, t) \left(-i\hbar \frac{\partial}{\partial y} \right) \Psi(\mathbf{r}, t) d\mathbf{r} \tag{3.56b}$$

and

$$\langle p_z \rangle = \int \Psi^*(\mathbf{r}, t)\left(-\mathrm{i}\hbar\frac{\partial}{\partial z}\right)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}. \tag{3.56c}$$

The three equations (3.56) are equivalent to the single equation

$$\langle \mathbf{p} \rangle = \int \Psi^*(\mathbf{r}, t)(-\mathrm{i}\hbar\nabla)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}. \tag{3.57}$$

We also remark that equations (3.46) imply that the expectation values $\langle p_x \rangle$, $\langle p_y \rangle$ and $\langle p_z \rangle$ are real, so that the operators $(-\mathrm{i}\hbar\partial/\partial x)$, $(-\mathrm{i}\hbar\partial/\partial y)$ and $(-\mathrm{i}\hbar\partial/\partial z)$ acting on the wave function $\Psi(\mathbf{r}, t)$ are Hermitian.

The result (3.57) can be generalised to more complicated functions. For example, if n is a positive integer, we have by using a straightforward generalisation of the above method (Problem 3.3)

$$\langle p_x^n \rangle = \int \Psi^*(\mathbf{r}, t)\left(-\mathrm{i}\hbar\frac{\partial}{\partial x}\right)^n \Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}. \tag{3.58}$$

More generally, if $g(p_x, p_y, p_z, t)$ is a polynomial or an absolutely convergent series in p_x, p_y, p_z, one has

$$\langle g(p_x, p_y, p_z, t) \rangle = \int \Psi^*(\mathbf{r}, t) g\left(-\mathrm{i}\hbar\frac{\partial}{\partial x}, -\mathrm{i}\hbar\frac{\partial}{\partial y}, -\mathrm{i}\hbar\frac{\partial}{\partial z}, t\right)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} \tag{3.59}$$

or, using a more compact notation

$$\langle g(\mathbf{p}, t) \rangle = \int \Psi^*(\mathbf{r}, t) g(-\mathrm{i}\hbar\nabla, t)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} \tag{3.60}$$

and we note that the operator $g(-\mathrm{i}\hbar\nabla, t)$ is Hermitian if the function g is real.

Looking back at the expectation values (3.41)–(3.44) and (3.56)–(3.60) obtained from the wave function $\Psi(\mathbf{r}, t)$ in configuration space, we see that they can all be written in the form

$$\langle A \rangle = \int \Psi^*(\mathbf{r}, t) A \Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} \tag{3.61}$$

where A is the operator associated with the quantity whose average value is to be evaluated. If we are dealing with a function $f(\mathbf{r}, t)$ of the coordinates of the particles and of the time, then the action of A on Ψ consists of multiplying the wave function Ψ by the function $f(\mathbf{r}, t)$. If the quantity whose expectation value is to be calculated is a function $g(\mathbf{p}, t)$, the operator A is obtained by making in $g(\mathbf{p}, t)$ the substitution $\mathbf{p} \to -\mathrm{i}\hbar\nabla$; we note that this is precisely the substitution which allowed us to obtain the Schrödinger equation (see (3.13)).

It is important to remark that the operators which we have considered thus far are either multipliers or derivatives, and hence belong to the category of *linear* operators. An operator A is said to be linear if its action on any two functions Ψ_1 and Ψ_2 is such that

$$A(c_1\Psi_1 + c_2\Psi_2) = c_1(A\Psi_1) + c_2(A\Psi_2) \tag{3.62}$$

where c_1 and c_2 are arbitrary complex numbers. Most of the operators relevant in quantum mechanics are linear, and in what follows, unless otherwise stated, the term 'operator' will mean a linear operator.

Until now we have considered quantities which are *either* functions $f(\mathbf{r}, t)$ of $\mathbf{r}$ and t *or* functions $g(\mathbf{p}, t)$ of $\mathbf{p}$ and t. However, some dynamical variables can be functions of $\mathbf{r}$, $\mathbf{p}$ and t, and thus can contain $\mathbf{r}$ and $\mathbf{p}$ simultaneously. This is the case, for example, for the total energy $E = \mathbf{p}^2/2m + V(\mathbf{r}, t)$ of a particle moving in a potential, to which is associated the Hamiltonian operator (3.20), namely $H = -(\hbar^2/2m)\nabla^2 + V(\mathbf{r}, t)$. In order to find a method for evaluating the average value of E, we shall in accordance with the correspondence principle, require that

$$\langle E\rangle = \left\langle \frac{\mathbf{p}^2}{2m}\right\rangle + \langle V\rangle \tag{3.63}$$

so that we obtain the correct averages in the classical limit (see (3.22)–(3.23)). Remembering the substitution rules (3.25) we may also write the relation (3.63) as

$$\left\langle \mathrm{i}\hbar\frac{\partial}{\partial t}\right\rangle = \left\langle -\frac{\hbar^2}{2m}\nabla^2\right\rangle + \langle V\rangle \tag{3.64}$$

and we see that the above equation is consistent with the Schrödinger equation (3.19) provided that the expectation value is defined in the general case with the operator acting on the right on Ψ, and multiplied on the left by Ψ^*. Thus we have

$$\begin{aligned}\langle E\rangle &= \int \Psi^*(\mathbf{r}, t)\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\right)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}\\ &= \int \Psi^*(\mathbf{r}, t)H\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} = \int \Psi^*(\mathbf{r}, t)\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)\right]\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}\\ &= \langle H\rangle.\end{aligned} \tag{3.65}$$

Generalising the above results, we are therefore led to postulate that if the dynamical state of a particle is described by the configuration space wave function $\Psi(\mathbf{r}, t)$, normalised to unity, the expectation value of a dynamical variable must be calculated as follows.

(1) One first associates with the dynamical variable $\mathcal{A} \equiv A(\mathbf{r}, \mathbf{p}, t)$ representing a physical quantity, the linear operator

$$A(\mathbf{r}, -\mathrm{i}\hbar\nabla, t) \tag{3.66}$$

obtained by performing the substitution $\mathbf{p} \to -\mathrm{i}\hbar\nabla$ wherever the momentum $\mathbf{p}$ occurs. This rule, however, needs some qualifications, which will be discussed shortly.

(2) One then calculates the required expectation value from the expression

$$\langle A\rangle = \int \Psi^*(\mathbf{r}, t)A(\mathbf{r}, -\mathrm{i}\hbar\nabla, t)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}. \tag{3.67}$$

Table 3.1 Physical quantities and corresponding operators acting in configuration space.

Physical quantity	*Operator*
Position coordinate x	x
Position vector $\mathbf{r}$	$\mathbf{r}$
x component of momentum p_x	$-i\hbar\frac{\partial}{\partial x}$
Momentum $\mathbf{p}$	$-i\hbar\nabla$
Kinetic energy $T = \frac{\mathbf{p}^2}{2m}$	$-\frac{\hbar^2}{2m}\nabla^2$
Potential energy $V(\mathbf{r}, t)$	$V(\mathbf{r}, t)$
Total energy $\frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, t)$	$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)$

If the wave function $\Psi(\mathbf{r}, t)$ is not normalised to unity, the expression (3.67) must of course be replaced by

$$\langle A\rangle = \frac{\int \Psi^*(\mathbf{r}, t)A(\mathbf{r}, -i\hbar\nabla, t)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}}{\int \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}}. \tag{3.68}$$

The operators A associated with physical quantities $\mathcal{A}$ are subject to an important restriction, which arises in the following way. The results of measurements of $\mathcal{A}$, and hence the expectation value $\langle A\rangle$, must obviously be *real* quantities. As a consequence, for any wave function Ψ, the condition

$$\int \Psi^* A\Psi \mathrm{d}\mathbf{r} = \int (A\Psi)^*\Psi \mathrm{d}\mathbf{r} \tag{3.69}$$

has to be satisfied, which means that the operator A associated with the dynamical quantity $\mathcal{A}$ must be *Hermitian*. A few important (linear) Hermitian operators acting in configuration space are listed in Table 3.1, together with the physical quantities to which they correspond.

As we have already seen, the requirement of the reality of expectation values – and hence the Hermitian character of the operators A associated with dynamical quantities – is automatically satisfied for real functions $f(\mathbf{r}, t)$ or $g(\mathbf{p}, t)$. However, for functions which depend on *both* $\mathbf{r}$ and $\mathbf{p}$, this is not necessarily the case. Consider, for example, a particle moving in one dimension, described by the wave function $\Psi(x, t)$, normalised to unity, and suppose that we wish to calculate the expectation value of the quantity xp_x. Following the rule stated above, we write

$$\langle xp_x\rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t)x\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi(x, t)\mathrm{d}x. \tag{3.70}$$

Integrating by parts and dropping the arguments of Ψ and Ψ^* to simplify the notation, we have

$$\langle xp_x\rangle = [-i\hbar x\Psi^*\Psi]_{-\infty}^{+\infty} + i\hbar\int_{-\infty}^{+\infty} \Psi\frac{\partial}{\partial x}(x\Psi^*)\mathrm{d}x. \tag{3.71}$$

The integrated part vanishes since $|\Psi| \to 0$ when $|x| \to \infty$. Thus

$$\begin{aligned}\langle xp_x\rangle &= \mathrm{i}\hbar\int_{-\infty}^{+\infty}\Psi x\frac{\partial\Psi^*}{\partial x}\mathrm{d}x + \mathrm{i}\hbar\int_{-\infty}^{+\infty}\Psi^*\Psi\mathrm{d}x\\ &= \langle xp_x\rangle^* + \mathrm{i}\hbar \end{aligned}\tag{3.72}$$

where $\langle xp_x\rangle^*$ denotes the complex conjugate of $\langle xp_x\rangle$. Since the second term on the right of (3.72) is non-zero, it is clear that $\langle xp_x\rangle$ is *not* a real quantity, and therefore that the operator $xp_x \equiv x(-\mathrm{i}\hbar\partial/\partial x)$ is not Hermitian. Similarly, it is readily checked (Problem 3.4) that

$$\langle p_x x\rangle = \langle p_x x\rangle^* - \mathrm{i}\hbar \tag{3.73}$$

so that $\langle p_x x\rangle$ is not real and the operator $p_x x \equiv (-\mathrm{i}\hbar\partial/\partial x)x$ is not Hermitian. However, a glance at equations (3.72) and (3.73) shows that

$$\left\langle\frac{xp_x + p_x x}{2}\right\rangle = \left\langle\frac{xp_x + p_x x}{2}\right\rangle^* \tag{3.74}$$

so that the operator $(xp_x + p_x x)/2$, obtained by taking the *mean* of the possible orders in which x and p_x appear, is Hermitian.

It is important to stress that in contrast to classical mechanics, where all quantities obey the rules of ordinary algebra, we are dealing in quantum mechanics with *operators*, which in general *do not commute* with each other. That is, if A and B are two operators, the product AB is not necessarily equal to the product BA. The *commutator* of two operators A and B is defined as the difference $AB - BA$ and is denoted by the symbol $[A, B]$:

$$[A, B] = AB - BA. \tag{3.75}$$

If their commutator vanishes, the two operators A and B commute: $AB = BA$.

As an example of operators which do not commute, let us consider the two operators x and $p_x = -\mathrm{i}\hbar\partial/\partial x$. For any wave function $\Psi(\mathbf{r}, t)$, we have

$$\begin{aligned}[x, p_x]\Psi &= (xp_x - p_x x)\Psi\\ &= -\mathrm{i}\hbar\left[x\frac{\partial\Psi}{\partial x} - \frac{\partial}{\partial x}(x\Psi)\right]\\ &= \mathrm{i}\hbar\Psi\end{aligned}\tag{3.76}$$

so that we may write the relation $[x, p_x] = \mathrm{i}\hbar$. More generally,

$$[x, p_x] = [y, p_y] = [z, p_z] = \mathrm{i}\hbar. \tag{3.77}$$

As a consequence of the non-commutativity of operators, different quantum mechanical operators may correspond to equivalent classical quantities. For example, to the three equivalent classical expressions

$$xp_x,\ p_x x,\ \tfrac{1}{2}(xp_x + p_x x) \tag{3.78}$$

correspond the three different operators

$$x\left(-i\hbar\frac{\partial}{\partial x}\right),\ \left(-i\hbar\frac{\partial}{\partial x}\right)x,\ \frac{1}{2}\left[x\left(-i\hbar\frac{\partial}{\partial x}\right)+\left(-i\hbar\frac{\partial}{\partial x}\right)x\right] \tag{3.79}$$

and we have seen above that only the last one is Hermitian.

We can now give a more precise meaning to the rule (3.66) which associates a linear operator A with a dynamical quantity. As stated previously, we must perform the substitution $\mathbf{p} \to -i\hbar\nabla$ wherever the momentum $\mathbf{p}$ appears. However, when necessary, we must also remove the ambiguity in the order of the factors of x and p_x (and similarly for y, p_y and z, p_z). To this end we shall require that the resulting operator A be Hermitian. In the case of the products xp_x and p_xx we have seen that this 'Hermitisation' can be accomplished by taking the mean between the two possible orders of x and p_x. This result can be generalised (Problem 3.5) and, in practice, the following procedure can be used:

(1) The function is ordered in such a way that all the factors involving x occur together, as do all the factors involving p_x (and similarly for y, p_y and z, p_z).

(2) One then replaces $x^k p_x^l$ by $(x^k p_x^l + p_x^l x^k)/2$, which guarantees that the operator A will be Hermitian. Although this procedure is still not completely unambiguous[4], it will be fully adequate to handle all the cases studied in this book.

We conclude this section with the following remark. Although we started our discussion of expectation values by giving equal emphasis to the configuration-space wave function $\Psi(\mathbf{r}, t)$ and the momentum-space wave function $\Phi(\mathbf{p}, t)$ (compare for example equations (3.41) and (3.45)), we continued our treatment by using exclusively the configuration-space wave function $\Psi(\mathbf{r}, t)$. The reason is that the Schrödinger equation and its interpretation have been developed earlier in this chapter in the more familiar configuration space. At the end of this chapter we shall restore the symmetry between the treatments in configuration and momentum space by discussing the Schrödinger equation, as well as operators and expectation values, in momentum space.

3.4 Transition from quantum mechanics to classical mechanics. The Ehrenfest theorem

According to the correspondence principle, we expect that the motion of a wave packet should agree with that of the corresponding classical particle whenever the distances and momenta involved in describing the motion of the particle are so large that the uncertainty principle may be ignored. In order to investigate this point, we

---

[4] For a detailed discussion of this point, see Bohm (1951), Chapter 9.

shall prove a theorem which is due to P. Ehrenfest (1927). It states that Newton's fundamental equations of classical dynamics, written in the form[5]

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = \frac{\mathbf{p}}{m} \tag{3.80a}$$

and

$$\frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = -\boldsymbol{\nabla} V \tag{3.80b}$$

are exactly satisfied by the *expectation (average) values* of the corresponding operators in quantum mechanics, these expectation values being calculated according to equation (3.67), where $\Psi(\mathbf{r}, t)$ is a square-integrable solution of the Schrödinger equation (3.19), normalised to unity. It is worth stressing that well-defined trajectories do not exist in quantum mechanics, so that equations such as (3.80) which give the values of $\mathrm{d}\mathbf{r}/\mathrm{d}t$ and $\mathrm{d}\mathbf{p}/\mathrm{d}t$ along a classical path cannot be written. However, it is possible to study the *time rates of change of the expectation values* $\langle\mathbf{r}\rangle$ and $\langle\mathbf{p}\rangle$.

Let us consider first the expectation value of x, which is given by (3.42a). The time rate of change of $\langle x\rangle$ is

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle &= \frac{\mathrm{d}}{\mathrm{d}t}\int \Psi^*(\mathbf{r}, t)x\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} \\ &= \int \Psi^*(\mathbf{r}, t)x\frac{\partial\Psi(\mathbf{r}, t)}{\partial t}\mathrm{d}\mathbf{r} + \int \frac{\partial\Psi^*(\mathbf{r}, t)}{\partial t}x\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}.\end{aligned} \tag{3.81}$$

This equation can be transformed by using the Schrödinger equation (3.21) and its complex conjugate (3.36). Dropping the arguments of Ψ and Ψ^* for notational simplicity, we have in this way

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle &= (\mathrm{i}\hbar)^{-1}\left[\int \Psi^* x(H\Psi)\mathrm{d}\mathbf{r} - \int (H\Psi)^* x\Psi\mathrm{d}\mathbf{r}\right] \\ &= (\mathrm{i}\hbar)^{-1}\left[\int \Psi^* x\left(-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi\right)\mathrm{d}\mathbf{r}\right. \\ &\qquad \left. - \int \left(-\frac{\hbar^2}{2m}\nabla^2\Psi^* + V\Psi^*\right)x\Psi\mathrm{d}\mathbf{r}\right].\end{aligned} \tag{3.82}$$

The terms involving the potential V cancel out, so that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle = \frac{\mathrm{i}\hbar}{2m}\int [\Psi^* x(\nabla^2\Psi) - (\nabla^2\Psi^*)x\Psi]\mathrm{d}\mathbf{r}. \tag{3.83}$$

---

[5] Note that equations (3.80) indeed reduce to the familiar Newtonian equations

$$m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = \frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = \mathbf{F}$$

where the force $\mathbf{F}$ is assumed to derive from a potential, $\mathbf{F} = -\boldsymbol{\nabla} V$.

Let us consider the second contribution to the integral. Using Green's first identity[6] and remembering that the volume V is the entire space, we obtain

$$\int (\nabla^2\Psi^*)x\Psi \mathrm{d}\mathbf{r} = \int_S x\Psi(\nabla\Psi^*).\mathrm{d}\mathbf{S} - \int (\nabla\Psi^*).\nabla(x\Psi)\mathrm{d}\mathbf{r}. \tag{3.84}$$

The first integral on the right is over the infinite bounding surface S, and hence is equal to zero because the wave function Ψ vanishes at large distances. Consequently, we have

$$\int (\nabla^2\Psi^*)x\Psi \mathrm{d}\mathbf{r} = -\int (\nabla\Psi^*).\nabla(x\Psi)\mathrm{d}\mathbf{r}. \tag{3.85}$$

Using again Green's first identity, we have

$$-\int (\nabla\Psi^*).\nabla(x\Psi)\mathrm{d}\mathbf{r} = -\int_S \Psi^*\nabla(x\Psi).\mathrm{d}\mathbf{S} + \int \Psi^*\nabla^2(x\Psi)\mathrm{d}\mathbf{r}. \tag{3.86}$$

Again the surface integral vanishes, so that

$$\int (\nabla^2\Psi^*)x\Psi \mathrm{d}\mathbf{r} = \int \Psi^*\nabla^2(x\Psi)\mathrm{d}\mathbf{r}. \tag{3.87}$$

Putting this result back into the equation (3.83) for $\mathrm{d}\langle x\rangle/\mathrm{d}t$, we find that

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle &= \frac{\mathrm{i}\hbar}{2m}\int \Psi^*[x\nabla^2\Psi - \nabla^2(x\Psi)]\mathrm{d}\mathbf{r} \\ &= -\frac{\mathrm{i}\hbar}{m}\int \Psi^*\frac{\partial\Psi}{\partial x}\mathrm{d}\mathbf{r}. \end{aligned} \tag{3.88}$$

On the other hand, the expectation value of the x-component of the momentum is given by (3.56a), so that we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle = \frac{\langle p_x\rangle}{m} \tag{3.89}$$

which is the quantum counterpart of the x-component of the classical equation (3.80a).

Let us now calculate the time rate of change of $\langle p_x\rangle$. We have from (3.56a)

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\langle p_x\rangle &= -\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\int \Psi^*\frac{\partial\Psi}{\partial x}\mathrm{d}\mathbf{r} \\ &= -\mathrm{i}\hbar\left[\int \Psi^*\frac{\partial}{\partial x}\frac{\partial\Psi}{\partial t}\mathrm{d}\mathbf{r} + \int \frac{\partial\Psi^*}{\partial t}\frac{\partial\Psi}{\partial x}\mathrm{d}\mathbf{r}\right]. \end{aligned} \tag{3.90}$$

---

[6] Green's first identity states that if $u(x, y, z)$ and $v(x, y, z)$ are scalar functions of position with continuous derivatives of at least the second order, then

$$\int_V [u(\nabla^2 v) + (\nabla u).(\nabla v)]\mathrm{d}\mathbf{r} = \int_S u(\nabla v).\mathrm{d}\mathbf{S}$$

where V is a volume bounded by the closed surface S. To obtain (3.84) set $u = x\Psi$ and $v = \Psi^*$.

Replacing, respectively, $\partial\Psi/\partial t$ and $\partial\Psi^*/\partial t$ according to the Schrödinger equation (3.21) and its complex conjugate (3.36), we obtain

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle p_x\rangle &= -\int \Psi^*\frac{\partial}{\partial x}\left(-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi\right)\mathrm{d}\mathbf{r} + \int\left(-\frac{\hbar^2}{2m}\nabla^2\Psi^* + V\Psi^*\right)\frac{\partial\Psi}{\partial x}\mathrm{d}\mathbf{r}\\ &= \frac{\hbar^2}{2m}\int\left[\Psi^*\left(\nabla^2\frac{\partial\Psi}{\partial x}\right) - (\nabla^2\Psi^*)\frac{\partial\Psi}{\partial x}\right]\mathrm{d}\mathbf{r}\\ &\quad - \int\Psi^*\left[\frac{\partial}{\partial x}(V\Psi) - V\frac{\partial\Psi}{\partial x}\right]\mathrm{d}\mathbf{r}. \qquad \textbf{(3.91)}\end{aligned}$$

Assuming that $\partial\Psi/\partial x$, as well as Ψ, vanishes at large distances, the first integral on the right of (3.91) is equal to zero by Green's second identity[7], in which $u = \Psi^*$ and $v = \partial\Psi/\partial x$. The second integral on the right of (3.91) is just

$$\begin{aligned}-\int\Psi^*\left[\frac{\partial}{\partial x}(V\Psi) - V\frac{\partial\Psi}{\partial x}\right]\mathrm{d}\mathbf{r} &= -\int\Psi^*\frac{\partial V}{\partial x}\Psi\mathrm{d}\mathbf{r}\\ &= -\left\langle\frac{\partial V}{\partial x}\right\rangle \qquad \textbf{(3.92)}\end{aligned}$$

so that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p_x\rangle = -\left\langle\frac{\partial V}{\partial x}\right\rangle \qquad \textbf{(3.93)}$$

which is the quantum counterpart of the x-component of the classical equation (3.80b). Equations (3.89) and (3.93), together with similar ones for the y- and z-components, constitute the mathematical formulation of the Ehrenfest theorem.

3.5 The time-independent Schrödinger equation. Stationary states

Let us now consider the particular case such that the potential energy V of the particle does not depend on the time. The Hamiltonian operator $H = -(\hbar^2/2m)\nabla^2 + V(\mathbf{r})$ is then also time-independent, and the time-dependent Schrödinger equation (3.19) simplifies considerably. Indeed, we shall show below that it admits particular solutions of the form

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})f(t) \qquad \textbf{(3.94)}$$

which are products of functions of $\mathbf{r}$ and t separately; we shall also see that the general solution of (3.19) can be expressed as a sum of such 'separable' solutions.

---

[7] Green's second identity states that if $u(x, y, z)$ and $v(x, y, z)$ are scalar functions of position with continuous derivatives of at least the second order, then

$$\int_V [u(\nabla^2 v) - v(\nabla^2 u)]\mathrm{d}\mathbf{r} = \int_S [u(\nabla v) - v(\nabla u)].\mathrm{d}\mathbf{S}$$

where V is a volume bounded by the closed surface S.

In order to prove that particular solutions of the Schrödinger equation (3.19) can be written in the product form (3.94) when V is independent of t, we apply to that equation the method of *separation of variables*. Substituting (3.94) into (3.19), we have

$$\mathrm{i}\hbar\psi(\mathbf{r})\frac{\mathrm{d}f(t)}{\mathrm{d}t} = \left[-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r})\right]f(t). \tag{3.95}$$

Dividing both sides of this equation by $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})f(t)$, we find that

$$\mathrm{i}\hbar\frac{1}{f(t)}\frac{\mathrm{d}f(t)}{\mathrm{d}t} = \frac{1}{\psi(\mathbf{r})}\left[-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r})\right]. \tag{3.96}$$

Since the left-hand side depends only on t and the right-hand side only on $\mathbf{r}$, both sides must be equal to a constant. As this constant has the dimensions of an energy, we shall denote it tentatively by E. We therefore obtain the two equations

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}f(t) = Ef(t) \tag{3.97}$$

and

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{3.98}$$

The first equation can be immediately integrated to give

$$f(t) = C\exp(-\mathrm{i}Et/\hbar) \tag{3.99}$$

where C is an arbitrary constant. Because the solution (3.94) is in product form and equations (3.97) and (3.98) are homogeneous, there is no loss of generality in taking $C = 1$ and writing the particular solution (3.94) in the form

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\exp(-\mathrm{i}Et/\hbar). \tag{3.100}$$

Equation (3.98), which must be satisfied by the function $\psi(\mathbf{r})$, is called the *time-independent Schrödinger equation*. In contrast to the time-dependent Schrödinger equation (3.19), which describes the time development of the wave function $\Psi(\mathbf{r}, t)$, we shall see shortly that equation (3.98) is an *eigenvalue equation*. Before proceeding with the analysis of (3.98), it is therefore useful to review a few basic features of eigenvalue equations.

Eigenvalue equations are equations of the type

$$A\psi_n = a_n\psi_n \tag{3.101}$$

where A is an operator and a_n is a number. A solution ψ_n of such an equation is called an *eigenfunction* corresponding to the *eigenvalue* a_n of the operator A. We see that the eigenvalue equation (3.101) states that the operator A, acting on certain functions ψ_n (the eigenfunctions) will give back these functions multiplied by constants a_n (the eigenvalues). In order that this eigenvalue problem be well defined, the conditions of regularity and the boundary conditions to be satisfied by the functions ψ_n must be specified. If more than one linearly independent eigenfunction corresponds to the same eigenvalue a_n, this eigenvalue is said to be *degenerate*; the *degree of degeneracy* is defined as the number of linearly independent eigenfunctions corresponding to that eigenvalue.

Let us now return to the time-independent Schrödinger equation (3.98). Remembering that the Hamiltonian operator of the particle is given by $H = -(\hbar^2/2m)\nabla^2 + V(\mathbf{r})$, we may write this equation in the form of the eigenvalue equation

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{3.102}$$

where it is understood that the eigenfunction $\psi(\mathbf{r})$ corresponds to the eigenvalue E. When we wish to emphasise this fact we shall add a subscript E to the eigenfunction $\psi(\mathbf{r})$, thus writing $\psi_E(\mathbf{r}) \equiv \psi(\mathbf{r})$. We remark that since H is assumed to be time-independent, a 'separable' solution (3.100) of the Schrödinger equation (3.19) is also an eigenfunction of H corresponding to the eigenvalue E, and hence satisfies the equation

$$H\Psi = E\Psi. \tag{3.103}$$

This last conclusion can also be reached by acting on the wave function (3.100) with the total energy operator $E_{\text{op}} = \mathrm{i}\hbar\partial/\partial t$. We obtain in this way

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi = E\Psi \tag{3.104}$$

which shows that the 'separable' wave function (3.100) is an eigenfunction of the energy operator $\mathrm{i}\hbar\partial/\partial t$ with eigenvalue E. Using (3.104) and the fact that (3.100) is a solution of (3.21) when H is time-independent we retrieve the result (3.103), as expected.

The above discussion strongly suggests that the wave function (3.100) corresponds to a state in which the total energy has the precise (numerical) value E. To show that this is the case, we first note that E is *real*. Indeed, for any 'separable' wave function of the form (3.100) the position probability density is given by

$$\begin{aligned} P(\mathbf{r}, t) &= \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t) \\ &= \psi^*(\mathbf{r})\psi(\mathbf{r}) \exp\left[-\frac{\mathrm{i}}{\hbar}(E - E^*)t\right]. \end{aligned} \tag{3.105}$$

Assuming that Ψ is square integrable, we have from probability conservation, as expressed by equation (3.29)

$$(E - E^*)\int \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} = 0 \tag{3.106}$$

where the integration is over all space. Hence $E = E^*$ and E is real. Now we have seen in Section 3.2 that the probability conservation equation (3.29) implies that the Hamiltonian operator H is Hermitian. We may therefore say that the eigenvalues E of the time-independent Schrödinger equation (3.102) are real because the Hamiltonian H is Hermitian. More generally, we shall see in Chapter 5 that the eigenvalues of *any* Hermitian operator are always real.

Let us now calculate the expectation value of the total energy in a state described by the wave function (3.100). Using (3.65), (3.21) and (3.103), we have

$$\begin{aligned}\langle E\rangle &= \int \Psi^*(\mathbf{r},t)\left(\mathrm{i}\hbar\frac{\partial}{\partial t}\right)\Psi(\mathbf{r},t)\mathrm{d}\mathbf{r} = \int \Psi^*(\mathbf{r},t)H\Psi(\mathbf{r},t)\mathrm{d}\mathbf{r}\\ &= E\end{aligned} \tag{3.107}$$

where we have assumed that the wave function (3.100) is normalised to unity. From (3.64) and (3.65) we may also write the above relation as

$$E = \langle H\rangle = \langle T\rangle + \langle V\rangle. \tag{3.108}$$

Thus the number E is the expectation value of the total energy in the state (3.100). More generally, we see that for a state (3.100) normalised to unity we have

$$\langle E^n\rangle = \int \Psi^*(\mathbf{r},t)H^n\Psi(\mathbf{r},t)\mathrm{d}\mathbf{r} = E^n. \tag{3.109}$$

Hence, if $f(E)$ is a function of the energy which can be expanded in an absolutely convergent power series in E,

$$f(E) = \sum_n a_n E^n \tag{3.110}$$

its expectation value, in a state (3.100) normalised to unity, is given by

$$\langle f(E)\rangle = \sum_n a_n\langle E^n\rangle = \sum_n a_n E^n = f(E) \tag{3.111}$$

so that the wave function (3.100) describes a state in which the total energy has the definite numerical value E. In other words, a measurement of the energy on any member of an ensemble of identically prepared systems described by the wave function (3.100) will produce the same numerical value E. For this reason the eigenvalues E appearing in the time-independent Schrödinger equation (3.102) are called *energy eigenvalues*, the corresponding eigenfunctions $\psi_E(\mathbf{r}) \equiv \psi(\mathbf{r})$ of the Hamiltonian operator H being the *energy eigenfunctions*. Since $\psi(\mathbf{r})$ and the 'separable' state (3.100) differ only by the time-dependent phase factor $\exp(-\mathrm{i}Et/\hbar)$, the spatial factor $\psi(\mathbf{r})$ is called a *time-independent wave function*.

Stationary states

The states (3.100) corresponding to a precise value E of the total energy have interesting properties. First of all, since E is real, we see from (3.105) that the position probability density corresponding to these states is given by

$$P(\mathbf{r}) = \psi^*(\mathbf{r})\psi(\mathbf{r}) = |\psi(\mathbf{r})|^2 \tag{3.112}$$

and hence is constant in time. For this reason the states (3.100) are called *stationary states*. We also note from (3.34) and (3.100) that the probability current density corresponding to stationary states reads

$$\mathbf{j}(\mathbf{r}) = \frac{\hbar}{2m\mathrm{i}}\{\psi^*(\mathbf{r})[\nabla\psi(\mathbf{r})] - [\nabla\psi^*(\mathbf{r})]\psi(\mathbf{r})\} \tag{3.113}$$

and is also constant in time. Moreover, the continuity equation (3.39) reduces to

$$\nabla.\mathbf{j}(\mathbf{r}) = 0. \tag{3.114}$$

An example of a stationary state is the plane wave (3.9), which can be written in the 'separable' form (3.100), with $\psi(\mathbf{r}) = A\exp(\mathrm{i}\mathbf{p}.\mathbf{r}/\hbar)$. It is a stationary state describing a free particle of well-defined momentum $\mathbf{p}$ and definite energy $E = \mathbf{p}^2/2m$.

It is important to note that for stationary states (3.100) the expectation value of any operator A is independent of the time t, provided that A itself does not depend explicitly on t. Indeed, for such an operator we have, from (3.68) and (3.100),

$$\begin{aligned}\langle A\rangle &= \frac{\int \Psi^*(\mathbf{r},t)A(\mathbf{r}, -\mathrm{i}\hbar\nabla)\Psi(\mathbf{r},t)\mathrm{d}\mathbf{r}}{\int \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)\mathrm{d}\mathbf{r}}\\ &= \frac{\int \psi^*(\mathbf{r})A(\mathbf{r}, -\mathrm{i}\hbar\nabla)\psi(\mathbf{r})\mathrm{d}\mathbf{r}}{\int \psi^*(\mathbf{r})\psi(\mathbf{r})\mathrm{d}\mathbf{r}}\end{aligned} \tag{3.115}$$

and we see that $\langle A\rangle$ is time-independent. In particular, since the time-independent operators $\mathbf{r}$ and $-\mathrm{i}\hbar\nabla$ are associated respectively with the basic dynamical variables $\mathbf{r}$ and $\mathbf{p}$, the expectation values of $\mathbf{r}$ and $\mathbf{p}_{\mathrm{op}} = -\mathrm{i}\hbar\nabla$ are independent of time for stationary states.

It is apparent from the time-independent Schrödinger equation (3.102) that if ψ is a solution of that equation corresponding to the eigenvalue E, all multiplies of ψ are also solutions of (3.102) corresponding to that eigenvalue. Since wave functions differing by a constant multiplicative factor describe the same physical state, we shall not regard two solutions of (3.102) to be distinct if they differ only by a constant factor. Note that since $\Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t) = \psi^*(\mathbf{r})\psi(\mathbf{r})$ for a stationary state (3.100), it follows that if this state is normalised to unity, then

$$\int \psi^*(\mathbf{r})\psi(\mathbf{r})\mathrm{d}\mathbf{r} = 1 \tag{3.116}$$

so that the energy eigenfunctions $\psi(\mathbf{r})$ are also normalised to unity. Clearly, in this case two solutions of (3.102) which are multiples of each other can differ only by a constant 'phase factor' of unit modulus, having the form $\exp(\mathrm{i}\alpha)$, where α is a real constant.

3.6 Energy quantisation

We have seen above that the time-independent Schrödinger equation (3.102) is an *eigenvalue equation.* We shall now show that *physically acceptable* solutions of that equation exist only for certain values of the total energy E.

To see how this comes about, let us consider the simple case of a particle moving in one dimension in a potential $V(x)$. The stationary states (3.100) then read

$$\Psi(x,t) = \psi(x)\exp(-\mathrm{i}Et/\hbar) \tag{3.117}$$

and the energy eigenfunctions $\psi(x)$ are solutions of the time-independent Schrödinger equation

$$H\psi(x) \equiv -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x) \tag{3.118}$$

which we shall rewrite for convenience as

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = \frac{2m}{\hbar^2}[V(x) - E]\psi(x). \tag{3.119}$$

Since this is a second-order linear differential equation, it always has two linearly independent solutions, for *any* E. Provided $V(x)$ is finite everywhere, we see from (3.119) that the second derivative $\mathrm{d}^2\psi(x)/\mathrm{d}x^2$ is also finite, so that $\mathrm{d}\psi(x)/\mathrm{d}x$, and, therefore, $\psi(x)$ are *continuous* for all x, in agreement with the general continuity properties of the wave function noted at the end of Section 3.1. Moreover, in order to maintain the probabilistic interpretation of the wave function discussed in Chapter 2 and in Section 3.2, we shall impose the *physical* requirement that a solution $\psi(x)$ of equation (3.119) must be *finite* and single-valued everywhere. The eigenfunctions $\psi(x)$ we are looking for are therefore solutions of equation (3.119), such that each solution is finite, continuous and has a continuous derivative over the entire interval $(-\infty, +\infty)$. It is worth noting that since both E and $V(x)$ are *real*, if $\psi(x)$ is an eigenfunction of equation (3.119), so is also its complex conjugate $\psi^*(x)$. Consequently, the real part $[\psi(x) + \psi^*(x)]/2$ and the imaginary part $[\psi(x) - \psi^*(x)]/2\mathrm{i}$ of an eigenfunction $\psi(x)$ are also solutions of (3.119). Because both $[\psi(x) + \psi^*(x)]/2$ and $[\psi(x) - \psi^*(x)]/2\mathrm{i}$ are *real* functions, we only need to know the real eigenfunctions of (3.119) to construct all the eigenfunctions corresponding to a given eigenvalue. In the remaining part of this section we shall take advantage of this fact which allows us to restrict our attention to the real solutions of (3.119), without loss of generality. In particular, this will permit us to plot real solutions $\psi(x)$ in the usual way, instead of representing for instance the real and imaginary parts of a complex $\psi(x)$.

As an example, let us study the case of a potential $V(x)$ having the form shown in Fig. 3.1. This potential is equal to the value V_- for $x \to -\infty$. As x increases, $V(x)$ decreases and attains a minimum value $V_{\text{min}} = V(x_0)$ at $x = x_0$. For values of x larger than x_0 the potential $V(x)$ is assumed to increase until it eventually becomes equal to the value V_+ when $x \to +\infty$. Four cases must be distinguished, depending on the value of the energy E (see Fig. 3.1).

Case 1: $E < V_{\text{min}}$

In this case the quantity $V(x) - E$ is always positive, so that from (3.119) it is apparent that the second derivative of the wave function, $\mathrm{d}^2\psi(x)/\mathrm{d}x^2$, has always the same

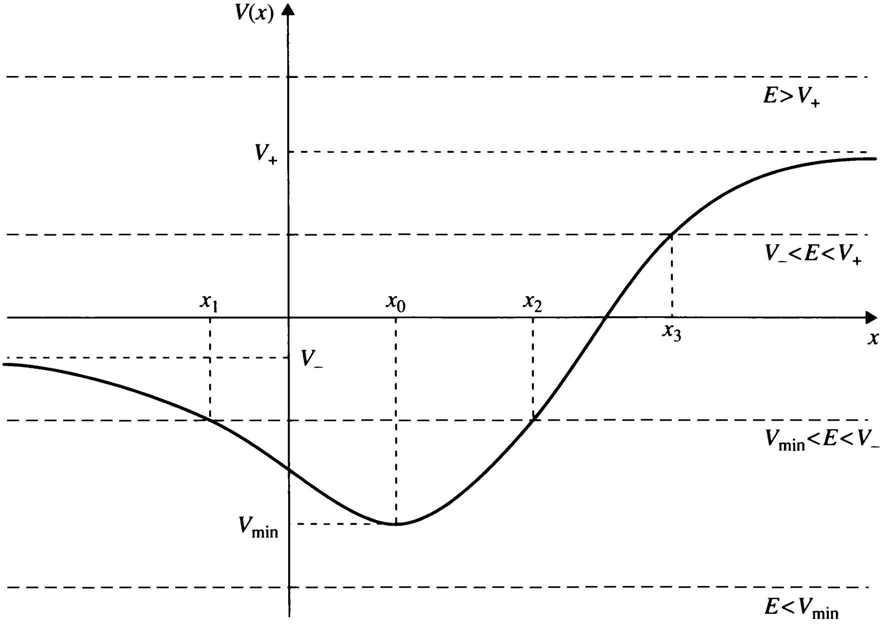


Figure 3.1 Illustration of the one-dimensional potential well $V(x)$ considered in the text. For $x \to -\infty$ the potential $V(x)$ tends to V_- and for $x \to +\infty$ it tends to V_+. At $x = x_0$ it attains the minimum value V_{min}. Also shown are four values of the total energy E (represented by horizontal lines) corresponding to the four cases which can occur. The points x_1 and x_2 are the classical turning points corresponding to the case $V_{min} < E < V_-$, and x_3 is the classical turning point corresponding to the case $V_- < E < V_+$.

sign as $\psi(x)$. Now the behaviour of a function $\psi(x)$ near a point $x = \bar{x}$, where $\psi(x)$ and $\mathrm{d}^2\psi(x)/\mathrm{d}x^2$ have the same sign is easily predicted and is illustrated in Fig. 3.2. If $\psi(\bar{x}) > 0$, then $\psi(x)$ will be concave upwards in the vicinity of $x = \bar{x}$ (see Fig. 3.2(a)); if $\psi(\bar{x}) < 0$ then $\psi(x)$ will be concave downwards in this vicinity (see Fig. 3.2(b)); if $\psi(\bar{x}) = 0$ then $\psi(x)$ will 'escape' away from the x-axis on both sides of the point $x = \bar{x}$ (see Fig. 3.2(c)). Since $V(x) - E > 0$ for *all* x, it is clear that a solution $\psi(x)$ of (3.119) which remains finite everywhere cannot be found. Indeed, $|\psi(x)|$ grows without limit either (a) as $x \to +\infty$ *and* $x \to -\infty$ or (b) as $x \to +\infty$ *or* $x \to -\infty$. The best we can do is to select from among the two linearly independent solutions of (3.119) a function $\psi(x)$ which approaches the x-axis asymptotically either on the left side (see Fig. 3.3(a)) or on the right side (see Fig. 3.3(b)), but then this solution will necessarily 'blow up' on the other side. We therefore conclude that there is *no physically acceptable solution* of equation (3.119) when $E < V(x)$ for all x. We also remark that because the kinetic energy $E - V(x)$ is everywhere negative, no classical motion would be possible in this case.

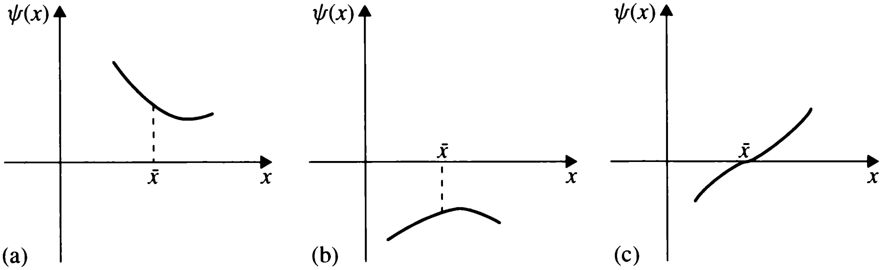


Figure 3.2 The local behaviour of a real solution $\psi(x)$ of equation (3.119) near a point $x = \bar{x}$, when $E < V_{\text{min}}$, for the three cases (a) $\psi(\bar{x}) > 0$, (b) $\psi(\bar{x}) < 0$ and (c) $\psi(\bar{x}) = 0$.

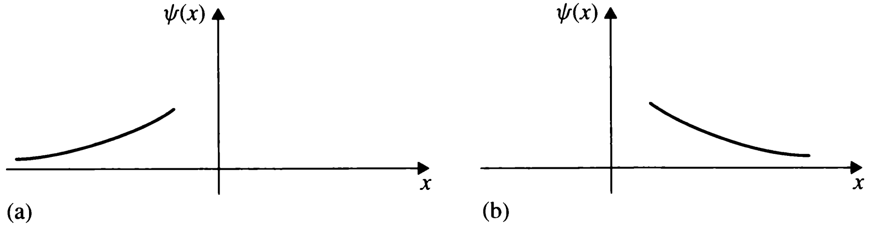


Figure 3.3 Illustration of solutions $\psi(x)$ of equation (3.119) approaching the x-axis asymptotically (a) on the left side and (b) on the right side, for the case $E < V_{\text{min}}$. In both cases it is assumed that $\psi(x) > 0$.

Case 2: $V_{\text{min}} < E < V_-$

Referring to Fig. 3.1, we see that $E - V(x)$ vanishes at the two points $x = x_1$ and $x = x_2$. The points for which $E = V(x)$ are called the classical *turning points* because they are the limits of the motion of a classical particle of energy E. Indeed, the regions for which the kinetic energy $E - V(x)$ is negative are inaccessible to a classical particle. At a turning point the kinetic energy is zero, so that a classical particle would stop and turn around at this point. In the present case the motion of a classical particle would therefore be confined to the interval $x_1 \leqslant x \leqslant x_2$.

Quantum mechanically, we shall now show that physically admissible solutions only exist for certain *discrete* values of the energy E. To see this, let us examine the behaviour of the solutions $\psi(x)$ of (3.119) in the 'internal' region $x_1 < x < x_2$ and in the two 'external' regions $x < x_1$ and $x > x_2$. In the internal region, where $E - V(x) > 0$, $\mathrm{d}^2\psi(x)/\mathrm{d}x^2$ is of opposite sign to $\psi(x)$. As a result, if $\bar{x}$ is a point belonging to that region, and if $\psi(\bar{x}) > 0$, then $\psi(x)$ will be concave downwards in the vicinity of $x = \bar{x}$ (see Fig. 3.4(a)); if $\psi(\bar{x}) < 0$ then $\psi(x)$ will be concave upwards in this vicinity (see Fig. 3.4(b)); if $\psi(\bar{x}) = 0$, then $\psi(x)$ will turn towards the x-axis on both sides of $\bar{x}$ (see Fig. 3.4(c)). Thus, when $x_1 < x < x_2$, $\psi(x)$ is always concave towards the x-axis and hence exhibits an *oscillatory* behaviour. It is worth noting that $\psi(x)$ might have several zeros in the internal region. The general solution of (3.119) in the internal region is a linear combination of two linearly independent

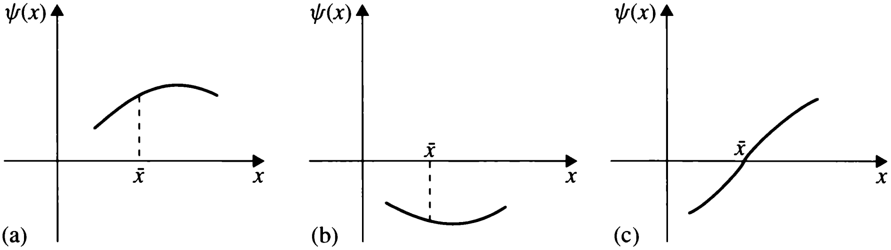


Figure 3.4 The local behaviour of a real solution $\psi(x)$ of equation (3.119) near a point $x = \bar{x}$ belonging to the internal region where $E - V(x) > 0$ for the three cases: (a) $\psi(\bar{x}) > 0$, (b) $\psi(\bar{x}) < 0$, and (c) $\psi(\bar{x}) = 0$.

solutions, both of which are oscillatory.

In the external region $x < x_1$ the second derivative $\mathrm{d}^2\psi(x)/\mathrm{d}x^2$ has the same sign as $\psi(x)$, and therefore two linearly independent solutions of (3.119) can be found, one which tends to zero as $x \to -\infty$, the other one being such that $|\psi(x)|$ increases without limit as $x \to -\infty$. The general solution of (3.119) in the external region $x < x_1$ is a linear combination of these two particular solutions. Likewise, in the external region $x > x_2$, two particular linearly independent solutions of (3.119) can be obtained: one which tends to zero as $x \to +\infty$ and the other one such that $|\psi(x)|$ 'blows up' as $x \to +\infty$. Again, the general solution of (3.119) in the region $x > x_2$ is a linear combination of these two particular solutions.

Now, the only physically admissible solution in the external region $x < x_1$ is the one tending to zero as $x \to -\infty$, and this solution is *unique*, apart from an irrelevant multiplicative constant. The continuity of $\psi(x)$ and $\mathrm{d}\psi(x)/\mathrm{d}x$ at $x = x_1$ then provides two conditions[8] which determine a unique linear combination of the two independent oscillatory solutions in the internal region $x_1 < x < x_2$. Similarly, the continuity of $\psi(x)$ and $\mathrm{d}\psi(x)/\mathrm{d}x$ at $x = x_2$ provides two conditions which determine a *unique* linear combination of the two independent solutions (one tending to zero and the other one blowing up as $x \to \infty$) in the external region $x > x_2$. Thus, in general, for a given value of E such that $V_{\min} < E < V_-$, the unique solution $\psi(x)$ of (3.119) which tends to zero as $x \to -\infty$ will contain in the region $x > x_2$ a component such that $|\psi(x)|$ increases without limit as $x \to +\infty$ (see Fig. 3.5(a) and 3.5(b)); it is therefore physically inadmissible. However, since the value of $\mathrm{d}^2\psi(x)/\mathrm{d}x^2$ and, hence, the curvature of the solution $\psi(x)$ depend on the energy E, there may be certain discrete value of E for which the solution in the internal region will join smoothly to the solutions in the external regions which tend to zero as $x \to -\infty$ and $x \to +\infty$ (see Fig. 3.5(c)). Such solutions, which are finite, continuous and having a continuous derivative everywhere are *eigenfunctions* of (3.119). Since the probability density $P(x) = |\psi(x)|^2$ corresponding to these physically admissible solutions decreases to

---

[8] The two conditions that $\psi(x)$ and $\mathrm{d}\psi(x)/\mathrm{d}x$ be continuous at a given point are often referred to as the conditions for 'smooth' matching (or joining) at that point.

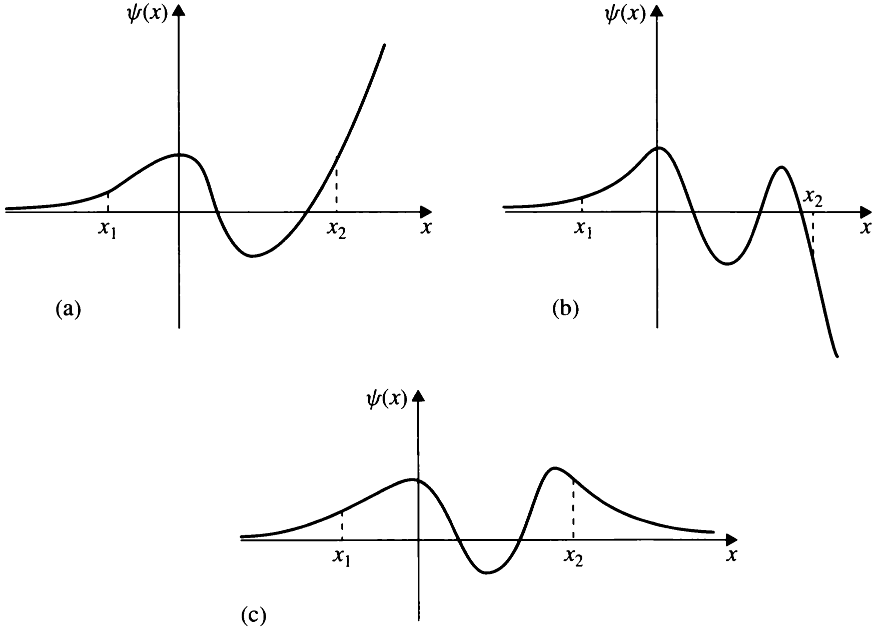


Figure 3.5 Diagrams (a), (b) and (c) show the behaviour of the solution of equation (3.119) at energies just below, just above, and at a bound state energy, respectively. All three solutions decrease to zero as $x \to -\infty$. It is seen that in cases (a) and (b) the solutions diverge as $x \to +\infty$, while in case (c) the solution tends asymptotically to zero as $x \to +\infty$.

zero as $|x| \to \infty$, these eigenfunctions are said to represent *bound states*, and the corresponding *discrete* energies are called *bound-state energies*. We have therefore obtained a fundamental result: the *quantisation of the bound-state energies*, and we see that the determination of the quantised energies appears in Schrödinger's wave mechanics as an eigenvalue problem. The number of discrete energy levels depends on the nature of the potential $V(x)$; it can be finite or infinite.

It is important to remark that in contrast to classical mechanics, where in the case $V_{\text{min}} < E < V_-$ the motion is strictly confined to the internal region (between the turning points), a quantum mechanical bound-state wave function $\psi(x)$ extends outside the internal region and vanishes only in the limits $x \to \pm\infty$. Thus, although the position probability density $P(x) = |\psi(x)|^2$ decreases as one goes deeper and deeper into the classically forbidden regions, it is nevertheless non-vanishing at finite distances, and becomes equal to zero only in the limits $x \to \pm\infty$.

It is apparent from the above discussion that apart from a multiplicative constant the physically admissible wave function corresponding to an allowed energy value is *unique*, so that *in one dimension the bound-state (discrete) energy eigenvalues are non-degenerate*. (In more than one dimension they may be degenerate.) This property can also be proved as follows. Let us suppose for a moment that the contrary is true, and let $\psi_1(x)$ and $\psi_2(x)$ be two linearly independent eigenfunctions of (3.119) corresponding to the same energy eigenvalue E. Since both $\psi_1(x)$ and $\psi_2(x)$ satisfy the equation (3.119), we have

$$\frac{\psi_1''}{\psi_1} = \frac{\psi_2''}{\psi_2} = \frac{2m}{\hbar^2}(V - E) \tag{3.120}$$

where we have used the notation $\psi_1'' \equiv \mathrm{d}^2\psi_1/\mathrm{d}x^2$ and $\psi_2'' \equiv \mathrm{d}^2\psi_2/\mathrm{d}x^2$. Using (3.120) we see that

$$\psi_1\psi_2'' - \psi_2\psi_1'' = (\psi_1\psi_2')' - (\psi_2\psi_1')' = 0 \tag{3.121}$$

where the prime denotes a derivative with respect to x. Integrating this relation, we find that

$$\psi_1\psi_2' - \psi_2\psi_1' = \text{ constant.} \tag{3.122}$$

We recognise on the left-hand side of this equation the *Wronskian*[9] of the two solutions ψ_1 and ψ_2. Since we are dealing with bound states, both ψ_1 and ψ_2 vanish at infinity, so that the constant in (3.122) must be equal to zero. Hence the Wronskian of ψ_1 and ψ_2 vanishes over the entire interval $(-\infty, +\infty)$ and

$$\frac{\psi_1'}{\psi_1} = \frac{\psi_2'}{\psi_2}. \tag{3.123}$$

---

[9] The *Wronskian* (determinant) of the two functions $f(x)$ and $g(x)$ is defined as

$$W[f, g] = \begin{vmatrix} f & g \\ f' & g' \end{vmatrix} = fg' - gf'.$$

If $W[f, g] = 0$ at a point x_0 of the x-axis, then $f'/f = g'/g$ at that point, so that the two functions f and g have the same logarithmic derivative at the point x_0. If $W[f, g]$ vanishes over the entire interval $(-\infty, +\infty)$ the two functions f and g are multiples of each other. Suppose now that $f(x)$ and $g(x)$ are, respectively, solutions of the equations

$$f'' + F(x)f = 0 \tag{1}$$
$$g'' + G(x)g = 0 \tag{2}$$

in an interval (a, b) where the functions $F(x)$ and $G(x)$ are piecewise continuous. Multiplying (1) by g, (2) by f and subtracting term by term, we obtain

$$fg'' - gf'' = (F - G)fg. \tag{3}$$

The left-hand side of this equation is just the derivative of the Wronskian $W[f, g]$. Upon integration over the interval (a, b), we therefore find that the overall variation of the Wronskian in the interval (a, b) is given by

$$W[f, g]_a^b = \int_a^b [F(x) - G(x)]f(x)g(x)\mathrm{d}x. \tag{4}$$

This property is known as the *Wronskian theorem*. As a consequence of this theorem, we see that if ψ_1 and ψ_2 are two solutions of the Schrödinger equation (3.119) corresponding to the *same* energy eigenvalue E, their Wronskian is independent of x and is therefore a constant:

$$W[\psi_1, \psi_2] = \text{ constant.} \tag{5}$$

Integrating this equation once more, we find that $\psi_1 = c\psi_2$, where c is a constant; this result is in contradiction to the assumed linear independence of the two eigenfunctions.

Case 3: $V_- < E < V_+$

Looking again at Fig. 3.1, we note that in this energy interval there is only one classical turning point, at $x = x_3$, no classical motion being allowed in the region $x > x_3$ for which the kinetic energy $E - V(x)$ is negative. A classical particle moving to the right would thus be reflected at the turning point. Note that classically the particle is *unbound* since it can move in an infinite region of the x-axis.

Quantum mechanically, we see that for $x < x_3$ there are two linearly independent solutions of (3.119) both of which are oscillatory, while for $x > x_3$ two linearly independent solutions can be found, one which tends to zero as $x \to +\infty$ and the other which is unbounded when $x \to +\infty$. The only physically admissible solution in the region $x > x_3$ is the one tending to zero as $x \to +\infty$, and this solution is *unique* (except for a multiplicative constant). The continuity of $\psi(x)$ and $\mathrm{d}\psi(x)/\mathrm{d}x$ at $x = x_3$ then yields two conditions which determine a *unique* linear combination of the two independent oscillatory solutions in the region $x < x_3$. A typical eigenfunction obtained in this way is illustrated in Fig. 3.6(a). It is important to remark that this 'smooth matching' at $x = x_3$ can be made for *every* energy E in the interval $V_- < E < V_+$. We therefore conclude that in this energy interval the allowed energies form a *continuum* and are *non-degenerate*.

We also note that in the present case the physically acceptable solutions of (3.119) tend to zero as $x \to +\infty$, but are non-zero and finite as $x \to -\infty$, so that the particle can be found 'at infinity'. Wave functions which are non-zero and finite at infinity are said to correspond to *unbound* (or *scattering*) states. Such wave functions are clearly not square integrable, and hence cannot be normalised by imposing the condition (3.28). We shall return to this point in the next section.

Case 4: $E > V_+$

In this case the kinetic energy $E - V(x)$ is everywhere positive. Classically, the particle is *unbound* and there are two independent states of motion, one in which the particle moves from left to right, and the other one in which it moves from right to left. Since $\mathrm{d}^2\psi(x)/\mathrm{d}x^2$ is opposite in sign to $\psi(x)$ for all x in this energy region, *two* linearly independent *oscillatory* solutions of (3.119) exist which are physically admissible for every energy. Thus when $E > V_+$ the energy eigenvalues of (3.119) form a continuum and are doubly degenerate. The corresponding eigenfunctions $\psi(x)$ are non-zero and finite as $x \to +\infty$ and $x \to -\infty$; they describe *unbound* (*scattering*) states. A typical eigenfunction of this kind is displayed in Fig. 3.6(b).

To summarise, we see that the eigenfunctions (that is the physically admissible solutions) of the time-independent Schrödinger equation (3.119) correspond to *bound* or *unbound* (*scattering*) states according to whether they vanish or are merely finite at infinity. The values of the total energy E for which the time-independent Schrödinger

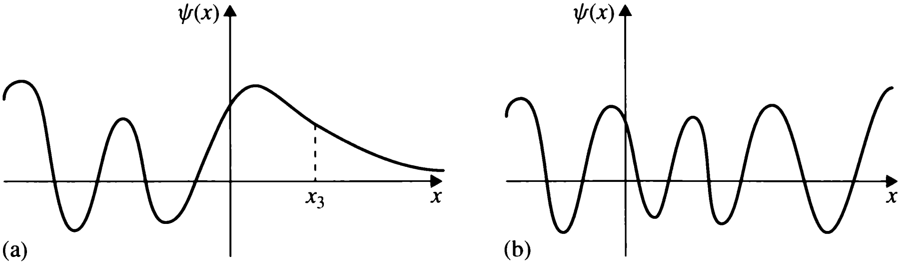


Figure 3.6 Typical eigenfunctions of the Schrödinger equation (3.119): (a) for the case $V_- < E < V_+$, and (b) for the case $E > V_+$.

equation has physically admissible solutions constitute the *energy spectrum*. For a particle moving in a bounded potential $V(x)$ this energy spectrum may contain a set of *discrete* energy levels corresponding to the *bound states*; in addition, it contains a *continuous* range of energies extending to $E = +\infty$, which corresponds to the *unbound states* (see Fig. 3.7). The bound-state energies must belong to a region in which the total energy E is such that the classical motion would be bound. Moreover, the energies of the bound states are *quantised*, since only a discrete set of them is allowed. As we have already seen in Section 1.4, the lowest discrete energy level is called the *ground-state energy* of the system, and all discrete higher energy levels are said to correspond to *excited* states. The energies of the unbound states are such that the particle would classically also be unbound; since these energies form a continuum there is no energy quantisation for unbound states.

Similar conclusions can be reached for the case of a particle of mass m moving in three dimensions in a potential $V(\mathbf{r})$. To be physically acceptable, a solution $\psi(\mathbf{r})$ of the time-independent Schrödinger equation (3.98) and its partial derivatives of the first order must be *continuous, single-valued* and *bounded* over all space. According to whether they vanish or are merely finite at infinity, the eigenfunctions of (3.98) are said to correspond to *bound states* or to *unbound* (*scattering*) states. It can be shown that if $V(\mathbf{r})$ is finite as $r \to \infty$ in any direction, the energy spectrum may contain a certain number of *discrete* (quantised) energy levels, corresponding to *bound states*; in addition it contains a *continuous* range of energies corresponding to unbound states. The bound states are analogous to the closed orbits of classical mechanics; their energies cannot exceed the minimum value V_- that $V(\infty)$ has in any direction; their number is finite (including zero) or infinite depending on the form of V. The scattering states are analogous to the open orbits of classical mechanics; their energies extend continuously from V_- to $+\infty$. A number of examples will be analysed in Chapters 4 and 7 to illustrate, respectively, the one-dimensional and three-dimensional situations.

It is interesting to note that if the potential energy V is changed by a constant (finite) amount, the eigenfunctions of the time-independent Schrödinger equation (3.98) are unchanged, while the eigenenergies are shifted by that constant (Problem 3.8). Indeed, the addition of a constant to the potential energy has no physical effect (the force

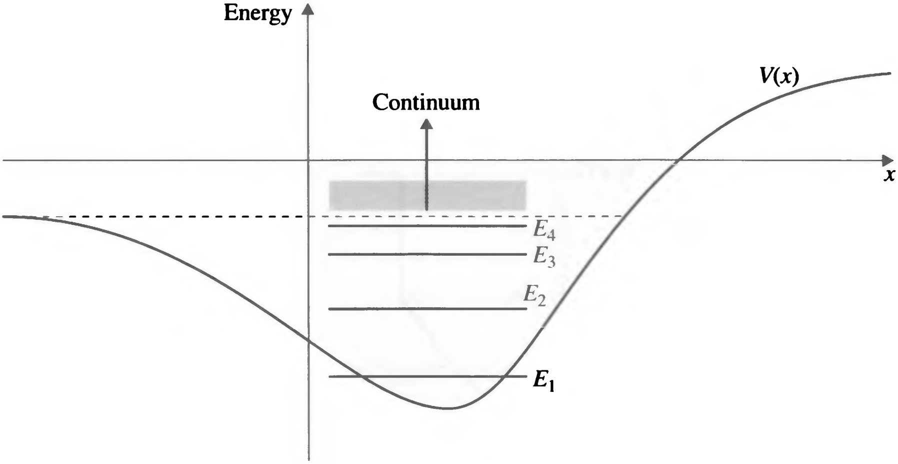


Figure 3.7 A typical energy spectrum for a one-dimensional potential well, containing both discrete and continuum energy levels.

corresponding to a constant potential energy being equal to zero) and corresponds simply to a change in the origin of the energy scale. We may therefore choose this constant as we please. For example, if $V(\mathbf{r})$ is bounded as $r \to \infty$, it is convenient to choose V_- (the smallest value of $V(\infty)$ in any direction) to be zero. In this case the discrete bound-state energies (if any) will be negative and the continuous spectrum will extend from $E = 0$ to $E = +\infty$.

Infinite potential energy

Until now we have considered potentials which are *finite* everywhere; this clearly includes potentials which exhibit discontinuities of the first kind (finite jumps). However, when the potential energy V is infinite[10] anywhere, the boundary conditions to be satisfied by the solutions of the time-independent Schrödinger equation must be modified. Indeed, because a particle cannot have an infinite potential energy, it cannot penetrate in a region of space where $V = \infty$. Consequently, its wave function $\Psi(\mathbf{r}, t)$ – and hence also the time-independent wave function $\psi(\mathbf{r})$ – must *vanish* everywhere in that region. The continuity of the wave function then requires that it also vanishes on the border of that region. We remark that since V exhibits a discontinuity of the second kind (infinite jump) across that border, $\nabla^2\psi$ will also exhibit such a discontinuity, so that $\boldsymbol{\nabla}\psi$ will be *discontinuous* (and hence undetermined) there. In particular, a boundary surface at which there is an infinite potential step acts like a perfectly rigid, impenetrable 'wall' where the wave function of the particle vanishes and its gradient is undetermined.

---

[10] Potentials which have discontinuities (finite or infinite) are of course mathematical idealisations of actual physical potentials.

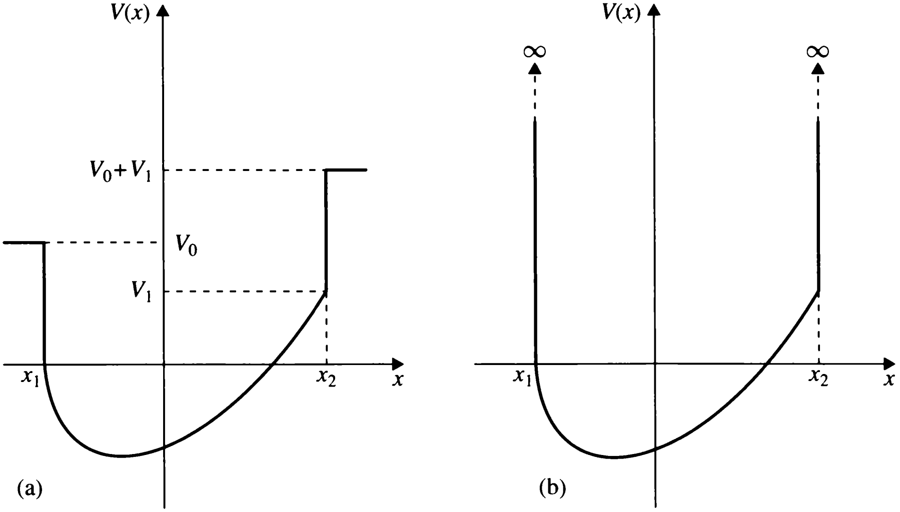


Figure 3.8 Illustration of the two potential wells described in the text: (a) $V(x)$ jumps upwards at $x = x_1$ and $x = x_2$ by the finite amount $V_0 > 0$, (b) corresponds to the case $V_0 \to \infty$.

The foregoing considerations will be illustrated in Section 4.3, where we shall study in detail the one-dimensional potential step. Here, we analyse briefly another example, which will be useful shortly in connection with the 'normalisation' of unbound wave functions. We consider a one-dimensional potential well such as that represented in Fig. 3.8(a). We assume that $V(x)$ is finite for $x_1 < x < x_2$. At $x = x_1$ it 'jumps' upwards from zero to the finite value V_0, and remains equal to V_0 for $x < x_1$. Similarly at $x = x_2$, the potential 'jumps' by the positive amount V_0 from the value V_1 (which for definiteness is taken to be positive) and is equal to $V_1 + V_0$ for $x > x_2$. According to the analysis made earlier in this section, when the total energy E is smaller than V_0, there may be a certain number of discrete bound states, while for $E > V_0$ the allowed energies form a continuum. Thus, as V_0 increases the continuum part of the spectrum will shrink and in the limit $V_0 \to +\infty$ (see Fig. 3.8(b)) the energy spectrum will be *entirely discrete*, the allowed energy levels being determined by the boundary conditions

$$\psi(x_1) = \psi(x_2) = 0 \tag{3.124}$$

which express the fact that the energy eigenfunctions must vanish at the two impenetrable walls of this one-dimensional box. The explicit determination of the energy levels and eigenfunctions will be done in Section 4.5 for the particular case of an infinite square well.

The above results are readily generalised to three dimensions. If we enclose a three-dimensional system in a box with impenetrable walls, its energy spectrum will be *entirely discrete*, the allowed energies being obtained from the requirement that the wave function vanishes at the walls. The energy levels and eigenfunctions of a 'free' particle constrained to move inside a three-dimensional box will be obtained in this way in Section 7.1.

Finally, we remark that as the walls of the box recede towards infinity, we expect on physical grounds that the energy spectrum will resemble more and more closely that corresponding to the potential without walls. This fact will be verified explicitly on the examples studied in Sections 4.5 and 7.1.

3.7 Properties of the energy eigenfunctions

In this section we shall obtain some important results concerning the energy eigenfunctions, that is the physically acceptable solutions of the time-independent Schrödinger equation (3.102). It will be convenient here to use the more explicit notation $\psi_E(\mathbf{r})$ to denote an energy eigenfunction corresponding to the eigenvalue E.

First of all, let us examine the question of the *normalisation* of the energy eigenfunctions. We have seen in the preceding section that there are two kinds of eigenfunctions of (3.102): the bound states, which vanish at infinity and correspond to discrete energies, and the unbound (scattering) states, which are only finite at infinity, and whose corresponding energies form a continuum. The bound-state eigenfunctions are square integrable, and hence can readily be normalised to unity in the familiar fashion (see (3.116)). However, the unbound states cannot be normalised in that way. As a result, one cannot define absolute probabilities and expectation values of physical quantities in such unbound states. A way of avoiding this difficulty, which we shall adopt here, is to enclose the system in a box with impenetrable walls, so that the entire eigenvalue spectrum becomes discrete. Since all the eigenfunctions now correspond to bound states, they can be normalised according to

$$\int_V \psi_E^*(\mathbf{r})\psi_E(\mathbf{r})\mathrm{d}\mathbf{r} = 1 \tag{3.125}$$

where V denotes the volume of the box. We shall choose the box to be very large (macroscopic) so that its effect on the energy spectrum is essentially negligible[11]. From now on all the integrals in this section will be assumed to be performed over the volume of a very large box.

We shall now demonstrate that two energy eigenfunctions ψ_E and $\psi_{E'}$ corresponding to *unequal* eigenvalues E and E' are *orthogonal*, namely

$$\int \psi_{E'}^*(\mathbf{r})\psi_E(\mathbf{r})\mathrm{d}\mathbf{r} = 0, \qquad E \neq E'. \tag{3.126}$$

The proof is very simple. First, since $H\psi_E = E\psi_E$ we have, upon premultiplying both sides by $\psi_{E'}^*$

$$\psi_{E'}^*(H\psi_E) = E\psi_{E'}^*\psi_E \tag{3.127}$$

---

[11] Alternative procedures to 'normalise' unbound states will be discussed in Sections 4.2 and 5.3.

where we have omitted the arguments of the functions, for notational simplicity. Now, because $H\psi_{E'} = E'\psi_{E'}$, we can also write

$$(H\psi_{E'})^* = E'\psi^*_{E'} \tag{3.128}$$

where we have used the fact that E' is real. Multiplying both sides of (3.128) on the right by ψ_E, we obtain

$$(H\psi_{E'})^*\psi_E = E'\psi^*_{E'}\psi_E. \tag{3.129}$$

Subtracting (3.129) from (3.127) and integrating over the volume V, we obtain

$$\begin{aligned}(E - E')\int \psi^*_{E'}\psi_E \mathrm{d}\mathbf{r} &= \int [\psi^*_{E'}(H\psi_E) - (H\psi_{E'})^*\psi_E]\mathrm{d}\mathbf{r} \\ &= 0\end{aligned} \tag{3.130}$$

where in the last step we have used the fact that H is Hermitian. Since we have assumed that $E \neq E'$ we see that (3.126) follows from (3.130).

Combining the normalisation relation (3.125) and the orthogonality relation (3.126), we can say that the energy eigenfunctions ψ_E satisfy the *orthonormality* relations

$$\int \psi^*_{E'}(\mathbf{r})\psi_E(\mathbf{r})\mathrm{d}\mathbf{r} = \delta_{EE'} \tag{3.131}$$

where $\delta_{EE'}$ is the Kronecker δ-symbol, such that

$$\delta_{EE'} = \begin{cases} 1 & \text{if } E = E' \\ 0 & \text{if } E \neq E' \end{cases}. \tag{3.132}$$

We have just seen that eigenfunctions corresponding to *different* energy eigenvalues are orthogonal. Let us now see what happens when an energy eigenvalue is degenerate, so that there is more than one linearly independent eigenfunction of (3.102) corresponding to that eigenvalue. Assuming that the degeneracy of E is of order α, we denote by $\psi_{E1}, \psi_{E2}, \ldots, \psi_{E\alpha}$ a set of α linearly independent eigenfunctions corresponding to that energy and normalised according to (3.125). The orthogonality proof given above, which made use of the fact that $E \neq E'$, is clearly not applicable in the present case. Indeed, in general, the eigenfunctions $\psi_{Er} (r = 1, 2, \ldots, \alpha)$ belonging to a degenerate eigenvalue E are not orthogonal. However, given a set of α linearly independent, normalisable functions, it is always possible to construct a new set of α mutually *orthogonal* functions by using the *Schmidt orthogonalisation* *procedure*. Starting from the function ψ_{E1}, we form the sequence

$$\phi_{E1} = \psi_{E1} \tag{3.133a}$$

$$\phi_{E2} = a_{21}\phi_{E1} + \psi_{E2} \tag{3.133b}$$

$$\phi_{E3} = a_{31}\phi_{E1} + a_{32}\phi_{E2} + \psi_{E3} \tag{3.133c}$$

$$\phi_{E\alpha} = a_{\alpha 1}\phi_{E1} + a_{\alpha 2}\phi_{E2} + \cdots + a_{\alpha,\alpha-1}\phi_{E\alpha-1} + \psi_{E\alpha} \tag{3.133d}$$

where a_{ij} denote the coefficients which we shall determine in such a way that each function of the sequence be orthogonal to all the preceding ones.

First, from the orthogonality requirement

$$\int \phi^*_{E1}\phi_{E2}\mathrm{d}\mathbf{r} = 0 \tag{3.134}$$

we deduce by using (3.133a) and (3.133b) that

$$a_{21}\int \phi^*_{E1}\phi_{E1}\mathrm{d}\mathbf{r} + \int \phi^*_{E1}\phi_{E2}\mathrm{d}\mathbf{r} = 0 \tag{3.135}$$

and since $\phi_{E1}(= \psi_{E1})$ is normalised to unity, we have

$$a_{21} = -\int \phi^*_{E1}\psi_{E2}\mathrm{d}\mathbf{r}. \tag{3.136}$$

With the coefficient a_{21} determined in this way we obtain from (3.133b) a function

$$\phi_{E2} = \left[-\int \phi^*_{E1}\psi_{E2}\mathrm{d}\mathbf{r}\right]\phi_{E1} + \psi_{E2} \tag{3.137}$$

orthogonal to ϕ_{E1}. Note that since the (normalised) functions ϕ_{E1} and ψ_{E2} are linearly independent it follows from the Schwarz inequality that $|a_{21}| < 1$. Consequently, using (3.133b), (3.136) and the fact that the functions ϕ_{E1} and ϕ_{E2} are orthogonal, it is seen that the normalisation integral for ϕ_{E2} never vanishes, so that the function ϕ_{E2} is normalisable.

Next, from the two orthogonality conditions

$$\int \phi^*_{E1}\phi_{E3}\mathrm{d}\mathbf{r} = 0 \tag{3.138a}$$

and

$$\int \phi^*_{E2}\phi_{E3}\mathrm{d}\mathbf{r} = 0 \tag{3.138b}$$

one deduces in a similar way that

$$a_{31} + \int \phi^*_{E1}\psi_{E3}\mathrm{d}\mathbf{r} = 0 \tag{3.139a}$$

and

$$a_{32}\int \phi^*_{E2}\phi_{E2}\mathrm{d}\mathbf{r} + \int \phi^*_{E2}\psi_{E3}\mathrm{d}\mathbf{r} = 0 \qquad \textbf{(3.139b)}$$

where we have used (3.134). From (3.133c) and (3.139) we obtain in this fashion a function

$$\phi_{E3} = \left[-\int \phi^*_{E1}\psi_{E3}\mathrm{d}\mathbf{r}\right]\phi_{E1} + \left[-\frac{\int \phi^*_{E2}\psi_{E3}\mathrm{d}\mathbf{r}}{\int \phi^*_{E2}\phi_{E2}\mathrm{d}\mathbf{r}}\right]\phi_{E2} + \psi_{E3} \qquad \textbf{(3.140)}$$

which is orthogonal to ϕ_{E1} and ϕ_{E2}, and normalisable, since ϕ_{E1}, ϕ_{E2} and ψ_{E3} are linearly independent.

This process can be continued until we arrive at the function

$$\phi_{E\alpha} = -\sum_{i=1}^{\alpha-1}\frac{\int \phi^*_{Ei}\psi_{E\alpha}\mathrm{d}\mathbf{r}}{\int \phi^*_{Ei}\phi_{Ei}\mathrm{d}\mathbf{r}}\phi_{Ei} + \psi_{E\alpha} \qquad \textbf{(3.141)}$$

which is orthogonal to the functions $\phi_{E1}, \phi_{E2}, \ldots, \phi_{E,\alpha-1}$ and is normalisable. The set of orthogonal functions $\phi_{Er}(r = 1, 2, \ldots, \alpha)$ being determined in this way[12], we can construct the functions

$$\chi_{Er} = \frac{\phi_{Er}}{\left[\int \phi^*_{Er}\phi_{Er}\mathrm{d}\mathbf{r}\right]^{1/2}}, \quad r = 1, 2, \ldots, \alpha \qquad \textbf{(3.142)}$$

which constitute a set of *mutually orthogonal* functions, *normalised to unity*. These functions satisfy, therefore, the orthonormality relations

$$\int \chi^*_{Es}(\mathbf{r})\chi_{Er}(\mathbf{r})\mathrm{d}\mathbf{r} = \delta_{rs} \quad (r, s = 1, 2, \ldots, \alpha). \qquad \textbf{(3.143)}$$

To summarise, we see that although the α linearly independent eigenfunctions $\psi_{Er}(r = 1, 2, \ldots, \alpha)$ corresponding to the eigenenergy E need not be mutually orthogonal, it is always possible to construct from linear combinations of them a new set of α eigenfunctions which are orthonormal. From now on we shall assume that this orthogonalisation procedure has already been carried out for each degenerate energy eigenvalue. Since, in addition, the eigenfunctions corresponding to different energy eigenvalues are orthogonal, it follows that *all* the energy eigenfunctions can be assumed to satisfy the orthonormality relations

$$\int \psi^*_{E's}(\mathbf{r})\psi_{Er}(\mathbf{r})\mathrm{d}\mathbf{r} = \delta_{EE'}\delta_{rs} \qquad \textbf{(3.144)}$$

and hence form an *orthonormal set.*

We shall postulate that the energy spectrum obtained by solving the time-independent Schrödinger equation (3.102) represents all the physically

---

[12] Note that this set is by no means unique, since we could for example have started the sequence of functions ϕ_{Er} by identifying ϕ_{E1} with ψ_{E2}, or with a linear combination of ψ_{E1} and ψ_{E2}. Thus there are infinitely many possible sets of orthogonal functions ϕ_{Er}.

realisable energies of the system. This implies that the set of energy eigenfunctions is *complete*, in the sense that any physically admissible wave function can be expressed as a superposition of them. The *general* solution $\Psi(\mathbf{r}, t)$ of the time-dependent Schrödinger equation (3.21) can therefore be expanded in terms of the energy eigenfunctions as

$$\Psi(\mathbf{r}, t) = \sum_E C_E(t)\psi_E(\mathbf{r}) \tag{3.145}$$

where the expansion coefficients $C_E(t)$ depend on the time. In writing the above equation, we have dropped the degeneracy index for notational simplicity, it being understood that the summation includes α times an energy eigenvalue whose degeneracy is of order α.

The formula (3.145) is analogous to the familiar expression giving the expansion of a vector in terms of a complete set of orthonormal basis vectors in a vector space. The complete set of orthonormal functions ψ_E plays the role of a set of basis vectors, and the wave function Ψ may be thought of as a 'vector' whose 'components' along the basis 'vectors' ψ_E are the coefficients C_E. This analogy with ordinary vector spaces has a profound significance, as we shall see in Chapter 5.

We remark that since the 'vector' Ψ evolves in time according to the time-dependent Schrödinger equation (3.21), its components C_E must also be functions of the time. If $\Psi(\mathbf{r}, t)$ is given at a particular time, its 'components' are readily obtained in the following way. Multiplying (3.145) on the left by $\psi^*_{E'}(\mathbf{r})$, integrating over the volume V of our (large) box and making use of the orthonormality relations satisfied by the energy eigenfunctions, we find that

$$\begin{aligned}\int \psi^*_{E'}(\mathbf{r})\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} &= \sum_E C_E(t) \int \psi^*_{E'}(\mathbf{r})\psi_E(\mathbf{r})\mathrm{d}\mathbf{r}\\ &= \sum_E C_E(t)\delta_{EE'}\\ &= C_{E'}(t).\end{aligned} \tag{3.146}$$

We conclude this section by mentioning an interesting property of the energy eigenfunctions corresponding to *bound states* of *one-dimensional* systems. Since we are dealing here exclusively with bound states there is no need to enclose the system in a finite box. Assuming that the potential energy $V(x)$ is finite everywhere, we have seen in the previous section that the bound state eigenfunctions vanish when $x \to \pm\infty$. Now, if bound-state energies exist and if they are placed in order of increasing magnitude ($E_1 < E_2 < E_3 < \cdots$), then the corresponding eigenfunctions $\psi_1(x)$, $\psi_2(x)$, $\psi_3(x)$, ..., will occur in increasing number of their zeros, the nth eigenfunction $\psi_n(x)$ having $(n-1)$ zeros for finite values of x. Moreover, between two consecutive zeros of $\psi_n(x)$, the following eigenfunctions will have at least one zero. This is known as the *oscillation theorem* (see Problem 3.9). If the particle is enclosed in a one-dimensional box with impenetrable walls such that $V(x_1) = V(x_2) = +\infty$, then its motion is confined to the interval $x_1 < x < x_2$ and the $(n-1)$ zeros of $\psi_n(x)$ referred to in the oscillation theorem will occur *within* that interval. In addition, of course, $\psi_n(x)$ must vanish in this case at the walls (i.e. at $x = x_1$ and $x = x_2$) so that the total number of its zeros will be $n+1$.

3.8 General solution of the time-dependent Schrödinger equation for a time-independent potential

In the preceding section we have seen that the general solution $\Psi(\mathbf{r}, t)$ of the time-dependent Schrödinger equation (3.21) can be expanded in terms of the energy eigenfunctions $\psi_E(\mathbf{r})$ according to (3.145). We shall now determine the expansion coefficients $C_E(t)$ for the case of a particle moving in a *time-independent* potential $V(\mathbf{r})$. To this end, we substitute (3.145) in the Schrödinger wave equation (3.21), and use the facts that the Hamiltonian H is time-independent and that $H\psi_E = E\psi_E$. Thus

$$\begin{aligned} \mathrm{i}\hbar\frac{\partial}{\partial t}\sum_E C_E(t)\psi_E(\mathbf{r}) &= H\sum_E C_E(t)\psi_E(\mathbf{r}) \\ &= \sum_E C_E(t)H\psi_E(\mathbf{r}) \\ &= \sum_E C_E(t)E\psi_E(\mathbf{r}). \end{aligned} \qquad (3.147)$$

Premultiplying both sides of this equation by $\psi^*_{E'}(\mathbf{r})$ and integrating over the volume V of the box we get

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\sum_E C_E(t)\int \psi^*_{E'}(\mathbf{r})\psi_E(\mathbf{r})\mathrm{d}\mathbf{r} = \sum_E C_E(t)E\int \psi^*_{E'}(\mathbf{r})\psi_E(\mathbf{r})\mathrm{d}\mathbf{r}. \qquad (3.148)$$

Now, since the energy eigenfunctions are orthonormal, this equation reduces to

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}C_E(t) = EC_E(t) \qquad (3.149)$$

where we have written $\mathrm{d}/\mathrm{d}t$ instead of $\partial/\partial t$ since only the time variable appears in (3.149). This equation is readily integrated to yield

$$C_E(t) = C_E(t_0)\exp[-\mathrm{i}E(t-t_0)/\hbar]. \qquad (3.150)$$

Using (3.145) and the above result, we thus find that the *general* solution of the time-dependent Schrödinger equation (3.21) may be written for a *time-independent potential* as

$$\Psi(\mathbf{r}, t) = \sum_E C_E(t_0)\exp[-\mathrm{i}E(t-t_0)/\hbar]\psi_E(\mathbf{r}) \qquad (3.151)$$

or

$$\Psi(\mathbf{r}, t) = \sum_E c_E \psi_E(\mathbf{r}) \exp(-\mathrm{i}Et/\hbar) \tag{3.152}$$

where the constants c_E are given by

$$c_E = C_E(t_0) \exp(\mathrm{i}Et_0/\hbar). \tag{3.153}$$

Remembering that in the case of a time-independent potential the *stationary states* $\psi_E(\mathbf{r}) \exp(-\mathrm{i}Et/\hbar)$ are particular solutions of the time-dependent Schrödinger equation, we see that the general solution (3.152) is an *arbitrary linear superposition of stationary states.* This is to be expected since according to the discussion of Section 3.1 an arbitrary linear superposition of solutions of the time-dependent Schrödinger equation must also be a solution of that equation, as required by the superposition principle.

The constants c_E can be evaluated from the knowledge of the wave function Ψ at any particular time t_0. Indeed, using (3.153) and (3.146), we have

$$c_E = \exp(\mathrm{i}Et_0/\hbar) \int \psi_E^*(\mathbf{r})\Psi(\mathbf{r}, t_0)\mathrm{d}\mathbf{r} \tag{3.154}$$

so that the general solution (3.152) may be written as

$$\Psi(\mathbf{r}, t) = \sum_E \left[\int \psi_E^*(\mathbf{r}')\Psi(\mathbf{r}', t_0)\mathrm{d}\mathbf{r}'\right] \exp[-\mathrm{i}E(t - t_0)/\hbar]\psi_E(\mathbf{r}). \tag{3.155}$$

This expression gives $\Psi(\mathbf{r}, t)$ at any time, once it is known at the time $t = t_0$. If we define the function

$$K(\mathbf{r}, t; \mathbf{r}', t_0) = \sum_E \psi_E^*(\mathbf{r}')\psi_E(\mathbf{r}) \exp[-\mathrm{i}E(t - t_0)/\hbar] \tag{3.156}$$

we see that we may recast (3.155) in the simpler form

$$\Psi(\mathbf{r}, t) = \int K(\mathbf{r}, t; \mathbf{r}', t_0)\Psi(\mathbf{r}', t_0)\mathrm{d}\mathbf{r}'. \tag{3.157}$$

This shows that the 'propagation' of the wave function from the time t_0 to the time t is controlled by the function $K(\mathbf{r}, t; \mathbf{r}', t_0)$, which is therefore called a *propagator.*

Let us now return to the form (3.152) of our general solution. In what follows we shall also need the complex conjugate of that solution

$$\Psi^*(\mathbf{r}, t) = \sum_{E'} c_{E'}^* \psi_{E'}^*(\mathbf{r}) \exp(\mathrm{i}E't/\hbar) \tag{3.158}$$

where we have used a different (dummy) summation symbol for further convenience. If we require that the general solution (3.152) be normalised to unity, we see from (3.152) and (3.158) that we must have

$$\int \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)\mathrm{d}\mathbf{r} = \sum_E \sum_{E'} c_{E'}^* c_E \exp[-\mathrm{i}(E-E')t/\hbar] \int \psi_{E'}^*(\mathbf{r})\psi_E(\mathbf{r})\mathrm{d}\mathbf{r}$$
$$= 1 \qquad \textbf{(3.159)}$$

where the integration is over the volume of the box. Now, because the energy eigenfunctions are orthonormal, we have

$$\sum_E \sum_{E'} c_{E'}^* c_E \exp[-\mathrm{i}(E-E')t/\hbar] \int \psi_{E'}^*(\mathbf{r})\psi_E(\mathbf{r})\mathrm{d}\mathbf{r}$$
$$= \sum_E \sum_{E'} c_{E'}^* c_E \exp[-\mathrm{i}(E-E')t/\hbar]\delta_{EE'}$$
$$= \sum_E |c_E|^2 \qquad \textbf{(3.160)}$$

and therefore the normalisation condition (3.159) reduces to

$$\sum_E |c_E|^2 = 1. \qquad \textbf{(3.161)}$$

It is important to note that in contrast to the case of stationary states, the position probability density corresponding to a superposition of stationary states is *time-dependent*. Indeed, using (3.152) and (3.158), this probability density is given by

$$\begin{aligned} P(\mathbf{r},t) &= \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t) \\ &= \sum_E \sum_{E'} c_{E'}^* c_E \exp[-\mathrm{i}(E-E')t/\hbar]\psi_{E'}^*(\mathbf{r})\psi_E(\mathbf{r}) \\ &= \sum_E |c_E|^2|\psi_E(\mathbf{r})|^2 + \sum_{\substack{E \\ E \neq E'}} \sum_{E'} c_{E'}^* c_E \exp[-\mathrm{i}(E-E')t/\hbar]\psi_{E'}^*(\mathbf{r})\psi_E(\mathbf{r}) \end{aligned} \qquad \textbf{(3.162)}$$

where in the last line we have separated the contributions to $P(\mathbf{r},t)$ arising from the diagonal ($E = E'$) and non-diagonal ($E \neq E'$) terms in the double summation on E and E'. We see that the non-diagonal terms are responsible for the time-dependence of $P(\mathbf{r},t)$.

Since a wave function $\Psi(\mathbf{r},t)$ which is a superposition of stationary states leads to a time-dependent position probability density, it follows that the expectation values of physical quantities in a state described by such a wave function depend in general on the time. An exception occurs for the total energy, whose expectation value in a state described by the general wave function (3.152) is

$$\begin{aligned}\langle E\rangle &= \langle H\rangle = \int \Psi^*(\mathbf{r},t)H\Psi(\mathbf{r},t)\mathrm{d}\mathbf{r}\\ &= \sum_E\sum_{E'} c^*_{E'}c_E \exp[-\mathrm{i}(E-E')t/\hbar]\int \psi^*_{E'}(\mathbf{r})H\psi_E(\mathbf{r})\mathrm{d}\mathbf{r}\\ &= \sum_E\sum_{E'} c^*_{E'}c_E \exp[-\mathrm{i}(E-E')t/\hbar]\ E\int \psi^*_{E'}(\mathbf{r})\psi_E(\mathbf{r})\mathrm{d}\mathbf{r}\\ &= \sum_E\sum_{E'} c^*_{E'}c_E \exp[-\mathrm{i}(E-E')t/\hbar]\ E\ \delta_{EE'}\\ &= \sum_E |c_E|^2 E \qquad\qquad \textbf{(3.163)}\end{aligned}$$

where we have used the fact that $H\psi_E = E\psi_E$ and the orthonormality of the energy eigenfunctions. As seen from (3.163) the average value of the total energy is time-independent, as expected.

It is important to remember that the summation on E in all the previous equations also includes implicitly a sum over a degeneracy index for degenerate energy eigenvalues. If we write this index explicitly, the general solution (3.152) reads

$$\Psi(\mathbf{r},t) = \sum_E\sum_r c_{Er}\psi_{Er}(\mathbf{r})\exp(-\mathrm{i}Et/\hbar). \qquad \textbf{(3.164)}$$

Assuming (without loss of generality) that the energy eigenfunctions satisfy the orthonormality relations (3.144), the normalisation condition becomes

$$\sum_E\sum_r |c_{Er}|^2 = 1 \qquad \textbf{(3.165)}$$

and equation (3.163) is replaced by

$$\langle E\rangle = \sum_E\sum_r |c_{Er}|^2 E. \qquad \textbf{(3.166)}$$

Since we have assumed that the energy spectrum obtained by solving the time-independent Schrödinger equation (3.102) represents all the physically realisable energies of the system, it follows that the energy eigenvalues E are the only possible results of precise measurements of the total energy of the particle. The above relations then suggest that we interpret the quantity

$$P(E) = |c_E|^2 \qquad \textbf{(3.167)}$$

as the *probability that a measurement of the total energy will yield the value* E, provided that this energy value is *non-degenerate*; the coefficient c_E is the corresponding *probability amplitude*. If the energy eigenvalue E is α times degenerate, it follows from (3.165) and (3.166) that the probability of obtaining this value is

$$P(E) = \sum_{r=1}^{\alpha} |c_{Er}|^2. \tag{3.168}$$

Equation (3.166) gives the average of the values found in a large number of precise measurements of the total energy, performed on equivalent, independent systems described by the same wave function (3.164). It should be noted that in general $\langle E \rangle$ will not be equal to one of the energy eigenvalues. However, if the system is in a particular stationary state corresponding to a given *non-degenerate* energy eigenvalue $\bar{E}$ then its wave function reduces to

$$\Psi(\mathbf{r}, t) = \psi_{\bar{E}}(\mathbf{r}) \exp(-\mathrm{i}\bar{E}t/\hbar) \tag{3.169}$$

so that $c_{\bar{E}} = 1$ and all the other coefficients vanish. Consequently $\langle E \rangle = \bar{E}$ and, upon measurement of the total energy, we are certain to obtain the value $\bar{E}$. If the energy eigenvalue $\bar{E}$ is α times *degenerate* and the system is in an arbitrary superposition of states corresponding to that energy eigenvalue, then its wave function is given by

$$\Psi(\mathbf{r}, t) = \sum_{r=1}^{\alpha} c_{\bar{E}r} \psi_{\bar{E}r}(\mathbf{r}) \exp(-\mathrm{i}\bar{E}t/\hbar). \tag{3.170}$$

Upon comparison with (3.164) we see that all the coefficients c_{Er} vanish for $E \neq \bar{E}$. Hence, using (3.166) and (3.165) we have $\langle E \rangle = \bar{E}$, and a measurement of the total energy will certainly give the value $\bar{E}$.

Until now we have enclosed the system in a large box of volume V, so that the entire energy spectrum is discrete. If we remove that constraint, the energy spectrum will in general contain a discrete and a continuous part. The general solution of the time-dependent Schrödinger equation for a time-independent potential will then still be given by the expression (3.152) (or more explicitly by (3.164)), provided the summation over the allowed energies E also includes an *integration* over the continuous part of the energy spectrum. In what follows the summation symbol on E will always be understood to have that meaning, when necessary. The normalisation of general wave functions (3.152) (or (3.164)) which contain unbound states will be discussed in Chapter 5.

3.9 The Schrödinger equation in momentum space

In Chapter 2 we defined the momentum space wave function $\Phi(\mathbf{p}, t)$ of a particle as the Fourier transform of its configuration space wave function $\Psi(\mathbf{r}, t)$, and we saw that $\Phi(\mathbf{p}, t)$ plays in momentum space the role assigned to the wave function $\Psi(\mathbf{r}, t)$ in configuration space. In particular, assuming that $\Phi(\mathbf{p}, t)$ is normalised to unity, $\Pi(\mathbf{p}, t)\mathrm{d}\mathbf{p} = |\Phi(\mathbf{p}, t)|^2\mathrm{d}\mathbf{p}$ is the probability of finding at time t the momentum of the particle within the volume element

$\mathrm{d}\mathbf{p} \equiv \mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$ about the point $\mathbf{p}$ in momentum space. In this section we shall further pursue the analogy between the formulations of quantum mechanics in configuration and momentum space.

Since the configuration space wave function $\Psi(\mathbf{r}, t)$ satisfies the time-dependent Schrödinger equation (3.19), we can readily obtain the corresponding time-dependent Schrödinger equation for the momentum space wave function $\Phi(\mathbf{p}, t)$. Remembering that $H = \mathbf{p}^2/2m + V(\mathbf{r}, t)$, we can transform (3.19) in momentum space by writing first

$$\begin{aligned} &\mathrm{i}\hbar\frac{\partial}{\partial t}\left[(2\pi\hbar)^{-3/2}\int \mathrm{e}^{-\mathrm{i}\mathbf{p}.\mathbf{r}/\hbar}\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}\right] \\ &\quad = (2\pi\hbar)^{-3/2}\int \mathrm{e}^{-\mathrm{i}\mathbf{p}.\mathbf{r}/\hbar}\left[\frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, t)\right]\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} \end{aligned} \tag{3.171}$$

which, upon using (2.61), becomes

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Phi(\mathbf{p}, t) = \frac{\mathbf{p}^2}{2m}\Phi(\mathbf{p}, t) + (2\pi\hbar)^{-3/2}\int \mathrm{e}^{-\mathrm{i}\mathbf{p}.\mathbf{r}/\hbar}V(\mathbf{r}, t)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}. \tag{3.172}$$

The second term on the right-hand side can be transformed by using the convolution theorem for Fourier transforms (see equations (A.53)–(A.54) of Appendix A). In this way (3.172) becomes

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Phi(\mathbf{p}, t) = \frac{\mathbf{p}^2}{2m}\Phi(\mathbf{p}, t) + \int \tilde{V}(\mathbf{p} - \mathbf{p}', t)\Phi(\mathbf{p}', t)\mathrm{d}\mathbf{p}' \tag{3.173}$$

where

$$\tilde{V}(\mathbf{p} - \mathbf{p}', t) = (2\pi\hbar)^{-3}\int \mathrm{e}^{-\mathrm{i}(\mathbf{p}-\mathbf{p}').\mathbf{r}/\hbar}V(\mathbf{r}, t)\mathrm{d}\mathbf{r}. \tag{3.174}$$

Equation (3.173) is the time-dependent Schrödinger equation for the momentum space wave function. Because of the integral on the right this equation is generally more complicated than the corresponding time-dependent Schrödinger equation (3.19) in configuration space. This explains why the configuration space Schrödinger equation is used in most applications.

Expectation values

In Section 3.3 we used the momentum space wave function to obtain in a natural way the expectation values of the momentum $\mathbf{p}$ (see (3.45)) and of arbitrary functions $g(\mathbf{p}, t)$ of $\mathbf{p}$ and t (see (3.47)). We shall now generalise these results in order to be able to calculate the expectation values of other dynamical variables in terms of $\Phi(\mathbf{p}, t)$.

Let us consider first the expectation value of x. Starting from (3.42a) and expressing $\Psi(\mathbf{r}, t)$ and $\Psi^*(\mathbf{r}, t)$ in terms of $\Phi(\mathbf{p}, t)$ and $\Phi^*(\mathbf{p}, t)$, we obtain by following an argument similar to that used after (3.50) (Problem 3.13)

$$\langle x\rangle = \int \Phi^*(\mathbf{p}, t)\left(\mathrm{i}\hbar\frac{\partial}{\partial p_x}\right)\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p} \tag{3.175a}$$

where the wave function $\Psi(\mathbf{r}, t)$ – and hence $\Phi(\mathbf{p}, t)$ – is normalised to unity. Similarly, we have

$$\langle y \rangle = \int \Phi^*(\mathbf{p}, t)\left(\mathrm{i}\hbar \frac{\partial}{\partial p_y}\right)\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p} \tag{3.175b}$$

and

$$\langle z \rangle = \int \Phi^*(\mathbf{p}, t)\left(\mathrm{i}\hbar \frac{\partial}{\partial p_z}\right)\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p}. \tag{3.175c}$$

The above equations imply that in momentum space the dynamical variables x, y and z are represented respectively by the differential operators $\mathrm{i}\hbar\partial/\partial p_x$, $\mathrm{i}\hbar\partial/\partial p_y$ and $\mathrm{i}\hbar\partial/\partial p_z$. We remark that since the expectation values $\langle x \rangle$, $\langle y \rangle$ and $\langle z \rangle$ are real these operators acting on $\Phi(\mathbf{p}, t)$ are Hermitian. The three equations (3.175) can be summarised by writing

$$\langle \mathbf{r} \rangle = \int \Phi^*(\mathbf{p}, t)(\mathrm{i}\hbar\nabla_{\mathbf{p}})\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p} \tag{3.176}$$

so that in momentum space the dynamical variable $\mathbf{r}$ is represented by the operator

$$\mathbf{r}_{\mathrm{op}} = \mathrm{i}\hbar\nabla_{\mathbf{p}} \tag{3.177}$$

where the gradient must be taken with respect to $\mathbf{p}$. On the other hand, it is clear from (3.45) that the action of $\mathbf{p}$ on $\Phi(\mathbf{p}, t)$ consists of multiplying the wave function $\Phi(\mathbf{p}, t)$ by $\mathbf{p}$. More generally, we see from (3.47) that the action of a function $g(\mathbf{p}, t)$ on $\Phi(\mathbf{p}, t)$ consists of multiplying $\Phi(\mathbf{p}, t)$ by $g(\mathbf{p}, t)$.

Following a reasoning similar to that used in Section 3.3 we can therefore formulate the following rules for obtaining the expectation value of a dynamical variable in a state specified by the momentum space wave function $\Phi(\mathbf{p}, t)$ normalised to unity.

(1) One associates with the dynamical variable $\mathcal{A} \equiv A(\mathbf{r}, \mathbf{p}, t)$ the linear operator

$$A(\mathrm{i}\hbar\nabla_{\mathbf{p}}, \mathbf{p}, t) \tag{3.178}$$

obtained by performing the substitution $\mathbf{r} \to \mathrm{i}\hbar\nabla_{\mathbf{p}}$ wherever the position vector $\mathbf{r}$ occurs. In addition, we must require that the operator A be Hermitian. A few important Hermitian operators acting in momentum space are listed in Table 3.2, together with the corresponding physical quantities. This Table should be compared with Table 3.1, where this correspondence was given for operators acting in configuration space.

(2) One then calculates the required expectation value from the expression

$$\langle A \rangle = \int \Phi^*(\mathbf{p}, t)A(\mathrm{i}\hbar\nabla_{\mathbf{p}}, \mathbf{p}, t)\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p}. \tag{3.179}$$

If the wave function $\Phi(\mathbf{p}, t)$ is not normalised to unity, the above expression must be replaced by

$$\langle A \rangle = \frac{\int \Phi^*(\mathbf{p}, t)A(\mathrm{i}\hbar\nabla_{\mathbf{p}}, \mathbf{p}, t)\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p}}{\int \Phi^*(\mathbf{p}, t)\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p}}. \tag{3.180}$$

Table 3.2 Physical quantities and corresponding operators acting in momentum space.

Physical quantity	*Operator*
Position coordinate x	$i\hbar \frac{\partial}{\partial p_x}$
Position vector $\mathbf{r}$	$i\hbar \nabla_{\mathbf{p}}$
x-component of momentum p_x	p_x
Momentum $\mathbf{p}$	$\mathbf{p}$
Kinetic energy $T = \frac{\mathbf{p}^2}{2m}$	$\frac{\mathbf{p}^2}{2m}$
Potential energy $V(\mathbf{r}, t)$	$V(i\hbar\nabla_{\mathbf{p}}, t)$
Total energy $\frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, t)$	$H = \frac{\mathbf{p}^2}{2m} + V(i\hbar\nabla_{\mathbf{p}}, t)$

Stationary states

If the potential energy V is time-independent, the time-dependent Schrödinger equation (3.173) admits particular solutions of the separable form

$$\Phi(\mathbf{p}, t) = \phi(\mathbf{p}) \exp(-\mathrm{i}Et/\hbar) \tag{3.181}$$

corresponding to precise values of the total energy E. The probability density in momentum space corresponding to these states is

$$\Pi(\mathbf{p}) = |\phi(\mathbf{p})|^2 = \phi^*(\mathbf{p})\phi(\mathbf{p}) \tag{3.182}$$

and hence is constant in time. The separable solutions (3.181) are clearly the Fourier transforms of the stationary states $\psi(\mathbf{r}) \exp(-\mathrm{i}Et/\hbar)$ given by (3.100), so that the time-independent wave functions $\psi(\mathbf{r})$ and $\phi(\mathbf{p})$ are related by the Fourier transformation

$$\phi(\mathbf{p}) = (2\pi\hbar)^{-3/2} \int \mathrm{e}^{-\mathrm{i}\mathbf{p}.\mathbf{r}/\hbar} \psi(\mathbf{r}) \mathrm{d}\mathbf{r}, \tag{3.183a}$$

$$\psi(\mathbf{r}) = (2\pi\hbar)^{-3/2} \int \mathrm{e}^{\mathrm{i}\mathbf{p}.\mathbf{r}/\hbar} \phi(\mathbf{p}) \mathrm{d}\mathbf{p}. \tag{3.183b}$$

Upon substitution of (3.181) into the Schrödinger equation (3.173), we find that the wave function $\phi(\mathbf{p})$ must satisfy the time-independent Schrödinger eigenvalue equation

$$\frac{\mathbf{p}^2}{2m}\phi(\mathbf{p}) + \int \tilde{V}(\mathbf{p} - \mathbf{p}')\phi(\mathbf{p}')\mathrm{d}\mathbf{p}' = E\phi(\mathbf{p}) \tag{3.184}$$

where

$$\tilde{V}(\mathbf{p} - \mathbf{p}') = (2\pi\hbar)^{-3} \int \mathrm{e}^{-\mathrm{i}(\mathbf{p}-\mathbf{p}').\mathbf{r}/\hbar} V(\mathbf{r}) \mathrm{d}\mathbf{r}. \tag{3.185}$$

The equation (3.184) is an integral equation, and hence is generally more difficult to solve than the corresponding time-independent Schrödinger equation (3.98) in configuration space.

Problems **3.1** In obtaining equations (3.33) and (3.39) we have assumed that the potential $V(\mathbf{r}, t)$ is a real quantity.

(a) Prove that if $V(\mathbf{r}, t)$ is complex the continuity equation (3.39) becomes

$$\frac{\partial}{\partial t}P(\mathbf{r}, t) + \boldsymbol{\nabla}.\mathbf{j}(\mathbf{r}, t) = \frac{2}{\hbar}[\mathrm{Im}\, V(\mathbf{r}, t)]P(\mathbf{r}, t)$$

so that the addition of an imaginary part of the potential describes the presence of sources if $\mathrm{Im}\, V > 0$ or sinks (absorbers) if $\mathrm{Im}\, V < 0$. Show that if the wave function $\Psi(\mathbf{r}, t)$ is square integrable

$$\frac{\partial}{\partial t}\int P(\mathbf{r}, t)\mathrm{d}\mathbf{r} = \frac{2}{\hbar}\int [\mathrm{Im}\, V(\mathbf{r}, t)]P(\mathbf{r}, t)\mathrm{d}\mathbf{r}.$$

(b) Assuming that $\mathrm{Im}\, V$ is time-independent and that $\Psi(\mathbf{r}, t)$ is normalised to unity at $t = 0$, prove that if $P(\mathbf{r}, t)$ is expanded about $t = 0$ as

$$P(\mathbf{r}, t) = P_0(\mathbf{r}) + P_1(\mathbf{r})\, t + \cdots$$

then

$$\int P(\mathbf{r}, t)\mathrm{d}\mathbf{r} = 1 + Ct + \cdots$$

Find an expression for C in terms of $P_0(\mathbf{r})$ and $\mathrm{Im}\, V(\mathbf{r})$, and verify that if $\mathrm{Im}\, V(\mathbf{r}) < 0$ the quantity $\int P(\mathbf{r}, t)\mathrm{d}\mathbf{r}$ decreases with increasing time, so that absorption occurs.

3.2 Prove that the operator $p_x = -\mathrm{i}\hbar\partial/\partial x$ is Hermitian.
(*Hint*: consider the expectation value

$$\langle p_x \rangle = \int \Psi^*(\mathbf{r}, t)\left[-\mathrm{i}\hbar\frac{\partial}{\partial x}\right]\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r}$$

and integrate by parts.)

3.3 Starting from the expression

$$\langle p_x^n \rangle = \int \Phi^*(\mathbf{p}, t)p_x^n\Phi(\mathbf{p}, t)\mathrm{d}\mathbf{p}$$

where n is a positive integer, prove equation (3.58).

3.4 Prove equation (3.73).

3.5 Show that the operator $x^k p_x^l$ is not Hermitian (where k and l are positive integers), but that the combination $(x^k p_x^l + p_x^l x^k)/2$ is Hermitian.

3.6 Show that, for a general one-dimensional free-particle wave packet

$$\Psi(x,t) = (2\pi\hbar)^{-1/2}\int_{-\infty}^{+\infty} \exp[\mathrm{i}(p_x x - p_x^2 t/2m)/\hbar]\phi(p_x)\mathrm{d}p_x$$

(a) the expectation value $\langle p_x \rangle$ of the momentum does not change with time, and
(b) the expectation value $\langle x \rangle$ of the position coordinate satisfies the equation

$$\langle x \rangle = \langle x \rangle_{t=t_0} + \frac{\langle p_x \rangle}{m}(t - t_0)$$

in agreement with the correspondence principle.

(*Hints*: Part (a) may be proved by obtaining the result

$$\langle p_x \rangle = \int_{-\infty}^{+\infty} \phi^*(p_x) p_x \phi(p_x)\mathrm{d}p_x.$$

For part (b), use the fact that

$$\frac{\partial}{\partial p_x}\exp[\mathrm{i}(p_x x - p_x^2 t/2m)/\hbar] = \frac{\mathrm{i}}{\hbar}(x - p_x t/m)\exp[\mathrm{i}(p_x x - p_x^2 t/2m)/\hbar]$$

to show that

$$\langle x \rangle = \int_{-\infty}^{+\infty} \phi^*(p_x)\left[\mathrm{i}\hbar\frac{\partial}{\partial p_x} + \frac{p_x}{m}t\right]\phi(p_x)\mathrm{d}p_x.)$$

3.7 Show that if $\Psi(\mathbf{r}, t)$ is a square integrable wave function normalised to unity, then

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2 \rangle = \frac{1}{m}[\langle x p_x \rangle + \langle p_x x \rangle]$$

where the expectation values are defined according to (3.67).

3.8 Prove that if a constant V_0 is added to the potential energy $V(\mathbf{r})$

(a) the energy eigenvalues of the time-independent Schrödinger equation (3.98) are shifted from E to $E + V_0$; and
(b) the corresponding eigenfunctions $\psi(\mathbf{r})$ remain unchanged.

3.9 Consider a one-dimensional system with bound-state energies placed in order of increasing magnitude ($E_1 < E_2 < E_3 < \cdots$) and let $\psi_1(x)$, $\psi_2(x)$, $\psi_3(x), \ldots,$ be the corresponding energy eigenfunctions. Prove that between two consecutive zeros of $\psi_n(x)$, the eigenfunction $\psi_{n+1}(x)$ must possess at least one zero. Note that the bound states of one-dimensional systems are non-degenerate, and that the energy eigenfunctions $\psi_n(x)$ can be taken to be real.

(*Hint*: From the Wronskian theorem (p. 110) and the Schrödinger eigenvalue equations satisfied by ψ_n and ψ_{n+1}, obtain first the relationship

$$[\psi_n'\psi_{n+1} - \psi_{n+1}'\psi_n]_a^b = \frac{2m}{\hbar^2}(E_{n+1} - E_n)\int_a^b \psi_n\psi_{n+1}\mathrm{d}x.$$

Then complete the proof by taking a and b to be two consecutive zeros of ψ_n.)

3.10 Let $H = \mathbf{p}^2/2m + V(\mathbf{r})$ be a time-independent Hamiltonian. Prove that the propagator $K(\mathbf{r}, t; \mathbf{r}', t_0)$ defined by (3.156) satisfies the time-dependent Schrödinger equation

$$\left[\mathrm{i}\hbar\frac{\partial}{\partial t} - H\right]K(\mathbf{r}, t; \mathbf{r}', t_0) = 0$$

subject to the condition

$$K(\mathbf{r}, t_0, \mathbf{r}', t_0) = \delta(\mathbf{r} - \mathbf{r}').$$

3.11 Show that the general one-dimensional free-particle wave packet $\Psi(x, t)$ of Problem 3.6 can be expressed in terms of its initial value $\Psi(x, t_0)$ as

$$\Psi(x, t) = \int_{-\infty}^{+\infty} K(x, t; x', t_0)\Psi(x', t_0)\mathrm{d}x'$$

where the propagator $K(x, t; x', t_0)$ is given by

$$K(x, t; x', t_0) = \left[\frac{m}{2\pi\mathrm{i}\hbar(t - t_0)}\right]^{1/2}\exp\left[\frac{\mathrm{i}m(x - x')^2}{2\hbar(t - t_0)}\right]$$

(*Hint*: Use the result (2.48), which also holds if α is purely imaginary, provided it is regarded as a limit. That is, if $\alpha = a + \mathrm{i}b$, $a > 0$, it is the limit in which $a \to 0$.)

3.12 Let E_n denote the bound-state energy eigenvalues of a one-dimensional system and let $\psi_n(x)$ denote the corresponding energy eigenfunctions. Let $\Psi(x, t)$ be the wave function of the system, normalised to unity, and suppose that at $t = 0$ it is given by

$$\Psi(x, t = 0) = \frac{1}{\sqrt{2}}\mathrm{e}^{\mathrm{i}\alpha_1}\psi_1(x) + \frac{1}{\sqrt{3}}\mathrm{e}^{\mathrm{i}\alpha_2}\psi_2(x) + \frac{1}{\sqrt{6}}\mathrm{e}^{\mathrm{i}\alpha_3}\psi_3(x)$$

where the α_i are real constants.

(a) Write down the wave function $\Psi(x, t)$ at time t.

(b) Find the probability that at time t a measurement of the energy of the system gives the value E_2.

(c) Does $\langle x\rangle$ vary with time? Does $\langle p_x\rangle$ vary with time? Does $E = \langle H\rangle$ vary with time?

3.13 Prove equations (3.175).

3.14 Prove that the time-dependent Schrödinger equation (3.173) for the momentum space wave function can be written in the form

$$i\hbar\frac{\partial}{\partial t}\Phi(\mathbf{p},t) = \frac{\mathbf{p}^2}{2m}\Phi(\mathbf{p},t) + V(i\hbar\nabla_{\mathbf{p}},t)\Phi(\mathbf{p},t)$$

provided $V(\mathbf{r},t)$ is an analytic function of x, y, z.

(*Hint*: Show first that

$$V(\mathbf{r},t) = \exp\left(\frac{i}{\hbar}\mathbf{p}.\mathbf{r}\right)V(i\hbar\nabla_{\mathbf{p}},t)\exp\left(-\frac{i}{\hbar}\mathbf{p}.\mathbf{r}\right).)$$

4 One-dimensional examples

In this chapter we shall study a few simple one-dimensional quantum mechanical problems in order to acquire some practice in dealing with the Schrödinger equation, and to analyse various interesting phenomena predicted by the quantum theory. One-dimensional problems are of interest not only because several physical situations are effectively one-dimensional, but also because a number of more complicated problems can be reduced to the solution of equations similar to the one-dimensional Schrödinger equation, as we shall see later in this book.

4.1 General formulae

We consider a particle of mass m moving on the x-axis in a time-independent potential $V(x)$. The time-dependent Schrödinger equation corresponding to this one-dimensional motion is

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(x,t) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x,t). \tag{4.1}$$

As we have shown in Chapter 3, the fact that the potential is time-independent implies that we can look for stationary-state solutions of (4.1) having the form

$$\Psi(x,t) = \psi(x)\exp(-\mathrm{i}Et/\hbar) \tag{4.2}$$

where E is the energy of the stationary state. The general solution of (4.1) is an arbitrary superposition of stationary states (4.2). The time-independent wave function

$\psi(x)$ is a solution of the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x) \tag{4.3}$$

which, in the present one-dimensional case, is just an ordinary differential equation. It is this equation which we shall solve below for several particular forms of the potential $V(x)$.

We also recall that the position probability density associated with a wave function $\Psi(x,t)$ is given by

$$P(x,t) = |\Psi(x,t)|^2 \tag{4.4}$$

and that the corresponding probability current density (or probability flux) is

$$j(x,t) = \frac{\hbar}{2\mathrm{i}m}\left[\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x} - \Psi(x,t)\frac{\partial\Psi^*(x,t)}{\partial x}\right]. \tag{4.5}$$

For stationary states (4.2) both P and j are, of course, time-independent. In particular, since $|\Psi(x,t)|^2 = |\psi(x)|^2$, the position probability density is given by

$$P(x) = |\psi(x)|^2. \tag{4.6}$$

Moreover, for one-dimensional stationary states (4.2) the equation (3.39) expressing probability conservation reduces to $\mathrm{d}j/\mathrm{d}x = 0$, so that the probability current density

$$j = \frac{\hbar}{2\mathrm{i}m}\left[\psi^*(x)\frac{\mathrm{d}\psi(x)}{\mathrm{d}x} - \psi(x)\frac{\mathrm{d}\psi^*(x)}{\mathrm{d}x}\right] \tag{4.7}$$

is also independent of x.

4.2 The free particle

Let us start by considering the simplest case, namely that of a potential which is constant: $V(x) = V_0$. The force acting on the particle, $F(x) = -\mathrm{d}V/\mathrm{d}x$, then vanishes so that the particle is free. Without loss of generality we can take the constant V_0 to be zero, since the addition of a constant amount to the potential energy merely shifts the energy eigenvalues of the Schrödinger equation (4.3) by that amount and leaves the eigenfunctions $\psi(x)$ unchanged (see Problem 3.8).

We must therefore solve the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = E\psi(x). \tag{4.8}$$

Writing

$$k = \left(\frac{2m}{\hbar^2}E\right)^{1/2} \tag{4.9}$$

we see that two linearly independent solutions of (4.8) are $\exp(\mathrm{i}kx)$ and $\exp(-\mathrm{i}kx)$ or, equivalently, the pair of real solutions $\sin kx$ and $\cos kx$. The general solution of (4.8) is therefore the linear combination

$$\psi(x) = A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx} \tag{4.10}$$

where A and B are arbitrary constants. It is clear that for a solution to be physically acceptable the quantity k cannot have an imaginary part, because if it did $\psi(x)$ would increase exponentially at one of the limits $x = -\infty$ or $x = +\infty$, and possibly at both limits. Since $E = \hbar^2k^2/2m$, we must therefore have $E \geqslant 0$, which confirms the statement made in Section 3.6 that the energy cannot remain lower than the potential (here $V = 0$) over the entire interval $(-\infty, +\infty)$. Because any non-negative value of E is allowed, the energy spectrum is *continuous*, extending from $E = 0$ to $E = +\infty$. This, of course, is not surprising, since E is the kinetic energy of the free particle. Note that each positive energy eigenvalue is *doubly degenerate* because there are two linearly independent eigenfunctions, $\exp(\mathrm{i}kx)$ and $\exp(-\mathrm{i}kx)$, corresponding to the same positive energy $E = \hbar^2k^2/2m$. We also remark that the basic solutions of (4.8) may be written in the form

$$\psi_{k_x}(x) = C\exp(\mathrm{i}k_x x) \tag{4.11a}$$

or

$$\psi_{p_x}(x) = C\exp(\mathrm{i}p_x x/\hbar) \tag{4.11b}$$

where C is a constant, $k_x = \pm k$ and $p_x = \hbar k_x$ is the momentum of the particle, of magnitude $p = |p_x| = \hbar k$.

Momentum eigenfunctions

The functions (4.11) are not only eigenfunctions of the free-particle Hamiltonian $p_{\text{op}}^2/2m = -(\hbar^2/2m)\partial^2/\partial x^2$ corresponding to the energy $E = p^2/2m = \hbar^2k^2/2m$, they are also *momentum eigenfunctions*, that is eigenfunctions of the momentum operator $p_{\text{op}} = -\mathrm{i}\hbar\partial/\partial x$. Indeed, the eigenvalue equation for the momentum operator reads

$$-\mathrm{i}\hbar\frac{\partial}{\partial x}\psi_{p_x}(x) = p_x\psi_{p_x}(x) \tag{4.12}$$

and we see immediately that the functions (4.11) are solutions of this equation. The eigenvalues $p_x = \hbar k_x$ must be real, so that the eigenfunctions (4.11) remain finite as x tends to $+\infty$ or $-\infty$. Since this is the only constraint on p_x, the spectrum of the operator p_{op} is *continuous*, extending from $-\infty$ to $+\infty$. Note that the two functions $\exp(\mathrm{i}kx)$ and $\exp(-\mathrm{i}kx)$, which are eigenfunctions of the free-particle Hamiltonian corresponding to the same energy $E = \hbar^2k^2/2m$, are eigenfunctions of the momentum operator p_{op} corresponding to the two different eigenvalues $p_x = \hbar k$ and $p_x = -\hbar k$, respectively. Finally, we remark that according to the Fourier analysis of Section 2.4, any physically admissible wave function $\Psi(x, t)$ can be expressed as a superposition of the momentum eigenfunctions (4.11).

Physical interpretation of the free-particle solutions

Let us now return to the general solution (4.10) of the free-particle Schrödinger equation (4.8). Substituting (4.10) into (4.2), we find that a stationary state of energy $E > 0$ for a free particle has the general form

$$\begin{aligned}\Psi(x, t) &= (A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx})\mathrm{e}^{-\mathrm{i}Et/\hbar} \\ &= A\mathrm{e}^{\mathrm{i}(kx-\omega t)} + B\mathrm{e}^{-\mathrm{i}(kx+\omega t)}\end{aligned} \qquad \textbf{(4.13)}$$

where $\omega = E/\hbar$ is the angular frequency.

In order to interpret the wave function (4.13) physically, let us consider some particular cases. If we set $B = 0$ in (4.13), the resulting wave function is the *plane wave*

$$\Psi(x, t) = A\mathrm{e}^{\mathrm{i}(kx-\omega t)} \qquad \textbf{(4.14)}$$

which, as we have seen in Chapter 2, is associated with a free particle of mass m moving along the x-axis in the positive direction with a definite momentum of magnitude $p = \hbar k$ (so that $p_x = \hbar k$) and a corresponding energy $E = p^2/2m = \hbar^2k^2/2m$. This plane wave has an angular frequency $\omega = E/\hbar = \hbar k^2/2m$ and a wave number $k = p/\hbar = 2\pi/\lambda$, where λ is the de Broglie wavelength of the particle. It represents a vibration *travelling* in the positive x-direction with a phase velocity $v_{\mathrm{ph}} = \omega/k = \hbar k/2m$. We recall that the particle velocity $v = p/m = \hbar k/m$ is *not* equal to the phase velocity v_{ph}, but is equal to the group velocity $v_{\mathrm{g}} = \mathrm{d}\omega/\mathrm{d}k$ of the wave packet formed by superposing plane waves of different wave numbers.

The position probability density corresponding to the plane wave (4.14) is

$$P = |\Psi(x, t)|^2 = |A|^2. \qquad \textbf{(4.15)}$$

It is not only independent of time (as for any stationary state), but is also independent of the variable x, so that the position of the particle on the x-axis is completely unknown. This is in accordance with the Heisenberg uncertainty relation (2.70) which implies that a particle moving along the x-axis with a perfectly well-defined momentum ($\Delta p_x = 0$) cannot be localised at all along this axis ($\Delta x = \infty$). We may thus think of the plane wave (4.14) as representing the idealised situation of a particle of perfectly known momentum, moving somewhere in a beam of infinite length.

Using (4.7) with $\psi(x) = A\exp(\mathrm{i}kx)$, we find that the probability current density corresponding to the plane wave (4.14) is given by

$$\begin{aligned}j &= \frac{\hbar}{2\mathrm{i}m}(A^*\mathrm{e}^{-\mathrm{i}kx}A\mathrm{i}k\mathrm{e}^{\mathrm{i}kx} - A\mathrm{e}^{\mathrm{i}kx}A^*(-\mathrm{i}k)\mathrm{e}^{-\mathrm{i}kx}) \\ &= \frac{\hbar k}{m}|A|^2 = \frac{p}{m}|A|^2 = v|A|^2\end{aligned} \qquad \textbf{(4.16)}$$

and is independent of x and t, in agreement with the general result obtained at the end of Section 4.1 for one-dimensional stationary states. It is also interesting to note that by using (4.15) we can rewrite (4.16) in the form $j = vP$. This relation is the same as the familiar one between flux, velocity and density in classical hydrodynamics. In particular, if the position probability density P is equal to unity (i.e. to one particle per unit length), the probability per unit time that the particle will cross the point x in the direction of increasing x is equal to its velocity v, as we expect.

Another particular case of (4.13) is obtained by setting $A = 0$. This gives the plane wave

$$\Psi(x, t) = B\mathrm{e}^{-\mathrm{i}(kx+\omega t)}. \tag{4.17}$$

The corresponding position probability density is

$$P = |\Psi(x, t)|^2 = |B|^2 \tag{4.18}$$

and the probability current density, obtained from (4.7) with $\psi(x) = B\exp(-\mathrm{i}kx)$, is

$$j = -\frac{\hbar k}{m}|B|^2 = -\frac{p}{m}|B|^2 = -v|B|^2. \tag{4.19}$$

Thus the plane wave (4.17) corresponds to a vibration of wave number $k = p/\hbar$ and angular frequency $\omega = E/\hbar = \hbar k^2/2m$ travelling in the *negative* x-direction with a phase velocity $v_{\mathrm{ph}} = \omega/k = \hbar k/2m$. It is associated with a free particle moving along the x-axis in the negative direction with a well-defined momentum of magnitude $p = mv = \hbar k$ (so that $p_x = -\hbar k$) and a given energy $E = p^2/2m = \hbar^2k^2/2m$, but whose position on the x-axis is completely unknown.

Two other interesting particular cases of (4.13) are obtained by choosing $A = B$ or $A = -B$. If we first set $A = B$, so that we add two plane waves travelling in opposite directions with equal amplitudes, the wave function (4.13) becomes

$$\begin{aligned}\Psi(x, t) &= A(\mathrm{e}^{\mathrm{i}kx} + \mathrm{e}^{-\mathrm{i}kx})\mathrm{e}^{-\mathrm{i}\omega t}\\ &= C\cos kx\,\mathrm{e}^{-\mathrm{i}\omega t}\end{aligned} \tag{4.20}$$

where $C = 2A$. In contrast to the travelling waves (4.14) and (4.17), this is a *standing wave* whose nodes are fixed in space at values

$$x_n = \pm\left(\frac{\pi}{2} + n\pi\right)\Big/ k, \qquad n = 0, 1, 2, \ldots \tag{4.21}$$

for which $\cos kx$ vanishes. The position probability density associated with the wave function (4.20) is

$$P(x) = |C|^2\cos^2 kx \tag{4.22}$$

and from (4.7), with $\psi(x) = C\cos kx$, the corresponding probability flux is given by

$$\begin{aligned}j &= \frac{\hbar}{2\mathrm{i}m}(-C^*\cos kxCk\sin kx + C\cos kxC^*k\sin kx)\\ &= 0.\end{aligned} \tag{4.23}$$

More generally, the probability flux (4.7) is seen to vanish for any function $\psi(x)$ which is real, apart from a multiplicative constant. In the present case, the result (4.23) is readily understood, since the probability flux $v|A|^2$ associated with the plane wave $A\exp[\mathrm{i}(kx - \omega t)]$ is cancelled by the probability flux $-v|A|^2$ corresponding to the plane wave $A\exp[-\mathrm{i}(kx + \omega t)]$; the net probability per unit time that the particle will cross a point x is thus equal to zero. We can therefore associate the standing wave (4.20) with a free particle moving along the x-axis with a momentum whose magnitude $p = \hbar k$ is known precisely, but whose direction is unknown.

It is also worth noting that the position probability density (4.22) vanishes at the points x_n given by (4.21), so that a free particle in the state described by the wave function (4.20) can never be found at these points. This is clearly an interference effect between the two travelling plane waves from which the standing wave (4.20) was constructed; it is entirely due to the wave properties associated with the particle.

If we set $A = -B$ in (4.13), we obtain another standing wave, namely

$$\begin{aligned}\Psi(x,t) &= A(\mathrm{e}^{\mathrm{i}kx} - \mathrm{e}^{-\mathrm{i}kx})\mathrm{e}^{-\mathrm{i}\omega t}\\ &= D\sin kx\,\mathrm{e}^{-\mathrm{i}\omega t}, \qquad D = 2\mathrm{i}A\end{aligned} \tag{4.24}$$

with properties similar to those discussed above for the standing wave (4.20). In particular, the probability flux associated with the wave function (4.24) is equal to zero, and its position probability density

$$P(x) = |D|^2\sin^2 kx \tag{4.25}$$

vanishes at the values $x_n = \pm n\pi/k (n = 0, 1, 2, \dots)$ for which $\sin kx = 0$.

Let us now return to the general free-particle stationary state (4.13), which is the superposition of two plane waves travelling in opposite directions along the x-axis, both with phase velocity $v_{\text{ph}} = \omega/k = \hbar k/2m$ and with amplitudes A and B, respectively. The position probability density corresponding to the wave function (4.13) is readily obtained by substituting (4.10) into (4.6); it is given by

$$P(x) = |A|^2 + |B|^2 + (AB^*\mathrm{e}^{2\mathrm{i}kx} + A^*B\mathrm{e}^{-2\mathrm{i}kx}) \tag{4.26}$$

and exhibits interference effects of the two plane waves. Using (4.7) and (4.10) we also find that the probability current density associated with the wave function (4.13) is given by

$$j = v[|A|^2 - |B|^2] \tag{4.27}$$

which, as we expect, is just the sum of the probability current densities (4.16) and (4.19).

'Normalisation' of the free-particle wave function

Since the integral

$$I = \int_{-\infty}^{+\infty} |A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}|^2\mathrm{d}x \tag{4.28}$$

is infinite for all values of A and B (except, of course $A = B = 0$) the free-particle wave functions (4.10) and momentum eigenfunctions cannot be made to satisfy the normalisation condition

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 \mathrm{d}x = 1. \tag{4.29}$$

As we pointed out in Chapter 2, for wave functions of this kind which are not square integrable we can only speak of *relative probabilities*. This will be sufficient for treating applications in this chapter involving such eigenfunctions, corresponding to continuous eigenvalues, which remain finite at great distances. Nevertheless, it is often desirable to be able to treat these eigenfunctions on the same footing as the square integrable eigenfunctions corresponding to discrete eigenvalues. There are several ways of doing this. For example, we may recognise that the momentum of a particle is never known exactly, and work with wave packets. However, this approach is cumbersome, and would prevent us from using simple and convenient wave functions such as the plane wave $\exp(ikx)$, which is the idealisation of a very broad, square integrable wave packet.

An alternative way is to 'normalise' such wave functions in a sense different from that of (4.29). In particular, we may enclose the particle in a box (in the present case a 'one-dimensional' box of length L) at the walls of which the wave function of the particle must obey boundary conditions. In order to illustrate this *box normalisation* procedure, let us consider the momentum eigenfunctions (i.e. the plane waves) given by (4.11a). In this case, it is convenient to require that these wave functions satisfy *periodic boundary conditions* at the walls, so that $\psi_{k_x}(x + L) = \psi_{k_x}(x)$. Because of this periodicity condition, k_x is no longer an arbitrary real quantity; it is restricted to the values

$$k_x = \frac{2\pi}{L} n, \qquad n = 0, \pm 1, \pm 2, \ldots . \tag{4.30}$$

As a result, the spectrum of energy eigenvalues of the Schrödinger equation (4.8) becomes discrete:

$$E_n = \frac{\hbar^2 k_x^2}{2m} = \frac{2\pi^2 \hbar^2}{mL^2} n^2 \tag{4.31}$$

each eigenvalue (except $E = 0$) being doubly degenerate. Note that as L increases, the spacing of the successive energy levels decreases, so that for a macroscopic 'box' the spectrum is essentially continuous. The momentum eigenfunctions (4.11a) can now be normalised by requiring that, in the basic 'box' $(0, L)$ or $(-L/2, +L/2)$ of side L,

$$\int_{-L/2}^{+L/2} |\psi_{k_x}(x)|^2 \mathrm{d}x = 1 \tag{4.32}$$

so that $|C|^2 = L^{-1}$. Choosing the arbitrary phase of the normalisation constant C to be zero, we have $C = L^{-1/2}$, and the normalised momentum eigenfunctions (4.11a) are given by

$$\psi_{k_x}(x) = L^{-1/2}\exp(\mathrm{i}k_x x). \tag{4.33}$$

We note that these eigenfunctions are *orthonormal* since

$$\begin{aligned}\int_{-L/2}^{+L/2} \psi^*_{k'_x}(x)\psi_{k_x}(x)\mathrm{d}x &= L^{-1}\int_{-L/2}^{+L/2} \exp[\mathrm{i}(k_x - k'_x)x]\mathrm{d}x \\ &= \delta_{k_x k'_x}\end{aligned} \tag{4.34}$$

where we have used the periodicity condition expressed by (4.30). We also remark that the momentum eigenfunctions (4.11) cannot be normalised by choosing a box with impenetrable (rigid) walls, since these eigenfunctions never vanish anywhere, and therefore cannot exist within such a box.

Instead of imposing a box normalisation with periodic boundary conditions, we can also use the Dirac delta function (discussed in Appendix A) to set up a *delta-function normalisation* similar to that given by (4.34), but which allows the momentum eigenfunctions (4.11a) to retain their form over the entire x-axis, for all real values of k_x. Indeed, using equation (A.18) of Appendix A, we have

$$\int_{-\infty}^{+\infty} \exp[\mathrm{i}(k_x - k'_x)x]\mathrm{d}x = 2\pi\delta(k_x - k'_x). \tag{4.35}$$

Taking the arbitrary phase of the normalisation constant C in (4.11a) to be zero, we see that if we choose $C = (2\pi)^{-1/2}$, the momentum eigenfunctions

$$\psi_{k_x}(x) = (2\pi)^{-1/2}\exp(\mathrm{i}k_x x) \tag{4.36}$$

satisfy the orthonormality relation

$$\int_{-\infty}^{+\infty} \psi^*_{k'_x}(x)\psi_{k_x}(x)\mathrm{d}x = \delta(k_x - k'_x). \tag{4.37}$$

We also see with the help of (A.18) that the wave functions (4.36) satisfy the *closure relation*

$$\int_{-\infty}^{+\infty} \psi^*_{k_x}(x')\psi_{k_x}(x)\mathrm{d}k_x = \delta(x - x'). \tag{4.38}$$

A similar relation can also be established in the limit of large L for the momentum eigenfunctions (4.33) satisfying the box normalisation with periodic boundary conditions (Problem 4.1).

The normalisation condition expressed by (4.37) is often referred to as *k-normalisation.* Other delta-function normalisations for wave functions belonging to the continuous spectrum may be used. For example, the momentum eigenfunctions

$$\psi_{p_x}(x) = (2\pi\hbar)^{-1/2}\exp(\mathrm{i}p_x x/\hbar) \tag{4.39}$$

are such that

$$\int_{-\infty}^{+\infty} \psi^*_{p'_x}(x)\psi_{p_x}(x)\mathrm{d}x = \delta(p_x - p'_x) \tag{4.40}$$

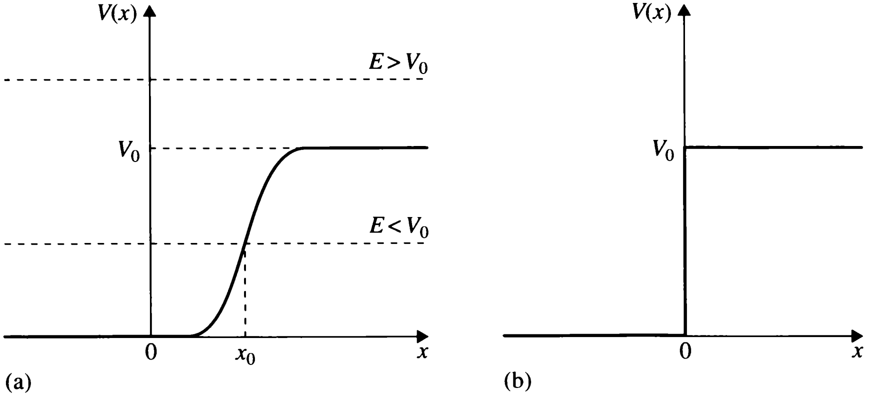


Figure 4.1 (a) A smoothly varying, infinitely wide potential barrier $V(x)$, tending to zero as one goes to the left, and to the constant value $V_0 > 0$ as one goes to the right. Two values of the total energy of the particle are indicated by dashed lines, corresponding to the cases $E < V_0$ and $E > V_0$. When $E < V_0$ there is a classical turning point at $x = x_0$, where $E = V(x_0)$.
(b) The step potential (4.41).

and this normalisation is called *p-normalisation*. Another frequently used normalisation, called the energy normalisation, is the subject of Problem 4.2.

4.3 The potential step

Our next example is that of a particle moving in a potential $V(x)$ which has the form of an infinitely wide potential barrier (see Fig. 4.1(a)). As we go to the left, the potential tends to the constant value zero, while as we go to the right it tends to the constant value $V_0 > 0$. We have also indicated in Fig. 4.1(a) two values of the total energy E of the particle. According to classical mechanics a particle incident from the left with an energy $E < V_0$ would always be *reflected* at the *turning point* x_0, where its kinetic energy vanishes. The region to the right of x_0 is therefore classically forbidden for the particle. On the other hand, following classical mechanics, a particle incident from the left with an energy $E > V_0$ would never be reflected, but would always be *transmitted.*

Let us now study this problem by using quantum mechanics. Since the potential is time-independent the motion of a particle of energy E is described by the wave function $\Psi(x,t) = \psi(x)\exp(-\mathrm{i}Et/\hbar)$, where $\psi(x)$ is a solution of the time-independent Schrödinger equation (4.3). To simplify our task we shall replace the smoothly varying potential of Fig. 4.1(a) by the *step potential* shown in Fig. 4.1(b). Note that we have chosen the turning point x_0 to be at the origin, so that

$$V(x) = \begin{cases} 0, & x < 0 \\ V_0, & x > 0. \end{cases} \tag{4.41}$$

It is clear that this potential step is an idealisation of potentials of the form shown in Fig. 4.1(a). It is the simplest example of a *piecewise constant* potential which is pieced together from constant portions in adjacent ranges of the x-axis. Other examples of piecewise constant potentials will be considered later in this chapter.

Before solving the time-independent Schrödinger equation (4.3) for the potential step (4.41), we recall from our discussion of Section 3.6 that the total energy E can never be lower than the absolute minimum of the potential. Thus for the potential step (4.41) there is no acceptable solution of the Schrödinger equation (4.3) when $E < 0$. In what follows we shall study successively the two cases $0 < E < V_0$, and $E > V_0$.

Case 1: $0 < E < V_0$

Since the step potential (4.41) is such that $V(x) = 0$ for $x < 0$ and $V(x) = V_0 > E$ for $x > 0$, the Schrödinger equation (4.3) becomes, in this case,

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + k^2\psi(x) = 0, \qquad k = \left(\frac{2m}{\hbar^2}E\right)^{1/2}, \qquad x < 0 \tag{4.42a}$$

and

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} - \kappa^2\psi(x) = 0, \qquad \kappa = \left[\frac{2m}{\hbar^2}(V_0 - E)\right]^{1/2}, \qquad x > 0. \tag{4.42b}$$

Equation (4.42a), valid for $x < 0$, describes the motion of a free particle of wave number k. Its general solution is

$$\psi(x) = A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}, \qquad x < 0 \tag{4.43a}$$

where A and B are arbitrary constants. The second equation (4.42b), valid for $x > 0$, has the general solution

$$\psi(x) = C\mathrm{e}^{\kappa x} + D\mathrm{e}^{-\kappa x}, \qquad x > 0 \tag{4.43b}$$

where C and D are arbitrary constants.

It follows from the discussion of Section 3.6 that in order to be an acceptable solution of the Schrödinger equation (4.3) the eigenfunction $\psi(x)$ and its first derivative $\mathrm{d}\psi(x)/\mathrm{d}x$ must be *finite* and *continuous* for all values of x. Now, if $C \neq 0$ it is clear that the eigenfunction $\psi(x)$ given by (4.43b) for $x > 0$ will not remain finite in the limit $x \to +\infty$, since $\exp(\kappa x)$ diverges in that limit. To prevent this unacceptable behaviour, we must choose the constant $C = 0$, so that for $x > 0$ the eigenfunction $\psi(x)$ is given by $\psi(x) = D\exp(-\kappa x)$. Thus we have

$$\psi(x) = \begin{cases} A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}, & x < 0 \qquad \text{(4.44a)} \\ D\mathrm{e}^{-\kappa x}, & x > 0 \qquad \text{(4.44b)} \end{cases}$$

and we note that, since one of the two linearly independent solutions for $x > 0$ has been excluded, the energy eigenvalues for $0 < E < V_0$ are non-degenerate.

Next, let us consider the point of discontinuity of the potential at $x = 0$. We recall from our discussion of Section 3.1 that the existence of discontinuities of the first kind (i.e. finite jumps) in the potential does not modify the conditions of continuity imposed on the function $\psi(x)$ and on its first derivative $\mathrm{d}\psi(x)/\mathrm{d}x$. Indeed, at a finite discontinuity of the potential it follows from the Schrödinger equation (4.3) that the *second* derivative $\mathrm{d}^2\psi(x)/\mathrm{d}x^2$ will exhibit a finite jump, but the integral of $\mathrm{d}^2\psi(x)/\mathrm{d}x^2$ remains continuous, so that $\mathrm{d}\psi(x)/\mathrm{d}x$, and hence $\psi(x)$, are continuous everywhere. This means that at $x = 0$ the solutions (4.44a) and (4.44b) must join 'smoothly' in such a way that $\psi(x)$ and $\mathrm{d}\psi(x)/\mathrm{d}x$ are continuous. The condition that $\psi(x)$ be continuous at $x = 0$ gives the relation

$$A + B = D \tag{4.45a}$$

while the requirement that $\mathrm{d}\psi(x)/\mathrm{d}x$ be continuous at $x = 0$ yields

$$\mathrm{i}k(A - B) = -\kappa D. \tag{4.45b}$$

From equations (4.45) we deduce that

$$A = \frac{1 + \mathrm{i}\kappa/k}{2} D, \qquad B = \frac{1 - \mathrm{i}\kappa/k}{2} D \tag{4.46}$$

so that the solution $\psi(x)$ of the Schrödinger equation (4.42) is given by equations (4.44), with A and B obtained in terms of D from (4.46). Note that since the oscillatory part (4.44a) of $\psi(x)$ can be joined smoothly to its exponential part (4.44b) for all values of E between 0 and V_0, the spectrum is *continuous*. The remaining constant D can be determined by 'normalising' the eigenfunction $\psi(x)$, but this will not be required in what follows. We also remark that since the quantity

$$\frac{B}{A} = \frac{1 - \mathrm{i}\kappa/k}{1 + \mathrm{i}\kappa/k} = \frac{1 - \mathrm{i}(V_0/E - 1)^{1/2}}{1 + \mathrm{i}(V_0/E - 1)^{1/2}} \tag{4.47}$$

is of modulus one it may be written in the form

$$\frac{B}{A} = \mathrm{e}^{\mathrm{i}\alpha}, \qquad \alpha = 2\tan^{-1}\left[-\left(\frac{V_0}{E} - 1\right)^{1/2}\right] \tag{4.48}$$

while

$$\frac{D}{A} = \frac{2}{1 + \mathrm{i}\kappa/k} = \frac{2}{1 + \mathrm{i}(V_0/E - 1)^{1/2}} = 1 + \mathrm{e}^{\mathrm{i}\alpha}. \tag{4.49}$$

Hence the eigenfunction (4.44) can be rewritten in terms of the constant A as

$$\psi(x) = \begin{cases} 2A\mathrm{e}^{\mathrm{i}\alpha/2}\cos\left(kx - \frac{\alpha}{2}\right), & x < 0 \qquad (4.50\mathrm{a}) \\ 2A\mathrm{e}^{\mathrm{i}\alpha/2}\cos\frac{\alpha}{2}\mathrm{e}^{-\kappa x}, & x > 0 \qquad (4.50\mathrm{b}) \end{cases}$$

and is seen to be real, apart from a multiplicative constant. As an example, the eigenfunction (4.50) with $A = 2^{-1}\exp(-\mathrm{i}\alpha/2)$ is shown in Fig. 4.2 for the case $\alpha = -\pi/3$, which corresponds to $E = 0.75V_0$.

We may readily interpret the solution $\psi(x)$ as follows. Let us first consider the region $x < 0$ and return to equation (4.44a). We have seen in Section 4.2 that

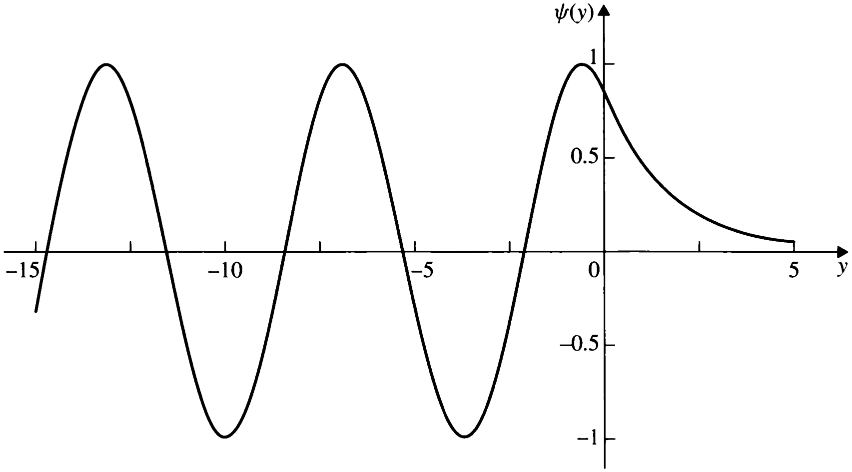


Figure 4.2 The eigenfunction ψ given by equations (4.50) with $A = 2^{-1}\exp(-i\alpha/2)$, as a function of the variable $y = kx$, for the case $\alpha = -\pi/3$, corresponding to an incident particle energy $E = 0.75V_0$.

the functions $\exp(ikx)$ and $\exp(-ikx)$, when multiplied by the factor $\exp(-iEt/\hbar)$, represent plane waves moving towards the right and towards the left, respectively. Moreover, the probability current density corresponding to the wave function (4.44a) is given (see (4.27)) by

$$j = v[|A|^2 - |B|^2], \qquad x < 0 \tag{4.51}$$

where $v = \hbar k/m$ is the magnitude of the velocity of the particle. The first term $A\exp(ikx)$ of $\psi(x)$ in the region $x < 0$ therefore corresponds to a plane wave of amplitude A *incident* from the left on the potential step, while the second term $B\exp(-ikx)$ corresponds to a *reflected* plane wave of amplitude B. The *reflection coefficient* R is defined as the ratio of the intensity of the reflected probability current density $(v|B|^2)$ to the intensity of the incident probability current density $(v|A|^2)$. Thus

$$R = \frac{v|B|^2}{v|A|^2} = \frac{|B|^2}{|A|^2} \tag{4.52}$$

and we see that the quantity R is also equal to the ratio of the intensity of the reflected wave to that of the incident wave. Note that R is independent of the absolute normalisation of the wave function $\psi(x)$. Now, from (4.48) we have $|A|^2 = |B|^2$, so that $R = 1$ and the reflection is *total*. This result is in agreement with the prediction of classical mechanics, according to which all particles with total energy $E < V_0$ are reflected by the potential step. However, we see from (4.6) and (4.50a) that to the left of the barrier the position probability density

$$P(x) = 4|A|^2\cos^2\left(kx - \frac{\alpha}{2}\right), \qquad x < 0 \tag{4.53}$$

exhibits an oscillatory behaviour, which is a purely quantum mechanical interference effect between the incident and reflected waves.

Since $|A|^2 = |B|^2$, the probability current density (4.51) vanishes for $x < 0$. By substituting the expression of $\psi(x)$ given by (4.44b) on the right of equation (4.7), it is also readily verified that $j = 0$ for $x > 0$. Hence there is no net current anywhere and therefore no net momentum in the state (4.44). This result could have been predicted directly by looking at the form (4.50) of the wave function. Indeed, as we already remarked in Section 4.2, the probability current density (4.7) vanishes for any function $\psi(x)$ which is real except for a multiplicative constant.

Let us now examine in more detail the eigenfunction $\psi(x)$ in the region $x > 0$, as given by (4.44b). The interesting feature is that this function *does not vanish* in this region. Thus, using (4.6) and (4.44b), we find that the position probability density is given to the right of the potential step by

$$P(x) = |D|^2 e^{-2\kappa x}, \qquad x > 0. \tag{4.54}$$

Although this expression decreases rapidly with increasing x, *there is a finite probability of finding the particle in the classically inaccessible region* $x > 0$. This striking non-classical phenomenon of *barrier penetration* is of great importance in the understanding of various phenomena in quantum physics, and will be illustrated in the following sections. In the present case, however, the wave-like property of penetration into the classically excluded region cannot be demonstrated experimentally. Indeed, in order to observe the particle in the region $x > 0$, it must be localised within a distance of order $\Delta x \simeq \kappa^{-1}$, for which the probability (4.54) is appreciable. As a result, its momentum would be uncertain by an amount

$$\Delta p_x \gtrsim \frac{\hbar}{\Delta x} \simeq \hbar\kappa = [2m(V_0 - E)]^{1/2} \tag{4.55}$$

and its energy would be uncertain by a quantity

$$\Delta E = \frac{(\Delta p_x)^2}{2m} \gtrsim V_0 - E \tag{4.56}$$

so that it would no longer be possible to state with certainty that the total energy E of the particle is less than V_0.

It is interesting to examine the limiting case of an infinitely high potential barrier, so that $V_0 \to \infty$ (the energy E being kept constant). Then $\kappa \to \infty$ and we see from (4.44b) that $\psi(x) \to 0$ in the classically forbidden region $x > 0$. From (4.47)–(4.49) we also deduce that

$$\lim_{V_0\to\infty} \frac{B}{A} = -1, \qquad \lim_{V_0\to\infty} \frac{D}{A} = 0 \tag{4.57}$$

so that as $V_0 \to \infty$ we have $B = -A$ and $D = 0$. The wave function (4.44) therefore becomes, in this case,

$$\psi(x) = \begin{cases} A(\mathrm{e}^{\mathrm{i}kx} - \mathrm{e}^{-\mathrm{i}kx}), & x < 0 \\ 0, & x > 0. \end{cases} \tag{4.58}$$

Thus, for an infinitely high barrier the wave function vanishes at the barrier (for $x = 0$) and beyond it (for $x > 0$), in agreement with the discussion of Section 3.6. We also remark that at the point $x = 0$, where the potential makes an infinite jump, the slope of the wave function (4.58) changes suddenly from the finite value $2\mathrm{i}kA$ to zero. Note that this discontinuity of the slope is not in contradiction with the condition of 'smooth' joining (which requires both $\psi(x)$ and $\mathrm{d}\psi(x)/\mathrm{d}x$ to be continuous) which only holds when the potential is either continuous or exhibits *finite* jumps.

Case 2: $E > V_0$

Let us now return to finite potential steps and consider the case for which the total energy E exceeds V_0. The Schrödinger equation (4.3) then becomes

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + k^2\psi(x) = 0, \qquad k = \left(\frac{2m}{\hbar^2}E\right)^{1/2}, \qquad x < 0 \tag{4.59a}$$

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + k'^2\psi(x) = 0, \qquad k' = \left[\frac{2m}{\hbar^2}(E - V_0)\right]^{1/2}, \qquad x > 0 \tag{4.59b}$$

and is readily solved to give

$$\psi(x) = \begin{cases} A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}, & x < 0 \quad \text{(4.60a)} \\ C\mathrm{e}^{\mathrm{i}k'x} + D\mathrm{e}^{-\mathrm{i}k'x}, & x > 0 \quad \text{(4.60b)} \end{cases}$$

where A, B, C and D are integration constants. We see that in both regions $x < 0$ and $x > 0$ the wave function (4.60) has an oscillatory character. Moreover, it is doubly degenerate since it consists of a linear combination of two linearly independent solutions corresponding to the same energy.

In order to make progress in the interpretation of the wave function (4.60), we must specify the physical situation which we want to study. Clearly, the particle can be incident on the step either from the left or from the right. We shall consider here the case when the particle is incident from the left. We must then discard the second term $D\exp(-\mathrm{i}k'x)$ on the right of (4.60b), since this term corresponds to a reflected wave travelling in the direction of decreasing x in the region $x > 0$, and there is nothing for x large and positive which can cause such a reflection. Hence we must set $D = 0$, so that the wave function (4.60) becomes

$$\psi(x) = \begin{cases} A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}, & x < 0 \quad \text{(4.61a)} \\ C\mathrm{e}^{\mathrm{i}k'x}, & x > 0. \quad \text{(4.61b)} \end{cases}$$

We see that it consists of an *incident* wave (of amplitude A) and a *reflected* wave (of amplitude B), both of wave number k, in the region $x < 0$, and of a *transmitted* wave (of amplitude C) of wave number k' in the region $x > 0$. Thus, in contrast with classical mechanics which says that a particle with energy $E > V_0$ will always pass the potential step, quantum mechanics predicts that the incident wave will be partly transmitted and partly reflected.

The constants A, B and C in (4.61) can be related by joining 'smoothly' the solutions (4.61a) and (4.61b), so that $\psi(x)$ and $\mathrm{d}\psi(x)/\mathrm{d}x$ are continuous at $x = 0$. Continuity of $\psi(x)$ at $x = 0$ requires that

$$A + B = C \tag{4.62a}$$

and continuity of $\mathrm{d}\psi(x)/\mathrm{d}x$ at $x = 0$ yields the further condition

$$k(A - B) = k'C. \tag{4.62b}$$

These two equations are readily solved to give

$$\frac{B}{A} = \frac{k - k'}{k + k'} \tag{4.63}$$

and

$$\frac{C}{A} = \frac{2k}{k + k'}. \tag{4.64}$$

Since the two solutions (4.61a) and (4.61b) can be joined smoothly in this way for all values of $E > V_0$, the spectrum is again *continuous*.

Let us now consider the probability current density j associated with the wave function (4.61). Substituting this wave function in (4.7), we find that

$$j = v[|A|^2 - |B|^2], \qquad x < 0 \tag{4.65a}$$

$$= v'|C|^2, \qquad x > 0 \tag{4.65b}$$

where $v = \hbar k/m$ and $v' = \hbar k'/m$ are the magnitudes of the particle velocity in the regions $x < 0$ and $x > 0$, respectively. Using (4.63) and (4.64) we have

$$\frac{|B|^2}{|A|^2} + \frac{v'}{v}\frac{|C|^2}{|A|^2} = 1 \tag{4.66}$$

so that $v'|C|^2 = v[|A|^2 - |B|^2]$ and the probability current density j has the same constant value everywhere, as it should for any one-dimensional stationary state. Note, however, that in contrast to the case $0 < E < V_0$ studied above, this constant value is not zero in the present situation.

The *reflection coefficient* R has been defined in (4.52) to be the ratio of the intensity of the reflected probability current density to that of the incident probability current density. Using (4.63), we therefore have

$$R = \frac{|B|^2}{|A|^2} = \frac{(k - k')^2}{(k + k')^2} = \frac{[1 - (1 - V_0/E)^{1/2}]^2}{[1 + (1 - V_0/E)^{1/2}]^2}, \qquad E > V_0. \tag{4.67}$$

The reflection coefficient is plotted in Fig. 4.3 as a function of the ratio E/V_0. We have also included in this graph the case $E/V_0 < 1$ studied above, for which $R = 1$.

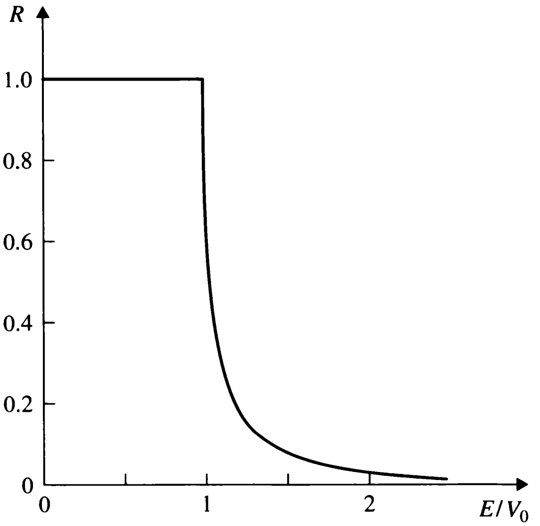


Figure 4.3 The reflection coefficient R for particles incident on the step potential (4.41), as a function of the ratio E / V_0.

Note that $R = 1$ when $E = V_0$. As E/V_0 continues to increase beyond unity, R decreases monotonically and tends to zero when $E/V_0 \to \infty$.

We can also define the *transmission coefficient* T as the ratio of the intensity of the transmitted probability current density to that of the incident probability current density. Thus T, like R, is independent of the absolute normalisation of the wave function $\psi(x)$. Using (4.64) we obtain

$$T = \frac{v'|C|^2}{v|A|^2} = \frac{4kk'}{(k+k')^2} = \frac{4(1 - V_0/E)^{1/2}}{[1 + (1 - V_0/E)^{1/2}]^2}, \qquad E > V_0 \qquad \textbf{(4.68)}$$

and we see that both R and T depend only on the ratio V_0/E. Moreover, we deduce from (4.66) that

$$R + T = 1. \qquad \textbf{(4.69)}$$

We have seen above that the wave function describing the motion of the particle is partially reflected and partially transmitted at the potential step. Similarly, the probability flux incident upon the potential step is split into a reflected flux and a transmitted flux, the total probability flux being conserved by virtue of (4.69). The particle itself is of course not split at the potential step, since particles are always observed as complete entities. In any particular event the particle will either be reflected or transmitted, the probability of reflection being R and that of transmission being T for a large number of events.

The fact that potential steps can reflect particles for which $E > V_0$ (i.e. having enough energy to be classically transmitted) is clearly due to the *wave-like* properties of particles embodied in the quantum mechanical formalism. It is therefore not surprising that this behaviour is analogous to a phenomenon occurring in classical *wave optics*, namely the reflection of light at a boundary where the index of refraction changes abruptly. Indeed, let us consider the regions to the left and to the right of the potential step as two 'optical media'. In the first medium ($x < 0$) the de Broglie wavelength of the particle is $\lambda = 2\pi/k$, and in the second medium ($x > 0$) it is given by $\lambda' = 2\pi/k'$. The index of refraction n of medium 2 relative to medium 1 is defined in the usual way as the ratio of the two wavelengths

$$n = \frac{\lambda}{\lambda'} = \frac{k'}{k} = \left(1 - \frac{V_0}{E}\right)^{1/2} \tag{4.70}$$

and in terms of this index of refraction we have

$$R = \left(\frac{1-n}{1+n}\right)^2 \tag{4.71}$$

which is precisely the result obtained in wave optics.

Until now we have analysed the situation for which the particle is incident from the left, but it is also instructive to consider the case when the particle is incident on the potential step from the right. We must then set $A = 0$ in the general wave function (4.60), since the term $A \exp(ikx)$ now corresponds to a reflected wave in the region $x < 0$, and there is no reflector for $x \to -\infty$. Following the method given above, it is straightforward to obtain the reflection and transmission coefficients for this case (Problem 4.3). It is found that they are the same as those given by (4.67) and (4.68) for a particle incident from the left, a result which could have been anticipated since both R and T remain unchanged if k and k' are exchanged. This clearly shows that partial reflection is not due to an increase of $V(x)$ in the direction of motion of the particle, but results from an *abrupt change* in the potential (and hence in the de Broglie wavelength of the particle), just as optical reflection occurs at a boundary where the index of refraction changes abruptly. Thus, if we return to the smoothly varying potential shown in Fig. 4.1(a), we can predict that partial reflection of particles with energy $E > V_0$ will only occur significantly if the potential $V(x)$ changes by an appreciable amount over a short distance. This can be proved by solving explicitly the Schrödinger equation (4.3) for potentials of the form shown in Fig. 4.1(a). It is found that partial reflection for $E > V_0$ occurs if the potential $V(x)$ varies significantly over a distance of the order of the de Broglie wavelength λ of the incident particle. On the other hand, reflection is negligible when the potential varies slowly over that de Broglie wavelength. This, of course, is the case in the classical limit for which any realistic potential $V(x)$ of the form shown in Fig. 4.1(a) changes by a negligible amount over the de Broglie wavelength, which tends to zero in that limit.

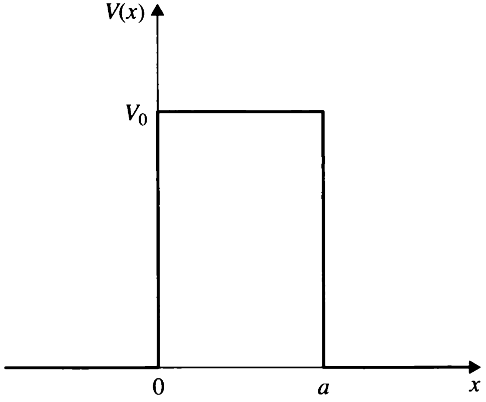


Figure 4.4 A rectangular potential barrier of height V_0 and thickness a.

4.4 The potential barrier

We now proceed to study the motion of a particle in a potential $V(x)$ which has the form of the rectangular barrier shown in Fig. 4.4. Thus

$$V(x) = \begin{cases} 0, & x < 0 \\ V_0, & 0 < x < a \\ 0, & x > a \end{cases} \tag{4.72}$$

with $V_0 > 0$. According to classical mechanics, a particle of total energy E incident upon this barrier would always be reflected if $E < V_0$ and it would be transmitted if $E > V_0$. In view of what we learned in the preceding section, we expect that quantum mechanics will lead to a different prediction. Indeed, as we shall now see, the quantum mechanical treatment of this problem leads to the conclusion that both reflection and transmission happen with finite probability for most (positive) values of the particle energy.

We begin by remarking that, as in the case of the potential step, there is no admissible solution of the Schrödinger equation (4.3) for the potential (4.72) when $E < 0$. We shall thus assume that $E > 0$. Note that the problem we want to analyse belongs to the category of one-dimensional *scattering problems*, in which a particle of energy $E > 0$ interacts with a potential in a given interval, and is free outside this interval. In the present case the particle interacts with the potential in the interval $(0, a)$. In the external regions $x < 0$ and $x > a$ the particle is free, and the general solution of the Schrödinger equation (4.3) is given by

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < 0 \qquad \textbf{(4.73a)} \\ Ce^{ikx} + De^{-ikx}, & x > a \qquad \textbf{(4.73b)} \end{cases}$$

where A, B, C, D are constants and $k = (2mE/\hbar^2)^{1/2}$. It is interesting to remark that solutions of the form (4.73) are valid in the force-free regions that are external to the interval in which *any* scattering potential acts.

The particle can obviously be incident upon the barrier either from the left or from the right. We shall study here the case when it is incident on the barrier from the left. Since there is nothing at large positive values of x to cause a reflection, we must set $D = 0$ in (4.73b). The wave function is therefore given in the external regions by

$$\psi(x) = \begin{cases} A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}, & x < 0 \qquad \textbf{(4.74a)} \\ C\mathrm{e}^{\mathrm{i}kx}, & x > a. \qquad \textbf{(4.74b)} \end{cases}$$

We see that in the region $x < 0$ the wave function consists of an *incident wave* of amplitude A and a *reflected wave* of amplitude B, both of wave number k. In the region $x > a$ it is a pure *transmitted* wave of amplitude C and wave number k. This interpretation is readily checked by substituting the wave function (4.74) into (4.7). The resulting probability current density (which is constant since we are dealing with one-dimensional stationary states) is given by

$$j = \begin{cases} v[|A|^2 - |B|^2], & x < 0 \qquad \textbf{(4.75a)} \\ v|C|^2, & x > a \qquad \textbf{(4.75b)} \end{cases}$$

where $v = \hbar k/m$ is the magnitude of the particle velocity. The quantities $v|A|^2$, $v|B|^2$ and $v|C|^2$ are, respectively, the intensities of the incident, reflected and transmitted probability current densities. Following the definitions of Section 4.3, a *reflection coefficient* R and a *transmission coefficient* T can be introduced, which are independent of the absolute normalisation of the wave function $\psi(x)$. They are given by

$$R = \frac{|B|^2}{|A|^2}, \qquad T = \frac{|C|^2}{|A|^2}. \qquad \textbf{(4.76)}$$

Note that in writing the expression for T we have used the fact that the velocity v of the particle is the same in both regions $x < 0$ and $x > a$.

Until now we have studied the solution $\psi(x)$ of the Schrödinger equation in the external regions $x < 0$ and $x > a$. The nature of the solution in the internal region $0 < x < a$ depends on whether $E < V_0$ or $E > V_0$. We shall analyse these two cases in succession.

Case 1: $E < V_0$

Remembering that $V(x) = V_0$ for $0 < x < a$, and setting $\kappa = [2m(V_0 - E)/\hbar^2]^{1/2}$ as in (4.42b), the solution of the Schrödinger equation in the internal region is given by

$$\psi(x) = F\mathrm{e}^{\kappa x} + G\mathrm{e}^{-\kappa x}, \qquad 0 < x < a. \qquad \textbf{(4.77)}$$

The five constants A, B, C, F and G can be related by requiring that $\psi(x)$ and $\mathrm{d}\psi(x)/\mathrm{d}x$ be continuous at both points $x = 0$ and $x = a$ where the potential is discontinuous. Thus at $x = 0$ we have, from (4.74a) and (4.77),

$$A + B = F + G \tag{4.78a}$$

$$\mathrm{i}k(A - B) = \kappa(F - G) \tag{4.78b}$$

while at $x = a$ we find from (4.74b) and (4.77) that

$$C\mathrm{e}^{\mathrm{i}ka} = F\mathrm{e}^{\kappa a} + G\mathrm{e}^{-\kappa a} \tag{4.79a}$$

$$\mathrm{i}kC\mathrm{e}^{\mathrm{i}ka} = \kappa(F\mathrm{e}^{\kappa a} - G\mathrm{e}^{-\kappa a}). \tag{4.79b}$$

Eliminating F and G and solving for the ratios B/A and C/A, we obtain

$$\frac{B}{A} = \frac{(k^2 + \kappa^2)(\mathrm{e}^{2\kappa a} - 1)}{\mathrm{e}^{2\kappa a}(k + \mathrm{i}\kappa)^2 - (k - \mathrm{i}\kappa)^2} \tag{4.80a}$$

and

$$\frac{C}{A} = \frac{4\mathrm{i}k\kappa \mathrm{e}^{-\mathrm{i}ka}\mathrm{e}^{\kappa a}}{\mathrm{e}^{2\kappa a}(k + \mathrm{i}\kappa)^2 - (k - \mathrm{i}\kappa)^2} \tag{4.80b}$$

so that the reflection and transmission coefficients are given by

$$R = \frac{|B|^2}{|A|^2} = \left[1 + \frac{4k^2\kappa^2}{(k^2 + \kappa^2)^2 \sinh^2(\kappa a)}\right]^{-1} = \left[1 + \frac{4E(V_0 - E)}{V_0^2 \sinh^2(\kappa a)}\right]^{-1} \tag{4.81a}$$

and

$$T = \frac{|C|^2}{|A|^2} = \left[1 + \frac{(k^2 + \kappa^2)^2 \sinh^2(\kappa a)}{4k^2\kappa^2}\right]^{-1} = \left[1 + \frac{V_0^2 \sinh^2(\kappa a)}{4E(V_0 - E)}\right]^{-1}. \tag{4.81b}$$

It is also readily verified that $R + T = 1$, which expresses conservation of the probability flux.

The above equations lead to the remarkable prediction that a particle has a certain probability of 'leaking through' a potential barrier which is completely 'opaque' from the point of view of classical mechanics. This phenomenon, which is one of the most striking features of quantum mechanics, is known as *barrier penetration* or the *tunnel effect*, and is quite common in atomic, nuclear and solid state physics. For example, the tunnel effect is fundamental in explaining the emission of alpha particles by radioactive nuclei, a process which we shall study in Chapter 8 after learning how to calculate the transmission coefficient for more general potential barriers than the rectangular one considered here. In Fig. 4.5 we illustrate schematically the tunnel effect by showing the modulus square of the wave function, $|\psi(x)|^2$, for a rectangular potential barrier (4.72) such that $mV_0a^2/\hbar^2 = 0.25$ and an incident particle energy $E = 0.75V_0$. Of particular interest is the fact that in the region $x > a$, one has $|\psi(x)|^2 = |C|^2$, which is non-zero. We also note the attenuation of $|\psi(x)|^2$ inside the barrier, and the fact that since $R < 1$ we have $|B| < |A|$, so that the wave function $\psi(x)$ – and hence $|\psi(x)|^2$ – never goes through zero in the region $x < 0$.

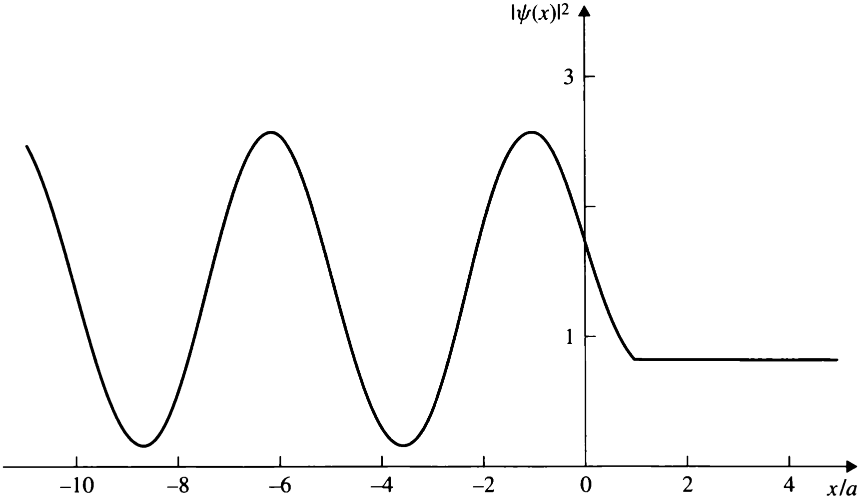


Figure 4.5 The modulus square of the wave function, $|\psi(x)|^2$, for the case of a rectangular barrier such that $mV_0a^2/\hbar^2 = 0.25$. The incident particle energy is $E = 0.75V_0$. The coefficient A in (4.73a) has been taken to be $A = 1$.

Going back to equation (4.81b), we see that $T \to 0$ in the limit $E \to 0$, and that T is a monotonically increasing function of E. Also, when the particle energy approaches the top of the barrier (from below), we have

$$\lim_{E\to V_0} T = \left(1 + \frac{mV_0a^2}{2\hbar^2}\right)^{-1} \tag{4.82}$$

Note that the dimensionless number $mV_0a^2/\hbar^2$ may be considered as a measure of the 'opacity' of the barrier. In the classical limit this opacity becomes very large, and the transmission coefficient T remains vanishingly small for all energies E such that $0 \leqslant E \leqslant V_0$. Finally, if $\kappa a \gg 1$ we can write $\sinh(\kappa a) \simeq 2^{-1}\exp(\kappa a)$, so that the transmission coefficient is given approximately by

$$T \simeq \frac{16E(V_0 - E)}{V_0^2}\mathrm{e}^{-2\kappa a} \tag{4.83}$$

and is very small.

The formula (4.83) has an important application in the *scanning tunnelling microscope*. A sharp metal needle is brought very close to a metal. The energy of the electrons within the needle and the surface is less than in the gap between them, so that a potential barrier exists through which the electrons can tunnel. If an electrical voltage is applied between the needle and the surface, a current will flow, whose magnitude depends on the transmission coefficient (4.83), in which the width a of the barrier is the height of the needle above the surface. Because of the exponential dependence of the transmission coefficient T on a, the current is a sensitive measure

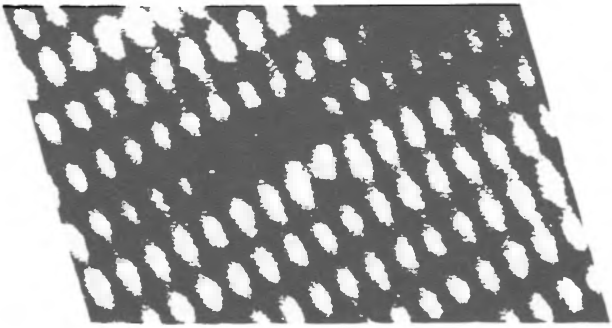


Figure 4.6 A scanning tunnelling microscope image of the surface of a silicon crystal.

of the height of the needle above the surface. This height can be adjusted as the needle scans the surface so that the current remains constant. In this way contour maps of surfaces have been obtained with an accuracy better than 10^{-11} m in the direction perpendicular to the surface and with a resolution of 0.5×10^{-9} m in directions parallel to the surface. In Fig. 4.6 a constant-current image of the surface of a silicon crystal is shown. A periodic array is seen corresponding to surface unit cells. The black area near the centre is caused by a small defect. Further applications of tunnelling are discussed in Section 8.4.

Case 2: $E > V_0$

The solution of the Schrödinger equation in the internal region is now given by

$$\psi(x) = F\mathrm{e}^{\mathrm{i}k'x} + G\mathrm{e}^{-\mathrm{i}k'x} \qquad 0 < x < a \tag{4.84}$$

where $k' = [2m(E - V_0)/\hbar^2]^{1/2}$ as in (4.59b).

The conditions that $\psi(x)$ and $\mathrm{d}\psi(x)/\mathrm{d}x$ be continuous at the two points $x = 0$ and $x = a$ provide four relations between the five constants A, B, C, F and G. Thus, after elimination of F and G, we can solve again for the ratios B/A and C/A. Actually, it is easier to obtain these ratios directly by replacing κ by $\mathrm{i}k'$ in the equations (4.80). We find in this way that the reflection and transmission coefficients are now given by

$$R = \frac{|B|^2}{|A|^2} = \left[1 + \frac{4k^2k'^2}{(k^2 - k'^2)^2\sin^2(k'a)}\right]^{-1} = \left[1 + \frac{4E(E - V_0)}{V_0^2\sin^2(k'a)}\right]^{-1} \tag{4.85a}$$

$$T = \frac{|C|^2}{|A|^2} = \left[1 + \frac{(k^2 - k'^2)^2\sin^2(k'a)}{4k^2k'^2}\right]^{-1} = \left[1 + \frac{V_0^2\sin^2(k'a)}{4E(E - V_0)}\right]^{-1} \tag{4.85b}$$

and we see again that $R + T = 1$. The most important point about these equations is that the transmission coefficient T is in general less than unity, in contradiction to the classical prediction that the particle should always pass the potential barrier when $E > V_0$. In fact, we see from (4.85b) that we only have $T = 1$ when $k'a = \pi, 2\pi, 3\pi, \ldots,$ namely whenever the thickness a of the barrier is equal to a half-integral or integral

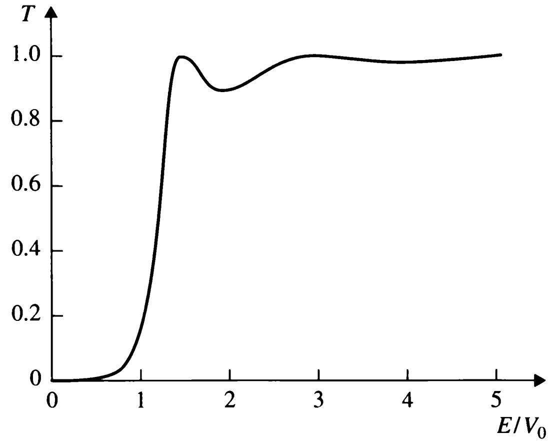


Figure 4.7 The transmission coefficient for a rectangular potential barrier such that $mV_0a^2/\hbar^2 = 10$, as a function of the ratio E/V_0.

number of de Broglie wavelengths $\lambda' = 2\pi/k'$ in that region. This effect results from destructive interference between reflections at the two points $x = 0$ and $x = a$. We also remark that when E tends to V_0 (this time from above), T joins smoothly to the value given by (4.82), while T becomes asymptotically equal to unity when E is large compared to V_0.

In Fig. 4.7 we show the transmission coefficient T, obtained from equations (4.81b) and (4.85b), as a function of E/V_0, for a barrier such that $mV_0a^2/\hbar^2 = 10$. Note that even when E is somewhat smaller than V_0 the transmission coefficient T is not negligible, which shows the importance of the tunnel effect in this case.

Since the phenomena of barrier penetration are characteristic of waves, we should not be surprised that they have a classical analogue in wave optics. Consider for example two optical media 1 and 2 (such as glass and air) having refractive indices n_1 and n_2, with $n_1 > n_2$, and suppose that a plane wave is incident from the optical medium 1 on the plane interface of the two media (see Fig. 4.8(a)). If the angle of incidence θ is larger than the critical angle θ_c, and if the optical medium 2 extends to infinity below the interface, the wave will be *totally reflected*, as shown in Fig. 4.8(a). However, despite the fact that the wave does not propagate in the optical medium 2, classical electromagnetic theory shows that the electric field does penetrate in that medium, its amplitude decreasing exponentially as one goes further away from the interface. This situation is therefore analogous to the potential step problem with $E < V_0$, for which we saw in the previous section that the reflection is total ($R = 1$), but the wave function $\psi(x)$ does penetrate in the classically forbidden region ($x > 0$) and decreases exponentially in that region (see (4.44b)).

Consider now the situation depicted in Fig. 4.8(b), where the optical medium 2 is reduced to a thin layer separating two optical media of type 1. In this case, a wave incident at an angle $\theta > \theta_c$ will be *partly reflected* and *partly transmitted*.

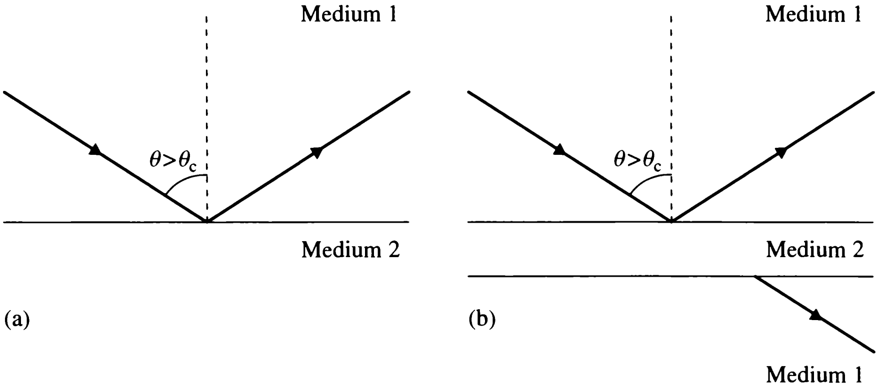


Figure 4.8 (a) Illustration of the total reflection of a plane electromagnetic wave at the plane interface of two media having different refractive indices. (b) Illustration of frustrated total reflection.

This phenomenon, called *frustrated total reflection*, can be fully understood by using classical electromagnetic theory, and is the analogue of the quantum mechanical tunnel effect. Just as the reduction of the optical medium 2 to a layer allows the transmission of the electromagnetic wave to occur, so does the reduction of a step potential (having infinite thickness) to a barrier potential (of finite thickness) permit the transmission of particles of energy $E < V_0$ in the quantum mechanical problem.

4.5 The infinite square well

Thus far we have only considered examples for which the Schrödinger eigenvalue equation (4.3) has solutions for every positive value of the energy, so that the energy spectrum forms a *continuum*. This is the case whenever the classical motion is not confined to a given region of space. We shall now study the opposite case of a particle of mass m which is *bound* so that the corresponding classical motion is periodic. In contrast with classical mechanics, solutions of the Schrödinger equation (4.3) then exist only for certain *discrete* values of the energy, as we have seen in Section 3.6. In this section we shall analyse a simple example such that the energy spectrum consists only of discrete bound states. This is the infinite square well potential, corresponding to the motion of a particle constrained by impenetrable walls to move in a region of width L, where the potential energy is constant. Taking this constant to be zero, and defining $a = L/2$, the potential energy for this problem is

$$V(x) = \begin{cases} 0, & -a < x < a \\ \infty, & |x| > a \end{cases} \qquad \textbf{(4.86)}$$

where we have chosen the origin of the x-axis to be at the centre of the well. This potential is illustrated in Fig. 4.9.

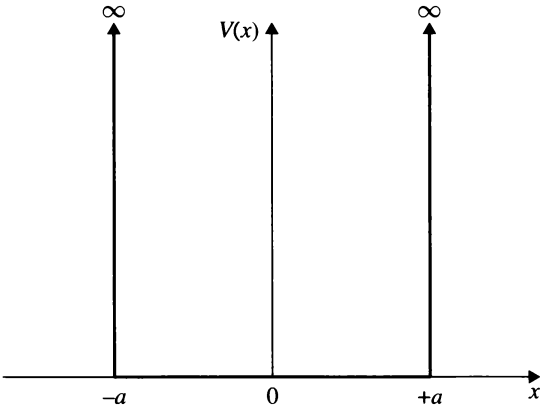


Figure 4.9 The infinite square well potential.

As the potential energy is infinite at $x = \pm a$, the probability of finding the particle outside the well is zero. The wave function $\psi(x)$ must therefore vanish for $|x| > a$, and we only need to solve the Schrödinger equation (4.3) inside the well. Moreover, since the wave function must be continuous, $\psi(x)$ must vanish at the constraining walls, namely

$$\psi(x) = 0 \qquad \text{at} \qquad x = \pm a. \tag{4.87}$$

We shall see shortly that this *boundary condition* leads to the quantisation of the energy. Note that the derivative of the wave function, $\mathrm{d}\psi(x)/\mathrm{d}x$, cannot vanish at $x = \pm a$, since then the eigenfunction $\psi(x)$ would be the trivial solution $\psi = 0$. Thus $\mathrm{d}\psi(x)/\mathrm{d}x$ will be discontinuous at the points $x = \pm a$, where the potential makes infinite jumps. As we have already remarked in Section 3.6, discontinuities of $\mathrm{d}\psi(x)/\mathrm{d}x$ are allowed at the points where the potential exhibits infinite discontinuities.

The Schrödinger equation for $|x| < a$ is simply

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = E\psi(x). \tag{4.88}$$

Setting $k = (2mE/\hbar^2)^{1/2}$, the general solution of (4.88) is a linear combination of the two linearly independent solutions $\exp(\mathrm{i}kx)$ and $\exp(-\mathrm{i}kx)$ or, equivalently, of the pair of real solutions $\sin kx$ and $\cos kx$. In the present problem it is convenient to use the real solutions, so that we shall write the general solution in the form

$$\psi(x) = A\cos kx + B\sin kx, \qquad k = \left(\frac{2m}{\hbar^2}E\right)^{1/2} \tag{4.89}$$

Let us now apply the boundary conditions (4.87). We find in this way that the following two conditions must be obeyed

$$A\cos ka = 0, \qquad B\sin ka = 0. \tag{4.90}$$

It is clear that we cannot allow both A and B to vanish, since this would yield the physically uninteresting trivial solution $\psi(x) = 0$. Also, we cannot make both $\cos ka$ and $\sin ka$ to vanish for a given value of k. Hence, there are *two* possible classes of solutions. For the *first class* $B = 0$ and $\cos ka = 0$, so that the only allowed values of k are

$$k_n = \frac{n\pi}{2a} = \frac{n\pi}{L} \tag{4.91}$$

with $n = 1, 3, 5, \ldots$. The corresponding eigenfunctions $\psi_n(x) = A_n \cos k_n x$ can be normalised so that

$$\int_{-a}^{+a} \psi_n^*(x)\psi_n(x)\mathrm{d}x = 1 \tag{4.92}$$

from which the normalisation constants are found (within an arbitrary multiplicative factor of modulus one) to be given by $A_n = a^{-1/2}$. The normalised eigenfunctions of the first class can therefore be written as

$$\psi_n(x) = \frac{1}{\sqrt{a}} \cos \frac{n\pi}{2a} x, \qquad n = 1, 3, 5, \ldots . \tag{4.93}$$

In the same way, we find that for the *second class* of solutions $A = 0$ and $\sin ka = 0$, so that the allowed values of k are given by (4.91), with $n = 2, 4, 6, \ldots$. The normalised eigenfunctions of the second class are therefore

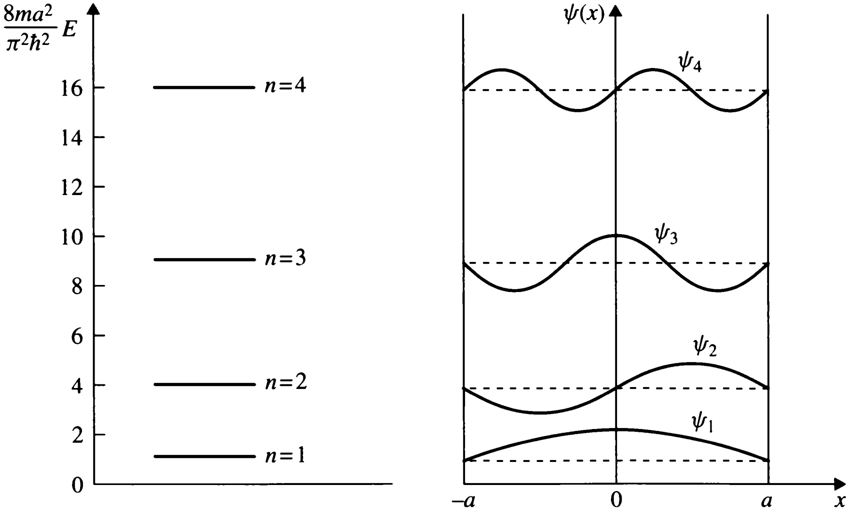
$$\psi_n(x) = \frac{1}{\sqrt{a}} \sin \frac{n\pi}{2a} x, \qquad n = 2, 4, 6, \ldots . \tag{4.94}$$

For both classes of eigenfunctions it is unnecessary to consider negative values of n, since these lead to solutions which are not linearly independent of those corresponding to positive n.

Taking into account the two classes of solutions, we find that the values of k are quantised, being given by $k_n = n\pi/L$, with $n = 1, 2, 3, \ldots$. The corresponding de Broglie wavelengths are $\lambda_n = 2\pi/k_n = 2L/n$, so that eigenfunctions are only obtained if a half-integral or integral number of de Broglie wavelengths can fit into the box. In contrast with the classical result, according to which a particle can move in the potential (4.86) with any positive energy, we see that in the quantum mechanical problem the energy is *quantised*, the *energy eigenvalues* being

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{8m}\frac{\pi^2 n^2}{a^2} = \frac{\hbar^2}{2m}\frac{\pi^2 n^2}{L^2}, \qquad n = 1, 2, 3, \ldots \tag{4.95}$$

so that the energy spectrum consists of an *infinite number* of *discrete* energy levels corresponding to *bound states*. Note that there is just one eigenfunction for each level, so that the energy levels are *non-degenerate*. We also see from (4.93) and (4.94) that the nth eigenfunction has $(n - 1)$ nodes within the potential, and that the (real)



(a) Energy levels (b) Wave functions (relative scale)

Figure 4.10 (a) The first four energy eigenvalues and (b) the corresponding eigenfunctions of the infinite square well. In (b) the x-axis for the eigenfunction ψ_n is drawn at a height corresponding to the energy E_n.

eigenfunctions $\psi_n(x)$ and $\psi_m(x)$ corresponding to different eigenvalues E_n and E_m are orthogonal:

$$\int_{-a}^{+a} \psi_m^*(x)\psi_n(x)\mathrm{d}x = 0, \qquad n \neq m. \tag{4.96}$$

All these results are in agreement with the discussion of Sections 3.6 and 3.7. The first few energy eigenvalues and corresponding eigenfunctions are shown in Fig. 4.10. It is worth noting that the lowest energy or *zero-point* energy is $E_{n=1} = \hbar^2\pi^2/8ma^2$, so that there is no state of zero energy. This is in agreement with the requirements of the uncertainty principle. Indeed, the position uncertainty is roughly given by $\Delta x \simeq a$. The corresponding momentum uncertainty is therefore $\Delta p_x \gtrsim \hbar/a$, leading to a minimum kinetic energy of order $\hbar^2/ma^2$, in qualitative agreement with the value of E_1.

Parity

There is an important difference between the two classes of eigenfunction which we have obtained. That is, the eigenfunctions (4.93) belonging to the first class are such that $\psi_n(-x) = \psi_n(x)$ and are therefore *even* functions of x, while the eigenfunctions (4.94) of the second class are such that $\psi_n(-x) = -\psi_n(x)$ and hence are *odd*. This division of the eigenfunctions $\psi_n(x)$ into eigenfunctions having a definite *parity* (even for the first class, odd for the second class) is a direct consequence of the fact that the potential is *symmetric* about $x = 0$, i.e. is an even function, $V(-x) = V(x)$, as we shall now show.

For this purpose let us study the behaviour of the Schrödinger eigenvalue equation (4.3) under the operation of *reflection through the origin*, $x \to -x$, which is also called the *parity* operation. If the potential is symmetric, the Hamiltonian $H = -(\hbar^2/2m)\mathrm{d}^2/\mathrm{d}x^2 + V(x)$ does not change when x is replaced by $-x$: it is *invariant* under the parity operation. Thus, if we change the sign of x in the Schrödinger equation (4.3), we have

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(-x)}{\mathrm{d}x^2} + V(x)\psi(-x) = E\psi(-x) \tag{4.97}$$

so that both $\psi(x)$ and $\psi(-x)$ are solutions of the same equation, with the same eigenvalue E. Two cases may arise.

Case 1: The eigenvalue E is non-degenerate

The two eigenfunctions $\psi(x)$ and $\psi(-x)$ can then differ only by a multiplicative constant

$$\psi(-x) = \alpha\psi(x). \tag{4.98}$$

Changing the sign of x in this equation yields

$$\psi(x) = \alpha\psi(-x) \tag{4.99}$$

and by combining these two equations we find that $\psi(x) = \alpha^2\psi(x)$. Hence $\alpha^2 = 1$ so that $\alpha = \pm 1$ and

$$\psi(-x) = \pm\psi(x) \tag{4.100}$$

which shows that the eigenfunctions $\psi(x)$ have a *definite parity*, being either even or odd for the parity operation $x \to -x$.

In particular, since bound states in one dimension are non-degenerate, every one-dimensional bound-state wave function in a symmetric potential must be either even or odd. Moreover, even functions clearly have an even number (including zero) of nodes, and odd functions have an odd number of nodes. As a consequence, if the energy levels are ordered by increasing energy values, the corresponding eigenfunctions are alternately even or odd, with the ground-state wave function being always an even function. As seen from (4.93) and (4.94), the results we have obtained above for the infinite square well are in agreement with these conclusions.

Case 2: The eigenvalue E is degenerate

In this case more than one linearly independent eigenfunction corresponds to the eigenvalue E, and these eigenfunctions need not have a definite parity. However, it is always possible to construct linear combinations of these eigenfunctions, such that each has definite parity. Indeed, let us assume that the eigenfunction $\psi(x)$ does not have a definite parity. We may then write

$$\psi(x) = \psi_+(x) + \psi_-(x) \tag{4.101}$$

where

$$\psi_+(x) = \tfrac{1}{2}[\psi(x) + \psi(-x)] \tag{4.102a}$$

obviously has even parity, while

$$\psi_-(x) = \tfrac{1}{2}[\psi(x) - \psi(-x)] \tag{4.102b}$$

is odd. Substituting (4.101) into the Schrödinger equation (4.3) we have

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) - E\right]\psi_+(x) + \left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) - E\right]\psi_-(x) = 0. \tag{4.103}$$

Changing x to $-x$ and using the fact that $V(-x) = V(x)$, $\psi_+(-x) = \psi_+(x)$ and $\psi_-(-x) = -\psi_-(x)$, we find that

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) - E\right]\psi_+(x) - \left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) - E\right]\psi_-(x) = 0. \tag{4.104}$$

Therefore, upon adding and subtracting (4.103) and (4.104), we see that $\psi_+(x)$ and $\psi_-(x)$ are separately solutions of the Schrödinger equation (4.3), corresponding to the same eigenvalue E. This completes the proof that *for a symmetric* (even) *potential the eigenfunctions $\psi(x)$ of the one-dimensional Schrödinger equation* (4.3) *can always be chosen to have definite parity*, without loss of generality.

The fact that eigenfunctions of the Schrödinger equation (4.3) can always be chosen to be even or odd when $V(-x) = V(x)$ often simplifies the calculations. In particular, we only have to obtain these eigenfunctions for positive values of x, and we know that odd functions vanish at the origin, while even functions must have zero slope at $x = 0$. This is apparent in the case of the infinite square well, and will again be illustrated below in our study of the finite square well and the linear harmonic oscillator.

Wave function regeneration

The general solution of the time-dependent Schrödinger equation (4.1) for a particle in the infinite square well (4.86) is given by

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) \exp(-\mathrm{i}E_n t/\hbar) \tag{4.105}$$

where the energy eigenvalues E_n are given by (4.95), and the corresponding eigenfunctions are given by (4.93) for n odd and (4.94) for n even. The constants c_n can be determined from the knowledge of the wave function $\Psi(x, t)$ at any particular time t_0. Following the procedure leading to (3.154), and setting $t_0 = 0$, we have

$$c_n = \int_{-a}^{+a} \psi_n^*(x)\Psi(x, t = 0)\mathrm{d}x \tag{4.106}$$

where we have used the normalisation condition (4.92) and the orthogonality relation (4.96).

As the time passes, the form of the wave packet $\Psi(x, t)$ changes. However, we shall now show that at the time $t = T$, where $T = 2\pi\hbar/E_1$, the wave packet is regenerated, so that

$$\Psi(x, t = T) = \Psi(x, t = 0). \tag{4.107}$$

Indeed, from (4.105), and since $E_n = n^2 E_1$, we have

$$\begin{aligned}\Psi(x, t = T) &= \sum_{n=1}^{\infty} c_n \psi_n(x) \exp\left(-\mathrm{i}n^2 E_1 \frac{2\pi}{E_1}\right) \\ &= \sum_{n=1}^{\infty} c_n \psi_n(x) \exp(-\mathrm{i}2\pi n^2).\end{aligned} \tag{4.108}$$

Since $2n^2$ is an even integer, it follows that $\exp(-\mathrm{i}2\pi n^2) = 1$, and hence

$$\Psi(x, t = T) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \Psi(x, t = 0). \tag{4.109}$$

By repeating this argument, we see that the wave function is completely regenerated at times sT, where $s = 1, 2, 3, \ldots$ is a positive integer.

Another interesting feature of the infinite square well wave function is that

$$\Psi(x, t = (2s - 1)T/2) = -\Psi(-x, t = 0) \tag{4.110}$$

which means that the wave function at times $(2s - 1)T/2$ is a reflection of that at $t = 0$ through the origin. To prove this, we note that

$$\Psi(x, t = (2s - 1)T/2) = \sum_{n=1}^{\infty} c_n \psi_n(x) \exp[-\mathrm{i}\pi n^2(2s - 1)]. \tag{4.111}$$

When n is odd, n^2 is odd and $\exp[-\mathrm{i}\pi n^2(2s - 1)] = -1$. On the other hand, when n is even, n^2 is even and $\exp[-\mathrm{i}\pi n^2(2s - 1)] = 1$. Thus

$$\Psi(x, t = (2s - 1)T/2) = \sum_{n=1}^{\infty} c_n(-1)^n \psi_n(x). \tag{4.112}$$

Since $\psi_n(x) = \psi_n(-x)$ when n is odd, and $\psi_n(x) = -\psi_n(-x)$ when n is even, the result (4.110) follows.

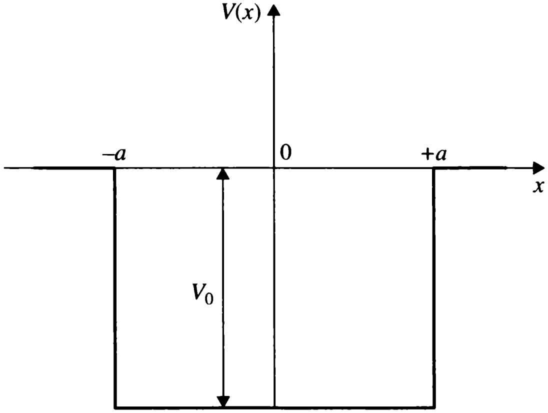


Figure 4.11 The one-dimensional square well potential (4.113) of depth V_0 and range a.

4.6 The square well

Let us now consider the square (or rectangular) well potential such that

$$V(x) = \begin{cases} -V_0, & |x| < a \\ 0, & |x| > a \end{cases} \tag{4.113}$$

where the positive constant V_0 is the depth of the well and a is its range. This potential is illustrated in Fig. 4.11. As in the case of the infinite square well studied in the preceding section, we have chosen the origin of the x-axis at the centre of the well, so that the potential is symmetric about $x = 0$. Two cases must be distinguished, corresponding respectively to positive or negative values of the energy E. When $E > 0$ the particle is *unconfined*; the corresponding *scattering* problem will be analysed later. The case $E < 0$ corresponds to a particle which is *confined* and hence is in a *bound state*; it is this situation which we shall study first.

Case 1: $E < 0$

Since the energy E cannot be lower than the absolute minimum of the potential, we must have $-V_0 \leqslant E < 0$. Inside the well the Schrödinger equation (4.3) reads

$$\frac{d^2\psi(x)}{dx^2} + \alpha^2\psi(x) = 0, \qquad \alpha = \left[\frac{2m}{\hbar^2}(V_0 + E)\right]^{1/2} = \left[\frac{2m}{\hbar^2}(V_0 - |E|)\right]^{1/2}, \qquad |x| < a \tag{4.114a}$$

and outside the well it can be written as

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} - \beta^2\psi(x) = 0, \quad \beta = \left(-\frac{2m}{\hbar^2}E\right)^{1/2} = \left(\frac{2m}{\hbar^2}|E|\right)^{1/2}, \quad |x| > a \tag{4.114b}$$

where we have introduced the *binding energy* $|E| = -E$ of the particle.

The potential being an even function of x, we know that the solutions have definite parity, and hence are determined by positive values of x. The *even* solutions of equations (4.114) are given for $x > 0$, by

$$\psi(x) = A\cos\alpha x, \qquad 0 < x < a \tag{4.115a}$$

and

$$\psi(x) = C\mathrm{e}^{-\beta x}, \qquad x > a. \tag{4.115b}$$

In writing this last equation we have taken into account the fact that the wave function cannot contain a term like $D\exp(\beta x)$, which would become infinite when $x \to +\infty$; we must therefore set $D = 0$. The requirements that ψ and $\mathrm{d}\psi/\mathrm{d}x$ be continuous at $x = a$ yield the two equations

$$A\cos\alpha a = C\mathrm{e}^{-\beta a} \tag{4.116a}$$

$$-\alpha A\sin\alpha a = -\beta C\mathrm{e}^{-\beta a} \tag{4.116b}$$

from which we deduce that

$$\alpha\tan\alpha a = \beta. \tag{4.117}$$

Note that instead of requiring both ψ and $\mathrm{d}\psi/\mathrm{d}x$ to be continuous at $x = a$, we may simply ask that the *logarithmic derivative* of the wave function, $\psi^{-1}(\mathrm{d}\psi/\mathrm{d}x)$, be *continuous* at $x = a$. Indeed, this condition yields directly equation (4.117), since the normalisation constants A and C disappear by taking the ratio $\psi^{-1}(\mathrm{d}\psi/\mathrm{d}x)$. The requirement of continuity for the logarithmic derivative is therefore a simple way of expressing the conditions of smooth joining.

The *odd* solutions of equations (4.114) are given for positive x by

$$\psi(x) = B\sin\alpha x, \qquad 0 < x < a \tag{4.118a}$$

and

$$\psi(x) = C\mathrm{e}^{-\beta x}, \qquad x > a. \tag{4.118b}$$

By requiring that $\psi^{-1}(\mathrm{d}\psi/\mathrm{d}x)$ be continuous at $x = a$ we obtain the equation

$$\alpha\cot\alpha a = -\beta. \tag{4.119}$$

The *energy levels* of the bound states are found by solving the transcendental equations (4.117) and (4.119), either numerically or graphically. We shall use here a simple graphical procedure to obtain the allowed values of the energy. We first introduce the dimensionless quantities $\xi = \alpha a$ and $\eta = \beta a$, so that the equations to be solved are

$$\xi \tan \xi = \eta \qquad \text{(for even states)} \tag{4.120a}$$

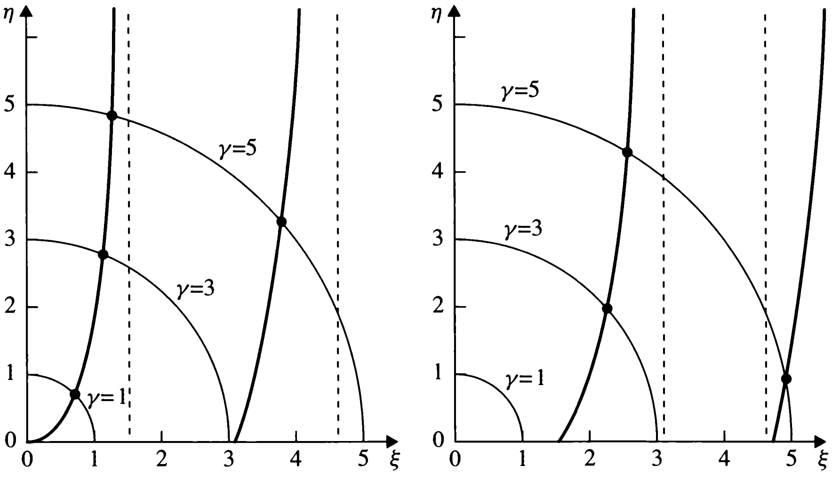
$$\xi \cot \xi = -\eta \qquad \text{(for odd states).} \tag{4.120b}$$

Note that both ξ and η must be positive, and such that

$$\xi^2 + \eta^2 = \gamma^2 \tag{4.121}$$

where $\gamma = (2mV_0 a^2/\hbar^2)^{1/2}$. The energy levels may therefore be found by determining the points of intersection of the circle $\xi^2 + \eta^2 = \gamma^2$, of known radius γ, with the curve $\eta = \xi \tan \xi$ (for even states), or with the curve $\eta = -\xi \cot \xi$ (for odd states). This is illustrated in Fig. 4.12(a) for even states and in Fig. 4.12(b) for odd states. Several conclusions can be deduced from these figures by inspection. First, the bound-state energy levels are seen to be *non-degenerate*, as expected since we are dealing with a one-dimensional problem. Second, their number is *finite* and depends on the dimensionless parameter γ, which may be called the 'strength parameter' of the potential. Note that for a fixed value of the mass m of the particle, γ depends on the parameters of the square well through the combination $V_0 a^2$. In particular, we see from Fig. 4.12(a) that if $0 < \gamma \leqslant \pi$ there is one even bound state, while if $\pi < \gamma \leqslant 2\pi$ there are two such bound states. More generally, it is clear that there will be N_e even-parity bound states if $(N_e - 1)\pi < \gamma \leqslant N_e \pi$. On the other hand, we note from Fig. 4.12(b) that if $0 < \gamma \leqslant \pi/2$, there is no bound state of odd parity, while if $\pi/2 < \gamma \leqslant 3\pi/2$, there is one such bound state. More generally, there are N_0 odd parity bound states if $(N_0 - 1/2)\pi < \gamma \leqslant (N_0 + 1/2)\pi$. This brings us to our third conclusion, namely that as the strength parameter γ increases, energy levels corresponding respectively to even and odd solutions appear successively (see Fig. 4.13), the total number of bound states being equal to N, if $(N - 1)\pi/2 < \gamma \leqslant N\pi/2$. Hence the bound-state spectrum consists of *alternating even and odd states*, the ground state being always even, the next state odd, and so on.

Having solved the equations (4.120) to determine the bound-state energy levels, we can readily obtain explicitly the corresponding normalised eigenfunctions from equations (4.115) (for even states) and (4.118) (for odd states). As an example, we illustrate in Fig. 4.14 the four energy eigenfunctions of a square well for which $\gamma = 5$. The corresponding eigenenergies are found to be given respectively by $E_1 = -0.93V_0$, $E_2 = -0.73V_0$, $E_3 = -0.41V_0$ and $E_4 = -0.04V_0$. The eigenfunctions $\psi_1(x)$ and $\psi_3(x)$ are seen to be even, while $\psi_2(x)$ and $\psi_4(x)$ are odd, as expected from the foregoing discussion. Moreover, the nth eigenfunction has $(n - 1)$ nodes, in agreement with the oscillation theorem (see Section 3.7). It is worth stressing that the eigenfunctions extend into the classically forbidden region $|x| > a$. In fact, we see from (4.115b) and (4.118b) that in this region the eigenfunctions fall off like $\exp(-\beta|x|)$, so that they extend to a distance given roughly by $\beta^{-1} = \hbar/(2m|E|)^{1/2}$ which increases as the binding energy $|E|$ of the particle decreases.



(a) (b)

Figure 4.12 Graphical determination of the energy levels for a one-dimensional square well potential (a) for even states and (b) for odd states. The energy levels are obtained by finding the points of intersection of the circle $\xi^2 + \eta^2 = \gamma^2$, of known radius $\gamma = (2mV_0a^2/\hbar^2)^{1/2}$ with the curve $\eta = \xi \tan \xi$ (for even states), or with the curve $\eta = -\xi \cot \xi$ (for odd states). The graphical solution of equations (4.120) is illustrated for three values of γ. When $\gamma = 1$ there is one (even) bound state, when $\gamma = 3$ there are two bound states (one even, one odd) and when $\gamma = 5$ there are four bound states (two even, two odd). The asymptotes are indicated by vertical dashed lines.

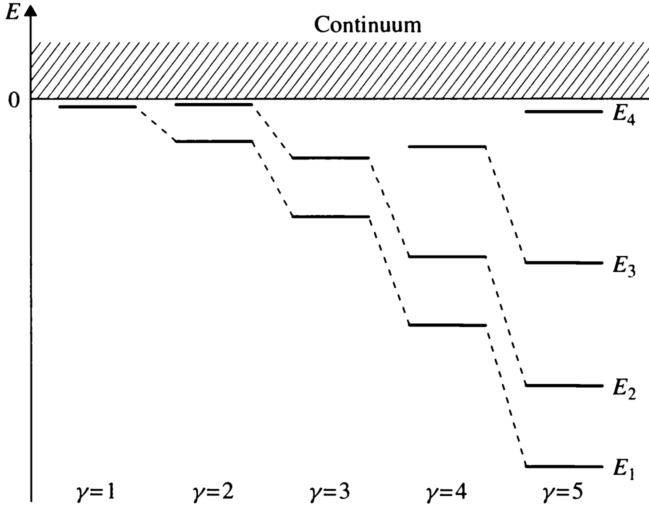


Figure 4.13 The energy level spectra for one-dimensional square wells of various depths V_0. The value of the strength parameter $\gamma = (2mV_0a^2/\hbar^2)^{1/2}$ corresponding to each energy level spectrum is indicated. The energy levels E_1 and E_3 correspond to even solutions, while E_2 and E_4 correspond to odd solutions.

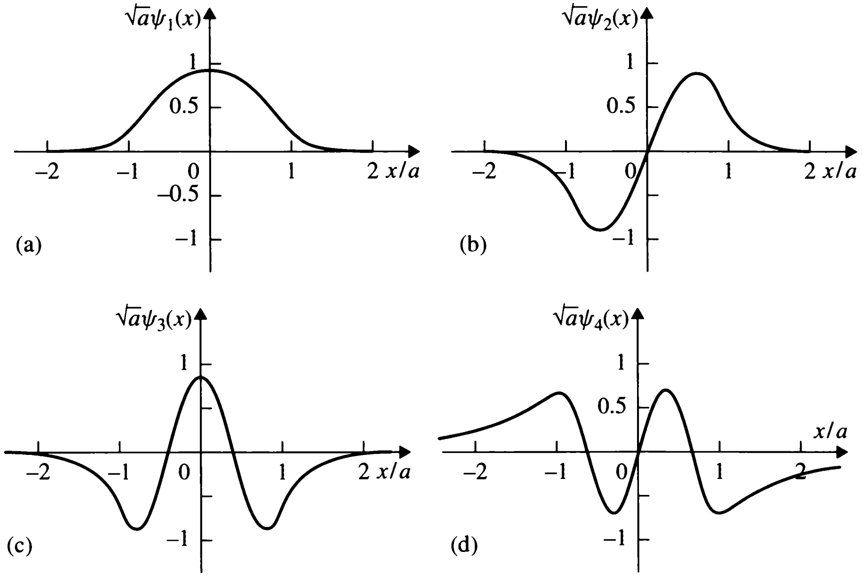


Figure 4.14 The four energy eigenfunctions of a one-dimensional square well potential such that $\gamma = 5$.

Finally, let us examine the limiting case of an infinitely deep square well, for which $V_0 \to \infty$ (so that $\gamma \to \infty$). In order to make contact with the results of Section 4.5, it is convenient to start from a slightly different finite square well, such that $V(x) = 0$ for $|x| < a$ and $V(x) = V_0$ for $|x| > a$. This corresponds to making an upward shift of the zero of the energies by an amount V_0. As we know (Problem 3.8), such a shift has the effect of adding the constant V_0 to all the energy eigenvalues, and leaves the corresponding eigenfunctions unchanged. Thus the bound states occur for $0 \leqslant E < V_0$; they are still determined by the transcendental equations (4.117) (for even states) and (4.119) (for odd states), where now $\alpha = (2mE/\hbar^2)^{1/2}$ and $\beta = [2m(V_0 - E)/\hbar^2]^{1/2}$. When $V_0 \to \infty$, it is apparent that the roots of equations (4.120) will be given by

$$\xi_n = n\frac{\pi}{2}, \qquad n = 1, 2, \ldots \tag{4.122}$$

and since $\xi = \alpha a = (2mE/\hbar^2)^{1/2}a$, the corresponding energy eigenvalues are

$$E_n = \frac{\hbar^2}{8m}\frac{\pi^2 n^2}{a^2} \tag{4.123}$$

in agreement with the result (4.95). Moreover, since $\beta \to \infty$ when $V_0 \to \infty$, the eigenfunctions (4.115) and (4.118) then vanish for $|x| \geqslant a$, as we found in Section 4.5 for the infinite square well.

Case 2: $E > 0$

Let us return to the square well (4.113), and consider the case of positive energies, so that the particle is not bound. Assuming that the particle is incident upon the well from the left, the solution of the Schrödinger equation (4.3) in the *external regions* $x < -a$ and $x > a$ is given by

$$\psi(x) = \begin{cases} A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}, & x < -a \qquad \textbf{(4.124a)} \\ C\mathrm{e}^{\mathrm{i}kx}, & x > a \qquad \textbf{(4.124b)} \end{cases}$$

where $k = (2mE/\hbar^2)^{1/2}$, A, B, C are constants, and we have used the fact that there is no reflector at large positive values of x (so that there is no term of the form $\exp(-\mathrm{i}kx)$ in (4.124b)). In the region $x < -a$ the wave function is seen to consist of an *incident wave* of amplitude A and a *reflected wave* of amplitude B, while in the region $x > a$ it is a pure *transmitted wave* of amplitude C. In the *internal region* $-a < x < a$, the solution of the Schrödinger equation is

$$\psi(x) = F\mathrm{e}^{\mathrm{i}\alpha x} + G\mathrm{e}^{-\mathrm{i}\alpha x} \qquad \textbf{(4.125)}$$

where $\alpha = [2m(V_0 + E)/\hbar^2]^{1/2}$.

Looking back at equations (4.74) and (4.84), we see that the present problem of scattering by a square well is closely related to the scattering by a potential barrier (with $E > V_0$) which was studied in Section 4.4. We shall therefore only outline the solution here, leaving the details of the calculations as an exercise (Problem 4.9). It is worth noting that in one-dimensional scattering problems there is a lack of symmetry between the external regions to the left and to the right of the potential, since the particle is assumed to be incident on the potential in a given direction. Hence in this case there is no advantage in dealing with solutions having a definite parity.

The five constants A, B, C, F and G appearing in (4.124) and (4.125) can be related by requiring that the wave function $\psi(x)$ and its derivative $\mathrm{d}\psi(x)/\mathrm{d}x$ be continuous at $x = \pm a$. This smooth joining of the external and internal solutions can be done for any positive value of E, so that the spectrum is *continuous* for $E > 0$. After eliminating F and G, one can solve for the ratios B/A and C/A and obtain the *reflection coefficient* $R = |B/A|^2$ and the *transmission coefficient* $T = |C/A|^2$. These are given by

$$R = \left[1 + \frac{4k^2\alpha^2}{(k^2 - \alpha^2)^2 \sin^2(\alpha L)}\right]^{-1} = \left[1 + \frac{4E(V_0 + E)}{V_0^2 \sin^2(\alpha L)}\right]^{-1} \qquad \textbf{(4.126a)}$$

and

$$T = \left[1 + \frac{(k^2 - \alpha^2)^2 \sin^2(\alpha L)}{4k^2\alpha^2}\right]^{-1} = \left[1 + \frac{V_0^2 \sin^2(\alpha L)}{4E(V_0 + E)}\right]^{-1} \qquad \textbf{(4.126b)}$$

where we have written $L = 2a$. We have, of course, $R + T = 1$. We also remark that the above results may be obtained from the corresponding ones given in (4.85) for the potential barrier by making the obvious substitutions $V_0 \to -V_0$, $k' \to \alpha$ and

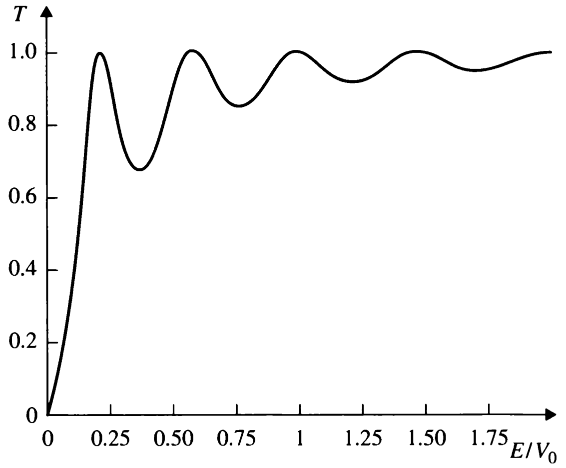


Figure 4.15 The transmission coefficient for a square well potential such that $\gamma = 10$, as a function of the ratio E / V_0.

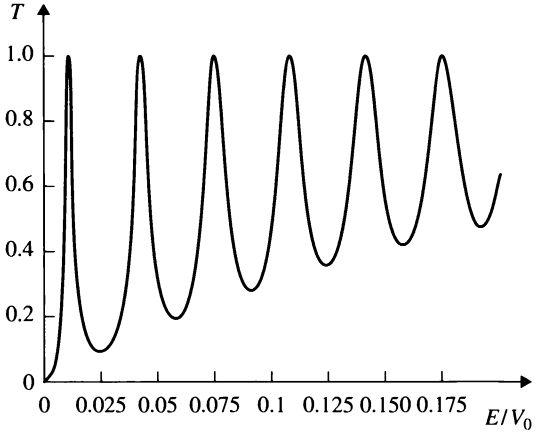


Figure 4.16 The transmission coefficient for a strong square well potential such that $\gamma = 100$, as a function of the ratio E / V_0.

$a \to L$ (we recall that the thickness of the potential barrier considered in Section 4.4 was denoted by a, while here the corresponding quantity is called L).

An important point about the results (4.126) is again that the transmission coefficient T is in general less than unity, in contradiction to the classical prediction according to which the particle should always be transmitted. The behaviour of T as a function of the energy E is readily deduced from (4.126b). We see that $T = 0$ when $E = 0$. As E increases, T rises and then fluctuates between its maximum value ($T = 1$) reached when $\alpha L = n\pi (n = 1, 2, \dots)$ and minima near $\alpha L = (2n+1)\pi/2$. Note that, as in the case of the potential barrier, perfect transmission occurs when the thickness L is equal to an integral or half-integral number of de Broglie wavelengths $(2\pi/\alpha)$ in the internal region. Finally, when E is large compared with V_0, the transmission coefficient becomes asymptotically equal to unity. This is illustrated in Fig. 4.15, where T is plotted as a function of E/V_0 for a square well whose strength parameter is $\gamma = 10$.

The case of a particle of low energy scattered by a very strong well is of particular interest. Using (4.126b) we see that the transmission coefficient is then small almost everywhere, except for a series of *sharp maxima* (where $T = 1$), which are reached when the condition $\alpha L = n\pi$ is obeyed. Such pronounced peaks in the transmission coefficient are said to represent *resonances*; they are clearly typical of the wave-like behaviour of the particle, and are illustrated in Fig. 4.16 for a square well such that $\gamma = 100$.

4.7 The linear harmonic oscillator

We shall now study the one-dimensional motion of a particle of mass m which is attracted to a fixed centre by a force proportional to the displacement from that centre. Thus, choosing the origin as the centre of force, the restoring force is given by $F = -kx$ (Hooke's law), where k is the force constant. This force can thus be represented by the potential energy

$$V(x) = \tfrac{1}{2}kx^2 \tag{4.127}$$

which is shown in Fig. 4.17(a). Such a parabolic potential is of great importance in quantum physics as well as in classical physics, since it can be used to approximate an arbitrary continuous potential $W(x)$ in the vicinity of a stable equilibrium position at $x = a$ (see Fig. 4.17(b)). Indeed, if we expand $W(x)$ in a Taylor series about $x = a$, we have

$$W(x) = W(a) + (x-a)W'(a) + \tfrac{1}{2}(x-a)^2W''(a) + \cdots \tag{4.128a}$$

with

$$W'(a) = \left(\frac{\mathrm{d}W(x)}{\mathrm{d}x}\right)_{x=a}, \qquad W''(a) = \left(\frac{\mathrm{d}^2W(x)}{\mathrm{d}x^2}\right)_{x=a}. \tag{4.128b}$$

Because $W(x)$ has a minimum at $x = a$ we have $W'(a) = 0$ and $W''(a) > 0$. Choosing a as the origin of coordinates and $W(a)$ as the origin of the energy scale, we see that the harmonic oscillator potential (4.127) (with $k = W''(a)$) is the first approximation to $W(x)$. The linear harmonic oscillator is therefore the prototype for systems in which there exist small vibrations about a point of stable equilibrium. This will be illustrated in Chapter 10 for the case of the vibrational motion of nuclei in molecules.

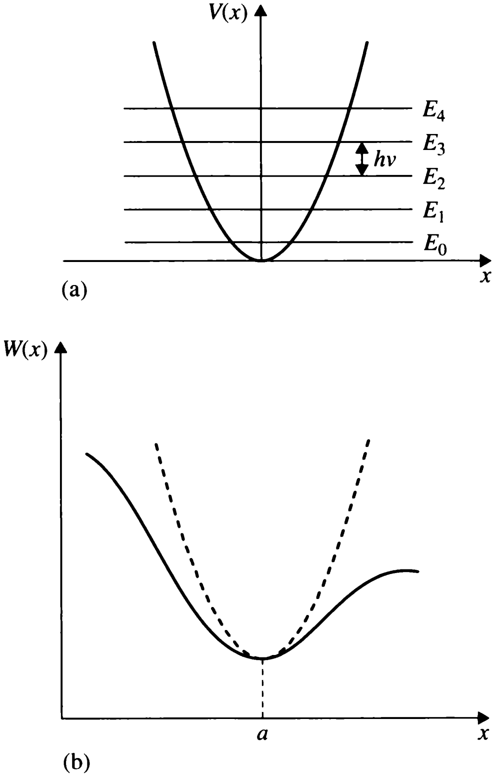


Figure 4.17 (a) The parabolic potential well $V(x) = \frac{1}{2}kx^2$. This is the potential of the linear harmonic oscillator. Also shown are the first few energy eigenvalues (4.151). (b) A continuous potential well $W(x)$, represented by the solid line can be approximated in the vicinity of a stable equilibrium position at $x = a$ by a linear harmonic oscillator potential, shown as the dashed line.

As the potential energy for a linear harmonic oscillator is given by (4.127), the corresponding Hamiltonian operator is

$$H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}kx^2 \tag{4.129}$$

and the Schrödinger eigenvalue equation reads

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x). \tag{4.130}$$

Clearly, all eigenfunctions correspond to bound states of positive energy. It is convenient to rewrite (4.130) in terms of dimensionless quantities. To this end we first introduce the dimensionless eigenvalues

$$\lambda = \frac{2E}{\hbar\omega} \tag{4.131}$$

where

$$\omega = \left(\frac{k}{m}\right)^{1/2} \tag{4.132}$$

is the angular frequency of the corresponding classical oscillator. We shall also use the dimensionless variable

$$\xi = \alpha x \tag{4.133}$$

where

$$\alpha = \left(\frac{mk}{\hbar^2}\right)^{1/4} = \left(\frac{m\omega}{\hbar}\right)^{1/2} \tag{4.134}$$

The Schrödinger equation (4.130) then becomes

$$\frac{\mathrm{d}^2\psi(\xi)}{\mathrm{d}\xi^2} + (\lambda - \xi^2)\psi(\xi) = 0. \tag{4.135}$$

Let us first analyse the behaviour of ψ in the asymptotic region $|\xi| \to \infty$. For any finite value of the total energy E the quantity λ becomes negligible with respect to ξ^2 in the limit $|\xi| \to \infty$, so that in this limit equation (4.135) reduces to

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\xi^2} - \xi^2\right)\psi(\xi) = 0. \tag{4.136}$$

For large enough $|\xi|$ it is readily verified that the functions

$$\psi(\xi) = \xi^p \mathrm{e}^{\pm\xi^2/2} \tag{4.137}$$

satisfy the equation (4.136) so far as the leading terms (which are of order $\xi^2\psi$) are concerned, when p has any finite value. Because the wave function ψ must be bounded everywhere, including at $\xi = \pm\infty$, the physically acceptable solution must contain only the minus sign in the exponent. The asymptotic analysis therefore suggests looking for solutions to equation (4.135) which are valid for all ξ having the form

$$\psi(\xi) = \mathrm{e}^{-\xi^2/2}H(\xi) \tag{4.138}$$

where $H(\xi)$ are functions which must not affect the asymptotic behaviour of ψ. Substituting (4.138) into (4.135) we obtain for $H(\xi)$ the differential equation

$$\frac{\mathrm{d}^2H}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}H}{\mathrm{d}\xi} + (\lambda - 1)H = 0 \tag{4.139}$$

which is called the *Hermite equation*.

In order to solve this equation, let us expand $H(\xi)$ in a power series in ξ. Since the harmonic oscillator potential (4.127) is such that $V(-x) = V(x)$, we know from our discussion of Section 4.5 that the eigenfunctions $\psi(x)$ of the Schrödinger equation (4.130) must have a definite parity. We shall therefore consider separately the even and odd states.

Even states

For these states we have $\psi(-\xi) = \psi(\xi)$ and also, therefore, $H(-\xi) = H(\xi)$, so that we can write for $H(\xi)$ the power series

$$H(\xi) = \sum_{k=0}^{\infty} c_k \xi^{2k}, \qquad c_0 \neq 0 \tag{4.140}$$

which contains only *even* powers of ξ. Substituting (4.140) into the Hermite equation (4.139), we find that

$$\sum_{k=0}^{\infty} [2k(2k-1)c_k\xi^{2(k-1)} + (\lambda - 1 - 4k)c_k\xi^{2k}] = 0 \tag{4.141}$$

or

$$\sum_{k=0}^{\infty} [2(k+1)(2k+1)c_{k+1} + (\lambda - 1 - 4k)c_k]\xi^{2k} = 0. \tag{4.142}$$

This equation will be satisfied provided the coefficient of each power of ξ separately vanishes, so that we obtain the *recursion relation*

$$c_{k+1} = \frac{4k + 1 - \lambda}{2(k+1)(2k+1)} c_k. \tag{4.143}$$

Thus, given $c_0 \neq 0$, all the coefficients c_k can be determined successively by using the above equation. We have therefore obtained a series representation of the even solution (4.140) of the Hermite equation.

If this series does not terminate, we see from (4.143) that for large k

$$\frac{c_{k+1}}{c_k} \sim \frac{1}{k}. \tag{4.144}$$

This ratio is the same as that of the series for $\xi^{2p}\exp(\xi^2)$, where p has a finite value. Using (4.138), we then find that the wave function $\psi(\xi)$ has an asymptotic behaviour of the form

$$\psi(\xi) \underset{|\xi| \to \infty}{\sim} \xi^{2p} e^{\xi^2/2} \tag{4.145}$$

which is obviously unacceptable. The only way to avoid this divergence of $\psi(\xi)$ at large $|\xi|$ is to require that the series (4.140) *terminates*, which means that $H(\xi)$ must be a *polynomial* in the variable ξ^2. Let the highest power of ξ^2 appearing in this polynomial be ξ^{2N}, where $N = 0, 1, 2, \ldots,$ is a positive integer or zero. Thus in (4.140) we have $c_N \neq 0$, while the coefficient c_{N+1} must vanish. Using the recursion relation (4.143) we see that this will happen if and only if λ takes on the discrete values

$$\lambda = 4N + 1, \qquad N = 0, 1, 2, \ldots. \tag{4.146}$$

To each value $N = 0, 1, 2, \ldots,$ of N will then correspond an even function $H(\xi)$ which is a polynomial of order $2N$ in ξ, and an even, physically acceptable, wave function $\psi(\xi)$ which is given by (4.138).

Odd states

In this case we have $\psi(-\xi) = -\psi(\xi)$, and hence $H(-\xi) = -H(\xi)$. Thus we begin by writing for $H(\xi)$ the power series

$$H(\xi) = \sum_{k=0}^{\infty} d_k \xi^{2k+1}, \qquad d_0 \neq 0 \tag{4.147}$$

which contains only *odd* powers of ξ. Substituting (4.147) into the Hermite equation (4.139), we obtain for the coefficients d_k the recursion relation

$$d_{k+1} = \frac{4k+3-\lambda}{2(k+1)(2k+3)} d_k. \tag{4.148}$$

For large k we have $d_{k+1}/d_k \sim k^{-1}$, so that the wave function $\psi(\xi)$, given by (4.138), will again diverge at large $|\xi|$ unless the series (4.147) for $H(\xi)$ terminates. Let the highest power of ξ in (4.147) be ξ^{2N+1}, where $N = 0, 1, 2, \dots$. Since $d_N \neq 0$, while d_{N+1} is required to vanish, we see from the recursion relation (4.148) that λ must take one of the discrete values

$$\lambda = 4N + 3, \qquad N = 0, 1, 2, \dots. \tag{4.149}$$

To each value $N = 0, 1, 2, \dots$, of N will then correspond an odd function $H(\xi)$ which is a polynomial of order $2N + 1$ in ξ, and an odd, physically acceptable wave function $\psi(\xi)$ given by (4.138).

Energy levels

Putting together the results which we have obtained for the even and odd cases, we see from (4.146) and (4.149) that the eigenvalue λ must take on one of the discrete values

$$\lambda = 2n + 1, \qquad n = 0, 1, 2, \dots \tag{4.150}$$

where the quantum number n is a positive integer or zero. Using (4.131) we therefore find that the energy spectrum of the linear harmonic oscillator is given by

$$\begin{aligned} E_n &= \left(n + \tfrac{1}{2}\right)\hbar\omega = \left(n + \tfrac{1}{2}\right)h\nu, \\ & \qquad\qquad n = 0, 1, 2, \dots \end{aligned} \tag{4.151}$$

where $\nu = \omega/2\pi$ is the frequency of the corresponding classical oscillator.

In contrast with classical mechanics, which predicts that the energy E of a linear harmonic oscillator can have any value, we see from (4.151) that its quantum mechanical energy spectrum consists of an infinite sequence of *discrete* levels (see Fig. 4.17(a)). For any finite eigenvalue (4.151) the particle is *bound*. The energy levels (4.151) are equally spaced and are similar to those discovered in 1900 by Planck for the radiation field modes (see Section 1.1). This is due to the fact that a decomposition of the electromagnetic field into normal modes is essentially a decomposition into uncoupled harmonic oscillators. We notice, however, that according to (4.151) the linear harmonic oscillator even in its lowest state ($n = 0$), has the energy $\hbar\omega/2$. The finite value $\hbar\omega/2$ of the ground-state energy level, which is called the *zero-point energy* of the linear harmonic oscillator, is clearly also a quantum phenomenon. As in the case of the infinite square well discussed in Section 4.5, the existence of this zero-point energy is directly related to the uncertainty principle (see Problem 4.12). In classical mechanics the lowest possible energy of the oscillator would of course be zero, corresponding to the particle being at rest at the origin, but in quantum mechanics this is forbidden by the uncertainty relation (2.70). We also remark that the eigenvalues (4.151) are *non-degenerate*, since for each value of the quantum number n there exists only one eigenfunction (apart from an arbitrary multiplicative constant); this is in agreement with the observation, already made, that one-dimensional bound states are non-degenerate.

Hermite polynomials

Let us now return to the wave functions $\psi(\xi)$. Using (4.138) and collecting our results for both even and odd cases, we see that the physically acceptable solutions of equation (4.135), corresponding to the eigenvalues (4.150), are given by

$$\psi_n(\xi) = \mathrm{e}^{-\xi^2/2} H_n(\xi) \tag{4.152}$$

where the functions $H_n(\xi)$ are polynomials of order n. Both $\psi_n(\xi)$ and $H_n(\xi)$ have the parity of n. Moreover, the polynomials $H_n(\xi)$ satisfy the Hermite equation (4.139) with $\lambda = 2n + 1$, namely

$$\frac{\mathrm{d}^2 H_n}{\mathrm{d}\xi^2} - 2\xi \frac{\mathrm{d}H_n}{\mathrm{d}\xi} + 2nH_n = 0. \tag{4.153}$$

The polynomials $H_n(\xi)$ are called *Hermite polynomials*. It is clear from the foregoing discussion that they are uniquely defined, except for an arbitrary multiplicative constant. This constant is traditionally chosen so that the highest power of ξ appears with the coefficient 2^n in $H_n(\xi)$. This is consistent with the following definition of the Hermite polynomials:

$$H_n(\xi) = (-1)^n \mathrm{e}^{\xi^2} \frac{\mathrm{d}^n \mathrm{e}^{-\xi^2}}{\mathrm{d}\xi^n} \tag{4.154a}$$

$$= \mathrm{e}^{\xi^2/2} \left(\xi - \frac{\mathrm{d}}{\mathrm{d}\xi} \right)^n \mathrm{e}^{-\xi^2/2}. \tag{4.154b}$$

The first few Hermite polynomials, obtained from (4.154), are

$$\begin{aligned}
H_0(\xi) &= 1 \\
H_1(\xi) &= 2\xi \\
H_2(\xi) &= 4\xi^2 - 2 \\
H_3(\xi) &= 8\xi^3 - 12\xi \\
H_4(\xi) &= 16\xi^4 - 48\xi^2 + 12 \\
H_5(\xi) &= 32\xi^5 - 160\xi^3 + 120\xi.
\end{aligned} \tag{4.155}$$

Note that the definition (4.154) implies that $H_n(\xi)$ has n real zeros.

Another definition of the Hermite polynomials $H_n(\xi)$, which is equivalent to (4.154) involves the use of a *generating function* $G(\xi, s)$. That is

$$G(\xi, s) = \mathrm{e}^{-s^2+2s\xi} \tag{4.156a}$$

$$= \sum_{n=0}^{\infty} \frac{H_n(\xi)}{n!} s^n. \tag{4.156b}$$

These relations mean that if the function $\exp(-s^2+2s\xi)$ is expanded in a power series in s, the coefficients of successive powers of s are just $1/n!$ times the Hermite polynomials $H_n(\xi)$. Using equations (4.156) it is straightforward to prove (Problem 4.13) that the Hermite polynomials satisfy the recursion relations

$$H_{n+1}(\xi) - 2\xi H_n(\xi) + 2nH_{n-1}(\xi) = 0 \tag{4.157}$$

and

$$\frac{\mathrm{d}H_n(\xi)}{\mathrm{d}\xi} = 2nH_{n-1}(\xi). \tag{4.158}$$

The lowest-order differential equation for H_n which can be constructed from these two recursion relations is then readily seen to be the equation (4.153) satisfied by the Hermite polynomials. Moreover, the equivalence of the two definitions (4.154) and (4.156) of the Hermite polynomials can be proved by using both expressions for $G(\xi, s)$ given in (4.156), differentiating n times with respect to s, and then letting s tend to zero (Problem 4.14).

The wave functions for the linear harmonic oscillator

Using (4.152), we see that to each of the discrete values E_n of the energy, given by (4.151), there corresponds one, and only one, physically acceptable eigenfunction, namely

$$\psi_n(x) = N_n \mathrm{e}^{-\alpha^2 x^2/2} H_n(\alpha x) \tag{4.159}$$

where we have returned to our original variable x. Both $H_n(\alpha x)$ and $\psi_n(x)$ have the parity of n and have n real zeros. The quantity N_n, written on the right of (4.159) is a constant which (apart from an arbitrary phase factor) can be determined by requiring that the wave function (4.159) be normalised to unity. That is

$$\int_{-\infty}^{+\infty} |\psi_n(x)|^2 \mathrm{d}x = \frac{|N_n|^2}{\alpha} \int_{-\infty}^{+\infty} \mathrm{e}^{-\xi^2} H_n^2(\xi) \mathrm{d}\xi = 1. \tag{4.160}$$

In order to evaluate the integral on the right of (4.160), we consider the generating function $G(\xi, s)$ given by (4.156) as well as the second generating function

$$G(\xi, t) = \mathrm{e}^{-t^2+2t\xi}$$

$$= \sum_{m=0}^{\infty} \frac{H_m(\xi)}{m!} t^m. \tag{4.161}$$

Using (4.156) and (4.161), we may then write

$$\int_{-\infty}^{+\infty} \mathrm{e}^{-\xi^2} G(\xi, s) G(\xi, t) \mathrm{d}\xi = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{s^n t^m}{n! m!} \int_{-\infty}^{+\infty} \mathrm{e}^{-\xi^2} H_n(\xi) H_m(\xi) \mathrm{d}\xi. \quad \textbf{(4.162)}$$

Since

$$\int_{-\infty}^{+\infty} \mathrm{e}^{-x^2} \mathrm{d}x = \sqrt{\pi} \quad \textbf{(4.163)}$$

the integral on the left-hand side of (4.162) is simply

$$\begin{aligned} \int_{-\infty}^{+\infty} \mathrm{e}^{-\xi^2} \mathrm{e}^{-s^2+2s\xi} \mathrm{e}^{-t^2+2t\xi} \mathrm{d}\xi &= \mathrm{e}^{2st} \int_{-\infty}^{+\infty} \mathrm{e}^{-(\xi-s-t)^2} d(\xi - s - t) \\ &= \sqrt{\pi} \mathrm{e}^{2st} \\ &= \sqrt{\pi} \sum_{n=0}^{\infty} \frac{(2st)^n}{n!}. \end{aligned} \quad \textbf{(4.164)}$$

Equating the coefficients of equal powers of s and t on the right-hand sides of (4.162) and (4.164), we find that

$$\int_{-\infty}^{+\infty} \mathrm{e}^{-\xi^2} H_n^2(\xi) \mathrm{d}\xi = \sqrt{\pi} 2^n n! \quad \textbf{(4.165)}$$

and

$$\int_{-\infty}^{+\infty} \mathrm{e}^{-\xi^2} H_n(\xi) H_m(\xi) \mathrm{d}\xi = 0, \qquad n \neq m. \quad \textbf{(4.166)}$$

From (4.160) and (4.165) we see that apart from an arbitrary complex multiplicative factor of modulus one the normalisation constant N_n is given by

$$N_n = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} \quad \textbf{(4.167)}$$

so that the normalised linear harmonic oscillator eigenfunctions are given by

$$\psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} \mathrm{e}^{-\alpha^2 x^2/2} H_n(\alpha x). \quad \textbf{(4.168)}$$

Moreover, the result (4.166) implies that

$$\int_{-\infty}^{+\infty} \psi_n^*(x) \psi_m(x) \mathrm{d}x = 0, \qquad n \neq m \quad \textbf{(4.169)}$$

so that the (real) harmonic oscillator wave functions $\psi_n(x)$ and $\psi_m(x)$ are *orthogonal* if $n \neq m$, in agreement with the fact that they correspond to non-degenerate energy eigenvalues. We may of course summarise equations (4.160) and (4.169) by writing that the set of normalised eigenfunctions (4.168) satisfies the relations

$$\int_{-\infty}^{+\infty} \psi_n^*(x) \psi_m(x) \mathrm{d}x = \delta_{nm} \quad \textbf{(4.170)}$$

and hence is *orthonormal*.

It is worth noting at this point that other integrals involving harmonic oscillator wave functions can also be evaluated by using the generating function (4.156) of the Hermite polynomials. For example, let us consider the integral

$$x_{nm} = \int_{-\infty}^{+\infty} \psi_n^*(x) x \psi_m(x) \mathrm{d}x = \frac{N_n N_m}{\alpha^2} \int_{-\infty}^{+\infty} \mathrm{e}^{-\xi^2} \xi H_n(\xi) H_m(\xi) \mathrm{d}\xi \qquad \textbf{(4.171)}$$

which we shall need further in this book. Using again the two generating functions $G(\xi, s)$ and $G(\xi, t)$, we now look at the quantity

$$\int_{-\infty}^{+\infty} \mathrm{e}^{-\xi^2} \xi G(\xi, s) G(\xi, t) \mathrm{d}\xi = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{s^n t^m}{n! m!} \int_{-\infty}^{+\infty} \mathrm{e}^{-\xi^2} \xi H_n(\xi) H_m(\xi) \mathrm{d}\xi. \qquad \textbf{(4.172)}$$

Using the result (4.163), one finds that the integral on the left-hand side is given by

$$\begin{aligned} \int_{-\infty}^{+\infty} \mathrm{e}^{-\xi^2} \xi \mathrm{e}^{-s^2+2s\xi} \mathrm{e}^{-t^2+2t\xi} \mathrm{d}\xi &= \sqrt{\pi}(s+t)\mathrm{e}^{2st} \\ &= \sqrt{\pi} \sum_{n=0}^{\infty} \frac{2^n}{n!} (s^{n+1} t^n + s^n t^{n+1}). \end{aligned} \qquad \textbf{(4.173)}$$

Upon comparison of the coefficients of equal powers of s and t on the right-hand sides of (4.172) and (4.173), and using (4.167), we see that

$$x_{nm} = \begin{cases} 0, & m \neq n \pm 1 \\ \dfrac{1}{\alpha}\left(\dfrac{n+1}{2}\right)^{1/2}, & m = n+1 \\ \dfrac{1}{\alpha}\left(\dfrac{n}{2}\right)^{1/2}, & m = n-1. \end{cases} \qquad \textbf{(4.174)}$$

This result may also be obtained (Problem 4.15) by using the recurrence relation (4.157) together with the orthonormality relation (4.170) and the result (4.167). We remark in particular that for any harmonic oscillator wave function ψ_n the expectation value of x vanishes:

$$\langle x \rangle = x_{nn} = \int_{-\infty}^{+\infty} \psi_n^*(x) x \psi_n(x) \mathrm{d}x = 0. \qquad \textbf{(4.175)}$$

This could have been anticipated on general symmetry grounds. Indeed, the harmonic oscillator wave functions have a *definite* parity (even when n is even, odd when n is odd), so that $|\psi_n(x)|^2$ is an *even* function of x. The integrand $x|\psi_n(x)|^2$ appearing in (4.175) is therefore an *odd* function of x, so that its integral taken from $-\infty$ to $+\infty$ vanishes.

Comparison with classical theory

The eigenfunctions $\psi_n(x)$ of the linear harmonic oscillator corresponding to the four lowest eigenvalues ($n = 0$ to 3) are plotted on the left of Fig. 4.18. On the right are displayed the corresponding position probability densities $|\psi_n|^2$, together with the limits of motion for a classical oscillator having the corresponding energy E_n, and the classical probability density P_c for such an oscillator. According to classical mechanics, the position of the particle is given by $x = x_0 \sin \omega t$ (where x_0 is the amplitude of oscillation), its speed is $v = \omega x_0 \cos \omega t$, and its energy is $E = m\omega^2 x_0^2/2$. The classical motion takes place between the turning points, such that $E = V(x)$, located at $\pm x_0 = \pm(2E/m\omega^2)^{1/2}$. The probability $P_c(x)\mathrm{d}x$ that the classical particle will be found in the interval dx in a random observation is equal to the fraction of the total time spent by the particle in that interval. If $T = 2\pi/\omega$ denotes the period of oscillation, we therefore have

$$P_c(x)\mathrm{d}x = \frac{1}{T}\frac{2\mathrm{d}x}{v} = \frac{\mathrm{d}x}{\pi(x_0^2 - x^2)^{1/2}}. \tag{4.176}$$

As expected, the classical probability density $P_c(x)$ is largest in the vicinity of the turning points $\pm x_0$, where the speed of the classical particle vanishes. In terms of the reduced variable $\xi = \alpha x$ the classical turning points are located at $\pm\xi_0 = \pm\alpha x_0 = \pm\lambda^{1/2}$ (where we recall that $\lambda = 2E/\hbar\omega$), and the classical probability density is

$$P_c(\xi) = \frac{1}{\pi(\xi_0^2 - \xi^2)^{1/2}}. \tag{4.177}$$

It is clear from Fig. 4.18 that for low values of the quantum number n the quantum mechanical position probability densities $|\psi_n|^2$ are very different from the corresponding densities P_c for the classical oscillator. For example, in the case of the ground state ($n = 0$), the quantum mechanical probability density $|\psi_0|^2$ has its maximum at $x = 0$, while classically the particle is most likely to be found at the end-points of its motion, as we have seen above. As predicted on general grounds (see Section 3.6) the wave functions ψ_n curve towards the axis and have n zeros in the classically allowed region of motion. Outside that region the wave functions curve away from the axis and decrease rapidly, but there is nevertheless a finite probability of finding the particle outside the classically permitted region. As n increases the agreement between the classical and quantum mechanical probability densities improves. This is in accordance with Bohr's *correspondence principle*, and is further illustrated in Fig. 4.19, where the quantum mechanical position probability density $|\psi_n|^2$ for $n = 20$ is plotted together with the probability density P_c of the corresponding classical oscillator, having a total energy $E_{n=20} = (41/2)\hbar\omega$. Apart from the rapid fluctuations of the quantum mechanical curve, the general agreement between the classical and quantum results is seen to be quite good.

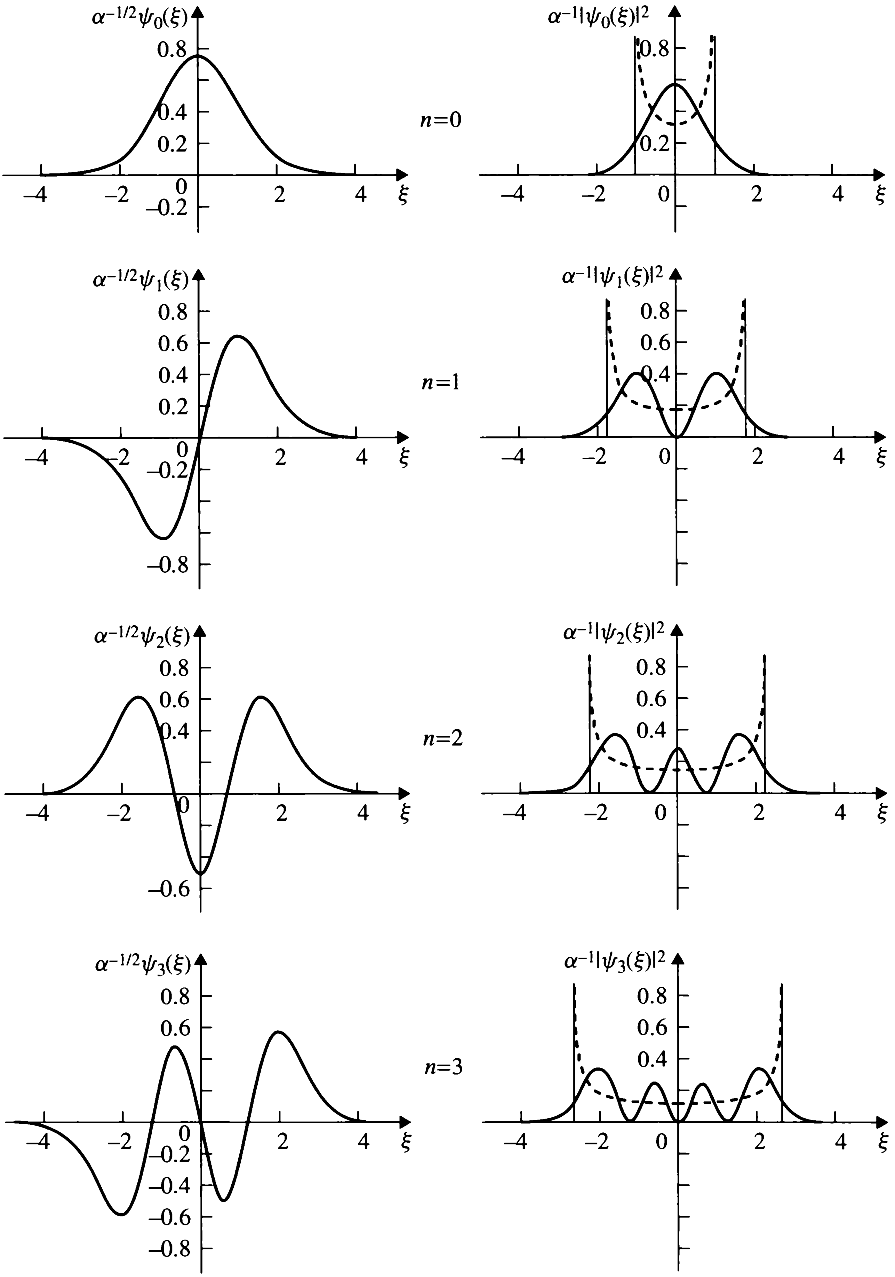


Figure 4.18 The first four energy eigenfunctions $\psi_n(\xi)$, $n = 0, 1, 2, 3$, of the linear harmonic oscillator are plotted on the left. On the right are shown the corresponding position probability densities $|\psi_n(\xi)|^2$ (solid curves), together with the limits of motion for a classical oscillator having the energy E_n, and the classical probability density $P_c(\xi)$ for such an oscillator (dashed curve).

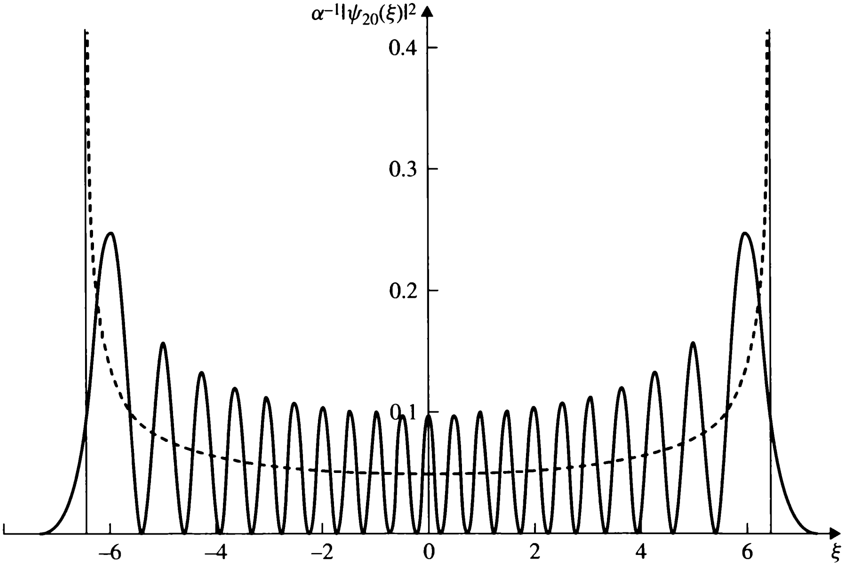


Figure 4.19 Comparison of the quantum mechanical position probability density for the state $n = 20$ of a linear harmonic oscillator (solid curve) with the probability density of the corresponding classical oscillator (dashed curve), having a total energy $E_{n=20} = (41/2)\hbar\omega$.

It is also interesting to evaluate the expectation value of the potential energy in the state ψ_n, namely

$$\begin{aligned}\langle V\rangle &= \int_{-\infty}^{+\infty} \psi_n^*(x)\frac{1}{2}kx^2\psi_n(x)\mathrm{d}x \\ &= \frac{1}{2}k\langle x^2\rangle \end{aligned} \tag{4.178}$$

where

$$\langle x^2\rangle = \int_{-\infty}^{+\infty} \psi_n^*(x)x^2\psi_n(x)\mathrm{d}x. \tag{4.179}$$

The integral on the right of this equation can be evaluated by using the generating function (4.156), or by making use of the recursion relation (4.157) in conjunction with the orthonormality relation (4.170). The result is (Problem 4.16)

$$\langle x^2\rangle = \frac{2n+1}{2\alpha^2} = \left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega} \tag{4.180}$$

so that, using (4.132), (4.178) and (4.151), we have

$$\langle V\rangle = \tfrac{1}{2}\left(n+\tfrac{1}{2}\right)\hbar\omega = \tfrac{1}{2}E_n. \tag{4.181}$$

From this result we can also deduce the average value of the kinetic energy operator $T = p_x^2/2m = -(\hbar^2/2m)\mathrm{d}^2/\mathrm{d}x^2$ in the state ψ_n. That is

$$\langle T \rangle = E_n - \langle V \rangle = \tfrac{1}{2}E_n. \tag{4.182}$$

Thus, for any harmonic oscillator eigenstate ψ_n, the average potential and kinetic energies are each equal to one-half of the total energy, as in the case of the classical oscillator.

We have seen above that $\langle x \rangle = 0$ for any harmonic oscillator eigenfunction ψ_n. By using the relation (4.158) together with the orthonormality relation (4.170), it is readily proved (Problem 4.16) that

$$\langle p_x \rangle = \int \psi_n^*(x)\left(-\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)\psi_n(x)\mathrm{d}x = 0 \tag{4.183}$$

and from (4.182) we also deduce that

$$\langle p_x^2 \rangle = 2m\langle T \rangle = mE_n = \left(n + \tfrac{1}{2}\right)m\hbar\omega. \tag{4.184}$$

4.8 The periodic potential

As our final example of one-dimensional problems, we shall consider the motion of a particle in a periodic potential of period l, so that

$$V(x + l) = V(x). \tag{4.185}$$

As an illustration we show in Fig. 4.20 a periodic potential with rectangular sections, called the *Kronig–Penney* potential, which can be used as a model of the interaction to which an electron is subjected in a crystal lattice consisting of a regular array of single atoms separated by the distance l.

Bloch waves

We shall first deduce some general consequences due to the periodicity of the potential (4.185). Although a real crystal is of course of finite length, we shall assume, as a useful idealisation, that equation (4.185) is true for all values of x, over the entire x-axis. Thus, if $\psi(x)$ is a solution of the Schrödinger equation (4.3), corresponding to the energy E, so also is $\psi(x + l)$. In addition, because the Schrödinger equation (4.3) is a second-order linear equation, any solution $\psi(x)$ may be represented as a linear combination of two linearly independent solutions $\psi_1(x)$ and $\psi_2(x)$

$$\psi(x) = c_1\psi_1(x) + c_2\psi_2(x). \tag{4.186}$$

Now $\psi_1(x + l)$ and $\psi_2(x + l)$ are also solutions of (4.3), and hence may be represented as linear combinations of $\psi_1(x)$ and $\psi_2(x)$

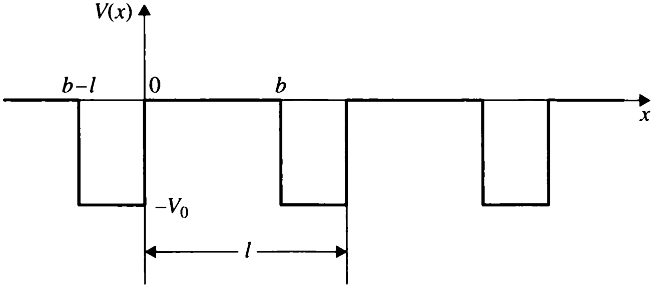


Figure 4.20 A periodic potential with rectangular sections, called the *Kronig–Penney* potential. The period has length *l*. The wells represent schematically the attraction exerted by the atoms (ions) of the crystal lattice on the electrons.

$$\begin{aligned}\psi_1(x+l) &= a_{11}\psi_1(x) + a_{12}\psi_2(x)\\ \psi_2(x+l) &= a_{21}\psi_1(x) + a_{22}\psi_2(x).\end{aligned} \tag{4.187}$$

Thus, using (4.186), (4.187) and the fact that $\psi(x+l)$ is also a solution, we may write

$$\begin{aligned}\psi(x+l) &= (c_1a_{11} + c_2a_{21})\psi_1(x) + (c_1a_{12} + c_2a_{22})\psi_2(x)\\ &= d_1\psi_1(x) + d_2\psi_2(x).\end{aligned} \tag{4.188}$$

The relation between the coefficients (c_1, c_2) and (d_1, d_2) clearly involves the matrix multiplication

$$\begin{pmatrix} d_1 \\ d_2 \end{pmatrix} = \begin{pmatrix} a_{11} & a_{21} \\ a_{12} & a_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}. \tag{4.189}$$

Let us see what happens if we diagonalise the 2 × 2 matrix in this equation. We must then solve the equation

$$\begin{vmatrix} a_{11}-\lambda & a_{21} \\ a_{12} & a_{22}-\lambda \end{vmatrix} = 0 \tag{4.190}$$

which is a quadratic equation for λ, having two solutions λ_1 and λ_2. If (c_1, c_2) is an eigenvector corresponding to one of the eigenvalues $\lambda = \lambda_i (i = 1, 2)$, we have $d_1 = \lambda c_1$ and $d_2 = \lambda c_2$. Thus, among the solutions, $\psi(x)$, there are two having the property

$$\psi(x+l) = \lambda\psi(x) \tag{4.191}$$

where λ is a constant factor. This result is known as *Floquet's theorem*. Of course, we see immediately from (4.191) that

$$\psi(x+nl) = \lambda^n\psi(x), \qquad n = 0, \pm1, \pm2, \ldots . \tag{4.192}$$

Now, let ψ_{λ_1} and ψ_{λ_2} be two solutions of the Schrödinger equation (4.3) corresponding to the energy E, which satisfy (4.191) and correspond respectively to the eigenvalues λ_1 and λ_2 of equation (4.190). Let ψ'_{λ_1} and ψ'_{λ_2} denote their respective derivatives. If

$$W = \begin{vmatrix} \psi_{\lambda_1} & \psi_{\lambda_2} \\ \psi'_{\lambda_1} & \psi'_{\lambda_2} \end{vmatrix} \tag{4.193}$$

denotes the Wronskian determinant of ψ_{λ_1} and ψ_{λ_2}, we have from (4.191)

$$W(x+l) = \lambda_1 \lambda_2 W(x). \tag{4.194}$$

Since the Wronskian of two solutions of the Schrödinger equation (4.3) corresponding to the same energy eigenvalue E is a constant (see footnote[9] of Chapter 3, p. 110) it follows that

$$\lambda_1 \lambda_2 = 1. \tag{4.195}$$

Let us now return to (4.191). If $|\lambda| > 1$, it is clear from (4.192) that ψ will grow above all limits when $x \to +\infty$, and decrease below all limits if $x \to -\infty$. The opposite will happen if $|\lambda| < 1$. Hence, physically admissible solutions of the Schrödinger equation exist only if $|\lambda| = 1$. Taking into account the result (4.195), we may therefore write the two quantities λ_1 and λ_2 in the form

$$\lambda_1 = \mathrm{e}^{\mathrm{i}Kl}, \qquad \lambda_2 = \mathrm{e}^{-\mathrm{i}Kl} \tag{4.196}$$

where K is a real number. Since $\exp(\mathrm{i}2\pi n) = 1$, it is clear that a complete set of wave functions can be obtained by restricting the values of K to the interval

$$-\frac{\pi}{l} \leqslant K \leqslant \frac{\pi}{l}. \tag{4.197}$$

Therefore, all physically admissible solutions must satisfy the relation

$$\psi(x+nl) = \mathrm{e}^{\mathrm{i}nKl}\psi(x), \qquad n = 0, \pm 1, \pm 2, \ldots \tag{4.198}$$

which is known as the *Bloch condition*. If we write the solution $\psi(x)$ in the form

$$\psi(x) = \mathrm{e}^{\mathrm{i}Kx} u_K(x) \tag{4.199}$$

it follows from (4.198) that

$$u_K(x+l) = u_K(x). \tag{4.200}$$

This result is known as *Bloch's theorem*. We see that the *Bloch wave function* (4.199) represents a travelling wave of wavelength $2\pi/K$, whose amplitude $u_K(x)$ is periodic, with the same period l as that of the crystal lattice.

Energy bands

Let us now discuss the energy spectrum. For simplicity, we shall focus our attention on the Kronig–Penney potential (see Fig. 4.20) which exhibits the basic features of the interaction felt by an electron in a crystal and leads to a readily solvable problem. We choose the zero of the energy scale to coincide with the top of the wells, and consider successively the two cases for which the electron energy E is such that $-V_0 < E < 0$ and $E > 0$.

Case 1: $-V_0 < E < 0$

The Schrödinger equation is

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \alpha^2\psi(x) = 0 \qquad \text{inside the wells} \tag{4.201a}$$

and

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} - \beta^2\psi(x) = 0 \qquad \text{between the wells} \tag{4.201b}$$

where (see (4.114))

$$\alpha = \left[\frac{2m}{\hbar^2}(V_0 + E)\right]^{1/2}, \qquad \beta = \left(-\frac{2m}{\hbar^2}E\right)^{1/2} \tag{4.202}$$

Let us solve the equations (4.201) for a given 'cell', for example that extending from $b - l$ to b. We have

$$\psi(x) = A\mathrm{e}^{\mathrm{i}\alpha x} + B\mathrm{e}^{-\mathrm{i}\alpha x}, \qquad b - l < x < 0 \tag{4.203a}$$

$$\psi(x) = C\mathrm{e}^{\beta x} + D\mathrm{e}^{-\beta x}, \qquad 0 < x < b. \tag{4.203b}$$

Now, according to the Bloch theorem, the solution $\psi(x)$ of the Schrödinger equation for a periodic potential has the general form (4.199), where the amplitude $u_K(x)$ has the same period l as that of the crystal lattice. In other words, the electron does not 'belong' to any one atom (ion) of the lattice, but has an equal probability of being found in the neighbourhood of any of them. Using (4.199) and (4.203), we find in the 'cell' $(b - l, b)$

$$u_K(x) = A\mathrm{e}^{\mathrm{i}(\alpha - K)x} + B\mathrm{e}^{-\mathrm{i}(\alpha + K)x}, \qquad b - l < x < 0 \tag{4.204a}$$

$$u_K(x) = C\mathrm{e}^{(\beta - \mathrm{i}K)x} + D\mathrm{e}^{-(\beta + \mathrm{i}K)x}, \qquad 0 < x < b \tag{4.204b}$$

and since $u_K(x)$ is periodic, the equations (4.204) determine $u_K(x)$ – and hence also $\psi(x)$ – for all values of x. For example, if we want to write the function $u_K(x)$ in the region $b < x < l$ we use the fact that $u_K(x) = u_K(x - l)$, and upon replacing x by $x - l$ in (4.204a), we have

$$u_K(x) = A\mathrm{e}^{\mathrm{i}(\alpha - K)(x - l)} + B\mathrm{e}^{-\mathrm{i}(\alpha + K)(x - l)}, \qquad b < x < l. \tag{4.205}$$

In order to be a physically acceptable solution of the Schrödinger equation, the wave function $\psi(x)$ and its first derivative $\mathrm{d}\psi(x)/\mathrm{d}x$ – and hence $u_K(x)$ and $\mathrm{d}u_K(x)/\mathrm{d}x$

– must be continuous at both edges of each potential well. The periodicity of $u_K(x)$ guarantees that if $u_K(x)$ and $\mathrm{d}u_K(x)/\mathrm{d}x$ are continuous at the edges of just *one* well, they will be continuous at the edges of *every* well. Now, from (4.204) we see that by requiring $u_K(x)$ and $\mathrm{d}u_K(x)/\mathrm{d}x$ to be continuous at $x = 0$ we obtain the two relations

$$A + B = C + D, \tag{4.206a}$$

$$\mathrm{i}(\alpha - K)A - \mathrm{i}(\alpha + K)B = (\beta - \mathrm{i}K)C - (\beta + \mathrm{i}K)D \tag{4.206b}$$

while the continuity conditions applied at $x = b$ to the functions (4.204b) and (4.205) yield the two equations

$$A\mathrm{e}^{-\mathrm{i}(\alpha-K)c} + B\mathrm{e}^{\mathrm{i}(\alpha+K)c} = C\mathrm{e}^{(\beta-\mathrm{i}K)b} + D\mathrm{e}^{-(\beta+\mathrm{i}K)b} \tag{4.206c}$$

$$\begin{aligned} \mathrm{i}(\alpha - K)A\mathrm{e}^{-\mathrm{i}(\alpha-K)c} - \mathrm{i}(\alpha + K)B\mathrm{e}^{\mathrm{i}(\alpha+K)c} &= (\beta - \mathrm{i}K)C\mathrm{e}^{(\beta-\mathrm{i}K)b} \\ &\quad -(\beta + \mathrm{i}K)D\mathrm{e}^{-(\beta+\mathrm{i}K)b} \end{aligned} \tag{4.206d}$$

where $c = l - b$.

The equations (4.206) constitute a system of four homogeneous equations for the four unknown quantities A, B, C and D. In order for this system to have a non-trivial solution the determinant of the coefficients of A, B, C and D must vanish. This results in the condition

$$\cos \alpha c \cosh \beta b - \frac{\alpha^2 - \beta^2}{2\alpha\beta} \sin \alpha c \sinh \beta b = \cos Kl \tag{4.207}$$

which is an implicit equation for the energy E.

Case 2: $E > 0$

The modifications required to treat the case $E > 0$ are very simple. We see from (4.202) that when the energy E is positive the quantity β becomes imaginary. We shall therefore set $\beta = \mathrm{i}k$, with $k = (2mE/\hbar^2)^{1/2}$. Since no assumption about the reality of β has been made in deriving (4.207), we may at once rewrite this equation for the case $E > 0$ as

$$\cos \alpha c \cos kb - \frac{\alpha^2 + k^2}{2\alpha k} \sin \alpha c \sin kb = \cos Kl \tag{4.208}$$

and we see that this is again an implicit equation for the energy E.

We can summarise both equations (4.207) and (4.208) by writing

$$F(E) = \cos Kl \tag{4.209}$$

where the function $F(E)$ represents the left-hand sides of (4.207) and (4.208). In writing the equation (4.209) we have used the fact that the two left-hand sides join smoothly at $E = 0$, so that only one function $F(E)$ is required for the full energy range $E > -V_0$. The function $F(E)$ is shown in Fig. 4.21 for typical values of b, l and V_0. The remarkable feature which emerges from this graph is that the equation (4.209) cannot be satisfied for certain ranges of values of E. Indeed, since K is real, we have

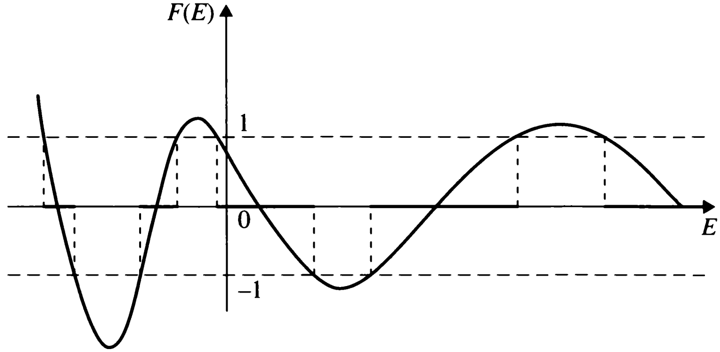


Figure 4.21 Plot of $F(E)$, which represents the left-hand sides of equations (4.207) and (4.208), as a function of the energy E. The heavy lines on the abscissa show the allowed values of E, corresponding to conduction bands; they are separated by forbidden energy gaps.

$|\cos Kl| \leqslant 1$, so that the values of E for which $|F(E)| > 1$ are inaccessible. As a result, the allowed values of E fall into bands satisfying the condition $|F(E)| \leqslant 1$, which are indicated by heavy lines in Fig. 4.21. These bands are known as the *conduction bands* of the lattice; they are separated by *forbidden energy gaps*.

It can be proved (Problem 4.20) that if the periodic distance l is increased without changing c or V_0 (i.e. if the separation between the wells is increased) the energy bands for $-V_0 < E < 0$ become narrower, and contract in the limit $l \to \infty$ into the discrete energy levels of an isolated potential well. This behaviour, which is illustrated in Fig. 4.22, is easy to understand. Indeed, as the spacing l between atoms is increased, the motion of an electron in one of the atoms of the crystal will be less and less affected by the presence of the other atoms, so that each atom will behave as if it were isolated. We also see from Fig. 4.21 that the bands corresponding to the lowest-lying levels are the narrowest; this is due to the fact that the electrons which are most tightly bound to the atoms are less likely to be perturbed by the presence of the other atoms. Note that the electrons in the low-lying bands (with energies $E < 0$) can only go from one atom to the other by 'tunnelling' through the potential barriers between the wells.

Until now we have not discussed the *boundary conditions* which must be satisfied by the wave function $\psi(x)$ at each end of the linear chain of atoms (i.e. at the 'surface' of the one-dimensional crystal we are considering). We could obviously ask that $\psi = 0$ at both ends of the chain so that the electrons cannot escape from the crystal. Unfortunately, this requirement, which leads to standing wave solutions of the Schrödinger equation, is not easy to implement. In particular, we see that the Bloch wave functions (4.199), which are travelling waves, do not satisfy such boundary conditions, so that superpositions of Bloch waves would be necessary to construct the required standing waves. For this reason, we shall disregard the (small) surface effects and adopt *periodic boundary conditions*, such that the wave function ψ is required to take the same value at both ends of the chain. This means that an

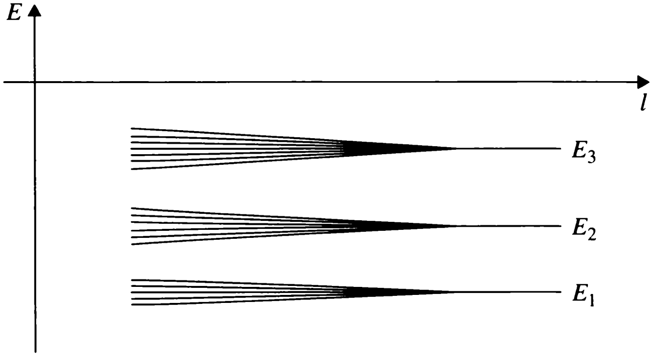


Figure 4.22 When the separation between the wells is increased, the energy bands for $-V_0 < E < 0$ shrink and in the limit $l \to \infty$ contract into the discrete energy levels of an isolated potential well.

electron leaving the crystal at one end simultaneously re-enters it at the corresponding point on the opposite face with its momentum unchanged.

An equivalent way of formulating the periodic boundary conditions is to consider that the one-dimensional lattice has the form of a *closed loop* containing N atoms (where $N \simeq 10^{23}$ is of the order of Avogadro's number). In order for the wave function to be single-valued, we must therefore have

$$\psi(x + Nl) = \psi(x) \tag{4.210}$$

and from (4.198) we see that this requirement is equivalent to the condition

$$e^{iNKl} = 1. \tag{4.211}$$

As a result, the possible values of K are discrete and are given by

$$K = \frac{2\pi n}{Nl}, \qquad n = 0, \pm 1, \pm 2, \dots, \tag{4.212}$$

Moreover, we see from (4.199), (4.207) and (4.208) that the wave function $\psi(x)$, as well as the corresponding energy E, are unchanged if K is increased or decreased by an integral multiple of $2\pi/l$. We may therefore, without any loss of generality, assume that K is confined within a given interval of length $2\pi/l$, for example the interval (4.197). From (4.197) and (4.212) we immediately deduce that there are N allowed values of K. As K takes on each of these possible values, the energy is equal to every one of its corresponding allowed values in each band. Hence every conduction band contains N allowed energy levels. This result is readily explained if one remembers that in the limit $l \to \infty$ each band contracts into a single level which is N-fold degenerate, since the electron can be bound to any one of the N atoms. For finite values of l this degeneracy is removed and each discrete atomic level spreads into a band of N energy levels.

Problems

4.1 Show that the momentum eigenfunctions

$$\psi_{k_x}(x) = L^{-1/2}\exp(\mathrm{i}k_x x)$$

satisfying the periodic boundary conditions $k_x = 2\pi n/L (n = 0, \pm 1, \pm 2, \ldots)$ obey in the limit $L \to \infty$ the closure relation

$$\int_{-\infty}^{+\infty} \psi^*_{k_x}(x')\psi_{k_x}(x)\mathrm{d}k_x = \delta(x - x').$$

(*Hint*: Convert the sum $\sum_{n=-\infty}^{+\infty}$ to the integral

$$\int_{-\infty}^{+\infty} \mathrm{d}n = (L/2\pi)\int_{-\infty}^{+\infty} \mathrm{d}k_x.)$$

4.2 Consider the momentum eigenfunctions

$$\psi_E(x) = c(E)\exp(\mathrm{i}kx).$$

Determine $c(E)$ so that $\psi_E(x)$ is 'normalised' on the energy scale according to

$$\int_{-\infty}^{+\infty} \psi^*_{E'}(x)\psi_E(x)\mathrm{d}x = \delta(E - E').$$

(*Hint*: Use equation (A.32) of Appendix A to obtain the relation

$$\delta(\sqrt{E} - \sqrt{E'}) = 2\sqrt{E}\delta(E - E'), \qquad E \neq 0.)$$

4.3 Consider a particle incident from the right on the potential step (4.41). Prove that the reflection and transmission coefficients are the same as when the particle is incident on the potential step from the left.

4.4 Consider an electron of energy E incident on the potential step (4.41), where $V_0 = 10$ eV. Calculate the reflection coefficient R and the transmission coefficient T (a) when $E = 5$ eV, (b) when $E = 15$ eV and (c) when $E = 10$ eV.

4.5 Determine the reflection coefficient R and transmission coefficient T:

(a) of an electron of energy $E = 1$ eV for a rectangular barrier potential (4.72) such that $V_0 = 2$ eV and $a = 1$ Å; and
(b) of a proton of the same energy for the same potential barrier.

4.6 Consider a particle of mass m moving in one dimension in an infinite square well of width L, such that the origin 0 has been chosen to be the left corner of the well. Show that the energy eigenvalues are given by (4.95), while the corresponding normalised eigenfunctions are

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi}{L}x\right), \qquad n = 1, 2, 3, \ldots$$

and compare these eigenfunctions with those obtained in the text (see (4.93) and (4.94)).

4.7 A particle of mass m moves in one dimension in the infinite square well (4.86). Suppose that at time $t = 0$ its wave function is

$$\Psi(x, t = 0) = A(a^2 - x^2)$$

where A is a normalisation constant.

(a) Find the probability P_n of obtaining the value E_n of the particle energy, where E_n is one of the energy eigenvalues.

(b) Determine the expectation value $\langle E \rangle$ of the energy.

4.8 Solve numerically the equations (4.120) to obtain the energy levels and corresponding normalised eigenfunctions of a one-dimensional square well (4.113) such that $\gamma = (2mV_0a^2/\hbar^2)^{1/2} = 5$.

4.9 Derive the results (4.126) for the reflection and transmission coefficients corresponding to a one-dimensional square well.

4.10 Consider a particle of mass m moving in one dimension in the potential well

$$V(x) = \begin{cases} 0, & 0 \leqslant |x| < a \\ V_0, & a < |x| < b \\ \infty, & |x| > b \end{cases}$$

where V_0, a and b are positive quantities and $b > a$. The energy E of the particle is such that $0 < E < V_0$.

(a) The eigenfunctions of the Schrödinger equation (4.3) for this potential can be assumed to be either even or odd. Why?

(b) Determine the normalised even eigenfunctions $\psi_n^+(x)$ and write down an expression allowing the corresponding energy eigenvalues E_n^+ to be obtained.

(c) Repeat the calculation of (b) for the normalised odd eigenfunctions $\psi_n^-(x)$ and the corresponding energy levels E_n^-.

(d) Show that when $a = b$ one retrieves the eigenfunctions and energy eigenvalues of a particle in the infinite square well (4.86).

4.11 Consider the one-dimensional motion of a particle of mass m in the double potential well

$$V(x) = \begin{cases} V_0, & 0 \leqslant |x| < b \\ 0, & b < |x| < c \\ \infty, & |x| > c \end{cases}$$

where V_0, b and c are positive quantities and $b < c$. The energy E of the particle is such that $0 < E < V_0$.

(a) Let $\psi_n^+(x)$ and $\psi_n^-(x)$ denote respectively the normalised even and odd eigenfunctions of the Schrödinger equation (4.3) for this potential, and let E_n^+ and E_n^- be the corresponding energy eigenvalues. Determine the functions $\psi_n^+(x)$ and $\psi_n^-(x)$ and write down the energy quantisation conditions giving E_n^+ and E_n^-.

(b) Show that for each doublet (E_n^+, E_n^-) the lowest energy level is E_n^+.

(c) Prove that when $V_0 \to \infty$ (so that an infinite barrier separates the two wells), each doublet (E_n^+, E_n^-) merges into a single (twofold degenerate) energy level E_n, the energy values $E_n = (\hbar^2/2m)(\pi^2 n^2/L^2)$, $n = 1, 2, 3, \ldots$, being those of the infinite square well (see (4.95)) with $L = c - b$.

4.12 By using the uncertainty relation (2.70) obtain an estimate of the zero-point energy of a linear harmonic oscillator.

4.13 Prove equations (4.157) and (4.158) by using the generating function (4.156) of the Hermite polynomials.

4.14 Prove that the definition (4.154a) of the Hermite polynomials is equivalent to the definition by means of the generating function given in equations (4.156).

4.15 Obtain the result (4.174) for x_{nm} by using the recurrence relation (4.157) of the Hermite polynomials, the orthonormality relation (4.170), and the result (4.167).

4.16 Prove equations (4.180) and (4.183).

4.17 Show that $f(\xi) = \xi \exp(\xi^2/2)$ is an eigenfunction of the linear harmonic oscillator equation (4.135) corresponding to the eigenvalue $\lambda = -3$. Is this eigenfunction physically acceptable? Explain.

4.18 Consider the motion of a particle of mass m in a one-dimensional potential $V(x) = \lambda\delta(x)$, where $\delta(x)$ is the Dirac delta function.

(a) Assuming that $\lambda > 0$, obtain the reflection coefficient R and the transmission coefficient T.

(*Hint*: For a potential of the form $V(x) = \lambda\delta(x)$, the integration of the Schrödinger eigenvalue equation (4.3) from $-\varepsilon$ to $+\varepsilon$ gives

$$\left.\frac{d\psi}{dx}\right|_{x=+\varepsilon} - \left.\frac{d\psi}{dx}\right|_{x=-\varepsilon} = \frac{2m}{\hbar^2}\lambda\int_{-\varepsilon}^{+\varepsilon}\delta(x)\psi(x)dx$$

$$= \frac{2m}{\hbar^2}\lambda\psi(x=0).)$$

(b) Consider now the case for which $\lambda < 0$. Show that there is only one bound state and find its energy as a function of $|\lambda|$. Using (4.120), verify that your result agrees with that obtained for the square well in the limit $V_0 \to \infty$, $a \to 0$, in such a way that $2aV_0$ is held fixed and equal to $|\lambda|$.

4.19 Consider the motion of a particle of mass m in the one-dimensional periodic potential

$$V(x) = \frac{V_0}{l} \sum_{n=-\infty}^{+\infty} \delta(x - nl)$$

where δ denotes the Dirac delta function and l is the periodic distance. Prove that for such a potential equation (4.209) reads

$$\cos kl + \frac{mV_0}{\hbar^2} \frac{\sin kl}{kl} = \cos Kl$$

where $k = (2mE/\hbar^2)^{1/2}$, and show that the band edges occur when $Kl = n\pi$, $n = 0, \pm 1, \pm 2, \ldots$.

4.20 Prove that, in the Kronig–Penney model, if the distance l is increased without changing c or V_0, the energy bands for $-V_0 < E < 0$ become narrower, and contract in the limit $l \to \infty$ into the discrete energy levels of an isolated potential well.

5 The formalism of quantum mechanics

The basic ideas of quantum mechanics were introduced in Chapters 2 and 3 by using a formulation of the theory known as *wave mechanics*. These ideas were applied in Chapter 4 to some simple one-dimensional problems. In this chapter we shall present the principles of quantum mechanics in a more general way, as a set of postulates justified by the experimental verification of their consequences. In particular, we shall see that there exist alternative ways of formulating quantum mechanics which are equivalent to wave mechanics. We shall also in the course of this chapter develop the mathematical tools necessary to make progress in the theory.

5.1 The state of a system

In classical physics, the dynamical state of a system is determined at each instant of time by the knowledge of the physical quantities–dynamical variables–such as the position vectors and the momenta of the particles which constitute the system. It is postulated that all the dynamical variables associated with the system may, in principle, be measured simultaneously with infinite precision.

The situation is very different in quantum physics, because of the central role played by the *measurement* process. Indeed, when a given dynamical variable is measured, the dynamical state of the system is in general modified in an unpredictable way, and we have seen in Chapter 2 that according to the Heisenberg uncertainty relations this sets a limit to the precision with which 'complementary' dynamical variables can be measured simultaneously. One is therefore led to abandon the classical assumption that all the dynamical variables of a system have well-defined values at every instant. Instead, quantum mechanics only predicts the number n of times that a particular result will be obtained when a large number N of identical, independent, identically prepared physical systems (called a *statistical ensemble* or, for short, an *ensemble*) are subjected to a measurement process. In other words, quantum mechanics predicts the *statistical frequency* n/N or *probability* of an event. In order to make these predictions, a set of postulates are required, which we shall now formulate.

Postulate 1

To an ensemble of physical systems one can, in certain cases, associate a *wave function* or *state function* which contains all the information that can be known about the ensemble. This function is in general complex; it may be multiplied by an arbitrary complex number without altering its physical significance.

Let us make the following two remarks about this first postulate:

(1) The words 'in certain cases' mean that some ensembles cannot be described by a single state function (determined apart from a complex multiplicative constant). Such ensembles will not be considered here; they will be discussed in Chapter 14.

(2) Although in principle one should always use ensembles, it is common practice to speak of the wave function associated with a particular system, and we shall often do so for convenience. However, as stated in Section 2.2, it should always be understood that this is shorthand for the wave function associated with an ensemble.

Let us first consider a physical system consisting of a single particle in a given potential $V(\mathbf{r}, t)$. We assume that the particle is structureless, i.e. has no internal degrees of freedom such as spin[1]. Expressed in configuration space, the state function associated with an ensemble of such systems is a wave function $\Psi(\mathbf{r}, t)$ depending on the position vector $\mathbf{r}$ of the particle and on the time t. As we saw in Section 2.2, a wave function $\Psi(\mathbf{r}, t)$ is said to be *square integrable* if its normalisation integral

$$I = \int |\Psi(\mathbf{r}, t)|^2 \mathrm{d}\mathbf{r} \tag{5.1}$$

is finite, where the integration is over all space. Since, according to Postulate 1, two wave functions Ψ and $c\Psi$ which differ by an arbitrary complex multiplicative

---

[1] The case of particles with spin will be discussed in Chapter 6.

constant c represent the same state, it is convenient when working with square integrable functions to choose this constant so that the wave function is normalised to unity:

$$\int |\Psi(\mathbf{r}, t)|^2 \mathrm{d}\mathbf{r} = 1. \tag{5.2}$$

The quantity

$$P(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 \tag{5.3}$$

can then be interpreted as a position probability density, as explained in Section 2.2. We note that the wave functions Ψ and $\exp(\mathrm{i}\alpha)\Psi$ which differ by the phase factor $\exp(\mathrm{i}\alpha)$–where α is a real number–not only describe the same state, but also have the same normalisation. We also recall that some wave functions, such as plane waves, are not square integrable, in which case other 'normalisation' procedures can be used, for example enclosing the system in a large box, or using the Dirac delta function 'normalisation'.

The generalisation of these considerations to the case of a physical system containing N structureless particles is straightforward. The state function associated with an ensemble of such systems, expressed in configuration space, is a wave function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t)$ which depends on the position vectors $\mathbf{r}_1, \dots, \mathbf{r}_N$ of the particles and on the time t. This wave function is said to be square integrable if the normalisation integral

$$I = \int |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t)|^2 \mathrm{d}\mathbf{r}_1 \dots \mathrm{d}\mathbf{r}_N \tag{5.4}$$

is finite. Again, since Ψ and $c\Psi$ (where c is a complex multiplicative constant) describe the same state, we can choose c so that the wave function is normalised to unity:

$$\int |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t)|^2 \mathrm{d}\mathbf{r}_1 \dots \mathrm{d}\mathbf{r}_N = 1 \tag{5.5}$$

in which case a constant phase factor of the form $\exp(\mathrm{i}\alpha)$ is still left undetermined. When the wave function is normalised to unity, the quantity

$$P(\mathbf{r}_1, \dots, \mathbf{r}_N, t) = |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t)|^2 \tag{5.6}$$

can be interpreted as a position probability density, in the sense that $P(\mathbf{r}_1, \dots, \mathbf{r}_N, t)\mathrm{d}\mathbf{r}_1 \dots \mathrm{d}\mathbf{r}_N$ is the probability of finding at time t particle 1 in the volume element $\mathrm{d}\mathbf{r}_1$ about $\mathbf{r}_1$, particle 2 in the volume element $\mathrm{d}\mathbf{r}_2$ about $\mathbf{r}_2$, and so on. We remark that

$$P_1(\mathbf{r}_1, t) \equiv \int P(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)\mathrm{d}\mathbf{r}_2 \dots \mathrm{d}\mathbf{r}_N \tag{5.7}$$

is the position probability density of particle 1 at the point $\mathbf{r}_1$ at time t, independently of the positions of the other particles. Similar position probability densities can clearly be introduced for the other particles.

Postulate 2

The superposition principle.

According to the *superposition principle*, which we have already discussed in Chapters 2 and 3, the dynamical states of a quantum system are linearly superposable. Thus, if the state function Ψ_1 is associated with one possible state of a statistical ensemble of physical systems, and the state function Ψ_2 with another state of this ensemble, then any linear combination

$$\Psi = c_1\Psi_1 + c_2\Psi_2 \tag{5.8}$$

where c_1 and c_2 are complex constants, is also a state function associated with a possible state of the ensemble. As we already stressed in Section 2.2, the *relative* phase of Ψ_1 and Ψ_2 in (5.8) is important, since it does affect the physical quantity $|\Psi|^2$ (see (2.10)).

Momentum space wave functions

Instead of using the configuration space wave function $\Psi(\mathbf{r}, t)$ to describe the state of an ensemble of one-particle systems, we could as well use the corresponding *momentum space* wave function $\Phi(\mathbf{p}, t)$, which is the Fourier transform of $\Psi(\mathbf{r}, t)$ (see (2.61)). We saw in Section 2.4 that if the configuration space wave function $\Psi(\mathbf{r}, t)$ is normalised to unity, the corresponding momentum space wave function $\Phi(\mathbf{p}, t)$ will also be normalised to unity in momentum space:

$$\int |\Phi(\mathbf{p}, t)|^2 \mathrm{d}\mathbf{p} = 1 \tag{5.9}$$

so that the quantity

$$\Pi(\mathbf{p}, t) = |\Phi(\mathbf{p}, t)|^2 \tag{5.10}$$

can be interpreted as the probability density in momentum space for finding the momentum of the particle in the volume element $\mathrm{d}\mathbf{p}$ about $\mathbf{p}$. Likewise the state function associated with an ensemble of N-particle physical systems can be 'represented' by a momentum space wave function $\Phi(\mathbf{p}_1, \ldots, \mathbf{p}_N, t)$ which is the Fourier transform of the configuration space wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t)$:

$$\Phi(\mathbf{p}_1, \ldots, \mathbf{p}_N, t) = (2\pi\hbar)^{-3N/2} \int \exp\left[-\frac{\mathrm{i}}{\hbar}(\mathbf{p}_1.\mathbf{r}_1 + \cdots + \mathbf{p}_N.\mathbf{r}_N)\right] \times \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t)\mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N. \tag{5.11}$$

If $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t)$ is normalised to unity according to (5.5), then by a direct generalisation of the Parseval theorem discussed in Appendix A, we have in momentum space

$$\int |\Phi(\mathbf{p}_1, \dots, \mathbf{p}_N, t)|^2 \mathrm{d}\mathbf{p}_1 \dots \mathrm{d}\mathbf{p}_N = 1 \tag{5.12}$$

so that the quantity

$$\Pi(\mathbf{p}_1, \dots, \mathbf{p}_N, t) = |\Phi(\mathbf{p}_1, \dots, \mathbf{p}_N, t)|^2 \tag{5.13}$$

is the probability density in momentum space for finding the momentum of particle 1 in the volume element $\mathrm{d}\mathbf{p}_1$ about $\mathbf{p}_1$, the momentum of particle 2 in the volume element $\mathrm{d}\mathbf{p}_2$ about $\mathbf{p}_2$, and so on.

The fact that both the wave function Ψ in configuration space and the wave function Φ in momentum space 'represent' the same state suggests that a more abstract quantity can be introduced of which Ψ and Φ are two explicit representations. We shall return to this point in Section 5.6.

Dirac bracket notation

A very convenient notation, due to Dirac, will now be introduced. The scalar product of two square integrable functions $\Psi_1(\mathbf{r})$ and $\Psi_2(\mathbf{r})$ is denoted by the symbol $\langle\Psi_1|\Psi_2\rangle$, namely

$$\langle\Psi_1|\Psi_2\rangle \equiv \int \Psi_1^*(\mathbf{r})\Psi_2(\mathbf{r})\mathrm{d}\mathbf{r} \tag{5.14a}$$

and the generalisation to functions $\Psi_1(\mathbf{r}_1, \dots, \mathbf{r}_N)$ and $\Psi_2(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is straightforward. That is,

$$\langle\Psi_1|\Psi_2\rangle \equiv \int \Psi_1^*(\mathbf{r}_1, \dots, \mathbf{r}_N)\Psi_2(\mathbf{r}_1, \dots, \mathbf{r}_N)\mathrm{d}\mathbf{r}_1 \dots \mathrm{d}\mathbf{r}_N. \tag{5.14b}$$

The symbol $|\Psi_2\rangle$ is known as a *ket* while $\langle\Psi_1|$ is known as a *bra*. From the definition (5.14) we have

$$\langle\Psi_1|\Psi_2\rangle = \langle\Psi_2|\Psi_1\rangle^*. \tag{5.15a}$$

Moreover, if c is a complex number and Ψ_3 a third function, we also have

$$\langle\Psi_1|c\Psi_2\rangle = c\langle\Psi_1|\Psi_2\rangle, \tag{5.15b}$$

$$\langle c\Psi_1|\Psi_2\rangle = c^*\langle\Psi_1|\Psi_2\rangle, \tag{5.15c}$$

$$\langle\Psi_3|\Psi_1 + \Psi_2\rangle = \langle\Psi_3|\Psi_1\rangle + \langle\Psi_3|\Psi_2\rangle. \tag{5.15d}$$

Two functions Ψ_1 and Ψ_2 are said to be orthogonal if their scalar product vanishes:

$$\langle\Psi_1|\Psi_2\rangle = 0. \tag{5.16}$$

Using the Dirac bracket notation, we see that the normalisation condition (5.5) can be written compactly as

$$\langle\Psi|\Psi\rangle = 1. \tag{5.17}$$

We remark that this notation can be used just as well for momentum space wave functions. For example, the normalisation condition (5.12) can be written as $\langle\Phi|\Phi\rangle = 1$.

5.2 Dynamical variables and operators

We have seen in Chapter 2 and 3 that with each dynamical variable is associated an operator acting on the wave function. Following this idea, one can formulate the next postulate as follows.

Postulate 3

With every dynamical variable is associated a linear operator.

We recall that an operator A is linear if it has the property (see (3.62))

$$A(c_1\Psi_1 + c_2\Psi_2) = c_1(A\Psi_1) + c_2(A\Psi_2) \tag{5.18}$$

where Ψ_1 and Ψ_2 are two functions and c_1 and c_2 are complex constants.

The rules for associating a linear operator with a dynamical variable have already been discussed in Sections 3.3 and 3.9 for the case of one-particle systems. The generalisation of these rules to systems of N particles is as follows. If the dynamical state of the system is described by a wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t)$ in configuration space, one associates with the dynamical variable $\mathcal{A} = A(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N, t)$ the linear operator

$$A(\mathbf{r}_1, \ldots, \mathbf{r}_N, -\mathrm{i}\hbar\nabla_1, \ldots, -\mathrm{i}\hbar\nabla_N, t) \tag{5.19}$$

obtained by performing the *substitution* $\mathbf{p}_i \to -\mathrm{i}\hbar\nabla_i (i = 1, 2, \ldots, N)$ whenever the momentum $\mathbf{p}_i$ occurs. If, on the other hand, the dynamical state of the system is described by a wave function $\Phi(\mathbf{p}_1, \ldots, \mathbf{p}_N, t)$ in momentum space, one associates with the dynamical variable $\mathcal{A} = A(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N, t)$ the linear operator

$$A(\mathrm{i}\hbar\nabla_{\mathbf{p}_1}, \ldots, \mathrm{i}\hbar\nabla_{\mathbf{p}_N}, \mathbf{p}_1, \ldots, \mathbf{p}_N, t) \tag{5.20}$$

obtained by performing the *substitution* $\mathbf{r}_i \to \mathrm{i}\hbar\nabla_{\mathbf{p}_i} (i = 1, 2, \ldots, N)$ whenever the position vector $\mathbf{r}_i$ occurs.

It is worth noting that these substitution rules only apply to dynamical variables expressed in Cartesian coordinates. We shall also see in Chapter 6 that quantum mechanics uses operators such as the spin which have no classical analogue, and which therefore cannot be obtained from the substitution rules.

Eigenvalues and eigenfunctions

We have seen in Section 3.5 that a function ψ_n is said to be an *eigenfunction* of an operator A if the result of operating on ψ_n with A is to multiply ψ_n by a number a_n called an eigenvalue:

$$A\psi_n = a_n\psi_n. \tag{5.21}$$

Postulate 4

The only result of a precise measurement of the dynamical variable $\mathcal{A}$ is one of the eigenvalues a_n of the linear operator A associated with $\mathcal{A}$.

The totality of the eigenvalues of an operator A is called the *spectrum of* A. Since the results of measurements are real numbers it follows that the spectrum of any operator representing a dynamical variable must be real. In some cases the spectrum of an operator consists only of discrete eigenvalues, in others it consists of a continuous range of eigenvalues, or a mixture of both.

Hermitian operators

We shall now discuss the consequences of the requirement that the allowed class of linear operators representing dynamical variables must have real eigenvalues. The operators required are called *Hermitian operators*, and are defined by the condition

$$\langle \mathrm{X}|(A\Psi)\rangle = \langle (A\mathrm{X})|\Psi\rangle \tag{5.22}$$

where Ψ and X are square-integrable functions. We note that if $\Psi = \mathrm{X}$,

$$\langle \Psi|(A\Psi)\rangle = \langle (A\Psi)|\Psi\rangle \tag{5.23}$$

which for a one-particle system is identical to (3.69). Although it appears that (5.22) is a more general definition of Hermiticity than (5.23), the two definitions are in fact equivalent (see Problem 5.2). The matrix element $\langle \mathrm{X}|(A\Psi)\rangle$ is usually written in the Dirac notation as

$$\langle \mathrm{X}|(A\Psi)\rangle \equiv \langle \mathrm{X}|A|\Psi\rangle \tag{5.24}$$

and from (5.23) we see that if A is Hermitian the matrix element $\langle \Psi|A|\Psi\rangle$ is real.

If ψ_n is an eigenfunction of the operator A corresponding to the eigenvalue a_n, then from (5.21) we have

$$\langle \psi_n|A|\psi_n\rangle = a_n\langle \psi_n|\psi_n\rangle. \tag{5.25}$$

In addition, since

$$(A\psi_n)^* = a_n^*\psi_n^* \tag{5.26}$$

we also have

$$\langle (A\psi_n)|\psi_n\rangle = a_n^*\langle \psi_n|\psi_n\rangle. \tag{5.27}$$

If A is Hermitian, the left-hand sides of (5.25) and (5.27) are equal, and hence $a_n = a_n^*$. Therefore a sufficient (but not a necessary) condition for an operator to have real eigenvalues is for it to be Hermitian. From now on the linear operator A associated with a dynamical variable $\mathcal{A}$ will be taken to be Hermitian. If the operator A obtained by using the substitution rules (5.19) and (5.20) is not Hermitian, the Hermitisation procedure discussed in Section 3.3 must be carried out.

If the wave function of a system is one of the eigenfunctions ψ_n of the operator A, corresponding to the eigenvalue a_n, then a measurement of the dynamical variable $\mathcal{A}$ will certainly produce the result a_n. In this case we shall say that the system is in an eigenstate of A characterised by the eigenvalue a_n. On the other hand, if the wave function is not an eigenfunction of A, then in a measurement of $\mathcal{A}$ any one of the results $a_1, a_2, \ldots,$ can be obtained. Which result will be obtained is impossible to predict. However, as we shall see later, the *probability* of obtaining a particular result a_n can be obtained.

Postulate 5

If a series of measurements is made of the dynamical variable A on an ensemble of systems^2, described by the wave function Ψ, the expectation or average value of this dynamical variable is

$$\langle A\rangle = \frac{\langle \Psi|A|\Psi\rangle}{\langle \Psi|\Psi\rangle}. \tag{5.28}$$

Since A is a Hermitian operator it follows that $\langle A\rangle$ is real. If the wave function Ψ is normalised to unity, we have $\langle \Psi|\Psi\rangle = 1$ and

$$\langle A\rangle = \langle \Psi|A|\Psi\rangle. \tag{5.29}$$

It is important to stress that $\langle A\rangle$ does not represent the average of a classical statistical distribution of the dynamical variable A between the systems being measured. Each systems is identical and is in the *same* state described by the wave function Ψ. The actual value of A obtained in an experiment on a single system is inherently unpredictable (unless Ψ is an eigenfunction of A). Since Ψ contains the maximum possible information about the system, there is no way of specifying the state more completely in a way which would allow the value of A to be predicted.

Some measurements are not immediately repeatable, for example if the energy of a particle is measured by noting the length of the track it makes while slowing down in a photographic plate. In contrast, measurements of the component in a certain direction of the magnetic moment of an atom in a Stern–Gerlach experiment (see Chapter 1) can be repeated immediately by passing the beam through a second apparatus. In such a case, it is reasonable to expect that if a particular result a_n is obtained in the first measurement, the same result will be obtained if the measurement is repeated immediately. Since the result of the second measurement can be predicted with certainty, we deduce that after the first measurement the state of the system is described by the eigenfunction ψ_n of A belonging to the eigenvalue a_n. Hence, in this case the act of measurement has a 'filtering' effect so that whatever the state of the system before the measurement, it is certainly in an eigenstate of the measured quantity immediately afterwards.

Adjoint operator

It is useful to introduce an operator $A^\dagger$, called the *adjoint* or *Hermitian conjugate* of a linear operator A by the relation

$$\begin{aligned} \langle \mathrm{X}|A^\dagger|\Psi\rangle &= \langle (A\mathrm{X})|\Psi\rangle \\ &= \langle \Psi|A|\mathrm{X}\rangle^* \end{aligned} \tag{5.30}$$

where Ψ and X are any pair of square-integrable functions.

If we define a bra $\langle\Phi|$ by the relation

$$\langle\Phi| = \langle \mathrm{X}|A^\dagger \tag{5.31}$$

where the operator $A^\dagger$ acts to the left on the bra $\langle \mathrm{X}|$, then it follows from (5.30) that the kets $|\Phi\rangle$ and $|\mathrm{X}\rangle$ are related by

$$|\Phi\rangle = A|\mathrm{X}\rangle \tag{5.32}$$

A linear operator A satisfying

$$A = A^\dagger \tag{5.33}$$

is said to be *self-adjoint*, and from (5.22) we see that a self-adjoint operator is Hermitian. The adjoint of an operator is the operator generalisation of the complex conjugate of a complex number, and a self-adjoint operator is the operator generalisation of a real number. It is important to note that the operator $A^\dagger$ is not, in general, equal to the operator A^* (obtained by replacing every i appearing in A by $-$i). For example, the configuration space operator $p_x = -\mathrm{i}\hbar\partial/\partial x$ is Hermitian, so that $p_x^\dagger = p_x$, while $p_x^* = \mathrm{i}\hbar\partial/\partial x = -p_x$. Hence $p_x^\dagger \neq p_x^*$.

Three important properties of the adjoint operator (see Problem 5.4) are

$$(cA)^\dagger = c^* A^\dagger \tag{5.34}$$

where c is a complex number,

$$(A + B)^\dagger = A^\dagger + B^\dagger \tag{5.35}$$

and

$$(AB)^\dagger = B^\dagger A^\dagger. \tag{5.36}$$

Functions of operators

If a function $f(z)$ can be expanded in a power series,

$$f(z) = \sum_{i=0}^{\infty} c_i z^i \tag{5.37}$$

then the operator function $f(A)$ can be defined as

$$f(A) = \sum_{i=0}^{\infty} c_i A^i . \tag{5.38}$$

Consequently, if ψ_n is one of the eigenfunctions of A, corresponding to the eigenvalue a_n, $A^i \psi_n = (a_n)^i \psi_n$ and thus

$$f(A)\psi_n = f(a_n)\psi_n . \tag{5.39}$$

The adjoint operator to $f(A)$ can be obtained as follows. Using (5.34)–(5.36) and (5.38), we see that

$$\begin{aligned} [f(A)]^\dagger &= \sum_{i=0}^{\infty} c_i^* (A^i)^\dagger = \sum_{i=0}^{\infty} c_i^* (A^\dagger)^i \\ &= f^*(A^\dagger). \end{aligned} \tag{5.40}$$

In particular, if A is a self-adjoint operator, we have

$$[f(A)]^\dagger = f^*(A). \tag{5.41}$$

Inverse and unitary operators

The unit operator I is the operator that leaves any function Ψ unchanged

$$I\Psi = \Psi . \tag{5.42}$$

If, given an operator A, there exists another operator B such that

$$BA = AB = I \tag{5.43}$$

then B is said to be the *inverse* of A and one writes

$$B = A^{-1} . \tag{5.44}$$

A linear operator U is said to be *unitary* if

$$U^{-1} = U^\dagger \tag{5.45a}$$

or

$$UU^\dagger = U^\dagger U = I . \tag{5.45b}$$

Such an operator can be expressed in the form

$$U = e^{iA} \tag{5.46}$$

where A is a Hermitian operator. Indeed, using (5.41), we see that

$$U^\dagger = (e^{iA})^\dagger = e^{-iA} \tag{5.47}$$

from which (5.45b) follows.

Projection operators

An operator Λ is said to be *idempotent* if

$$\Lambda^2 = \Lambda. \tag{5.48}$$

If, in addition, Λ is Hermitian, it is called a *projection operator.*

Any function Ψ can be expressed in terms of two orthogonal functions Φ and X by means of a projection operator. This can be seen as follows. We first write

$$\Psi = \Phi + X \tag{5.49}$$

with $\Phi = \Lambda\Psi$ and $X = (I - \Lambda)\Psi$. Now

$$\begin{aligned} \langle\Phi|X\rangle &= \langle\Lambda\Psi|(I - \Lambda)\Psi\rangle \\ &= \langle\Psi|\Lambda - \Lambda^2|\Psi\rangle \\ &= 0 \end{aligned} \tag{5.50}$$

where in the second line we have used the fact that Λ is Hermitian and in the third line we have used (5.48). Note that $I - \Lambda$ is also a projection operator, since it is Hermitian, and

$$\begin{aligned} (I - \Lambda)^2 &= I - 2\Lambda + \Lambda^2 \\ &= I - \Lambda. \end{aligned} \tag{5.51}$$

5.3 Expansions in eigenfunctions

We shall now study in more detail the properties of the solutions of eigenvalue equations such as (5.21), generalising the discussion of Section 3.7. We assume that in (5.21) the operator A is a linear, Hermitian operator representing a dynamical variable, so that the eigenvalues a_n are real. We first consider the case where all the eigenfunctions ψ_n are square integrable and hence can be taken to be normalised to unity:

$$\langle\psi_n|\psi_n\rangle = 1. \tag{5.52}$$

Orthogonality

If ψ_i and ψ_j are two eigenfunctions of A corresponding to *different* eigenvalues a_i and a_j, then

$$A\psi_i = a_i\psi_i \tag{5.53a}$$

and

$$A\psi_j = a_j\psi_j. \tag{5.53b}$$

Hence

$$\begin{aligned}(a_i - a_j)\langle\psi_i|\psi_j\rangle &= \langle a_i\psi_i|\psi_j\rangle - \langle\psi_i|a_j\psi_j\rangle \\ &= \langle(A\psi_i)|\psi_j\rangle - \langle\psi_i|(A\psi_j)\rangle \\ &= 0\end{aligned} \tag{5.54}$$

where we have used the fact that A is Hermitian. Since $a_i \neq a_j$ it follows from (5.54) that

$$\langle\psi_i|\psi_j\rangle = 0, \qquad i \neq j \tag{5.55}$$

so that eigenfunctions belonging to different eigenvalues are *orthogonal.*

Degeneracy

We have seen in Section 3.5 that an eigenvalue a_n is said to be *degenerate* if there is more than one linearly independent eigenfunction belonging to that eigenvalue, the *degree* of degeneracy being the number of such linearly independent eigenfunctions.

Suppose that α is the degree of degeneracy of the eigenvalue a_n, so that the corresponding eigenfunctions can be labelled ψ_{nr} (with $r = 1, 2, \dots, \alpha$), and

$$A\psi_{nr} = a_n\psi_{nr}, \qquad r = 1, 2, \dots, \alpha. \tag{5.56}$$

By using the Schmidt orthogonalisation procedure discussed in Section 3.7, it is always possible to arrange that all the eigenfunctions ψ_{nr} are mutually orthogonal and each of them can be normalised to unity. Since the eigenfunctions belonging to different eigenvalues are mutually orthogonal, there is no loss of generality in writing that all the eigenfunctions satisfy the *orthonormality relations*

$$\langle\psi_{ir}|\psi_{js}\rangle = \delta_{ij}\delta_{rs} \tag{5.57}$$

where δ_{mn} is the Kronecker delta symbol such that

$$\delta_{mn} = \begin{cases} 1, & m = n \\ 0, & m \neq n. \end{cases} \tag{5.58}$$

To avoid cumbersome subscripts, unless it is necessary to distinguish the eigenfunctions belonging to a degenerate eigenvalue explicitly, we shall label all the orthonormal eigenfunctions of the operator A by a single index and write

$$\langle\psi_m|\psi_n\rangle = \delta_{mn}. \tag{5.59}$$

Postulate 6

A wave function representing any dynamical state can be expressed as a linear combination of the eigenfunctions of A, where A is the operator associated with a dynamical variable.

For the case of purely discrete eigenvalues, which we shall consider first, we have

$$\Psi = \sum_n c_n\psi_n. \tag{5.60}$$

The number of eigenfunctions in the set $\{\psi_n\}$ is in some cases finite, and in others infinite. Since *all* wave functions can be expanded in the set of eigenfunctions $\{\psi_n\}$, the set is said to be *complete*. The completeness of the set of eigenfunctions of some operators can be proved, but in general it must be postulated, as stated above. It should be noted that not all Hermitian operators possess a complete set of eigenfunctions; those that do are called *observables*.

The coefficients of the expansion (5.60) can be found by using the orthonormality relation (5.59). Taking the scalar product (see (5.14)) of both sides of (5.60) with the eigenfunction ψ_m, we obtain

$$\begin{aligned}\langle\psi_m|\Psi\rangle &= \sum_n c_n\langle\psi_m|\psi_n\rangle \\ &= \sum_n c_n\delta_{mn} \\ &= c_m.\end{aligned} \tag{5.61}$$

More explicitly, for the case of a one-particle system, we have

$$\begin{aligned}\Psi(\mathbf{r},t) &= \sum_n\left[\int\psi_n^*(\mathbf{r}')\Psi(\mathbf{r}',t)\mathrm{d}\mathbf{r}'\right]\psi_n(\mathbf{r}) \\ &= \int\left[\sum_n\psi_n^*(\mathbf{r}')\psi_n(\mathbf{r})\right]\Psi(\mathbf{r}',t)\mathrm{d}\mathbf{r}'\end{aligned} \tag{5.62}$$

and hence

$$\sum_n\psi_n^*(\mathbf{r}')\psi_n(\mathbf{r}) = \delta(\mathbf{r}-\mathbf{r}') \tag{5.63a}$$

where we have used the property (A.51) of the Dirac delta function. The relation (5.63a) is called the *closure* relation; it expresses the completeness of the set of functions $\{\psi_n\}$. The obvious generalisation of this relation for systems of N particles is

$$\sum_n \psi_n^*(\mathbf{r}_1', \dots, \mathbf{r}_N')\psi_n(\mathbf{r}_1, \dots, \mathbf{r}_N) = \delta(\mathbf{r}_1 - \mathbf{r}_1')\dots\delta(\mathbf{r}_N - \mathbf{r}_N'). \qquad \textbf{(5.63b)}$$

Using the closure relation (5.63a) we can write the scalar product of two wave functions as

$$\begin{aligned}\langle \mathrm{X}|\Psi\rangle &= \int \mathrm{X}^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)\mathrm{d}\mathbf{r} \\ &= \int \mathrm{X}^*(\mathbf{r}, t)\delta(\mathbf{r} - \mathbf{r}')\Psi(\mathbf{r}', t)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\ &= \sum_n \int \mathrm{X}^*(\mathbf{r}, t)\psi_n(\mathbf{r})\mathrm{d}\mathbf{r} \int \psi_n^*(\mathbf{r}')\Psi(\mathbf{r}', t)\mathrm{d}\mathbf{r}' \\ &= \sum_n \langle \mathrm{X}|\psi_n\rangle\langle\psi_n|\Psi\rangle \qquad \textbf{(5.64)}\end{aligned}$$

where we have considered the one-particle case for ease of notation. We see from (5.64) that in the Dirac notation the closure relation can be written in the compact form

$$\sum_n |\psi_n\rangle\langle\psi_n| = I \qquad \textbf{(5.65)}$$

where I is the unit operator.

Probability amplitudes

In the state described by a wave function Ψ, normalised to unity, the expectation value of an observable A is given by (5.29). Expanding Ψ in the complete orthonormal set of eigenfunctions $\{\psi_n\}$ of A according to (5.60), and expanding Ψ^* similarly, we have

$$\begin{aligned}\langle A\rangle &= \langle\Psi|A|\Psi\rangle \\ &= \sum_m\sum_n c_m^* c_n \langle\psi_m|A|\psi_n\rangle \\ &= \sum_m\sum_n c_m^* c_n a_n \langle\psi_m|\psi_n\rangle \\ &= \sum_n |c_n|^2 a_n \qquad \textbf{(5.66)}\end{aligned}$$

where the orthonormality relation (5.59) has been used to obtain the last line. Since Ψ is normalised to unity, $\langle\Psi|\Psi\rangle = 1$, we also have

$$\sum_n |c_n|^2 = 1. \tag{5.67}$$

In view of the fact that the possible results of measurements of A are the eigenvalues a_n, and since the average value obtained in series of measurements of a large number of identically prepared systems, all in the same state described by Ψ, is the expectation value $\langle A\rangle$, it is reasonable, following M. Born, to interpret the quantity

$$P_n = |c_n|^2 = |\langle\psi_n|\Psi\rangle|^2 \tag{5.68}$$

as the probability that in a given measurement the particular value a_n will be obtained. The condition (5.67) is thus seen to express the fact that the probability of obtaining some result is unity. The coefficients $c_n = \langle\psi_n|\Psi\rangle$ are called *probability amplitudes*.

In obtaining the above results we have implicitly included the degeneracy index in the summations. If a particular eigenvalue a_n is α times degenerate, and $\psi_{nr}(r = 1, \dots, \alpha)$ are the corresponding orthonormal eigenfunctions, we have instead of (5.60) the explicit expansion

$$\Psi = \sum_n \sum_{r=1}^{\alpha} c_{nr}\psi_{nr} \tag{5.69}$$

with

$$c_{nr} = \langle\psi_{nr}|\Psi\rangle. \tag{5.70}$$

A simple reworking of (5.66) then yields

$$\langle A\rangle = \sum_n \sum_{r=1}^{\alpha} |c_{nr}|^2 a_n \tag{5.71}$$

so that the probability of obtaining upon measurement of A the degenerate eigenvalue a_n is

$$P_n = \sum_{r=1}^{\alpha} |c_{nr}|^2 = \sum_{r=1}^{\alpha} |\langle\psi_{nr}|\Psi\rangle|^2. \tag{5.72}$$

After a measurement leading to the value a_n, the system is described by the (unnormalised) wave function

$$\Psi_n = \sum_{r=1}^{\alpha} c_{nr}\psi_{nr} \tag{5.73}$$

and if the measurement is immediately repeated the value a_n will be obtained with certainty.

The continuous spectrum

So far in this chapter, observables which possess only a spectrum of discrete eigenvalues have been considered. Our discussion is therefore not sufficiently general, as we have already encountered observables for which the spectrum is purely continuous, or for which the spectrum possesses both a discrete and a continuum part. For example, the momentum operator p_x belongs to the former category (see Section 4.2) and the Hamiltonian operator for a particle in an attractive one-dimensional square well belongs to the latter category (see Section 4.6). Thus, in general, in order to expand an arbitrary wave function in the complete set of eigenfunctions of an operator, eigenfunctions corresponding to continuous as well as discrete eigenvalues are required. As we have seen in Chapters 3 and 4, the eigenfunctions corresponding to the continuous spectrum are not normalisable in the usual sense. One way of avoiding this difficulty is to render the spectrum purely discrete by enclosing the system in a large box with walls which are either impenetrable, or where periodic boundary conditions are imposed. In that case, the various expansion and closure formulae remain the same as for the discrete case. The physical results obtained from the theory are independent of the size of the normalisation box, provided that it is large enough. The alternative is to 'normalise' the eigenfunctions corresponding to the continuous eigenvalues in terms of the Dirac delta functions, as we did for the plane waves in Section 4.2.

Consider an observable A with a spectrum containing both discrete eigenvalues a_n and a continuous range of eigenvalues which we denote by a. The corresponding eigenfunctions are ψ_n and ψ_a, respectively. For the sake of simplicity we shall not display the degeneracy indices. Thus we have

$$A\psi_n = a_n\psi_n, \qquad A\psi_a = a\psi_a. \tag{5.74}$$

The continuous eigenvalues must clearly be real, as are the discrete ones. The discrete eigenfunctions will be taken to be orthonormal, as before.

According to the 'expansion' Postulate 6, an arbitray wave function Ψ must be expandable in the complete set $\{\psi_n, \psi_a\}$,

$$\Psi = \sum_n c_n\psi_n + \int c(a)\psi_a \mathrm{d}a \tag{5.75}$$

where the integral runs over the whole range of values of a. Taking the case in which Ψ is normalised to unity, the expectation value of the observable A is given from (5.29) and (5.75) by

$$
\begin{aligned}
\langle A\rangle &= \langle\Psi|A|\Psi\rangle \\
&= \sum_m\sum_n c_m^* c_n\langle\psi_m|A|\psi_n\rangle + \sum_m\int \mathrm{d}a c_m^* c(a)\langle\psi_m|A|\psi_a\rangle \\
&\quad + \sum_n\int \mathrm{d}a' c^*(a')c_n\langle\psi_{a'}|A|\psi_n\rangle + \int \mathrm{d}a\int \mathrm{d}a' c^*(a')c(a)\langle\psi_{a'}|A|\psi_a\rangle \\
&= \sum_m\sum_n c_m^* c_n a_n\langle\psi_m|\psi_n\rangle + \sum_m\int \mathrm{d}a c_m^* c(a)a\langle\psi_m|\psi_a\rangle \\
&\quad + \sum_n\int \mathrm{d}a' c^*(a')c_n a_n\langle\psi_{a'}|\psi_n\rangle \\
&\quad + \int \mathrm{d}a\int \mathrm{d}a' c^*(a')c(a)a\langle\psi_{a'}|\psi_a\rangle
\end{aligned}
\qquad \mathbf{(5.76)}
$$

where in writing the last two lines we have used (5.74).

Now, in order to maintain the interpretation of the coefficients c_n and $c(a)$ as probability amplitudes, we demand that the generalisation of the basic results (5.66) should be, in the present case,

$$\langle A\rangle = \sum_n |c_n|^2 a_n + \int |c(a)|^2 a\mathrm{d}a. \qquad \mathbf{(5.77)}$$

Comparing (5.76) with (5.77) and recollecting that $\langle\psi_m|\psi_n\rangle = \delta_{mn}$, we deduce the following:

(1) All the eigenfunctions belonging to the continuum spectrum must be orthogonal to all those belonging to the discrete spectrum:

$$\langle\psi_m|\psi_a\rangle = 0. \qquad \mathbf{(5.78)}$$

(2) The eigenfunctions belonging to the continuum spectrum must satisfy the orthonormality condition

$$\langle\psi_{a'}|\psi_a\rangle = \delta(a-a'). \qquad \mathbf{(5.79)}$$

Using these results, together with (5.75), we then find that the coefficients c_n and $c(a)$ are given, respectively, by

$$c_n = \langle\psi_n|\Psi\rangle, \qquad c(a) = \langle\psi_a|\Psi\rangle. \qquad \mathbf{(5.80)}$$

The closure relation (5.63a) for a one-particle system now reads

$$\sum_n \psi_n^*(\mathbf{r}')\psi_n(\mathbf{r}) + \int \psi_a^*(\mathbf{r}')\psi_a(\mathbf{r})\mathrm{d}a = \delta(\mathbf{r}-\mathbf{r}') \qquad \mathbf{(5.81a)}$$

and the corresponding result for a N-particle system is

$$\sum_n \psi_n^*(\mathbf{r}_1', \dots, \mathbf{r}_N')\psi_n(\mathbf{r}_1, \dots, \mathbf{r}_N) + \int \psi_a^*(\mathbf{r}_1', \dots, \mathbf{r}_N')\psi_a(\mathbf{r}_1, \dots, \mathbf{r}_N)\mathrm{d}a$$

$$= \delta(\mathbf{r}_1 - \mathbf{r}_1') \dots \delta(\mathbf{r}_N - \mathbf{r}_N'). \qquad \textbf{(5.81b)}$$

If the box normalisation is employed (so that the entire spectrum becomes discrete) and we denote by ψ_i the normalised eigenfunction corresponding to the discrete eigenvalue $a_i (i = 1, 2, \dots)$, the connection between the eigenfunction ψ_i and the continuum eigenfunction ψ_a can be established as follows. Assuming the normalisation box to be very large, the eigenvalues a_i corresponding to the continuous spectrum are densely distributed, and for these eigenvalues the index i can be treated as a continuous variable. Hence, setting $i \equiv i(a)$ and introducing a *density of states*

$$\rho(a) = \frac{\mathrm{d}i}{\mathrm{d}a} \qquad \textbf{(5.82)}$$

which is equal to the number of discrete states within a unit range of a, we have

$$\sum_i c_i\psi_i \rightarrow \int c_i\psi_i \mathrm{d}i = \int \rho(a)c_i\psi_i \mathrm{d}a. \qquad \textbf{(5.83)}$$

Requiring that

$$\int \rho(a)c_i\psi_i \mathrm{d}a = \int c(a)\psi_a \mathrm{d}a \qquad \textbf{(5.84)}$$

and also (from the closure relation and with $\sum_i \rightarrow \int \rho(a)\mathrm{d}a$)

$$\int \rho(a)\psi_i^*(\mathbf{r}')\psi_i(\mathbf{r})\mathrm{d}a = \int \psi_a^*(\mathbf{r}')\psi_a(\mathbf{r})\mathrm{d}a \qquad \textbf{(5.85)}$$

one can make the identifications

$$\psi_a = [\rho(a)]^{1/2}\psi_i \qquad \textbf{(5.86a)}$$

and

$$c(a) = [\rho(a)]^{1/2}c_i \qquad \textbf{(5.86b)}$$

which allow one to 'translate' formulae written using the 'box normalisation' into those written using the delta function 'normalisation'.

5.4 Commuting observables, compatibility and the Heisenberg uncertainty relations

We saw in Chapter 3 that the *commutator* of two operators A and B is defined as

$$[A, B] = AB - BA. \qquad \textbf{(5.87)}$$

If the commutator vanishes when acting on *any* wave function, the two operators A and B are said to commute, $AB = BA$. The operators representing the 'canonically conjugate' position and momentum variables of a particle satisfy the fundamental commutation relations (see (3.77))

$$[x, p_x] = [y, p_y] = [z, p_z] = \mathrm{i}\hbar \tag{5.88}$$

with all other pairs of operators (for example y and p_x) commuting. If a system contains several particles with position vectors $\mathbf{r}_i$ and momenta $\mathbf{p}_i$ $(i = 1, 2, \dots, N)$, it is clear that *all operators referring to one particle commute with all those referring to another.* The only pairs out of the operators (x_1, y_1, z_1), $(x_2, y_2, z_2), \dots,$ and (p_{1x}, p_{1y}, p_{1z}), $(p_{2x}, p_{2y}, p_{2z}), \dots,$ which do not commute are the canonically conjugate pairs (x_i, p_{ix}), (y_i, p_{iy}) and (z_i, p_{iz}) for which, in conformity with (5.88)

$$[x_i, p_{ix}] = [y_i, p_{iy}] = [z_i, p_{iz}] = \mathrm{i}\hbar \qquad (i = 1, 2, \dots, N). \tag{5.89}$$

Commuting observables

Let us suppose that A and B are two observables. If there exists a complete set of functions ψ_n such that each function is simultaneously an eigenfunction of A and of B, the observables A and B are said to be *compatible.* If the eigenvalues of A and B corresponding to the eigenfunction ψ_n are denoted by a_n and b_n, respectively, then

$$A\psi_n = a_n\psi_n, \qquad B\psi_n = b_n\psi_n. \tag{5.90}$$

In a state described by ψ_n, a measurement of A must produce the precise result a_n and a measurement of B the precise result b_n, with no limit on the precision with which A and B can be measured simultaneously. Examples of such compatible observables are the Cartesian components x, y and z of the position vector $\mathbf{r}$ of a particle, and others are the Cartesian components p_x, p_y and p_z of its momentum $\mathbf{p}$. In contrast, x and p_x are not compatible, since, by the uncertainty relations, both of these quantities cannot be measured simultaneously to arbitrary precision. More generally, several observables $A, B, C, \dots,$ are said to be compatible if they possess a common set of eigenfunctions. In this case, all these observables can be measured simultaneously to arbitrary precision.

If A and B are two compatible observables, and ψ_n is a common eigenfunction, we have

$$\begin{aligned} AB\psi_n &= a_n b_n \psi_n \\ &= b_n a_n \psi_n \\ &= BA\psi_n. \end{aligned} \tag{5.91}$$

Since any wave function Ψ can be expanded in the complete set of eigenfunctions ψ_n according to (5.60)[3], we find, using (5.91),

$$(AB - BA)\Psi = \sum_n c_n(AB - BA)\psi_n = 0 \tag{5.92}$$

so that

$$[A, B] = 0 \tag{5.93}$$

and two compatible observables commute.

The converse of this result, that two operators which commute possess a complete set of common eigenfunctions, will now be proved. First, consider the case for which A has *non-degenerate* eigenvalues a_n. Then if A and B commute,

$$A(B\psi_n) = BA\psi_n = a_n(B\psi_n) \tag{5.94}$$

and therefore $(B\psi_n)$ is an eigenfunction of A belonging to the eigenvalue a_n. Since a_n is non-degenerate, $(B\psi_n)$ can only differ from ψ_n by a multiplicative constant which we call b_n

$$B\psi_n = b_n\psi_n. \tag{5.95}$$

Thus we see that ψ_n is simultaneously an eigenfunction of the operators A and B belonging to the eigenvalues a_n and b_n, respectively.

Now consider the case in which a_n is a degenerate eigenvalue of A, of degree α, with corresponding linearly independent eigenfunctions $\psi_{nr} (r = 1, 2, \dots , \alpha)$. Since A and B commute, $(B\psi_{nr})$ is an eigenfunction of A belonging to the degenerate eigenvalue a_n. It follows that $(B\psi_{nr})$ can be expanded in terms of the α linearly independent functions $\psi_{n1}, \psi_{n2}, \dots , \psi_{n\alpha}$

$$B\psi_{nr} = \sum_{s=1}^{\alpha} c_{rs}\psi_{ns} \tag{5.96}$$

where c_{rs} are the expansion coefficients. Let us form a linear combination of the functions ψ_{nr} with α constants d_r, so that

$$B\sum_{r=1}^{\alpha} d_r\psi_{nr} = \sum_{r=1}^{\alpha}\sum_{s=1}^{\alpha} d_r c_{rs}\psi_{ns}. \tag{5.97}$$

Therefore, $\sum_r d_r\psi_{nr}$ is an eigenfunction of B belonging to an eigenvalue b_n provided that

$$\sum_{r=1}^{\alpha} d_r c_{rs} = b_n d_s, \qquad s = 1, 2, \dots , \alpha. \tag{5.98}$$

---

[3] For notational simplicity we only treat here the case of a discrete spectrum.

This is a system of α homogeneous linear equations for the α constants d_r. This system has a non-trivial solution if

$$\det|c_{rs} - b_n\delta_{rs}| = 0 \tag{5.99}$$

where det means the determinant. This is an equation of order α for b_n, having α roots. Corresponding to each root, $b_n = b_n^{(k)}$, where $k = 1, 2, \dots, \alpha$, is a solution $d_r^{(k)}$ of (5.98) and we see by construction that

$$\phi_n^{(k)} = \sum_{r=1}^{\alpha} d_r^{(k)} \psi_{nr} \tag{5.100}$$

is simultaneously an eigenfunction of A, belonging to the eigenvalue a_n, and of B, belonging to the eigenvalue $b_n^{(k)}$. The eigenvalue a_n together with the eigenvalue $b_n^{(k)}$ completely specify a particular simultaneous eigenfunction $\phi_n^{(k)}$ of A and B, so that when both operators are considered together the degeneracy is removed.

The foregoing analysis can be extended to show that if $A, B, C, \dots$, are a set of commuting observables, then a complete set of simultaneous eigenfunctions of these observables exists. The largest set of commuting observables which can be found (for a given system) is called a *complete set of commuting observables*. In this case the eigenvalues $a_n, b_n, c_n \dots$, completely specify a simultaneous eigenfunction ψ_n of $A, B, C, \dots$ (apart from a multiplicative constant), so that the degeneracy is completely removed.

Commutator algebra

The following relations satisfied by commutators are useful and are readily proved (see Problem 5.6)

$$[A, B] = -[B, A] \tag{5.101a}$$

$$[A, B + C] = [A, B] + [A, C] \tag{5.101b}$$

$$[A, BC] = [A, B]C + B[A, C] \tag{5.101c}$$

$$[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0 \tag{5.101d}$$

The Heisenberg uncertainty relations

In Section 2.5 we discussed the Heisenberg uncertainty principle, and found the 'order of magnitude' uncertainty relations (2.71) for the position and momentum of a particle. We shall now obtain a precise form of these uncertainty relations by adopting an accurate definition of the uncertainties Δx, $\Delta p_x, \dots$, which appear in these relations. At the same time, we shall derive a more general expression of the Heisenberg uncertainty relations, which is valid for two canonically conjugate observables A and B, such that $[A, B] = i\hbar$.

Let us consider two observables A and B. Let $\langle A\rangle \equiv \langle\Psi|A|\Psi\rangle$ be the expectation value of A in a given state Ψ (normalised to unity) and let $\langle B\rangle \equiv \langle\Psi|B|\Psi\rangle$ be the expectation value of B in the state Ψ. We define the uncertainty ΔA to be

$$\Delta A = [\langle (A - \langle A\rangle)^2\rangle]^{1/2} \tag{5.102}$$

so that

$$(\Delta A)^2 = \langle (A - \langle A\rangle)^2\rangle = \langle A^2\rangle - \langle A\rangle^2 \tag{5.103}$$

is the mean-square deviation about the expectation value $\langle A\rangle$. Similarly, we define the uncertainty ΔB to be

$$\Delta B = [\langle (B - \langle B\rangle)^2\rangle]^{1/2}. \tag{5.104}$$

We shall now prove that

$$\Delta A \Delta B \geqslant \frac{1}{2}|\langle [A, B]\rangle|. \tag{5.105}$$

To this end, we first introduce the linear Hermitian operators

$$\bar{A} = A - \langle A\rangle, \qquad \bar{B} = B - \langle B\rangle \tag{5.106}$$

which are such that their expectation values vanish. In terms of these operators, we have

$$(\Delta A)^2 = \langle \bar{A}^2\rangle, \qquad (\Delta B)^2 = \langle \bar{B}^2\rangle \tag{5.107}$$

and we also note that

$$[\bar{A}, \bar{B}] = [A - \langle A\rangle, B - \langle B\rangle] = [A, B]. \tag{5.108}$$

Next, we consider the linear (but not Hermitian) operator

$$C = \bar{A} + \mathrm{i}\lambda\bar{B} \tag{5.109}$$

where λ is a real constant. The adjoint of C is the operator $C^\dagger = \bar{A} - \mathrm{i}\lambda\bar{B}$ and we note that the expectation value of $CC^\dagger$ is real and non-negative, since

$$\langle CC^\dagger\rangle = \langle \Psi|CC^\dagger|\Psi\rangle = \langle C^\dagger\Psi|C^\dagger\Psi\rangle \geqslant 0. \tag{5.110}$$

From (5.109) and (5.110) it follows that the expectation value

$$\langle (\bar{A} + \mathrm{i}\lambda\bar{B})(\bar{A} - \mathrm{i}\lambda\bar{B})\rangle = \langle \bar{A}^2 + \lambda^2\bar{B}^2 - \mathrm{i}\lambda[\bar{A}, \bar{B}]\rangle \tag{5.111}$$

is real and non-negative. Using (5.111), (5.107) and (5.108), we see that the function

$$\begin{aligned} f(\lambda) &= \langle \bar{A}^2\rangle + \lambda^2\langle \bar{B}^2\rangle - \mathrm{i}\lambda\langle [\bar{A}, \bar{B}]\rangle \\ &= (\Delta A)^2 + \lambda^2(\Delta B)^2 - \mathrm{i}\lambda\langle [A, B]\rangle \end{aligned} \tag{5.112}$$

is also real and non-negative, which implies that $\langle [A, B]\rangle$ is purely imaginary. Now, the function $f(\lambda)$ has a minimum for

$$\lambda_0 = \frac{\mathrm{i}}{2}\frac{\langle [A, B]\rangle}{(\Delta B)^2} \tag{5.113}$$

and the value of $f(\lambda)$ at the minimum is

$$f(\lambda_0) = (\Delta A)^2 + \frac{1}{4}\frac{(\langle[A, B]\rangle)^2}{(\Delta B)^2}. \tag{5.114}$$

Since this value is non-negative, we must have

$$(\Delta A)^2(\Delta B)^2 \geqslant -\frac{1}{4}(\langle[A, B]\rangle)^2 \tag{5.115}$$

and the property (5.105) follows by remembering that $\langle[A, B]\rangle$ is purely imaginary.

For two observables which are canonically conjugate, so that $[A, B] = \mathrm{i}\hbar$ we have $\langle[A, B]\rangle = \mathrm{i}\hbar$ and we therefore deduce from (5.115) that

$$\Delta A \Delta B \geqslant \frac{\hbar}{2}. \tag{5.116}$$

In particular, for the pairs of canonically conjugate variables (x, p_x), (y, p_y) and (z, p_z), we can state the position–momentum uncertainty relations in the precise form

$$\Delta x \Delta p_x \geqslant \frac{\hbar}{2}, \qquad \Delta y \Delta p_y \geqslant \frac{\hbar}{2}, \qquad \Delta z \Delta p_z \geqslant \frac{\hbar}{2} \tag{5.117}$$

with

$$\Delta x = [\langle(x - \langle x\rangle)^2\rangle]^{1/2}, \qquad \Delta p_x = [\langle(p_x - \langle p_x\rangle)^2\rangle]^{1/2} \tag{5.118}$$

and similar definitions for Δy, Δp_y, Δz and Δp_z.

The minimum uncertainty wave packet

It is clear that the equality sign in (5.105), giving the minimum uncertainty product, holds when $\lambda = \lambda_0$ and $C^\dagger \Psi = 0$ (see (5.110) and (5.114)) so that

$$(\bar{A} - \mathrm{i}\lambda_0 \bar{B})\Psi = 0. \tag{5.119}$$

This equation can be used to find the wave function Ψ such that the product $\Delta A \Delta B$ takes its minimum value.

As an example, let us consider the motion of a particle in one dimension. Setting $A = x$ and $B = p_x$, the minimum value of the uncertainty product $\Delta x \Delta p_x$ at a definite instant of time (say $t = 0$) is given by

$$\Delta x \Delta p_x = \frac{\hbar}{2}. \tag{5.120}$$

Writing $\psi(x) \equiv \Psi(x, t = 0)$, and using (5.119) with $\bar{A} = x - \langle x\rangle$, $\bar{B} = p_x - \langle p_x\rangle$ and $\lambda_0 = \mathrm{i}\langle[x, p_x]\rangle/[2(\Delta p_x)^2] = -\hbar/[2(\Delta p_x)^2]$, we find that

$$\left(-\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x} - \langle p_x\rangle\right)\psi(x) = \frac{2\mathrm{i}(\Delta p_x)^2}{\hbar}(x - \langle x\rangle)\psi(x). \tag{5.121}$$

This first order differential equation is readily integrated to give the *minimum uncertainty wave function*

$$\psi(x) = C \exp\left(\frac{\mathrm{i}}{\hbar}\langle p_x \rangle x\right) \exp\left[-\frac{(\Delta p_x)^2 (x - \langle x \rangle)^2}{\hbar^2}\right] \tag{5.122}$$

where C is a normalisation constant. This wave function is seen to be a Gaussian wave packet.

5.5 Unitary transformations

We shall now show that by acting with a unitary operator on the wave function describing a state of a system, one obtains a new wave function which provides a completely equivalent description of this state. The application of a unitary operator to every wave function associated with a system is called a unitary transformation.

Let Ψ and X be two functions and let A be a linear, Hermitian operator such that

$$A\Psi = \mathrm{X}. \tag{5.123}$$

Let us apply the unitary transformation U, so that

$$\Psi' = U\Psi, \qquad \mathrm{X}' = U\mathrm{X}. \tag{5.124}$$

Writing

$$A'\Psi' = \mathrm{X}' \tag{5.125}$$

we have

$$A'U\Psi = U\mathrm{X} = UA\Psi \tag{5.126}$$

so that

$$A'U = UA. \tag{5.127}$$

Since $UU^\dagger = U^\dagger U = I$ (see (5.45b)), it follows at once from (5.127) that

$$A' = UAU^\dagger, \qquad A = U^\dagger A' U. \tag{5.128}$$

A number of results will now be proved.

(1) If A is Hermitian, then A' is also Hermitian.
From (5.128) we have

$$A'^\dagger = (UAU^\dagger)^\dagger = UA^\dagger U^\dagger \tag{5.129}$$

and since $A = A^\dagger$, we find that

$$A'^\dagger = UAU^\dagger = A'. \tag{5.130}$$

(2) Operator equations remain unchanged in form.
Consider for example the operator equation

$$A = c_1 B + c_2 CD \tag{5.131}$$

where c_1 and c_2 are complex constants and B, C, D are operators. Using again the fact that $UU^\dagger = U^\dagger U = I$, we have

$$UAU^\dagger = c_1 UBU^\dagger + c_2 UCU^\dagger UDU^\dagger \tag{5.132}$$

or

$$A' = c_1 B' + c_2 C'D' \tag{5.133}$$

where A', B', C' and D' are the transforms of A, B, C and D, respectively. We also note that if A and B are two operators such that $[A, B] = c$, where c is a complex number, and A' and B' are their transforms, then

$$[A, B] = [A', B'] = c. \tag{5.134}$$

It follows that the fundamental commutation relations (5.88) remain unchanged under unitary transformations.

(3) The eigenvalues of A' are the same as those of A.
Indeed, we can rewrite the eigenvalue equation (5.21) as

$$AU^\dagger U\psi_n = a_n U^\dagger U\psi_n. \tag{5.135}$$

Operating from the left throughout with U, we obtain

$$(UAU^\dagger)(U\psi_n) = a_n(UU^\dagger)(U\psi_n) \tag{5.136}$$

so that

$$A'\psi'_n = a_n\psi'_n \tag{5.137}$$

with $\psi'_n = U\psi_n$. Hence $A' = UAU^\dagger$ has the same eigenvalues as A.

(4) The quantities $\langle \mathrm{X}|A|\Psi\rangle$ are unchanged by a unitary transformation.
The proof is as follows:

$$\begin{aligned}\langle \mathrm{X}|A|\Psi\rangle &= \langle \mathrm{X}|U^\dagger UAU^\dagger U|\Psi\rangle \\ &= \langle (U\mathrm{X})|UAU^\dagger|(U\Psi)\rangle \\ &= \langle \mathrm{X}'|A'|\Psi'\rangle \end{aligned} \tag{5.138}$$

where in the second line we have used (5.30). A corollary of (5.138) is that expectation values remain unchanged under unitary transformations:

$$\langle \Psi|A|\Psi\rangle = \langle \Psi'|A'|\Psi'\rangle. \tag{5.139}$$

By choosing $A = I$ in (5.138), we also see that

$$\langle \mathrm{X}|\Psi\rangle = \langle \mathrm{X}'|\Psi'\rangle \tag{5.140}$$

so that the scalar product is invariant under unitary transformations. Consequently, the normalisation is also preserved in such transformations, since

$$\langle \Psi | \Psi \rangle = \langle \Psi' | \Psi' \rangle. \tag{5.141}$$

From the above results we see that physical quantities such as eigenvalues and expectation values can be equally well calculated from the transformed wave functions $\Psi', \mathrm{X}', \ldots$, and operators $A', B', \ldots$, as from the original ones. This raises the possibility that a dynamical problem may be easier to solve by finding a suitable unitary transformation leading to a new set of wave functions and operators. It is also worth noting that each different unitary transformation leads to a new form or 'representation' of the operators associated with the basic dynamical variables x, y, z and p_x, p_y, p_z, while the fundamental commutation relations (5.88) remain invariant. This suggests that an alternative formulation of quantum mechanics can be developed by considering the commutation relations (5.88) as one of the basic postulates of the theory[4].

As an example, consider a particle moving in one dimension, for which the wave function in the position representation is $\Psi(x, t)$, the position and momentum operators being given in that representation by $x_{\text{op}} = x$ and $(p_x)_{\text{op}} = -\mathrm{i}\hbar\partial/\partial x$, respectively. The Fourier transform (2.43) of $\Psi(x, t)$ defines the momentum space wave function $\Phi(p_x, t)$, and this transformation is unitary. Indeed, we can write

$$\begin{aligned} \Phi(p_x, t) &= U\Psi(x, t) \\ &= (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} \mathrm{e}^{-\mathrm{i}p_x x/\hbar} \Psi(x, t) \mathrm{d}x, \end{aligned} \tag{5.142}$$

the inverse transformation (2.42) being

$$\begin{aligned} \Psi(x, t) &= U^{-1}\Phi(p_x, t) \\ &= (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} \mathrm{e}^{\mathrm{i}p_x x/\hbar} \Phi(p_x, t) \mathrm{d}p_x \\ &= U^{\dagger}\Phi(p_x, t). \end{aligned} \tag{5.143}$$

Thus

$$U^{\dagger}U\Psi(x, t) = U^{\dagger}\Phi(p_x, t) = \Psi(x, t) \tag{5.144a}$$

and also

$$UU^{\dagger}\Phi(p_x, t) = U\Psi(x, t) = \Phi(p_x, t) \tag{5.144b}$$

---

[4] See Dirac (1958).

from which we see that $U^\dagger U = UU^\dagger = I$, so that the integral operator U defined by (5.142) is unitary. By Parseval's theorem (see equation (A.43) of Appendix A)

$$\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \mathrm{d}x = \int_{-\infty}^{+\infty} |\Phi(p_x,t)|^2 \mathrm{d}p_x \tag{5.145}$$

which is just a particular case of (5.141).

As we saw in Table 3.2, in the momentum representation the position and momentum operators are given by $x_{\mathrm{op}} = \mathrm{i}\hbar\partial/\partial p_x$ and $(p_x)_{\mathrm{op}} = p_x$, respectively. It is straightforward to verify that in both the position and momentum representations the commutation relation $[x_{\mathrm{op}}, (p_x)_{\mathrm{op}}] = \mathrm{i}\hbar$ is satisfied, which illustrates the invariance of the basic commutation relations (5.88) under unitary transformations.

Infinitesimal unitary transformations

If the unitary operator U is very close to the unit operator I, the unitary transformation is said to be infinitesimal. We may then write

$$U = I + \mathrm{i}\varepsilon F \tag{5.146}$$

where ε is a real, arbitrary small parameter, and F is an operator which must be *Hermitian*. Indeed, from (5.45) and (5.146) we deduce that to first order in ε

$$I = U^\dagger U = (I - \mathrm{i}\varepsilon F^\dagger)(I + \mathrm{i}\varepsilon F) \simeq I - \mathrm{i}\varepsilon F^\dagger + \mathrm{i}\varepsilon F \tag{5.147}$$

from which $\varepsilon(F - F^\dagger) = 0$ and

$$F = F^\dagger. \tag{5.148}$$

The operator F is called the *generator* of the infinitesimal unitary transformation. We remark that if an infinitesimal unitary transformation is performed, the transformed wave functions are given by

$$\Psi' \equiv \Psi + \delta\Psi = (I + \mathrm{i}\varepsilon F)\Psi \tag{5.149}$$

so that

$$\delta\Psi = \mathrm{i}\varepsilon F\Psi \tag{5.150}$$

while from (5.128), (5.146) and (5.148) the transformed operators are

$$\begin{aligned} A' \equiv A + \delta A &= (I + \mathrm{i}\varepsilon F)A(I - \mathrm{i}\varepsilon F) \\ &= A + \mathrm{i}\varepsilon FA - \mathrm{i}\varepsilon AF + \mathcal{O}(\varepsilon^2) \\ &= A + \mathrm{i}\varepsilon[F, A] + \mathcal{O}(\varepsilon^2) \end{aligned} \tag{5.151}$$

and therefore, to first order in ε,

$$\delta A = \mathrm{i}\varepsilon[F, A]. \tag{5.152}$$

5.6 Matrix representations of wave functions and operators

Let us consider a complete set of orthonormal functions $\{\psi_n\}$. To simplify the notation we shall assume that the index n is discrete. Any physical wave function Ψ can be expanded in terms of this set according to equation (5.60), where the coefficients c_n are determined by $c_n = \langle\psi_n|\Psi\rangle$ (see (5.61)). For a given set of functions $\{\psi_n\}$, the numbers c_n specify the wave function Ψ completely. The coefficients c_n are said to *represent* Ψ in the *basis* (or *representation*) $\{\psi_n\}$. We can think of the set of functions $\{\psi_n\}$ as being analogous to a set of orthogonal axes and the numbers c_n as being analogous to the components of a 'vector' Ψ along each of these axes.

The action of a linear and Hermitian operator A on a wave function produces another wave function

$$\mathrm{X} = A\Psi. \tag{5.153}$$

The wave function X can also be expanded in terms of the basis $\{\psi_n\}$ as

$$\mathrm{X} = \sum_m d_m\psi_m \tag{5.154}$$

where the coefficients of the expansion are given by $d_m = \langle\psi_m|\mathrm{X}\rangle$. Using (5.153) and (5.60), we have

$$\begin{aligned} d_m &= \langle\psi_m|\mathrm{X}\rangle \\ &= \langle\psi_m|A|\Psi\rangle \\ &= \sum_n \langle\psi_m|A|\psi_n\rangle c_n. \end{aligned} \tag{5.155}$$

The quantities

$$A_{mn} = \langle\psi_m|A|\psi_n\rangle \tag{5.156}$$

are called the *matrix elements* of the operator A in the basis $\{\psi_n\}$. The equation (5.155) can thus be written as

$$d_m = \sum_n A_{mn}c_n. \tag{5.157}$$

It relates the coefficients c_n which uniquely define Ψ to the coefficients d_m which uniquely define X, and is completely equivalent to the operator equation (5.153). Thus the set of matrix elements A_{mn} completely specifies the operator A within the basis $\{\psi_n\}$. We remark that equation (5.157) can be written as a *matrix equation*

$$\mathbf{d} = \mathbf{A}\mathbf{c} \tag{5.158}$$

or

$$\begin{pmatrix} d_1 \\ d_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \vdots & \vdots & \dots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \tag{5.159}$$

where **d** and **c** are column vectors and **A** is a square matrix. If the basis $\{\psi_n\}$ contains a finite number of functions, the matrix **A** is of finite dimension; otherwise **A** is of infinite dimension. Clearly there are as many different representations of wave functions and operators as there are basis sets of functions $\{\psi_n\}$.

Using (5.64) and the fact that $c_n = \langle\psi_n|\Psi\rangle$ and $d_n^* = \langle \mathrm{X}|\psi_n\rangle$, the scalar product $\langle \mathrm{X}|\Psi\rangle$ can be expressed as

$$\langle \mathrm{X}|\Psi\rangle = \sum_n d_n^* c_n = \mathbf{d}^{\dagger}.\mathbf{c} \tag{5.160}$$

where **c** is a column vector with elements c_n and $\mathbf{d}^{\dagger}$ is a row vector with elements d_n^*. Thus (5.160) can be displayed as

$$\langle \mathrm{X}|\Psi\rangle = (d_1^* \ d_2^* \dots) \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}. \tag{5.161}$$

Matrix properties and definitions

Two matrices **A** and **B** can be added when they have the same number of rows and the same number of columns. Addition is commutative

$$\mathbf{A} + \mathbf{B} = \mathbf{B} + \mathbf{A} \tag{5.162}$$

and if $\mathbf{C} = \mathbf{A} + \mathbf{B}$ is the matrix sum, then

$$C_{mn} = A_{mn} + B_{mn}. \tag{5.163}$$

If $\mathbf{C} = \mathbf{AB}$ denotes the product of two matrices **A** and **B**, then

$$C_{mn} = \sum_k A_{mk} B_{kn} \tag{5.164}$$

which requires that the number of rows of **B** must be equal to the number of columns of **A**. It follows from (5.163) and (5.164) that multiplications is distributive

$$\mathbf{A}(\mathbf{B} + \mathbf{C}) = \mathbf{AB} + \mathbf{AC} \tag{5.165}$$

and associative

$$\mathbf{A}(\mathbf{BC}) = (\mathbf{AB})\mathbf{C}. \tag{5.166}$$

It is also apparent from (5.164) that, in general, **AB** is not equal to **BA**. If $\mathbf{AB} = \mathbf{BA}$, the two matrices **A** and **B** are said to commute.

The inverse $\mathbf{A}^{-1}$ of a matrix $\mathbf{A}$ is such that

$$\mathbf{A}\mathbf{A}^{-1} = \mathbf{A}^{-1}\mathbf{A} = \mathbf{I} \tag{5.167}$$

where $\mathbf{I}$ is the unit matrix, having elements $I_{mn} = \delta_{mn}$. A matrix which possesses an inverse is said to be *non-singular*.

The matrix $\mathbf{A}^{\mathrm{T}}$ is the transpose of $\mathbf{A}$ if

$$(A^{\mathrm{T}})_{mn} = A_{nm} \tag{5.168}$$

and $\mathbf{A}^{\dagger}$ is the adjoint of $\mathbf{A}$ if

$$(A^{\dagger})_{mn} = A^*_{nm}. \tag{5.169}$$

A matrix is Hermitian if it is equal to its adjoint:

$$\mathbf{A} = \mathbf{A}^{\dagger} \tag{5.170}$$

so that

$$A_{mn} = A^*_{nm}. \tag{5.171}$$

If the inverse of a matrix is equal to its adjoint, this matrix is said to be unitary. Hence, for a unitary matrix $\mathbf{U}$,

$$\mathbf{U}^{-1} = \mathbf{U}^{\dagger} \tag{5.172a}$$

or

$$\mathbf{U}\mathbf{U}^{\dagger} = \mathbf{U}^{\dagger}\mathbf{U} = \mathbf{I}. \tag{5.172b}$$

The trace of a matrix is the sum of its diagonal elements:

$$\mathrm{Tr}\mathbf{A} = \sum_m A_{mm}. \tag{5.173}$$

Using these definitions, it is easy to prove (see Problem 5.10) that a Hermitian operator is represented by a Hermitian matrix, a unitary operator by a unitary matrix, the operator sum $A + B$ by the matrix sum $\mathbf{A} + \mathbf{B}$, and the operator product $C = AB$ by the matrix product $\mathbf{C} = \mathbf{AB}$, so that the algebraic properties of operators are mirrored by their matrix representations. For example, consider the operator product $C = AB$. We have

$$\begin{aligned} C_{mn} &= \langle \psi_m | AB | \psi_n \rangle \\ &= \sum_k \langle \psi_m | A | \psi_k \rangle \langle \psi_k | B | \psi_n \rangle \\ &= \sum_k A_{mk} B_{kn} \end{aligned} \tag{5.174}$$

where in the second line the closure relation (5.65) has been used. Looking back at (5.164), it follows that the matrix $\mathbf{C}$ is equal to the matrix product of $\mathbf{A}$ and $\mathbf{B}$.

A square matrix **A** is said to be *diagonal* if it has non-vanishing elements A_{mn} only when $m = n$. If the complete set of orthonormal eigenfunctions $\{\psi_n\}$ of an observable A is used as a basis, then the matrix **A** representing A in this basis is diagonal, the diagonal elements being the eigenvalues a_n of A. Indeed, since $A\psi_n = a_n\psi_n$, the matrix elements of A in the basis $\{\psi_n\}$ are

$$\begin{aligned} A_{mn} &= \langle\psi_m|A|\psi_n\rangle \\ &= a_n\langle\psi_m|\psi_n\rangle \\ &= a_n\delta_{mn}. \end{aligned} \tag{5.175}$$

Let **A** be the matrix representing the observable A in a given basis. The eigenvalue equation $A\psi_n = a_n\psi_n$ for the operator A becomes, in that representation, the matrix eigenvalue equation

$$\mathbf{A}\mathbf{u}_n = a_n\mathbf{u}_n \tag{5.176}$$

where $\mathbf{u}_n$ is called an *eigenvector* of the matrix **A**, belonging to the eigenvalue a_n. It is often convenient to use the Dirac ket notation and to write the eigenvector $\mathbf{u}_n$ belonging to the eigenvalue a_n as the *eigenket* $|a_n\rangle$. Correspondingly, the row vector $\mathbf{u}_n^\dagger$ will be written as the bra $\langle a_n|$. More generally, a simultaneous eigenvector of the matrices **A**, **B**, **C**, ..., corresponding to eigenvalues $a_n, b_m, c_j, \ldots$, will be denoted by $|a_n, b_m, c_j, \ldots\rangle$.

The eigenvalues a_n of the matrix equation (5.176) are real since **A** is Hermitian; they are solutions of the 'secular' equation

$$\det|\mathbf{A} - a_n\mathbf{I}| = 0. \tag{5.177}$$

The properties of the eigenfunctions ψ_n of A are mirrored by those of the eigenvectors $\mathbf{u}_n$ of **A**. In particular, two eigenvectors belonging to different eigenvalues are orthogonal (see (5.55)). Also, by using the Schmidt orthogonalisation procedure, it is possible to ensure that linearly independent eigenvectors $\mathbf{u}_{ir}$ belonging to degenerate eigenvalues a_i are mutually orthogonal. All eigenvectors can also be normalised to unity. Thus we have (compare with (5.57))

$$\mathbf{u}_{ir}^\dagger.\mathbf{u}_{js} = \delta_{ij}\delta_{rs} \tag{5.178}$$

where the indices r and s refer to the degeneracy. Finally, we remark that in the basis $\{\psi_n\}$ of the eigenfunctions of A, in which the matrix **A** assumes the diagonal form (5.175), all the elements of the normalised eigenvector $\mathbf{u}_n$ are equal to zero, except the nth element, which is unity.

Change of representation and unitary transformations

We have already shown that different representations of quantum mechanical operators and wave functions can be obtained through unitary transformations. In the particular case of transformations between different matrix representations, the transforming operators are unitary matrices, as we shall now see. Suppose that $\{\psi_n\}$

and $\{\phi_m\}$ are two different orthonormal bases. Each member of the set $\{\psi_n\}$ can be expanded in the basis $\{\phi_m\}$ as

$$\psi_n = \sum_m U_{mn}\phi_m \tag{5.179}$$

where the expansion coefficients U_{mn} are obtained by taking the scalar product of both sides of (5.179) with ϕ_m, and are given by

$$U_{mn} = \langle\phi_m|\psi_n\rangle. \tag{5.180}$$

We shall now prove that the set of numbers U_{mn} are the elements of a *unitary* matrix. Indeed,

$$\begin{aligned}(UU^\dagger)_{mn} &= \sum_k U_{mk}(U^\dagger)_{kn} \\ &= \sum_k U_{mk}U^*_{nk} \\ &= \sum_k \langle\phi_m|\psi_k\rangle\langle\psi_k|\phi_n\rangle \\ &= \langle\phi_m|\phi_n\rangle = \delta_{mn}\end{aligned} \tag{5.181a}$$

where we have used the closure relation (5.65). Similarly

$$(U^\dagger U)_{mn} = \delta_{mn} \tag{5.181b}$$

so that $\mathbf{U}\mathbf{U}^\dagger = \mathbf{U}^\dagger\mathbf{U} = \mathbf{I}$, and $\mathbf{U}$ is a unitary matrix.

Suppose now that a wave function Ψ is represented in the basis $\{\psi_n\}$ by the coefficients c_n (forming a column vector $\mathbf{c}$) and in the basis $\{\phi_m\}$ by the coefficients c'_m (forming a column vector $\mathbf{c}'$). That is

$$\Psi = \sum_n c_n\psi_n = \sum_m c'_m\phi_m \tag{5.182a}$$

with

$$c_n = \langle\psi_n|\Psi\rangle, \qquad c'_m = \langle\phi_m|\Psi\rangle. \tag{5.182b}$$

Using the closure relation (5.65) and equation (5.180), we have

$$\begin{aligned}c'_m &= \langle\phi_m|\Psi\rangle \\ &= \sum_n \langle\phi_m|\psi_n\rangle\langle\psi_n|\Psi\rangle \\ &= \sum_n U_{mn}c_n,\end{aligned} \tag{5.183}$$

a result which can be written in matrix form as

$$\mathbf{c}' = \mathbf{U}\mathbf{c}. \tag{5.184}$$

Similarly, if **A** is a matrix representing the operator A in the basis $\{\psi_n\}$ and **A**$'$ the matrix representing that operator in the basis $\{\phi_m\}$, then

$$\begin{aligned} A'_{mn} &= \langle\phi_m|A|\phi_n\rangle \\ &= \sum_k\sum_l \langle\phi_m|\psi_k\rangle\langle\psi_k|A|\psi_l\rangle\langle\psi_l|\phi_n\rangle \\ &= \sum_k\sum_l U_{mk}A_{kl}(U^\dagger)_{ln} \end{aligned} \tag{5.185}$$

so that

$$\mathbf{A}' = \mathbf{U}\mathbf{A}\mathbf{U}^\dagger \qquad \text{and} \qquad \mathbf{A} = \mathbf{U}^\dagger\mathbf{A}'\mathbf{U}. \tag{5.186}$$

We saw earlier that if two Hermitian operators are connected by a unitary transformation they have the same eigenvalues. This property is mirrored for Hermitian matrices, so that the problem of solving the matrix eigenvalue equationn (5.176) can be viewed as that of finding a unitary transformation which converts the Hermitian matrix **A** into a matrix $\mathbf{A}' = \mathbf{U}\mathbf{A}\mathbf{U}^\dagger$ which is diagonal. It is a fundamental theorem of matrix algebra that *any Hermitian matrix can be diagonalised by a unitary transformation.* Another important theorem states that in order that two Hermitian matrices **A** and **B** can be diagonalised by the same unitary transformation, it is necessary and sufficient that they commute ($\mathbf{AB} = \mathbf{BA}$).

Finally, an important property of unitary transformations is that they leave the trace of a matrix unaltered. Indeed, if the matrices **A** and **A**$'$ are connected by a unitary transformation, so that $\mathbf{A}' = \mathbf{U}\mathbf{A}\mathbf{U}^\dagger$, we have

$$\begin{aligned} \mathrm{Tr}\,\mathbf{A}' &= \sum_m A'_{mm} \\ &= \sum_k\sum_l\sum_m U_{mk}A_{kl}(U^\dagger)_{lm} \\ &= \sum_k\sum_l\sum_m [(U^\dagger)_{lm}U_{mk}]A_{kl} \\ &= \sum_k\sum_l \delta_{lk}A_{kl} \\ &= \sum_k A_{kk} = \mathrm{Tr}\,\mathbf{A}. \end{aligned} \tag{5.187}$$

It follows from (5.187), and the fundamental diagonalisation theorem, that the trace of a Hermitian matrix is equal to the sum of its eigenvalues.

The state vector

By now we have seen that the wave functions and operators which appear in quantum mechanics can be represented in many ways, all connected by unitary transformations. This fact led Dirac to suggest that the state of a system could be described by a more abstract quantity called a *state vector*, denoted by a ket $|\Psi\rangle$. With each state vector is associated a conjugate quantity or bra $\langle\Psi|$ such that $\langle\Psi|\Psi\rangle$ is a real number representing the square of the 'length' or norm of $|\Psi\rangle$. The various representations we have studied correspond to specifying the 'components' of $|\Psi\rangle$ along different directions in the abstract space, just as ordinary three-dimensional vectors can be represented by components along any three independent directions. The linear Hermitian operators, corresponding to dynamical variables, act on the abstract state vectors, converting one into another. In Dirac's formulation of quantum theory the fundamental commutation relations play a central role, since these are independent of the choice of basis. Indeed, the superposition principle, together with the commutation relations for the basic operators (x, y, z) and (p_x, p_y, p_z) can be used to determine the physical quantities, such as expectation values or eigenvalues, without introducing a specific basis. In what follows we shall illustrate Dirac's approach by obtaining the energy levels of a linear harmonic oscillator.

The linear harmonic oscillator revisited

Let us consider a one-dimensional harmonic oscillator, the Hamiltonian of which is

$$H = \frac{p_x^2}{2m} + \frac{1}{2}kx^2 = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2x^2 \tag{5.188}$$

with $\omega = (k/m)^{1/2}$. In Section 4.7 we obtained the eigenvalues and eigenfunctions of this Hamiltonian by working in the position representation. We shall now find the eigenvalues of H by using a method due to Dirac, which does not make reference to any particular representation.

Let us introduce the operators

$$a_{\pm} = \frac{1}{\sqrt{2}}\left[\left(\frac{m\omega}{\hbar}\right)^{1/2} x \mp \mathrm{i}\frac{p_x}{(m\hbar\omega)^{1/2}}\right]. \tag{5.189}$$

Since x and p_x are Hermitian operators, a_+ and a_- are adjoints of each other: $a_+ = a_-^\dagger$ and $a_- = a_+^\dagger$. Using the basic commutation relation $[x, p_x] = \mathrm{i}\hbar$, it is readily verified (Problem 5.12) that a_+ and a_- satisfy the commutation relation

$$[a_-, a_+] = 1. \tag{5.190}$$

In terms of the operators a_+ and a_-, the Hamiltonian (5.188) can be rewritten in either of the forms

$$H = \frac{\hbar\omega}{2}(a_-a_+ + a_+a_-) = \hbar\omega\left(a_-a_+ - \tfrac{1}{2}\right) = \hbar\omega\left(a_+a_- + \tfrac{1}{2}\right) = \hbar\omega\left(N + \tfrac{1}{2}\right) \tag{5.191}$$

where

$$N = a_+a_-. \tag{5.192}$$

Furthermore, we have (Problem 5.12)

$$[H, a_\pm] = \pm\hbar\omega a_\pm. \tag{5.193}$$

If $|E\rangle$ is an eigenvector (eigenket) of H belonging to the eigenvalue E, so that

$$H|E\rangle = E|E\rangle \tag{5.194}$$

we have from (5.193) that

$$\begin{aligned} Ha_\pm|E\rangle &= (a_\pm H \pm \hbar\omega a_\pm)|E\rangle \\ &= (E \pm \hbar\omega)a_\pm|E\rangle. \end{aligned} \tag{5.195}$$

It follows that the kets $a_\pm|E\rangle$ are also eigenvectors of H, belonging to the eigenvalues $E \pm \hbar\omega$. As a_+ raises and a_- lowers the value of E, the operators a_+ and a_- are called *raising* and *lowering* operators, respectively. Since H only contains the squares of the operators p_x and x, the expectation value of H in any state cannot be negative, and hence the eigenvalues of H must be non-negative. Let E_0 be the smallest of these eigenvalues, and $|E_0\rangle$ be the corresponding eigenket. We must have

$$a_-|E_0\rangle = 0 \tag{5.196}$$

for otherwise $a_-|E_0\rangle$ would be an eigenket corresponding to the eigenvalue $E_0 - \hbar\omega$, contrary to the hypothesis that E_0 is the lowest eigenvalue. Operating on (5.196) with $\hbar\omega a_+$, and using (5.191) and (5.192), we have

$$\hbar\omega a_+ a_-|E_0\rangle = \hbar\omega N|E_0\rangle = \left(H - \tfrac{1}{2}\hbar\omega\right)|E_0\rangle = 0 \tag{5.197}$$

from which we deduce that the lowest eigenvalue E_0 is given by $E_0 = \hbar\omega/2$. Using (5.195) we see that by operating repeatedly with a_+ on the eigenket $|E_0\rangle$, we obtain the sequence of (unnormalised) eigenkets

$$|E_0\rangle, a_+|E_0\rangle, a_+^2|E_0\rangle, \dots, \tag{5.198}$$

the eigenket $a_+^n|E_0\rangle$ corresponding to the eigenvalue

$$E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega, \qquad n = 0, 1, 2, \dots \tag{5.199}$$

Let $|E_n\rangle$ be the normalised eigenket corresponding to the eigenvalue E_n and $|E_{n+1}\rangle$ be that corresponding to the eigenvalue E_{n+1}. From (5.198), we have

$$|E_{n+1}\rangle = C_{n+1}a_+|E_n\rangle \tag{5.200}$$

where C_{n+1} is a normalisation coefficient. Since $\langle E_{n+1}|E_{n+1}\rangle = 1$ and $a_- = a_+^\dagger$, we find that

$$|C_{n+1}|^2\langle E_n|a_- a_+|E_n\rangle = 1. \tag{5.201}$$

Now, since $a_- a_+ = (H/\hbar\omega) + 1/2$, and $H|E_n\rangle = E_n|E_n\rangle$, with $E_n = (n + 1/2)\hbar\omega$, and remembering that $\langle E_n|E_n\rangle = 1$, we have

$$C_{n+1} = (n + 1)^{-1/2} \tag{5.202}$$

where we have taken C_{n+1} to be real. From (5.200) and (5.201) we see that

$$a_+|E_n\rangle = (n+1)^{1/2}|E_{n+1}\rangle. \tag{5.203}$$

By starting from $n = 0$ and using repeatedly the relation (5.203), all the eigenvectors $|E_n\rangle$ can be obtained from $|E_0\rangle$:

$$|E_n\rangle = (n!)^{-1/2}a_+^n|E_0\rangle \tag{5.204}$$

Let $|E_{n-1}\rangle$ be the normalised eigenket corresponding to the eigenvalue E_{n-1}. From (5.200) and (5.202), we have

$$|E_n\rangle = C_n a_+|E_{n-1}\rangle \tag{5.205}$$

with $C_n = n^{-1/2}$. Operating on both sides of this equation with a_-, we find that

$$a_-|E_n\rangle = n^{-1/2}a_-a_+|E_{n-1}\rangle \tag{5.206}$$

Since $a_-a_+ = (H/\hbar\omega) + 1/2$ and $H|E_{n-1}\rangle = (n - 1/2)\hbar\omega|E_{n-1}\rangle$, we obtain

$$a_-|E_n\rangle = n^{1/2}|E_{n-1}\rangle \tag{5.207}$$

The operators a_+ and a_- can be used to calculate any property of the system. As an example, let us evaluate the expectation value of x^4 in the ground state $|E_0\rangle$ of the linear harmonic oscillator. From (5.189), we have

$$x = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(a_+ + a_-) \tag{5.208}$$

and therefore

$$\begin{aligned}\langle E_0|x^4|E_0\rangle = \frac{\hbar^2}{4m^2\omega^2}\langle E_0|&a_+^4 + a_+^3a_- + a_+^2a_-a_+ + a_+^2a_-^2\\ &+a_+a_-a_+^2 + a_+a_-a_+a_- + a_+a_-^2a_+ + a_+a_-^3\\ &+a_-a_+^3 + a_-a_+^2a_- + a_-a_+a_-a_+ + a_-a_+a_-^2\\ &+a_-^2a_+^2 + a_-^2a_+a_- + a_-^3a_+ + a_-^4|E_0\rangle.\end{aligned} \tag{5.209}$$

We now observe that since $a_-|E_0\rangle = 0$, and also $\langle E_0|a_+ = \langle E_0|a_-^\dagger = \langle a_-E_0| = 0$, (5.209) reduces to

$$\langle E_0|x^4|E_0\rangle = \frac{\hbar^2}{4m^2\omega^2}\langle E_0|a_-a_+^3 + a_-a_+a_-a_+ + a_-^2a_+^2 + a_-^3a_+|E_0\rangle. \tag{5.210}$$

Since we are evaluating a diagonal matrix element, we must also exclude all terms in which the number of operators a_+ is not equal to the number of operators a_-. Hence

$$\langle E_0|x^4|E_0\rangle = \frac{\hbar^2}{4m^2\omega^2}\langle E_0|a_-a_+a_-a_+ + a_-^2a_+^2|E_0\rangle. \tag{5.211}$$

Using the relations (5.203) and (5.207), we have

$$\begin{aligned} a_-a_+a_-a_+|E_0\rangle &= a_-a_+a_-|E_1\rangle \\ &= a_-a_+|E_0\rangle \\ &= a_-|E_1\rangle \\ &= |E_0\rangle . \end{aligned} \tag{5.212}$$

Similarly,

$$\begin{aligned} a_-^2a_+^2|E_0\rangle &= a_-^2a_+|E_1\rangle \\ &= a_-^2\sqrt{2}|E_2\rangle \\ &= a_-2|E_1\rangle \\ &= 2|E_0\rangle \end{aligned} \tag{5.213}$$

and hence

$$\langle E_0|x^4|E_0\rangle = \frac{3\hbar^2}{4m^2\omega^2} \tag{5.214}$$

Matrix representation in the $\{|E_n\rangle\}$ basis

In terms of the orthonormal set $\{|E_n\rangle\}$ with $n = 0, 1, 2, \ldots$, the matrix representation of H is a diagonal matrix with elements $E_n = (n + 1/2)\hbar\omega$, and that of the operator N is a diagonal matrix with elements n. That is

$$\mathbf{H} = \hbar\omega \begin{pmatrix} \frac{1}{2} & 0 & 0 & \ldots \\ 0 & \frac{3}{2} & 0 & \ldots \\ 0 & 0 & \frac{5}{2} & \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}, \qquad \mathbf{N} = \begin{pmatrix} 0 & 0 & 0 & \ldots \\ 0 & 1 & 0 & \ldots \\ 0 & 0 & 2 & \\ \vdots & & & \vdots \end{pmatrix}. \tag{5.215}$$

From (5.200) and the orthogonality of eigenvectors corresponding to different eigenvalues, we have

$$\langle E_k|E_{n+1}\rangle = C_{n+1}\langle E_k|a_+|E_n\rangle = \delta_{k,n+1} \tag{5.216}$$

where the indices k and n can take the values $0, 1, 2, \ldots$. Hence, the matrix elements of a_+ in the $\{|E_n\rangle\}$ representation are, using (5.202),

$$(a_+)_{kn} = (n+1)^{1/2}\delta_{k,n+1} \tag{5.217}$$

and we see that $\mathbf{a}_+$ is a real matrix whose only non-zero elements are those of the diagonal immediately below the main diagonal. Moreover, since $\mathbf{a}_- = \mathbf{a}_+^\dagger$ and $\mathbf{a}_+$ is a real matrix, we find that the matrix elements of $\mathbf{a}_-$ are

$$(a_-)_{kn} = (k+1)^{1/2}\delta_{k+1,n} \tag{5.218}$$

so that $\mathbf{a}_-$ is a real matrix whose only non-zero elements lie on the diagonal immediately above the main diagonal. Explicitly,

$$\mathbf{a}_+ = \begin{pmatrix} 0 & 0 & 0 & \ldots \\ \sqrt{1} & 0 & 0 & \ldots \\ 0 & \sqrt{2} & 0 & \ldots \\ 0 & 0 & \sqrt{3} & \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad \mathbf{a}_- = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \ldots \\ 0 & 0 & \sqrt{2} & 0 & \ldots \\ 0 & 0 & 0 & \sqrt{3} & \ldots \\ \vdots & \vdots & \vdots & & \ddots \end{pmatrix}. \tag{5.219}$$

The matrix elements of x and p_x can be found immediately by using (5.189) (see Problem 5.14).

Transition from the $\{|E_n\rangle\}$ to the position representation

We shall now show how the linear harmonic oscillator eigenfunctions, given by (4.168) in the position representation, can be found by using the operators a_+ and a_-. We first recall that in the position representation the operator x is represented by ordinary multiplication by x, while the operator p_x is represented by $-\mathrm{i}\hbar\partial/\partial x$ (with $\partial/\partial x \equiv \mathrm{d}/\mathrm{d}x$ in the present case). Hence, the operators $a_\pm$ introduced in (5.189) become

$$a_\pm = \frac{1}{\sqrt{2}}\left[\left(\frac{m\omega}{\hbar}\right)^{1/2} x \mp \frac{1}{(m\hbar\omega)^{1/2}}\frac{\mathrm{d}}{\mathrm{d}x}\right] \tag{5.220}$$

or, in terms of the variable $\xi = (m\omega/\hbar)^{1/2}x = \alpha x$

$$a_\pm = \frac{1}{\sqrt{2}}\left(\xi \mp \frac{\mathrm{d}}{\mathrm{d}\xi}\right). \tag{5.221}$$

Thus, in the position representation, the equation (5.196) becomes

$$\left(\xi + \frac{\mathrm{d}}{\mathrm{d}\xi}\right)\psi_0(\xi) = 0. \tag{5.222}$$

This equation has the solution

$$\psi_0(\xi) = N_0 \mathrm{e}^{-\xi^2/2} \tag{5.223}$$

where N_0 is a constant. Hence

$$\psi_0(x) = N_0 \mathrm{e}^{-\alpha^2 x^2/2}. \tag{5.224}$$

If N_0 is chosen to be real and such that $\psi_0(x)$ is normalised to unity, we have

$$N_0 = \left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2} \tag{5.225}$$

All the other eigenfunctions can be found by using equation (5.204), which in the position representation becomes

$$\psi_n(\xi) = (n!)^{-1/2}\left[\frac{1}{\sqrt{2}}\left(\xi - \frac{\mathrm{d}}{\mathrm{d}\xi}\right)\right]^n \psi_0(\xi) \tag{5.226}$$

Using (4.154b), (5.223) and (5.225), we obtain

$$\psi_n(\xi) = \left(\frac{\alpha}{\sqrt{\pi}2^n n!}\right)^{1/2} e^{-\xi^2/2} H_n(\xi) \quad \textbf{(5.227)}$$

where $H_n(\xi)$ is the Hermite polynomial of order n. Upon returning to the variable x, we see that (5.227) is identical to (4.168).

5.7 The Schrödinger equation and the time evolution of a system

The next postulate of quantum mechanics concerns the time evolution of a quantum system and may be formulated as follows.

Postulate 7

The time evolution of the wave function of a system is determined by the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(t) = H\Psi(t) \quad \textbf{(5.228)}$$

where H is the Hamiltonian, or total energy operator of the system.

Assuming that the system has a classical analogue, its Hamiltonian operator can be obtained by applying the substitution rule (5.19) in the position representation, or (5.20) in the momentum representation, and carrying out the Hermitisation procedure described in Section 3.3, if necessary.

As a first example, let us consider a system of N spinless particles having masses m_i, position coordinates $\mathbf{r}_i$, momenta $\mathbf{p}_i$, and such that its potential energy $V(\mathbf{r}_1, \dots, \mathbf{r}_N, t)$ depends only on the positions $\mathbf{r}_i$ and the time t. The (non-relativistic) Hamiltonian operator of this system is given by

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{r}_1, \dots, \mathbf{r}_N, t) \quad \textbf{(5.229)}$$

where $\mathbf{p}_i = -i\hbar\nabla_i$ if one is working in the position representation.

As a second example, consider a particle of mass m and charge q moving in an electromagnetic field described by a vector potential $\mathbf{A}(\mathbf{r}, t)$ and a scalar potential $\phi(\mathbf{r}, t)$. Its (non-relativistic) classical Hamiltonian can be obtained (Goldstein 1980) by starting from the field free expression $E = \mathbf{p}^2/2m$ between the energy and the momentum of the particle, and making in it the substitutions

$$E \to E - q\phi, \quad \mathbf{p} \to \mathbf{p} - q\mathbf{A}. \quad \textbf{(5.230)}$$

The resulting Hamiltonian

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi \tag{5.231a}$$

becomes the (non-relativistic) quantum mechanical Hamiltonian operator by replacing the generalised momentum **p** by the corresponding momentum operator ($\mathbf{p}_{\text{op}} = -\text{i}\hbar\nabla$ in the position representation). Applying the 'Hermitisation' procedure discussed in Section 3.3 to the term $-(q/m)\mathbf{A}.\mathbf{p}$, this Hamiltonian operator can be written in the form

$$H = \frac{\mathbf{p}^2}{2m} - \frac{q}{2m}(\mathbf{A}.\mathbf{p} + \mathbf{p}.\mathbf{A}) + \frac{q^2}{2m}\mathbf{A}^2 + q\phi \tag{5.231b}$$

where we have omitted the subscript on the momentum operator in order to simplify the notation.

The evolution operator

Since the Schrödinger equation (5.228) is a first-order differential equation in time, the state vector $\Psi(t)$ is determined for all t once it is specified at any given time t_0. We may therefore introduce an *evolution* operator $U(t, t_0)$ such that

$$\Psi(t) = U(t, t_0)\Psi(t_0) \tag{5.232}$$

with

$$U(t_0, t_0) = I. \tag{5.233}$$

Applying twice the definition (5.232), we also have

$$U(t, t_0) = U(t, t')U(t', t_0) \tag{5.234}$$

and

$$U^{-1}(t, t_0) = U(t_0, t) \tag{5.235}$$

so that the evolution operator exhibits the *group property*.

Substituting (5.232) into the Schrödinger equation (5.228), we see that the evolution operator $U(t, t_0)$ satisfies the equation

$$\text{i}\hbar\frac{\partial}{\partial t}U(t, t_0) = HU(t, t_0) \tag{5.236}$$

subject to the initial condition (5.233). We remark that the differential equation (5.236) together with the initial condition (5.233) can be replaced by the integral equation

$$U(t, t_0) = I - \frac{\text{i}}{\hbar}\int_{t_0}^{t} HU(t', t_0)\text{d}t'. \tag{5.237}$$

Conservation of probability requires that

$$\langle\Psi(t)|\Psi(t)\rangle = \langle\Psi(t_0)|\Psi(t_0)\rangle. \tag{5.238}$$

However, from (5.232)

$$\begin{aligned}\langle\Psi(t)|\Psi(t)\rangle &= \langle U(t,t_0)\Psi(t_0)|U(t,t_0)\Psi(t_0)\rangle \\ &= \langle\Psi(t_0)|U^\dagger(t,t_0)U(t,t_0)|\Psi(t_0)\rangle \end{aligned} \qquad \textbf{(5.239)}$$

from which

$$U^\dagger(t,t_0)U(t,t_0) = I. \qquad \textbf{(5.240a)}$$

Likewise, starting from $\langle\Psi(t_0)|\Psi(t_0)\rangle$, we obtain

$$U(t,t_0)U^\dagger(t,t_0) = I \qquad \textbf{(5.240b)}$$

so that from these two equations we conclude that $U(t,t_0)$ is a *unitary* operator.

The unitary character of the evolution operator is clearly connected to the Hermiticity of the Hamiltonian. We can display the connection by studying the change in the evolution operator induced after an arbitrary small time δt. We first have from (5.236)

$$\mathrm{i}\hbar[U(t_0+\delta t,t_0) - U(t_0,t_0)] = HU(t_0+\delta t,t_0)\delta t. \qquad \textbf{(5.241)}$$

Hence, to first order in δt, and using the initial condition (5.233), we have

$$U(t_0+\delta t,t_0) = I - \frac{\mathrm{i}}{\hbar}H\delta t. \qquad \textbf{(5.242)}$$

The Hamiltonian H is therefore the generator of an infinitesimal unitary transformation (see (5.146)) – in fact, an infinitesimal *time translation* – described by the evolution operator $U(t_0+\delta t,t_0)$.

Let us consider the particular case for which the Hamiltonian H is time-independent. A solution of (5.236) satisfying the initial condition (5.233) is then given by

$$U(t,t_0) = \exp\left[-\frac{\mathrm{i}}{\hbar}H(t-t_0)\right] \qquad \textbf{(5.243)}$$

as is readily checked by recollecting that a function of an operator can be defined by its series expansion (see (5.38)) so that

$$\exp\left[-\frac{\mathrm{i}}{\hbar}H(t-t_0)\right] = \sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{\mathrm{i}}{\hbar}\right)^n H^n(t-t_0)^n. \qquad \textbf{(5.244)}$$

Thus a formal solution of the time-dependent Schrödinger equation for a time-independent Hamiltonian H is given by

$$\Psi(t) = \exp\left[-\frac{\mathrm{i}}{\hbar}H(t-t_0)\right]\Psi(t_0). \qquad \textbf{(5.245)}$$

As an example, suppose that we are dealing with the motion of a structureless particle in a time-independent potential $V(\mathbf{r})$. From (5.245) we may write the wave function $\Psi(\mathbf{r}, t)$ as

$$\begin{aligned}\Psi(\mathbf{r}, t) &= \exp\left[-\frac{\mathrm{i}}{\hbar}H(t-t_0)\right]\Psi(\mathbf{r}, t_0)\\ &= \int \exp\left[-\frac{\mathrm{i}}{\hbar}H(t-t_0)\right]\delta(\mathbf{r}-\mathbf{r}')\Psi(\mathbf{r}', t_0)\mathrm{d}\mathbf{r}'. \end{aligned}\tag{5.246}$$

Now, according to the closure relation satisfied by the energy eigenfunctions, we have

$$\sum_E \psi_E^*(\mathbf{r}')\psi_E(\mathbf{r}) = \delta(\mathbf{r}-\mathbf{r}')\tag{5.247}$$

so that we can recast (5.246) in the form

$$\Psi(\mathbf{r}, t) = \sum_E \int \exp\left[-\frac{\mathrm{i}}{\hbar}H(t-t_0)\right]\psi_E^*(\mathbf{r}')\psi_E(\mathbf{r})\Psi(\mathbf{r}', t_0)\mathrm{d}\mathbf{r}'.\tag{5.248}$$

Since $H\psi_E = E\psi_E$, it follows that

$$\Psi(\mathbf{r}, t) = \sum_E \left[\int \psi_E^*(\mathbf{r}')\Psi(\mathbf{r}', t_0)\mathrm{d}\mathbf{r}'\right]\exp[-\mathrm{i}E(t-t_0)/\hbar]\psi_E(\mathbf{r})\tag{5.249}$$

in agreement with the result (3.155) obtained in Chapter 3.

Time variation of expectation values

Let us consider an observable A. The expectation value $\langle A\rangle$ of this observable in the state Ψ, normalised to unity, is given by $\langle\Psi|A|\Psi\rangle$. The rate of change of this expectation value is therefore

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle &= \frac{\mathrm{d}}{\mathrm{d}t}\langle\Psi|A|\Psi\rangle\\ &= \left\langle\frac{\partial\Psi}{\partial t}|A|\Psi\right\rangle + \left\langle\Psi\left|\frac{\partial A}{\partial t}\right|\Psi\right\rangle + \left\langle\Psi|A|\frac{\partial\Psi}{\partial t}\right\rangle\\ &= -(\mathrm{i}\hbar)^{-1}\langle H\Psi|A|\Psi\rangle + \left\langle\Psi\left|\frac{\partial A}{\partial t}\right|\Psi\right\rangle + (\mathrm{i}\hbar)^{-1}\langle\Psi|AH|\Psi\rangle\end{aligned}\tag{5.250}$$

where in writing the last line we have used the Schrödinger equation (5.228) and its complex conjugate. Since H is Hermitian, the first matrix element on the right of (5.250) may be written as $\langle\Psi|HA|\Psi\rangle$ so that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle = (\mathrm{i}\hbar)^{-1}\langle[A, H]\rangle + \left\langle\frac{\partial A}{\partial t}\right\rangle\tag{5.251}$$

where

$$\langle[A, H]\rangle = \langle\Psi|[A, H]|\Psi\rangle = \langle\Psi|AH - HA|\Psi\rangle\tag{5.252}$$

and

$$\left\langle\frac{\partial A}{\partial t}\right\rangle = \left\langle\Psi\left|\frac{\partial A}{\partial t}\right|\Psi\right\rangle.\tag{5.253}$$

In particular, if the operator A does not depend explicitly on time (that is, if $\partial A/\partial t = 0$) equation (5.251) reduces to

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle = (\mathrm{i}\hbar)^{-1}\langle [A, H]\rangle. \tag{5.254}$$

Hence, if $\partial A/\partial t = 0$ and the operator A commutes with H, its expectation value does not vary in time, and we can say that *the observable A is a constant of the motion.*

Time-independent Hamiltonian

As an example of the preceding discussion, consider a system for which the Hamiltonian is *time-independent* ($\partial H/\partial t = 0$). Using (5.254) with $A = H$, we see that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle H\rangle = (\mathrm{i}\hbar)^{-1}\langle [H, H]\rangle = 0 \tag{5.255}$$

so that the total energy is a constant of the motion. This is the analogue of energy conservation for conservative system in classical mechanics.

Let ψ_E be an eigenfunction of the time-independent Hamiltonian H corresponding to the eigenenergy E. For a *stationary state* $\Psi_E = \psi_E \exp(-\mathrm{i}Et/\hbar)$ and a *time-independent* operator A it is clear that the expectation value $\langle \Psi_E|A|\Psi_E\rangle = \langle \psi_E|A|\psi_E\rangle$ does not depend on the time. Hence in this case (5.254) reduces to

$$\langle \psi_E|[A, H]|\psi_E\rangle = 0. \tag{5.256}$$

The virial theorem

We now apply the above result to the particular case of a particle of mass m moving in a potential $V(\mathbf{r})$, so that the corresponding Hamiltonian is

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}). \tag{5.257}$$

Moreover, we choose A to be the time-independent operator $\mathbf{r.p}$. We then have from (5.256)

$$\langle \psi_E|[\mathbf{r.p}, H]|\psi_E\rangle = 0. \tag{5.258}$$

Using the algebraic properties (5.101) of the commutators, together with the fundamental commutation relations (5.88) and the fact that $\mathbf{p} = -\mathrm{i}\hbar\boldsymbol{\nabla}$ in the position representation, we find that

$$\begin{aligned}
[\mathbf{r.p}, H] &= \left[(xp_x + yp_y + zp_z), \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z)\right] \\
&= \frac{\mathrm{i}\hbar}{m}(p_x^2 + p_y^2 + p_z^2) - \mathrm{i}\hbar\left(x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z}\right) \\
&= 2\mathrm{i}\hbar T - \mathrm{i}\hbar(\mathbf{r}.\boldsymbol{\nabla}V)
\end{aligned} \tag{5.259}$$

where $T = \mathbf{p}^2/2m = -(\hbar^2/2m)\nabla^2$ is the kinetic energy operator. From (5.258) and (5.259) we therefore deduce that, for a *stationary state*

$$2\langle T\rangle = \langle \mathbf{r}.\boldsymbol{\nabla} V\rangle \tag{5.260}$$

which is known as the *virial theorem*[5]. We remark that the result (5.260) may also be obtained by choosing the operator A to be $\mathbf{p}.\mathbf{r}$ instead of $\mathbf{r}.\mathbf{p}$. Indeed, the difference between $\mathbf{r}.\mathbf{p}$ and $\mathbf{p}.\mathbf{r}$ is a constant, and hence commutes with H. We also note that if the interaction potential V is spherically symmetric and proportional to r^s, one has for a stationary state

$$\begin{aligned} 2\langle T\rangle &= \left\langle r\frac{\partial V}{\partial r}\right\rangle \\ &= s\langle V\rangle . \end{aligned} \tag{5.261}$$

The generalisation of the virial theorem (5.260) to a system of N particles is the subject of Problem 5.16.

The Schrödinger equation for a two-body system

As an example of the time evolution of a system we shall consider the case of two particles, of masses m_1 and m_2, interacting via a time-independent potential $V(\mathbf{r}_1 - \mathbf{r}_2)$ which depends only upon the relative coordinate $\mathbf{r}_1 - \mathbf{r}_2$. The classical Hamiltonian of the system is therefore given by

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(\mathbf{r}_1 - \mathbf{r}_2). \tag{5.262}$$

Making the substitutions $\mathbf{p}_1 \to -\mathrm{i}\hbar\boldsymbol{\nabla}_{\mathbf{r}_1}$ and $\mathbf{p}_2 \to -\mathrm{i}\hbar\boldsymbol{\nabla}_{\mathbf{r}_2}$, we obtain the quantum mechanical Hamiltonian operator, and the corresponding time-dependent Schrödinger equation reads in configuration space

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \left[-\frac{\hbar^2}{2m_1}\nabla^2_{\mathbf{r}_1} - \frac{\hbar^2}{2m_2}\nabla^2_{\mathbf{r}_2} + V(\mathbf{r}_1 - \mathbf{r}_2)\right]\Psi(\mathbf{r}_1, \mathbf{r}_2, t). \tag{5.263}$$

---

[5] In classical mechanics the *virial* of a particle is defined as the quantity $-(1/2)\overline{\mathbf{F}.\mathbf{r}}$, where $\mathbf{F}$ is the force acting on the particle and the bar denotes a *time average*. If the motion is periodic (or even if the motion is not periodic, but the coordinates and velocity of the particle remain finite) and $\bar{T}$ denotes the time average of the kinetic energy of the particle, one has

$$\bar{T} = -\frac{1}{2}\overline{\mathbf{F}.\mathbf{r}}$$

and this relation is known as the *virial theorem*. If the force is derivable from a potential V the virial theorem becomes

$$2\bar{T} = \overline{\mathbf{r}.\boldsymbol{\nabla} V}$$

which is the classical analogue of (5.260).

This is a seven-dimensional partial-differential equation. However, just as in classical mechanics, the problem can be reduced by introducing the *relative coordinate*

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \tag{5.264}$$

and the vector

$$\mathbf{R} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2} \tag{5.265}$$

which determines the position of the *centre of mass* (CM) of the system. Changing variables from the coordinates $(\mathbf{r}_1, \mathbf{r}_2)$ to the new coordinates $(\mathbf{r}, \mathbf{R})$, we find after a straightforward calculation (Problem 5.18) that

$$-\frac{\hbar^2}{2m_1}\nabla^2_{\mathbf{r}_1} - \frac{\hbar^2}{2m_2}\nabla^2_{\mathbf{r}_2} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} \tag{5.266}$$

where

$$M = m_1 + m_2 \tag{5.267}$$

is the *total mass* of the system and

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{5.268}$$

is the *reduced mass* of the two particles. The Schrödinger equation (5.263) therefore becomes

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{R}, \mathbf{r}, t) = \left[-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right]\Psi(\mathbf{R}, \mathbf{r}, t). \tag{5.269}$$

This equation can also be obtained by introducing the *relative momentum*

$$\mathbf{p} = \frac{m_2 \mathbf{p}_1 - m_1 \mathbf{p}_2}{m_1 + m_2} \tag{5.270}$$

together with the *total momentum*

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2. \tag{5.271}$$

Since

$$\frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} \tag{5.272}$$

the classical Hamiltonian (5.262) can be written as

$$H = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} + V(\mathbf{r}). \tag{5.273}$$

Performing the substitutions $\mathbf{P} \to -\mathrm{i}\hbar\nabla_{\mathbf{R}}$ and $\mathbf{p} \to -\mathrm{i}\hbar\nabla_{\mathbf{r}}$ in (5.273), we then obtain the quantum mechanical Hamiltonian operator

$$H = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r}) \tag{5.274}$$

leading to the Schrödinger equation (5.269).

Two separations of the equation (5.269) can now be made. The time dependence can first be separated as in Section 3.5 since the potential $V(\mathbf{r})$ is independent of time. Second, the spatial part of the wave function $\Psi(\mathbf{R}, \mathbf{r}, t)$ can be separated into a product of functions of the centre of mass coordinate $\mathbf{R}$ and of the relative coordinate $\mathbf{r}$. Thus the Schrödinger equation (5.269) admits solutions of the form

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \Phi(\mathbf{R})\psi(\mathbf{r}) \exp[-\mathrm{i}(E_{\mathrm{CM}} + E)t/\hbar] \tag{5.275}$$

where the functions $\Phi(\mathbf{R})$ and $\psi(\mathbf{r})$ satisfy, respectively, the equations

$$-\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2\Phi(\mathbf{R}) = E_{\mathrm{CM}}\Phi(\mathbf{R}) \tag{5.276}$$

and

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{5.277}$$

We see that the equation (5.276) is a time-independent Schrödinger equation describing the centre of mass as a free particle of mass M and energy E_{CM}. The second time-independent Schrödinger equation (5.277) describes the relative motion of the two particles; it is the same as the equation corresponding to the motion of a particle having the reduced mass μ in the potential $V(\mathbf{r})$. The total energy of the system is clearly

$$E_{\mathrm{tot}} = E_{\mathrm{CM}} + E. \tag{5.278}$$

We have therefore 'decoupled' the original two-body problem into two one-body problems: that of a free particle (the centre of mass) and that of a single particle of reduced mass μ in the potential $V(\mathbf{r})$. We remark that if we elect to work in the centre-of-mass system of the two particles, we need not be concerned with the motion of the centre of mass, the coordinates of which are eliminated.

5.8 The Schrödinger and Heisenberg pictures

Although there are many representations of wave functions and observables connected by unitary transformations, it is useful to distinguish certain classes of representations, called *pictures*, which differ in the way the time evolution of the system is treated.

The *Schrödinger picture*, which we have used until now, is one in which the operators (either in differential or matrix form) representing the position and momentum variables $\mathbf{r}_i$ and $\mathbf{p}_i$, are *time-independent*. The time evolution of a system is determined in this picture by a *time-dependent* wave function $\Psi(t)$ satisfying the Schrödinger equation (5.228). According to (5.232), the wave function $\Psi(t)$ is related to its value at time t_0 by performing the unitary transformation $\Psi(t) = U(t, t_0)\Psi(t_0)$, where $U(t, t_0)$ is the evolution operator. The time dependence of the expectation values of the basic time-independent operators $\mathbf{r}_i$ and $\mathbf{p}_i$ is given by (5.254). On the other hand, the rate of change of the expectation value of an operator which depends explicitly on time (such as a time-dependent potential $V(\mathbf{r}, t)$) is determined by equation (5.251).

The *Heisenberg picture* is obtained from the Schrödinger picture by applying to the Schrödinger wave function $\Psi(t)$ the unitary operator $U^\dagger(t, t_0) = U(t_0, t)$. The resulting wave function is the Heisenberg wave function (or state function) Ψ_H such that

$$\Psi_H = U^\dagger(t, t_0)\Psi(t) = U(t_0, t)\Psi(t) = \Psi(t_0). \tag{5.279}$$

Hence, in the Heisenberg picture, the wave function Ψ_H is *time-independent* and coincides at some particular fixed time t_0 with the Schrödinger wave function $\Psi(t_0)$. Using (5.279) and (5.128) we see that if A is an operator in the Schrödinger picture and A_H is the corresponding operator in the Heisenberg picture, we have

$$\begin{aligned} A_H(t) &= U^\dagger(t, t_0)AU(t, t_0) \\ &= U(t_0, t)AU^\dagger(t_0, t) \end{aligned} \tag{5.280}$$

and we note that $A_H(t)$ is time-dependent even if A does not depend on time.

The time variation of $A_H(t)$ can be determined as follows. Writing $U \equiv U(t_0, t)$, we first have from (5.280)

$$\frac{\mathrm{d}}{\mathrm{d}t}A_H(t) = \frac{\partial U}{\partial t}AU^\dagger + U\frac{\partial A}{\partial t}U^\dagger + UA\frac{\partial U^\dagger}{\partial t}. \tag{5.281}$$

Using (5.236) and the facts that H is Hermitian and U is unitary, we then find that

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}A_H(t) &= (\mathrm{i}\hbar)^{-1}(-UHAU^\dagger + UAHU^\dagger) + U\frac{\partial A}{\partial t}U^\dagger \\ &= (\mathrm{i}\hbar)^{-1}(-UHU^\dagger UAU^\dagger + UAU^\dagger UHU^\dagger) + U\frac{\partial A}{\partial t}U^\dagger. \end{aligned} \tag{5.282}$$

Defining the Heisenberg operators

$$H_H = UHU^\dagger \tag{5.283}$$

and

$$\left(\frac{\partial A}{\partial t}\right)_H = U\frac{\partial A}{\partial t}U^\dagger \tag{5.284}$$

we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}A_H(t) = (\mathrm{i}\hbar)^{-1}[A_H, H_H] + \left(\frac{\partial A}{\partial t}\right)_H \tag{5.285}$$

which is the *Heisenberg equation of motion* for the operator A_H.

As an example, let us consider the case of the x-components of the position and momentum of a particle, x and p_x. Since these operators are time-independent in the Schrödinger picture ($\partial x/\partial t = \partial p_x/\partial t = 0$), we see from (5.284) and (5.285) that

$$\frac{\mathrm{d}x_H}{\mathrm{d}t} = (\mathrm{i}\hbar)^{-1}[x_H, H_H] \tag{5.286a}$$

and

$$\frac{\mathrm{d}(p_x)_H}{\mathrm{d}t} = (\mathrm{i}\hbar)^{-1}[(p_x)_H, H_H]. \tag{5.286b}$$

Using the fact that the basic commutation relations (5.88) are unchanged by unitary transformations, together with the results of Problem 5.7, one has

$$\frac{\mathrm{d}x_H}{\mathrm{d}t} = \frac{\partial H_H}{\partial (p_x)_H} \tag{5.287a}$$

and

$$\frac{\mathrm{d}(p_x)_H}{\mathrm{d}t} = -\frac{\partial H_H}{\partial x_H} \tag{5.287b}$$

which are formally identical to Hamilton's canonical equations in classical mechanics. Thus we see that the Heisenberg picture corresponds to a formulation of quantum dynamics which is formally close to classical mechanics.

It is clear that since the Schrödinger and Heisenberg pictures are related by a unitary transformation, all physical quantities such as eigenvalues and expectation values of observables are identical when calculated in either picture.

We also remark that if the Hamiltonian operator H in the Schrödinger picture is *time-independent*, the evolution operator in that picture is given by (5.243). The Heisenberg wave function Ψ_H is then related to the Schrödinger wave function by

$$\Psi_H \equiv \Psi(t_0) = \exp\left[\frac{\mathrm{i}}{\hbar}H(t-t_0)\right]\Psi(t) \tag{5.288}$$

and we see from (5.283) that $H_H = H$.

It is sometimes useful to define other pictures in which a unitary transformation is applied to the Schrödinger wave function $\Psi(t)$ using not the full Hamiltonian H as in (5.288), but part of it. Such pictures are called *interaction pictures*.

5.9 Path integrals

As we saw in Section 3.1, the Schrödinger equation can be obtained from the classical Hamiltonian function by replacing the coordinates and momenta by the appropriate operators. An alternative formulation of quantum mechanics, developed by R. P. Feynman, is closely related to the classical Lagrangian function, and provides new insights into the structure of quantum mechanics and its classical limit. It has also provided a very useful framework in which a large variety of problems occurring in high-energy and statistical physics can be studied. To avoid a complicated notation Feynman's formulation, based on *path integrals*, will be discussed for the motion in one dimension of a particle of mass m moving in a time-independent potential $V(x)$. The classical Lagrangian function for this system is

$$L = T - V(x) \tag{5.289}$$

where T is the kinetic energy

$$T = \frac{1}{2}m\dot{x}^2 \tag{5.290}$$

and the dot denotes a derivative with respect to time. The equation of motion written in terms of L, is the *Euler–Lagrange* equation[6]

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{x}}\right) - \frac{\partial L}{\partial x} = 0 \tag{5.291}$$

and the solution of this second order equation, with boundary conditions $x(t_0) = a$, $\dot{x}(t_0) = b$, determines the classical path

$$x = x(t). \tag{5.292}$$

The equation of motion (5.291) follows from Hamilton's principle which states that the motion of the system from time t_0 to t_1 is such that the *action I* is stationary, where I is defined as

$$I(t_1, t_0) = \int_{t_0}^{t_1} L(\dot{x}(t), x(t))\mathrm{d}t, \tag{5.293}$$

and the integral is taken along the classical path (5.292).

The stationary condition means that if the line integral (5.293) is taken along a neighbouring path to (5.292) so that

$$x = x(t) + \epsilon\eta(t) \tag{5.294}$$

where ϵ is a small quantity and $\eta(t)$ is an arbitary function such that

$$\eta(t_0) = \eta(t_1) = 0, \tag{5.295}$$

then the change in I is of the order ϵ^2.

The Schrödinger wave function $\Psi(x, t_1)$ satisfies the equation (3.157), which for one-dimensional motion is

$$\Psi(x, t_1) = \int_{-\infty}^{\infty} K(x, t_1; x', t_0)\Psi(x', t_0)\mathrm{d}x'. \tag{5.296}$$

Feynman showed that the propagator K could be expressed as

$$K(x, t_1; x', t_0) = \sum_p W_p \exp[\mathrm{i}I_p(t_1, t_0)/\hbar] \tag{5.297}$$

where $I_p(t_1, t_0)$ is the classical action (5.293), in which the integration is taken along a path $x = x_p(t)$, the sum over p is over *all* paths $x_p(t)$ which connect $x(t_1)$ with $x(t_0)$, and W_p is a weighting factor (see Fig. 5.1). Since there is a continuum of such paths the sum over p represents a kind of integral called a path integral, which will be defined later.

---

[6] See for example Goldstein (1980) or Kibble and Berkshire (1996).

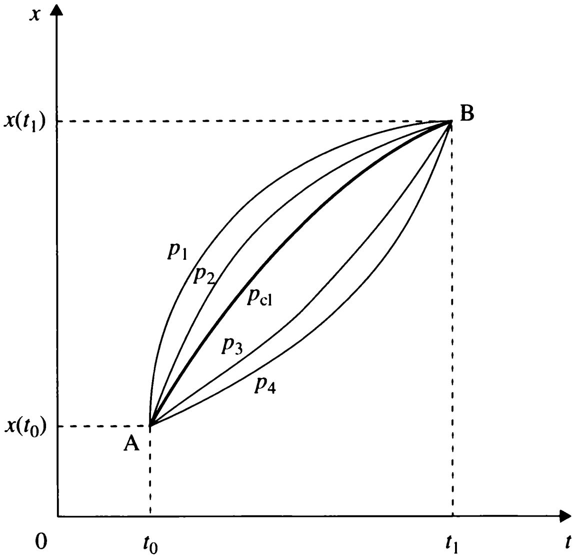


Figure 5.1 Different paths p_1, $p_2 \ldots$ linking the end points A and B for motion in one dimension between times t_0 and t_1. The classical path is marked as p_{cl}.

For a particle with a wavelength which is short compared with the range of the potential, $I/\hbar$ is a very large quantity. The change in I between neighbouring paths is also large, so that the exponential in (5.297) oscillates rapidly with the consequence that the sum over paths averages to zero. The exceptional case is when I is stationary, so that the change in I is zero between neighbouring paths and a finite contribution to the sum results. This only occurs for the classical path p_{cl}, which is the only significant path for a macroscopic system. In contrast, for a microscopic particle, such as an electron moving in a potential of atomic dimensions, $I/\hbar$ is not large, so that many paths contribute to the propagator and the classical path is no longer dominant.

To derive equation (5.297), we write the propagator K in the form

$$K(x, t_1; x', t_0) = \exp\left(-\frac{\mathrm{i}}{\hbar} H(t_1 - t_0)\right)\delta(x - x') \tag{5.298}$$

which is obtained by comparing (5.245) and (5.296). In the present case the Hamiltonian H is

$$H = \frac{p_x^2}{2m} + V(x). \tag{5.299}$$

The time interval $(t_1 - t_0)$ can be divided into N equal segments of width $\Delta t = (t_1 - t_0)/N$, so that the evolution operator $\exp[-\mathrm{i}H(t_1 - t_0)/\hbar]$ can be expressed as a product of N terms:

$$\begin{aligned}\exp\left(-\frac{\mathrm{i}}{\hbar}H(t_1-t_0)\right) &= \exp\left(-\frac{\mathrm{i}}{\hbar}HN\Delta t\right)\\ &= \left[\exp\left(-\frac{\mathrm{i}}{\hbar}H\Delta t\right)\right]^N\\ &= \exp\left(-\frac{\mathrm{i}}{\hbar}H\Delta t\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H\Delta t\right)\ldots\exp\left(-\frac{\mathrm{i}}{\hbar}H\Delta t\right).\end{aligned} \tag{5.300}$$

Using this expression in (5.298) and inserting a delta function between each factor of $\exp(-\mathrm{i}H\Delta t/\hbar)$, the propagator K can be put in the form

$$\begin{aligned}K(x_N,t_1;x_0,t_0) = &\int_{-\infty}^{\infty}\mathrm{d}x_1\ldots\int_{-\infty}^{\infty}\mathrm{d}x_{N-1}\exp\left(-\frac{\mathrm{i}}{\hbar}H\Delta t\right)\delta(x_N-x_{N-1})\\ &\times\exp\left(-\frac{\mathrm{i}}{\hbar}H\Delta t\right)\delta(x_{N-1}-x_{N-2})\ldots\\ &\times\delta(x_2-x_1)\exp\left(-\frac{\mathrm{i}}{\hbar}H\Delta t\right)\delta(x_1-x_0)\end{aligned} \tag{5.301}$$

where we have set $x = x_N$ and $x' = x_0$ for notational convenience.

By taking N to be large so that Δt is small and $(\Delta t)^2 \ll \Delta t$, it can be seen using (5.244) that

$$\exp\left(-\frac{\mathrm{i}}{\hbar}H\Delta t\right) \simeq \exp\left[-\frac{\mathrm{i}}{\hbar}\frac{p_x^2}{2m}\Delta t\right]\exp\left(-\frac{\mathrm{i}}{\hbar}V(x)\Delta t\right) \tag{5.302}$$

This relation is correct up to terms of order $(\Delta t)^2$ and is exact in the limit $N \to \infty$, that is $\Delta t \to 0$. Each of the delta functions in (5.301) can be expressed by the relation (A.18) of appendix A in the form

$$\delta(x_n - x_{n-1}) = (2\pi)^{-1}\int_{-\infty}^{\infty}\mathrm{d}k\exp[\mathrm{i}k(x_n-x_{n-1})], \quad n = 1,2,\ldots N \tag{5.303}$$

Since the plane wave $\exp[\mathrm{i}k(x_n - x_{n-1})]$ is an eigenfunction of the kinetic energy operator $p_x^2/2m$ belonging to the eigenvalue $\hbar^2k^2/2m$, we have from (5.302) that in the limit of small Δt

$$\begin{aligned}&\exp\left(-\frac{\mathrm{i}}{\hbar}H\Delta t\right)\delta(x_n-x_{n-1})\\ &= (2\pi)^{-1}\int_{-\infty}^{\infty}\mathrm{d}k\exp\left(-\mathrm{i}\frac{\hbar k^2}{2m}\Delta t+\mathrm{i}k(x_n+x_{n-1})\right)\\ &\quad\times\exp\left(-\frac{\mathrm{i}}{\hbar}V(x_{n-1})\Delta t\right).\end{aligned} \tag{5.304}$$

Using the integral (2.48), which holds for imaginary values of α and β, we find with $\alpha = \mathrm{i}\hbar\Delta t/(2m)$ and $\beta = \mathrm{i}(x_n - x_{n-1})$ that

$$\begin{aligned}
&\exp\left(-\frac{\mathrm{i}}{\hbar}H\Delta t\right)\delta(x_n - x_{n-1}) \\
&= \left(\frac{m}{2\pi\mathrm{i}\hbar\Delta t}\right)^{1/2}\exp\left[\frac{\mathrm{i}m(x_n - x_{n-1})^2}{2\hbar\Delta t}\right]\exp\left[-\frac{\mathrm{i}}{\hbar}V(x_{n-1})\Delta t\right]. \qquad \textbf{(5.305)}
\end{aligned}$$

It should be noted that when $V = 0$, this expression reduces to the free particle propagator which expresses $\Psi(x_n, t_0 + \Delta t)$ in terms of $\Psi(x_{n-1}, t_0)$ (see Problem 3.11).

From (5.301), (5.304) and (5.305) and taking the limit $N \to \infty$, we obtain an exact expression for the propagator K

$$\begin{aligned}
K(x_N, t_1; x_0, t_0) = \lim_{N\to\infty}&\left[\frac{m}{2\pi\mathrm{i}\hbar\Delta t}\right]^{N/2}\int_{-\infty}^{\infty}\mathrm{d}x_1\dots\int_{-\infty}^{\infty}\mathrm{d}x_{N-1} \\
&\times\exp\left\{\frac{\mathrm{i}}{\hbar}\Delta t\sum_{n=1}^{N}\left[\frac{m(x_n - x_{n-1})^2}{2(\Delta t)^2} - V(x_{n-1})\right]\right\}. \qquad \textbf{(5.306)}
\end{aligned}$$

The point x_n is the value of x at time $t_0 + n\Delta t$ and the set of points x_n, $n = 1, 2, 3, \dots N$ defines a path between the end points (x_0, t_0) and (x_N, t_N) as shown in Fig. 5.2. The integrals over $x_1, x_2 \dots x_{N-1}$ result in a sum over all paths and in the limit $N \to \infty$ define a path integral. In this limit

$$\lim_{\Delta t\to 0}\frac{(x_n - x_{n-1})^2}{(\Delta t)^2} \to (\dot{x}(t))^2 \qquad \textbf{(5.307)}$$

and

$$\Delta t\sum_{n=1}^{N} \to \int \mathrm{d}t \qquad \textbf{(5.308)}$$

so that the exponent in (5.306) can be written in terms of the classical action

$$\begin{aligned}
&\lim_{N\to\infty}\frac{\mathrm{i}}{\hbar}\Delta t\sum_{n=1}^{N}\left[\frac{m(x_n - x_{n-1})^2}{2(\Delta t)^2} - V(x_{n-1})\right] \\
&= \frac{\mathrm{i}}{\hbar}\int_{t_0}^{t_1}\left[\frac{1}{2}m(\dot{x}(t))^2 - V(x(t))\right]\mathrm{d}t \\
&= \frac{\mathrm{i}}{\hbar}I(t_1, t_0). \qquad \textbf{(5.309)}
\end{aligned}$$

If the infinitely dimensional integral in (5.306) is written symbolically as

$$\int\mathcal{D}(x(t)) = \lim_{N\to\infty}\left[\frac{m}{2\pi\mathrm{i}\hbar\Delta t}\right]^{N/2}\int_{-\infty}^{\infty}\mathrm{d}x_1\dots\int_{-\infty}^{\infty}\mathrm{d}x_{N-1} \qquad \textbf{(5.310)}$$

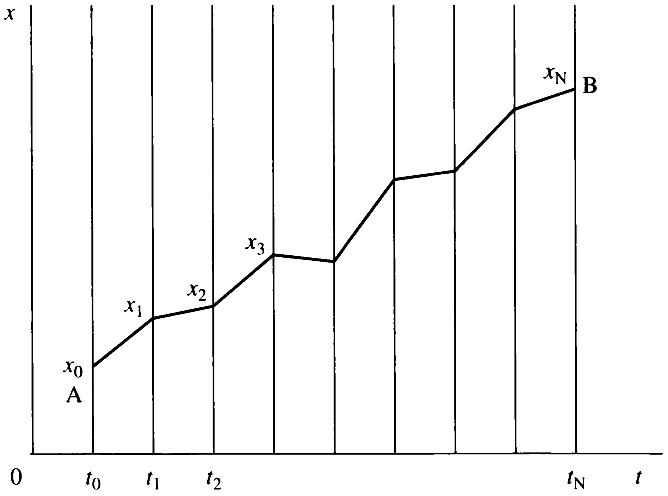


Figure 5.2 A path between $A(x_0, t_0)$ and $B(x_N, t_N)$ is defined by a series of points x_n at times $t_n = t_0 + n\Delta t$. By integrating over $x_1, x_2 \dots x_{N-1}$ a sum over all paths is obtained.

the path integral form of K can be written as

$$K(x_N, t_1; x_0, t_0) = \int \mathcal{D}(x(t)) \exp\left(\frac{\mathrm{i}}{\hbar} I(t_1, t_0)\right). \tag{5.311}$$

Although it is convenient to express the sum over all paths by an integral symbol, it must not be forgotten that the path integral is defined as the limit $N \to \infty$ of the discretised expression (5.306).

In this discussion the propagator, and hence the wave function, have been expressed in path integral form by using the evolution operator (5.243) which was in turn derived from the Schrödinger equation. Alternatively it is possible to postulate the expression (5.311) where I is the classical action, and to develop quantum mechanics from it.

With the exception of a few potentials, including the harmonic oscillator, the propagator K cannot be evaluated exactly starting from (5.311), so that the path integral expression has a limited use in practical calculations. However, path integral methods can lead to an understanding of physical effects both in non-relativistic quantum mechanics and in its generalisation to relativistic quantum field theory (see for example Huang, 1998).

5.10 Symmetry principles and conservation laws

In this section we shall discuss the connection between symmetry principles and conservation laws. The symmetry operations with which we are concerned are transformations of the dynamical variables that leave the time-independent Hamiltonian operator of an *isolated system* invariant. We shall show that for each operation that leaves the Hamiltonian invariant there is a corresponding dynamical variable that is a constant of the motion and is conserved.

Spatial translations and conservation of momentum

Let us begin by analysing the connection between the translational properties of a system and the conservation of momentum. We shall make the basic assumption that the physical properties of an *isolated* physical system cannot be altered by a translation of the system by an arbitrary amount **a**. Such a translation has of course the same effect as one in which the system is undisturbed, but the origin of coordinates is displaced[7] by an amount $-\mathbf{a}$. Thus the new position vector of a point, $\mathbf{r}'$, is related to the old one, **r**, by

$$\mathbf{r}' = T(\mathbf{a})\mathbf{r} \equiv \mathbf{r} + \mathbf{a} \tag{5.312}$$

where $T(\mathbf{a})$ is the operator effecting the transformation. The inverse translation $T^{-1}(\mathbf{a})$ is then defined by

$$\mathbf{r} = T^{-1}(\mathbf{a})\mathbf{r}' \equiv \mathbf{r}' - \mathbf{a}. \tag{5.313}$$

Let us now consider the simple case of a system consisting of a single structureless particle described at a given time by the spatial wave function $\psi(\mathbf{r})$. Let the system after being translated by an amount **a** be described by the wave function $\psi'(\mathbf{r})$. The two wave functions $\psi(\mathbf{r})$ and $\psi'(\mathbf{r})$ can be connected by an operator $U_{\mathrm{T}}(\mathbf{a})$ defined so that

$$\psi'(\mathbf{r}) = U_{\mathrm{T}}(\mathbf{a})\psi(\mathbf{r}). \tag{5.314}$$

Since this active translation of the system by the amount **a** is equivalent to shifting the coordinate origin by $-\mathbf{a}$, it is clear that

$$\begin{aligned} \psi'(\mathbf{r}+\mathbf{a}) &= \psi'(T\mathbf{r}) \\ &= \psi(\mathbf{r}) \end{aligned} \tag{5.315}$$

or, alternatively,

$$\begin{aligned} \psi'(\mathbf{r}) &= U_{\mathrm{T}}(\mathbf{a})\psi(\mathbf{r}) = \psi(T^{-1}\mathbf{r}) \\ &= \psi(\mathbf{r}-\mathbf{a}). \end{aligned} \tag{5.316}$$

Because the physical properties of the system cannot be altered by this transformation, $U_{\mathrm{T}}(\mathbf{a})$ must be a *unitary operator* (see Section 5.5). The explicit form of $U_{\mathrm{T}}(\mathbf{a})$

---

[7] Transformations in which the system is moved relative to a particular coordinate system are said to be 'active' transformations. If, on the other hand, the system is considered to be fixed and the coordinate system is moved the transformations are said to be 'passive'.

can be determined by considering first the effect of an *infinitesimal translation* $\delta\mathbf{a}$ on the wave function. Using (5.316) and keeping terms to first order in $\delta\mathbf{a}$, we have

$$\begin{aligned}\psi'(\mathbf{r}) &= \psi(\mathbf{r}-\delta\mathbf{a})\\ &= \psi(\mathbf{r}) - \delta a_x\frac{\partial\psi(\mathbf{r})}{\partial x} - \delta a_y\frac{\partial\psi(\mathbf{r})}{\partial y} - \delta a_z\frac{\partial\psi(\mathbf{r})}{\partial z}\\ &= (I - \delta\mathbf{a}.\boldsymbol{\nabla})\psi(\mathbf{r}). \end{aligned}\qquad \textbf{(5.317)}$$

Comparing (5.317) with (5.314), we see that the infinitesimal unitary translation operator is

$$\begin{aligned}U_{\mathrm{T}}(\delta\mathbf{a}) &= I - \delta\mathbf{a}.\boldsymbol{\nabla}\\ &= I - \frac{\mathrm{i}}{\hbar}\delta\mathbf{a}.\mathbf{p}_{\mathrm{op}}\end{aligned}\qquad \textbf{(5.318)}$$

where $\mathbf{p}_{\mathrm{op}} = -\mathrm{i}\hbar\boldsymbol{\nabla}$ is the momentum operator of the particle in the position representation. Thus we see that the momentum operator $\mathbf{p}_{\mathrm{op}}$ is the generator of the infinitesimal translations.

A finite translation can be obtained by performing successive infinitesimal translations in steps of $\delta\mathbf{a}$. Let us write $\delta\mathbf{a} = \mathbf{a}/n$, where n is an integer, and take the limit $n \to \infty$. We then have

$$\begin{aligned}U_{\mathrm{T}}(\mathbf{a}) &= \lim_{n\to\infty}\left(I - \frac{\mathrm{i}}{\hbar}\frac{\mathbf{a}.\mathbf{p}_{\mathrm{op}}}{n}\right)^n\\ &= \exp\left(-\frac{\mathrm{i}}{\hbar}\mathbf{a}.\mathbf{p}_{\mathrm{op}}\right).\end{aligned}\qquad \textbf{(5.319)}$$

If the wave function $\psi(\mathbf{r})$ is an eigenstate of the momentum operator $\mathbf{p}_{\mathrm{op}}$ corresponding to an eigenvalue $\mathbf{p}$

$$\mathbf{p}_{\mathrm{op}}\psi = \mathbf{p}\psi \qquad \textbf{(5.320)}$$

it follows that

$$U_{\mathrm{T}}(\mathbf{a})\psi = \exp\left(-\frac{\mathrm{i}}{\hbar}\mathbf{a}.\mathbf{p}\right)\psi. \qquad \textbf{(5.321)}$$

Thus the action of $U_{\mathrm{T}}(\mathbf{a})$ is to alter ψ by a phase factor, which clearly does not change the state of the system. Conversely, we see that if the state of a system is unaltered by a translation, it is an eigenstate of the momentum operator.

These results can be immediately generalised to a system of N particles. In this case, the infinitesimal unitary translation operator is given by

$$U_{\mathrm{T}}(\delta\mathbf{a}) = I - \frac{\mathrm{i}}{\hbar}\delta\mathbf{a}.\mathbf{P}_{\mathrm{op}} \qquad \textbf{(5.322)}$$

where the generator of the transformation, $\mathbf{P}_{\mathrm{op}}$, is the total momentum operator

$$\mathbf{P}_{\mathrm{op}} = (\mathbf{p}_1)_{\mathrm{op}} + (\mathbf{p}_2)_{\mathrm{op}} + \cdots + (\mathbf{p}_N)_{\mathrm{op}}. \qquad \textbf{(5.323)}$$

Likewise, the unitary operator corresponding to a finite translation is given for an N-particle system by

$$U_{\mathrm{T}}(\mathbf{a}) = \exp\left(-\frac{\mathrm{i}}{\hbar}\mathbf{a}.\mathbf{P}_{\mathrm{op}}\right). \tag{5.324}$$

Since the Hamiltonian H of an isolated system is invariant under any translation, it follows that

$$H' = U_{\mathrm{T}}(\mathbf{a})HU_{\mathrm{T}}^{\dagger}(\mathbf{a}) = H. \tag{5.325}$$

In particular, for an infinitesimal translation we have from (5.322), to order $\delta\mathbf{a}$

$$U_{\mathrm{T}}(\delta\mathbf{a})HU_{\mathrm{T}}^{\dagger}(\delta\mathbf{a}) = H - \frac{\mathrm{i}}{\hbar}\delta\mathbf{a}.[\mathbf{P}_{\mathrm{op}}, H] \tag{5.326}$$

and therefore, upon comparison of (5.326) with (5.325), we find that

$$[\mathbf{P}_{\mathrm{op}}, H] = 0 \tag{5.327}$$

so that the total momentum is a constant of the motion (see (5.254)). Thus we see that *the conservation of the total momentum of an isolated system results from the invariance of its Hamiltonian under translations.*

Conservation laws and continuous symmetry transformations

The foregoing discussion can readily be generalised to any continuous symmetry transformation. Let the Hamiltonian H of an isolated system be invariant under a symmetry transformation S. If U_S is the unitary operator effecting this transformation, its action on the wave function Ψ of the system is given by

$$\Psi' = U_S\Psi. \tag{5.328}$$

Let A be an observable and A' its transform by the symmetry operation. Because the expectation value of measurements of A' made on the system in the dynamical state Ψ' must be equal to the expectation value of measurements of A made on the system in the dynamical state Ψ, we must have

$$\begin{aligned}\langle\Psi|A|\Psi\rangle &= \langle\Psi'|A'|\Psi'\rangle \\ &= \langle U_S\Psi|A'|U_S\Psi\rangle\end{aligned} \tag{5.329}$$

so that

$$A' = U_S A U_S^{\dagger}, \qquad A = U_S^{\dagger}A'U_S. \tag{5.330}$$

In particular, since the Hamiltonian H is invariant under the symmetry operation S,

$$H' = U_S H U_S^{\dagger} = H. \tag{5.331}$$

If the symmetry transformation is a continuous one, any operator U_S can be expressed as a product of operators $U_{\delta S}$ corresponding to infinitesimal symmetry transformations, such that

$$U_{\delta S}(\varepsilon) = I + \mathrm{i}\varepsilon F_S \tag{5.332}$$

where ε is a real, arbitrarily small parameter and F_S, the generator of the infinitesimal unitary transformation, is an Hermitian operator. To first order in ε,

$$H' = U_{\delta S}(\varepsilon) H U^{\dagger}_{\delta S}(\varepsilon) = H + \mathrm{i}\varepsilon[F_S, H]. \tag{5.333}$$

Comparing (5.333) with (5.331), we see that

$$[F_S, H] = 0 \tag{5.334}$$

and it follows from (5.254) that if F_S is time-independent its expectation value $\langle F_S \rangle$ will not vary in time, so that F_S is a *constant of the motion.*

Equation (5.334) generalises to any continuous symmetry transformation the result (5.327) derived for spatial translations. In Chapter 6 we shall examine the case of rotations, and shall show that *the conservation of the angular momentum of an isolated system is the consequence of the invariance of its Hamiltonian under rotations.* Here we consider briefly *time translations*, which, as we have seen in Section 5.7, are effected for a time-independent Hamiltonian by the evolution operator

$$U(t, t_0) = \exp\left[-\frac{\mathrm{i}}{\hbar} H(t - t_0)\right]. \tag{5.335}$$

The generator of the corresponding infinitesimal transformation is the Hamiltonian H, and as H commutes with itself, it follows that if H is time-independent the energy is conserved. Thus, *the conservation of energy of an isolated system is a consequence of the invariance of its Hamiltonian with respect to time translations.*

Space reflection and parity conservation

Until now we have discussed continuous symmetry transformations. We now turn our attention to a *discrete* symmetry transformation: the *reflection* through the origin 0 of the coordinate system. This operation is also known as an *inversion* or *parity* operation. Corresponding to such an operation, there is a unitary operator, usually denoted by $\mathcal{P}$, and called the *parity* operator. It is such that, for a single particle (spatial) wave function $\psi(\mathbf{r})$,

$$\mathcal{P}\psi(\mathbf{r}) = \psi(-\mathbf{r}) \tag{5.336a}$$

and for several particles

$$\mathcal{P}\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi(-\mathbf{r}_1, -\mathbf{r}_2, \dots, -\mathbf{r}_N). \tag{5.336b}$$

The parity operator $\mathcal{P}$ is Hermitian ($\mathcal{P}^\dagger = \mathcal{P}$) since, for any two wave functions $\psi(\mathbf{r})$ and $\phi(\mathbf{r})$, we have

$$\begin{aligned}\int \phi^*(\mathbf{r})\mathcal{P}\psi(\mathbf{r})\mathrm{d}\mathbf{r} &= \int \phi^*(\mathbf{r})\psi(-\mathbf{r})\mathrm{d}\mathbf{r} \\ &= \int \phi^*(-\mathbf{r})\psi(\mathbf{r})\mathrm{d}\mathbf{r} \\ &= \int [\mathcal{P}\phi(\mathbf{r})]^*\psi(\mathbf{r})\mathrm{d}\mathbf{r} \end{aligned} \tag{5.337}$$

and the generalisation to several-particle wave functions is obvious.

It follows from the definition (5.336) that

$$\mathcal{P}^2 = I \tag{5.338}$$

so that the eigenvalues of $\mathcal{P}$ are $+1$ or -1, and the corresponding eigenstates are said to be *even* or *odd*. Thus, if $\psi_+(\mathbf{r})$ is an even eigenstate of $\mathcal{P}$ and $\psi_-(\mathbf{r})$ is an odd eigenstate, we have

$$\mathcal{P}\psi_+(\mathbf{r}) = \psi_+(-\mathbf{r}) = \psi_+(\mathbf{r}) \tag{5.339a}$$

and

$$\mathcal{P}\psi_-(\mathbf{r}) = \psi_-(-\mathbf{r}) = -\psi_-(\mathbf{r}). \tag{5.339b}$$

We note that

$$\begin{aligned}\int \psi_+^*(\mathbf{r})\psi_-(\mathbf{r})\mathrm{d}\mathbf{r} &= \int \psi_+^*(-\mathbf{r})\psi_-(-\mathbf{r})\mathrm{d}\mathbf{r} \\ &= -\int \psi_+^*(\mathbf{r})\psi_-(\mathbf{r})\mathrm{d}\mathbf{r}. \end{aligned} \tag{5.340}$$

Hence

$$\int \psi_+^*(\mathbf{r})\psi_-(\mathbf{r})\mathrm{d}\mathbf{r} = 0 \tag{5.341}$$

so that the eigenstates $\psi_+(\mathbf{r})$ and $\psi_-(\mathbf{r})$ are *orthogonal*, in accordance with the fact that they belong to different eigenvalues of $\mathcal{P}$. They also form a complete set, since any function can be written as

$$\psi(\mathbf{r}) = \psi_+(\mathbf{r}) + \psi_-(\mathbf{r}) \tag{5.342}$$

where

$$\psi_+(\mathbf{r}) = \tfrac{1}{2}[\psi(\mathbf{r}) + \psi(-\mathbf{r})] \tag{5.343}$$

has even parity, while

$$\psi_-(\mathbf{r}) = \tfrac{1}{2}[\psi(\mathbf{r}) - \psi(-\mathbf{r})] \tag{5.344}$$

has odd parity. Again, the generalisation to systems of N particles is obvious.

The action of the parity operator $\mathcal{P}$ on the observables $\mathbf{r}$ and $\mathbf{p}_{\text{op}}$ is given by

$$\mathcal{P}\mathbf{r}\mathcal{P}^\dagger = -\mathbf{r} \tag{5.345}$$

and

$$\mathcal{P}\mathbf{p}_{\text{op}}\mathcal{P}^\dagger = -\mathbf{p}_{\text{op}}. \tag{5.346}$$

and we recall that $\mathcal{P}^\dagger = \mathcal{P}$.

The parity operation is equivalent to transforming a right-handed system of coordinates into a left-handed one. From our general discussion, we know that if the parity operator commutes with the Hamiltonian of the system, then parity is conserved and simultaneous eigenstates of the Hamiltonian and the parity operator can be formed. If the weak interaction (which is responsible, for example, for the beta-decay of nuclei) is disregarded, the parity operator commutes with the Hamiltonians of atomic and nuclear systems

$$[\mathcal{P}, H] = 0 \tag{5.347}$$

and parity is conserved.

Time-reversal invariance

A second important discrete transformation is one in which the time is reversed, $t \to -t$. Before we examine the effect of this transformation in quantum mechanics, it is instructive to recall how time-reversal invariance occurs in classical mechanics. For this purpose, we start from Newton's law of motion for a mass point,

$$m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = \mathbf{F} \tag{5.348}$$

and assume that the force $\mathbf{F}$ only depends explicitly on the position coordinates. Then, because Newton's equations are of second order in t, we can associate to every solution $\mathbf{r}(t)$ of equation (5.348) another solution

$$\mathbf{r}'(t) = \mathbf{r}(-t). \tag{5.349}$$

The correspondence between the two solutions is illustrated by Fig. 5.3. We remark that the position of the particle at time t_0 in case (a) is the same as its position at time $-t_0$ in case (b), while the velocities (and hence the momenta) are reversed. Indeed,

$$\mathbf{v}'(t_0) = \left[\frac{\mathrm{d}\mathbf{r}'(t)}{\mathrm{d}t}\right]_{t=t_0} = -\left[\frac{\mathrm{d}\mathbf{r}(-t)}{\mathrm{d}(-t)}\right]_{t=t_0} = -\left[\frac{\mathrm{d}\mathbf{r}(t')}{\mathrm{d}t'}\right]_{t'=-t_0} = -\mathbf{v}(-t_0). \tag{5.350}$$

Let us now investigate the effect of the time-reversal transformation $t \to -t$ in quantum mechanics. We begin by considering the case of a spinless particle of mass m moving in a real time-independent potential $V(\mathbf{r})$. The corresponding time-dependent Schrödinger equation reads

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}, t). \tag{5.351}$$

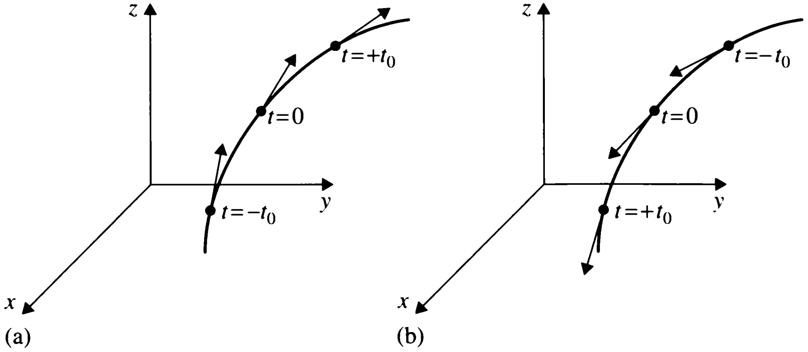


Figure 5.3 Two classical trajectories (a) and (b) which correspond by time reversal.

Changing t into $-t$, we obtain

$$-i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, -t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}, -t) \tag{5.352}$$

and we see that by taking the complex conjugate we can restore the form of the original equation (5.351):

$$i\hbar\frac{\partial}{\partial t}\Psi^*(\mathbf{r}, -t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi^*(\mathbf{r}, -t). \tag{5.353}$$

It follows that if $\Psi(\mathbf{r}, t)$ is a solution of the time-dependent Schrödinger equation (5.351), so also is the 'time-reversed' wave function

$$\Psi'(\mathbf{r}, t) = \Psi^*(\mathbf{r}, -t). \tag{5.354}$$

It should be noted that this result depends on our choice of representation. For example, if we write (see (2.60))

$$\Psi(\mathbf{r}, t) = (2\pi\hbar)^{-3/2}\int e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}\Phi(\mathbf{p}, t)d\mathbf{p} \tag{5.355}$$

and

$$\Psi'(\mathbf{r}, t) = (2\pi\hbar)^{-3/2}\int e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}\Phi'(\mathbf{p}, t)d\mathbf{p} \tag{5.356}$$

we see from (5.354) that the momentum space wave functions $\Phi(\mathbf{p}, t)$ and $\Phi'(\mathbf{p}, t)$ are related by

$$\Phi'(\mathbf{p}, t) = \Phi^*(-\mathbf{p}, -t). \tag{5.357}$$

Thus in momentum space, as we change t into $-t$ we must not only take the complex conjugate of the wave function, but also change $\mathbf{p}$ into $-\mathbf{p}$. This last finding is consistent with the classical result (5.350).

Let us now consider a more general case, starting from the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(t) = H\Psi(t) \tag{5.358}$$

and assuming that the Hamiltonian H is time-independent. Changing t into $-t$, and taking the complex conjugate, we obtain

$$i\hbar\frac{\partial}{\partial t}\Psi^*(-t) = H^*\Psi^*(-t). \tag{5.359}$$

Let us first assume that the Hamiltonian H is real $(H^* = H)$. Then, if $\Psi(t)$ is a solution of the time-dependent Schrödinger equation, so is also the time-reversed state vector

$$\Psi'(t) = \Psi^*(-t) = K\Psi(-t). \tag{5.360}$$

Here K denotes the operator of complex conjugation. We remark that this operator is anti-unitary[8], and such that $K^2 = I$ or $K = K^\dagger$.

In general, however, H is not real. In this case we suppose that there exists a unitary[9] operator U_τ, such that

$$U_\tau H^* U_\tau^\dagger = H. \tag{5.361}$$

This operator U_τ should obviously reduce to the unit operator I when H is real. Operating on both sides of (5.359) with U_τ and using (5.361), we find that

$$i\hbar\frac{\partial}{\partial t}U_\tau\Psi^*(-t) = HU_\tau\Psi^*(-t). \tag{5.362}$$

Hence, if $\Psi(t)$ is a solution of the time-dependent Schrödinger equation, so also is

$$\begin{aligned}\Psi'(t) &= U_\tau\Psi^*(-t) = U_\tau K\Psi(-t)\\ &= \mathcal{T}\Psi(-t)\end{aligned} \tag{5.363}$$

where

$$\mathcal{T} = U_\tau K \tag{5.364}$$

is the *time-reversal operator*. In analogy with our foregoing discussion we call $\Psi'(t)$ the time-reversed state vector corresponding to $\Psi(t)$. We remark that since K is anti-unitary and U_τ is unitary the time-reversal operator $\mathcal{T}$ is anti-unitary.

---

[8] An operator B is said to be *anti-linear* if

$$B(c_1\Psi_1 + c_2\Psi_2) = c_1^*(B\Psi_1) + c_2^*(B\Psi_2)$$

where Ψ_1 and Ψ_2 are two functions and c_1 and c_2 are complex constants. An *anti-unitary* operator V is anti-linear and, in addition, satisfies the relation

$$VV^\dagger = V^\dagger V = I.$$

[9] The condition that U_τ be a unitary operator is imposed by the requirement of preserving the normalisation of the state vector.

We have seen above that when the Hamiltonian H is real the operator U_τ reduces to the unit operator, so that in this case the time-reversal operator $\mathcal{T}$ is just the operator K of complex conjugation. When $H^* \neq H$ it is usually a simple matter to obtain the appropriate operator U_τ (and hence $\mathcal{T}$) by using the following considerations. First of all, we require that the position operator **r** be left unchanged under time reversal:

$$\mathbf{r}' = \mathcal{T}\mathbf{r}\mathcal{T}^\dagger = \mathbf{r}. \tag{5.365}$$

Hence, if we work in the position representation (where **r** is a purely real operator), we must have

$$\mathcal{T}\mathbf{r}\mathcal{T}^\dagger = U_\tau K\mathbf{r}K^\dagger U_\tau^\dagger = U_\tau\mathbf{r}U_\tau^\dagger = \mathbf{r} \tag{5.366}$$

so that U_τ must commute with **r**. We also require that the momentum operator shall change sign under the time-reversal operation

$$\mathbf{p}'_{\mathrm{op}} = \mathcal{T}\mathbf{p}_{\mathrm{op}}\mathcal{T}^\dagger = -\mathbf{p}_{\mathrm{op}}. \tag{5.367}$$

Since $\mathbf{p}_{\mathrm{op}} = -\mathrm{i}\hbar\boldsymbol{\nabla}$ is a purely imaginary operator in the position representation, we have in that representation

$$\mathcal{T}\mathbf{p}_{\mathrm{op}}\mathcal{T}^\dagger = U_\tau K(-\mathrm{i}\hbar\boldsymbol{\nabla})K^\dagger U_\tau^\dagger = U_\tau(\mathrm{i}\hbar\boldsymbol{\nabla})U_\tau^\dagger = -\mathbf{p}_{\mathrm{op}} = \mathrm{i}\hbar\boldsymbol{\nabla} \tag{5.368}$$

which implies that U_τ must also commute with $\mathbf{p}_{\mathrm{op}} = -\mathrm{i}\hbar\boldsymbol{\nabla}$.

Let us now return once more to the time-dependent Schrödinger equation (5.358). Changing t into $-t$ and inserting $\mathcal{T}^\dagger\mathcal{T}(= I)$ between H and Ψ, we obtain

$$-\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(-t) = H\mathcal{T}^\dagger\mathcal{T}\Psi(-t) \tag{5.369}$$

and therefore

$$-\mathcal{T}\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(-t) = \mathcal{T}H\mathcal{T}^\dagger\mathcal{T}\Psi(-t). \tag{5.370}$$

Now, using (5.363) and (5.364), we have

$$-U_\tau K\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(-t) = -U_\tau(-\mathrm{i})\hbar\frac{\partial}{\partial t}\Psi^*(-t) = \mathcal{T}H\mathcal{T}^\dagger\Psi'(t) \tag{5.371}$$

or

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi'(t) = \mathcal{T}H\mathcal{T}^\dagger\Psi'(t) \tag{5.372}$$

and we want this equation to be identical with the original Schrödinger equation (5.358). Hence, provided that a unitary operator U_τ satisfying (5.361) exists, we see that the requirement

$$\mathcal{T}H\mathcal{T}^\dagger = H \tag{5.373}$$

or

$$[\mathcal{T}, H] = 0 \tag{5.374}$$

is the necessary and sufficient condition for the time-reversal invariance of the Schrödinger equation. At one time it was supposed that all fundamental Hamiltonians satisfied the time-reversal invariance condition (5.374), but it is now known that the Hamiltonian corresponding to the weak interaction is not time-reversal invariant, as well as not being invariant under the parity operation.

Galilean transformations

Let us consider a frame of reference S specified by Cartesian axes OX, OY, OZ and a second frame S' with Cartesian axes $O'X$, $O'Y$, $O'Z$ such that the axes in the two frames are parallel, but the origin O' moves with a constant velocity $\mathbf{v}$ with respect to O. If $\mathbf{r}$ is the position vector of a particle in S at time t and $\mathbf{r}'$ is the position vector of the same particle at the same time in S', then

$$\mathbf{r}' = \mathbf{r} - \mathbf{v}t \tag{5.375}$$

where we have taken O and O' to coincide at the time $t = 0$. The transformation (5.375) is known as a *Galilean transformation*. In non-relativistic classical mechanics, if Newton's laws of motion are obeyed in a frame S (an *inertial frame*), then they also hold in all frames S' which can be obtained by a Galilean transformation from S.

We shall now examine how the Schrödinger equation for a single particle of mass m moving in a potential $V(\mathbf{r}, t)$ changes under the Galilean transformation (5.375). If $\Psi(\mathbf{r}, t)$ is the wave function in the frame S, it satisfies the Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}, t)\right]\Psi(\mathbf{r}, t) \tag{5.376}$$

To rewrite this equation in terms of $\mathbf{r}'$ we note that

$$\Psi(\mathbf{r}, t) = \Psi(\mathbf{r}' + \mathbf{v}t, t) \tag{5.377a}$$

$$\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \frac{\partial}{\partial t}\Psi(\mathbf{r}' + \mathbf{v}t, t) - \mathbf{v}.\nabla_{\mathbf{r}'}\Psi(\mathbf{r}' + \mathbf{v}t, t) \tag{5.377b}$$

$$\nabla_{\mathbf{r}}\Psi(\mathbf{r}, t) = \nabla_{\mathbf{r}'}\Psi(\mathbf{r}' + \mathbf{v}t, t) \tag{5.377c}$$

so that (5.376) can be written as

$$\begin{aligned}&\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}' + \mathbf{v}t, t) - \mathrm{i}\hbar\mathbf{v}.\nabla_{\mathbf{r}'}\Psi(\mathbf{r}' + \mathbf{v}t, t)\\ &\quad = \left(-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}'}^2 + V(\mathbf{r}' + \mathbf{v}t, t)\right)\Psi(\mathbf{r}' + \mathbf{v}t, t)\end{aligned} \tag{5.378}$$

This equation, although correct, is not in the form of a Schrödinger equation because of the term in $\mathbf{v}.\nabla_{\mathbf{r}'}$ on the left-hand side. A wave function $\Psi'(\mathbf{r}', t)$ which satisfies a standard Schrödinger equation in the frame S' can be introduced by making the unitary transformation

$$\Psi(\mathbf{r}' + \mathbf{v}t, t) = \exp[\mathrm{i}(m\mathbf{v}.\mathbf{r}' + mv^2t/2)/\hbar]\Psi'(\mathbf{r}', t) \tag{5.379}$$

The plane wave exponential factor takes account of the fact that a particle at rest in the frame S' has a momentum $m\mathbf{v}$ and a kinetic energy $mv^2/2$ when viewed from the frame S. Inserting (5.379) into (5.378) it is found that (Problem 5.21)

$$i\hbar\frac{\partial\Psi'(\mathbf{r}',t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}'} + V'(\mathbf{r}',t)\right)\Psi'(\mathbf{r}',t) \tag{5.380}$$

where the potential in the S' frame, $V'(\mathbf{r}',t)$, is defined as

$$V'(\mathbf{r}',t) = V(\mathbf{r}-\mathbf{v}t,t) \tag{5.381}$$

It is seen that $\Psi'(\mathbf{r}',t)$ satisfies a normal Schrödinger equation. If the potential V is zero, so is the potential V', with the consequence that both Ψ and Ψ' satisfy the same Schrödinger equation for a free particle; that is, the free-particle Schrödinger equation is invariant under a Galilean transformation.

We shall now show that the Schrödinger equation for an isolated system of particles is also invariant under a Galilean transformation. To see this, consider first the Schrödinger equation for an isolated two-body system which is written in terms of the relative coordinate $\mathbf{r}$ and the centre of mass coordinate $\mathbf{R}$ in equation (5.269). There are no external interactions but the two particles interact by the potential $V(\mathbf{r})$. Under a Galilean transformation the relative coordinate $\mathbf{r}$ is unchanged, but the position $\mathbf{R}'$ of the centre of mass in S' is related to $\mathbf{R}$ by

$$\mathbf{R}' = \mathbf{R} - \mathbf{v}t \tag{5.382}$$

In the frame S' the wave function $\Psi(\mathbf{R},\mathbf{r},t)$ becomes $\Psi(\mathbf{R}'+\mathbf{v}t,\mathbf{r},t)$ and introducing the unitary transformation

$$\Psi(\mathbf{R}'+\mathbf{v}t,t) = \exp[i(M\mathbf{v}.\mathbf{R}' + Mv^2t/2)\hbar]\Psi'(\mathbf{R}',\mathbf{r},t) \tag{5.383}$$

it is found that $\Psi'(\mathbf{R}',\mathbf{r},t)$ satisfies

$$i\hbar\frac{\partial\Psi'(\mathbf{R}',\mathbf{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}'} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right]\Psi'(\mathbf{R}',\mathbf{r},t) \tag{5.384}$$

where we recall that $M = m_1 + m_2$ is the total mass of the system and $\mu = m_1m_2/(m_1+m_2)$ is the reduced mass of the two particles. The equation (5.384) is identical in form to (5.269) so that the two-body Schrödinger equation for an isolated system is invariant under a Galilean transformation. Clearly this argument can be repeated for a many-body system in which there are no external interactions and the interactions between particles only depend on internal coordinates $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$.

5.11 The classical limit

The transition from quantum mechanics to classical mechanics was discussed briefly in Section 3.4. In this section, we shall examine this question in more detail.

The Ehrenfest theorem

We begin by re-deriving the Ehrenfest theorem, using commutator algebra. Consider a particle of mass m moving in a potential $V(\mathbf{r}, t)$, so that its Hamiltonian is given by

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, t) \tag{5.385}$$

Using equation (5.254) for the operator x, we find that

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle &= (\mathrm{i}\hbar)^{-1}\langle [x, H]\rangle \\ &= (\mathrm{i}\hbar)^{-1}\left\langle \left[x, \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, t)\right]\right\rangle \end{aligned} \tag{5.386}$$

Since x commutes with $V(\mathbf{r}, t)$ and also with p_y and p_z, we have

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle &= \frac{1}{2m\mathrm{i}\hbar}\langle [x, p_x^2]\rangle \\ &= \frac{1}{2m\mathrm{i}\hbar}\langle [x, p_x]p_x + p_x[x, p_x]\rangle \end{aligned} \tag{5.387}$$

But $[x, p_x] = \mathrm{i}\hbar$ and therefore

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle = \frac{\langle p_x\rangle}{m} \tag{5.388}$$

Proceeding in the same way with the expectation values of y and z, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \mathbf{r}\rangle = \frac{\langle \mathbf{p}\rangle}{m} \tag{5.389}$$

which is the first Ehrenfest relation.

Using now equation (5.254) for the operator p_x, we have

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\langle p_x\rangle &= (\mathrm{i}\hbar)^{-1}\langle [p_x, H]\rangle \\ &= (\mathrm{i}\hbar)^{-1}\left\langle \left[p_x, \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, t)\right]\right\rangle \\ &= -\left\langle \frac{\partial V}{\partial x}\right\rangle \end{aligned} \tag{5.390}$$

where we have used the fact that $[p_x, \mathbf{p}^2] = 0$ together with the equation

$$[p_x, V] = -\mathrm{i}\hbar\frac{\partial V}{\partial x} \tag{5.391}$$

Repeating the argument for p_y and p_z, we find that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \mathbf{p}\rangle = -\langle \boldsymbol{\nabla} V(\mathbf{r}, t)\rangle \tag{5.392}$$

which is the second Ehrenfest relation.

The Ehrenfest relations do not imply that classical mechanics holds for the expectation (average) values of **r** and **p**. For this to be true, we must have in addition that

$$\langle \nabla V(\mathbf{r}, t)\rangle = \nabla V(\langle \mathbf{r}\rangle, t). \tag{5.393}$$

This can only be approximately satisfied if the width of the position probability distribution is small compared with the distance over which the potential V varies appreciably.

To examine this point further, let us consider the simple case of one-dimensional motion in a potential $V(x)$. Expanding $\mathrm{d}V(x)/\mathrm{d}x \equiv V'(x)$ about the (time-dependent) expectation value $\langle x\rangle$, we have

$$V'(x) = V'(\langle x\rangle) + (x - \langle x\rangle)V''(\langle x\rangle) + \frac{1}{2}(x - \langle x\rangle)^2 V'''(\langle x\rangle) + \cdots \tag{5.394}$$

so that

$$\langle V'(x)\rangle = V'(\langle x\rangle) + \frac{1}{2}\langle (x - \langle x\rangle)^2\rangle V'''(\langle x\rangle) + \cdots \tag{5.395}$$

where we have used the fact that $\langle x - \langle x\rangle\rangle = 0$. The quantity $-V'(\langle x\rangle)$ is just the classical force at the point $\langle x\rangle$. Thus, if only the first term is retained on the right of (5.395), we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p_x\rangle = -V'(\langle x\rangle), \tag{5.396}$$

which shows that the expectation values $\langle x\rangle$ and $\langle p_x\rangle$ obey Newton's law. However, the condition that the second and higher terms in the expansion (5.395) are small is a necessary, but not sufficient, condition for the motion to be classical. For example, in the case of the harmonic oscillator, where $V(x)$ is quadratic in x, the second and higher terms in (5.395) vanish, and yet the classical limit can only be recovered if the spacing between the discrete energy levels is small compared with the energy of the oscillator; this occurs in the limit of large quantum numbers.

The Hamilton–Jacobi equation

Let us consider the time-dependent Schrödinger equation for a particle of mass m in a potential $V(\mathbf{r}, t)$:

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)\right]\Psi(\mathbf{r}, t) \tag{5.397}$$

and look for a solution of the form

$$\Psi(\mathbf{r}, t) = \exp\left[\frac{\mathrm{i}}{\hbar}W(\mathbf{r}, t)\right]. \tag{5.398}$$

Substituting (5.398) into (5.397), we find that the function W must satisfy the equation

$$\frac{\partial W}{\partial t} + \frac{1}{2m}(\nabla W)^2 + V - \frac{\mathrm{i}\hbar}{2m}\nabla^2 W = 0 \tag{5.399}$$

which in the limit $\hbar \to 0$ reduces to

$$\frac{\partial W}{\partial t} + \frac{1}{2m}(\nabla W)^2 + V = 0. \tag{5.400}$$

This is the *Hamilton–Jacobi equation* for Hamilton's principal function W[10]. It can also be written as

$$\frac{\partial W}{\partial t} + H(\mathbf{r}, \mathbf{p}, t) = 0 \tag{5.401}$$

where H is the classical Hamiltonian, $\mathbf{r}$ and $\mathbf{p}$ are the classical position and (canonical conjugate) momentum respectively, and

$$\mathbf{p}(t) = \nabla W(\mathbf{r}, t). \tag{5.402}$$

Thus, for the one-body problem we are considering, the Hamilton–Jacobi equation is a first-order partial differential equation in the four variables x, y, z and t. Classical trajectories $\mathbf{r}(t)$, which depend on the initial values (at $t = t_0$) of the canonical variables $\mathbf{r}$ and $\mathbf{p}$, can be determined from the knowledge of the principal function $W(\mathbf{r}, t)$.

Let us now consider the case for which the potential $V(\mathbf{r})$ is time-independent, so that the Schrödinger equation (5.397) has stationary solutions of the form $\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp(-\mathrm{i}Et/\hbar)$. In that case, we can write

$$W(\mathbf{r}, t) = S(\mathbf{r}) - Et \tag{5.403}$$

so that

$$\psi(\mathbf{r}) = \exp\left[\frac{\mathrm{i}}{\hbar} S(\mathbf{r})\right]. \tag{5.404}$$

Substituting (5.403) into (5.399), we obtain for the function S the equation

$$\frac{1}{2m}(\nabla S)^2 - [E - V(\mathbf{r})] - \frac{\mathrm{i}\hbar}{2m}\nabla^2 S = 0 \tag{5.405}$$

In the limit $\hbar \to 0$, this equation reduces to

$$\frac{1}{2m}(\nabla S)^2 = E - V(\mathbf{r}) \tag{5.406}$$

which is the equation determining Hamilton's characteristic function $S(\mathbf{r})$. For a time-independent potential $V(\mathbf{r})$, it follows from (5.402) that the classical trajectories $\mathbf{r}(t)$ are orthogonal to the surfaces of constant W. In 1834, Hamilton observed that in analogy with optics (where the rays of geometrical optics are the normals to wave fronts of constant phase), we may interpret classical mechanics as the 'geometrical optics' limit of a wave motion, the classical orbits being orthogonal to the wave fronts W = constant. This idea was the starting point of the investigations of de Broglie

---

[10] It can be shown quite generally for any classical system that the numerical value of the action integral I introduced in Section 5.9 is the same as that of the corresponding Hamilton principal function W (see Goldstein 1980).

and Schrödinger, which led to the formulation of wave mechanics. In Section 8.4, we shall show how the semi-classical approximation method of Wentzel, Kramers and Brillouin can be based on these considerations.

Problems

5.1 The operators $A_i (i = 1, \dots, 6)$ are defined as follows

$$A_1\psi(x) = [\psi(x)]^2 \qquad A_4\psi(x) = x^2\psi(x)$$

$$A_2\psi(x) = \frac{\mathrm{d}}{\mathrm{d}x}\psi(x) \qquad A_5\psi(x) = \sin[\psi(x)]$$

$$A_3\psi(x) = \int_a^x \psi(x')\mathrm{d}x' \qquad A_6\psi(x) = \frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x).$$

Which of the operators A_i are linear operators? Which are Hermitian?

5.2 Using the definition of Hermiticity (3.69) show, by expressing the wave function Ψ in the form $\Psi = c_1\Psi_1 + c_2\Psi_2$, where Ψ_1, Ψ_2 are a pair of square-integrable functions and c_1, c_2 are complex constants, that

$$\int \Psi_1^* A\Psi_2 \mathrm{d}\mathbf{r} = \int (A\Psi_1)^*\Psi_2 \mathrm{d}\mathbf{r}$$

in conformity with the general definition of Hermiticity (5.22).

5.3 If A and B are two Hermitian operators (a) show that AB and BA may not be Hermitian, but that $(AB + BA)$ and $\mathrm{i}(AB - BA)$ are both Hermitian. (b) Prove that the expectation value of A^2 is always real and non-negative. (c) If $A^2 = 2$, find the eigenvalues of A.

5.4 Prove that (a) if A is a linear operator and c is a complex number then

$$(cA)^\dagger = c^* A^\dagger$$

(b) if A and B are linear operators then

$$(A + B)^\dagger = A^\dagger + B^\dagger, \quad \text{and} \quad (AB)^\dagger = B^\dagger A^\dagger.$$

5.5 Consider a free particle of mass m moving in one dimension so that its Hamiltonian is $H = p_x^2/2m$. Show that the eigenvalues of H are two-fold degenerate, and that the degeneracy can be removed by considering the simultaneous eigenfunctions of H and p_x.

5.6 Prove the relations (5.101) satisfied by commutators.

5.7 (a) Prove by induction that

$$[x^n, p_x] = \mathrm{i}\hbar n x^{n-1}$$

and that

$$[x, p_x^n] = \mathrm{i}\hbar n p_x^{n-1}$$

where n is a positive integer.

(b) Using these results show that if $f(x)$ can be expanded in a polynomial in x and $g(p_x)$ can be expanded in a polynomial in p_x, then

$$[f(x), p_x] = \mathrm{i}\hbar \mathrm{d}f/\mathrm{d}x$$

and

$$[x, g(p_x)] = \mathrm{i}\hbar \mathrm{d}g/\mathrm{d}p_x.$$

5.8 If A and B are two operators such that $[A, B] = \lambda$, where λ is a complex number, and if μ is a second complex number, prove that

$$\exp[\mu(A + B)] = \exp(\mu A)\exp(\mu B)\exp(-\mu^2\lambda/2).$$

5.9 Show that for a one-dimensional harmonic oscillator the uncertainty product $\Delta x \Delta p_x$ is equal to $\left(n + \frac{1}{2}\right)\hbar$ in the energy eigenstate $\psi_n(x)$, where Δx and Δp_x are defined by (5.118). Verify that the ground-state wave function has the form of a minimum uncertainty wave packet (5.122).

5.10 Prove that a Hermitian operator is represented by a Hermitian matrix, a unitary operator by a unitary matrix, and the operator sum $A + B$ by the matrix sum $\mathbf{A} + \mathbf{B}$.

5.11 The Hamiltonian operator H for a certain physical system is represented by the matrix

$$\mathbf{H} = \hbar\omega \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

while two other observables A and B are represented by the matrices

$$\mathbf{A} = \begin{pmatrix} 0 & \lambda & 0 \\ \lambda & 0 & 0 \\ 0 & 0 & 2\lambda \end{pmatrix}, \quad \mathbf{B} = \begin{pmatrix} 2\mu & 0 & 0 \\ 0 & 0 & \mu \\ 0 & \mu & 0 \end{pmatrix}$$

where λ and μ are real (non-zero) numbers.

(a) Find the eigenvalues and eigenvectors of $\mathbf{A}$ and $\mathbf{B}$.

(b) If the system is in a state described by the state vector

$$\mathbf{u} = c_1\mathbf{u}_1 + c_2\mathbf{u}_2 + c_3\mathbf{u}_3$$

where c_1, c_2 and c_3 are complex constants and

$$\mathbf{u}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \mathbf{u}_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \mathbf{u}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

(i) find the relationship between c_1, c_2 and c_3 such that **u** is normalised to unity; and

(ii) find the expectation values of H, A and B.

(iii) What are the possible values of the energy that can be obtained in a measurement when the system is described by the state vector **u**? For each possible result find the wave function in the matrix representation immediately after the measurement.

5.12 Prove the commutation relations (5.190) and (5.193).

5.13 Calculate for a linear harmonic oscillator the matrix elements $(x^i)_{nm}$, where $i = 2, 3, 4$:

(a) by using matrix multiplication, starting from the expressions for x_{nm} given by (4.174); and

(b) by using the raising and lowering operators a_+ and a_-.

5.14 Find the matrix elements of x and p_x for the linear harmonic oscillator using $(a_+)_{kn}$ and $(a_-)_{kn}$ given respectively by (5.217) and (5.218).

5.15 Consider a particle of mass m moving in a potential $V(\mathbf{r}, t)$, so that its Hamiltonian is given by

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, t).$$

Using the result (5.254) and commutator algebra, prove that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle = \frac{1}{m}(\langle xp_x\rangle + \langle p_x x\rangle).$$

5.16 Generalise the virial theorem (5.260) to a system of N particles, having a Hamiltonian of the form (5.229).

5.17 Consider a one-particle system, of which the Hamiltonian does not depend on x. Using (5.254), show that the x-component of the momentum is then a constant of the motion.

5.18 Prove equation (5.266).

5.19 Show that for a one-dimensional harmonic oscillator described in the Heisenberg picture by the Hamiltonian

$$H_H = \frac{1}{2m}p_H^2(t) + \frac{1}{2}k\,x_H^2(t)$$

where $p_H \equiv (p_x)_H$, the general solution of equations (5.287) is

$$x_H(t) = x_H(0)\cos\omega t + \frac{1}{m\omega}p_H(0)\sin\omega t,$$

$$p_H(t) = -m\omega\,x_H(0)\sin\omega t + p_H(0)\cos\omega t$$

where $\omega = (k/m)^{1/2}$.

Is the Hamiltonian H_H time-independent?

5.20 Consider the one-dimensional motion of a free particle and the three operators $H = p_x^2/2m$, p_x and $\mathcal{P}$ (the parity operator). Do these operators all mutually commute? If not, show that one can construct two different complete sets of commuting observables from these three operators.

5.21 Show that the wave function $\Psi'(\mathbf{r}', t)$ defined by the unitary transformation (5.379) satisfies the time-dependent Schrödinger equation (5.380).

6 Angular momentum

One of the most important concepts in classical mechanics is that of angular momentum. All isolated systems possess the fundamental invariance property that their total angular momentum is conserved. This property provides a powerful aid in studying a number of problems such as the dynamics of rigid bodies and the motion of planets. In this respect the angular momentum can be compared with the total energy and the total linear momentum, which are also conserved quantities for isolated systems.

The role of angular momentum in quantum mechanics is also of paramount importance. In this chapter, the necessary formalism for the description of angular momentum in quantum theory will be developed and some illustrative applications will be discussed. We shall see that the main differences from classical mechanics arise from the fact that in quantum physics the angular momentum is not an ordinary vector, but is a *vector operator*, whose three components do not commute with each other. We begin by considering the *orbital angular momentum*, and establish its relationship with rotations. Then, after analysing the general properties of angular momentum, we will study the important case of the *spin* (or intrinsic) angular momentum. Finally, we shall treat the problem of the addition of angular momenta.

6.1 Orbital angular momentum

Let us consider a particle of mass m. We denote by $\mathbf{p}$ its momentum and by $\mathbf{r}$ its position vector with respect to a fixed origin 0. In classical mechanics the orbital angular momentum of this particle with respect to 0 is defined as a vector $\mathbf{L}$, such that

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{6.1}$$

This vector points in a direction at right angles to the plane containing $\mathbf{r}$ and $\mathbf{p}$, and is of magnitude $L = rp \sin\alpha$, where α is the angle between $\mathbf{r}$ and $\mathbf{p}$. The Cartesian components of $\mathbf{L}$ are

$$L_x = yp_z - zp_y \tag{6.2a}$$

$$L_y = zp_x - xp_z \tag{6.2b}$$

$$L_z = xp_y - yp_x. \tag{6.2c}$$

The corresponding operators representing L_x, L_y and L_z in quantum mechanics are obtained by replacing x, y, z and p_x, p_y, p_z by the appropriate operators obeying the fundamental commutation relations (5.88). Using the position representation of wave mechanics, such that $x_{\text{op}} = x$, $y_{\text{op}} = y$, $z_{\text{op}} = z$ and $(p_x)_{\text{op}} = -\mathrm{i}\hbar\partial/\partial x$, $(p_y)_{\text{op}} = -\mathrm{i}\hbar\partial/\partial y$, $(p_z)_{\text{op}} = -\mathrm{i}\hbar\partial/\partial z$, we find that the operators L_x, L_y and L_z are given by

$$L_x = -\mathrm{i}\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{6.3a}$$

$$L_y = -\mathrm{i}\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{6.3b}$$

$$L_z = -\mathrm{i}\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \tag{6.3c}$$

In other words the orbital angular momentum is represented in the position representation of wave mechanics by the *vector operator*

$$\mathbf{L} = -\mathrm{i}\hbar(\mathbf{r} \times \boldsymbol{\nabla}) \tag{6.4}$$

whose Cartesian components are the differential operators given by (6.3). It is easy to verify (Problem 6.1) that $\mathbf{L}$ is Hermitian.

Using the rules (5.101) of commutator algebra and the basic commutation relations (5.88), one readily obtains the commutation relations satisfied by the operators L_x, L_y and L_z. For example, we have

$$\begin{aligned}[L_x, L_y] &= [(yp_z - zp_y), (zp_x - xp_z)] \\ &= [yp_z, zp_x] + [zp_y, xp_z] - [yp_z, xp_z] - [zp_y, zp_x].\end{aligned} \tag{6.5}$$

The first commutator on the right of this equation is

$$[yp_z, zp_x] = yp_z zp_x - zp_x yp_z. \tag{6.6}$$

Since y and p_x commute with each other and with z and p_z, we can write

$$\begin{aligned}[yp_z, zp_x] &= yp_x[p_z, z] \\ &= -i\hbar yp_x. \end{aligned} \tag{6.7}$$

Similarly, the second commutator on the right of (6.5) becomes

$$\begin{aligned}[zp_y, xp_z] &= zp_y xp_z - xp_z zp_y \\ &= xp_y[z, p_z] \\ &= i\hbar xp_y. \end{aligned} \tag{6.8}$$

The third commutator on the right of (6.5) vanishes because y, x and p_z mutually commute, and so also does the last commutator, since z, p_y and p_x mutually commute. Thus we find that

$$\begin{aligned}[L_x, L_y] &= i\hbar(xp_y - yp_x) \\ &= i\hbar L_z. \end{aligned} \tag{6.9a}$$

Similarly, one obtains

$$[L_y, L_z] = i\hbar L_x \tag{6.9b}$$

and

$$[L_z, L_x] = i\hbar L_y. \tag{6.9c}$$

The three commutation relations (6.9) are readily shown (Problem 6.2) to be equivalent to the vector commutation relation

$$\mathbf{L} \times \mathbf{L} = i\hbar\mathbf{L}. \tag{6.10}$$

Note that the operator character of **L** is clearly exhibited by this equation, since the vector product **L** × **L** would vanish if **L** were an ordinary vector.

It is apparent from equations (6.9) that the operators representing any two components of the orbital angular momentum do not commute. From the results of Section 5.4 it follows that they are not simultaneously measurable. As a result, it is, in general[1], impossible to assign simultaneously definite values for all components of the orbital angular momentum. Thus, if the system is in an eigenstate of one orbital angular momentum component (so that a measurement of that component will produce a definite value), it will in general not be in an eigenstate of either of the two other components.

The operator representing the square of the magnitude of the orbital angular momentum is defined as

$$\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2 \tag{6.11}$$

---

[1] The words 'in general' are required because we shall see shortly that functions which depend only on the magnitude r of the position vector $\mathbf{r}$ are simultaneous eigenstates of L_x, L_y and L_z with eigenvalue zero.

Using the rules of commutator algebra and the commutation relations (6.9), it is easy to show that $\mathbf{L}^2$ commutes with each of the three components of $\mathbf{L}$. For example, let us look at the commutator

$$[\mathbf{L}^2, L_x] = [L_x^2 + L_y^2 + L_z^2, L_x]. \tag{6.12}$$

Since the commutator of L_x with itself vanishes, we have $[L_x^2, L_x] = 0$ and

$$\begin{aligned}[\mathbf{L}^2, L_x] &= [L_y^2 + L_z^2, L_x] \\ &= [L_y^2, L_x] + [L_z^2, L_x] \\ &= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z \\ &= -\mathrm{i}\hbar(L_yL_z + L_zL_y) + \mathrm{i}\hbar(L_zL_y + L_yL_z) \\ &= 0. \end{aligned} \tag{6.13a}$$

In the same way, we also find that

$$[\mathbf{L}^2, L_y] = [\mathbf{L}^2, L_z] = 0 \tag{6.13b}$$

and we may summarise the equations (6.13) by writing

$$[\mathbf{L}^2, \mathbf{L}] = 0. \tag{6.14}$$

It follows that simultaneous eigenfunctions of $\mathbf{L}^2$ and any one component of $\mathbf{L}$ can be found, so that both the magnitude of the orbital angular momentum and the value of any one of its components can be determined precisely. Furthermore, $\mathbf{L}^2$ and that component of $\mathbf{L}$ (say for example L_z) form a complete set for the specification of angular momentum states.

In obtaining the eigenvalues and eigenfunctions of $\mathbf{L}^2$ and of one of the components of $\mathbf{L}$, which we shall carry out in Section 6.3, it is convenient to express the orbital angular momentum operators in spherical polar coordinates (r, θ, ϕ) which are related to the Cartesian coordinates (x, y, z) of the vector $\mathbf{r}$ by

$$\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned} \tag{6.15}$$

with $0 \leqslant r \leqslant \infty$, $0 \leqslant \theta \leqslant \pi$, $0 \leqslant \phi \leqslant 2\pi$ (see Fig. 6.1). After some algebra (Problem 6.3) it is found that

$$L_x = -\mathrm{i}\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \tag{6.16a}$$

$$L_y = -\mathrm{i}\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \tag{6.16b}$$

$$L_z = -\mathrm{i}\hbar\frac{\partial}{\partial\phi} \tag{6.16c}$$

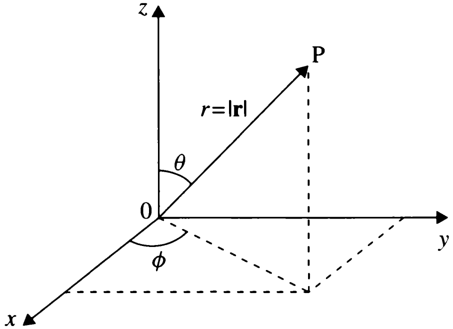


Figure 6.1 The spherical polar coordinates (r, θ, ϕ) of a point P. The position vector of P with respect to the origin is **r**.

and

$$\mathbf{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]. \qquad \textbf{(6.17)}$$

It should be noted that L_x, L_y, L_z and $\mathbf{L}^2$ are purely angular operators, which do not operate on the radial coordinate r. Therefore these operators commute with any function of r

$$[L_x, f(r)] = [L_y, f(r)] = [L_z, f(r)] = [\mathbf{L}^2, f(r)] = 0. \qquad \textbf{(6.18)}$$

From the expressions (6.16) and (6.17) it is also clear that if a function is independent of θ and ϕ (and hence depends only on r), then it is simultaneously an eigenfunction of L_x, L_y, L_z and $\mathbf{L}^2$ corresponding in each case to the eigenvalue zero. This is the single exception to the rule that eigenfunctions of one component of **L** cannot be simultaneously eigenfunctions of either of the two other components.

Thus far we have considered the three Cartesian components of the orbital angular momentum operator **L**, but in what follows we shall also need its component L_n along an arbitrary direction determined by the unit vector $\hat{\mathbf{n}} \equiv (n_x, n_y, n_z)$. For this purpose we use the following definition. If **V** is a vector operator which has Cartesian components V_x, V_y, V_z, the component V_n of **V** along the unit vector $\hat{\mathbf{n}}$ is

$$V_n \equiv \hat{\mathbf{n}}.\mathbf{V} = n_x V_x + n_y V_y + n_z V_z. \qquad \textbf{(6.19)}$$

In this way, one may define the three components V_u, V_v, V_w of **V** in any Cartesian frame whose axes are directed along the unit vectors $\hat{\mathbf{u}}$, $\hat{\mathbf{v}}$ and $\hat{\mathbf{w}}$ such that $\hat{\mathbf{w}} = \hat{\mathbf{u}} \times \hat{\mathbf{v}}$. In particular, the three components of **L** along $\hat{\mathbf{u}}$, $\hat{\mathbf{v}}$ and $\hat{\mathbf{w}}$ are given respectively by

$$L_u \equiv \hat{\mathbf{u}}.\mathbf{L}, \qquad L_v \equiv \hat{\mathbf{v}}.\mathbf{L}, \qquad L_w \equiv \hat{\mathbf{w}}.\mathbf{L} \qquad \textbf{(6.20)}$$

and it is readily verified (Problem 6.5) that the three commutation relations (6.9) for L_x, L_y and L_z imply analogous commutation relations for L_u, L_v and L_w, namely

$$[L_u, L_v] = \mathrm{i}\hbar L_w, \qquad [L_v, L_w] = \mathrm{i}\hbar L_u, \qquad [L_w, L_u] = \mathrm{i}\hbar L_v. \qquad \textbf{(6.21)}$$

Let us now consider an isolated system of N structureless particles. If $\mathbf{r}_i$ and $\mathbf{p}_i$ are respectively the position and momentum vectors of the ith particle, its orbital angular momentum is defined to be

$$\mathbf{L}_i = \mathbf{r}_i \times \mathbf{p}_i \tag{6.22}$$

so that in the position representation $\mathbf{L}_i$ is represented by the operator $-i\hbar(\mathbf{r}_i \times \boldsymbol{\nabla}_i)$ where $\boldsymbol{\nabla}_i$ is the gradient operator with respect to $\mathbf{r}_i$, having Cartesian components $(\partial/\partial x_i, \partial/\partial y_i, \partial/\partial z_i)$. The total orbital angular momentum $\mathbf{L}$ of the system is the vector sum of the orbital angular momenta of the N constituents:

$$\mathbf{L} = \sum_{i=1}^{N} \mathbf{L}_i. \tag{6.23}$$

Since the operators acting on different variables commute, all the components of $\mathbf{L}_i$ commute with all the components of $\mathbf{L}_k (i \neq k)$, and we have

$$\begin{aligned} \mathbf{L} \times \mathbf{L} &= (\mathbf{L}_1 + \mathbf{L}_2 + \cdots + \mathbf{L}_N) \times (\mathbf{L}_1 + \mathbf{L}_2 + \cdots + \mathbf{L}_N) \\ &= \mathbf{L}_1 \times \mathbf{L}_1 + \mathbf{L}_2 \times \mathbf{L}_2 + \cdots + \mathbf{L}_N \times \mathbf{L}_N \\ &= i\hbar(\mathbf{L}_1 + \mathbf{L}_2 + \cdots + \mathbf{L}_N) = i\hbar\mathbf{L} \end{aligned} \tag{6.24}$$

so that the components of the total orbital angular momentum satisfy the commutation relations

$$[L_x, L_y] = i\hbar L_z, \qquad [L_y, L_z] = i\hbar L_x, \qquad [L_z, L_x] = i\hbar L_y \tag{6.25}$$

as in the case of one particle.

6.2 Orbital angular momentum and spatial rotations

Considerable insight into the nature of the orbital angular momentum operator is obtained by analysing its connection with rotations in space. First of all, as in the case of the translations studied in Chapter 5, we must distinguish between the *passive* and *active* points of view in considering the effect of rotations on a physical system. According to the passive viewpoint, the coordinate axes are rotated while the system itself is untouched, while in the active viewpoint the axes are fixed and the system is rotated. The two viewpoints are equivalent in the sense that rotating the physical system about an axis or rotating the coordinate axes in the opposite direction amounts to the same thing. In what follows we shall adopt the active viewpoint and rotate the physical system.

Let us assume that we are dealing with an *isolated* system. Since space is intrinsically *isotropic* (i.e. all directions are equivalent), the physics of this system must be the same before and after a rotation is performed on it. Using the results of Section 5.10, it follows that under a rotation R the state vector Ψ describing the system must transform as

$$\Psi' = U_R \Psi \tag{6.26}$$

where U_R is a unitary operator (such that $U_R U_R^\dagger = U_R^\dagger U_R = I$). The normalisation is then preserved

$$\langle \Psi' | \Psi' \rangle = \langle U_R \Psi | U_R \Psi \rangle = \langle \Psi | U_R^\dagger U_R | \Psi \rangle = \langle \Psi | \Psi \rangle \tag{6.27}$$

and the probability amplitude $\langle \mathrm{X} | \Psi \rangle$ that the system described by Ψ will be found in a state X is also unchanged by the rotation.

Consider now a dynamical variable (observable) to which corresponds an operator A, and let A' be the transform of A under the rotation R. Since the average value of A in a state Ψ must be equal to the average value of A' in the state $\Psi' = U_R \Psi$, we must have

$$\langle \Psi' | A' | \Psi' \rangle = \langle \Psi | U_R^\dagger A' U_R | \Psi \rangle = \langle \Psi | A | \Psi \rangle \tag{6.28}$$

and hence

$$A = U_R^\dagger A' U_R \qquad \text{or} \qquad A' = U_R A U_R^\dagger . \tag{6.29}$$

In particular, the Hamiltonian H of an isolated system must be *invariant* for spatial rotations. As a result, we have

$$H' = U_R H U_R^\dagger = H \tag{6.30}$$

so that $U_R H = H U_R$ and

$$[U_R, H] = 0. \tag{6.31}$$

In order to obtain an explicit form for the unitary rotation operator U_R, we begin by considering the case of a single structureless particle, whose wave function at a given time is $\psi(\mathbf{r})$. Under a rotation R the point $\mathbf{r}$ is moved to $\mathbf{r}' = R\mathbf{r}$. Except for a phase factor, which may be chosen equal to unity[2] the wave function ψ' describing the rotated state at $\mathbf{r}'$ must be equal to the original wave function ψ at the point $\mathbf{r}$, namely

$$\psi'(\mathbf{r}') = \psi(\mathbf{r}). \tag{6.32}$$

According to (6.26) we want to relate ψ and ψ' by a unitary operator U_R such that

$$\psi'(\mathbf{r}) = U_R \psi(\mathbf{r}). \tag{6.33}$$

Now, from (6.32) we have $\psi'(\mathbf{r}') = \psi(R^{-1}\mathbf{r}')$, and since this relation is valid for all points in space, it follows that $\psi'(\mathbf{r}) = \psi(R^{-1}\mathbf{r})$. We therefore obtain for the determination of U_R the relation

$$\psi'(\mathbf{r}) = U_R \psi(\mathbf{r}) = \psi(R^{-1}\mathbf{r}) \tag{6.34}$$

which specifies the one-to-one correspondence (6.26) in the position representation.

As a first example, let us consider an *infinitesimal rotation* by an angle $\delta\alpha$ in the positive (right-handed) sense about the z-axis, and let us denote by $U_z(\delta\alpha)$ the

---

[2] This point is discussed in detail by A. Messiah (1968), Chapter 15.

corresponding rotation operator U_R. To first order in $\delta\alpha$, the coordinates (x', y', z') of $\mathbf{r}' = R\mathbf{r}$ are given by

$$\begin{aligned} x' &= x - y\delta\alpha \\ y' &= x\delta\alpha + y \\ z' &= z \end{aligned} \tag{6.35}$$

and those of $R^{-1}\mathbf{r}$ are obtained by changing $\delta\alpha$ into $-\delta\alpha$. Using (6.33), we have

$$\psi'(\mathbf{r}) = U_z(\delta\alpha)\psi(\mathbf{r}) = \psi(R^{-1}\mathbf{r}) = \psi(x + y\delta\alpha, y - x\delta\alpha, z) \tag{6.36}$$

and retaining only first-order terms in $\delta\alpha$, we find that

$$\begin{aligned} U_z(\delta\alpha)\psi(\mathbf{r}) &= \psi(x, y, z) + y\delta\alpha\frac{\partial\psi}{\partial x} - x\delta\alpha\frac{\partial\psi}{\partial y} \\ &= \left[I - \delta\alpha\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right]\psi(\mathbf{r}) \\ &= \left[I - \frac{\mathrm{i}}{\hbar}\delta\alpha L_z\right]\psi(\mathbf{r}) \end{aligned} \tag{6.37}$$

where we have used (6.3c). Hence we obtain the important relation

$$U_z(\delta\alpha) = I - \frac{\mathrm{i}}{\hbar}\delta\alpha L_z \tag{6.38}$$

between the infinitesimal rotation operator $U_z(\delta\alpha)$ and the z-component of the orbital angular momentum. Note that since $U_z(\delta\alpha)$ is an infinitesimal unitary transformation it follows from the discussion of Section 5.5 that L_z must be Hermitian.

Relations similar to (6.38) are readily derived for infinitesimal rotations about the x- and y-axes. As expected, they involve respectively the x- and y-components of $\mathbf{L}$,

$$U_x(\delta\alpha) = I - \frac{\mathrm{i}}{\hbar}\delta\alpha L_x, \qquad U_y(\delta\alpha) = I - \frac{\mathrm{i}}{\hbar}\delta\alpha L_y. \tag{6.39}$$

More generally, let us consider an infinitesimal rotation by an angle $\delta\alpha$ in the positive sense about an axis oriented along an arbitrary unit vector $\hat{\mathbf{n}}$, so that

$$\mathbf{r}' = R\mathbf{r} = \mathbf{r} + \delta\alpha\hat{\mathbf{n}} \times \mathbf{r}. \tag{6.40}$$

Denoting by $U_{\hat{\mathbf{n}}}(\delta\alpha)$ the corresponding infinitesimal rotation operator, we have

$$U_{\hat{\mathbf{n}}}(\delta\alpha)\psi(\mathbf{r}) = \psi(R^{-1}\mathbf{r}) = \psi(\mathbf{r} - \delta\alpha\hat{\mathbf{n}} \times \mathbf{r}). \tag{6.41}$$

Keeping terms to first order in $\delta\alpha$, we find that

$$\begin{aligned} U_{\hat{\mathbf{n}}}(\delta\alpha)\psi(\mathbf{r}) &= \psi(\mathbf{r}) - (\delta\alpha\hat{\mathbf{n}} \times \mathbf{r}).\nabla\psi(\mathbf{r}) \\ &= [I - \delta\alpha\hat{\mathbf{n}}.(\mathbf{r} \times \nabla)]\psi(\mathbf{r}) \\ &= \left[I - \frac{\mathrm{i}}{\hbar}\delta\alpha\hat{\mathbf{n}}.\mathbf{L}\right]\psi(\mathbf{r}) \end{aligned} \tag{6.42}$$

where we have used the definition (6.4) of the operator **L**, and we recall that $\hat{\mathbf{n}}.\mathbf{L}$ is the component of **L** along $\hat{\mathbf{n}}$. Hence

$$U_{\hat{\mathbf{n}}}(\delta\alpha) = I - \frac{\mathrm{i}}{\hbar}\delta\alpha\hat{\mathbf{n}}.\mathbf{L} \tag{6.43}$$

so that the orbital angular momentum operator **L** may be called the *generator of infinitesimal rotations.*

Except when they are performed about the same axis, rotations do not in general commute. Looking at (6.43), we therefore expect that the commutation relations (6.9) obeyed by the components of the orbital angular momentum operator could be re-derived by considering two successive infinitesimal rotations about different coordinate axes in opposite orders. To see this, let us perform an infinitesimal rotation R_x of angle $\delta\alpha$ about the x-axis, followed by an infinitesimal rotation R_y of angle $\delta\alpha$ about the y-axis. Let the corresponding infinitesimal rotation operators be $U_x(\delta\alpha)$ and $U_y(\delta\alpha)$, respectively. According to (6.41) we then have (remembering that the order of the operations reads from right to left),

$$\begin{aligned} U_y(\delta\alpha)U_x(\delta\alpha)\psi(\mathbf{r}) &= \psi[(R_yR_x)^{-1}\mathbf{r}] \\ &= \psi[R_x^{-1}R_y^{-1}\mathbf{r}] \\ &= \psi[R_x^{-1}(\mathbf{r} - \delta\alpha\hat{\mathbf{y}} \times \mathbf{r})] \\ &= \psi[\mathbf{r} - \delta\alpha\hat{\mathbf{y}} \times \mathbf{r} - \delta\alpha\hat{\mathbf{x}} \times (\mathbf{r} - \delta\alpha\hat{\mathbf{y}} \times \mathbf{r})] \end{aligned} \tag{6.44}$$

where $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ are unit vectors about the x- and y-axis, respectively. Similarly, if we perform first the infinitesimal rotation R_y about the y-axis, and then the infinitesimal rotation R_x about the x-axis, we obtain

$$U_x(\delta\alpha)U_y(\delta\alpha)\psi(\mathbf{r}) = \psi[\mathbf{r} - \delta\alpha\hat{\mathbf{x}} \times \mathbf{r} - \delta\alpha\hat{\mathbf{y}} \times (\mathbf{r} - \delta\alpha\hat{\mathbf{x}} \times \mathbf{r})]. \tag{6.45}$$

Subtracting (6.44) from (6.45), we find that the commutator of the two operators $U_x(\delta\alpha)$ and $U_y(\delta\alpha)$, acting on $\psi(\mathbf{r})$, gives

$$\begin{aligned} [U_x(\delta\alpha), U_y(\delta\alpha)]\psi(\mathbf{r}) &= \psi[\mathbf{r} - \delta\alpha(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \times \mathbf{r} + (\delta\alpha)^2\hat{\mathbf{y}} \times (\hat{\mathbf{x}} \times \mathbf{r})] \\ &\quad -\psi[\mathbf{r} - \delta\alpha(\hat{\mathbf{y}} + \hat{\mathbf{x}}) \times \mathbf{r} + (\delta\alpha)^2\hat{\mathbf{x}} \times (\hat{\mathbf{y}} \times \mathbf{r})] \\ &= (\delta\alpha)^2[\hat{\mathbf{y}} \times (\hat{\mathbf{x}} \times \mathbf{r}) - \hat{\mathbf{x}} \times (\hat{\mathbf{y}} \times \mathbf{r})].\boldsymbol{\nabla}\psi(\mathbf{r}) \\ &= (\delta\alpha)^2[y\hat{\mathbf{x}} - x\hat{\mathbf{y}}].\boldsymbol{\nabla}\psi(\mathbf{r} \\ &= -(\delta\alpha)^2(\hat{\mathbf{z}} \times \mathbf{r}).\boldsymbol{\nabla}\psi(\mathbf{r}) \\ &= -(\delta\alpha)^2[\hat{\mathbf{z}}.(\mathbf{r} \times \boldsymbol{\nabla})]\psi(\mathbf{r}) \\ &= -(\delta\alpha)^2\frac{\mathrm{i}}{\hbar}L_z\psi(\mathbf{r}) \end{aligned} \tag{6.46}$$

where we have kept terms to leading order $(\delta\alpha)^2$ on the right-hand side. On the other hand, it follows from (6.39) that

$$[U_x(\delta\alpha), U_y(\delta\alpha)]\psi(\mathbf{r}) = \left[\left(I - \frac{\mathrm{i}}{\hbar}\delta\alpha L_x\right)\left(I - \frac{\mathrm{i}}{\hbar}\delta\alpha L_y\right) - \left(I - \frac{\mathrm{i}}{\hbar}\delta\alpha L_y\right)\left(I - \frac{\mathrm{i}}{\hbar}\delta\alpha L_x\right)\right]\psi(\mathbf{r})$$
$$= -\frac{(\delta\alpha)^2}{\hbar^2}[L_x, L_y]\psi(\mathbf{r}) \qquad \textbf{(6.47)}$$

and therefore, upon comparison of (6.46) and (6.47) we find that $[L_x, L_y] = \mathrm{i}\hbar L_z$, which is the commutation relation (6.9a). The commutation relations (6.9b) and (6.9c) may clearly be obtained in a similar way. The non-commutativity of different components of the orbital angular momentum operator **L** is therefore a direct consequence of the non-commutativity of spatial rotations about different axes. Notice that, to the extend that $(\delta\alpha)^2$ can be neglected, infinitesimal rotations do, in fact, commute.

Let us now consider rotations through *finite* angles. Any such finite rotation about an axis oriented along an arbitrary unit vector $\hat{\mathbf{n}}$ can be built up by a succession of infinitesimal rotations about that axis. If $U_{\hat{\mathbf{n}}}(\alpha)$ is the unitary operator corresponding to a finite rotation of angle α, we may therefore write

$$U_{\hat{\mathbf{n}}}(\alpha + \delta\alpha) = U_{\hat{\mathbf{n}}}(\delta\alpha)U_{\hat{\mathbf{n}}}(\alpha)$$
$$= \left(I - \frac{\mathrm{i}}{\hbar}\delta\alpha\hat{\mathbf{n}}.\mathbf{L}\right)U_{\hat{\mathbf{n}}}(\alpha) \qquad \textbf{(6.48)}$$

where we have used (6.43). Thus

$$\mathrm{d}U_{\hat{\mathbf{n}}}(\alpha) = U_{\hat{\mathbf{n}}}(\alpha + \delta\alpha) - U_{\hat{\mathbf{n}}}(\alpha) = \left(-\frac{\mathrm{i}}{\hbar}\delta\alpha\hat{\mathbf{n}}.\mathbf{L}\right)U_{\hat{\mathbf{n}}}(\alpha) \qquad \textbf{(6.49)}$$

so that

$$\frac{\mathrm{d}U_{\hat{\mathbf{n}}}(\alpha)}{\mathrm{d}\alpha} = \left(-\frac{\mathrm{i}}{\hbar}\hat{\mathbf{n}}.\mathbf{L}\right)U_{\hat{\mathbf{n}}}(\alpha) \qquad \textbf{(6.50)}$$

and upon integration, we find that

$$U_{\hat{\mathbf{n}}}(\alpha) = \exp\left(-\frac{\mathrm{i}}{\hbar}\alpha\hat{\mathbf{n}}.\mathbf{L}\right) \qquad \textbf{(6.51)}$$

where the meaning of the operator $\exp(-\mathrm{i}\alpha\hat{\mathbf{n}}.\mathbf{L}/\hbar)$ is (see (5.38))

$$\exp\left(-\frac{\mathrm{i}}{\hbar}\alpha\hat{\mathbf{n}}.\mathbf{L}\right) = \sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{\mathrm{i}\alpha\hat{\mathbf{n}}.\mathbf{L}}{\hbar}\right)^n. \qquad \textbf{(6.52)}$$

The above considerations are readily extended to an isolated system of N structureless particles. In particular, replacing the vector coordinate $\mathbf{r}$ by the set of vector coordinates $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ of the N particles, one finds (Problem 6.6) that the unitary rotation operators U_R are still given by equations (6.43) (for infinitesimal rotations) and (6.51) (for finite rotations), where **L** now denotes the *total* orbital angular momentum (6.23).

Let us now return to the important equation (6.31), which expresses the invariance of the Hamiltonian H of an isolated system for spatial rotations. Because any rotation can be expressed as a product of infinitesimal rotations, and since the total orbital angular momentum is the generator of infinitesimal rotations (see (6.43)), it follows that the invariance of H under rotations implies that, for an isolated system of structureless particles,

$$[\mathbf{L}, H] = 0 \tag{6.53}$$

so that the *total orbital angular momentum is conserved.* Conversely, if the Hamiltonian H of a system of structureless particles commutes with the total orbital angular momentum operator **L**, then H is invariant under rotations. It also follows from (6.53) and (6.14) that the operators H, $\mathbf{L}^2$ and L_z mutually commute. Thus, the eigenfunctions of H can be found among those common to $\mathbf{L}^2$ and L_z, so that the eigenvalue problem of H considerably simplifies.

6.3 The eigenvalues and eigenfunctions of $\mathbf{L}^2$ and L_z

Let us consider a single particle, for which the orbital angular momentum operator **L** is given by (6.4). In Section 6.1 we learned that the operator $\mathbf{L}^2$ commutes with any component of **L**, but that two components of **L** cannot accurately be known simultaneously. Thus simultaneous eigenfunction of $\mathbf{L}^2$ and of one of its components can be found, and we shall obtain them in this section, using spherical polar coordinates. Since we have seen in Section 6.1 that the components of **L** as well as $\mathbf{L}^2$ are purely angular operators, we only need to consider the polar angles (θ, ϕ). Moreover, because the expression (6.16c) for L_z is simpler than those for L_x and L_y in spherical polar coordinates, it is convenient to look for simultaneous eigenfunctions of $\mathbf{L}^2$ and of the component L_z.

Eigenfunctions and eigenvalues of L_z

We begin by finding the eigenvalues and eigenfunctions of the operator L_z alone. Denoting the eigenvalues of L_z by $m\hbar$, and the corresponding eigenfunctions by $\Phi_m(\phi)$, we have

$$L_z \Phi_m(\phi) = m\hbar \Phi_m(\phi) \tag{6.54}$$

or

$$-\mathrm{i}\frac{\partial}{\partial \phi}\Phi_m(\phi) = m\Phi_m(\phi) \tag{6.55}$$

where we have used (6.16c). The solutions of this equation are

$$\Phi_m(\phi) = (2\pi)^{-1/2}\mathrm{e}^{\mathrm{i}m\phi} \tag{6.56}$$

where $(2\pi)^{-1/2}$ is a normalisation constant. The equation (6.55) is then satisfied for any value of m. However, for the wave function to be *single-valued*[3], we must require that $\Phi_m(2\pi) = \Phi_m(0)$, or

$$e^{i2\pi m} = 1. \tag{6.57}$$

This relation is satisfied if m is restricted to positive or negative integers, or zero. Hence the eigenvalues of the operator L_z are equal to $m\hbar$, where

$$m = 0, \pm 1, \pm 2, \ldots \tag{6.58}$$

and a measurement of the z-component of the orbital angular momentum can only yield the values 0, $\pm\hbar$, $\pm 2\hbar$, ... Because the z-axis can be chosen along an arbitrary direction, we see that the component of the orbital angular momentum about any axis is quantised. The quantum number m is usually called the *magnetic quantum number*, a name which, as we shall see later, is justified by its prominent role in the study of charged particles in magnetic fields.

The eigenfunctions $\Phi_m(\phi)$ given by (6.56) are *orthonormal* over the range $0 \leqslant \phi \leqslant 2\pi$,

$$\int_0^{2\pi} \Phi_{m'}^*(\phi)\Phi_m(\phi)d\phi = \delta_{mm'} \tag{6.59}$$

which means that they are normalised to unity and that eigenfunctions belonging to different eigenvalues ($m \neq m'$) are orthogonal. The eigenfunctions (6.56) also form a *complete set*, so that any function $f(\phi)$ defined on the interval $0 \leqslant \phi \leqslant 2\pi$ can be expanded as

$$f(\phi) = \sum_{m=-\infty}^{+\infty} a_m \Phi_m(\phi). \tag{6.60}$$

The coefficients a_m are found by multiplying both sides of (6.60) by $\Phi_{m'}^*(\phi)$, integrating over ϕ from 0 to 2π and using (6.59). This gives

$$a_m = \int_0^{2\pi} \Phi_m^*(\phi) f(\phi)d\phi. \tag{6.61}$$

Inserting this expression of a_m (in which we change the name of the integration variable from ϕ to ϕ') into (6.60) and using the property (A.26) of the delta function, we see that the eigenfunctions $\Phi_m(\phi)$ satisfy the *closure relation*

$$\sum_{m=-\infty}^{+\infty} \Phi_m^*(\phi')\Phi_m(\phi) = \delta(\phi - \phi'). \tag{6.62}$$

---

[3] It should be stressed that the requirement for single-valuedness of the wave function only applies to its spatial part. As we shall see in Section 6.9, certain wave functions depending on internal degrees of freedom may be double-valued; in particular, this is the case for spin wave functions corresponding to particles having half-odd integer spin (see (6.268)).

Simultaneous eigenfunctions of $\mathbf{L}^2$ and L_z

We now turn to the problem of obtaining the common eigenfunctions $Y_{lm}(\theta, \phi)$ of the operators $\mathbf{L}^2$ and L_z, satisfying the two eigenvalue equations

$$\mathbf{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi) \tag{6.63}$$

and

$$L_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi) \tag{6.64}$$

where the eigenvalues of $\mathbf{L}^2$ have been written as $l(l+1)\hbar^2$. From our study of the eigenfunctions of L_z, we see that equation (6.64) implies that the functions $Y_{lm}(\theta, \phi)$ must be of the form

$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi) \tag{6.65}$$

where the functions $\Phi_m(\phi)$ are given by (6.56), with $m = 0, \pm 1, \pm 2, \ldots$

Let us now turn to equation (6.63). Using the expression (6.17) of $\mathbf{L}^2$ in spherical polar coordinates, we have

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y_{lm}(\theta, \phi) = -l(l+1)Y_{lm}(\theta, \phi). \tag{6.66}$$

Substituting (6.65) into (6.66) and making use of (6.56), we obtain for $\Theta_{lm}(\theta)$ the differential equation

$$\left[\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\right) + \left\{l(l+1) - \frac{m^2}{\sin^2\theta}\right\}\right]\Theta_{lm}(\theta) = 0. \tag{6.67}$$

Our task is to find physically acceptable solutions of this equation over the range $0 \leqslant \theta \leqslant \pi$. For this purpose, it is convenient to introduce the new variable $w = \cos\theta$ and the new function

$$F_{lm}(w) = \Theta_{lm}(\theta) \tag{6.68}$$

so that (6.67) reads

$$\left[(1-w^2)\frac{\mathrm{d}^2}{\mathrm{d}w^2} - 2w\frac{\mathrm{d}}{\mathrm{d}w} + l(l+1) - \frac{m^2}{1-w^2}\right]F_{lm}(w) = 0 \tag{6.69}$$

with $-1 \leqslant w \leqslant 1$.

The case $m = 0$

It is easiest to start with the case $m = 0$, for which (6.69) reduces to

$$\left[(1-w^2)\frac{\mathrm{d}^2}{\mathrm{d}w^2} - 2w\frac{\mathrm{d}}{\mathrm{d}w} + l(l+1)\right]F_{l0}(w) = 0. \tag{6.70}$$

This differential equation is known as the *Legendre equation*. Since the point $w = 0$ is an ordinary (non-singular) point of this equation, we can try a power series solution of the form

$$F_{l0}(w) = \sum_{k=0}^{\infty} c_k w^k. \tag{6.71}$$

Inserting (6.71) into (6.70) and setting $\lambda = l(l+1)$, we find that

$$\sum_{k=0}^{\infty} [k(k-1)c_k w^{k-2} - k(k-1)c_k w^k - 2kc_k w^k + \lambda c_k w^k] = 0 \tag{6.72}$$

or

$$\sum_{k=0}^{\infty} [(k+1)(k+2)c_{k+2} + \{\lambda - k(k+1)\}c_k]w^k = 0. \tag{6.73}$$

This equation will be satisfied if the coefficient of each power of w vanishes. We therefore obtain for the coefficients c_k the *recursion relation*

$$c_{k+2} = \frac{k(k+1) - \lambda}{(k+1)(k+2)} c_k \tag{6.74}$$

so that the general power series solution of (6.70) is given by

$$\begin{aligned} F_{l0}(w) = {} & c_0\left[1 - \frac{\lambda}{2}w^2 - \frac{2.3 - \lambda}{3.4}\frac{\lambda}{2}w^4 + \cdots\right] \\ & + c_1\left[w + \frac{1.2 - \lambda}{2.3}w^3 + \frac{3.4 - \lambda}{4.5}\frac{1.2 - \lambda}{2.3}w^5 + \cdots\right] \end{aligned} \tag{6.75}$$

where c_0 and c_1 are arbitrary constants. Note that the first power series, which multiplies c_0 on the right of (6.75), contains only *even* powers of w, while the second power series (multiplying c_1) contains only *odd* powers of w. The occurrence of particular solutions which are either even functions of w (when $c_1 = 0$) or odd functions of w (when $c_0 = 0$) is to be expected, since equation (6.70) is invariant when $-w$ is substituted for w.

We see from (6.74) that if the series on the right of (6.75) do not terminate at some fixed values of k, then for large k we have $c_{k+2}/c_k \simeq k/(k+2)$, a behaviour which is similar to the divergent series Σk^{-1}, where k is even or odd. As a result, both series on the right of (6.75) diverge for $w^2 = 1$, i.e. for $w = \pm 1$, and in consequence do not yield an acceptable wave function[4]. Thus, in order to be satisfactory, the expression (6.75) for $F_{l0}(w)$ must contain only a finite number of terms. Using (6.74) and remembering that $\lambda = l(l+1)$, we see that by choosing l to be a positive integer to zero,

$$l = 0, 1, 2, \ldots \tag{6.76}$$

---

[4] This is not surprising, since $w = \pm 1$ are (regular) *singular* points of the Legendre equation (6.70). See, for example, Mathews and Walker (1973).

either the even or odd series in (6.75) can be terminated at the finite value $k = l$. The other series can be made to vanish by choosing $c_1 = 0$ (for even l) or $c_0 = 0$ (for odd l). The quantum number l, whose allowed values are given by (6.76), is called the *orbital angular momentum quantum number*.

The physically acceptable solutions of the Legendre equation (6.70), which exist only for $l = 0, 1, 2, \ldots$, are thus polynomials of degree l, called *Legendre polynomials*, and denoted by $P_l(w)$. From the above discussion it is clear that they are uniquely defined, apart from an arbitrary multiplicative constant. By convention this constant is chosen so that

$$P_l(1) = 1. \qquad \textbf{(6.77)}$$

Since the Legendre polynomial $P_l(w)$ is in even or odd powers of w, depending on whether l is even or odd, we have

$$P_l(-w) = (-1)^l P_l(w). \qquad \textbf{(6.78)}$$

An equivalent definition of the Legendre polynomials is

$$P_l(w) = (2)^{-l}(l!)^{-1}\frac{\mathrm{d}^l}{\mathrm{d}w^l}(w^2 - 1)^l \qquad \textbf{(6.79)}$$

which is known as the Rodrigues formula. It is readily verified that the Legendre polynomials given by (6.79) satisfy the Legendre equation (6.70) and the relation (6.77). The Rodrigues formula can be used to prove various important properties of the Legendre polynomials. In particular, by performing integrations by parts, one finds that (Problem 6.7)

$$\int_{-1}^{+1} P_l(w)P_{l'}(w)\mathrm{d}w = \frac{2}{2l+1}\delta_{ll'} \qquad \textbf{(6.80)}$$

so that the Legendre polynomials are orthogonal for $l \neq l'$ over the range $-1 \leqslant w \leqslant 1$, but they are not normalised to unity. Of course, physically acceptable solutions of the Legendre equation (6.70) which are orthogonal for $l \neq l'$ and normalised to unity are easily constructed. From (6.80) we see that apart from a phase factor $\exp(\mathrm{i}\alpha)$ of modulus one they are given by

$$F_{l0}(w) = \left(\frac{2l+1}{2}\right)^{1/2} P_l(w). \qquad \textbf{(6.81)}$$

Another equivalent definition of the Legendre polynomials may be given in terms of a *generating function*, by

$$\begin{aligned} T(w,s) &= (1 - 2ws + s^2)^{-1/2} \\ &= \sum_{l=0}^{\infty} P_l(w)s^l, \qquad |s| < 1. \end{aligned} \qquad \textbf{(6.82)}$$

By differentiating this generating function with respect to w and s one can show (Problem 6.8) that the Legendre polynomials satisfy the recurrence relations

$$(l+1)P_{l+1}(w) = (2l+1)wP_l(w) - lP_{l-1}(w) \tag{6.83a}$$

and

$$(1-w^2)\frac{\mathrm{d}P_l}{\mathrm{d}w} = -lwP_l(w) + lP_{l-1}(w). \tag{6.83b}$$

The lowest-order differential equation for P_l which can be constructed from these two recurrence relations is then seen to be the Legendre equation (6.70). Note that from (6.82) we immediately have $P_l(1) = 1$.

The Legendre polynomials $P_l(w)$ form a *complete set* on the interval $-1 \leqslant w \leqslant 1$, so that any function $f(w)$, defined on this interval, can be expanded as

$$f(w) = \sum_{l=0}^{\infty} a_l P_l(w) \tag{6.84}$$

and by using (6.80) we have

$$a_l = \frac{2l+1}{2}\int_{-1}^{+1} P_l(w) f(w)\mathrm{d}w. \tag{6.85}$$

Inserting this expression of a_l into (6.84) and using (6.80), we also find that the Legendre polynomials satisfy the *closure relation*

$$\frac{1}{2}\sum_{l=0}^{\infty}(2l+1)P_l(w')P_l(w) = \delta(w-w'). \tag{6.86}$$

The first few Legendre polynomials are

$$\begin{aligned}
P_0(w) &= 1\\
P_1(w) &= w\\
P_2(w) &= \tfrac{1}{2}(3w^2-1)\\
P_3(w) &= \tfrac{1}{2}(5w^3-3w)\\
P_4(w) &= \tfrac{1}{8}(35w^4-30w^2+3)\\
P_5(w) &= \tfrac{1}{8}(63w^5-70w^3+15w).
\end{aligned} \tag{6.87}$$

The general case

Having solved the Legendre equation (6.70) we shall now obtain the physically acceptable solutions of equation (6.69), for which m is not necessarily equal to zero. Since (6.69) is independent of the sign of m, the solutions of this equation can be characterised by l and $|m|$. Let us define the *associated Legendre function* $P_l^{|m|}(w)$ of degree $l (l = 0, 1, 2, \dots)$ and order $|m| \leqslant l$ by the relation

$$P_l^{|m|}(w) = (1-w^2)^{|m|/2}\frac{\mathrm{d}^{|m|}}{\mathrm{d}w^{|m|}}P_l(w), \qquad |m| = 0, 1, 2, \dots \tag{6.88}$$

We note that for $m = 0$ we have $P_l^0(w) = P_l(w)$. Upon differentiating $|m|$ times the Legendre equation (6.70) satisfied by $P_l(w)$, we obtain

$$\left[(1-w^2)\frac{\mathrm{d}^{|m|+2}}{\mathrm{d}w^{|m|+2}} - 2(|m|+1)w\frac{\mathrm{d}^{|m|+1}}{\mathrm{d}w^{|m|+1}} + \{l(l+1) - |m|(|m|+1)\}\frac{\mathrm{d}^{|m|}}{\mathrm{d}w^{|m|}}\right]P_l(w) = 0. \tag{6.89}$$

Using (6.88) we then find that $P_l^{|m|}(w)$ satisfies the equation

$$\left[(1-w^2)\frac{\mathrm{d}^2}{\mathrm{d}w^2} - 2w\frac{\mathrm{d}}{\mathrm{d}w} + l(l+1) - \frac{m^2}{1-w^2}\right]P_l^{|m|}(w) = 0 \tag{6.90}$$

which is the same as (6.69). Apart from an arbitrary multiplicative constant, the associated Legendre functions $P_l^{|m|}(w)$ are the only physically acceptable solutions of (6.69). We emphasise that the orbital angular momentum quantum number l is restricted to one of the values $l = 0, 1, 2, \ldots$ Regarding the magnetic quantum number m, we note from (6.88) that since $P_l(w)$ is a polynomial of degree, l, its $|m|$th derivative, and hence $P_l^{|m|}(w)$, will vanish if $|m| > l$. Hence for a fixed value of l there are $(2l+1)$ allowed values of m given by

$$m = -l, -l+1, \ldots, l. \tag{6.91}$$

This result can readily be understood as follows. Since $\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2$, the expectation value of $\mathbf{L}^2$ in a given state Ψ is

$$\langle \mathbf{L}^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle. \tag{6.92}$$

Now, since L_x and L_y are Hermitian, $\langle L_x^2 \rangle \geqslant 0$ and $\langle L_y^2 \rangle \geqslant 0$, so that

$$\langle \mathbf{L}^2 \rangle \geqslant \langle L_z^2 \rangle. \tag{6.93}$$

Taking Ψ to be such that its angular part is an eigenfunction $Y_{lm}(\theta, \phi)$ common to $\mathbf{L}^2$ and L_z, we have from (6.63), (6.64) and (6.93)

$$l(l+1) \geqslant m^2 \tag{6.94}$$

and as l and m can only take the values $l = 0, 1, 2, \ldots$, and $m = 0, \pm 1, \pm 2, \ldots$, we see that m is restricted for a given l to the $(2l+1)$ values given by (6.91).

We note from (6.88) that the associated Legendre function $P_l^{|m|}(w)$ is the product of the quantity $(1-w^2)^{|m|/2}$ and of a polynomial of degree $l - |m|$. Using (6.78) and (6.88) it is straightforward to show that (Problem 6.9)

$$P_l^{|m|}(-w) = (-1)^{l-|m|}P_l^{|m|}(w). \tag{6.95}$$

A generating function for the $P_l^{|m|}$ can be obtained by differentiating (6.82) $|m|$ times with respect to w and multiplying by $(1-w^2)^{|m|/2}$ as required by (6.88). We obtain in this way

$$T_{|m|}(w,s) = \frac{(2|m|)!(1-w^2)^{|m|/2}s^{|m|}}{2^{|m|}(|m|)!(1-2ws+s^2)^{|m|+1/2}}$$
$$= \sum_{l=|m|}^{\infty} P_l^{|m|}(w)s^l, \qquad |s| < 1. \tag{6.96}$$

We also remark that the functions $P_l^{|m|}$ satisfy the recurrence relations (Problem 6.10)

$$(2l+1)wP_l^{|m|}(w) = (l-|m|+1)P_{l+1}^{|m|}(w) + (l+|m|)P_{l-1}^{|m|}(w) \tag{6.97a}$$

$$(2l+1)(1-w^2)^{1/2}P_l^{|m|-1}(w) = P_{l+1}^{|m|}(w) - P_{l-1}^{|m|}(w) \tag{6.97b}$$

$$\begin{aligned}(1-w^2)\frac{\mathrm{d}P_l^{|m|}}{\mathrm{d}w} &= -lwP_l^{|m|}(w) + (l+|m|)P_{l-1}^{|m|}(w)\\ &= (l+1)wP_l^{|m|}(w) - (l+1-|m|)P_{l+1}^{|m|}(w)\end{aligned} \tag{6.97c}$$

$$\begin{aligned}(1-w^2)\frac{\mathrm{d}P_l^{|m|}}{\mathrm{d}w} &= (1-w^2)^{1/2}P_l^{|m|+1}(w) - |m|wP_l^{|m|}(w)\\ &= -(1-w^2)^{1/2}(l+|m|)(l-|m|+1)P_l^{|m|-1}(w) + |m|wP_l^{|m|}(w)\end{aligned} \tag{6.97d}$$

and the orthogonality relations

$$\int_{-1}^{+1} P_l^{|m|}(w)P_{l'}^{|m|}(w)\mathrm{d}w = \frac{2}{2l+1}\frac{(l+|m|)!}{(l-|m|)!}\delta_{ll'}. \tag{6.98}$$

Finally, it can be shown that the $P_l^{|m|}$ form a complete set.

The first few associated Legendre functions are given explicitly by

$$\begin{aligned}P_1^1(w) &= (1-w^2)^{1/2}\\ P_2^1(w) &= 3(1-w^2)^{1/2}w\\ P_2^2(w) &= 3(1-w^2)\\ P_3^1(w) &= \tfrac{3}{2}(1-w^2)^{1/2}(5w^2-1)\\ P_3^2(w) &= 15w(1-w^2)\\ P_3^3(w) &= 15(1-w^2)^{3/2}\end{aligned} \tag{6.99}$$

It should be noted from (6.98) that the functions $P_l^{|m|}(w)$ are not normalised to unity. However, by multiplying $P_l^{|m|}(w)$ by an appropriate normalisation factor, physically acceptable solutions $F_{lm}(w)$ of equation (6.69) which are normalised to unity can be determined to within an arbitrary phase factor of modulus one. We shall not quote these, but instead we write down the corresponding physically admissible solutions $\Theta_{lm}(\theta)$ of equation (6.67), normalised so that

$$\int_0^\pi \Theta_{l'm}^*(\theta)\Theta_{lm}(\theta)\sin\theta d\theta = \delta_{ll'}. \tag{6.100}$$

These functions are given in terms of the associated Legendre functions by

$$\begin{aligned}\Theta_{lm}(\theta) &= (-1)^m\left[\frac{(2l+1)(l-m)!}{2(l+m)!}\right]^{1/2} P_l^m(\cos\theta), \qquad m \geqslant 0\\ &= (-1)^m\Theta_{l|m|}(\theta), \qquad m<0\end{aligned} \tag{6.101}$$

where the choice of the phase factor is a conventional one.

Spherical harmonics

The eigenfunctions $Y_{lm}(\theta,\phi)$, common to the operators $\mathbf{L}^2$ and L_z (see (6.63) and (6.64)) and normalised to unity on the unit sphere, are called *spherical harmonics*. Using (6.65), (6.56) and (6.101), we see that they are given for non-negative values of m by

$$Y_{lm}(\theta,\phi) = (-1)^m\left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right]^{1/2} P_l^m(\cos\theta)\mathrm{e}^{\mathrm{i}m\phi}, \qquad m \geqslant 0 \tag{6.102a}$$

and for negative values of m we have

$$Y_{lm}(\theta,\phi) = (-1)^m Y_{l,-m}^*(\theta,\phi) \tag{6.102b}$$

where the phase convention adopted here is a frequently used one. We recall that the quantum number l can only take the values $l = 0, 1, 2, \dots$, (see (6.76)) and that for a fixed value of l the allowed values of m are $m = -l, -l+1, \dots, l$ (see (6.91)).

From (6.65), (6.56) and (6.101) we also note that the spherical harmonics satisfy the *orthonormality relations*

$$\begin{aligned}\int Y_{l'm'}^*(\theta,\phi)Y_{lm}(\theta,\phi)\mathrm{d}\Omega &= \int_0^{2\pi}\mathrm{d}\phi\int_0^\pi \mathrm{d}\theta\sin\theta Y_{l'm'}^*(\theta,\phi)Y_{lm}(\theta,\phi)\\ &= \delta_{ll'}\delta_{mm'}\end{aligned} \tag{6.103}$$

where we have written $\mathrm{d}\Omega \equiv \sin\theta\mathrm{d}\theta\mathrm{d}\phi$ and the symbol $\int \mathrm{d}\Omega$ means that we integrate over the full range of the angular variables (θ,ϕ), namely

$$\int \mathrm{d}\Omega \equiv \int_0^{2\pi}\mathrm{d}\phi\int_0^\pi \mathrm{d}\theta\sin\theta. \tag{6.104}$$

It can also be proved that the Y_{lm} form a *complete set*, so that a function $f(\theta,\phi)$ can be expanded in terms of them as

$$f(\theta,\phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l} a_{lm}Y_{lm}(\theta,\phi) \tag{6.105}$$

By using the orthonormality relation (6.103), the coefficients of the expansion are seen to be given by

$$a_{lm} = \int Y_{lm}^*(\theta, \phi) f(\theta, \phi) \mathrm{d}\Omega. \tag{6.106}$$

Substituting (6.106) into (6.105) and using (6.103) we obtain the *closure relation*

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} Y_{lm}^*(\theta', \phi') Y_{lm}(\theta, \phi) = \delta(\Omega - \Omega'),$$

$$\delta(\Omega - \Omega') = \frac{\delta(\theta - \theta')\delta(\phi - \phi')}{\sin\theta} \tag{6.107}$$

It is clear from (6.102) and our study of associated Legendre functions that $Y_{lm}(\theta, \phi)$ is the product of $\exp(im\phi)\sin^{|m|}\theta$ times a polynomial in $\cos\theta$ of degree $(l - |m|)$. In particular, for $m = 0$ and $m = l$, we have, respectively,

$$Y_{l,0}(\theta) = \left(\frac{2l+1}{4\pi}\right)^{1/2} P_l(\cos\theta) \tag{6.108}$$

and

$$Y_{l,l}(\theta, \phi) = (-1)^l \left[\frac{2l+1}{4\pi} \frac{(2l)!}{2^{2l}(l!)^2}\right]^{1/2} \sin^l\theta \mathrm{e}^{il\phi}. \tag{6.109}$$

The behaviour of the spherical harmonics under the *parity* operation $\mathbf{r} \to -\mathbf{r}$ is of special interest. Under this operation the spherical polar coordinates (r, θ, ϕ) transform as

$$r \to r, \qquad \theta \to \pi - \theta, \qquad \phi \to \phi + \pi. \tag{6.110}$$

Thus, if $\mathcal{P}$ is the parity operator defined in (5.336), we have

$$\mathcal{P}[Y_{lm}(\theta, \phi)] = Y_{lm}(\pi - \theta, \phi + \pi). \tag{6.111}$$

Now, from (6.95) we have

$$P_l^{|m|}[\cos(\pi - \theta)] = P_l^{|m|}(-\cos\theta) = (-1)^{l-|m|} P_l^{|m|}(\cos\theta) \tag{6.112}$$

while from (6.56) we deduce that

$$\Phi_m(\phi + \pi) = (-1)^m \Phi_m(\phi). \tag{6.113}$$

Hence

$$Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi) \tag{6.114}$$

so that Y_{lm} has the parity of l (even for even l, odd for odd l).

Following a notation originally introduced in spectroscopy, it is customary to designate the states corresponding to the values $l = 0, 1, 2, 3, 4, 5, \ldots$, of the orbital angular momentum quantum number l of a particle by the symbols s, p, d, f, g, h, ... When there is more than one particle, capital letters S, P, D, F, G, H, ..., are used for the total orbital angular momentum. The first few spherical harmonics, corresponding

Table 6.1 Low-order spherical harmonics.

l	*m*	*Spherical harmonic* $Y_{lm}(\theta, \phi)$
0	0	$Y_{0,0} = \dfrac{1}{(4\pi)^{1/2}}$
1	0	$Y_{1,0} = \left(\dfrac{3}{4\pi}\right)^{1/2} \cos\theta$
	±1	$Y_{1,\pm1} = \mp\left(\dfrac{3}{8\pi}\right)^{1/2} \sin\theta \mathrm{e}^{\pm\mathrm{i}\phi}$
2	0	$Y_{2,0} = \left(\dfrac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$
	±1	$Y_{2,\pm1} = \mp\left(\dfrac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta \mathrm{e}^{\pm\mathrm{i}\phi}$
	±2	$Y_{2,\pm2} = \left(\dfrac{15}{32\pi}\right)^{1/2} \sin^2\theta \mathrm{e}^{\pm2\mathrm{i}\phi}$
3	0	$Y_{3,0} = \left(\dfrac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
	±1	$Y_{3,\pm1} = \mp\left(\dfrac{21}{64\pi}\right)^{1/2} \sin\theta(5\cos^2\theta - 1)\mathrm{e}^{\pm\mathrm{i}\phi}$
	±2	$Y_{3,\pm2} = \left(\dfrac{105}{32\pi}\right)^{1/2} \sin^2\theta \cos\theta \mathrm{e}^{\pm2\mathrm{i}\phi}$
	±3	$Y_{3,\pm3} = \mp\left(\dfrac{35}{64\pi}\right)^{1/2} \sin^3\theta \mathrm{e}^{\pm3\mathrm{i}\phi}$

to the s, p, d and f states are listed in Table 6.1, and polar plots of the corresponding probability distributions

$$|Y_{lm}(\theta, \phi)|^2 = (2\pi)^{-1}|\Theta_{lm}(\theta)|^2 \tag{6.115}$$

are shown in Fig. 6.2.

It is also interesting to study the effect of the operators L_x and L_y on Y_{lm}. For this purpose, it is convenient to introduce the two operators

$$L_+ = L_x + \mathrm{i}L_y, \qquad L_- = L_x - \mathrm{i}L_y. \tag{6.116}$$

We note that these operators are not Hermitian, but are mutually adjoint, since $L_+^\dagger = L_x - \mathrm{i}L_y = L_-$ and $L_-^\dagger = L_x + \mathrm{i}L_y = L_+$. Because L_x and L_y commute with $\mathbf{L}^2$, we have

$$[\mathbf{L}^2, L_\pm] = 0. \tag{6.117}$$

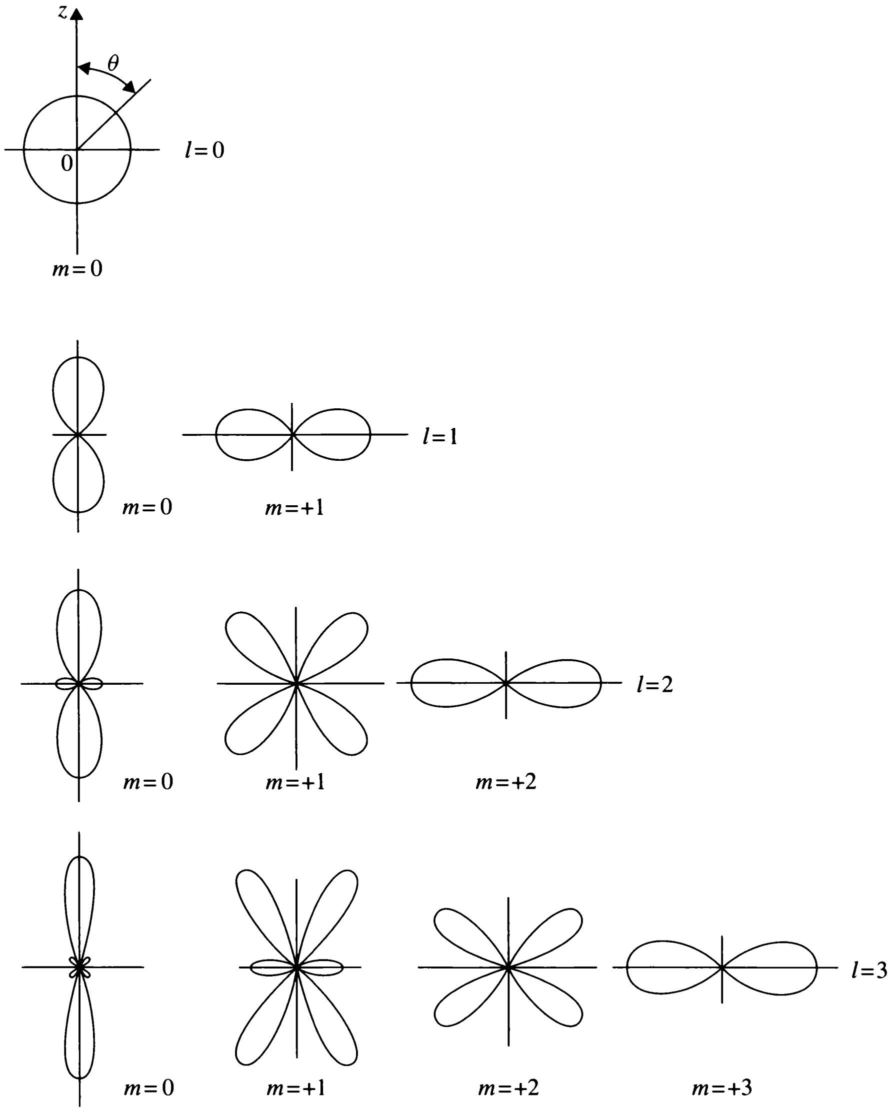


Figure 6.2 Polar plots of the probability distributions $|Y_{lm}(\theta, \phi)|^2 = (2\pi)^{-1}|\Theta_{lm}(\theta)|^2$.

It is also readily verified from the commutation relations (6.9) that (Problem 6.11)

$$L_\pm L_\mp = \mathbf{L}^2 - L_z^2 \pm \hbar L_z \qquad \textbf{(6.118a)}$$

$$[L_+, L_-] = 2\hbar L_z \qquad \textbf{(6.118b)}$$

and

$$[L_z, L_\pm] = \pm\hbar L_\pm. \tag{6.118c}$$

Acting on both sides of (6.64) with $L_\pm$ and using (6.118c), we find that

$$L_z(L_\pm Y_{lm}) = (m \pm 1)\hbar(L_\pm Y_{lm}). \tag{6.119}$$

Also, if we act on both sides of (6.63) with $L_\pm$ and use the fact that $\mathbf{L}^2$ commutes with $L_\pm$, we have

$$\mathbf{L}^2(L_\pm Y_{lm}) = l(l+1)\hbar^2(L_\pm Y_{lm}). \tag{6.120}$$

Thus the operator L_+ acting on a simultaneous eigenfunction Y_{lm} of $\mathbf{L}^2$ and L_z generates a new common eigenfunction of these two operators, for which the eigenvalue of $\mathbf{L}^2$ remains equal to $l(l+1)\hbar^2$, while the eigenvalue of L_z is increased by one unit of $\hbar$ to become $(m+1)\hbar$. Similarly, $(L_- Y_{lm})$ is a simultaneous eigenfunction of $\mathbf{L}^2$ and L_z with eigenvalues given, respectively, by $l(l+1)\hbar^2$ and $(m-1)\hbar$. Hence

$$L_\pm Y_{lm}(\theta, \phi) = c^\pm_{lm} Y_{l,m\pm 1}(\theta, \phi) \tag{6.121}$$

where $c^\pm_{lm}$ are constants. With regard to the eigenvalue equation (6.64) the operators L_+ and L_- are therefore respectively *raising* and *lowering* operators; we see that they play a role similar to that of the ladder operators a_+ and a_- introduced in Section 5.6 to study the spectrum of the linear harmonic oscillator.

In order to obtain the constants $c^\pm_{lm}$ of (6.121), we use the expressions (6.16a) and (6.16b) of the operators L_x and L_y to write $L_\pm$ in spherical polar coordinates. The result is

$$L_\pm = \hbar e^{\pm i\phi}\left[\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right]. \tag{6.122}$$

From (6.64) and (6.16c) we know that by acting with $\partial/\partial\phi$ on $Y_{lm}(\theta, \phi)$, one obtains $(im)Y_{lm}(\theta, \phi)$. The action of $\partial/\partial\theta$ on $Y_{lm}(\theta, \phi)$ may be studied by using (6.102) and the recurrence relations (6.97d) satisfied by the associated Legendre functions (in which one sets $w = \cos\theta$). In this way it is found that

$$L_\pm Y_{lm}(\theta, \phi) = \hbar[l(l+1) - m(m\pm 1)]^{1/2} Y_{l,m\pm 1}(\theta, \phi) \tag{6.123a}$$

or

$$L_\pm|lm\rangle = \hbar[l(l+1) - m(m\pm 1)]^{1/2}|lm\pm 1\rangle \tag{6.123b}$$

where in the last line we have used the Dirac ket notation, the ket $|lm\rangle$ being represented in the position representation by the spherical harmonic $Y_{lm}(\theta, \phi)$. From (6.123) and the fact that

$$L_x = \frac{1}{2}(L_+ + L_-), \qquad L_y = \frac{1}{2i}(L_+ - L_-) \tag{6.124}$$

the result of the action of the operators L_x and L_y on Y_{lm} (or $|lm\rangle$) is then immediately obtained.

Let us now consider a particle which is in the orbital angular momentum state $|lm\rangle$, so that the angular part of its wave function Ψ (which we assume to be normalised to unity) is given by $Y_{lm}(\theta, \phi)$. Thus we have $\mathbf{L}^2|lm\rangle = l(l+1)\hbar^2|lm\rangle$ and $L_z|lm\rangle = m\hbar|lm\rangle$. Although we have seen that two components of the orbital angular momentum cannot in general be assigned precise values simultaneously, it is nevertheless possible to say something about the components L_x and L_y. Indeed, from (6.123) and (6.124) the expectation value of L_x in the state $|lm\rangle$ is given by

$$\langle L_x\rangle = \langle lm|L_x|lm\rangle = \tfrac{1}{2}\langle lm|L_+ + L_-|lm\rangle. \tag{6.125}$$

Now, from (6.123b) we have

$$\begin{aligned}\langle lm|L_\pm|lm\rangle &= \hbar[l(l+1) - m(m\pm 1)]^{1/2}\langle lm|lm\pm 1\rangle \\ &= 0\end{aligned} \tag{6.126}$$

where we have used the fact that the spherical harmonics satisfy the orthonormality relations (6.103) so that $\langle lm|l'm'\rangle = \delta_{ll'}\delta_{mm'}$. Thus

$$\langle L_x\rangle = 0 \tag{6.127a}$$

and similarly

$$\langle L_y\rangle = 0. \tag{6.127b}$$

On the other hand, from (6.124), (6.118a) and (6.126) we obtain

$$\begin{aligned}\langle L_x^2\rangle &= \langle L_y^2\rangle = \tfrac{1}{2}\langle \mathbf{L}^2 - L_z^2\rangle \\ &= \tfrac{1}{2}[l(l+1) - m^2]\hbar^2.\end{aligned} \tag{6.128}$$

Note that when $m = +l$ or $m = -l$, so that the orbital angular momentum is respectively 'parallel' or 'anti-parallel' to the z-axis, its x- and y-components are still not zero, although the average values of L_x and L_y always vanish. It is convenient to visualise these results in terms of a *vector model* (see Fig. 6.3). According to this model, the orbital angular momentum vector $\mathbf{L}$, of length $\sqrt{l(l+1)}\hbar$, precesses about the z-axis, the $(2l+1)$ allowed projections of $\mathbf{L}$ on this axis being given by $m\hbar$, with $m = -l, -l+1, \dots, +l$. Thus the vector $\mathbf{L}$ may be viewed as lying on the surface of a cone with altitude $m\hbar$ which has the z-axis as its symmetry axis, all orientations of $\mathbf{L}$ on the surface of the cone being equally likely.

We conclude this section by mentioning an important property of the Y_{lm} called the *addition theorem* of the spherical harmonics. Let $\mathbf{r}_1$ and $\mathbf{r}_2$ be two vectors having polar angles (θ_1, ϕ_1) and (θ_2, ϕ_2), respectively, and let θ be the angle between them. The addition theorem states that

$$P_l(\cos\theta) = \frac{4\pi}{2l+1}\sum_{m=-l}^{+l} Y_{lm}^*(\theta_1, \phi_1)Y_{lm}(\theta_2, \phi_2). \tag{6.129}$$

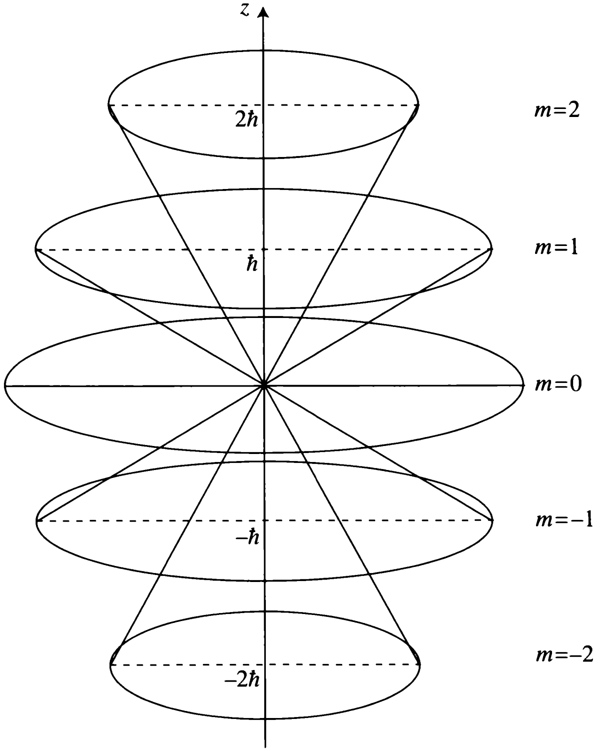


Figure 6.3 The vector model of angular momentum, illustrated here for the orbital angular momentum **L** when $l = 2$. The vector **L**, of length $\sqrt{l(l+1)}\hbar$, precesses about the axis of quantisation, the $(2l + 1)$ allowed projections of **L** on this axis being given by $m\hbar$, with $m = -l, l+1, \ldots, +l$.

Note that since the Y_{lm} satisfy (6.102b) and the summation runs over the entire set $m = -l, -l+1, \ldots, +l$, of allowed values of m, the complex-conjugate sign can be put either on $Y_{lm}(\theta_1, \phi_1)$ or on $Y_{lm}(\theta_2, \phi_2)$.

6.4 Particle on a sphere and the rigid rotator

In this section we shall illustrate the results obtained above on a simple example. Let us consider a particle of mass μ and let $\mathbf{p} = -i\hbar\boldsymbol{\nabla}$ be its momentum operator in the position representation of wave mechanics. The kinetic energy operator of the particle is therefore given in this representation by $T = \mathbf{p}^2/2\mu = -(\hbar^2/2\mu)\nabla^2$. Expressing the Laplacian operator ∇^2 in spherical polar coordinates[5], we may also

---

[5] See, for example, Byron and Fuller (1969).

write for $r \neq 0$

$$T = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{6.130a}$$

or

$$T = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\mathbf{L}^2}{\hbar^2 r^2}\right] \tag{6.130b}$$

where we have used the expression (6.17) of the operator $\mathbf{L}^2$.

Let us now assume that the particle is constrained to move on the surface of a sphere of radius a. Taking the centre of the sphere as the origin of coordinates, r has the *fixed* value $r = a$. Hence the first term in the square brackets on the right of (6.130b) does not occur, and the kinetic energy operator of the particle reduces to

$$T = \frac{\mathbf{L}^2}{2\mu a^2} = \frac{\mathbf{L}^2}{2I} \tag{6.131}$$

where $I = \mu a^2$ is the moment of inertia of the particle with respect to the origin. Moreover, its potential energy V is clearly independent of r. If we suppose that V is also time-independent, the Hamiltonian of the particle is given by

$$H = \frac{\mathbf{L}^2}{2I} + V(\theta, \phi) \tag{6.132}$$

and the time-independent Schrödinger equation reads

$$\left[\frac{\mathbf{L}^2}{2I} + V(\theta, \phi)\right]\psi(\theta, \phi) = E\psi(\theta, \phi). \tag{6.133}$$

Rigid rotator

We now focus our attention on the simple case in which the particle is *free* (except for being constrained to move on the sphere) so that $V = 0$ and we are dealing with a rigid rotator. In this case the Hamiltonian (6.132) reduces to

$$H = \frac{\mathbf{L}^2}{2I} \tag{6.134}$$

and the Schrödinger equation (6.133) becomes

$$\frac{\mathbf{L}^2}{2I}\psi(\theta, \phi) = E\psi(\theta, \phi). \tag{6.135}$$

Since the eigenfunctions of $\mathbf{L}^2$ are the spherical harmonics $Y_{lm}(\theta, \phi)$, and its eigenvalues are given by $l(l+1)\hbar^2$ (with $l = 0, 1, 2, \ldots$) we see that the eigenfunctions of the rigid-rotator Hamiltonian (6.134) are also the Y_{lm}, the corresponding energy eigenvalues being

$$E_l = \frac{\hbar^2}{2I}l(l+1), \qquad l = 0, 1, 2, \ldots \tag{6.136}$$

It is worth stressing that these energy eigenvalues are independent of the quantum number m. Thus, the $(2l+1)$ eigenfunctions $Y_{lm}(\theta, \phi)$ with $m = -l, -l+1, \dots, l$, correspond to the same energy, so that the energy level E_l is $(2l+1)$-*fold degenerate*. This degeneracy arises from the fact that the Hamiltonian (6.134) of the rigid rotator commutes with the orbital angular momentum operator $\mathbf{L}$ (see (6.14)) and is therefore invariant under rotations. Hence for this system all directions of space are physically equivalent. Now we have seen in Section 6.3 that $m\hbar$ measures the projection of the orbital angular momentum $\mathbf{L}$ on the z-axis, and thus is determined by the orientation of $\mathbf{L}$. The $(2l+1)$-fold degeneracy with respect to the quantum number m therefore results from the fact that the Hamiltonian (6.134) is independent of this orientation, so that its energy levels cannot depend on the magnitude of the component of $\mathbf{L}$ in any particular direction.

Rotational energy levels of a diatomic molecule

The result (6.136) giving the eigenvalues of the rigid-rotator Hamiltonian can be used to obtain an approximation for the rotational energy levels of a diatomic molecule. As far as its rotational motion is concerned, a diatomic molecule can be considered (in first approximation) as a rigid 'dumb-bell' with the nuclei of the two atoms A and B held a fixed distance R_0 apart (see Fig. 6.4). Classically the (kinetic) energy of rotation is

$$T = \frac{1}{2}I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{\mathbf{L}^2}{2I} \tag{6.137}$$

where ω is the angular frequency of rotation, I is the moment of inertia and $L = I\omega$ is the magnitude of the angular momentum of the molecule with respect to the axis of rotation, which is perpendicular to the symmetry axis of the molecule (i.e. the line joining the two nuclei) and passes through the centre of mass. Denoting respectively by M_A and M_B the masses of the nuclei A and B, and by R_A and R_B their distances from the centre of mass, we have (see Fig. 6.4)

$$I = M_\mathrm{A}R_\mathrm{A}^2 + M_\mathrm{B}R_\mathrm{B}^2 = \mu R_0^2 \tag{6.138}$$

where $\mu = M_\mathrm{A}M_\mathrm{B}/(M_\mathrm{A}+M_\mathrm{B})$ is the reduced mass. In obtaining the above result we have used the relations $M_\mathrm{A}R_\mathrm{A} = M_\mathrm{B}R_\mathrm{B}$ and $R_0 = R_\mathrm{A} + R_\mathrm{B}$. Since there is no potential energy, the Hamiltonian of the system is just $H = \mathbf{L}^2/2I$, so that the energy eigenvalues are given by (6.136), as in the case of the rigid rotator. The only difference is that the quantity μ which appears in the moment of inertia (6.138) is now the reduced mass μ of the two nuclei.

As an example, the constant $\hbar^2/2I$ has the value 1.3×10^{-3} eV in the lowest electronic state of the molecule HCl. Transitions between rotational states which differ in the quantum number l give rise to a series of closely spaced lines, called a *band spectrum* because it appears as a band when the structure due to the lines is not resolved. Pure rotational spectra of this kind lie in the far infrared and microwave

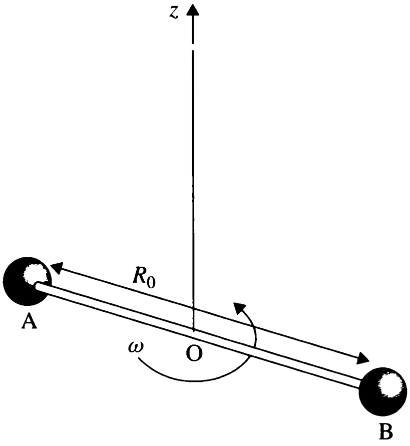


Figure 6.4 Rotation of a diatomic molecule considered as a rigid 'dumb-bell', the nuclei of the two atoms A and B being a distance R_0 apart. The rotation is about an axis Oz perpendicular to the symmetry axis of the molecule and passing through the centre of mass. The classical energy of rotation is $I\omega^2/2$, where I is the moment of inertia (6.138) and ω is the angular frequency of rotation.

regions[6].

Thus far we have assumed that the molecule is completely rigid. In fact, the nuclei can vibrate about their equilibrium position, and we shall see in Chapter 10 that the spacing of the corresponding vibrational energy levels is of the order of 0.1 eV, i.e. is about one hundred times larger than typical spacings of rotational levels. Transitions in which *both* the vibrational and rotational quantum numbers change give rise to the *vibration–rotation* (also called *rovibrational*) spectra of molecules, which appear in the infrared part of the electromagnetic spectrum. Finally, *electronic spectra* of molecules are observed when changes occur in the electronic as well as in the vibrational and rotational states of the molecule. As we shall show in Chapter 10, typical energy separations between low-lying electronic levels of molecules are of the order of a few eV, so that the corresponding electronic spectra appear in the ultraviolet and visible regions.

6.5 General angular momentum. The spectrum of $\mathbf{J}^2$ and J_z

In Chapter 1 we saw that experiments demonstrate that particles can be assigned an intrinsic angular momentum, the *spin* $\mathbf{S}$, and a spin quantum number s. For example, the electron has a spin quantum number $s = 1/2$, so that the component of its spin angular momentum $\mathbf{S}$ in a given direction can only take the values $\pm\hbar/2$.

---

[6] See Bransden and Joachain (1983), Chapter 10.

Such values are excluded for the component of the *orbital* angular momentum **L** in a given direction, which can only take the values $m\hbar$, where $m = -l, -l+1, \dots, l$, is either zero or a positive or negative integer (see (6.76) and (6.91)). This arises from the condition that the wave function should have a unique value at each point in space. Since the spin angular momentum of a particle is not associated with the spatial dependence of the wave function, this restriction need not apply for the spin. The theory developed so far for the orbital angular momentum is therefore not comprehensive enough to include also the spin angular momentum.

Because the commutation relations play a fundamental role in quantum mechanics, the way forward is to adopt the following general definition of angular momentum: *a vector operator* **J** *is an angular momentum if its components are Hermitian operators satisfying the commutation relations*

$$[J_x, J_y] = \mathrm{i}\hbar J_z, \qquad [J_y, J_z] = \mathrm{i}\hbar J_x, \qquad [J_z, J_x] = \mathrm{i}\hbar J_y \tag{6.139}$$

which are equivalent to the vector commutation relation

$$\mathbf{J} \times \mathbf{J} = \mathrm{i}\hbar \mathbf{J}. \tag{6.140}$$

Moreover, using the commutation relations (6.139), and proceeding as in the cases of the orbital angular momentum (see (6.20) and (6.21)), one finds that if J_u, J_v and J_w, are, respectively, the components of **J** along the three orthogonal unit vectors $\hat{\mathbf{u}}$, $\hat{\mathbf{v}}$ and $\hat{\mathbf{w}} = \hat{\mathbf{u}} \times \hat{\mathbf{v}}$, then

$$[J_u, J_v] = \mathrm{i}\hbar J_w, \qquad [J_v, J_w] = \mathrm{i}\hbar J_u, \qquad [J_w, J_u] = \mathrm{i}\hbar J_v. \tag{6.141}$$

From the commutation relations (6.139), one also deduces that the square of the angular momentum operator,

$$\mathbf{J}^2 = J_x^2 + J_y^2 + J_z^2 \tag{6.142}$$

commutes with J_x, J_y and J_z, namely

$$[\mathbf{J}^2, J_x] = [\mathbf{J}^2, J_y] = [\mathbf{J}^2, J_z] = 0. \tag{6.143}$$

The proof is entirely similar to that given in Section 6.1 for the orbital angular momentum (see (6.13)). We shall summarise the relations (6.143) by writing

$$[\mathbf{J}^2, \mathbf{J}] = 0. \tag{6.144}$$

Because $\mathbf{J}^2$ commutes with each of the components of **J**, simultaneous eigenfunctions of $\mathbf{J}^2$ and any component of **J** (for example J_z) can be found. Starting with the definition of the angular momentum based on the commutation relations (6.139), and without adopting any specific representation, we shall now obtain the eigenvalues of $\mathbf{J}^2$ and J_z, which will be seen to include both integer and half-odd-integer values of the angular momentum quantum numbers.

The eigenvalues of $\mathbf{J}^2$ and J_z are real, since $\mathbf{J}^2$ and J_z are Hermitian operators. Moreover, the eigenvalues of $\mathbf{J}^2$ must be either positive or zero. For later convenience we shall write the eigenvalues of $\mathbf{J}^2$ in the form $j(j+1)\hbar^2$ and those of J_z in the form[7] $m\hbar$, with $j \geqslant 0$. Denoting the simultaneous eigenvectors of $\mathbf{J}^2$ and J_z by $|jm\rangle$, we have

$$\mathbf{J}^2|jm\rangle = j(j+1)\hbar^2|jm\rangle \tag{6.145}$$

and

$$J_z|jm\rangle = m\hbar|jm\rangle. \tag{6.146}$$

Because the expectation value of the square of a Hermitian operator must be positive (or zero), we have

$$\begin{aligned}\langle \mathbf{J}^2\rangle &= \langle J_x^2\rangle + \langle J_y^2\rangle + \langle J_z^2\rangle \\ &\geqslant \langle J_z^2\rangle\end{aligned} \tag{6.147}$$

and it follows that

$$j(j+1) \geqslant m^2. \tag{6.148}$$

We now introduce the raising and lowering operators (compare with (6.116))

$$J_+ = J_x + \mathrm{i}J_y, \qquad J_- = J_x - \mathrm{i}J_y \tag{6.149}$$

and we note that

$$J_+^\dagger = J_-, \qquad J_-^\dagger = J_+. \tag{6.150}$$

As in the case of the orbital angular momentum (see (6.117) and (6.118)) we have the relations

$$[\mathbf{J}^2, J_\pm] = 0 \tag{6.151a}$$

$$J_\pm J_\mp = \mathbf{J}^2 - J_z^2 \pm \hbar J_z \tag{6.151b}$$

$$[J_+, J_-] = 2\hbar J_z \tag{6.151c}$$

and

$$[J_z, J_\pm] = \pm\hbar J_\pm. \tag{6.151d}$$

Using (6.151a) and (6.151d), we see that $J_\pm|jm\rangle$ are simultaneous eigenvectors of $\mathbf{J}^2$ and J_z belonging, respectively, to the eigenvalues $j(j+1)\hbar^2$ and $(m \pm 1)\hbar$. Indeed, since $[\mathbf{J}^2, J_\pm] = 0$ we have

$$\mathbf{J}^2(J_\pm|jm\rangle) = J_\pm\mathbf{J}^2|jm\rangle = j(j+1)\hbar^2(J_\pm|jm\rangle) \tag{6.152}$$

and from (6.151d) we find that

$$\begin{aligned}J_z(J_\pm|jm\rangle) &= J_\pm(J_z|jm\rangle) \pm \hbar J_\pm|jm\rangle \\ &= (m \pm 1)\hbar(J_\pm|jm\rangle).\end{aligned} \tag{6.153}$$

---

[7] For notational simplicity we shall use here the symbol m for the 'magnetic' quantum number associated with the operator J_z. Whenever it will be necessary, we shall add subscripts and write m_l, m_s or m_j to denote the magnetic quantum numbers associated with the operators L_z, S_z or J_z.

By operating repeatedly with J_+, a sequence of eigenvectors of J_z can be constructed, with eigenvalues $(m+1)\hbar$, $(m+2)\hbar$, and so on, each of which being an eigenvector of $\mathbf{J}^2$ corresponding to the eigenvalue $j(j+1)\hbar^2$. Similarly, by repeated operation with J_-, a sequence of eigenvectors of J_z can be constructed, with eigenvalues $(m-1)\hbar$, $(m-2)\hbar$, etc., and again each of them is an eigenvector of $\mathbf{J}^2$ with the same eigenvalue $j(j+1)\hbar^2$. Now, in view of (6.148) for each j there must be a maximum (top) eigenvalue, say $m_\mathrm{T}\hbar$, and also a minimum (bottom) eigenvalue $m_\mathrm{B}\hbar$, so that the ladder of eigenvalues of J_z cannot continue indefinitely in either direction. Therefore, the quantity $m_\mathrm{T} - m_\mathrm{B}$ must be a positive integer or zero

$$m_\mathrm{T} - m_\mathrm{B} = n, \qquad n = 0, 1, 2, \ldots \tag{6.154}$$

If J_+ is applied to the state $|jm_\mathrm{T}\rangle$, the sequence terminates and

$$J_+|jm_\mathrm{T}\rangle = 0. \tag{6.155}$$

From the above result and from (6.151b), we have

$$\begin{aligned} J_-(J_+|jm_\mathrm{T}\rangle) &= (\mathbf{J}^2 - J_z^2 - \hbar J_z)|jm_\mathrm{T}\rangle \\ &= [j(j+1) - m_\mathrm{T}^2 - m_\mathrm{T}]\hbar^2|jm_\mathrm{T}\rangle \\ &= 0 \end{aligned} \tag{6.156}$$

where we have used the fact that $J_z|jm_\mathrm{T}\rangle = m_\mathrm{T}\hbar|jm_\mathrm{T}\rangle$. Thus

$$j(j+1) = m_\mathrm{T}^2 + m_\mathrm{T}. \tag{6.157}$$

Similarly, if J_- is applied to the state $|jm_\mathrm{B}\rangle$, the sequence terminates, so that

$$J_-|jm_\mathrm{B}\rangle = 0. \tag{6.158}$$

From this relation and from (6.151b), we have in this case

$$\begin{aligned} J_+(J_-|jm_\mathrm{B}\rangle) &= (\mathbf{J}^2 - J_z^2 + \hbar J_z)|jm_\mathrm{B}\rangle \\ &= [j(j+1) - m_\mathrm{B}^2 + m_\mathrm{B}]\hbar^2|jm_\mathrm{B}\rangle \\ &= 0 \end{aligned} \tag{6.159}$$

since $J_z|jm_\mathrm{B}\rangle = m_\mathrm{B}\hbar|jm_\mathrm{B}\rangle$. Hence

$$j(j+1) = m_\mathrm{B}^2 - m_\mathrm{B}. \tag{6.160}$$

The two equations (6.157) and (6.160) require that

$$m_\mathrm{T}^2 + m_\mathrm{T} = m_\mathrm{B}^2 - m_\mathrm{B}. \tag{6.161}$$

This equation has two solutions:

$$m_\mathrm{T} = -m_\mathrm{B}, \qquad m_\mathrm{T} = m_\mathrm{B} - 1. \tag{6.162}$$

The second solution contradicts (6.154), so that we must have $m_\mathrm{T} = -m_\mathrm{B}$, and hence also $m_\mathrm{T} \geqslant 0$. Going back to (6.157) and using the fact that j is also non-negative, we find that the only acceptable solution of this equation is $m_\mathrm{T} = j$. Thus

$$m_\mathrm{T} = j, \qquad m_\mathrm{B} = -j. \tag{6.163}$$

Now, as $m_\mathrm{T} - m_\mathrm{B}$ is a positive integer or zero (see (6.154)), $2j$ must also be a positive integer or zero, so that the allowed values of the angular momentum quantum number j are

$$j = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \tfrac{5}{2}, \ldots \tag{6.164}$$

Moreover, because the maximum value of the magnetic quantum number m is $m_\mathrm{T} = j$ and its minimum value is $m_\mathrm{B} = -j$, the allowed values of m, for a given j, are the $(2j + 1)$ values

$$-j, -j+1, \ldots, j. \tag{6.165}$$

Our general definition of angular momentum, based on the commutation relations (6.139), therefore leads to *integer* (including zero) and *half-odd-integer* values for j (and hence for m). As we have seen above, half-odd-integer values of j are excluded in the case of the orbital angular momentum, where $j = l = 0, 1, 2$, etc. On the other hand, in the case of the spin angular momentum the quantum number j has a fixed value s which is an integer (or zero) for some particles, and a half-odd-integer for others. For example, pions have spin zero ($s = 0$), photons have spin one ($s = 1$), electrons, protons and neutrons have spin 1/2, the Ω^- particle (a particle with a mass roughly 1.8 times that of the proton and a lifetime of about 10^{-10} s) has spin 3/2.

6.6 Matrix representations of angular momentum operators

Let us consider the simultaneous eigenvectors $|jm\rangle$ of $\mathbf{J}^2$ and J_z. These eigenvectors can be chosen to be normalised to unity, $\langle jm|jm\rangle = 1$. Moreover, the eigenvectors of Hermitian operators belonging to different eigenvalues are orthogonal. We can therefore adopt the orthonormality conditions

$$\langle j'm'|jm\rangle = \delta_{jj'}\delta_{mm'}. \tag{6.166}$$

Using as a basis the eigenvectors $|jm\rangle$ of $\mathbf{J}^2$ and J_z, it is easy to find a matrix representation of the angular momentum operators. First, we note that the matrices representating the operators $\mathbf{J}^2$ and J_z are diagonal, with elements

$$\begin{aligned}(\mathbf{J}^2)_{j'm',jm} &= \langle j'm'|\mathbf{J}^2|jm\rangle \\ &= j(j+1)\hbar^2\delta_{jj'}\delta_{mm'}\end{aligned} \tag{6.167}$$

and

$$\begin{aligned}(J_z)_{j'm',jm} &= \langle j'm'|J_z|jm\rangle \\ &= m\hbar\delta_{jj'}\delta_{mm'}.\end{aligned} \tag{6.168}$$

In order to find the matrix elements of J_x and J_y, it is convenient to obtain first those of the operators J_+ and J_-. To this end, we remark that

$$J_\pm|jm\rangle = N_\pm|jm \pm 1\rangle \tag{6.169}$$

where $N_\pm$ are normalisation factors. Since both $|jm\rangle$ and $|jm \pm 1\rangle$ are normalised to unity

$$\begin{aligned}|N_\pm|^2 &= \langle jm|J_\pm^\dagger J_\pm|jm\rangle \\ &= \langle jm|J_\mp J_\pm|jm\rangle \\ &= [j(j+1) - m(m \pm 1)]\hbar^2\end{aligned} \tag{6.170}$$

where we have used (6.150) in the second line and (6.151b) in the last line. Adopting the convention that $N_\pm$ are real and positive, we have

$$N_\pm = [j(j+1) - m(m \pm 1)]^{1/2}\hbar. \tag{6.171}$$

The matrix representation of J_+ follows. It is

$$\begin{aligned}(J_+)_{j'm',jm} &= \langle j'm'|J_+|jm\rangle \\ &= [j(j+1) - m(m+1)]^{1/2}\hbar\delta_{jj'}\delta_{m'm+1}.\end{aligned} \tag{6.172}$$

In the same way, we find that

$$(J_-)_{j'm',jm} = [j(j+1) - m(m-1)]^{1/2}\hbar\delta_{jj'}\delta_{m'm-1}. \tag{6.173}$$

The matrix representations of J_x and J_y can be found at once from those of J_+ and J_- by using the relations (see (6.149))

$$J_x = \frac{1}{2}(J_+ + J_-), \qquad J_y = \frac{1}{2\mathrm{i}}(J_+ - J_-). \tag{6.174}$$

It is clear from the above results that the matrices representing the angular momentum operators J_x, J_y, J_z, J_+, J_- and $\mathbf{J}^2$ in the basis $|jm\rangle$ are diagonal in j. We therefore have an infinite number of representations for these matrices, each of them characterised by a given value of j ($j = 0, 1/2, 1, 3/2, \ldots$) and having $2j + 1$ columns and rows, labelled respectively by the values of m and m'. One may take all these representations together to form one single representation of infinite rank, or we may consider each of the representations of dimension $2j + 1$ separately. The first three finite-dimensional representations, for $j = 0$, 1/2 and 1, are given below for the operators J_x, J_y, J_z and $\mathbf{J}^2$.

(1) For $j = 0$

$$J_x = (0), \qquad J_y = (0), \qquad J_z = (0), \qquad \mathbf{J}^2 = (0) \tag{6.175a}$$

where (0) is the null matrix of unit rank.

(2) For $j = 1/2$

$$J_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad J_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}$$

$$J_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad \mathbf{J}^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{6.175b}$$

(3) For $j = 1$

$$J_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad J_y = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{pmatrix}$$

$$J_z = \hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \qquad \mathbf{J}^2 = 2\hbar^2\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{6.175c}$$

Since the orbital angular momentum **L** is a particular angular momentum for which the quantum number $j(= l)$ is an integer or zero, one can use the matrix representations with $j = l = 0, 1, 2, \ldots$ for the orbital angular momentum operators. In fact, when $j(= l)$ is an integer or zero, the basic results (6.167), (6.168), (6.172) and (6.173) can be obtained by using the properties of the spherical harmonics $Y_{lm}(\theta, \phi)$, which represent the kets $|lm\rangle$ in the position representation. Indeed, from (6.63), (6.64) and the orthonormality property (6.103) of the spherical harmonics, we have

$$\begin{aligned}(\mathbf{L}^2)_{l'm',lm} &= \int Y^*_{l'm'}(\theta, \phi)\mathbf{L}^2 Y_{lm}(\theta, \phi)\mathrm{d}\Omega \\ &= l(l+1)\hbar^2\delta_{ll'}\delta_{mm'}\end{aligned} \tag{6.176}$$

and

$$\begin{aligned}(L_z)_{l'm',lm} &= \int Y^*_{l'm'}(\theta, \phi)L_z Y_{lm}(\theta, \phi)\mathrm{d}\Omega \\ &= m\hbar\delta_{ll'}\delta_{mm'}\end{aligned} \tag{6.177}$$

while from (6.123) we obtain the matrix representations of the operators L_+ and L_-

$$\begin{aligned}(L_\pm)_{l'm',lm} &= \int Y^*_{l'm'}(\theta, \phi)L_\pm Y_{lm}(\theta, \phi)\mathrm{d}\Omega \\ &= [l(l+1) - m(m \pm 1)]^{1/2}\hbar\delta_{ll'}\delta_{m'm\pm 1}.\end{aligned} \tag{6.178}$$

The vector model introduced in Section 6.3 to visualise the orbital angular momentum can readily be extended to all angular momenta. To see this, we first note from (6.172)–(6.174) that

$$\langle J_x \rangle \equiv \langle jm|J_x|jm\rangle = 0 \tag{6.179a}$$

and similarly

$$\langle J_y \rangle \equiv \langle jm|J_y|jm\rangle = 0. \tag{6.179b}$$

Also, from (6.174), (6.151b) and the fact that $\langle jm|J_\pm|jm\rangle = 0$, we have

$$\begin{aligned}\langle J_x^2 \rangle &= \langle J_y^2 \rangle = \tfrac{1}{2}\langle \mathbf{J}^2 - J_z^2 \rangle \\ &= \tfrac{1}{2}[j(j+1) - m^2]\hbar^2 \end{aligned} \tag{6.180}$$

so that an angular momentum $\mathbf{J}$ can be viewed as a vector, of length $\sqrt{j(j+1)}\hbar$, precessing about the z-axis, the $2j+1$ allowed projections of $\mathbf{J}$ on this axis being given by $m\hbar$, with $m = -j, -j+1, \dots, +j$.

6.7 Spin angular momentum

In Chapter 1, we reviewed some of the evidence showing that 'elementary' particles possess an internal degree of freedom which behaves like an angular momentum and is termed *spin*. In what follows we shall use the symbol $\mathbf{S}$ to denote the spin angular momentum operator of a particle, rather than $\mathbf{J}$ which we used in the two previous sections to denote angular momentum in general.

Since the spin operator $\mathbf{S}$ is an angular momentum, its Cartesian components S_x, S_y and S_z are Hermitian operators satisfying the commutation relations (see (6.139))

$$[S_x, S_y] = \mathrm{i}\hbar S_z, \qquad [S_y, S_z] = \mathrm{i}\hbar S_x, \qquad [S_z, S_x] = \mathrm{i}\hbar S_y \tag{6.181}$$

which may also be rewritten as

$$\mathbf{S} \times \mathbf{S} = \mathrm{i}\hbar\mathbf{S}. \tag{6.182}$$

From the general theory of angular momentum discussed in Section 6.5, we know that the square of the spin angular momentum operator,

$$\mathbf{S}^2 = S_x^2 + S_y^2 + S_z^2 \tag{6.183}$$

commutes with S_x, S_y and S_z. Thus simultaneous eigenvectors of $\mathbf{S}^2$ and S_z can be found, corresponding to eigenvalues $s(s+1)\hbar^2$ and $m_s\hbar$, respectively. In the notation of Section 6.5 these eigenvectors, normalised to unity would be written $|sm_s\rangle$. In what follows, however, it will be more convenient to denote them by the symbol χ_{s,m_s}. We therefore have

$$\mathbf{S}^2\chi_{s,m_s} = s(s+1)\hbar^2\chi_{s,m_s} \tag{6.184}$$

and

$$S_z\chi_{s,m_s} = m_s\hbar\chi_{s,m_s}. \tag{6.185}$$

It follows from the general discussion of Section 6.5 that the spin quantum number s (usually abbreviated as spin) can be an integer (including zero) or half an odd integer. Particles having integer spin ($s = 0, 1, 2, \dots$) are called *bosons* while those having half-odd-integer spin ($s = 1/2, 3/2, \ldots$) are called *fermions*. Regarding the quantum number m_s, we know from the general theory developed in Section 6.5 that it has $(2s + 1)$ allowed values, given by $-s, -s + 1, \ldots, +s$. Furthermore, from the orthonormality condition (6.166), we have

$$\langle \chi_{s,m'_s} | \chi_{s,m_s} \rangle = \delta_{m_s m'_s} . \tag{6.186}$$

If the $(2s + 1)$ eigenvectors χ_{s,m_s} are used as a basis, the spin operators S_x, S_y, S_z and $\mathbf{S}^2$ are represented by $(2s + 1) \times (2s + 1)$ matrices, which are of course the same matrices as those appearing in the $(2j + 1)$ dimensional representation of the general angular momentum operators J_x, J_y, J_z and $\mathbf{J}^2$, with $j = s$. The eigenvectors χ_{s,m_s} are then represented by *column vectors* with $(2s + 1)$ components, all components being equal to zero except one, which is equal to unity. For example, in the case of spin one ($s = 1$) we see from (6.175c) that

$$S_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad S_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{pmatrix}$$

$$S_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \mathbf{S}^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{6.187}$$

and it is readily verified that the three spin eigenvectors

$$\chi_{1,1} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad \chi_{1,0} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \qquad \chi_{1,-1} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \tag{6.188}$$

correspond respectively to eigenvalues $+\hbar$, 0 and $-\hbar$ of S_z and to the eigenvalue $2\hbar^2$ of $\mathbf{S}^2$. We remark that in matrix notation the orthonormality relations (6.186) read

$$\chi^{\dagger}_{s,m'_s} \chi_{s,m_s} = \delta_{m_s m'_s} \tag{6.189}$$

where $\chi^{\dagger}_{s,m'_s}$, the Hermitian adjoint of χ_{s,m'_s}, is a *row vector*. For example, the Hermitian adjoints of the spin-one eigenvectors (6.188) are

$$\chi^{\dagger}_{1,1} = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix}, \qquad \chi^{\dagger}_{1,0} = \begin{pmatrix} 0 & 1 & 0 \end{pmatrix}, \qquad \chi^{\dagger}_{1,-1} = \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \tag{6.190}$$

and the orthonormality relations (6.189) can easily be checked by using the rules of matrix multiplication. For instance

$$\chi^{\dagger}_{1,1} \chi_{1,1} = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = 1,$$

$$\chi^{\dagger}_{1,1} \chi_{1,0} = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = 0. \tag{6.191}$$

In the position representation – in which $\mathbf{r}$ is diagonal – the state vector $|\Psi(t)\rangle$ of a *spinless* particle is represented by a wave function $\Psi(\mathbf{r}, t)$ which is in general a function of the three dynamical variables x, y, z describing its position, and of the time t. From the foregoing discussion it is apparent that in the case of a particle having spin s the wave function must also depend on an additional *spin variable* describing the spin orientation of the particle. In a representation in which $\mathbf{r}$ and S_z are diagonal, the state vector $|\Psi(t)\rangle$ will therefore be represented by a wave function $\Psi(\mathbf{r}, t, \sigma)$, in which the spin variable σ, denoting the component of the spin along the z-axis, can only take on $2s+1$ values $-s\hbar, (-s+1)\hbar, \dots, s\hbar$ corresponding to the $2s+1$ possible values of the quantum number m_s. We emphasise that in contrast to the position variables x, y and z, which vary in a continuous way, the spin variable σ can only take on *discrete* values; this variable has no classical analogue.

We shall assume that the basic postulates of quantum mechanics discussed in Chapter 5 also apply to the new independent spin variable σ. In particular, we may expand a general wave function $\Psi(\mathbf{r}, t, \sigma)$ for a particle having spin in terms of the basic spin eigenfunctions χ_{s,m_s}. That is

$$\Psi(\mathbf{r}, t, \sigma) = \sum_{m_s=-s}^{+s} \Psi_{m_s}(\mathbf{r}, t)\chi_{s,m_s} \tag{6.192}$$

so that a particle of spin s is described by a wave function Ψ having $2s+1$ components $\Psi_{m_s}(\mathbf{r}, t)$, each of them corresponding to a particular value of the spin variable σ. For example, in the case of spin one we may use the three spin eigenvectors (6.188) to write the wave function Ψ as a column vector:

$$\begin{aligned}\Psi(\mathbf{r}, t, \sigma) &= \Psi_1(\mathbf{r}, t)\begin{pmatrix}1\\0\\0\end{pmatrix} + \Psi_0(\mathbf{r}, t)\begin{pmatrix}0\\1\\0\end{pmatrix} + \Psi_{-1}(\mathbf{r}, t)\begin{pmatrix}0\\0\\1\end{pmatrix}\\ &= \begin{pmatrix}\Psi_1(\mathbf{r}, t)\\ \Psi_0(\mathbf{r}, t)\\ \Psi_{-1}(\mathbf{r}, t)\end{pmatrix}\end{aligned} \tag{6.193}$$

where the three components Ψ_1, Ψ_0 and Ψ_{-1} correspond respectively to the values $+\hbar$, 0 and $-\hbar$ of the spin variable σ. We note that the requirement that the wave function (6.192) be normalised to unity reads

$$\langle\Psi|\Psi\rangle = 1 \tag{6.194a}$$

where

$$\begin{aligned}\langle\Psi|\Psi\rangle &= \int \Psi^\dagger(\mathbf{r}, t, \sigma)\Psi(\mathbf{r}, t, \sigma)\mathrm{d}\mathbf{r}\\ &= \sum_{m_s=-s}^{+s} \int |\Psi_{m_s}(\mathbf{r}, t)|^2\mathrm{d}\mathbf{r}\end{aligned} \tag{6.194b}$$

and we have used (6.192) and (6.189). For instance, in the case of the spin-one wave function (6.193) we have

$$\begin{aligned}\langle\Psi|\Psi\rangle &= \int \left(\Psi_1^*(\mathbf{r},t)\ \Psi_0^*(\mathbf{r},t)\ \Psi_{-1}^*(\mathbf{r},t)\right)\begin{pmatrix}\Psi_1(\mathbf{r},t)\\ \Psi_0(\mathbf{r},t)\\ \Psi_{-1}(\mathbf{r},t)\end{pmatrix}\mathrm{d}\mathbf{r}\\ &= \int [|\Psi_1(\mathbf{r},t)|^2 + |\Psi_0(\mathbf{r},t)|^2 + |\Psi_{-1}(\mathbf{r},t)|^2]\mathrm{d}\mathbf{r}.\end{aligned} \tag{6.195}$$

Having expanded the wave function Ψ according to (6.192), we may interpret the quantity $|\Psi_{m_s}(\mathbf{r},t)|^2\mathrm{d}\mathbf{r}$ as the probability of finding the particle at time t in the volume element $\mathrm{d}\mathbf{r}$ *with the component of its spin along the z-axis equal to* $m_s\hbar$, provided the wave function Ψ is normalised to unity. The probability that the particle be found at time t in the volume element $\mathrm{d}\mathbf{r}$, independently of its spin orientation, is equal to

$$\sum_{m_s=-s}^{+s} |\Psi_{m_s}(\mathbf{r},t)|^2\mathrm{d}\mathbf{r} \tag{6.196}$$

and the integral

$$\int |\Psi_{m_s}(\mathbf{r},t)|^2\mathrm{d}\mathbf{r} \tag{6.197}$$

gives the probability that the component of the spin along the z-axis is equal to $m_s\hbar$ at the time t. We remark that if the particle is in an eigenstate of S_z corresponding to a definite value $\bar{m}_s$ of m_s, its wave function has the form

$$\Psi(\mathbf{r},t,\sigma) = \Psi_{\bar{m}_s}(\mathbf{r},t)\chi_{s,\bar{m}_s} \tag{6.198}$$

and hence all the components of Ψ are zero except the one corresponding to the value $\bar{\sigma} = \bar{m}_s\hbar$ of the spin variable σ.

The expectation value of an operator A is given by the usual expression (see (5.28))

$$\langle A\rangle = \frac{\langle\Psi|A|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{6.199}$$

where $\langle\Psi|\Psi\rangle$ is given by (6.194b). Using (6.192) and (6.189), the matrix element $\langle\Psi|A|\Psi\rangle$ reads

$$\begin{aligned}\langle\Psi|A|\Psi\rangle &= \int \Psi^\dagger(\mathbf{r},t,\sigma)A\Psi(\mathbf{r},t,\sigma)\mathrm{d}\mathbf{r}\\ &= \sum_{m_s=-s}^{+s}\sum_{m_s'=-s}^{+s}\int \Psi_{m_s}^*(\mathbf{r},t)A_{m_s m_s'}\Psi_{m_s'}(\mathbf{r},t)\mathrm{d}\mathbf{r}\end{aligned} \tag{6.200}$$

where

$$A_{m_s m_s'} = \langle\chi_{s,m_s}|A|\chi_{s,m_s'}\rangle \tag{6.201}$$

is the $(2s+1)\times(2s+1)$ matrix representing the operator A in ‘spin space’.

It is important to note that the position and time variables on the one hand, and the spin variable on the other, can be studied separately and can then be assembled by using (6.192). One can therefore focus the attention on the spin properties, and temporarily disregard the dependence of the wave function Ψ on the position and time variable. The (spin) state of a particle of spin s is then determined by a wave function χ_s which is in general an arbitrary superposition of the $(2s+1)$ basic spin eigenstates χ_{s,m_s}, namely

$$\chi_s = \sum_{m_s=-s}^{+s} a_{m_s} \chi_{s,m_s} \tag{6.202}$$

where the a_{m_s} are complex coefficients. If χ_s is normalised to unity, so that $\chi_s^\dagger \chi_s = 1$, then $|a_{m_s}|^2$ is the probability of finding the particle in the basic spin state χ_{s,m_s}, and from the orthonormality relations (6.189) we have

$$\sum_{m_s=-s}^{+s} |a_{m_s}|^2 = 1. \tag{6.203}$$

It is also interesting to note from (6.184) and (6.202) that for an *arbitrary* spin function χ_s one has $\mathbf{S}^2\chi_s = s(s+1)\hbar^2\chi_s$. More generally, since the operator $\mathbf{S}^2$ does not act on the variables $\mathbf{r}$ and t, we can write the relation

$$\mathbf{S}^2\Psi = s(s+1)\hbar^2\Psi \tag{6.204}$$

for an arbitrary wave function (6.192) corresponding to a particle of spin s. The above relation means that in contrast to the case of the orbital angular momentum, the operator $\mathbf{S}^2$ is a purely numerical one, which can be written as

$$\mathbf{S}^2 = s(s+1)\hbar^2. \tag{6.205}$$

Finally, we remark that if spin-dependent interactions are negligible, so that the Hamiltonian H of the particle is spin-independent, the wave function $\Psi(\mathbf{r}, t, \sigma)$ of a particle of spin s will simply be the product

$$\Psi(\mathbf{r}, t, \sigma) = \Psi(\mathbf{r}, t)\chi_s \tag{6.206}$$

where $\Psi(\mathbf{r}, t)$ is a (spinless) solution of the Schrödinger equation $i\hbar\partial\Psi/\partial t = H\Psi$, and χ_s is the spin function of the particle. From (6.192) and (6.202) the $2s+1$ components of the wave function are then given by

$$\Psi_{m_s}(\mathbf{r}, t) = \Psi(\mathbf{r}, t)a_{m_s}. \tag{6.207}$$

6.8 Spin one-half

In this section we shall now discuss in more detail the simplest non-trivial case of spin quantum mechanics, namely that of particles of spin $s = 1/2$. The non-relativistic theory of spin-1/2 particles was first developed by W. Pauli in 1927. It is a very important case, since *electrons* and *nucleons* (protons and neutrons), the building blocks of atomic and nuclear physics, have spin 1/2. Moreover, it is also believed that all the *hadrons* (the strongly interacting particles), including the proton and the neutron, are made of more elementary constituents, the *quarks*, which also have spin 1/2.

Since for a particle of spin $s = 1/2$ the only possible values of m_s are $m_s = \pm 1/2$, the spin variable σ can only take the *two* values $+\hbar/2$ and $-\hbar/2$, and there are only *two* independent normalised spin eigenfunctions χ_{s,m_s}, namely $\chi_{1/2,1/2}$ and $\chi_{1/2,-1/2}$. We shall denote them by α and β, respectively. Thus

$$\alpha \equiv \chi_{\frac{1}{2},\frac{1}{2}}, \qquad \beta \equiv \chi_{\frac{1}{2},-\frac{1}{2}} \tag{6.208}$$

and we see from (6.184) and (6.185) that

$$\mathbf{S}^2\alpha = \frac{3}{4}\hbar^2\alpha, \qquad \mathbf{S}^2\beta = \frac{3}{4}\hbar^2\beta \tag{6.209}$$

and

$$S_z\alpha = \frac{\hbar}{2}\alpha, \qquad S_z\beta = -\frac{\hbar}{2}\beta. \tag{6.210}$$

The two basic spin-1/2 eigenfunctions α and β are said to correspond respectively to '*spin-up*' (↑) and '*spin-down*' (↓) states. They satisfy the orthonormality relations (see (6.186))

$$\begin{aligned} \langle\alpha|\alpha\rangle &= \langle\beta|\beta\rangle = 1 \\ \langle\alpha|\beta\rangle &= \langle\beta|\alpha\rangle = 0. \end{aligned} \tag{6.211}$$

Introducing the raising and lowering operators

$$S_\pm = S_x \pm \mathrm{i}S_y \tag{6.212}$$

and using the general relations (6.169) and (6.171) with $j = 1/2$ and $m = \pm 1/2$, we find that

$$S_+\alpha = 0, \qquad S_+\beta = \hbar\alpha, \tag{6.213a}$$

$$S_-\alpha = \hbar\beta, \qquad S_-\beta = 0. \tag{6.213b}$$

From (6.210), (6.212) and (6.213) we can construct a table which tells us how the components of $\mathbf{S}$ act on α and β. That is

$$\begin{aligned} S_x\alpha &= \frac{\hbar}{2}\beta, & S_x\beta &= \frac{\hbar}{2}\alpha \\ S_y\alpha &= \frac{\mathrm{i}\hbar}{2}\beta, & S_y\beta &= -\frac{\mathrm{i}\hbar}{2}\alpha \\ S_z\alpha &= \frac{\hbar}{2}\alpha, & S_z\beta &= -\frac{\hbar}{2}\beta \end{aligned} \tag{6.214}$$

According to (6.192), a general wave function for a particle of spin 1/2 can be expanded in terms of the two basic spin states α and β as

$$\Psi(\mathbf{r}, t, \sigma) = \Psi_{1/2}(\mathbf{r}, t)\alpha + \Psi_{-1/2}(\mathbf{r}, t)\beta. \tag{6.215}$$

If we concentrate our attention on the spin variable only, we can, following (6.202), write a general spin-1/2 function as

$$\chi = a\alpha + b\beta \tag{6.216}$$

where in order to simplify the notation we have set $\chi \equiv \chi_{1/2}, a \equiv a_{1/2}$ and $b \equiv a_{-1/2}$. If χ is normalised to unity, so that $\langle\chi|\chi\rangle = 1$, then using (6.211) we have

$$|a|^2 + |b|^2 = 1. \tag{6.217}$$

The probability of finding the particle in the 'spin-up' state α (i.e. the probability that a measurement of S_z will yield the value $+\hbar/2$) is given by $|a|^2$, while $|b|^2$ is the probability of finding the particle in the 'spin-down' state β (i.e. the probability that the value $-\hbar/2$ will be found upon measuring S_z).

Using (6.204) with $s = 1/2$, we see that for an arbitrary spin-1/2 wave function (6.215) we have $\mathbf{S}^2\Psi = (3/4)\hbar^2\Psi$, so that $\mathbf{S}^2$ is the purely numerical operator

$$\mathbf{S}^2 = \frac{3}{4}\hbar^2. \tag{6.218}$$

In addition, it follows from (6.214) that for any spin-1/2 wave function (6.215) one has

$$S_x^2\Psi = \frac{\hbar^2}{4}\Psi \tag{6.219}$$

with a similar result for S_y^2 and S_z^2. We can therefore write

$$S_x^2 = S_y^2 = S_z^2 = \frac{\hbar^2}{4}. \tag{6.220}$$

Let us now explore in more detail the algebra of spin-1/2 operators. From (6.213) we deduce at once that $S_\pm^2 = 0$ and hence, using (6.212) and (6.220), we find that

$$\begin{aligned} 0 = (S_x \pm \mathrm{i}S_y)^2 &= S_x^2 - S_y^2 \pm \mathrm{i}(S_xS_y + S_yS_x) \\ &= \pm\mathrm{i}(S_xS_y + S_yS_x) \end{aligned} \tag{6.221}$$

so that

$$S_xS_y + S_yS_x = 0. \tag{6.222}$$

It is easy to verify (Problem 6.15) that the same relation holds between any different pair of components. If we introduce the *anticommutator* $[A, B]_+$ of two operators A and B, which is defined by the relation

$$[A, B]_+ = AB + BA \tag{6.223}$$

we have

$$[S_x, S_y]_+ = 0, \qquad [S_y, S_z]_+ = 0, \qquad [S_z, S_x]_+ = 0 \tag{6.224}$$

so that the operators S_x, S_y and S_z *anticommute in pairs*. Combining the above anticommutation relations with the basic commutation relations (6.181), we find that

$$S_i S_j = \frac{\mathrm{i}\hbar}{2} S_k \tag{6.225}$$

where $i, j, k = x, y$ or z, in cyclic order. This relation is very useful because when used together with (6.220) it allows one to reduce an arbitrary product of spin-1/2 operators either to a *spin-independent* term or to a term *linear* in S_x, S_y and S_z. For example

$$\begin{aligned} S_x S_y S_z S_y S_z S_x &= S_x S_y S_z S_y \left(\frac{\mathrm{i}\hbar}{2}\right) S_y = S_x S_y S_z \frac{\hbar^2}{4}\left(\frac{\mathrm{i}\hbar}{2}\right) = S_x \left(\frac{\mathrm{i}\hbar}{2}\right) S_x \frac{\hbar^2}{4}\left(\frac{\mathrm{i}\hbar}{2}\right) \\ &= \frac{\hbar^2}{4}\left(\frac{\mathrm{i}\hbar}{2}\right)\frac{\hbar^2}{4}\left(\frac{\mathrm{i}\hbar}{2}\right) = -\frac{\hbar^6}{64} \end{aligned} \tag{6.226a}$$

and

$$\begin{aligned} S_x S_y S_x S_y S_z S_x &= S_x S_y S_x S_y \left(\frac{\mathrm{i}\hbar}{2}\right) S_y = S_x S_y S_x \frac{\hbar^2}{4}\left(\frac{\mathrm{i}\hbar}{2}\right) \\ &= S_x \left(-\frac{\mathrm{i}\hbar}{2}\right) S_z \frac{\hbar^2}{4}\left(\frac{\mathrm{i}\hbar}{2}\right) = \left(-\frac{\mathrm{i}\hbar}{2}\right) S_y \left(-\frac{\mathrm{i}\hbar}{2}\right)\frac{\hbar^2}{4}\left(\frac{\mathrm{i}\hbar}{2}\right) \\ &= -\frac{\mathrm{i}\hbar^5}{32} S_y. \end{aligned} \tag{6.226b}$$

As a result, the most general spin-1/2 operator can be written in the form

$$\begin{aligned} A &= A_0 + A_x S_x + A_y S_y + A_z S_z \\ &= A_0 + \mathbf{A.S} \end{aligned} \tag{6.227}$$

where the operators A_0, A_x, A_y and A_z are spin-independent.

It follows from the general theory of angular momentum which was developed earlier in this chapter that one cannot ascribe any meaning to the statement that the spin vector **S** is in a given direction. Indeed, this would imply that its three components S_x, S_y and S_z could be measured simultaneously with arbitrary precision, which is impossible since they do not commute. In particular, we see from (6.220) that when the particle is in the 'spin-up' state α or the 'spin-down' state β the expectation values of S_x^2 and S_y^2 are given by $\langle S_x^2 \rangle = \langle S_y^2 \rangle = \hbar^2/4$, so that the x- and y-components of the spin are not zero. However, one can speak of the *average* spin direction. For example, if the particle is in the 'spin-up' state α, one finds from (6.211) and (6.214) that the average value of S_z is given by $\langle S_z \rangle = \hbar/2$, while $\langle S_x \rangle = \langle S_y \rangle = 0$. Similarly, if the particle is in the 'spin-down' state β, one has $\langle S_z \rangle = -\hbar/2$ while $\langle S_x \rangle = \langle S_y \rangle = 0$. In what follows it is always in this average sense that a spin-1/2 particle will be said to have its spin 'up' or 'down'. These results, which are particular cases of those

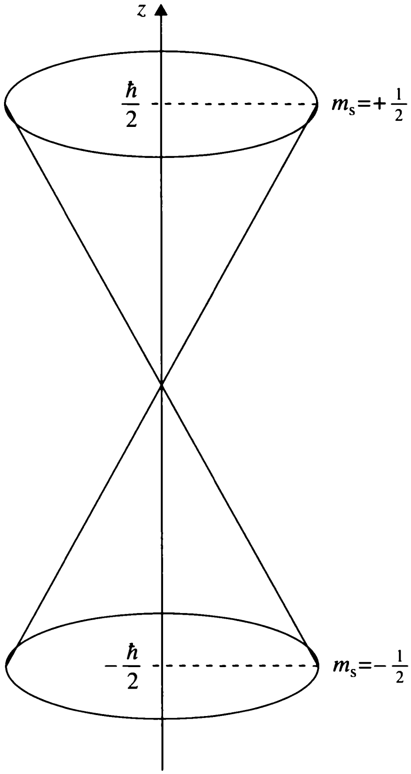


Figure 6.5 The vector model of the spin, for a particle of spin 1/2. The spin vector **S**, of length $\sqrt{3/4}\hbar$, precesses about the *z*-axis, the only allowed projections of **S** on the *z*-axis being $m_s\hbar$, with $m_s = \pm 1/2$.

obtained in Section 6.6 for a general angular momentum (see (6.179) and (6.180)) can conveniently be visualised with the help of the vector model, as illustrated in Fig. 6.5.

If the two basic spin-1/2 eigenvectors α and β are used as a basis, the spin operators are represented by 2 × 2 matrices. Thus, using our previous results (6.175b) with $j = s = 1/2$, we have

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \tag{6.228a}$$

$$S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad \mathbf{S}^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{6.228b}$$

and from (6.172) and (6.173) we also deduce that

$$S_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \qquad S_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \tag{6.229}$$

The normalised spin-1/2 eigenvectors α and β are given by the two component column vectors

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{6.230}$$

and may be considered as the basis vectors of a two-dimensional 'spin space'. The orthonormality relations (6.211) can then be written in the form

$$\begin{aligned} \alpha^\dagger \alpha &= \beta^\dagger \beta = 1 \\ \alpha^\dagger \beta &= \beta^\dagger \alpha = 0 \end{aligned} \tag{6.231}$$

where the Hermitian adjoints $\alpha^\dagger$ and $\beta^\dagger$ are the row vectors

$$\alpha^\dagger = \begin{pmatrix} 1 & 0 \end{pmatrix}, \qquad \beta^\dagger = \begin{pmatrix} 0 & 1 \end{pmatrix}. \tag{6.232}$$

From (6.216) and (6.230), we see that a general spin-1/2 function χ is now represented as

$$\chi = a \begin{pmatrix} 1 \\ 0 \end{pmatrix} + b \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix}. \tag{6.233}$$

If χ is normalised to unity, we have

$$\chi^\dagger \chi = \begin{pmatrix} a^* & b^* \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 1 \tag{6.234}$$

so that $|a|^2 + |b|^2 = 1$, in agreement with (6.217). More generally, if we take into account the position coordinates $\mathbf{r}$ of the particle and the time t, we can write a general wave function (6.215) for a particle of spin 1/2 in the form of a two-component wave function (also called a Pauli wave function)

$$\begin{aligned} \Psi(\mathbf{r}, t, \sigma) &= \Psi_{1/2}(\mathbf{r}, t) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \Psi_{-1/2}(\mathbf{r}, t) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= \begin{pmatrix} \Psi_{1/2}(\mathbf{r}, t) \\ \Psi_{-1/2}(\mathbf{r}, t) \end{pmatrix}. \end{aligned} \tag{6.235}$$

The Pauli spin matrices

When working with the spin operators for spin 1/2, it is convenient to introduce the Pauli vector operator $\boldsymbol{\sigma}$ by the relation

$$\mathbf{S} = \frac{\hbar}{2} \boldsymbol{\sigma}. \tag{6.236}$$

From the basic commutation relations (6.181) we deduce immediately that

$$[\sigma_x, \sigma_y] = 2\mathrm{i}\sigma_z, \qquad [\sigma_y, \sigma_z] = 2\mathrm{i}\sigma_x, \qquad [\sigma_z, \sigma_x] = 2\mathrm{i}\sigma_y \tag{6.237}$$

and by using (6.220) we infer that

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1. \tag{6.238}$$

We also note from (6.224) that σ_x, σ_y and σ_z anticommute in pairs, so that we may write

$$[\sigma_i, \sigma_j]_+ = 2\delta_{ij} \qquad (i, j = x, y \text{ or } z). \tag{6.239}$$

From (6.225) and (6.236) we also have

$$\sigma_i \sigma_j = \mathrm{i}\sigma_k \tag{6.240}$$

where $i, j, k = x, y$ or z, in cyclic order. From (6.239) and (6.240) it also follows (Problem 6.16) that

$$(\boldsymbol{\sigma}.\mathbf{A})(\boldsymbol{\sigma}.\mathbf{B}) = \mathbf{A}.\mathbf{B} + \mathrm{i}\boldsymbol{\sigma}.(\mathbf{A} \times \mathbf{B}) \tag{6.241}$$

where **A** and **B** are two vectors, or two vector operators whose components commute with those of $\boldsymbol{\sigma}$. In the latter case the order of **A** and **B** on both sides of (6.241) must be respected. For example

$$(\boldsymbol{\sigma}.\mathbf{r})(\boldsymbol{\sigma}.\mathbf{p}) = \mathbf{r}.\mathbf{p} + \mathrm{i}\boldsymbol{\sigma}.(\mathbf{r} \times \mathbf{p}). \tag{6.242}$$

Using (6.236) and the matrix representation (6.228) of the spin-1/2 operators S_x, S_y and S_z, we find that σ_x, σ_y and σ_z are represented by the matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{6.243}$$

which are known as the *Pauli spin matrices*. We see that the traces of all Pauli spin matrices vanish,

$$\mathrm{Tr}\sigma_x = \mathrm{Tr}\sigma_y = \mathrm{Tr}\sigma_z = 0 \tag{6.244}$$

and that

$$\det\sigma_x = \det\sigma_y = \det\sigma_z = -1 \tag{6.245}$$

where det means the determinant. Moreover, the unit 2 × 2 matrix I and the three Pauli matrices (6.243) are four linearly independent matrices. They form a complete set of 2 × 2 matrices, in the sense that an arbitrary 2 × 2 matrix can always be expressed as a linear combination of I, σ_x, σ_y and σ_z, with coefficients which can be complex.

Eigenvalues and eigenfunctions of an arbitrary spin-1/2 component

Let $\hat{\mathbf{n}}$ be a unit vector with polar angles (θ, ϕ) as shown in Fig. 6.6. The component of the spin vector **S** along $\hat{\mathbf{n}}$ is $S_n = \hat{\mathbf{n}}.\mathbf{S}$. In order to find the eigenvalues and eigenfunctions of S_n, we must solve the eigenvalue equation

$$S_n \chi = \nu\hbar\chi \tag{6.246}$$

where we have written the eigenvalue as $\nu\hbar$ for further convenience. Since the Cartesian components of $\hat{\mathbf{n}}$ are $(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, we find with the help

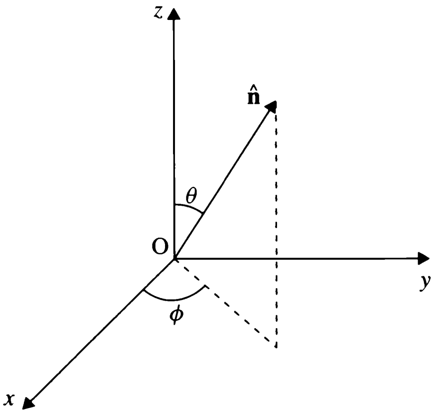


Figure 6.6 The unit vector $\hat{\mathbf{n}}$ of the text, having spherical polar angles (θ, ϕ).

of (6.228) that

$$\begin{aligned} S_n &= S_x \sin\theta\cos\phi + S_y \sin\theta\sin\phi + S_z\cos\theta \\ &= \frac{\hbar}{2}\begin{pmatrix} \cos\theta & \sin\theta e^{-i\phi} \\ \sin\theta e^{i\phi} & -\cos\theta \end{pmatrix}. \end{aligned} \tag{6.247}$$

Writing the spin function as $\chi = \begin{pmatrix} a \\ b \end{pmatrix}$, we have

$$S_n\chi = \frac{\hbar}{2}\begin{pmatrix} a\cos\theta + b\sin\theta e^{-i\phi} \\ a\sin\theta e^{i\phi} - b\cos\theta \end{pmatrix}. \tag{6.248}$$

Hence (6.246) reduces to the set of two linear, homogeneous equations

$$(\cos\theta - 2\nu)a + \sin\theta e^{-i\phi} b = 0 \tag{6.249a}$$

$$\sin\theta e^{i\phi} a - (\cos\theta + 2\nu) b = 0 \tag{6.249b}$$

which have non-trivial solutions only if

$$\begin{vmatrix} \cos\theta - 2\nu & \sin\theta e^{-i\phi} \\ \sin\theta e^{i\phi} & -(\cos\theta + 2\nu) \end{vmatrix} = 0. \tag{6.250}$$

The determinant on the left-hand side being equal to $4\nu^2 - 1$, we must have $\nu = \pm 1/2$.

If $\nu = +1/2$, we see from (6.249) that

$$\frac{b}{a} = \tan\frac{\theta}{2} e^{i\phi}. \tag{6.251}$$

Hence, apart from an irrelevant phase factor common to a and b the corresponding spin function $\chi_\uparrow$, normalised according to (6.234), may be written as

$$\chi_\uparrow = \begin{pmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2} e^{i\phi} \end{pmatrix}. \tag{6.252}$$

We note that the expectation values of the components of **S** in this state $\chi_\uparrow$ are (Problem 6.17)

$$\begin{aligned}\langle S_x\rangle &= \frac{\hbar}{2}\sin\theta\cos\phi \\ \langle S_y\rangle &= \frac{\hbar}{2}\sin\theta\sin\phi \\ \langle S_z\rangle &= \frac{\hbar}{2}\cos\theta\end{aligned} \tag{6.253}$$

so that the polar angles θ and ϕ give the direction of $\langle\mathbf{S}\rangle$. In this sense we shall say that the spin is 'up' in the direction of $\hat{\mathbf{n}}$. Using (6.233), we also remark that if the z-component of the spin of a particle in the state $\chi_\uparrow$ is measured, the probability of finding the spin 'up' is $|a|^2 = \cos^2(\theta/2)$. As θ varies between 0 and π, $|a|^2$ varies between 1 and 0.

If $\nu = -1/2$, we have from (6.249),

$$\frac{b}{a} = -\cot\frac{\theta}{2}\mathrm{e}^{\mathrm{i}\phi} \tag{6.254}$$

and the corresponding normalised spin function $\chi_\downarrow$ may be written (apart from an arbitrary phase factor common to a and b) as

$$\chi_\downarrow = \begin{pmatrix}\sin\frac{\theta}{2} \\ -\cos\frac{\theta}{2}\mathrm{e}^{\mathrm{i}\phi}\end{pmatrix}. \tag{6.255}$$

Upon calculating the expectation values of the components of **S** in the state $\chi_\downarrow$, it is readily verified (Problem 6.17) that the direction of $\langle\mathbf{S}\rangle$ is now given by the polar angles $(\pi - \theta, \phi + \pi)$, and we shall say that the spin is 'down' in the $\hat{\mathbf{n}}$ direction.

It is a simple matter to check (Problem 6.18) that the two spin functions $\chi_\uparrow$ and $\chi_\downarrow$ form a complete orthonormal set. We also remark that when $\theta = 0$ the spin function $\chi_\uparrow$ reduces to

$$\alpha = \begin{pmatrix}1\\0\end{pmatrix},$$

while the spin function $\chi_\downarrow$ reduces (apart from a phase factor) to

$$\beta = \begin{pmatrix}0\\1\end{pmatrix},$$

as expected.

6.9 Total angular momentum

Let us conside a particle which possesses a spin angular momentum. If **S** denotes its spin angular momentum operator, and **L** its orbital angular momentum operator, the *total angular momentum operator* of this particle is

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \tag{6.256}$$

Since the orbital angular momentum **L** and the spin angular momentum **S** operate on different variables (**L** operates on the angular variables and **S** on the spin variable), all the components of **L** commute with all those of **S**. As a result, the commutation relations for the components of **J** are the same as those for the components of **L** and those of **S**, and are given by (6.139).

More generally, let us consider an isolated system of N particles. Its total angular momentum operator is the sum of the angular momentum operators of the individual particles,

$$\mathbf{J} = \sum_{i=1}^{N} \mathbf{J}_i \tag{6.257}$$

where $\mathbf{J}_i$, the angular momentum operator of the ith particle, is the sum of its orbital angular momentum operator $\mathbf{L}_i$ and of its spin angular momentum operator $\mathbf{S}_i$ (if any)

$$\mathbf{J}_i = \mathbf{L}_i + \mathbf{S}_i. \tag{6.258}$$

Note that (6.257) may also be written in the form of equation (6.256), provided that **L** now denotes the *total orbital angular momentum* operator of the system, as defined by (6.23), and **S** is now the *total spin* operator

$$\mathbf{S} = \sum_{i=1}^{N} \mathbf{S}_i. \tag{6.259}$$

We observed at the end of Section 6.1 that because operators acting on different, independent variables commute, all the components of $\mathbf{L}_i$ commute with all those of $\mathbf{L}_k$ when $i \neq k$, so that the components of the total orbital angular momentum **L** obey the same basic commutation relations (6.25) as those obtained for the case of a single particle. Likewise, when $i \neq k$ all the components of $\mathbf{S}_i$ commute with all those of $\mathbf{S}_k$, and all the components of $\mathbf{J}_i$ commute with all those of $\mathbf{J}_k$. As a consequence, the components of the total spin operator (6.259) and those of the total angular momentum operator (6.257) also obey the basic commutation relations (6.139) characteristic of angular momenta.

Total angular momentum and rotations

In Section 6.2 we considered the effect of spatial rotations on an isolated system of N *spinless* particles, and we found that the component of the total orbital angular momentum **L** along an axis is the generator of infinitesimal rotations about that axis (see (6.43)). The *key properties* of the generators L_x, L_y and L_z corresponding respectively to infinitesimal rotations about the x-, y- and z-axes are the basic *commutation relations* (6.25). Similarly, the generators $L_u \equiv \hat{\mathbf{u}}.\mathbf{L}$, $L_v \equiv \hat{\mathbf{v}}.\mathbf{L}$ and $L_w \equiv \hat{\mathbf{w}}.\mathbf{L}$

corresponding respectively to infinitesimal rotations about the three orthogonal unit vectors $\hat{\mathbf{u}}$, $\hat{\mathbf{v}}$ and $\hat{\mathbf{w}} = \hat{\mathbf{u}} \times \hat{\mathbf{v}}$ satisfy the basic commutation relations (6.21).

Likewise, in the case of a system of particles possessing both orbital angular momentum and spin, we can take the generators of infinitesimal rotations about the x-, y- and z-axes to be given respectively by the Cartesian components J_x, J_y and J_z of the *total* angular momentum **J** of the system, which satisfy the basic commutation relations (6.139). In the same way, the generators of infinitesimal rotations about the three orthogonal unit vectors $\hat{\mathbf{u}}$, $\hat{\mathbf{v}}$ and $\hat{\mathbf{w}} = \hat{\mathbf{u}} \times \hat{\mathbf{v}}$ can be taken, respectively, to be the components $J_u \equiv \hat{\mathbf{u}}.\mathbf{J}$, $J_v \equiv \hat{\mathbf{v}}.\mathbf{J}$ and $J_w \equiv \hat{\mathbf{w}}.\mathbf{J}$ which also satisfy the basic commutation relations (see (6.141)). Thus, in analogy with (6.43), the unitary operator corresponding to an infinitesimal rotation by an angle $\delta\alpha$ in the positive sense about an axis oriented along an arbitrary vector $\hat{\mathbf{n}}$ is now given by

$$U_{\hat{\mathbf{n}}}(\delta\alpha) = I - \frac{\mathrm{i}}{\hbar}\delta\alpha\hat{\mathbf{n}}.\mathbf{J} \tag{6.260}$$

and we shall say that the *total* angular momentum **J** of the system is the *generator of infinitesimal rotations* in the combined space of spatial plus spin variables. The unitary operator corresponding to a *finite* rotation of angle α about $\hat{\mathbf{n}}$ is

$$U_{\hat{\mathbf{n}}}(\alpha) = \exp\left(-\frac{\mathrm{i}}{\hbar}\alpha\hat{\mathbf{n}}.\mathbf{J}\right) \tag{6.261}$$

which is the direct generalisation of (6.51). From (6.26) and (6.261) the state vector describing the system must therefore transform under a rotation of angle α about $\hat{\mathbf{n}}$ as

$$\begin{aligned}\Psi' &= U_{\hat{\mathbf{n}}}(\alpha)\Psi \\ &= \exp\left(-\frac{\mathrm{i}}{\hbar}\alpha\hat{\mathbf{n}}.\mathbf{J}\right)\Psi.\end{aligned} \tag{6.262}$$

Since the Hamiltonian of an isolated system is invariant under rotations, and because **J** is the generator of infinitesimal rotations, it follows from (6.31) and (6.260) that for an isolated system

$$[\mathbf{J}, H] = 0 \tag{6.263}$$

so that the *total angular momentum is conserved.* Conversely, if the Hamiltonian H of a system of particles commutes with the total angular momentum operator **J**, then H is invariant under rotations. Equation (6.263) is the generalisation of equation (6.53) to particles or systems of particles which may possess a spin angular momentum. From (6.263) and (6.144) it follows that the operators H, $\mathbf{J}^2$ and J_z mutually commute, so that the eigenfunctions of H can be searched for among those common to $\mathbf{J}^2$ and J_z, a fact which greatly simplifies the eigenvalue problem of H. If the eigenvalues of $\mathbf{J}^2$ and J_z are denoted respectively by $j(j+1)\hbar^2$ and $m\hbar$, the energy eigenvalues corresponding to the same value of j but different values of m must be identical. This is because there is no preferred direction of space for an isolated system, so that the energy eigenvalues cannot depend on the projection of the total angular momentum on the z-axis, and hence are independent of the quantum number m.

Rotations in 'spin space'

Let us return to the equation (6.262), which tells us how the state vector describing a system transforms under a rotation of angle α about the unit vector $\hat{\mathbf{n}}$. In what follows we shall concentrate on the transformation properties of *spin* functions under rotations. Since $\mathbf{J} = \mathbf{L} + \mathbf{S}$ and the orbital angular momentum $\mathbf{L}$ acts only on the angular variables, it follows from (6.262) that under a rotation of angle α about $\hat{\mathbf{n}}$, a spin function χ_s for a particle of spin s transforms into a new spin function χ'_s such that

$$\chi'_s = \exp\left(-\frac{\mathrm{i}}{\hbar}\alpha\hat{\mathbf{n}}.\mathbf{S}\right)\chi_s. \tag{6.264}$$

In particular, for a spin-1/2 particle we have (dropping the subscript 1/2)

$$\begin{aligned}\chi' &= \exp\left(-\mathrm{i}\frac{\alpha}{2}\hat{\mathbf{n}}.\boldsymbol{\sigma}\right)\chi \\ &= \left(I\cos\frac{\alpha}{2} - \mathrm{i}\hat{\mathbf{n}}.\boldsymbol{\sigma}\sin\frac{\alpha}{2}\right)\chi\end{aligned} \tag{6.265}$$

where I denotes the unit 2×2 matrix and we have used the equations (6.236) and (6.241). For example, in the case of a rotation of angle α about the z-axis we have

$$\begin{aligned}\chi' &= \left(I\cos\frac{\alpha}{2} - \mathrm{i}\sigma_z\sin\frac{\alpha}{2}\right)\chi \\ &= \begin{pmatrix} \mathrm{e}^{-\mathrm{i}\alpha/2} & 0 \\ 0 & \mathrm{e}^{\mathrm{i}\alpha/2}\end{pmatrix}\chi.\end{aligned} \tag{6.266}$$

An object χ with one column and two rows which transforms under spatial rotations according to (6.265) is called a *spinor*. We remark that if a full rotation of angle $\alpha = 2\pi$ is made, we have $\chi' = -\chi$. This change of sign of spinors under rotations should not deter us from using them, since all the matrix elements giving measurable quantities (such as expectation values) depend bi-linearly on the spinors.

Let us now return to (6.264) giving the transformation property of a general spin function under rotations. For a rotation of angle α about the z-axis, we have

$$\chi'_s = \exp\left(-\frac{\mathrm{i}}{\hbar}\alpha S_z\right)\chi_s. \tag{6.267}$$

Using (6.185) and (6.202), we see that for a rotation of angle $\alpha = 2\pi$

$$\begin{aligned}\chi'_s &= \exp(-2\pi\mathrm{i}m_s)\chi_s \\ &= (-1)^{2m_s}\chi_s = (-1)^{2s}\chi_s\end{aligned} \tag{6.268}$$

where we have used the fact that $2s$ has the same parity as $2m_s$. Hence, when a full rotation of angle 2π is made, the wave functions corresponding to particles of integer spin return to their original values, while those corresponding to half-odd integer values of $s(s = 1/2, 3/2, \dots)$ change sign.

6.10 The addition of angular momenta

In many situations of physical interest we are dealing with systems whose Hamiltonian H is invariant under rotations, and hence commutes with the total angular momentum operator $\mathbf{J}$ (see (6.263)). We can then search for the eigenfunctions of H among the simultaneous eigenfunctions of $\mathbf{J}^2$ and J_z. Consequently, it is very important to determine the common eigenfunctions of $\mathbf{J}^2$ and J_z.

Now, the total angular momentum operator $\mathbf{J}$ of a system is in general a sum of angular momentum operators referring either to distinct sets of dynamical variables of the system (such as the orbital angular momentum $\mathbf{L}$ and the spin angular momentum $\mathbf{S}$ of equation (6.256)) or to distinct sub-systems (such as the individual angular momenta $\mathbf{J}_i$ of equation (6.257)). Since these 'separate' angular momenta whose sum gives $\mathbf{J}$ correspond to distinct, independent quantities, they all mutually commute (i.e. all the components of one of them commute with all the components of the others). In addition, the components of each separate angular momentum satisfy the basic commutation relations (6.139). As observed in Section 6.9, it follows that the components of $\mathbf{J}$ also satisfy the commutation relations (6.139) characteristic of angular momenta. Thus simultaneous eigenvectors of $\mathbf{J}^2$ and J_z can be found, which correspond to eigenvalues $j(j+1)\hbar^2$ and $m\hbar$, respectively. As usual, for a given value of j the quantum number m can take one of the $2j+1$ values $-j, -j+1, \dots, j$. Now, in general, we can obtain the eigenvectors and eigenvalues of the 'separate' angular momentum operators. The addition problem consists of determining the eigenvectors and eigenvalues of $\mathbf{J}^2$ and J_z in terms of those of the separate, independent angular momentum operators.

In what follows we shall treat the simplest addition problem, namely that of adding *two* commuting angular momenta. Thus we have

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2 \tag{6.269}$$

where $\mathbf{J}_1$ and $\mathbf{J}_2$ are any two angular momenta corresponding respectively to the independent sub-systems (or sets of dynamical variables) 1 and 2.

Let $|j_1 m_1\rangle$ be a normalised simultaneous eigenvector of $\mathbf{J}_1^2$ and J_{1z}, so that

$$\mathbf{J}_1^2 |j_1 m_1\rangle = j_1(j_1 + 1)\hbar^2 |j_1 m_1\rangle \tag{6.270}$$

and

$$J_{1z} |j_1 m_1\rangle = m_1 \hbar |j_1 m_1\rangle. \tag{6.271}$$

Similary, let $|j_2 m_2\rangle$ be a normalised simultaneous eigenvector of $\mathbf{J}_2^2$ and J_{2z}, whence

$$\mathbf{J}_2^2 |j_2 m_2\rangle = j_2(j_2+1)\hbar^2 |j_2 m_2\rangle \tag{6.272}$$

and

$$J_{2z} |j_2 m_2\rangle = m_2 \hbar |j_2 m_2\rangle. \tag{6.273}$$

A normalised simultaneous eigenvector of $\mathbf{J}_1^2$, $\mathbf{J}_2^2$, J_{1z} and J_{2z} belonging respectively to the eigenvalues $j_1(j_1+1)\hbar^2$, $j_2(j_2+1)\hbar^2$, $m_1\hbar$ and $m_2\hbar$ is therefore given by the 'direct product'

$$|j_1 j_2 m_1 m_2\rangle = |j_1 m_1\rangle |j_2 m_2\rangle. \tag{6.274}$$

For a fixed value of j_1, m_1 can take one of the $2j_1+1$ values $-j_1, -j_1+1, \ldots, j_1$, and for a fixed value of j_2 the $2j_2+1$ allowed values of m_2 are $-j_2, -j_2+1, \ldots, j_2$. Hence, for given values of j_1 and j_2 there are $(2j_1+1)(2j_2+1)$ 'direct products' (6.274) which form a complete orthonormal set, i.e. a basis in the 'product space' of the combined system $(1+2)$.

It is instructive to rewrite the direct products (6.274) in a more explicit way. Suppose that instead of using the abstract eigenvector $|j_1 m_1\rangle$ we denote by $\psi_{j_1 m_1}(1)$ a normalised simultaneous eigenfunction of $\mathbf{J}_1^2$ and J_{1z} corresponding respectively to the eigenvalues $j_1(j_1+1)\hbar^2$ and $m_1\hbar$. Likewise, instead of using the abstract eigenvector $|j_2 m_2\rangle$ let us denote by $\psi_{j_2 m_2}(2)$ a normalised simultaneous eigenfunction of $\mathbf{J}_2^2$ and J_{2z} belonging to the eigenvalues $j_2(j_2+1)\hbar^2$ and $m_2\hbar$, respectively. The normalised simultaneous eigenfunctions of $\mathbf{J}_1^2$, $\mathbf{J}_2^2$, J_{1z} and J_{2z} corresponding respectively to the eigenvalues $j_1(j_1+1)\hbar^2$, $j_2(j_2+1)\hbar^2$, $m_1\hbar$ and $m_2\hbar$ are then given by

$$\psi_{j_1 j_2 m_1 m_2}(1,2) = \psi_{j_1 m_1}(1)\psi_{j_2 m_2}(2). \tag{6.275}$$

We emphasise that when operating on $\psi_{j_1 j_2 m_1 m_2}(1,2)$ the components of $\mathbf{J}_1$ only act on the variables denoted collectively by 1, while the components of $\mathbf{J}_2$ only act on the variables denoted by 2. In particular, from (6.269) and (6.275) we have

$$\begin{aligned} J_z \psi_{j_1 j_2 m_1 m_2}(1,2) &= (J_{1z}+J_{2z})\psi_{j_1 m_1}(1)\psi_{j_2 m_2}(2) \\ &= [J_{1z}\psi_{j_1 m_1}(1)]\psi_{j_2 m_2}(2) + \psi_{j_1 m_1}(1)[J_{2z}\psi_{j_2 m_2}(2)] \\ &= m_1\hbar\psi_{j_1 m_1}(1)\psi_{j_2 m_2}(2) + m_2\hbar\psi_{j_1 m_1}(1)\psi_{j_2 m_2}(2) \\ &= (m_1+m_2)\hbar\ \psi_{j_1 j_2 m_1 m_2}(1,2) \end{aligned} \tag{6.276}$$

which means that $\psi_{j_1 j_2 m_1 m_2}(1,2)$ is also an eigenfunction of J_z corresponding to the eigenvalue $(m_1+m_2)\hbar$. In terms of abstract eigenvectors we can write the above result as

$$J_z |j_1 j_2 m_1 m_2\rangle = (m_1+m_2)\hbar\ |j_1 j_2 m_1 m_2\rangle. \tag{6.277}$$

The fact that simultaneous eigenfunctions of $\mathbf{J}_1^2$, $\mathbf{J}_2^2$, J_{1z} and J_{2z} are also eigenfunctions of J_z could have been anticipated by noting that $J_z = J_{1z} + J_{2z}$ commutes with $\mathbf{J}_1^2$, $\mathbf{J}_2^2$, J_{1z} and J_{2z}.

Let us now consider the operator $\mathbf{J}^2$. From (6.269) we have

$$\mathbf{J}^2 = (\mathbf{J}_1 + \mathbf{J}_2)^2 = \mathbf{J}_1^2 + \mathbf{J}_2^2 + 2\mathbf{J}_1.\mathbf{J}_2. \qquad \textbf{(6.278a)}$$

Because all the components of $\mathbf{J}_1$ commute with all those of $\mathbf{J}_2$, and since $[\mathbf{J}_1^2, \mathbf{J}_1] = [\mathbf{J}_2^2, \mathbf{J}_2] = 0$ it follows that $\mathbf{J}^2$ commutes with $\mathbf{J}_1^2$ and $\mathbf{J}_2^2$. However, as

$$\mathbf{J}_1.\mathbf{J}_2 = J_{1x}J_{2x} + J_{1y}J_{2y} + J_{1z}J_{2z} \qquad \textbf{(6.278b)}$$

and since J_{1z} does not commute with J_{1x} or J_{1y}, we see that $\mathbf{J}^2$ does *not* commute with J_{1z}; likewise $\mathbf{J}^2$ does *not* commute with J_{2z}. Consequently, the simultaneous eigenfunctions of $\mathbf{J}^2$ and J_z are eigenfunctions of $\mathbf{J}_1^2$ and $\mathbf{J}_2^2$, but not (in general) of J_{1z} and J_{2z}. There are therefore two complete, but distinct descriptions of the system: either in terms of the eigenfunctions of $\mathbf{J}_1^2$, $\mathbf{J}_2^2$, J_{1z} and J_{2z}, given by (6.275), or in terms of the eigenfunctions of $\mathbf{J}_1^2$, $\mathbf{J}_2^2$, $\mathbf{J}^2$ and J_z. We shall denote the latter (normalised to unity) by $\Phi_{j_1 j_2}^{jm}(1,2)$. Thus we have in particular

$$\mathbf{J}^2\Phi_{j_1 j_2}^{jm}(1,2) = j(j+1)\hbar^2\Phi_{j_1 j_2}^{jm}(1,2) \qquad \textbf{(6.279)}$$

and

$$\mathbf{J}_z\Phi_{j_1 j_2}^{jm}(1,2) = m\hbar\Phi_{j_1 j_2}^{jm}(1,2). \qquad \textbf{(6.280)}$$

Like the functions $\psi_{j_1 j_2 m_1 m_2}(1,2)$, the functions $\Phi_{j_1 j_2}^{jm}(1,2)$ form a complete orthonormal set, and hence are another basis in the 'product space' of the system $(1+2)$. These two basis sets of orthonormal eigenfunctions can therefore be related by a *unitary* transformation

$$\Phi_{j_1 j_2}^{jm}(1,2) = \sum_{m_1 m_2} \langle j_1 j_2 m_1 m_2 | jm\rangle \psi_{j_1 j_2 m_1 m_2}(1,2) \qquad \textbf{(6.281)}$$

where the summation must only be performed over m_1 and m_2, since j_1 and j_2 are assumed to have fixed values. The coefficients $\langle j_1 j_2 m_1 m_2 | jm\rangle$ of that unitary transformation are called *Clebsch–Gordan* or *vector addition coefficients*. In the Dirac notation we can write the unitary transformation (6.281) as

$$|j_1 j_2 jm\rangle = \sum_{m_1 m_2} \langle j_1 j_2 m_1 m_2 | jm\rangle |j_1 j_2 m_1 m_2\rangle \qquad \textbf{(6.282)}$$

where $|j_1 j_2 m_1 m_2\rangle$ is given by (6.274).

In order to find out what are the allowed values of j for given j_1 and j_2 we proceed as follows. We first notice that since $\psi_{j_1 j_2 m_1 m_2}$ is an eigenfunction of J_z belonging to the eigenvalue $(m_1 + m_2)\hbar$ (see (6.276)) we must have

$$m = m_1 + m_2 \qquad \textbf{(6.283)}$$

so that the double sum in (6.282) reduces to a single sum. In other words the Clebsch–Gordan coefficients must vanish unless $m = m_1 + m_2$:

$$\langle j_1 j_2 m_1 m_2 | jm\rangle = 0 \qquad \text{if} \qquad m \neq m_1 + m_2. \qquad \textbf{(6.284)}$$

Moreover, because the maximum allowed values of m_1 and m_2 are given respectively by j_1 and j_2, the relation (6.283) tells us that the maximum possible value of m is $j_1 + j_2$. Since m can only take on the $2j + 1$ values $-j, -j + 1, \dots, j$, it follows that the maximum possible value of j is $j_1 + j_2$. We remark that for $j = j_1 + j_2$ and $m = j_1 + j_2$ there is only one term in the sum on the right of (6.282), namely that corresponding to $m_1 = j_1$ and $m_2 = j_2$. Thus

$$\Phi_{j_1 j_2}^{j_1+j_2, j_1+j_2}(1,2) = \langle j_1 j_2 j_1 j_2 | j_1 + j_2, j_1 + j_2 \rangle \psi_{j_1 j_2 j_1 j_2}(1,2) \qquad \textbf{(6.285)}$$

and since the eigenfunctions $\Phi_{j_1 j_2}^{jm}$ and $\psi_{j_1 j_2 m_1 m_2}$ are normalised to unity, we have

$$|\langle j_1 j_2 j_1 j_2 | j_1 + j_2, j_1 + j_2 \rangle| = 1. \qquad \textbf{(6.286)}$$

Next, let us consider a state $\Phi_{j_1 j_2}^{jm}$ for which $m = j_1 + j_2 - 1$. In this case there are two possibilities for the values of m_1 and m_2: we can either have $m_1 = j_1$ and $m_2 = j_2 - 1$ or $m_1 = j_1 - 1$ and $m_2 = j_2$. Thus a state $\Phi_{j_1 j_2}^{j, j_1+j_2-1}$ must be a linear combination of the two linearly independent eigenfunctions $\psi_{j_1 j_2 j_1 j_2 - 1}$ and $\psi_{j_1 j_2 j_1 - 1 j_2}$. Moreover, there are two such linear combinations, one of them belonging to the set of eigenfunctions with $j = j_1 + j_2$ while the other (orthogonal) combination must be a member of a set of eigenfunctions for which the maximum value of m is $j_1 + j_2 - 1$; this latter set must therefore be such that $j = j_1 + j_2 - 1$. Proceeding further to states $\Phi_{j_1 j_2}^{jm}$ with $m = j_1 + j_2 - 2$, we see that three linearly independent states of this kind exist, corresponding to the values $j = j_1 + j_2$, $j_1 + j_2 - 1$ and $j_1 + j_2 - 2$, respectively. Repeating this argument successively, it is found that the minimum value of j is $|j_1 - j_2|$, because when j reaches this smallest value all the combinations have been exhausted. This is readily checked by noting that there must be the same number of eigenfunctions in the basis set $\{\Phi_{j_1 j_2}^{jm}\}$ as in the basis set $\{\psi_{j_1 j_2 m_1 m_2}\}$. As we have shown above, the latter set contains $(2j_1 + 1)(2j_2 + 1)$ eigenfunctions. Now, for each value of j there are $2j + 1$ values of m so that the total number of eigenfunctions $\Phi_{j_1 j_2}^{jm}$ is given by

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j + 1) = (2j_1 + 1)(2j_2 + 1). \qquad \textbf{(6.287)}$$

This is illustrated in Table 6.2 for the case $j_1 = 1$, $j_2 = 3/2$, where the number of $(m_1 m_2)$ and of (jm) combinations are both seen to be equal to 12.

We have therefore obtained the following fundamental result: for given values of j_1 and j_2 the allowed values of j are

$$j = |j_1 - j_2|, |j_1 - j_2| + 1, \dots, j_1 + j_2 \qquad \textbf{(6.288)}$$

so that the three angular momentum quantum numbers j_1, j_2 and j must satisfy the *triangular condition*

$$|j_1 - j_2| \leqslant j \leqslant j_1 + j_2. \qquad \textbf{(6.289)}$$

Moreover, for each value of j there are $2j + 1$ eigenfunctions $\Phi_{j_1 j_2}^{jm}$, such that $m = -j, -j + 1, \dots, +j$.

Table 6.2 Allowed values of $(m_1 m_2)$ and (jm) for $j_1 = 1$ and $j_2 = 3/2$.

m_1	m_2	m	j
1	3/2	5/2	5/2
0 1	3/2 1/2	3/2	5/2,3/2
−1 0 1	3/2 1/2 −1/2	1/2	5/2,3/2,1/2
−1 0 1	1/2 −1/2 −3/2	−1/2	5/2,3/2,1/2
−1 0	−1/2 −3/2	−3/2	5/2,3/2
−1	−3/2	−5/2	5/2
Total: $(2j_1+1)(2j_2+1) = 12$		Total: $\sum_{j=\lvert j_1-j_2\rvert}^{j_1+j_2} (2j+1) = 12$	

The Clebsch–Gordan coefficients $\langle j_1 j_2 m_1 m_2 | jm\rangle$ can be determined by applying the raising and lowering operators $J_\pm = J_x \pm \mathrm{i}J_y$ to (6.281) (or (6.282)), so that recursion relations are obtained. First of all, it follows from the foregoing discussion that they must satisfy the *selection rules* (6.283) and (6.289). Furthermore, in order that this determination be unambiguous, the relative phases of the eigenvectors $|j_1 j_2 m_1 m_2\rangle$ and $|j_1 j_2 jm\rangle$ must be specified. A frequently used convention, which we shall adopt here, is that of Condon and Shortely and of Wigner, namely

(1) $$J_\pm |j_1 j_2 jm\rangle = [j(j+1) - m(m\pm 1)]^{1/2}\hbar |j_1 j_2 jm \pm 1\rangle \qquad \textbf{(6.290a)}$$

with similar relationships for $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ (see (6.169) and (6.171)); and

(2) $\langle j_1 j_2 j_1 (j - j_1) | jj\rangle$ is real and positive. **(6.290b)**

With this phase convention, the Clebsch–Gordan coefficients are real. It can also be proved[8] that they satisfy the orthogonality relations

$$\sum_{m_1 m_2} \langle j_1 j_2 m_1 m_2 | jm\rangle\langle j_1 j_2 m_1 m_2 | j'm'\rangle = \delta_{jj'}\delta_{mm'}$$

$$\sum_{jm} \langle j_1 j_2 m_1 m_2 | jm\rangle\langle j_1 j_2 m'_1 m'_2 | jm\rangle = \delta_{m_1 m'_1}\delta_{m_2 m'_2} \qquad \textbf{(6.291)}$$

---

[8] See, for example, Edmonds (1957).

Table 6.3 Clebsch–Gordan coefficients.

$\langle j_1 \tfrac{1}{2} m_1 m_2 | jm\rangle$

j	$m_2 = \frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j_1 + \frac{1}{2}$	$\left(\frac{j_1+m+\frac{1}{2}}{2j_1+1}\right)^{1/2}$	$\left(\frac{j_1-m+\frac{1}{2}}{2j_1+1}\right)^{1/2}$
$j_1 - \frac{1}{2}$	$-\left(\frac{j_1-m+\frac{1}{2}}{2j_1+1}\right)^{1/2}$	$\left(\frac{j_1+m+\frac{1}{2}}{2j_1+1}\right)^{1/2}$

$\langle j_1 1 m_1 m_2 | jm\rangle$

j	$m_2 = 1$	$m_2 = 0$	$m_2 = -1$
$j_1 + 1$	$\left[\frac{(j_1+m)(j_1+m+1)}{(2j_1+1)(2j_1+2)}\right]^{1/2}$	$\left[\frac{(j_1-m+1)(j_1+m+1)}{(2j_1+1)(j_1+1)}\right]^{1/2}$	$\left[\frac{(j_1-m)(j_1-m+1)}{(2j_1+1)(2j_1+2)}\right]^{1/2}$
j_1	$-\left[\frac{(j_1+m)(j_1-m+1)}{2j_1(j_1+1)}\right]^{1/2}$	$\left[\frac{m^2}{j_1(j_1+1)}\right]^{1/2}$	$\left[\frac{(j_1-m)(j_1+m+1)}{2j_1(j_1+1)}\right]^{1/2}$
$j_1 - 1$	$\left[\frac{(j_1-m)(j_1-m+1)}{2j_1(2j_1+1)}\right]^{1/2}$	$-\left[\frac{(j_1-m)(j_1+m)}{j_1(2j_1+1)}\right]^{1/2}$	$\left[\frac{(j_1+m+1)(j_1+m)}{2j_1(2j_1+1)}\right]^{1/2}$

and the symmetry relations

$$\begin{aligned}
\langle j_1 j_2 m_1 m_2 | jm\rangle &= (-)^{j_1+j_2-j}\langle j_2 j_1 m_2 m_1 | jm\rangle \\
&= (-)^{j_1+j_2-j}\langle j_1 j_2 - m_1 - m_2 | j - m\rangle \\
&= \langle j_2 j_1 - m_2 - m_1 | j - m\rangle \\
&= (-)^{j_1-m_1}\left(\frac{2j+1}{2j_2+1}\right)^{1/2}\langle j_1 j m_1 - m | j_2 - m_2\rangle \\
&= (-)^{j_2+m_2}\left(\frac{2j+1}{2j_1+1}\right)^{1/2}\langle j j_2 - m m_2 | j_1 - m_1\rangle. \qquad \textbf{(6.292)}
\end{aligned}$$

Details concerning the explicit computation of the Clebsch–Gordan coefficients, together with tables, can be found for example in Edmonds (1957) or Rose (1957). In Table 6.3 the Clebsch–Gordan coefficients $\langle j_1 j_2 m_1 m_2 | jm\rangle$ are given for the cases $j_2 = 1/2$ and $j_2 = 1$. By using the symmetry relations, all the coefficients with any one of j_1, j_2 or j equal to 1/2 or to 1 can be obtained.

Addition of the orbital angular momentum and spin of a particle

As a first example, let us consider a particle of spin s. Let $\mathbf{L}$ be its orbital angular momentum operator and $\mathbf{S}$ its spin angular momentum operator. The total angular momentum operator of the particle is therefore $\mathbf{J} = \mathbf{L} + \mathbf{S}$. We shall denote by m_l, m_s and m_j the quantum numbers corresponding to the operators L_z, S_z and J_z, respectively. In the position representation the simultaneous eigenfunctions of the operators $\mathbf{L}^2$ and L_z are the spherical harmonics $Y_{lm_l}(\theta, \phi)$ with $l = 0, 1, 2, \ldots,$ and

$m_l = -l, -l+1, \dots, l$. The simultaneous eigenfunctions of the operators $\mathbf{S}^2$ and S_z are the spin functions χ_{s,m_s} (with $m_s = -s, -s+1, \dots, s$) which as we have seen in Section 6.7 can be represented by column vectors with $(2s+1)$ positions, having zeros in all positions except one. Hence the simultaneous eigenfunctions of the operators $\mathbf{L}^2$, $\mathbf{S}^2$, L_z and S_z are represented in the direct product 'coordinate–spin' space by the spin-angle functions

$$\psi_{lsm_lm_s} = Y_{lm_l}(\theta, \phi)\chi_{s,m_s}. \tag{6.293}$$

According to the fundamental result (6.288), the allowed values of the total angular momentum quantum number j of the particle are

$$j = |l-s|, |l-s|+1, \dots, l+s. \tag{6.294}$$

The simultaneous normalised eigenfunctions of the operators $\mathbf{L}^2$, $\mathbf{S}^2$, $\mathbf{J}^2$ and J_z (which are usually denoted by the symbol $\mathcal{Y}_{ls}^{jm_j}$) are seen from (6.281) to be the spin-angle functions

$$\begin{aligned}\mathcal{Y}_{ls}^{jm_j} &= \sum_{m_lm_s} \langle lsm_lm_s|jm_j\rangle \psi_{lsm_lm_s} \\ &= \sum_{m_lm_s} \langle lsm_lm_s|jm_j\rangle Y_{lm_l}(\theta, \phi)\chi_{s,m_s}.\end{aligned} \tag{6.295}$$

In particular, for a particle of spin $s = 1/2$ we see from (6.294) that for a given value of the orbital angular momentum quantum number l the total angular momentum quantum number j can take the two values

$$j = l - \tfrac{1}{2}, l + \tfrac{1}{2} \tag{6.296}$$

except when $l = 0$ (s-state) in which case the only allowed value of j is $j = 1/2$. By using the Clebsch–Gordan coefficients displayed in Table 6.3 we find that (Problem 6.21)

$$\mathcal{Y}_{l,\frac{1}{2}}^{l\pm\frac{1}{2},m_j} = \begin{pmatrix} \pm\left[\dfrac{l\pm m_j+\frac{1}{2}}{2l+1}\right]^{1/2} & Y_{l,m_j-\frac{1}{2}}(\theta,\phi) \\ \left[\dfrac{l\mp m_j+\frac{1}{2}}{2l+1}\right]^{1/2} & Y_{l,m_j+\frac{1}{2}}(\theta,\phi) \end{pmatrix} \tag{6.297}$$

Addition of two spins 1/2

As a second example, let us consider two particles whose spin operators are $\mathbf{S}_1$ and $\mathbf{S}_2$, respectively. The total spin angular momentum is thus

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2. \tag{6.298}$$

If the two particles have spin 1/2, the direct-product spin space of the combined system $(1+2)$ has four dimensions. The simultaneous eigenfunctions of the operators $\mathbf{S}_1^2$

and S_{1z} for the first particle are the two basic spinors $\alpha(1)$ and $\beta(1)$ corresponding respectively to 'spin up' ($m_{s_1} = +1/2$) and 'spin down' ($m_{s_1} = -1/2$) for that particle. Likewise, the simultaneous eigenfunctions of the operators $\mathbf{S}_2^2$ and S_{2z} for particle 2 are the two basic spinors $\alpha(2)$ and $\beta(2)$ corresponding respectively to 'spin up' ($m_{s_2} = +1/2$) and 'spin down' ($m_{s_2} = -1/2$) for the second particle. The direct-product eigenfunctions $\psi_{j_1 j_2 m_1 m_2}(1, 2)$ are therefore in the present case the four spin functions

$$\alpha(1)\alpha(2), \qquad \alpha(1)\beta(2), \qquad \beta(1)\alpha(2), \qquad \beta(1)\beta(2) \tag{6.299}$$

which constitute a basis in the four-dimensional spin space of the combined system. If we denote by $M_s\hbar$ the eigenvalues of the operator S_z, we see that $M_s = m_{s_1} + m_{s_2}$, so that the four eigenfunctions (6.299) correspond respectively to the values $M_s = 1, 0, 0$ and -1.

From the basic result (6.288), the allowed values of the total spin quantum number S are given by

$$S = 0, 1. \tag{6.300}$$

The simultaneous normalised eigenfunctions of $\mathbf{S}_1^2$, $\mathbf{S}_2^2$, $\mathbf{S}^2$ and S_z, which we shall denote by χ_{S,M_s}, are readily obtained from (6.281), (6.299) and the Table 6.3 of Clebsch–Gordan coefficients. We find in this way that when $S = 0$ there is only *one* such eigenfunction,

$$\chi_{0,0} = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{6.301}$$

which is called a *singlet* spin state. We note that it is an eigenstate of S_z corresponding to the quantum number $M_s = 0$ and that it is *antisymmetric* in the interchange of the spin coordinates of the two particles. When $S = 1$ we obtain *three* simultaneous normalised eigenfunctions of $\mathbf{S}_1^2$, $\mathbf{S}_2^2$, $\mathbf{S}^2$ and S_z, namely

$$\begin{aligned}
\chi_{1,1} &= \alpha(1)\alpha(2) \\
\chi_{1,0} &= \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\
\chi_{1,-1} &= \beta(1)\beta(2)
\end{aligned} \tag{6.302}$$

which are said to form a spin *triplet*. These three states, which are *symmetric* in the interchange of the spin coordinates of the two particles, are respectively eigenstates of S_z corresponding to the values $M_s = +1, 0, -1$ of the quantum number M_s.

As an example, the lowest state of the helium atom (which contains two electrons) is a single state ($S = 0$), while excited states can be either singlet or triplet. Another example is the deuteron, the nucleus composed of one proton and one neutron, whose only bound state is a triplet spin state ($S = 1$). Both the helium atom and the deuteron will be studied in Chapter 10.

Problems

6.1 Prove that the orbital angular momentum operator **L** is a Hermitian operator.

6.2 Show that the three commutation relations (6.9) are equivalent to the vector commutation relation (6.10).

6.3 Prove equations (6.16) and (6.17).

6.4 Prove that

(a) $[L_i, x_j] = \mathrm{i}\hbar\varepsilon_{ijk}x_k \qquad (i, j, k = 1, 2, 3)$
where $L_1 = L_x, L_2 = L_y, L_3 = L_z$ and $x_1 = x$, $x_2 = y$ and $x_3 = z$. The symbol ε_{ijk}, called the Levi–Civita antisymmetric symbol, is such that

$$\varepsilon_{ijk} = \begin{cases} 1, & \text{if } ijk = 123, 231, 312 \\ -1, & \text{if } ijk = 321, 213, 132 \\ 0, & \text{otherwise.} \end{cases}$$

(b) $[L_i, p_j] = \mathrm{i}\hbar\varepsilon_{ijk}p_k$,
where $p_1 = p_x, p_2 = p_y, p_3 = p_z$.

(c) $\mathbf{L.r} = \mathbf{L.p} = 0$.

6.5 Prove equations (6.21).

6.6 Show that for a system of N structureless particles the rotation operators U_R are given by (6.43) for infinitesimal rotations, and by (6.51) for finite rotations, where **L** is the total orbital angular momentum operator of the system.

6.7 Prove equation (6.80) by using the Rodrigues formula.

6.8 Prove the recurrence relations (6.83) for the Legendre polynomials.

6.9 Prove equation (6.95).

6.10 Establish the recurrence relations (6.97) for the associated Legendre functions.

6.11 Prove the relations (6.118) for L_+ and L_-.

6.12 Let $\hat{\mathbf{n}}$ be a unit vector in a direction specified by the polar angles (θ, ϕ). Show that the component of the angular momentum in the direction $\hat{\mathbf{n}}$ is

$$\begin{aligned} L_n &= \sin\theta\cos\phi L_x + \sin\theta\sin\phi L_y + \cos\theta L_z \\ &= \tfrac{1}{2}\sin\theta(\mathrm{e}^{-\mathrm{i}\phi}L_+ + \mathrm{e}^{\mathrm{i}\phi}L_-) + \cos\theta L_z. \end{aligned}$$

If the system is in simultaneous eigenstates of $\mathbf{L}^2$ and L_z belonging to the eigenvalues $l(l+1)\hbar^2$ and $m\hbar$,

(a) what are the possible results of a measurement of L_n?

(b) what are the expectation values of L_n and L_n^2?

6.13 Consider a free particle of mass μ constrained to move on a ring of radius a.

(a) Show that the Hamiltonian of this system is

$$H = L_z^2/2I$$

where the z-axis is through the centre O of the ring and is perpendicular to its plane, and I is the moment of inertia of the particle with respect to the centre O.

(b) Find the energy eigenfunctions for the system and write down a general expression for the solution of the time-dependent Schrödinger equation.

6.14 Using as a basis the eigenvectors $|jm\rangle$ of $\mathbf{J}^2$ and J_z, obtain the matrix representation of the angular momentum operators J_x, J_y, J_z and $\mathbf{J}^2$ for the case $j = \frac{3}{2}$.

6.15 Verify the anticommutation relations (6.224).

6.16 Prove equation (6.241).

6.17 Calculate the expectation values of the components of $\mathbf{S}$ for a spin-$\frac{1}{2}$ particle

(a) in the state $\chi_\uparrow$ given by (6.252); and
(b) in the state $\chi_\downarrow$ given by (6.255).

6.18 (a) Verify that the two eigenvectors $\chi_\uparrow$ and $\chi_\downarrow$ of the operator S_n given respectively by (6.252) and (6.255) are orthogonal.

(b) By using $\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ as a basis, prove that $\chi_\uparrow$ and $\chi_\downarrow$ satisfy the closure relation

$$|\chi_\uparrow\rangle\langle\chi_\uparrow| + |\chi_\downarrow\rangle\langle\chi_\downarrow| = I.$$

6.19 Obtain the eigenvalues and the corresponding normalised eigenfunctions of S_x and S_y for a spin-$\frac{1}{2}$ particle and check your results by referring to (6.252) and (6.255).

6.20 Obtain the eigenvalues and corresponding normalised eigenvectors of $S_n = \hat{\mathbf{n}}.\mathbf{S}$ for a particle of spin 1, where $\hat{\mathbf{n}}$ is a unit vector defined by the polar angles (θ, ϕ).

6.21 Using the Clebsch–Gordan coefficients given in Table 6.3, obtain the result (6.297).

6.22 Two particles of spin-$\frac{1}{2}$ have spin operators $\mathbf{S}_1$ and $\mathbf{S}_2$. Find the expectation values of the product $\mathbf{S}_1.\mathbf{S}_2$ in the singlet and triplet spin states, for which the wave functions are given by (6.301) and (6.302), respectively.
(*Hint*: $\mathbf{S}_1.\mathbf{S}_2 = (\mathbf{S}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2)/2$.)

6.23 The spin properties of a system of two spin-$\frac{1}{2}$ particles are described by the singlet and triplet wave functions (6.301) and (6.302). If a third particle of spin-$\frac{1}{2}$ is added to the system, show that the total spin quantum number of the three-particle system can be $S = \frac{3}{2}$ (a quartet state) or $S = \frac{1}{2}$ (a doublet state), and find the corresponding spin functions.

(*Hint*: Treat the original two-particle system as a single entity of either spin 1 or spin 0.)

6.24 Let $\mathcal{T}$ be the time-reversal operator introduced in Section 5.9. According to (5.364) this operator is given by $\mathcal{T} = U_\tau K$, where U_τ is a unitary operator and K is the operator of complex conjugation.

(a) Using the results (5.365) and (5.367), show that the orbital angular momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ changes sign under the operation of time reversal:

$$\mathbf{L}' = \mathcal{T}\mathbf{L}\mathcal{T}^\dagger = -\mathbf{L}.$$

(b) The natural extension of this result is to require that the spin angular momentum operator $\mathbf{S}$ changes sign under the operation of time reversal:

$$\mathbf{S}' = \mathcal{T}\mathbf{S}\mathcal{T}^\dagger = -\mathbf{S}.$$

Using this relation, show that for a spin-1/2 particle the operator $\mathcal{T}$ is given by

$$\mathcal{T} = U_\tau K \qquad \text{with} \qquad U_\tau = \mathrm{i}\sigma_y$$

where σ_y is the second of the Pauli spin matrices (6.243).

7 The Schrödinger equation in three dimensions

In Chapter 4 we solved the time-independent Schrödinger equation for several one-dimensional problems. We shall now generalise our treatment to study in three dimensions the non-relativistic motion of a particle in a time-independent potential $V(\mathbf{r})$, where $\mathbf{r}$ denotes the position vector of the particle. In fact, we can treat a slightly more general problem at no extra cost. Indeed, we have seen in Section 5.7 that the motion of two particles A and B, of masses m_A and m_B, interacting via a time-independent potential $V(\mathbf{r})$ which depends only on their relative coordinate $\mathbf{r} = \mathbf{r}_A - \mathbf{r}_B$, reduces in the centre-of-mass system to a one-body problem: the motion of a particle of mass $\mu = m_A m_B/(m_A + m_B)$ in the potential $V(\mathbf{r})$. The two problems can therefore be treated on the same footing, the time-independent Schrödinger equation to be solved being

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{7.1}$$

This is a second-order partial differential equation, in contrast to the one-dimensional case, where the time-independent Schrödinger equation (4.3) is a second-order ordinary differential equation. As a result, the solution of the three-dimensional Schrödinger equation (7.1) can only be obtained exactly and explicitly in a few simple cases. In particular, the potential may be such that the technique of *separation of variables* may be used. The original three-dimensional problem then reduces to simpler problems of lower dimensionality.

In this chapter we shall examine several cases for which a separation of variables can be made in the three-dimensional Schrödinger equation (7.1), and its solutions can be obtained. We shall first consider some simple examples where the Schrödinger equation is separable in Cartesian coordinates. The most interesting case, however, is that of *central* potentials, that is potentials $V(r)$ which depend only upon the magnitude $r = |\mathbf{r}|$ of the vector $\mathbf{r}$. For such spherically symmetric potentials the Schrödinger equation (7.1) can be separated in spherical polar coordinates. As in classical mechanics, the orbital angular momentum plays an essential role in this problem. In fact, using results obtained in Chapter 6 we shall be able to write down the angular part of the eigenfunctions, so that the solution of the Schrödinger equation (7.1) will reduce to that of a differential equation involving only the radial coordinate r. This radial equation will then be solved for several important problems: the free particle, the spherical square well, the hydrogenic atom and the isotropic three-dimensional harmonic oscillator.

7.1 Separation of the Schrödinger equation in Cartesian coordinates

Let us first consider the simple case where the potential $V(\mathbf{r})$ has the special form

$$V(\mathbf{r}) = V_1(x) + V_2(y) + V_3(z) \tag{7.2}$$

The Hamiltonian $H = -(\hbar^2/2\mu)\nabla^2 + V(\mathbf{r})$ may then be written as

$$H = H_x + H_y + H_z \tag{7.3}$$

where

$$H_x = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + V_1(x), \tag{7.4a}$$

$$H_y = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial y^2} + V_2(y), \tag{7.4b}$$

$$H_z = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial z^2} + V_3(z) \tag{7.4c}$$

and the Schrödinger equation (7.1) becomes

$$\begin{aligned}\bigg\{\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + V_1(x)\right] + \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial y^2} + V_2(y)\right]& \\ +\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial z^2} + V_3(z)\right]\bigg\}\psi(x, y, z) &= E\psi(x, y, z).\end{aligned} \tag{7.5}$$

The form of this equation suggests that we seek solutions which are products of three functions, each of a single variable

$$\psi(x, y, z) = X(x)Y(y)Z(z). \tag{7.6}$$

Substituting (7.6) into (7.5) and dividing through by ψ, we find that

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}+V_1(x)\right]+\left[-\frac{\hbar^2}{2\mu}\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}+V_2(y)\right]$$
$$+\left[-\frac{\hbar^2}{2\mu}\frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2}+V_3(z)\right]=E. \tag{7.7}$$

Each expression in square brackets can only be a function of one of the variables x, y, z. Moreover, the sum of these three expressions must be equal to the constant E. Hence each separate expression must itself be equal to a constant, the sum of these constants being equal to E. We therefore obtain the three ordinary differential equations

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+V_1(x)\right]X(x) = E_xX(x) \tag{7.8a}$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}y^2}+V_2(y)\right]Y(y) = E_yY(y) \tag{7.8b}$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}z^2}+V_3(z)\right]Z(z) = E_zZ(z) \tag{7.8c}$$

with the condition

$$E = E_x + E_y + E_z. \tag{7.9}$$

Each of the equations (7.8) has the form of the one-dimensional time-independent Schrödinger equation (4.3) discussed in Chapter 4. The three-dimensional states are therefore expressible in terms of familiar one-dimensional states.

The free particle

As a first example, let us consider the motion of a free particle of mass μ. In this case $V = 0$ in all space, and the Schrödinger equation (7.1) becomes

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{7.10}$$

This equation is of course separable in Cartesian coordinates with $V_1 = V_2 = V_3 = 0$. In particular, equation (7.8a) reduces to

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2X(x)}{\mathrm{d}x^2} = E_xX(x). \tag{7.11}$$

From our discussion of Chapter 4, we know that acceptable solutions of (7.11) exist for any value $E_x \geqslant 0$, and are given by

$$X(x) = A\exp(\mathrm{i}|k_x|x) + B\exp(-\mathrm{i}|k_x|x) \tag{7.12}$$

where A and B are arbitrary complex constants, and $|k_x| = (2\mu E_x/\hbar^2)^{1/2}$.

Proceeding in a similar way with equations (7.8b) and (7.8c), we see that the three-dimensional free-particle solutions $\psi(x, y, z) = X(x)Y(y)Z(z)$ of the Schrödinger equation (7.10) can be written as linear combinations of *plane-wave* states

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r}) &= C\exp[\mathrm{i}(k_x x + k_y y + k_z z)] \\ &= C\exp(\mathrm{i}\mathbf{k}.\mathbf{r}) \end{aligned} \tag{7.13}$$

where the propagation vector (or wave vector) **k** has Cartesian components (k_x, k_y, k_z), and C is a 'normalisation' constant. Moreover, from (7.9) we have

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2\mu}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{2\mu} = \frac{p^2}{2\mu} \tag{7.14}$$

where p is the magnitude of the linear momentum $\mathbf{p} = \hbar\mathbf{k}$.

The fact that the free-particle Schrödinger equation (7.10) has plane-wave solutions of the form (7.13) is in accordance with our discussion in Chapter 3. We also recall that the plane-wave state (7.13) is a *momentum eigenfunction*, that is an eigenstate of the momentum operator $\mathbf{p}_{\mathrm{op}} = -\mathrm{i}\hbar\boldsymbol{\nabla}$, with the eigenvalue $\mathbf{p} = \hbar\mathbf{k}$ corresponding to a definite linear momentum. The plane waves (7.13) are thus simultaneous eigenfunctions of energy and linear momentum; more precisely, they are simultaneous eigenfunctions of the free-particle Hamiltonian $H = -(\hbar^2/2\mu)\nabla^2$ and of the three operators $(p_x)_{\mathrm{op}} = -\mathrm{i}\hbar\partial/\partial x$, $(p_y)_{\mathrm{op}} = -\mathrm{i}\hbar\partial/\partial y$ and $(p_z)_{\mathrm{op}} = -\mathrm{i}\hbar\partial/\partial z$.

Because every non-negative value of the energy E is allowed, the spectrum is *continuous*. Moreover, each energy eigenvalue is *infinitely degenerate*, since the condition (7.14) only restricts the magnitude of the vector **k**, so that there are infinitely many possible orientations of this vector for a given value of E.

The plane wave (7.13) can be 'normalised' by a simple extension of the procedures described in Section 4.2 for the one-dimensional case. Generalising (4.37) to three dimensions, we obtain the 'delta function' normalisation

$$\int \psi_{\mathbf{k}'}^*(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})\mathrm{d}\mathbf{r} = \delta(\mathbf{k} - \mathbf{k}') \tag{7.15}$$

where the three-dimensional Dirac delta function $\delta(\mathbf{k} - \mathbf{k}')$ is given by

$$\begin{aligned} \delta(\mathbf{k} - \mathbf{k}') &= \delta(k_x - k_x')\delta(k_y - k_y')\delta(k_z - k_z') \\ &= (2\pi)^{-3}\int_{-\infty}^{+\infty}\exp[\mathrm{i}(k_x - k_x')x]\mathrm{d}x \int_{-\infty}^{+\infty}\exp[\mathrm{i}(k_y - k_y')y]\mathrm{d}y \\ &\quad\times \int_{-\infty}^{+\infty}\exp[\mathrm{i}(k_z - k_z')z]\mathrm{d}z \\ &= (2\pi)^{-3}\int \exp[\mathrm{i}(\mathbf{k} - \mathbf{k}').\mathbf{r}]\mathrm{d}\mathbf{r}. \end{aligned} \tag{7.16}$$

Taking the arbitrary phase of the normalisation constant C in (7.13) to be zero, we see from (7.13), (7.15) and (7.16) that $C = (2\pi)^{-3/2}$, so that the plane-wave states

$\psi_{\mathbf{k}}(\mathbf{r})$, normalised in the sense of (7.15), are

$$\psi_{\mathbf{k}}(\mathbf{r}) = (2\pi)^{-3/2} \exp(i\mathbf{k}.\mathbf{r}). \tag{7.17}$$

Finally, we remark that the plane waves (7.17) form a *complete set*, so that an arbitrary state can be expressed as a superposition of these functions; this is precisely the Fourier expansion which was discussed in Chapter 2. The *closure relation* (5.63a) applied to the plane-wave eigenfunctions (7.17) reads

$$\begin{aligned}\int \psi^*_{\mathbf{k}}(\mathbf{r}')\psi_{\mathbf{k}}(\mathbf{r})\mathrm{d}\mathbf{k} &= (2\pi)^{-3} \int \exp[i\mathbf{k}.(\mathbf{r}-\mathbf{r}')]\mathrm{d}\mathbf{k} \\ &= \delta(\mathbf{r}-\mathbf{r}'). \end{aligned} \tag{7.18}$$

If we elect to work with discrete eigenvalues, we can restrict the domain of the plane waves (7.13) to an arbitrary large but finite cubical box of volume L^3, at the walls of which they obey *periodic boundary conditions*. By a straightforward generalisation of the one-dimensional treatment of Section 4.2 we then find that the components (k_x, k_y, k_z) of the wave vector $\mathbf{k}$ must satisfy the conditions

$$k_x = \frac{2\pi}{L}n_x, \qquad k_y = \frac{2\pi}{L}n_y, \qquad k_z = \frac{2\pi}{L}n_z \tag{7.19}$$

where n_x, n_y, n_z are positive or negative integers, or zero. The energy E, given by (7.14), can therefore take only discrete values in this case. The momentum eigenfunctions (7.13) can now be normalised by requiring that in the basic cube of side L

$$\int_0^L \mathrm{d}x \int_0^L \mathrm{d}y \int_0^L \mathrm{d}z |\psi_{\mathbf{k}}(\mathbf{r})|^2 = 1. \tag{7.20}$$

Hence, taking the arbitrary phase of the normalisation constant C to be zero, this constant is given by $C = L^{-3/2}$, and the normalised plane waves are

$$\psi_{\mathbf{k}}(\mathbf{r}) = L^{-3/2} \exp(i\mathbf{k}.\mathbf{r}). \tag{7.21}$$

These eigenfunctions form a complete set of orthonormal functions in terms of which an arbitrary state can be expanded by a Fourier series within the basic cube.

The three-dimensional box

As a second example, let us consider a particle of mass μ which is constrained by *impenetrable walls* to move in a rectangular box of sides L_1, L_2 and L_3. Inside the box the potential energy V is a constant which we choose to be zero, while at the walls V is infinite. This problem is therefore a generalisation of the one-dimensional infinite square well treated in Section 4.5.

The time-independent Schrödinger equation to be solved in the region inside the box is

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x, y, z) = E\psi(x, y, z). \tag{7.22}$$

In addition, we must have $\psi(x, y, z) = 0$ at each of the walls and beyond. Taking the origin to be at one corner of the box and writing $\psi(x, y, z)$ in the product form (7.6), we find that for $0 \leqslant x \leqslant L_1$ the function $X(x)$ satisfies the equation

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2X(x)}{\mathrm{d}x^2} = E_x X(x) \tag{7.23}$$

and that

$$X(x) = 0 \text{ for } x \leqslant 0 \text{ and } x \geqslant L_1. \tag{7.24}$$

From our results of Section 4.5 we see at once that the allowed values of E_x are given by

$$E_{n_x} = \frac{\hbar^2}{2\mu}\frac{\pi^2 n_x^2}{L_1^2}, \qquad n_x = 1, 2, 3, \dots \tag{7.25}$$

the corresponding normalised eigenfunctions being the standing waves

$$X_{n_x}(x) = \left(\frac{2}{L_1}\right)^{1/2} \sin\left(\frac{n_x\pi}{L_1}x\right). \tag{7.26}$$

Proceeding in a similar way for the functions $Y(y)$ and $Z(z)$, we find that the normalised eigenfunctions of the full three-dimensional problem are the standing waves

$$\psi_{n_x n_y n_z}(x, y, z) = \left(\frac{8}{V}\right)^{1/2} \sin\left(\frac{n_x\pi}{L_1}x\right)\sin\left(\frac{n_y\pi}{L_2}y\right)\sin\left(\frac{n_z\pi}{L_3}z\right) \tag{7.27}$$

where $V = L_1L_2L_3$ is the volume of the box and n_x, n_y, n_z are positive integers[1]. The allowed values of the energy $E = E_x + E_y + E_z$ are

$$E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2\mu}\left(\frac{n_x^2}{L_1^2} + \frac{n_y^2}{L_2^2} + \frac{n_z^2}{L_3^2}\right). \tag{7.28}$$

This energy spectrum does not exhibit regularities for general values of L_1, L_2 and L_3. Although it is strictly discrete, we see that as the dimensions of the box increase the spacing of the energy levels decreases, so that for a macroscopic box the spectrum is nearly continuous.

Let us now consider the simpler case of a cubical box of side L. The normalised eigenfunctions are then given by

$$\psi_{n_x n_y n_z}(x, y, z) = \left(\frac{8}{L^3}\right)^{1/2} \sin\left(\frac{n_x\pi}{L}x\right)\sin\left(\frac{n_y\pi}{L}y\right)\sin\left(\frac{n_z\pi}{L}z\right),$$
$$n_x, n_y, n_z = 1, 2, 3, \dots \tag{7.29}$$

---

[1] Note that if n_x, n_y or n_z is equal to zero one obtains the trivial non-physical solution $\psi = 0$, while changing n_x to $-n_x$ (and similarly for n_y or n_z) changes the sign of the wave function, which is not physically significant.

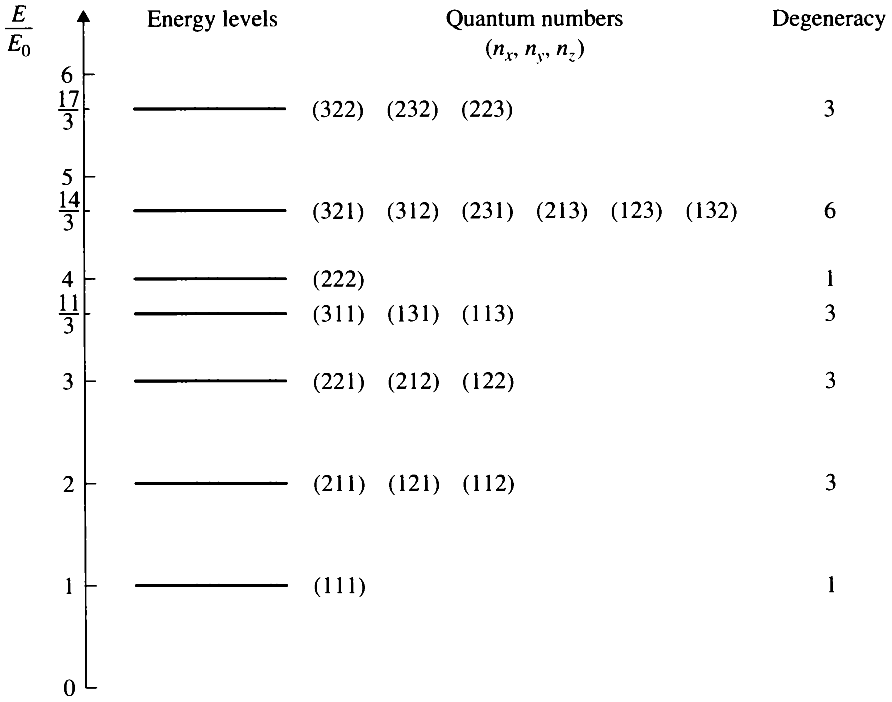


Figure 7.1 The first few energy levels of a particle in a cubical box of side L. Also shown are the quantum numbers (n_x, n_y, n_z) of the corresponding eigenfunctions, and the degeneracy of each energy level. The ground state energy is $E_0 = 3\hbar^2\pi^2/(2\mu L^2)$.

and the allowed energy values are

$$E_n = \frac{\hbar^2\pi^2}{2\mu L^2}n^2 \tag{7.30}$$

where

$$n^2 = n_x^2 + n_y^2 + n_z^2. \tag{7.31}$$

The ground state is such that $n_x = n_y = n_z = 1$, so that $n^2 = 3$ and the corresponding energy is $E_0 = 3\hbar^2\pi^2/(2\mu L^2)$; this level is non-degenerate. The next energy level has an energy $2E_0$ (corresponding to $n^2 = 6$), which can be obtained in three different ways by choosing the set of quantum numbers (n_x, n_y, n_z) to be $(2, 1, 1)$ or $(1, 2, 1)$ or $(1, 1, 2)$; this level is therefore three-fold degenerate. The next energy levels can be obtained in a similar way. The first few energy levels, together with their degeneracies, are shown in Fig. 7.1. It is apparent that since the energy eigenvalues (7.30) depend on the quantum numbers n_x, n_y and n_z only through the combination $n^2 = n_x^2 + n_y^2 + n_z^2$, they can generally be obtained from different sets of values of (n_x, n_y, n_z), and hence are usually degenerate. This is in contrast with the energy levels (7.28) corresponding to the rectangular box. Clearly the existence of degeneracies is directly related to the symmetry of the potential.

The three-dimensional harmonic oscillator

As another example of a three-dimensional system for which the Schrödinger equation is separable in Cartesian coordinates, we consider the motion of a particle of mass μ in the potential

$$V(\mathbf{r}) = \tfrac{1}{2}k_1x^2 + \tfrac{1}{2}k_2y^2 + \tfrac{1}{2}k_3z^2 \tag{7.32}$$

corresponding to a three-dimensional harmonic oscillator. The separated Schrödinger equations (7.8) are now of the form of the one-dimensional linear harmonic oscillator equation (4.130), namely

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2X(x)}{\mathrm{d}x^2} + \frac{1}{2}k_1x^2X(x) = E_xX(x) \tag{7.33}$$

with similar equations for $Y(y)$ and $Z(z)$. Using the results of Section 4.7 we find that the spectrum is entirely discrete, the energy levels being given by

$$E_{n_xn_yn_z} = \left(n_x + \tfrac{1}{2}\right)\hbar\omega_1 + \left(n_y + \tfrac{1}{2}\right)\hbar\omega_2 + \left(n_z + \tfrac{1}{2}\right)\hbar\omega_3 \tag{7.34a}$$

where

$$\omega_1 = \left(\frac{k_1}{\mu}\right)^{1/2}, \qquad \omega_2 = \left(\frac{k_2}{\mu}\right)^{1/2}, \qquad \omega_3 = \left(\frac{k_3}{\mu}\right)^{1/2} \tag{7.34b}$$

and n_x, n_y, n_z are positive integers, or zero.

The corresponding normalised eigenfunctions can also be readily obtained by using (7.6) and the one-dimensional linear harmonic oscillator wave functions of Section 4.7. They are given by

$$\begin{aligned}\psi_{n_xn_yn_z}(x, y, z) &= N_{n_x}N_{n_y}N_{n_z}\exp\left[-\tfrac{1}{2}(\alpha_1^2x^2 + \alpha_2^2y^2 + \alpha_3^2z^2)\right] \\ &\quad \times H_{n_x}(\alpha_1x)H_{n_y}(\alpha_2y)H_{n_z}(\alpha_3z)\end{aligned} \tag{7.35a}$$

where $H_n(\xi)$ is the Hermite polynomial defined in (4.154) and

$$\alpha_1 = \left(\frac{\mu k_1}{\hbar^2}\right)^{1/4}, \qquad N_{n_x} = \left(\frac{\alpha_1}{\sqrt{\pi}2^{n_x}n_x!}\right)^{1/2} \tag{7.35b}$$

with similar expressions for α_2, α_3 and N_{n_y}, N_{n_z}. Note that if the three force constants k_1, k_2 and k_3 are all different, so that the harmonic oscillator is *anisotropic*, the energy levels (7.34) are, in general, non-degenerate.

Let us now consider the particular case of an *isotropic* three-dimensional harmonic oscillator, for which $k_1 = k_2 = k_3$. Calling this common value of the force constant k, we see that the potential

$$V(r) = \tfrac{1}{2}k(x^2 + y^2 + z^2) = \tfrac{1}{2}kr^2 \tag{7.36}$$

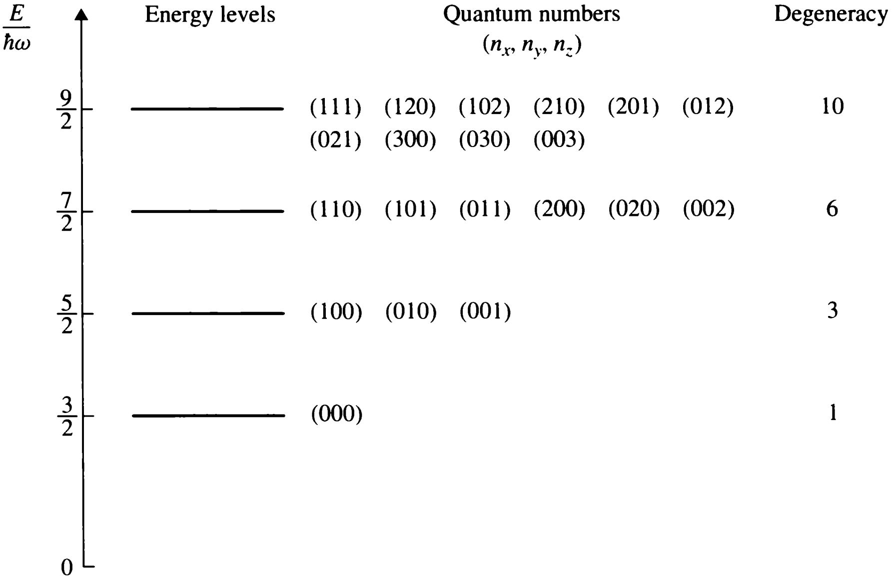


Figure 7.2 The first few energy levels of a three-dimensional isotropic harmonic oscillator. Also shown are the quantum numbers (n_x, n_y, n_z) of the corresponding eigenfunctions, and the degeneracy of each energy level.

is *central*. The motion of a particle in a central potential will be discussed at length in the remaining sections of this chapter. Here we only note that upon setting $k_1 = k_2 = k_3 = k$ in (7.34) the energy levels of the three-dimensional isotropic harmonic oscillator are given by

$$E_n = \left(n + \tfrac{3}{2}\right)\hbar\omega \tag{7.37}$$

where $\omega = (k/\mu)^{1/2}$. The quantum number n is such that

$$n = n_x + n_y + n_z \tag{7.38}$$

and thus can take on the values $n = 0, 1, 2, \ldots$. The eigenfunctions are given by (7.35) with $\alpha_1 = \alpha_2 = \alpha_3 = \alpha = (\mu k/\hbar^2)^{1/4}$. The ground state has the energy $E_{n=0} = 3\hbar\omega/2$ and is not degenerate, while all the other energy levels are degenerate. For example, the first excited level has an energy $E_{n=1} = 5\hbar\omega/2$ and is three-fold degenerate since it can be obtained in three different ways by taking the set of quantum numbers (n_x, n_y, n_z) to be $(1, 0, 0)$ or $(0, 1, 0)$ or $(0, 0, 1)$. The first few energy levels of the three-dimensional isotropic harmonic oscillator and their degeneracies are shown in Fig. 7.2. Note that the energy level $E_n = (n+3/2)\hbar\omega$ is $(n+1)(n+2)/2$-fold degenerate, since this is the number of ways that n can be obtained as the sum of the three non-negative integers n_x, n_y and n_z. Thus the three-dimensional isotropic harmonic oscillator provides another illustration of how the symmetry of the potential results in degeneracies.

7.2 Central potentials. Separation of the Schrödinger equation in spherical polar coordinates

We now turn to the main subject of this chapter: the study of the non-relativistic motion of a spinless particle of mass μ in a *central* potential (that is a potential $V(r)$ which depends only on the magnitude r of the position vector $\mathbf{r}$). We shall see that the properties of the orbital angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ obtained in Chapter 6 are of particular importance in this analysis.

Since $V(r)$ is spherically symmetric, it is natural to use the spherical polar coordinates defined in (6.15) and illustrated in Fig. 6.1. Our first task is to express the Hamiltonian operator

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r) \tag{7.39}$$

in these coordinates. The potential energy $V(r)$ is already given in terms of the polar coordinate r, and the expression of the kinetic-energy operator $T = -(\hbar^2/2\mu)\nabla^2$ in spherical polar coordinates is given by (6.130b) for $r \neq 0$. Hence the Hamiltonian (7.39) may be written in these coordinates (for $r \neq 0$) as

$$H = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r) \tag{7.40a}$$

or

$$H = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\mathbf{L}^2}{\hbar^2 r^2}\right] + V(r) \tag{7.40b}$$

where $\mathbf{L}^2$ is given by (6.17). The corresponding time-independent Schrödinger equation is

$$\left\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\mathbf{L}^2}{\hbar^2 r^2}\right] + V(r)\right\}\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{7.41}$$

In order to simplify the solution of this equation, we first recall that the operators L_x, L_y, L_z and $\mathbf{L}^2$ do not operate on the radial variable r. Hence, *for a spherically symmetric potential* $V(r)$, we have $[V(r), \mathbf{L}] = [V(r), \mathbf{L}^2] = 0$. Moreover, L_x, L_y, L_z and $\mathbf{L}^2$ also commute with the kinetic energy operator T, as is readily seen by using the expression (6.130b) of T and remembering that $[\mathbf{L}^2, \mathbf{L}] = 0$. Therefore,

$$[H, \mathbf{L}] = [H, \mathbf{L}^2] = 0. \tag{7.42}$$

Remembering that the operators L_x, L_y and L_z do not commute among themselves, we see that a set of commuting operators can be taken to be H, $\mathbf{L}^2$ and any one of L_x, L_y and L_z. Taking this set to be H, $\mathbf{L}^2$ and L_z, it follows that it is possible to find simultaneous eigenfunctions of these three operators, or in other words to obtain solutions of the Schrödinger equation (7.41) which are also eigenfunctions of $\mathbf{L}^2$ and L_z. Since the spherical harmonics $Y_{lm}(\theta, \phi)$ are simultaneous eigenfunctions of $\mathbf{L}^2$

and L_z (see (6.63) and (6.64)) we can look for solutions of the Schrödinger equation having the separable form

$$\psi_{Elm}(\mathbf{r}) = R_{Elm}(r)Y_{lm}(\theta, \phi) \tag{7.43}$$

where $R_{Elm}(r)$ is a *radial function* which remains to be found. It is worth stressing that the angular dependence of the eigenfunction (7.43) is entirely given by the spherical harmonic $Y_{lm}(\theta, \phi)$; it is the proper one associated with eigenvalues of $\mathbf{L}^2$ and L_z characterised by the orbital angular momentum quantum number l and the magnetic quantum number m. These two quantum numbers, together with the energy E, can thus be used to 'label' the eigenfunction ψ_{Elm}. We also remark (see Problem 7.3) that all the solutions of the Schrödinger equation (7.41) can be obtained as linear combinations of the separable solutions (7.43).

Inserting (7.43) into the Schrödinger equation (7.41) and using the fact that $\mathbf{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi)$, we obtain for the radial function the differential equation

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right) + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)\right]R_{El}(r) = ER_{El}(r). \tag{7.44}$$

Note that the magnetic quantum number m does not appear in this equation. The radial function is therefore independent of this quantum number. For this reason we have written $R_{El}(r) \equiv R_{Elm}(r)$, and equation (7.43) becomes

$$\psi_{Elm}(\mathbf{r}) = R_{El}(r)Y_{lm}(\theta, \phi). \tag{7.45}$$

Similarly, the eigenvalues E obtained from (7.44) are independent of the quantum number m. Thus, for a given value of l there are $(2l+1)$ eigenfunctions (7.45) corresponding to the $(2l+1)$ possible different values of $m (m = -l, -l+1, \dots, l)$ which all have the same energy E. The reason for this $(2l+1)$-*fold degeneracy* is that for a spherically symmetric potential no direction of space is physically different from another, or in other words the Hamiltonian (7.39) is *invariant under rotations*. Since $m\hbar$ measures the projection of the orbital angular momentum $\mathbf{L}$ on the z-axis (see Section 6.3) the energy levels cannot depend on the quantum number m.

Using (6.115), we see that the modulus squared of the eigenfunctions (7.45) is given by

$$\begin{aligned} |\psi_{Elm}(r, \theta, \phi)|^2 &= |R_{El}(r)|^2 |Y_{lm}(\theta, \phi)|^2 \\ &= |R_{El}(r)|^2 (2\pi)^{-1} |\Theta_{lm}(\theta)|^2 \end{aligned} \tag{7.46}$$

and hence does not depend on the angle ϕ. The behaviour of $|\psi_{Elm}|^2$ is thus completely specified by the *radial* quantity $|R_{El}(r)|^2$, which depends on the central potential $V(r)$ considered (see (7.44)) and on the *angular factor* $(2\pi)^{-1}|\Theta_{lm}(\theta)|^2$ which is independent of $V(r)$ and has been studied in Chapter 6. In particular, we refer the reader to the polar plots of $(2\pi)^{-1}|\Theta_{lm}(\theta)|^2$ shown in Fig. 6.2.

We also note that if an eigenfunction (7.45) corresponds to a *bound state* it is square integrable and thus can be normalised to unity by requiring that

$$\int_0^\infty \mathrm{d}r r^2 \int_0^\pi \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\phi |\psi_{Elm}(r,\theta,\phi)|^2 = 1. \tag{7.47}$$

Since the spherical harmonics are normalised on the unit sphere (see (6.103)), it follows from (7.46) and (7.47) that the radial bound-state eigenfunctions must satisfy the normalisation condition

$$\int_0^\infty |R_{El}(r)|^2 r^2 \mathrm{d}r = 1. \tag{7.48}$$

Another important remark concerns the *parity* of the states (7.45). We recall that under the parity operation $\mathbf{r} \to -\mathbf{r}$ the spherical polar coordinates (r, θ, ϕ) become $(r, \pi-\theta, \phi+\pi)$. The Hamiltonian for a particle in a central potential, given by (7.40), is clearly unaffected by this operation, so that the parity operator $\mathcal{P}$ commutes with the Hamiltonian (7.40). As a result, simultaneous eigenfunctions of the operators H and $\mathcal{P}$ can be found. Applying the parity operator to the wave function (7.45), we have

$$\begin{aligned} \mathcal{P}\psi_{Elm}(r,\theta,\phi) &= \mathcal{P}[R_{El}(r)Y_{lm}(\theta,\phi)] \\ &= R_{El}(r)Y_{lm}(\pi-\theta,\phi+\pi). \end{aligned} \tag{7.49}$$

Now, we have seen in Chapter 6 that $Y_{lm}(\pi-\theta,\phi+\pi) = (-1)^l Y_{lm}(\theta,\phi)$, so that Y_{lm} has the parity of l (see (6.114)). We have therefore

$$\begin{aligned} \mathcal{P}\psi_{Elm}(r,\theta,\phi) &= R_{El}(r)(-1)^l Y_{lm}(\theta,\phi) \\ &= (-1)^l \psi_{Elm}(r,\theta,\phi). \end{aligned} \tag{7.50}$$

As a result, the states (7.45) have a definite parity which, like that of the Y_{lm}, is the parity of l (even for even l and odd for odd l).

It is also interesting to examine the relation between the radial equation (7.44) and the one-dimensional Schrödinger equation (4.3). To this end, we introduce the new radial function

$$u_{El}(r) = rR_{El}(r). \tag{7.51}$$

Using (7.44) and (7.51), we obtain for $u_{El}(r)$ the radial equation

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2 u_{El}(r)}{\mathrm{d}r^2} + V_{\mathrm{eff}}(r)u_{El}(r) = Eu_{El}(r) \tag{7.52}$$

where

$$V_{\mathrm{eff}}(r) = V(r) + \frac{l(l+1)\hbar^2}{2\mu r^2} \tag{7.53}$$

is an *effective potential* which, in addition to the interaction potential $V(r)$, also contains the repulsive *centrifugal barrier* term $l(l+1)\hbar^2/2\mu r^2$. The equation (7.52) is then identical in form to the one-dimensional Schrödinger equation (4.3). However, it has significance only for positive values of r, and must be supplemented by a boundary condition at $r = 0$. We shall require that the radial function $R_{El}(r)$ remains finite at the origin[2]. Since $R_{El}(r) = r^{-1}u_{El}(r)$, this implies that we must have

$$u_{El}(0) = 0. \tag{7.54}$$

Let us examine more closely the behaviour of the function $u_{El}(r)$ near the origin. We shall first assume that in the vicinity of $r = 0$ the interaction potential $V(r)$ has the form

$$V(r) = r^p(b_0 + b_1 r + \cdots), \qquad b_0 \neq 0 \tag{7.55}$$

where p is an integer such that $p \geqslant -1$. In other words, the potential cannot be more singular than r^{-1} at the origin, which is the case for nearly all interactions of physical interest. Since $r = 0$ is a regular singular point[3] of the differential equation (7.52), we can expand the solution $u_{El}(r)$ in the vicinity of the origin as

$$u_{El}(r) = r^s \sum_{k=0}^{\infty} c_k r^k, \qquad c_0 \neq 0. \tag{7.56}$$

Substituting this expansion in (7.52), we find by looking at the coefficient of the lowest power of r (i.e. r^{s-2}) that the quantity s must satisfy the *indicial equation*

$$s(s-1) - l(l+1) = 0 \tag{7.57}$$

so that $s = l + 1$ or $s = -l$. The choice $s = -l$ corresponds to *irregular* solutions which do not satisfy the condition (7.54). The other choice $s = l + 1$ corresponds to *regular* solutions which are physically allowed, and are such that

$$u_{El}(r) \underset{r \to 0}{\sim} r^{l+1}. \tag{7.58}$$

Note that the corresponding admissible radial functions $R_{El}(r)$ behave like r^l near $r = 0$. We see that as l increases, the functions $u_{El}(r)$, or $R_{El}(r)$, become smaller and smaller in the neighbourhood of the origin. This is clearly due to the presence of the centrifugal barrier which for $l \neq 0$ 'blocks out' the region near the origin, the effect being more and more pronounced as l increases.

We now consider briefly the case for which the integer p in (7.55) is such that $p < -1$. If the interaction is *repulsive* near $r = 0$ (so that $b_0 > 0$), we may still impose the condition (7.54), since the radial function $R_{El}(r)$ itself must clearly vanish at the infinite wall at $r = 0$. On the other hand, if the potential is *attractive* in the neighbourhood of the origin (so that $b_0 < 0$) the nature of the singularity is important. For example, when $p = -2$ and $b_0 < 0$ in (7.55), it can be shown (Problem 7.4) that physically acceptable solutions of (7.52) exist only when $b_0 > -\hbar^2/8\mu$. In what

---

[2] The requirement of finiteness of $R_{El}(r)$ at $r = 0$ is in fact too stringent and must be relaxed in certain cases. However, it will be fully adequate for all the non-relativistic applications treated in this book.

[3] See, for example, Mathews and Walker (1973).

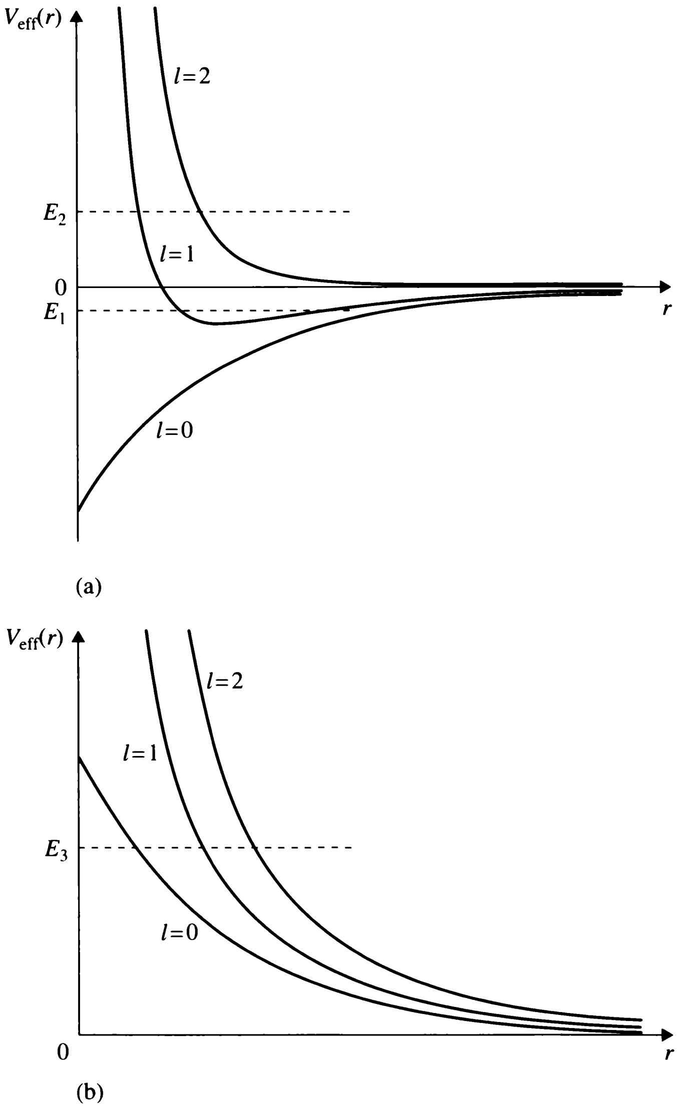


Figure 7.3 Illustration of the effective potential $V_{\rm eff}(r) = V(r) + l(l+1)\hbar^2/2\mu r^2$ for $l = 0, 1, 2$ (a) in the case of a typical attractive interaction $V(r)$, and (b) in the case of a typical repulsive interaction $V(r)$. The energy $E_1 < 0$ corresponds to a bound state, while the positive energies E_2 and E_3 correspond to states belonging to the continuous spectrum.

follows, the attractive potentials which we shall consider will always be assumed to be less singular than r^{-2} at the origin, so that the results (7.54) and (7.58) hold true.

In the remaining sections of this chapter we shall solve the radial equations (7.44) or (7.52) for several central potentials. Before doing this, however, it is instructive to examine the form of the effective potential (7.53) in some typical cases. In Fig. 7.3(a) we illustrate the effective potential $V_{\text{eff}}(r)$ for the first values of l for an attractive interaction $V(r)$, and in Fig. 7.3(b) this is done for a repulsive interaction. It is seen that in the first case the effect of the centrifugal barrier term $l(l+1)\hbar^2/2\mu r^2$ is to reduce the effective depth of the potential well. This effect obviously increases as l increases. Thus, in the example shown in Fig. 7.3(a), bound states of negative energy (such as E_1) could exist for the values $l = 0$ and 1, but we see that for $l \geqslant 2$ the effective potential is purely repulsive, so that no bound states can exist for $l \geqslant 2$. We also remark that for the example displayed in Fig. 7.3(a), solutions $u_{El}(r)$ of the radial equation (7.52) which exhibit an oscillatory behaviour at infinity exist for every l when $E > 0$; the spectrum is therefore continuous for every l in the case of positive energies (such as E_2). Turning now to the case of a repulsive interaction, it is clear from (7.53) that as l increases the effective potential becomes increasingly repulsive. This is illustrated in Fig. 7.3(b). The energy spectrum will therefore consist only of continuum states of positive energy (such as E_3), for all values of l.

7.3 The free particle

As a first example of motion in a central potential, we shall consider the very simple case of a free particle, for which $V(r) = 0$. Using Cartesian coordinates, we have obtained in Section 7.1 plane-wave solutions (7.13) of the free-particle Schrödinger equation (7.10). These plane-wave states are also momentum eigenfunctions, and hence are simultaneous eigenfunctions of the free-particle Hamiltonian $H = -(\hbar^2/2\mu)\nabla^2$ and of the (linear) momentum operator $\mathbf{p}_{\text{op}} = -\text{i}\hbar\boldsymbol{\nabla}$. Using spherical polar coordinates, we shall now look for solutions of the free-particle Schrödinger equation of the form (7.45), that is simultaneous eigenfunctions of H, $\mathbf{L}^2$ and L_z corresponding to definite values of E, l and m. The free-particle radial functions $R_{El}(r)$ are therefore solutions of the radial equation (7.44) with $V(r) = 0$, namely

$$\left[\frac{\text{d}^2}{\text{d}r^2} + \frac{2}{r}\frac{\text{d}}{\text{d}r} - \frac{l(l+1)}{r^2} + k^2\right]R_{El}(r) = 0 \tag{7.59}$$

where $k^2 = 2\mu E/\hbar^2$. Using (7.52) and the fact that in the present case the effective potential $V_{\text{eff}}(r)$ is just the centrifugal barrier term $l(l+1)\hbar^2/2\mu r^2$, we see that the free-particle functions $u_{El}(r) = rR_{El}(r)$ are solutions of the differential equation

$$\left[\frac{\text{d}^2}{\text{d}r^2} - \frac{l(l+1)}{r^2} + k^2\right]u_{El}(r) = 0. \tag{7.60}$$

Let us first consider the case $l = 0$. From (7.60) we see immediately that the solution $u_{E0}(r)$ which vanishes at the origin (in order to satisfy the boundary condition (7.54)) is given, up to a multiplicative constant, by $u_{E0}(r) = \sin kr$, so that $R_{E0}(r) \propto r^{-1}\sin kr$.

The spherical Bessel differential equation and its solutions

For $l \neq 0$ the equation (7.60) is more difficult to solve and it is convenient to return to the radial equation (7.59), which can be solved in terms of known functions for all values of $l (l = 0, 1, 2, \dots)$. Indeed, if we change variables in (7.59) to $\rho = kr$, and write $R_l(\rho) \equiv R_{El}(r)$, we obtain for $R_l(\rho)$ the equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + \frac{2}{\rho}\frac{\mathrm{d}}{\mathrm{d}\rho} + \left(1 - \frac{l(l+1)}{\rho^2}\right)\right] R_l(\rho) = 0 \tag{7.61}$$

which is called the *spherical Bessel differential equation*. Particular solutions of this equation are the *spherical Bessel functions*

$$j_l(\rho) = \left(\frac{\pi}{2\rho}\right)^{1/2} J_{l+\frac{1}{2}}(\rho) \tag{7.62a}$$

and the *spherical Neumann functions*

$$n_l(\rho) = (-1)^{l+1}\left(\frac{\pi}{2\rho}\right)^{1/2} J_{-l-\frac{1}{2}}(\rho) \tag{7.62b}$$

where $J_\nu(\rho)$ is an ordinary Bessel function[4] of order ν.

The functions $j_l(\rho)$ and $n_l(\rho)$ are also given by the expressions (Problem 7.5)

$$j_l(\rho) = (-\rho)^l \left(\frac{1}{\rho}\frac{\mathrm{d}}{\mathrm{d}\rho}\right)^l \frac{\sin\rho}{\rho} \tag{7.63a}$$

and

$$n_l(\rho) = -(-\rho)^l \left(\frac{1}{\rho}\frac{\mathrm{d}}{\mathrm{d}\rho}\right)^l \frac{\cos\rho}{\rho}. \tag{7.63b}$$

From the above equations, the first few functions $j_l(\rho)$ and $n_l(\rho)$ are readily found to be

$$j_0(\rho) = \frac{\sin\rho}{\rho}, \qquad n_0(\rho) = -\frac{\cos\rho}{\rho} \tag{7.64a}$$

$$j_1(\rho) = \frac{\sin\rho}{\rho^2} - \frac{\cos\rho}{\rho}, \qquad n_1(\rho) = -\frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho} \tag{7.64b}$$

$$j_2(\rho) = \left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\sin\rho - \frac{3}{\rho^2}\cos\rho, \quad n_2(\rho) = -\left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\cos\rho - \frac{3}{\rho^2}\sin\rho. \tag{7.64c}$$

These functions are plotted in Fig. 7.4.

---

[4] See, for example, Bell (1968) or Watson (1966).

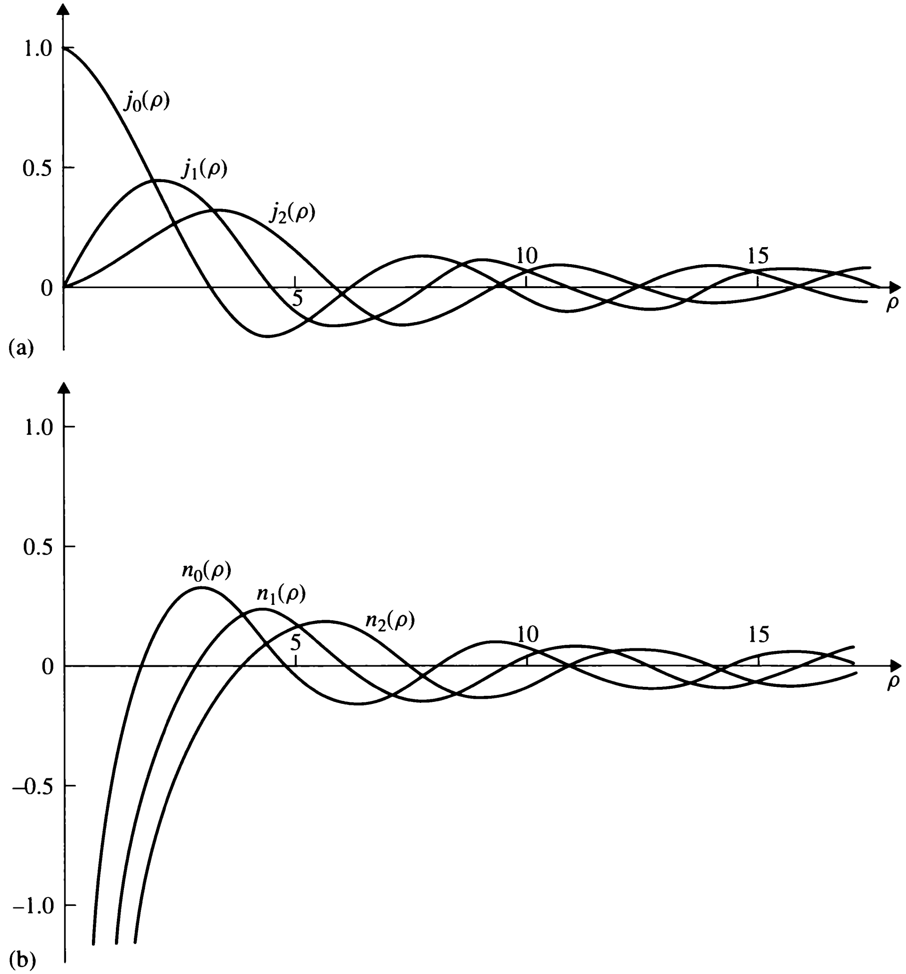


Figure 7.4 (a) The first three spherical Bessel functions. (b) The first three spherical Neumann functions.

We may also use equations (7.63) to obtain the leading term of $j_l(\rho)$ and $n_l(\rho)$ for small and large values of ρ (Problem 7.6). For small ρ, upon expanding $\rho^{-1} \sin \rho$ and $\rho^{-1} \cos \rho$ in a power series in ρ, it is found that

$$j_l(\rho) \underset{\rho \to 0}{\to} \frac{\rho^l}{1.3.5 \dots (2l+1)} \tag{7.65a}$$

$$n_l(\rho) \underset{\rho \to 0}{\to} -\frac{1.1.3.5 \dots (2l-1)}{\rho^{l+1}}. \tag{7.65b}$$

Asymptotically, for large values of ρ, the leading term is that proportional to ρ^{-1}, and one obtains

$$j_l(\rho) \underset{\rho\to\infty}{\to} \frac{1}{\rho}\sin\left(\rho - \frac{l\pi}{2}\right) \tag{7.66a}$$

$$n_l(\rho) \underset{\rho\to\infty}{\to} -\frac{1}{\rho}\cos\left(\rho - \frac{l\pi}{2}\right). \tag{7.66b}$$

Equations (7.66) are in fact useful approximations for ρ somewhat larger than $l(l+1)/2$.

For every l the two functions $\{j_l(\rho), n_l(\rho)\}$ provide a pair of linearly independent solutions of the spherical Bessel differential equation (7.61), so that the general solution of this equation can be written as a linear combination of these two functions. Another pair of linearly independent solutions of equation (7.61) is given by the *spherical Hankel functions* of the first and second kinds, which are defined respectively by

$$h_l^{(1)}(\rho) = j_l(\rho) + \mathrm{i}n_l(\rho) \tag{7.67a}$$

and

$$h_l^{(2)}(\rho) = j_l(\rho) - \mathrm{i}n_l(\rho) = [h_l^{(1)}(\rho)]^*. \tag{7.67b}$$

The first few spherical Hankel functions of the first kind are

$$h_0^{(1)}(\rho) = -\mathrm{i}\frac{\mathrm{e}^{\mathrm{i}\rho}}{\rho} \tag{7.68a}$$

$$h_1^{(1)}(\rho) = -\left(\frac{1}{\rho} + \frac{\mathrm{i}}{\rho^2}\right)\mathrm{e}^{\mathrm{i}\rho} \tag{7.68b}$$

$$h_2^{(1)}(\rho) = \left(\frac{\mathrm{i}}{\rho} - \frac{3}{\rho^2} - \frac{3\mathrm{i}}{\rho^3}\right)\mathrm{e}^{\mathrm{i}\rho}. \tag{7.68c}$$

Using (7.66) and (7.67) we also find that the asymptotic behaviour of the spherical Hankel functions is given by

$$h_l^{(1)}(\rho) \underset{\rho\to\infty}{\to} -\mathrm{i}\frac{\exp[\mathrm{i}(\rho - l\pi/2)]}{\rho} \tag{7.69a}$$

and

$$h_l^{(2)}(\rho) \underset{\rho\to\infty}{\to} \mathrm{i}\frac{\exp[-\mathrm{i}(\rho - l\pi/2)]}{\rho}. \tag{7.69b}$$

The eigenfunctions of the free particle in spherical polar coordinates

As seen from (7.65b), the spherical Neumann function $n_l(\rho)$ has a pole of order $l+1$ at the origin, and is therefore an *irregular* solution of equation (7.61). From their definition (7.67), we note that the spherical Hankel functions, which contain $n_l(\rho)$, are also irregular solutions of (7.61). On the other hand, the spherical Bessel function

$j_l(\rho)$ is finite at the origin and is thus a *regular* solution of (7.61). In fact $j_l(\rho)$ is finite everywhere, so that the radial eigenfunction of the Schrödinger equation (7.59) for a free particle is

$$R_{El}(r) = Cj_l(kr) \tag{7.70}$$

where C is a constant. Using (7.65a), we see that near $r = 0$ this free-particle radial wave function behaves like r^l, in agreement with the remark following (7.58).

Having obtained the free-particle radial functions we may now, using (7.45) and (7.70), write down the full eigenfunctions of the free particle in spherical polar coordinates as

$$\psi_{Elm}(\mathbf{r}) = Cj_l(kr)Y_{lm}(\theta, \phi). \tag{7.71}$$

These wave functions will be called *spherical waves*.

The eigenvalues k^2 of (7.59) can take on any value in the interval $(0, \infty)$, so that the energy $E = \hbar^2k^2/2\mu$ can assume any value in this interval, and the spectrum is continuous, as we found in Section 7.1. Every free-particle eigenfunction (7.71) can thus be labelled by the two discrete indices l and m and by the continuous index E (or k). It can be shown that the ensemble of the spherical waves forms a complete orthonormal set. Note that each energy eigenvalue is *infinitely degenerate*, since for a fixed value of E the eigenfunctions (7.71) are labelled by the two quantum numbers l and m, such that $l = 0, 1, 2, \ldots$, and $m = -l, -l + 1, \ldots, l$.

Expansion of a plane wave in spherical harmonics

We found in Section 7.1 that the stationary states of a free particle can be written as linear combinations of plane waves of the form (7.13). These plane-wave states are simultaneous eigenfunctions of the free-particle Hamiltonian $H = -(\hbar^2/2\mu)\nabla^2$, and of the three Cartesian components $(p_x)_{\text{op}}$, $(p_y)_{\text{op}}$ and $(p_z)_{\text{op}}$ of the linear momentum operator $\mathbf{p}_{\text{op}} = -\text{i}\hbar\boldsymbol{\nabla}$. They are characterised by the three well-defined Cartesian components $p_x = \hbar k_x$, $p_y = \hbar k_y$, $p_z = \hbar k_z$ of the momentum $\mathbf{p}$, and by the energy $E = \hbar^2k^2/2\mu$. Note that since the operators $(p_x)_{\text{op}}$, $(p_y)_{\text{op}}$ and $(p_z)_{\text{op}}$ do *not* simultaneously commute with $\mathbf{L}^2$ and L_z, the plane-wave states (7.13) cannot be labelled by the quantum numbers (l, m), so that the orbital angular momentum is poorly defined in those states. On the other hand, the spherical wave states (7.71) are states of well-defined orbital angular momentum, which are characterised by the quantum numbers (l, m), and for which the linear momentum is poorly defined.

Since both the plane-wave states (7.13) and the spherical-wave states (7.71) form a complete set, an arbitrary state can be expressed as a superposition of either of them. In particular, a plane wave $\exp(\text{i}\mathbf{k}.\mathbf{r})$ can be expanded in terms of spherical waves, so that we may write

$$\text{e}^{\text{i}\mathbf{k}.\mathbf{r}} = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l} c_{lm}j_l(kr)Y_{lm}(\theta, \phi) \tag{7.72}$$

where the coefficients c_{lm} (which are independent of $\mathbf{r}$) must be determined. In order to do this, we first consider the special case in which the vector $\mathbf{k}$ lies along the z-axis. The left-hand side of (7.72) then reads $\exp(\mathrm{i}\mathbf{k}.\mathbf{r}) = \exp(\mathrm{i}kr\cos\theta)$, which is independent of ϕ, so that the expansion (7.72) reduces to one in terms of the Legendre polynomials $P_l(\cos\theta)$

$$e^{\mathrm{i}\mathbf{k}.\mathbf{r}} = \sum_{l=0}^{\infty} a_l j_l(kr) P_l(\cos\theta). \tag{7.73}$$

The coefficients a_l of this expansion can be determined in the following way. Using the relation (6.80) satisfied by the Legendre polynomials, we have

$$\frac{2}{2l+1} a_l j_l(kr) = \int_{-1}^{+1} \exp(\mathrm{i}krw) P_l(w) \mathrm{d}w \tag{7.74}$$

where we have set $w = \cos\theta$. Integrating by parts, we find that

$$\frac{2}{2l+1} a_l j_l(kr) = \left[\frac{\exp(\mathrm{i}krw)}{\mathrm{i}kr} P_l(w)\right]_{w=-1}^{w=+1} - \int_{-1}^{+1} \frac{\exp(\mathrm{i}krw)}{\mathrm{i}kr} \left[\frac{\mathrm{d}}{\mathrm{d}w} P_l(w)\right] \mathrm{d}w. \tag{7.75}$$

Let us now examine this equation in the limit of large r. Using the asymptotic expression (7.66a) for $j_l(kr)$, and noting that the second term on the right of (7.75) is of order r^{-2} (which can be seen by performing a second integration by parts), we find that in the large r limit equation (7.75) reduces to

$$\begin{aligned}\frac{2}{2l+1} a_l \frac{1}{kr} \sin\left(kr - \frac{l\pi}{2}\right) &= \frac{1}{\mathrm{i}kr}[e^{\mathrm{i}kr} P_l(1) - e^{-\mathrm{i}kr} P_l(-1)] \\ &= \frac{1}{\mathrm{i}kr}[e^{\mathrm{i}kr} - (-1)^l e^{-\mathrm{i}kr}]\end{aligned} \tag{7.76}$$

from which we deduce that $a_l = (2l+1)\mathrm{i}^l$. The expansion of a plane wave $\exp(\mathrm{i}\mathbf{k}.\mathbf{r})$ in Legendre polynomials is therefore given by

$$e^{\mathrm{i}\mathbf{k}.\mathbf{r}} = \sum_{l=0}^{\infty} (2l+1)\mathrm{i}^l j_l(kr) P_l(\cos\theta). \tag{7.77}$$

Using the addition theorem of the spherical harmonics (see (6.129)) we can also write the above formula in the form of equation (7.72). That is

$$e^{\mathrm{i}\mathbf{k}.\mathbf{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \mathrm{i}^l j_l(kr) Y_{lm}^*(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}}) \tag{7.78}$$

where $\hat{\mathbf{v}}$ denotes the polar angles of a vector $\mathbf{v}$. Upon comparison of (7.72) and (7.78) we see that the coefficients c_{lm} of the expansion (7.72) are given by $c_{lm}(\hat{\mathbf{k}}) = 4\pi \mathrm{i}^l Y_{lm}^*(\hat{\mathbf{k}})$.

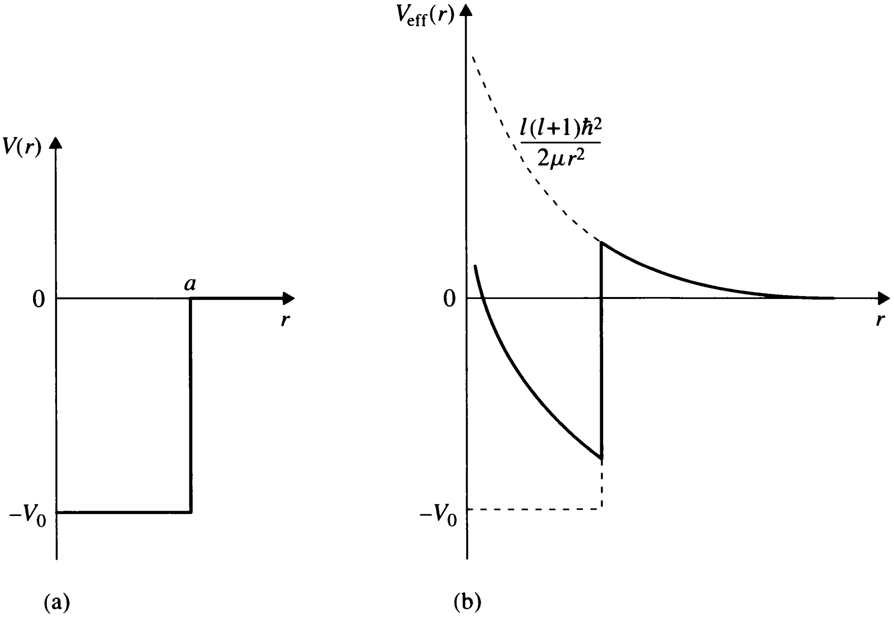


Figure 7.5 (a) The spherically symmetric square well potential of depth V_0 and range a. (b) The corresponding effective potential (solid line) $V_{\text{eff}}(r) = V(r) + l(l+1)\hbar^2/2\mu r^2$, for $l \neq 0$.

7.4 The three-dimensional square well potential

The next example of central potential which we shall analyse is the three-dimensional spherically symmetric square well of depth V_0 and range a

$$\begin{aligned} V(r) &= -V_0, \qquad r < a \\ &= 0, \qquad\quad r > a \end{aligned} \tag{7.79}$$

where V_0 and a are positive constants (see Fig. 7.5(a)). The corresponding effective potential (7.53) is shown in Fig. 7.5(b). Since $V_{\text{eff}}(r)$ vanishes as $r \to \infty$, solutions $u_{El}(r)$ of the radial equation (7.52) for $E \geqslant 0$ will have an oscillatory behaviour at infinity and will be acceptable eigenfunctions for any non-negative value of E. We therefore have a continuous spectrum for $E \geqslant 0$; the corresponding unbound states will be studied in Chapter 13, where we investigate collision phenomena. Here we shall only be interested in the *bound states*, for which the energy is such that $-V_0 \leqslant E < 0$.

Because the potential (7.79) is central we know that there exist solutions of the Schrödinger equation having the form (7.45). The radial functions $R_{El}(r)$ are solutions of the differential equation (7.44), which in the present case becomes

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right)+\frac{l(l+1)\hbar^2}{2\mu r^2}\right]R_{El}(r)=(E+V_0)R_{El}(r), \qquad r<a \tag{7.80a}$$

and

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right)+\frac{l(l+1)\hbar^2}{2\mu r^2}\right]R_{El}(r)=ER_{El}(r), \qquad r>a. \tag{7.80b}$$

Interior solution

Let us first analyse the equation (7.80a), which holds inside the well ($r < a$). If we define the quantity

$$K=\left[\frac{2\mu}{\hbar^2}(E+V_0)\right]^{1/2} \tag{7.81}$$

change variables to $\rho = Kr$, and write $R_l(\rho) \equiv R_{El}(r)$, we find that for $r < a$ the radial function $R_l(\rho)$ satisfies the spherical Bessel differential equation (7.61). Just as in the case of the free particle, the condition that $R_l(\rho)$ must be finite everywhere – including at the origin – restricts us to the spherical Bessel functions j_l, and we have, inside the well,

$$R_{El}(r)=Aj_l(Kr), \qquad r<a \tag{7.82}$$

where A is a constant.

Exterior solution

We now turn to the equation (7.80b), which is valid outside the well ($r > a$). This equation is formally identical to the free-particle equation (7.59), but we must remember that $E < 0$ in the present case. It is convenient to write $E = -(\hbar^2/2\mu)\lambda^2$, so that

$$\lambda=\left(-\frac{2\mu}{\hbar^2}E\right)^{1/2} \tag{7.83}$$

In order to put (7.80b) in the form of the spherical Bessel equation (7.61) we must redefine the variable ρ to be given by $\rho = \mathrm{i}\lambda r$, which amounts to replacing k by $\mathrm{i}\lambda$ in the free-particle treatment. Note that since $r > a$ in (7.80b), the domain of ρ does *not* extend down to zero, so that there is no reason to limit our choice to the spherical Bessel function, j_l, which is regular at the origin. Instead, a linear combination of the functions j_l and n_l (or $h_l^{(1)}$ and $h_l^{(2)}$) is perfectly admissible. The proper linear combination can be determined by looking at the asymptotic behaviour of the solutions. Using the asymptotic formulae (7.66) and (7.69), with $\rho = \mathrm{i}\lambda r$, we see that for large r the functions $j_l(\mathrm{i}\lambda r)$, $n_l(\mathrm{i}\lambda r)$ and $h_l^{(2)}(\mathrm{i}\lambda r)$ all increase exponentially (like $r^{-1}\exp(\lambda r)$) and must therefore be excluded. The only admissible solution is $h_l^{(1)}(\mathrm{i}\lambda r)$, which is proportional to $r^{-1}\exp(-\lambda r)$ for large r. Hence the desired solution of (7.80b), outside the well, is

$$\begin{aligned} R_{El}(r) &= Bh_l^{(1)}(\mathrm{i}\lambda r) \\ &= B[j_l(\mathrm{i}\lambda r) + \mathrm{i}n_l(\mathrm{i}\lambda r)], \qquad r > a \end{aligned} \tag{7.84}$$

where B is a constant. From (7.68) we see that the first three functions $h_l^{(1)}(\mathrm{i}\lambda r)$ are

$$h_0^{(1)}(\mathrm{i}\lambda r) = -\frac{1}{\lambda r}\mathrm{e}^{-\lambda r} \tag{7.85a}$$

$$h_1^{(1)}(\mathrm{i}\lambda r) = \mathrm{i}\left(\frac{1}{\lambda r} + \frac{1}{\lambda^2 r^2}\right)\mathrm{e}^{-\lambda r} \tag{7.85b}$$

$$h_2^{(1)}(\mathrm{i}\lambda r) = \left(\frac{1}{\lambda r} + \frac{3}{\lambda^2 r^2} + \frac{3}{\lambda^3 r^3}\right)\mathrm{e}^{-\lambda r}. \tag{7.85c}$$

Energy levels

As in the analogous one-dimensional problem studied in Section 4.6, the energy levels are obtained by requiring that the eigenfunction and its derivative be continuous at the discontinuity ($r = a$) of the potential. Thus the logarithmic derivative $(1/R_{El})(\mathrm{d}R_{El}/\mathrm{d}r)$ must be continuous at $r = a$. By applying this condition to the interior solution (7.82) and the exterior solution (7.84), we have

$$\left[\frac{\mathrm{d}j_l(Kr)/\mathrm{d}r}{j_l(Kr)}\right]_{r=a} = \left[\frac{\mathrm{d}h_l^{(1)}(\mathrm{i}\lambda r)/\mathrm{d}r}{h_l^{(1)}(\mathrm{i}\lambda r)}\right]_{r=a}. \tag{7.86}$$

This transcendental equation is complicated for arbitrary l, but for $l = 0$ we find with the help of (7.64a) and (7.85a) that it reduces to the equation

$$K \cot Ka = -\lambda \tag{7.87}$$

which we have already analysed in Section 4.6 when we studied the *odd parity* solutions of the one-dimensional square well. Thus, setting $\xi = Ka$ and $\eta = \lambda a$ and using (7.81) and (7.83), we have to solve the equation

$$\xi \cot \xi = -\eta \tag{7.88}$$

with

$$\xi^2 + \eta^2 = \frac{2\mu}{\hbar^2}V_0 a^2 = \gamma^2 \tag{7.89}$$

where $\gamma = (2\mu V_0 a^2/\hbar^2)^{1/2}$ is the 'strength parameter' of the square well. From our work of Section 4.6, we deduce that there is no ($l = 0$) bound state if $\gamma \leqslant \pi/2$, one ($l = 0$) bound state if $\pi/2 < \gamma \leqslant 3\pi/2$, and so on. The radial functions $R_{E0}(r)$ are illustrated in Fig. 7.6 for a spherical square well with $\gamma = 6$ which can support two $l = 0$ bound states.

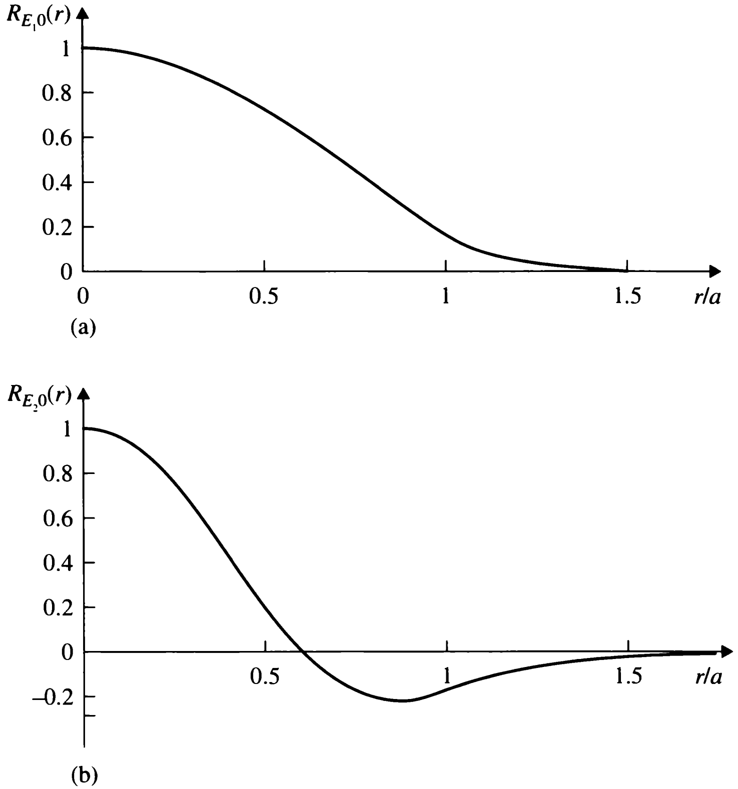


Figure 7.6 Illustration of the two $l = 0$ (s-wave) (unnormalised) radial eigenfunctions $R_{E0}(r)$ for a spherical square well potential such that $\gamma = 6$, corresponding to the bound state energies (a) $E = E_1 = -0.80V_0$ and (b) $E = E_2 = -0.24V_0$.

For the case $l = 1$ one readily finds (Problem 7.9) by using (7.64b) and (7.85b) that equation (7.86) reduces to

$$\frac{\cot\xi}{\xi} - \frac{1}{\xi^2} = \frac{1}{\eta} + \frac{1}{\eta^2} \tag{7.90}$$

where again $\xi^2 + \eta^2 = \gamma^2$. This equation must be solved numerically or graphically. It is worth noting that one can easily predict the number of $l = 1$ bound states as a function of the parameter γ without actually solving equation (7.90). Indeed, a new $l = 1$ bound state will appear whenever $\eta = 0$ or $\cot\xi$ is infinite. This will happen when $\xi = \pi, 2\pi, \ldots$, so that there is no $l = 1$ bound state when $\gamma \leqslant \pi$, one $l = 1$ bound state when $\pi < \gamma \leqslant 2\pi$, etc. We also remark that the smallest value of the 'strength parameter' γ for which the spherical square well can support an $l = 1$ bound state is larger than the corresponding value of γ for the $l = 0$ case. In fact, it can be shown (Problem 7.11) that the minimum value of γ

necessary to bind a particle of angular momentum l in the square well increases as l increases. This is physically reasonable in view of the presence of the repulsive centrifugal barrier term in the effective potential $V_{\text{eff}}(r) = V(r) + l(l+1)\hbar^2/2\mu r^2$ (see Fig. 7.5(b)).

Finally, we remark that in general there is no degeneracy between the energy levels obtained from equation (7.86) for different l values. Of course, each energy level of orbital angular momentum quantum number l is $(2l+1)$-fold degenerate with respect to the magnetic quantum number m, a feature which is common to all central potentials, as was shown in Section 7.2.

7.5 The hydrogenic atom

Let us now consider a hydrogenic atom containing an atomic nucleus of charge Ze and an electron of charge $-e$ interacting by means of the Coulomb potential

$$V(r) = -\frac{Ze^2}{(4\pi\varepsilon_0)r} \tag{7.91}$$

where r is the distance between the two particles. We denote by m the mass of the electron and by M the mass of the nucleus. Since the interaction potential (7.91) depends only on the relative coordinate of the two particles, we may use the results of Section 5.7 to separate the motion of the centre of mass. Thus, working in the centre-of-mass system (where the total momentum **P** of the atom is equal to zero), the Hamiltonian of the atom reduces to that describing the relative motion of the two particles:

$$H = \frac{\mathbf{p}^2}{2\mu} - \frac{Ze^2}{(4\pi\varepsilon_0)r} \tag{7.92}$$

where **p** is the relative momentum and

$$\mu = \frac{mM}{m+M} \tag{7.93}$$

is the reduced mass of the two particles. The corresponding one-body Schrödinger equation describing the relative motion is

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r}\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{7.94}$$

Since the Coulomb potential is central, this equation admits solutions of the form $\psi_{Elm}(\mathbf{r}) = R_{El}(r)Y_{lm}(\theta,\phi)$. Writing $u_{El}(r) = rR_{El}(r)$ and using (7.52) and (7.53), we see that the functions $u_{El}(r)$ must satisfy the equation

$$\frac{\mathrm{d}^2u_{El}(r)}{\mathrm{d}r^2} + \frac{2\mu}{\hbar^2}[E - V_{\text{eff}}(r)]u_{El}(r) = 0 \tag{7.95a}$$

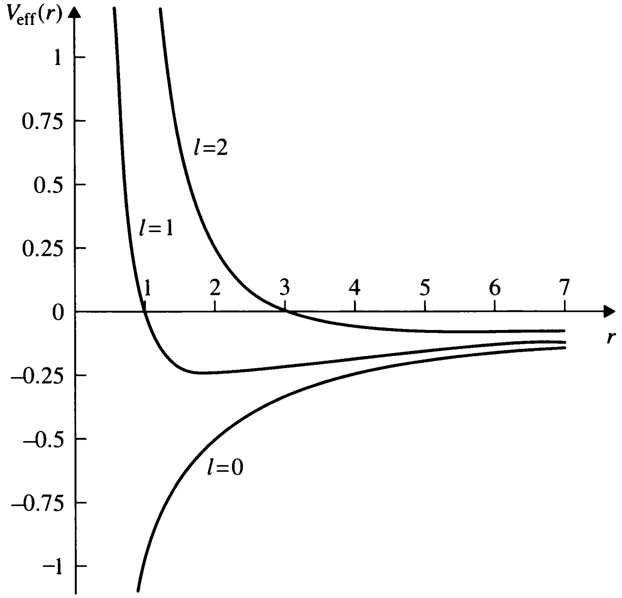


Figure 7.7 The effective potential $V_{\text{eff}}(r)$ given by (7.95b) for the case $Z = 1$ and for the values $l = 0, 1, 2$. The unit of length is $a_\mu = (m/\mu)a_0$ where a_0 is the Bohr radius (1.66). The unit of energy is $e^2/(4\pi\varepsilon_0 a_\mu)$.

where

$$V_{\text{eff}}(r) = -\frac{Ze^2}{(4\pi\varepsilon_0)r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \tag{7.95b}$$

is the effective potential. Fig. 7.7 shows this effective potential for the case $Z = 1$ and for the values $l = 0, 1, 2$ of the orbital angular momentum quantum number. Because $V_{\text{eff}}(r)$ tends to zero for large r, the solution $u_{El}(r)$ for $E > 0$ will have an oscillatory behaviour at infinity and will be an acceptable eigenfunction for any positive value of E. We therefore have a *continuous spectrum* for $E > 0$. The corresponding unbound (scattering) states play an important role in the analysis of collision phenomena between electrons and ions. In what follows, however, we shall focus our attention on the *bound states*, for which $E < 0$.

We now proceed to solve equation (7.95), subject to the condition $u_{El}(0) = 0$ (see (7.54)). It is convenient to introduce the dimensionless quantities

$$\rho = \left(-\frac{8\mu E}{\hbar^2}\right)^{1/2} r \tag{7.96}$$

and

$$\lambda = \frac{Ze^2}{(4\pi\varepsilon_0)\hbar}\left(-\frac{\mu}{2E}\right)^{1/2} = Z\alpha\left(-\frac{\mu c^2}{2E}\right)^{1/2} \tag{7.97}$$

where $\alpha = e^2/(4\pi\varepsilon_0\hbar c) \simeq 1/137$ is the fine-structure constant and we recall that $E < 0$. In terms of the new quantities ρ and λ, (7.95) becomes

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}\right] u_{El}(\rho) = 0. \tag{7.98}$$

Let us first examine the asymptotic behaviour of $u_{El}(\rho)$. To this end, we remark that when $\rho \to \infty$ the terms in ρ^{-1} and ρ^{-2} become negligible with respect to the constant term $(-1/4)$. Hence for large ρ equation (7.98) reduces to the 'asymptotic' equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \frac{1}{4}\right] u_{El}(\rho) = 0, \tag{7.99}$$

the solutions of which are proportional to $\exp(\pm\rho/2)$. Since the function $u_{El}(\rho)$ must be bounded everywhere, including at infinity, we must keep only the exponentially decreasing function, so that

$$u_{El}(\rho) \underset{\rho\to\infty}{\sim} \exp(-\rho/2), \tag{7.100}$$

This result suggests that we look for a solution of the radial equation (7.98) having the form

$$u_{El}(\rho) = \mathrm{e}^{-\rho/2} f(\rho) \tag{7.101}$$

where we have written $f(\rho) \equiv f_{El}(\rho)$ to simplify the notation. Substituting (7.101) into (7.98), we obtain for $f(\rho)$ the equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \frac{\mathrm{d}}{\mathrm{d}\rho} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho}\right] f(\rho) = 0. \tag{7.102}$$

We now write a series expansion for $f(\rho)$ in the form

$$f(\rho) = \rho^{l+1} g(\rho) \tag{7.103}$$

where

$$g(\rho) = \sum_{k=0}^{\infty} c_k \rho^k, \qquad c_0 \neq 0 \tag{7.104}$$

and we have used the fact (see (7.58)) that $u_{El}(\rho)$, and thus also $f(\rho)$, behaves like ρ^{l+1} in the vicinity of the origin. Inserting (7.103) into (7.102), we find that the function $g(\rho)$ satisfies the differential equation

$$\left[\rho\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + (2l+2-\rho)\frac{\mathrm{d}}{\mathrm{d}\rho} + (\lambda - l - 1)\right] g(\rho) = 0. \tag{7.105}$$

Using the expansion (7.104) to solve this equation, we have

$$\sum_{k=0}^{\infty} [k(k-1)c_k\rho^{k-1} + (2l+2-\rho)kc_k\rho^{k-1} + (\lambda - l - 1)c_k\rho^k] = 0 \tag{7.106}$$

or

$$\sum_{k=0}^{\infty}\{[k(k+1)+(2l+2)(k+1)]c_{k+1}+(\lambda-l-1-k)c_k\}\rho^k=0 \tag{7.107}$$

so that the coefficients c_k must satisfy the recursion relation

$$c_{k+1}=\frac{k+l+1-\lambda}{(k+1)(k+2l+2)}c_k. \tag{7.108}$$

If the series (7.104) does not terminate, we see from (7.108) that for large k

$$\frac{c_{k+1}}{c_k}\sim\frac{1}{k} \tag{7.109}$$

a ratio which is the same as that of the series for $\rho^p\exp(\rho)$, where p has a finite value. Thus in this case we deduce by using (7.101) and (7.103) that the function $u_{El}(r)$ has an asymptotic behaviour of the type

$$u_{El}(\rho)\underset{\rho\to\infty}{\sim}\rho^{l+1+p}e^{\rho/2} \tag{7.110}$$

which is clearly unacceptable.

The series (7.104) must therefore terminate, which means that $g(\rho)$ must be a *polynomial* in ρ. Let the highest power of ρ appearing in $g(\rho)$ be ρ^{n_r}, where the *radial quantum number* $n_r=0,1,2,\dots$, is a positive integer or zero. Then the coefficient $c_{n_r+1}=0$, and from the recursion formula (7.108) we have

$$\lambda=n_r+l+1. \tag{7.111}$$

Let us introduce the *principal quantum number*

$$n=n_r+l+1 \tag{7.112}$$

which is a positive integer ($n=1,2,\dots$) since both n_r and l can take on positive integer or zero values. From (7.111) and (7.112) we see that the eigenvalues of equation (7.98) corresponding to the bound-state spectrum ($E<0$) are given by

$$\lambda=n. \tag{7.113}$$

Energy levels

Replacing in (7.97) the quantity λ by its value (7.113), we obtain the bound-state energy eigenvalues

$$\begin{aligned}E_n&=-\frac{\mu}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{1}{n^2}\\&=-\frac{e^2}{(4\pi\varepsilon_0)a_\mu}\frac{Z^2}{2n^2}\\&=-\frac{1}{2}\mu c^2\frac{(Z\alpha)^2}{n^2},\qquad n=1,2,3,\dots\end{aligned} \tag{7.114}$$

where $\alpha \simeq 1/137$ is the fine-structure constant and a_μ denotes the modified Bohr radius

$$a_\mu = \frac{(4\pi\varepsilon_0)\hbar^2}{\mu e^2} = \frac{m}{\mu}a_0 \tag{7.115}$$

with $a_0 = (4\pi\varepsilon_0)\hbar^2/(me^2)$ being the Bohr radius (1.66).

The energy levels (7.114), which we have obtained here by solving the Schrödinger equation for one-electron atoms, agree exactly with those found in Section 1.4 from the Bohr model. The agreement of this energy spectrum with the main features of the experimental spectrum was pointed out when we analysed the Bohr results. This agreement, however, is not perfect and various corrections (such as the fine structure arising from relativistic effects and the electron spin, the Lamb shift and the hyperfine structure due to nuclear effects) must be taken into account in order to explain the details of the experimental spectrum[5].

We remark from (7.114) that since n may take on all integral values from 1 to $+\infty$, the bound-state energy spectrum corresponding to the Coulomb potential (7.91) contains an *infinite number of discrete energy levels* extending from $-(\mu/2\hbar^2)(Ze^2/4\pi\varepsilon_0)^2$ to zero. This is due to the fact that the magnitude of the Coulomb potential falls off slowly at larger r. On the contrary, short-range potentials – such as the square well studied in the previous section – have a finite (sometimes zero) number of bound states.

Another striking feature of the result (7.114) is that the energy eigenvalues E_n depend only on the principal quantum number n, and are therefore degenerate with respect to the quantum numbers l and m. Indeed, for each value of n the orbital angular momentum quantum number l may take on the values $0, 1, \dots, n-1$, and for each value of l the magnetic quantum number m may take the $(2l+1)$ possible values $-l, -l+1, \dots, +l$. The total degeneracy of the bound-state energy level E_n is therefore given by

$$\sum_{l=0}^{n-1}(2l+1) = 2\frac{n(n-1)}{2} + n = n^2. \tag{7.116}$$

As we have shown in Section 7.2, the degeneracy with respect to the quantum number m is present for any central potential $V(r)$. On the other hand, the degeneracy with respect to l is characteristic of the Coulomb potential; it is removed if the dependence of the potential on r is modified. For example, we have seen in Section 7.4 that there is no degeneracy with respect to l in the case of a square well. Another illustration is provided by the spectrum of alkali atoms. Many properties of these atoms can be understood in terms of the motion of a single 'valence' electron in a central potential which is Coulombic (i.e. proportional to r^{-1}) at large distances, but which deviates from the Coulomb behaviour as r decreases because of the presence of the 'inner' electrons. As a result, the energy of the valence electron does depend on l, and the degeneracy with respect to l is removed, leading to n distinct levels

---

[5] See Bransden and Joachain (1983), Chapter 5.

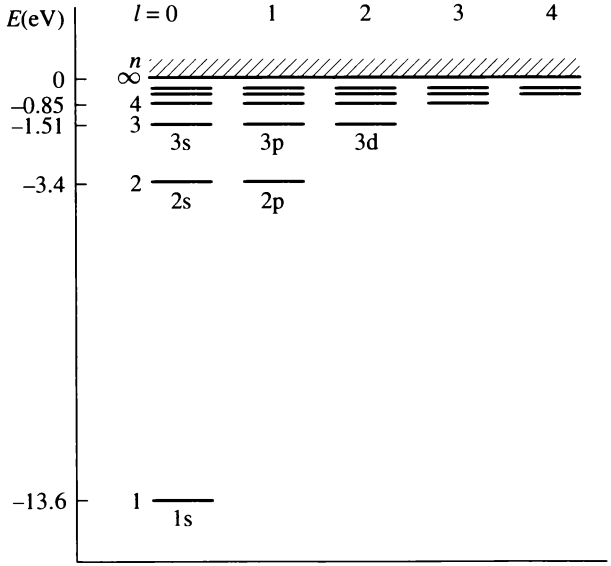


Figure 7.8 The energy-level diagram of atomic hydrogen.

$E_{nl}(l = 0, 1, \ldots, n - 1)$ for a given principal quantum number n. Finally, if an external magnetic field is applied to the atom, we shall see in Chapter 12 that the $(2l + 1)$ degeneracy with respect to the magnetic quantum number m is removed.

Figure 7.8 shows the energy-level diagram of the hydrogen atom; it is similar to that displayed in Fig. 1.11, except that the degenerate levels with the same n but different l are shown separately. Following the usual spectroscopic notation, these levels are labelled by two symbols. The first one gives the value of the principal quantum number n; the second one is a code letter which indicates the value of the orbital angular momentum quantum number l according to the correspondence discussed in Chapter 6, namely

Value of l	0	1	2	3	4	5
	$\updownarrow$	$\updownarrow$	$\updownarrow$	$\updownarrow$	$\updownarrow$	$\updownarrow$
Code letter	s	p	d	f	g	h

Looking at the hydrogen atom spectrum illustrated in Fig. 7.8, we see that the ground state ($n = 1$) is a 1s state, the first excited state ($n = 2$) is four-fold degenerate and contains one 2s state and three 2p states (with $m = -1, 0, +1$), the second excited state ($n = 3$) is nine-fold degenerate and contains one 3s state, three 3p states (with $m = -1, 0, +1$) and five 3d states (with $m = -2, -1, 0, +1, +2$), etc.

Having obtained the energy levels of one-electron atoms within the framework of the Schrödinger non-relativistic quantum theory, we may now inquire about the *spectral lines* corresponding to transitions from one energy level to another. This problem has already been discussed in Chapter 1, where the frequencies of the spectral lines were obtained by using the Bohr model. We shall return to this question in detail in Chapter 11, where the interaction of atomic systems with electromagnetic radiation will be studied quantum mechanically. In particular, we shall re-derive in that chapter the Bohr result (1.61) giving the frequencies of the spectral lines, and we shall calculate the transition rates for the most common transitions, the so-called electric dipole transitions.

The eigenfunctions of the bound states

Until now we have seen that the energy levels predicted by the Schrödinger theory for hydrogenic atoms agree with those already obtained in Section 1.4 by using the Bohr model. However, the Schrödinger theory has much more predictive power than the old quantum theory since it also yields the *eigenfunctions* which enable one to calculate probability densities, expectation values of operators, transition rates, etc.

The radial eigenfunctions of the bound states

In order to obtain these eigenfunctions explicitly, let us return to (7.105). This equation can be identified with the *Kummer–Laplace differential equation*

$$z\frac{\mathrm{d}^2 w}{\mathrm{d}z^2} + (c-z)\frac{\mathrm{d}w}{\mathrm{d}z} - aw = 0 \tag{7.117}$$

with $z = \rho$, $w = g$, $a = l + 1 - \lambda$ and $c = 2l + 2$. Within a multiplicative constant, the solution of (7.117), regular at the origin, is the *confluent hypergeometric function*

$$\begin{aligned} {}_1F_1(a, c, z) &= 1 + \frac{az}{c1!} + \frac{a(a+1)z^2}{c(c+1)2!} + \cdots \\ &= \sum_{k=0}^{\infty} \frac{(a)_k\, z^k}{(c)_k\, k!} \end{aligned} \tag{7.118a}$$

where

$$\alpha_k = \alpha(\alpha+1)\ldots(\alpha+k-1), \qquad (\alpha)_0 = 1. \tag{7.118b}$$

In general, for large positive values of its argument the confluent hypergeometric series (7.118) behaves asymptotically as

$${}_1F_1(a, c, z) \to \frac{\Gamma(c)}{\Gamma(a)} \mathrm{e}^{z} z^{a-c} \tag{7.119}$$

where Γ is Euler's gamma function. Thus, in the present case the series (7.118) for ${}_1F_1(l + 1 - \lambda, 2l + 2, \rho)$ is in general proportional to $\rho^{-l-1-\lambda}\exp(\rho)$ for large ρ, leading to a function $u_{El}(\rho)$ having the unacceptable asymptotic behaviour $u_{El}(\rho) \sim \rho^{-\lambda}\exp(\rho/2)$ (see (7.101) and (7.103)). The only way to obtain physically acceptable solutions of (7.105) is to require that the hypergeometric series for ${}_1F_1(l + 1 - \lambda, 2l + 2, \rho)$ terminates, which implies that $l + 1 - \lambda = -n_r (n_r = 0, 1, 2, \ldots)$, and hence $\lambda = n_r + l + 1 = n$. The confluent hypergeometric function ${}_1F_1(l+1-\lambda, 2l+2, \rho) \equiv {}_1F_1(-n_r, 2l+2, \rho)$ then reduces to a *polynomial* of degree n_r, namely

$$\begin{aligned} &{}_1F_1(l+1-n, 2l+2, \rho) \\ &= \sum_{k=0}^{n-l-1} \frac{(k+l-n)(k-1+l-n)\dots(1+l-n)}{(k+2l+1)(k-1+2l+1)\dots(1+2l+1)} \frac{\rho^k}{k!} \end{aligned} \qquad \textbf{(7.120)}$$

in accordance with our foregoing discussion. We may readily verify the correctness of this result by using the recursion relation (7.108) which we derived above for the coefficients c_k of the function $g(\rho)$. Thus, setting $c_0 = 1$ and using the fact that $\lambda = n$, we find from (7.108) that

$$c_k = \frac{(k+l-n)(k-1+l-n)\dots(1+l-n)}{(k+2l+1)(k-1+2l+1)\dots(1+2l+1)} \frac{1}{k!} \qquad \textbf{(7.121)}$$

in agreement with (7.120). We also remark from (7.96) and (7.114) that

$$\rho = \frac{2Z}{na_\mu} r = \frac{2Z}{na_0} \frac{\mu}{m} r. \qquad \textbf{(7.122)}$$

The physically admissible solutions $g(\rho)$ of (7.105), corresponding to $\lambda = n$, may also be expressed in terms of *associated Laguerre polynomials*. To see how this comes about, we first define the *Laguerre polynomials* $L_q(\rho)$ by the relation

$$L_q(\rho) = \mathrm{e}^{\rho} \frac{\mathrm{d}^q}{\mathrm{d}\rho^q} (\rho^q \mathrm{e}^{-\rho}) \qquad \textbf{(7.123)}$$

and we note that these Laguerre polynomials may also be obtained from the generating function

$$\begin{aligned} U(\rho, s) &= \frac{\exp[-\rho s/(1-s)]}{1-s} \\ &= \sum_{q=0}^{\infty} \frac{L_q(\rho)}{q!} s^q, \qquad |s| < 1. \end{aligned} \qquad \textbf{(7.124)}$$

Differentiation of this generating function with respect to s yields the recurrence formula (Problem 7.12)

$$L_{q+1}(\rho) + (\rho - 1 - 2q) L_q(\rho) + q^2 L_{q-1}(\rho) = 0. \qquad \textbf{(7.125)}$$

Similarly, upon differentiation of $U(\rho, s)$ with respect to ρ, we find that

$$\frac{\mathrm{d}}{\mathrm{d}\rho} L_q(\rho) - q \frac{\mathrm{d}}{\mathrm{d}\rho} L_{q-1}(\rho) + q L_{q-1}(\rho) = 0. \qquad \textbf{(7.126)}$$

Using (7.125) and (7.126), it is readily shown that the lowest order differential equation involving only $L_q(\rho)$ is

$$\left[\rho \frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + (1-\rho) \frac{\mathrm{d}}{\mathrm{d}\rho} + q\right] L_q(\rho) = 0. \qquad \textbf{(7.127)}$$

Next, we define the *associated Laguerre polynomials* $L_q^p(\rho)$ by the relation

$$L_q^p(\rho) = \frac{\mathrm{d}^p}{\mathrm{d}\rho^p} L_q(\rho). \tag{7.128}$$

Differentiating (7.127) p times, we find that $L_q^p(\rho)$ satisfies the differential equation (Problem 7.13)

$$\left[\rho\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + (p+1-\rho)\frac{\mathrm{d}}{\mathrm{d}\rho} + (q-p)\right]L_q^p(\rho) = 0. \tag{7.129}$$

Setting $\lambda = n$ in (7.105) and comparing with (7.129), we see that the physically acceptable solution $g(\rho)$ of (7.105) is given (up to a multiplicative constant) by the associated Laguerre polynomial $L_{n+l}^{2l+1}(\rho)$. Note that this polynomial is of order $(n+l)-(2l+1) = n-l-1 = n_r$, in accordance with the discussion following (7.110).

The generating function for the associated Laguerre polynomials may be obtained by differentiating (7.124) p times with respect to ρ. That is,

$$\begin{aligned} U_p(\rho, s) &= \frac{(-s)^p \exp[-\rho s/(1-s)]}{(1-s)^{p+1}} \\ &= \sum_{q=p}^{\infty} \frac{L_q^p(\rho)}{q!} s^q, \qquad |s| < 1. \end{aligned} \tag{7.130}$$

An explicit expression for $L_{n+l}^{2l+1}(\rho)$ is given by

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+1} \frac{[(n+l)!]^2}{(n-l-1-k)!(2l+1+k)!} \frac{\rho^k}{k!} \tag{7.131}$$

and is readily verified by substitution into (7.130), with $q = n+l$ and $p = 2l+1$.

Since the physically admissible solutions $g(\rho)$ of (7.105) are given within a multiplicative constant either by the confluent hypergeometric function ${}_1F_1(l+1-n, 2l+2, \rho)$ or by the associated Laguerre polynomial $L_{n+l}^{2l+1}(\rho)$, it is clear that these two functions differ only by a constant factor. This factor is readily found by comparing (7.120) and (7.131) at $\rho = 0$ and remembering that the confluent hypergeometric function is equal to unity at the origin (see (7.118)). Thus we have

$$L_{n+l}^{2l+1}(\rho) = -\frac{[(n+l)!]^2}{(n-l-1)!(2l+1)!}\, {}_1F_1(l+1-n, 2l+2, \rho). \tag{7.132}$$

Using (7.51), (7.101), (7.103) and the foregoing results, we may now write the full hydrogenic radial functions as

$$R_{nl}(r) = N\mathrm{e}^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho) \tag{7.133a}$$

$$= \tilde{N}\mathrm{e}^{-\rho/2}\rho^l\, {}_1F_1(l+1-n, 2l+2, \rho) \tag{7.133b}$$

where N and $\tilde{N}$ are constants which will be determined below (apart from an arbitrary phase factor) by the normalisation condition. In (7.133) we have used the notation

R_{nl} (which displays explicitly the quantum numbers n and l) instead of the symbol R_{El}, and we recall that $\rho = (2Z/na_\mu)r$ (see (7.122)).

The hydrogenic wave functions of the discrete spectrum

Using (7.45), we see that the full eigenfunctions of the discrete spectrum for hydrogenic atoms may be written as

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi) \tag{7.134}$$

where the radial functions are given by (7.133) and the spherical harmonics provide the angular part of the wave functions. We require that the eigenfunctions (7.134) be normalised to unity, so that

$$\int_0^\infty \mathrm{d}r r^2 \int_0^\pi \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\phi |\psi_{nlm}(r,\theta,\phi)|^2 = 1. \tag{7.135}$$

Because the spherical harmonics are normalised on the unit sphere (see (6.103)), the normalisation condition (7.135) implies that

$$\int_0^\infty |R_{nl}(r)|^2 r^2 \mathrm{d}r = 1 \tag{7.136}$$

or

$$|N|^2 \left(\frac{na_\mu}{2Z}\right)^3 \int_0^\infty \mathrm{e}^{-\rho}\rho^{2l}[L_{n+l}^{2l+1}(\rho)]^2 \rho^2 \mathrm{d}\rho = 1 \tag{7.137}$$

where we have used (7.133a). The integral over ρ can be evaluated by using the generating function (7.130) for the associated Laguerre polynomials (see Problem 7.15). The result is

$$\int_0^\infty \mathrm{e}^{-\rho}\rho^{2l}[L_{n+l}^{2l+1}(\rho)]^2 \rho^2 \mathrm{d}\rho = \frac{2n[(n+l)!]^3}{(n-l-1)!} \tag{7.138}$$

so that the normalised radial functions for the bound states of hydrogenic atoms may be written as

$$R_{nl}(r) = -\left\{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2} \mathrm{e}^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho) \tag{7.139a}$$

or

$$R_{nl}(r) = \frac{1}{(2l+1)!}\left\{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n+l)!}{2n(n-l-1)!}\right\}^{1/2} \times \mathrm{e}^{-\rho/2}\rho^l {}_1F_1(l+1-n, 2l+2, \rho) \tag{7.139b}$$

with

$$\rho = \frac{2Z}{na_\mu}r, \qquad a_\mu = \frac{(4\pi\varepsilon_0)\hbar^2}{\mu \mathrm{e}^2} \tag{7.139c}$$

where a constant multiplicative factor of modulus one is still arbitrary. In writing (7.139b) we have used equation (7.132) which relates the associated Laguerre polynomial $L_{n+l}^{2l+1}(\rho)$ to the confluent hypergeometric function ${}_1F_1(l+1-n, 2l+2, \rho)$.

The first few radial eigenfunctions (7.139) are given by

$$\begin{aligned}
R_{10}(r) &= 2(Z/a_\mu)^{3/2}\exp(-Zr/a_\mu) \\
R_{20}(r) &= 2(Z/2a_\mu)^{3/2}(1 - Zr/2a_\mu)\exp(-Zr/2a_\mu) \\
R_{21}(r) &= \frac{1}{\sqrt{3}}(Z/2a_\mu)^{3/2}(Zr/a_\mu)\exp(-Zr/2a_\mu) \\
R_{30}(r) &= 2(Z/3a_\mu)^{3/2}(1 - 2Zr/3a_\mu + 2Z^2r^2/27a_\mu^2)\exp(-Zr/3a_\mu) \\
R_{31}(r) &= \frac{4\sqrt{2}}{9}(Z/3a_\mu)^{3/2}(1 - Zr/6a_\mu)(Zr/a_\mu)\exp(-Zr/3a_\mu) \\
R_{32}(r) &= \frac{4}{27\sqrt{10}}(Z/3a_\mu)^{3/2}(Zr/a_\mu)^2\exp(-Zr/3a_\mu)
\end{aligned} \tag{7.140}$$

and are illustrated in Fig. 7.9.

Using the radial wave functions (7.140), together with the explicit expressions of the spherical harmonics given in Table 6.1, we display in Table 7.1 the full normalised bound-state hydrogenic eigenfunctions $\psi_{nlm}(r, \theta, \phi)$ for the first three shells (that is, the K, L and M shells corresponding, respectively, to the values $n = 1, 2, 3$ of the principal quantum number). We have also indicated in Table 7.1 the spectroscopic notation, introduced in the discussion of the energy levels, with the subscripts corresponding to the values of the magnetic quantum number m (when $l \neq 0$).

According to the interpretation of the wave function discussed in Chapter 2, the quantity

$$|\psi_{nlm}(r, \theta, \phi)|^2 \mathrm{d}\mathbf{r} = \psi_{nlm}^*(r, \theta, \phi)\psi_{nlm}(r, \theta, \phi)r^2\mathrm{d}r\sin\theta\mathrm{d}\theta\mathrm{d}\phi \tag{7.141}$$

represents the probability of finding the electron in the volume element $\mathrm{d}\mathbf{r}$ (given in spherical polar coordinates by $\mathrm{d}\mathbf{r} = r^2\mathrm{d}r\sin\theta\mathrm{d}\theta\mathrm{d}\phi$) when the system is in the stationary state specified by the quantum numbers (n, l, m). In agreement with the discussion following (7.46), the *position probability density*

$$|\psi_{nlm}(r, \theta, \phi)|^2 = |R_{nl}(r)|^2(2\pi)^{-1}|\Theta_{lm}(\theta)|^2 \tag{7.142}$$

does not depend on the coordinate ϕ. It is the product of the *angular factor* $(2\pi)^{-1}|\Theta_{lm}(\theta)|^2$, studied in Chapter 6 and of the quantity $|R_{nl}(r)|^2$, which gives the *electron density* as a function of r *along a given direction.* The *radial distribution function*

$$D_{nl}(r) = r^2|R_{nl}(r)|^2 \tag{7.143}$$

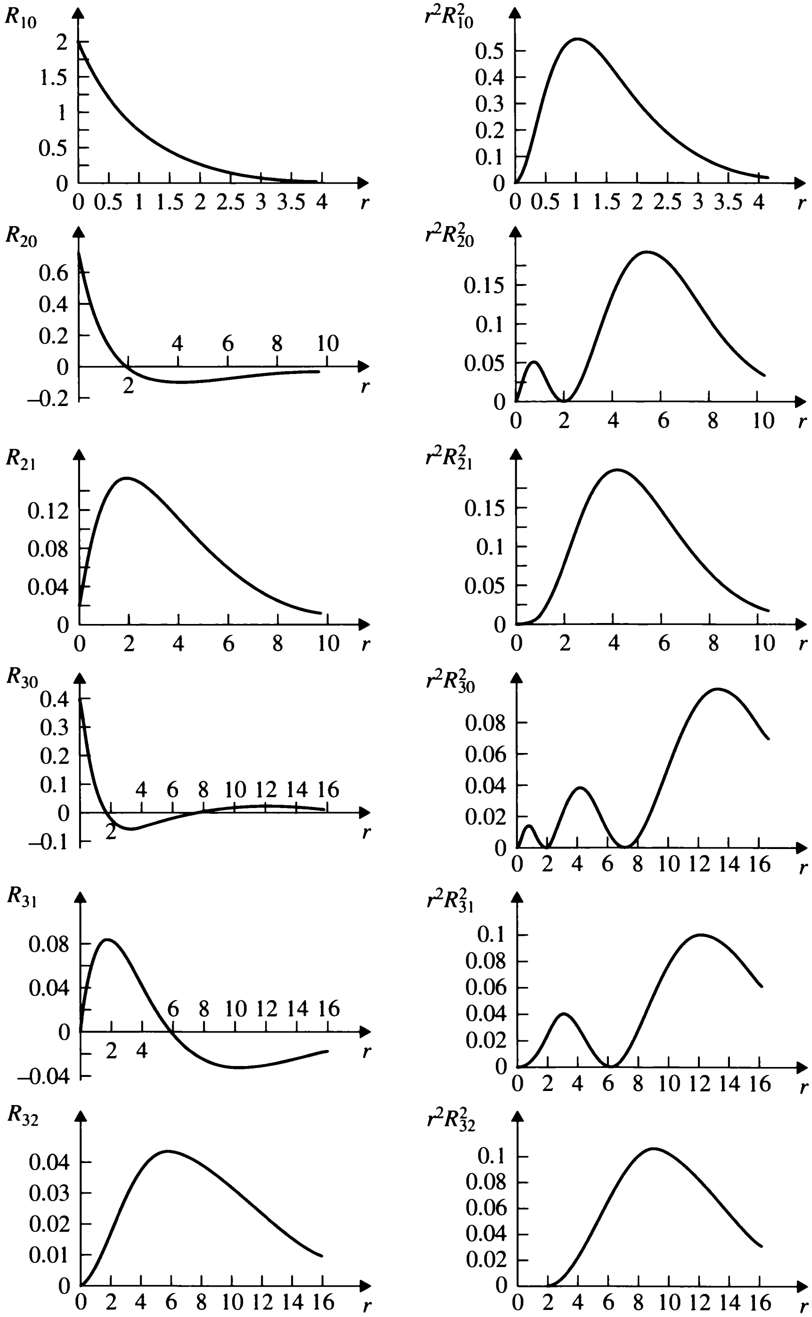


Figure 7.9 Radial functions $R_{nl}(r)$ and radial distribution functions $r^2R^2_{nl}(r)$ for atomic hydrogen. The unit of length is $a_\mu = (m/\mu)a_0$, where a_0 is the first Bohr radius (1.66).

Table 7.1 The complete normalised hydrogenic wave functions corresponding to the first three shells.

	Quantum numbers			*Spectroscopic*	*Wave function* $\psi_{nlm}(r,\theta,\phi)$
Shell	*n*	*l*	*m*	*notation*	
K	1	0	0	1s	$\frac{1}{\sqrt{\pi}}(Z/a_\mu)^{3/2}\exp(-Zr/a_\mu)$
L	2	0	0	2s	$\frac{1}{2\sqrt{2\pi}}(Z/a_\mu)^{3/2}(1-Zr/2a_\mu)\exp(-Zr/2a_\mu)$
	2	1	0	2p_0	$\frac{1}{4\sqrt{2\pi}}(Z/a_\mu)^{3/2}(Zr/a_\mu)\exp(-Zr/2a_\mu)\cos\theta$
	2	1	±1	$2\text{p}_{\pm1}$	$\mp\frac{1}{8\sqrt{\pi}}(Z/a_\mu)^{3/2}(Zr/a_\mu)\exp(-Zr/2a_\mu)\sin\theta\exp(\pm i\phi)$
M	3	0	0	3s	$\frac{1}{3\sqrt{3\pi}}(Z/a_\mu)^{3/2}(1-2Zr/3a_\mu+2Z^2r^2/27a_\mu^2)\exp(-Zr/3a_\mu)$
	3	1	0	3p_0	$\frac{2\sqrt{2}}{27\sqrt{\pi}}(Z/a_\mu)^{3/2}(1-Zr/6a_\mu)(Zr/a_\mu)\exp(-Zr/3a_\mu)\cos\theta$
	3	1	±1	$3\text{p}_{\pm1}$	$\mp\frac{2}{27\sqrt{\pi}}(Z/a_\mu)^{3/2}(1-Zr/6a_\mu)(Zr/a_\mu)\exp(-Zr/3a_\mu)\sin\theta\exp(\pm i\phi)$
	3	2	0	3d_0	$\frac{1}{81\sqrt{6\pi}}(Z/a_\mu)^{3/2}(Z^2r^2/a_\mu^2)\exp(-Zr/3a_\mu)(3\cos^2\theta-1)$
	3	2	±1	$3\text{d}_{\pm1}$	$\mp\frac{1}{81\sqrt{\pi}}(Z/a_\mu)^{3/2}(Z^2r^2/a_\mu^2)\exp(-Zr/3a_\mu)\sin\theta\cos\theta\exp(\pm i\phi)$
	3	2	±2	$3\text{d}_{\pm2}$	$\frac{1}{162\sqrt{\pi}}(Z/a_\mu)^{3/2}(Z^2r^2/a_\mu^2)\exp(-Zr/3a_\mu)\sin^2\theta\exp(\pm 2i\phi)$

gives the probability per unit length that the electron is to be found at a distance r from the nucleus. Indeed, by integrating (7.141) over the polar angles θ and ϕ and using (7.134) and (6.103), we see that

$$\begin{aligned}
&\int_0^\pi \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\phi |\psi_{nlm}(r,\theta,\phi)|^2 r^2 \mathrm{d}r \\
&= r^2 |R_{nl}(r)|^2 \mathrm{d}r \int_0^\pi \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\phi |Y_{lm}(\theta,\phi)|^2 \\
&= r^2 |R_{nl}(r)|^2 \mathrm{d}r \\
&= D_{nl}(r)\mathrm{d}r \qquad \textbf{(7.144)}
\end{aligned}$$

represents the probability of finding the electron between the distances r and $r + \mathrm{d}r$ from the nucleus, regardless of direction. The radial distribution functions $D_{nl}(r)$ corresponding to the first few radial functions are plotted in Fig. 7.9.

Several interesting features emerge from the examination of the radial eigenfunctions $R_{nl}(r)$ and the radial distribution functions $D_{nl}(r)$.

(1) Only for s states ($l = 0$) are the radial eigenfunctions different from zero at $r = 0$. We also note that since $Y_{00} = (4\pi)^{-1/2}$ is independent of θ and ϕ, one has from (7.134) and (7.139)

$$|\psi_{n00}(0)|^2 = \frac{1}{4\pi}|R_{n0}(0)|^2 = \frac{Z^3}{\pi a_\mu^3 n^3}. \qquad \textbf{(7.145)}$$

Moreover, each of the s-state radial eigenfunctions R_{n0} are such that $\mathrm{d}R_{n0}/\mathrm{d}r \neq 0$ at $r = 0$. This peculiar behaviour is due to the fact that the potential energy (7.91) is infinite at the origin.

(2) We also verify from (7.139) that the radial eigenfunctions $R_{nl}(r)$ are proportional to r^l near the origin, in agreement with our general discussion of Section 7.2. Thus, for $l \neq 0$ the radial wave functions are forced to remain small over distances which increase with l. As we have seen in Section 7.2, this behaviour is due to the centrifugal barrier term $l(l+1)\hbar^2/2\mu r^2$ contained in the effective potential. Among the radial eigenfunctions $R_{nl}(r)$ having the same principal quantum number n, the one with the lowest value of l has the largest amplitude in the vicinity of the nucleus.

(3) The associated Laguerre polynomial $L_{n+l}^{2l+1}(\rho)$ is a polynomial of degree $n_r = n - l - 1$ having n_r radial nodes (zeros). Thus the radial distribution function $D_{nl}(r)$ has $n - l$ maxima. We remark that there is only one maximum when, for a given n, the orbital angular momentum quantum number l has its largest value $l = n - 1$. In that case $n_r = 0$ and we see from (7.131) and (7.139) that

$$R_{n,n-1}(r) \sim r^{n-1} \exp(-Zr/na_\mu). \qquad \textbf{(7.146)}$$

Hence $D_{n,n-1}(r) = r^2 R^2_{n,n-1}(r)$ will exhibit a maximum at a value of r obtained by solving the equation

$$\frac{\mathrm{d}D_{n,n-1}}{\mathrm{d}r} = \left(2nr^{2n-1} - \frac{2Z}{na_\mu} r^{2n}\right) \exp(-2Zr/na_\mu) = 0 \tag{7.147}$$

i.e. at

$$r = \frac{n^2 a_\mu}{Z}. \tag{7.148}$$

This is precisely the value (1.74) given by the Bohr model. However, in contrast to the Bohr model, the diffuseness of the electron cloud implies that the concept of size is less precise in the quantum mechanical theory, so that the value (7.148) should be interpreted as a 'most probable distance'. We see from (7.148) that this most probable distance is proportional to n^2 and is inversely proportional to Z. More generally, the maximum value of $D_{nl}(r)$ recedes from the nucleus with increasing values of n (see Fig. 7.9) and becomes closer to the nucleus (by a factor of Z^{-1}) when Z increases.

To conclude our study of the hydrogenic bound state wave functions we recall that all wave functions of the form (7.45) transform under the *parity* operation according to (7.50). In particular, the action of the parity operator $\mathcal{P}$ on the hydrogenic wave function (7.134) yields

$$\begin{aligned} \mathcal{P}\psi_{nlm}(r,\theta,\phi) &= \mathcal{P}[R_{nl}(r)Y_{lm}(\theta,\phi)] \\ &= R_{nl}(r)(-1)^l Y_{lm}(\theta,\phi) \\ &= (-1)^l \psi_{nlm}(r,\theta,\phi) \end{aligned} \tag{7.149}$$

so that the hydrogenic states ψ_{nlm} have the parity of l, in agreement with the general discussion of Section 7.2.

Hydrogen iso-electronic sequence; hydrogen isotopes; positronium; muonium; antihydrogen

Let us recall some important results we have obtained for hydrogenic systems. The energy eigenvalues are given by (7.114) and the eigenfunctions by (7.134). In particular, the ionisation potential $I_{\mathrm{P}} = |E_{n=1}|$ is

$$I_{\mathrm{P}} = \frac{e^2}{(4\pi\varepsilon_0)a_\mu}\frac{Z^2}{2} \tag{7.150}$$

and the 'extension' a of the wave function describing the relative motion of the system is roughly given in the ground state (see (7.148)) by

$$a = \frac{a_\mu}{Z} = \frac{(4\pi\varepsilon_0)\hbar^2}{Z\mu e^2}. \tag{7.151}$$

The hydrogenic systems we have considered so far correspond to an atomic nucleus of mass M and charge Ze and an electron of mass m and charge $-e$ interacting by means of the Coulomb potential (7.91). The 'normal' hydrogen atom, containing a proton and an electron is the prototype of these hydrogenic systems. The hydrogenic ions He^+ $(Z = 2)$, Li^{2+} $(Z = 3)$, Be^{3+} $(Z = 4)$, etc., which belong to the *hydrogen iso-electronic sequence* are also examples of such systems. Note that apart from small reduced mass effects the ionisation potential I_{P} of these hydrogenic ions is increased by a factor of Z^2, while the value of a for these ions is decreased by a factor of Z with respect to the hydrogen atom.

The (neutral) *isotopes* of atomic hydrogen, deuterium and tritium, also provide examples of hydrogenic systems. Here the proton is replaced by a nucleus having the same charge $+e$, namely a deuteron (containing a proton and a neutron) in the case of deuterium and a triton (containing one proton and two neutrons) in the case of tritium. Since $M_{\mathrm{d}} \simeq 2M_{\mathrm{p}}$ and $M_{\mathrm{t}} \simeq 3M_{\mathrm{p}}$, where M_{p} is the mass of the proton, M_{d} the mass of the deuteron and M_{t} the mass of the triton, we see from (7.93) that the reduced mass μ is slightly different for (normal) hydrogen, deuterium and tritium; the relative differences are of the order of 10^{-3}. Thus the quantities I_{P} and a are nearly identical for these three atoms, the small differences in the value of μ giving rise to *isotopic shifts* of the spectral lines which we have already discussed in Section 1.4.

In addition to deuterium and tritium, there exist also other 'isotopes' of hydrogen, in which the role of the nucleus is played by another particle. For example, *positronium* (e^+e^-) is a bound hydrogenic system made of a positron e^+ (the antiparticle of the electron, having the same mass m as the electron, but the opposite charge) and an electron e^-. *Muonium* (μ^+e^-) is another 'isotope' of hydrogen, in which the proton has been replaced by a positive muon μ^+, a particle which is very similar to the positron e^+, except that it has a mass $M_\mu \simeq 207m$ and that it is unstable, with a lifetime of about 2.2×10^{-6} s. Positronium and muonium may thus be considered as light 'isotopes' of hydrogen. Positronium was first observed in 1951 and muonium in 1960. Table 7.2 gives the values of the reduced mass μ, the 'radius' a and the ionisation potential I_{P} for positronium and muonium, compared with those of the hydrogen atom. It should be noted that both positronium and muonium are *unstable*. Indeed, muonium has a lifetime of 2.2×10^{-6} s (which is the lifetime of the muon μ^+ itself) while in positronium the electron and the positron may annihilate, their total energy including their rest mass energy being completely converted into electromagnetic radiation (photons).

Positronium and muonium have attracted a great deal of interest because they contain only *leptons* (i.e. particles which are not affected by the strong interactions) and hence are particularly suitable systems in which the predictions of quantum electrodynamics can be accurately verified.

Finally, we mention that atoms of antihydrogen $(\bar{p}e^+)$, a bound system made of an antiproton $\bar{p}$ and a positron e^+, have been observed in an experiment performed at CERN in 1995 by G. Baur *et al.*

Muonic atoms

In all the hydrogenic atoms we have considered until now the negative particle is an electron. In 1947, J. A. Wheeler suggested that other negative particles could form

Table 7.2 The reduced mass μ, 'radius' a and ionisation potential I_P of some special hydrogenic systems, compared with the corresponding quantities for the hydrogen atom (pe^-). The following 'atomic units' are used: unit of mass = electron mass m; unit of length = Bohr radius a_0 (see (1.66)); unit of energy = $e^2/[(4\pi\varepsilon_0)a_0]$, i.e. twice the ionisation potential of atomic hydrogen (with an infinite nuclear mass).

System	*Reduced mass* μ	*'Radius'* a	*Ionisation potential* I_P
(pe^-), $(\bar{p}e^+)$	$\frac{1836}{1837} \simeq 1$	$\simeq a_0 = 1$	$\simeq \frac{e^2}{(4\pi\varepsilon_0)2a_0} = 0.5$
(e^+e^-)	0.5	2	0.25
(μ^+e^-)	$\frac{207}{208} \simeq 1$	$\simeq a_0 = 1$	$\simeq 0.5$
$(p\mu^-)$	$\simeq 186$	$\simeq 5.4 \times 10^{-3}$	$\simeq 93$

a bound system with a nucleus. This, in particular, is the case for a lepton such as the *negative muon* μ^-, which is the antiparticle of the positive muon μ^+, having the same mass $M_\mu \simeq 207m$ and the same lifetime (2.2×10^{-6} s) but a negative charge $-e$. The negative muon μ^- is therefore a kind of 'heavy electron'. As it is slowing down in bulk matter, it can be captured by the Coulomb attraction of a nucleus of charge Z, thus forming a *muonic atom.*

The simplest example of muonic atom is the bound system $(p\mu^-)$ consisting of a proton p and a negative muon μ^-. Since the muon has a mass $M_\mu \simeq 207m$, the reduced mass of the muon with respect to the proton is approximately 186 times the electron mass. As a result, we see from (7.151) that the 'radius' a of muonic hydrogen $(p\mu^-)$ is 186 times smaller than that of the ordinary hydrogen atom (pe^-). On the other hand, using (7.150) we see that the ionisation potential I_P of the muonic atom $(p\mu^-)$ is 186 times larger than the corresponding quantity for ordinary atomic hydrogen (see Table 7.2). The frequencies of the spectral lines corresponding to transitions between the energy levels of $(p\mu^-)$ may thus be obtained from those of the hydrogen atom by multiplying the latter by a factor of 186. For transitions between the lowest energy levels of $(p\mu^-)$ the spectral lines are therefore lying in the X-ray region.

7.6 The three-dimensional isotropic oscillator

As a last example of central field, we shall consider the motion of a particle of mass μ in the potential

$$V(r) = \frac{1}{2}kr^2 = \frac{1}{2}\mu\omega^2 r^2 \tag{7.152}$$

which corresponds to an isotropic three-dimensional oscillator of classical angular frequency $\omega = (k/\mu)^{1/2}$. In Section 7.1 we solved the corresponding Schrödinger equation in Cartesian coordinates. In particular, we found that the energy levels are given by $E_n = (n + 3/2)\hbar\omega$, where $n = 0, 1, 2, \ldots$, each energy level E_n being $(n + 1)(n + 2)/2$-fold degenerate.

In this section we want to analyse this problem using spherical polar coordinates, so that we look for solutions of the Schrödinger equation having the form (7.45). The radial equation (7.52) for the function $u_{El}(r) = rR_{El}(r)$ becomes in the present case

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} + \frac{2\mu E}{\hbar^2} - \frac{\mu^2\omega^2 r^2}{\hbar^2}\right]u_{El}(r) = 0. \tag{7.153}$$

It is convenient to introduce the dimensionless variable

$$\rho = \alpha r \tag{7.154}$$

where

$$\alpha = \left(\frac{\mu k}{\hbar^2}\right)^{1/4} = \left(\frac{\mu\omega}{\hbar}\right)^{1/2} \tag{7.155}$$

and the dimensionless eigenvalue

$$\lambda = \frac{2E}{\hbar\omega} \tag{7.156}$$

so that (7.153) now reads

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \frac{l(l+1)}{\rho^2} + \lambda - \rho^2\right]u_{El}(\rho) = 0. \tag{7.157}$$

Let us first study the asymptotic behaviour of $u_{El}(\rho)$. When $\rho \to \infty$ we may neglect the terms $l(l + 1)/\rho^2$ and λ compared to ρ^2, so that (7.157) reduces to

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \rho^2\right]u_{El}(\rho) = 0 \tag{7.158}$$

which is the same asymptotic equation as that studied in Section 4.7 in the one-dimensional case (see (4.136)). For sufficiently large ρ the functions $u_{El}(\rho) = \rho^p \exp(\pm\rho^2/2)$ satisfy (7.158) as far as the leading terms, which are of order $\rho^2 u_{El}(\rho)$, are concerned when p has any finite value. Since the function $u_{El}(r)$ must be bounded everywhere, we only keep the minus sign in the exponent. This suggests looking for solutions of (7.157) in the form

$$u_{El}(\rho) = \mathrm{e}^{-\rho^2/2}v(\rho) \tag{7.159}$$

where we have written $v(\rho) \equiv v_{El}(\rho)$. Substituting (7.159) in (7.157) we obtain for $v(\rho)$ the equation

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - 2\rho\frac{\mathrm{d}}{\mathrm{d}\rho} - \frac{l(l+1)}{\rho^2} + \lambda - 1\right)v(\rho) = 0. \tag{7.160}$$

From the general discussion of Section 7.2 we know that $u_{El}(\rho)$ – and hence also $v(\rho)$ – behaves like ρ^{l+1} near the origin. We therefore seek a solution of (7.160) of the form

$$v(\rho) = \rho^{l+1} w(\rho). \tag{7.161}$$

Upon substitution of (7.161) in (7.160) we find that the function $w(\rho)$ satisfies the differential equation

$$\frac{d^2 w}{d\rho^2} + 2\left(\frac{l+1}{\rho} - \rho\right)\frac{dw}{d\rho} + \left[\lambda - 2\left(l + \frac{3}{2}\right)\right] w(\rho) = 0. \tag{7.162}$$

By introducing the new independent variable $\zeta = \rho^2$, this equation goes over to the differential equation

$$\zeta \frac{d^2 w}{d\zeta^2} + \left[\left(l + \frac{3}{2}\right) - \zeta\right]\frac{dw}{d\zeta} - \left[\frac{1}{2}\left(l + \frac{3}{2}\right) - \frac{\lambda}{4}\right] w(\zeta) = 0 \tag{7.163}$$

which is just the Kummer–Laplace differential equation (7.117), with $z = \zeta$, $a = (l + 3/2)/2 - \lambda/4$ and $c = l + 3/2$. The solution of (7.163), regular at the origin, is thus given by

$$w(\zeta) = C\, {}_1F_1\left[\frac{1}{2}\left(l + \frac{3}{2}\right) - \frac{\lambda}{4}, l + \frac{3}{2}, \zeta\right] \tag{7.164}$$

where C is a constant.

Energy levels

Let us examine the solution (7.164) in the limit of large ζ. From (7.119), we remark that in this limit the confluent hypergeometric series (7.118) for ${}_1F_1[(l + 3/2)/2 - \lambda/4, l + 3/2, \zeta]$ is proportional to $\zeta^{-(l+3/2+\lambda/2)/2} \exp(\zeta)$. Thus, using (7.159) and (7.161), we see that if this series does not terminate, the function $u_{El}(\rho)$ will have an asymptotic behaviour of the type

$$u_{El}(\rho) \underset{\rho \to \infty}{\sim} \rho^{-(\lambda+1)/2} e^{\rho^2/2} \tag{7.165}$$

which is inadmissible. The only way to avoid this divergence is to transform the confluent hypergeometric series into a *polynomial* of degree n_r, by requiring that

$$\frac{1}{2}\left(l + \frac{3}{2}\right) - \frac{\lambda}{4} = -n_r \tag{7.166}$$

where the *radial quantum number* $n_r = 0, 1, 2, \ldots$ is a positive integer or zero. This condition may also be written in the form

$$\lambda = 2\left(n + \frac{3}{2}\right) \tag{7.167}$$

with

$$n = 2n_r + l, \qquad n = 0, 1, 2, \ldots \tag{7.168}$$

and from (7.156) we see that the energy levels are given by

$$E_n = \left(n + \frac{3}{2}\right)\hbar\omega, \qquad n = 0, 1, 2, \dots \tag{7.169}$$

in agreement with the result (7.37) of Section 7.1.

The eigenfunctions of the three-dimensional isotropic oscillator

Using (7.154), (7.159), (7.161), (7.164) and (7.166), we find that the radial eigenfunctions $R_{El}(r) = r^{-1}u_{El}(r)$ of the three-dimensional isotropic oscillator are given by

$$R_{El}(r) = N\mathrm{e}^{-\alpha^2 r^2/2} r^l \, {}_1F_1\left(-n_r, l + \tfrac{3}{2}, \alpha^2 r^2\right) \tag{7.170}$$

where $\alpha = (\mu\omega/\hbar)^{1/2}$ and N is a normalisation constant. Hence, from (7.45) the complete three-dimensional isotropic oscillator eigenfunctions are given in spherical polar coordinates by

$$\psi_{Elm}(r, \theta, \phi) = N\mathrm{e}^{-\alpha^2 r^2/2} r^l \, {}_1F_1\left(-n_r, l + \tfrac{3}{2}, \alpha^2 r^2\right) Y_{lm}(\theta, \phi). \tag{7.171}$$

Except for the ground state ($n = 0$), the energy levels (7.169) are *degenerate*. Indeed, for even n there are $n/2 + 1$ partitions of n according to (7.168), and for odd n there are $(n + 1)/2$ partitions. Moreover, for each value of l, there is a $(2l + 1)$ degeneracy with respect to the magnetic quantum number m (which can take on the values $-l, -l + 1, \dots, l$). As a result, there is only one eigenfunction for $n = 0$, there are three linearly independent eigenfunctions for $n = 1$ (corresponding to $l = 1$ and $m = -1, 0, +1$), six for $n = 2$ (one corresponding to $l = 0$ and five to $l = 2$), etc. In general, there are $(n + 1)(n + 2)/2$ linearly independent eigenfunctions for each value of n, in agreement with the conclusion reached in Section 7.1.

Problems

7.1 Consider a particle of mass μ confined within a box with impenetrable walls of sides L_1, L_2 and L_3. If $L_1 = L_2$, obtain the allowed energies and discuss the degeneracy of the first few energy levels.

7.2 Consider an anisotropic harmonic oscillator described by the Hamiltonian

$$H = \frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) + \frac{1}{2}k_1(x^2 + y^2) + \frac{1}{2}k_2 z^2.$$

(a) Find the energy levels and the corresponding energy eigenfunctions using Cartesian coordinates. What are the degeneracies of the levels, assuming that $\omega_1 = (k_1/\mu)^{1/2}$ and $\omega_2 = (k_2/\mu)^{1/2}$ are incommensurable?

(b) Can the stationary states be eigenstates of $\mathbf{L}^2$? of L_z?

7.3 Show that all solutions of the Schrödinger equation (7.41) can be obtained as linear combinations of separable solutions of the form (7.43).

(*Hint*: Use the orthonormality and closure relations satisfied by the spherical harmonics.)

7.4 Show that when $p = -2$ and $b_0 < 0$ in (7.55), physically acceptable solutions of (7.52) exist only if $b_0 > -\hbar^2/8\mu$.

7.5 Prove that the spherical Bessel and Neumann functions defined by (7.63a) and (7.63b) satisfy the differential equation (7.61).

7.6 Using equations (7.63) obtain the leading term of $j_l(\rho)$ and $n_l(\rho)$ for small and large values of ρ.

7.7 Consider a particle of mass μ confined in a spherical box of radius a.

(a) Write down the equation which determines the allowed energy levels.
(b) Solve this equation explicitly for the case $l = 0$.

7.8 Solve equation (7.87) numerically to obtain the $l = 0$ energy levels and corresponding normalised radial functions for a three-dimensional square well such that

$$\gamma = (2\mu V_0 a^2/\hbar^2)^{1/2} = 5.$$

7.9 Prove equation (7.90).

7.10 Consider a particle of mass μ moving in a very deep square well potential for which $Ka \gg l$. Show that for the bound states with $|E| \ll V_0$, equation (7.86) reduces to

$$Ka - l\pi/2 \simeq (n + \tfrac{1}{2})\pi; \qquad n = 0, 1, 2, \ldots$$

and that the energy levels are given approximately by

$$E \simeq -2V_0\{1 - [n + (l + 1)/2]\pi/\gamma\}.$$

7.11 (a) Show that for a square well potential, bound states of zero energy for $l > 0$ occur when

$$j_{l-1}(\gamma) = 0.$$

(b) Deduce from this condition that the value of γ necessary to bind a particle of angular momentum quantum number l increases with increasing l.

7.12 (a) Prove the relations (7.125) and (7.126) satisfied by the Laguerre polynomials.
(b) Show that the lowest order differential equation involving only $L_q(\rho)$ is given by (7.127).

7.13 Prove equation (7.129).

7.14 Any region of space in which the kinetic energy T of a particle would become negative is forbidden for classical motion. For a hydrogen atom in the ground state:

(a) find the classically forbidden region; and
(b) using the ground-state wave function $\psi_{100}(r)$, calculate the probability of finding the electron in this region.

7.15 Using the generating function (7.130) and proceeding as in the case of the linear harmonic oscillator (see Section 4.7) evaluate the integral (7.138).

7.16 Using the generating function (7.130), show that the average values

$$\langle r^k\rangle_{nlm} = \int \psi^*_{nlm}(\mathbf{r})r^k\psi_{nlm}(\mathbf{r})\mathrm{d}\mathbf{r} = \int_0^\infty |R_{nl}(r)|^2 r^{k+2}\mathrm{d}r$$

are given respectively for $k = 1, -1, -2$ and -3 by

$$\begin{aligned}
\langle r\rangle_{nlm} &= a_\mu\frac{n^2}{Z}\left\{1+\frac{1}{2}\left[1-\frac{l(l+1)}{n^2}\right]\right\} && (1)\\
\langle r^{-1}\rangle_{nlm} &= \frac{Z}{a_\mu n^2} && (2)\\
\langle r^{-2}\rangle_{nlm} &= \frac{Z^2}{a_\mu^2 n^3\left(l+\frac{1}{2}\right)} && (3)\\
\langle r^{-3}\rangle_{nlm} &= \frac{Z^3}{a_\mu^3 n^3 l\left(l+\frac{1}{2}\right)(l+1)}. && (4)
\end{aligned}$$

7.17 Using the result (2) of the preceding problem, together with (7.114) show that for a hydrogenic atom, the average values of the kinetic energy operator T and of the potential energy V in a bound state (nlm) are such that

$$2\langle T\rangle_{nlm} = -\langle V\rangle_{nlm}.$$

Relate your result to the virial theorem of Section 5.7.

7.18 Consider a hydrogen atom whose wave function at $t = 0$ is the following superposition of energy eigenfunctions $\psi_{nlm}(\mathbf{r})$:

$$\Psi(\mathbf{r}, t=0) = \frac{1}{\sqrt{14}}[2\psi_{100}(\mathbf{r}) - 3\psi_{200}(\mathbf{r}) + \psi_{322}(\mathbf{r})].$$

(a) Is this wave function an eigenfunction of the parity operator?
(b) What is the probability of finding the system in the ground state (100)? In the state (200)? In the state (322)? In another energy eigenstate?
(c) What is the expectation value of the energy; of the operator $\mathbf{L}^2$; of the operator L_z?

7.19 Find the energy levels and the corresponding eigenfunctions of a particle of mass μ in the potential $V(r) = (A/r^2 + Br^2)$, where $A \geqslant 0$ and $B > 0$. In the case $A = 0$ compare your result with that obtained in Section 7.6 for the three-dimensional isotropic oscillator.

(*Hint*: Set $l'(l'+1) = l(l+1) + 2\mu A/\hbar^2$ and compare the radial equation you obtain with (7.153).)

7.20 A two-dimensional harmonic oscillator has the Hamiltonian

$$H = -\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right] + \frac{1}{2}k_1 x^2 + \frac{1}{2}k_2 y^2.$$

(a) Show that the energy levels are given by

$$E_{n_x n_y} = \left(n_x + \frac{1}{2}\right)\hbar\omega_1 + \left(n_y + \frac{1}{2}\right)\hbar\omega_2, \qquad \begin{array}{l} n_x = 0, 1, 2, \ldots \\ n_y = 0, 1, 2, \ldots \end{array}$$

where $\omega_1 = (k_1/\mu)^{1/2}$ and $\omega_2 = (k_2/\mu)^{1/2}$. Obtain the corresponding energy eigenfunctions in terms of the one-dimensional linear harmonic oscillator wave functions of Section 4.7.

(b) Assuming that the harmonic oscillator is isotropic ($k_1 = k_2 = k$), what is the degeneracy of each energy level?

(c) Solve the Schrödinger equation for the two-dimensional isotropic oscillator in plane polar coordinates (r, ϕ). Using the fact that the Laplacian operator is given in these coordinates by

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$$

and introducing the dimensionless quantities

$$\rho = \alpha r, \qquad \lambda = 2E/\hbar\omega,$$

where $\alpha = (\mu k/\hbar^2)^{1/4} = (\mu\omega/\hbar)^{1/2}$, show first that the eigenfunctions are of the form

$$\psi = \mathrm{e}^{-\rho^2/2}\rho^{|m|}g(\rho)\mathrm{e}^{im\phi}, \qquad m = 0, \pm 1, \pm 2, \ldots$$

where the function $g(\rho)$ must satisfy the differential equation

$$\frac{\mathrm{d}^2 g}{\mathrm{d}\rho^2} + \left[\frac{2|m|+1}{\rho} - 2\rho\right]\frac{\mathrm{d}g}{\mathrm{d}\rho} - [2(|m|+1) - \lambda]g = 0. \tag{1}$$

Then, taking $v = \rho^2$ as a new variable, prove that equation (1) is transformed into the Kummer–Laplace equation

$$v\frac{\mathrm{d}^2 g}{\mathrm{d}v^2} + [(|m|+1) - v]\frac{\mathrm{d}g}{\mathrm{d}v} - \frac{1}{2}\left[(|m|+1) - \frac{\lambda}{2}\right]g = 0 \tag{2}$$

whose solution regular at $v = 0$ is the confluent hypergeometric function

$$g(v) = {}_1F_1(a, c, v) \tag{3}$$

with

$$a = \frac{1}{2}\left(|m| + 1 - \frac{\lambda}{2}\right), \qquad c = |m| + 1. \tag{4}$$

Using these results, show that the eigenfunctions are given by

$$\psi_{n_r,m}(\rho,\phi) = N\mathrm{e}^{-\rho^2/2}\rho^{|m|}\ {}_1F_1(-n_r, |m|+1, \rho^2)\mathrm{e}^{\mathrm{i}m\phi} \tag{5}$$

where $n_r = 0, 1, 2, \ldots$, $m = 0, \pm 1, \pm 2, \ldots$ and N is a normalisation constant. Prove that the energy levels are given by

$$E_n = \hbar\omega(n+1) \tag{6}$$

where

$$n = 2n_r + |m| = 0, 1, 2, \ldots \tag{7}$$

Discuss the degeneracy of the energy levels and compare your results with those obtained by using Cartesian coordinates.

7.21 The parabolic coordinates (ξ, η, ϕ) of a point in three-dimensional space are defined by the relations

$$\begin{aligned} x &= \sqrt{\xi\eta}\cos\phi, & \xi &= r+z \\ y &= \sqrt{\xi\eta}\sin\phi, & \eta &= r-z \\ z &= \tfrac{1}{2}(\xi-\eta), & \phi &= \tan^{-1}(y/x) \\ r &= \tfrac{1}{2}(\xi+\eta) \end{aligned}$$

and the Laplacian operator is given in these coordinates by

$$\nabla^2 = \frac{4}{\xi+\eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right)\right] + \frac{1}{\xi\eta}\frac{\partial^2}{\partial\phi^2}$$

(a) Prove that the Schrödinger equation (7.94) with a Coulomb potential is separable in these coordinates.
(*Hint*: Write the eigenfunctions in the form

$$\psi = f_1(\xi)f_2(\eta)\mathrm{e}^{\mathrm{i}m\phi}, \qquad m = 0, \pm 1, \pm 2, \ldots$$

and show that the Schrödinger equation can be replaced by the two differential equations

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}\xi}\left(\xi\frac{\mathrm{d}f_1}{\mathrm{d}\xi}\right) - \left(\frac{1}{4}\lambda^2\xi + \frac{m^2}{4\xi} + \nu_1\right)f_1 &= 0 \\ \frac{\mathrm{d}}{\mathrm{d}\eta}\left(\eta\frac{\mathrm{d}f_2}{\mathrm{d}\eta}\right) - \left(\frac{1}{4}\lambda^2\eta + \frac{m^2}{4\eta} + \nu_2\right)f_2 &= 0 \end{aligned}$$

where $\lambda^2 = -2\mu E/\hbar^2$ and the constants of separation ν_1 and ν_2 are related by

$$\nu_1 + \nu_2 = -\frac{Ze^2}{4\pi\varepsilon_0}\frac{\mu}{\hbar^2}.)$$

(b) Taking the energy to be negative (discrete spectrum), obtain the functions $f_1(\xi)$ and $f_2(\eta)$, and hence the eigenfunctions and energy levels. Compare your results with those derived in the text in spherical polar coordinates.

8 Approximation methods for stationary problems

As in the case of classical mechanics, there are relatively few physically interesting problems in quantum mechanics which can be solved exactly. Approximation methods are therefore very important in nearly all the applications of the theory. In this chapter and the next one we shall develop several approximation methods to study mainly the bound states of physical systems; approximation methods for collision problems, which deal with the continuous part of the spectrum, will be considered in Chapter 13.

Approximation methods can be conveniently divided into two groups, according to whether the Hamiltonian of the system is time-independent or time-dependent. The latter case will be considered in Chapter 9. In the present chapter we are concerned with the approximate determination of the discrete eigenenergies and corresponding eigenfunctions for the stationary states of a time-independent Hamiltonian. We shall begin by discussing perturbation theory, which studies the changes induced in a system by a small disturbance. In Section 8.1 we shall develop a stationary perturbation method for the case of a non-degenerate energy level. The generalisation to degenerate energy levels will be considered in Section 8.2. The next section is devoted to the variational method. Finally, in Section 8.4 we shall discuss the semi-classical approximation method of Wentzel, Kramers and Brillouin, which is known as the WKB approximation.

8.1 Time-independent perturbation theory for a non-degenerate energy level

In this section and the following one we shall discuss the *Rayleigh–Schrödinger perturbation theory*, which analyses the modifications of discrete energy levels and of the corresponding eigenfunctions of a system when a perturbation is applied.

Let us suppose that the time-independent Hamiltonian H of a system can be expressed as

$$H = H_0 + \lambda H' \tag{8.1}$$

where the 'unperturbed' Hamiltonian H_0 is sufficiently simple so that the corresponding time-independent Schrödinger equation

$$H_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \tag{8.2}$$

can be solved, and $\lambda H'$ is a small perturbation. The quantity λ is a real parameter, which will be used below to distinguish between the various orders of the perturbation calculation. We can let λ tend to zero, in which case the Hamiltonian H reduces to the unperturbed Hamiltonian H_0, or we may let λ reach its full value, which we shall choose to be $\lambda = 1$.

We assume that the known eigenfunctions $\psi_n^{(0)}$ corresponding to the known eigenvalues $E_n^{(0)}$ of H_0 form a complete orthonormal set (which may be partly continuous). Thus, if $\psi_i^{(0)}$ and $\psi_j^{(0)}$ are two members of that set, we have

$$\langle \psi_i^{(0)} | \psi_j^{(0)} \rangle = \delta_{ij} \tag{8.3}$$

where for notational simplicity the meaning of δ_{ij} is implicitly extended to cover the possibility of $\psi_i^{(0)}$ and $\psi_j^{(0)}$ being discrete or continuous states. The eigenvalue problem which we want to solve is

$$H \psi_n = E_n \psi_n. \tag{8.4}$$

Let us consider a *particular* unperturbed, discrete energy level $E_n^{(0)}$, which we assume to be *non-degenerate* (other unperturbed energy levels may be degenerate). We suppose that the perturbation $\lambda H'$ is small enough so that the perturbed energy level E_n is much closer to $E_n^{(0)}$ than to any other unperturbed level. As λ tends to zero, we have

$$\lim_{\lambda \to 0} E_n = E_n^{(0)}. \tag{8.5}$$

Similarly, since the state n is non-degenerate, the perturbed eigenfunction ψ_n must approach the unperturbed eigenfunction $\psi_n^{(0)}$ as λ approaches zero:

$$\lim_{\lambda \to 0} \psi_n = \psi_n^{(0)}. \tag{8.6}$$

The basic idea of perturbation theory is to assume that both the eigenvalues and eigenfunctions of H can be expanded in powers of the perturbation parameter λ. That is

$$E_n = \sum_{j=0}^{\infty} \lambda^j E_n^{(j)} \tag{8.7}$$

and

$$\psi_n = \sum_{j=0}^{\infty} \lambda^j \psi_n^{(j)} \tag{8.8}$$

where j, the power of λ, is the order of the perturbation. Substituting the expansions (8.7) and (8.8) into the Schrödinger equation (8.4), we have

$$\begin{aligned}(H_0 + \lambda H')(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots) = {} & (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots) \\ & \times(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots).\end{aligned} \tag{8.9}$$

We now equate the coefficients of equal powers of λ on both sides of this equation. Beginning with λ^0, we find, as expected, that $H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$. Next, the coefficients of λ give

$$H_0\psi_n^{(1)} + H'\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} \tag{8.10}$$

while those of λ^2 yield

$$H_0\psi_n^{(2)} + H'\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}. \tag{8.11}$$

More generally, by equating the coefficients of λ^j in (8.9) we have for $j \geqslant 1$

$$H_0\psi_n^{(j)} + H'\psi_n^{(j-1)} = E_n^{(0)}\psi_n^{(j)} + E_n^{(1)}\psi_n^{(j-1)} + \cdots + E_n^{(j)}\psi_n^{(0)}. \tag{8.12}$$

In order to obtain the first-order energy correction $E_n^{(1)}$, we premultiply (8.10) by $\psi_n^{(0)*}$ and integrate over all coordinates. This gives

$$\langle\psi_n^{(0)}|H_0 - E_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|H' - E_n^{(1)}|\psi_n^{(0)}\rangle = 0. \tag{8.13}$$

Now, using (8.2) and the fact that the operator H_0 is Hermitian, we have

$$\begin{aligned}\langle\psi_n^{(0)}|H_0|\psi_n^{(1)}\rangle &= \langle\psi_n^{(1)}|H_0|\psi_n^{(0)}\rangle^* \\ &= E_n^{(0)}\langle\psi_n^{(1)}|\psi_n^{(0)}\rangle^* \\ &= E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle\end{aligned} \tag{8.14}$$

so that the first term on the left of (8.13) vanishes. Moreover, since $\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle = 1$, we see that (8.13) reduces to

$$E_n^{(1)} = \langle\psi_n^{(0)}|H'|\psi_n^{(0)}\rangle. \tag{8.15}$$

This is a *very important result.* It tells us that the first-order correction to the energy for a non-degenerate level is just the perturbation H' averaged over the corresponding unperturbed state of the system.

Proceeding in a similar way with equation (8.11), we have

$$\langle\psi_n^{(0)}|H_0 - E_n^{(0)}|\psi_n^{(2)}\rangle + \langle\psi_n^{(0)}|H' - E_n^{(1)}|\psi_n^{(1)}\rangle - E_n^{(2)} = 0. \tag{8.16}$$

Again the first term vanishes, so that the second-order energy correction is given by

$$E_n^{(2)} = \langle \psi_n^{(0)} | H' - E_n^{(1)} | \psi_n^{(1)} \rangle. \tag{8.17}$$

Expressions for higher-order energy corrections can be obtained in a similar way from (8.12). In particular, one has (Problem 8.2)

$$E_n^{(3)} = \langle \psi_n^{(1)} | H' - E_n^{(1)} | \psi_n^{(1)} \rangle - 2E_n^{(2)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle. \tag{8.18}$$

It is interesting to note that the knowledge of the unperturbed wave function $\psi_n^{(0)}$ yields $E_n^{(0)}$ and $E_n^{(1)}$, while that of the first-order wave function correction $\psi_n^{(1)}$ gives $E_n^{(2)}$ and $E_n^{(3)}$. More generally, if $\psi_n^{(0)}, \psi_n^{(1)}, \dots, \psi_n^{(s)}$, are known, the energy corrections can be obtained up to and including $E_n^{(2s+1)}$ (see Problem 8.3).

Let us now return to equation (8.10). The Rayleigh–Schrödinger method attempts to obtain the solution $\psi_n^{(1)}$ of this equation in the following way. First, the 'unperturbed' equation (8.2) is solved for all eigenvalues and eigenfunctions (including those belonging to the continuous part of the spectrum, if one exists). The unknown function $\psi_n^{(1)}$ is then expanded in the basis set of the unperturbed eigenfunctions, namely

$$\psi_n^{(1)} = \sum_k a_{nk}^{(1)} \psi_k^{(0)} \tag{8.19}$$

where the sum over k means a summation over the discrete part of the set and an integration over its continuous part. Substituting the expansion (8.19) into (8.10), we obtain

$$(H_0 - E_n^{(0)}) \sum_k a_{nk}^{(1)} \psi_k^{(0)} + (H' - E_n^{(1)}) \psi_n^{(0)} = 0. \tag{8.20}$$

Premultiplying by $\psi_l^{(0)*}$, integrating over all coordinates, and using equations (8.2) and (8.3), we find that

$$a_{nl}^{(1)} (E_l^{(0)} - E_n^{(0)}) + H'_{ln} - E_n^{(1)} \delta_{nl} = 0 \tag{8.21}$$

where we have written $H'_{ln} \equiv \langle \psi_l^{(0)} | H' | \psi_n^{(0)} \rangle$.

For $l = n$, equation (8.21) reduces to $E_n^{(1)} = H'_{nn}$, which is the result (8.15). On the other hand, for $l \neq n$, we have

$$a_{nl}^{(1)} = \frac{H'_{ln}}{E_n^{(0)} - E_l^{(0)}}, \qquad l \neq n. \tag{8.22}$$

From this result and equation (8.19), we see that a sufficient condition for the applicability of the Rayleigh–Schrödinger perturbation method is that

$$\left| \frac{H'_{ln}}{E_n^{(0)} - E_l^{(0)}} \right| \ll 1, \qquad l \neq n. \tag{8.23}$$

We also remark that the coefficient $a_{nn}^{(1)} = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle$, which is the 'component' of $\psi_n^{(1)}$ along $\psi_n^{(0)}$, cannot be obtained from equation (8.21). We shall return shortly to the determination of $a_{nn}^{(1)}$.

The Rayleigh–Schrödinger method can also be applied to solve higher-order equations such as (8.11). In this case, expanding $\psi_n^{(2)}$ as

$$\psi_n^{(2)} = \sum_k a_{nk}^{(2)} \psi_k^{(0)} \tag{8.24}$$

substituting in (8.11) and using (8.19), we have

$$(H_0 - E_n^{(0)}) \sum_k a_{nk}^{(2)} \psi_k^{(0)} + (H' - E_n^{(1)}) \sum_k a_{nk}^{(1)} \psi_k^{(0)} - E_n^{(2)} \psi_n^{(0)} = 0. \tag{8.25}$$

Premultiplying by $\psi_l^{(0)*}$, integrating over all coordinates and using (8.2) and (8.3), we find that

$$a_{nl}^{(2)} (E_l^{(0)} - E_n^{(0)}) + \sum_k H'_{lk} a_{nk}^{(1)} - E_n^{(1)} a_{nl}^{(1)} - E_n^{(2)} \delta_{nl} = 0. \tag{8.26}$$

Let us first examine what happens for $l = n$. The above equation then yields

$$\begin{aligned} E_n^{(2)} &= \sum_k H'_{nk} a_{nk}^{(1)} - H'_{nn} a_{nn}^{(1)} \\ &= \sum_{k \neq n} H'_{nk} a_{nk}^{(1)} \end{aligned} \tag{8.27}$$

where we have used the fact that $E_n^{(1)} = H'_{nn}$. With the help of (8.22) we can therefore write

$$E_n^{(2)} = \sum_{k \neq n} \frac{H'_{nk} H'_{kn}}{E_n^{(0)} - E_k^{(0)}} \tag{8.28a}$$

$$= \sum_{k \neq n} \frac{|H'_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}. \tag{8.28b}$$

The second-order energy correction $E_n^{(2)}$ can therefore be obtained by performing a summation over all the states $\psi_k^{(0)}$, with $k \neq n$, as indicated in (8.28). The states $\psi_k^{(0)}$ over which the summation is performed are often called 'intermediate' states. Indeed, we see from (8.28a) that each term in the summation may be viewed as a succession of two first-order transitions, weighted by the energy denominator $E_n^{(0)} - E_k^{(0)}$, in which the system leaves the state $\psi_n^{(0)}$, 'propagates' in the intermediate state $\psi_k^{(0)}$ and then 'falls back' to the state $\psi_n^{(0)}$. We also remark from (8.28b) that if the level n which we are studying corresponds to the *ground state* of the system, then $E_n^{(0)} - E_k^{(0)} < 0$ for $k \neq n$; hence in that case the second-order energy correction $E_n^{(2)}$ is always *negative*, for any perturbation H'.

Summarising the results we have obtained thus far for the perturbed energy level E_n, we see from (8.15) and (8.28) that to second order in the perturbation, we have

$$E_n = E_n^{(0)} + H'_{nn} + \sum_{k \neq n} \frac{|H'_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} \tag{8.29}$$

where we have set $\lambda = 1$.

Let us now return to (8.26). Using (8.22) and the fact that $E_n^{(1)} = H'_{nn}$, we have for $l \neq n$

$$a_{nl}^{(2)} = \frac{1}{E_n^{(0)} - E_l^{(0)}} \sum_{k \neq n} \frac{H'_{lk} H'_{kn}}{E_n^{(0)} - E_k^{(0)}} - \frac{H'_{nn} H'_{ln}}{(E_n^{(0)} - E_l^{(0)})^2} - a_{nn}^{(1)} \frac{H'_{ln}}{E_n^{(0)} - E_l^{(0)}} \tag{8.30}$$

and we note that no information can be obtained from (8.26) – and hence from (8.11) – concerning the coefficient $a_{nn}^{(2)}$. Similarly, we recall that $a_{nn}^{(1)}$ could not be determined from equation (8.10). More generally, if we denote by

$$a_{nn}^{(j)} = \langle \psi_n^{(0)} | \psi_n^{(j)} \rangle, \qquad j \geqslant 1 \tag{8.31}$$

the 'component' of $\psi_n^{(j)}$ along $\psi_n^{(0)}$, we see by pre-multiplying equation (8.12) with $\psi_n^{(0)*}$ and integrating over all coordinates that this equation does not determine $a_{nn}^{(j)}$.

Since our basic perturbation equations (8.10)–(8.12) leave the coefficients $a_{nn}^{(j)}$ undetermined, it is clear that the choice of these quantities can have no physical consequences. We may, for example, require that the $a_{nn}^{(j)}$ be chosen in such a way that the perturbed wave function ψ_n, calculated through order λ^j, be normalised to unity in the sense that

$$\begin{aligned} \langle \psi_n | \psi_n \rangle &\simeq \langle \psi_n^{(0)} + \lambda \psi_n^{(1)} + \cdots + \lambda^j \psi_n^{(j)} | \psi_n^{(0)} + \lambda \psi_n^{(1)} + \cdots + \lambda^j \psi_n^{(j)} \rangle \\ &= 1 + \mathcal{O}(\lambda^{j+1}) \end{aligned} \tag{8.32}$$

where $\mathcal{O}(\lambda^{j+1})$ denotes a correction of order λ^{j+1}. In particular, since $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$, we find from (8.32), to first order in λ

$$\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle = 0 \tag{8.33a}$$

or, using (8.31),

$$a_{nn}^{(1)} + a_{nn}^{(1)*} = 0 \tag{8.33b}$$

so that the real part of $a_{nn}^{(1)}$ must vanish. Similarly, to second order in λ, the normalisation condition (8.32) gives

$$\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle = 0. \tag{8.34a}$$

Using (8.31), (8.19) and (8.3), this equation yields

$$a_{nn}^{(2)} + a_{nn}^{(2)*} + \sum_k |a_{nk}^{(1)}|^2 = 0 \tag{8.34b}$$

which is an equation for the real part of $a_{nn}^{(2)}$. This procedure can be continued to higher orders in λ. Note, however, that the imaginary parts of the coefficients $a_{nn}^{(j)}$ cannot be determined from the normalisation condition (8.32). This remaining arbitrariness corresponds to the fact that without changing its normalisation we can multiply the perturbed wave function ψ_n by an arbitrary phase factor $\exp(\mathrm{i}\alpha)$, where α is a real quantity which may depend on λ. We can therefore require without loss of generality that the imaginary parts of the coefficients $a_{nn}^{(j)}$ vanish, in which case we have, through second order in λ,

$$a_{nn}^{(1)} = 0, \qquad a_{nn}^{(2)} = -\frac{1}{2}\sum_{k\neq n} |a_{nk}^{(1)}|^2. \tag{8.35}$$

As a result of this discussion, the normalised perturbed wave function is given to second order by

$$\psi_n = \psi_n^{(0)} + \psi_n^{(1)} + \psi_n^{(2)} \tag{8.36a}$$

where

$$\psi_n^{(1)} = \sum_{l\neq n} \frac{H'_{ln}}{E_n^{(0)} - E_l^{(0)}}\psi_l^{(0)}, \tag{8.36b}$$

$$\begin{aligned}\psi_n^{(2)} = {} & \sum_{l\neq n}\left[\sum_{k\neq n} \frac{H'_{lk}H'_{kn}}{(E_n^{(0)} - E_l^{(0)})(E_n^{(0)} - E_k^{(0)})} - \frac{H'_{nn}H'_{ln}}{(E_n^{(0)} - E_l^{(0)})^2}\right]\psi_l^{(0)} \\ & -\frac{1}{2}\sum_{k\neq n}\frac{|H'_{kn}|^2}{(E_n^{(0)} - E_k^{(0)})^2}\psi_n^{(0)}\end{aligned} \tag{8.36c}$$

and we have set $\lambda = 1$.

We have discussed above a possible choice of the coefficients $a_{nn}^{(j)}$ which ensures that the perturbed wave function ψ_n be normalised to a given order in λ. Another way of choosing the coefficients $a_{nn}^{(j)}$ which is often used in perturbation calculations is to require that

$$a_{nn}^{(j)} = 0, \qquad j \geqslant 1. \tag{8.37}$$

In this case it is clear that the first correction $\psi_n^{(1)}$ is identical to that found above, equation (8.36b), so that the perturbed wave function ψ_n is still normalised to unity to first order in λ. However, we see from (8.35) that this is not the case beyond first order. Nevertheless, if desired, we can always obtain a normalised perturbed eigenfunction at the end of the calculation (performed to a given order in λ) by multiplying ψ_n by a constant $N(\lambda)$ such that $\langle N(\lambda)\psi_n | N(\lambda)\psi_n\rangle = 1$.

Finally, we remark that if the expression (8.36b) for $\psi_n^{(1)}$ is substituted into (8.17) we retrieve the second-order energy correction $E_n^{(2)}$ given by (8.28). The third-order correction $E_n^{(3)}$ can be obtained in a similar way by using (8.18) and (8.36b). Remembering that $\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = a_{nn}^{(1)} = 0$, one finds (Problem 8.5) that

$$E_n^{(3)} = \sum_{k\neq n}\sum_{m\neq n}\frac{H'_{nk}H'_{km}H'_{mn}}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_m^{(0)})} - H'_{nn}\sum_{k\neq n}\frac{|H'_{kn}|^2}{(E_n^{(0)} - E_k^{(0)})^2}. \tag{8.38}$$

Perturbed harmonic oscillator

As a first example of the application of Rayleigh–Schrödinger perturbation theory to non-degenerate energy levels, we shall consider a problem which can be solved exactly, so that we may check our perturbative results against exact expressions. The unperturbed Hamiltonian is that of a linear harmonic oscillator

$$H_0 = \frac{p_x^2}{2m} + \frac{1}{2}kx^2, \qquad k > 0 \tag{8.39}$$

and the perturbation, proportional to x^2, is written as

$$H' = \frac{1}{2}k'x^2, \qquad k' > 0 \tag{8.40}$$

where we have set $\lambda = 1$ (in fact the parameter λ may be thought of as being absorbed in the quantity k'). The unperturbed energy levels are

$$E_n^{(0)} = \hbar\omega\left(n + \tfrac{1}{2}\right), \qquad n = 0, 1, 2, \ldots \tag{8.41}$$

with $\omega = (k/m)^{1/2}$. The corresponding unperturbed eigenfunctions are the linear harmonic oscillator wave functions $\psi_n(x)$ given by (4.168).

Since the full Hamiltonian

$$H = \frac{p_x^2}{2m} + \frac{1}{2}kx^2 + \frac{1}{2}k'x^2 \tag{8.42}$$

is that of a linear harmonic oscillator with a force constant $K = k + k'$, the perturbed eigenfunctions and eigenvalues can readily be obtained exactly by replacing k by $k + k'$ in the expressions of the unperturbed eigenfunctions and eigenenergies. In particular, the perturbed energy levels are given by

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)\left(1 + \frac{k'}{k}\right)^{1/2}, \qquad n = 0, 1, 2, \ldots . \tag{8.43}$$

Let us now calculate the perturbed energies through second order in perturbation theory. According to (8.15), the first-order correction to the energy of the nth state is

$$E_n^{(1)} = H'_{nn} = \tfrac{1}{2}k'(x^2)_{nn} \tag{8.44}$$

and from (8.28) we see that the second-order energy correction is

$$E_n^{(2)} = \frac{1}{4}(k')^2 \sum_{k \neq n} \frac{|(x^2)_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} \tag{8.45}$$

where

$$(x^2)_{kn} = \langle\psi_k^{(0)}|x^2|\psi_n^{(0)}\rangle \tag{8.46}$$

denotes the matrix element of x^2 between a pair of unperturbed linear harmonic oscillator wave functions $\psi_k^{(0)}(x)$ and $\psi_n^{(0)}(x)$.

The matrix elements (8.46) can be evaluated in a variety of ways (see Problem 5.13). The result is

$$\begin{aligned}(x^2)_{kn} &= \frac{1}{2\alpha^2}[(n+1)(n+2)]^{1/2}, && k = n+2\\ &= \frac{1}{2\alpha^2}[2n+1], && k = n\\ &= \frac{1}{2\alpha^2}[n(n-1)]^{1/2}, && k = n-2\\ &= 0 && \text{otherwise}\end{aligned} \tag{8.47}$$

where $\alpha = (mk/\hbar^2)^{1/4} = (m\omega/\hbar)^{1/2}$. Thus

$$E_n^{(1)} = \frac{1}{2}k'\frac{1}{2\alpha^2}(2n+1) = \hbar\omega\left(n+\frac{1}{2}\right)\left(\frac{1}{2}\frac{k'}{k}\right) \tag{8.48}$$

and

$$\begin{aligned}E_n^{(2)} &= \frac{1}{4}k'^2\left\{\frac{[(x^2)_{n-2,n}]^2}{2\hbar\omega} + \frac{[(x^2)_{n+2,n}]^2}{-2\hbar\omega}\right\}\\ &= \hbar\omega\left(n+\frac{1}{2}\right)\left(-\frac{1}{8}\frac{k'^2}{k^2}\right)\end{aligned} \tag{8.49}$$

in agreement with the expansion of the exact result (8.43) through second order in k'/k. Note that this expansion converges only if $k'/k < 1$. As the ratio $E_n^{(j+1)}/E_n^{(j)}$ is independent of n, the condition for convergence does not depend on the size of the energy shift, which can be large for large n. This feature is peculiar to this example.

As a second example, let us consider the case of an anharmonic oscillator whose Hamiltonian is

$$H = \frac{p_x^2}{2m} + \frac{1}{2}kx^2 + ax^3 + bx^4. \tag{8.50}$$

As seen from (4.128), the anharmonic terms ax^3 and bx^4 arise in correcting the approximation to a continuous potential well $W(x)$ given by the linear harmonic oscillator potential $kx^2/2$. In particular, such anharmonic corrections occur in the study of the vibrational spectra of molecules. We shall assume here that $b > 0$ since otherwise the potential energy would tend to $-\infty$ for $x \to \pm\infty$, with the consequence that the energy spectrum would be continuous and unbounded towards negative as well as positive energies.

The unperturbed Hamiltonian H_0 is still that of the linear harmonic oscillator (see (8.39)) and with $\lambda = 1$ we have

$$H' = ax^3 + bx^4. \tag{8.51}$$

The first-order correction to the energy of the nth state is therefore

$$\begin{aligned} E_n^{(1)} &= a(x^3)_{nn} + b(x^4)_{nn} \\ &= \int_{-\infty}^{+\infty} (ax^3 + bx^4)|\psi_n^{(0)}(x)|^2 \mathrm{d}x. \end{aligned} \qquad \textbf{(8.52)}$$

Now in Section 4.7 we showed that the linear harmonic oscillator wave functions (4.168) have a *definite* parity (even when n is even, odd when n is odd), so that $|\psi_n^{(0)}(x)|^2$ is always an *even* function of x. On the other hand, x^3 is an *odd* function of x. As a result, the diagonal matrix element $(x^3)_{nn}$ vanishes, and the term ax^3 does not contribute to $E_n^{(1)}$. The matrix element $(x^4)_{nn}$ is given by (Problem 5.13)

$$(x^4)_{nn} = \frac{3}{4\alpha^4}(2n^2 + 2n + 1) \qquad \textbf{(8.53)}$$

so that the first-order energy shift is

$$E_n^{(1)} = b(x^4)_{nn} = \frac{3}{4} b \left(\frac{\hbar}{m\omega}\right)^2 (2n^2 + 2n + 1). \qquad \textbf{(8.54)}$$

Note that for a fixed value of b the quantity $E_n^{(1)}$ grows rapidly with n. This is not surprising, since the higher excited states of the linear harmonic oscillator extend to larger and larger values of x (see Fig. 4.18), so that the perturbation bx^4 can have an increasingly important effect. Because the validity of the perturbation method requires that the magnitude of the correction term be small compared to the spacing between the unperturbed levels (given in the present case by $\hbar\omega$), we see from (8.54) that the higher the value of n the smaller are the values of the parameter b for which reliable results may be obtained from the perturbative result (8.54).

The second-order correction to the energy of the state n is

$$E_n^{(2)} = \sum_{k \neq n} \frac{|a(x^3)_{kn} + b(x^4)_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}. \qquad \textbf{(8.55)}$$

Using the results of Problem 5.13 for the required off-diagonal matrix elements of x^3 and x^4 one finds (Problem 8.8) that

$$\begin{aligned} E_n^{(2)} = &-\frac{15}{4}\frac{a^2}{\hbar\omega}\left(\frac{\hbar}{m\omega}\right)^3 \left(n^2 + n + \frac{11}{30}\right) \\ &-\frac{1}{8}\frac{b^2}{\hbar\omega}\left(\frac{\hbar}{m\omega}\right)^4 (34n^3 + 51n^2 + 59n + 21) \end{aligned} \qquad \textbf{(8.56)}$$

and we see that $|E_n^{(2)}|$ grows rapidly with n. Thus, as n increases, reliable results[1] will only be obtained from (8.56) for smaller and smaller values of a^2 and b^2.

---

[1] In fact, the perturbation series for this problem does not converge, but is an *asymptotic*, or *semi-convergent*, series. (See Matthews and Walker, 1973.)

Finally, we remark that the second-order corrections (8.45) and (8.55) could be calculated relatively easily because (a) the spectrum of the unperturbed Hamiltonian (the linear harmonic oscillator) is entirely discrete, and (b) only a small number of the required matrix elements of the perturbation are non-vanishing. When these conditions are not satisfied, the calculation of the second- (and higher) order corrections to the energy can become very difficult and must usually be performed approximately.

Gravitational energy shift in atomic hydrogen

As a final example of the application of perturbation theory for non-degenerate energy levels, let us consider an ordinary hydrogen atom (proton + electron) whose unperturbed Hamiltonian is

$$H_0 = \frac{\mathbf{p}^2}{2\mu} - \frac{e^2}{(4\pi\varepsilon_0)r} \tag{8.57}$$

where $\mu = mM_\mathrm{p}/(m + M_\mathrm{p})$ is the reduced mass, m being the mass of the electron and M_p that of the proton. Now the proton and the electron interact not only through the electrostatic potential $-e^2/(4\pi\varepsilon_0 r)$, but also by means of the gravitational interaction. The perturbation H' due to the gravitational force is (with $\lambda = 1$)

$$H' = -G\frac{mM_\mathrm{p}}{r} \tag{8.58}$$

where $G = 6.672 \times 10^{-11}$ N m^2 kg^{-2} is the gravitational constant. To first order in perturbation theory, the energy shift of the ground (1s) state of atomic hydrogen (which is non-degenerate) due to this perturbation is

$$\begin{aligned} E_{1s}^{(1)} &= \langle\psi_{1s}|H'|\psi_{1s}\rangle \\ &= \frac{1}{\pi a_\mu^3}\int\left(-G\frac{mM_\mathrm{p}}{r}\right)\exp(-2r/a_\mu)\mathrm{d}\mathbf{r} \\ &= -\frac{GmM_\mathrm{p}}{a_\mu} \end{aligned} \tag{8.59}$$

where $a_\mu = 4\pi\varepsilon_0\hbar^2/\mu e^2$. Since the unperturbed ground state energy of atomic hydrogen is given (see (7.114)) by

$$E_{1s}^{(0)} = -\frac{e^2}{(4\pi\varepsilon_0)2a_\mu} \tag{8.60}$$

the relative energy shift is

$$\frac{E_{1s}^{(1)}}{E_{1s}^{(0)}} = \frac{8\pi\varepsilon_0 GmM_\mathrm{p}}{e^2} \simeq 8.8 \times 10^{-40} \tag{8.61}$$

which is a truly small number! Needless to say, it is not necessary to calculate higher-order corrections in the present case.

8.2 Time-independent perturbation theory for a degenerate energy level

Until now we have assumed that the perturbed eigenfunction ψ_n differs slightly from a given function $\psi_n^{(0)}$, a solution of the 'unperturbed' equation (8.2). When the unperturbed energy level $E_n^{(0)}$ is α-fold degenerate, there are *several* 'unperturbed' wave functions $\psi_{nr}^{(0)}(r = 1, 2, \dots, \alpha)$ corresponding to this level, and we do not know *a priori* to which functions the perturbed eigenfunctions tend when $\lambda \to 0$. This implies that the treatment of Section 8.1 – in particular the basic expansion (8.8) – must be modified to deal with the degenerate case.

The α unperturbed wave functions $\psi_{nr}^{(0)}$ corresponding to the level $E_n^{(0)}$ are of course orthogonal to the unperturbed wave functions $\psi_l^{(0)}$ corresponding to *other* energy levels $E_l^{(0)} \neq E_n^{(0)}$. Although they need not be orthogonal among themselves, it is always possible to construct from linear combinations of them a new set of α unperturbed wave functions which are mutually orthogonal and normalised to unity. We may therefore assume without loss of generality that this has already been done, so that

$$\langle \psi_{nr}^{(0)} | \psi_{ns}^{(0)} \rangle = \delta_{rs} \quad (r, s = 1, 2, \dots, \alpha). \tag{8.62}$$

Let us now introduce the correct zero-order functions $\chi_{nr}^{(0)}$ which yield the first term in the expansion of the exact wave functions ψ_{nr} in powers of λ. That is

$$\psi_{nr} = \chi_{nr}^{(0)} + \lambda \psi_{nr}^{(1)} + \lambda^2 \psi_{nr}^{(2)} + \cdots \tag{8.63}$$

We shall also write the perturbed energy E_{nr} as

$$E_{nr} = E_n^{(0)} + \lambda E_{nr}^{(1)} + \lambda^2 E_{nr}^{(2)} + \cdots \tag{8.64}$$

with $E_n^{(0)} \equiv E_{nr}^{(0)}$ $(r = 1, 2, \dots, \alpha)$ since the unperturbed level $E_n^{(0)}$ is α-fold degenerate. Substituting the expansions (8.63) and (8.64) in equation (8.4) and equating the coefficients of λ, we find that

$$H_0 \psi_{nr}^{(1)} + H' \chi_{nr}^{(0)} = E_n^{(0)} \psi_{nr}^{(1)} + E_{nr}^{(1)} \chi_{nr}^{(0)}. \tag{8.65}$$

Since the functions $\chi_{nr}^{(0)}$ are linear combinations of the unperturbed wave functions $\psi_{nr}^{(0)}$, we may write

$$\chi_{nr}^{(0)} = \sum_{s=1}^{\alpha} c_{rs} \psi_{ns}^{(0)}, \qquad (r = 1, 2, \dots, \alpha) \tag{8.66}$$

where the coefficients c_{rs} are to be determined. Similarly, expanding $\psi_{nr}^{(1)}$ in the basis set of the unperturbed wave functions, we have

$$\psi_{nr}^{(1)} = \sum_k \sum_s a_{nr,ks}^{(1)} \psi_{ks}^{(0)} \tag{8.67}$$

where the indices r and s refer explicitly to the degeneracy. Substituting the expressions (8.66) and (8.67) in equation (8.65) and using the fact that $H_0\psi_{ks}^{(0)} = E_k^{(0)}\psi_{ks}^{(0)}$, we find that

$$\sum_k \sum_s a_{nr,ks}^{(1)}(E_k^{(0)} - E_n^{(0)})\psi_{ks}^{(0)} + \sum_s c_{rs}(H' - E_{nr}^{(1)})\psi_{ns}^{(0)} = 0. \tag{8.68}$$

Premultiplying by $\psi_{nu}^{(0)*}$ and integrating over all coordinates, we obtain

$$\sum_k \sum_s a_{nr,ks}^{(1)}(E_k^{(0)} - E_n^{(0)})\langle\psi_{nu}^{(0)}|\psi_{ks}^{(0)}\rangle + \sum_s c_{rs}[H'_{nu,ns} - E_{nr}^{(1)}\delta_{us}] = 0,$$
$$(u = 1, 2, \dots, \alpha) \tag{8.69}$$

where we have used (8.62) and written

$$H'_{nu,ns} \equiv \langle\psi_{nu}^{(0)}|H'|\psi_{ns}^{(0)}\rangle. \tag{8.70}$$

Since $\langle\psi_{nu}^{(0)}|\psi_{ks}^{(0)}\rangle = 0$ when $k \neq n$ and $E_k^{(0)} = E_n^{(0)}$ if $k = n$, we see that (8.69) reduces to

$$\sum_{s=1}^{\alpha} c_{rs}[H'_{nu,ns} - E_{nr}^{(1)}\delta_{us}] = 0, \qquad (u = 1, 2, \dots, \alpha). \tag{8.71}$$

This is a linear, homogeneous system of equations for the α unknown quantities $c_{r1}, c_{r2}, \dots, c_{r\alpha}$. A non-trivial solution is obtained if the determinant of the quantity in square brackets vanishes:

$$\det|H'_{nu,ns} - E_{nr}^{(1)}\delta_{us}| = 0, \qquad (s, u = 1, 2, \dots, \alpha). \tag{8.72}$$

This equation, which is of degree α in $E_{nr}^{(1)}$, is often called a *secular* equation by analogy with similar equations occurring in classical mechanics. It has α real roots $E_{n1}^{(1)}, E_{n2}^{(1)}, \dots, E_{n\alpha}^{(1)}$. If all these roots are *distinct* the degeneracy is completely removed to first order in the perturbation. On the other hand, if some (or all) roots of (8.72) are identical the degeneracy is only *partially* (or *not at all) removed.* The residual degeneracy may then either be removed in higher-order perturbation theory, or it may persist to all orders. The latter case occurs when the operators H_0 and H' share symmetry properties.

For a given value of r, the coefficients $c_{rs}(s = 1, 2, \dots, \alpha)$ which determine the 'correct' unperturbed zero-order wave function $\chi_{nr}^{(0)}$ via (8.66) may be obtained by substituting the value of $E_{nr}^{(1)}$ in the system (8.71) and solving for the coefficients $c_{r1}, c_{r2}, \dots, c_{r\alpha}$, in terms of one of them. The last coefficient is then obtained (up to a phase) by requiring that the function $\chi_{nr}^{(0)}$ be normalised to unity. Clearly, this procedure does not lead to a unique result when two or more roots $E_{nr}^{(1)}$ of the secular equation (8.72) coincide, since in this case the degeneracy is not fully removed.

It is apparent from the foregoing discussion that the determination of the correct zero-order wave functions $\chi_{nr}^{(0)}(r = 1, 2, \dots, \alpha)$ amounts to finding the proper orthonormal linear combinations of the original zero-order degenerate states $\psi_{nr}^{(0)}$, such that the matrix

$$\tilde{H}'_{nr,ns} = \langle \chi_{nr}^{(0)} | H' | \chi_{ns}^{(0)} \rangle, \qquad (r, s = 1, 2, \dots, \alpha) \tag{8.73}$$

be diagonal with respect to the indices r and s. The diagonal elements of this matrix are equal to the corresponding first-order energy corrections

$$E_{nr}^{(1)} = \tilde{H}'_{nr,nr}, \qquad (r = 1, 2, \dots, \alpha). \tag{8.74}$$

Once the correct zero-order wave functions $\chi_{nr}^{(0)}$ have been determined, the first-order correction $\psi_{nr}^{(1)}$ to the wave function and the second-order energy correction $E_{nr}^{(2)}$ can be obtained in a way similar to that followed in Section 8.1 for the non-degenerate case.

It is also interesting to note that if all the original *off-diagonal* matrix elements $H'_{nr,ns} = \langle \psi_{nr}^{(0)} | H' | \psi_{ns}^{(0)} \rangle, r \neq s$, vanish (i.e. if the degenerate states $\psi_{nr}^{(0)} (r = 1, 2, \dots, \alpha)$ belonging to the level $E_n^{(0)}$ are not connected to first order), then the secular equation (8.72) takes the simple diagonal form

$$\begin{vmatrix} H'_{n1,n1} - E_{nr}^{(1)} & 0 & 0 \;\dots & 0 \\ 0 & H'_{n2,n2} - E_{nr}^{(1)} & 0 \;\dots & 0 \\ 0 & 0 & & \vdots \\ \vdots & \vdots & & 0 \\ 0 & 0 & \dots\; 0 & H'_{n\alpha,n\alpha} - E_{nr}^{(1)} \end{vmatrix} = 0. \tag{8.75}$$

In this case, we see from (8.66) and (8.71) that our initial unperturbed wave functions $\psi_{nr}^{(0)}$ are already the correct zero-order wave functions for the perturbation H'. Moreover, the roots $E_{nr}^{(1)}$ of equation (8.75) are given immediately by the formula

$$E_{nr}^{(1)} = H'_{nr,nr}, \qquad (r = 1, 2, \dots, \alpha) \tag{8.76}$$

and upon comparison with (8.15) we see that the degeneracy plays no role in the analysis. This situation occurs whenever the unperturbed states can be uniquely specified in terms of a set of operators which all commute with the perturbation H'.

Doubly degenerate energy level

As a simple illustration of our general discussion, let us consider the case of an unperturbed energy level $E_n^{(0)}$ which is doubly degenerate. Dropping the index n for notational simplicity, we denote by $\psi_1^{(0)}$ and $\psi_2^{(0)}$ two linearly independent orthonormal zero order wave functions corresponding to this level. The system of linear homogeneous equation (8.71) reduces to a set of two equations which we write in matrix form as

$$\begin{pmatrix} H'_{11} - E_r^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_r^{(1)} \end{pmatrix} \begin{pmatrix} c_{r1} \\ c_{r2} \end{pmatrix} = 0 \tag{8.77}$$

with $H'_{ij} = \langle\psi_i^{(0)}|H'|\psi_j^{(0)}\rangle$ and $i, j = 1, 2$. The secular equation (8.72) reads

$$\begin{vmatrix} H'_{11} - E_r^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_r^{(1)} \end{vmatrix} = 0 \tag{8.78}$$

and yields the two first-order energy corrections

$$E_1^{(1)} = \frac{1}{2}(H'_{11} + H'_{22}) + \frac{1}{2}[(H'_{11} - H'_{22})^2 + 4|H'_{12}|^2]^{1/2} \tag{8.79a}$$

and

$$E_2^{(1)} = \frac{1}{2}(H'_{11} + H'_{22}) - \frac{1}{2}[(H'_{11} - H'_{22})^2 + 4|H'_{12}|^2]^{1/2} \tag{8.79b}$$

where we have used the fact that $H'_{21} = H'^{*}_{12}$.

Given the above values of $E_r^{(1)} (r = 1, 2)$, we may now return to the system of two homogeneous equations (8.77), which gives

$$\frac{c_{r1}}{c_{r2}} = -\frac{H'_{12}}{H'_{11} - E_r^{(1)}} = -\frac{H'_{22} - E_r^{(1)}}{H'_{21}}, \qquad r = 1, 2. \tag{8.80}$$

The normalised correct zero-order wave function for $r = 1$ is therefore given by

$$\chi_1^{(0)} = c_{11}\psi_1^{(0)} + c_{12}\psi_2^{(0)} \tag{8.81a}$$

and that corresponding to $r = 2$ is given by

$$\chi_2^{(0)} = c_{21}\psi_1^{(0)} + c_{22}\psi_2^{(0)} \tag{8.81b}$$

where the coefficients c_{rs} (with $r, s = 1, 2$) are obtained from (8.80) and the normalisation condition

$$|c_{r1}|^2 + |c_{r2}|^2 = 1, \qquad r = 1, 2. \tag{8.82}$$

Choosing the phase of c_{r1} so that this coefficient be real and positive, one obtains (Problem 8.9)

$$c_{r1} = \frac{1}{\sqrt{2}}\left[1 - (-1)^r \frac{H'_{11} - H'_{22}}{[(H'_{11} - H'_{22})^2 + 4|H'_{12}|^2]^{1/2}}\right]^{1/2} \tag{8.83a}$$

and

$$c_{r2} = (-1)^{r+1}\frac{|H'_{12}|}{H'_{12}}\frac{1}{\sqrt{2}}\left[1 + (-1)^r \frac{H'_{11} - H'_{22}}{[(H'_{11} - H'_{22})^2 + 4|H'_{12}|^2]^{1/2}}\right]^{1/2} \tag{8.83b}$$

An interesting special case is that for which

$$\begin{aligned} H'_{11} &= H'_{22} = 0, \\ H'_{12} &= H'^{*}_{21} \neq 0. \end{aligned} \tag{8.84}$$

We then obtain from (8.79) the simple results

$$E_1^{(1)} = +|H'_{12}|, \qquad E_2^{(1)} = -|H'_{12}| \tag{8.85}$$

and we see from (8.80) and (8.85) that

$$\frac{c_{11}}{c_{12}} = -\frac{c_{21}}{c_{22}} = \frac{H'_{12}}{|H'_{12}|}. \tag{8.86}$$

Note that the original degenerate states $\psi_1^{(0)}$ and $\psi_2^{(0)}$ are fully mixed, since $|c_{r1}| = |c_{r2}|$.

Another particular case arises when the off-diagonal matrix elements vanish

$$H'_{12} = H'^{*}_{21} = 0 \tag{8.87}$$

so that the two degenerate states $\psi_1^{(0)}$ and $\psi_2^{(0)}$ are not connected to first order. We then have

$$E_1^{(1)} = H'_{11}, \qquad E_2^{(1)} = H'_{22} \tag{8.88}$$

which is of course a special case of (8.76).

Fine structure of hydrogenic atoms

As a second example of degenerate perturbation theory, we shall calculate the corrections to the Schrödinger (Bohr) energy levels of one-electron atoms due to *relativistic effects*. We assume that the nucleus is 'infinitely heavy' so that the reduced mass μ coincides with m, the mass of the electron. The unperturbed Hamiltonian is then

$$H_0 = \frac{\mathbf{p}^2}{2m} + V(r) \tag{8.89}$$

where $V(r)$ is the Coulomb potential

$$V(r) = -\frac{Ze^2}{(4\pi\varepsilon_0)r}. \tag{8.90}$$

The perturbation H' is given by[2]

$$H' = H'_1 + H'_2 + H'_3 \tag{8.91}$$

where

$$H'_1 = -\frac{\mathbf{p}^4}{8m^3c^2} \tag{8.92}$$

$$H'_2 = \frac{1}{2m^2c^2}\frac{1}{r}\frac{\mathrm{d}V}{\mathrm{d}r}\mathbf{L}.\mathbf{S} \tag{8.93}$$

and

$$H'_3 = \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\delta(\mathbf{r}). \tag{8.94}$$

---

[2] The Hamiltonian H' can be obtained by starting from the Dirac relativistic wave equation for the electron, and keeping terms up to order v^2/c^2 (where v is the electron velocity and c the velocity of light) in the Dirac Hamiltonian. This will be shown in Chapter 15.

The first term, H_1', is readily seen to be a *relativistic correction to the kinetic energy* (Problem 8.10). The second term, H_2', involving the scalar product **L**.**S** of the orbital angular momentum **L** and the spin operator **S** of the electron, is called the *spin–orbit* term. Its physical origin is the interaction between the intrinsic magnetic dipole moment of the electron, due to its spin, and the internal magnetic field of the atom, related to the electron's orbital angular momentum. The third term, H_3', is a relativistic correction to the potential energy, called the *Darwin term* which is proportional to the delta function $\delta(\mathbf{r})$ and hence acts only at the origin.

Before we proceed to the evaluation of the energy shifts due to these three terms by using perturbation theory, we remark that the Schrödinger theory of one-electron atoms discussed in Chapter 7 does not include the spin of the electron. In order to calculate corrections involving the spin operator, such as those arising from H_2', we shall thus start from the 'unperturbed' equation

$$H_0\psi^{(0)}_{nlm_lm_s} = E^{(0)}_n\psi^{(0)}_{nlm_lm_s} \tag{8.95}$$

where $E^{(0)}_n$ are the Schrödinger energy eigenvalues (7.114) with $\mu = m$. The zero-order wave functions $\psi^{(0)}_{nlm_lm_s}$ are the Pauli two-component hydrogenic spin-orbitals

$$\psi^{(0)}_{nlm_lm_s} = \psi^{(0)}_{nlm_l}(\mathbf{r})\chi_{\frac{1}{2},m_s} \tag{8.96}$$

where the functions $\psi^{(0)}_{nlm_l}(\mathbf{r})$ are the hydrogenic Schrödinger eigenfunctions such that

$$H_0\psi^{(0)}_{nlm_l}(\mathbf{r}) = E^{(0)}_n\psi^{(0)}_{nlm_l}(\mathbf{r}) \tag{8.97}$$

and $\chi_{\frac{1}{2},m_s}$ are the two-component spin-1/2 eigenfunctions, with $m_s = \pm 1/2$. We remark that the spin-orbitals $\psi^{(0)}_{nlm_lm_s}$ are simultaneous eigenfunctions of the operators H_0, $\mathbf{L}^2$, L_z, $\mathbf{S}^2$ and S_z with eigenvalues $E^{(0)}_n$, $l(l+1)\hbar^2$, $m_l\hbar$, $(3/4)\hbar^2$ and $m_s\hbar$, respectively. To each energy level $E^{(0)}_n$ correspond $2n^2$ spin-orbitals $\psi^{(0)}_{nlm_lm_s}$, the factor of two being due to the two possible values $m_s = \pm 1/2$ of the quantum number m_s.

We shall now calculate the first-order energy corrections to the energy levels $E^{(0)}_n$ due to the three terms (8.92)–(8.94), using the Pauli spin-orbitals $\psi^{(0)}_{nlm_lm_s}$ as our zero-order wave functions.

Energy shift due to the term H_1' (relativistic correction to the kinetic energy)

Since the unperturbed energy level $E^{(0)}_n$ is $2n^2$-degenerate, we should use degenerate perturbation theory. However, we first note that H_1' does not act on the spin variable. Furthermore, it commutes with the components of the orbital angular momentum so that the degenerate states belonging to the level $E^{(0)}_n$ are not connected to first order by H_1'. Hence, according to (8.76), the first-order energy correction ΔE_1 due to H_1'

is given by

$$\begin{aligned}\Delta E_1 &= \left\langle \psi^{(0)}_{nlm_lm_s} \left| -\frac{\mathbf{p}^4}{8m^3c^2} \right| \psi^{(0)}_{nlm_lm_s} \right\rangle \\ &= \left\langle \psi^{(0)}_{nlm_l} \left| -\frac{\mathbf{p}^4}{8m^3c^2} \right| \psi^{(0)}_{nlm_l} \right\rangle \\ &= -\frac{1}{2mc^2} \langle \psi^{(0)}_{nlm_l} | T^2 | \psi^{(0)}_{nlm_l} \rangle \qquad \textbf{(8.98)}\end{aligned}$$

where $T = \mathbf{p}^2/2m$ is the kinetic energy operator. From (8.89) and (8.90), we have

$$T = H_0 - V(r) = H_0 + \frac{Ze^2}{(4\pi\varepsilon_0)r} \qquad \textbf{(8.99)}$$

so that

$$\begin{aligned}\Delta E_1 &= -\frac{1}{2mc^2} \left\langle \psi^{(0)}_{nlm_l} \left| \left(H_0 + \frac{Ze^2}{(4\pi\varepsilon_0)r} \right) \left(H_0 + \frac{Ze^2}{(4\pi\varepsilon_0)r} \right) \right| \psi^{(0)}_{nlm_l} \right\rangle \\ &= -\frac{1}{2mc^2} \left[(E_n^{(0)})^2 + 2E_n^{(0)} \left(\frac{Ze^2}{4\pi\varepsilon_0} \right) \left\langle \frac{1}{r} \right\rangle_{nlm_l} + \left(\frac{Ze^2}{4\pi\varepsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle_{nlm_l} \right] \qquad \textbf{(8.100)}\end{aligned}$$

where we have used (8.97). Now $E_n^{(0)}$ is given by (7.114) with $\mu = m$, and the required average values of r^{-1} and r^{-2} can be obtained from the results of Problem 7.16, in which μ is set equal to m (so that $a_\mu = a_0$, the first Bohr radius). Hence

$$\begin{aligned}\Delta E_1 &= -\frac{1}{2mc^2} \left\{ \left[\frac{mc^2(Z\alpha)^2}{2n^2} \right]^2 - 2\left(\frac{Ze^2}{4\pi\varepsilon_0} \right) \frac{mc^2(Z\alpha)^2}{2n^2} \frac{Z}{a_0n^2} \right. \\ &\qquad \left. + \left(\frac{Ze^2}{4\pi\varepsilon_0} \right)^2 \frac{Z^2}{a_0^2 n^3(l+1/2)} \right\} \\ &= \frac{1}{2} mc^2 \frac{(Z\alpha)^2}{n^2} \frac{(Z\alpha)^2}{n^2} \left[\frac{3}{4} - \frac{n}{l+1/2} \right] \\ &= -E_n^{(0)} \frac{(Z\alpha)^2}{n^2} \left[\frac{3}{4} - \frac{n}{l+1/2} \right] \qquad \textbf{(8.101)}\end{aligned}$$

where $\alpha = e^2/(4\pi\varepsilon_0\hbar c) \simeq 1/137$ is the fine-structure constant.

Energy shift due to the term H_2' (spin–orbit term)

Let us first rewrite this term as

$$H_2' = \xi(r)\mathbf{L}.\mathbf{S} \qquad \textbf{(8.102)}$$

where the quantity $\xi(r)$ is given from (8.90) and (8.93) by

$$\begin{aligned}\xi(r) &= \frac{1}{2m^2c^2}\frac{1}{r}\frac{\mathrm{d}V}{\mathrm{d}r} \\ &= \frac{1}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\frac{1}{r^3}.\end{aligned} \tag{8.103}$$

Because the operator $\mathbf{L}^2$ does not act on the spin variable, and commutes with the components of $\mathbf{L}$ and with any function of the radial variable r, we see from (8.102) that $\mathbf{L}^2$ commutes with H_2'. Thus the perturbation H_2' does not connect states with different values of the orbital angular momentum quantum number l. Since for a fixed value of n and l there are $2(2l+1)$ degenerate eigenstates of H_0 ($2l+1$ allowed values of m_l given by $m_l = -l, -l+1, \dots, +l$, and a factor of two due to the two spin states), we see that the calculation of the energy shift arising from H_2' requires the diagonalisation of $2(2l+1) \times 2(2l+1)$ sub-matrices.

This diagonalisation can be greatly simplified by making a judicious choice of the set of zero-order wave functions, the best choice being obviously that for which $\mathbf{L.S}$ is diagonal. Now, the zero-order wave functions $\psi^{(0)}_{nlm_lm_s}$ given by (8.96) are simultaneous eigenfunctions of H_0, $\mathbf{L}^2$, L_z, $\mathbf{S}^2$ and S_z and hence are not convenient since $\mathbf{L.S}$ does not commute with L_z or S_z. However, we shall now show that adequate zero-order wave functions may be obtained by forming appropriate linear combinations of the functions $\psi^{(0)}_{nlm_lm_s}$. To this end, we introduce the total angular momentum of the electron

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{8.104}$$

and since

$$\mathbf{J}^2 = \mathbf{L}^2 + 2\mathbf{L.S} + \mathbf{S}^2 \tag{8.105}$$

we may write

$$\mathbf{L.S} = \tfrac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2). \tag{8.106}$$

Consider now wave functions $\psi^{(0)}_{nljm_j}$ which are eigenstates of the operators H_0, $\mathbf{L}^2$, $\mathbf{S}^2$, $\mathbf{J}^2$ and J_z, the corresponding eigenvalues being $E^{(0)}_n$, $l(l+1)\hbar^2$, $(3/4)\hbar^2$, $j(j+1)\hbar^2$ and $m_j\hbar$. Using our study of the addition of angular momenta made in Section 6.10, and remembering that $s = 1/2$ in the present case, we see that the allowed values of the total angular momentum quantum number j are

$$\begin{aligned} j &= l \pm 1/2, \qquad l \neq 0 \\ j &= 1/2, \qquad l = 0 \end{aligned} \tag{8.107}$$

and that the corresponding magnetic quantum number m_j can take on the $(2j+1)$ allowed values

$$m_j = -j, -j+1, \dots, +j. \tag{8.108}$$

Moreover, we can construct the functions $\psi^{(0)}_{nljm_j}$ from linear combinations of the functions $\psi^{(0)}_{nlm_lm_s}$. Using (6.295), we obtain

$$\psi^{(0)}_{nljm_j} = \sum_{m_lm_s} \langle lsm_lm_s|jm_j\rangle \psi^{(0)}_{nlm_lm_s}, \qquad s = 1/2 \tag{8.109}$$

where $\langle lsm_lm_s|jm_j\rangle$ are Clebsch–Gordan coefficients.

Since **L.S** commutes with $\mathbf{L}^2$, $\mathbf{S}^2$, $\mathbf{J}^2$ and J_z it is clear that the new zero-order wave functions $\psi^{(0)}_{nljm_j}$ form a satisfactory basis set in which the operator **L.S** (and hence the perturbation H_2') is diagonal. From (8.102) and (8.106) we see that for $l \neq 0$ the energy shift due to the term H_2' is given by

$$\begin{aligned} \Delta E_2 &= \langle \psi^{(0)}_{nljm_j}|\tfrac{1}{2}\xi(r)[\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2]|\psi^{(0)}_{nljm_j}\rangle \\ &= \frac{\hbar^2}{2}\langle \xi(r)\rangle \big[j(j+1) - l(l+1) - \tfrac{3}{4}\big] \end{aligned} \tag{8.110}$$

where $\langle \xi(r)\rangle$ denotes the average value of $\xi(r)$ in the state $\psi^{(0)}_{nljm_j}$. Using (8.103) and the average value of r^{-3} calculated in Problem 7.16 (with $a_\mu = a_0$), we have

$$\begin{aligned} \langle \xi(r)\rangle &= \frac{1}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\left\langle \frac{1}{r^3}\right\rangle \\ &= \frac{1}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\frac{Z^3}{a_0^3n^3l(l+1/2)(l+1)}. \end{aligned} \tag{8.111}$$

Hence, for $l \neq 0$, we find from (8.110) and (8.111) that

$$\begin{aligned} \Delta E_2 &= \frac{mc^2(Z\alpha)^4}{4n^3l(l+1/2)(l+1)} \times \begin{cases} l & \text{for } j = l + 1/2 \\ -l-1 & \text{for } j = l - 1/2 \end{cases} \\ &= -E_n^{(0)}\frac{(Z\alpha)^2}{2nl(l+1/2)(l+1)} \times \begin{cases} l & \text{for } j = l + 1/2 \\ -l-1 & \text{for } j = l - 1/2 \end{cases} \end{aligned} \tag{8.112}$$

For $l = 0$ the spin–orbit interaction (8.102) vanishes so that $\Delta E_2 = 0$ in that case.

Energy shift due to the term H_3' (Darwin term)

This term does not act on the spin variable and commutes with the operators $\mathbf{L}^2$ and L_z. Moreover, since H_3' acts only at the origin and the hydrogenic wave functions vanish at $r = 0$ when $l \neq 0$, we have only to consider the case $l = 0$. Calling ΔE_3