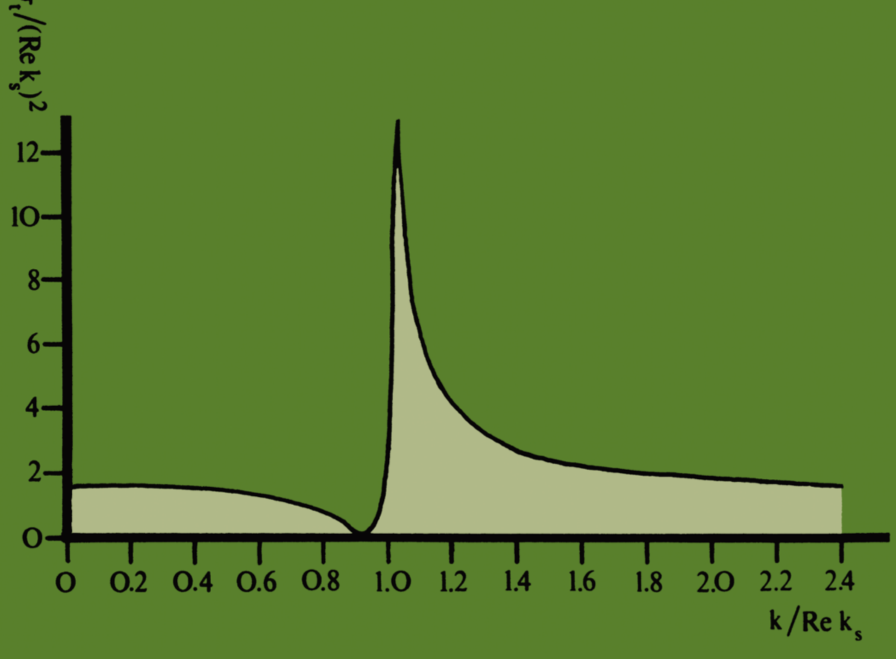
BASIC QUANTUM MECHANICS

Second Edition

J. M. Cassels



Basic quantum mechanics

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J. M. Cassels, FRS

Lyon Jones Professor of Physics
University of Liverpool, Liverpool, UK

Second edition

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Preface to the second edition

I am glad to have the opportunity to write a preface to a second edition of *Basic Quantum Mechanics.* The first edition has been out of print for a few years but, with the permission of the publishers, it has been circulating vigorously among students in photocopied form. This has encouraged me to believe that it would be worthwhile to produce an improved version of the book.

There are two major changes that I have made. In chapter 3 there is now a much more thorough account of the relationship between potential energy curves, energy levels, and wave functions. A difficulty here is that the discussion rests on the WKB approximation, an analysis of which would hold up progress at a point at which speedy movement is vital. My solution is to state and use the important features of the WKB approximation without proofs, which come later—in the same place as in the first edition, chapter 5. Since the statements required are few and succinct I believe this procedure will be acceptable.

The second major change is to the treatments of radioactive states and the related resonant scattering, in chapters 8 and 9. It has always surprised me to notice how many physicists spend careers measuring widths and inferring lifetimes without asking for proofs of the formulae required. Certainly few elementary books on quantum mechanics are of any use to them in this respect. In the first edition I worked out decay and scattering for the same particular potential, pointed out the relationship of interest, and stated the general extension. That was better than nothing, but not really satisfactory. Now in this second edition I have given a more general treatment, based on the S-matrix, which owes much to research papers by Ning Hu and by Peierls, published thirty-three and twenty years ago, respectively. I intend the version in this book to be comprehensible at the transition between British undergraduate and postgraduate studies, like the treatments of other advanced topics.

I have also made many minor changes that are intended to improve the balance of the argument and to smooth the reader's path. Referring to the preface to the first edition, I cannot yet claim that the book is as easy to read as a novel, but perhaps it is now more nearly so.

I have changed over to SI units throughout. This seems to be mandatory now, but I regret the clumsiness that has been introduced into many of the formulae thereby.

Finally I should thank Professor Sir Rudolf Peierls, and Drs Allcock and Huby for valuable advice, Dr Wormald for computational help, Misses Calland and Owen for typing the manuscript, and Mrs Cheyne for tracing the diagrams. I thank also Dr Carroll for help with the proofs.

Liverpool, 1981 J. M. CASSELS

Preface to the first edition

When I first learnt about quantum mechanics, I thought it was horrible. The trouble was that the course was taught in a semi-historical spirit, with a conscious attempt to bring in new ideas only very gradually. Every calculation involved further tinkering with the rules, until a point was reached when I had lost all confidence that a stable new view of physics would be achieved. It was a great relief in the following year to attend the lectures of Professor Dirac, which followed essentially the plan of his evergreen book, *The Principles of Quantum Mechanics* (Oxford University Press). I learnt at last that quantum mechanics had an extremely clear and logical structure, and that classical mechanics could be seen as a limiting case, in a very beautiful way.

My lectures to third year Honours Physics students at Liverpool have therefore followed the logical approach, albeit at a more elementary level than Professor Dirac's. This book follows the same plan at the same level; all the new concepts are in chapter 1 and the rest of the book simply follows the consequences.

A commitment to the logical approach also seems to me to make it advisable to give a full account of the mathematics. I have therefore tried very hard to avoid simply quoting 'well-known' mathematical results which in fact might well be encountered for the first time.

I should make it clear that the book is about mechanics, and makes no claim to be a connected account of elementary atomic, nuclear, or particle physics. I have provided examples from these fields, however, to illustrate every important point in the discussion.

I am aware that my emphasis on logic and basic structure, on full presentation of mathematical argument, and on overall brevity has produced a book which is not easy to read like, say, a novel. Possibly users of it may wish to work with another book in parallel which covers the same ground in a more relaxed, readable, and necessarily less thoroughgoing way. Another book, *Introduction to Quantum Mechanics* by Professor Matthews (McGraw-Hill), has always seemed to me to be an excellent essay in this manner.

I should mention that my commitment to the logical approach does not in any way reflect disrespect for the history of quantum mechanics. On the contrary I believe that the whole development represents an adventure of the human spirit worthy to rank in the top dozen since the Renaissance. I feel, though, that the history of quantum mechanics is best appreciated by those who understand how it works. Once that is assured, I recommend strongly a study of *The Conceptual Development of Quantum Mechanics* by Professor Jammer (McGraw-Hill).

During the writing of this book, I received much helpful advice from many colleagues at Liverpool, particularly Drs Huby and Allcock.

At various times four departmental secretaries have worked on the typing of the manuscript, and I mention particularly Mrs Valerie Turnbull who broke the back of the job. I wish to thank also members of the departmental drawing office for their help with the diagrams.

Liverpool, 1969 J. M. CASSELS

List of abbreviations

MPD	Momentum probability density
PCD	Probability current density
PPD	Position probability density
RPCD	Radial probability current density
RPPD	Radial position probability density
TDSE	Time-dependent Schrödinger equation
TISE	Time-independent Schrödinger equation
WKB	Wentzel, Kramers, and Brillouin

1

Fundamentals of particle quantum mechanics

§1 Introduction

Non-relativistic quantum mechanics is an elegant, logical, and complete branch of physical theory, but for several reasons the early steps towards its understanding are not easy.

First, a number of unfamiliar concepts are involved in the basic skeleton of the theory, and it is difficult to appreciate the significance of any one of them until the others are understood. The initial conceptual investment is therefore high. Secondly, much of the discussion centres round the wave function ψ which, to be sure, can be calculated explicitly enough once the physical scene is set. Nevertheless, ψ has a purely abstract significance; an electromagnetic field carries the power to move objects, whereas ψ carries nothing more tangible than information. Thirdly, the methods for tapping this source of information are somewhat indirect. Fourthly, the predictions of the theory are often only statistical; the probabilities of this or that result for an experiment may be all that is available.

It should be mentioned at once, before premature despair takes hold, that the mathematical operations involved in the theory are often very simple indeed. Thus encouraged the physicist's instincts, at first frozen by unfamiliarity, soon resume their normal functions; the right way to think about problems comes to feel completely natural.

The best answer to the problem of understanding the basic skeleton of the theory is surely to describe it all in one place, as clearly and briefly as possible, in order to facilitate reference and concentrated study; section 2 does just this, and the sections beyond do not call for further adjustments to basic concepts.

Meanwhile nothing becomes a skeleton so much as flesh, and the rest of section 1 aims to provide some. A few very simple examples will be worked through in detail, to provide a quite informal mixture of information and exercise. The intention is that this preview should be read as lightly as possible, but that it should be frequently rechecked to see how general principles work out in practice.

Informal preview The first point to understand is that the physical condition of a particle, its state, is described by a wave function ψ of position and time. One of the basic assumptions is that ψ obeys a partial differential equation called Schrödinger's equation, first published in 1926. Solution of this gives the value of ψ for all positions and all times.

The simplest example is provided by a particle of mass m that is completely free to move in one dimension. Schrödinger's equation then takes the form

$$\frac{\partial}{\partial t}\psi(x,t)=\frac{i\hbar}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) \tag{1.1}$$

where $\hbar$ is a universal constant, in fact Planck's constant h divided by 2π. Of course x measures the position and t the time.

Two simplifying features should be noticed, and it is fortunate that they are common to all examples of Schrödinger's equation. First, it is *linear* in ψ, so that no awkward terms proportional to, say, ψ^3 or $(\partial\psi/\partial x)^2$ appear. Secondly, it is *homogeneous*; all the terms are linear in ψ and there is none that is independent of ψ.

A third feature is not universal but is found in this particular example. The coefficients qualifying the terms are constant, and not functions of x or, more complicated still, functions of both x and t.

It is well known that a differential equation with the three features mentioned can be solved by an exponential function whose argument is linear in the variables, here x and t. With a little forethought this function may be written

$$\psi=A\mathrm{e}^{i(kx-\omega t)}\equiv A\mathrm{e}^{2\pi i\{(x/\lambda)-\nu t\}} \tag{1.2}$$

where $k \equiv 2\pi/\lambda$, $\omega \equiv 2\pi\nu$, and where A is a normalising constant, which may be chosen to be complex if desired. Obviously ψ behaves in a wavelike manner, k being the circular wavenumber,† $|\lambda|$ the wavelength, ω the circular frequency, and ν the ordinary frequency.

Substitution into equation (1.1) verifies the solution, provided only that a *dispersion relation* is always maintained between ω and k:

$$\omega = \frac{\hbar k^2}{2m} \tag{1.3}$$

The dispersion relation is non-linear, and elementary wave theory signals a warning. A complicated, that is anharmonic, wave function can be considered to be a superposition of harmonic wave functions of more than one frequency. The shape of such a wave function must change as the harmonic waves propagate forwards in time, since the wave velocity ω/k depends on k and ω.‡ An example will be examined in section 6.

For the moment attention will be confined to free particle wave functions of a single circular frequency, say ω_1. Furthermore, the discussion will concentrate on a finite region of space, such that $-L/2 \leqslant x \leqslant L/2$. It will appear later, in section 4, that there is then a reason for requiring that L should be an integral multiple of the wavelength $|\lambda_1|$ of the wave function, and obviously the simplest choice is

$$L = |\lambda_1| \tag{1.4}$$

---

† The term *wavenumber* is unfortunate, though standard, since k clearly has the dimensions of an inverse length.

‡ In classical physics a displacement of a stretched string, or a pressure fluctuation in a gas, obeys the common wave equation

$$\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} = \frac{\partial^2\psi}{\partial x^2}$$

which again is linear, homogeneous, and has constant coefficients. Therefore equation (1.2) holds good, but the dispersion relation then has the simple and familiar linear form

$$\omega = \pm ck$$

where c is a constant velocity, independent of k and ω. A complicated disturbance can therefore propagate without distortion.

The associated circular wavenumbers and frequency are (equations (1.2) and (1.3))

$$k_1 = \pm 2\pi/L, \qquad \omega_1 = 2\pi^2\hbar/mL^2 \tag{1.5}$$

Three particular wave functions of frequency ω_1 will be discussed. They are

$$\left.\begin{aligned} \psi_a &= L^{-1/2}e^{i(k_1x-\omega_1t)} \\ \psi_b &= L^{-1/2}e^{i(-k_1x-\omega_1t)} \\ \psi_c &= -i2^{-1/2}\psi_a + i2^{-1/2}\psi_b \\ &= (2/L)^{1/2}\sin(k_1x)e^{-i\omega_1t} \end{aligned}\right\} \tag{1.6}$$

For the sake of definiteness k_1 is now taken to be positive throughout, and a negative wavenumber is shown explicitly by a minus sign.

Clearly ψ_a and ψ_b are progressive waves, towards positive and negative x respectively, and ψ_c is a standing wave. As usual a superposition of solutions of a linear differential equation is itself a solution of that equation; this is a fact of fundamental importance to quantum mechanics.

A most important point is that ψ itself cannot be measured directly by any kind of experiment. However, ψ does carry information about all the usual dynamical variables of the particle, such as its position, momentum, kinetic energy, potential energy, and so on, and this information can be extracted by appropriate mathematical operations.

Predictions about the position of the particle can be made directly from the wave function, in the manner first suggested by Born in 1926. In fact $|\psi|^2$ is the *position probability density* (PPD),† so called because $|\psi|^2\,dx$ is the chance that the particle will be found between x and $x+dx$. For the sample wave functions of equation (1.6),

$$\left.\begin{aligned} |\psi_a|^2 &= |\psi_b|^2 = 1/L \\ |\psi_c|^2 &= (2/L)\sin^2(k_1x) \end{aligned}\right\} \tag{1.7}$$

In the states represented by ψ_a and ψ_b the particle might equally well be found anywhere, whereas in that represented by ψ_c it is most likely to be found near the points where x is an odd multiple of $L/4$

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† To avoid verbosity several longwinded titles, after their first occurrences, are abbreviated to sets of initials in capital letters. A list of abbreviations will be found at the front of the book.

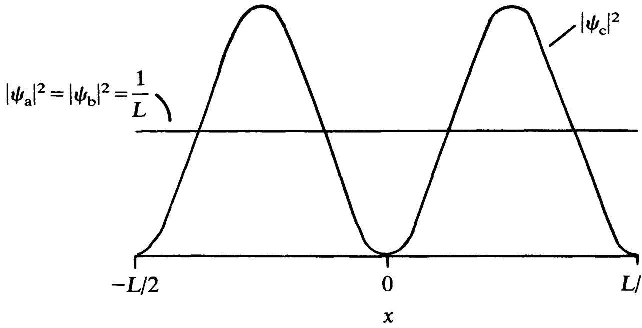

Figure 1.1 PPDs for the three wave functions ψ_a, ψ_b, and ψ_c.

(figure 1.1). Clearly quantum mechanics is making only predictions of a statistical nature here.

In all three examples the wave function is normalised so that the chance of finding it somewhere in the region of special interest is unity,

$$\int_{-L/2}^{L/2} |\psi|^2 \, dx = 1 \tag{1.8}$$

It should be realised, of course, that the wavefunctions and PPDs repeat themselves over and over again at intervals of L on either side of the region of special interest, so that other particles could be found out there. It is obviously not possible to produce a localised PPD with harmonic wave functions of a single frequency, ω_1, in this case.†

The other properties of the particle have to be discussed in a less explicit way. Such things as the momentum, kinetic energy, potential energy, and in fact all the objectives of measurement in experimental physics, are called observables. Each observable is represented in the theory by an operator, which gives instructions for a mathematical operation on ψ. Forecasts of the result of measuring an observable are made by studying the effect of carrying out the associated mathematical operation on ψ.

The momentum of the particle in a one-dimensional problem, for example, is represented by the operator $\hat{p} = -i\hbar(\partial/\partial x)$, which acts on

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† Note that in section 7 and figure 7.10 the wave functions are harmonic inside the range $-L/2 \leqslant x \leqslant L/2$, but zero outside it. A superposition of harmonic waves of an infinite number of frequencies is required to bring this about (*vide* problem 3.12).

ψ to produce $-i\hbar(\partial\psi/\partial x)$.† If this operator is applied to ψ_a or ψ_b,

$$\left.\begin{aligned}\hat{p}\psi_a &= -i\hbar\frac{\partial\psi_a}{\partial x} = \hbar k_1\psi_a\\ \hat{p}\psi_b &= -i\hbar\frac{\partial\psi_b}{\partial x} = -\hbar k_1\psi_b\end{aligned}\right\} \tag{1.9}$$

A significant feature is that the action of $\hat{p}$ on ψ_a or ψ_b has not changed their shapes, but only multiplied them by the factors $\hbar k_1$ or $-\hbar k_1$ respectively. The interpretation of this special mathematical situation is that a measurement of the momentum of the particle in the state represented by ψ_a or ψ_b is sure to produce the result $\hbar k_1$ or $-\hbar k_1$ respectively. The predictions here are definite and not statistical.

The relationship between the momentum p and the wavelength $2\pi/k_1$ in the state represented by ψ_a was verified in electron diffraction experiments by Davisson and Germer, and independently by G. P. Thomson, in 1927.

When $\hat{p}$ is applied to ψ_c the result is not so simple:

$$\begin{aligned}\hat{p}\psi_c &= -i\hbar\frac{\partial}{\partial x}\{(2/L)^{1/2}\sin(k_1x)e^{-i\omega_1t}\}\\ &= -i(2/L)^{1/2}\hbar k_1\cos(k_1x)e^{-i\omega_1t}\end{aligned} \tag{1.10}$$

Here the action of $\hat{p}$ has changed the shape of ψ_c, and the interpretation is that the momentum of the particle in the state represented by ψ_c cannot be definitely predicted. Nevertheless, some information about it is available, from an inspection of the third of equations (1.6). There it is seen that ψ_c can be expanded in terms of ψ_a and ψ_b, both associated with definite momenta. The interpretation is that the momentum in the state represented by ψ_c could be found to be either $\hbar k_1$ or $-\hbar k_1$. The chance of getting one or the other result is proportional to the square of the modulus of the expansion coefficient in the third of equations (1.6), that is $|-i2^{-1/2}|^2=\frac{1}{2}$ for the result $\hbar k_1$, and $|i2^{-1/2}|^2=\frac{1}{2}$ for the result $-\hbar k_1$. The prediction here is statistical again, and it is significant that a slightly more definite prediction about the position of the particle in the state represented by ψ_c has been accompanied by a more indefinite prediction about its momentum.

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† Operators will be distinguished by a circumflex accent throughout.

A third observable may also be considered, the kinetic energy T. In classical mechanics $T = p^2/2m$ and in quantum mechanics the operator $\hat{T}$ which represents the kinetic energy is connected with $\hat{p}$ by the same relation. Thus,

$$\hat{T} = \frac{\hat{p}^2}{2m} = \left(-i\hbar\frac{\partial}{\partial x}\right)^2 \frac{1}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{1.11}$$

and

$$\left.\begin{aligned} \hat{T}\psi_{\mathrm{a}} &= -\frac{\hbar^2}{2m}\frac{\partial^2\psi_a}{\partial x^2} = \frac{\hbar^2 k_1^2}{2m}\psi_{\mathrm{a}} \\ \hat{T}\psi_{\mathrm{b}} &= -\frac{\hbar^2}{2m}\frac{\partial^2\psi_{\mathrm{b}}}{\partial x^2} = \frac{\hbar^2 k_1^2}{2m}\psi_{\mathrm{b}} \\ \hat{T}\psi_{\mathrm{c}} &= -\frac{\hbar^2}{2m}\frac{\partial^2\psi_{\mathrm{c}}}{\partial x^2} = \frac{\hbar^2 k_1^2}{2m}\psi_{\mathrm{c}} \end{aligned}\right\} \tag{1.12}$$

In each of these operations the wave function is left unchanged except for a constant multiplicative factor and, as before, the interpretation is that the kinetic energy of the particle is certainly $(\hbar^2 k_1^2/2m)$. The relationship between the predicted kinetic energy $(\hbar^2 k_1^2/2m)$ and the predicted momentum or momenta ($\hbar k_1$ or $-\hbar k_1$) is always the same as in classical physics. Clearly this is the result of equation (1.11), where the operators in quantum mechanics were set up to obey the corresponding relationship. That input has quickly produced an output reminiscent of classical physics, but with some added subtlety, like the uncertain prediction of the sign of the momentum in the state represented by ψ_{c}.

Table 1.1 summarises conclusions about the states represented by ψ_{a}, ψ_{b}, and ψ_{c}. A striking feature is that the position of the particle for all three states, and the momentum for that represented by ψ_{c}, have not been definitely predicted. It might be thought that this is trivially the result of imprecise specification of the physical conditions. However, it will soon appear† that a lack of full determinacy is a fundamental feature of quantum mechanics; it always turns up in some observables or other, whatever state may be considered. The potentially complete certainty of classical physics, with all its philosophical implications, must for ever be surrendered.

---

† *Vide* section 5

Table 1.1 Predictions about the results of measuring various observables, for the three states represented by ψ_a, ψ_b, and ψ_c (equations (1.6))

Wave function	Position	Momentum	Kinetic energy
ψ_a	Uniform probability density	$\hbar k_1$	$\hbar^2 k_1^2/2m$
ψ_b	Uniform probability density	$-\hbar k_1$	$\hbar^2 k_1^2/2m$
ψ_c	Probability density peaked at odd multiples of $L/4$	$\hbar k_1$ (probability $\frac{1}{2}$) $-\hbar k_1$ (probability $\frac{1}{2}$)	$\hbar^2 k_1^2/2m$

§2 Basic assumptions

The basic assumptions of particle quantum mechanics can be set out formally under seven main headings, and for the sake of clarity and ease of reference this will now be done. The result may make somewhat forbidding reading at first sight, and frequent reference back to section 1 is recommended. Simple examples of nearly all that is involved have been given there.

Wave functions and probability density *The state of a particle is represented by a complex function $\psi(\mathbf{r}, t)$, such that $|\psi|^2\,d\tau$ is the probability of finding the particle at the time t in the element of volume $d\tau$ at the point* $\mathbf{r}$.

The function ψ is called the *wave function* because it must satisfy an equation (2.18) whose solution in some circumstances has the form of stationary or travelling waves; $|\psi|^2$ is called the *position probability density* (PPD). The complex conjugate wave function ψ^* is obtained by changing the sign of the imaginary part of ψ at every $\mathbf{r}$ and t.

The wave function will usually be *normalised* so that

$$\int |\psi|^2\,d\tau = \int \psi^*\psi\,d\tau = 1 \qquad (2.1)$$

where the integration is carried through all the space available to the particle.† Physically this normalisation means that just one particle is present. The creation and destruction of particles will not be considered, so the time dependence of ψ must be such that the normalisation is preserved for all t.

Linear superposition of states *If two possible states of the particle are represented by ψ_1 and ψ_2, then a possible state of the particle is also represented by $\psi = c_1\psi_1 + c_2\psi_2$, where the coefficients c_1 and c_2 are arbitrary complex numbers, independent of* $\mathbf{r}$ *but possibly functions of t.*

Obviously, by continued superposition, any number of wave functions may be used to build up a new ψ:

$$\psi = c_1\psi_1 + c_2\psi_2 + \cdots + c_s\psi_s + \cdots + c_n\psi_n = \sum_{s=1}^{n} c_s\psi_s \tag{2.2}$$

Observables and operators *Observables are represented by linear operators which multiply, differentiate, or otherwise act on the wave function ψ to produce a new function.*‡

Thus an observable l will be represented by a linear operator $\hat{l}$, and symbolically the result of applying $\hat{l}$ to ψ can be written $\hat{l}\psi$. By definition a linear operator satisfies§

$$\left.\begin{aligned} \hat{l}(c\psi) &= c\hat{l}\psi \\ \hat{l}(c_1\psi_1 + c_2\psi_2) &= c_1\hat{l}\psi_1 + c_2\hat{l}\psi_2 \end{aligned}\right\} \tag{2.3}$$

Operators may be handled algebraically when rules for their equation, addition, subtraction, and multiplication have been provided.

The equation $\hat{l} = \hat{m}$ of two operators means that they produce the same result when they act on an arbitrary wave function ψ. The sum $\hat{l} + \hat{m}$ or difference $\hat{l} - \hat{m}$ of two operators is defined by

$$(\hat{l} \pm \hat{m})\psi = \hat{l}\psi \pm \hat{m}\psi \tag{2.4}$$

---

† For free particles a 'region of special interest' is usually considered (cf. section 1, and the discussion of periodic boundary conditions in section 4).

‡ Cf. $\hat{p}$ and $\hat{T}$ in section 1; these particular operators may be substituted into some of the equations which follow in order to gain a clearer view of their meaning.

§ In view of the possible time dependence of c it may be remarked that $\hat{l}$ can always be expressed in a form which avoids differentiation or integration with respect to t.

Clearly $\hat{l}+\hat{m}=\hat{m}+\hat{l}$ and $\hat{l}-\hat{m}=-\hat{m}+\hat{l}$, so that addition and subtraction are commutative. More complicated sums and differences may be built up by repeated use of the basic rule. A simple example shows that addition and subtraction are associative,

$$(\hat{l}+\hat{m})+\hat{n}=\hat{l}+(\hat{m}+\hat{n}) \tag{2.5}$$

since both sides act on ψ to produce $\hat{l}\psi+\hat{m}\psi+\hat{n}\psi$.

The product $\hat{l}\hat{m}$ is defined to be the operator whose instructions are that $\hat{m}$ should act first, and then $\hat{l}$ should act on the result,

$$(\hat{l}\hat{m})\psi=\hat{l}(\hat{m}\psi) \tag{2.6}$$

More complicated products may again be built up by repeated use of the basic rule. A simple example shows that multiplication is associative,

$$(\hat{l}\hat{m})\hat{n}=\hat{l}(\hat{m}\hat{n}) \tag{2.7}$$

since both sides instruct that $\hat{n}$ should act first, then $\hat{m}$, and finally $\hat{l}$. Another example shows that multiplication of linear operators is distributive,

$$\hat{l}(\hat{m}+\hat{n})=(\hat{l}\hat{m})+(\hat{l}\hat{n}) \tag{2.8}$$

since both sides act on ψ to produce $\hat{l}(\hat{m}\psi)+\hat{l}(n\psi)$.

Multiplication of operators is not guaranteed to be commutative, however. The product $\hat{m}\hat{l}$ may produce a quite different result from $\hat{l}\hat{m}$, since the order of the component operations is reversed. The operators $\hat{l}$ and $\hat{m}$, and the observables associated with them, are said to commute[†] if it does happen that $\hat{m}\hat{l}=\hat{l}\hat{m}$. Obviously any operator commutes with itself.

The possible failure of the commutative law of multiplication is the only difference between the algebra of linear operators and ordinary elementary algebra; extra care must be taken with the order of the products.

It is clear that functions of operators can be constructed if a suitable recipe is given in terms of additions, subtractions, and multiplications of the arguments.

[†] $\hat{p}$ and $\hat{T}$ in section 1 are operators which commute, since

$$\hat{p}\hat{T}=\hat{T}\hat{p}=\frac{i\hbar^3}{2m}\frac{\partial^3}{\partial x^3}$$

Predictions of the result of measuring an observable *When $\hat{l}$ operates on a particular wave function, u_s say, it may produce a function which differs from u_s only by a constant multiplicative factor l_s:*

$$\hat{l}u_s = l_s u_s \tag{2.9}$$

If so, then a measurement of l is certain to yield the numerical value l_s. The particle is said to be in an *eigenstate* of l belonging to the *eigenvalue* l_s, and the wave function u_s is called an *eigenfunction* of l belonging to the eigenvalue l_s.†

It is taken for granted‡ that the eigenfunctions associated with an operator $\hat{l}$ form a complete set, in the sense that any wave function whatever can be formed by superposing them:

$$\psi = \sum_{s=1}^{n} c_s u_s \tag{2.10}$$

where ψ and all the u_s are normalised.

The expansion (2.10) may be used as the basis for a more general assumption, which includes the one already made as a special case; *the probability of l being found to have the eigenvalue l_s is equal to* $|c_s|^2$. No result other than an eigenvalue can be obtained,§ for it will appear in section 4 that

$$\sum_{s=1}^{n} |c_s|^2 = 1 \tag{2.11}$$

Hermitian operators *Only a certain kind of linear operator is suitable for representing an observable. If ψ_1 and ψ_2 are any two wave functions, then $\hat{l}$ must satisfy*

$$\int \psi_1^*(\hat{l}\psi_2)\,\mathrm{d}\tau = \int (\hat{l}\psi_1)^*\psi_2\,\mathrm{d}\tau \tag{2.12}$$

where the integrals are again to be taken over all the space available to the particle. Operators which satisfy this relation are called *Hermitian.*

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† Cf. equations (1.9), which shows that ψ_a and ψ_b are eigenfunctions of p, belonging to the eigenvalues $\hbar k_1$ and $-\hbar k_1$ respectively.

‡ Proofs of completeness are conventionally, and conveniently, not required by ordinary physicists.

§ Cf. equations (1.6), where the momentum eigenfunctions and ψ_c were all properly normalised, and the total probability of finding one momentum value or the other in the state represented by ψ_c was $\frac{1}{2}+\frac{1}{2}=1$ (*vide* also problem 1.3).

Momentum and energy operators The use of functions of position to represent the states of the particle fixes the form of the operator $\hat{\mathbf{r}}$ which represents the position $\mathbf{r}$ of the particle. The instructions given by $\hat{\mathbf{r}}$ are in fact that the wave function $\psi(\mathbf{r}, t)$ is to be multiplied at each point by the value of $\mathbf{r}$ at that point,

$$\hat{\mathbf{r}}\psi = \mathbf{r}\psi \tag{2.13}$$

For consider a wave function u_s which is zero except at the point $\mathbf{r}_s$. The particle is then certainly located at $\mathbf{r}_s$ since the probability density is zero elsewhere, and so u_s must be an eigenfunction of $\mathbf{r}$ belonging to the eigenvalue $\mathbf{r}_s$. This is ensured by the multiplicative form of $\hat{\mathbf{r}}$, for then $\hat{\mathbf{r}}u_s = \mathbf{r}u_s = \mathbf{r}_s u_s$.

In three-dimensional Cartesian coordinates the position components x, y, z are represented by operators which multiply the wave function by x, y, and z respectively. In one dimension, of course $\hat{x} = x$.

The operator which represents the momentum is assumed to be

$$\hat{\mathbf{p}} = -i\hbar\nabla \tag{2.14}$$

which acts on ψ to produce $-i\hbar\nabla\psi$. Thus in three-dimensional Cartesian coordinates the momentum components p_x, p_y, p_z are represented by†

$$\left.\begin{aligned} \hat{p}_x &= -i\hbar(\partial/\partial x) \\ \hat{p}_y &= -i\hbar(\partial/\partial y) \\ \hat{p}_z &= -i\hbar(\partial/\partial z) \end{aligned}\right\} \tag{2.15}$$

Operators for the position and momentum of the particle are now available, and these can be used to build up other operators. *If an observable may be written in classical mechanics as a function $F(\mathbf{r}, \mathbf{p})$ of the position and momentum of the particle, then it is assumed that in quantum mechanics the observable is represented by the operator $F(\hat{\mathbf{r}}, \hat{\mathbf{p}})$.*‡

Thus in classical mechanics the kinetic energy T of the particle is equal to $p^2/2m$, and in quantum mechanics T is represented by the differential operator

$$\hat{T} = \frac{1}{2m}(\hat{\mathbf{p}})^2 = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{2.16}$$

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† Cf. section 1.

‡ The fact that some components of $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ do not commute does not raise difficulties in practice.

Similarly, a potential energy $V(\mathbf{r}, t)$ is represented by an operator $\hat{V}$ which instructs that the wave function is to be multiplied by $V(\mathbf{r}, t)$.

Until chapter 6 attention will be confined to problems in which the forces on the particle can be described by a potential. The total energy H of the particle is then equal to $T+V$, and it is represented by

$$\hat{H}=\hat{T}+\hat{V}=-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r}, t) \tag{2.17}$$

Time dependence of ψ *The rate of change of* ψ *is given by*

$$i\hbar\frac{\partial\psi}{\partial t}=\hat{H}\psi \tag{2.18}$$

so that the operator $\hat{H}$ has the dual role of representing the energy of the particle and controlling the time dependence of ψ; equation (2.18) is called the time-dependent Schrödinger equation (TDSE).

The equation shows that if ψ is completely specified at any time, then its rate of change is also specified. Thus the development in time of ψ is completely determined by its initial shape, so long as the particle is left undisturbed.

A measurement of some property of the particle generally does constitute a disturbance. The wave function ψ carries information about what *might* happen when the measurement is made. If an observer, presumably intelligent, sees what actually *does* happen, then some of the possibilities allowed by the wave function may cease to be compatible with reality. The wave function must jump discontinuously at the moment of observation in order to discard these redundant possibilities, and this jump is not described by any equation like (2.18). If, for example, a particle in a state represented by a diffuse wave function is seen to produce a water droplet in a cloud chamber, then the wave function and the position probability density immediately become concentrated at this point. Since the wave function has been changed fundamentally by the position measurement it is not generally possible to go on and measure some other observable and regard the result as a property of the original state. After each measurement, then, the Schrödinger equation must be solved again with a new set of initial conditions which takes into account the information that has been obtained.

Problems

1.1 All the mathematical expressions in section 2 are in three-dimensional form. Read the section again and jot down the corresponding one-dimensional expressions, where appropriate. Thus

$$\psi(\mathbf{r}, t) \rightarrow \psi(x, t)$$
$$|\psi|^2\,\mathrm{d}\tau = |\psi|^2\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \rightarrow |\psi|^2\,\mathrm{d}x$$

and so on. Check with section 1 where possible, and in particular show that the TDSE of equation (2.18) is translated into equation (1.1) when there is no potential energy.

1.2 Show by direct integration that the ψ_a and ψ_b given by equations (1.6) are *orthogonal* in the interval $-L/2 \leqslant x \leqslant L/2$, which means that

$$\int_{-L/2}^{L/2} \psi_b^* \psi_a\,\mathrm{d}x = 0 = \int_{-L/2}^{L/2} \psi_a^* \psi_b\,\mathrm{d}x$$

If the frequency were raised from ω_1 to $\omega' = 3\omega_1/2$, would the corresponding wave functions ψ_a' and ψ_b' be orthogonal in the same interval? [*Comment*: The wave functions involving ω' are not periodic in the special interval $-L/2 \leqslant x \leqslant L/2$ and it will appear in section 4 that they are lacking in certain essential qualities.]

1.3 Consider a wave function formed from the ψ_a and ψ_b given in equations (1.6),

$$\psi = c_a\psi_a + c_b\psi_b$$

where c_a and c_b are complex constants. Use the orthogonality of ψ_a and ψ_b to demonstrate that

$$\int_{-L/2}^{L/2} \psi^*\psi\,\mathrm{d}x = |c_a|^2 + |c_b|^2$$

Hence deduce that, if ψ is normalised to unity, the chances of finding p with the values $\hbar k_1$ or $-\hbar k_1$ add up to unity when the particle is in the state represented by ψ. [*Comment*: ψ_c in equations (1.6) is a particular example of ψ with $c_a = -i2^{-1/2}$ and $c_b = i2^{-1/2}$.]

1.4 Verify that the momentum operator $\hat{p}$ is Hermitian in the examples

$$\int_{-L/2}^{L/2} (\hat{p}\psi_a)^* \psi_a \, dx = \int_{-L/2}^{L/2} \psi_a^* (\hat{p}\psi_a) \, dx$$

$$\int_{-L/2}^{L/2} (\hat{p}\psi_a)^* \psi_b \, dx = \int_{-L/2}^{L/2} \psi_a^* (\hat{p}\psi_b) \, dx$$

$$\int_{-L/2}^{L/2} (\hat{p}\psi_a)^* \psi_c \, dx = \int_{-L/2}^{L/2} \psi_a^* (\hat{p}\psi_c) \, dx$$

where ψ_a, ψ_b, and ψ_c are given in equations (1.6). [*Comment*: The quickest results are obtained by free use of equations (1.9), together with the orthogonality of ψ_a and ψ_b. The Hermiticity of $\hat{p}$ and the reality of the eigenvalues of p are evidently closely related.]

1.5 According to classical mechanics a particle subject to a restoring force proportional to x should vibrate harmonically, say with circular frequency ω. Find the classical expression for the potential energy in terms of ω.

Hence write down the quantum mechanical energy operator $\hat{H}$ for the same problem. [*Comment*: The completed expression may be checked with equation (8.1).]

1.6 Show that the wave function $\psi e^{i\delta}$, with δ real, gives rise to the same physical predictions as the wave function ψ. Hence conclude that they represent the same state. [*Hint*: Substitute $\psi e^{i\delta}$ for ψ in equations (2.1) and (2.10). *Comment*: Although the *overall* phase of a wave function is not significant, the *relative* phase of two superposed wave functions is very important. For example $\psi_1 + \psi_2$ and $\psi_1 - \psi_2$ generally represent quite different states.]

2

Mathematical and physical development of the basic assumptions

§3 Solutions to Schrödinger's equation

The TDSE (equation (2.18)) is a partial differential equation involving both position and time as independent variables. The problem of solving it systematically is greatly eased when the variables can be separated, which is possible when the potential is independent of time and $\hat{H}$ does not mention t, a very common situation. Then

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \tag{3.1}$$

and there are energy eigenfunctions u_s which depend on $\mathbf{r}$ but not on t,

$$\hat{H}u_s(\mathbf{r}) = E_s u_s(\mathbf{r}) \tag{3.2}$$

To each u_s there corresponds a solution of the TDSE: if the circular† frequency ω_s and the wave function ψ_s are defined by

$$\hbar\omega_s \equiv E_s$$

$$\psi_s(\mathbf{r}, t) \equiv u_s(\mathbf{r})e^{-i\omega_s t} \tag{3.3}$$

then

$$i\hbar\frac{\partial\psi_s}{\partial t} = \hat{H}\psi_s \tag{3.4}$$

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† The adjective 'circular' will usually be left implicit in future.

as required. In view of the special relationship between the ψ_s and u_s, equation (3.2) is called the time-independent Schrödinger equation (TISE).†

The physical properties of the energy eigenstate represented by ψ_s do not change with time, because ψ_s varies only by an overall phase factor.‡ Such a state is therefore called *stationary*.

A general wave function ψ at $t=0$ may be expanded§ in terms of the u_s, since they form a complete set,

$$\psi(\mathbf{r}, 0)=\sum_s c_s u_s(\mathbf{r}) \tag{3.5}$$

The continued development of $\psi(\mathbf{r}, t)$ according to the TDSE is then obviously given by

$$\psi(\mathbf{r}, t)=\sum_s c_s u_s(\mathbf{r})e^{-i\omega_s t} \tag{3.6}$$

Thus all problems giving rise to time-independent energy operators are easily handled once the energy eigenfunctions u_s and the energy eigenvalues E_s (or frequencies ω_s) are known. The solution of the TISE is therefore a prime objective in practical calculations.

Probability current density (PCD) As a preliminary step equation (2.18) may be written out in full, together with its complex

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† The relationship between the TDSE and the TISE in quantum mechanics is similar to that between the common wave equation and the Helmholtz equation in the classical theory of wave motion. For example a displacement ψ in a stretched string satisfies the wave equation

$$\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}=\frac{\partial^2\psi}{\partial x^2}$$

and, if ψ_s varies with the particular frequency ω_s,

$$\psi_s=u_s(x)\cos(\omega_s t+\alpha_s)$$

where α_s is a phase angle. Substitution into the wave equation gives the Helmholtz equation

$$\frac{d^2u_s}{dx^2}=-k_s^2u_s$$

with $ck_s\equiv\omega_s$.

‡ *Vide* problem 1.6.

§ An explicit formula for the constants c_s will be derived later (equation (4.16)).

conjugate:

$$\left.\begin{aligned} i\hbar\frac{\partial\psi}{\partial t} &= -\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r}, t)\psi \\ -i\hbar\frac{\partial\psi^*}{\partial t} &= -\frac{\hbar^2}{2m}\nabla^2\psi^* + V(\mathbf{r}, t)\psi^* \end{aligned}\right\} \tag{3.7}$$

When the first equation, multiplied by $(i/\hbar)\psi^*$, is added to the second equation, multiplied by $-(i/\hbar)\psi$,

$$\begin{aligned} -\frac{\partial}{\partial t}(\psi^*\psi) &= -\psi^*\left(\frac{\partial\psi}{\partial t}\right) - \left(\frac{\partial\psi^*}{\partial t}\right)\psi \\ &= \frac{i\hbar}{2m}\{(\nabla^2\psi^*)\psi - \psi^*(\nabla^2\psi)\} \end{aligned} \tag{3.8}$$

Now the vector **j**, known as the probability current density or PCD, can be defined by

$$\mathbf{j}(\mathbf{r}, t) \equiv \frac{i\hbar}{2m}\{(\nabla\psi^*)\psi - \psi^*(\nabla\psi)\} \tag{3.9}$$

and an *equation of continuity*† can readily be established between the PCD and the PPD:

$$\nabla \cdot \mathbf{j} + \frac{\partial}{\partial t}(\psi^*\psi) = 0 \tag{3.10}$$

The physical significance of the PCD and the equation of continuity can be exposed with the help of Gauss's theorem, applied to an arbitrary volume W enclosed by the surface S:

$$\frac{\partial}{\partial t}\int_W \psi^*\psi \, d\tau = -\int_W \nabla \cdot \mathbf{j} \, d\tau = -\int_S \mathbf{j} \cdot d\mathbf{S} \tag{3.11}$$

The rate of change of the probability of finding the particle inside the volume W is equal to the inward flux of the PCD. Thus $\mathbf{j} \cdot d\mathbf{S}$ may be interpreted as the probability per unit time that a particle passes through $d\mathbf{S}$.

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† Similar equations in the classical theory of wave motion connect energy fluxes and densities.

§4 Mathematical properties of wave functions and operators

Hermitian operators The five operators introduced in section 2 must be shown to be Hermitian, as defined by equation (2.12). Certainly $\hat{\mathbf{r}}$ is Hermitian because it is multiplicative, and $\mathbf{r}$ is real:

$$\int \psi_1^*(\hat{\mathbf{r}}\psi_2)\,\mathrm{d}\tau = \int \psi_1^*\mathbf{r}\psi_2\,\mathrm{d}\tau = \int (\mathbf{r}\psi_1)^*\psi_2\,\mathrm{d}\tau = \int (\hat{\mathbf{r}}\psi_1)^*\psi_2\,\mathrm{d}\tau \tag{4.1}$$

Similarly $\hat{V}$ is Hermitian, because it is multiplicative and V is a real function† of $\mathbf{r}$ and t.

The Hermitian characteristics of $\hat{\mathbf{p}}$ and $\hat{T}$ are less straightforward to discuss. In one dimension, an integration by parts from x_1 to x_2 gives

$$\int_{x_1}^{x_2} \psi_1^*\left(-i\hbar\frac{\partial\psi_2}{\partial x}\right)\mathrm{d}x = \int_{x_1}^{x_2} \left(-i\hbar\frac{\partial\psi_1}{\partial x}\right)^*\psi_2\,\mathrm{d}x - i\hbar\Big[\psi_1^*\psi_2\Big]_{x_1}^{x_2} \tag{4.2}$$

Similarly, after two integrations by parts,

$$\int_{x_1}^{x_2} \psi_1^*\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi_2}{\partial x^2}\right)\mathrm{d}x = \int_{x_1}^{x_2} \left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi_1}{\partial x^2}\right)^*\psi_2\,\mathrm{d}x - \frac{\hbar^2}{2m}\left[\psi_1^*\frac{\partial\psi_2}{\partial x} - \frac{\partial\psi_1^*}{\partial x}\psi_2\right]_{x_1}^{x_2} \tag{4.3}$$

Obviously $\hat{p}$ and $\hat{T}$ are Hermitian in the range $x_1 \leqslant x \leqslant x_2$ if the second terms on the right-hand sides of these equations can be discarded.

In many problems the particle is in a bound state so that its wave function is localised near some finite value of x; the wave functions are either zero at x_1 and x_2 or else they tend to zero exponentially as $x_1 \to -\infty$, $x_2 \to +\infty$. In either situation the unwanted terms disappear.

Sometimes it is not convenient to consider a region of space sufficiently large to embrace the entire wave function. For example,

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† Sometimes, though not in this book, a complex and non-Hermitian V is used as a calculational device, to describe the disappearance of particles into states that the physicist does not want to discuss. Only a partial picture of the situation can be gained from such calculations.

a beam of particles may be accelerated (x very negative), scattered by a field of force ($x \approx 0$), and finally detected (x very positive). The accelerator and detector play an essential part experimentally, but it is hardly desirable to include descriptions of them in a quantum mechanical analysis of the scattering process. This may be avoided if finite limits x_1 and x_2 are chosen so that the scattering region is included but the accelerator and detector are excluded. The artificial restriction of the space under scrutiny ($x_1 \leqslant x \leqslant x_2$) has to be matched by an artificial restriction on the wave functions; they have to satisfy boundary conditions at x_1 and x_2 such that the unwanted terms in equations (4.2) and (4.3) vanish.

A possible boundary condition to impose on every ψ, including of course ψ_1 and ψ_2, is that

$$\psi(x_1) = \psi(x_2) = 0 \tag{4.4}$$

However, it is usually better to work with the *periodic boundary conditions*

$$\psi(x_1) = \psi(x_2), \qquad \left(\frac{\partial\psi}{\partial x}\right)_{x_1} = \left(\frac{\partial\psi}{\partial x}\right)_{x_2} \tag{4.5}$$

The advantage is that ψ can be a momentum eigenfunction, or a superposition of momentum eigenfunctions.†

Similar considerations apply in three dimensions. If the particle is not localised, a possible boundary condition is

$$(\psi)_S = 0 \tag{4.6}$$

on the surface S of some suitable volume of space. Alternatively there are again the periodic boundary conditions, active on the surfaces of a cube of side L,

$$\left.\begin{aligned} \psi(-L/2, y, z) &= \psi(L/2, y, z) \\ (\nabla\psi)_{-L/2,y,z} &= (\nabla\psi)_{L/2,y,z} \end{aligned}\right\} \tag{4.7}$$

with corresponding equations for $y = \pm L/2$, $z = \pm L/2$.

Finally, the Hermiticity of $\hat{H}$ is guaranteed because it is the sum of other operators, $\hat{T}$ and $\hat{V}$, which are Hermitian. The number of particles is consequently conserved:

$$\frac{\partial}{\partial t}\int \psi^*\psi \, \mathrm{d}\tau = -\frac{i}{\hbar}\left\{\int \psi^*(\hat{H}\psi)\, \mathrm{d}\tau - \int (\hat{H}\psi)^*\psi \, \mathrm{d}\tau\right\} = 0 \tag{4.8}$$

---

† Cf. ψ_a, ψ_b, and ψ_c in section 1.

Dirac notation Many times already the complex conjugate of one function of position has been multiplied by another function of position and the product has been integrated over all space, or over all of a special region of space if the particles are not localised. Such integrations are indeed very characteristic of quantum mechanics, and it will be worthwhile having a nomenclature and a shorthand notation for them. The integral on the left-hand side of the identity

$$\int_{\text{all space}} \psi_1^* \psi_2 \,\mathrm{d}\tau \equiv \langle \psi_1 \mid \psi_2 \rangle \tag{4.9}$$

is called the *scalar product of* ψ_2 *with* ψ_1, and on the right-hand side this is expressed in the neat notation invented by Dirac. Obviously

$$\langle \psi_1 \mid \psi_2 \rangle = \langle \psi_2 \mid \psi_1 \rangle^* \tag{4.10}$$

The normalisation integral (equation (2.1)) is now written

$$\langle \psi \mid \psi \rangle = 1 \tag{4.11}$$

and the Hermitian condition (equation (2.12)) becomes

$$\begin{aligned} \langle \psi_1 \mid \hat{l}\psi_2 \rangle &= \langle \hat{l}\psi_1 \mid \psi_2 \rangle \\ &\equiv \langle \psi_1 | \, \hat{l} \, | \psi_2 \rangle \end{aligned} \tag{4.12}$$

The extension to the Dirac notation in the second line here has a symmetrical form which reflects the fact that $\hat{l}$ may equally well operate on ψ_2 or ψ_1. Obviously this notation would be meaningless and inappropriate if the operator concerned were not Hermitian. In future $\langle \psi_1 | \, \hat{l} \, | \psi_2 \rangle$ will be called the *matrix element of* $\hat{l}$ *taken between* ψ_2 *and* ψ_1.

An operator which is not Hermitian, $\hat{k}$ say, also has a matrix element taken between ψ_2 and ψ_1, but this must be understood to mean $\langle \psi_1 \mid \hat{k}\psi_2 \rangle$ and not $\langle \hat{k}\psi_1 \mid \psi_2 \rangle$.

Orthogonality of eigenfunctions If u_1, u_2 are two eigenfunctions of l belonging to the eigenvalues l_1, l_2,

$$\begin{aligned} \langle u_1 | \, \hat{l} \, | u_2 \rangle &= \langle u_1 \mid \hat{l}u_2 \rangle = l_2 \langle u_1 \mid u_2 \rangle \\ &= \langle \hat{l}u_1 \mid u_2 \rangle = l_1 \langle u_1 \mid u_2 \rangle \end{aligned} \tag{4.13}$$

and so $(l_2 - l_1)\langle u_1 \mid u_2 \rangle = 0$. If l_1 and l_2 are different,

$$\langle u_1 \mid u_2 \rangle = 0 \tag{4.14}$$

and u_1, u_2 are said to be *orthogonal.*† Generally, if u_r and u_s are any two eigenfunctions of $\hat{l}$,

$$\langle u_s \mid u_r \rangle = \delta_{sr} \tag{4.15}$$

where the Kronecker symbol δ_{sr} is zero if $r \neq s$ and 1 if $r = s$. A collection of all the normalised mutually orthogonal eigenfunctions obeying equation (4.15) will be called a *complete orthonormal set.*

None of the functions in the set can be expressible in terms of the others, or equation (4.15) would fail: in other words all the functions must be linearly independent.

Sometimes two or more eigenfunctions, orthonormal and linearly independent though they may be, belong to the same eigenvalue of some observable. This is called *degeneracy*, and the eigenfunctions and states involved are said to be degenerate. The observable concerned should be stated, or at least kept in mind, because two eigenfunctions which are degenerate with respect to one observable are not necessarily so with respect to another.‡ The possible existence of degeneracy complicates many otherwise simple theorems in quantum mechanics, but further remarks in section 12 will show how best to deal with it.

Expansion in eigenfunctions The interpretative structure of the theory makes it very important to be able to expand any ψ in terms of eigenfunctions. The expansion is easily carried out if the eigenfunctions are arranged into a complete orthonormal set. For if

$$\psi = \sum_s c_s u_s$$

the coefficient c_s may be determined by forming the scalar product of ψ with u_s,

$$\langle u_s \mid \psi \rangle = \sum_r \langle u_s \mid c_r u_r \rangle = \sum_r c_r \langle u_s \mid u_r \rangle = \sum_r c_r \delta_{sr} = c_s \tag{4.16}$$

and therefore the required expansion§ is

$$\psi = \sum_s \langle u_s \mid \psi \rangle u_s \tag{4.17}$$

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† Cf. problem 1.2.

‡ Cf. table 1.1: ψ_a and ψ_b are degenerate in energy, but not in momentum. The latter fact is quite enough to guarantee that they are orthogonal.

§ Cf. the third of equations (1.6), where $\langle \psi_a \mid \psi_c \rangle = -i2^{-1/2}$ and $\langle \psi_b \mid \psi_c \rangle = i2^{-1/2}$.

If ψ is normalised,

$$\langle\psi \mid \psi\rangle=\sum_r\sum_s\langle c_r u_r \mid c_s u_s\rangle=\sum_r\sum_s c_r^* c_s \delta_{rs}=\sum_s |c_s|^2=1 \qquad (4.18)$$

as promised in equation (2.11).

Closure According to equation (4.17) two functions ϕ_r ane ϕ_s, not necessarily normalised, may be expanded in terms of a complete orthornormal set by means of the relations $\phi_r=\sum_k\langle u_k \mid \phi_r\rangle u_k$ and $\phi_s=\sum_j\langle u_j \mid \phi_s\rangle u_j$. Then,

$$\begin{aligned}\langle\phi_r \mid \phi_s\rangle&=\sum_k\sum_j\langle u_k \mid \phi_r\rangle^*\langle u_j \mid \phi_s\rangle\langle u_k \mid u_j\rangle\\&=\sum_k\sum_j\langle\phi_r \mid u_k\rangle\langle u_j \mid \phi_s\rangle\delta_{kj}\\&=\sum_k\langle\phi_r \mid u_k\rangle\langle u_k \mid \phi_s\rangle \qquad (4.19)\end{aligned}$$

This is the closure relation, of which equation (4.18) is actually a special example. Another useful special form arises if ϕ_r is identified with $\hat{l}u_r$ and ϕ_s with $\hat{l}u_s$:

$$\langle u_r|\, \hat{l}^2\, |u_s\rangle=\langle\hat{l}u_r \mid \hat{l}u_s\rangle=\sum_k\langle u_r|\, \hat{l}\, |u_k\rangle\langle u_k|\, \hat{l}\, |u_s\rangle \qquad (4.20)$$

Pictorial summary Many of the results obtained so far can be summarised in a pictorial way. The illustrations exploit analogies between ordinary unit vectors and their scalar products, on the one hand, and normalised wave functions and their scalar products, on the other.

In figure 4.1 a complete orthonormal set of eigenfunctions of l is represented pictorially by orthogonal unit base vectors. The set in this example has three members, but in general the number may be more or less, or even infinite. The scalar product of any pair of base vectors in the picture is of course zero, and so is the scalar product of any pair of eigenfunctions in the theory.

In figure 4.2 a general normalised wave function ψ is represented by another unit vector, oriented so that its direction cosine with respect to each base vector u_s is the scalar product $\langle u_s \mid \psi\rangle$.† The projection of the unit vector ψ on the base vector u_s is $\langle u_s \mid \psi\rangle=c_s$,

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† The fact that $\langle u_s \mid \psi\rangle$ may be a complex number does not receive pictorial recognition.

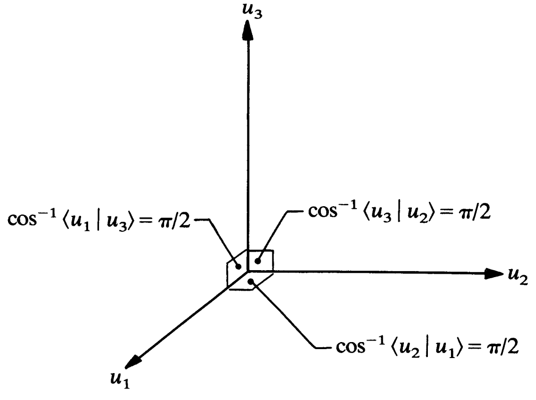

Figure 4.1 A picture of a set of three orthogonal eigenfunctions.

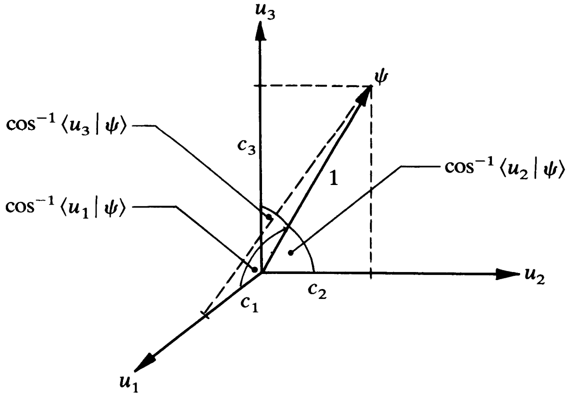

Figure 4.2 A picture of a general normalised wave function ψ, and its projections on to the three basic eigenfunctions of figure 4.1.

and the square of the length of this projection is $|c_s|^2$, the chance of l being found to have the value l_s. The equation $|c_1|^2 + |c_2|^2 + |c_3|^2 = 1$ corresponds to the usual relation for the sum of the squares of direction cosines.

In general the vector representing ψ changes its direction as time goes on. One exception occurs if ψ represents a stationary state of energy E_n, and $\hat{l}$ does not mention t explicitly; then the vector representing ψ does not move because the projection of ψ on each u_s varies only by the overall phase factor $e^{-i\omega_n t}$ and is therefore of constant length. Another exception occurs (equation (3.6)) when the u_s are energy eigenfunctions and $\hat{H}$ does not mention t; the projection of ψ on each u_s is then again constant in length but varies with its own particular phase factor $e^{-i\omega_s t}$.

The abstract space in these illustrations is called *Hilbert space.*

Expectation values of observables If the state represented by ψ is set up many times, and the value of l measured each time, then the average of all the results is called the *expectation value* of l. It will be written as $\langle l \rangle$.

The expectation value of $\mathbf{r}$ is easily calculated from the position probability density,

$$\langle \mathbf{r} \rangle = \int \mathbf{r}\, |\psi|^2\, d\tau = \int \psi^* \mathbf{r} \psi\, d\tau = \langle \psi | \,\hat{\mathbf{r}}\, | \psi \rangle \tag{4.21}$$

The form of this result is in fact quite general. If again

$$\psi = \sum_s c_s u_s$$

where the u_s are the eigenfunctions of l,

$$\begin{aligned} \langle \psi | \,\hat{l}\, | \psi \rangle &= \langle \psi \mid \hat{l}\psi \rangle = \sum_{r,s} \langle c_r u_r \mid \hat{l} c_s u_s \rangle \\ &= \sum_{r,s} c_r^* c_s l_s \langle u_r \mid u_s \rangle = \sum_{r,s} c_r^* c_s l_s \delta_{rs} \\ &= \sum_s |c_s|^2 l_s \end{aligned} \tag{4.22}$$

But

$$\langle l \rangle = \sum_s |c_s|^2 l_s,$$

since the probability of getting the result l_s is $|c_s|^2$, and so,

$$\langle l \rangle = \langle \psi | \,\hat{l}\, | \psi \rangle \tag{4.23}$$

Products of operators It is easily seen that the one-dimensional position and momentum of a particle do not commute,

$$(\hat{p}\hat{x})\psi = -i\hbar \frac{\partial}{\partial x}(x\psi) = -i\hbar x \frac{\partial \psi}{\partial x} - i\hbar\psi = (\hat{x}\hat{p} - i\hbar)\psi \tag{4.24}$$

so that

$$\hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar \tag{4.25}$$

This intriguing and beautiful equation was first obtained by Born and Jordan in 1925.

The commutator of two operators $\hat{l}$ and $\hat{m}$ is defined to be $\hat{l}\hat{m}-\hat{m}\hat{l}$ and written as $[\hat{l}, \hat{m}]$. Thus,

$$[\hat{x}, \hat{p}] = i\hbar \tag{4.26}$$

Typical commutation relations for the three-dimensional position and momentum of a particle are

$$\left.\begin{aligned}(\hat{p}_x\hat{x})\psi &= -i\hbar\frac{\partial}{\partial x}(x\psi) = -i\hbar x\frac{\partial\psi}{\partial x} - i\hbar\psi = (\hat{x}\hat{p}_x - i\hbar)\psi \\ (\hat{p}_x\hat{y})\psi &= -i\hbar\frac{\partial}{\partial x}(y\psi) = -i\hbar y\frac{\partial\psi}{\partial x} = (\hat{y}\hat{p}_x)\psi\end{aligned}\right\} \tag{4.27}$$

and generally,

$$[\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij} \tag{4.28}$$

where the suffixes i, j take the values 1, 2, 3 for the x, y, z components of $\mathbf{r}$ and $\mathbf{p}$ respectively.

If l does not commute with m it may be shown that $\hat{l}\hat{m}$ is not a Hermitian operator, and therefore does not represent an observable. In general,†

$$\begin{aligned}\langle\psi_1 \mid \hat{l}\hat{m}\psi_2\rangle = \langle\hat{l}\psi_1 \mid \hat{m}\psi_2\rangle &= \langle\hat{m}\hat{l}\psi_1 \mid \psi_2\rangle \\ &\neq \langle\hat{l}\hat{m}\psi_1 \mid \psi_2\rangle\end{aligned} \tag{4.29}$$

The form of this equation shows that the symmetrical product $\hat{l}\hat{m}+\hat{m}\hat{l}$ is always a Hermitian operator. Of course if $\hat{l}$ and $\hat{m}$ do commute, then $\hat{l}\hat{m}$, and indeed any real function of $\hat{l}$ and $\hat{m}$, are Hermitian operators.

A particularly simple product operator is $\hat{l}\hat{l} = \hat{l}^2$, which does represent an observable l^2 because $\hat{l}$ certainly commutes with itself. An eigenfunction u_s of l belonging to the eigenvalue l_s is also an

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† The first step here assumes that equation (2.12) still holds good if $\hat{m}\psi_2$ is substituted for ψ_2 itself. This is usually true, except when $\hat{l}$ is a differential operator and the particle is not localised. The Hermitian character of $\hat{l}$ must then be enforced by boundary conditions, but $\hat{m}\psi_2$ does not necessarily obey the conditions which ψ_2 itself does. In a one-dimensional problem with periodic boundary conditions, for example, $\hat{x}\psi_2 = x\psi_2$ could not have the same value at the boundaries x_1 and x_2. Whenever product operators are handled in this way the results must therefore be used with due discrimination. This is particularly important in section 5.

eigenfunction of l^2 belonging to the eigenvalue l_s^2,

$$\hat{l}^2 u_s = \hat{l}(\hat{l}u_s) = \hat{l}(l_s u_s) = l_s \hat{l} u_s = l_s^2 u_s \tag{4.30}$$

Clearly l^2 cannot have negative eigenvalues. It follows, for example, that a measurement of the kinetic energy of a particle ($T = \mathbf{p}^2/2m$) never gives a negative result.

Symmetric energy operators and parity The observables considered so far have all been familiar from classical physics, but there are others that can be conceived only in the framework of quantum mechanics. They are defined by means of the linear and Hermitian operators that represent them. One such observable is the *parity* Π represented by the operator $\hat{\Pi}$, whose instructions in one dimension are that $\psi(x)$ is to be replaced by $\psi(-x)$ at every point x. Thus

$$\hat{\Pi}\psi(x) = \psi(-x) \tag{4.31}$$

This amounts to a reflection of the wave function about the point $x = 0$. If ψ happens to be an even function of x,

$$\hat{\Pi}\psi(x) = \psi(-x) = \psi(x) \tag{4.32}$$

and the parity evidently has the eigenvalue +1. Similarly, if ψ happens to be an odd function of x, the parity has the eigenvalue −1. There is no other possible eigenvalue, apart from ±1, because any ψ is an eigenfunction of Π^2 belonging to the eigenvalue +1,

$$\hat{\Pi}^2\psi(x) = \hat{\Pi}\psi(-x) = \psi(x) \tag{4.33}$$

The commutation relation of $\hat{\Pi}$ with $\hat{H}$ is of interest, particularly when $V(x)$ is an even function of x. Then

$$\hat{\Pi}V(x) = V(-x)\hat{\Pi} = V(x)\hat{\Pi} \tag{4.34}$$

As for $\hat{T}$,

$$\left.\begin{aligned} \hat{\Pi}\frac{\partial}{\partial x} &= \frac{\partial}{\partial(-x)}\hat{\Pi} = \frac{\partial}{\partial x}\frac{\mathrm{d}x}{\mathrm{d}(-x)}\hat{\Pi} = -\frac{\partial}{\partial x}\hat{\Pi} \\ \hat{\Pi}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right) &= \frac{\hbar^2}{2m}\frac{\partial}{\partial x}\hat{\Pi}\frac{\partial}{\partial x} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\hat{\Pi} \end{aligned}\right\} \tag{4.35}$$

Thus, when $V(x)$ is an even function of x,

$$[\hat{\Pi}, \hat{H}] = 0 \tag{4.36}$$

In section 5 it will appear that interesting general consequences follow when two observables commute, particularly when one is the energy. In anticipation it can be stated that a consequence of equation (4.36) is that the energy eigenfunctions, if they are not degenerate, must be parity eigenfunctions also, that is even or odd functions of x. Further, parity is conserved and in particular an eigenfunction of parity remains so for all time. Since an eigenfunction of parity, belonging to either eigenvalue, has a PPD which is an even function of x, any departure from parity conservation can be detected. If that were to happen it would be a sure sign that $V(x)$ and therefore $\hat{H}$ was not in fact symmetric about $x = 0$.

In three dimensions $\hat{\Pi}$ can be specified in either Cartesian or spherical polar coordinates:

$$\left.\begin{aligned}\hat{\Pi}\psi(x, y, z) &= \psi(-x, -y, -z)\\ \hat{\Pi}\psi(r, \theta, \phi) &= \psi(r, \pi-\theta, \phi+\pi)\end{aligned}\right\} \tag{4.37}$$

From the second form it is easy to see that a spherically symmetric $\hat{H}$, as in the hydrogen atom, leads again to equation (4.36) and its consequences.

Continuous eigenvalues† It has so far been tacitly assumed that the eigenvalues of l are discrete, although the position operator is an obvious exception. If in fact the eigenvalues of l are continuously distributed from l_1 to l_2, then the expansion in eigenfunctions (equation (2.9)) has to be written as an integral over l,

$$\psi = \int_{l_1}^{l_2} c(l) u_l \, \mathrm{d}l \tag{4.38}$$

and the interpretation must be altered to say that, if $\langle\psi \mid \psi\rangle = 1$, *the chance of getting a value of l between l and $l + \mathrm{d}l$ is* $|c(l)|^2 \, \mathrm{d}l$. Then $|c(l)|^2$ may be referred to as the *probability density* for the observable l.

The orthogonality of eigenfunctions belonging to different eigenvalues (equation (4.15)) is now expressed by

$$\langle u_l \mid u_{l'}\rangle = \delta(l - l') \tag{4.39}$$

where the Dirac δ-function $\delta(l - l')$ is zero when $l - l' \neq 0$. Its value at $l - l' = 0$, which fixes the normalisation of u_l, is defined to be

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† This topic may be skipped at a first reading.

positively infinite in such a way that

$$\int_{l_1}^{l_2} \delta(l-l')\,\mathrm{d}l' = 1 \tag{4.40}$$

Clearly $\delta(l-l')$ is a highly singular mathematical function, which only has a meaning when it appears in an integral similar to the one that defines it. An elementary property is

$$\begin{aligned}\int_{l_1}^{l_2} c(l')\delta(l-l')\,\mathrm{d}l' &= \int_{l_1}^{l_2} c(l)\delta(l-l')\,\mathrm{d}l' \\ &= c(l)\int_{l_1}^{l_2} \delta(l-l')\,\mathrm{d}l' = c(l)\end{aligned} \tag{4.41}$$

The δ-function is only non-zero when its argument is zero, and so a reversal in sign of the argument has no effect. The last two equations are still satisfied when $\delta(l'-l)$ is substituted for $\delta(l-l')$.

The orthonormality of the eigenfunctions, as defined by equations (4.39) and (4.40), ensures that the total chance of getting a result from a measurement of l is unity. For,

$$\begin{aligned}\langle\psi \mid \psi\rangle &= \int_{l_1}^{l_2}\int_{l_1}^{l_2} \langle c(l)u_l \mid c(l')u_{l'}\rangle\,\mathrm{d}l'\,\mathrm{d}l \\ &= \int_{l_1}^{l_2}\int_{l_1}^{l_2} c^*(l)c(l')\langle u_l \mid u_{l'}\rangle\,\mathrm{d}l'\,\mathrm{d}l \\ &= \int_{l_1}^{l_2} c^*(l)\left\{\int_{l_1}^{l_2} c(l')\delta(l-l')\,\mathrm{d}l'\right\}\mathrm{d}l \\ &= \int_{l_1}^{l_2} c^*(l)c(l)\,\mathrm{d}l\end{aligned} \tag{4.42}$$

Since $\langle\psi \mid \psi\rangle = 1$,

$$\int_{l_1}^{l_2} |c(l)|^2\,\mathrm{d}l = 1 \tag{4.43}$$

in correspondence with equation (2.11).

Finally it may be shown that the expansion coefficient $c(l)$ in equation (4.38) is equal to $\langle u_l \mid \psi\rangle$,

$$\langle u_l \mid \psi\rangle = \int_{l_1}^{l_2} \langle u_l \mid c(l')u_{l'}\rangle \, \mathrm{d}l' = \int_{l_1}^{l_2} c(l')\langle u_l \mid u_{l'}\rangle \, \mathrm{d}l'$$
$$= \int_{l_1}^{l_2} c(l')\delta(l-l') \, \mathrm{d}l' = c(l) \tag{4.44}$$

in correspondence with equation (4.16).

§5 General properties of quantum mechanics

Correspondence to classical mechanics The expectation value of an observable l was defined in section 4 and calculated in equation (4.23); its rate of change with time is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle l\rangle = \frac{\mathrm{d}}{\mathrm{d}t}\langle\psi| \,\hat{l}\, |\psi\rangle \tag{5.1}$$

Differentiating each of the three parts of the integrand in turn,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle l\rangle = \left\langle\frac{\partial\psi}{\partial t}\right| \hat{l} \left|\psi\right\rangle + \left\langle\psi\right| \frac{\partial\hat{l}}{\partial t} \left|\psi\right\rangle + \left\langle\psi\right| \hat{l} \left|\frac{\partial\psi}{\partial t}\right\rangle \tag{5.2}$$

and, with the aid of Schrödinger's equation,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle l\rangle = \frac{i}{\hbar}\langle\hat{H}\psi| \,\hat{l}\, |\psi\rangle + \left\langle\psi\right| \frac{\partial\hat{l}}{\partial t} \left|\psi\right\rangle - \frac{i}{\hbar}\langle\psi| \,\hat{l}\, |\hat{H}\psi\rangle$$
$$= \left\langle\psi\right| \left\{\frac{\partial\hat{l}}{\partial t} - \frac{i}{\hbar}(\hat{l}\hat{H} - \hat{H}\hat{l})\right\} \left|\psi\right\rangle \tag{5.3}$$

The right-hand side here is clearly the expectation value of the operator in the parentheses, so that,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle l\rangle = \left\langle\frac{\partial\hat{l}}{\partial t} - \frac{i}{\hbar}[\hat{l}, \hat{H}]\right\rangle \tag{5.4}$$

As an example the general observable l may be identified with the momentum $\mathbf{p}$. Since $\mathbf{p}$ and T commute,[†]

$$\begin{aligned}[\hat{\mathbf{p}}, \hat{H}] &= \hat{\mathbf{p}}\hat{V} - \hat{V}\hat{\mathbf{p}} = -i\hbar\nabla V + i\hbar V\nabla \\ &= -i\hbar(\nabla V) \end{aligned} \tag{5.5}$$

Clearly $\partial\hat{\mathbf{p}}/\partial t = 0$, since $\hat{\mathbf{p}}$ does not mention t, and so equation (5.4) becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathbf{p}\rangle = \langle -(\nabla V)\rangle \tag{5.6}$$

which recalls at once the classical relation $\mathrm{d}\mathbf{p}/\mathrm{d}t = -\nabla V$. This is an example of a general rule, known as the *correspondence principle*, that the expectation values of observables in quantum mechanics behave in the same way as the observables themselves do in classical mechanics.[‡] The characteristic feature of quantum mechanics is the frequently occurring fluctuations of the measured values of observables around their expectation values, a topic that will be examined soon.

A second example of the correspondence principle in action arises when l is identified with the position $\mathbf{r}$. Since $\mathbf{r}$ and V commute,

$$[\hat{\mathbf{r}}, \hat{H}] = \frac{1}{2m}[\hat{\mathbf{r}}, \hat{\mathbf{p}}^2] \tag{5.7}$$

The ith component is

$$[\hat{r}_i, \hat{\mathbf{p}}^2] = [\hat{r}_i, \hat{p}_i^2] = [\hat{r}_i, \hat{p}_i]\hat{p}_i + \hat{p}_i[\hat{r}_i, \hat{p}_i] = 2i\hbar\hat{p}_i \tag{5.8}$$

and so

$$[\hat{\mathbf{r}}, \hat{\mathbf{p}}^2] = 2i\hbar\hat{\mathbf{p}} \tag{5.9}$$

Since $\partial\hat{\mathbf{r}}/\partial t = 0$, equation (5.4) becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathbf{r}\rangle = \frac{1}{m}\langle\mathbf{p}\rangle \tag{5.10}$$

which corresponds to the classical equation $\mathrm{d}\mathbf{r}/\mathrm{d}t = \mathbf{p}/m$.

[†] If operator equations seem obscure at first it will be found worthwhile to include the wave function explicitly. Then the last step in this particular equation will be seen to involve nothing more difficult than the derivative of the product of two functions,

$$\nabla V\psi = (\nabla V)\psi + V\nabla\psi$$

[‡] Equation (5.6) is also known as Ehrenfest's theorem. Vaguer and more elusive versions of the correspondence principle are sometimes encountered.

As a final example, the total energy H may be considered in the situation where the potential V is not a function of t. Then $\partial\hat{H}/\partial t = 0$, and of course the commutator of $\hat{H}$ with itself vanishes, so

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle H\rangle = 0 \tag{5.11}$$

corresponding to the classical conservation of the total energy in the same situation.

Heisenberg's uncertainty principle The first part of section 5 has described how the expectation values of observables in quantum mechanics behave like the corresponding classical observables. In quantum mechanics, of course, the actual measured value of an observable is liable to differ from its expectation value, except when the particle is in an eigenstate of that particular observable. It is not in fact possible for a particle to be in an eigenstate of every observable simultaneously, so that there cannot be a physical situation in which all the observables are free from uncertainty.

It is easy to find a condition which must be satisfied if a wave function ψ is to be an eigenfunction of two observables l and m. If $\hat{l}\psi = l_s\psi$ and $\hat{m}\psi = m_r\psi$,

$$\left.\begin{aligned}\hat{l}\hat{m}\psi &= \hat{l}(m_r\psi) = m_r(\hat{l}\psi) = m_r l_s\psi\\ \hat{m}\hat{l}\psi &= \hat{m}(l_s\psi) = l_s(m\psi) = l_s m_r\psi\end{aligned}\right\} \tag{5.12}$$

Obviously $m_r l_s\psi = l_s m_r\psi$, so that

$$(\hat{l}\hat{m} - \hat{m}\hat{l})\psi = [\hat{l}, \hat{m}]\psi = 0 \tag{5.13}$$

Sometimes the commutation relations between $\hat{l}$ and $\hat{m}$ are such that this condition can never be satisfied. In one-dimensional problems, for example, the position and momentum observables obey the commutation relation $[\hat{x}, \hat{p}] = i\hbar$; but if ψ is normalised $i\hbar\psi$ cannot be zero everywhere. It follows that simultaneous eigenstates of x and p do not exist, and these observables are therefore said to be *complementary*. In three-dimensional problems x and p_x, y and p_y, z and p_z are pairs of complementary observables because of the commutation relations $[\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij}$.

Sometimes l and m do not commute, but $[\hat{l}, \hat{m}]$ is equal to an operator rather than a constant. This situation produces a modified type of complementarity, less absolute than that involving x and p. The point is that the operator just mentioned may produce zero for some very particular wave functions ψ, though not for all. The complementarity of l and m is then abated for these very particular wave functions. The orbital angular momentum components in section 10 provide a fine example.

So far a necessary but not sufficient condition has been derived for ψ to be a simultaneous eigenfunction of l and m. However, the discussion can be sharpened further; if $[\hat{l}, \hat{m}]\psi = 0$ and if ψ is an eigenfunction of l belonging to the eigenvalue l_s,

$$\hat{l}(\hat{m}\psi) = \hat{m}(\hat{l}\psi) = l_s(\hat{m}\psi) \tag{5.14}$$

Here $\hat{m}\psi$ is seen also to be an eigenfunction of l, belonging to the same eigenvalue l_s. *Provided that this eigenvalue is non-degenerate*, $\hat{m}\psi$ can differ from ψ only by a multiplicative constant, m_r say. Thus $\hat{m}\psi = m_r\psi$ and ψ is definitely an eigenfunction of m also.

The uncertainties which must be associated with a pair of complementary observables can be discussed quantitatively. A measure Δl of the uncertainty of l is given by

$$\begin{aligned}(\Delta l)^2 = \langle l^2\rangle - \langle l\rangle^2 &= \langle\psi|\, \hat{l}^2\, |\psi\rangle - \langle\psi|\, \hat{l}\, |\psi\rangle^2 \\ &= \langle\psi|\, (\hat{l} - \langle\psi|\, \hat{l}\, |\psi\rangle)^2\, |\psi\rangle \\ &= \langle\psi|\, \hat{l}'^2\, |\psi\rangle\end{aligned} \tag{5.15}$$

where $\hat{l}' = \hat{l} - \langle\psi|\, \hat{l}\, |\psi\rangle$, the second term being simply multiplicative. The uncertainty of the complementary observable m is similarly measured by Δm. Then,

$$\begin{aligned}(\Delta l)^2(\Delta m)^2 &= \langle\psi|\, \hat{l}'^2\, |\psi\rangle\langle\psi|\, \hat{m}'^2\, |\psi\rangle \\ &= \langle\hat{l}'\psi \mid \hat{l}'\psi\rangle\langle\hat{m}'\psi \mid \hat{m}'\psi\rangle\end{aligned} \tag{5.16}$$

Now Schwarz's inequality† states that for any two complex functions f and g,

$$\int f^*f\, d\tau \int g^*g\, d\tau \geqslant \left|\int f^*g\, d\tau\right|^2 \tag{5.17}$$

and, obviously,

$$\left|\int f^*g\, d\tau\right|^2 \geqslant \left\{\int \mathrm{Im}\,(f^*g)\, d\tau\right\}^2 = \left\{\int \frac{1}{2i}(f^*g - g^*f)\, d\tau\right\}^2 \tag{5.18}$$

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† The inequality may be obtained by considering that $\int h^*h\, d\tau \geqslant 0$, where $h \equiv (\int f^*g\, d\tau)f - (\int f^*f\, d\tau)g$.

If f is identified with $\hat{l}'\psi$, and g with $\hat{m}'\psi$, these two inequalities may be used in the right-hand side of equation (5.16):

$$
\begin{aligned}
(\Delta l)^2(\Delta m)^2 &\geqslant \left\{\frac{1}{2i}\left(\langle \hat{l}'\psi \mid \hat{m}'\psi\rangle - \langle \hat{m}'\psi \mid \hat{l}'\psi\rangle\right)\right\}^2 \\
&\geqslant \left\langle \psi \left| \frac{1}{2i}(\hat{l}'\hat{m}' - \hat{m}'\hat{l}') \right| \psi \right\rangle^2 \\
&\geqslant \left\langle \frac{1}{2i}[\hat{l}', \hat{m}'] \right\rangle^2
\end{aligned}
\tag{5.19}
$$

Obviously,

$$[\hat{l}', \hat{m}'] = [\hat{l}, \hat{m}] \tag{5.20}$$

and so finally,

$$\Delta l \, \Delta m \geqslant \left| \left\langle \frac{1}{2i}[\hat{l}, \hat{m}] \right\rangle \right| \tag{5.21}$$

This is the mathematical expression of *Heisenberg's uncertainty principle*. It may be applied at once to the one-dimensional position and momentum to give the example

$$\Delta x \, \Delta p \geqslant \hbar/2 \tag{5.22}$$

The certainty of the classical theory would be regained if $\hbar$ were actually zero; this is a general feature of the uncertainty principle, since a non-vanishing $[\hat{l}, \hat{m}]$ always contains a factor $\hbar$.

When attention is artificially restricted to a region of special interest the uncertainty principle must be applied with care. In section 1, for example, it has to be remembered that ψ_a, ψ_b, and ψ_c really repeat themselves over and over again outside the region $-L/2 \geqslant x \geqslant L/2$. *Physically* Δx is infinite, and so Δp can be zero for ψ_a and ψ_b. *Mathematically* the failure of equation (5.22), when attention is restricted to a special region, is explained by the footnote on page 26.

The uncertainty principle will be extended later (sections 25, 26) to discuss the spread ΔE of an energy measurement carried out in a finite time interval Δt. The considerations involved are qualitatively somewhat different from those presented here.

Conservation of observables Usually $\partial \hat{l}/\partial t = 0$, and in some physical situations it may happen that $[\hat{l}, \hat{H}] = 0$. According to equation (5.4) $\langle l \rangle$ is invariant, and so are $\langle l^2 \rangle$, Δl, and indeed the expectation value of any function of l. The observable l is then said to be conserved. In particular, if a measurement of l is certain to yield the eigenvalue l_s at some time, then it is certain to do so at all times.

The simplest example is the conservation of energy whenever $\partial\hat{H}/\partial t = 0$ (equation (5.11)). Another instructive example is the conservation of linear momentum for a free particle, when $\hat{H} = \hat{\mathbf{p}}^2/2m$ and $[\hat{p}, \hat{H}] = 0$. All the conservation laws of classical mechanics are reproduced in this way.

Problems

2.1 Suppose that the eigenfunctions of l are not degenerate, and that $u_s(\mathbf{r})$ and $u_s'(\mathbf{r})$ are both normalised eigenfunctions of l belonging to the eigenvalue l_s. Show that the most general possible relationship between the two eigenfunctions is

$$u_s(\mathbf{r}) = u_s'(r)e^{i\delta}$$

where δ is constant and real.

2.2 Show that a non-degenerate solution to the simplest form of TISE (equation (3.2) with $\hat{H}$ given by equation (3.1)) can be expressed as a function which is real everywhere.

Show further that the PCD for the solution is zero everywhere.

[*Hint*: Suppose u_s to be a solution, write it in the form $v_s + iw_s$ where v_s and w_s are real everywhere, substitute into the TISE, and separate the real and imaginary parts of the equation. The absence of degeneracy points to a relationship between v_s and w_s. *Comment*: A complete set of real functions which solve the TISE can also be found when there is degeneracy, but a set of complex functions may be more convenient if its members are simultaneous eigenfunctions of energy and some other important observable. Thus in equations (1.6) ψ_a and ψ_b are eigenfunctions of momentum, but ψ_c is not.]

2.3 Use equation (3.9) to calculate the PCD for the states represented by ψ_a and ψ_b in equations (1.6). Verify that the PCD is equal to p/m times the PPD for these momentum eigenstates, as might be expected from the classical relation $p = mv$.

2.4 In spherical polar coordinates the components of the operator $\boldsymbol{\nabla}$ in the directions in which r only, θ only, and ϕ only increase are

$$\nabla_r = \frac{\partial}{\partial r}$$

$$\nabla_\theta = \frac{1}{r}\frac{\partial}{\partial \theta}$$

$$\nabla_\phi = \frac{1}{r \sin\theta}\frac{\partial}{\partial \phi}$$

The radial probability current density (RPCD) is the flux of the PCD through a spherical surface of radius r.

If

$$\psi = (1/2\pi^{1/2} r) S(r)$$

show that the RPCD is

$$\frac{i\hbar}{2m}\left(\frac{\mathrm{d}S^*}{\mathrm{d}r} S - S^* \frac{\mathrm{d}S}{\mathrm{d}r}\right)$$

If in fact $S = \mathrm{e}^{ikr}$, where k is real, then show that the RPCD is $\hbar k/m$.

2.5 The matrix elements of an operator are so called because they can be arranged in the form of a square matrix; if $\hat{l}$ in particular is a Hermitian operator, then $\langle\psi_m|\, \hat{l}\, |\psi_n\rangle$ appears in the mth row and the nth column. If this matrix element is labelled l_{mn}, then a Hermitian matrix is one in which $l_{nm} = l_{mn}^*$. Show that the $\langle\psi_m|\, \hat{l}\, |\psi_n\rangle$ form a Hermitian matrix and that the diagonal elements $(m = n)$ are therefore real.

Show further that if the wave functions used to form the matrix elements are in fact the eigenfunctions of l, and if there is no degeneracy, then the diagonal elements of the matrix are the eigenvalues of l and the off-diagonal elements vanish.

Jot down the 2×2 matrix associated with p, ψ_a, and ψ_b in section 1.

2.6 Suppose that $\hat{l}$ does not mention t, that $[\hat{l}, \hat{H}] = 0$, that the $u_\mathrm{s}(r)$ form a complete orthonormal set of non-degenerate eigenfunctions of l, and that

$$\psi(r, t) = \sum_s c_\mathrm{s}(t) u_\mathrm{s}(\mathbf{r})$$

Show that

$$\frac{\mathrm{d}}{\mathrm{d}t}|c_s|^2=0$$

for any s, as would be expected when l is conserved. [*Hint:* In the circumstances that are postulated an eigenfunction of l is also an eigenfunction of H. *Comment*: The extension to cover degeneracy is quite difficult, but it can in fact be proved that the overall probability of l being found to have each eigenvalue is invariant.]

2.7 The energy operator for a particle moving in a three-dimensional potential field $V(r)$ has the form

$$\hat{H}=-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\hat{\mathbf{l}}^2}{2mr^2}+V(r,\theta,\phi)$$

in spherical polar coordinates r, θ, ϕ. The operator $\mathbf{l}$ represents the angular momentum of the particle round the origin: it mentions θ and ϕ, but not r.

Show that the angular momentum is conserved, if the potential is central and described simply by $V(r)$.

3

One-dimensional applications

§6 Free particles: momentum probability density

Stationary states It is a wise habit to start the quantum mechanical analysis of a physical situation by writing down the energy operator $\hat{H}$, whenever possible. For free particles

$$\hat{H}=\hat{T}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{6.1}$$

Normally the next steps would be to write down the TISE, and solve it to find the stationary state wave functions $u_s(x)$ and the energy eigenvalues $E_s=\hbar\omega_s$. The problem in hand is so simple, however, that the TDSE has already been written down and solved directly in section 1. According to equation (1.2) the solutions are wavelike, and a typical one after normalisation can be written

$$\psi_s(x,t)=L^{-1/2}e^{i(k_sx-\omega_st)} \tag{6.2}$$

If attention is again confined to the finite region $-L/2\leqslant x\leqslant L/2$, then periodic boundary conditions should be imposed. In essence they require that the interval L should be an integral multiple of the wavelength $2\pi/k_s$. Then

$$k_s=2\pi s/L, \qquad s=0,\pm1,\pm2,\dots \tag{6.3}$$

where s is the first example of a *quantum number*, whose value must be chosen from a set of permissible values, not necessarily integral in every problem. The function of a quantum number is to ensure that a general solution to the TDSE or TISE, like equation (6.2), is specialised to conform to the boundary conditions.

The value of each ω_s can be obtained from k_s by means of the dispersion relation, equation (1.3). Thus

$$\omega_s = 2\pi^2 s^2 \hbar / mL^2 \tag{6.4}$$

The transition from the mathematical style of section 1 to the more standard one of section 3 is made by writing equation (6.2) in the form of equations (3.3):

$$\left.\begin{aligned} \psi_s(x, t) &= u_s(x)\mathrm{e}^{-i\omega_s t} \\ u_s(x) &= L^{-1/2}\mathrm{e}^{ik_s x} \end{aligned}\right\} \tag{6.5}$$

It is readily shown that u_s is an eigenfunction both of momentum and energy,† belonging to the eigenvalues $\hbar k_s$ and $\hbar\omega_s$ respectively. In fact

$$\left.\begin{aligned} \hat{p}u_s &= \hbar k_s u_s \\ \hat{H}u_s &= (\hbar^2 k_s^2/2m)u_s = \hbar\omega_s u_s \end{aligned}\right\} \tag{6.6}$$

Discrete eigenvalues of momentum According to equations (6.3) and (6.6),

$$p_s = 2\pi s\hbar / L \tag{6.7}$$

Since the quantum number s must be integral, the momentum eigenvalue spectrum is discrete: there is a gap between successive eigenvalues, equal to $2\pi\hbar/L$. Obviously this gap may be made as small as desired by taking L suitably large, but it is always possible to count the number of eigenvalues which lie in a certain interval of momentum. It will appear later that this is indeed a very important kind of operation.

If a momentum interval δp_s is considered, then division of δp_s by the gap between eigenvalues will yield the corresponding number δN of momentum eigenvalues:

$$\left.\begin{aligned} &\delta N = (L/2\pi\hbar)\delta p_s \\ &\frac{\delta N}{\delta p_s} = \frac{L}{2\pi\hbar} \end{aligned}\right\} \tag{6.8}$$

This may be called the *density of states in momentum space.*

---

† Notice that $\hat{p}$ commutes with $\hat{H}$ for free particles.

Discrete eigenvalues of energy The energy eigenvalue spectrum is also discrete, because

$$E_s = 2\pi^2 s^2 \hbar^2 / mL^2 \tag{6.9}$$

The gaps between successive energy eigenvalues become larger as E_s and s increase, because of the dependence on s^2. This means that the density of states in energy space decreases as the energy increases.†

Wave packets It has been seen that a wave function proportional to $e^{ik'x}$ represents a state in which the particle has the momentum $\hbar k'$. On the other hand the position of the particle is undefined, since the PPD is constant. It is interesting to consider the effect of localising the particle, by putting into the wave function a modulating amplitude proportional to $e^{-a^2x^2/2}$, where a is a real constant. After normalisation‡ the resulting wave function, which is an example of a *wave packet*, has the form

$$\psi(x, 0) = \pi^{-1/4} a^{1/2} e^{-a^2x^2/2} e^{ik'x} \tag{6.10}$$

at $t = 0$.

The energy operator $\hat{H}$ is of course unchanged, and use of it shows that $\psi(x, 0)$ does not obey the TISE, and so it is not an energy eigenfunction and does not represent a stationary state. For the time being the discussion will be confined to the state of affairs at $t = 0$.

The PPD is immediately calculable, and it has the Gaussian shape shown in figure 6.1. The PPD is symmetric about $x = 0$, and

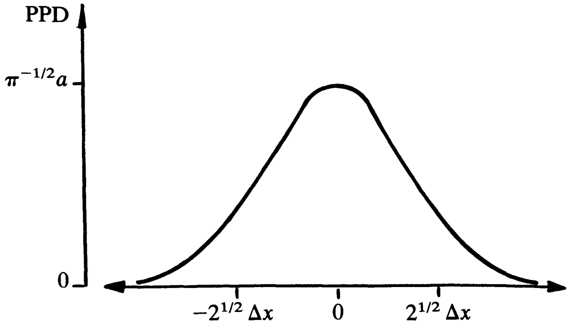

Figure 6.1 The PPD of the wave packet at $t = 0$.

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† *Vide* problem 3.2.

‡ *Vide* appendix, equation (1).

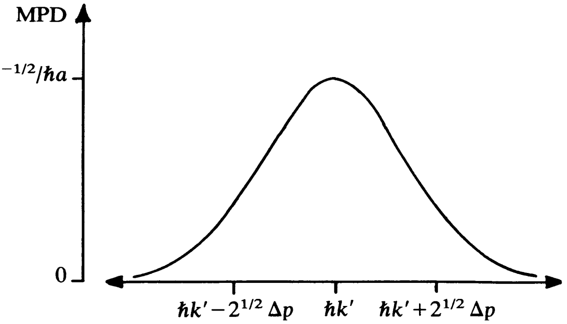

Figure 6.2 The MPD of the wave packet at $t = 0$.

therefore the expectation value of x must be zero. Indeed

$$\begin{aligned}\langle x\rangle &= \langle\psi(x,0)|\,x\,|\psi(x,0)\rangle\\ &= \frac{a}{\pi^{1/2}}\int_{-\infty}^{\infty} x\mathrm{e}^{-a^2x^2}\,\mathrm{d}x = 0\end{aligned} \tag{6.11}$$

because the integrand is an odd function of x.

As for the expectation value of x^2 and the uncertainty of position Δx,

$$\left.\begin{aligned}\langle x^2\rangle &= \frac{a}{\pi^{1/2}}\int_{-\infty}^{\infty} x^2\mathrm{e}^{-a^2x^2}\,\mathrm{d}x = 1/2a^2\\ \Delta x &= (\langle x^2\rangle - \langle x\rangle^2)^{1/2} = 1/2^{1/2}a\end{aligned}\right\} \tag{6.12}$$

with the help of the appendix, equation (2). It follows that the PPD falls to 1/e of its peak value† at $x = \pm a^{-1} = \pm 2^{1/2}\Delta x$.

Obviously $\psi(x, 0)$ is not an eigenfunction of the momentum, but the expectation value $\langle p\rangle$ is unchanged by the introduction of the factor $\mathrm{e}^{-a^2x^2/2}$:

$$\begin{aligned}\langle p\rangle &= \langle\psi|\,\hat{p}\,|\psi\rangle = \left\langle\psi\,\middle|\,-i\hbar\frac{\partial\psi}{\partial x}\right\rangle\\ &= -\frac{i\hbar a}{\pi^{1/2}}\int_{-\infty}^{\infty}(ik' - a^2x)\mathrm{e}^{-a^2x^2}\,\mathrm{d}x = \hbar k'\end{aligned} \tag{6.13}$$

---

† Of course there is the same relationship between any Gaussian distribution and its standard deviation.

The value of $\langle p^2 \rangle$ is

$$\begin{aligned}\langle p^2\rangle &= \langle \psi |\, \hat{p}^2 \,| \psi\rangle \\ &= -\frac{\hbar^2 a}{\pi^{1/2}} \int_{-\infty}^{\infty} (-a^2 - k'^2 - 2ia^2k'x + a^4x^2)\mathrm{e}^{-a^2x^2}\,\mathrm{d}x \\ &= \hbar^2(k'^2 + a^2/2) \qquad (6.14)\end{aligned}$$

and so the uncertainty Δp in the momentum of the particle is given by

$$\Delta p = (\langle p^2\rangle - \langle p\rangle^2)^{1/2} = \hbar a/2^{1/2} \qquad (6.15)$$

The product $\Delta x\, \Delta p$ has the value

$$\Delta x\, \Delta p = \hbar/2 \qquad (6.16)$$

which is in fact the minimum allowed by the uncertainty principle. This is a special property of the Gaussian modulation of $\psi(x, 0)$.

Momentum probability density (MPD) Some theoretical development is needed to get detailed information about the momentum of the particle. When a wavefunction ψ is not an eigenfunction of momentum it is necessary to expand it in terms of a complete orthonormal set of momentum eigenfunctions. Such a set is provided by the second of equations (6.5), and the chance that the momentum will be found to have the value p_s is

$$|c_s|^2 = |\langle L^{-1/2}\mathrm{e}^{\mathrm{i}p_sx/\hbar} \,|\, \psi\rangle|^2 \qquad (6.17)$$

according to equation (4.17). The limits of integration are $x = \pm L/2$, and the arbitrary length L must be set very large so that all values of x for which ψ is significant are covered.

With that condition $|c_s|^2$ is proportional to $1/L$, which looks puzzling at first sight. However, the output of real physical interest is the MPD, $|c(p_s)|^2$, defined so that the chance of the momentum being found with a value between p_s and $p_s + \delta p_s$ is $|c(p_s)|^2\, \delta p_s$. When L is very large there are many momentum eigenvalues in the range δp_s, and so the density of states in momentum space, which is proportional to L, becomes a factor. Then, as $L \to \infty$,

$$\left.\begin{aligned}|c(p_s)|^2\, \delta p_s &= |c_s|^2\, \delta N \\ |c(p_s)|^2 &= |c_s|^2 \frac{L}{2\pi\hbar}\end{aligned}\right\} \qquad (6.18)$$

according to equations (6.8). After the superfluous suffix s has been dropped,

$$c(p) = \langle (2\pi\hbar)^{-1/2} e^{ipx/\hbar} \mid \psi \rangle \tag{6.19}$$

which is happily independent of L.

If the wave function $\psi(x, 0)$ is substituted into the general formula†

$$\begin{aligned} c(p) &= \left(\frac{a}{2\pi^{3/2}\hbar}\right)^{1/2} \int_{-\infty}^{\infty} e^{-i(p/\hbar)x + ik'x - (a^2x^2/2)} \mathrm{d}x \\ &= \left(\frac{1}{\pi^{1/2}\hbar a}\right)^{1/2} e^{-(\hbar k' - p)^2/2\hbar^2 a^2} \end{aligned} \tag{6.20}$$

and therefore,

$$|c(p)|^2 = \left(\frac{1}{\pi^{1/2}\hbar a}\right) e^{-(\hbar k' - p)^2/\hbar^2 a^2} \tag{6.21}$$

This distribution, which is again of Gaussian form, is shown in figure 6.2. The MPD is largest when $p = \langle p \rangle$, and it falls to 1/e of its peak value at $p = \langle p \rangle \pm 2^{1/2} \Delta p$.

Continuous eigenvalues of momentum‡ The MPD was calculated by expanding ψ in eigenfunctions of p belonging to discrete eigenvalues, and then letting $L \to \infty$ so that the spectrum went over to a continuum. The same final result can be obtained more directly by using the continuous eigenvalue theory developed in section 4.

In fact equation (6.19) for $c(p)$ corresponds exactly to equation (4.44) and it is only necessary to show that the eigenfunction $u_p = (2\pi\hbar)^{-1/2} e^{ipx/\hbar}$ is correctly normalised; to check with equation (4.39) it must be proved that $\langle u_p \mid u_{p'} \rangle = \delta(p - p')$.

It is hardly surprising, in view of its equation with a δ-function, that $\langle u_p \mid u_{p'} \rangle$ is positively infinite when $p' = p$. This can be seen by defining the infinite integral in the usual way:

$$\begin{aligned} \langle u_p \mid u_{p'} \rangle &= \lim_{X \to \infty} \frac{1}{2\pi\hbar} \int_{-X}^{X} e^{i(p'-p)x/\hbar} \mathrm{d}x \\ &= \lim_{X \to \infty} \frac{\sin\{(p'-p)X/\hbar\}}{\pi(p'-p)} \end{aligned} \tag{6.22}$$

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† *Vide* appendix, equation (3).

‡ This sub-section, which ends on page 44, may be skipped at a first reading.

The function whose limit is to be taken has the value $X/\pi\hbar$ when $p'=p$, and so the final result is clearly infinite.

It is irritating that the expression (6.22) does not settle down to zero when $p'\neq p$, in the limit $X\to\infty$. Instead it oscillates finitely around the mean value zero as X increases, with the amplitude $\{\pi(p'-p)\}^{-1}$. Steps may reasonably be taken to damp out these oscillations, by modifying the momentum eigenfunctions at extremely large values of $|x|$. After all, the eigenfunctions actually enter into calculations when scalar products with them of physical wave functions ψ are taken. It is unlikely that ψ will be significant as far away as the moon, let alone at infinity. Thus the scalar products will not be affected by the introduction of a factor which differs from unity only at extremely large $|x|$.

The damping can be accomplished by introducing a factor $e^{-\varepsilon|x|/2\hbar}$, where ε is real, positive, and very small. This is the simplest factor which will suit the purpose in hand; it has the disadvantage that the momentum eigenfunctions are not differentiable, and hence cannot respond properly to $\hat{p}$, at $x=0$, but this fault may be excused since the uncertainty in the differential goes to zero in the limit $\varepsilon\to+0$. Thus,

$$\begin{aligned}\langle u_p \mid u_{p'}\rangle &= \lim_{\varepsilon\to+0}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{\{i(p'-p)x-\varepsilon|x|\}/\hbar}\,dx\\ &= \lim_{\varepsilon\to+0}\frac{i}{2\pi}\left(\frac{1}{p-p'+i\varepsilon}-\frac{1}{p-p'-i\varepsilon}\right)\\ &= \lim_{\varepsilon\to+0}\frac{\varepsilon}{\pi\{(p-p')^2+\varepsilon^2\}} \qquad (6.23)\end{aligned}$$

The separate terms in the second line appear when the integral is taken in two bites, from $-\infty$ to 0 and from 0 to $+\infty$.

The expression (6.23) may be completely identified† with $\delta(p-p')$. It is positively infinite when $p'=p$, zero when $p'\neq p$, and yields unity when integrated over all p'.

Time dependence of wave packets Some important facts about the development with time of the wave packet can be seen without examining the wave function in detail. The momentum is conserved, since $\hat{p}$ is an operator which commutes with $\hat{H}$ and does not depend

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† In shorthand, $\int_{-\infty}^{\infty} e^{i(k'-k)x}\,dx = 2\pi\delta(k-k') = 2\pi\delta(k'-k)$.

on t. Therefore,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p\rangle = \frac{\mathrm{d}}{\mathrm{d}t}\langle p^2\rangle = 0$$

and $\langle p\rangle$, $\langle p^2\rangle$, and hence Δp preserve at all times the values already computed for $t=0$.

The value of $\langle x\rangle$ can also be found quickly. From equation (5.4),

$$\left.\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle = -\frac{i}{\hbar}\langle[\hat{x},\hat{H}]\rangle = -\frac{i}{2\hbar m}\langle[\hat{x},\hat{p}^2]\rangle \\ &[\hat{x},\hat{p}^2] = [\hat{x},\hat{p}]\hat{p} + \hat{p}[\hat{x},\hat{p}] = 2i\hbar\hat{p} \end{aligned}\right\} \tag{6.24}$$

with the help of equation (4.26). So

$$\left.\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle = \frac{1}{m}\langle p\rangle = \frac{\hbar k'}{m} \\ &\langle x\rangle_t = \langle x\rangle_0 + \hbar k' t/m \end{aligned}\right\} \tag{6.25}$$

The first equation here shows the expectation value of x moving along at a velocity which is equal to $1/m$ times the expectation value of p: that is just what would be expected from the correspondence principle.

In order to evaluate $\langle x\rangle_t$ and $(\Delta x)_t$ it is necessary to follow the development of the wave function from $\psi(x,0)$ to $\psi(x,t)$. That involves a straightforward but unfortunately lengthy calculation.† The final result is

$$\left.\begin{aligned} &\langle x^2\rangle_t = \langle x^2\rangle_0 + \frac{\hbar^2 a^2 t^2}{2m^2} \\ &(\Delta x)_t^2 = (\Delta x)_0^2 + (\Delta p)^2 t^2/m^2 \end{aligned}\right\} \tag{6.26}$$

The same result is predicted by the correspondence principle. An uncertainty Δp in momentum produces an uncertainty in position $(\Delta p)t/m$ after time t: the usual square law has to be used to combine this with the original uncertainty $(\Delta x)_0$.

The product $(\Delta x)_t\ \Delta p$, which at $t=0$ had the minimum value allowed by the uncertainty principle, increases without limit as time goes on.

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† *Vide* problem 3.5.

§7 Solutions of the TISE

General features It was explained in section 3 that the TISE (equation (3.2)) plays a central role when $\hat{H}$ does not mention t. A qualitative discussion of its solutions is therefore appropriate now.

In a region of x where $E > V(x)$ the TISE, with the label s implicit, can be written as

$$\frac{\mathrm{d}^2u}{\mathrm{d}x^2} = -k^2(x)u \tag{7.1}$$

where

$$k(x) \equiv |[2m\{E - V(x)\}/\hbar^2]^{1/2}|$$

This linear and homogeneous equation is of the second order, which means that it involves the second but no higher derivative of u with respect to x. Consequently it must have two linearly independent solutions before boundary conditions are taken into account.

Where $k(x)$ is constant a general solution looks like the superposition of two standing waves,

$$u = A\cos(kx) + B\sin(kx) \tag{7.2}$$

where A and B are arbitrary constants. Alternatively, by taking suitable linear combinations of the terms, u can be made to look like two travelling waves,

$$u = C\mathrm{e}^{ikx} + D\mathrm{e}^{-ikx} \tag{7.3}$$

where C and D are arbitrary constants. As a rule bound particle states are better represented by standing waves and free particle states by travelling waves.

Where $k(x)$ varies slowly† these simple solutions become mildly distorted, as the left-hand side of figure 7.1 shows. The wavelength and the two amplitudes at each point are proportional to the local values of k^{-1} and $k^{-1/2}$ respectively.‡ The variation of the wavelength is intuitively obvious, while that of the amplitudes gives unidirectional travelling waves a constant PCD, a necessity on physical grounds.§ The two constants, A and B say, may now be the amplitudes of the two distorted waves at some reference value of x.

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† The criterion is $|\mathrm{d}k/\mathrm{d}x| \ll k^2$.

‡ Expressions for these solutions will be developed in section 18, but they are not quoted here because they involve phase integrals, which may appear abstruse at first sight. Problem 3.7 is intended to make the concept more familiar.

§ *Vide* problem 3.8.

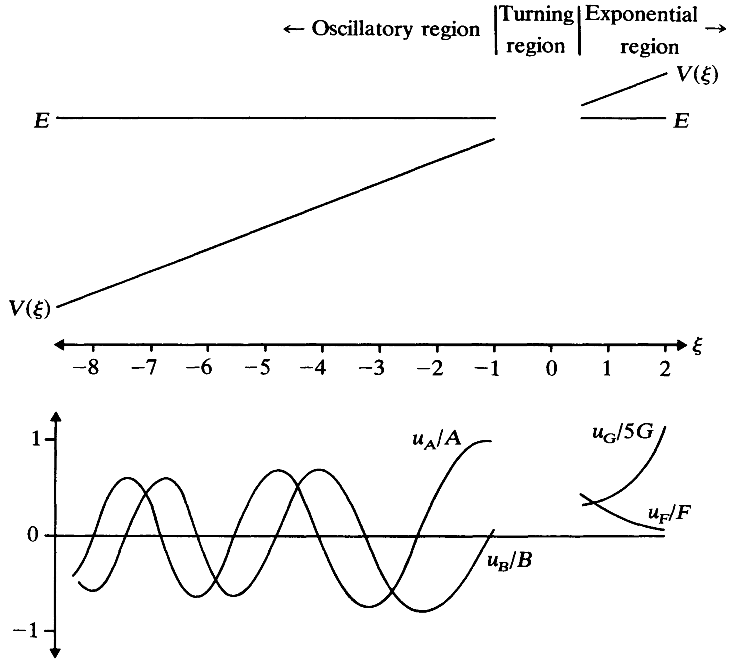

Figure 7.1 The left-hand side shows the behaviour of the two terms in equation (7.2) when they are distorted by a slow linear variation in the potential energy $V(\xi)$. The right-hand side shows the two terms in equation (7.5) similarly distorted. The variable $\xi = |\{2m\hbar^{-2}(\mathrm{d}V/\mathrm{d}x)\}^{1/3}|\,x$ is proportional to x but dimensionless. As a matter of fact u_A is continuous with u_F through the turning region if $A = F$, and so is u_B with u_G if $B = G$.

Where $k(x)$ changes rapidly the solutions just discussed break down, but usually the affected region of x is quite small and the qualitative behaviour of u within it can be guessed successfully.

In a region of x where $E < V(x)$ the TISE becomes

$$\frac{\mathrm{d}^2u}{\mathrm{d}x^2} = \kappa^2(x)u \tag{7.4}$$

where

$$\kappa(x) \equiv |[2m\{V(x) - E\}/\hbar^2]^{1/2}|$$

Where $\kappa(x)$ is constant the general solution looks like the superposition of two exponentials, one decaying and one growing with x,

$$u = F\mathrm{e}^{-\kappa x} + G\mathrm{e}^{\kappa x} \tag{7.5}$$

where F and G are arbitrary constants.

Where $\kappa(x)$ varies slowly† this simple solution becomes mildly distorted, although this is not very obvious in the right-hand side of figure 7.1. The attenuation length and the two amplitudes are proportional to the local values of κ^{-1} and $\kappa^{-1/2}$ respectively. The arbitrary constants F and G may now be the values of the distorted exponentials at a second reference value of x.

Where $\kappa(x)$ changes rapidly the solution just discussed breaks down, but again the qualitative behaviour of u can be guessed successfully.

In figure 7.1, and in figures 7.2–7.4 below, it is assumed that the wave functions are real everywhere. There is no loss of generality because non-degenerate solutions of the TISE are being sought.‡

The behaviour of u is clearly very different in the two regions. Where $E > V(x)$ the signs of $\mathrm{d}^2u/\mathrm{d}x^2$ and u are opposite: then the curve of u against x is concave towards the $u = 0$ axis, and is apt to cross it repeatedly at nodes. Where $E < V(x)$ the signs of $\mathrm{d}^2u/\mathrm{d}x^2$ and u are the same: then the curve of u against x is convex towards the $u = 0$ axis, and therefore if it crosses the axis once§ it cannot do so again within the region. If the region extends over all positive x, and if $u \to 0$ as $x \to \infty$, then it does not cross the axis at all within the region.

A region of x where $k(x)$ is constant or slowly varying is called *oscillatory*, and so is the behaviour of u there. Similarly a region of x where $\kappa(x)$ is constant or slowly varying is called *exponential*, and so is the behaviour of u there.

Continuity through a turning region An oscillatory region is separated from an exponential one by a *turning region*, within which lies a *turning point* where $E = V(x)$. Classically a particle projected from an oscillatory region towards a turning point would be turned back precisely there. In quantum mechanics k (or κ) varies rapidly in that part of the turning region that lies between the turning point and the oscillatory (exponential) region.¶

A particular approximate u in the oscillatory region, involving definite values for A and B, specifies the exact u to which it is an approximation. The exact u can then be followed through the

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† The criterion is $|\mathrm{d}\kappa/\mathrm{d}x| \ll \kappa^2$.

‡ *Vide* problem 2.2.

§ F and G would have to be of opposite sign.

¶ Note that k^2 (or κ^2) is small near the turning point.

turning region† and into the exponential region, where in turn it specifies another particular approximate u, involving definite values for F and G. When A and B are given, F and G can in principle be determined. More precisely, F and G are connected with A and B by two linear homogeneous equations.

Boundary conditions at infinity It is usual in physics for the general solutions of differential equations to be specialised by *boundary conditions* in particular problems, and the solutions of the TISE are no exception. For example the second term in equation (7.5) must be excluded when an exponential region persists as $x \to \infty$. Otherwise the PPD would become infinite where classically no particle could penetrate, and that would be unphysical. The boundary condition can say simply that $G = 0$, or alternatively that $u \to 0$ as $x \to \infty$. A third, and particularly simple, linear homogeneous equation for the arbitrary constants has appeared here.

When an exponential region persists as $x \to -\infty$ then $F = 0$, or $u \to 0$ as $x \to -\infty$.

Construction of part of an overall solution The next step is to consider the construction of a solution that passes current all the way from an oscillatory region through a turning region to an exponential region of infinite extent (figure 7.2). The four constants A, B, F, G, are here connected by three linear homogeneous equations, two for the connection through the turning region and one for the boundary condition as $x \to \infty$. Therefore u is determined apart from an overall scale factor, which may as well be identified with F. In figure 7.2 F has a positive real value but it might equally well have been negative, and then u would have approached the x-axis from underneath as $x \to \infty$.

The solution in figure 7.2 has been computed exactly, but a result not much inferior might have been obtained by taking the very simple approximate u in the exponential region, extrapolating by eye across the turning region, and continuing with an approximate u in the oscillatory region. The extrapolation relies on the fact that u and du/dx must be continuous if $V(x)$ is well behaved.‡

The vertical dotted line in figure 7.2 is a reminder that d^2u/dx^2 changes sign at the turning point, although u does not.

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† A glance forward to figure 18.1 may be helpful.

‡ If they were not continuous, then d^2u/dx^2 would not exist, in general contradiction of the TISE.

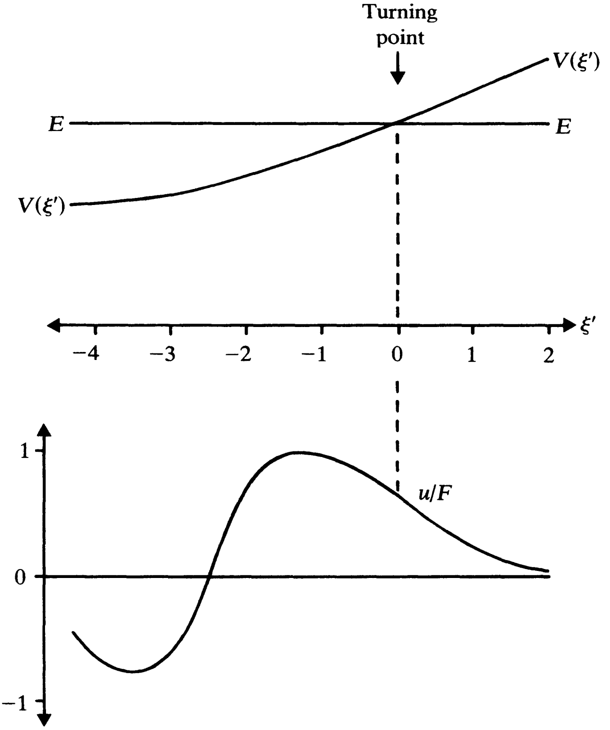

Figure 7.2 A wave function current through a turning point, and obeying the usual boundary condition for an exponential region of infinite extent. The variable $\xi' = |\{2m\hbar^{-2}(\mathrm{d}V/\mathrm{d}x)_0\}^{1/3}|\,x$ is proportional to x but dimensionless.

Bound states When $V(x)$ takes on the shape of a *potential well*, as in figure 7.3, there is a possibility that bound states can be formed.

The partial solution u_+ in figure 7.3 is similar to the solution constructed for figure 7.2: it is valid in the central oscillatory region and in the right-hand turning and exponential regions. Let it be proportional to the scale factor F_+.

The second partial solution u_- is valid only in the left-hand exponential region. In view of the boundary condition as $x \longrightarrow -\infty$, u_- consists of a single term decaying with $-x$, and proportional to the scale factor G_-.

To form a complete solution u_+ and u_- must be extrapolated through the left-hand turning region to a smooth junction at the

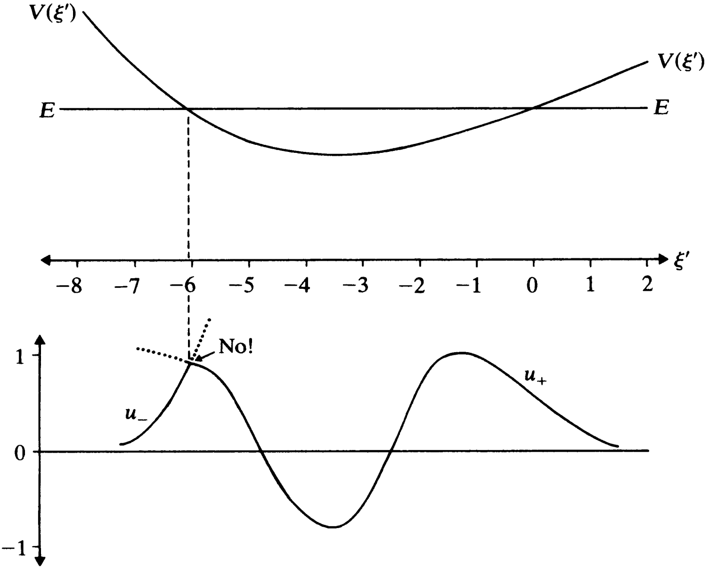

Figure 7.3 An attempt to construct a wave function current through all regions fails because the slopes of u_+ and u_- do not match at the left-hand turning point.

left-hand turning point. Now the ratio F_+/G_- can be adjusted so that u_+ is continuous with u_- at the turning point, but no scope remains for an adjustment to constants which will make $\mathrm{d}u_+/\mathrm{d}x$ continuous with $\mathrm{d}u_-/dx$ there. In general it will not be so,† and figure 7.3 shows an example. The defect is unacceptable, and the only cure is to vary E: if E is increased (reduced) the turning points move further apart (closer together) and the wavelengths of the oscillations are reduced (increased). Either way a legitimate eigenfunction of energy can be obtained (figure 7.4), and further variation of E will find more. As E is increased (decreased) a node in u_+ may appear (disappear) and the sign of G_- or F_+ has to be changed to maintain u_+ continuous with u_-. That is why one eigenfunction in

---

† A more mathematical analysis would note that there are six amplitudes, for two solutions to the TISE in each of three regions of x. There are also six linear homogeneous equations connecting the amplitudes, two to satisfy boundary conditions as $x \rightarrow \pm\infty$ and four to ensure the continuities of u and $\mathrm{d}u/\mathrm{d}x$ at two turning points. There is no non-trivial solution unless the determinant formed from the coefficients of the amplitudes is zero, and that will not generally happen.

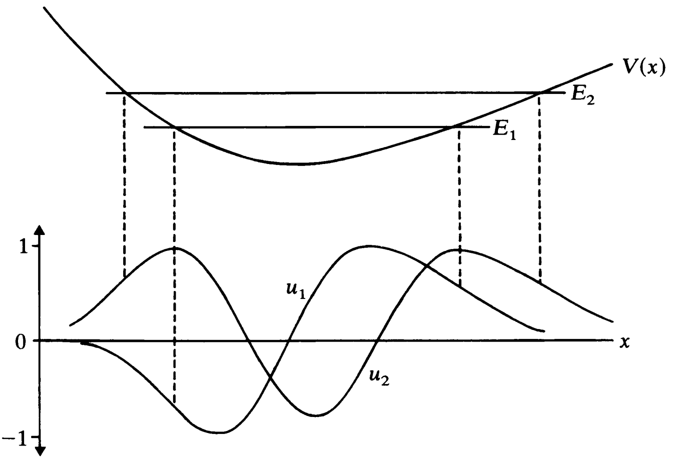

Figure 7.4 Decrease or increase of E in figure 7.3 produces satisfactory energy eigenfunctions u_1 or u_2, which have one or two nodes respectively. Further decrease of E would set up u_0, while further increase would set up u_3, $u_4, \ldots$. The eigenfunctions here have not yet been normalised.

figure 7.4 approaches the $u = 0$ axis from above as $x \rightarrow -\infty$, and the other from underneath.

When the energy eigenfunctions in figure 7.4 have been normalised they are then completely determined apart from a trivial ambiguity in sign.†

When the genesis of the two energy eigenfunctions in figure 7.4 has been fully pondered, some very important facts about bound states in simple one-dimensional potential wells will become obvious. *The energy eigenvalues of these states have a discrete spectrum, and the energy eigenfunctions are non-degenerate. If the eigenvalues in order of increasing energy are E_0, E_1, $E_2, \ldots$, then the corresponding eigenfunctions u_0, u_1, $u_2, \ldots$ have* 0, 1, 2, . . . *nodes*‡ *respectively in the oscillatory region.*

The lowest energy eigenvalue E_0 is bound to lie above the minimum potential energy.§ The difference is called the *zero-point energy.*

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† A particular example of a trivial phase factor, the subject of problem 1.6.

‡ The quantum number conventionally assigned to a bound state is often equal to the number of nodes, or the number of nodes plus one.

§ *Vide* problem 3.9.

The potential $V(x)$ in figure 7.4 was deliberately made asymmetric for the sake of generality. *If* $V(x)$ *had been symmetric, the theorems about parity proved in section* 4 *would have come into force:* $u_0, u_2, u_4, \ldots$ *would have belonged to the parity eigenvalue* $+1$ (*even parity*), *while* $u_1, u_3, u_5, \ldots$ *would have belonged to the parity eigenvalue* -1 (*odd parity*).†

Reflection and transmission at a potential step It is useful to consider next some solutions to the TISE which represent free particle states.

The potential step shown in figure 7.5 is a simplified description of a situation where a very large force to the left acts on the particles over a very small interval of x near $x = 0$.

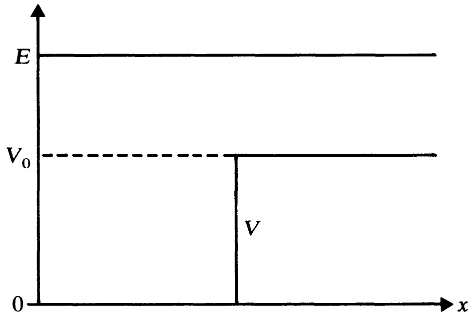

Figure 7.5 A potential step such that $V(x)$ does not exceed E. Both regions are oscillatory, but the wave function discussed in the text is not shown because it is complex, the PCD being non-zero.

For negative x the general solution of the TISE is‡

$$u = A\mathrm{e}^{ikx} + B\mathrm{e}^{-ikx} \tag{7.6}$$

whereas for $E > V_0$ and positive x it is

$$u' = C\mathrm{e}^{ik'x} + D\mathrm{e}^{-ik'x} \tag{7.7}$$

Calculation of the PCD verifies that u describes particle fluxes equal to $(\hbar k/m)\,|A|^2$ to the right and $(\hbar k/m)\,|B|^2$ to the left, and likewise

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† Clearly an eigenfunction of parity with an even (odd) number of nodes must belong to even (odd) parity.

‡ In future the formulae for wave numbers $k(x)$ and absorption coefficients $\kappa(x)$ (lines following equations (7.1) and (7.4)) will usually be taken for granted.

that u' describes particle fluxes equal to $(\hbar k'/m)\,|C|^2$ to the right and $(\hbar k'/m)\,|D|^2$ to the left.

The change in V at $x=0$ is not singular enough to destroy the continuity† of u' with u and of $\mathrm{d}^2u'/\mathrm{d}x^2$ with $\mathrm{d}^2u/\mathrm{d}x^2$. Thus there are two linear homogeneous equations connecting the four constants A, B, C, and D. Since there are no boundary conditions at $x=\pm\infty$, there are two linearly independent solutions‡ for each value of $E>V_0$. By setting $D=0$, one of these can be chosen to represent a state where no particles enter from the right. Now there are three linear homogeneous equations for four constants, and so this solution certainly exists for any $E>V_0$. *The energy eigenvalues of free particle states have a continuous spectrum.*

When the continuity conditions at $x=0$ are put into mathematical form,

$$\left.\begin{aligned} A+B&=C \\ k(A-B)&=k'C \end{aligned}\right\} \tag{7.8}$$

Reflection and transmission coefficients for particles entering from the left and encountering the step may be defined and evaluated in an obvious manner:

$$\left.\begin{aligned} \mathcal{R}&=\frac{(\text{flux to left})_{x<0}}{(\text{flux to right})_{x<0}}=\left|\frac{B}{A}\right|^2=\left(\frac{k'-k}{k'+k}\right)^2 \\ \mathcal{T}&=\frac{(\text{flux to right})_{x>0}}{(\text{flux to left})_{x<0}}=\frac{k'}{k}\left|\frac{C}{A}\right|^2=\frac{4k'k}{(k'+k)^2} \end{aligned}\right\} \tag{7.9}$$

Physically it is satisfying and indeed necessary that $\mathcal{R}$ and $\mathcal{T}$ are real and positive, that

$$\mathcal{R}+\mathcal{T}=1 \tag{7.10}$$

and that $\mathcal{R}\to 0$ when $V_0\to 0$.

If $0<E<V_0$ then equation (7.7) must be altered to read

$$u'=F\mathrm{e}^{-\kappa x}+G\mathrm{e}^{\kappa x} \tag{7.11}$$

The boundary condition $G=0$ is now mandatory, and so there are four constants connected by three linear homogeneous equations. A

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† For finite V_0 the TISE requires only that $\mathrm{d}^2u'/\mathrm{d}x^2$ should be discontinuous with $\mathrm{d}^2u/\mathrm{d}x^2$.

‡ In counting constants and linear homogeneous equations there is no need to worry whether or not the wave function is complex. A complex constant contains two real constants, but then a complex equation provides two real equations.

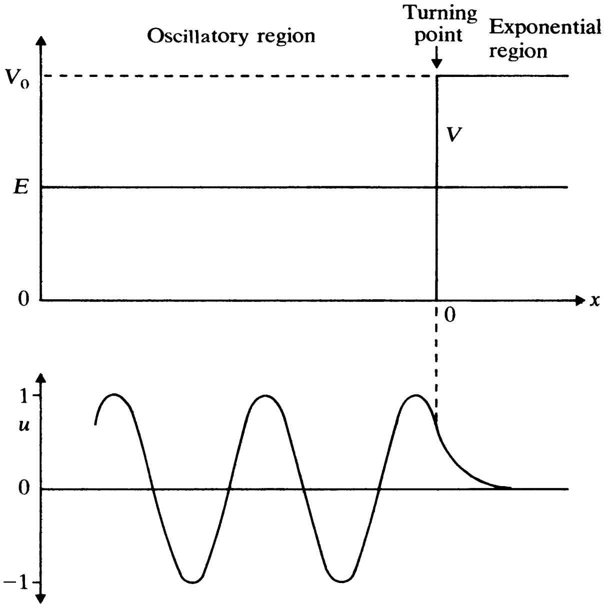

Figure 7.6 A finite potential step such that $V(x)$ does exceed E. The wave function in the oscillatory region is a harmonic standing wave. The wave function can be shown because it is real, the PCD being zero everywhere.

single solution always exists and therefore the spectrum of energy eigenvalues is continuous. Since there is no degeneracy the eigenfunction can be expressed in real form (figure 7.6).† Finally, because the PCD is zero for a real wave function, it may be concluded that $\mathcal{R}=1$, $\mathcal{T}=0$.

Reflection and transmission at a barrier A 'rectangular' barrier of height V_0 and width a is shown in figure 7.7. If $E>V_0$, and if attention is restricted to situations in which all particles enter from the left,

$$\left.\begin{aligned} u &= Ae^{ikx}+Be^{-ikx}, && x<0 \\ u' &= Ce^{ik'x}+De^{-ik'x}, && 0\leqslant x\leqslant a \\ u'' &= Fe^{ikx}, && x>a \end{aligned}\right\} \qquad (7.12)$$

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† *Vide* problem 3.11.

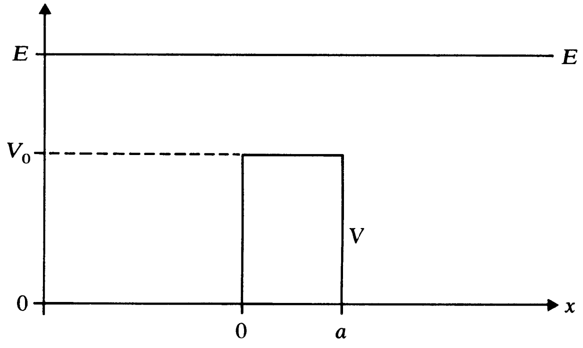

Figure 7.7 A potential barrier of width a and height V_0.

There are five constants connected by four equations, which ensure that the wave function and its derivative are continuous at $x=0$ and $x=a$. The other constants, and in particular F, can therefore be expressed in terms of A alone. A mildly tedious calculation gives the result

$$\frac{F}{A}=\frac{4kk'\mathrm{e}^{\mathrm{i}(\alpha-\beta)}}{(k+k')^2-(k-k')^2\mathrm{e}^{2\mathrm{i}\alpha}} \tag{7.13}$$

where $\alpha \equiv k'a$ and $\beta \equiv ka$. Thus

$$\begin{aligned}\mathcal{T}=\left|\frac{F}{A}\right|^2&=\frac{8k^2k'^2}{k^4+6k^2k'^2+k'^4-(k^2-k'^2)^2\cos 2\alpha}\\&=\left|1+\frac{V_0^2\sin^2\alpha}{4E(E-V_0)}\right|^{-1}\end{aligned} \tag{7.14}$$

The variation of $\mathcal{T}$ for values of V_0/E in the range -1 to $+1$ is shown in figure 7.8. Transmission is complete when V_0/E is zero, for the obvious reason that there is then no barrier. It is also complete whenever $\alpha=n\pi$, with $n=1,2,3,\ldots$: the waves reflected† at $x=0$ and $x=a$ then superpose with opposite sign in the region where $x<0$.

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† Similar effects in optics are exploited when camera lenses are coated to promote transmission of light.

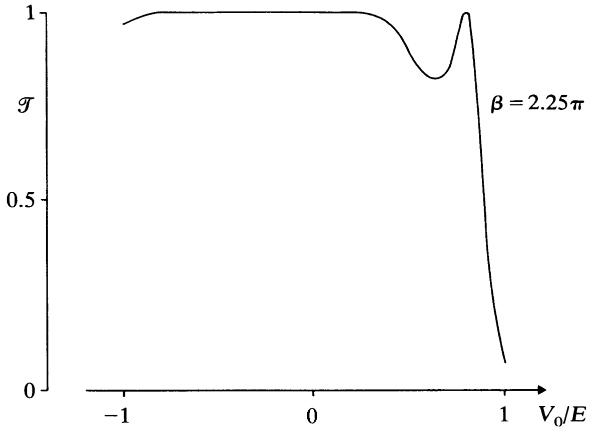

Figure 7.8 Transmission through a potential barrier.

Transmission through a classically impenetrable barrier When $E = V_0$,

$$\mathcal{T} = 1/(1 + \beta^2/4) > 0 \tag{7.15}$$

and so it looks likely that finite transmission will persist when $E > V_0$. That can be checked by working with a trio of equations like equations (7.12), but with $i\kappa$ substituted for k'. The solution will be like equation (7.14), but again $i\kappa$ must be substituted for k'. Then†

$$\mathcal{T} = \left\{1 + \frac{V_0^2 \sinh^2(\kappa a)}{4E(V_0 - E)}\right\}^{-1} \tag{7.16}$$

and so

$$\mathcal{T} \approx 16E(V_0 - E)V_0^{-2}e^{-2\kappa a}, \qquad \kappa a \gg 1 \tag{7.17}$$

The most important factor here is the exponential $e^{-2\kappa a}$, which makes $\mathcal{T}$ extremely sensitive to the value of κa. This is a feature of the theory of α-decay that was developed by Gurney and Condon, and independently by Gamow, in 1928. The α-particle has to penetrate the Coulomb barrier, outside the range of nuclear forces but inside the radius at which it is classically free. The decay lifetime is indeed a very sensitive function of the α-particle energy (Geiger–Nuttall relation).

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† Note that $\sin(ix) = i \sinh x$.

Particle trapped between impenetrable walls An understanding of the behaviour of wave functions at potential steps makes it possible to discuss the simplest of all bound state problems, that of the trapped particle, and the results exemplify very well the earlier exposition of the general properties of bound states.

The appropriate potential is illustrated in figure 7.9. With the two walls the particle is free to move and $V(x)=0$, while at each wall $(x=\pm L/2)$ there is an infinite potential step. There is no transmission to the region outside either wall,† and so two boundary conditions are imposed on a general energy eigenfunction u_s:

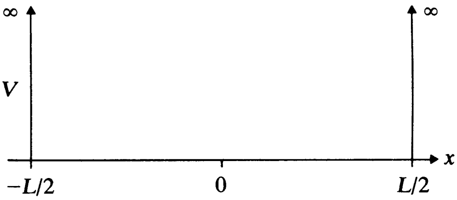

Figure 7.9 Potential for an infinitely deep particle trap.

$$u_s(x)=0, \qquad x=\pm L/2 \tag{7.18}$$

The energy operator in the region between the walls is

$$\hat{H}=\hat{T}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, \qquad -L/2\leqslant x\leqslant L/2 \tag{7.19}$$

and the TISE is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u_s}{\mathrm{d}x^2}=E_su_s, \qquad -L/2\leqslant x\leqslant L/2 \tag{7.20}$$

Obviously the solutions are harmonic and depend as usual on a wavenumber k_s. Since this is a bound state problem a representation in terms of standing rather than travelling waves will prove to be most convenient:

$$u_s=A_s\cos(k_sx)+B_s\sin(k_sx) \tag{7.21}$$

Further specialisation is introduced by the fact that the potential in figure 7.9 is symmetric about $x=0$, so that u_s should‡ have even

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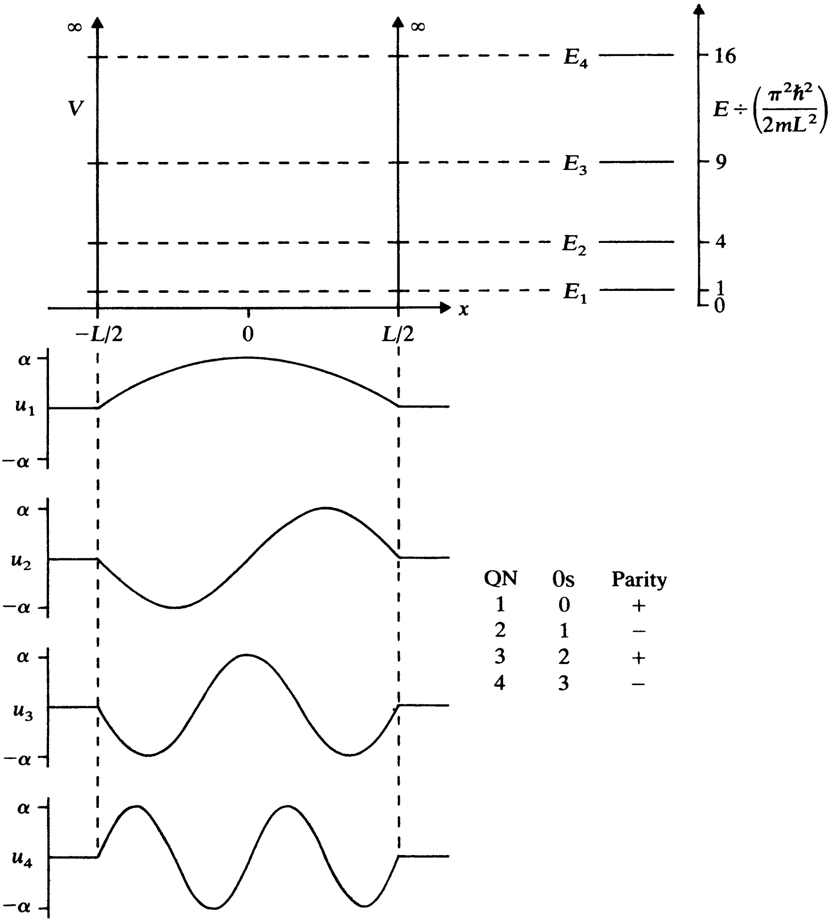
† *Vide* problem 3.11.

‡ There is no question of degeneracy in this problem.

parity ($B_s = 0$) or odd parity ($A_s = 0$). Thus, when the boundary conditions (7.18) are taken into account, and the eigenfunctions are normalised,

$$u_s = \left\{\begin{array}{ll} (2/L)^{1/2}\cos(\pi s x/L), & s = 1, 3, 5, \ldots \\ (2/L)^{1/2}\sin(\pi s x/L), & s = 2, 4, 6, \ldots \end{array}\right\} \tag{7.22}$$



QN	0s	Parity
1	0	+
2	1	−
3	2	+
4	3	−

Figure 7.10 Unified diagram for the energy eigenstates of a particle in an infinitely deep trap. The potential energy (top left), energy eigenvalues (top right), energy eigenfunctions (bottom left), the quantum numbers, zeros, and parities (bottom right) are shown. The dashed lines are related to the turning points of the classical motion. The ordinate scale for the eigenfunctions is set by $\alpha \equiv (2/L)^{1/2}$.

The usual relation between E_s and k_s gives†

$$E_s = \hbar^2 k_s^2/2m = \pi^2\hbar^2 s^2/2mL^2 \tag{7.23}$$

A bound state problem in quantum mechanics is apt to give rise to three different types of diagram: a plot of $V(x)$ against x (as in figure 7.9), a display in which the eigenenergies are drawn as horizontal lines against a vertical energy scale, and plots of some of the $u_s(x)$ against x. In figure 7.10 all three are presented in a unified form which emphasises the connections between them. The horizontal dashed lines show how the eigenenergies are related to the turning points, and the vertical dashed lines are reminders that the latter are the points at which d^2u_s/dx^2 changes sign.

The available space at the bottom right accommodates information on the quantum numbers (QN), numbers of nodes (0s) and parities (Π).

§8 The linear harmonic oscillator

Energy eigenvalues Classically a particle which is subjected to a restoring force $-(m\omega^2)x$ oscillates about $x=0$ at the frequency $\omega/2\pi$. The restoring force can be described by the potential energy $V(x) = m\omega^2x^2/2$ (figure 8.1, top left) and in quantum mechanics this appears in the operator which represents the total energy,

$$\hat{H} = \hat{T} + \hat{V} = \frac{1}{2m}\hat{p}^2 + \frac{m\omega^2}{2}\hat{x}^2 \tag{8.1}$$

The energy eigenvalues E_n can of course be obtained by substituting the appropriate operators into Schrödinger's equation $\hat{H}u_n = E_n u_n$, but the resulting differential equation requires to be solved in series. This tiresome procedure can be avoided by attacking the problem in a more indirect way, which makes use of simple non-commutative operator algebra.

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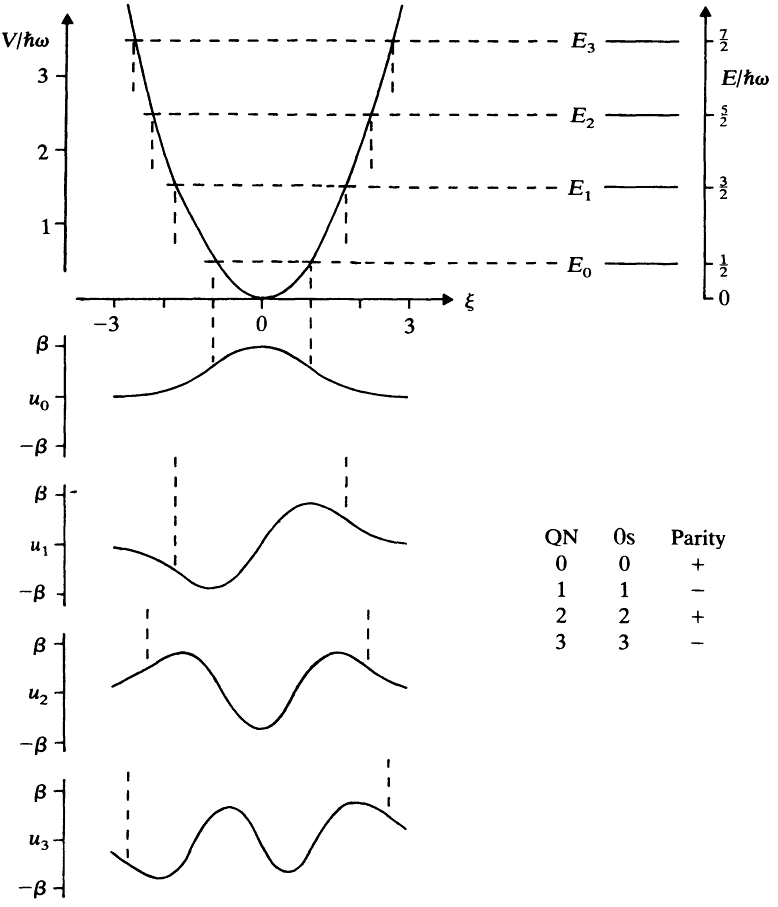
† An analogous problem in classical physics is provided by a stretched string clamped at both ends, as in a guitar. The eigenfrequencies there are proportional to the harmonic number s, and not s^2 as they are here. The difference arises entirely from the different dispersion relation (equation (1.3) and subsequent footnote).



QN	0s	Parity
0	0	+
1	1	−
2	2	+
3	3	−

Figure 8.1 Unified diagram for the energy eigenstates of a particle in a linear harmonic oscillator potential. The ordinate scale for the eigenfunctions is set by $\beta \equiv (m\omega/\pi\hbar)^{1/4}$. Note the strong family resemblance to figure 7.10.

It is convenient to define two dimensionless operators $\hat{a}$ and $\hat{a}^*$ by the equations

$$\left.\begin{aligned} \hat{a} &= \frac{1}{\sqrt{2}}\{i(\hbar m\omega)^{-1/2}\hat{p} + (m\omega/\hbar)^{1/2}\hat{x}\} \\ \hat{a}^* &= \frac{1}{\sqrt{2}}\{-i(\hbar m\omega)^{-1/2}\hat{p} + (m\omega/\hbar)^{1/2}\hat{x}\} \end{aligned}\right\} \tag{8.2}$$

Since $\hat{p}$ and $\hat{x}$ are Hermitian it can be seen that $\langle\psi_1 \mid \hat{a}\psi_2\rangle = \langle\hat{a}^*\psi_1 \mid \psi_2\rangle$ and $\langle\psi_1 \mid \hat{a}^*\psi_2\rangle = \langle\hat{a}\psi_1 \mid \psi_2\rangle$ for any two wave functions ψ_1 and ψ_2. Thus the operators $\hat{a}$ and $\hat{a}^*$ are not Hermitian; they do not represent observables and the symmetrical notation (equation (4.12)) for their matrix elements is not appropriate. However $\hat{a}\hat{a}^*$ and $\hat{a}^*\hat{a}$ are Hermitian operators, because they can be expressed as real functions of $\hat{H}$,

$$\left.\begin{aligned} \hat{a}\hat{a}^* &= \frac{1}{\hbar\omega}\left(\frac{1}{2m}\hat{p}^2 + \frac{m\omega^2}{2}\hat{x}^2\right) - \frac{i}{2\hbar}[\hat{x}, \hat{p}] = \frac{\hat{H}}{\hbar\omega} + \frac{1}{2} \\ \hat{a}^*\hat{a} &= \frac{1}{\hbar\omega}\left(\frac{1}{2m}\hat{p}^2 + \frac{m\omega^2}{2}\hat{x}^2\right) + \frac{i}{2\hbar}[\hat{x}, \hat{p}] = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2} \end{aligned}\right\} \qquad (8.3)$$

and so

$$\hat{H} = (\hat{a}\hat{a}^* - \tfrac{1}{2})\hbar\omega = (\hat{a}^*\hat{a} + \tfrac{1}{2})\hbar\omega; \qquad [\hat{a}, \hat{a}^*] = 1 \qquad (8.4)$$

These equations may be used to investigate the commutation relation between $\hat{H}$ and $\hat{a}$,

$$\begin{aligned} \hat{H}\hat{a} &= (\hat{a}\hat{a}^*\hat{a} - \tfrac{1}{2}\hat{a})\hbar\omega \\ &= \hat{a}(\hat{a}^*\hat{a} - \tfrac{1}{2})\hbar\omega = \hat{a}(\hat{H} - \hbar\omega) \end{aligned} \qquad (8.5)$$

If both sides of this equation are applied to an energy eigenfunction u_n belonging to the eigenvalue E_n, then $\hat{H}(\hat{a}u_n) = \hat{a}(\hat{H} - \hbar\omega)u_n = (E_n - \hbar\omega)(\hat{a}u_n)$. *Clearly $\hat{a}u_n$ is also an energy eigenfunction, but it belongs to the eigenvalue $E_n - \hbar\omega$; the effect of $\hat{a}$ on u_n is to produce a new eigenfunction whose energy is lower by $\hbar\omega$. This amount of energy is called a quantum, and $\hat{a}$ is referred to as the quantum destruction operator.* Similarly,

$$\begin{aligned} \hat{H}\hat{a}^* &= (\hat{a}^*\hat{a}\hat{a}^* + \tfrac{1}{2}\hat{a}^*)\hbar\omega \\ &= \hat{a}^*(\hat{a}\hat{a}^* + \tfrac{1}{2})\hbar\omega = \hat{a}^*(\hat{H} + \hbar\omega) \end{aligned} \qquad (8.6)$$

and so $\hat{H}(\hat{a}^*u_n) = (E_n + \hbar\omega)(\hat{a}^*u_n)$. *The effect of $\hat{a}^*$ on u_n is to produce a new eigenfunction whose energy is higher by $\hbar\omega$, and $\hat{a}^*$ is referred to as the quantum creation operator.*

The energy eigenvalues cannot be negative since $\hat{H}$ is the sum of the squares of Hermitian operators. There must exist an eigenfunction u_0 belonging to the minimum energy E_0, and when the quantum destruction operator is used the equation $\hat{H}(\hat{a}u_0) = (E_0 - \hbar\omega)(\hat{a}u_0)$ can only be satisfied by the disappearance of $\hat{a}u_0$. Thus,

$$\hat{a}u_0 = 0 \qquad (8.7)$$

and with the help of equation (8.3),

$$\begin{aligned}(\hat{H}-\tfrac{1}{2}\hbar\omega)u_0 &= \hbar\omega\hat{a}^*(\hat{a}u_0)=0\\ \hat{H}u_0 &= \tfrac{1}{2}\hbar\omega u_0 \end{aligned} \tag{8.8}$$

so that $E_0=\frac{1}{2}\hbar\omega$. Successive applications of the quantum destruction operator to any u_n must eventually reduce it to the form u_0, since the production of negative energy eigenvalues can be avoided in no other way. If n applications are required, then

$$E_n=(n+\tfrac{1}{2})\hbar\omega \tag{8.9}$$

where n is an integer (figure 8.1, top right)

The minimum energy $\hbar\omega/2$ is of course the zero-point energy. An oscillator in the nth stationary state is said to have n quanta, the zero-point energy being ignored.

The relationship (8.9) between the classical frequency ω and the quantised energy step $\hbar\omega$ is just the one brilliantly though indirectly conceived by Planck on 7 October 1900. He was thinking of 'resonators' in the walls of a cavity and coupled to the electromagnetic field inside, and his idea resolved serious difficulties that had appeared in the theory of black body radiation.

Energy eigenfunctions The explicit expressions for the quantum destruction and creation operators can be obtained by substituting $\hat{p}=-i\hbar\,\partial/\partial x$ in equation (8.2),

$$\left.\begin{aligned}\hat{a} &= \frac{1}{\sqrt{2}}\{(\hbar/m\omega)^{1/2}\frac{\partial}{\partial x}+(m\omega/\hbar)^{1/2}x\}=\frac{1}{\sqrt{2}}\left(\frac{\partial}{\partial\xi}+\xi\right)\\ \hat{a}^* &= \frac{1}{\sqrt{2}}\left(-\frac{\partial}{\partial\xi}+\xi\right)\end{aligned}\right\} \tag{8.10}$$

where $\xi=+(m\omega/\hbar)^{1/2}x$. Thus equation (8.7) for u_0, and its normalised solution, may be written

$$\frac{\mathrm{d}u_0}{\mathrm{d}\xi}=-\xi u_0, \qquad u_0=\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\mathrm{e}^{-\xi^2/2} \tag{8.11}$$

The other eigenfunctions can be obtained from u_0 by successive applications of the quantum creation operator; obviously u_n is proportional to $(\hat{a}^*)^n u_0$. The normalisation may be kept in order by observing that

$$\begin{aligned}\langle \hat{a}^* u_s \mid \hat{a}^* u_s\rangle &= \langle u_s \mid \hat{a}\hat{a}^* u_s\rangle \\ &= \left\langle u_s \,\middle|\, \left(\frac{\hat{H}}{\hbar\omega}+\frac{1}{2}\right) u_s\right\rangle = (s+1)\langle u_s \mid u_s\rangle \qquad (8.12)\end{aligned}$$

so that if u_s is normalised so is $u_{s+1} = (s+1)^{-1/2}\hat{a}^* u_s$. Therefore,

$$\begin{aligned} u_n &= (1\,.\,2\,.\,3\ldots n)^{-1/2}(\hat{a}^*)^n u_0 \\ &= (2^n n!)^{-1/2}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\left(-\frac{\mathrm{d}}{\mathrm{d}\xi}+\xi\right)^n \mathrm{e}^{-\xi^2/2} \qquad (8.13)\end{aligned}$$

This expression may be simplified to some extent by means of the operator identities

$$\left.\begin{aligned} -\frac{\mathrm{d}}{\mathrm{d}\xi}+\xi &= -\mathrm{e}^{\xi^2/2}\frac{\mathrm{d}}{\mathrm{d}\xi}\mathrm{e}^{-\xi^2/2} \\ \left(-\frac{\mathrm{d}}{\mathrm{d}\xi}+\xi\right)^n &= (-1)^n \mathrm{e}^{\xi^2/2}\left(\frac{\mathrm{d}}{\mathrm{d}\xi}\right)^n \mathrm{e}^{-\xi^2/2}\end{aligned}\right\} \qquad (8.14)$$

so that

$$\begin{aligned} u_n &= (2^n n!)^{-1/2}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\mathrm{e}^{-\xi^2/2}\left\{(-1)^n \mathrm{e}^{\xi^2}\left(\frac{\mathrm{d}}{\mathrm{d}\xi}\right)^n \mathrm{e}^{-\xi^2}\right\} \\ &= (2^n n!)^{-1/2}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\mathrm{e}^{-\xi^2/2}H_n(\xi) \qquad (8.15)\end{aligned}$$

Table 8.1 Stationary state wave functions of a linear harmonic oscillator. The last bracket in each is the Hermite polynomial

n	u_n
0	$\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\mathrm{e}^{-\xi^2/2}(1)$
1	$(2)^{-1/2}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\mathrm{e}^{-\xi^2/2}(2\xi)$
2	$(8)^{-1/2}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\mathrm{e}^{-\xi^2/2}(4\xi^2-2)$
3	$(48)^{-1/2}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\mathrm{e}^{-\xi^2/2}(8\xi^3-12\xi)$

where the function in the braces defines $H_n(\xi)$, the Hermite polynomial of degree n.†

The first few eigenfunctions are given in table 8.1 and illustrated in figure 8.1 (bottom left). The peaks in the $n=2$ and $n=3$ eigenfunctions show clearly the approximate $k^{-1/2}$ factor in the amplitude (figure 7.1).

Parity Clearly u_0 has even parity because it is an even function of ξ, or x. In general the parity is even if n is even, and odd if n is odd.‡

Zero-point energy and the uncertainty principle When the oscillator is in the lowest energy state,

$$\langle H\rangle=\frac{\hbar\omega}{2}=\langle V+T\rangle=\frac{m\omega^2}{2}\langle x^2\rangle+\frac{1}{2m}\langle p^2\rangle \tag{8.16}$$

Now if a, b, c are any three real numbers such that $a+b=c$, then $ab\leqslant c^2/4$. Application of this inequality to $m\omega^2\langle x^2\rangle$, $(1/m)\langle p^2\rangle$, and $\hbar\omega$ gives

$$\Delta x\,\Delta p=\surd(\langle x^2\rangle\langle p^2\rangle)\leqslant\hbar/2 \tag{8.17}$$

since $\langle x\rangle$ and $\langle p\rangle=(\mathrm{d}/\mathrm{d}t)\langle x\rangle$ are obviously zero. This equation may be compared with the uncertainty principle, $\Delta x\,\Delta p\geqslant\hbar/2$, to see that in fact $\Delta x\,\Delta p=\hbar/2$. Obviously the zero-point energy could not have been any lower than $\hbar\omega/2$ without violating the uncertainty principle.

Matrix elements of the destruction and creation operators The matrix elements of $\hat{a}$ and $\hat{a}^*$ will be of interest later. They are readily calculated from the relation $u_{s+1}=(s+1)^{-1/2}\hat{a}^*u_s$,

$$\begin{aligned}\langle u_s\mid \hat{a}u_n\rangle&=\langle \hat{a}^*u_s\mid u_n\rangle=(s+1)^{1/2}\langle u_{s+1}\mid u_n\rangle\\&=(s+1)^{1/2}\delta_{s+1,n}=n^{1/2}\delta_{s,n-1}\end{aligned} \tag{8.18}$$

and,

$$\langle u_s\mid a^*u_n\rangle=(n+1)^{1/2}\langle u_s\mid u_{n+1}\rangle=(n+1)^{1/2}\delta_{s,n+1} \tag{8.19}$$

Finally it may be noted that $(\hat{a}^*\hat{a})u_n=\{(\hat{H}/\hbar\omega)-\tfrac{1}{2}\}u_n=nu_n$. The Hermitian operator $\hat{a}^*\hat{a}$ represents an observable whose eigenvalues are the number of quanta which the oscillator can have, and $\hat{a}^*\hat{a}$ is therefore called the *number operator.*

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† The leading term in $H_n(\xi)$ is readily seen to be proportional to ξ^n.

‡ *Vide* problem 3.13.

Problems

3.1 Show that the eigenfunctions of momentum and energy given by the second of equations (6.5) form an orthonormal set. In mathematical terms the required result is

$$\langle u_r(x) \mid u_s(x)\rangle = \delta_{rs}$$

3.2 For free particles show that the density of states in energy space is given by

$$\frac{\delta N}{\delta E_s} = \frac{L}{2\pi h}\left(\frac{m}{2E}\right)^{1/2}$$

[*Hint:* Use the relation

$$\frac{\delta N}{\delta E_s} = \frac{\delta N}{\delta p_s}\frac{\delta p_s}{\delta E_s}$$

together with equations (6.8).]

3.3 If ψ is expanded in terms of the normalised momentum eigenfunctions identified before equation (6.22),

$$\psi = \int_{-\infty}^{\infty} c(p)u_p\, \mathrm{d}p = (2\pi\hbar)^{-1/2}\int_{-\infty}^{\infty} c(p)\mathrm{e}^{ipx/\hbar}\, \mathrm{d}p$$

According to equation (6.19),

$$c(p) = (2\pi\hbar)^{-1/2}\int_{-\infty}^{\infty} \psi \mathrm{e}^{-ipx/\hbar}\mathrm{d}x$$

Check that this pair of equations exemplifies Fourier's theorem, which states that if

$$f(x) = (2\pi)^{-1/2}\int_{-\infty}^{\infty} g(k)\mathrm{e}^{ikx}\,\mathrm{d}k$$

then

$$g(k) = (2\pi)^{-1/2}\int_{-\infty}^{\infty} f(x)\mathrm{e}^{-ikx}\,\mathrm{d}x$$

Note that $f(x)$ is called the Fourier transform of $g(k)$, and vice versa.

3.4 The process of going over in one dimension from an expansion in discrete momentum eigenfunctions to one in continuous momentum eigenfunctions can be summarised as follows:

$$\lim_{L\to\infty} \sum_s L^{-1} \to \int_{-\infty}^{\infty} (2\pi\hbar)^{-1}\,\mathrm{d}p$$

Understand this statement. [*Hint:* Write out the expansion of a general ψ in terms of normalised discrete momentum eigenfunctions, with c_s expressed as a scalar product. Repeat in terms of normalised continuous momentum eigenfunctions, with $c(p)$ similarly expressed.]

3.5 In equation (6.10) a wave function $\psi(x, 0)$ representing a particular wave packet was given. Subsequently $\psi(x, 0)$ was expanded in momentum wavefunctions

$$\psi(x, 0) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{\infty} c(p)\mathrm{e}^{\mathrm{i}px/\hbar}\,\mathrm{d}p$$

where $c(p)$ was expressed in the second of equations (6.20).

Now momentum eigenfunctions are also energy eigenfunctions for free particles, and so the TDSE can be solved at once by extending equation (3.6) to integral form:

$$\psi(x, t) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{\infty} c(p)\mathrm{e}^{\mathrm{i}px/\hbar}\mathrm{e}^{-\mathrm{i}p^2t/2\hbar m}\,\mathrm{d}p$$

Carry out the integration with the help of the appendix, equation (3), and show that

$$\psi(x, t) = \pi^{-1/4}a^{1/2}\{1 + (i\hbar a^2t/m)\}^{-1/2} \times \exp\left\{\frac{-a^2x^2/2 + ik'x - (i\hbar k'^2t/2m)}{1 + (i\hbar a^2t/m)}\right\}$$

[*Hint:* It is tidier to work with $k' = p/\hbar$ as the variable of integration. *Comment:* Note how $\psi(x, t)$ goes back to $\psi(x, 0)$ when $t = 0$.]

3.6 Form the PPD from $\psi(x, t)$ in problem 3.5 and verify equations (6.26).

3.7 Where k is constant equation (7.6) can be written

$$u = A \cos\left(\int_0^x k \, dx\right) + B \sin\left(\int_0^x k \, dx\right)$$

Where k varies slowly show that the appropriate generalisation is

$$u = A\left(\frac{k_0}{k}\right)^{1/2} \cos\left\{\int_0^x k(x) \, dx\right\} + B\left(\frac{k_0}{k}\right)^{1/2} \sin\left\{\int_0^x k(x) \, dx\right\}$$

and certainly not

$$u = A\left(\frac{k_0}{k}\right)^{1/2} \cos\{k(x)x\} + B\left(\frac{k_0}{k}\right)^{1/2} \sin\{k(x)x\}$$

Ignore the amplitude factors $(k_0/k)^{1/2}$ in this discussion.

3.8 The distorted unidirectional travelling wave

$$u = (k_0/k)^{1/2} \exp\left\{i \int_{x_0}^x k(x) \, dx\right\}$$

is said in section 7 to be an approximate solution to the TISE where $k(x)$ varies slowly. Check this by direct differentiation.

According to equation (3.10) the PCD in a stationary state must conform to the equation

$$\nabla \cdot \mathbf{j} = 0$$

and in one dimension the PCD must therefore be constant. Check that u is satisfactory from this point of view, and hence justify the $k^{-1/2}$ factor in the amplitude. [*Hint:* Use the condition $|dk/dx| \ll k^2$ at each differentiation.]

3.9 If the lowest bound state in a potential well $V(x)$ has the eigenfunction u_0 and the energy E_0, show that the zero-point energy is

$$E_0 - V_{\min} = \int_{-\infty}^{\infty} \left[\{V(x) - V_{\min}\} |u_0|^2 + \frac{\hbar^2}{2m} \left| \frac{\mathrm{d}u_0}{\mathrm{d}x} \right|^2 \right] \mathrm{d}x$$

Explain qualitatively why the first term must be greater than or equal to zero, and the second greater than zero. [*Hint:* Express E_0 in terms of $\langle V \rangle$ and $\langle T \rangle$, and use the hermiticity of $\hat{p}$.]

3.10 Suppose that the turning points in problem 3.9 are a distance $2d$ apart, and that u_0 can be approximated by a Gaussian function. Show with the help of the appendix, equation (2), that

$$\int_{-\infty}^{\infty} \frac{\hbar^2}{2m} \left| \frac{\mathrm{d}u_0}{\mathrm{d}x} \right|^2 \mathrm{d}x \approx \hbar^2/4md^2$$

Relate this result to the uncertainty principle, equation (5.22). [*Hint:* Arrange that a normalised Gaussian function has $\mathrm{d}^2u_0/\mathrm{d}x^2 = 0$ at $x = \pm d$. For the final part recall that $(\Delta p)^2 = \langle p^2 \rangle - \langle p \rangle^2$.]

3.11 Show that the wave function in figure 7.6 may be expressed in the form

$$u = A' \cos(kx + \phi), \qquad x \leqslant 0$$
$$u' = A' \cos \phi \, \mathrm{e}^{-\kappa x}, \qquad x > 0$$

with

$$\tan \phi = \frac{\kappa}{k}$$

If the potential step is infinitely high show further that $\kappa/k \rightarrow \infty$ and $u \rightarrow 0$ at the barrier, while $u' \rightarrow 0$ there and at all points to the right. [*Comment*: In the last part of the problem the gradient of the wave function is not continuous at $x = 0$. This exceptional behaviour arises because the potential is infinite.]

3.12 Find the MPD for a particle trapped between rigid walls and in its ground state. [*Comment*: Recall the discussions below equation (1.8).]

3.13 Show that the parity operator $\hat{\Pi}$ and the quantum destruction operator $\hat{a}^*$ (equations (8.10)) anticommute, that is

$$\hat{\Pi}\hat{a}^* = -\hat{a}^*\hat{\Pi}$$

Hence show that a linear harmonic oscillator in the state belonging to the eigenenergy $(n+\frac{1}{2})h\omega$ also belongs to the parity $(-1)^n$.

3.14 Use classical mechanics to consider a particle subject to a restoring force proportional to its displacement, and so acting as a linear harmonic oscillator. If the amplitude is A, find an expression for the time-averaged probability of finding the particle between x and $x+\delta x$, and plot it as a function of x.

Use quantum mechanics, and a computer, to make a similar plot of the PPD when the particle is in its 10th eigenstate. Hence show the general correspondence of the two plots when the turning points are made to coincide:

$$(n+\tfrac{1}{2})h\omega = m\omega^2 A^2/2$$

[*Hint:* The Hermite polynominal of degree 10 can be looked up in the *Handbook of Mathematical Functions* (ed. M. Abramowitz and I. A. Stegun), Dover Publications, New York, 1965.]

3.15 A wave packet moves along at the group velocity $d\omega/dk$. Recall the dispersion relation (equation (1.3)) and so check the remarks in the text under the first equation (6.25). [*Comment:* this is a very easy and beautiful example of the correspondence principle.]

4

Three-dimensional applications

§9 Free particles

Stationary states For free particles in three dimensions the total energy operator is

$$\hat{H} = \hat{T} = -\frac{\hbar^2}{2m}\nabla^2 \tag{9.1}$$

In Cartesian coordinates a stationary state wave function $u_{\mathbf{k}}$ belonging to the energy $E_{\mathbf{k}}$ obeys the TISE

$$-\frac{\hbar^2}{2m}\nabla^2 u_{\mathbf{k}} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)u_{\mathbf{k}} = E_{\mathbf{k}}u_{\mathbf{k}} \tag{9.2}$$

It is convenient to restrict attention to a cube of volume L^3, bounded by the planes $x = \pm L/2$, $y = \pm L/2$, $z = \pm L/2$. The operators $\hat{\mathbf{p}}$ and $\hat{T}$ will be kept Hermitian by means of the periodic boundary conditions given in equation (4.7).

The variables may be separated by the substitution $u_{\mathbf{k}}(x, y, z) = f(x)g(y)h(z)$; after division by fgh the Schrödinger equation becomes

$$\frac{\hbar^2}{2mf}\frac{\partial^2 f}{\partial x^2}+\frac{\hbar^2}{2mg}\frac{\partial^2 g}{\partial y^2}+\frac{\hbar^2}{2mh}\frac{\partial^2 h}{\partial z^2}+E_{\mathbf{k}}=0 \tag{9.3}$$

The first term is the only one which depends on x, and so the equation can only be correct for all x if this term is separately equal to a constant, which may be written in the form $-\hbar^2 k_x^2/2m$. Then,

$$\frac{d^2 f}{dx^2} + k_x^2 f = 0 \tag{9.4}$$

Similar constants k_y and k_z may be defined so that

$$\frac{d^2 g}{dy^2} + k_y^2 g = 0; \qquad \frac{d^2 h}{dz^2} + k_z^2 h = 0 \tag{9.5}$$

and equation (9.3) is satisfied if $(\hbar^2/2m)(k_x^2 + k_y^2 + k_z^2) = E_\mathbf{k}$. Solutions for these three equations are readily found and normalised:

$$f = L^{-1/2} e^{ik_x x}, \qquad g = L^{-1/2} e^{ik_y y}, \qquad h = L^{-1/2} e^{ik_z z} \tag{9.6}$$

Now $\mathbf{k}$ may be defined as the vector whose components are k_x, k_y, k_z; the stationary state wave functions may then be written in the form

$$\left.\begin{array}{ll} u_\mathbf{k} = fgh = L^{-3/2} e^{i\mathbf{k}.\mathbf{r}}; & E_\mathbf{k} = \dfrac{\hbar^2 k^2}{2m} \\ k_x = 2\pi s_x/L, & s_x = 0, \pm 1, \pm 2, \ldots \\ k_y = 2\pi s_y/L, & s_y = 0, \pm 1, \pm 2, \ldots \\ k_z = 2\pi s_z/L, & s_z = 0, \pm 1, \pm 2, \ldots \end{array}\right\} \tag{9.7}$$

where the conditions on k_x, k_y, k_z ensure that the periodic boundary conditions are satisfied.

The wave function associated with the vector $\mathbf{k}$ and the energy $E_\mathbf{k}$ is also an eigenfunction of the momentum belonging to the eigenvalue $\mathbf{p}_\mathbf{k} = \hbar\mathbf{k}$:

$$\hat{\mathbf{p}} u_\mathbf{k} = -i\hbar\nabla(L^{-3/2} e^{i\mathbf{k}.\mathbf{r}}) = \hbar\mathbf{k}(L^{-3/2} e^{i\mathbf{k}.\mathbf{r}}) = \hbar\mathbf{k} u_\mathbf{k} \tag{9.8}$$

This is only possible because the momentum and total energy for free particles commute, as they did in one dimension.

Density of states To every set of integers s_x, s_y, s_z there corresponds a distinct stationary state. Now the relations between† p_x, k_x, and s_x are precisely the same as those between p_s, k_s, and s in one

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† From this point the suffix '$\mathbf{k}$' on $E_\mathbf{k}$ and $\mathbf{p}_\mathbf{k}$ will often be left implicit.

dimension, and therefore equation (6.8) can be taken over to see that the number of p_x eigenvalues in the interval δp_x is $(L/2\pi\hbar)\delta p_x$.

Similarly the numbers of p_y and p_z eigenvalues in the intervals δp_y and δp_z are $(L/2\pi\hbar)\delta p_y$ and $(L/2\pi\hbar)\delta p_z$ respectively. The number of eigenvalues of $\mathbf{p}$ where the three components lie in the intervals δp_x, δp_y, δp_z is the product,

$$\delta N = \left(\frac{L}{2\pi\hbar}\right)^3 \delta p_x\, \delta p_y\, \delta p_z \tag{9.9}$$

A momentum space may be constructed in which p_x, p_y, p_z are Cartesian coordinates. In this space $\delta p_x\, \delta p_y\, \delta p_z$ is an elementary volume, and equation (9.9) shows that there are simply $(L/2\pi\hbar)^3$ free particle stationary states per unit volume.

Later on the number of states in the energy interval δE will be required. Since $E = (\hbar^2 k^2/2m) = p^2/2m$, the corresponding momentum interval is $\delta p = (\mathrm{d}p/\mathrm{d}E)\delta E = (m/p)\, \delta E$. If the direction of $\mathbf{p}$ is left unspecified the associated momentum space is a spherical shell of radius p and thickness δp. The volume of this is $4\pi p^2\, \delta p = 4\pi mp\, \delta E$ and therefore

$$\left.\begin{aligned} \delta N &= \left(\frac{L}{2\pi\hbar}\right)^3 4\pi mp\, \delta E = \frac{L^3 mp}{2\pi^2\hbar^3}\, \delta E \\ \frac{\delta N}{\delta E} &= \rho_E = \frac{L^3 mp}{2\pi^2\hbar^3} \end{aligned}\right\} \tag{9.10}$$

The density of states is of course reduced by the factor $\mathrm{d}\omega/4\pi$ if $\mathbf{p}$ is required to point into an elementary solid angle $\mathrm{d}\omega$ in some particular direction.

Momentum distribution The wave functions given in equations (9.7) form a complete orthonormal set of momentum eigenfunctions, which can be used to find the momentum probability distribution in a general state represented by $\psi(\mathbf{r})$. If

$$\psi(\mathbf{r}) = \sum_k c_{\mathbf{k}} u_{\mathbf{k}}$$

then

$$c_{\mathbf{k}} = \langle L^{-3/2} e^{i\mathbf{p}.\mathbf{r}/\hbar} \mid \psi\rangle \tag{9.11}$$

since $\mathbf{p} = \hbar\mathbf{k}$. Obviously L must be chosen very large so that ψ is negligibly small at distances of the order of $L/2$ from the origin; the exact limits of integration will turn out to be unimportant.

The overall probability of finding the momentum with components in the intervals δp_x, δp_y, δp_z is $|c_{\mathbf{k}}|^2\,\delta N = (L/2\pi\hbar)^3\,|c_{\mathbf{k}}|^2\,\delta p_x\,\delta p_y\,\delta p_z$. This is equal to $|c(\mathbf{p})|^2\,\delta p_x\,\delta p_y\,\delta p_z$ if $c(\mathbf{p})$ is defined by

$$c(\mathbf{p}) = \langle (2\pi\hbar)^{-3/2} e^{i\mathbf{p}.\mathbf{r}/\hbar} \mid \psi \rangle \tag{9.12}$$

The result here is independent of L, which may thus be allowed to become infinite so that the eigenvalues of $\mathbf{p}$ go over to a continuum.

Momentum with continuous eigenvalues† As in one dimension, $c(\mathbf{p})$ can be computed directly from continuous eigenvalue theory if correctly normalised momentum eigenfunctions are available. The result of equation (9.12) shows at once that these are $u_{\mathbf{p}} = (2\pi\hbar)^{-3/2} e^{i\mathbf{p}.\mathbf{r}/\hbar}$. An obvious extension of the calculation in section 6 verifies that

$$\langle u_{\mathbf{p}} \mid u_{\mathbf{p}'} \rangle = \delta(p_x - p_x')\,\delta(p_y - p_y')\,\delta(p_z - p_z') = \delta(\mathbf{p} - \mathbf{p}') \tag{9.13}$$

which serves also to introduce and define the vector Dirac function $\delta(\mathbf{p} - \mathbf{p}')$.

§10 Orbital angular momentum

Operators In classical mechanics the orbital momentum $\mathbf{l}$ of a particle round a point is defined by

$$\mathbf{l} = \mathbf{r} \times \mathbf{p} \tag{10.1}$$

where $\mathbf{r}$ is the radius vector of the particle from the point, and $\mathbf{p}$ is its linear momentum. As usual the quantum mechanical operator $\mathbf{l}$ must be connected with the operators $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ by the same equation. If Cartesian coordinates are set up with the point of reference for $\mathbf{l}$ at the origin,

$$\left.\begin{aligned} \hat{l}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \hat{l}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \hat{l}_z &= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{aligned}\right\} \tag{10.2}$$

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† This sub-section may be skipped at a first reading.

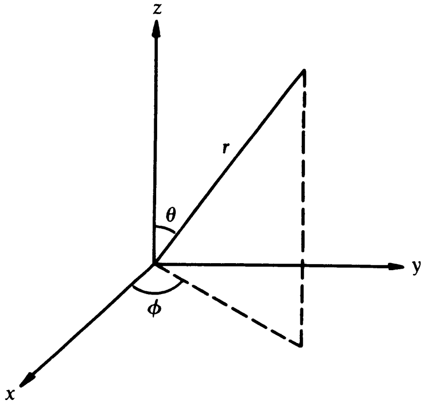

Figure 10.1 The standard relationship between Cartesian and spherical polar coordinates.

The passage to quantum mechanics is quite straightforward because no products of non-commuting operators are involved.

Often it will be convenient to work in spherical polar coordinates (figure 10.1), defined in the standard way so that $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, $z = r\cos\theta$. When the variables are changed,

$$\left.\begin{aligned} \hat{l}_x &= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\ \hat{l}_y &= i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\ \hat{l}_z &= -i\hbar\frac{\partial}{\partial\phi} \end{aligned}\right\} \tag{10.3}$$

The coordinate r does not appear in any of these operators, which therefore commute with any operator involving r alone.

The square of the total orbital angular momentum is represented by

$$\hat{\mathbf{l}}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\} \tag{10.4}$$

Commutation relations According to equation (4.28) each component of linear momentum fails to commute with the corresponding component of position. Thus,

$$\begin{aligned}[\hat l_x, \hat l_y] &= [\hat y\hat p_z - \hat z\hat p_y, \hat z\hat p_x - \hat x\hat p_z] \\ &= \hat y\hat p_x[\hat p_z, \hat z] + \hat x\hat p_y[\hat z, \hat p_z] \\ &= i\hbar(\hat x\hat p_y - \hat y\hat p_x) = i\hbar\hat l_z \qquad (10.5)\end{aligned}$$

Similar equations for the commutators $[\hat l_y, \hat l_z]$ and $[\hat l_z, \hat l_x]$ may be written down immediately, because all the equations involved remain true when x, y, z are cyclically interchanged. To summarise,†

$$[\hat l_x, \hat l_y] = i\hbar\hat l_z, \qquad [\hat l_y, \hat l_z] = i\hbar\hat l_x, \qquad [\hat l_z, \hat l_x] = i\hbar\hat l_y \qquad (10.6)$$

The square of the total angular momentum, on the other hand, commutes with any of the three components. For example,

$$\begin{aligned}[\hat{\mathbf{l}}^2, \hat l_x] &= [\hat l_y^2, \hat l_x] + [\hat l_z^2, \hat l_x] \\ &= \hat l_y[\hat l_y, \hat l_x] + [\hat l_y, \hat l_x]\hat l_y + \hat l_z[\hat l_z, \hat l_x] + [\hat l_z, \hat l_x]\hat l_z \\ &= i\hbar(-\hat l_y\hat l_z - \hat l_z\hat l_y + \hat l_z\hat l_y + \hat l_y\hat l_z) = 0 \qquad (10.7)\end{aligned}$$

Since $\hat{\mathbf{l}}^2$ is unaffected by cyclic interchange of x, y, z,

$$[\hat{\mathbf{l}}^2, \hat l_x] = [\hat{\mathbf{l}}^2, \hat l_y] = [\hat{\mathbf{l}}^2, \hat l_z] = 0 \qquad (10.8)$$

Complementarity The commutation relations between the three components of $\mathbf{l}$ suggest that an eigenstate of one component is not in general an eigenstate of the other two.

It may indeed be proved that an eigenstate of any two components must also be an eigenstate of the third, belonging to the eigenvalue zero for all three. For equation (5.13) shows that if u_{n00} is an eigenfunction‡ of, say, l_x and l_y,

$$[\hat l_x, \hat l_y]u_{n00} = i\hbar\hat l_z u_{n00} = 0 \qquad (10.9)$$

so that u_{n00} is also an eigenfunction of l_z, belonging to the eigenvalue zero. Once this is established, equation (5.13) can be used twice more:

$$\left.\begin{aligned}[\hat l_y, \hat l_z]u_{n00} = i\hbar\hat l_x u_{n00} = 0 \\ [\hat l_z, \hat l_x]u_{n00} = i\hbar\hat l_y u_{n00} = 0\end{aligned}\right\} \qquad (10.10)$$

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† In vector notation $\hat{\mathbf{l}} \times \hat{\mathbf{l}} = i\hbar\hat{\mathbf{l}}$; this equation looks strange at first sight but corresponds to the classical $\mathbf{l} \times \mathbf{l} = 0$ as $\hbar \to 0$.

‡ This and subsequent eigenfunctions are labelled by three suffices. The second and third serve to indicate the eigenvalues of $\mathbf{l}^2$ and l_z to which the eigenfunctions belong (equations (10.11)). The first is connected with their radial variation (equation (11.2)), which must be decided by reference to another observable because the operators for angular momentum depend on θ, ϕ only.

Thus u_{n00} must belong to the eigenvalue zero for l_x, l_y, l_z, and consequently $\mathbf{l}^2$ also.

This argument shows that, *if the total angular momentum is not zero, then only one of its three components can be definitely specified.* Conventionally l_z is picked out for this special attention, and no generality is lost because the orientation of the basic coordinate system can be chosen arbitrarily. There is, of course, no obstacle to the specification of both $\mathbf{l}^2$ and l_z at the same time, since these two observables commute. A general angular momentum eigenfunction will therefore be written u_{nlm}, with

$$\left.\begin{aligned}\hat{\mathbf{l}}^2 u_{nlm} &= l(l+1)\hbar^2 u_{nlm}\\ \hat{l}_z u_{nlm} &= m\hbar u_{nlm}\end{aligned}\right\} \tag{10.11}$$

where the form of the u_{nlm} and the possible values† of the numbers l and m, which fix the eigenvalues of $\mathbf{l}^2$ and l_z, remain to be investigated. Negative values of l need not be considered because $\mathbf{l}^2$, which is represented by the sum of the squares of Hermitian operators, cannot have negative eigenvalues.

Sometimes l is called the *orbital angular momentum quantum number,* and m the *magnetic quantum number.* An eigenstate of $\mathbf{l}^2$ belonging to the eigenvalue $l(l+1)\hbar^2$ may conveniently, but somewhat loosely, be referred to as a 'state of orbital angular momentum l'.

Eigenvalues The eigenvalues can best be found by operator algebra‡ based on equations (10.6) and (10.8). It is convenient to define two operators $\hat{l}_+$ and $\hat{l}_-$ by the relations

$$\hat{l}_+ = \hat{l}_x + i\hat{l}_y, \qquad \hat{l}_- = \hat{l}_x - i\hat{l}_y \tag{10.12}$$

Since $\hat{l}_x$ and $\hat{l}_y$ are Hermitian it is clear that $\langle\psi_1 \mid \hat{l}_+\psi_2\rangle = \langle\hat{l}_-\psi_1 \mid \psi_2\rangle$ and $\langle\psi_1 \mid \hat{l}_-\psi_2\rangle = \langle\hat{l}_+\psi_1 \mid \psi_2\rangle$ for any two wave functions ψ_1 and ψ_2. Thus the operators $\hat{l}_+$ and $\hat{l}_-$ are not Hermitian and they do not represent observables. However $\hat{l}_+\hat{l}_1$ and $\hat{l}_-\hat{l}_+$ are Hermitian operators, because they can be expressed as real functions of $\hat{\mathbf{l}}^2$

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† The eigenvalue in the first of equations (10.11) is written in the way that it is because l will later turn out to be integral; however, this is in no way assumed at this point.

‡ The procedure here is very similar to that followed in section 8 to find the energy eigenvalues of the linear harmonic oscillator.

and $\hat{l}_z$,

$$\left.\begin{aligned}\hat{l}_+\hat{l}_- &= (\hat{l}_x+i\hat{l}_y)(\hat{l}_x-i\hat{l}_y) = \hat{l}_x^2+\hat{l}_y^2-i[\hat{l}_x, \hat{l}_y]\\ &= \hat{l}_x^2+\hat{l}_y^2+\hbar\hat{l}_z = \hat{\mathbf{l}}^2-\hat{l}_z(\hat{l}_z-\hbar)\\ \hat{l}_-\hat{l}_+ &= \hat{l}_x^2+\hat{l}_y^2-\hbar\hat{l}_z = \hat{\mathbf{l}}^2-\hat{l}_z(\hat{l}_z+\hbar)\end{aligned}\right\} \quad (10.13)$$

Obviously $\hat{\mathbf{l}}^2$ commutes with $\hat{l}_+$, because it commutes with both $\hat{l}_x$ and $\hat{l}_y$. On the other hand,

$$\left.\begin{aligned}[\hat{l}_z, \hat{l}_+] &= [\hat{l}_z, \hat{l}_x]+i[\hat{l}_z, \hat{l}_y] = i\hbar\hat{l}_y+\hbar\hat{l}_x = \hbar\hat{l}_+\\ \hat{l}_z\hat{l}_+ &= \hat{l}_+(\hat{l}_z+\hbar)\end{aligned}\right\} \quad (10.14)$$

The result of applying $\hat{l}_+$ to the angular momentum eigenfunction u_{nlm} (equations (10.11)) may now be considered. Since $[\hat{\mathbf{l}}^2, \hat{l}_+]=0$,

$$\hat{\mathbf{l}}^2(\hat{l}_+u_{nlm}) = \hat{l}_+\hat{\mathbf{l}}^2u_{nlm} = l(l+1)\hbar^2(\hat{l}_+u_{nlm}) \quad (10.15)$$

so that $\hat{l}_+u_{nlm}$ is also an eigenfunction of $\mathbf{l}^2$ belonging to the same eigenvalue as u_{nlm} itself. On the other hand, by equations (10.14),

$$\hat{l}_z(\hat{l}_+u_{nlm}) = \hat{l}_+(\hat{l}_z+\hbar)u_{nlm} = (m+1)\hbar(\hat{l}_+u_{nlm}) \quad (10.16)$$

so that $\hat{l}_+u_{nlm}$ is also an eigenfunction of l_z, but it belongs to the eigenvalue $(m+1)\hbar$. *The effect of $\hat{l}_+$ on u_{nlm} is to produce a new angular momentum eigenfunction, belonging to the same eigenvalue of $\mathbf{l}^2$ but with the eigenvalue of l_z increased by $\hbar$. For this reason $\hat{l}_+$ is called the positive shift operator for orbital angular momentum.*

Similarly $\hat{\mathbf{l}}^2$ commutes with $\hat{l}_-$, and $\hat{l}_z\hat{l}_- = \hat{l}_-(\hat{l}_z-\hbar)$. The result of applying $\hat{l}_-$ to u_{nlm} is then expressed by the equations

$$\left.\begin{aligned}\hat{\mathbf{l}}^2(\hat{l}_-u_{nlm}) &= l(l+1)\hbar^2(\hat{l}_-u_{nlm})\\ \hat{l}_z(\hat{l}_-u_{nlm}) &= (m-1)\hbar(\hat{l}_-u_{nlm})\end{aligned}\right\} \quad (10.17)$$

The effect of $\hat{l}_-$ on u_{nlm} is to produce a new angular momentum eigenfunction, belonging to the same eigenvalue of $\mathbf{l}^2$ but with the eigenvalue of l_z decreased by $\hbar$. Correspondingly $\hat{l}_-$ is called the negative shift operator for orbital angular momentum.

There are limits to the amounts by which the l_z eigenvalue can be raised or lowered by successive applications of the shift operators. The observable $\mathbf{l}^2-l_z^2 = l_x^2+l_y^2$ cannot have negative eigenvalues; for a given eigenvalue of $\mathbf{l}^2$ there must be maximum and minimum eigenvalues of l_z, which may be denoted by $m_+\hbar$ and $m_-\hbar$ respectively.

When $\hat{l}_+$ is applied to u_{nlm_+}, equation (10.16) can only be satisfied because u_{nlm_+} vanishes everywhere. An equation for m_+ in terms of

l can then be found with the help of equations (10.13),

$$\left.\begin{array}{l}\hat{l}_-(\hat{l}_+u_{nlm_+})=\{l(l+1)-m_+(m_++1)\}\hbar^2u_{nlm_+}=0\\ m_+(m_++1)=l(l+1)\end{array}\right\} \qquad (10.18)$$

so that $m_+=l$ or $-(l+1)$. Similarly $\hat{l}_-u_{nlm_-}$ must also vanish everywhere, and this leads to an equation for m_- in terms of l,

$$\left.\begin{array}{l}\hat{l}_+(\hat{l}_-u_{nlm_-})=\{l(l+1)-m_-(m_--1)\}\hbar^2u_{nlm_-}=0\\ m_-(m_--1)=l(l+1)\end{array}\right\} \qquad (10.19)$$

so that $m_-=-l$ or $(l+1)$. Now obviously $m_+\geqslant m_-$, which rules out the second of the two possible solutions for m_+ and m_-. Therefore,

$$m_+=l, \qquad m_-=-l \qquad (10.20)$$

Successive applications of the positive shift operator to u_{nlm_-} must eventually bring it to the form u_{nlm_+}, because the production of negative eigenvalues of $\mathbf{l}^2-l_z^2$ can be avoided in no other way. Since the eigenvalue of l_z increases by $\hbar$ at each application, the value of m increases by integral steps from m_- to m_+. It follows that $m_+-m_-=2l$ must be integral, *and therefore l must be integral or half-integral.*

Similarly it can be seen that any allowed value of m differs from m_+ by an integer. *It follows that, for a given l, all the possible values of m are contained in the series which climbs by integral steps from $-l$ to $+l$* (figure 10.2). For a given l there are obviously $(2l+1)$ possible values of m.

This completes the information which can be extracted from the commutation relations for the components of $\mathbf{l}$. It will appear shortly that in fact no suitable eigenfunctions of r, θ, ϕ can be found for the half-integral values of l and m, and so the corresponding eigenvalues are ruled out for orbital angular momentum. Nevertheless these values are shown by open circles in figure 10.2, and they will be discussed later in connection with the concept of spin angular momentum.

Eigenfunctions A frontal assault on the problem of finding the u_{nlm} could be made by putting the various values of l and m into equations (10.11), together with the explicit expressions for $\hat{\mathbf{l}}^2$ and $\hat{l}_z$ in terms of θ and ϕ. Unfortunately the second-order differential equation involving $\hat{\mathbf{l}}^2$ is laborious to discuss, although it is very well known in mathematical physics.

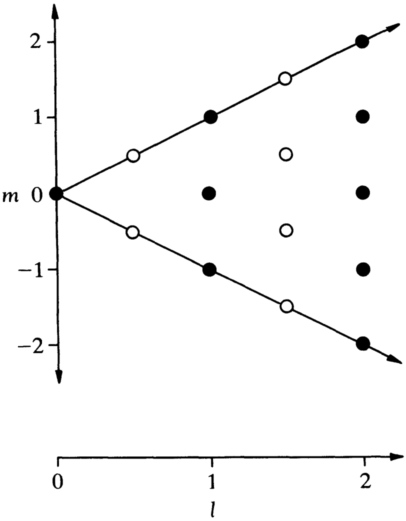

Figure 10.2 The allowed values for angular momentum quantum numbers. The half-integral values shown by the open circles are not suitable for orbital angular momentum.

This difficulty can be avoided by starting with the $u_{nl,-l}$, which obey the first-order differential equation $\hat{l}_- u_{nl,-l} = 0$. Subsequently the general eigenfunction u_{nlm} can be found by applying the positive shift operator $l+m$ times to $u_{nl,-l}$. In these operations the normalisation can be kept in order by noting that

$$\begin{aligned}\langle \hat{l}_+ u_{nlm'} \mid \hat{l}_+ u_{nlm'}\rangle &= \langle u_{nlm'} \mid \hat{l}_- \hat{l}_+ u_{nlm'}\rangle \\ &= \{l(l+1) - m'(m'+1)\}\hbar^2 \langle u_{nlm'} \mid u_{nlm'}\rangle \\ &= (l+m'+1)(l-m')\hbar^2 \langle u_{nlm'} \mid u_{nlm'}\rangle \qquad (10.21)\end{aligned}$$

so that, if $u_{nlm'}$ is normalised, then so is

$$u_{nl,m'+1} = \{(l+m'+1)(l-m')\}^{-1/2}\hbar^{-1}\hat{l}_+ u_{nlm'} \qquad (10.22)$$

Since $m' \leqslant l$ the numerical coefficient here has been chosen in such a way that it is always real, and never negative. This is a generally accepted convention.

Separation of variables The u_{nlm} may conveniently be written as the product of separate functions of r, θ, ϕ:

$$u_{nlm} = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi) \qquad (10.23)$$

The logical arrangement of most of the suffices can be easily understood. The operator $\hat{l}_z$ depends only on ϕ, and so the second of equations (10.11) reduces simply to $\hat{l}_z\Phi_m = m\hbar\Phi_m$. Thus the function Φ_m depends only on the value of m. Similarly the operator $\hat{\mathbf{l}}^2$ depends only on θ and ϕ, and so the first of equations (10.11) reduces to $\hat{\mathbf{l}}^2\Theta_{lm}\Phi_m = l(l+1)\hbar^2\Theta_{lm}\Phi_m$. This equation obviously depends on l, and it also depends on m through Φ_m. Thus both must be specified in order to label Θ_{lm}. The suffices attached to R_{nl} cannot be discussed until section 11, however.

The normalisation of u_{nlm} requires that

$$\langle u_{nlm} \mid u_{nlm}\rangle = \int\limits_{r=0}^{\infty} \int\limits_{\theta=0}^{\pi} \int\limits_{\phi=0}^{2\pi} (R^*_{nl}R_{nl})(\Theta^*_{lm}\Theta_{lm})(\Phi^*_m\Phi_m) \times r^2 \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\phi = 1 \tag{10.24}$$

and this can conveniently be arranged by three separate normalisations:

$$\left.\begin{aligned} \int_0^{2\pi} \Phi^*_m\Phi_m \, \mathrm{d}\phi &= 1 \\ \int_0^{\pi} \Theta^*_{lm}\Theta_{lm} \sin\theta \, \mathrm{d}\theta &= 1 \\ \int_0^{\infty} R^*_{nl}R_{nl}r^2 \, \mathrm{d}r &= 1 \end{aligned}\right\} \tag{10.25}$$

Azimuthal angle functions Φ_m It has already been pointed out that Φ_m obeys the simple equation

$$\hat{l}_z\Phi_m = -i\hbar\frac{\mathrm{d}}{\mathrm{d}\phi}\Phi_m = m\hbar\Phi_m \tag{10.26}$$

whose correctly normalised solution is

$$\Phi_m = \left(\frac{1}{2\pi}\right)^{1/2} \mathrm{e}^{im\phi} \tag{10.27}$$

A restriction on the values of m now becomes apparent. The wave functions cannot be properly interpreted if they are not single-valued functions of position; but $\Phi_m(\phi+2\pi)=\Phi_m(\phi)$ only if m be integral. For orbital angular momentum attention must therefore be restricted to the eigenvalues which are indicated by filled circles in figure 10.2.

Polar angle functions Θ_{lm} A plan for finding these by means of the shift operators has already been outlined. Explicit expressions for $\hat{l}_+$ and $\hat{l}_-$ will be needed:

$$\left.\begin{aligned}\hat{l}_+ &= \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta}+i\cot\theta\frac{\partial}{\partial\phi}\right)\\ &= \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta}-\hbar^{-1}\cot\theta l_z\right)\\ \hat{l}_- &= \hbar e^{-i\phi}\left(-\frac{\partial}{\partial\theta}+i\cot\theta\frac{\partial}{\partial\phi}\right)\\ &= -\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta}+\hbar^{-1}\cot\theta l_z\right)\end{aligned}\right\} \tag{10.28}$$

The function $\Theta_{l,-l}$ is found first by writing down the equation $\hat{l}_-R_{nl}\Theta_{l,-l}\Phi_{-l}=0$. Since $\hat{l}_-$ does not affect R_{nl},

$$-\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta}+\hbar^{-1}\cot\theta l_z\right)\Theta_{l,-l}\Phi_{-l}=0 \tag{10.29}$$

After substituting $l_z=-l\hbar\Phi_{-l}$ and removing the factor $-\hbar e^{-i\phi}\Phi_{-l}$,

$$\left(\frac{d}{d\theta}-l\cot\theta\right)\Theta_{l,-l}=0 \tag{10.30}$$

which has the simple solution $\Theta_{l,-l}=A\sin^l\theta$. The normalising factor A can be found from the second of equations (10.25) by repeated partial integration. The result is

$$\Theta_{l,-l}=\{\tfrac{1}{2}(2l+1)!\}^{1/2}\left(\frac{1}{2^l l!}\right)\sin^l\theta \tag{10.31}$$

Now Θ_{lm} can be found by using the upward shift operator $l+m$ times, a typical step being given by equation (10.22). Again R_{nl} is not affected by $\hat{l}_+$, and so equation (10.22) becomes

$$\Theta_{l,m'+1}\Phi_{m'+1}=\{(l+m'+1)(l-m')\}^{-1/2}e^{i\phi}\left(\frac{\partial}{\partial\theta}-\hbar^{-1}\cot\theta\hat{l}_z\right)\Theta_{lm'}\Phi_{m'} \tag{10.32}$$

After substituting $\hat{l}_z\Phi_{m'} = m'\hbar\Phi_{m'}$ and cancelling a factor $\Phi_{m'+1} = e^{i\phi}\Phi_{m'}$ from both sides,

$$\begin{aligned}\Theta_{l,m'+1} &= \{(l+m'+1)(l-m')\}^{-1/2}\left(\frac{d}{d\theta} - m' \cot\theta\right)\Theta_{lm'} \\ &= \{(l+m'+1)(l-m')\}^{-1/2}\left(\sin^{m'}\theta \frac{d}{d\theta}\sin^{-m'}\theta\right)\Theta_{lm'}\end{aligned} \tag{10.33}$$

This operation must be carried out $l+m$ times, starting with $m' = -l$ and the $\Theta_{l,-l}$ given by equation (10.31), and ending with $m' = m-1$. After cancelling many intermediate factors of $\sin\theta$ the result is

$$\begin{aligned}\Theta_{lm} &= \left[\frac{(2l+1)(l-m)!}{2(l+m)!}\right]^{1/2}\left[\left(\frac{1}{2^l l!}\right)\sin^m\theta\left(\frac{1}{\sin\theta}\frac{d}{d\theta}\right)^{l+m}\sin^{2l}\theta\right] \\ &= \left[\frac{(2l+1)(l-m)!}{2(l+m)!}\right]^{1/2}\left\{\frac{(-1)^m}{2^l l!}\sin^m\theta\frac{d^{l+m}}{d(\cos\theta)^{l+m}}(\cos^2\theta-1)^l\right\} \\ &= \left[\frac{(2l+1)(l-m)!}{2(l+m)!}\right]^{1/2} P_l^m(\cos\theta)\end{aligned} \tag{10.34}$$

where the expression in the braces defines $P_l^m(\cos\theta)$, the associated Legendre function† labelled by l and m. When $m = 0$ this function is identical with $P_l(\cos\theta)$, the Legendre polynomial of degree‡ l, and the upper suffix is then omitted. Thus,

$$\begin{aligned}\Theta_{l0} &= \{\tfrac{1}{2}(2l+1)\}^{1/2}\left\{\frac{1}{2^l l!}\frac{d^l}{d(\cos\theta)^l}(\cos^2\theta-1)^l\right\} \\ &= \{\tfrac{1}{2}(2l+1)\}^{1/2}P_l(\cos\theta)\end{aligned} \tag{10.35}$$

***Spherical harmonics* $Y_{lm}(\theta, \phi)$** The product $Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$ is called a spherical harmonic. The first few of them are set out in table 10.1, and figure 10.3 gives a polar diagram which illustrates their behaviour on the $y = 0$ ($\phi = 0, \pi$) plane.

An inspection of the examples in table 10.1 *shows that the angular dependence of the position probability density,* $u^*_{nlm}u_{nlm} \propto |Y_{lm}(\theta, \phi)|^2$,

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† Various definitions of $P_l^m(\cos\theta)$ are current, many of them inconsistent by factors of -1 for some values of m. The definition used here has the merit of being valid for both positive and negative m, and it agrees with the one given in *Higher Transcendental Functions*, Vol. I, Bateman Manuscript Project, McGraw-Hill (1953). A useful relation is $\Theta_{lm} = (-1)^m\Theta_{l,-m}$.

‡ The leading term in $P_l(\cos\theta)$ is easily seen to be proportional to $\cos^l\theta$.

Table 10.1 Spherical harmonics for $l = 0, 1, 2$. The minus signs occur for odd positive values of m only

l	m	$Y_{lm}(\theta, \phi)$	l	m	$Y_{lm}(\theta, \phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$	2	2	$\left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{2i\phi}$
1	1	$-\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi}$		1	$-\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{i\phi}$
	0	$\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$		0	$\left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$
	-1	$\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi}$		-1	$\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{-i\phi}$
				-2	$\left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{-2i\phi}$

can be expressed simply in terms of a polynomial of degree 2l in $\cos\theta$. For example, $|Y_{10}|^2 \propto \cos^2\theta$ and $|Y_{21}|^2 \propto \sin^2\theta\cos^2\theta = -\cos^4\theta + \cos^2\theta$. A little study of equation (10.34) can easily put this remark on a general basis.

This kind of relationship between the angular distribution of the position probability density and the angular momentum of the particle concerned is widely exploited in atomic, nuclear, and particle physics.

It is also worth remarking that spherical harmonics belonging to different eigenvalues of $\mathbf{l}^2$ or l_z must of course be orthogonal, and therefore

$$\int_0^{\pi}\int_0^{2\pi} Y^*_{l'm'}(\theta, \phi) Y_{lm}(\theta, \phi) \sin\theta \, d\theta \, d\phi = \delta_{l'l}\,\delta_{m'm} \qquad (10.36)$$

Parity In three dimensions the instructions of the parity operator $\hat{\Pi}$ are

$$\hat{\Pi}\psi(x, y, z) = \psi(-x, -y, -z) \qquad (10.37)$$

The various theorems proved about parity in one dimension are readily extended to three, and in particular the two possible eigenvalues of Π are again $+1$ (even parity states) and -1 (odd parity states).

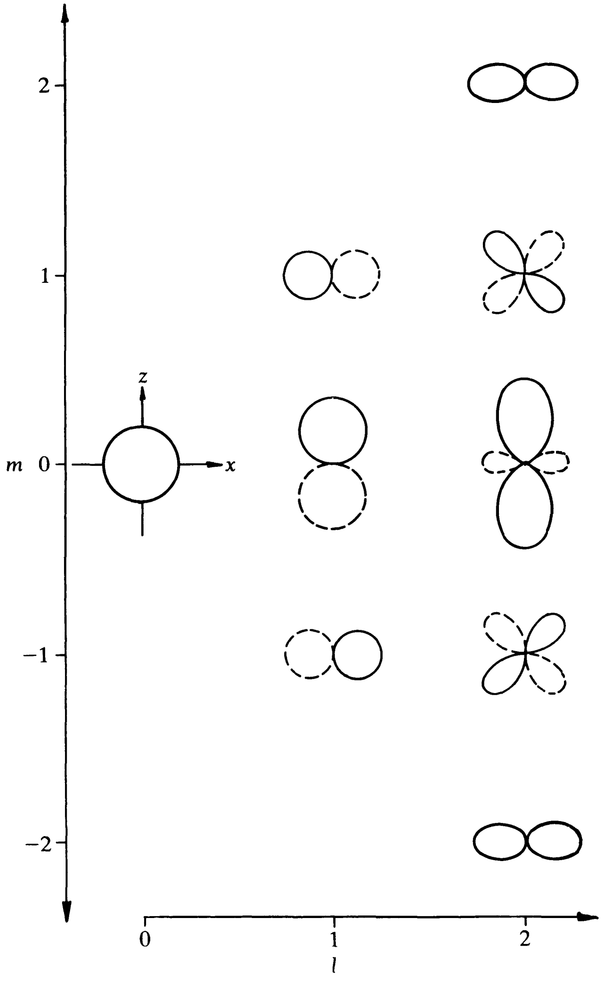

Figure 10.3 Polar diagrams of the spherical harmonics with $l \leqslant 2$ on the $\phi = 0$, π or z, x plane. The directions of z and x are shown on the Y_{00} diagram only, to avoid clutter. Negative values are indicated by dashed lines, and the parities of the spherical harmonies should be noted. The scale is fixed by the radius of the Y_{00} diagram, which is of course $(4\pi)^{-1/2}$.

When the instructions of $\hat{\Pi}$ are translated into spherical polar coordinates and applied to u_{nlm},

$$\hat{\Pi}R_{nl}(r)Y_{lm}(\theta,\phi)=R_{nl}(r)Y_{lm}(\pi-\theta,\phi+\pi) \tag{10.38}$$

so that the form of $R_{nl}(r)$ is immaterial so far as the parity is concerned. The parity properties of $Y_{lm}(\theta,\phi)$, on the other hand, can be established in a clear and simple form.

The first point to notice is that $\hat{\Pi}$ commutes with all angular momentum operators, including the shift operators. For example,

$$\begin{aligned}\hat{\Pi}\hat{l}_z&=-i\hbar\left\{-x\frac{\partial}{\partial(-y)}+y\frac{\partial}{\partial(-x)}\right\}\hat{\Pi}\\&=i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\hat{\Pi}=\hat{l}_z\hat{\Pi}\end{aligned} \tag{10.39}$$

Next, it is easy to see from equation (10.38) that $Y_{l,-l}(\theta,\phi)\propto\sin^l\theta e^{-il\phi}$ has parity $(-1)^l$, since $\sin(\pi-\theta)=\sin\theta$ and $e^{-il(\phi+\pi)}=e^{-il\pi}e^{-il\phi}=(-1)^le^{-il\phi}$.

Finally, since $\hat{\Pi}$ commutes with $\hat{l}_+$ and $Y_{lm}(\theta,\phi)$ is proportional to $(\hat{l}_+)^{l+m}Y_{l,-l}(\theta,\phi)$, it follows that $Y_{lm}(\theta,\phi)$ has the same parity as $Y_{l,-l}(\theta,\phi)$. *Thus it is seen that states of even (odd) orbital angular momentum have even (odd) parity.*

Properties of the shift operators For future reference the properties of the shift operators may conveniently be summarised at this point. With the normalisation established by equation (10.22),

$$\left.\begin{aligned}\hat{l}_+u_{nlm}&=\begin{cases}+\{(l+m+1)(l-m)\}^{1/2}\hbar u_{nl,m+1}, & -l\leqslant m\leqslant l-1\\ 0, & m=l\end{cases}\\ \hat{l}_-u_{nlm}&=\begin{cases}+\{(l-m+1)(l+m)\}^{1/2}\hbar u_{nl,m-1}, & -l+1\leqslant m\leqslant l\\ 0, & m=-l\end{cases}\end{aligned}\right\} \tag{10.40}$$

The third equation may be obtained from the first by replacing m by $m-1$, applying $\hat{l}_-$ to both sides, and using equations (10.13) for $\hat{l}_-\hat{l}_+$.

Spectroscopic notation For historical reasons states of orbital angular momentum $0,1,2,3,4,5,\ldots$ are called s, p, d, f, g, h, ... states respectively.

§11 Central potentials

Stationary states and radial functions $R_{nl}(r)$ A central potential $V(r)$ is one which depends only on the magnitude of r and not on the value of θ or ϕ. A particle moving in such a field is subject to forces which are always directed to or from the origin of the coordinate system.

The total energy operator† is $\hat{H} = -(\hbar^2/2m_0)\nabla^2 + V(r)$, and in spherical polar coordinates this becomes

$$\begin{aligned}\hat{H} = &-\frac{\hbar^2}{2m_0}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right.\\ &\left.+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}+V(r)\\ = &-\frac{\hbar^2}{2m_0r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\hat{\mathbf{l}}^2}{2m_0r^2}+V(r)\end{aligned} \tag{11.1}$$

The second term, which stands alongside $V(r)$, is called the centrifugal potential. In classical mechanics its negative gradient would be the centrifugal force, $(\mathbf{l}^2/m_0r^4)\mathbf{r}$.

None of the angular momentum operators mentions r, and all of them commute with $\mathbf{l}^2$; therefore all of them commute here with $\hat{H}$. This has the usual consequence that the orbital angular momentum is conserved, just as it would be in classical mechanics.

A further consequence is that the stationary states can be eigenstates of l_z and $\mathbf{l}^2$, as well as H, and the corresponding eigenfunctions can therefore be written in the form $u_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi)$. The time-independent Schrödinger equation, $\hat{H}u_{nlm} = E_{nl}u_{nlm}$, is readily simplified by operating with $\mathbf{l}^2$ and cancelling the Y_{lm} throughout. The result is

$$\left\{-\frac{\hbar^2}{2m_0r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right)+\frac{l(l+1)\hbar^2}{2m_0r^2}+V(r)\right\}R_{nl} = E_{nl}R_{nl} \tag{11.2}$$

This equation does not mention m, which is the reason why R_{nl} and E_{nl} are given only two distinguishing suffices.

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† In this section the masses of particles will be given a suffix (e.g. m_0, m_e, m_p) in order to avoid all possibility of confusion with the magnetic quantum number m.

A more convenient equation can be obtained by the substitution $R_{nl} = S_{nl}/r$; after multiplication by r,

$$\left\{-\frac{\hbar^2}{2m_0}\frac{d^2}{dr^2}+\frac{l(l+1)\hbar^2}{2m_0 r^2}+V(r)\right\}S_{nl}=E_{nl}S_{nl} \tag{11.3}$$

This has the same mathematical form as a one-dimensional Schrödinger equation, with the centrifugal potential added to $V(r)$.

According to equations (10.25), S_{nl} is correctly normalised by†

$$\int_0^\infty S_{nl}^* S_{nl}\, dr = 1 \tag{11.4}$$

Boundary conditions Near the origin S_{nl} must tend to zero at least as fast as r, in order to avoid having an infinite position probability density at that point. At very large r, on the other hand, equation (11.3) takes the form

$$\frac{\hbar^2}{2m_0}\frac{d^2 S_{nl}}{dr^2}=\{V(r)-E_{nl}\}S_{nl} \tag{11.5}$$

As r increases $V(r)-E_{nl}$ must become positive for bound states, and the solutions of the equation either increase or decrease exponentially. The increasing solutions must obviously be rejected, because they do not represent states in which the particle is to be found near the origin.

§12 The hydrogen atom

Stationary states The simplest of all atomic systems is the hydrogen atom, consisting of an electron (mass m_e, charge $-e$) bound electrically to a proton (mass m_p, charge e). Since $m_e \ll m_p$, the proton may to a good approximation‡ be considered stationary at the origin of the coordinate system, and the Coulomb forces acting on the electron are then described by the central potential $V(r) = -e^2/4\pi\varepsilon_0 r$.

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† Note carefully that S_{nl} is normalised so that there is no factor of 4π in this integral. In future $|S_{nl}|^2$ will be called the *radial position probability density* (RPPD).

‡ As shown in section 14, this approximation may easily be avoided by replacing m_e with the reduced mass $\mu = m_e m_p/(m_e + m_p)$.

As usual a stationary state of orbital angular momentum l is associated with a radial function S_{nl} obeying equation (11.3):

$$\left\{-\frac{\hbar^2}{2m_e}\frac{d^2}{dr^2}+\frac{l(l+1)\hbar^2}{2m_e r^2}-\frac{e^2}{4\pi\varepsilon_0 r}\right\}S_{nl}=E_{nl}S_{nl} \tag{12.1}$$

This equation is cluttered with coefficients and in need of rationalisation. As a first step a positive number n may be defined:

$$n\equiv\left|\left(\frac{-m_e}{2\hbar^2 E_{nl}}\right)^{1/2}\right|\left(\frac{e^2}{4\pi\varepsilon_0}\right) \tag{12.2}$$

It should be noted that E_{nl} is negative for bound states and that the spectrum of n is discrete† because the spectrum of E_{nl} is discrete.

Next a natural length a_0 may be constructed from the physical constants present, namely $\hbar$, m_e, and $e^2/4\pi\varepsilon_0$. *It is*

$$a_0\equiv 4\pi\varepsilon_0\hbar^2/m_e e^2=5.292\times 10^{-11}\ \mathrm{m} \tag{12.3}$$

and is called the Bohr radius: it sets the scale of all atomic and molecular systems and processes.

Finally a dimensionless variable ρ proportional to r may be defined:

$$\rho\equiv\left(\frac{m_e e^2}{2\pi\varepsilon_0 n\hbar^2}\right)r=\frac{2r}{na_0} \tag{12.4}$$

Use of ρ in place of r in the equation has the effect of introducing a natural length varying with the energy eigenvalue. This unusual step is justified by the mathematical simplification that is gained.

When the first equation (12.4) is used on the left-hand side of equation (12.1), and equation (12.2) on the right-hand side,

$$\frac{d^2S_{nl}}{d\rho^2}+\left\{-\frac{1}{4}+\frac{n}{\rho}-\frac{l(l+1)}{\rho^2}\right\}S_{nl}=0 \tag{12.5}$$

At very large values of r, or ρ, the equation takes the asymptotic form $(d^2/d\rho^2)S_{nl}=S_{nl}/4$, which has the exponentially decreasing solution $S_{nl}\sim e^{-\rho/2}$. A suitable solution to equation (12.5) would be $S_{nl}=f(\rho)e^{-\rho/2}$ where $f(\rho)$ is a function whose behaviour at large ρ does not dominate that of the factor $e^{-\rho/2}$. After substituting for S_{nl},

$$\frac{d^2f}{d\rho^2}-\frac{df}{d\rho}+\left\{\frac{n}{\rho}-\frac{l(l+1)}{\rho^2}\right\}f=0 \tag{12.6}$$

---

† n will later turn out to be integral; however, this is in no way assumed at this point.

An expression for f may be sought in the form of a series in ascending powers of ρ: $f=(a_0\rho^\sigma+a_1\rho^{\sigma+1}+a_2\rho^{\sigma+2}+\cdots)=\rho^\sigma\sum_s a_s\rho^s$. When this is put into equation (12.6) every power of ρ must of course vanish separately. The terms of lowest power, $\rho^{\sigma-2}$, cancel if

$$\sigma(\sigma-1)=l(l+1) \qquad (12.7)$$

and so $\sigma=l+1$ or $-l$. The first choice must be adopted because $a_0\rho^{-l}$ would become infinite at $r=0$, contrary to the boundary conditions on S_{nl}. Once σ has been fixed, it may be seen that the terms proportional to ρ^{l+s} in equation (12.6) cancel if

$$a_{s+1}=\frac{l+s+1-n}{(s+1)(s+2l+2)}\,a_s \qquad (12.8)$$

This relates all the coefficients in the series to a_0, whose value can be decided by normalisation (equation (11.4)).

The docile behaviour of f at large ρ must still be checked. The highest powers of ρ are the most important from this point of view, and equation (12.8) shows that the ratio between successive coefficients becomes $a_{s+1}/a_s=1/s$ when s is very large. The same asymptotic ratio is found in the series expansion of e^ρ, and it may be concluded that f tends to behave like e^ρ for large ρ, which is contrary to specification. The difficulty can only be avoided if the series for f is in fact a polynomial in ρ of finite degree; this is true provided that n is integral and $n\geqslant l+1$, for then the numerator on the right-hand side of equation (12.8) vanishes after $n-l$ terms of the series. The denominator is never zero and so a_{n-1} and all higher coefficients vanish.

The integer n is called the *principal quantum number*, and in spectroscopic notation its value is often written in front of the letter indicating the orbital angular momentum. For example, a state with $n=2$ and $l=1$ is called a 2p state.

Energy eigenvalues The original definition of n relates the energy eigenvalues directly to the principal quantum number. In fact

$$E_n=-\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2n^2} \qquad (12.9)$$

where the suffix l has been dropped because the energy eigenvalues do not depend on l at all. This is a special property of the Coulomb potential and not generally true.

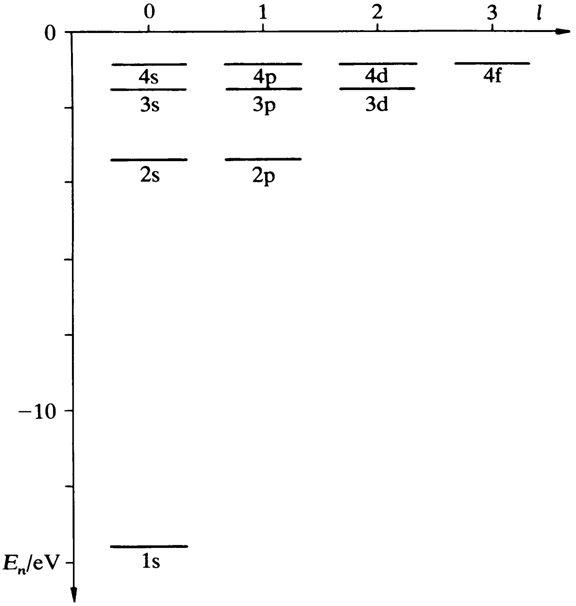

Figure 12.1 Energy levels and quantum numbers for the hydrogen atom. The spectroscopic label for each state is shown underneath the line which represents its energy. Only the states with principle quantum number $n \leqslant 4$ are shown, simply because the lines get crowded as $n \to \infty$ and $E_n \to 0$.

The scheme of quantum numbers and energy eigenvalues for the hydrogen atom is shown in figure 12.1.

The first semi-classical derivation of equation (12.9) was given by Bohr in 1913. He was able to account for many known features of the optical spectrum of the hydrogen atom, and so established beyond doubt that atomic structures were to be described by quantum mechanics. The first modern treatment of the hydrogen atom was published by Schrödinger in 1926, in the same paper that introduced the TDSE and TISE themselves.

The actual value of E_1 is -2.180×10^{-18} J or -13.61 eV when the proton mass is taken to be infinite.

Energy eigenfunctions The polynominal generated by the recurrence relation (12.8) may be connected with the associated Laguerre

Table 12.1 Radial functions $S_{nl} = rR_{nl}$ for the hydrogen atom, according to equation (12.11). Here $\rho_1 = 2r/a_0$, $\rho_2 = r/a_0$, and $\rho_3 = 2r/3a_0$, as specified by equation (12.4)

n	l	$a_0^{1/2}S_{nl}$
1	0	$-\rho_1 e^{-\rho_1/2}$
2	0	$-(\frac{1}{2})^{1/2}\rho_2 e^{-\rho_2/2}(1-\rho_2/2)$
	1	$-(\frac{1}{24})^{1/2}\rho_2^2 e^{-\rho_2/2}$
3	0	$-(\frac{1}{3})^{1/2}\rho_3 e^{-\rho_3/2}(1-\rho_3+\rho_3^2/6)$
	1	$-(\frac{2}{27})^{1/2}\rho_3^2 e^{-\rho_3/2}(1-\rho_3/4)$
	2	$-(\frac{1}{1080})^{1/2}\rho_3^3 e^{-\rho_3/2}$

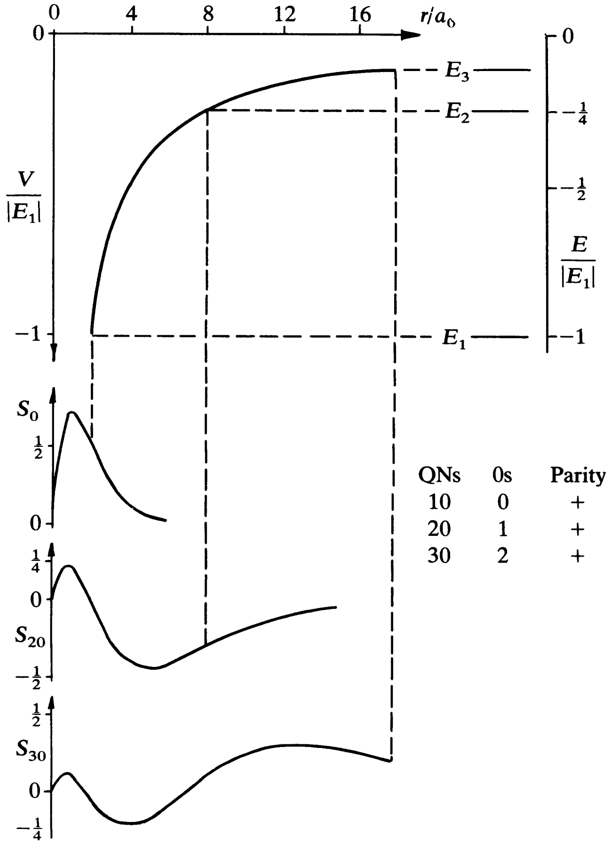

Figure 12.2 Unified diagram for the energy eigenstates of the hydrogen atom, with $l = 0$ (s states). Note that the radial wave functions are S_{10}, etc., and not R_{10}, etc.

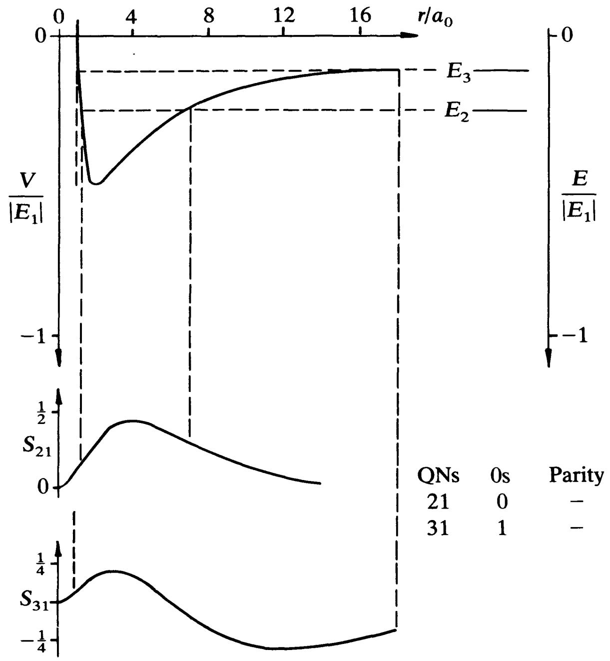

Figure 12.3 Unified diagram for the energy eigenstates of the hydrogen atom, with $l=1$ (p states). The centrifugal potential is present, in contrast with figure 12.2.

polynomial of degree $n-l-1$,

$$L_{n+l}^{2l+1}(\rho) = -\{(n+l)!\}^2 \sum_{\lambda=0}^{n-l-1} \frac{(-\rho)^\lambda}{\lambda!(n-l-1-\lambda)!(2l+1+\lambda)!} \tag{12.10}$$

and then

$$S_{nl} = a_0^{-1/2} \left[\frac{(n-l-1)!}{n^2\{(n+l)!\}^3} \right]^{1/2} e^{-\rho/2} \rho^{l+1} L_{n+l}^{2l+1}(\rho) \tag{12.11}$$

The normalisation is in accord with equation (11.4).

The first few of these eigenfunctions are listed in table 12.1. The three s wave functions for $n \leqslant 3$ are shown† in figure 12.2 and the two p wave functions for $n \leqslant 3$ in figure 12.3. The centrifugal potential has the important effect of moving the oscillatory region out from the origin, as well as raising the energy eigenvalue.

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† Note that these unified diagrams must deal with S_{nl} and not R_{nl}: only the former obeys a simple radial equation.

Degeneracy The problem of degeneracy mentioned in section 4 can now be discussed in more detail. For example, the stationary state wave functions for the hydrogen atom are clearly degenerate so far as the energy is concerned. Thus figure 12.1 shows nine states with $n = 3$ and energy $E_3 = -m_e e^4/288\pi^2\varepsilon_0^2 h^2$, namely one 3s state ($m = 0$), three 3p states ($m = 0, \pm 1$), and five 3d states ($m = 0, \pm 1, \pm 2$). If the energy eigenvalues alone had been calculated it would not be clear that the corresponding eigenfunctions are orthogonal. In fact they must be so, because they belong to different combinations of eigenvalues of $\mathbf{l}^2$ and l_z.

This example shows how to form a complete orthonormal set of eigenfunctions even when there is degeneracy. A *complete commuting set of observables* must be used, such that each eigenfunction belongs to a unique combination of eigenvalues. The set used here for the hydrogen atom comprised $\mathbf{l}^2$, l_z, and H.

§13 The three-dimensional harmonic oscillator

Stationary states A problem with important practical applications is provided by the three-dimensional harmonic oscillator, set up by subjecting a particle to the central potential $V(r) = m\omega^2 r^2/2$. This potential is illustrated by the full curve in figure 13.1, while the dashed curve illustrates the sort of potential which could represent the short-range nuclear forces binding a proton or neutron to a nucleus. The curves diverge widely outside a certain radius, but for

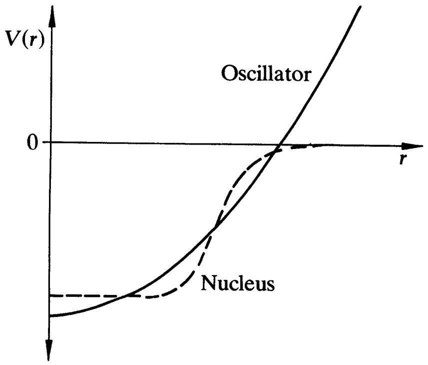

Figure 13.1 Qualitative comparison between the oscillator potential and a plausible potential for a neutron or proton bound in a nucleus. The Coulomb interaction of a proton has been ignored.

tightly bound states the wave functions are in any event small and decreasing exponentially in this region. The oscillator potential is therefore often used for simplified nuclear calculations.

It is perfectly possible to proceed in the standard way by writing the stationary state wave functions in the form $u_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi)$, and finding the R_{nl} by the method of section 11. This amounts, of course, to the selection of $\mathbf{l}^2$, l_z, and H as the complete set of commuting observables for the problem.

There are, however, some advantages in working with a different set, in order to make use of the work already done on the linear harmonic oscillator (section 8). The stationary state wave functions so obtained are not generally eigenfunctions of $\mathbf{l}^2$ or l_z, but it is instructive to discuss the possible values of these observables without making formal expansions in angular momentum eigenfunctions.

The energy operator can be expressed as the sum of three operators depending only on x, y, and z respectively,

$$\hat{H} \equiv \hat{H}_x + \hat{H}_y + \hat{H}_z \tag{13.1}$$

where H_x, for example, is given by equation (8.1) with the understanding that p there means p_x.

The stationary state eigenfunctions can be expressed as the product of three eigenfunctions depending only on x, y, and z respectively,

$$U_{n_x n_y n_z} = u_{n_x}(x)v_{n_y}(y)w_{n_z}(z) \tag{13.2}$$

where $u_{n_x}(x)$, for example, is given by equation (8.15) with the understanding that n there means n_x. Then

$$\hat{H}U_{n_x n_y n_z} = (n_x + n_y + n_z + \tfrac{3}{2})\hbar\omega = (N + \tfrac{3}{2})\hbar\omega \tag{13.3}$$

The energies for the lowest five values of N are given in table 13.1, column 2.

Table 13.1 Energies, multiplicities, parities, and quantum numbers for the three-dimensional harmonic oscillator

N	$E_N/\hbar\omega$	g_N	Π	n, l
0	$\frac{3}{2}$	1	+	1s
1	$\frac{5}{2}$	3	−	2p
2	$\frac{7}{2}$	6	+	2s, 3d
3	$\frac{9}{2}$	10	−	3p, 4f
4	$\frac{11}{2}$	15	+	3s, 4d, 5g

Energy degeneracy In general there are several different sets of n_x, n_y, n_z values for each value of N, so that the wave functions are degenerate with respect to energy. When N is given, n_x can take the values $0, 1, \ldots, N$, and for each n_x there are $N-n_x+1$ possible values of n_y, namely $0, 1, 2, \ldots, N-n_x$. Thus the total number of independent eigenfunctions belonging to the energy E_N is

$$g_N = \sum_{n_x=0}^{N} (N-n_x+1) = \tfrac{1}{2}(N+1)(N+2)$$

The values of g_N are given in table 13.1, column 3.

Parity The effect of using $\hat{\Pi}$ is equivalent to multiplication by $(-1)^{n_x}(-1)^{n_y}(-1)^{n_z} = (-1)^N$. States of even (odd) N therefore have even (odd) parity, as shown in table 13.1, column 4.

Angular momentum The leading term in $U_{n_x n_y n_z}$ may be written down in Cartesian coordinates and then transformed into spherical polar coordinates:

$$\begin{aligned} U_{n_x n_y n_z} &\propto e^{-m\omega(x^2+y^2+z^2)/2\hbar} x^{n_x} y^{n_y} z^{n_z} + \cdots \\ &= e^{-m\omega r^2/2\hbar} r^N \cos^{n_z}\theta \sin^{n_x+n_y}\theta \cos^{n_x}\phi \sin^{n_y}\phi + \cdots \end{aligned} \tag{13.4}$$

Comparison with the remarks below equation (10.35) about the angular complexity of $|Y_{lm}(\theta, \phi)|^2$ shows that an expansion of $U_{n_x n_y n_z}$ in angular momentum eigenfunctions contains only terms with $l \leq N$. Moreover, in view of the parities, the expansion contains only terms with l even (odd) if N is even (odd). These two rules lead quite simply to the angular momentum assignments indicated in table 13.1, column 5.

Thus the wave function with $N=0$ can only be associated with $l=0$, and so it must represent the lowest energy state of zero angular momentum, the 1s state.

The three linearly independent wave functions with $N=1$ can only be associated with $l=1$, and so they must be composed of linear combinations of the wave functions which represent the lowest energy states of angular momentum 1, the three 2p states.

The six linearly independent wave functions with $N=2$ can be associated with $l=0$ or 2. They cannot contain any 1s component, however, because they are all orthogonal to the $N=0$ wave function. Therefore they must be composed of linear combinations of the wave functions representing the next lowest energy state of zero

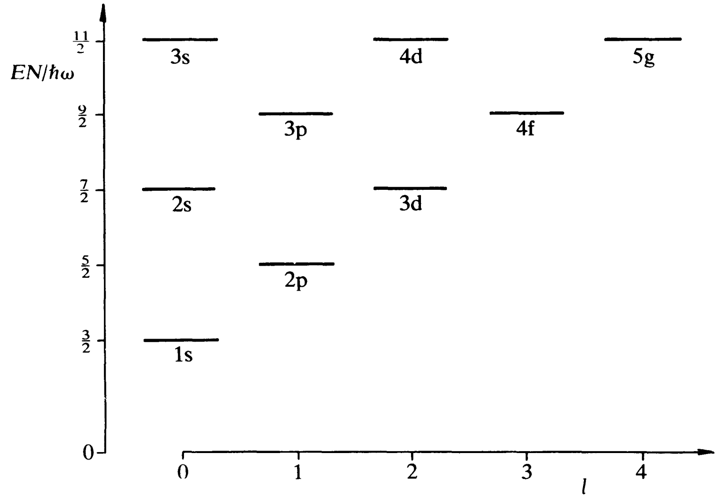

Figure 13.2 Energy levels and spectroscopic labels for the three-dimensional harmonic oscillator. The comparison with figure 12.1 is interesting: the Coulomb potential is relatively more effective at smaller radii and therefore for smaller l. Nuclear physicists using the oscillator potential often use the principal quantum number $n' = n - l$.

angular momentum, the 2s state, or the lowest energy states of angular momentum 2, the five 3d states. In fact these states must all be degenerate in energy, in order to provide the $1+5=6$ linearly independent combinations which are required. Thus the $N=2$ wave functions represent mixtures of 2s and 3d states.

The wave functions with $N=3$ and 4 can be analysed in the same way, and the level scheme shown in figure 13.2 is the result. It is interesting to compare this with figure 12.1.

§14 The deuteron

Structure The deuteron is a bound state of a neutron (mass m_n, position $\mathbf{r}_n$) and a proton (mass m_p, position $\mathbf{r}_p$). The two are held together by a short-range and strongly attractive nuclear force, which for many purposes may be described by the 'square well' potential shown in figure 14.1. The potential energy is supposed to depend only on the distance between the two particles, $|\mathbf{r}_n - \mathbf{r}_p|$; it is equal to $-V_0$ if this distance is less than or equal to the range a, and zero otherwise.

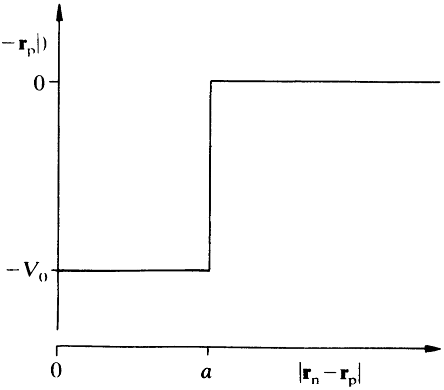

Figure 14.1 The 'square well' potential for the neutron–proton interaction.

Quantum mechanics of two-particle systems† Some modifications need to be made in the basic assumptions (section 2) when two particles are present, and in particular the wave function becomes a function of two position vectors as well as the time. In the deuteron problem, for example, the wave function is $\psi(\mathbf{r}_n, \mathbf{r}_p, t)$; physically $\psi^*\psi\, d\tau_n\, d\tau_p$ is the probability of finding the neutron in an elementary volume $d\tau_n$ at $\mathbf{r}_n$, and at the same time finding the proton in an elementary volume $d\tau_p$ at $\mathbf{r}_p$. The overall probability is proportional to both the elementary volumes, as it obviously must be.

The operators representing observables are formed in the same way as before. Thus the three components of momentum of the neutron are represented by $-i\hbar\,\partial/\partial x_n$, $-i\hbar\,\partial/\partial y_n$, $-i\hbar\,\partial/\partial z_n$, where x_n, y_n, z_n are the components of $\mathbf{r}_n$. Operators representing more complicated observables are again found by reference to their classical analogues, and in particular the total energy is represented by

$$\begin{aligned}\hat{H} &= \hat{T}_n + \hat{T}_p + \hat{V}_{np}\\ &= -\frac{\hbar^2}{2m_n}\nabla_n^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 + V(|\mathbf{r}_n - \mathbf{r}_p|) \qquad (14.1)\end{aligned}$$

where, for example, ∇_n^2 stands for the operator $\partial^2/\partial x_n^2 + \partial^2/\partial y_n^2 + \partial^2/\partial z_n^2$.

The interpretative structure of the theory is unaltered, and the TDSE still states that $i\hbar\,\partial\psi/\partial t = \hat{H}\psi$. If ψ is written in the form

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† Further points arise when the two particles are identical (section 24).

$u_s(\mathbf{r}_n, \mathbf{r}_p)e^{-iE_st/\hbar}$, then the TISE exhibits $u_s(\mathbf{r}_n, \mathbf{r}_p)$ as the usual eigenfunction of H belonging to the eigenvalue E_s:

$$\begin{aligned}\hat{H}u_s(\mathbf{r}_n, \mathbf{r}_p) &= \left\{-\frac{\hbar}{2m_n}\nabla_n^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 + V(|\mathbf{r}_n - \mathbf{r}_p|)\right\}u_s(\mathbf{r}_n, \mathbf{r}_p) \\ &= E_s u_s(\mathbf{r}_n, \mathbf{r}_p) \qquad (14.2)\end{aligned}$$

Centre of mass coordinates It is convenient to introduce new coordinates and masses by the relationships

$$\left.\begin{aligned} \mathbf{r} &= \mathbf{r}_n - \mathbf{r}_p, & \mathbf{R} &= \frac{m_n\mathbf{r}_n + m_p\mathbf{r}_p}{m_n + m_p} \\ \mu &= \frac{m_n m_p}{m_n + m_p}, & M &= m_n + m_p \end{aligned}\right\} \qquad (14.3)$$

Clearly $\mathbf{R}$ (with components X, Y, Z) is the position of the centre of mass of the deutron as a whole, and M is its total mass. On the other hand $\mathbf{r}$ (with components x, y, z) is the position of the neutron relative to that of the proton, and μ is called the *reduced mass* of the system. Now equation (14.2) may be transformed by introducing $\mathbf{R}$, $\mathbf{r}$, M, and μ, by writing $u_s(\mathbf{r}_n, \mathbf{r}_p) = F_s(\mathbf{R})f_s(\mathbf{r})$, and by dividing throughout by $F_s(\mathbf{R})f_s(\mathbf{r})$. The result is

$$\frac{1}{F_s(\mathbf{R})}\left\{-\frac{\hbar^2}{2M}\nabla_R^2\right\}F_s(\mathbf{R}) + \frac{1}{f_s(\mathbf{r})}\left\{-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right\}f_s(\mathbf{r}) = E_s \qquad (14.4)$$

where, for example, ∇_R^2 stands for the operator $\partial^2/\partial X^2 + \partial^2/\partial Y^2 + \partial^2/\partial Z^2$. Physically $F^*f^*Ff\,d\tau_R\,d\tau_r$ is the probability of finding the centre of mass of the deuteron within the element of volume $d\tau_R$ at $\mathbf{R}$, and at the same time finding the position of the neutron, relative to that of the proton, within the element of volume $d\tau_r$ at $\mathbf{r}$.

The first term in equation (14.4) is the only one that depends on $\mathbf{R}$, and so it must separately be equal to a constant, $E_{s,R}$ say:

$$-\frac{\hbar^2}{2M}\nabla_R^2 F_s(\mathbf{R}) = E_{s,R}F_s(\mathbf{R}) \qquad (14.5)$$

Similarly,

$$\left\{-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right\}f_s(\mathbf{r}) = E_{s,r}f_s(\mathbf{r}) \qquad (14.6)$$

with $E_{s,r}$ also a constant, such that $E_{s,R} + E_{s,r} = E_s$.

Comparison with equation (9.1) shows that equation (14.5) refers simply to the motion of the deuteron, considered as a free particle of mass M located at $\mathbf{R}$. The appropriate function for F_s (equations (9.7)) is a plane wave proportional to $e^{i\mathbf{K}_s\cdot\mathbf{R}}$, representing a state in which the deuteron has momentum $\hbar\mathbf{K}_s$ and kinetic energy $E_{s,R} = \hbar^2K_s^2/2M$.

On the other hand, equation (14.6), which is concerned only with the internal structure of the deuteron, is identical mathematically with the TISE for a single particle of mass μ subject to the fixed central potential $V(r)$. The appropriate methods for handling it have therefore been fully developed already.

Explicitly, $f_s(\mathbf{r})$ will be written in the form $r^{-1}S_{nl}(r)Y_{lm}(\theta, \phi)$, where the spherical polar coordinates r, θ, ϕ are related to x, y, z in the usual way (figure 10.1). If the internal energy $E_{s,r}$ is renamed E_{nl}, then the S_{nl} obey equation (11.3) exactly as before, except that m_0 is replaced by μ. The $Y_{lm}(\theta, \phi)$ are also unchanged (table 10.1), and they are eigenfunctions of the $\mathbf{l}^2$ and l_z defined by equations (10.3) and (10.4). The observable $\mathbf{l}$ will be referred to as the internal orbital angular momentum; it is actually the sum of the orbital angular momenta of the neutron and proton round the position of their centre of mass.

Ground state of the deuteron The stationary state of lowest internal energy has $l = 0$ in order to avoid a repulsive centrifugal potential, and $n = 1$ in order to minimize the number of nodes in the wave function and hence the kinetic energy. The appropriate radial equation is

$$\left\{-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r)\right\}S_{10} = E_{10}S_{10} \tag{14.7}$$

with $V(r)$ as shown in figure 14.1.† If the deuteron is bound, E must be negative, and for $r > a$,

$$\frac{d^2S}{dr^2} - \kappa^2 S = 0, \qquad \kappa = |(-2\mu E/\hbar^2)^{1/2}| \tag{14.8}$$

whose solution is $S = Ae^{-\kappa r}$. (The solution proportional to $e^{\kappa r}$ does not satisfy the boundary conditions at $r = \infty$.) Similarly for $r \leqslant a$,

$$\frac{d^2S}{dr^2} + k^2 S = 0, \qquad k = |\{2\mu(E + V_0)/\hbar^2\}^{1/2}| \tag{14.9}$$

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† The suffices 10 will be left implicit for the rest of this section.

whose solution is $S = B \sin(kr)$. The solution proportional to $\cos(kr)$ does not satisfy the boundary conditions at $r = 0$.) At $r = a$ the wave function and its first derivative must be continuous, and therefore

$$\left.\begin{aligned} A\mathrm{e}^{-\kappa a} &= B \sin(ka) \\ -\kappa A\mathrm{e}^{-\kappa a} &= kB \cos(ka) \end{aligned}\right\} \qquad (14.10)$$

When the second equation is divided by the first,

$$\cot(ka) = -\kappa/k \qquad (14.11)$$

This equation must be solved numerically in order to arrive at the appropriate value of E. A condition on the solution is $\pi/2 < ka < \pi$; the lower limit is set because $\cot(ka)$ is negative, and the upper limit because an $n = 1$ wave function has no nodes between $r = 0$ and $r = \infty$. The lower limit gives rise to a condition for a bound state of the deuteron to exist at all:

$$a\left(\frac{2\mu V_0}{\hbar^2}\right)^{1/2} > a\left\{\frac{2\mu}{\hbar^2}(E + V_0)\right\}^{1/2} > \frac{\pi}{2} \qquad (14.12)$$

since E is negative. In other words,

$$a^2 V_0 > \pi^2 \hbar^2 / 8\mu \qquad (14.13)$$

The deuteron is in fact only just bound, and the inequality only just satisfied; this gives information about $a^2 V_0$, but not about either the range or the depth of the potential separately.

Problems

4.1 Consider a mole of helium kept under standard pressure and temperature in a cubical box of side L (volume $= 2.24 \times 10^{-2}\ \mathrm{m}^3$). How many quantum states are available to the atoms, below a reasonably estimated maximum energy, say $2kT$ ($k = 1.38 \times 10^{-23}\ \mathrm{J\,K}^{-1}$, $T = 273\ \mathrm{K}$)? Hence estimate the probability of a quantum state being occupied.

4.2 Show that the PPD for each of the three p wave eigenfunctions can be expressed as a polynomial in $\cos\theta$ of degree 2. Show further that, if the PPDs (not the wave functions) are added together with equal weight, then the result is spherically symmetrical. Repeat, *mutatis mutandis*, for the d wave eigenfunctions. [*Comment*: The rule exposed here explains in part why a closed electron shell in an atom is so inert.]

4.3 The addition theorem for spherical harmonics refers to two sets of Cartesian axes **i**, **j**, **k**, and **i**′, **j**′, **k**′, together with a general point **r**. The polar and azimuthal angles of **r** relative to **i**, **j**, **k** are θ, ϕ and the corresponding angles of **k**′ relative to **i**, **j**, **k** are α, β. The angle between **r** and **k**′ is θ'. Then

$$P_l(\cos\theta') = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y^*_{lm}(\alpha, \beta) Y_{lm}(\theta, \phi)$$

Make a sketch to illustrate the angles θ, ϕ, α, β, and θ'.

A particle is in a p state belonging to the eigenvalue $l_{z'} = 0$. Use the addition theorem to show that the chances of finding $l_{x'}/\hbar = -1$, 0, or -1 are $\frac{1}{2}$, 0, or $\frac{1}{2}$ respectively. [*Hint:* Align **k** along **i**′. The angle β is arbitrary but that does not affect the result.]

4.4 Show that the TDSE for a free particle in an s state takes the simple form

$$i\hbar \frac{\partial \phi(r, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \phi(r, t)}{\partial r^2}$$

where

$$\phi(r, t) = r\psi(r, t)$$

Show further that a solution is

$$\phi(r, t) = (1/2\pi^{1/2}) S(r) \mathrm{e}^{-iEt/\hbar}$$

with

$$S(r) = A_- \mathrm{e}^{-ikr} + A_+ \mathrm{e}^{ikr}$$

and write down the consequent dispersion relation between k and E (or ω). [*Hint:* Treat the radial operator in ∇^2 as in equation (11.3). *Comment:* The boundary condition at $r = 0$ means that $A_+/A_- = -1$, but this would be modified if the particle were not free inside some definite radius, say a.]

5

Approximate methods for stationary states

§15 Perturbation theory

First-order perturbations The stationary state problems so far discussed have been solved exactly with the single exception of the deuteron problem, where numerical methods can be used to get a solution to any desired accuracy. Essentially the Schrödinger equation $\hat{H}u_s = E_s u_s$ has yielded the energy eigenfunctions u_s and the corresponding eigenvalues E_s.

In practice the energy H in these problems may very often be modified by the addition of a small perturbing term H', so causing the eigenfunctions to change by small amounts from u_s to $u_s + u_s'$ and the eigenvalues similarly from E_s to $E_s + E_s'$. The new Schrödinger equation,

$$(\hat{H} + \hat{H}')(u_s + u_s') = (E_s + E_s')(u_s + u_s') \tag{15.1}$$

may not be capable of exact solution. An approximate procedure is then to neglect terms of the second order of smallness, namely $\hat{H}'u_s'$ and $E_s'u_s'$. After cancellation of $\hat{H}u_s$ with $E_s u_s$,

$$\hat{H}u_s' + \hat{H}'u_s = E_s u_s' + E_s' u_s \tag{15.2}$$

As usual the original unperturbed eigenfunctions u_s form a complete set, so that each u_s' may be expanded in the form $u_s' = \sum_r c_{rs}' u_r$.

After $\hat{H}u_r$ has been put equal to $E_r u_r$, the equation becomes

$$\sum_r c'_{rs}E_r u_r + \hat{H}'u_s = \sum_r c'_{rs}E_s u_r + E'_s u_s \tag{15.3}$$

Every term may now be multiplied by u_k^* and integrated over all space. Since $\langle u_k \mid u_r\rangle = \delta_{kr}$,

$$c'_{ks}E_k + \langle u_k|\, \hat{H}'\, |u_s\rangle = c'_{ks}E_s + E'_s\delta_{ks} \tag{15.4}$$

The shift E'_s in the energy eigenvalues is obtained when k is put equal to s:

$$E'_s = \langle u_s|\, \hat{H}'\, |u_s\rangle = \langle H'\rangle \tag{15.5}$$

The change in the eigenfunctions is calculated by taking k not equal to s:

$$c'_{ks} = \frac{\langle u_k|\, \hat{H}'\, |u_s\rangle}{E_s - E_k}, \qquad k \neq s \tag{15.6}$$

This does not fix the value of c'_{ss}, which must be chosen so that $u_s + u'_s$ is suitably normalised. In fact it may be put equal to zero:

$$u'_s = \sum_{k\neq s} \frac{\langle u_k|\, \hat{H}'\, |u_s\rangle u_k}{E_s - E_k} \tag{15.7}$$

This is because all the u_k concerned are orthogonal to u_s, and so $\langle u_s + u'_s \mid u_s + u'_s\rangle = \langle u_s \mid u_s\rangle = 1$ to terms of the first order of smallness.

Degeneracy A condition for this procedure to work satisfactorily is that the c'_{ks} given by equation (15.6) are small compared to unity. This is obviously not true when there are u_k which are degenerate in energy with u_s (that is $E_s - E_k = 0$), and at the same time $\langle u_k|\, \hat{H}'\, |u_s\rangle \neq 0$. If this difficulty arises the eigenfunctions concerned must be rearranged into new linear combinations such that all the appropriate matrix elements of $\hat{H}'$ are zero. An example is given in section 16.

Second-order perturbations A second-order calculation of the energy shift is sometimes required, especially when $E'_s = 0$. This starts with the equation

$$(\hat{H} + \hat{H}')\left(u_s + \sum_k c'_{ks}u_k + u''_s\right) = (E_s + E'_s + E''_s)\left(u_s + \sum_k c'_{ks}u_k + u''_s\right) \tag{15.8}$$

where the c'_{ks} and E'_s have already been evaluated, and u''_s and E''_s are of the second order of smallness. The zero- and first-order terms already satisfy the equation, and when third- and higher-order terms are discarded,

$$\hat{H}u''_s + \sum_k c'_{ks}\hat{H}'u_k = E_s u''_s + E'_s \sum_k c'_{ks}u_k + E''_s u_s \tag{15.9}$$

Now u''_s may be written in the form $\sum_j c''_{js}u_j$ and the scalar product taken of every term with u_s. The result is

$$\begin{aligned} E''_s &= \sum_{k\neq s} \frac{\langle u_s|\,\hat{H}'\,|u_k\rangle\langle u_k|\,\hat{H}'\,|u_s\rangle}{E_s - E_k} \\ &= \sum_{k\neq s} \frac{|\langle u_k|\,\hat{H}'\,|u_s\rangle|^2}{E_s - E_k} \end{aligned} \tag{15.10}$$

For the ground state ($s=1$, say) E''_1 is necessarily negative, because $E_1 - E_k$ is always negative.

The summation in equation (15.10) may be difficult to evaluate, but a useful upper limit to $-E''_1$ may be found by replacing $E_k - E_1$ by its minimum value, $E_2 - E_1$. With the help of the closure relation of equation (4.19),

$$\begin{aligned} -E''_1 &\leq \left(\frac{1}{E_2 - E_1}\right) \sum_{k\neq 1} \langle u_1|\,\hat{H}'\,|u_k\rangle\langle u_k|\,\hat{H}'\,|u_1\rangle \\ &= \left(\frac{1}{E_2 - E_1}\right)\left(\sum_k \langle u_1|\,\hat{H}'\,|u_k\rangle\langle u_k|\,\hat{H}'\,|u_1\rangle - \langle u_1|\,\hat{H}'\,|u_1\rangle^2\right) \\ &= \left(\frac{1}{E_2 - E_1}\right)(\langle u_1|\,\hat{H}'^2\,|u_1\rangle - E_1'^2) \end{aligned} \tag{15.11}$$

§16 Hydrogen atom in an electric field

The perturbing potential in a uniform field The coordinate system may be chosen so that the electric field is directed along the z axis, and the potential energy of the electron (charge $-e$) then contains an extra term $e\mathscr{E}z = e\mathscr{E}r\cos\theta$. For any reasonable value of $\mathscr{E}$ this may certainly be regarded as small compared to the kinetic and Coulomb energy terms.

Ground state perturbation in first order According to equation (15.5) the first-order shift in the ground state energy is

$$\begin{aligned} E'_{100} &= \langle u_{100}|\, e\mathscr{E} r \cos\theta \,|u_{100}\rangle \\ &= e\mathscr{E}\int u^*_{100}(r\cos\theta)u_{100}\,\mathrm{d}\tau \end{aligned} \qquad (16.1)$$

Now u_{100} is a parity eigenfunction,† and so $u^*_{100}u_{100}$ is an even function of position. On the other hand the perturbation is an odd function and therefore the integrand as a whole is odd. Any contribution at the point **r** is cancelled by the contribution at −**r**, and it follows that $E'_{100}=0$.

A short way of stating this result is to say that the electric dipole moment of the system is zero. Obviously the same is true of any state of definite parity, provided that the calculation is not complicated by degeneracy.

Ground state perturbation in second order A limit to the second-order shift may be obtained from equation (15.11):

$$\begin{aligned} -E''_{100} &\leqslant \frac{\langle u_{100}|\, e^2\mathscr{E}^2 r^2\cos^2\theta \,|u_{100}\rangle}{(E_{200}-E_{100})} \\ &= \frac{32\varepsilon_0\mathscr{E}^2}{3a_0^2}\int_0^\infty\int_0^\pi\int_0^{2\pi} r^4 \mathrm{e}^{-2r/a_0}\cos^2\theta\sin\theta\,\mathrm{d}\phi\,\mathrm{d}\theta\,\mathrm{d}r \\ &= \frac{32\pi\varepsilon_0}{3}a_0^3\mathscr{E}^2 \end{aligned} \qquad (16.2)$$

The second-order shift may be written $-\frac{1}{2}\alpha\mathscr{E}^2$, where α is the polarisability of the system; evidently for the ground state of the hydrogen atom‡ $\alpha \leqslant (64\varepsilon_0/3)a_0^3$.

Perturbations of $n=2$ ***states in first order*** The $n=2$ eigenfunctions u_{200}, u_{211}, u_{210}, and u_{21-1} represent four states which are degenerate in energy in the simple theory of the hydrogen atom. They are also eigenfunctions of the parity, and in fact the energies associated with u_{211} and u_{21-1} are not shifted in first order by the electric field. However, the perturbation calculations for u_{200} and u_{210} are spoiled

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† It is in fact even parity, since $l=0$, but this is not essential to the argument.

‡ An exact calculation gives $\alpha=(18\varepsilon_0)a_0^3$, so that the upper limit is only about 20 per cent high.

by non-vanishing matrix elements,†

$$\langle u_{210}|\, e\mathscr{E}r\cos\theta\, |u_{200}\rangle = \langle u_{200}|\, e\mathscr{E}r\cos\theta\, |u_{210}\rangle^*$$

$$= \frac{e\mathscr{E}}{16\pi a_0^4}\int_0^\infty\int_0^\pi\int_0^{2\pi} r^4\left(1-\frac{r}{2a_0}\right)e^{-r/a_0}$$

$$\times\cos^2\theta\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi$$

$$= -3e\mathscr{E}a_0 \tag{16.3}$$

The remedy is to work with new normalised linear combinations of these two eigenfunctions, namely $u_2' = (1/\surd 2)(u_{200}+u_{210})$ and $u_2'' = (1/\surd 2)(u_{200}-u_{210})$. With the help of equation (16.3) it is easily seen that

$$\left.\begin{aligned}\langle u_2'|\, e\mathscr{E}r\cos\theta\, |u_2''\rangle &= \langle u_2''|\, e\mathscr{E}r\cos\theta\, |u_2'\rangle = 0\\ \langle u_2'|\, e\mathscr{E}r\cos\theta\, |u_2'\rangle &= -3e\mathscr{E}a_0\\ \langle u_2''|\, e\mathscr{E}r\cos\theta\, |u_2''\rangle &= 3e\mathscr{E}a_0\end{aligned}\right\} \tag{16.4}$$

The first equation checks that u_2' and u_2'' can be handled by perturbation methods, while the second and third give the corresponding energy shifts in first order.

The $n=2$ stationary states of the hydrogen atom in the electric field are therefore represented by u_{211}, u_{21-1}, u_2', and u_2'', whose energy eigenvalues are summarised in figure 16.1. Obviously u_2' and u_2'' are not eigenfunctions of $\mathbf{l}^2$ or Π, but this is not surprising because these observables do not commute with the total energy when the term $e\mathscr{E}r\cos\theta$ is present.

§17 The variational method

Upper limits to ground state energies It is obvious that the expectation value of the energy $\langle H\rangle$, computed from a normalised wave function v, cannot be less than the lowest energy eigenvalue E_0. Moreover, the difference is very small if v does not differ much from u_0, the ground state eigenfunction. For let v be expanded in energy eigenfunctions, $v = \sum_s c_s u_s$, where the coefficients c_s for $s \geqslant 1$ are

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† Matrix elements of $e\mathscr{E}r\cos\theta$ which connect two states of different magnetic quantum number vanish when the integration over ϕ is carried out.

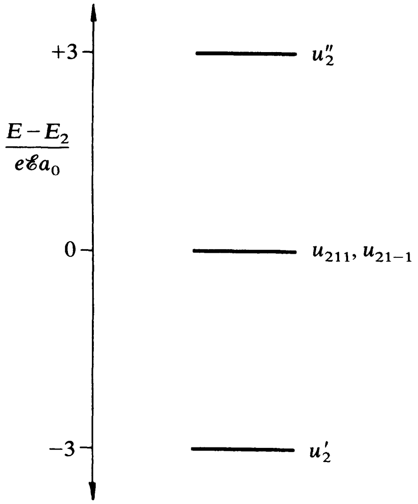

Figure 16.1 The $n=2$ energy levels of a hydrogen atom in a uniform electric field.

supposed to be of the first order of smallness. Then, because $\sum_s |c_s|^2 = 1$, we find

$$\langle H\rangle = \sum_{s=0}^{\infty} |c_s|^2 E_s = E_0 + \sum_{s=1}^{\infty} (E_s - E_0)\, |c_s|^2 \qquad (17.1)$$

which shows that $\langle H\rangle - E_0$ is of the second order of smallness.

The variational method for estimating a ground state energy is to write down a trial wave function depending on one adjustable parameter, whose value is then varied until $\langle H\rangle$ is a minimum. This minimum will not be far above E_0 if the trial wave function has been wisely chosen. Obviously it should have a general form which is appropriate to the state being investigated; the ground state of the helium atom, for example, should be represented by a spherically symmetrical electron wave function (no orbital angular momentum) with no nodes between zero and infinite radius (minimum kinetic energy). This particular problem will be worked out in detail later (section 24).

The variational principle A simple generalisation of equation (17.1) states that if a normalised v differs little from an eigenfunction u_s of l, belonging to the eigenvalue l_s, then $\langle v|\, l - l_s\, |v\rangle$ is of the second order of smallness. This principle can be applied to find approximations both to l_s and u_s, but considerable insight and subtlety are required to get useful results.

§18 The WKB approximation

This method of approximation was invented by Jeffreys in 1925 and introduced into quantum mechanics by Wentzel, Kramers, and Brillouin in 1926. It provides the mathematical support for the discussion given in section 7 and especially the part that related to figure 7.1, which should be studied again.

The oscillatory region Here $E-V(x)$ is positive and the TISE may be written

$$\frac{d^2u}{dx^2}=-k^2(x)u \tag{18.1}$$

where $k(x)$ is real and positive. The WKB approximation may be set up by writing $u=e^{iv}$. Then,

$$-\left(\frac{dv}{dx}\right)^2+i\frac{d^2v}{dx^2}=-k^2 \tag{18.2}$$

and

$$v=\pm\int^x\left(k^2+i\frac{d^2v}{dx^2}\right)^{1/2}dx \tag{18.3}$$

The fixed but arbitrary lower limit of integration will be chosen later, and the associated constants of integration left implicit up to that point.

Now if $k(x)$ had actually been a constant, k_0 say, the solutions $u=e^{\pm ik_0x}$ could have been written down at once. Then v would have been equal to $\pm k_0x$, and d^2v/dx^2 would have been zero. This suggests that, if k is actually varying slowly, a first approximation to v can be obtained by neglecting d^2v/dx^2 in equation (18.3) Thus,

$$v\approx v_1=\pm\int^x k\,dx \tag{18.4}$$

Now $d^2v_1/dx^2=\pm dk/dx$, and this can be put back into equation (18.3) to get a second approximation to v,

$$v\approx v_2=\pm\int^x\left(k^2\pm i\frac{dk}{dx}\right)^{1/2}dx \tag{18.5}$$

where, to be consistent, plus or minus signs must be used throughout. If the approximation is to work well v_2 should be close to v_1. So,

$$\left|\frac{\mathrm{d}k}{\mathrm{d}x}\right| \ll k^2 \tag{18.6}$$

which is the basic condition for applying the WKB approximation in the oscillatory region. If a 'wavelength' $\lambda(x)$ is defined by $\lambda = 2\pi/k$, an equivalent statement is that

$$\left|\frac{\mathrm{d}\lambda}{\mathrm{d}x}\right| \ll 2\pi \tag{18.7}$$

Thus the fractional change in wavelength from one oscillation to the next (an increase of x by about λ) must be small compared to 2π. Obviously this allows u to differ markedly from an oscillation of constant wavelength.

The expression for v_2 can be simplified by making further use of equation (18.6) to write

$$v_2 \approx \pm \int^x \left(k \pm \frac{i}{2k}\frac{\mathrm{d}k}{\mathrm{d}x}\right)\mathrm{d}x = \pm \int^x k\,\mathrm{d}x + \tfrac{1}{2}i \log k \tag{18.8}$$

In the oscillatory region, then, u can be approximated by

$$\mathrm{e}^{iv_2} = k^{-1/2} \exp\left(\mp i \int_x^{x_0} k\,\mathrm{d}x + c_{\mp}\right) \tag{18.9}$$

where the arbitrary limit of integration has been fixed at the position of the turning point (x_0) and the limits of integration have been reversed to make the integral positive. The constants of integration have also been made explicit; they can be complex to achieve any desired phase and normalisation.

In bound state problems it is convenient to use standing rather than progressive waves. They are produced by appropriate linear combination of the solutions (18.9),

$$u \approx u_0 = k^{-1/2} \cos(y_0 + \phi) \tag{18.10}$$

where

$$y_0 \equiv \int_x^{x_0} k\,\mathrm{d}x \tag{18.11}$$

In equation (18.10) a particular choice of normalisation has been made, but the phase angle ϕ is still arbitrary. Obviously two independent standing waves can always be obtained by choosing a pair of phase angles differing by $\pi/2$.

The exponential region Now equation (18.1) is replaced by

$$\frac{\mathrm{d}^2u}{\mathrm{d}x^2}=\kappa^2(x)u \tag{18.12}$$

where $\kappa(x)$ is real and positive. The WKB approximation to the solution of this equation can be obtained in a similar way, provided that

$$\left|\frac{\mathrm{d}\kappa}{\mathrm{d}x}\right| \ll \kappa^2 \tag{18.13}$$

The result is

$$u \approx u_\mathrm{E}=\kappa^{-1/2}\mathrm{e}^{\pm y_\mathrm{E}} \tag{18.14}$$

where

$$y_\mathrm{E}\equiv\int_{x_0}^{x}\kappa\,\mathrm{d}x \tag{18.15}$$

and an arbitrary choice of normalisation has been made. In practice the solution with a negative sign in the argument of the exponential is most often required, to suit a boundary condition.

Joining solutions through the turning region It will be realised that the WKB solutions (18.10) and (18.14) hold good whether or not $V(x)$ varies linearly with x, as it did in figure 7.1. It is only necessary that the conditions (18.6) and (18.13) are satisfied over a useful range of x.

To join up solutions through the turning region it is necessary to specify $V(x)$ there precisely. Clearly a linear variation is most generally appropriate,

$$V(x)=E(1+\alpha x) \tag{18.16}$$

where, for convenience, the origin of the coordinate system has been chosen so that $x_0=0$.

The TISE in the turning region has two independent solutions as usual. The first (second) may be arranged to connect a solution of

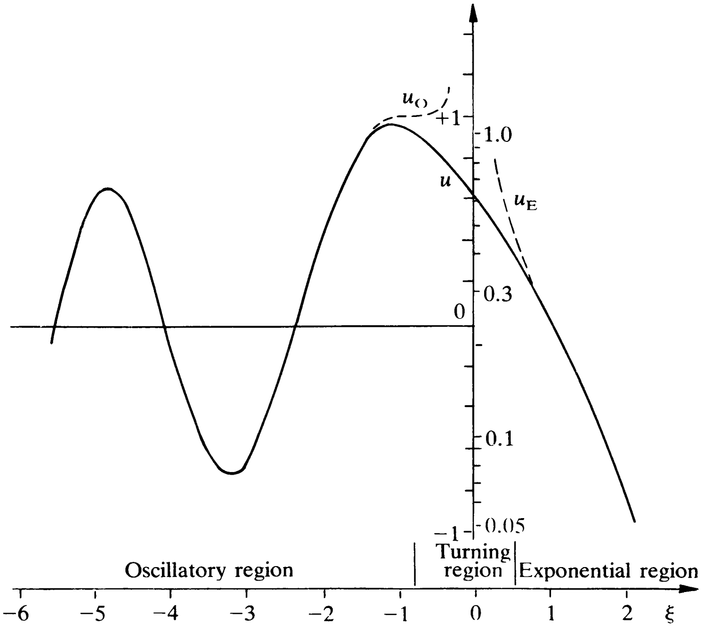

Figure 18.1 The exact wave function u near the turning point of a linearly varying potential, and the WKB approximations u_O and u_E. The vertical scale is linear to the left of turning point and logarithmic to the right.

the type (18.10) with $\phi = -\pi/4$ ($\phi = +\pi/4$) through to the solution of the type (18.14) which decreases (increases) exponentially. The connection formulae which give the internal normalisations are

$$\left.\begin{aligned} k^{-1/2}\cos(y_O - \pi/4) &\twoheadleftarrow\!\!\!\rightarrow \tfrac{1}{2}\kappa^{-1/2}e^{-y_E} \\ k^{-1/2}\cos(y_O + \pi/4) &\leftarrow\!\!\!\twoheadrightarrow \kappa^{-1/2}e^{+y_E} \end{aligned}\right\} \qquad (18.17)$$

The proof of these easily grasped results is both very tedious and quite advanced, and it will not be given here. However, figure 18.1 shows the first solution through all three regions, and the failure of the WKB approximations in the turning region can be seen. The position variable used in figure 18.1 is dimensionless,†

$$\xi = |(2m\alpha E/\hbar^2)^{1/3}|\, x = |\{2m\hbar^{-2}(\mathrm{d}V/\mathrm{d}x)\}^{1/3}|\, x \qquad (18.18)$$

The double and single arrowheads in equations (18.17) are a reminder of a point that must be kept in mind. If the exponentially

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† Equations (18.16) and (18.18) give $y_O = \frac{2}{3}(-\xi)^{3/2}$ and $y_E = \frac{2}{3}\xi^{3/2}$.

decreasing solution is found far inside the exponential region, then the phase of the wave function in the oscillatory region can be confidently inferred. The reverse is not true, for a small change in phase in the oscillatory region will introduce some of the exponentially increasing solution; the coefficient may be small, but nevertheless this solution will dominate far inside the exponential region. The first formula (18.17) can be used freely only in the direction of the double arrow. In the second formula the double arrow points in the opposite direction, obviously.

Potential increasing to the left The discussion so far has dealt entirely with a potential increasing to the right through the turning point x_0. However, the connection formulae can be used unchanged in the reverse situation, provided that the limits of integration in the formulae for y_O and y_E are both reversed.

Approximate energy eigenvalues for bound states The WKB approximation can be applied in an interesting way to estimate the energy eigenvalues of bound states.

If there is no node the angle $y_O + \phi$ (equations (18.10) and (18.11)) must increase from the value $-\pi/4$ at the reference turning point (x_1) through zero to the value $\pi/4$ at the other turning point (x_2). Thus

$$\int_{x_1}^{x_2} k\,\mathrm{d}x = \pi/2, \qquad \text{no node} \tag{18.19}$$

If there are nodes the phase integral must increase by π for each node,

$$\int_{x_1}^{x_2} k\,\mathrm{d}x = (n+\tfrac{1}{2})\pi, \qquad n \text{ nodes} \tag{18.20}$$

This equation expresses the Bohr–Sommerfeld quantisation rule, published in 1915.

As an example the energy levels of the linear harmonic oscillator may be estimated. With the notation of section 8,

$$\frac{m\omega}{\hbar}\int_{-(2E_n/m\omega^2)^{1/2}}^{+(2E_n/m\omega^2)^{1/2}} \left(\frac{2E_n}{m\omega^2} - x^2\right)^{1/2} \mathrm{d}x \approx (n+\tfrac{1}{2})\pi \tag{18.36}$$

and integration gives the remarkable result $E_n \approx (n+\frac{1}{2})\hbar\omega$. This formula is exactly correct in spite of the approximations made in the calculation.

Phase space and quantisation Classically a particle with energy E_n in a bound state bounces back and forth between the turning points x_1 and x_2, its momentum at any intermediate point being $p = \pm[2m\{E_n - V(x)\}]^{1/2}$.

Now phase space is constructed by using x and p as two orthogonal coordinates, and the classical trajectory of the particle in phase space may be plotted (figure 18.2) through one complete oscillation. This trajectory is of course closed, and symmetrical about the $p=0$ axis. The area inside is

$$2\int_{x_1}^{x_2} p\,\mathrm{d}x = (2n+1)\pi\hbar \tag{18.22}$$

according to equation (18.20).

The trajectory of a particle with E_{n-1} would lie entirely inside the one just discussed, and it would enclose an area $(2n-1)\pi\hbar$. Another version of the quantisation rule, therefore, is that each additional stationary state involves the enclosure in phase space of

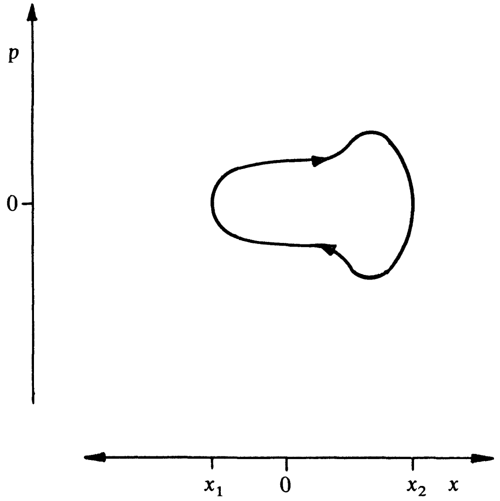

Figure 18.2 Classical trajectory in phase space of a particle in a bound state.

an extra area $2\pi\hbar$ by the corresponding classical motion. The similar rule in three-dimensional motion involves a volume $(2\pi\hbar)^3$ in phase space. Something like these rules has been seen before (equations (6.8) and (9.9)).

Problems

5.1 The proton would be more accurately described as a uniformly charged sphere of radius 10^{-14} m than as a point charge. Use perturbation theory to estimate the consequent small change in the binding energy of the 1s state of the hydrogen atom.

The change in the binding energy of the 2p state is even less. Why is this?

5.2 When a uniform electric field is applied to the 1s state of the hydrogen atom the wave function becomes distorted. Find the admixture of the following wave functions:

$$2\text{p}\,(m=0), \qquad 2\text{p}\,(m=1), \qquad 2\text{s}$$

5.3 A particle is subject to a square well potential of finite depth ($V=0$, $-L/2 \leqslant x \leqslant L/2$; $V=V_0$ elsewhere). Use the Bohr–Sommerfeld quantisation rule to find the number of bound states. Is the answer accurate?

5.4 Verify that the Bohr–Sommerfeld quantisation rule is not useful for estimating the energy of the 1s state of the hydrogen atom. The failure appears as a mathematical snag: what is the basic reason for it?

6

Magnetic fields and spin angular momentum

§19 Review of classical mechanics: general rules for quantisation

Introduction It has been assumed so far that the forces acting on a particle can be described by a scalar potential V. However, the forces produced on a charged particle by a magnetic field are not in this class; they depend on the particle's velocity as well as its position. To deal with these forces it is necessary to put the theory on a more general basis, which uses the advanced classical mechanics embodied in the Lagrangian and Hamiltonian equations of motion. A brief review of this classical theory follows, and then it will be seen that the passage to quantum mechanics can be very simply achieved.

Classical mechanics: Lagrangian equations of motion A Lagrangian function $L(x_i, \dot{x}_i, t)$ is assigned to the particle, where the x_i $(i = 1, 2, 3)$ are the Cartesian position coordinates and the $\dot{x}_i$ are the corresponding components of velocity; for mathematical purposes the x_i, $\dot{x}_i$, and t will be regarded as independent arguments in considering variations of L.

The Lagrangian equations of motion are given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{x}_j}-\frac{\partial L}{\partial x_j}=0 \qquad (19.1)$$

The physical content of these equations depends entirely on the choice of L. In the simple situation, with forces that can be described by a potential $V(x_i, t)$, the correct choice is easily seen to be $L = T - V$,

$$L(x_i, \dot{x}_i, t) = \sum_i \tfrac{1}{2} m \dot{x}_i^2 - V(x_i, t) \tag{19.2}$$

For then the Lagrangian equations take the form,

$$m\ddot{x}_j + \frac{\partial V}{\partial x_j} = 0 \tag{19.3}$$

or $m\dot{\mathbf{v}} = -\mathbf{grad}\ V$.

Classical mechanics: Hamiltonian equations of motion The Lagrangian equations can be cast into another form by defining new variables, the momenta p_i conjugate to the x_i, and a new function, the Hamiltonian H.

The momenta are defined by

$$p_i = \frac{\partial L}{\partial \dot{x}_i} \tag{19.4}$$

and the Hamiltonian function by

$$H = \sum_i p_i \dot{x}_i - L(x_i, \dot{x}_i, t) \tag{19.5}$$

When considering variations of H the p_i and $\dot{x}_i$ will be considered as independent arguments for the first term, and the x_i, the $\dot{x}_i$, and t for the second term. Then

$$\begin{aligned} \mathrm{d}H &= \sum_j \left\{ \dot{x}_j\, \mathrm{d}p_j + p_j\, \mathrm{d}\dot{x}_j - \frac{\partial L(x_i, \dot{x}_i, t)}{\partial x_j} \mathrm{d}x_j \right. \\ &\quad \left. - \frac{\partial L(x_i, \dot{x}_i, t)}{\partial \dot{x}_j} \mathrm{d}\dot{x}_j \right\} - \frac{\partial L(x_i, \dot{x}_i, t)}{\partial t} \mathrm{d}t \\ &= \sum_j \left(\dot{x}_j\, \mathrm{d}p_j - \frac{\partial L}{\partial x_j} \mathrm{d}x_j \right) - \frac{\partial L}{\partial t} \mathrm{d}t \\ &= \sum_j (\dot{x}_j\, \mathrm{d}p_j - \dot{p}_j\, \mathrm{d}x_j) - \frac{\partial L}{\partial t} \mathrm{d}t \end{aligned} \tag{19.6}$$

Here the second and fourth terms of the first equation cancelled because of the definition of the momenta, and the step between the second and third equations used the Lagrangian equations also.

It is clear from the last line of equation (19.6) that the x_j, the p_j, and t may conveniently be used as the independent arguments for H, when considering its variation as a whole. In this way the Hamiltonian equations of motion are obtained:

$$\frac{\partial H(x_i, p_i, t)}{\partial x_j} = -\dot{p}_j; \qquad \frac{\partial H(x_i, p_i, t)}{\partial p_j} = \dot{x}_j \tag{19.7}$$

All this takes on a very familiar appearance in the simple situation where the forces can be described by a potential V. Then L is given by equation (19.2) and the momenta defined by equation (19.4) are $p_i = m\dot{x}_i$, as usual. The Hamiltonian H, defined by equation (19.5), is

$$H = \sum_i p_i \dot{x}_i - T + V = T + V$$

thus H is in fact the total energy, in line with the notation used all along. Explicitly,

$$H(x_i, p_i, t) = \left(\sum_i p_i^2/2m\right) + V(x_i, t) \tag{19.8}$$

and the Hamiltonian equations are,

$$\frac{\partial V}{\partial x_j} = -\dot{p}_j; \qquad \frac{p_j}{m} = \dot{x}_j \tag{19.9}$$

In other words $\dot{\mathbf{p}} = -\mathbf{grad}\ V$ and $\mathbf{p} = m\mathbf{v}$, as usual.

Quantisation Two rules suffice for the passage from classical to quantum mechanics. First, the p_i conjugate to each x_i is to be replaced by the operator $-i\hbar(\partial/\partial x_i)$. Secondly, the Hamiltonian operator $\hat{H}\{x_i, -i\hbar(\partial/\partial x_i), t\}$ thus formed is to be used in the Schrödinger equation $i\hbar(\partial\psi/\partial t) = \hat{H}\psi$.

In the simple situation where the forces can be described by a potential these rules lead at once to equations (2.14) and (2.17). All conclusions up to the present point are thus automatically recovered.

§20 Magnetic fields

Classical mechanics An electric and magnetic field, specified by $\mathscr{E}$ and $\mathscr{B}$, can be described in terms of scalar and vector potentials ϕ

and **A**. The relations between the fields and the potentials are

$$\mathscr{E} = -\nabla\phi - \frac{\partial \mathbf{A}}{\partial t}, \qquad \mathscr{B} = \nabla \times \mathbf{A} \tag{20.1}$$

and the divergence of **A** may be fixed by the gauge condition,

$$\nabla \cdot \mathbf{A} + \frac{1}{c^2}\dot{\phi} = 0 \tag{20.2}$$

For a particle of charge e and mass m moving in this electromagnetic field the Lagrangian is in fact

$$L = T - e\phi + e\mathbf{v}\cdot\mathbf{A} = \sum_i \left(\tfrac{1}{2}m\dot{x}_i^2 + e\dot{x}_i A_i\right) - e\phi \tag{20.3}$$

To check this the Lagrangian equations must be shown to predict the correct electric and magnetic forces on the particle. In fact they state that

$$m\ddot{x}_j = e\left(-\frac{\partial\phi}{\partial x_j} - \dot{A}_j + \sum_i \dot{x}_i \frac{\partial A_i}{\partial x_j}\right) \tag{20.4}$$

Now there are two reasons why the value of **A** at the position of the particle may vary with time; one is that **A** itself may vary with time and the other is that the particle may be changing its position in the field with time. In other words,

$$\dot{A}_j = \frac{\partial A_j}{\partial t} + \sum_i \dot{x}_i \frac{\partial A_j}{\partial x_i} \tag{20.5}$$

and so

$$m\ddot{x}_j = e\left(-\frac{\partial\phi}{\partial x_j} - \frac{\partial A_j}{\partial t}\right) + e\sum_i \left(-\dot{x}_i \frac{\partial A_j}{\partial x_i} + \dot{x}_i \frac{\partial A_i}{\partial x_j}\right) \tag{20.6}$$

The expression in the first bracket is the jth component of $\mathscr{E}$, and in the second bracket two terms cancel and the remaining four can be identified with $\mathbf{v}\times\nabla\times\mathbf{A}$. Thus the Lagrangian equations simply show the particle accelerating under the usual Lorentz force,

$$m\dot{\mathbf{v}} = e(\mathscr{E} + \mathbf{v}\times\mathscr{B}) \tag{20.7}$$

Now that L has been decided, equation (19.4) can be used to find the momenta p_i conjugate to the x_i,

$$p_i = m\dot{x}_i + eA_i \tag{20.8}$$

or

$$\mathbf{p} = m\mathbf{v} + e\mathbf{A} \tag{20.9}$$

Then the Hamiltonian function can be found from equation (19.5),

$$\begin{aligned} H &= \sum_i (p_i\dot{x}_i - \tfrac{1}{2}m\dot{x}_i^2 - e\dot{x}_i A_i) + e\phi \\ &= \sum_i \frac{1}{2m}(p_i - eA_i)^2 + e\phi \qquad (20.10) \\ &= \frac{1}{2m}(\mathbf{p} - e\mathbf{A})^2 + e\phi \end{aligned}$$

Quantisation The rules for quantisation set out at the end of section 19 lead at once to the Hamiltonian operator

$$\begin{aligned} \hat{H} &= \frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - e\mathbf{A})^2 + e\phi \\ &= -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + \frac{i\hbar e}{2m}(\boldsymbol{\nabla}\,.\,\mathbf{A} + \mathbf{A}\,.\,\boldsymbol{\nabla}) + \frac{e^2}{2m}\mathbf{A}^2 + e\phi \qquad (20.11) \end{aligned}$$

Here the first term in the parentheses instructs that the differential operator should act on the product of A and any wave function to which $\hat{H}$ is applied. With the usual rule for the differentiation of products, and with the help of equation (20.2),

$$\boldsymbol{\nabla}\,.\,\mathbf{A} = \mathbf{A}\,.\,\boldsymbol{\nabla} + (\boldsymbol{\nabla}\,.\,\mathbf{A}) = \mathbf{A}\,.\,\boldsymbol{\nabla} - \frac{1}{c^2}\dot{\phi} \qquad (20.12)$$

where the parentheses indicate a multiplicative factor. Altogether then

$$\hat{H} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + \frac{i\hbar e}{m}\mathbf{A}\,.\,\boldsymbol{\nabla} + \frac{e^2}{2m}\mathbf{A}^2 + e\phi - \frac{i\hbar e}{2mc^2}\dot{\phi} \qquad (20.13)$$

Electrons in a uniform magnetic field The magnetic field may be supposed to have a uniform strength $\mathscr{B}$ directed along the z axis, since the orientation of the coordinate system can be chosen arbitrarily. The vector potential is then,

$$\left.\begin{aligned} &A_x = -\tfrac{1}{2}\mathscr{B}y; \qquad A_y = \tfrac{1}{2}\mathscr{B}x; \qquad A_z = 0 \\ &(\boldsymbol{\nabla}\times\mathbf{A})_x = (\boldsymbol{\nabla}\times\mathbf{A})_y = 0; \qquad (\boldsymbol{\nabla}\times\mathbf{A})_z = \mathscr{B} \end{aligned}\right\} \qquad (20.14)$$

The electric field is assumed to be static, so that $\dot{\phi} = 0$.

For reasonably weak magnetic fields $\mathbf{A}^2$ may be neglected, so that the second term in equation (20.13) is the only new one. Its value for an electron of charge $-e$ and mass m_e is,†

$$-\frac{i\hbar e}{m_e}\mathbf{A}\,.\,\boldsymbol{\nabla}=-\frac{i\hbar e\mathscr{B}}{2m_e}\left(-y\frac{\partial}{\partial x}+x\frac{\partial}{\partial y}\right)=\frac{e\mathscr{B}}{2m_e}\left(-ih\frac{\partial}{\partial\phi}\right) \tag{20.15}$$

The operator here is the familiar l_z, and so the effect of the magnetic field on an eigenstate of l_z is easily evaluated. The energy of the state is altered by the Zeeman shift ε_m, where

$$\varepsilon_m=\frac{e\hbar}{2m_e}m\mathscr{B} \tag{20.16}$$

It is obvious now why m was called the magnetic quantum number in section 10.

Classically the energy of a magnetic dipole in the magnetic field would be $-\mu_z\mathscr{B}$, where μ_z is the z-component of its magnetic moment. Thus the electron behaves as if it had a z-component of magnetic moment

$$\mu_z=-\left(\frac{e\hbar}{2m_e}\right)m=\mu_B m \tag{20.17}$$

where $\mu_B=-e\hbar/2m_e$ is a natural unit of magnetic moment for a particle of charge $-e$ and mass m_e. It is called the Bohr magnetic moment of the particle concerned, here an electron.

The Zeeman shift will often be written

$$\varepsilon_{m_l}=-\mu_B g_l m_l\mathscr{B} \tag{20.18}$$

where a subscript l has been added to the magnetic quantum number, to show that orbital angular momentum is involved, and a factor g_l equal to unity has been introduced. The significance of these steps will be understood in section 21.

Atoms in a non-uniform magnetic field Classically a force $\mu_z\mathscr{B}'$ in the z-direction is exerted on a magnetic dipole with z-component μ_z by a magnetic field whose z-component is $\mathscr{B}+\mathscr{B}'z$ ($\mathscr{B}, \mathscr{B}'$ constants). The effects of this force are also predicted by quantum mechanics, in accordance with the correspondence principle, but there is the important feature that μ_z is quantised by equation (20.17). From 1921 onwards Stern and Gerlach demonstrated this

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† Just at this point the same symbol ϕ is being used for both the scalar potential and the azimuthal angle. The context will show which is meant.

by using a non-uniform magnetic field to split collimated beams of randomly oriented atoms into $2l+1$ discrete components, each with a particular value of m. The importance of these observations was immediately clear, but some years passed before they could be fully interpreted.

§21 Spin angular momentum

Experiments on Zeeman shifts and Stern–Gerlach splittings show that equation (20.18) leads to the right order of magnitude for the effects observed, which are certainly of the kind predicted. There are, however, some very serious discrepancies in detail.

The first Stern–Gerlach experiment, for example, split a beam of silver atoms into *two* components, although $2l+1$ cannot be even for integral l. This is of course a complicated result to discuss here, because the silver atom contains many electrons.

It is simpler to consider a fact which was established with more difficulty, that the 1s level of the hydrogen atom is Zeeman shifted and split into two components, differing in energy by $2\mu_B\mathscr{B}$. This is just twice the normal spacing between states differing by unit m_l.

There are two important points to note. The first is that there are twice as many levels (2) as expected (1), and this feature turns out to be common to all levels of a single electron. The second is that the energy splitting is at least of the order of magnitude predicted.

These clues support the suggestion, first put forward by Uhlenbeck and Goudsmit in 1925, that the anomaly had something to do with an angular momentum of the electron such that two eigenvalues for its z-component exist. Consideration of figure 10.2 shows that the appropriate angular momentum has a squared value of $\frac{1}{2}(\frac{1}{2}+1)\hbar^2 = \frac{3}{4}\hbar^2$, with possible z-components of $\pm\frac{1}{2}\hbar$. Conveniently, but somewhat loosely, these eigenvalues may be said to belong to 'a state of angular momentum $\frac{1}{2}$'.

It is true that half-integral values were eschewed for orbital angular momentum, on the grounds that eigenfunctions single-valued in ϕ could not be found for them. The objection does not rule out the possibility that the particle itself has an intrinsic angular momentum, or *spin*, which is not directly related to its orbital motion; this spin angular momentum $\mathbf{s}$ may be represented by operators $\hat{\mathbf{s}}$ which have no other function except to act on spin eigenfunctions $\chi_{\pm\frac{1}{2}}$, which in turn have no other function than to respond to $\hat{\mathbf{s}}$. In particular the $\chi_{\pm\frac{1}{2}}$ are not represented by wave functions of some coordinate describing the orientation of the electron, so that no question arises of single-valuedness in such a coordinate. The quantum mechanical formalism for all this is perfectly normal, as will be seen, but no useful classical picture of the spin can be given because the angular momentum involved disappears in the limit $\hbar \rightarrow 0$. The same is not true for orbital angular momentum because the quantum numbers l and m may take arbitrarily large values.

In order to explain the double-sized Zeeman splitting the corresponding equation to equation (20.18) must be

$$\varepsilon_{m_s} = -\mu_B g_s m_s \mathscr{B}, \qquad m_s = \pm\tfrac{1}{2} \tag{21.1}$$

with $g_s = 2$. This means that the magnetic moment per unit of spin angular momentum is given just twice the value deduced for orbital angular momentum.

The introduction of spin $\frac{1}{2}$ (as it is loosely called) and the assignment $g_s = 2$ are presented here as responses to experimental facts. It should be mentioned that in fully relativistic quantum mechanics the Schrödinger equation is replaced by either the Klein–Gordon or the Dirac equation. The particles described by the Klein–Gordon equation have no spin, but those described by the Dirac equation have the spin $\frac{1}{2}$ and $g_s = 2$ 'built in' from the start. The latter class of particles includes the electron.

As a matter of fact the proton also has spin $\frac{1}{2}$, causing a further doubling of the number of levels of the hydrogen atom. The splittings are much smaller than those discussed here, because the Bohr magneton for the proton is smaller than that of the electron by the factor m_e/m_p.

Formal mathematical machinery The basic assumptions are that the spin angular momentum operators obey the same commutation rules as orbital angular momentum operators,

$$[\hat{s}_x, \hat{s}_y] = i\hbar\hat{s}_z; \qquad [\hat{s}_y, \hat{s}_z] = i\hbar\hat{s}_x; \qquad [\hat{s}_z, \hat{s}_x] = i\hbar\hat{s}_y \tag{21.2}$$

and that

$$\hat{\mathbf{s}} = s(s+1)\hbar^2 = \tfrac{3}{4}\hbar^2; \qquad s = \tfrac{1}{2} \tag{21.3}$$

Positive and negative shift operators, $\hat{s}_+ = \hat{s}_x + i\hat{s}_y$ and $\hat{s}_- = \hat{s}_x - i\hat{s}_y$, and a magnetic quantum number m_s can be defined in the manner of section 10, and the procedure of that section followed in a completely routine way. Two eigenfunctions χ_{m_s}, with $m_s = \pm\frac{1}{2}$, emerge with the following properties:

$$\left.\begin{array}{ccc} \hat{s}_z\chi_{-\frac{1}{2}} = -\frac{1}{2}\hbar\chi_{-\frac{1}{2}}, & \hat{s}_z\chi_{\frac{1}{2}} = +\frac{1}{2}\hbar\chi_{\frac{1}{2}}, & \hat{\mathbf{s}}^2\chi_{\pm\frac{1}{2}} = \frac{3}{4}\hbar^2\chi_{\pm\frac{1}{2}}, \\ \hat{s}_+\chi_{-\frac{1}{2}} = \hbar\chi_{\frac{1}{2}}; & \hat{s}_+\chi_{\frac{1}{2}} = 0 & \\ \hat{s}_-\chi_{-\frac{1}{2}} = 0; & \hat{s}_-\chi_{\frac{1}{2}} = \hbar\chi_{-\frac{1}{2}} & \end{array}\right\} \tag{21.4}$$

Scalar products of the two eigenfunctions are given the usual values for an orthornomal set,

$$\left.\begin{array}{c} \langle\chi_{\frac{1}{2}} \mid \chi_{\frac{1}{2}}\rangle = \langle\chi_{-\frac{1}{2}} \mid \chi_{-\frac{1}{2}}\rangle = 1 \\ \langle\chi_{\frac{1}{2}} \mid \chi_{-\frac{1}{2}}\rangle = \langle\chi_{-\frac{1}{2}} \mid \chi_{\frac{1}{2}}\rangle = 0 \end{array}\right\} \tag{21.5}$$

Since no actual coordinate is involved these are not integrals, but they may be visualised as scalar products in a two-dimensional Hilbert space (figures 4.1, 4.2).

There is no difficulty in forming the matrix elements of $\hat{\mathbf{s}}$. For example,

$$\langle\chi_{-\frac{1}{2}}|\ \hat{s}_z\ |\chi_{\frac{1}{2}}\rangle = \langle\chi_{-\frac{1}{2}} \mid \hat{s}_z\chi_{\frac{1}{2}}\rangle = +\tfrac{1}{2}\hbar\langle\chi_{-\frac{1}{2}} \mid \chi_{\frac{1}{2}}\rangle = 0 \tag{21.6}$$

Finally, the Hamiltonian for an electron (charge $-e$) in an electromagnetic field must be amended to include a term $(g_s e/2m_e c)\boldsymbol{\mathscr{B}}\cdot\mathbf{s}$, which obviously produces the right Zeeman splitting (equation (21.1)). This is actually one of four additions to equation (20.13) that are discussed in section 23.

§22 Combination of orbital and spin angular momenta

Full wave functions The full wave function of an electron must now carry information about the spin as well as the ordinary observables. It is appropriately formed by multiplying together the spin and ordinary wave functions. The operators representing observables act only on the part of the full wave function with which they are concerned, and they simply ignore the other part. Two examples follow, for the 2p ($m_s = +\frac{1}{2}$) state of the hydrogen atom,

$$\left.\begin{array}{l} \hat{l}_z u_{211}(r)\chi_{\frac{1}{2}} = (\hat{l}_z u_{211}(r))\chi_{\frac{1}{2}} = \hbar u_{211}(r)\chi_{\frac{1}{2}} \\ \hat{s}_z u_{211}(r)\chi_{\frac{1}{2}} = u_{211}(r)(\hat{s}_z\chi_{\frac{1}{2}}) = \frac{1}{2}\hbar u_{211}(r)\chi_{\frac{1}{2}} \end{array}\right\} \tag{22.1}$$

Both have the familiar form of an operator acting on a (full) wave function to generate an eigenvalue multiplied by a (full) wave function.

Addition of orbital and spin angular mometa The two kinds of angular momentum combine vectorially to give the total angular momentum,

$$\mathbf{j}=\mathbf{l}+\mathbf{s} \tag{22.2}$$

with the components $j_x = l_x + s_x$, $j_y = l_y + s_y$, $j_z = l_z + s_z$. From the properties of $\hat{\mathbf{l}}$ and $\hat{\mathbf{s}}$ it is clear that $\mathbf{j}$ obeys the usual commutation rules,

$$[\hat{j}_x, \hat{j}_y]=i\hbar\hat{j}_z; \qquad [\hat{j}_y, \hat{j}_z]=i\hbar\hat{j}_z; \qquad [\hat{j}_z, \hat{j}_x]=i\hbar\hat{j}_y \tag{22.3}$$

and therefore

$$[\hat{j}_x, \hat{\mathbf{j}}^2]=[\hat{j}_y, \hat{\mathbf{j}}^2]=[\hat{j}_z, \hat{\boldsymbol{j}}^2]=0 \tag{22.4}$$

Positive and negative shift operators, $\hat{j}_+=\hat{j}_x+i\hat{j}_y$ and $\hat{j}_-=\hat{j}_x-i\hat{j}_y$, and total and magnetic quantum numbers j, m_j can be defined in the usual way. The procedure of section 10 can be followed once more to see that the values of these quantum numbers are to be found in figure 10.2.

Three relations involving $\hat{\mathbf{j}}^2$ can usefully be written down at once:

$$\left.\begin{aligned}\hat{\mathbf{j}}^2&=\hat{\mathbf{l}}^2+\hat{\mathbf{s}}^2+2\hat{\mathbf{l}}\,.\,\hat{\mathbf{s}}\\&=\hat{\mathbf{l}}^2+\hat{\mathbf{s}}^2+2\hat{l}_z\hat{s}_z+\hat{l}_+\hat{s}_-+\hat{l}_-\hat{s}_+\\\hat{\mathbf{l}}\,.\,\hat{\mathbf{s}}&=\tfrac{1}{2}(\hat{\boldsymbol{j}}^2-\hat{\mathbf{l}}^2-\hat{\mathbf{s}}^2)\end{aligned}\right\} \tag{22.5}$$

The wave functions $Y_{lm_l}(\theta, \phi)\chi_{m_s}$ formed† in the manner of equations (22.1) are eigenfunctions of the commuting set $\hat{\mathbf{l}}^2$, $\hat{l}_z$, $\hat{\mathbf{s}}^2$, and $\hat{s}_z$. Often it is better to work with wave functions $W_{ls}^{jm_j}$ which are eigenfunctions of the commuting set $\hat{\mathbf{j}}^2$ $\hat{j}_z$, $\hat{\mathbf{l}}^2$, and $\hat{\mathbf{s}}^2$. Two non-vanishing commutators should be noticed at once:

$$\left.\begin{aligned}[\hat{\mathbf{j}}^2, \hat{l}_z]&=2\hat{s}_x[\hat{l}_x, \hat{l}_z]+2\hat{s}_y[\hat{l}_y, \hat{l}_z]\\&=\hbar(\hat{s}_+\hat{l}_--\hat{s}_-\hat{l}_+)\\[\hat{\mathbf{j}}^2, \hat{s}_z]&=-\hbar(\hat{s}_+\hat{l}_--\hat{s}_-\hat{l}_+)\end{aligned}\right\} \tag{22.6}$$

It follows that in general the eigenfunctions of $\hat{\mathbf{j}}^2$ *cannot be eigenfunctions of* l_z *and* s_z *also. An exception to this statement (cf. equation (5.13)) occurs when* m_l, m_s, *and* $m_j = m_l + m_s$ *all have their maximum values* l, s, *and* $j = l + s$: *the shift operators* $\hat{s}_+$ *and* $\hat{l}_+$ *in equations (22.6) then produce zero. A second exception occurs when* m_l, m_s, *and* m_j *all have their minimum values* $-l$, $-s$, *and* $-j=-l-s$; *the shift operators* $\hat{s}_-$ *and* $\hat{l}_-$ *then produce zero.*

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† The radial variation of the u_{nlm} is not involved in what follows, and it will be left implicit.

Apart from these two exceptions the $W^{jm_j}_{ls}$ will be superpositions of two $Y_{lm_l}\chi_{m_s}$, since $s=\frac{1}{2}$ and $m_j=m_l+m_s=m_l\pm\frac{1}{2}$. Explicitly,

$$W^{jm_j}_{l\frac{1}{2}}=C^{jm_j}_{l(m_j+\frac{1}{2})\frac{1}{2}-\frac{1}{2}}Y_{l(m_j+\frac{1}{2})}\chi_{-\frac{1}{2}}+C^{jm_j}_{l(m_j-\frac{1}{2})\frac{1}{2}\frac{1}{2}}Y_{l(m_j-\frac{1}{2})}\chi_{\frac{1}{2}} \tag{22.7}$$

The coefficients $C^{jm_j}_{lm_lsm_s}$ which appear here are called Clebsch–Gordan coefficients; their values in most practical situations may be found from published tables, similar to table 22.1. The first two sets of coefficients given there will now be derived in detail.

$l=0$, $s=\frac{1}{2}$ Matters are very simple here because all combinations are exceptional; either $m_l=0$ and $m_s=\frac{1}{2}$ (both maximum values), or $m_l=0$ and $m_s=-\frac{1}{2}$ (both minimum values). Since $\hat{\mathbf{j}}^2=\hat{\mathbf{s}}^2$,

$$W^{\frac{1}{2}\frac{1}{2}}_{0\frac{1}{2}}=Y_{00}\chi_{\frac{1}{2}},\qquad W^{\frac{1}{2}-\frac{1}{2}}_{0\frac{1}{2}}=Y_{00}\chi_{-\frac{1}{2}} \tag{22.8}$$

and $C^{\frac{1}{2}\frac{1}{2}}_{00\frac{1}{2}\frac{1}{2}}=C^{\frac{1}{2}-\frac{1}{2}}_{00\frac{1}{2}-\frac{1}{2}}=1$.

$l=1$, $s=\frac{1}{2}$ The exceptional combination $m_l=-1$, $m_s=-\frac{1}{2}$ may be considered first. With the help of the second of equations (22.5),

$$\begin{aligned}\hat{\mathbf{j}}^2Y_{1-1}\chi_{-\frac{1}{2}}&=(2+\tfrac{3}{4}+1)\hbar^2Y_{1-1}\chi_{-\frac{1}{2}}\\&=\tfrac{3}{2}(\tfrac{3}{2}+1)\hbar^2Y_{1-1}\chi_{-\frac{1}{2}}\end{aligned} \tag{22.9}$$

and so

$$W^{\frac{3}{2}-\frac{3}{2}}_{1\frac{1}{2}}=Y_{1-1}\chi_{-\frac{1}{2}} \tag{22.10}$$

Three more eigenfunctions of $\mathbf{j}^2$ with $j=\frac{3}{2}$ can be found by using the shift operator $\hat{j}_+=\hat{l}_++\hat{s}_+$. The normalisation is kept in order by factors similar to those in equations (10.22), (10.40), and (21.4). Thus

$$\begin{aligned}W^{\frac{3}{2}-\frac{1}{2}}_{1\frac{1}{2}}&=3^{-1/2}\hbar^{-1}(\hat{l}_++\hat{s}_+)Y_{1-1}\chi_{-\frac{1}{2}}\\&=(\tfrac{2}{3})^{1/2}Y_{10}\chi_{-\frac{1}{2}}+(\tfrac{1}{3})^{1/2}Y_{1-1}\chi_{\frac{1}{2}}\end{aligned} \tag{22.11}$$

and likewise

$$\left.\begin{aligned}W^{\frac{3}{2}\frac{1}{2}}_{1\frac{1}{2}}&=(\tfrac{1}{3})^{1/2}Y_{11}\chi_{-\frac{1}{2}}+(\tfrac{2}{3})^{1/2}Y_{10}\chi_{\frac{1}{2}}\\W^{\frac{3}{2}\frac{3}{2}}_{1\frac{1}{2}}&=Y_{11}\chi_{\frac{1}{2}}\end{aligned}\right\} \tag{22.12}$$

The last-mentioned eigenfunction of course involves the second exceptional combination $m_l=1$, $m_s=\frac{1}{2}$.

A normalised wave function orthogonal to $W^{\frac{3}{2}-\frac{1}{2}}_{1\frac{1}{2}}$ can be constructed from it by transposing the coefficients of $Y_{10}\chi_{-\frac{1}{2}}$ and $Y_{1-1}\chi_{\frac{1}{2}}$, at the same time changing the sign of one. This new wave function is still an eigenfunction of j_z. As for $\mathbf{j}^2$, the second of

Table 22.1 Clebsch–Gordan coefficients for the vectorial addition of the orbital and spin angular momenta of a single electron. The second column is redundant, since $m_j = m_l + m_s$, and it is only included for clarity. In (c) the coefficients are zero unless the square root of a positive quantity is indicated.

(a) $l = 0, s = \frac{1}{2}$

j	m_j	m_l	m_s	$C^{jm_j}_{00\frac{1}{2}m_s}$
$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	1
$\frac{1}{2}$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	1

(b) $l = 1, s = \frac{1}{2}$

j	m_j	m_l	m_s	$C^{jm_j}_{1m_l\frac{1}{2}m_s}$
$\frac{3}{2}$	$\frac{3}{2}$	1	$\frac{1}{2}$	1
$\frac{3}{2}$	$\frac{1}{2}$	1	$-\frac{1}{2}$	$(\frac{1}{3})^{1/2}$
		0	$\frac{1}{2}$	$(\frac{2}{3})^{1/2}$
$\frac{3}{2}$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$(\frac{2}{3})^{1/2}$
		-1	$\frac{1}{2}$	$(\frac{1}{3})^{1/2}$
$\frac{3}{2}$	$-\frac{3}{2}$	-1	$-\frac{1}{2}$	1
$\frac{1}{2}$	$\frac{1}{2}$	1	$-\frac{1}{2}$	$(\frac{2}{3})^{1/2}$
		0	$\frac{1}{2}$	$-(\frac{1}{3})^{1/2}$
$\frac{1}{2}$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$(\frac{1}{3})^{1/2}$
		-1	$\frac{1}{2}$	$-(\frac{2}{3})^{1/2}$

(c) General l, $s = \frac{1}{2}$

j	m_j	m_l	m_s	$C^{jm_j}_{l(m_j-m_s)\frac{1}{2}m_s}$
$l+\frac{1}{2}$	m_j	$m_j+\frac{1}{2}$	$-\frac{1}{2}$	$(l-m_j+\frac{1}{2})^{1/2}(2l+1)^{-1/2}$
		$m_j-\frac{1}{2}$	$\frac{1}{2}$	$(l+m_j+\frac{1}{2})^{1/2}(2l+1)^{-1/2}$
$l-\frac{1}{2}$	m_j	$m_j+\frac{1}{2}$	$-\frac{1}{2}$	$(l+m_j+\frac{1}{2})^{1/2}(2l+1)^{-1/2}$
		$m_j-\frac{1}{2}$	$\frac{1}{2}$	$-(l-m_j+\frac{1}{2})^{1/2}(2l+1)^{-1/2}$

equations (22.5) can be used to see that

$$\hat{\mathbf{j}}^2\{(\tfrac{1}{3})^{1/2}Y_{10}\chi_{-\frac{1}{2}}-(\tfrac{2}{3})^{1/2}Y_{1-1}\chi_{\frac{1}{2}}\}$$
$$=\tfrac{1}{2}(\tfrac{1}{2}+1)\hbar^2\{(\tfrac{1}{3})^{1/2}Y_{10}\chi_{-\frac{1}{2}}-(\tfrac{2}{3})^{1/2}Y_{1-1}\chi_{\frac{1}{2}}\} \quad (22.13)$$

so that,

$$W^{\frac{1}{2}-\frac{1}{2}}_{1\frac{1}{2}}=(\tfrac{1}{3})^{1/2}Y_{10}\chi_{-\frac{1}{2}}-(\tfrac{2}{3})^{1/2}Y_{1-1}\chi_{\frac{1}{2}} \quad (22.14)$$

Finally, with the help of $\hat{j}_+$,

$$W^{\frac{1}{2}\frac{1}{2}}_{1\frac{1}{2}} = \left(\tfrac{2}{3}\right)^{1/2} Y_{11}\chi_{-\frac{1}{2}} - \left(\tfrac{1}{3}\right)^{1/2} Y_{10}\chi_{\frac{1}{2}} \tag{22.15}$$

Six independent Ws have now been found, four belonging to $j=\frac{3}{2}$ and two to $j=\frac{1}{2}$. No others exist, because there are only $6=3\times 2$ independent products of Ys and χs available.

General addition of angular momenta When $\mathbf{j}=\mathbf{j}_1+\mathbf{j}_2$, with $j_1 \geqslant j_2$, the total angular momentum quantum number j may take any of the values j_1+j_2, $j_1+j_2-1, \ldots, j_1-j_2+1$, j_1-j_2. The number of independent eigenfunctions, either of the set $\mathbf{j}_1^2$, j_{1_z}, $\mathbf{j}_2^2$, j_{2_z} or of the set $\mathbf{j}^2$, j_z, $\mathbf{j}_1^2$, $\mathbf{j}_2^2$, is given by

$$(2j_1+1)(2j_2+1)=\sum_{j=j_1-j_2}^{j_1+j_2}(2j+1) \tag{22.16}$$

Spectroscopic notation The spectroscopic notation mentioned in section 10 is extended to label a state of principal quantum number n, spin multiplicity $2s+1$, orbital angular momentum l, and total angular momentum j. Such a state is called a $n^{2s+1}l_j$ state. The total angular momentum eigenfunctions derived earlier would thus be appropriate to $n^2\mathrm{s}_{\frac{1}{2}}$, $n^2\mathrm{p}_{\frac{3}{2}}$, and $n^2\mathrm{p}_{\frac{1}{2}}$ states. Of course the value of n is open until the radial part of the wave function is specified.

At times it is convenient to omit the values of n and $2s+1$, and write down simply l_j.

§23 Spin-orbit coupling and fine structure: Zeeman effects

It has already been mentioned that the correct relativistic equation for the electron is the Dirac equation, and really this should be used to determine the energy eigenvalues of the hydrogen atom. The work involved is beyond the scope of this book, but it leads to the conclusion that, to a good approximation, the normal Schrödinger equation and non-relativistic quantum mechanics can be used, provided that some extra terms are included in the Hamiltonian. This should be amended to read

$$\hat{H}=\frac{1}{2\mu}\hat{\mathbf{p}}^2+V(r)+\hat{H}'+\hat{H}''+\hat{H}''' \tag{23.1}$$

where μ is the reduced mass, $V(r)=-e^2/4\pi\varepsilon_0 r$, and the three last terms are new and small. They are given by

$$\left.\begin{aligned}\hat{H}'&=-\frac{\hat{\mathbf{p}}^4}{8\mu^3c^2}\\ \hat{H}''&=-\frac{\hbar^2}{4\mu^2c^2}\frac{\partial V}{\partial r}\frac{\partial}{\partial r}\\ \hat{H}'''&=\frac{1}{2\mu^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\hat{\mathbf{l}}\cdot\hat{\mathbf{s}}\end{aligned}\right\}\tag{23.2}$$

The classical and relativistic genealogy of two of these terms can be understood quite easily. The first, $\hat{H}'$, is the second term in the expansion of the relativistic kinetic energy in powers of $\mathbf{p}^2/\mu^2c^2$; apart from potential energy, $E^2=c^2\mathbf{p}^2+\mu^2c^4$, and the difference between E and the rest energy is $E-\mu c^2=(1/2\mu)\mathbf{p}^2-(1/8\mu^3c^2)\mathbf{p}^4+\cdots$

The second term, $\hat{H}''$, is known as the Darwin term and cannot be understood in a purely classical way.

The third term, $\hat{H}'''$, was first written down correctly by Thomas. A relativistic transformation of the Coulomb field into the rest frame of the electron gives rise to a small magnetic field, and $\hat{H}'''$ describes the energy of the electron's magnetic moment in this field. The situation is complicated by the fact that the electron rest frame precesses with a certain angular velocity relative to the centre of mass frame, and this halves the value of the term.

Since the third term contains $\hat{\mathbf{l}}\cdot\hat{\mathbf{s}}$ it is said to give rise to *spin-orbit coupling*. A term of this type arises in many other atomic and nuclear problems, and so it is important to understand how to deal with it.

General strategy The effect of the new small terms may be calculated with the help of the perturbation theory of section 15. The unperturbed wave functions must of course represent the stationary states of the original first two terms of equation (23.1).

It is at once obvious that the $R_{nl}(r)Y_{lm_l}\chi_{m_s}$ will not serve for the purpose; because of the $\hat{\mathbf{l}}\cdot\hat{\mathbf{s}}$ operator in $\hat{H}'''$ there will be finite matrix elements connecting degenerate states with the same values of n, l, and $m_j=m_l+m_s$, but different values of m_l, m_s. To see this it is only necessary to write $\hat{\mathbf{l}}\cdot\hat{\mathbf{s}}=l_zs_z+\frac{1}{2}(\hat{l}_+\hat{s}_-+\hat{l}_-\hat{s}_+)$ and to consider the effect of the shift operators on $Y_{lm_l}\chi_{m_s}$.

The remedy is to use the unperturbed wave functions $R_{nl}W^{jm_j}_{l\frac{1}{2}}$, the total angular momentum eigenfunctions of section 22. The point is that these are eigenfunctions of $\mathbf{l}\,.\,\mathbf{s}=\frac{1}{2}(\mathbf{j}^2-\mathbf{l}^2-\frac{3}{4})$, and the orthonormality of the $W^{jm_j}_{l\frac{1}{2}}$ can therefore be relied upon to suppress undesirable matrix elements of $\hat{H}'''$.

The actual eigenvalues of $\mathbf{l}\,.\,\mathbf{s}$ will be needed; they are equal to $\frac{1}{2}\{j(j+1)-l(l+1)-\frac{3}{4}\}\hbar^2$, or $\frac{1}{2}l\hbar^2$ for $j=l+\frac{1}{2}$ and $-\frac{1}{2}(l+1)\hbar^2$ for $j=l-\frac{1}{2}$.

Evaluation The calculation is straightforward once the correct unperturbed wave functions have been chosen. The first energy shift is

$$\begin{aligned}E' &= \langle R_{nl}W^{jm_j}_{l\frac{1}{2}}|\,\hat{H}'\,|R_{nl}W^{jm_j}_{l\frac{1}{2}}\rangle\\ &= -\frac{1}{2\mu c^2}\int_0^\infty\left(E_n+\frac{e^2}{4\pi\varepsilon_0 r}\right)^2 R_{nl}^2 r^2\,\mathrm{d}r\\ &= \frac{\alpha^2}{n^2}\left(\frac{n}{l+\frac{1}{2}}-\frac{3}{4}\right)E_n \end{aligned}\tag{23.3}$$

Here the TISE satisfied by the $R_{nl}W^{jm_j}_{l\frac{1}{2}}$ has been used to substitute for $(\hat{\mathbf{p}}^2/2\mu)^2$, and the final result is stated in terms of the fine structure constant $\alpha=e^2/4\pi\varepsilon_0\hbar c$. This is an important pure number with a value close to 1/137.

The second energy shift is

$$\begin{aligned}E'' &= \langle R_{nl}W^{jm_j}_{l\frac{1}{2}}|\,\hat{H}''\,|R_{nl}W^{jm_j}_{l\frac{1}{2}}\rangle\\ &= -\frac{\hbar^2e^2}{16\pi\varepsilon_0\mu^2c^2}\int_0^\infty R_{nl}\frac{\mathrm{d}R_{nl}}{\mathrm{d}r}\,\mathrm{d}r\\ &= \frac{\hbar^2\mathrm{e}^2}{32\pi\varepsilon_0\mu^2c^2}R_{nl}^2(0)=-\left(\frac{\alpha^2}{n}\right)E_n\delta_{l0} \end{aligned}\tag{23.4}$$

since $R_{nl}(0)=0$ if $l\neq 0$.

The third energy shift is zero if $l=0$, because there cannot then be any spin-orbit coupling. When l is not zero,

$$\begin{aligned}E''' &= \langle R_{nl}W^{jm_j}_{l\frac{1}{2}}|\,\hat{H}'''\,|R_{nl}W^{jm_j}_{l\frac{1}{2}}\rangle\\ &= \frac{\hbar^2e^2}{16\pi\varepsilon_0\mu^2c^2}\{j(j+1)-l(l+1)-\tfrac{3}{4}\}\int_0^\infty\frac{1}{r}R_{nl}^2\,\mathrm{d}r\\ &= -\frac{\alpha^2}{n}\left\{\frac{j(j+1)-l(l+1)-\frac{3}{4}}{l(l+1)(2l+1)}\right\}E_n;\qquad l\neq 0 \end{aligned}\tag{23.5}$$

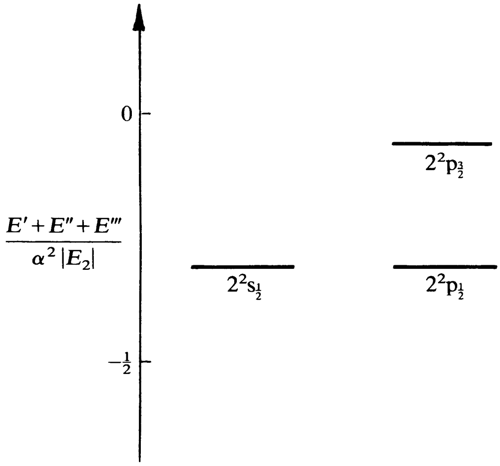

Figure 23.1 Fine structure of the $n=2$ energy levels of the hydrogen atom.

All three terms may be collected together to give the total fine structure energy,

$$E'+E''+E'''=\frac{\alpha^2}{n^2}\left\{\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right\}E_n \tag{23.6}$$

independent of whether $l=0$ or not, and whether $j=l+\frac{1}{2}$ or $l-\frac{1}{2}$.

Obviously the spin-orbit coupling gives rise to a splitting of levels that were previously degenerate. A simple example is the splitting of the $2^2p_{\frac{3}{2}}$ and $2^2p_{\frac{1}{2}}$ levels in hydrogen† (figure 23.1).

Weak magnetic field If a magnetic field $\mathscr{B}$ in the z direction is added, then there will be a further term in the Hamiltonian,

$$\hat{H}''''=-(\hat{l}_z+2\hat{s}_z)\hbar^{-1}\mu_B\mathscr{B} \tag{23.7}$$

The operator here has non-zero matrix elements connecting $W^{jm_j}_{l\frac{1}{2}}$ of differing j but the same l and m_j. Nevertheless, since just these levels are split by the spin-orbit term, a perturbation calculation based on the $W^{jm_j}_{l\frac{1}{2}}$ is valid if the magnetic field is weak. The criterion is that the Zeeman splitting energies must be small compared to the

---

† The $2^2s_{\frac{1}{2}}$ and $2^2p_{\frac{1}{2}}$ levels are still degenerate to this approximation. They are actually split by the Lamb shift, an effect smaller than the fine structure by another factor of α^2.

spin-orbit splitting. Provided that this is so,

$$\varepsilon_{jm_j} = -\langle W_{l\frac{1}{2}}^{jm_j} | \hat{l}_z + 2\hat{s}_z \, | W_{l\frac{1}{2}}^{jm_j} \rangle \hbar^{-1} \mu_{\mathrm{B}} \mathscr{B} \tag{23.8}$$

The matrix element can be calculated by expanding the $W_{l\frac{1}{2}}^{jm_j}$ in terms of the $Y_{lm_l}\chi_{m_s}$, with the help of Clebsch–Gordan coefficients. For example, when $j=\frac{3}{2}$ and $m_j=\frac{1}{2}$, equation (22.12) shows that the expectation value of l_z+2s_z is $\{\frac{1}{3}(1-1)+\frac{2}{3}(0+1)\}\hbar=\frac{2}{3}\hbar$. Similar evaluations for the other three $p_{\frac{3}{2}}$ wave functions show that

$$\varepsilon_{\frac{3}{2}m_j} = -\mu_{\mathrm{B}} g_{\frac{3}{2}} m_j \mathscr{B} \tag{23.9}$$

with $g_{\frac{3}{2}}=\frac{4}{3}$. For the two $p_{\frac{1}{2}}$ states the corresponding formula for $\varepsilon_{\frac{1}{2}m_j}$ has the factor $g_{\frac{1}{2}}=\frac{2}{3}$. These results determine the initial slopes of the lines in figure 23.2, which traces the energies of the 2p levels of hydrogen as a function of magnetic field.

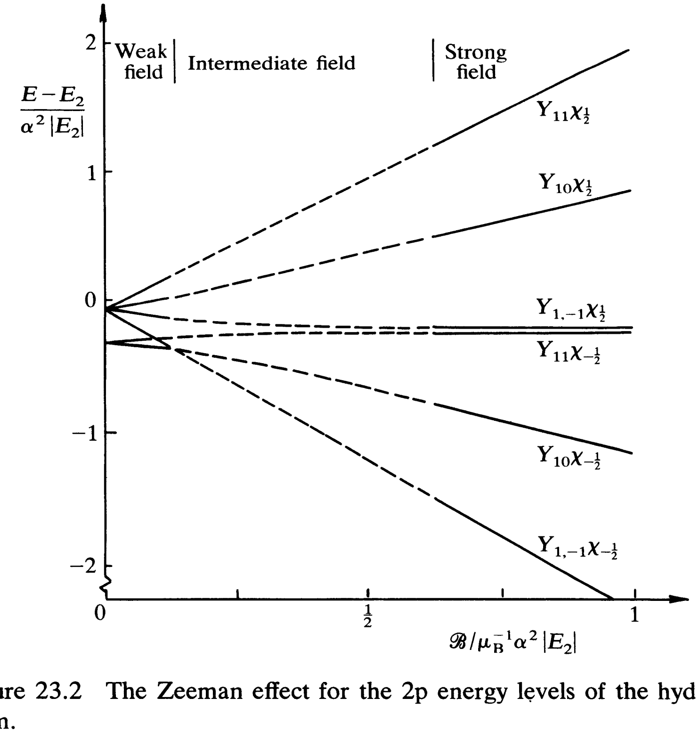

Figure 23.2 The Zeeman effect for the 2p energy levels of the hydrogen atom.

General values of g_j The general results are worth quoting. The Zeeman shift is

$$\varepsilon_{jm_j} = -\mu_B g_j m_j \mathscr{B} \tag{23.10}$$

with

$$g_j = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \tag{23.11}$$

Here g_j is called the Landé splitting factor.

Strong magnetic field When the Zeeman splitting energies are large compared to the spin-orbit splitting a reversal of policy on the choice of unperturbed wave functions is necessary. Now the $Y_{lm_l}\chi_{m_s}$ should be used, because they are eigenfunctions of l_z and s_z, and so of $\hat{H}''''$. Undesirable matrix elements of $\hat{H}''''$ are therefore suppressed.

The magnetic energy obviously has the value

$$\varepsilon_{m_l m_s} = -\mu_B(m_l + 2m_s)\mathscr{B} \tag{23.12}$$

The spin-orbit coupling can now be regarded as perturbing the $Y_{lm_l}\chi_{m_s}$, because the magnetic energy splits the previously degenerate states with the same $m_j = m_l + m_s$. The essential expectation value, that of $\hat{\mathbf{l}} \cdot \hat{\mathbf{s}} = \hat{l}_z\hat{s}_z + \frac{1}{2}(\hat{l}_+\hat{l}_- + \hat{l}_-\hat{l}_+)$, is easily calculated,

$$\langle Y_{lm_l}\chi_{m_s} | \hat{\mathbf{l}} \cdot \hat{\mathbf{s}} \, | Y_{lm_l}\chi_{m_s} \rangle = m_l m_s \hbar^2 \tag{23.13}$$

since the raising and lowering operators produce wave functions that are orthogonal to $Y_{lm_l}\chi_{m_s}$.

For the 2p stages of hydrogen the combined effect of $\hat{H}'$, $\hat{H}''$, and $\hat{H}'''$ is easily calculated by substituting $m_l m_s \hbar^2$ into equation (23.5), in place of the eigenvalues of $\hat{\mathbf{l}} \cdot \hat{\mathbf{s}}$. In this way a small energy shift,

$$E' + E'' + E''' = (\tfrac{7}{48} - \tfrac{1}{6}m_l m_s)\alpha^2 E_2 \tag{23.14}$$

is obtained for these particular states, and this must be added to the large magnetic energy given by equation (23.12).

The whole of figure 23.2 can now be understood. The weak field results at the left of the picture give way to the strong field results at the right. The change of pattern is known as the Paschen–Back effect. In the intermediate field region, which has not been discussed, the energy eigenvalues are indicated by dotted lines.

Problems

6.1 A hydrogen atom is in a 2p, $j=\frac{3}{2}$, $m_j=\frac{1}{2}$ state. Predict the results of measuring $\mathbf{l}^2$, $\mathbf{s}^2$, l_z, and s_z.

6.2 A hydrogen atom is in a 2p, $m_l=1$, $m_s=-\frac{1}{2}$ state. Predict the results of measuring $\mathbf{j}^2$ and j_z.

6.3 Draw the diagram corresponding to figure 23.1 for the $n=3$ levels of the hydrogen atom. Compare quantitatively the $\mathrm{p}_{\frac{1}{2}}$–$\mathrm{p}_{\frac{3}{2}}$ splitting in the two diagrams.

6.4 Draw the diagram corresponding to figure 23.2 for the 3d levels of the hydrogen atom.

7

Identical particles and the Pauli principle

§24 Identical particles

The wave function† for two particles, first discussed in section 14, has the form $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$ when the particles are labelled 1 and 2. The probability at time t of finding particle 1 in the elementary volume $d\tau_1$, and particle 2 in $d\tau_2$, is $|\Psi|^2\, d\tau_1\, d\tau_2$. Other observables, for example momentum, are represented by operators mentioning $\mathbf{r}_1$ and $\mathbf{r}_2$ in the appropriate way.

The exchange operator Although the labels 1 and 2 are explicit in the wave function, it seems that no physical distinction can be made between particles that are identical. This is the *principle of indistinguishability*, and it gives rise to an important property of the wave function. No difference can be detected between the state described by $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$ and that described by $\Psi(\mathbf{r}_2, \mathbf{r}_1, t)$, where the role of particle 1 has been taken by particle 2, and vice versa. This means that the second wave function can differ from the first at most by a phase factor $e^{i\delta}$, with δ real. Mathematically, if $\hat{P}_{12}$ is the operator that exchanges particle 1 for particle 2 (and vice versa),

$$\hat{P}_{12}\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \Psi(\mathbf{r}_2, \mathbf{r}_1, t) = e^{i\delta}\Psi(\mathbf{r}_1, \mathbf{r}_2, t) \qquad (24.1)$$

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† Spin variables may be added to $\mathbf{r}_1$ and $\mathbf{r}_2$, for particles with spin.

If $\hat{P}_{12}$ is applied twice,

$$\hat{P}_{12}^2\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \hat{P}_{12}e^{i\delta}\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = e^{2i\delta}\Psi(\mathbf{r}_1, \mathbf{r}_2, t) \qquad (24.2)$$

After two exchanges of the particles the wave function must be back to its initial form, so also,

$$\hat{P}_{12}^2\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \Psi(\mathbf{r}_1, \mathbf{r}_2, t) \qquad (24.3)$$

Thus $e^{2i\delta} = 1$ and $e^{i\delta} = \pm 1$.

It is not hard to see that $\hat{P}_{12}$ is a Hermitian operator, as defined by equation (2.12). Obviously $\hat{P}_{12}$ is linear, and so it is fit to represent an observable, the *exchange parity*. The eigenvalues of exchange parity are +1 (symmetric or even state) and −1 (antisymmetric or odd state).

It is clear that the energy operator $\hat{H}$ must involve the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ in a symmetrical way,† and it follows that $[\hat{P}_{12}, \hat{H}] = 0$. All the work done in section 4 with ordinary parity can then be repeated with $\hat{P}_{12}$ substituted for $\hat{\Pi}$.

One consequence is that any stationary state is automatically represented by an eigenfunction of exchange parity, unless there is degeneracy.

A second consequence is that exchange parity is conserved. If two particles are created in a particular state of exchange parity, they will so continue for all time.

It happens that fermions,‡ or particles of half-integral spin, are found only in states of odd exchange parity; on the other hand bosons,§ or particles of integral spin, are found only in states of even exchange parity. The first of these rules is referred to as the *Pauli exclusion principle*, for reasons that will become clear shortly. Both rules can actually be deduced from relativistic quantum mechanics.

Two independent fermions The Schrödinger equation, for two identical fermions moving without mutual interaction and without spin-dependent forces, has the form,

$$\{\hat{H}(\mathbf{r}_1) + \hat{H}(\mathbf{r}_2)\}\Psi(\mathbf{r}_1, \mathbf{r}_2)X(m_s^{(1)}, m_s^{(2)}) = E\Psi(\mathbf{r}_1, \mathbf{r}_2)X(m_s^{(1)}, m_s^{(2)}) \qquad (24.4)$$

where the spin wave function X has been made explicit.

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† For example equation (24.10).

‡ Electrons, muons, protons, and neutrons are fermions.

§ Pions, kaons, and photons are bosons.

The appropriate ΨX can be built up very easily out of the solutions to the Schrödinger equation for each particle individually. These solutions have the form

$$\left.\begin{array}{l}\hat{H}(\mathbf{r}_1)\psi_a(\mathbf{r}_1)\chi^{(1)}_{+\frac12}=E_a\psi_a(\mathbf{r}_1)\chi^{(1)}_{+\frac12}\\ \hat{H}(\mathbf{r}_2)\psi_b(\mathbf{r}_2)\chi^{(2)}_{+\frac12}=E_b\psi_b(\mathbf{r}_2)\chi^{(2)}_{+\frac12}\end{array}\right\}\tag{24.5}$$

It is easily checked that the product $\Psi X=\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)\chi^{(1)}_{+\frac12}\chi^{(2)}_{+\frac12}$ solves equation (24.4) with $E=E_a+E_b$. When it is remembered that $\hat{H}(\mathbf{r}_1)+\hat{H}(\mathbf{r}_2)$ mentions $\mathbf{r}_1$ and $\mathbf{r}_2$ symmetrically, and the spins not at all, it becomes clear that the solution is at least eightfold degenerate. The spin wave functions can be any one of the four combinations $\chi^{(1)}_{\pm\frac12}\chi^{(2)}_{\pm\frac12}$, and the spatial wave function can be $\psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)$ instead of $\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$. None of these are eigenfunctions of P_{12}, and the next step is to write down linear combinations that are so.

The four symmetric and normalised[†] combinations are

$$\left.\begin{array}{l}\frac{1}{\sqrt2}(\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)+\psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2))\left\{\begin{array}{l}\chi^{(1)}_{+\frac12}\chi^{(2)}_{+\frac12}\\ \frac{1}{\sqrt2}(\chi^{(1)}_{+\frac12}\chi^{(2)}_{-\frac12}+\chi^{(1)}_{-\frac12}\chi^{(2)}_{+\frac12})\\ \chi^{(1)}_{-\frac12}\chi^{(2)}_{-\frac12}\end{array}\right.\\ \frac{1}{\sqrt2}(\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)-\psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2))\cdot\frac{1}{\sqrt2}(\chi^{(1)}_{+\frac12}\chi^{(2)}_{-\frac12}-\chi^{(1)}_{-\frac12}\chi^{(2)}_{+\frac12})\end{array}\right\}\tag{24.6}$$

and the four antisymmetric and normalised[†] combinations are

$$\left.\begin{array}{l}\frac{1}{\sqrt2}(\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)+\psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2))\cdot\frac{1}{\sqrt2}(\chi^{(1)}_{+\frac12}\chi^{(2)}_{-\frac12}-\chi^{(1)}_{-\frac12}\chi^{(2)}_{+\frac12})\\ \frac{1}{\sqrt2}(\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)-\psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2))\left\{\begin{array}{l}\chi^{(1)}_{+\frac12}\chi^{(2)}_{+\frac12}\\ \frac{1}{\sqrt2}(\chi^{(1)}_{+\frac12}\chi^{(2)}_{-\frac12}+\chi^{(1)}_{-\frac12}\chi^{(2)}_{+\frac12})\\ \chi^{(1)}_{-\frac12}\chi^{(2)}_{-\frac12}\end{array}\right.\end{array}\right\}\tag{24.7}$$

The Pauli exclusion principle states that none of the symmetric wave functions are allowed for two fermions. The antisymmetric wave functions, on the other hand, vanish identically if the two fermions are in the same state (that is $a=b$ and $m_s^{(1)}=m_s^{(2)}$). *A consequence of the Pauli exclusion principle, applicable to non-interacting fermions, is that two fermions cannot be in the same state.*

[†] When $a=b$ the normalising factor for the spatial part of the wave function is $\frac12$, not $1/\sqrt2$. Obviously $\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2)$ is correctly normalised.

Total spin wave functions The spin angular momenta of two fermions can be added vectorially to give the total spin,

$$\mathbf{S} = \mathbf{s}^{(1)} + \mathbf{s}^{(2)} \tag{24.8}$$

The observables of interest are S_z and $\mathbf{S}^2$, represented by operators such that

$$\left.\begin{aligned} \hat{S}_z &= \hat{s}_z^{(1)} + \hat{s}_z^{(2)} \\ \hat{\mathbf{S}}^2 &= \hat{\mathbf{s}}^{2_{(1)}} + \hat{\mathbf{s}}^{2_{(2)}} + 2\hat{\mathbf{s}}^{(1)} \cdot \hat{\mathbf{s}}^{(2)} \\ &= \tfrac{3}{2}\hbar^2 + 2\hat{s}_z^{(1)}\hat{s}_z^{(2)} + \hat{s}_+^{(1)}\hat{s}_-^{(2)} + \hat{s}_-^{(1)}\hat{s}_+^{(2)} \end{aligned}\right\} \tag{24.9}$$

where $\hat{s}_+^{(1)}$, $\hat{s}_+^{(2)}$, $\hat{s}_-^{(1)}$, $\hat{s}_-^{(2)}$ are the usual raising and lowering operators. The methods of section 22 can be used again to see that the three symmetric spin wave functions which appear in equations (24.6) and (24.7) are eigenstates of S_z, belonging to the eigenvalues $1, 0, -1$ respectively, and that all three are also eigenstates of $\mathbf{S}^2$, belonging to the eigenvalue $1(1+1)\hbar^2 = 2\hbar^2$; they are referred to as the triplet spin states or, more loosely, as states of total spin 1. Similarly, the antisymmetric spin wave function belongs to the eigenvalues 0, 0 for S_z, $\mathbf{S}^2$. It is referred to as the singlet spin state, or as the state of total spin 0.

The Clebsch–Gordan coefficients for combining two spin $\frac{1}{2}$ angular momenta are given in table 24.1.

Table 24.1 Clebsch–Gordan coefficients for the vectorial addition of two spin angular momenta

S	m_s	$m_s^{(1)}$	$m_s^{(2)}$	$C^{Sm_s}_{\frac{1}{2}m_s^{(1)}\frac{1}{2}m_s^{(2)}}$
1	1	$\frac{1}{2}$	$\frac{1}{2}$	1
1	0	$\frac{1}{2}$	$-\frac{1}{2}$	$2^{-1/2}$
		$-\frac{1}{2}$	$\frac{1}{2}$	$2^{-1/2}$
1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	1
0	0	$\frac{1}{2}$	$-\frac{1}{2}$	$2^{-1/2}$
		$-\frac{1}{2}$	$\frac{1}{2}$	$-2^{-1/2}$

Ground state of helium The helium atom has a nucleus of charge $2e$ and two electrons, for which the operator $\hat{H}$ has the form

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{2\pi\varepsilon_0 r_1} - \frac{e^2}{2\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \tag{24.10}$$

As a first approximation the last term may be ignored, and the two electrons then become independent. Each electron is represented by a wave function similar to that of the hydrogen atom, with $2e^2$ substituted for e^2 throughout. The ground state is obviously obtained by putting both electrons into the 1s state, necessarily producing a symmetric spatial part of the wave function. It follows, because electrons are fermions, that the ground state contains an antisymmetric, or singlet, spin wave factor. In fact,†

$$(\Psi X)_0 \approx \frac{8}{\pi a_0^3} \exp\left(-\frac{2r_1}{a_0} - \frac{2r_2}{a_0}\right) \cdot \frac{1}{\sqrt{2}} \left(\chi_{+\frac{1}{2}}^{(1)}\chi_{-\frac{1}{2}}^{(2)} - \chi_{-\frac{1}{2}}^{(1)}\chi_{+\frac{1}{2}}^{(2)}\right) \tag{24.11}$$

where a_0 is given by equation (12.3) as usual. The associated energy eigenvalue‡ is $-me^4/4\pi^2\varepsilon_0^2\hbar^2$.

It is important to notice that the total spin is forced to be zero by the Pauli principle and the associated symmetry considerations, even though $\hat{H}$ mentions no spin-dependent interaction. The lowest energy for a triplet spin state, to the same approximation, has an energy of $-5me^4/32\pi^2\varepsilon_0^2\hbar^2$, when one electron is in the 1s state and the other in a 2s or 2p state.

A more accurate energy for the ground state may be obtained by the variational method of section 17. The charge on the nucleus is $+2e$, but each electron partially screens the other so that the 'effective charge' lies between e and $2e$. Thus suggests that the effective charge should be written ze, and that z should be varied to minimize $\langle\Psi|\hat{H}|\Psi\rangle$. The spin wave function is not involved, and it will be left implicit. The trial wave function is simply

$$\Psi = \frac{z^3}{\pi a_0^3} \mathrm{e}^{-(z/a_0)(r_1+r_2)} \tag{24.12}$$

---

† *Vide* tables 10.1 and 12.1 with e^2 replaced by $2e^2$, and equation (24.7) and its associated footnote.

‡ That is two electrons each four times as strongly bound as in the hydrogen 1s state (equation (12.9)).

The calculation of $\langle\Psi|\hat{H}|\Psi\rangle$ is straightforward so far as the first four terms of equation (24.10) are concerned. They produce together an expectation energy equal to $(z^2-4z)(me^4/16\pi^2\varepsilon_0^2\hbar^2)$.

The fifth term in equation (24.10) can be handled by means of an expansion involving Legendre polynomials. If $r_1 < r_2$

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}=\frac{1}{r_2}+\frac{r_1}{r_2^2}P_1(\cos\theta')+\frac{r_1^2}{r_2^3}P_2(\cos\theta') \qquad (24.13)$$

where θ' is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. If $r_2 < r_1$ then the roles of r_1 and r_2 should be exchanged on the right-hand side.

Only the first term of each expansion needs to be considered, because Ψ is spherically symmetric. The result is an expectation energy equal to $(5z/8)(me^4/16\pi^2\varepsilon_0^2\hbar^2)$. Altogether then

$$\langle\Psi|\hat{H}|\Psi\rangle=\left(z^2-\frac{27z}{8}\right)\frac{me^4}{16\pi^2\varepsilon_0^2\hbar^2} \qquad (24.14)$$

This expression has a minimum when $z=27/16=1.688$. The corresponding energy is 2.85 $(me^4/16\pi^2\varepsilon_0^2\hbar^2)$, a result which is accurate to 2 per cent.

Spectroscopic notation Once more the spectroscopic notation is extended. A state of spin multiplicity $2S+1$, orbital angular momentum $L\hbar$, and total angular momentum $J\hbar$ is referred to as a $^{2S+1}L_J$ state. The capital letters conventionally signify vectorial addition of the angular momenta of two or more electrons.

Another notation may be used to show how the individual electrons are disposed, by specifying the number of electrons in each state. Obviously lower case letters are used to specify these.

Thus the ground state of helium is a $^1S_0$ state, and its invididual particle configuration is $(1s)^2$.

Excited states of helium: exchange interaction According to equation (24.7) four different states of helium can be built up from the individual particle configuration (1s) (2s). The spatial wave function may be symmetric and the spin wave function antisymmetric, so giving rise to a $^1S_0$ state or, alternatively, the spatial wave function may be antisymmetric and the spin wave function symmetric, so giving rise to three degenerate $^3S_1$ states.

When the mutual interaction of the two electrons is ignored the $^1S_0$ and the $^3S_1$ states have the same energy. The degeneracy is lifted, however, when the mutual interaction is taken into account.

A perturbation calculation of the effect of the fifth term in equation (24.10) shows this clearly. For the $^1S_0$ state,

$$\begin{aligned}\left\langle \Psi_{^1S_0} \left| \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_1-\mathbf{r}_2|} \right| \Psi_{^1S_0} \right\rangle &= \iint u^*_{100}(\mathbf{r}_1)u^*_{200}(\mathbf{r}_2)\left\{\frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_1-\mathbf{r}_2|}\right\} \\ &\quad \times u_{100}(\mathbf{r}_1)u_{200}(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \\ &\quad + \iint u^*_{100}(\mathbf{r}_1)u^*_{200}(\mathbf{r}_2)\left\{\frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_1-\mathbf{r}_2|}\right\} \\ &\quad \times u_{200}(\mathbf{r}_1)u_{100}(\mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \\ &\equiv I_\mathrm{C}+I_\mathrm{E} \end{aligned} \tag{24.15}$$

Here the wave functions are the same as those in section 12, except that $2e^2$ replaces e^2 throughout. The two terms are called the Coulomb integral (I_C) and the exchange integral (I_E). For the $^3S_1$ state,

$$\left\langle \Psi_{^3S_1} \left| \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_1-\mathbf{r}_2|} \right| \Psi_{^3S_1} \right\rangle = I_\mathrm{C}-I_\mathrm{E} \tag{24.16}$$

Obviously I_C is positive, and this turns out to be true for I_E also; essentially the reason is that the interaction is strongest when $\mathbf{r}_1 \approx \mathbf{r}_2$, so that there is not a great deal of difference between I_C and I_E. It follows that the $^1S_0$ state has higher energy (less binding) than the $^3S_1$ state. Here again there is a remarkable difference in energy between singlet and triplet spin states, even though $\hat{H}$ does not mention spin.

Problems

7.1 Three fermions labelled 1, 2, 3 are to be put into three quantum states labelled *a*, *b*, *c*. Form a properly antisymmetrical and normalised wave function for this.

What would happen if the three particles were bosons instead, with the further assumption that $E_a < E_b < E_c$ and the gaps between energy levels are large compared to kT?

8

Transitions

§25 Spin precession and magnetic resonance

So far the discussion has been mainly concerned with the properties of stationary states, although the wave packet in section 6 was an exception. In this chapter some situations that call for the TDSE will be discussed. The two problems that follow, both concerned with the behaviour of spin $\frac{1}{2}$ in magnetic fields, offer the attraction that exact solutions are possible and convenient. The first, about spin precession, illustrates the use of equation (3.6) when $\hat{H}$ is independent of time. The second, about magnetic resonance, involves a time-dependent $\hat{H}$ so that equation (3.6) is not applicable. It is typically convenient to expand the wave function in terms of the stationary states of the time-independent part of $\hat{H}$, but the expansion coefficients are, of course, functions of time that require calculation.

Spin precession A particle of spin $\frac{1}{2}$ will be considered whose state is represented by $\psi(r)\chi_{\pm\frac{1}{2}}$, and it will be supposed that $\psi(r)$ is not coupled to a magnetic field of strength $\mathscr{B}$ in the z direction. This would be true if the particle were bound in an s state, for example. The space part of the wave function can then be left implicit when considering the effect of the magnetic field on the spin angular momentum.

The Hamiltonian is given by $\hat{H} = -(g_s e/2m)\mathscr{B}\hat{s}_z$, where e and m are the charge and mass of the particle. The factor g_s is very close to 2 for the electron or muon, but it takes other values for particles that are subject to nuclear forces, such as the proton. The stationary states are represented by $\chi_{+\frac{1}{2}}$ and $\chi_{-\frac{1}{2}}$, belonging to the eigenvalues $\pm\frac{1}{2}\hbar$ for s_z and $\mp (g_s e\hbar/4m)\mathscr{B}$ for the energy. The *Larmor precession frequency* ω_L may be defined by

$$\omega_L \equiv -\frac{g_s e\mathscr{B}}{2m} \tag{25.1}$$

and the energy eigenvalues are then given by $\pm\frac{1}{2}\hbar\omega_L$.

When $t = 0$ the spin wave function ϕ will be taken to be

$$\phi(0) = \frac{1}{\sqrt{2}}(\chi_{+\frac{1}{2}} + \chi_{-\frac{1}{2}}) \tag{25.2}$$

Obviously s_z is equally likely to have the two possible values $\pm\frac{1}{2}\hbar$, but $\phi(0)$ is actually an eigenfunction of s_x, belonging to the eigenvalue $+\frac{1}{2}\hbar$,

$$\begin{aligned}\hat{s}_x\phi(0) &= \tfrac{1}{2}\{(\hat{s}_x + i\hat{s}_y) + (\hat{s}_x - i\hat{s}_y)\}\phi(0)\\ &= 2^{-3/2}(\hat{s}_-\chi_{\frac{1}{2}} + \hat{s}_+\chi_{-\frac{1}{2}}) = \tfrac{1}{2}\hbar\phi(0)\end{aligned} \tag{25.3}$$

where the properties of the shift operators $\hat{s}_+$, $\hat{s}_-$ have been recalled.

The subsequent development of $\phi(t)$ can be written down at once by means of equation (3.6):

$$\phi(t) = \frac{1}{\sqrt{2}}(e^{-i\omega_L t/2}\chi_{\frac{1}{2}} + e^{+i\omega_L t/2}\chi_{-\frac{1}{2}}) \tag{25.4}$$

It is clear that the particle is repeatedly in an eigenstate of s_x, belonging to the eigenvalue $+\hbar/2$, when t is an integral multiple of $2\pi/\omega_L$; at such times $\phi(t) = \pm\phi(0)$. This suggests that the spin rotates, or precesses, in the xy plane and this idea is easy to verify. A unit vector $\mathbf{n}$ may be defined that starts off in the x direction and rotates in the xy plane, round the z-axis, with angular velocity ω_L. A positive (negative) ω_L corresponds to clockwise (anticlockwise) rotation when viewed along the z-axis. The component of $\mathbf{s}$ along $\mathbf{n}$ is represented by the operator

$$\begin{aligned}\hat{\mathbf{s}}\,.\,\mathbf{n} &= \hat{s}_x n_x + \hat{s}_y n_y = \hat{s}_x \cos(\omega_L t) + \hat{s}_y \sin(\omega_L t)\\ &= \tfrac{1}{2}(\hat{s}_+ e^{-i\omega_L t} + \hat{s}_- e^{i\omega_L t})\end{aligned} \tag{25.5}$$

and it is easy to check that

$$(\hat{\mathbf{s}}\,.\,\mathbf{n})\phi(t) = 2^{-3/2}(e^{i\omega_L t/2}\hat{s}_-\chi_{\frac{1}{2}} + e^{-i\omega_L t/2}\hat{s}_+\chi_{-\frac{1}{2}}) = \tfrac{1}{2}\hbar\phi(t) \tag{25.6}$$

Here it is seen that the spin steadily maintains the eigenvalue $\hbar/2$ in the direction of the rotating vector $\mathbf{n}$. This behaviour corresponds to the classical precession of a gyroscope that is subjected to a couple at right angles to its angular momentum.

Magnetic resonance Another situation of great practical interest arises when a static magnetic field of strength $\mathscr{B}$ is maintained in the z-direction, while a rather weak magnetic field $\mathscr{B}'$ is arranged to rotate in the xy plane at angular velocity ω. The components of the rotating field in the x- and y-directions are $\mathscr{B}' \cos(\omega t)$ and $\mathscr{B}' \sin(\omega t)$, so that a positive (negative) ω corresponds to clockwise (anticlockwise) rotation when viewed along the z-axis. The Hamiltonian is

$$\begin{aligned}\hat{H} &= -(g_s e/2m)(\mathscr{B}\hat{s}_z + \mathscr{B}' \cos(\omega t)\hat{s}_x + \mathscr{B}' \sin(\omega t)\hat{s}_y) \\ &= \omega_L \hat{s}_z + \tfrac{1}{2}(\lambda \hat{s}_+ e^{-i\omega t} + \lambda \hat{s}_- e^{i\omega t}) \qquad (25.7)\end{aligned}$$

where λ is defined to be the angular frequency $-(g_s e\mathscr{B}'/2m)$.

The spin wave function at $t=0$ may be supposed to be $\chi_{-\frac{1}{2}}$, so that the particle would be in the stationary state represented by $\chi_{-\frac{1}{2}} e^{i\omega_L t/2}$ if $\mathscr{B}'$ were zero. When $\mathscr{B}'$ is not zero,†

$$\phi(t) = c_+(t)\chi_{\frac{1}{2}} e^{-i\omega_L t/2} + c_-(t)\chi_{-\frac{1}{2}} e^{i\omega_L t/2} \qquad (25.8)$$

with $c_+(0)=0$, $c_-(0)=1$. Clearly $|c_+(t)|^2$ is the probability at time t that there has been a transition to the state with $s_z = +\hbar/2$.

When $\hat{H}$ is given by equation (25.7), the TISE says that

$$i\dot{c}_+\chi_{\frac{1}{2}} e^{-i\omega_L t/2} + i\dot{c}_-\chi_{-\frac{1}{2}} e^{i\omega_L t/2} = \tfrac{1}{2}\lambda c_- \chi_{\frac{1}{2}} e^{i(\frac{1}{2}\omega_L - \omega)t} + \tfrac{1}{2}\lambda c_+ \chi_{-\frac{1}{2}} e^{-i(\frac{1}{2}\omega_L - \omega)t} \qquad (25.9)$$

The scalar product of this equation may be formed with $\chi_{\frac{1}{2}} e^{-i\omega_L t/2}$ and $\chi_{-\frac{1}{2}} e^{i\omega_L t/2}$ to get two equations, involving c_+, $\dot{c}_+$, c_-, and $\dot{c}_-$,

$$\left.\begin{aligned} i\dot{c}_+ &= \tfrac{1}{2}\lambda c_- \, e^{i(\omega_L - \omega)t} \\ i\dot{c}_- &= \tfrac{1}{2}\lambda c_+ \, e^{-i(\omega_L - \omega)t} \end{aligned}\right\} \qquad (25.10)$$

The first of these may be differentiated to get

$$\ddot{c}_+ - i(\omega_L - \omega)\dot{c}_+ + \tfrac{1}{4}\lambda^2 c_+ = 0 \qquad (25.11)$$

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† The exclusion of the exponential factors from $c_+(t)$ and $c_-(t)$ greatly simplifies the following equations. In advanced quantum mechanics this is called 'working in the interaction representation'.

This linear and homogeneous differential equation may be solved as usual by the substitution $c_+ = \mathrm{e}^{pt}$, which gives a quadratic equation for p with the two solutions

$$p_{1,2} = \tfrac{1}{2}i[(\omega_L - \omega) \pm \{(\omega_L - \omega)^2 + \lambda^2\}^{1/2}] \tag{25.12}$$

The constants in the general solution $c_+ = A\mathrm{e}^{p_1 t} + B\mathrm{e}^{p_2 t}$ can be obtained by considering that $c_+(0) = 0$, and by looking at the first of equations (25.10) at $t = 0$. The final result is

$$c_+ = -\frac{i\lambda \mathrm{e}^{i(\omega_L - \omega)t/2} \sin[\tfrac{1}{2}\{(\omega_L - \omega)^2 + \lambda^2\}^{1/2} t]}{\{(\omega_L - \omega)^2 + \lambda^2\}^{1/2}}$$

$$|c_+|^2 = \frac{\lambda^2 \sin^2[\tfrac{1}{2}\{(\omega_L - \omega)^2 + \lambda^2\}^{1/2} t]}{(\omega_L - \omega)^2 + \lambda^2} \tag{25.13}$$

There are several instructive general points that are exemplified in this formula. In the first place it is clear that, for $\lambda \ll \omega_L$ (or $\mathscr{B}' \ll \mathscr{B}$), the transitions from $s_z = -\hbar/2$ to $s_z = +\hbar/2$ occur for a sharply limited range of angular frequencies ω. This is illustrated in figure 25.1, which shows $|c_+|^2$ for $t = \pi/\lambda$, when the transition can be complete for the first time. The relationship between the effective range of applied frequencies and the energy change between the two

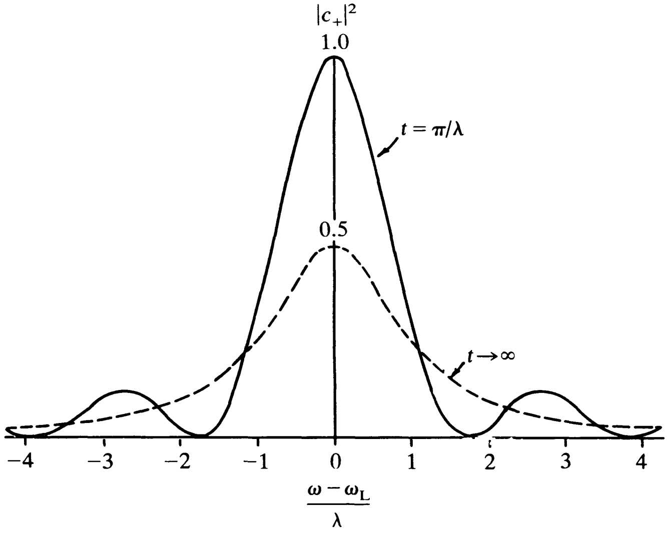

Figure 25.1 The probability $|c_+|^2$ of s_z being found to be $+\hbar/2$ at the time $t = \pi/\lambda$ and as a function of ω. The probability as $t \to \infty$ is also shown, with the assumption that experimental conditions are not ideal.

states concerned is given by the formula

$$E_f - E_i \approx \hbar\omega \tag{25.14}$$

where E_i and E_f are the energy eigenvalues of the initial and final states.

For the sake of definiteness the discussion will temporarily be specialised by supposing that the particle is in fact an electron, which has negative charge and a positive ω_L (clockwise when viewed along the steady magnetic field). Then equation (25.14) shows that energy is being supplied by the source of the rotating magnetic field to the electron. At exact resonance the flow of energy is reversed after $t = \pi/\lambda$ until the initial situation is restored at $t = 2\pi/\lambda$.

For slight variations of frequency, inhomogeneities of field, and long periods of time the trigonometric function in equation (25.13) averages out to the value $\frac{1}{2}$. The remaining factor then controls the final dependence of $|c_+|^2$ on ω_L and the population of the $s_z = +\hbar/2$ state fluctuates around the dashed line in figure 25.1. If there is no other process involving the electron spin the net flow of energy from the source of the magnetic field ceases after this initial investment has been made. In solids or liquids there is often some other method of *spin relaxation* by which the electron is returned to the $s_z = -\hbar/2$ state, and then the flow of energy from the source is continuous and can be macroscopically detected.

Alternatively the transitions can be microscopically detected in free particles, atoms, or ions by a change in the effect of an inhomogeneous magnetic field, applied before and after the magnetic fields discussed here. The Stern–Gerlach experiments mentioned in section 20 were powerfully extended in this direction by Rabi and his collaborators.

A second point of interest is that equation (25.14) becomes more and more exact as λ/ω_L is reduced, as figure 25.1 indeed makes obvious. Of course the time required for the transition to occur is increased, in inverse proportion to λ. The error ΔE in measuring $E_f - E_i$ is related to the time Δt before a transition is likely to be observed by

$$\Delta E\,\Delta t \approx \hbar\lambda\,.\,\frac{1}{\lambda} = \hbar \tag{25.15}$$

as foreshadowed in section 5 when the uncertainty principle was first discussed.

Finally, the correspondence principle can again be seen at work.

A classical magnetic dipole associated with an angular momentum would precess round $\mathcal{B}$ at the angular frequency ω_L, as discussed earlier. The magnetic field $\mathcal{B}'$, rotating at the same angular frequency, would point consistently along the vector **n**, so producing a further precession round that vector at the angular frequency λ. The component s_z of the particle's angular momentum would thus be proportional to $-\cos(\lambda t)$ at exact resonance. The quantum mechanical formula (25.13) shows that $\langle s_z\rangle$ is indeed proportional to

$$|c_+|^2-|c_-|^2=2\,|c_+|^2-1=2\sin^2(\tfrac{1}{2}\lambda t)-1=-\cos(\lambda t) \qquad (25.16)$$

There is a point of experimental technique that should be mentioned. A linearly oscillatory magnetic field is usually applied, rather than a pure rotating field. The linear field can, however, be decomposed into a superposition of two rotating fields, with angular frequencies $\pm\omega$. When $\omega\approx\omega_L$ the component at angular frequency $-\omega$ does not produce a significant effect.

§26 Transitions caused by a perturbation independent of time

A non-stationary situation of very general interest can be discussed with the help of figure 26.1, which shows the energy eigenvalues associated with a time-independent Hamiltonian $\hat{H}$. By hypothesis the state labelled s is an isolated one, whereas those labelled r (or k) are closely spaced and their energies E_r (or E_k) extend indefinitely above and below E_s. At $t=0$ the system starts off in the state s, which would of course be stationary if the Hamiltonian comprised $\hat{H}$ alone. In fact it will be supposed that a second time-independent

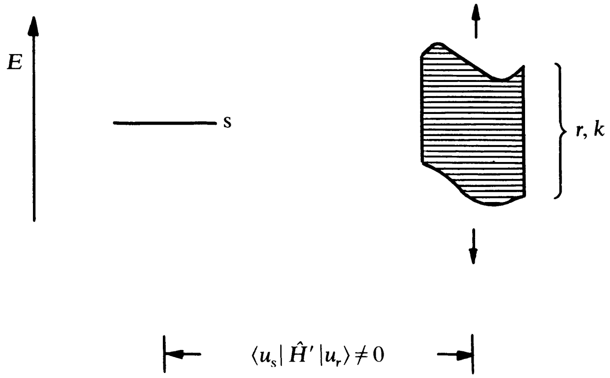

Figure 26.1 The structure assumed for the energy eigenvalues of H alone.

term $\hat{H}'$ is also included in the total Hamiltonian, and the aim is to see what happens after $t=0$ because of this fact. An important role in the calculation will be played by the matrix elements $\langle u_r|\,\hat{H}'\,|u_s\rangle$ (or $\langle u_k|\,\hat{H}'\,|u_s\rangle$) which are assumed to be non-zero. Other conditions on them will appear later.

The energy eigenfunctions of $\hat{H}$ alone form a complete orthonormal set, and so ψ can be expanded in terms of them:

$$\left.\begin{array}{l} \psi = c_s(t)u_s\mathrm{e}^{-i(E_s+E_s')t/\hbar} + \sum\limits_r c_r(t)u_r\mathrm{e}^{-i(E_r+E_r')t/\hbar} \\ \begin{cases} c_s(0)=1 \\ c_r(0)=0 \end{cases} \qquad \begin{cases} E_s' = \langle u_s|\,\hat{H}'\,|u_s\rangle \\ E_r' = \langle u_r|\,\hat{H}'\,|u_r\rangle \end{cases} \end{array}\right\} \tag{26.1}$$

The complex exponential factors are included as a matter of convenience, because later equations will be simplified thereby, but of course the as yet uncalculated $c_s(t)$, $c_r(t)$ allow full freedom to the variation of ψ. The energies E_s', E_r' defined here would, in other circumstances, be the first-order energy corrections to E_s, E_r caused by $\hat{H}'$ (section 15).

The actual time variation of ψ is described by the TDSE

$$i\hbar\frac{\partial\psi}{\partial t} = (\hat{H}+\hat{H}')\psi \tag{26.2}$$

and so

$$\begin{aligned} (i\hbar\dot{c}_s + E_s'c_s)u_s\mathrm{e}^{-i(E_s+E_s')t/\hbar} &+ \sum_r (i\hbar\dot{c}_r + E_r'c_r)u_r\mathrm{e}^{-i(E_r+E_r')t/\hbar} \\ &= c_s\hat{H}'u_s\mathrm{e}^{-i(E_s+E_s')t/\hbar} + \sum_r c_r\hat{H}'u_r\mathrm{e}^{-i(E_r+E_r')t/\hbar} \end{aligned} \tag{26.3}$$

since $\hat{H}u_s = E_su_s$ and $\hat{H}u_r = E_ru_r$.

The scalar product of equation (26.3) may be formed, first with u_s and then with one of the u_r, say u_k. Some terms are eliminated by orthonormality of the eigenfunctions, and others cancel because of the definitions of E_s' and E_r' (or E_k'). The results are

$$\left.\begin{aligned} ih\dot{c}_s &= \sum_r c_r\langle u_s|\,\hat{H}'\,|u_r\rangle\mathrm{e}^{-i\omega_{rs}t} \\ i\hbar\dot{c}_k &= c_s\langle u_k|\,\hat{H}'\,|u_s\rangle\mathrm{e}^{i\omega_{ks}t} + \sum_{r\neq k} c_r\langle u_k|\,\hat{H}'\,|u_r\rangle\mathrm{e}^{i\omega_{kr}t} \end{aligned}\right\} \tag{26.4}$$

where, for example,

$$\hbar\omega_{ks} = (E_k + E_k') - (E_s + E_s') \tag{26.5}$$

An integral equation for c_s So far the calculation has been exact, but further progress depends on getting rid of the last term in the second of equations (26.4), by putting† $\langle u_k | \hat{H}' | u_r \rangle = 0$ for $r \neq k$. In words it is usual to say that 'the final states do not interact'. This is often an exactly fulfilled requirement, for example in the nuclear beta decay calculation of section 27, where $\hat{H}'$ includes a charge operator. In other situations the final states do in fact interact, and the omission of the terms under discussion is a regrettable approximation which impairs the credibility of the final result.

When the final states do not interact, E_k' and E_s' are also apt to be zero. It is therefore consistent to simplify equation (26.5) to read,

$$\hbar\omega_{ks} = E_k - E_s \tag{26.6}$$

It is an easy matter to reinstate E_k' and E_s' alongside E_k and E_s in succeeding formulae, if desired.

The second of equations (26.4), with its last term now dropped, may be integrated and put into the first of equations (26.4),

$$\dot{c}_s = -\frac{1}{\hbar^2} \sum_k |\langle u_k | \hat{H}' | u_s \rangle|^2 e^{-i\omega_{ks}t} \left\{ \int_0^t c_s(t') e^{i\omega_{ks}t'} \, dt' \right\} \tag{26.7}$$

The next step is to recognise that the states k are all of the same type, so that $|\langle u_k | \hat{H}' | u_s \rangle|^2$ will vary smoothly with E_k, or ω_{ks}. Moreover, if the number dN of states k in the energy interval dE_k is given by

$$\frac{dN}{dE_k} \equiv \rho_E = \frac{1}{\hbar} \frac{dN}{d\omega_{ks}} \tag{26.8}$$

then ρ_E can be assumed to be large and also to vary smoothly with ω_{ks}. Thus the summation in equation (26.7) can be replaced by integration over ω_{ks},

$$\dot{c}_s = -\frac{1}{\hbar} \int |\langle u_k | \hat{H}' | u_s \rangle|^2 e^{-i\omega_{ks}t} \left\{ \int_0^t c_s(t') e^{i\omega_{ks}t'} \, dt' \right\} \rho_E \, d\omega_{ks} \tag{26.9}$$

A final approximation, of physical significance, is to assume that the time integral in equation (26.9) is negligibly small outside a small interval of ω_{ks} near $\omega_{ks} = 0$. If this is so, then $|\langle u_k | \hat{H}' | u_s \rangle|^2$ and ρ_E may be regarded as constants, and the range of integration over ω_{ks}

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† Note that the possible values of r specifically exclude s (figure 26.1).

extended from $-\infty$ to $+\infty$,

$$\dot{c}_s = -\frac{1}{\hbar}|\langle u_k|\,\hat{H}'\,|u_s\rangle|^2\rho_E \int_{-\infty}^{\infty} \mathrm{e}^{-i\omega_{ks}t}\left\{\int_0^t c_s(t')\mathrm{e}^{i\omega_{ks}t'}\,\mathrm{d}t'\right\}\mathrm{d}\omega_{ks} \tag{26.10}$$

The conditions for the validity of this final approximation will be discussed later.

Solution of the integral equation The key to the solution of equation (26.10) is to remember the exponential decay law of radioactivity. A nucleus in a state s, able to make transitions into states k which include one or more free particles, does so in such a way that $|c_s|^2 = \mathrm{e}^{-\lambda t}$, where λ may be called either the *transition rate* or the *decay constant.*

An obvious suggestion is therefore that $c_s(t) = \mathrm{e}^{-\lambda t/2}$ should be tried. The time integration in equation (26.10) then gives,

$$\int_0^t \mathrm{e}^{(-\lambda/2+i\omega_{ks})t'}\,\mathrm{d}t' = \frac{-i\{\mathrm{e}^{(-\lambda/2+i\omega_{ks})t}-1\}}{\omega_{ks}+i\lambda/2} \tag{26.11}$$

and the ω_{ks} integration gives†

$$-i\int_{-\infty}^{\infty}\left(\frac{\mathrm{e}^{-\lambda t/2}-\mathrm{e}^{-i\omega_{ks}t}}{\omega_{ks}+i\lambda/2}\right)\mathrm{d}\omega_{ks} = \pi\mathrm{e}^{-\lambda t/2} \tag{26.12}$$

Since $\dot{c}_s = -\frac{1}{2}\lambda\mathrm{e}^{-\lambda t/2}$ it is now clear that equation (26.10) is satisfied if

$$\lambda = \frac{2\pi}{\hbar}|\langle u_k|\,\hat{H}'\,|u_s\rangle|^2\rho_E \tag{26.13}$$

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† *Vide* the appendix, equation (4). An alternative and altogether more dashing treatment results from reversing the order of integration over t' and ω_{ks}, and using the fact (section 6) that

$$\int_{-\infty}^{\infty} \mathrm{e}^{i\omega_{ks}(t'-t)}\,\mathrm{d}\omega_{ks} = 2\pi\,\delta(t'-t)$$

Then,

$$2\pi\int_0^t \mathrm{e}^{-\lambda t'/2}\,\delta(t'-t)\,\mathrm{d}t = \pi\int_0^\infty \mathrm{e}^{-\lambda t'/2}\,\delta(t'-t)\,\mathrm{d}t' = \pi\mathrm{e}^{-\lambda t/2}$$

This important formula is often referred to as the Golden Rule. It obviously involves two distinct parts, the square of the modulus of the matrix element and the density ρ_E. The latter is often called the phase space factor, because it is equal to $(2\pi\hbar)^{-3}$ multiplied by the volume of phase space embraced when a unit increase is made in E_k (section 18).

Very often the matrix element cannot be precisely calculated, because of lack of knowledge about $\hat{H}$, u_k, and u_s, but it is usually possible to make some statements about it (for example angular distribution or dependence on E_s). The phase space factor can always be calculated, and useful predictions may sometimes be made from the behaviour of this factor alone (section 27).

Decay width The chance $I(\omega_{ks}, t)\,\mathrm{d}\omega_{ks}$ of finding the system at time t in one of the states k lying in the interval $\mathrm{d}\omega_{ks}$ is given by integration of the second of equations (26.4):

$$\begin{aligned} I(\omega_{ks}, t)\,\mathrm{d}\omega_{ks} &= |c_k(t)|^2\,\hbar\rho_E\,\mathrm{d}\omega_{ks} \\ &= \frac{1}{\hbar}\left|\int_0^t \langle u_k|\,\hat{H}'\,|u_s\rangle \mathrm{e}^{(-\lambda/2+\mathrm{i}\omega_{ks})t'}\,\mathrm{d}t'\right|^2 \rho_E\,\mathrm{d}\omega_{ks} \qquad (26.14) \end{aligned}$$

With the help of equations (26.11) and (26.13),

$$\begin{aligned} I(\omega_{ks}, t) &= \frac{\lambda}{2\pi}\left|\frac{\mathrm{e}^{(-\lambda/2+\mathrm{i}\omega_{ks})t}-1}{\omega_{ks}+i\lambda/2}\right|^2 \\ &= \frac{\lambda/2}{\pi(\omega_{ks}^2+\lambda^2/4)}\{1+\mathrm{e}^{-\lambda t}-2\mathrm{e}^{-\lambda t/2}\cos(\omega_{ks}t)\} \qquad (26.15) \end{aligned}$$

At infinitely large times,

$$I(\omega_{ks}, \infty) = \frac{\lambda/2}{\pi(\omega_{ks}^2+\lambda^2/4)} \qquad (26.16)$$

Figure 26.2 shows how I depends on ω_{ks} for $\lambda t = 1, 2$, and ∞. The characteristic bell-shaped form of the last of these should be noted, together with the fact that

$$\int_{-\infty}^{\infty} I(\omega_{ks}, \infty)\,\mathrm{d}\omega_{ks} = 1$$

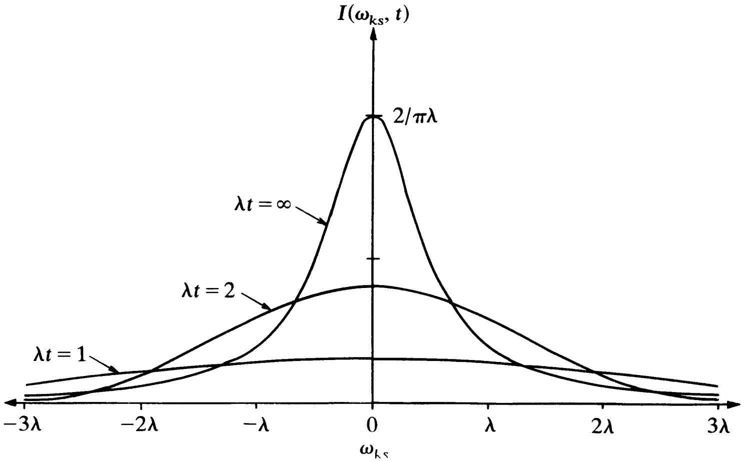

Figure 26.2 The probability distribution for ω_{ks}, at various times.

In nuclear and particle physics it is more usual to express I in terms of E_k rather than the frequency ω_{ks}. Thus,†

$$I(E_k, \infty) = \frac{\Gamma/2}{\pi\{(E_k - E_s)^2 + \Gamma^2/4\}} \tag{26.17}$$

where $\Gamma = \hbar\lambda$ is an energy called the *decay width*; it is the full width of the energy interval within which $I(E_k, \infty)$ has more than half its maximum value.

The uncertainty principle involving energy and time is again exemplified here. An observer attempting to determine E_s by one measurement of E_k must wait for the transition to occur, which takes a time Δt of the order of $1/\lambda$. But the error ΔE in identifying E_s with E_k is of the order $\Gamma = \hbar\lambda$, so $\Delta E \Delta t \approx \hbar$ as before (equation (25.15)). Obviously the limitation can be overcome by repeating the experiment many times, so building up an experimental distribution curve to compare with figure 26.2

The approximation leading to equation (26.10) It is now clear that the important final states are those for which $|E_k - E_s| \approx \Gamma$, and a retrospective look at the derivation of equation (26.10) shows that u_k and ρ_E must not change appreciably for these values of E_k. This

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† If E_k' and E_s' had been carried along the denominator would involve the energy $(E_k + E_k' - E_s - E_s')^2$

is assured if $\Gamma \ll T_k$, where T_k is the kinetic energy of the particle or particles involved.

More vaguely, the condition can be stated in the form that $\hat{H}' \ll \hat{H}$, and for this reason the derivation of the Golden Rule is described as a perturbation theory of transitions.

Selection rules The matrix element $\langle u_k | \hat{H}' | u_s \rangle$ may be zero for all $E_k \approx E_s$, and then the transition rate vanishes to first order. Often this does not happen by accident, but rather because of symmetry properties of $\hat{H}'$, u_s, and u_k. If $\hat{H}'$ were an odd parity operator, for example, then u_s and u_k would have to have opposite parity to achieve a non-zero transition rate.† Similar situations crop up in connection with angular momentum, where matrix elements often vanish on angular integration except in special circumstances. Considerations of this kind give rise to *selection rules* governing the nature of the transitions that are allowed to occur.

Second-order transitions If the first-order transition rate is small or forbidden by a selection rule, then the more complicated situation shown in figure 26.3 may have to be considered. The *virtual states q* are such that $E_q \neq E_s$, and they have finite matrix elements

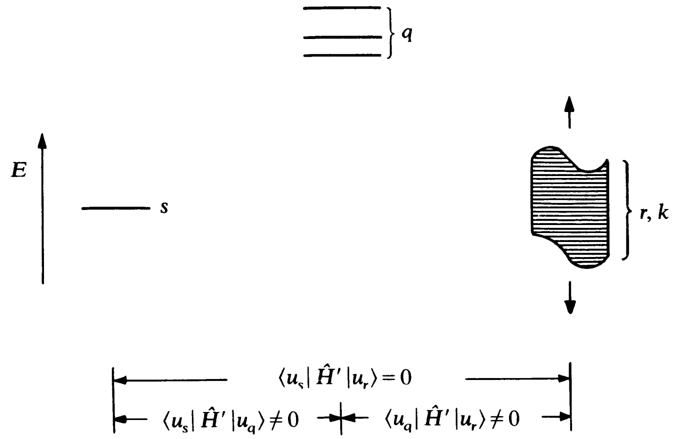

Figure 26.3 The structure assumed for the energy eigenvalues of H alone, when transitions only occur in second order.

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† Cf. previous remarks about electric dipole moments (section 16).

of $\hat{H}'$, both with u_s and u_r (or u_k). It is assumed as before that the final states do not interact ($\langle u_k|\hat{H}'|u_r\rangle = 0$, $r \neq k$), and that E'_k and E'_s are zero.

The new form of ψ may be written

$$\begin{aligned}\psi = c_s(t)\left[u_s + \sum_q \left\{\frac{\langle u_q|\hat{H}'|u_s\rangle}{E_s - E_q}\right\}u_q e^{-i(E_s+E''_s)t/\hbar}\right]\\ + \sum_r c_r(t)\left[u_r + \sum_q \left\{\frac{\langle u_q|\hat{H}'|u_r\rangle}{E_r - E_q}\right\}u_q\right]e^{-i(E_r+E''_r)t/\hbar}\end{aligned} \tag{26.18}$$

where

$$E''_s = \sum_q \frac{|\langle u_q|\hat{H}'|u_s\rangle|^2}{E_s - E_q}, \qquad E''_r = \sum_q \frac{|\langle u_q|\hat{H}'|u_r\rangle|^2}{E_r - E_q}$$

Here the wave functions in the square brackets are stationary to terms of first order in the presence of $\hat{H}'$ (equation (15.7)). As before the exponential factors are chosen for future convenience; in other circumstances E''_s, E''_r would be the second-order energy corrections to E_s, E_r caused by $\hat{H}'$ (equation (15.10)).

When the expression for ψ is substituted into equation (26.2), scalar products are taken with u_s and u_k, and all appropriate cancellations are made:

$$\left.\begin{aligned}i\hbar\dot{c}_s &= \sum_r c_r\left\{\sum_q \frac{\langle u_s|\hat{H}'|u_q\rangle\langle u_q|\hat{H}'|u_r\rangle}{E_r - E_q}\right\}e^{-i\omega_{rs}t}\\ i\hbar\dot{c}_k &= c_s\left\{\sum_q \frac{\langle u_k|\hat{H}'|u_q\rangle\langle u_q|\hat{H}'|u_s\rangle}{E_s - E_q}\right\}e^{i\omega_{ks}t}\end{aligned}\right\} \tag{26.19}$$

These equations are the same as equations (26.4) (final state interactions neglected), except that the summations over the virtual states q replace the direct matrix elements that appeared previously. Continuation of the calculation along the same lines as before carries this feature into the answer, the second-order Golden Rule,

$$\lambda = \frac{2\pi}{\hbar}\left|\sum_q \frac{\langle u_k|\hat{H}'|u_q\rangle\langle u_q|\hat{H}'|u_s\rangle}{E_s - E_q}\right|^2 \rho_E \tag{26.20}$$

The only new condition is that $\Gamma = \hbar\lambda$ must be small compared to $|E_s - E_q|$ for all q, so that the summation denominators can always be written as $E_s - E_q$.

The denominator $E_s - E_q$ exercises some restraint on the energy of the virtual states through which the decay proceeds. If this restraint be sacrificed an upper limit for the second-order transition rate can be found by replacing $E_s - E_q$ by $E_s - E_{q'}$, where $E_{q'}$ is the energy of the lowest effective virtual state. With the help of the closure relation (equation (4.19)),

$$\lambda \leqslant \frac{2\pi}{\hbar} \frac{|\langle u_k| \hat{H}'^2 |u_s\rangle|^2}{(E_s - E_{q'})^2} \rho_E \tag{26.21}$$

Obviously this is much smaller than a typical first-order transition rate produced by $\hat{H}'$ and not forbidden by a selection rule, since $\hat{H}'$ is small and $E_s - E_{q'}$ will be of the order of $\hat{H}$.

§27 Nuclear beta decay

The Golden Rule can be applied with confidence when $\hat{H}'$ corresponds to an electromagnetic interaction, or to the weak Fermi interaction responsible for, among other processes, nuclear beta decay. As an example the latter process will be discussed in order to bring out some general points of interest.

The process $A \rightarrow B + e^- + \bar{\nu}_e$ will be analysed, where A, B are the initial and final nuclei, e^- is an electron, and $\bar{\nu}_e$ is an antineutrino of the electron-associated variety. The differential decay constant $d\lambda(E_e)$ for transitions in which an electron is produced with total energy between E_e and $E_e + dE_e$ is

$$\begin{aligned} d\lambda(E_e) &= \frac{2\pi}{\hbar} |\langle \psi_e \psi_{\bar{\nu}} \Psi_B| \hat{H}' |\Psi_A\rangle^2 \rho \, dE_e \\ &= \frac{2\pi}{\hbar} |\langle L^{-3/2} e^{i\mathbf{k}_e \cdot \mathbf{r}_e} . L^{-3/2} e^{i\mathbf{k}_{\bar{\nu}} \cdot \mathbf{r}_{\bar{\nu}}} \Psi_B| \hat{H}' |\Psi_A\rangle^2 \rho \, dE_e \end{aligned} \tag{27.1}$$

where $\hbar\mathbf{k}_e$ and $\hbar\mathbf{k}_{\bar{\nu}}$ are the momenta of the emitted electron and antineutrino respectively. They are free particles apart from $\hat{H}'$ (and neglected Coulomb interactions between the electron and the nuclear charges), and therefore have the usual plane wave functions (section 9). Provided that the electron and antineutrino wavelengths are long compared to nuclear dimensions, and this is a good approximation, only the constant 1 need be kept in the expansions $e^{i\mathbf{k}_e \cdot \mathbf{r}_e} = 1 + i\mathbf{k}_e . \mathbf{r}_e + \cdots$ and $e^{i\mathbf{k}_{\bar{\nu}} \cdot \mathbf{r}_{\bar{\nu}}} = 1 + i\mathbf{k}_{\bar{\nu}} . \mathbf{r}_{\bar{\nu}} + \cdots$. The spins of both are ignored.

The meaning in equation (27.1) of the phase space factor ρ needs some thought, since there are two free particles of variable energy in the final state. Of course ρ contains a factor ρ_{E_e}, such that $\rho_{E_e} \, dE_e$ is the number of electron states with electron energy in the range dE_e.

But for each electron state there is an energy density of final states obtained by varying the antineutrino energy $E_{\bar{\nu}}$. Thus ρ also contains a second factor $\rho_{E_{\bar{\nu}}}$, evaluated at the antineutrino energy $E_{\bar{\nu}}$ which is given by overall energy conservation. The integral involving a δ-function at the end of equation (27.2) is a convenient way of writing down this second factor.

Next, $\hat{H}'$ may be taken to be a scalar constant g, whose dimensions are energy×volume, multiplied by a charge operator $\mathcal{T}$ that changes a neutron into a proton.

This is a very simplified assumption, which does not, however, affect the general points at which this discussion is aimed. In truth the interaction is a mixture of vector and axial vector interactions, which involve the neglected spins of the electron and antineutrino.

With the above simplified form of $\hat{H}'$, the differential decay constant is

$$\mathrm{d}\lambda(E_e) = \frac{2\pi g^2 M^2}{\hbar L^6}\, \rho_{E_e}\, \mathrm{d}E_e \int_0^{E_0 - mc^2} \rho_{E_{\bar{\nu}}}\, \delta(E_0 - E_e - E_{\bar{\nu}})\, \mathrm{d}E_{\bar{\nu}} \tag{27.2}$$

where $M = |\langle \Psi_B | \mathcal{T} | \Psi_A \rangle|$ is of order unity, unless it vanishes because of a selection rule. In the δ-function, E_0 is the total energy available for the two particles, including that required for the mass energy of the electron.

A minor deviation is needed to recalculate equation (9.10) relativistically. This is necessary for the massless antineutrino, and might as well be done for the electron as well. Thus, for either particle, $\rho_E = \mathrm{d}N/\mathrm{d}E = (\mathrm{d}N/\mathrm{d}p)(\mathrm{d}p/\mathrm{d}E)$ and, since $E^2 = c^2p^2 + m^2c^4$,

$$\left.\begin{aligned} \frac{\mathrm{d}N}{\mathrm{d}p} &= \left(\frac{L}{2\pi\hbar}\right)^3 4\pi p^2 = \frac{L^3}{2\pi^2 c^2 \hbar^3}(E^2 - m^2c^4) \\ \frac{\mathrm{d}p}{\mathrm{d}E} &= \frac{E}{c^2 p} = \frac{E}{c}(E^2 - m^2c^4)^{-1/2} \end{aligned}\right\} \tag{27.3}$$

where the phase space rule mentioned in section 18 has been used to count the states. Thus,

$$\frac{\mathrm{d}\lambda(E_e)}{\mathrm{d}E_e} = \left(\frac{2\pi g^2 M^2}{\hbar L^6}\right)\left(\frac{L^3}{2\pi^2 c^3 \hbar^3}\right)\{E_e(E_e^2 - m^2c^4)^{1/2}\}$$

$$\times \int_0^{E_0 - mc^2} \frac{L^3}{2\pi^2 c^3 \hbar^3} E_{\bar{\nu}}^2 \delta(E_0 - E_e - E_{\bar{\nu}})\, \mathrm{d}E_{\bar{\nu}}$$

$$= \frac{g^2 M^2}{2\pi^3 c^6 \hbar^7}\{E_e(E_e^2 - m^2c^4)^{1/2}(E_0 - E_e)^2\} \tag{27.4}$$

It is seen here that the shape of the electron spectrum has been entirely determined by the phase space factor; it is called the 'allowed' shape and has been experimentally checked with great accuracy in numerous transitions.

The total transition rate obtained by integrating equation (27.4) over E_e is given by

$$\lambda = \frac{g^2 M^2 m^5 c^4}{2\pi^3 \hbar^7} f(\eta_0) \tag{27.5}$$

where,

$$\left.\begin{aligned} \eta_0 &= (E_0^2 - m^2c^4)^{1/2}/mc^2 \\ f(\eta_0) &= -\tfrac{1}{4}\eta_0 - \tfrac{1}{12}\eta_0^3 + \tfrac{1}{30}\eta_0^5 + \tfrac{1}{4}(1+\eta_0^2)^{1/2}\ln\{\eta_0 + (1+\eta_0^2)^{1/2}\} \end{aligned}\right\} \tag{27.6}$$

The value of M might conceivably be accurately zero, for example if A had the opposite parity to B; this would be an example of a selection rule at work. In such a case the second terms in the expansion of $e^{i\mathbf{k}_e\cdot\mathbf{r}_e}$ and $e^{i\mathbf{k}_{\bar{\nu}}\cdot\mathbf{r}_{\bar{\nu}}}$ would have to be brought into play. The electron spectrum would be modified into a 'forbidden' shape, and M^2 would be reduced by a factor of the order of $(E_0 a/\hbar c)^2$, where a is the nuclear radius. This is about a factor 100, and the effect of this can be clearly seen in a group of experimental values of λ.

The experimental half-life of the neutron (about 10^3 s) leads to a value for g of about 1.5×10^{-49} MeV m^3, since M should be close to 1 in this transition. The interaction is certainly weak compared to the ordinary potential energy describing the nuclear force, say 30 MeV, multiplied by the cube of its range, say 3×10^{-45} m^3, giving a typical product of about 10^{-43} MeV m^3. The ratio of the weak $\hat{H}'$ to the nuclear $\hat{H}$, about 10^{+6}, amply justifies the use of perturbation theory for this problem.

Nuclear double β-decay Certain nuclei are unstable against the emission of two electrons and two antineutrinos. A typical example is $^{48}\text{Ca}\ (\rightarrow {}^{48}\text{Sc} + e^- + \bar{\nu}_e) \rightarrow {}^{48}\text{Ti} + 2e^- + 2\bar{\nu}_e$, where the virtual state configuration is indicated in brackets; the energy available for the whole process is 4.3 MeV. Although ^{48}Ca is energetically unstable for single β-decay to ^{48}Sc, the process is very highly forbidden because of angular momentum selection rules. A value of $|(E_s - E_{q'})|$ of about 1 MeV may be adopted as an estimate of the minimum energy required to raise the ^{48}Sc to a virtual state of more suitable nuclear spin. An upper limit for the integrated double beta decay rate is, according to equation (26.21),

$$\lambda \leqslant \frac{2\pi g^4}{\hbar(E_s - E_{q'})^2 L^{12}} |\langle \Psi_{\mathrm{Ti}}| \mathcal{T}^2 |\Psi_{\mathrm{Ca}}\rangle|^2 \left(\frac{L^3}{2\pi^2 c^3 \hbar^3}\right)^4$$

$$\times \int\!\!\int\!\!\int\!\!\int E_{e_1}(E_{e_1}^2 - m^2c^4)^{1/2} E_{e_2}(E_{e_2}^2 - m^2c^4)^{1/2}$$

$$\times E_{\bar{\nu}_1}^2 E_{\bar{\nu}_2}^2 \delta(E_0 - E_{e_1} - E_{e_2} - E_{\bar{\nu}_1} - E_{\bar{\nu}_2})\, dE_{e_1}\, dE_{e_2}\, dE_{\bar{\nu}_1}\, dE_{\bar{\nu}_2} \quad (27.7)$$

The phase space integral may be made dimensionless by bringing out a factor† of $(mc^2)^{11}$, and it will then be of order unity, like the matrix element, M. Thus,

$$\lambda \leqslant \frac{2\pi g^4}{\hbar(E_s - E_{q'})^2 L^{12}} \left(\frac{L^3}{2\pi^2 c^3 \hbar^3}\right)^4 (mc^2)^{11} \approx 5 \times 10^{-28}\,\mathrm{s}^{-1} \quad (27.8)$$

The lifetime $1/\lambda$ is thus about 10^{20} years, but experimentally the process just evades detection at the time of writing.

§28 Radioactivity

The immediate objective here is to give a mathematical description of the emission of particles in radioactivity, and to develop a relation between the energy spectrum of the particles and the decay lifetime.‡ However, some of the equations that will be written down will be useful again in section 31, where the remarkable relationships between bound or radioactive states and scattering will come to light.

A central force of definite range a will be supposed to act on a particle of mass m,

$$V(\mathbf{r}) = \begin{cases} V(r), & r \leqslant a \\ 0, & r > a \end{cases} \quad (28.1)$$

No attempt will be made to specify $V(\mathbf{r})$ in detail, and so it will not be possible to write down the wave function inside a. That does not matter; it is the wave function outside a that carries the information sought. In that region the TDSE for an s state takes the simple

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† From its definition a δ function obviously has dimensions reciprocal to those of its argument.

‡ The relation was seen already at equation (26.7), but the derivation there is subject to the limitations of perturbation theory.

form†

$$i\hbar\frac{\partial\phi(r,t)}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\phi(r,t)}{\partial r^2},\qquad r>a \tag{28.2}$$

where

$$\phi(r,t)\equiv r\psi(r,t)$$

If $V(r)$ is attractive enough a bound s state with negative energy E_0 can be formed. Outside a, and therefore outside the outer turning point, the wave function decays exponentially with r:

$$\phi_0(r,t)=A_0\mathrm{e}^{-\kappa_0 r}\mathrm{e}^{-iE_0t/\hbar},\qquad r>a \tag{28.3}$$

where

$$\kappa_0=|(-2mE_0/\hbar)^{1/2}|$$

When the force is not quite so attractive a radioactive s state may be formed. A major part of the wave function represents a stationary state of energy E_s in the usual way, but there is an extra factor $\mathrm{e}^{-\lambda_s t/2}$ which introduces exponential decay with the decay constant λ_s. Thus

$$\phi_s(r,t)=\begin{cases}\left.\begin{array}{l}(\lambda_s/4\pi v_s)^{1/2}(\mathrm{e}^{ik_sr}\mathrm{e}^{-iE_st/\hbar})\mathrm{e}^{-\lambda_st/2}\\ (\lambda_s/4\pi v_s)^{1/2}\mathrm{e}^{ik_sr}\mathrm{e}^{-i(E_s-\frac{1}{2}i\Gamma_s)t/\hbar}\end{array}\right\} & a<r\leqslant v_st\\ \\ 0 & r>v_st\end{cases} \tag{28.4}$$

where the *width* $\Gamma_s=\hbar\lambda_s$. If $\Gamma_s\ll E_s$, and this will be assumed to the end of this section, the waveform emitted from the central region will be well preserved as it travels outwards‡ with the group velocity v_s (figure 28.1); in other words the RPPD is a function only of the retarded time $t-v_s^{-1}r$, and it is zero for negative retarded times. Now the RPPD is

$$4\pi\,|\phi_s|^2=(\lambda_s/v_s)\mathrm{e}^{-2(\mathrm{Im}\,k_s)r-\lambda_st},\qquad a<r\leqslant v_st \tag{28.5}$$

and this is a function of the retarded time only if

$$-2\,\mathrm{Im}\,k_s=\lambda_s/v_s \tag{28.6}$$

The probability of decay occurring by the time t should be $1-\mathrm{e}^{-\lambda_st}$, and the normalisation of ϕ_s ensures this. Provided that a is much smaller than v_s/λ_s, the radius reached by the wavefront after the

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† *Vide* problem 4.4.

‡ Like toothpaste squirted from the tube.

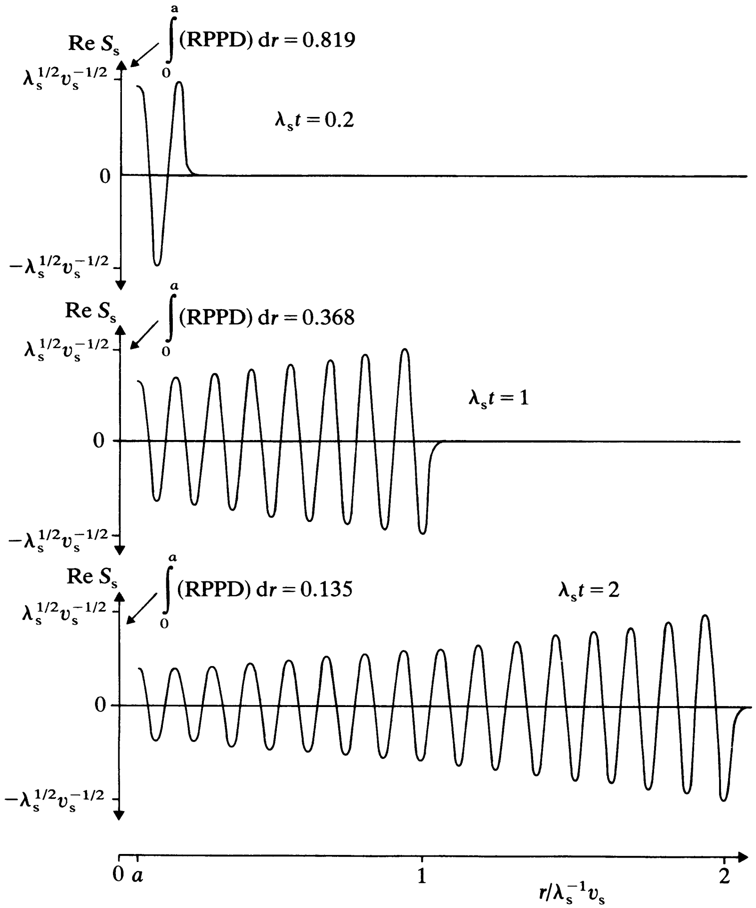

Figure 28.1 The wave functions of a particle emitted from a radioactive state.

mean lifetime of the decay, the normalising integral is

$$(\lambda_s/v_s)\int_a^{v_s t} e^{-\lambda_s(t-v_s^{-1}r)}\,dr \approx 1-e^{-\lambda_s t}, \qquad a \ll v_s/\lambda_s \qquad (28.7)$$

Since equation (28.2), the TDSE, is satisfied

$$k_s = \{(2m/\hbar^2)(E_s - \tfrac{1}{2}i\Gamma_s)\}^{1/2}$$

and

$$\begin{aligned}\operatorname{Re} k_s &\approx |(2mE_s/\hbar^2)^{1/2}|\\ \operatorname{Im} k_s &\approx -\operatorname{Re} k_s(\Gamma_s/4E_s)\end{aligned} \tag{28.8}$$

The two equations for $\operatorname{Im} k_s$ are compatible because $E_s \approx \frac{1}{2}mv_s^2$, as the correspondence principle requires.

The particle kinetic energy spectrum According to the usual interpretative rules, the chance of finding the particle with kinetic energy T and $T+\delta T$ is $I(T, \infty)$, with

$$I(T, \infty) = \lim_{t\to\infty} |\langle u_T|\,\phi_s\rangle|^2 \frac{\mathrm{d}N}{\mathrm{d}T} \tag{28.9}$$

Here $u_T = (1/2\pi^{1/2})S_T(r)$ is an angular momentum and kinetic energy eigenfunction belonging to the eigenvalues 0 and T, respectively, and $\mathrm{d}N/\mathrm{d}T$ is the density of kinetic energy eigenstates. After appropriate substitution,† and omission of factors of modulus unity

$$\begin{aligned}I(T, \infty) &= \lim_{t\to\infty} \left| \int_a^{v_s t} \sin(k_T r) e^{ik_s r - \frac{1}{2}\lambda_s t} \mathrm{d}r \right|^2 \frac{2\lambda_s}{\pi\hbar v_s}\left(\frac{m}{2T}\right)^{1/2}\\ &= \left| \frac{1}{k_T - \operatorname{Re} k_s - i \operatorname{Im} k_s} + \frac{1}{k_T + \operatorname{Re} k_s + i \operatorname{Im} k_s} \right|^2\\ &\quad \times \frac{\lambda_s}{2\pi\hbar v_s}\left(\frac{m}{2T}\right)^{1/2}\\ &\approx \frac{(T/E_s)^{1/2}(\Gamma_s/2\pi)}{(T-E_s)^2 + \frac{1}{4}\Gamma_s^2}, \qquad \Gamma_s \ll E_s\end{aligned} \tag{28.10}$$

An example is shown in figure 28.2. The full width of the spectrum at half height (say ΔE) is close to Γ_s, while the mean lifetime of the state (say Δt) is $\lambda_s^{-1} = \hbar/\Gamma_s$, and so $\Delta E\,\Delta t \approx \hbar$ as the uncertainty principle requires.

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† *Vide* problem 8.3.

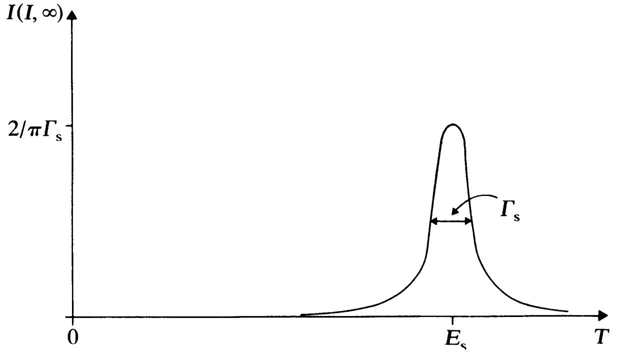

Figure 28.2 The kinetic energy spectrum of a particle emitted from a radioactive state. The shorter the lifetime of the state, the broader is the spectrum.

Problems

8.1 Sketch the diagram analogous to figure 25.1, with $t = 3\pi/\lambda$ instead of π/λ. Interpret the result in the light of the uncertainty principle.

8.2 The maximum kinetic energy of the electrons emitted in the beta decay of ^{3}H to ^{3}He is 18.6 keV. Estimate the half-life of the decay.

8.3 Verify that the radial wavefunction

$$\begin{aligned} S_T(r) &= (2/R)^{1/2} \sin(k_T r) \\ &= -i(2R)^{-1/2}(e^{ik_T r} - e^{-ik_T r}) \end{aligned}$$

is an eigenfunction of the kinetic energy T belonging to the eigenvalue $\hbar^2 k_T^2/2m$.

Note that S_T satisfies the boundary condition $S_T = 0$ both at zero radius and at the arbitrarily large radius R, in order to ensure that T is Hermitian. Hence show that the density of states is

$$\frac{dN}{dT} = \left(\frac{dN}{dk_T}\right)\left(\frac{dk_T}{dT}\right) = \frac{R}{\pi h}\left(\frac{m}{2T}\right)^{1/2}$$

9

Scattering

§29 Introduction: analysis into partial waves of definite angular momentum

In atomic, nuclear, and particle physics scattering experiments are a standard means of investigating interactions and structures. Typically a collimated beam of particles, as monoenergetic as possible, is directed on to a target consisting of many atoms. The interactions of the incident particles with the target cause some of them to be scattered out of the beam, and the numbers appearing at various angles may be measured. The energy of the beam and the nature of the particles in it determines whether each atom as a whole acts as a scattering centre, or whether the nucleus or the particles within it are the effective centres. Sometimes indeed, when the wavelength of the incident particles matches the interatomic spacing, the collaborative effects of many atoms must be considered. For simplicity, the wavelengths will here be assumed to be small compared to interatomic distances so that superposition effects do not come in. In such conditions it is enough to analyse the scattering of the incident particles by a single atom or nucleus, the separate effects of the various scattering centres being simply additive.

Some features of the interaction between the incident particle and the scatterer show up quite directly. The *range* of the interaction may sometimes be indicated by sharp minima in the intensity of the scattered particles as a function of scattering angle (section 32); at other times an *upper limit to the range* is a fair deduction from a featureless angular distribution (section 29). If the system 'particle plus scatterer' has bound states, then the scattering at low beam energies is predictable (sections 30, 31). If the same system has radioactive states with positive energies, then the intensity of scattering shows dramatic maxima or *resonances* at just those energies (section 31).

On the other hand, the establishment of the fine details of the interaction between the scatterer and the incident particle requires very patient investigation. In general, data are collected for many angles and energies and compared with the predictions of various assumed interactions. It often takes much effort to reach a satisfactory description, ideally in terms of a potential energy between the particle and the scatterer that is specified for all separations between them. Often the interaction is too complicated to describe in these terms although, even then, an effective potential which gives the right answer in some conditions may be a useful abstraction.

The discussion is often much simplified by dealing one at a time with the various angular momenta of the incident particles around the scatterer. To see how to do this, the beam alone will be considered first.

The incident beam: no scatterer present A collimated beam of free particles, moving co-axially along the z-axis with momentum $\hbar k$ and energy $E=\hbar k^2/2m$, can be represented by the wave function $\psi=e^{ikz}$ in the bombarded region (x, y small). The time-dependent factor $e^{-iEt/\hbar}$ is left implicit, and normalisation will not be necessary. The collimating diaphragms are supposed to be wide enough to avoid trouble from diffraction effects.

The particles obviously have zero z-component of angular momentum l_z, but a measurement of the square of the total angular momentum may yield any of the eigenvalues of $\mathbf{l}^2$. When ψ is expanded in eigenfunctions of $\mathbf{l}^2$ and l_z, belonging to the eigenvalue 0 for the latter,

$$\psi=e^{ikz}=\sum_{l=0}^{\infty}\frac{1}{r}S_l'(r)Y_{l0}(\theta,\phi) \tag{29.1}$$

where r, θ, ϕ are related to x, y, z in the usual way. Since $\hat{\mathbf{l}}^2$ and $\hat{H}$ commute, $(\hat{\mathbf{l}}^2)^n\psi$ also obeys the Schrödinger equation for arbitrary integral n, and so each term in the expansion must separately be a solution. Thus S_l' obeys the usual radial equation (equation (11.3)) with $V(r) = 0$,

$$\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2}\right\} S_l'(r) = ES_l'(r) = \left(\frac{\hbar^2 k^2}{2m}\right) S_l'(r) \qquad (29.2)$$

The boundary condition $S_l'(0) = 0$ applies as before.

The $l = 0$ or s wave is particularly easy to discuss. The radial function S_0' may be obtained from equation (29.1) by using the orthonormality of the Y_{l0}, expressed in equation (10.36). After writing $z = r\cos\theta$ and remembering that $Y_{00} = (1/4\pi)^{1/2}$,

$$\left.\begin{aligned} \frac{1}{r}S_0' &= \int_0^{\pi}\int_0^{2\pi}\left(\frac{1}{4\pi}\right)^{1/2} e^{ikr\cos\theta}\sin\theta\, d\theta\, d\phi \\ &= \frac{i\pi^{1/2}}{kr}\left[e^{ikr\cos\theta}\right]_{\theta=0}^{\pi} = \frac{(4\pi)^{1/2}}{kr}\sin(kr) \\ S_0' &= \frac{(4\pi)^{1/2}}{k}\sin(kr) \end{aligned}\right\} \qquad (29.3)$$

As expected this is a solution of the $l = 0$ version of equation (29.2),

$$-\left(\frac{\hbar^2}{2m}\right)\frac{d^2 S_0'}{dr^2} = \left(\frac{\hbar^2 k^2}{2m}\right) S_0' \qquad (29.4)$$

with $S_0'(0) = 0$. The full s wave including Y_{00} is

$$\frac{1}{r}S_0' Y_{00} = \frac{1}{kr}\sin(kr) = \frac{i}{2kr}(e^{-ikr} - e^{ikr}) \qquad (29.5)$$

Scatterer present The scatterer, centred on the origin of the coordinate system, will be supposed to exert only central forces that can be described by a potential $V(r)$. Very often $V(r)$ is zero for r greater than some range a, and this too will be assumed. At some distance from the origin the stationary state wave function will now take the modified form,

$$\psi \approx e^{ikz} + \frac{f(\theta)}{r}e^{ikr}, \qquad r \gg a \qquad (29.6)$$

Again ψ is independent of ϕ because the angular momentum is conserved for central forces, so that l_z still has the eigenvalue 0.

Upstream in the incident beam (small x, y, and large negative z) the first term in equation (29.6) is dominant. Calculation of the probability current density $\mathbf{j}$ yields a flux of v incident particles per unit time and area, where v is the velocity $\hbar k/m$.

Well outside the incident beam (large x, y) the first term in equation (29.6) is cut off by the collimators, and the second becomes dominant. Another calculation of $\mathbf{j}$ shows a flow of $v\,|f(\theta)|^2\,\mathrm{d}\Omega$ scattered particles per unit time passing through an area subtending the elementary solid angle $\mathrm{d}\Omega$ at the origin. The fact that this flow is directed radially outwards is the physical justification for the general form of equation (29.6), and in particular for the positive sign in the exponent of the second term. This term represents an outgoing travelling wave.

The *differential scattering cross-section* $\mathrm{d}\sigma/\mathrm{d}\Omega$ is defined as the scattered flow per unit time and solid angle, divided by the incident flux,

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}=|f(\theta)|^2 \tag{29.7}$$

From equation (29.6) it is obvious that $f(\theta)$ has the dimensions of a length, as the nomenclature implies. In a purely statistical sense $\mathrm{d}\sigma$ may be thought of as the effective target area that the incident particles have to hit in order to score a scatter into the solid angle $\mathrm{d}\Omega$.

The *total scattering cross-section* σ_{t} is the integral of $\mathrm{d}\sigma/\mathrm{d}\Omega$ over all directions,

$$\sigma_{\mathrm{t}}=\int_0^{\pi}\int_0^{2\pi}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi=2\pi\int_0^{\pi}|f(\theta)|^2\sin\theta\,\mathrm{d}\theta \tag{29.8}$$

Obviously $f(\theta)$ contains all information about the scattering. It can be calculated by solving the Schrödinger equation, including $V(r)$, over the whole region of the beam, including the origin. The boundary conditions state that ψ must remain finite at $r=0$, and conform to equation (29.6) at large radii.

Again ψ may be expanded in angular momentum eigenfunctions, belonging to the eigenvalue 0 for l_z,

$$\psi=\sum_{l=0}^{\infty}\frac{1}{r}S_l(r)Y_{l0}(\theta,\phi) \tag{29.9}$$

Since the forces are central $\hat{\mathbf{l}}^2$ and $\hat{H}$ continue to commute, and each term in the expansion must obey the Schrödinger equation separately. Thus,

$$\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{l(l+1)\hbar^2}{2mr^2}+V(r)\right\}S_l(r)=\left(\frac{\hbar^2k^2}{2m}\right)S_l(r) \qquad (29.10)$$

with $S_l(0)=0$. At large radii equation (29.6) will be achieved if the S_l can be related to the S_l':

$$\sum_{l=0}^{\infty}\frac{1}{r}\{S_l(r)-S_l'(r)\}Y_{l0}(\theta,\phi)\xrightarrow[kr\to\infty]{}\frac{f(\theta)}{r}e^{ikr} \qquad (29.11)$$

This is possible because the second and third terms on the left-hand side of equation (29.10), and the second on the left-hand side of equation (29.2), are negligible at large radii. The two equations become identical and simple, and the solutions are harmonic functions of kr, like S_0' in equation (29.3). The harmonic functions can be expressed as superpositions of in-going and out-going travelling waves, like S_0' in equation (29.5). If S_l is normalised so that its in-going part is matched to that of S_l', then equation (29.11) will be satisfied.

For the s wave in particular, the $l=0$ version of equation (29.10) is

$$\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+V(r)\right\}S_0(r)=\left(\frac{\hbar k^2}{2m}\right)S_0(r) \qquad (29.12)$$

with $S_0(0)=0$. Outside a, the second term on the left-hand side is zero and S_0 must take the form $A\sin(kr+\delta_0)$, where A is a normalising constant and δ_0 is a real angle called the *s wave phase shift*. The value of A can be fixed to match the in-going part (cf. equation (29.5)) of S_0':

$$\left.\begin{aligned} S_0&=\frac{(4\pi)^{1/2}}{k}e^{i\delta_0}\sin(kr+\delta_0)\\ \frac{1}{r}S_0Y_{00}&=\frac{i}{2kr}(e^{-ikr}-e^{2i\delta_0}e^{ikr})\\ \frac{1}{r}(S_0-S_0')Y_{00}&=\frac{i}{2kr}(1-e^{2i\delta_0})e^{ikr}, \qquad r\geqslant a \end{aligned}\right\} \qquad (29.13)$$

For the s waves there is no need to go to the limit of large radii because the centrifugal potential is absent.

Neglect of scattering in states of high l The second term on the left-hand side of equation (29.10), the centrifugal potential, will equal the energy of the particles at a radius b_l given by the relation $l(l+1)/b_l^2 = k^2$. When l is large enough b_l will be considerably larger than a, the range of the scattering potential. Between a and b_l the dominant terms in equation (29.10) state that

$$\frac{\mathrm{d}^2 S_l}{\mathrm{d}r^2} \approx \frac{l(l+1)}{r^2} S_l, \qquad b_l \geqslant r \geqslant a,\, b_l \gg a \tag{29.14}$$

which has the general solution $S_l \approx B_l r^{l+1} + C_l r^{-l}$. The ratio of B_l to C_l is of course fixed by the solution of equation (29.10) inside a, and the boundary condition at the origin, but it would be an extremely exceptional situation if B_l were precisely zero. In general the radially increasing term $B_l r^{l+1}$ will become completely dominant at b_l, whatever the behaviour of $V(r)$ inside a may be. The effective boundary condition offered to S_l at larger radii is thus independent of $V(r)$, and the same as if there were no scatterer present at all. Thus $S_l \approx S_l'$ and the scattering will be negligible for angular momentum l such that

$$\left.\begin{array}{c} b_l \gg a \\ l(l+1) \gg (ka)^2 = (a/\lambdabar)^2 \end{array}\right\} \tag{29.15}$$

The classical analogue of this conclusion is easy to see. A particle with linear momentum $\hbar k$ and angular momentum $\hbar ka$ would pass the origin at the distance a, just touching the scattering potential. If the angular momentum were greater than $\hbar ka$, no interaction at all would take place.

It follows that the scattered wave described by equation (29.11) involves the sum of a limited number of spherical harmonics of low l. If $\mathrm{d}\sigma/\mathrm{d}\Omega$ is expressed in powers of $\cos\theta$, no power greater than (say) $6a/\lambdabar$ will be significant.

In particular, at energies low enough for the inequality $2 \gg (a/\lambdabar)^2$ to hold good, only $l=0$ or s wave scattering will occur. The angular distribution of the scattered particles is then isotropic.

s wave approximation There is now only one term in equation (29.11), and this is written down in equations (29.13). Thus,

$$\left.\begin{aligned} f(\theta) &= \frac{i}{2k}(1-\mathrm{e}^{2i\delta_0}) = \left(\frac{1}{k}\right)\mathrm{e}^{i\delta_0}\sin\delta_0 \equiv a_0 \\ \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= \left(\frac{1}{k}\right)^2 \sin^2\delta_0 = \lambdabar^2\sin^2\delta_0 = |a_0|^2 \\ \sigma_t &= 4\pi\lambdabar^2\sin^2\delta_0 = 4\pi\,|a_0|^2 \end{aligned}\right\} \tag{29.16}$$

where a_0, the s wave scattering amplitude, has been defined.

Obviously the total s wave scattering cross-section cannot be greater than $4\pi\bar{\lambda}^2$.

Calculation of δ_0, a_0 The scattering cross-section has now been firmly tied to the phase shift δ_0, which can only be obtained by solving equation (29.12) inside a, with $S_0(0)=0$. The solution must be joined smoothly (S_0, $\mathrm{d}S_0/\mathrm{d}r$ continuous) at a to the S_0 written down in equations (29.13). The two joining equations give the normalisation of the internal solution (not interesting here) and the phase shift δ_0 in the external solution (all important). In fact the fixing of δ_0 may be isolated by requiring $(1/S_0)\,\mathrm{d}S_0/\mathrm{d}r$ to be continuous at a:

$$\left(\frac{1}{S_0}\frac{\mathrm{d}S_0}{\mathrm{d}r}\right)_a = k\cot(ka+\delta_0)$$

This equation suggests that a_0 should be expressed in terms of cot $(ka+\delta_0)$, rather than $\sin\delta_0$. This can be done by means of the trigonometric identity

$$\begin{aligned} a_0 &= \left(\frac{1}{k}\right)\mathrm{e}^{i\delta_0}\sin\delta_0 \\ &\equiv \mathrm{e}^{-2ika}\left\{\frac{1}{k\cot(ka+\delta_0)-ik} - \frac{\mathrm{e}^{ika}\sin(ka)}{k}\right\} \end{aligned} \tag{29.17}$$

which may be checked by using the standard trigonometrical expressions for $\sin(ka+\delta_0)$, $\cos(ka+\delta_0)$ in terms of $\sin(ka)$, $\cos(ka)$, $\sin\delta_0$, and $\cos\delta_0$.

Now ka is small for the s wave approximation to be valid at all, and so equation (29.17) can be written in the approximate form

$$\begin{aligned} a_0 &\approx \frac{1}{k\cot(ka+\delta_0)-ik} - a \\ &= \frac{1}{\left(\dfrac{1}{S_0}\dfrac{\mathrm{d}S_0}{\mathrm{d}r}\right)_a - ik} - a \end{aligned} \tag{29.18}$$

The first term here is called the resonance term, and it is only significant if a near-cancellation of its denominator occurs; such an event is apt to be connected with the existence of bound or radioactive states at about the same energy of the system 'particle + scatterer' (sections 30, 31), The second term is called the potential scattering term, and it is constant and determined by the range of the interaction between particle and scatterer.

As k, $E \rightarrow 0$, the right-hand side of equation (29.12) will lose its influence inside a. Correspondingly $S_0(r<a)$, $\{(1/S_0)\,dS_0/dr\}_a$, a_0, and hence σ_t must become independent of energy. If in particular $a_0 \rightarrow a_0'$, then $-a_0'$ is called the *scattering length.*

Formulae for general l For reference some of the formulae for general l may be set down. A full analysis of equation (29.1) shows that

$$e^{ikz} = \sum_{l=0}^{\infty} (2l+1)i^l \left(\frac{\pi}{2kr}\right)^{1/2} J_{l+\frac{1}{2}}(kr) P_l(\cos\theta) \qquad (29.19)$$

where $J_{l+\frac{1}{2}}(kr)$ is the Bessel function of order $l+\frac{1}{2}$. At large radii,

$$\left(\frac{\pi}{2kr}\right)^{1/2} J_{l+\frac{1}{2}}(kr) \xrightarrow[kr\rightarrow\infty]{} \left(\frac{1}{kr}\right) \sin(kr - \tfrac{1}{2}l\pi) \qquad (29.20)$$

The right-hand side here shows the harmonic dependence on kr that is expected from the earlier discussion. When the scatterer is present the sine function is replaced by $e^{i\delta_l} \sin(kr - \frac{1}{2}l\pi + \delta_l)$, the in-going travelling wave being preserved. The real angle δ_l is of course called the l wave phase shift. Then,

$$\left.\begin{aligned} f(\theta) &= \left(\frac{1}{k}\right) \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin\delta_l P_l(\cos\theta) \\ \frac{d\sigma}{d\Omega} &= \lambda\!\!\!^{-2} \left| \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin\delta_l P_l(\cos\theta) \right|^2 \\ \sigma_t &= 4\pi \lambda\!\!\!^{-2} \sum_{l=0}^{\infty} (2l+1) \sin^2\delta_l \end{aligned}\right\} \qquad (29.21)$$

It is interesting to notice that, since $P_l(1) = 1$ and $\operatorname{Im} e^{i\delta_l} = \sin\delta_l$,

$$\sigma_t = \frac{4\pi}{k} \operatorname{Im} f(0) \qquad (29.22)$$

This result is known as the *optical theorem.*

As k, $E \rightarrow 0$ it can be shown that δ_l must become proportional to k^{2l+1}, and correspondingly the contribution of the lth partial wave to σ_t will be proportional to k^{4l} or E^{2l}.

§30 Neutron–proton scattering at low energies

This problem involves two particles, but the methods of section 14 can be used to reduce it to single-particle form. The analysis of section 29 holds good, provided that $\mu = m_n m_p/(m_n + m_p)$ is written in place of m, and also that $\mathbf{r}$ (components x, y, z) is interpreted as the position of the neutron relative to the proton (equation (14.3)). The interaction between neutron and proton will be the same as that used to calculate the binding energy of the deuteron (figure 14.1)

The zero range approximation will be adopted; this says that a is extremely small and V_0 extremely large, while the product $a^2 V_0$ just satisfies the inequality of equation (14.13).

Since a is extremely small the s wave approximation will be valid, the scattering will be isotropic, and the potential scattering term in equation (29.18) will be negligible.

In the interaction region ($r \leqslant a$) the solution to equation (29.12) with the right boundary condition at the origin is $S_0 \propto \sin[\{2\mu(E+V_0)/\hbar^2\}^{1/2} r]$, where $E = \hbar^2 k^2/2\mu$. Since V_0 is extremely large, and a is extremely small,

$$\left(\frac{1}{S_0}\frac{\mathrm{d}S_0}{\mathrm{d}r}\right)_a \approx \left(\frac{2\mu V_0}{\hbar^2}\right)^{1/2} \cot\left\{\left(\frac{2\mu V_0}{\hbar^2}\right)^{1/2} a\right\} \tag{30.1}$$

Under the same conditions, equation (14.11) says that

$$\left(\frac{2\mu V_0}{\hbar^2}\right)^{1/2} \cot\left\{\left(\frac{2\mu V_0}{\hbar^2}\right)^{1/2} a\right\} \approx -\left(\frac{-2\mu E_{10}}{\hbar^2}\right)^{1/2} \tag{30.2}$$

where E_{10} is the (negative) energy of the bound state of the deuteron. The resonant scattering term is therefore

$$\left.\begin{aligned} a_0 &\approx \frac{1}{-\{(-2\mu E_{10})/\hbar^2\}^{1/2} - ik} \\ \sigma_t &\approx \frac{2\pi\hbar^2}{\mu}\left(\frac{1}{|E_{10}| + E}\right) \end{aligned}\right\} \tag{30.3}$$

It is clear that the binding energy of the deuteron and the neutron–proton scattering cross-section are very closely related; the smaller the binding energy, the larger the cross-section. In practice the situation is complicated by the fact that both particles have spin $\frac{1}{2}$, and the interaction between them is spin dependent. The total spin of the deuteron is actually 1, and so equation (30.3) only apply to the scattering which takes place when the spins of the neutron and proton are set up to form total spin 1. More usually the spins are at random, and a slightly more complicated formula than equations (30.3) must then be used. The details will not be pursued here.

Transformation to laboratory system In actual practice experimental measurements are made in the laboratory frame of reference; in a typical collision the proton is initially at rest and the neutron is projected towards it with velocity v (figure 30.1(a)). In this picture the centre of mass, located at the point $\mathbf{R}$ (equation (14.3)), is moving to the right at the velocity $\{m_n/(m_n+m_p)\}v$.

Since the motion of $\mathbf{R}$ is undisturbed by the collision, it is convenient to follow developments in a frame of reference in which $\mathbf{R}$ is constant. This is the centre of mass frame of reference. A picture of the initial situation in this frame (figure 30.1(b)) may be obtained by giving both particles an additional velocity $\{m_n/(m_n+m_p)\}v$ to the left. The velocity of the neutron is reduced to the value $\{m_p/(m_n+m_p)\}v$ to the right by this transformation.

In the centre of mass frame after the collision (figure 30.1(c)) the conservation of energy and linear momentum require the velocities of the particles to be unchanged in magnitude, although directed differently. The final direction of $\mathbf{r}$ determines the angle of scattering θ.

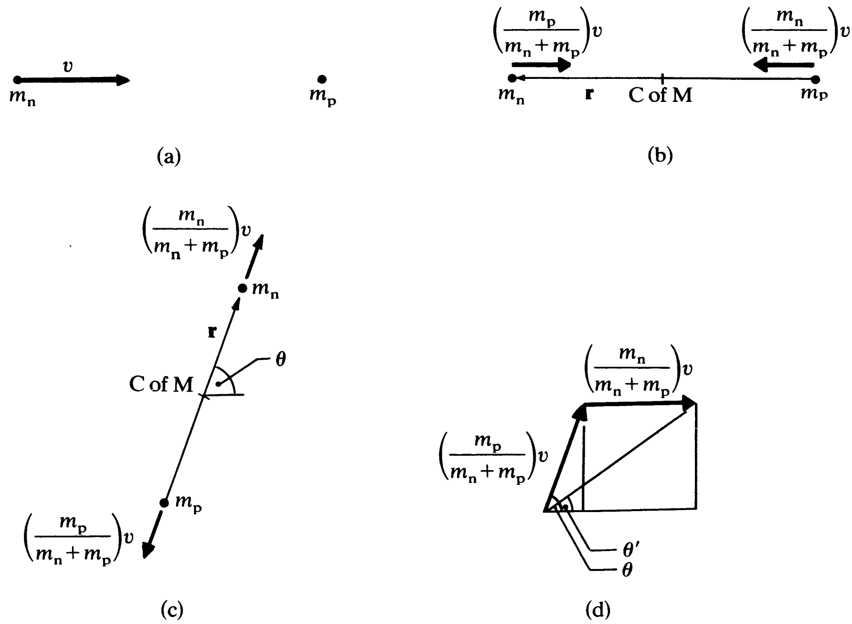

Figure 30.1 Neutron–proton scattering in the laboratory and centre of mass frames.

The final velocity of the neutron in the laboratory frame (figure 30.1(d)) may be obtained by adding back the velocity $\{m_n/(m_n + m_p)\}v$ to the right. The laboratory angles of scattering θ', ϕ' are evidently given by

$$\left.\begin{aligned} \tan\theta' &= \frac{m_p \sin\theta}{m_p\cos\theta + m_n} = \frac{\sin\theta}{\cos\theta+\gamma} \\ \phi' &= \phi \end{aligned}\right\} \qquad (30.4)$$

where $\gamma = m_n/m_p$.

The fictitious particles with reduced mass μ and position $\mathbf{r}$ have the initial velocity $\dot{r} = v$; their momentum is $\mu v = \hbar k$, their energy is $E = \frac{1}{2}\mu v^2 = \hbar^2 k^2/2\mu$, their position probability density in the incident beam is normalised to unity, and their incident flux is v.

The neutrons in laboratory space with mass m_n and position $\mathbf{r}_n$ have the initial velocity $\dot{r}_n = v$; their momentum is $m_n v = \hbar k' = (m_n/\mu)k$, their energy is $E' = \frac{1}{2}m_n v^2 = (m_n/\mu)E$, their position probability density is unity, and their incident flux is therefore v also.

To each scattering of a fictitious particle at the angles θ, ϕ there corresponds a scattering of a neutron at the angles θ', ϕ'. When an elementary solid angle $d\Omega$ is traced out by $\mathbf{r}$, a corresponding elementary solid angle $d\Omega'$ is traced out by $\mathbf{r}_n$. According to equation (30.4),

$$\frac{d\Omega}{d\Omega'} = \left|\frac{\sin\theta\, d\theta\, d\phi}{\sin\theta'\, d\theta'\, d\phi'}\right| = \frac{(1+2\gamma\cos\theta+\gamma^2)^{3/2}}{|1+\gamma\cos\theta|} \qquad (30.5)$$

The solid angle transformation gives rise to a difference between the outgoing flows per unit solid angle of scattered neutrons at θ', ϕ' and fictitious particles at θ, ϕ. Since the incident fluxes are the same, the differential cross-section for neutron scattering in the laboratory frame is given by

$$\frac{d\sigma'}{d\Omega'} = \left(\frac{d\sigma}{d\Omega}\right)\frac{(1+2\gamma\cos\theta+\gamma^2)^{3/2}}{|1+\gamma\cos\theta|} \qquad (30.6)$$

The scattering of the neutron in the laboratory frame is not isotropic, obviously.

Since the total numbers of scattering events are identical, the total cross-section for neutron scattering in the laboratory frame is

$$\sigma_t' = \sigma_t = \frac{8\pi\hbar^2}{m_n}\left(\frac{1}{2\,|E_{10}| + E'}\right) \qquad (30.7)$$

Here equation (30.3) has been rewritten in terms of E', with the approximation $\gamma \approx 1$.

§31 Resonant scattering

As in section 28, it will be supposed that the particle is subject to a central force of definite range a. The energy of the particle is supposed to be low enough to ensure that only s wave scattering occurs.

The TDSE again takes the form†

$$i\hbar \frac{\partial \phi(r, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \phi(r, t)}{\partial r^2}, \qquad r > a \tag{31.1}$$

whose solution is

$$\phi(r, t) = (A_- e^{-ikr} + A_+ e^{ikr}) e^{-iEt/\hbar} \tag{31.2}$$

where $k = |(2mE/\hbar^2)^{1/2}|$.

The ratio of A_+ to A_- for a given k is fixed by the boundary condition at $r = 0$. It would always be -1 if the potential $V(r)$ inside a were not present.

All this looks like the familiar progression from the TDSE through the TISE to an energy eigenvalue and a stationary state wave function, but this is not so. Unusually, E will be allowed to be complex as well as real, so bringing in states in which the wave function grows or decays exponentially. The wave function of equation (28.4) and figure 28.1 is an example of a decaying state. The normalised wave function in a growing or decaying state is confined to a changing region of space bounded by a wave front. The writ of equation (31.2) does not run everywhere, and therefore there is no question of saying that the energy has a complex eigenvalue: rather it has a spectrum of real values when a proper analysis is made (equation (28.10)).

***The* S*-matrix*‡** The scattering of particles is often described by means of the S-matrix. When elastic s wave scattering alone is involved the S-matrix becomes a 1×1 matrix, or just an ordinary

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† *Vide* problem 4.4.

‡ A capital S sans serif will be used to denote the S-matrix. There should be no confusion with $S(r) = rR(r)$, a persistent usage since section 11. The former appears only in section 31, the latter not at all in section 31.

function, actually of k. It may be defined by reference to equation (31.2),

$$\mathsf{S}(k) \equiv -A_+/A_- \qquad (31.3)$$

When k is varied it is to be expected that $\mathsf{S}(k)$ varies analytically, but there are situations in which it becomes infinite.

For example the bound state of section 28 may be considered. If k is given the particular value $i\kappa_0$ in equation (31.2), and if the result is then compared with equation (28.3), it is clear that A_+ can be identified with A_0, and A_- with zero. Thus $\mathsf{S}(i\kappa_0)$ has an infinite value or, in other words, the S-matrix has a pole when k takes the value $i\kappa_0$.

The radioactive state represented by equation (28.4) may be considered similarly, and the conclusion is that the S-matrix has a pole when k takes the value k_s.

An alternative way of writing the wave function in equation (31.2) is

$$\phi(r, t) = (A_+ e^{-i(-k)r} + A_- e^{i(-k)r}) e^{-iEt/\hbar}, \qquad r > a \qquad (31.4)$$

from which is it apparent that

$$\left.\begin{aligned} \mathsf{S}(-k) = -A_-/A_+ = 1/\mathsf{S}(k) \\ \mathsf{S}(k)\mathsf{S}(-k) = 1 \end{aligned}\right\} \qquad (31.5)$$

Thus it follows† from the identification above of poles that if there is a bound state S has a zero at $k = -i\kappa_0$, and if there is a radioactive state S has a zero at $k = -k_s$.

If $\psi(r, t)$ is a solution of the TDSE then it can be shown that $\psi^*(r, -t)$ is another.‡ Thus equation (31.2) implies the existence of a solution which can be written§

$$\phi(r, t) = (A_-^* e^{-i(-k^*)r} + A_+^* e^{i(-k^*)r}) e^{-iE^*t/\hbar}, \qquad r > a \qquad (31.6)$$

so that

$$\mathsf{S}(-k^*) = -A_+^*/A_-^* = \mathsf{S}(k)^* \qquad (31.7)$$

Thus poles and zeros not on the imaginary k-axis occur in pairs; the radioactive state also gives rise to a pole at $-k_s^*$ and a zero at k_s^*, in addition to the pole and zero already noted.

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† Attention may be drawn to figures 31.1 and 31.2 at this point.

‡ *Vide* problem 9.2.

§ Since, for example, $(ikr)^* = -ik^*r = i(-k^*)r$.

Connection between S(k) ***and the scattering amplitude*** When k is real and positive S(k) can be connected with the scattering amplitude. According to the second of equations (29.13),

$$\mathsf{S}(k) = e^{2i\delta_0}, \qquad k \text{ real}, + \tag{31.8}$$

and then the first of equations (29.17) gives

$$a_0 = \frac{i}{2k}(1 - \mathsf{S}), \qquad k \text{ real}, + \tag{31.9}$$

Two more conditions on S The description of pure scattering must show as many particles going out as coming in, and so $|A_-|^2 = |A_+|^2$ for real and positive k in equation (31.2). Furthermore, as was noted below equation (29.18), the scattering amplitude tends to a constant a_0' at low energies. Therefore

$$\left.\begin{aligned} &|\mathsf{S}| = 1 \\ &\lim_{k\to 0} \frac{1}{k} \arg \mathsf{S} = 2a_0' \qquad k \text{ real}, + \end{aligned}\right\} \tag{31.10}$$

Scattering when there is a bound state An expression for S can be constructed which reproduces the features of figure 31.1 and obeys equations (31.5), (31.7), and (31.10). It is

$$\mathsf{S} = -\frac{k + i\kappa_0}{k - i\kappa_0} \tag{31.11}$$

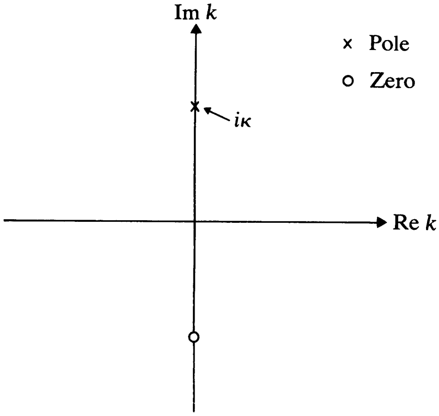

Figure 31.1 The pole and zero of the S-matrix when there is a bound state of the 'particle plus scatterer'.

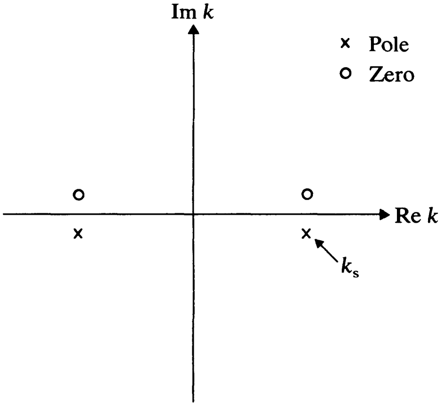

Figure 31.2 Poles and zeros of the **S**-matrix when there is a radioactive state of the 'particle plus scatterer'.

This gives

$$\sigma = 4\pi\,|a_0|^2 = \frac{\pi}{k^2}\left|1 + \frac{k + i\kappa_0}{k - i\kappa_0}\right|^2$$
$$= \frac{\pi}{k^2}\left(\frac{k^2}{k^2+\kappa_0^2}\right) = \frac{2\pi\hbar^2}{m}\left(\frac{1}{E+|E_0|}\right), \qquad k \text{ real, } + \tag{31.12}$$

in complete agreement with equation (30.3) when minor differences of notation are taken into account.

Scattering when there is a radioactive state The features of figure 31.2 and equations (31.5), (31.7), and (31.10) indicate that

$$\mathbf{S} = \frac{(k - k_s^*)(k + k_s)}{(k - k_s)(k + k_s^*)} \tag{31.13}$$

For real and positive k,† while $|\mathbf{S}| = 1$ as already mentioned, arg **S** starts at 0 when $k = 0$, increases through π when k is near Re k_s, and approaches 2π as $k \to \infty$.

A resonance is said to occur when arg $\mathbf{S} = \pi$ precisely, and $\mathbf{S} = -1$. The cross-section at that particular value of k, say k_{res}, is

$$\sigma_t(k_{\text{res}}) = \frac{4\pi}{k_{\text{res}}^2} = 4\pi\lambda_{\text{res}}^2 \tag{31.14}$$

which is the maximum value possible.

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† The moduli and arguments of the four factors should be considered in order to follow these remarks. For example $|k - k_s^*| = |k - k_s|$ and $|k + k_s| = |k + k_s^*|$ for real k.

An expression for the cross-section may be obtained as follows:

$$\begin{aligned}\sigma_t = 4\pi\,|a_0|^2 &= \frac{\pi}{k^2}\left|1 - \frac{(k-k_s^*)(k+k_s)}{(k-k_s)(k+k_s^*)}\right|^2\\ &= \frac{\pi}{k^2}\frac{|2k(k_s^*-k_s)|^2}{|k-k_s|^2\,|k+k_s|^2}\\ &= \frac{\pi\Gamma_s^2/(\operatorname{Re} k_s)^2}{(E-E_s)^2+\Gamma_s^2/4}, \qquad k \text{ real}, + \qquad (31.15)\end{aligned}$$

where equation (28.8) has been used.

In figure 31.3 a plot of σ_t against E, for the particular case $\Gamma_s = E_s/10$, shows the resonance at energies near to E_s. The full width of the peak at half height is always equal to Γ_s, and thus Γ_s is usually called the width of the resonance or, equally, of the radioactive state.

A comparison between figures 28.2 and 31.3 shows remarkable similarities. *It may be concluded that the energies of radioactive states can be determined in two ways, either by measuring the most probable energies of emitted particles or by finding the resonance energies for scattering of the same particles by the residual systems.*

The lifetimes of the radioactive states can be found in three ways. The decays with time of the fluxes of emitted particles may be followed, or the widths of the emitted particles measured, or the widths

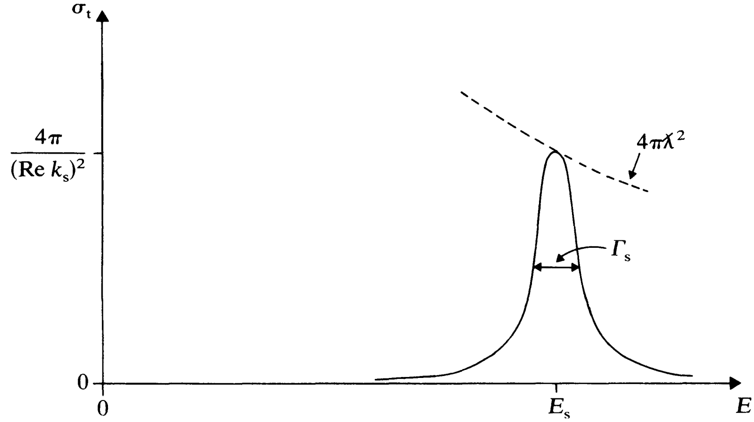

Figure 31.3 Resonance scattering, when there is a radioactive state of 'particle plus scatterer'. The shorter the lifetime of the state, the broader is the resonance.

of resonance scattering measured. The first method is most convenient for long lifetimes, and the other two for short lifetimes.

Applications in atomic, nuclear, and particle physics are widespread.

§32 The Born approximation

A completely different approach to the scattering problem may be developed by regarding the interaction $\hat{H}'$ of the particles with the scattering centre as weak compared to their kinetic energy $\hat{H}$. The momentum eigenfunctions $L^{-3/2}e^{i\mathbf{k}\cdot\mathbf{r}}$ discussed in section 9 may be used as unperturbed eigenfunctions of $\hat{H}$. These eigenfunctions obey periodic boundary conditions at the faces of a cube of side L. The conditions are enforced by the restrictions of equation (9.7) on the components of k, and these in turn determine the density of states (equation (9.10)).

The perturbation $\hat{H}'$ causes transitions of particles from a state with the initial momentum $\hbar\mathbf{k}_i$ to other states with the final momentum $\hbar\mathbf{k}_f$. Conservation of energy in the usual way ensures that $|\mathbf{k}_f^2| \approx |\mathbf{k}_i^2| \equiv k^2$. The density of final states is found by putting $p = \hbar k$ in equation (9.10), with an additional factor of $d\Omega/4\pi$ when attention is focused on those final states where $\mathbf{k}_f$ points into the solid angle $d\Omega$.

The initial state has a flux vL^{-3} particles per unit area and time, so that the rate at which the specified transitions occur must be $vL^{-3}\,d\sigma$. This may be equated with the transition rate given† by the Golden Rule,

$$vL^{-3}\,d\sigma = \frac{2\pi}{\hbar}\left| -\langle L^{-3/2}e^{i\mathbf{k}_f\cdot\mathbf{r}} \,|\hat{H}'|\, L^{-3/2}e^{i\mathbf{k}_i\cdot\mathbf{r}} \right|^2 \frac{L^3 mk}{8\pi^3\hbar^2}\,d\Omega \qquad (32.1)$$

The factors of L cancel as usual, and L may therefore be allowed to become infinite. If $\hat{H}$ is represented by the scattering potential $V(r)$,

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{4\pi^2\hbar^4}\left| -\int V(r)e^{i(\mathbf{k}_i-\mathbf{k}_f)\cdot\mathbf{r}}\,d\tau \right|^2 \qquad (32.2)$$

---

† A negative sign is included to indicate the phase of $f(\theta)$ (see equations (29.6) and (29.7)) and this is faithfully preserved through equation (32.4). The phase is not readily deduced here, but there are other ways of obtaining the Born approximation which do supply this information. The amplitude does not obey the optical theorem (equation (29.22)).

At this point is is convenient to define the vector $\mathbf{K} \equiv \mathbf{k}_i - \mathbf{k}_f$; an elementary construction shows that the magnitude K is equal to $2k \sin(\theta/2)$. Evidently $\hbar\mathbf{K}$ is the *momentum transfer* from the scattered particle to the scattering centre in the collision concerned.

Now the direction of $\mathbf{K}$ can be taken as the polar axis of a set of spherical coordinates r, θ', ϕ'. Integration of the right-hand side of equation (32.2) is trivial over ϕ', and simple over θ',

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{4\pi^2\hbar^4}\left| -\int_0^\infty \int_0^\pi \int_0^{2\pi} V(r) e^{iKr\cos\theta'} r^2 \sin\theta' \, d\phi' \, d\theta' \, dr \right|^2$$

$$= \frac{m^2}{\hbar^4}\left| -\int_0^\infty V(r)\left[\left(\frac{i}{Kr}\right) e^{iKr\cos\theta'}\right]_{\theta'=0}^{\pi} r^2 \, dr \right|^2 \tag{32.3}$$

which leads to the standard Born approximation formula,

$$\frac{d\sigma}{d\Omega} = \frac{4m^2}{\hbar^4}\left| -\int_0^\infty V(r)\left\{\frac{\sin Kr}{Kr}\right\} r^2 \, dr \right|^2 \tag{32.4}$$

It is worth noting that $d\sigma/d\Omega$ depends on the kinematics of the collision only through the variable $K = 2k \sin(\theta/2)$. This means, for example, that quadrupling the energy of the particle and halving the value of $\sin(\theta/2)$ would leave $d\sigma/d\Omega$ unchanged.

Validity The accuracy of the Born formula is not easily discussed in a general way, but some criteria can be obtained when the potential $V(r)$ may be given some sort of average value V' up to its range a.

The scattered wave will not be a serious perturbation of the incident wave if the phase shifts are small, and in particular the s wave phase shift δ_0 is small. According to equation (29.16),

$$k\left(1 - \frac{V'}{E}\right)^{1/2} \cot\left\{ka\left(1 - \frac{V'}{E}\right)^{1/2}\right\} = k \cot(ka + \delta_0) \tag{32.5}$$

At *high energies* ($E \gg V'$) it is clear that δ_0 will be small if the cotangent on the left-hand side has an argument differing by a small angle from ka. Since $\{1 - (V'/E)\}^{1/2} \approx 1 - \frac{1}{2}(V'/E)$, the condition is

$$\left|\frac{kaV'}{2E}\right| = \left|\frac{aV'}{\hbar v}\right| \ll 1 \tag{32.6}$$

where v is the classical velocity of the incident particles. It is satisfactory to note that in this situation the Born approximation is complementary to the s wave approximation, which applies at low energies.

It is possible for the Born approximation to be valid at *low energies*, when $ka \ll 1$, V' is negative, and $E \ll |V'|$. Then equation (32.5) says

$$\tan\delta_0 \approx (-E/V')^{1/2}\tan\{(-2mV')^{1/2}a/\hbar\} \tag{32.7}$$

Thus δ_0 will be small provided that $(-2mV')^{1/2}a/\hbar$ does not approach $\pi/2$ very closely.

If $V(r) = -V_0$ (V_0 positive) when $r \leqslant a$, and $V(r) = 0$ otherwise, the condition says that

$$a^2V_0 < \pi^2h^2/8m \tag{32.8}$$

Comparison with equation (14.13) shows that the Born approximation is valid at low energies provided that the scattered particle cannot have, or nearly have, a bound state in the interaction potential. The Born approximation could not therefore be used to obtain equation (30.3), for example.

Neutron scattering by nuclei at intermediate energies A suitable use for the Born approximation is to calculate the scattering of, say, 400 MeV neutrons by nuclei. The interaction can be represented by a constant potential $-V_0$ extending up to the nuclear radius a. Typical values are $V_0 \sim 40$ MeV and $a \sim 2.5 \times 10^{-15}$ m for carbon, so that $V_0/E \approx 0.1$ and $aV_0/\hbar v \approx \frac{1}{2}$; thus equation (32.6) is rather sparsely satisfied. The calculation will therefore not be extremely accurate.

The appropriate substitutions in equation (32.4) yield the result

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= \frac{4m^2V_0^2}{\hbar^4}\left\{K^{-3}\int_0^{Ka} Ka\sin(Ka)\,d(Ka)\right\}^2 \\ &= \frac{4m^2V_0^2a^6}{9\hbar^4}[-3(Ka)^{-3}\{\sin(Ka) - Ka\cos(Ka)\}]^2 \\ &= \frac{4m^2V_0^2a^6}{9\hbar^4}\{-3(Ka)^{-1}j_1(Ka)\}^2 \end{aligned} \tag{32.9}$$

where the spherical Bessel function of order 1 has been identified.

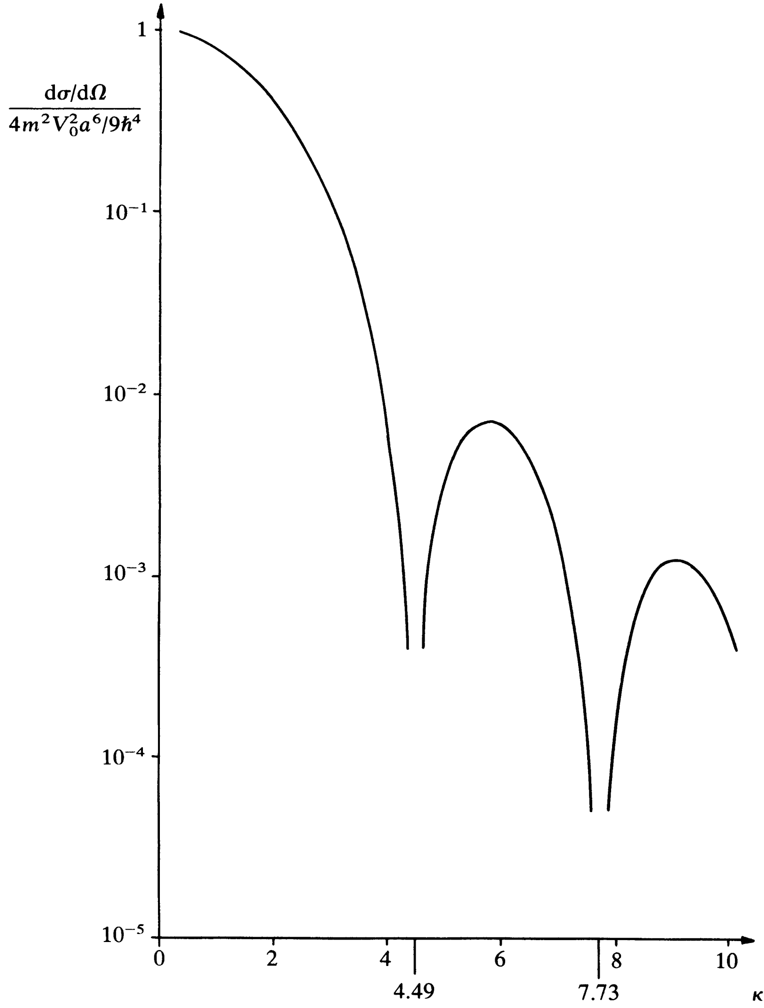

Figure 32.1 Neutron scattering by nuclei of intermediate energies, calculated by means of the Born approximation. Diffraction minima are seen.

The dependence of $d\sigma/d\Omega$ on Ka is shown in figure 32.1. The diffraction minima are quite characteristic, and experimental studies of them are often used to establish the radii of nuclei and particles. When the calculations are made exactly the minima actually occur at slightly smaller values of Ka.

Problems

9.1 At first sight equation (29.6) conveys the impression that the number of particles is not conserved. The beam appears to continue undisturbed downstream from the target, while scattered particles travel away from the target in other directions.

Prove in fact that particles disappear in the forward direction because of a destructive superposition of the two terms in equation (29.6). The overall number of particles is conserved as a consequence of the optical theorem, equation (29.22).

9.2 Show that if $\psi(r, t)$ is a solution of the TDSE then so is $\psi^*(r, -t)$. [*Hint:* Write down the TDSE,

$$i\hbar\frac{\partial\psi(r, t)}{\partial t}=\left\{-\frac{\hbar^2}{2m}\nabla^2+V(r)\right\}\psi(r, t)$$

and then write down its complex conjugate, which is not a TDSE because of a minus sign on the left-hand side. This can be corrected by substitution of $\psi^*(r, -t)$ for $\psi^*(r, t)$.]

9.3 Show that $\psi^*(r, -t)$ represents a physical state which is the same as that represented by $\psi(r, t)$, except that it develops in the reverse order of time.

9.4 Show that S cannot have a pole where the real and imaginary parts of k are both positive. Since poles are paired this means that S cannot have poles in the upper half plane, apart from those on the imaginary axis due to bound states. [*Hint:* Attempt to construct an analogue to figure 28.1 with proper attention to normalisation.]

9.5 Show that the maximum value of σ_t, given by equation (31.15), occurs when $E=E_s$. Show further that resonance occurs at the slightly higher $E=|(E_s^2+\Gamma_s/4)^{1/2}|$. [*Hint:* In the second part find where the maximum of $\sigma_t/4\pi\lambda^2$ occurs.]

9.6 Show that the potential scattering is described by $\mathsf{S}=\mathrm{e}^{-2ika}$, and that equations (31.5), (31.7), and (31.10) are duly satisfied. When the potential scattering is not neglected, and

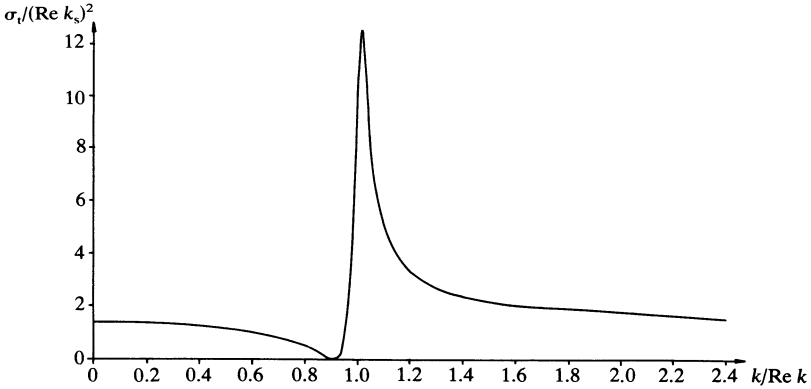

Figure 9P.1 Resonance and potential scattering, showing constructive superposition above resonance and destructive superposition below it.

when there is a radioactive state,

$$\mathsf{S}=e^{-2ika}\frac{(k-k_s^*)(k+k_s)}{(k-k_s)(k+k_s^*)}$$

Sketch Argand diagrams for S and $1-\mathsf{S}$, and hence show that the resonance and potential scattering superpose constructively above resonance and destructively below it. [*Comment:* Figure 9P.1 shows a computed example.]

10

Radiation

§33 Quantisation of the radiation field

A single oscillator: classical version In a vacuum, with no charges or currents present, the electromagnetic field is called a pure radiation field. It can be described by a vector potential $\mathbf{A}(\mathbf{r}, t)$, the scalar potential $\phi(\mathbf{r}, t)$ being zero. The vector potential obeys the equations

$$\left.\begin{aligned} \nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} = 0 \\ \operatorname{div}\mathbf{A} = 0 \end{aligned}\right\} \tag{33.1}$$

and the electric and magnetic fields are

$$\mathscr{E} = -\dot{\mathbf{A}}, \qquad \mathscr{B} = \mathbf{curl}\ \mathbf{A} \tag{33.2}$$

A Fourier analysis of $\mathbf{A}$ can be made in terms of travelling waves obeying periodic boundary conditions in a cube of space with side L. For the moment attention will be restricted to a situation in which just one of these waves is present:

$$\mathbf{A} = \left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)^{1/2} \boldsymbol{\varepsilon}_{\mathbf{k}j}\{a_{\mathbf{k}j}(t)\mathrm{e}^{i\mathbf{k}.\mathbf{r}} + a_{\mathbf{k}j}^*(t)\mathrm{e}^{-i\mathbf{k}.\mathbf{r}}\} \tag{33.3}$$

Here $\mathbf{k}$ is the propagation vector of the wave, and $(\hbar/2\varepsilon_0 kcL^3)^{1/2}a_{\mathbf{k}j}(t)$ is a complex amplitude:† $\mathbf{A}$ is kept real by the addition of the second term involving the complex conjugate amplitude. The wave is transversely polarised in the direction of the unit vector $\boldsymbol{\varepsilon}_{\mathbf{k}j}$, which must be orthogonal to $\mathbf{k}$ in view of the second of equations (33.1). Two orthogonal choices for $\boldsymbol{\varepsilon}_{\mathbf{k}j}$ are required, and these may be decided and labelled by $j=1,2$ in any convenient manner. In order to satisfy the periodic boundary conditions,

$$k_x = 2\pi s_x/L, \qquad k_y = 2\pi s_y/L, \qquad k_z = 2\pi s_z/L \tag{33.4}$$

with s_x, s_y, s_z integral.

When the expression for $\mathbf{A}$ is substituted into the first of equations (33.1) the time dependence of a is exposed:‡

$$\ddot{a} + \omega^2 a = 0, \qquad \omega \equiv ck \tag{33.5}$$

The appropriate solution is

$$a \propto e^{-i\omega t} \tag{33.6}$$

since $\mathbf{A}$ will then be a harmonic function of $\mathbf{k}\,.\,\mathbf{r} - \omega t$: this makes the wave travel in the direction of $\mathbf{k}$ with velocity c.

The real observables Q and P can be defined by

$$\left.\begin{aligned} Q &\equiv \left(\frac{\hbar}{2\omega}\right)^{1/2}(a + a^*) \\ P &\equiv \dot{Q} = -i\left(\frac{\hbar\omega}{2}\right)^{1/2}(a - a^*) \end{aligned}\right\} \tag{33.7}$$

since $\dot{a} = -i\omega a$ and $\dot{a}^* = i\omega a^*$. After inversion,

$$\left.\begin{aligned} a &= \frac{1}{\sqrt{2}}\left\{i\left(\frac{1}{\hbar\omega}\right)^{1/2} P + \left(\frac{\omega}{\hbar}\right)^{1/2} Q\right\} \\ a^* &= \frac{1}{\sqrt{2}}\left\{-i\left(\frac{1}{\hbar\omega}\right)^{1/2} P + \left(\frac{\omega}{\hbar}\right)^{1/2} Q\right\} \end{aligned}\right\} \tag{33.8}$$

---

† It might seem strange that the arbitrary normalising factor contains $\hbar^{1/2}$, while the discussion remains strictly classical. Later on this is matched by a factor $\hbar^{1/2}$ in the definitions of Q and P (equations (33.7)), so that in fact no trace of $\hbar$ remains when those observables are used. The factors are so chosen in order to prepare for a close analogy between a and a^*, on the one hand, and the quantum destruction and creation operators $\hat{a}$ and $\hat{a}^*$ of section 8, on the other.

‡ The suffices $\mathbf{k}j$ will be left implicit while one particular wave is being discussed.

The electric and magnetic fields given by equations (33.2) can now be calculated, first in terms of a and a^* and then in terms of Q and P:

$$\begin{aligned}\mathcal{E} &= i\left(\frac{\hbar\omega}{2\varepsilon_0 L^3}\right)^{1/2} \boldsymbol{\varepsilon}(a e^{i\mathbf{k}.\mathbf{r}} - a^* e^{-i\mathbf{k}.\mathbf{r}}) \\ &= -\left(\frac{1}{\varepsilon_0 L^3}\right)^{1/2} \boldsymbol{\varepsilon}(P \cos \mathbf{k}\,.\,\mathbf{r} + \omega Q \sin \mathbf{k}\,.\,\mathbf{r}) \qquad (33.9)\end{aligned}$$

and

$$\begin{aligned}\mathcal{B} &= i\left(\frac{\mu_0 \hbar\omega}{2L^3}\right)^{1/2} \left(\frac{\mathbf{k}\times\boldsymbol{\varepsilon}}{\mathbf{k}}\right)(a e^{i\mathbf{k}.\mathbf{r}} - a^* e^{-i\mathbf{k}.\mathbf{r}}) \\ &= -\left(\frac{\mu_0}{L^3}\right)^{1/2} \left(\frac{\mathbf{k}\times\boldsymbol{\varepsilon}}{k}\right)(P \cos \mathbf{k}\,.\,\mathbf{r} + \omega Q \sin \mathbf{k}\,.\,\mathbf{r}) \qquad (33.10)\end{aligned}$$

Thus the total energy H of the electromagnetic field can be found:

$$H = \tfrac{1}{2}(\varepsilon_0 \overline{\mathcal{E}^2} + \mu_0^{-1} \overline{\mathcal{B}^2})L^3 = \tfrac{1}{2}(P^2 + \omega^2 Q^2) \qquad (33.11)$$

The total energy has deliberately been called H in order to suggest that it may be regarded as a Hamiltonian depending on a 'coordinate' Q and a conjugate 'momentum' P. The corresponding Hamiltonian equations (equations (19.7)) are indeed correct,

$$\frac{\partial H}{\partial Q} = \omega^2 Q = -\dot{P}, \qquad \frac{\partial H}{\partial P} = P = \dot{Q} \qquad (33.12)$$

which agree with equation (33.7).

An analogy between the electromagnetic wave and the linear harmonic oscillator of section 8 is now quite obvious. The Hamiltonian of equation (33.11) is the same as that of a linear oscillator of unit mass and frequency ω. The electromagnetic wave may be quantised simply by pursuing this analogy to its logical conclusions.

A single oscillator: quantised version The quantum mechanical description of the wave involves the operators $\hat{Q}$, $\hat{P}$, $\hat{H}$, $\hat{a}$, and $\hat{a}^*$ whose mathematical properties reproduce those of the operators $\hat{x}$, $\hat{p}$, $\hat{H}$, $\hat{a}$, and $\hat{a}^*$ of section 8. Thus $[\hat{Q}, \hat{P}] = i\hbar$, and the operator algebra based on this leads to the inevitable consequence that the wave has quantised energy eigenvalues,

$$E_n = (n + \tfrac{1}{2})\hbar\omega \qquad (33.13)$$

In the nth state the wave is said to involve n photons, each of energy $\hbar\omega$. Since any transition involves the creation or destruction of integral numbers of photons, it is reasonable to think of them as particles.

The operators just mentioned must operate on wave functions $u_n(Q)e^{-iE_nt/\hbar}$, which corresponds to the oscillator wave functions $u_n(x)e^{-iE_nt/\hbar}$. Obviously $u_n^*(Q)u_n(Q)\,dQ$ is the probability of field measurements on the wave leading to the conclusion that Q lies in the range dQ. In fact such measurements are seldom discussed, and the number of photons in the wave is nearly always the point of interest. In order to recognise this it is reasonable to develop a notation which promotes n to a more prominent position and omits to mention the wave function explicitly. This will be done from equation (33.15) onwards.

The photon destruction and creation operators (equations (8.2), (33.8), and (8.18)) have the following non-vanishing matrix elements:

$$\left.\begin{aligned} \langle u_s \mid \hat{a}u_n\rangle &= n^{1/2}\delta_{s,n-1} \\ \langle u_s \mid \hat{a}^*u_n\rangle &= (n+1)^{1/2}\delta_{s,n+1} \end{aligned}\right\} \tag{33.14}$$

The vector potential can be expressed in terms of $\hat{a}$ and $\hat{a}^*$, and so it takes on the properties of an operator $\hat{\mathbf{A}}$. Its non-vanishing matrix elements are obtained from equations (33.3) and (33.14):

$$\left.\begin{aligned} \langle n-1|\,\hat{\mathbf{A}}\,|n\rangle &= n^{1/2}\left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)^{1/2}\boldsymbol{\varepsilon}e^{i\mathbf{k}.\mathbf{r}} \\ \langle n+1|\,\hat{\mathbf{A}}\,|n\rangle &= (n+1)^{1/2}\left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)^{1/2}\boldsymbol{\varepsilon}e^{-i\mathbf{k}.\mathbf{r}} \end{aligned}\right\} \tag{33.15}$$

Very often the radiation process under discussion is the emission of a photon where none was present before. The relevant matrix element is then

$$\langle 1|\,\hat{\mathbf{A}}\,|0\rangle = \left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)\boldsymbol{\varepsilon}e^{-i\mathbf{k}.\mathbf{r}} \tag{33.16}$$

The exponential factors here and in the previous equation are signals that the photon has momentum $\hbar\mathbf{k}$.† Thus the relation between the energy and momentum of the photon is

$$E = \hbar\omega = \hbar ck = cp \tag{33.17}$$

which is the appropriate relativistic formula for a particle of zero rest mass.

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† *Vide* problem 10.1.

A full set of oscillators When the most general variation of the classical **A** is considered, equation (33.3) must be replaced by

$$\mathbf{A} = \sum_{\mathbf{k}j} \left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)^{1/2} \boldsymbol{\varepsilon}_{\mathbf{k}j}\{a_{\mathbf{k}j}(t)\mathrm{e}^{i\mathbf{k.r}} + a^*_{\mathbf{k}j}(t)\mathrm{e}^{-i\mathbf{k.r}}\} \tag{33.18}$$

Because of equation (33.4) the waves can be counted in the manner of section 9. Thus the number with k vectors whose magnitudes lie in the interval $\mathrm{d}k$ is given by

$$\frac{\mathrm{d}N}{\mathrm{d}k} = \frac{L^3k^2}{2\pi^2} \tag{33.19}$$

After quantisation this leads, through equation (33.17), to an energy density ρ_E for oscillators with a single photon of specified polarisation:

$$\rho_\mathrm{E} = \frac{L^3k^2}{2\pi^2\hbar c} \tag{33.20}$$

If the polarisation is not specified, then the right-hand sides of the last two equations should be doubled, to allow for summation over $j = 1, 2$. If $\mathbf{k}$ is restricted to point into the solid angle $\mathrm{d}\Omega$ then a factor of $\mathrm{d}\Omega/4\pi$ should be included.

The next step is to calculate the Hamiltonian in terms of the full set of $\omega_{\mathbf{k}j}$, $Q_{\mathbf{k}j}$, and $P_{\mathbf{k}j}$. The result replacing equation (33.11) is

$$H = \tfrac{1}{2}(\varepsilon_0\overline{\mathscr{E}^2} + \mu_0^{-1}\overline{\mathscr{B}^2})L^3 = \sum_{\mathbf{k}j}\tfrac{1}{2}(P_{\mathbf{k}j} + \omega^2_{\mathbf{k}j}Q^2_{\mathbf{k}j}) \tag{33.21}$$

which shows that each oscillator makes its own separate contribution. In general the cross-terms between pairs of waves vanish on spatial averaging, since they come from two different values of $\mathbf{k}$ and therefore vary spatially through an integral number of cycles. Even if the pair has a common $\mathbf{k}$ the cross-terms for the two orthogonal polarisations vanish. Finally, when the cross-terms between a pair of waves of indices $\mathbf{k}$, j and $-\mathbf{k}$, j are considered, the contributions to $\frac{1}{2}\varepsilon_0\overline{\mathscr{E}^2}$ and $\frac{1}{2}\mu_0^{-1}\overline{\mathscr{B}^2}$ are equal in magnitude but opposite in sign. This is seen most easily from the fact that $\mathbf{k}$, $\mathscr{E}$, and $\mathscr{B}$ always form an orthogonal right-handed set of vectors.

The Hamiltonian equations now state that each $P_{\mathbf{k}j}$ is conjugate to $Q_{\mathbf{k}j}$, and uncoupled to the coordinates of any other oscillator. After quantisation $[\hat{Q}_{\mathbf{k}j}, \hat{P}_{\mathbf{k}'j'}] = i\hbar$ if $\mathbf{k} = \mathbf{k}'$, $j = j'$, and zero otherwise. Thus the operator algebra for finding the energy eigenvalues can be carried through for each oscillator separately, the inevitable result being

$$E=\sum_{\mathbf{k}j}(n_{\mathbf{k}j}+\tfrac{1}{2})\hbar\omega_{\mathbf{k}j} \tag{33.22}$$

Since there is an infinite number of oscillators there is an infinite zero-point energy, $\sum_{\mathbf{k}j}\frac{1}{2}\hbar\omega_{\mathbf{k}j}$. However, this energy does not change in transitions, and is therefore unobserved and capable of being ignored.

The matrix element given by equation (33.16) must now be modified slightly in order to specify which oscillator gains a photon:

$$\langle 1_{\mathbf{k}j}|\,\hat{\mathbf{A}}\,|0\rangle=\left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)^{1/2}\boldsymbol{\varepsilon}_{\mathbf{k}j}\mathrm{e}^{-i\mathbf{k}.\mathbf{r}} \tag{33.23}$$

General remarks on radiative transitions When a charged particle and a radiation field are considered together, the total Hamiltonian H_t is the sum of the Hamiltonian H_p for the particle alone, H_r for the radiation field alone, and H_i for the interaction between the two:

$$\hat{H}_\mathrm{t}=\hat{H}_\mathrm{p}+\hat{H}_\mathrm{r}+\hat{H}_\mathrm{i} \tag{33.24}$$

It will soon appear that $\hat{H}_\mathrm{i}$ can be treated as a perturbation, so that the stationary states of the system can be well represented by products of the eigenfunctions of $\hat{H}_\mathrm{p}$ and $\hat{H}_\mathrm{r}$. Transitions will be induced by $\hat{H}_\mathrm{i}$ in which the states both of the particle and of the radiation field change simultaneously, the latter by the creation or destruction of one photon since $\hat{H}_\mathrm{i}$ is actually proportional to $\hat{\mathbf{A}}$. In section 26 it was seen that energy is approximately conserved in such transitions. When, for example, the particle starts in an eigenstate of $\hat{H}_\mathrm{p}$ belonging to the energy eigenvalue E_i and ends in one belonging to E_f, and simultaneously a photon of energy $h\omega_{\mathbf{k}j}$ appears in the radiation field where none was present before,

$$h\omega_{\mathbf{k}j}\approx E_\mathrm{i}-E_\mathrm{f} \tag{33.25}$$

This formula, and its twin for processes in which a photon disappears, played a vital part in Einstein's discussion of the photoelectric effect (1905) and Bohr's of the spectrum of the hydrogen atom (1913).

The interaction term most prominently involved in radiative transitions is the second one in equation (20.13),†

$$H_{\mathrm{i}} = -\frac{e}{m}\hat{\mathbf{A}}\,.\,\hat{\mathbf{p}} \tag{33.26}$$

for a particle of charge e.

According to section 26 the Golden Rule (equation (26.13)) will give an accurate radiative decay rate if the width Γ is small compared to the photon energies involved. An order of magnitude assessment gives

$$\frac{\Gamma}{\hbar\omega} = \frac{\lambda}{\omega} \approx \left(\frac{2\pi}{\hbar}\right)\left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)\left(\frac{ep}{m}\right)^2\left(\frac{L^3k^2}{2\pi^2\hbar c}\right)\left(\frac{1}{\omega}\right)$$

$$\approx 2(e^2/4\pi\varepsilon_0\hbar c)(v^2/c^2) \leqslant \tfrac{2}{137} \tag{33.27}$$

where the fine structure constant $\alpha = e^2/4\pi\varepsilon_0\hbar c \approx 1/137$ has been identified. Clearly the validity of the Golden Rule is assured.

In this estimate it was assumed that the factor $\mathrm{e}^{-i\mathbf{k}.\mathbf{r}}$ in the matrix element is well approximated by unity. This is called the electric dipole approximation. Because of a selection rule the matrix element of $\mathbf{p}$ may vanish, and then a higher term in the series expansion of $\mathrm{e}^{-i\mathbf{k}.\mathbf{r}}$ must be considered. If the sth term is the lowest effective one then the radiative width will be reduced by a factor of about $(kR)^{2s} = (R/\lambda\!\!\!^{-})^{2s}$, where R is a typical dimension in the particle system. This is apt to be a severe and experimentally obvious inhibition.

If n photons are already present in an oscillator involved in an emission process, then the corresponding transition rate is increased by the extra factor‡ $n+1$ in the square of the matrix element (equation (33.15)). This is the fundamental basis of stimulated emission devices such as the laser, in which a large collection of excited atoms is induced to co-operate in emitting energy into particular radiation oscillators.

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† It is worth noticing that the third term, involving $\hat{\mathbf{A}}^2$, is responsible for low energy or Thomson scattering of radiation by a charged particle.

‡ This same factor appeared in the early and simple calculations by Einstein of his 'A and B coefficients' for induced radiative transition probabilities (1917).

§34 The 2p–1s radiative transition in the hydrogen atom

The value of k can be calculated immediately from equation (12.9), corrected by use of the reduced mass μ, and equation (33.25). It is

$$k=\frac{\omega}{c}=\frac{\mu e^4}{32\pi^2\varepsilon_0^2\hbar^3 c}\left(1-\tfrac{1}{4}\right) \tag{34.1}$$

When this value of k is multiplied by the Bohr radius a small number is obtained,

$$ka_0=\frac{3}{8}\frac{e^2}{4\pi\varepsilon_0\hbar c}=\frac{3}{8}\cdot\frac{1}{137} \tag{34.2}$$

where the fine structure constant α has been identified again. The smallness of ka_0 permits the use of the electric dipole approximation, since no problem arises with the matrix element for the transition under discussion.

According to the Golden Rule the differential transition rate $\mathrm{d}\lambda_m$ from the 2p state with magnetic quantum number m, when the photon propagation vector k is required to point into the solid angle $\mathrm{d}\Omega$, is given by

$$\left.\begin{aligned}\mathrm{d}\lambda_m &= \sum_{j=1,2}\frac{2\pi}{\hbar}\left|\left(\frac{e}{\mu}\right)\left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)^{1/2}\boldsymbol{\varepsilon}_{\mathbf{k}j}\right.\\ &\qquad\times\langle u_{100}|\,\hat{\mathbf{p}}\,|u_{21m}\rangle|^2\frac{L^3k^2}{2\pi^2\hbar c}\frac{\mathrm{d}\Omega}{4\pi}\\ \frac{\mathrm{d}\lambda_m}{\mathrm{d}\Omega}&=\frac{1}{2\pi}\left(\frac{e^2k}{4\pi\varepsilon_0\mu^2\hbar c^2}\right)\sum_{j=1,2}|\boldsymbol{\varepsilon}_{\mathbf{k}j}\cdot\langle u_{100}|\,\hat{\mathbf{p}}\,|u_{21m}\rangle|^2\end{aligned}\right\} \tag{34.3}$$

As usual L has cancelled out and may conveniently be allowed to become infinite. According to equations (5.7) and (5.9),

$$\hat{\mathbf{p}}=-\frac{i\mu}{\hbar}[\hat{\mathbf{r}}_{\mathrm{e}},\hat{H}] \tag{34.4}$$

where, for clarity, the position of the electron is labelled with a suffix to distinguish it from the coordinate involved in the classical vector potential $\mathbf{A}$. Then,

$$\begin{aligned}\langle u_{100}|\,\hat{\mathbf{p}}\,|u_{21m}\rangle &= -\frac{i\mu}{\hbar}\{\langle u_{100}|\,\hat{\mathbf{r}}_{\mathrm{e}}\,|\hat{H}u_{21m}\rangle-\langle\hat{H}u_{100}|\,\hat{\mathbf{r}}_{\mathrm{e}}\,|u_{21m}\rangle\}\\ &= -\frac{i\mu}{\hbar}(E_2-E_1)\langle u_{100}|\,\mathbf{r}_{\mathrm{e}}\,|u_{21m}\rangle\\ &= -i\mu kc\langle u_{100}|\,\mathbf{r}_{\mathrm{e}}\,|u_{21m}\rangle\end{aligned} \tag{34.5}$$

Thus,

$$\frac{\mathrm{d}\lambda_m}{\mathrm{d}\Omega}=\frac{1}{2\pi}\left(\frac{e^2k^3}{4\pi\varepsilon_0\hbar}\right)\sum_{j=1,2}|\boldsymbol{\varepsilon}_{\mathbf{k}j}\cdot\langle u_{100}|\,\mathbf{r}_e\,|u_{21m}\rangle|^2 \tag{34.6}$$

This new form of the matrix element explains why the electric dipole approximation is so called. The next step is to express the vector matrix element in terms of ordinary vectors with real components by the definitions

$$\langle u_{100}|\,\mathbf{r}_e\,|u_{21m}\rangle\equiv\mathbf{M}_{mr}+i\mathbf{M}_{mi} \tag{34.7}$$

The angle between $\boldsymbol{\varepsilon}_{\mathbf{k}j}$ and, say, $\mathbf{M}_{mr}$ will be called Θ_{jmr}, and so on. Then,

$$\frac{\mathrm{d}\lambda_m}{\mathrm{d}\Omega}=\frac{1}{2\pi}\left(\frac{e^2k^3}{4\pi\varepsilon_0\hbar}\right)\{(\cos^2\Theta_{1mr}+\cos^2\Theta_{2mr})\mathbf{M}^2_{mr}$$
$$+(\cos^2\Theta_{1mi}+\cos^2\Theta_{2mi})\mathbf{M}^2_{mi}\} \tag{34.8}$$

Since $\mathbf{k}$, $\boldsymbol{\varepsilon}_{\mathbf{k}1}$, and $\boldsymbol{\varepsilon}_{\mathbf{k}2}$ are an orthogonal set of vectors, the sum of the direction cosines of any vector with respect to them is unity. Thus,

$$\frac{\mathrm{d}\lambda_m}{\mathrm{d}\Omega}=\frac{1}{2\pi}\left(\frac{e^2k^3}{4\pi\varepsilon_0\hbar}\right)\{(1-\cos^2\Theta_{kmr})\mathbf{M}^2_{mr}+(1-\cos^2\Theta_{kmi})\mathbf{M}^2_{mi}\} \tag{34.9}$$

where, for example, Θ_{kmr} is the angle between $\mathbf{k}$ and $\mathbf{M}_{mr}$.

The total transition rate is obtained by integrating over all directions of $\mathbf{k}$, when the average values of both $\cos^2\Theta_{kmr}$ and $\cos^2\Theta_{kmi}$ will be $\frac{1}{3}$. So,

$$\lambda_m=\frac{4}{3}\left(\frac{e^2k^3}{4\pi\varepsilon_0\hbar}\right)(\mathbf{M}^2_{mr}+\mathbf{M}^2_{mi})$$
$$=\frac{4}{3}\left(\frac{e^2k^3}{4\pi\varepsilon_0\hbar}\right)\langle u_{21m}|\,\mathbf{r}_e\,|u_{100}\rangle\cdot\langle u_{100}|\,\mathbf{r}_e\,|u_{21m}\rangle \tag{34.10}$$

The components of $\mathbf{M}_{mr}$ and $\mathbf{M}_{mi}$ are easily calculated (Table 34.1) by writing

$$x_e=\left(\frac{2\pi}{3}\right)^{1/2}r_e(-Y^*_{11}+Y^*_{1,-1})$$
$$y_e=\left(\frac{2\pi}{3}\right)^{1/2}ir_e(-Y^*_{11}-Y^*_{1,-1}) \tag{34.11}$$
$$z_e=\left(\frac{4\pi}{3}\right)^{1/2}r_eY^*_{10}$$

Table 34.1 Components of the electric dipole matrix elements, with the radial factor removed, for the 2p–1s transition in hydrogen

Vector	Components divided by I_r		
	x	y	z
$\mathbf{M}_{1r}$	$-\sqrt{\frac{1}{6}}$	0	0
$\mathbf{M}_{1i}$	0	$-\sqrt{\frac{1}{6}}$	0
$\mathbf{M}_{0r}$	0	0	$\sqrt{\frac{1}{3}}$
$\mathbf{M}_{0i}$	0	0	0
$\mathbf{M}_{-1r}$	$\sqrt{\frac{1}{6}}$	0	0
$\mathbf{M}_{-1i}$	0	$-\sqrt{\frac{1}{6}}$	0

and remembering the $l'=l=1$ version of equation (10.36),

$$\int_0^{\pi}\int_0^{2\pi} Y^*_{1m'}Y_{1m}\sin\theta_e\,\mathrm{d}\phi_e\,\mathrm{d}\theta_e=\delta_{m'm} \tag{34.12}$$

Each component contains the radial integral

$$I_r=\int_0^{\infty} r_e^3R^*_{10}R_{21}\,\mathrm{d}r_e=2^{15/2}3^{-9/2}a_0 \tag{34.13}$$

which is not included in the data given in table 34.1 *Equation (34.10) shows that the transition rate is independent of the value of the initial state magnetic quantum number m; this is a particular example of a general result. Very often the initial state is a mixture, with equal probability but random relative phase, of all the states of different m; the transition rate remains the same.* It is given here by

$$\begin{aligned}\lambda&=2^{11}3^{-8}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)\left(\frac{\mu e^4}{32\pi^2\varepsilon_0^2\hbar^3c}\right)a_0^2\\&=2(2/3)^8\alpha^3\hbar^{-1}\,|E_1|\end{aligned} \tag{34.14}$$

This has a value of $6.26\times10^8\,\mathrm{s}^{-1}$, the corresponding lifetime being $1.60\times10^{-9}\,\mathrm{s}$.

Selection rules It is obvious from equation (34.6) that the matrix element would have vanished if the initial and final states had not been of opposite parity. It is also clear from equations (34.11) and (10.36) that only a p state has a non-vanishing matrix element for an electric dipole transition to an s state. *These are particular examples of the electric dipole selection rules; the transitions allowed are those with* $\Delta l = 1$, $\Delta m = 0, \pm 1$, *and change of parity.*

Angular distributions According to equation (34.9) and table 34.1, the angular distribution of the photons from the $m = 0$ initial state is proportional to $\sin^2 \Theta_{kz}$, where Θ_{kz} is the angle between $\mathbf{k}$ and the z-axis.

Similarly the angular distribution of photons from the $m = \pm 1$ initial state is proportional to $\frac{1}{2}(1 - \cos^2 \Theta_{kx}) + \frac{1}{2}(1 - \cos^2 \Theta_{ky}) = 1 - \frac{1}{2} \sin^2 \Theta_{kz}$.

If all three initial states are populated, with equal probability but random relative phase, the angular distribution is isotropic. This corresponds to a general rule that such a prescription makes all orientations of the initial system equally likely.

Polarisation: transition from the* 2p** $(m = 0)$ ***state The rules governing linear polarisation of the photons can be found from equations (34.6), (34.7), and table 34.1. When the initial state has $m = 0$, the matrix element of $\mathbf{r}_e$ reduces simply to the z-component of $\mathbf{M}_{0r}$.

It then follows that all photons emitted in the equatorial (or x, y) plane are plane polarised parallel to the z-axis.

No photons are emitted along the z-axis, so that no question of their polarisation arises. In figures 34.1 and 34.2 this pattern of polarisation will be referred to as type $p1$.

Polarisation: transition from the* 2p** $(m = 1)$ ***state Here $\mathbf{M}_{1r}$ has only an x-component, and $\mathbf{M}_{1i}$ only a y-component.

It follows that photons emitted in the equatorial plane are plane polarised in the equatorial plane, obviously at right angles to $\mathbf{k}$.

Photons emitted along the z-axis have both an x-component and a y-component of polarisation. It is then interesting to consider whether these are phased in such a way that the polarisation is circular. In fact the analysis that follows will show that photons emitted in the positive z-direction are right circularly polarised, and those emitted in the negative z-direction are left circularly

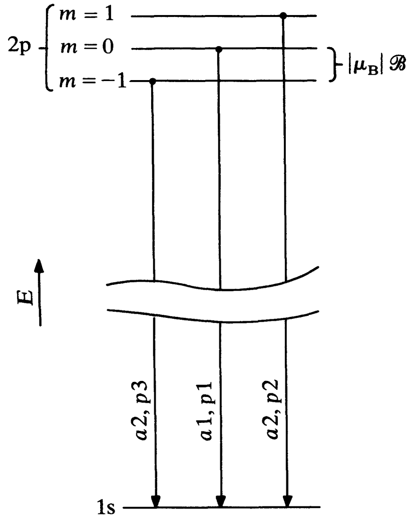

Figure 34.1 The 2p–1s transitions including Zeeman effect, with spin neglected. The angular distributions of the photons are proportional to $\sin^2 \Theta_{kz}(a1)$, or to $1-\frac{1}{2}\sin^2 \Theta_{kz}(a2)$. The polarisation patterns $p1$, $p2$ and $p3$ are described in the text.

polarised. This pattern of polarisation will be referred to as type $p2$ in figures 34.1 and 34.2.

In order to discuss circular polarisation of photons, the first point to recognise is that the classical vector potential **A** could have been expanded in terms of right and left circularly polarised travelling waves, in place of the plane polarised waves that were actually used.

When only a single right circularly polarised wave is present, equation (33.3) would be replaced by

$$\mathbf{A} = \left(\frac{\hbar}{2\varepsilon_0 k c L^3}\right)^{1/2} \left\{ \frac{1}{\sqrt{2}} (\boldsymbol{\varepsilon}_{\mathbf{k}1} + i\boldsymbol{\varepsilon}_{\mathbf{k}2}) a_{\mathbf{k}R} \mathrm{e}^{i\mathbf{k}.\mathbf{r}} + \frac{1}{\sqrt{2}} (\boldsymbol{\varepsilon}_{\mathbf{k}1} - i\boldsymbol{\varepsilon}_{\mathbf{k}2}) a^*_{\mathbf{k}R} \mathrm{e}^{-i\mathbf{k}.\mathbf{r}} \right\} \tag{34.15}$$

where $\mathbf{k}$, $\boldsymbol{\varepsilon}_1$, and $\boldsymbol{\varepsilon}_2$ form a right-handed orthogonal set of vectors.

The discussion then proceeds along the same lines as before. Real observables $P_{\mathbf{k}R}$, $Q_{\mathbf{k}R}$ are constructed from $a_{\mathbf{k}R}$, $a^*_{\mathbf{k}R}$ by equations like equation (33.6). A Hamiltonian for the wave is thus $H = \frac{1}{2}(P^2_{\mathbf{k}R} + \omega^2 Q^2_{\mathbf{k}R})$. When the oscillator is quantised $a_{\mathbf{k}R}$ becomes a

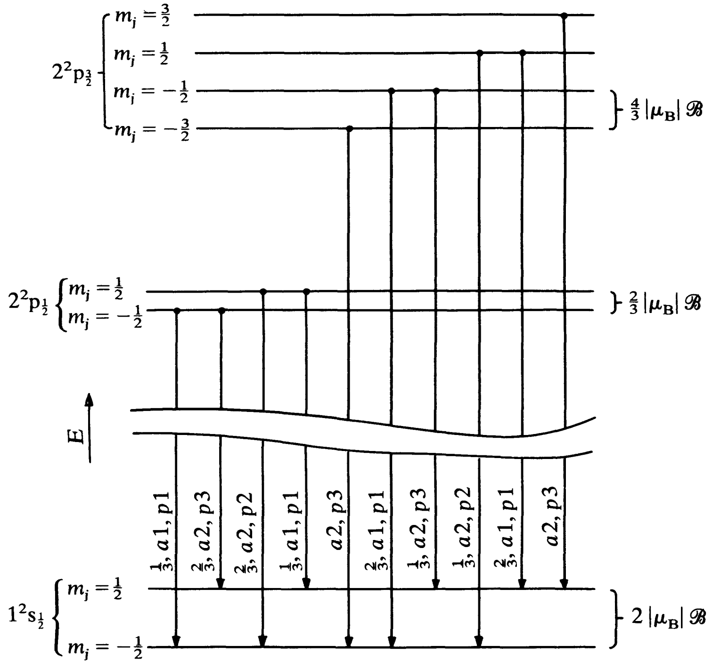

Figure 34.2 The 2p–1s transitions including Zeeman effect, with spin. Where appropriate the branching ratios are given, as well as the photon angular distribution and polarisation patterns.

right circularly polarised photon destruction operator, and $a^*_{\mathbf{k}R}$ similarly a right circularly polarised photon creation operator. The matrix elements of $a_{\mathbf{k}R}$ and $a^*_{\mathbf{k}R}$ are given again by equations like equation (33.15). So, when only one right circularly polarised oscillator is considered, the matrix elements of $\mathbf{A}$ are

$$\left.\begin{aligned}\langle (n-1)_{\mathbf{k}R}|\,\hat{\mathbf{A}}\,|n_{\mathbf{k}R}\rangle &= (n_{\mathbf{k}R})^{1/2}\left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)^{1/2}\\ &\qquad\times\frac{1}{\sqrt{2}}(\boldsymbol{\varepsilon}_{\mathbf{k}1}+i\boldsymbol{\varepsilon}_{\mathbf{k}2})\mathrm{e}^{i\mathbf{k}.\mathbf{r}}\\ \langle (n+1)_{\mathbf{k}R}|\,\hat{\mathbf{A}}\,|n_{\mathbf{k}R}\rangle &= \{(n+1)_{\mathbf{k}R}\}^{1/2}\left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)^{1/2}\\ &\qquad\times\frac{1}{\sqrt{2}}(\boldsymbol{\varepsilon}_{\mathbf{k}1}-i\boldsymbol{\varepsilon}_{\mathbf{k}2})\mathrm{e}^{-i\mathbf{k}.\mathbf{r}}\end{aligned}\right\}\qquad(34.16)$$

A full set of oscillators, both left and right circularly polarised, can be handled without difficulty because once again the Hamiltonian does not contain cross-terms. Thus equations (34.16) hold good for each right circularly polarised oscillator separately. The similar matrix elements for left circularly polarised oscillators are

$$\left.\begin{aligned}\langle (n-1)_{\mathbf{k}L}|\,\hat{\mathbf{A}}\,|n_{\mathbf{k}L}\rangle &= (n_{\mathbf{k}L})^{1/2}\left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)^{1/2}\\ &\quad\times\frac{1}{\sqrt{2}}(\boldsymbol{\varepsilon}_{\mathbf{k}1}-i\boldsymbol{\varepsilon}_{\mathbf{k}2})\mathrm{e}^{i\mathbf{k}.\mathbf{r}}\\ \langle (n+1)_{\mathbf{k}L}|\,\hat{\mathbf{A}}\,|n_{\mathbf{k}L}\rangle &= \{(n+1)_{\mathbf{k}L}\}^{1/2}\left(\frac{\hbar}{2\varepsilon_0 kcL^3}\right)^{1/2}\\ &\quad\times\frac{1}{\sqrt{2}}(\boldsymbol{\varepsilon}_{\mathbf{k}1}+i\boldsymbol{\varepsilon}_{\mathbf{k}2})\mathrm{e}^{-i\mathbf{k}.\mathbf{r}}\end{aligned}\right\}\qquad(34.17)$$

When the perturbation calculation of the 2p–1s transition rate is carried out once more, equation (34.6) is obviously to be replaced by

$$\begin{aligned}\frac{\mathrm{d}\lambda_m}{\mathrm{d}\Omega}=\frac{1}{2\pi}\left(\frac{e^3k^3}{4\pi\varepsilon_0\hbar}\right)&\left\{\left|\frac{1}{\sqrt{2}}(\boldsymbol{\varepsilon}_1-i\boldsymbol{\varepsilon}_2)\,.\,\langle u_{100}|\,\mathbf{r}_\mathrm{e}\,|u_{21m}\rangle\right|^2\right.\\ &\left.+\left|\frac{1}{\sqrt{2}}(\boldsymbol{\varepsilon}_1+i\boldsymbol{\varepsilon}_2)\,.\,\langle u_{100}|\,\mathbf{r}_\mathrm{e}\,|u_{21m}\rangle\right|^2\right\}\qquad(34.18)\end{aligned}$$

where the first term corresponds to right circularly polarised photons, and the second to left. A little thought will show that the total transition rates given by equations (34.6) and (34.18) are the same.

Now the particular problem in hand can be taken up again. For emission along the positive z-axis the polarisation vector $\boldsymbol{\varepsilon}_1$ can lie along the positive x-axis, and $\boldsymbol{\varepsilon}_2$ along the positive y-axis. Consideration of the components of $\mathbf{M}_{1r}$ and $\mathbf{M}_{1i}$ in table 34.1 then shows that only the first term of equation (34.18) contributes; therefore the photons are right circularly polarised.

For emission along the negative z-axis, $\boldsymbol{\varepsilon}_1$ can lie along the positive x-axis and $\boldsymbol{\varepsilon}_2$ along the *negative* y-axis, so forming $\mathbf{k}$, $\boldsymbol{\varepsilon}_1$, and $\boldsymbol{\varepsilon}_2$ into the required right-handed set. It is then obvious that only the second term in equation (34.18) contributes, and the photons are left circularly polarised.

Photons moving along the z-axis cannot carry a z-component of orbital angular momentum, but in the transition under discussion one unit of l_z disappears from the electron. The missing angular momentum can be accounted for if the photon is given one unit of intrinsic angular momentum, or spin. When the photon is right (left) circularly polarised the component of the spin along $\mathbf{k}$ is supposed to be $+\hbar$ $(-\hbar)$. This simple picture of the photon's spin cannot be taken too far, because the expected third state of alignment is missing. However, within its limits, the idea is a useful one.

Polarisation: transition from the* 2p ($m=-1$) *state Here, as would be expected, the photons emitted along the positive (negative) z-axis are left (right) circularly polarised. This pattern of polarisation is referred to as type $p3$ in figures 34.1 and 34.2.

Zeeman effect: spin neglected When a uniform magnetic field $\mathcal{B}$ is applied along the z-axis, the three initial states have slightly different energies, and correspondingly there are three slightly different values of k. Each of the three spectral lines has a unique combination of angular distribution and polarisation pattern. The predictions are illustrated in figure 34.1.

Zeeman effect: spin included The actual experimental results differ from figure 34.1, because the electron has spin $\frac{1}{2}$ and there is a spin-orbit term in its energy. With the help of chapter 6 the amended predictions of figure 34.2 can be constructed. The initial states are shown split according to the weak field part of figure 23.2. The final state is of course a doublet, since spin angular momentum alone is present. The magnitude of all the Zeeman splittings are controlled by the Landé g-factor (equation (23.11)).

The initial states are eigenfunctions of $\mathbf{j}^2$ and j_z. When discussing radiative transitions these must be considered as superpositions of eigenfunctions of l_z and s_z, because $\mathbf{s}$ is not mentioned in equation (33.26) and so s_z cannot change in the transition. Those initial states which contain two terms of different s_z will decay by two routes, with branching ratios controlled by the squares of the corresponding Clebsch–Gordon coefficients. The branching ratios are shown in figure 34.2 along with the angular distributions and polarisation patterns.

When this extraordinary wealth of experimentally accessible information is considered, it will be readily understood how atomic spectroscopy came to be the principal testing ground for the quantum theory in its early days.

Problems

10.1 Write down the matrix element for the emission of a quantum of radiation by a free particle. If the initial momentum of the particle is $\mathbf{p}_i$ and its final momentum is $\mathbf{p}_f$, show that the matrix element averages to zero over the usual cube of side L unless

$$\mathbf{p}_i = \mathbf{p}_f + \hbar \mathbf{k}$$

[*Comment:* Energy is not conserved in this process, so that it can only be part of a more complicated event.]

10.2 Calculate the lifetime for the 3s–2p transition in the H atom.

Appendix

A few non-elementary integrals

$$\int_{-\infty}^{\infty} \mathrm{e}^{-a^2x^2}\,\mathrm{d}x = \frac{\pi^{1/2}}{a} \tag{1}$$

$$\int_{-\infty}^{\infty} x^2\mathrm{e}^{-a^2x^2}\,\mathrm{d}x = \frac{\pi^{1/2}}{2a^3} \tag{2}$$

$$\int_{-\infty}^{\infty} \mathrm{e}^{-2bcx-c^2x^2}\,\mathrm{d}x = \frac{\pi^{1/2}\mathrm{e}^{b^2}}{c} \tag{3}$$

Completion of the square in the exponent leads to a version of equation (1):

$$\int_{-\infty}^{\infty} \left(\frac{\mathrm{e}^{-\lambda t/2} - \mathrm{e}^{-i\omega t}}{\omega + i\lambda/2}\right)\mathrm{d}\omega = i\pi\mathrm{e}^{-\lambda t/2} \tag{4}$$

This is most easily verified by contour integration in the complex ω plane. The contour extends from $-\infty$ to $+\infty$ along a real axis (giving the integral required), and returns by clockwise traversal of an infinite semicircle in the lower half plane. The integral is regular at $\omega = -i\lambda/2$, and so the integral required is the negative of the contour integral round the semicircle. The second term in the numerator contributes nothing to this (Jordan's lemma, slightly modified) but the first term gives rise to the result stated.

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