

## Chapter 2

# Quantum mechanics

The charge carriers in semiconductor devices—electrons and holes—are quantum particles. Any researcher in device modelling must have a thorough grounding in the theory of quantum mechanics, because there is no point in finding solutions to the quantum equations without being able to sensibly interpret these solutions in the quantum context.

### 2.1 The physical basis of quantum mechanics

The subject of quantum mechanics had a very messy beginning. The old certainties of Newtonian mechanics were swept away when new observations negated these ideas, and a traumatic period followed during which its replacement theory, in the form of quantum mechanics, developed in fits and starts.

Up to about 1900, the old ideas of classical physics were accepted. Among them were:

- The success of Newton's laws of motion.
- Variables representing observable quantities were real numbers, usually continuous over some interval. For example, the energy of simple harmonic motion  $\ddot{x} = -\omega x$  is  $\frac{1}{2}m A^2 \omega^2$ , where  $A$  is the amplitude and  $m$  is the mass; this energy could have any non-negative value by adjusting the value of  $A$ .
- Any two or more observables on a system could be measured simultaneously and precisely; for example, the position  $x(t)$  and momentum  $m\dot{x}(t)$  of the particle, or the  $x$  and  $y$  components of angular momentum.
- Light travelled in waves and could be reflected, refracted and diffracted. Young's diffraction experiments (1803) confirmed this, with further confirmation by Maxwell's electromagnetic theory (1864).
- Discovery of X-rays by Roentgen in 1895. They were diffracted as light by von Laue.
- Discovery of the electron in 1897. J.J. Thompson showed that the electron behaved as a Newtonian particle, and measured the ratio charge/mass.

- Measurements could be made with unlimited accuracy, or would be eventually.

But experiments were beginning to be performed, the outcomes of which could not be explained by the ideas of classical physics:

1. A *blackbody* is one which absorbs all incident radiation with no reflection. It was found that the calculated spectrum of radiation from a blackbody at temperature  $T$  did not correspond with experimental results. In fact, the total energy of the radiation calculated using the classical theory of radiation gave an infinite answer (the *ultraviolet catastrophe*).
2. The calculated temperature dependence of specific heats  $dU/dT$  of bodies at low temperatures did not agree with experimental results. Experiment showed a fall-off at low temperatures, while calculation showed no fall-off.
3. Electrons are ejected from a solid which is radiated with light. Classical theory could not explain why the energies of the emitted electrons depended strongly on the frequency of the incident radiation, rather than its intensity (Hertz 1887).
4. The *Compton effect* (1923): X-rays with frequency  $\nu$  strike a block of paraffin. Electrons are knocked out, together with radiation of frequency  $\nu'$ . The energy of the ejected electrons was  $E = h\nu - h\nu'$ . Hence the X-rays behaved as though they had particle momentum. This effect was also seen in problem 3.
5. In the *Davisson-Germer* experiment of 1927, a beam of electrons aimed at a crystal lattice produced a diffraction pattern on a screen placed behind the crystal; the electrons behaved as though they possessed some sort of wave motion.
6. The spectral experiments of Ritz on radiation emitted from solids showed that the wavelengths appeared as a set of discrete values.
7. The classical idea of the atom was that of a charged electron in orbit about a nucleus. However, the acceleration of the charged particle should cause it to radiate, lose energy, and spiral into the nucleus. This did not happen.

In 1901, Max Planck resolved problem (1) by suggesting that electromagnetic radiation was emitted in discrete packets, or *quanta*. The energy of each quantum is

$$E = h\nu$$

where  $\nu$  is the frequency of the radiation and  $h$  is a constant (now known as Planck's constant) with the value  $h = 6.626 \times 10^{-34}$  Joule-secs. Using this suggestion, Einstein resolved problem (3) in 1905 and problem (2) in 1907. The quantum of light is called the *photon*. The three main conclusions from all of this were (i) energy appears in discrete quanta; (ii) electromagnetic radiation and matter both have a particle—wave duality; (iii) certain observable quantities have only discrete values.

To explain the particle—wave duality aspect, it is found that the momentum  $p$  of a particle and its associated radiation wavelength  $\lambda$  must be related by the *de Broglie relation*

$$p\lambda = h.$$

This explains the Compton effect and the diffraction pattern associated with electrons striking a crystal lattice. Hence

$$E = h\nu, \quad (2.1)$$

$$p\lambda = h, \quad (2.2)$$

$$\hbar \equiv h/(2\pi) = 1.05 \times 10^{-34} \text{ Joule-secs.}$$

The *Uncertainty Principle* deals with the fact that certain pairs of observables cannot be measured simultaneously and precisely. For example, consider an experiment in which light is beamed at a screen containing two slits. The light passes through the slits and a diffraction pattern is formed on a photosensitive screen placed behind the slits. This illustrates the particle—wave duality of the incoming radiation: its wave property causes the wave fronts to spread out from the two slits and to interact constructively and destructively on the screen behind the slits; its particle property causes electrons to be ejected from this screen to enable the diffraction pattern to be seen. Now reduce the intensity of the light so that only one photon at a time passes through the apparatus: over a length of time the same diffraction pattern will build up. Now put detectors behind the slits so that we can determine through which slit the individual photon passes—this destroys the diffraction pattern. So we cannot know the slit through which the photon passes (its position) while knowing its momentum (through measurement of the diffraction pattern).

Any experiment, thought or otherwise, will produce the following result: that if  $\Delta x$  and  $\Delta p_x$  are the uncertainties in the  $x$  components of position and momentum, then

$$\Delta x \Delta p_x \geq \frac{1}{2} \hbar. \quad (2.3)$$

Similarly, if  $\Delta E$  and  $\Delta t$  are the uncertainties in the measurement of the energy of a system and the time at which it is measured, then

$$\Delta t \Delta E \geq \frac{1}{2} \hbar. \quad (2.4)$$

These results will be derived later using the operator formalism.

## 2.2 The Schrödinger equation

All this suggests that a particle can be thought of as a *wave packet*, which is composed of a group of plane waves of nearly the same wavelength  $\lambda$  which interfere destructively except around a certain point. The de Broglie relation in Equation (2.2) gives

$$p = \frac{h}{\lambda}, \quad \text{or} \quad \Delta p = -\frac{h}{\lambda^2} \Delta \lambda.$$

This result corresponds neatly with the uncertainty relation of Equation (2.3):

- a small spread in  $\lambda$  ( $\Delta \lambda$  small,  $\Delta p$  small) gives a large spread in  $x$  ( $\Delta x$  large);
- a large spread in  $\lambda$  ( $\Delta \lambda$  large,  $\Delta p$  large) gives a small spread in  $x$  ( $\Delta x$  small).

A wave function  $\Psi(\mathbf{r}, t)$  will be associated with the particle, where  $\mathbf{r}$  represents a space position and  $t$  represents time. Postulate that  $|\Psi(\mathbf{r}, t)|^2 d^3\mathbf{r}$  is the probability of finding the particle in the element of volume  $d^3\mathbf{r}$  surrounding the point with position  $\mathbf{r}$  at time  $t$  (postulate of Max Born 1926). We must find an evolution equation for the wave function, the form of which has universal validity; that is, its coefficients, apart from the value of the particle mass and potential, should be constants so that different solutions may be superposed.

### 2.2.1 Derivation of the time-dependent Schrödinger equation

A very crude derivation will be given of this evolution equation in a very special case. Suppose the particle has a constant mass  $m$  and is moving in one dimension along the  $x$  axis, in the direction of increasing  $x$ . It is moving in a constant potential  $V$  and has energy  $E$ . Suppose that its momentum  $p$  is known exactly ( $\Delta p = 0$ ), so that nothing is known of its position ( $\Delta x = \infty$ ). Then  $|\Psi(\mathbf{r}, t)|^2$  is a constant for all  $x$  and  $t$ . The particle will be represented by a plane wave with wavelength  $\lambda = h/p$ . The solutions of the wave equation

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{k^2}{\omega^2} \frac{\partial^2 \Psi}{\partial t^2}$$

are  $\Psi = e^{\pm i(kx - \omega t)}$ , where  $\omega = 2\pi\nu$  and  $k = 2\pi/\lambda$ : the positive sign in the solution is taken for motion along the positive  $x$  direction. Now

$$\begin{aligned} \omega &= 2\pi\nu = \frac{2\pi E}{h} = \frac{E}{\hbar} \quad \text{and} \\ k &= \frac{2\pi}{\lambda} = \frac{2\pi p}{h} = \frac{p}{\hbar}. \end{aligned}$$

Hence

$$\Psi(x, t) = e^{\frac{i}{\hbar}(px - Et)} \quad (2.5)$$

It follows from this result that

$$i\hbar \frac{\partial \Psi}{\partial t} = E\Psi \quad (2.6)$$

$$-i\hbar \frac{\partial \Psi}{\partial x} = p\Psi \quad (2.7)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = \frac{p^2}{2m} \Psi \quad (2.8)$$

Hence the classical energy equation  $E = p^2/(2m) + V$  leads to the suggested replacement

$$\begin{aligned}
 E\Psi &= \frac{p^2}{2m}\Psi + V\Psi \quad \Rightarrow \\
 i\hbar \frac{\partial \Psi}{\partial t} &= -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi.
 \end{aligned}
 \tag{2.9}$$

This suggested substitution has been made in the very special case of a particle whose momentum is known exactly, and is moving in one dimension in a constant potential. Now postulate that the equation holds for a particle moving in three dimensions in a potential  $V(\mathbf{r}, t)$ :

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t) + V(\mathbf{r}, t) \Psi(\mathbf{r}, t). \tag{2.10}$$

This is the *Time-Dependent Schrödinger Equation* (TDSE).

### 2.2.2 The time-independent Schrödinger equation

The Schrödinger equation separates when the potential  $V$  is independent of  $t$ :  $V \equiv V(\mathbf{r})$ . In this case, look for a solution in the form

$$\Psi(\mathbf{r}, t) = u(\mathbf{r})v(t). \tag{2.11}$$

Then Equation (2.10) becomes

$$i\hbar u \frac{dv}{dt} = -\frac{\hbar^2}{2m} v \nabla^2 u + V(\mathbf{r})uv$$

or

$$i\hbar \frac{1}{v} \frac{dv}{dt} = -\frac{\hbar^2}{2m} \frac{1}{u} \nabla^2 u + V(\mathbf{r}) \equiv C \tag{2.12}$$

where  $C$  is a constant of separation. The resulting equation for  $v(t)$  has the solution  $v(t) = \exp(-\frac{i}{\hbar} Ct)$ , and so

$$\Psi(\mathbf{r}, t) = u_C(\mathbf{r})e^{-\frac{i}{\hbar} Ct}, \tag{2.13}$$

where  $u \equiv u_C$  denotes the fact that  $u$  is now a function of  $C$ . Differentiation of Equation (2.13) with respect to  $t$  shows that  $i\hbar \frac{\partial \Psi}{\partial t} = C\Psi$ , and comparison of this result with that in Equation (2.6) leads to the identification  $C \equiv E$ . Hence Equation (2.13) becomes

$$\Psi(\mathbf{r}, t) = u_E(\mathbf{r})e^{-\frac{i}{\hbar} Et}. \tag{2.14}$$

Since the Schrödinger equation is linear, the general solution is the superposition

$$\Psi(\mathbf{r}, t) = \sum_E u_E(\mathbf{r})e^{-\frac{i}{\hbar} Et}, \tag{2.15}$$

where the range over which  $E$  is summed will depend on the particular system being considered. The spatial part of Equation (2.12) gives

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)u(\mathbf{r}) = Eu(\mathbf{r}). \quad (2.16)$$

This is the *Time-Independent Schrödinger Equation* (TISE).

By defining the *Hamiltonian* operator

$$H \equiv -\frac{\hbar^2}{2m}\nabla^2 + V, \quad (2.17)$$

the TISE Equation (2.16) can be written

$$Hu(\mathbf{r}) = Eu(\mathbf{r}). \quad (2.18)$$

The full Schrödinger Equation (2.10) then becomes

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi. \quad (2.19)$$

## 2.3 Boundary and continuity conditions, and parity

The solution of the Schrödinger equation is not complete without the specification of boundary conditions and continuity conditions. Further, certain properties are held by the solution when the potential possesses some symmetry.

### 2.3.1 Boundary and continuity conditions

Since  $|\Psi(\mathbf{r}, t)|^2$  is interpreted as a probability density, we should attempt to normalise the solution using the condition

$$\int |\Psi(\mathbf{r}, t)|^2 d^3\mathbf{r} = 1$$

where the integral is taken over the whole of the physical region of the system. In general, there are two main types of wave function:

1. those for which the normalisation integral converges. These correspond to well localised wave packets, restrained by the potential  $V(\mathbf{r})$ .
2. those for which the normalisation integral diverges. These correspond to travelling harmonic waves which are not localised or restrained. In this case, we require that the wave function is bounded at great distances in all directions; we

are not interested in those solutions which are unbounded, since these correspond to indefinitely increasing probability.

In all cases, we require that both  $\Psi$  and  $\nabla\Psi$  are continuous, finite and single valued in order to uniquely represent a definite physical situation. This ensures that the probability density  $|\Psi|^2$  is finite and continuous. However, we must relax the condition that  $\nabla\Psi$  is continuous at certain infinite discontinuities in the potential.

### 2.3.2 Parity

Suppose that the potential is an even function of  $\mathbf{r}$ , that is,  $V(\mathbf{r}) = V(-\mathbf{r})$ . Then

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}) + V(\mathbf{r})\Psi(\mathbf{r}) &= E\Psi(\mathbf{r}), \quad \text{and} \\ -\frac{\hbar^2}{2m}\nabla^2\Psi(-\mathbf{r}) + V(\mathbf{r})\Psi(-\mathbf{r}) &= E\Psi(-\mathbf{r}). \end{aligned}$$

Hence  $\Psi(\mathbf{r})$  and  $\Psi(-\mathbf{r})$  satisfy the same equation for a given value of  $E$ . Unless there are two or more linearly independent solutions corresponding to the energy  $E$ , then  $\Psi(-\mathbf{r}) = \alpha\Psi(\mathbf{r})$  for some constant  $\alpha$ . Hence  $\Psi(\mathbf{r}) = \alpha\Psi(-\mathbf{r})$ , from which it follows that  $\alpha = \pm 1$ . It then follows that  $\Psi(-\mathbf{r}) = \pm\Psi(\mathbf{r})$ , and hence the solutions for an even function  $V(\mathbf{r})$  are even or odd: they are said to have *even parity* or *odd parity* respectively.

## 2.4 The probability current density

An overline on any complex quantity will denote its complex conjugate so that, in particular,  $|\Psi|^2 = \overline{\Psi}\Psi$ . It follows from Equation (2.10) that

$$\begin{aligned} \frac{\partial\Psi}{\partial t} &= -\frac{\hbar}{2im}\nabla^2\Psi + \frac{1}{ih}V\Psi \\ \frac{\partial\overline{\Psi}}{\partial t} &= \frac{\hbar}{2im}\nabla^2\overline{\Psi} - \frac{1}{ih}V\overline{\Psi} \end{aligned}$$

where the reality of the potential  $V$  has been used:  $\overline{V} = V$ . Hence

$$\begin{aligned} \frac{\partial}{\partial t}|\Psi|^2 &= \frac{\partial}{\partial t}(\Psi\overline{\Psi}) = \overline{\Psi}\frac{\partial\Psi}{\partial t} + \Psi\frac{\partial\overline{\Psi}}{\partial t} \\ &= -\frac{\hbar}{2im}\overline{\Psi}\nabla^2\Psi + \frac{\hbar}{2im}\Psi\nabla^2\overline{\Psi} \\ &= -\frac{\hbar}{2im}\nabla \cdot (\overline{\Psi}\nabla\Psi - \Psi\nabla\overline{\Psi}) \\ &= -\nabla \cdot \mathbf{s} \end{aligned} \tag{2.20}$$

where the vector quantity  $\mathbf{s}$  is defined as

$$\mathbf{s} \equiv \frac{\hbar}{2im} (\bar{\Psi} \nabla \Psi - \Psi \nabla \bar{\Psi}). \quad (2.21)$$

This leads to the *continuity equation*

$$\frac{\partial}{\partial t} |\Psi|^2 + \nabla \cdot \mathbf{s} = 0. \quad (2.22)$$

The probability of finding the particle at time  $t$  in the fixed volume  $R$  surrounded by surface  $A$  is  $P_t = \int_R |\Psi|^2 d^3\mathbf{r}$ . Hence

$$\frac{dP_t}{dt} = \int_R \frac{\partial}{\partial t} |\Psi|^2 d^3\mathbf{r} = - \int_R (\nabla \cdot \mathbf{s}) d^3\mathbf{r} = - \int_A s_n dA.$$

Hence  $s_n dA$  is the probability per unit time that the particle crosses out of the area  $dA$  at the point on the surface at which the unit normal vector is  $\mathbf{n}$ . For this reason, the quantity  $\mathbf{s}$  defined in Equation (2.21) is called the *probability current density*.

## 2.5 One dimensional motion

In all of the following sections we consider cases in which the potential  $V$  is independent of time, with motion confined to the  $x$ -direction. We will solve the TISE exactly only for a small number of special cases.

### 2.5.1 General considerations

Suppose that, without loss of generality, the potential  $V(x)$  is given by

$$\begin{aligned} V(x) &\rightarrow 0 \quad \text{as } x \rightarrow -\infty \\ &\rightarrow V_0 > 0 \quad \text{as } x \rightarrow \infty \end{aligned}$$

with  $V_{\min} \equiv \min\{V(x)\}$ . The situation is shown generally in Fig. 2.1.

A particle with mass  $m$  and energy  $E$  moves in this potential. The TISE is

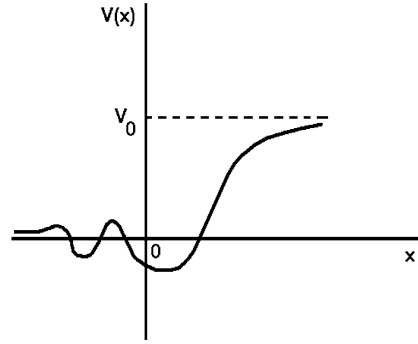
$$Eu = Tu + V(x)u$$

where  $T$  is the kinetic operator  $-\hbar^2/(2m)d^2/(dx^2)$ . We will use angular brackets on any observable quantity  $A$  to denote its average, or *expectation value*  $\langle A \rangle$ —an exact definition of expectation value will be given in Sect. 2.6. It follows that

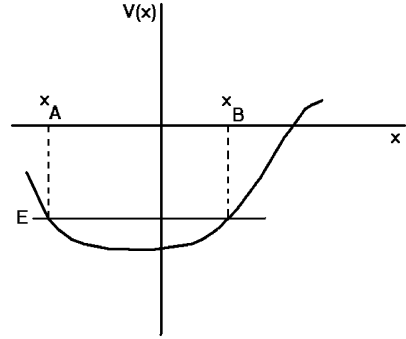
$$E = \langle T \rangle + \langle V \rangle \geq V_{\min}$$



**Fig. 2.1** The potential having the properties  
 $V(x) \rightarrow 0$  as  $x \rightarrow -\infty$  and  
 $V(x) \rightarrow V_0 > 0$  as  $x \rightarrow \infty$ .



**Fig. 2.2** The points at which the potential  $V(x)$  meet the energy  $E$ .



since  $\langle T \rangle \geq 0$ .

(i) *Bound state*

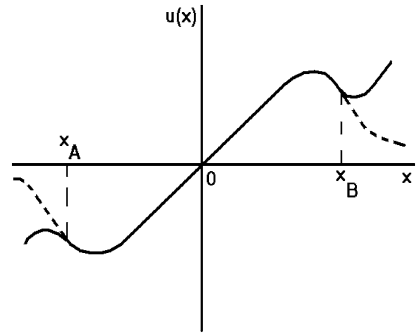
As  $x \rightarrow \pm\infty$ , the TISE Equation (2.16) becomes

$$u'' = \frac{2m}{\hbar^2}(V_0 - E)u \quad \text{as } x \rightarrow \infty$$

$$u'' = -\frac{2m}{\hbar^2}Eu \quad \text{as } x \rightarrow -\infty.$$

For a bound state in which the particle is not allowed to go to infinity in either direction, we must have  $u \rightarrow 0$  as  $x \rightarrow \pm\infty$ . This means that  $V_0 - E > 0$  and  $E < 0$ . Hence bound states occur only if  $V_{\min} \leq E < 0$ . In this case, let  $V(x) = E$  at the positions  $x = x_A$  and  $x = x_B$  as shown in Fig. 2.2. Since  $u'' = (2m/\hbar^2)(V(x) - E)u$ , then for  $x_A < x < x_B$  we have the two cases ( $u > 0$ ,  $u'' < 0$ ,  $u'$  decreases), and ( $u < 0$ ,  $u'' > 0$ ,  $u'$  increases). Hence in both cases we get an oscillating behaviour of  $u$  inside the given range, and the curve of  $u(x)$  against  $x$  bends towards the  $x$ -axis. This behaviour is shown in Fig. 2.3. Immediately outside the interval  $x_A < x < x_B$  we have the two possibilities ( $u > 0$ ,  $u'' > 0$ ,  $u'$  increases) and ( $u < 0$ ,  $u'' < 0$ ,  $u'$  decreases). Hence in both cases of  $u$  the curve of  $u(x)$  against  $x$  bends away from the  $x$ -axis. Generally, the curves bend exponentially away from the  $x$ -axis as  $x \rightarrow \pm\infty$ , and the solution then becomes infinite.

**Fig. 2.3** The oscillating behaviour of  $u(x)$  as it bends towards the  $x$ -axis.



These curves will tail off to zero only for certain values of  $E$  (the dotted lines in Fig. 2.3). Thus we get a discrete spectrum for the bound states. Depending on the particular problem, there will be a finite or an infinite number of, or even no, discrete energy levels. When they exist, these energy levels will be *non-degenerate*. Degeneracy and non-degeneracy will be defined properly later: we say that an energy level is non-degenerate if there corresponds to it only one solution. To prove the above statement, let  $u_1$  and  $u_2$  be two solutions corresponding to the energy  $E$  in the range  $V_{min} < E < 0$ . Then

$$\frac{u_1''}{u_1} = \frac{2m}{\hbar^2}(V - E) = \frac{u_2''}{u_2}.$$

Hence

$$u_1''u_2 - u_2''u_1 = 0, \quad \text{or} \quad u_1'u_2 - u_1u_2' = \text{constant}.$$

This constant is called the *Wronskian*. Since  $u_1 = u_2 = 0$  at  $x = \pm\infty$ , the constant must be zero. Then  $u_1'/u_1 = u_2'/u_2$ , or  $u_1 = \text{const} \times u_2$ . Hence  $u_1$  and  $u_2$  are the same up to a multiplicative constant.

(ii)  $0 < E < V_0$

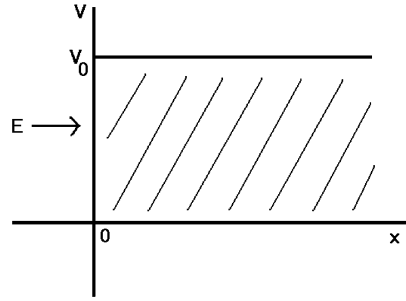
If  $x$  is sufficiently large and negative, then we can neglect  $V(x)$ . The corresponding TISE is then  $u'' + (2m/\hbar^2)Eu$  which has solution  $u = a \cos(kx + \delta)$  where  $k \equiv \sqrt{2mE/\hbar^2}$ . Then  $|u|$  does not tend to zero as  $x \rightarrow -\infty$ , and the particle is not bounded for large negative  $x$ . On the other hand, as  $x \rightarrow \infty$ , the TISE becomes  $u'' = (2m/\hbar^2)(V_0 - E)u$  which has solution  $u = be^{-k_1x}$  where  $k_1 \equiv \sqrt{2m(V_0 - E)/\hbar^2}$ . Now there is no term  $e^{k_1x}$  since this would cause the solution to diverge as  $x \rightarrow \infty$ . The energies  $E$  are again non-degenerate since the quantity  $u_1'u_2 - u_1u_2'$  vanishes as  $x \rightarrow \infty$ .

(iii)  $E > V_0$

Let us first look at the effect of the momentum operator  $p$  on the quantities  $e^{\pm ikx}$ , where  $k$  is a positive constant. From Equation (2.7) we have

$$pe^{\pm ikx} = -i\hbar \frac{d}{dx}e^{\pm ikx} = \pm \hbar k e^{\pm ikx}.$$

**Fig. 2.4** The potential of a single finite step with height  $V_0$  situated at  $x = 0$ .



Hence the term  $e^{ikx}$  corresponds to a particle moving to the right, while the term  $e^{-ikx}$  corresponds to a particle moving to the left. Then as  $x \rightarrow -\infty$ , the solution of the TISE is

$$u \rightarrow a \cos(kx + \delta) = pe^{ikx} + qe^{-ikx}$$

and, as  $x \rightarrow \infty$ , the TISE  $u'' = -(2m/\hbar^2)(E - V_0)$  has solution

$$u \rightarrow re^{ik_2x} + se^{-ik_2x}$$

where  $k_2 \equiv \sqrt{2m(E - V_0)/\hbar^2}$ . From what we have seen above, the separate terms relate to motion in the positive and negative directions. The solutions are now doubly degenerate, since both of the independent solutions  $e^{\pm ikx}$  and  $e^{\pm ik_2x}$  correspond to a given value of  $E$ .

### 2.5.2 Reflection and Transmission coefficients

Consider the piecewise constant potential step shown in Fig. 2.4. The potential is again given by

$$\begin{aligned} V(x) &\rightarrow 0 & \text{as } x &\rightarrow -\infty \\ &\rightarrow V_0 > 0 & \text{as } x &\rightarrow \infty \end{aligned}$$

A particle of mass  $m$  with energy  $E$  is incident on the barrier from the left. If  $E < V_0$ , then classically the particle does not have enough energy to surmount the barrier, and will be reflected back. Quantum mechanically, however, there will be a probability that the particle will cross the barrier—this is the process of *tunneling* which will be quantified later. If  $E > V_0$ , then classically the carrier will carry on over the barrier, but with reduced velocity. Quantum mechanically, there is a probability that the particle will be reflected back. In order to see this, we solve the TISE

$$u'' + \frac{2m}{\hbar^2}(E - V(x))u = 0$$

for the case  $E > V_0$ :

$$u \rightarrow Ae^{ikx} + Be^{-ikx} \quad \text{as } x \rightarrow -\infty \quad (2.23)$$

$$u \rightarrow Ce^{ik_2x} \quad \text{as } x \rightarrow \infty \quad (2.24)$$

where the constants  $k$  and  $k_2$  are defined as

$$k \equiv \sqrt{\frac{2mE}{\hbar^2}}, \quad k_2 \equiv \sqrt{\frac{2m(E - V_0)}{\hbar^2}}.$$

The first term on the right hand side of Equation (2.23) represents the incident wave, while the second represents the reflected wave. The term on the right hand side of Equation (2.24) represents the transmitted wave: note that there is no reflected wave in that region. The one-dimensional equivalent of the probability current density defined in Equation (2.21) is

$$s \equiv \frac{\hbar}{2im} \left( \bar{u} \frac{du}{dx} - u \frac{d\bar{u}}{dx} \right). \quad (2.25)$$

Evaluating and equating this quantity at both ends of the  $x$ -axis, it is easily shown that

$$\frac{\hbar}{m} k |A|^2 - \frac{\hbar}{m} k |B|^2 = \frac{\hbar}{m} k_2 |C|^2 \quad (2.26)$$

Note that the quantity on the left hand side of this equation does not contain cross terms involving  $A$  and  $B$ . Consequently, the probability current densities of the incident, reflected and transmitted parts separately are

$$s_{inc} = \frac{\hbar k}{m} |A|^2, \quad s_{ref} = -\frac{\hbar k}{m} |B|^2, \quad s_{tr} = \frac{\hbar k_2}{m} |C|^2.$$

The *reflection coefficient*  $R$  and the *transmission coefficient*  $T$  are defined by

$$\text{Reflection coefficient: } R \equiv \left| \frac{s_{ref}}{s_{inc}} \right| = \left| \frac{B}{A} \right|^2 \quad (2.27)$$

$$\text{Transmission coefficient: } T \equiv \left| \frac{s_{tr}}{s_{inc}} \right| = \frac{k_2}{k} \left| \frac{C}{A} \right|^2. \quad (2.28)$$

Using Equation (2.26) it is easily shown that

$$T + R = 1. \quad (2.29)$$

It is also easily shown that these coefficients are the same for incidence in either direction for the case  $E > V_0$ . This is easily proved by noting that, for particles moving from the right, the solution of the TISE is

$$u_1 \rightarrow C_1 e^{-ikx} \quad \text{as } x \rightarrow -\infty$$

$$u_1 \rightarrow A_1 e^{-ik_2x} + B_1 e^{ik_2x} \quad \text{as } x \rightarrow \infty.$$

Evaluation of the Wronskian  $uu'_1 - u_1u'$  at both ends gives  $kAC_1 = k_2A_1C$ . Hence

$$\begin{aligned} \text{Transmission coefficient (L to R)} &= \frac{k_2}{k} \left| \frac{C}{A} \right|^2 \\ &= \frac{k}{k_2} \left| \frac{C_1}{A_1} \right|^2 \\ &= \text{Transmission coefficient (R to L).} \end{aligned}$$

### 2.5.3 Single finite step for $E < V_0$

Fig. 2.4 shows a single time-independent finite step of height  $V_0$  at  $x = 0$ , with the potential given by

$$V(x) = \begin{cases} 0 & \text{for } x \leq 0 \\ V_0 & \text{for } x > 0 \end{cases} \quad (2.30)$$

A particle of constant mass  $m$  approaches the barrier from the left, now with energy  $E < V_0$ . The TISE is written down for the two regions:

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dx^2} = Eu \quad (x \leq 0) \quad (2.31)$$

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dx^2} + V_0u = Eu \quad (x > 0), \quad (2.32)$$

and these have solutions

$$u(x) = \begin{cases} A \sin \alpha x + B \cos \alpha x & \text{for } x \leq 0 \\ C e^{-\beta x} + D e^{\beta x} & \text{for } x > 0 \end{cases} \quad (2.33)$$

where

$$\alpha \equiv \frac{1}{\hbar} \sqrt{2mE}, \quad \beta \equiv \frac{1}{\hbar} \sqrt{2m(V_0 - E)}.$$

Since  $u(x)$  must be bounded everywhere, then  $D = 0$ . Since  $u$  and  $u'$  are continuous at  $x = 0$ , then

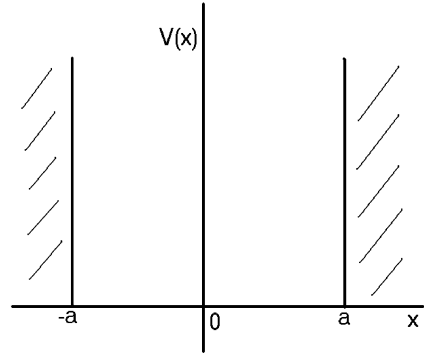
$$B = C, \quad A\alpha = -\beta C. \quad (2.34)$$

Hence

$$u(x) = \begin{cases} A(\sin \alpha x - \frac{\alpha}{\beta} \cos \alpha x) & \text{for } x \leq 0 \\ -\frac{\alpha}{\beta} A e^{-\beta x} & \text{for } x \geq 0. \end{cases} \quad (2.35)$$

This simple problem illustrates one of the important differences between the classical and quantum interpretations of the situation. Classically, since the energy  $E$  of the incoming particle is less than the height of the barrier, then the particle would

**Fig. 2.5** The potential of the infinite square well with width  $2a$  centred on  $x = 0$ .



bounce back, and not appear to the right of the barrier. However, this quantum calculation shows that there is a non-zero probability of the particle being to the right of the barrier. This tunnelling process plays an important part in the transmission of electrons through potential barriers in semiconductors.

### 2.5.4 Infinite barrier

The particle now approaches an infinite barrier at  $x = 0$ . We can use the result found in the previous section by taking the limit  $V_0 \rightarrow \infty$ . In this limit,  $\beta \rightarrow \infty$ , and so Equation (2.34) shows that we must have  $C \rightarrow 0$  in order to keep  $A$  finite. Hence  $u(x) = 0$  for all  $x \geq 0$ : this means that there is now zero probability that the particle will cross the barrier to the other side. The infinite potential means that the particle encounters an impenetrable barrier.

### 2.5.5 Infinite square well

The particle is now confined in an infinite square well, shown in Fig. 2.5. The potential is given by

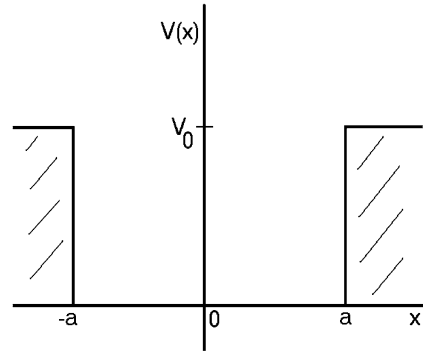
$$V(x) = \begin{cases} 0 & \text{for } x > -a \text{ and } x < a \\ \infty & \text{otherwise} \end{cases} \quad (2.36)$$

The TISE to be solved in the region  $-a < x < a$  is

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2} = Eu \quad (E > 0), \quad (2.37)$$

which has the solution

**Fig. 2.6** The potential of the finite square well with width  $2a$  and depth  $V_0$ .



$$u(x) = A \sin kx + B \cos kx, \quad k \equiv \frac{1}{\hbar} \sqrt{2mE}. \quad (2.38)$$

Since  $u = 0$  at  $x = \pm a$ , then

$$\begin{aligned} A \sin ka + B \cos ka &= 0 \\ -A \sin ka + B \cos ka &= 0 \end{aligned}$$

giving

$$A \sin ka = 0, \quad B \cos ka = 0.$$

Since  $A$  and  $B$  cannot simultaneously be zero (otherwise there would be zero probability of finding the particle in the box), then we have the two possible cases

1.  $A = 0$  and  $\cos ka = 0$ , giving  $ka = n\pi/2$  where  $n$  is an odd integer,
2.  $B = 0$  and  $\sin ka = 0$ , giving  $ka = n\pi/2$  where  $n$  is an even integer.

Hence

$$u_n(x) = \begin{cases} B \cos \frac{n\pi x}{2a} & \text{for } n \text{ odd} \\ A \sin \frac{n\pi x}{2a} & \text{for } n \text{ even.} \end{cases} \quad (2.39)$$

Note the even and odd parity in this solution, since the potential  $V(x)$  is symmetric. Since  $k^2 = n^2\pi^2/(4a^2)$ , then the allowed energy levels are given by

$$E \equiv E_n = \frac{\pi^2 \hbar^2 n^2}{8ma^2}, \quad n = 1, 2, 3, \dots \quad (2.40)$$

Note that the value  $E = 0$  (or  $n = 0$ ) is not allowed, since this again would imply that the particle is not in the region. Normalisation gives  $A = B = 1/\sqrt{a}$ .

### 2.5.6 Finite square well

The particle now moves in a finite square well, shown in Fig. 2.6. The potential is given by

$$V(x) = \begin{cases} 0 & \text{for } x > -a \text{ and } x < a \\ V_0 > 0 & \text{otherwise} \end{cases} \quad (2.41)$$

Then  $E > V_{min} = 0$ . The Schrödinger equation is written down for the two regions:

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2} = Eu \quad (|x| \leq a) \quad (2.42)$$

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2} + V_0 u = Eu \quad (|x| \geq a), \quad (2.43)$$

and for bound states with  $0 < E < V_0$  these equations have solutions

$$u(x) = \begin{cases} A \sin kx + B \cos kx & \text{for } |x| \leq a \\ C e^{-k_1 x} + D e^{k_1 x} & \text{for } |x| \geq a \end{cases} \quad (2.44)$$

where

$$\alpha \equiv \frac{1}{\hbar} \sqrt{2mE}, \quad \beta \equiv \frac{1}{\hbar} \sqrt{2m(V_0 - E)}.$$

In order to keep the solution finite, we must have  $C = 0$  in the region  $x < -a$ , and  $D = 0$  in the region  $x > a$ . Since  $u$  and  $u'$  are continuous at  $x = \mp a$ , we must also have

$$\begin{aligned} A \sin ka + B \cos ka &= C e^{-k_1 a} \\ -A \sin ka + B \cos ka &= D e^{-k_1 a} \\ kA \cos ka - kB \sin ka &= -k_1 C e^{-k_1 a} \\ kA \cos ka + kB \sin ka &= k_1 D e^{-k_1 a} \end{aligned}$$

Hence it follows that

$$\begin{aligned} 2A \sin ka &= (C - D) e^{-k_1 a}, & 2kA \cos ka &= -k_1 (C - D) e^{-k_1 a} \\ 2B \cos ka &= (C + D) e^{-k_1 a}, & 2kB \sin ka &= k_1 (C + D) e^{-k_1 a}. \end{aligned}$$

The only possible solutions are given by

1. even parity  $A = 0, C = D, k \tan ka = k_1$ ,
2. odd parity  $B = 0, C = -D, k \cot ka = -k_1$ .

Hence the energy levels are given by

$$\sqrt{E} \tan \left( a \sqrt{2mE/\hbar^2} \right) = \sqrt{V_0 - E} \quad (2.45)$$

$$\sqrt{E} \cot \left( a \sqrt{2mE/\hbar^2} \right) = -\sqrt{V_0 - E}. \quad (2.46)$$

See Problems 2.1 and 2.2.



### 2.5.7 $\delta$ -function potential

Consider the  $\delta$ -function potential centred at  $x = 0$ :

$$V(x) = V_0\delta(x). \quad (2.47)$$

We first consider the case  $V_0 > 0$ , so that  $E > 0$ . The TISE to be solved is

$$-\frac{\hbar^2}{2m}u'' + V_0\delta(x)u = Eu, \quad (2.48)$$

which has solution

$$u = Ae^{ikx} + Be^{-ikx} \quad (x < 0) \quad (2.49)$$

$$u = Ce^{ik_2x} \quad (x > 0), \quad (2.50)$$

where  $k \equiv \sqrt{2mE/\hbar^2}$ . Integrating both sides of Equation (2.48) from  $-\varepsilon$  to  $+\varepsilon$  where  $\varepsilon > 0$ , we have

$$-\frac{\hbar^2}{2m}[u'(\varepsilon) - u'(-\varepsilon)] + V_0u(0) = E \int_{-\varepsilon}^{\varepsilon} u(x)dx.$$

Hence as  $\varepsilon \rightarrow 0$  and using the fact that  $u$  is continuous at  $x = 0$ , it follows that

$$\lim_{\varepsilon \rightarrow 0}[u'(\varepsilon) - u'(-\varepsilon)] = \frac{2m}{\hbar^2}V_0u(0).$$

On using Equations (2.49) and (2.50), this becomes

$$\lim_{\varepsilon \rightarrow 0}[ikCe^{ik\varepsilon} - ikAe^{-ik\varepsilon} + ikBe^{-ik\varepsilon}] = C \frac{2m}{\hbar^2}V_0,$$

or

$$ikC - ikA + ikB = \frac{2mV_0}{\hbar^2}C.$$

This result, combined with the continuity condition  $A + B = C$ , eventually gives

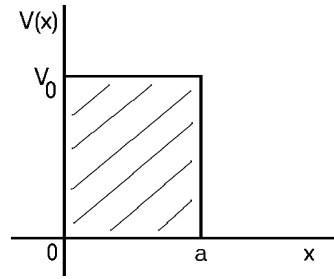
$$B = \frac{-\frac{imV_0}{\hbar^2k}A}{1 + \frac{mV_0}{\hbar^2k}i}, \quad C = \frac{A}{1 + \frac{mV_0}{\hbar^2k}i},$$

giving the reflection coefficient

$$R = \left| \frac{B}{A} \right| = \frac{1}{\frac{\hbar^4k^2}{m^2V_0^2} + 1}. \quad (2.51)$$

This result holds for both  $V_0 > 0$  and  $V_0 < 0$ . If  $V_0 > 0$  then  $E > 0$ . If  $V_0 < 0$  then we can also have  $E < 0$ : in this case, the solution will be

**Fig. 2.7** The potential of the square barrier with width  $a$  and height  $V_0$ .



$$u(x) = \begin{cases} P e^{-k'x} & \text{for } x > 0 \\ Q e^{k'x} & \text{for } x < 0 \end{cases}$$

where  $k' \equiv \sqrt{-2mE}/\hbar$ . The continuity conditions at  $x = 0$  will give

$$P = Q, \quad -k'P - k'Q = \frac{2m}{\hbar^2} V_0 P$$

giving  $k' = mV_0/\hbar^2$ . Hence there is only one allowed energy value, which is given by

$$E \equiv E_0 = -\frac{mV_0^2}{2\hbar^2}.$$

Then for  $E > 0$ , the reflection coefficient may be shown to be (see Problem 2.3)

$$R = \frac{|E|}{|E| + |E_0|}. \quad (2.52)$$

### 2.5.8 Square potential barrier

The potential of the square barrier is shown in Fig. 2.7. This is given by

$$V(x) = \begin{cases} 0 & \text{for } x < 0 \text{ and } x > a \\ V_0 > 0 & \text{for } 0 < x < a. \end{cases}$$

For  $E > V_0$ , the solution of the TISE is

$$u = A e^{ikx} + B e^{-ikx} \quad \text{for } x \leq 0 \quad (2.53)$$

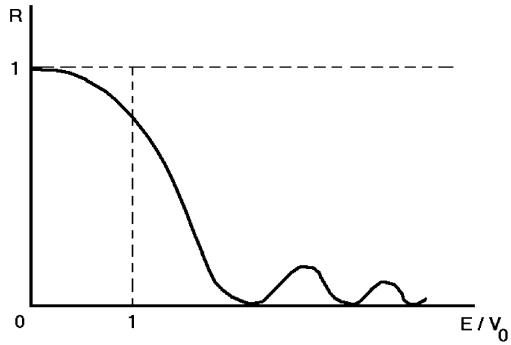
$$u = C e^{ikx} \quad \text{for } x \geq a \quad (2.54)$$

$$u = F e^{ik_2x} + G e^{-ik_2x} \quad \text{for } 0 \leq x \leq a \quad (2.55)$$

where

$$k \equiv \sqrt{\frac{2mE}{\hbar^2}}, \quad k_2 \equiv \sqrt{\frac{2m(E - V_0)}{\hbar^2}}.$$

**Fig. 2.8** Perfect transmission ( $R = 0, T = 1$ ) achieved when  $k_2 a = n\pi$  for  $n = 1, 2, \dots$



The continuity conditions at  $x = 0$  and  $x = a$  give

$$\begin{aligned} A + B &= F + G \\ ikA - ikB &= ik_2F - ik_2G \\ Ce^{ika} &= Fe^{ik_2a} + Ge^{-ik_2a} \\ ikCe^{ika} &= ik_2Fe^{ik_2a} - ik_2Ge^{-ik_2a}, \end{aligned}$$

which can be solved to give

$$\begin{aligned} B &= \frac{(k^2 - k_2^2)(1 - e^{2ik_2a})}{(k + k_2)^2 - (k - k_2)^2 e^{2ik_2a}} A, \\ C &= \frac{4kk_2 e^{i(k_2 - k)a}}{(k + k_2)^2 - (k - k_2)^2 e^{2ik_2a}} A. \end{aligned}$$

The transmission and reflection coefficients may then be calculated as

$$T = \left| \frac{C}{A} \right|^2 = \left( 1 + \frac{V_0^2 \sin^2(k_2 a)}{4E(E - V_0)} \right)^{-1}, \quad (2.56)$$

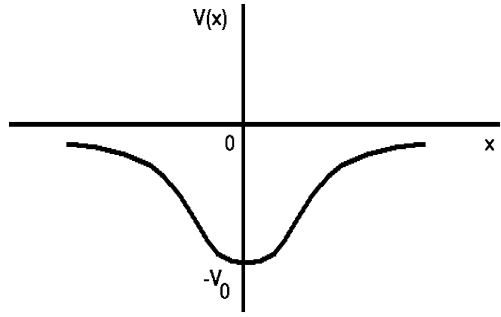
$$R = \left| \frac{B}{A} \right|^2 = \left( 1 + \frac{4E(E - V_0)}{V_0^2 \sin^2(k_2 a)} \right)^{-1}. \quad (2.57)$$

Perfect transmission ( $R = 0, T = 1$ ) is achieved when  $k_2 a = n\pi$  for  $n = 1, 2, \dots$ , that is, the barrier contains an integral number of half wavelengths. This is the case in the transmission of light through thin refracting layers. This situation is shown in Fig. 2.8.

In the case for which  $E < V_0$ , we may use the above results with  $k_2 = ik_3$ , together with the quantity  $k_3 \equiv \sqrt{2m(V_0 - E)}/\hbar$ . It then follows that

$$T = \left| \frac{C}{A} \right|^2 = \left( 1 + \frac{V_0^2 \sinh^2(k_3 a)}{4E(E - V_0)} \right)^{-1}, \quad (2.58)$$

**Fig. 2.9** The potential  
 $V(x) = \text{sech}^2 x$ .



$$R = \left| \frac{B}{A} \right|^2 = \left( 1 + \frac{4E(E - V_0)}{V_0^2 \sinh^2(k_3 a)} \right)^{-1}. \quad (2.59)$$

In the situation in which  $k_3 a \gg 1$ , then  $T \approx 16E(V_0 - E)V_0^{-2}e^{-2k_3 a}$  which is a very small quantity.

### 2.5.9 The $\text{sech}^2$ potential

We investigate the potential

$$V(x) = -V_0 \text{sech}^2 \alpha x \quad (2.60)$$

for  $V_0 > 0$ : this is plotted in Fig. 2.9. With a change of units, this potential is often used to illustrate multi-soliton solutions of the *Korteweg-de Vries (KdV) equation* (Korteweg and Vries 1895; Lax 1968). The corresponding TISE is

$$u'' + \frac{2m}{\hbar^2} (E + V_0 \text{sech}^2 \alpha x) u = 0. \quad (2.61)$$

In order to find a solution of this equation, it is convenient to make the substitutions

$$u \equiv \frac{w}{\cosh^s \alpha x}, \quad s \equiv \frac{1}{2} \left( -1 + \sqrt{1 + \frac{8mV_0}{\alpha^2 \hbar^2}} \right).$$

In terms of these new quantities, TISE then becomes

$$w'' - 2s\alpha(\tanh \alpha x)w' + \left( \alpha^2 s^2 + \frac{2mE}{\hbar^2} \right) w = 0.$$

On using the further new variables

$$y \equiv \sinh^2 \alpha x, \quad k \equiv \frac{1}{\alpha} \sqrt{-\frac{2mE}{\hbar^2}},$$

the equation becomes the *hypergeometric equation*

$$y(1+y)\frac{d^2w}{dy^2} + \left((1-s)y + \frac{1}{2}\right)\frac{dw}{dy} + \frac{1}{4}(s^2 - k^2)w = 0.$$

Since  $V(x) = V(-x)$ , then the solutions will have even and odd parity: they are

$$w_1 = F\left(-\frac{1}{2}s + \frac{1}{2}k, -\frac{1}{2}s - \frac{1}{2}k, \frac{1}{2}, -y\right), \quad (2.62)$$

$$w_2 = \sqrt{y}F\left(-\frac{1}{2}s + \frac{1}{2}k + \frac{1}{2}, -\frac{1}{2}s - \frac{1}{2}k + \frac{1}{2}, \frac{3}{2}, -y\right), \quad (2.63)$$

which are given in terms of the hypergeometric function  $F$ . We must be careful with the sign of  $x$  because as  $x$  changes sign,  $y$  retains the same sign but  $\sqrt{y}$  changes sign.

The cases  $E < 0$  and  $E > 0$ , and the KdV equation, will be considered separately:

#### Case $E < 0$

Look for a discrete spectrum. Now  $u = (1+y)^{-s/2}w_1 \rightarrow 0$  as  $y \rightarrow \infty$ . This implies that  $\frac{1}{2}k - \frac{1}{2}s$  is a negative integer or zero. The function  $F$  is then a polynomial of degree  $\frac{1}{2}s - \frac{1}{2}k$ . Similarly,  $u = (1+y)^{-s/2}w_2 \rightarrow 0$  as  $y \rightarrow \infty$ , and this implies that  $\frac{1}{2}k - \frac{1}{2}s + \frac{1}{2}$  is a negative integer. Hence  $s - k = n$  for  $n = 0, 1, 2, \dots, N$  for some integer  $N$ . Since  $s$  is fixed and  $k > 0$ , it follows that  $s - n > 0$ , and so  $n < s$ . Hence

$$2n < \sqrt{1 + \frac{8mV_0}{\alpha^2\hbar^2}} - 1,$$

and this determines the value of the integer  $N$ . Since

$$n = s - k = \frac{1}{2} \left( -1 + \sqrt{1 + \frac{8mV_0}{\alpha^2\hbar^2}} \right) - \frac{1}{\alpha} \sqrt{-\frac{2mE}{\hbar^2}},$$

then the energy levels are given by

$$E \equiv E_n = -\frac{\hbar^2\alpha^2}{8m} \left( -(1+2n) + \sqrt{1 + \frac{8mV_0}{\alpha^2\hbar^2}} \right)^2. \quad (2.64)$$

#### Case $E > 0$

Define  $\kappa \equiv \sqrt{2mE/\hbar^2}$ . Then  $k = i\kappa/\alpha$ , and the general solution becomes

$$w = \cosh^s \alpha x \left( C_1 F\left(-\frac{1}{2}s + \frac{1}{2}i\frac{\kappa}{\alpha}, -\frac{1}{2}s - \frac{1}{2}i\frac{\kappa}{\alpha}, \frac{1}{2}, -\sinh^2 \alpha x\right) \right)$$

$$+ C_2(\sinh \alpha x) F\left(-\frac{1}{2}s + \frac{1}{2}i\frac{\kappa}{\alpha} + \frac{1}{2}, -\frac{1}{2}s - \frac{1}{2}i\frac{\kappa}{\alpha} + \frac{1}{2}, \frac{3}{2}, -\sinh^2 \alpha x\right).$$

The ratio of  $C_1$  to  $C_2$  is chosen such that  $w$  has only the asymptotic form  $e^{i\kappa x}$  as  $x \rightarrow \infty$  (Gol'dman and Krivchenkov 1961). The reflection coefficient may then be calculated as

$$R = \frac{\cos^2(\frac{1}{2}\pi\sqrt{1 + \frac{8mV_0}{\alpha^2\hbar^2}})}{\sinh^2 \frac{\pi\kappa}{\alpha} + \cos^2(\frac{1}{2}\pi\sqrt{1 + \frac{8mV_0}{\alpha^2\hbar^2}})}. \quad (2.65)$$

### The KdV equation

The KdV equation can be obtained from the TISE by the replacement  $2m/\hbar^2 \rightarrow 1$ . Then in this case,

$$E_n = -\frac{\alpha^2}{4} \left( -(1+2n) + \sqrt{1 + \frac{4V_0}{\alpha^2}} \right)^2$$

with

$$2n < \sqrt{1 + \frac{4V_0}{\alpha^2}} - 1$$

and

$$R = \frac{\cos^2(\frac{1}{2}\pi\sqrt{1 + \frac{4V_0}{\alpha^2}})}{\sinh^2 \frac{\pi\kappa}{\alpha} + \cos^2(\frac{1}{2}\pi\sqrt{1 + \frac{4V_0}{\alpha^2}}}.$$

Two special cases are commonly associated with these results:

1.  $V(x) = -6 \operatorname{sech}^2 x$ , giving  $\alpha = 1$  and  $V_0 = 6$ . Then  $2n < \sqrt{25} - 1 = 4$ , or  $n = 0, 1$ . The energy levels are

$$E_0 = -\frac{1}{4}(-1+5)^2 = -4, \quad E_1 = -\frac{1}{4}(-(1+2)+5)^2 = -1,$$

and

$$R = \cos^2\left(\frac{1}{2}\pi\sqrt{1+24}\right) = 0.$$

2.  $V(x) = -2 \operatorname{sech}^2 x$ , giving  $\alpha = 1$  and  $V_0 = 2$ . Then  $2n < \sqrt{9} - 1 = 2$ , or  $n = 0$ . Hence there is only one energy value

$$E_0 = -\frac{1}{4}(-1+\sqrt{9})^2 = -1,$$

and

$$R = \cos^2\left(\frac{1}{2}\pi\sqrt{1+8}\right) = 0.$$

## 2.6 Operators and observables

Equations (2.6) and (2.7), namely

$$\left(i\hbar\frac{\partial}{\partial t}\right)\Psi = E\Psi \quad \text{and} \quad (2.66)$$

$$\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi = p\Psi, \quad (2.67)$$

suggest that to each observable there corresponds an *operator*, such that for each observable, the operator acting on a function produces the corresponding measure multiplied by that function. If the suffix *op* denotes the corresponding operator, the observables met so far suggest the following associations:

$$\text{momentum: } \mathbf{p}_{op} = -i\hbar\nabla$$

$$\text{energy: } E_{op} = i\hbar\frac{\partial}{\partial t}$$

$$\text{kinetic energy: } (K)_{op} = \frac{1}{2m}\mathbf{p}_{op}^2 = -\frac{\hbar^2}{2m}\nabla^2 \quad (\text{constant mass})$$

$$\text{potential energy: } V_{op} = V \quad (\text{multiplication operator})$$

$$\text{position: } \mathbf{r}_{op} = \mathbf{r} \quad (\text{multiplication operator})$$

$$\text{time: } t_{op} = t \quad (\text{multiplication operator})$$

From now on, it will be assumed that the observables are operators unless otherwise stated, and the suffix *op* will be omitted.

Let  $A$ ,  $B$ , etc. denote operators. Only *linear* operators  $A$ ,  $B$ , etc. will be considered. These have the properties that, for any complex numbers  $c$  and  $d$  and any functions  $\phi$  and  $\psi$ ,

$$\begin{aligned} (cA + dB)\psi &\equiv cA\psi + dB\psi \\ A(\psi + \phi) &= A\psi + A\phi \\ A(c\psi) &= cA\psi. \end{aligned} \quad (2.68)$$

The power  $A^q$  of an operator is defined inductively as  $(A^q)\psi = A^{q-1}(A\psi)$ . In this way it is possible to define a function  $f(A)$  of an operator  $A$  as a series expansion  $(\sum_{i=0}^N g_i A^i)$  of  $A$ .

Equations (2.66) and (2.67) are in the form of *eigenvalue equations*, in which an operator acting on a function (the *eigenfunction*) produces a number (the *eigenvalue*) multiplied by that function. Since appropriate boundary conditions on the eigenfunctions mean that the equation is valid for only a discrete set of eigenvalues, this is an appropriate way of building the discreteness of certain observable quantities into our theory.

Consider the eigenvalue equation

$$A\phi = a\phi \quad (2.69)$$

where  $A$  is an operator,  $\phi$  is a function, and  $a$  is a number. In general, there will be a set of eigenfunctions and eigenvalues corresponding to  $A$  when appropriate boundary conditions are applied to the solution:

$$A\phi_n = a_n\phi_n, \quad n = 1, 2, \dots \quad (2.70)$$

Hence, for a linear operator,

$$A\phi_n = a_n\phi_n \quad \Rightarrow \quad A^q\phi_n = a_n^q\phi_n, \quad (2.71)$$

and

$$f(A)\phi_n = \left( \sum_{i=0}^N g_i A^i \right) \phi_n = \sum_{i=0}^N g_i a_n^i \phi_n = f(a_n)\phi_n.$$

Hence

$$A\phi_n = a_n\phi_n \quad \Rightarrow \quad f(A)\phi_n = f(a_n)\phi_n. \quad (2.72)$$

**Definition 2.1.** The *inner product*  $(\psi, \phi)$  of any two functions  $\phi$  and  $\psi$  is

$$(\psi, \phi) \equiv \int \bar{\psi} \phi d^3 \mathbf{r}. \quad (2.73)$$

This inner product has the property that, for all functions  $\phi$  and  $\psi$ ,

$$\overline{(\psi, \phi)} = (\phi, \psi).$$

In particular, this result shows that the quantity  $(\psi, \psi)$  is real.

**Definition 2.2.** Functions  $\phi$  and  $\psi$  are *orthogonal* if  $\phi \neq 0$ ,  $\psi \neq 0$  and  $(\phi, \psi) = 0$ .

**Definition 2.3.** An operator  $A$  is *hermitian* if, for any functions  $\phi$  and  $\psi$ , we have

$$(\psi, A\phi) = (A\psi, \phi). \quad (2.74)$$

From the definition (2.73), it is easily verified that for any complex constants  $c$  and  $d$  and any functions  $\psi$ ,  $\psi_1$ ,  $\psi_2$ ,  $\phi$ ,  $\phi_1$  and  $\phi_2$ , then

$$(\psi, c\phi) = c(\psi, \phi) \quad (2.75)$$

$$(d\psi, \phi) = \bar{d}(\psi, \phi) \quad (2.76)$$

$$(\psi_1 + \psi_2, \phi_1 + \psi_2) = (\psi_1, \phi_1) + (\psi_1, \phi_2) + (\psi_2, \phi_1) + (\psi_2, \phi_2) \quad (2.77)$$

$$\overline{(\psi, \phi)} = (\phi, \psi) \quad (2.78)$$

$$(\psi, \psi) = 0 \quad \text{if and only if} \quad \psi = 0. \quad (2.79)$$

Now suppose that the operator  $A$  is hermitian. Then  $\overline{(\phi, A\phi)} = (A\phi, \phi) = (\phi, A\phi)$ . Hence

$$A \text{ hermitian} \quad \Rightarrow \quad (\phi, A\phi) \text{ is real.} \quad (2.80)$$



Further, if  $A$  is hermitian and

$$A\phi_n = a_n\phi_n \quad \text{with} \quad (\phi_n, \phi_n) \neq 0, \quad n = 1, 2, \dots,$$

then it follows that

$$a_n(\phi_n, \phi_n) = (\phi_n, a_n\phi_n) = (\phi_n, A\phi_n) = (A\phi_n, \phi_n) = (a_n\phi_n, \phi_n) = \overline{a_n}(\phi_n, \phi_n).$$

Hence  $\overline{a_n} = a_n$ , and so the eigenvalues of an hermitian operator are real. Further,

$$0 = (\phi_m, A\phi_n) - (A\phi_m, \phi_n) = (\phi_m, a_n\phi_n) - (a_m\phi_m, \phi_n) = (a_n - a_m)(\phi_m, \phi_n).$$

Hence if  $a_n \neq a_m$ , then  $(\phi_m, \phi_n) = 0$ . It follows that the eigenfunctions corresponding to distinct eigenvalues are orthogonal.

It is easily shown that the operators  $\mathbf{r}$ ,  $\mathbf{p}$  and the kinetic energy are hermitian. For example, since  $x$  is real, then

$$(\psi, x\phi) = \int \overline{\psi} x \phi d^3\mathbf{r} = \int x \overline{\psi} \phi d^3\mathbf{r} = (x\psi, \phi),$$

and

$$\begin{aligned} (\psi, p_x\phi) &= \int \overline{\psi} (-i\hbar\partial_x)\phi d^3\mathbf{r} = -i\hbar[\overline{\psi}\phi]_B + i\hbar \int (\partial_x\overline{\psi})\phi d^3\mathbf{r} \\ &= \int \overline{(-i\hbar\partial_x\psi)}\phi d^3\mathbf{r} = (p_x\psi, \phi) \end{aligned}$$

where we have used the fact that, for any real system, the functions  $\psi$  and  $\phi$  vanish at the boundaries  $B$ . Further, since  $K = \mathbf{p}^2/(2m)$  for a constant mass  $m$ , then

$$(\psi, K\phi) = \left( \psi, \frac{1}{2m}\mathbf{p}\mathbf{p}\phi \right) = \frac{1}{2m} (\psi, \mathbf{p}\mathbf{p}\phi) = \frac{1}{2m} (\mathbf{p}\mathbf{p}\psi, \phi) = (K\psi, \phi)$$

since  $m$  is real and  $\mathbf{p}$  is hermitian. Hence the kinetic energy operator  $K$  is hermitian.

Hermitian operators are very important in quantum mechanics. If we associate the eigenvalues and expectation values of operators with observed values, then we want these eigenvalues to be real. Hermitian operators have real eigenvalues, and we will see later that we postulate that an observable may be represented by a linear hermitian operator. However, an operator does not need to be hermitian to have real eigenvalues: for example, the operator  $H \equiv p^2 + ix^3$  is not hermitian (prove this) but it does have real eigenvalues. Later, however, when we seek an operator which represents an observable (in particular, the operator which represents kinetic energy for a particle with a position-dependent mass), we will always look for a hermitian operator. In that way, we can be sure that the operator will give real eigenvalues.

If the eigenfunctions  $\phi_n$  are normalised, that is,  $\int |\phi_n|^2 d^3\mathbf{r} = 1$ , then  $(\phi_n, \phi_n) = 1$ . Hence if  $\phi_n$  and  $\phi_m$  are normalised and belong to different eigenvalues, we have

$$(\phi_n, \phi_m) = \int \overline{\phi_n} \phi_m d^3 \mathbf{r} = \delta_{mn}. \quad (2.81)$$

In this case, we say that the  $\{\phi_n : n = 1, 2, \dots\}$  form an *orthonormal set*.

**Definition 2.4.** An eigenvalue is *non-degenerate* when there corresponds to it only one eigenfunction.

**Definition 2.5.** An eigenvalue is *degenerate* when there corresponds to it more than one eigenfunction. If, to the eigenvalue  $a_n$  there correspond the distinct eigenfunctions  $\phi_{n1}, \phi_{n2}, \dots, \phi_{np}$ , that is,  $A\phi_{ni} = a_n\phi_{ni}$ , ( $i = 1, \dots, p$ ), then we say that  $a_n$  is *p-fold degenerate*.

Any linear combination of the members of the set  $\{\phi_{ni}\}$  is also an eigenfunction corresponding to the eigenvalue  $a_n$ . The members of this set are not necessarily orthogonal among themselves, but a set of orthogonal eigenfunctions can be constructed from them using the *Schmidt Orthogonalisation Procedure*. For example, suppose that  $p = 2$ , and that  $(\phi_{n1}, \phi_{n2}) \neq 0$ . We require that  $\phi_{n1}$  and the linear combination  $\phi_{n1} + \alpha\phi_{n2}$  are orthogonal. Then

$$0 = (\phi_{n1}, \phi_{n1} + \alpha\phi_{n2}) = (\phi_{n1}, \phi_{n1}) + \alpha(\phi_{n1}, \phi_{n2})$$

giving  $\alpha = -(\phi_{n1}, \phi_{n1})/(\phi_{n1}, \phi_{n2})$ . Hence the eigenfunctions

$$\phi_{n1} \quad \text{and} \quad \phi_{n1} - \frac{(\phi_{n1}, \phi_{n1})}{(\phi_{n1}, \phi_{n2})} \phi_{n2}$$

are orthogonal.

**Definition 2.6.** The set of functions  $\phi_1, \phi_2, \dots, \phi_N$  is a *complete set* of orthonormal functions if

$$\sum_{i=1}^N d_i \phi_i = 0 \quad \Rightarrow \quad d_i = 0 \quad (i = 1, \dots, N)$$

and any arbitrary function can be expanded in terms of them:

$$\psi = \sum_{i=1}^N c_i \phi_i. \quad (2.82)$$

The coefficients  $c_i$  can be calculated, since

$$(\phi_j, \psi) = \left( \phi_j, \sum_i c_i \phi_i \right) = \sum_i c_i (\phi_j, \phi_i) = \sum_i c_i \delta_{ij} = c_j.$$

Hence Equation (2.82) becomes

$$\psi = \sum_{i=1}^N (\phi_i, \psi) \phi_i. \quad (2.83)$$

Suppose that the system is in state  $\Psi$ , and write  $\Psi = \sum_{i=1}^N c_i \phi_i$ . If  $\Psi$  is normalised, then

$$1 = (\Psi, \Psi) = \left( \sum_i c_i \phi_i, \sum_j c_j \phi_j \right) = \sum_i \sum_j \bar{c}_i c_j (\phi_i, \phi_j) = \sum_i |c_i|^2.$$

**Definition 2.7.** The *expectation value*  $\langle A \rangle$  of the operator  $A$  is defined as

$$\langle A \rangle \equiv (\Psi, A\Psi) = \left( \sum_i c_i \phi_i, A \sum_j c_j \phi_j \right) = \sum_i |c_i|^2 a_i. \quad (2.84)$$

This expectation value is real if  $A$  is hermitian since all the  $a_i$  will then be real. Note that the expectation value of any operator  $A$  is a linear combination of its eigenvalues; the significance of this linear combination will be discussed in Sect. 2.8.

**Definition 2.8.** For any operator  $A$  which is not necessarily hermitian, define the *adjoint* operator  $A^\times$  by

$$(\phi, A\psi) = (A^\times \phi, \psi) \quad \text{for all functions } \phi \text{ and } \psi. \quad (2.85)$$

Then for any operators  $A$  and  $B$  and any constant  $c$ , it is easily proved that

$$\begin{aligned} (A^\times)^\times &= A, & (cA)^\times &= \bar{c}A^\times, & (AB)^\times &= B^\times A^\times, \\ (A + A^\times)^\times &= (A + A^\times). \end{aligned} \quad (2.86)$$

Further, if  $f(x)$  is any complex function of  $x$ , then

$$[f(A)]^\times = \bar{f}(A^\times). \quad (2.87)$$

In particular, if  $A$  and  $B$  are both hermitian, then  $A^\times = A$ ,  $B^\times = B$  and  $(AB)^\times = BA$ .

**Definition 2.9.** An operator  $U$  is *unitary* if  $UU^\times = U^\times U = I$ .

Hence in this case,  $U^\times$  acts as the inverse operator. Also, for any functions  $\phi$  and  $\psi$ ,

$$(U\phi, U\psi) = (U^\times U\phi, \psi) = (\phi, \psi) \quad (U \text{ unitary}). \quad (2.88)$$

**Definition 2.10.** For any two operators  $A$  and  $B$ , their *commutator* is defined as

$$[A, B] \equiv AB - BA. \quad (2.89)$$

It is easily proved that if  $[A, B] = 0$  then  $[f(A), g(B)] = 0$  for functions  $f$  and  $g$ . For example, taking  $f(A) \equiv A^2$  and  $g(B) \equiv B$ , then the relation  $[A, B] = 0$  implies that

$$[A^2, B] = A^2 B - B A^2 = AAB - BAA = ABA - BAA = BAA - BAA = 0.$$

An important example of such a commutator occurs between position and momentum operators. For any function  $\psi$ ,

$$[x, p_x]\psi = x(-i\hbar\partial_x)\psi - (-i\hbar\partial_x)(x\psi) = -i\hbar x\partial_x\psi + i\hbar x\partial_x\psi + i\hbar\psi = i\hbar\psi.$$

A similar result holds between the energy and time operators. Some of the more important results are:

$$\begin{aligned} [x, p_x] &= [y, p_y] = [z, p_z] = i\hbar \\ [x, p_y] &= 0 \quad \text{etc.} \\ [x, y] &= [y, z] = [z, x] = 0 \\ [p_x, p_y] &= [p_y, p_z] = [p_z, p_x] = 0 \\ [x, t] &= [y, t] = [z, t] = 0 \\ [E, t] &= i\hbar. \end{aligned}$$

The following result will have an important consequence when we come to discuss the process of measurement in quantum mechanics in the next Section.

**Theorem 2.1.** *A necessary and sufficient condition for two operators to commute is that they possess a complete set of simultaneous orthogonal eigenfunctions.*

*Proof.* (i) Suppose that two linear operators  $A$  and  $B$  commute. Then  $AB = BA$ , and  $A$  commutes with any function  $f(B)$  of  $B$ :  $Af(B) = f(B)A$ . Further, let the eigenfunction  $\phi_n$  of  $A$  correspond to the eigenvalue  $a_n$ , and let the eigenfunction  $\xi_n$  of  $B$  correspond to the eigenvalue  $b_n$ . Since the set  $\{\xi_n\}$  is a complete set, then  $\phi_n$  can be expanded in terms of this set:

$$\phi_n = \sum_i c_{ni} \xi_i.$$

Let  $f(B)$  be an arbitrary function of  $B$ . Then

$$\begin{aligned} 0 &= Af(B)\phi_n - f(B)A\phi_n = Af(B)\phi_n - f(B)a_n\phi_n \\ &= (A - a_n)f(B) \sum_i c_{ni} \xi_i = (A - a_n) \sum_i c_{ni} f(b_i) \xi_i \\ &= \sum_i c_{ni} f(b_i) (A - a_n) \xi_i. \end{aligned}$$

Now, the function  $f$  is arbitrary. In particular, choose  $f$  such that  $f(x) = \delta_{x, b_k}$  for some eigenvalue  $b_k$  of  $B$ . Then

$$0 = \sum_{i(k)} c_{ni} (A - a_n) \xi_i$$

where  $\sum_{i(k)}$  denotes the summation over values of  $i$  for which  $b_i = b_k$ . Hence  $A\xi_i = a_n\xi_i$  for all those eigenfunctions  $\xi_i$  of  $B$  for which  $b_i = b_k$ .

(ii) Suppose that  $A$  and  $B$  possess a complete set of simultaneous eigenfunctions  $\phi_n$ :

$$A\phi_n = a_n\phi_n, \quad B\phi_n = b_n\phi_n.$$

Let  $\psi = \sum_i c_i \phi_i$  be an arbitrary function. Then

$$\begin{aligned} [A, B]\psi &= AB\psi - BA\psi = AB \sum_i c_i \phi_i - BA \sum_i c_i \phi_i \\ &= A \sum_i c_i b_i \phi_i - B \sum_i c_i a_i \phi_i = \sum_i c_i b_i a_i \phi_i - \sum_i c_i a_i b_i \phi_i \\ &= 0. \end{aligned}$$

Since the function  $\psi$  is arbitrary, then  $[A, B] = 0$ . This completes the proof.  $\square$

## 2.7 The Uncertainty Principle

Let  $A$  and  $B$  be two operators representing observables. Then  $A$  and  $B$  are hermitian. Let

$$[A, B] = iC \tag{2.90}$$

where  $C$  is an operator. Then for any functions  $\theta$  and  $\phi$ ,

$$\begin{aligned} (\theta, C\phi) &= \left( \theta, \frac{1}{i}(AB - BA)\phi \right) = \frac{1}{i}((BA - AB)\theta, \phi) = \left( -\frac{1}{i}(BA - AB)\theta, \phi \right) \\ &= (C\theta, \phi). \end{aligned}$$

Hence the operator  $C$  is hermitian. If  $\Psi$  is the state function of the system, then

$$\langle C \rangle = (\Psi, C\Psi) = (C\Psi, \Psi) = \overline{(\Psi, C\Psi)} = \overline{\langle C \rangle}$$

so that the expectation value  $\langle C \rangle$  of  $C$  is real. Now define the operators

$$\alpha \equiv A - \langle A \rangle \quad \text{and} \quad \beta \equiv B - \langle B \rangle$$

—these will both be hermitian, and

$$\alpha\beta - \beta\alpha = iC.$$

Now define  $\Delta a \equiv \sqrt{\langle \alpha^2 \rangle}$  and  $\Delta b \equiv \sqrt{\langle \beta^2 \rangle}$  to be the uncertainties in the measurements of the observables to which  $A$  and  $B$  correspond. Since  $\overline{(\beta\Psi, \alpha\Psi)} = (\alpha\Psi, \beta\Psi)$ , it follows that

$$\begin{aligned} 2i\text{Imag}(\beta\Psi, \alpha\Psi) &= (\beta\Psi, \alpha\Psi) - (\alpha\Psi, \beta\Psi) \\ &= (\Psi, \beta\alpha\Psi) - (\Psi, \alpha\beta\Psi) \\ &= (\Psi, [\beta, \alpha]\Psi) = -\langle [\alpha, \beta] \rangle \\ &= -i\langle C \rangle \end{aligned}$$

Hence

$$|\langle C \rangle| = 2|\text{Imag}(\beta\Psi, \alpha\Psi)| \leq 2|(\beta\Psi, \alpha\Psi)|. \quad (2.91)$$

Now for any functions  $f$  and  $g$  we have the *Schwartz inequality* (written in one dimension only)

$$\left( \int |f|^2 dx \right) \left( \int |g|^2 dx \right) \geq \left| \int \bar{f} g dx \right|^2,$$

or  $(f, f)(g, g) \geq |(f, g)|^2$ . Using this inequality with  $f \equiv \beta\Psi$  and  $g \equiv \alpha\Psi$ , Equation (2.91) becomes

$$\begin{aligned} \frac{1}{4}|\langle C \rangle|^2 &\leq |(\beta\Psi, \alpha\Psi)|^2 \\ &\leq (\beta\Psi, \beta\Psi)(\alpha\Psi, \alpha\Psi) = (\Psi, \beta^2\Psi)(\Psi, \alpha^2\Psi) = (\Delta a)^2(\Delta b)^2. \end{aligned}$$

Hence

$$\Delta a \cdot \Delta b \geq \frac{1}{2}|\langle C \rangle|. \quad (2.92)$$

This result shows that if  $\langle C \rangle \neq 0$ , then  $\Delta a$  and  $\Delta b$  cannot simultaneously both be zero. In terms of measurement, this is interpreted as meaning that the observables to which the operators  $A$  and  $B$  correspond cannot be measured simultaneously and precisely.

It has been shown in Sect. 2.6 that a necessary and sufficient condition for two linear operators to commute is that they possess a complete set of simultaneous eigenfunctions. Hence it follows from Equation (2.92) that two observables whose operators possess a complete set of simultaneous eigenfunctions can be simultaneously observable.

For example, we know that  $[x, p_x] = i\hbar$ , so that  $C = \hbar$  in this case. Result (2.92) then gives

$$\Delta x \cdot \Delta p_x \geq \frac{1}{2}\hbar,$$

so that  $x$  and  $p_x$  cannot be measured simultaneously and precisely. A similar result holds for the pairs  $\{y, p_y\}$  and  $\{z, p_z\}$ . However, since  $[x, p_y] = 0$  then we have  $\Delta x \cdot \Delta p_y \geq 0$  and so it is possible to measure the pair  $\{x, p_y\}$  simultaneously and precisely, with similar results for the remaining pairs. Further, since  $[E, t] = i\hbar$ , then  $\Delta E \cdot \Delta t \geq 0$ , and so the energy of a system and the time at which that energy is measured cannot be measured simultaneously and precisely.

Two simple examples will illustrate the application of the Uncertainty Principle.

1. Consider the creation of virtual  $\pi$ -mesons when a proton decays:  $p \rightarrow p + \pi^0$ . This process violates the classical principle of conservation of energy, since mass is seemingly created. However, the virtual particle lives for such a short time that the uncertainty principle does not allow us to see that the conservation principle is being violated. Writing  $\Delta t \cdot \Delta E \sim \hbar$  and taking  $\Delta E$  to be the pion mass

- (= 135 MeV), we find that  $\Delta t \sim \hbar/(\Delta E) \sim 5.2 \times 10^{-24}$  seconds: this is taken as a measure of the mean lifetime of the virtual pion.
2. When atoms radiate, electrons jump from an orbit with energy  $E_2$  to an orbit with lower energy  $E_1$ . The frequency of the emitted radiation is  $\nu$  where  $h\nu = E_2 - E_1$ . An excited state of an atom lasts approximately for a time  $\Delta t \sim 10^{-8}$  seconds. Hence by the uncertainty principle,  $\Delta E \neq 0$ , or equivalently  $\Delta\nu \neq 0$ . This uncertainty in the energy measurement manifests itself in the production of spectral lines of nonzero width.

## 2.8 The postulates of quantum mechanics

Having built up a somewhat loose picture of how quantum mechanics operates, and having found a mathematical framework for carrying these ideas, we may now formalise everything into a set of postulates which encapsulate these ideas.

### POSTULATE 1

A system is completely specified by a normalised state function  $\Psi$  which contains an arbitrary factor of modulus unity. This state function allows us to determine everything that can be known about the system.

The word “everything” in this postulates does not mean that we can know as much as we have come to expect from non-quantum classical mechanics. The determinism of classical mechanics is now replaced by a much lower expectation of knowledge based on the Uncertainty Principle. Now, the most we can predict are probabilities rather than certainties. The state function is normalised, which means that

$$|\Psi|^2 = (\Psi, \Psi) = 1, \quad (2.93)$$

and an arbitrary factor of modulus unity means that the state function remains normalised:

$$|e^{i\alpha}\Psi|^2 = |\Psi|^2. \quad (2.94)$$

### POSTULATE 2

To every observable there corresponds a linear hermitian operator for which a complete set of orthonormal eigenfunctions may be derived.

If the eigenvalues of the operator are non-degenerate, then the eigenfunctions are already orthogonal: all that is required is that this set be normalised. On the other hand, if the eigenvalues are degenerate, then a complete set of orthogonal eigenfunctions may be derived using the Schmidt Orthogonalisation procedure: this derived set may then be normalised.

*POSTULATE 3*

Let  $A$  be an operator representing an observable, and let  $a_n$  and  $\phi_n$  ( $n = 1, 2, \dots, N$ ) be the set of eigenvalues and eigenfunctions:

$$A\phi_n = a_n\phi_n, \quad (n = 1, 2, \dots, N). \quad (2.95)$$

Then the only possible outcome of a precise measurement of the observable is one of the eigenvalues  $a_n$ .

We need the  $a_n$  to be real if they are the outcomes of physical measurement: we have ensured this by taking the operator  $A$  to be hermitian. Further, this postulate does not say which of the eigenvalues will be observed in a precise measurement—only that one of them will be.

*POSTULATE 4*

An hermitian operator  $H$ , called the *Hamiltonian operator*, exists for each system. The time development of the system is governed by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi, \quad (2.96)$$

provided that the system is not disturbed.

In practice, this turns out to be a partial differential equation for which a solution is impossible to find except in the simplest and most artificial of cases. We very often end up having to make approximations, both mathematical and numerical, in order to get some sort of solution. The words “provided that the system is not disturbed” look harmless, until it is remembered that the process of measurement disturbs a system. Hence Equation (2.96) is valid for a system provided that we are not looking at it. We need some other way of describing the development of the system when we are looking at it.

*POSTULATE 5*

Let operator  $A$  correspond to an observable, and let  $a_n$  and  $\phi_n$  ( $n = 1, 2, \dots, N$ ) be the complete set of eigenvalues and orthonormal eigenfunctions of  $A$ . Order the eigenvalues so that  $a_1 \leq a_2 \leq a_3 \leq \dots \leq a_N$ . Let the state function be  $\Psi = \sum_{n=1}^N c_n \phi_n$ . Then the probability of finding a measured value of the observable in the given range  $a' \leq a \leq a''$  is

$$P(a', a'') \equiv \sum_i |c_i|^2 \quad (2.97)$$

where the summation is taken only over those values of  $i$  for which  $a_i$  lies in the given range.

One consequence of this postulate is that, if the eigenvalues are non-degenerate, then the probability that the eigenvalue  $a_i$  itself is measured is  $P(a_i, a_i) = |c_i|^2$ .



Further, with all summations running from 1 to  $N$ , we have

$$\begin{aligned} 1 = (\Psi, \Psi) &= \left( \sum_n c_n \phi_n, \sum_i c_i \phi_i \right) = \sum_n \sum_i \bar{c}_n c_i (\phi_n, \phi_i) \\ &= \sum_n \sum_i \bar{c}_n c_i \delta_{ni} = \sum_i |c_i|^2. \end{aligned}$$

Hence  $\sum_{i=1}^N |c_i|^2 = 1$ , and so the normalisation of the state function ensures that all the probabilities add to unity. We may evaluate the inner product

$$\begin{aligned} (\Psi, A\Psi) &= \left( \sum_i \phi_i, \sum_j c_j A\phi_j \right) = \sum_i \sum_j \bar{c}_i c_j a_j (\phi_i, \phi_j) \\ &= \sum_{i=1}^N |c_i|^2 a_i = \sum_{i=1}^N P(a_i, a_i) a_i. \end{aligned} \quad (2.98)$$

This quantity corresponds in some sense to the average value of the operator  $A$ , and is the expectation value defined in Equation (2.84). Finally, suppose that we know that the system is definitely in state  $\Psi = \phi_n$ . Then

$$\phi_n = \sum_{i=1}^N c_i \phi_i \quad \Rightarrow \quad c_n = 1 \text{ and } c_{(i \neq n)} = 0.$$

Hence the probability of measuring the value  $a_n$  is  $|c_n|^2 = 1$ : that is, we are certain to measure the value  $a_n$ .

### POSTULATE 6

Suppose a measurement is made of the observable to which the operator  $A$  corresponds, and the result is seen to lie in the range  $a' \leq a \leq a''$ . Then immediately after the measurement, the system is in the state

$$\Psi' = \frac{\sum_i c_j \phi_j}{\sqrt{\sum_j |c_j|^2}} \quad (2.99)$$

where the summations are over those values of  $j$  for which  $a' \leq a_j \leq a''$ .

Equation (2.96) describes how the system develops when we are not looking at it. Postulate 6 describes how the system develops when we are looking at it: the effect of this measurement on the state function is called the *collapse of the wave packet*. In practise, the differential equation Equation (2.96) governs the smooth development of the system when initial conditions are given. If a measurement is then made on the system at a later time, the wave packet collapses as described. The system subsequently develops according to Equation (2.96) using the new initial condition given by Equation (2.99). Note that the denominator on the right hand

side of Equation (2.99) is merely the inverse of the normalisation factor. Finally, if  $a' = a'' = a_i$ , then we have measured  $a_i$  exactly, and then

$$\Psi' = \frac{\sum_j c_j \phi_j}{\sqrt{\sum_j |c_j|^2}}$$

(where the summations are over those values of  $j$  for which  $\phi_j$ ) is an eigenfunction corresponding to the eigenvalue  $a_i$ . In particular, for non-degenerate  $a_i$ , the summation reduces to one term  $\Psi' = (c_i/|c_i|)\phi_i$ .

## 2.9 The harmonic oscillator

The study of the quantised harmonic oscillator is important in such fields as atomic vibrations and quantised wave fields. Classically, the one dimensional harmonic oscillator consists of a particle of mass  $m$  moving along the  $x$ -axis under the action of a force  $\mu|x|$  directed towards the origin  $O$ , where  $\mu$  is a positive constant. Its equation of motion is  $m\ddot{x} = -\mu x$ , or  $\ddot{x} = -\omega_c^2 x$  where  $\omega_c \equiv \sqrt{\mu/m}$  is the classical circular frequency. Its potential is  $V(x)$  where  $dV/dx = \mu x$ , or

$$V(x) = \frac{1}{2}\mu x^2 \quad (2.100)$$

which is determined up to an additive constant.

The equivalent quantum problem gives rise to the TISE

$$-\frac{\hbar^2}{2m} \frac{d^2 u(x)}{dx^2} + \frac{1}{2}\mu x^2 u(x) = E u(x). \quad (2.101)$$

It is required to find the energy eigenvalues  $E$  and eigenfunctions  $u(x)$  which satisfy the conditions that  $u(x)$  is finite everywhere, and  $u(x) \rightarrow 0$  as  $|x| \rightarrow \infty$ .

Although this equation looks simple, getting the solution is not a straightforward matter. Two methods will be described in order to generate the solution. The first method will be to solve the differential equation in terms of Hermite polynomials. This method will be used to generate properties of the solution which are useful when we come to evaluate integrals based on the solution. The second method will use the elegant *ladder operator* approach.

### 2.9.1 Solution of the differential equation

In this section, the purely algebraic manipulations will be left to the reader to complete. Define positive constants  $\alpha$  and  $\lambda$ , and a new independent variable  $\xi$ , by

$$\alpha^4 \equiv \frac{m\mu}{\hbar^2}, \quad \lambda^2 \equiv \frac{4E^2m}{\hbar^2\mu}, \quad \xi \equiv \alpha x. \quad (2.102)$$

Then writing  $w(\xi) \equiv u(x)$ , Equation (2.101) becomes

$$w'' + (\lambda - \xi^2)w = 0 \quad (2.103)$$

where primes denote differentiation with respect to  $\xi$ . Now make the substitution

$$w(\xi) \equiv H(\xi)e^{-\frac{1}{2}\xi^2} \quad (2.104)$$

into Equation (2.103) and obtain an equation for  $H(\xi)$ . Note that the function  $H(\xi)$  is not to be confused with the hamiltonian operator: no conflict of notation should arise in this section. The resulting equation is

$$H'' - 2\xi H' + (\lambda - 1)H = 0. \quad (2.105)$$

We now proceed by looking for a series solution of the form

$$H(\xi) = \xi^s(a_0 + a_1\xi + a_2\xi^2 + \dots) \quad (2.106)$$

where  $a_0 \neq 0$  and  $s \geq 0$ . This last condition ensures that  $H$  does not diverge at  $\xi = 0$ . The series is substituted into Equation (2.105), and coefficients of the various powers of  $\xi$  are set to zero. The first two coefficients give

$$s(s-1)a_0 = 0, \quad (s+1)sa_1 = 0,$$

while the evaluation of the general coefficient gives

$$(s+r+2)(s+r+1)a_{r+2} - (2s+2r+1-\lambda)a_r = 0. \quad (2.107)$$

The first of these equations shows that  $s = 0$  or  $s = 1$ . The second equation shows that  $a_1 = 0$  if  $s = 1$ , or that both  $s$  and  $a_1$  can be zero. Note that Equation (2.107) will give all the even-indexed coefficients  $a_2, a_4, a_6$  etc. proportional to  $a_0$ , and will give all of the odd-indexed coefficients proportional to  $a_1$ . Hence the series for  $H(\xi)$  splits into two alternating series—one proportional to  $a_0$  and the other proportional to  $a_1$ . Now

$$\begin{aligned} \frac{a_{r+2}}{a_r} &= \frac{2s+2r+1-\lambda}{(s+r+2)(s+r+1)} \\ &\rightarrow \frac{2}{r} \quad \text{as } r \rightarrow \infty, \end{aligned}$$

which is exactly the behaviour of the corresponding series for the function  $\xi^n e^{\xi^2}$ . Hence this comparison test shows that the series for  $H(\xi)$  would diverge if it were allowed to continue as an infinite series. In order to avoid this, the values of  $\lambda$  must be such that the series terminates. Since  $a_0$  is not zero, we must terminate this part

of the series to a polynomial, and we must not allow the other alternating series to start, otherwise it would leapfrog the  $a_0$  series and continue indefinitely. Hence we must take  $a_1 = 0$ , and if  $a_R$  is the last coefficient, we must have  $a_{R+2} = 0$ . It then follows from Equation (2.107) that

$$2s + 2R + 1 - \lambda = 0,$$

or  $\lambda = 2s + 2R + 1$ . Hence taking both of the cases  $s = 0$  or  $s = 1$  into account,  $\lambda$  must be of the form

$$\lambda = 2n + 1, \quad (n = 0, 1, 2, \dots). \quad (2.108)$$

Recalling that  $\lambda = 2E/(\hbar\omega_c)$ , it follows that the quantised energy levels are

$$E \equiv E_n = \left(n + \frac{1}{2}\right) \hbar\omega_c, \quad (n = 0, 1, 2, \dots). \quad (2.109)$$

The lowest, or *groundstate*, energy is

$$E_0 = \frac{1}{2} \hbar\omega_c. \quad (2.110)$$

From Equation (2.105), it can be seen that the function  $H_n(\xi)$  associated with the energy eigenvalue  $E_n$  will satisfy the equation

$$H_n'' - 2\xi H_n' + 2n H_n = 0, \quad (2.111)$$

and the eigenfunction corresponding to the energy level will be

$$u_n(x) = N_n H_n(\alpha x) e^{-\frac{1}{2}\alpha^2 x^2} \quad (2.112)$$

where  $N_n$  is the normalisation factor which will be found later.

The function  $H_n$  is called the *n*th *Hermite Polynomial*. Because of the leapfrog properties of the coefficients  $a_r$  in the expansion of  $H_n$ , the expansion splits into a part which is even in  $\xi$  and a part which is odd. One of these parts must terminate, while the other must be set to zero. Hence  $H_n(\xi)$  is either an even or odd function of  $\xi$ . Since the term  $e^{\frac{1}{2}\xi^2}$  is an even function of  $\xi$ , then it can be seen from Equation (2.104) that the eigenfunction  $u_n(x)$  is either even or odd.

Properties of the Hermite polynomials will now be derived which will be useful in evaluating the integrals involved in the determination of expectation values of operators. Consider the *generating function*  $G$  which generates a set of functions  $A_n(\xi)$ :

$$\begin{aligned} G(\xi, \sigma) &\equiv e^{\xi^2 - (\sigma - \xi)^2} = e^{-\sigma^2 + 2\sigma\xi} \\ &\equiv \sum_{n=0}^{\infty} \frac{1}{n!} A_n(\xi) \sigma^n, \end{aligned} \quad (2.113)$$

where  $0! = 1$  is taken by convention. By evaluating  $\partial G/\partial \xi$ , it may be shown that

$$\sum_{n=0}^{\infty} \frac{2}{n!} A_n(\xi) \sigma^{n+1} = \sum_{n=0}^{\infty} \frac{1}{n!} A'_n(\xi) \sigma^n,$$

from which it follows that

$$A'_n = 2n A_{n-1}. \quad (2.114)$$

Similarly, by evaluating  $\partial G/\partial \sigma$ , it may be shown that

$$\sum_{n=0}^{\infty} \frac{1}{n!} (-2\sigma + 2\xi) A_n(\xi) \sigma^n = \sum_{n=0}^{\infty} \frac{1}{(n-1)!} A_n(\xi) \sigma^{n-1},$$

from which it follows that

$$A_{n+1} = 2\xi A_n - 2n A_{n-1} = 2\xi A_n - A'_n.$$

On differentiating this result, and using Equation (2.114), it follows that

$$A''_n - 2\xi A'_n + 2n A_n = 0$$

—this is just the Equation (2.111) which was found for the Hermite polynomials. Hence  $G(\xi, \sigma)$  is the generating function for these polynomials. Now

$$\frac{\partial^n G}{\partial \sigma^n} = e^{\xi^2} \frac{\partial^n}{\partial \sigma^n} e^{-(\sigma-\xi)^2} = (-1)^n e^{\xi^2} \frac{\partial^n}{\partial \xi^n} e^{-(\sigma-\xi)^2},$$

and so it follows from Equation (2.113) that

$$H_n(\xi) = \left( \frac{\partial^n G}{\partial \sigma^n} \right)_{\sigma=0} = (-1)^n e^{\xi^2} \frac{\partial^n}{\partial \xi^n} e^{-\xi^2}. \quad (2.115)$$

The first four polynomials are easily calculated as

$$\begin{aligned} H_0(\xi) &= 1 \\ H_1(\xi) &= 2\xi \\ H_2(\xi) &= 4\xi^2 - 2 \\ H_3(\xi) &= 8\xi^3 - 12\xi. \end{aligned}$$

Note how each polynomial is either an even or an odd function of  $\xi$ .

Finally, the orthonormal properties of the energy eigenfunctions can be derived. By evaluating

$$\int_{-\infty}^{\infty} G(\xi, \sigma) G(\xi, \tau) e^{-\xi^2} d\xi$$

using Equation (2.113), we obtain

$$\begin{aligned}
 & \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{\sigma^n \tau^m}{n!m!} \int_{-\infty}^{\infty} H_n(\xi) H_m(\xi) e^{-\xi^2} d\xi \\
 &= \int_{-\infty}^{\infty} e^{-\sigma^2 + 2\sigma\xi} \cdot e^{-\tau^2 + 2\tau\xi} \cdot e^{-\xi^2} d\xi \\
 &= \int_{-\infty}^{\infty} e^{-(\xi - \sigma - \tau)^2 + 2\sigma\tau} d\xi = \sqrt{\pi} e^{2\sigma\tau} \\
 &= \sqrt{\pi} \sum_{r=0}^{\infty} \frac{1}{r!} (2\sigma\tau)^r.
 \end{aligned}$$

Then, by equating coefficients of various powers of  $\sigma$  and  $\tau$ , we get

$$\int_{-\infty}^{\infty} H_n(\xi) H_m(\xi) e^{-\xi^2} d\xi = \sqrt{\pi} 2^n n! \delta_{mn}. \quad (2.116)$$

The normalisation factor  $N_n$  can now be found, remembering that  $0! = 1$ . We require

$$1 = \int_{-\infty}^{\infty} |u_n(x)|^2 dx = \frac{N_n^2}{\alpha} \int_{-\infty}^{\infty} H_n(\xi)^2 e^{-\xi^2} d\xi = \frac{N_n^2}{\alpha} \sqrt{\pi} 2^n n!$$

and hence

$$N_n = \sqrt{\frac{\alpha}{\sqrt{\pi} 2^n n!}}. \quad (2.117)$$

Therefore the complete normalised solution of the TISE for the harmonic oscillator is

$$u_n(x) = \sqrt{\frac{\alpha}{\sqrt{\pi} 2^n n!}} H_n(\alpha x) e^{-\frac{1}{2}\alpha^2 x^2}, \quad (2.118)$$

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega_c, \quad \text{where} \quad (2.119)$$

$$\alpha^4 = \frac{\mu m}{\hbar^2}. \quad (2.120)$$

Note that  $n$  is uniquely determined for a fixed value of  $E_n$ , and  $H_n(\xi)$  is uniquely determined by the value of  $n$ . Hence the eigenvalues  $E_n$  are non degenerate in this one dimensional case, but we shall see how degeneracy may occur for an oscillator in more than one dimension.

### 2.9.2 The ladder operator method

The ladder operator method is an extremely elegant method of obtaining the energy eigenvalues of Equation (2.101). The method will be encountered again when dealing with spin angular momentum.

Operators  $r_+$  and  $r_-$  will be used to climb up and down the ladder whose rungs are the energy eigenvalues. Equation (2.101) can be written in the form

$$Hu_n = E_n u_n$$

where the Hamiltonian operator  $H$  (now not to be confused with the Hermite polynomial) is given by

$$H \equiv \frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} \mu x^2 = \frac{1}{2m} p^2 + \frac{1}{2} \mu x^2$$

and  $p = -i\hbar\partial/\partial x$  is the momentum operator in the  $x$  direction. Now define the ladder operators

$$r_+ \equiv \frac{1}{\sqrt{2m}} p + i\sqrt{\frac{\mu}{2}} x \quad (2.121)$$

$$r_- \equiv \frac{1}{\sqrt{2m}} p - i\sqrt{\frac{\mu}{2}} x. \quad (2.122)$$

Recalling that

$$[x, p] \equiv xp - px = i\hbar, \quad (2.123)$$

then it can be easily shown that

$$(r_+)^{\times} = r_-, \quad (r_-)^{\times} = r_+, \quad (2.124)$$

$$H = r_+ r_- + \frac{1}{2} \hbar \omega_c = r_- r_+ - \frac{1}{2} \hbar \omega_c, \quad (2.125)$$

$$[r_+, r_-] = -\hbar \omega_c, \quad (2.126)$$

$$[H, r_{\pm}] = \pm \hbar \omega_c r_{\pm}. \quad (2.127)$$

It can now be shown that the effect of the ladder operator  $r_+$  on  $u_n$ , which corresponds to the energy eigenvalue  $E_n$ , is to produce the eigenvalue  $E_n + \hbar \omega_c$ , while the effect of the operator  $r_-$  produces the eigenvalue  $E_n - \hbar \omega_c$ . Since  $Hu_n = E_n u_n$ , and since  $r_+$  is a linear operator, then

$$\begin{aligned} H(r_+ u_n) &= (H r_+) u_n \\ &= (r_+ H + \hbar \omega_c r_+) u_n \\ &= r_+ E_n u_n + \hbar \omega_c r_+ u_n \\ &= (E_n + \hbar \omega_c) r_+ u_n. \end{aligned} \quad (2.128)$$

Similarly, it can be shown that

$$H(r_-u_n) = (E_n - \hbar\omega_c)r_-u_n. \quad (2.129)$$

This demonstrates that the difference in consecutive energy eigenvalues is  $\hbar\omega_c$ , giving the result

$$E_n = E_0 + n\hbar\omega_c. \quad (2.130)$$

It now remains to determine the groundstate energy  $E_0$ , given by  $Hu_0 = E_0u_0$ . Applying the result of Equation (2.129), we have

$$H(r_-u_0) = (E_0 - \hbar\omega_c)r_-u_0.$$

However, since  $E_0$  is the lowest eigenvalue, this equation has seemingly produced an even lower one. This contradiction is resolved if we take  $r_-u_0 = 0$ . Then  $r_+(r_-u_0) = 0$ , and it follows from Equation (2.125) that

$$Hu_0 - \frac{1}{2}\hbar\omega_cu_0 = 0, \quad \text{or} \quad \left(E_0 - \frac{1}{2}\hbar\omega_c\right)u_0 = 0.$$

Since  $u_0$  is not identically zero, this result can only hold if  $E_0 = \frac{1}{2}\hbar\omega_c$ . The energy levels are then given from Equation (2.130) as

$$E_n = \frac{1}{2}\hbar\omega_c + n\hbar\omega_c = \left(n + \frac{1}{2}\right)\hbar\omega_c$$

as before.

Since the energy levels are non-degenerate, then Equation (2.128) shows that  $u_{n+1}$  is some multiple of  $r_+u_n$ :

$$u_{n+1} = c_{n+1}r_+u_n. \quad (2.131)$$

This multiple  $c_{n+1}$  can be found by normalisation:

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} \overline{u_n}u_ndx, \\ 1 &= \int_{-\infty}^{\infty} \overline{u_{n+1}}u_{n+1}dx = \int_{-\infty}^{\infty} \overline{c_{n+1}r_+u_n}c_{n+1}r_+u_ndx \\ &= |c_{n+1}|^2 \int_{-\infty}^{\infty} \overline{u_n}(r_+)^{\times}r_+u_ndx = |c_{n+1}|^2 \int_{-\infty}^{\infty} \overline{u_n}(r_-r_+)u_ndx \\ &= |c_{n+1}|^2 \int_{-\infty}^{\infty} \overline{u_n} \left(H + \frac{1}{2}\hbar\omega_c\right)u_ndx = |c_{n+1}|^2 \int_{-\infty}^{\infty} \overline{u_n} \left(E_n + \frac{1}{2}\hbar\omega_c\right)u_ndx \\ &= |c_{n+1}|^2(n+1)\hbar\omega_c. \end{aligned}$$



Hence

$$c_{n+1} = \frac{1}{\sqrt{\hbar\omega_c(n+1)}},$$

giving

$$u_{n+1} = c_{n+1}r_+u_n = \frac{1}{\sqrt{\hbar\omega_c(n+1)}}r_+u_n,$$

from which it follows that

$$u_n = \frac{1}{\sqrt{(\hbar\omega_c)^n n!}}(r_+)^n u_0. \quad (2.132)$$

### 2.9.3 Oscillations in more than one dimension

For oscillations in three dimensions, the generalisation of the potential energy given by Equation (2.100) is

$$V(x, y, z) = \frac{1}{2}\mu_1 x^2 + \frac{1}{2}\mu_2 y^2 + \frac{1}{2}\mu_3 z^2$$

where the positive constants  $\mu_1$ ,  $\mu_2$  and  $\mu_3$  are not necessarily equal. The TISE becomes

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) + \frac{1}{2}(\mu_1 x^2 + \mu_2 y^2 + \mu_3 z^2)u = Eu, \quad (2.133)$$

where  $u \equiv u(x, y, z)$ . We look for a separable solution

$$u(x, y, z) = X(x)Y(y)Z(z)$$

and substitute into Equation (2.133):

$$-\frac{\hbar^2}{2m} \left( \frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z} \right) + \frac{1}{2}(\mu_1 x^2 + \mu_2 y^2 + \mu_3 z^2) = E,$$

or

$$-\frac{\hbar^2}{2m} \frac{X''}{X} + \frac{1}{2}\mu_1 x^2 = E + \frac{\hbar^2}{2m} \left( \frac{Y''}{Y} + \frac{Z''}{Z} \right) - \frac{1}{2}(\mu_2 y^2 + \mu_3 z^2).$$

Since the left hand side is a function of  $x$  only, and the right hand side is a function of  $y$  and  $z$  only, then each side must be a constant  $E_1$ , giving

$$-\frac{\hbar^2}{2m} X'' + \frac{1}{2}\mu_1 x^2 X = E_1 X.$$

The function  $X(x)$  must have the same boundary conditions as the solution of the one dimensional oscillator, and hence, as before, the allowed energy levels associated with motion along the  $x$ -direction are

$$E_{1n_1} = \left(n_1 + \frac{1}{2}\right) \hbar \sqrt{\frac{\mu_1}{m}}, \quad (n_1 = 0, 1, 2, \dots)$$

with associated energy eigenfunctions

$$X_{n_1}(x) = \sqrt{\frac{\alpha_1}{\sqrt{\pi} 2^{n_1} n_1!}} H_{n_1}(\alpha_1 x) e^{-\frac{1}{2}\alpha_1^2 x^2}$$

where

$$\alpha_1^4 = \frac{\mu_1 m}{\hbar^2}.$$

Similar solutions are associated with the  $y$ - and  $z$ -directions, with  $E_{2n_2}$  and  $E_{3n_3}$  being the energy eigenvalues associated with the motions in these directions. The total energy is therefore

$$\begin{aligned} E_{n_1 n_2 n_3} &= E_{1n_1} + E_{2n_2} + E_{3n_3} \\ &= \left(n_1 + \frac{1}{2}\right) \hbar \sqrt{\frac{\mu_1}{m}} + \left(n_2 + \frac{1}{2}\right) \hbar \sqrt{\frac{\mu_2}{m}} + \left(n_3 + \frac{1}{2}\right) \hbar \sqrt{\frac{\mu_3}{m}} \end{aligned}$$

where  $n_1, n_2$  and  $n_3$  are all non-negative integers.

Note that degeneracy occurs when  $\mu_1 = \mu_2 = \mu_3 \equiv \mu$ , for then

$$E_{n_1 n_2 n_3} = \left(n_1 + n_2 + n_3 + \frac{3}{2}\right) \hbar \sqrt{\frac{\mu}{m}},$$

giving

$$N \equiv n_1 + n_2 + n_3 = \frac{1}{\hbar} \sqrt{\frac{m}{\mu}} E_{n_1 n_2 n_3} - \frac{3}{2}.$$

Then for a given energy  $E_{n_1 n_2 n_3}$ , all eigensolutions with integers  $n_1, n_2$  and  $n_3$  which total to  $N$  will correspond to this given value. By counting these permutations, it is easy to show that the degeneracy of the energy level  $E$  is

$$\frac{1}{2}(N+1)(N+2),$$

where

$$N \equiv \frac{1}{\hbar} \sqrt{\frac{m}{\mu}} E - \frac{3}{2}.$$

Note that the symmetry imposes degeneracy on the energy levels. We shall see this process happening later when evaluating energy levels in the quantum wells found at the material interfaces in semiconductor devices.

### 2.9.4 The displaced harmonic oscillator

It is now shown that the potential energy of the harmonic oscillator may have linear terms added to it, resulting in the overall nature of the solution being unchanged. Returning to the one dimensional case, the potential energy can be generalised to the form

$$V(x) = \frac{1}{2}\mu x^2 + \varepsilon\mu x + b\mu \quad (2.134)$$

where  $\varepsilon$  and  $b$  are constants. The TISE can then be written

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2} + \left( \frac{1}{2}\mu(x + \varepsilon)^2 + b\mu - \varepsilon^2 \right) u = Eu,$$

or

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2} + \frac{1}{2}\mu(x + \varepsilon)^2 u = (E + \varepsilon^2 - b\mu)u.$$

On changing the independent variable from  $x$  to  $x_1 \equiv x + \varepsilon$ , with  $v(x_1) \equiv u(x)$ , this equation becomes

$$-\frac{\hbar^2}{2m} \frac{d^2 v}{dx_1^2} + \frac{1}{2}\mu x_1^2 v = (E + \varepsilon^2 - b\mu)v.$$

This has the same form as Equation (2.101), and hence a similar method of solution will give the condition

$$E_n + \varepsilon^2 - b\mu = \left(n + \frac{1}{2}\right) \hbar \sqrt{\frac{\mu}{m}}.$$

The energy levels are then

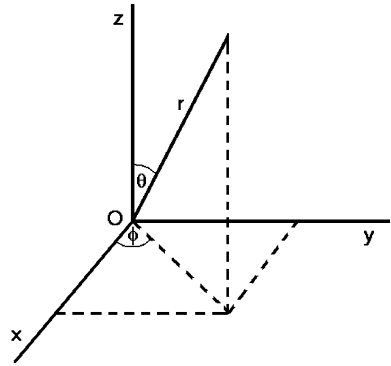
$$E_n = \left(n + \frac{1}{2}\right) \hbar \sqrt{\frac{\mu}{m}} - \varepsilon^2 + b\mu, \quad (n = 0, 1, 2, \dots).$$

Hence the energy levels are all displaced by the same amount  $b\mu - \varepsilon^2$ , and the centre of the oscillation is displaced from  $x = 0$  to  $x = -\varepsilon$ .

## 2.10 Spherically symmetric potentials

An important class of situations arises for those problems in which the potential depends only on the distance from a fixed point, and not on any angular distribution about that fixed point. In particular, the discussion of the hydrogen atom falls into this category.

**Fig. 2.10** The spherical polar coordinates  $r$ ,  $\theta$ , and  $\phi$ .



### 2.10.1 The Schrödinger equation in spherical polar coordinates

In problems involving a potential  $V(r)$  which depends only on the distance  $r$  from the centre  $O$ , it is most natural to use the spherical polar coordinates  $r$ ,  $\theta$ , and  $\phi$  shown in Fig. 2.10. The ranges of these coordinates are

$$0 \leq r, \quad 0 \leq \theta \leq \pi, \quad 0 \leq \phi \leq 2\pi.$$

The transformation between cartesian and spherical polar coordinates is given by

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta, \quad (2.135)$$

and the expression for  $\nabla^2$  in spherical polar coordinates is given by

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}. \quad (2.136)$$

In quantum mechanical problems involving a spherically symmetric potential, the quantity  $m$  normally denotes an integer. Consequently, particle mass will be denoted by  $m_e$ : the suffix  $e$  can denote the terms “electron” or, more generally, “effective”.

Using this expression in Equation (2.136), the TISE is

$$\begin{aligned} & -\frac{\hbar^2}{2m_e} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} u(r, \theta, \phi) \\ & + V(r)u(r, \theta, \phi) \\ & = Eu(r, \theta, \phi). \end{aligned} \quad (2.137)$$

It is required that the solution  $u(r, \theta, \phi)$  be finite and continuous everywhere. We look for a solution of the form

$$u(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

and use separation of variables to obtain the three equations

$$\frac{d^2\Phi}{d\phi^2} + f\Phi = 0, \quad (2.138)$$

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{d\Theta}{d\theta} \right) + \left( g - \frac{f}{\sin^2\theta} \right) \Theta = 0, \quad (2.139)$$

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left\{ \frac{2m_e}{\hbar^2} (E - V(r)) - \frac{g}{r^2} \right\} R = 0 \quad (2.140)$$

where  $f$  and  $g$  are constants of separation. Since the element of volume in spherical polar coordinates is  $r^2 \sin\theta \, dr \, d\theta \, d\phi$ , the normalisation condition is

$$\int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi r^2 \sin\theta |u(r, \theta, \phi)|^2 = 1,$$

or

$$\int_0^\infty r^2 |R(r)|^2 dr \int_0^\pi |\Theta(\theta)|^2 \sin\theta d\theta \int_0^{2\pi} d\phi |\Phi(\phi)|^2 = 1.$$

It can be seen from this result that each coordinate solution may be normalised separately.

Note that the potential function  $V(r)$  is contained only in the radial Equation (2.140). The angular solutions  $\Theta(\theta)$  and  $\Phi(\phi)$  are given in Equations (2.138) and (2.139). Consequently, the total angular part of the solution can be found without having to specify the form of  $V(r)$ .

### 2.10.2 Solution of the angular components

The solution of Equation (2.138) is easily obtained. For continuity, we require that  $\Phi(\phi + 2\pi) = \Phi(\phi)$  for all values of  $\phi$ . If  $f < 0$ , the solution must be written in terms of real exponentials  $\exp(\pm\sqrt{-f}\phi)$ , which will not satisfy this continuity requirement. Hence,  $f$  must be non-negative:  $f = m^2$  where  $m$  is real. The solution is then

$$\Phi(\phi) = Ae^{im\phi} + Be^{-im\phi}$$

where  $A$  and  $B$  are constants, and the above continuity condition will require that  $m = 0, \pm 1, \pm 2, \dots$ . Separate normalisation of this part of the solution means that

$$1 = \int_0^{2\pi} |\Phi(\phi)|^2 d\phi = 2\pi(|A|^2 + |B|^2).$$

Since there is no other condition which will provide the values of  $A$  and  $B$  separately, then without loss of generality we may take  $B = 0$  and  $A$  to be real, giving

$$\Phi(\phi) \equiv \Phi_n(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad (m = 0, \pm 1, \pm 2, \dots). \quad (2.141)$$

The solution of the Equation (2.139) for  $\Theta(\theta)$  is much more complicated. It involves a method using a series solution, much like the method which generated the Hermite polynomials for the linear harmonic oscillator. Using the fact that  $f = m^2$  where  $m$  is an integer, then Equation (2.139) is

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left( g - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0,$$

and using the substitution  $\omega \equiv \cos \theta$ ,  $P(\omega) \equiv \Theta(\theta)$ , this equation becomes

$$\frac{d}{d\omega} \left( (1 - \omega^2) \frac{dP}{d\omega} \right) + \left( g - \frac{m^2}{1 - \omega^2} \right) P = 0. \quad (2.142)$$

Since the value  $\omega^2 = 1$  relates to points on the  $z$ -axis, which is an arbitrary direction in space, we must ensure that the solution of this equation remains finite at  $\omega = \pm 1$ .

Of course, the function  $P(\omega)$  will depend on the value of  $m$  and so it will carry this index, but it will be omitted for the time being. The calculation leading to the solution for a general value of  $m$  is quite complicated, although the calculation for the case  $m = 0$  is relatively easy. Further, it turns out that the solution for a general value of  $m$  can be written in terms of the solution for which  $m = 0$ , and this simpler case will be considered first. For  $m = 0$ , Equation (2.142) becomes

$$\frac{d}{d\omega} \left( (1 - \omega^2) \frac{dP}{d\omega} \right) + gP = 0, \quad (2.143)$$

where  $g$  is a constant. Now look for a series solution

$$P(\omega) = \sum_{r=0}^{\infty} a_r \omega^r, \quad (2.144)$$

where the coefficients  $a_r$  are to be determined. Substitution into Equation (2.143) gives

$$\sum_{r=0}^{\infty} \{a_{r+2}(r+1)(r+2) - a_r[r(r+1) - g]\} \omega^r = 0.$$

Since this must be valid for all values of  $\omega$ , each coefficient must be zero, giving

$$\frac{a_{r+2}}{a_r} = \frac{r(r+1) - g}{(r+1)(r+2)}. \quad (2.145)$$

Note that this relation shows that the even coefficients  $a_2, a_4, a_6, \dots$  will be given in terms of  $a_0$ , and the odd coefficients  $a_3, a_5, a_7, \dots$  will be given in terms of  $a_1$ . Hence the series solution for  $P$  splits up into two separate series—one proportional to  $a_0$  and the other proportional to  $a_1$ . It can be seen from Equation (2.145) that

$a_{r+2}/a_r \rightarrow 1$  as  $r \rightarrow \infty$ , and so the series would diverge if this limit were allowed to happen. As in the case of the series solution for the Hermite polynomials, we must stop this happening by taking either  $a_0$  or  $a_1$  to be zero, and terminating the remaining series to a polynomial. If  $a_{r'}$  is the last term in the series, then it can be seen from Equation (2.145) that  $a_{r'+2} = 0$  giving  $g = r'(r' + 1)$ . Hence  $g$  has the form

$$g = l(l + 1) \quad (2.146)$$

where  $l \geq 0$  is an integer. We must take  $a_0 = 0$  if  $l$  is odd, and  $a_1 = 0$  if  $l$  is even, in order to avoid the leapfrogging of one sub-series to infinity. Hence the solution is either an even or an odd function of  $\omega$ . Equation (2.143) then becomes

$$\frac{d}{d\omega} \left( (1 - \omega^2) \frac{dP_l(\omega)}{d\omega} \right) + l(l + 1)P_l(\omega) = 0 \quad (2.147)$$

where we have now attached the suffix  $l$  to the solution. The polynomials  $P_l(\omega)$  are called *Legendre polynomials*, and it can be verified (Sneddon 1961) that their generating function is

$$\frac{1}{\sqrt{1 - 2\omega x + x^2}} = \sum_{l=0}^{\infty} P_l(\omega)x^l, \quad x < 1. \quad (2.148)$$

The first four polynomials can be calculated from Equations (2.145) and (2.146) as

$$\begin{aligned} P_0(\omega) &= 1 \\ P_1(\omega) &= \omega \\ P_2(\omega) &= \frac{1}{2}(3\omega^2 - 1) \\ P_3(\omega) &= \frac{1}{2}(5\omega^3 - 3\omega). \end{aligned}$$

Note how each polynomial is either an even or odd function of  $\omega$ .

We now return to the full Equation (2.142), remembering that its solution  $P(\omega)$  now depends on the integers  $l$  and  $m$ :  $P(\omega) \equiv P_l^m(\omega)$ . This equation is

$$\begin{aligned} \frac{d}{d\omega} \left( (1 - \omega^2) \frac{dP_l^m}{d\omega} \right) + \left( l(l + 1) - \frac{m^2}{1 - \omega^2} \right) P_l^m &= 0, \\ m = 0, \pm 1, \pm 2, \dots; \quad l = 0, 1, 2, \dots \end{aligned} \quad (2.149)$$

We again seek a series solution. A calculation, which is much more complex than for the case  $m = 0$ , gives the result (Sneddon 1961)

$$P_l^m(\omega) = (1 - \omega^2)^{\frac{1}{2}|m|} \frac{d^{|m|}}{d\omega^{|m|}} P_l(\omega), \quad (2.150)$$

and is called the *Associated Legendre polynomial*. Now  $P_l(\omega)$  is a polynomial of degree  $l$ . Hence the  $|m|$ th derivative of  $P_l(\omega)$  would be zero if  $|m| > l$ , since the derivative would vanish. This would give the physically unrealistic situation that the wave function, given in terms of  $P_l(\omega)$ , would vanish. Hence we must have  $|m| \leq l$ . This polynomial has the property

$$\int_0^\pi \overline{\Theta_l^m} \Theta_l^m \sin \theta d\theta = \int_{-1}^1 \overline{P_l^m} P_l^m d\omega = \frac{2}{2l+1} \frac{(l+|m|)!}{(l-|m|)!},$$

which provides the normalisation factor

$$\left[ \frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!} \right]^{\frac{1}{2}}.$$

Hence the total angular part of the solution, denoted by  $Y_{lm}(\theta, \phi)$ , to the spherically symmetric problem is

$$Y_{lm}(\theta, \phi) = \left[ \frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{\frac{1}{2}} P_l^m(\cos \theta) e^{im\phi}, \quad l \geq |m|. \quad (2.151)$$

These functions are called *spherical harmonics*. It is easily verified that the first few terms of the  $Y_{lm}$  are given by

$$\begin{aligned} Y_{00} &= \sqrt{\frac{1}{4\pi}} \\ Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos \theta \\ Y_{11} &= \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi} \\ Y_{1-1} &= \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}. \end{aligned}$$

See Problem 2.4.

### 2.10.3 Angular momentum

Classically, a particle with position vector  $\mathbf{r}$  and momentum  $\mathbf{p}$  has angular momentum  $\mathbf{M} = \mathbf{r} \times \mathbf{p}$ . Therefore the quantum mechanical operator corresponding to this classical angular momentum will be given by

$$\begin{aligned} \mathbf{M} &= \mathbf{r} \times \mathbf{p} \\ &= (x, y, z) \times \left( -i\hbar \frac{\partial}{\partial x}, -i\hbar \frac{\partial}{\partial y}, -i\hbar \frac{\partial}{\partial z} \right) \end{aligned}$$



$$\begin{aligned}
&= -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}, z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}, x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \\
&\equiv (M_x, M_y, M_z).
\end{aligned} \tag{2.152}$$

Using the coordinate transformation equations (2.135), these expressions can be written in terms of derivatives with respect to  $r$ ,  $\theta$  and  $\phi$ . For example,

$$\begin{aligned}
\frac{\partial}{\partial \phi} &= \frac{\partial x}{\partial \phi} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi} \frac{\partial}{\partial y} + \frac{\partial z}{\partial \phi} \frac{\partial}{\partial z} \\
&= -r \sin \theta \sin \phi \frac{\partial}{\partial x} + r \sin \theta \cos \phi \frac{\partial}{\partial y} + 0 \\
&= -y \frac{\partial}{\partial x} + x \frac{\partial}{\partial y} \\
&= \frac{M_x}{-i\hbar}.
\end{aligned}$$

Hence  $M_z = -i\hbar \partial/\partial \phi$ . Similar expressions can be found for  $M_x$  and  $M_y$ . The complete list is

$$M_x = i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \tag{2.153}$$

$$M_y = i\hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \tag{2.154}$$

$$M_z = -i\hbar \frac{\partial}{\partial \phi} \tag{2.155}$$

$$\begin{aligned}
M^2 &= M_x^2 + M_y^2 + M_z^2 \\
&= -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right].
\end{aligned} \tag{2.156}$$

Further, it follows that

$$\begin{aligned}
[M_x, M_y] &= -\hbar^2 \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\
&\quad + \hbar^2 \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\
&= -\hbar^2 \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) \\
&= i\hbar M_z.
\end{aligned}$$

Hence the angular momentum operators satisfy the commutation relations

$$\begin{aligned}
[M_x, M_y] &= i\hbar M_z \\
[M_y, M_z] &= i\hbar M_x \\
[M_z, M_x] &= i\hbar M_y \\
[M_x, M^2] &= [M_y, M^2] = [M_z, M^2] = 0.
\end{aligned} \tag{2.157}$$

We are now in a position to find the eigenvalues and eigenfunctions of the angular momentum operators. Using the expression for the spherical harmonic in Equation (2.151), we have

$$M_z Y_{lm}(\theta, \phi) = -i\hbar \frac{\partial}{\partial \phi} Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi). \tag{2.158}$$

Hence the  $Y_{lm}(\theta, \phi)$  are eigenfunctions of the operator  $M_z$  corresponding to the eigenvalue  $m\hbar$ . Further, using Equations (2.139) and (2.156), it can be shown that

$$M^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi). \tag{2.159}$$

Hence the  $Y_{lm}(\theta, \phi)$  are also eigenfunctions of the operator  $M^2$  corresponding to the eigenvalue  $l(l+1)\hbar^2$ . Since the value of  $m$  must be such that  $|m| \leq l$ , it follows that there are  $2l+1$  values of  $m$  corresponding to the eigenvalue  $l(l+1)\hbar^2$  of  $M^2$ . Therefore the eigenvalue  $l(l+1)\hbar^2$  of  $M^2$  is  $(2l+1)$ -fold degenerate. Since the operators  $M^2$  and  $M_z$  possess a set of simultaneous eigenfunctions, then they are simultaneously measurable. This fact is also evident from the relation  $[M^2, M_z] = 0$  of Equation (2.157). By symmetry, the operators  $M^2$  and  $M_x$  will also possess a set of simultaneous eigenfunctions, and so will the operators  $M^2$  and  $M_y$ . However, these will be *different* sets of simultaneous eigenfunctions, and the observables to which the pair  $M_x$  and  $M_y$  correspond (and  $M_y$  and  $M_z$ ) will not be simultaneously observable because each of these pairs does not possess a set of simultaneous eigenfunctions.

### 2.10.4 The hydrogen atom

We now consider the hydrogen atom as the quantum equivalent of the classical central orbit problem. Let  $q$  denote the magnitude of the electron charge. The atom consists of an electron with mass  $m_e$  and negative charge  $-q$  interacting with a nucleus with mass  $m_{nuc}$  and a positive charge  $Zq$ , where  $Z$  is a positive constant. For the hydrogen atom, we will take  $Z = 1$ , but we take  $Z = 2$  for the helium atom. Let the nucleus have coordinates  $(x_{nuc}, y_{nuc}, z_{nuc})$ , and let the electron have coordinates  $(x_e, y_e, z_e)$ . The potential will be

$$V(\mathbf{r}) = \frac{(Zq)(-q)}{r} = \frac{-Zq^2}{\sqrt{(x_e - x_{nuc})^2 + (y_e - y_{nuc})^2 + (z_e - z_{nuc})^2}}. \tag{2.160}$$

The hamiltonian operator for the system is then

$$H = -\frac{\hbar^2}{2m_{nuc}} \nabla_{nuc}^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 + V(x_e - x_{nuc}, y_e - y_{nuc}, z_e - z_{nuc}) \quad (2.161)$$

where  $\nabla_{nuc}^2$  and  $\nabla_e^2$  operate with respect to the coordinates of the nucleus and electron respectively.

The standard procedure in any two-body problem is to introduce the coordinates  $(X, Y, Z)$  of the centre of mass, and the position coordinates  $(x, y, z)$  relative to the centre of mass. The total mass is  $M = m_{nuc} + m_e$ . These coordinates are defined by

$$(X, Y, Z) \equiv \frac{m_e(x_e, y_e, z_e) + m_{nuc}(x_{nuc}, y_{nuc}, z_{nuc})}{M} \quad (2.162)$$

$$(x, y, z) \equiv (x_e, y_e, z_e) - (x_{nuc}, y_{nuc}, z_{nuc}). \quad (2.163)$$

Using the standard rules of partial differentiation, it can then be verified that the expression for  $H$  given by Equation (2.161) becomes

$$H = -\frac{\hbar^2}{2M} \nabla_{X,Y,Z}^2 - \frac{\hbar^2}{2\mu} \nabla_{x,y,z}^2 + V(x, y, z)$$

where

$$\mu \equiv \frac{m_e m_{nuc}}{m_e + m_{nuc}} \quad (2.164)$$

is called the *reduced mass* (so-called because it is less than both  $m_e$  and  $m_{nuc}$ ). We now look for a solution of the TISE in terms of separation of variables

$$u(x, y, z)U(X, Y, Z).$$

This produces the two separated equations

$$-\frac{\hbar^2}{2M} \nabla_{X,Y,Z}^2 U = E' U, \quad (2.165)$$

$$-\frac{\hbar^2}{2\mu} \nabla_{x,y,z}^2 u + V(r)u = Eu \quad (2.166)$$

where the total energy is given by  $E = E'$ .

Equation (2.165) is the equation of motion of the centre of mass, and shows that it moves as a free particle in a zero potential. Equation (2.166) is the equation of motion about the centre of mass, and it has the same form as Equation (2.137). This equation can then be separated into Equations (2.138)–(2.140) as before, with the total angular part of the solution being the spherical harmonics  $Y_{lm}(\theta, \phi)$ . The radial equation (2.140) becomes

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left\{ \frac{2\mu}{\hbar^2} \left( E + \frac{Zq^2}{r} \right) - \frac{l(l+1)}{r^2} \right\} R = 0. \quad (2.167)$$

As we would expect for a bound state, the energy  $E$  is negative (because positive energy would have to be supplied in order to drag the two particles an infinite distance apart). It follows that we can define real positive constants  $\alpha$  and  $\gamma$  by

$$\begin{aligned}\alpha^2 &\equiv -\frac{8\mu E}{\hbar^2}, \quad \alpha > 0, \\ \gamma &\equiv \frac{Zq^2}{\hbar} \left(-\frac{\mu}{2E}\right)^{\frac{1}{2}}.\end{aligned}\tag{2.168}$$

In order to proceed with the solution of Equation (2.167), define a new independent variable  $\rho$  and a new dependent solution  $L(\rho)$  such that

$$\begin{aligned}\rho &\equiv \alpha r, \\ R(r) &\equiv e^{-\frac{1}{2}\rho} \rho^s L(\rho), \quad s \geq 0\end{aligned}\tag{2.169}$$

for some constant  $s$  which must be non-negative to avoid divergence of the solution at  $\rho = 0$ . Then substitution of these quantities into Equation (2.167) can be shown to give the equation

$$\rho^2 L'' + \rho[2(s+1) - \rho]L' + [\rho(\gamma - s - 1) + s(s+1) - l(l+1)]L = 0.\tag{2.170}$$

Now look for a series solution of the form

$$L(\rho) = \sum_{i=0}^{\infty} a_i \rho^i, \quad a_0 \neq 0\tag{2.171}$$

—note that no generality has been lost in taking  $a_0 \neq 0$  since the value of  $s$  is to be determined using this condition. This series is substituted into Equation (2.170) and the coefficients of  $\rho^k$  are equated to zero for all values of  $k$ . For  $k = 0$ , this process gives

$$s(s+1) = l(l+1)$$

which has solution  $s = l$  and  $s = -(l+1)$ . The second solution must be discarded in view of the condition  $s \geq 0$ . Hence on dividing by  $\rho$ , Equation (2.170) becomes

$$\rho L'' + [2(l+1) - \rho]L' + (\gamma - l - 1)L = 0.\tag{2.172}$$

The series solution Equation (2.171) is substituted into this equation and an analysis is made of the coefficients, just as we made in obtaining the Hermite polynomials for the linear harmonic oscillator, and in obtaining the Legendre polynomials for the  $\theta$ -dependence. It is found that  $L(\rho)$  has to be terminated to a polynomial to avoid the solution diverging as  $\rho \rightarrow \infty$ . This leads to the condition that  $(\gamma - l - 1)$  has to be a non-negative integer. Hence  $\gamma$  must be a positive integer  $n$ :

$$\gamma = \frac{Zq^2}{\hbar} \left(-\frac{\mu}{2E}\right)^{\frac{1}{2}} = n, \quad n = 1, 2, 3, \dots,$$

giving

$$E \equiv E_n = -\frac{\mu Z^2 q^4}{2\hbar^2(n+1)^2}, \quad n = 0, 1, 2, \dots \quad (2.173)$$

The groundstate energy  $E_0$  is then given by

$$E_0 = -\frac{\mu Z^2 q^4}{2\hbar^2}, \quad (2.174)$$

so that

$$E_n = \frac{E_0}{(n+1)^2}, \quad n = 0, 1, 2, \dots \quad (2.175)$$

When the electron jumps from an orbit with energy  $E_{n_1}$  to an orbit with a lower energy  $E_{n_2}$ , a photon with frequency  $\lambda$  is emitted where

$$\frac{hc}{\lambda} = E_{n_1} - E_{n_2},$$

where  $c$  is the speed of light. This gives

$$\begin{aligned} \frac{1}{\lambda} &= \frac{1}{ch} \cdot \frac{\mu Z^2 q^4}{2\hbar^2} \left[ \frac{1}{(n_2+1)^2} - \frac{1}{(n_1+1)^2} \right] \\ &= R_y \left[ \frac{1}{(n_2+1)^2} - \frac{1}{(n_1+1)^2} \right] \end{aligned}$$

where  $R_y \equiv \mu Z^2 q^4 / (4\pi\hbar^3 c)$  is called the *Rydberg constant*, and has the value  $R_y = 1.0974 \times 10^7 \text{ m}^{-1}$  for the hydrogen atom.

This formula generates a number of series transitions:

- (i) The *Lyman series* is generated for transitions into the groundstate  $n_2 = 0$ :

$$\frac{1}{\lambda} = R_y \left[ 1 - \frac{1}{(n_1+1)^2} \right], \quad n_1 = 1, 2, 3, \dots$$

- (ii) The *Balmer series* is generated for transitions into the first excited state  $n_2 = 1$ :

$$\frac{1}{\lambda} = R_y \left[ \frac{1}{4} - \frac{1}{(n_1+1)^2} \right], \quad n_1 = 2, 3, 4, \dots$$

- (iii) The *Paschen series* is generated for transitions into the second excited state  $n_2 = 2$ :

$$\frac{1}{\lambda} = R_y \left[ \frac{1}{9} - \frac{1}{(n_1+1)^2} \right], \quad n_1 = 3, 4, 5, \dots$$

The quantity  $\lambda^{-1}$  is directly proportional to the reduced mass  $\mu$  which appears in the expression for  $R_y$ . For a nucleus consisting of a proton, the ratio  $m_{nuc}/m_e \approx 1836$ , and so it follows from Equation (2.164) that

$$\mu = \frac{m_e}{1 + \frac{m_e}{m_{nuc}}} \approx 0.99946m_e.$$

Although this value is very close to  $m_e$ , the effect of using  $\mu$  rather than  $m_e$  in the expression for  $R_\gamma$  is observed in a shift of the spectral lines.

Since  $\gamma$  has to be a positive integer, Equation (2.172) becomes

$$\rho L'' + [2(l+1) - \rho]L' + (n-l-1)L = 0 \quad (2.176)$$

with  $(n-l-1)$  being a non-negative integer. Hence  $n \geq l+1$ . The solution of this equation is the *Associated Laguerre polynomial* given by

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} \frac{(-1)^{k+1} [(n+l)!]^2}{(n-l-1-k)!(2l+1+k)!k!} \rho^k, \quad (2.177)$$

for which the generating function is

$$\frac{(-x)^p \exp(-\rho \frac{x}{1-x})}{(1-x)^{p+1}} = \sum_{q=p}^{\infty} \frac{1}{q!} L_q^p(\rho) x^q. \quad (2.178)$$

The functions

$$e^{-\frac{1}{2}\rho} \rho^s L_{n+l}^{2l+1}(\rho)$$

which appear in Equation (2.169) are called the *Laguerre functions*. Their properties are well known, and normalisation gives (Sneddon 1961)

$$R_{nl}(r) = \left[ \left( \frac{2Z\mu q^2}{n\hbar^2} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{\frac{1}{2}} e^{-\frac{1}{2}\alpha_n r} (\alpha_n r)^l L_{n+l}^{2l+1}(\alpha_n r) \quad (2.179)$$

where

$$\alpha_n^2 \equiv -\frac{8\mu E_{n-1}}{\hbar^2}, \quad n = 1, 2, 3, \dots \quad (2.180)$$

Finally, the complete solution of Equation (2.166) is then

$$u_{nlm}(r, \theta, \phi) = R_{nl} Y_{lm}(\theta, \phi). \quad (2.181)$$

The degeneracy of the energy eigenvalues is easily found. We have  $Hu_{nlm} = E_{n-1} \times u_{nlm}$  (remember,  $n$  starts from 1, but we count energy levels starting from the groundstate  $E_0$  by convention). The value of  $l$  must lie in the range  $0 \leq l \leq n-1$ , and there are  $(2l+1)$  values of  $m$  satisfying the condition  $|m| \leq l$ . Hence the total degeneracy of the energy  $E_{n-1}$  is

$$\sum_{l=0}^{n-1} (2l+1) = n^2. \quad (2.182)$$

## 2.11 Angular momentum and spin

The eigenvalues of the orbital angular momentum have been found in Sect. 2.10.3. However, observations show that these eigenvalues are split into many more levels than can be accounted for by orbital angular momentum alone. This leads to a more general definition of angular momentum, and to the introduction of *spin* angular momentum.

### 2.11.1 The necessity for extra energy levels

Suppose that an electron moves in a spherically symmetric potential, and a magnetic field  $B_z$  is applied in the  $z$  direction. Classically the hamiltonian becomes

$$H' = H^{(0)} + \frac{q}{2\mu c} B L_z \quad (2.183)$$

where  $\mu$  is the reduced mass of the electron,  $L_z$  is the  $z$  component of the angular momentum, the hamiltonian  $H^{(0)}$  is given by

$$H^{(0)} = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r), \quad (2.184)$$

and

$$H^{(0)} u_{nlm}(r, \theta, \phi) = E_n u_{nlm}(r, \theta, \phi) \quad (2.185)$$

where  $n, l$  and  $m$  take integer values. It is known that

$$L_z u_{nlm}(r, \theta, \phi) = -i\hbar \frac{\partial}{\partial \phi} Y_{lm}(\theta, \phi) R_{nl}(r) = n\hbar u_{nlm}(r, \theta, \phi), \quad (2.186)$$

and therefore

$$H' u_{nlm}(r, \theta, \phi) = \left( E_n + \frac{q\hbar m}{2\mu c} B_z \right) u_{nlm}(r, \theta, \phi) \quad (2.187)$$

for  $m = -l, -l+1, \dots, l-1, l$ . Hence on this calculation, the energy level  $E_n$  is split by adding any of  $(2l+1)$  values to it—this is the Normal Zeeman effect. However, it is observed that there is much more splitting than this, pointing to the fact that the electron possesses another degree of freedom. To introduce this extra freedom, we will generalise our notion of angular momentum.

The orbital angular momentum is defined as  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ , and using the commutation relations  $[x, p_x] = i\hbar$  and  $[x, p_y] = 0$  etc., it is easily shown that

$$\begin{aligned} [L_x, L_y] &= i\hbar L_z, & [L_y, L_z] &= i\hbar L_x, & [L_z, L_x] &= i\hbar L_y, \\ [L^2, L_x] &= [L^2, L_y] = [L^2, L_z] = 0, \end{aligned}$$

and that  $L^2$  has eigenvalues  $l(l+1)\hbar^2$  for  $l = 0, 1, 2, \dots$

### 2.11.2 Generalised angular momentum

We now use these commutation relations to *define* a more general angular momentum  $\mathbf{M}$  which is hermitian (that is,  $\mathbf{M}^\times = \mathbf{M}$ ) such that

$$[M_x, M_y] = i\hbar M_z, \quad [M_y, M_z] = i\hbar M_x, \quad [M_z, M_x] = i\hbar M_y, \quad (2.188)$$

and

$$[M^2, M_x] = [M^2, M_y] = [M^2, M_z] = 0. \quad (2.189)$$

Now let  $W$  represent an operator, or a set of operators, such that  $W$ ,  $M^2$  and  $M_z$  form a set of commuting operators, with  $W$  commuting with  $M_x$  and  $M_y$  also: this last condition represents spherical symmetry. Let  $w$ ,  $\mu^2$  and  $\mu_z$  represent the eigenvalues of  $W$ ,  $M^2$  and  $M_z$  respectively (with  $\mu \geq 0$ ), and let  $\psi(w, \mu^2, \mu_z)$  be a simultaneous eigenfunction:

$$\begin{aligned} W\psi(w, \mu^2, \mu_z) &= q\psi(w, \mu^2, \mu_z), \\ M^2\psi(w, \mu^2, \mu_z) &= \mu^2\psi(w, \mu^2, \mu_z), \\ M_z\psi(w, \mu^2, \mu_z) &= \mu_z\psi(w, \mu^2, \mu_z). \end{aligned}$$

It follows that

$$\begin{aligned} (M_x^2 + M_y^2)\psi(w, \mu^2, \mu_z) &= (M^2 - M_z^2)\psi(w, \mu^2, \mu_z) \\ &= (\mu^2 - \mu_z^2)\psi(w, \mu^2, \mu_z), \end{aligned}$$

and so  $\psi(w, \mu^2, \mu_z)$  is also an eigenfunction of the operator  $(M_x^2 + M_y^2)$  corresponding to the eigenvalue  $(\mu^2 - \mu_z^2)$ . This operator will have non-negative eigenvalues, and so  $\mu^2 \geq \mu_z^2$ , or  $|\mu_z| \leq \mu$ . Hence for a given value of  $\mu$ , the eigenvalues of  $M_z$  are bounded above and below. Now define the two operators

$$A_+ \equiv M_x + iM_y \quad (2.190)$$

$$A_- \equiv M_x - iM_y \quad (2.191)$$

Then  $A_+^\times = A_-$ . Using Equations (2.188) and (2.189), it is easily verified that

$$[A_\pm, M_z] = \mp\hbar A_\pm \quad (2.192)$$

$$[A_\pm, M^2] = 0 \quad (2.193)$$

$$A_+A_- = M^2 - M_z^2 + \hbar M_z \quad (2.194)$$

$$A_-A_+ = M^2 - M_z^2 - \hbar M_z. \quad (2.195)$$

It follows that

$$\begin{aligned} WA_\pm\psi(w, \mu^2, \mu_z) &= A_\pm W\psi(w, \mu^2, \mu_z) \\ &= wA_\pm\psi(w, \mu^2, \mu_z), \end{aligned} \quad (2.196)$$



$$\begin{aligned} M^2 A_{\pm} \psi(w, \mu^2, \mu_z) &= A_{\pm} M^2 \psi(w, \mu^2, \mu_z) \\ &= \mu^2 A_{\pm} \psi(w, \mu^2, \mu_z), \end{aligned} \quad (2.197)$$

$$\begin{aligned} M_z A_{\pm} \psi(w, \mu^2, \mu_z) &= (A_{\pm} M_z \pm \hbar A_{\pm}) \psi(w, \mu^2, \mu_z) \\ &= (\mu_z \pm \hbar) A_{\pm} \psi(w, \mu^2, \mu_z). \end{aligned} \quad (2.198)$$

These results show that the functions  $A_{\pm} \psi(w, \mu^2, \mu_z)$  are themselves simultaneous eigenfunctions of the operator  $W$  with eigenvalue  $w$ , of the operator  $M^2$  with eigenvalue  $\mu^2$  as before, and of the operator  $M_z$  with displaced eigenvalues  $(\mu_z \pm \hbar)$ .

Hence by repeatedly operating on the function  $\psi(w, \mu^2, \mu_z)$  with the operator  $A_+$  we generate a whole set of eigenvalues  $\mu^2$  of  $M^2$ , and eigenvalues  $\mu_z, \mu_z + \hbar, \mu_z + 2\hbar, \mu_z + 3\hbar, \dots$  of  $M_z$ . Similarly, by operating on the function  $\psi(w, \mu^2, \mu_z)$  with the operator  $A_-$  we generate a whole set of eigenvalues  $\mu^2$  of  $M^2$ , and eigenvalues  $\mu_z, \mu_z - \hbar, \mu_z - 2\hbar, \mu_z - 3\hbar, \dots$  of  $M_z$ . The operators  $A_{\pm}$  are ladder operators of a type encountered in the case of the harmonic oscillator.

Since the eigenvalues of  $M_z$  are bounded above and below, the eigenvalues of  $M_z$  cannot be generated indefinitely for a fixed value of  $\mu$ . Let the maximum eigenvalue of  $M_z$  be  $l\hbar$  for some value  $l$ :

$$M_z \psi(w, \mu^2, l\hbar) = l\hbar \psi(w, \mu^2, l\hbar).$$

Operating with  $A_+$  would then give

$$M_z A_+ \psi(w, \mu^2, l\hbar) = (l\hbar + \hbar) A_+ \psi(w, \mu^2, l\hbar). \quad (2.199)$$

However, this has generated an even larger eigenvalue of  $M_z$ , which is not allowed. Hence Equation (2.199) can hold only if

$$A_+ \psi(w, \mu^2, l\hbar) = 0,$$

or

$$A_- A_+ \psi(w, \mu^2, l\hbar) = 0.$$

Using Equation (2.195) this becomes

$$(M^2 - M_z^2 - \hbar M_z) \psi(w, \mu^2, l\hbar) = 0,$$

or

$$(\mu^2 - l^2 \hbar^2 - l \hbar^2) \psi(w, \mu^2, l\hbar) = 0.$$

Hence

$$\mu^2 = l(l+1) \hbar^2. \quad (2.200)$$

Similarly, there must be a least eigenvalue  $l' \hbar$  of  $M_z$  with

$$A_- \psi(w, \mu^2, l' \hbar) = 0,$$

or

$$A_+ A_- \psi(w, \mu^2, l' \hbar) = 0.$$

Using Equation (2.194), this becomes

$$(M^2 - M_z^2 + \hbar M_z)\psi(w, \mu^2, l'\hbar) = 0,$$

or

$$(\mu^2 - l'^2\hbar^2 + l'\hbar^2)\psi(w, \mu^2, l'\hbar) = 0.$$

Hence it follows that

$$l'(l' - 1)\hbar^2 = \mu^2 = l(l + 1)\hbar^2$$

which has solutions  $l' = l + 1$  (which is not physically acceptable, otherwise the lowest eigenvalue would be larger than the highest), or  $l' = -l$ . Hence for a given value of  $l$  the eigenvalues of  $M^2$  are  $\mu^2 = l(l + 1)\hbar^2$ , and the eigenvalues of  $M_z$  are  $n\hbar$  ( $n = -l, -l + 1, \dots, l - 1, l$ ). Since there must be an integral number of such values, then the only possibility is that

$$\begin{aligned} l &= \frac{1}{2} \times \text{integer} \\ &= 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots \end{aligned} \quad (2.201)$$

Therefore the quantity  $l$  can now take half-integer values as well as integer values. The half-integer values do not describe the orbital angular momentum  $\mathbf{L}$  (remember, these are described by integer values). This means that we have found an additional degree of freedom  $\mathbf{S}$ , called the *spin* angular momentum, when  $l = \frac{1}{2} \times \text{integer}$ . The total angular momentum is

$$\mathbf{M} = \mathbf{L} + \mathbf{S} \quad (2.202)$$

where both  $\mathbf{L}$  and  $\mathbf{S}$  obey the commutation rules of Equations (2.188) and (2.189).

The spin represents a new internal degree of freedom in the system. It is found that the behaviour of an electron in a magnetic field requires that the electron has spin  $l = \frac{1}{2}$ , so that  $S_z$  can have one of the two eigenvalues  $\pm \frac{1}{2}\hbar$  and  $S^2$  has eigenvalue  $\frac{3}{4}\hbar^2$ . Both  $S_x$  and  $S_y$  can also have values  $\pm \frac{1}{2}\hbar$  since there is nothing special about the direction of the  $z$  axis. However, we can specify  $S^2$  and only one of the quantities  $S_x$ ,  $S_y$  and  $S_z$  simultaneously, since these last three operators do not commute.

### 2.11.3 Particles with spin $\frac{1}{2}$

It is found that electrons, protons and neutrons have spin  $l = \frac{1}{2}$ , with  $n = (-\frac{1}{2}, \frac{1}{2})$ . Let the eigenfunctions of the operator  $S_z$  corresponding to the eigenvalues  $-\frac{1}{2}\hbar$  and  $\frac{1}{2}\hbar$  be  $a_-$  and  $a_+$  respectively. Then

$$S_z a_- = -\frac{1}{2}\hbar a_-, \quad S_z a_+ = \frac{1}{2}\hbar a_+.$$

The spin state of a particle can be described by a vector in the two dimensional spin space  $\mathcal{S}$ . Particles without spin are represented by wave functions in the *Hilbert space*  $\mathcal{H}$  spanned by a complete orthonormal set of functions  $\xi(\mathbf{r})$ . Hence in general, electron wave functions can be thought of as vectors in the product space  $\mathcal{H} \times \mathcal{S}$ , and can be written as

$$\psi = a_- \psi_-(\mathbf{r}) + a_+ \psi_+(\mathbf{r})$$

where

$$\psi_{\pm}(\mathbf{r}) \equiv \sum_k c_{\pm k}^{\pm} \xi_k(\mathbf{r}).$$

The probability of finding an electron in volume  $V$  with  $z$ -component of spin either  $+\frac{1}{2}\hbar$  or  $-\frac{1}{2}\hbar$  is

$$\int_V |\psi_{\pm}(\mathbf{r})|^2 d^3\mathbf{r}.$$

The probability of finding the electron in volume  $V$  regardless of spin is

$$\int_V [|\psi_+(\mathbf{r})|^2 + |\psi_-(\mathbf{r})|^2] d^3\mathbf{r},$$

with normalisation given by

$$\int [|\psi_+(\mathbf{r})|^2 + |\psi_-(\mathbf{r})|^2] d^3\mathbf{r} = 1,$$

where this integral is taken over all space. The electron wave function may also be written in the form

$$\begin{aligned} \psi(\mathbf{r}) &= \begin{pmatrix} \psi_+(\mathbf{r}) \\ \psi_-(\mathbf{r}) \end{pmatrix} \\ &= \psi_+(\mathbf{r}) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \psi_-(\mathbf{r}) \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \end{aligned}$$

Hence the eigenfunctions  $a_-$  and  $a_+$  can be represented by  $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$  and  $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$  respectively. The inner product in this representation of any two vectors  $\phi = \begin{pmatrix} \phi_+ \\ \phi_- \end{pmatrix}$  and  $\chi = \begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix}$  in  $\mathcal{H} \times \mathcal{S}$  is defined as

$$\begin{aligned} (\phi, \chi) &= \int \left\{ \overline{\phi_+}, \overline{\phi_-} \right\} \begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix} \right\} d^3\mathbf{r} \\ &= \int \{ \overline{\phi_+} \chi_+ + \overline{\phi_-} \chi_- \} d^3\mathbf{r} \end{aligned}$$

where the integrals are again taken over all space. In  $\mathcal{S}$  only, if we write  $\phi \equiv \begin{pmatrix} p \\ q \end{pmatrix}$ , then  $(\phi, \phi) = p^2 + q^2$ , and the corresponding normalised vector is  $\frac{1}{\sqrt{p^2+q^2}} \begin{pmatrix} p \\ q \end{pmatrix}$ .

Operators on these two-component vectors will be  $2 \times 2$  matrices with complex elements. Let the matrix  $\begin{pmatrix} a & b \\ c & d \end{pmatrix}$  correspond to the operator  $S_z$ . Then

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2}\hbar \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{1}{2}\hbar \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

These equations have solution  $b = c = 0$ ,  $a = \hbar/2$  and  $d = -\hbar/2$ . Hence

$$S_z = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Now  $S^2$ ,  $S_x$ ,  $S_y$  and  $S_z$  must obey the commutation relations in Equations (2.188) and (2.189). It is easily verified that these relations are satisfied if we take

$$S_x = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (2.203)$$

$$S_y = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (2.204)$$

$$S_z = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.205)$$

These results may be written in the form

$$\mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma} \quad (2.206)$$

where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (2.207)$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (2.208)$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (2.209)$$

are called the *Pauli spin matrices*. Note that the matrices corresponding to these operators are hermitian. Further, it follows that

$$S^2 = S_x^2 + S_y^2 + S_z^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (2.210)$$

### 2.11.4 Energy splitting using spin

We can now demonstrate how the spin splits the energy levels even further. Equation (2.187) can be written as

$$H' u_{nlm}(r, \theta, \phi) = E'_{nm} u_{nlm}(r, \theta, \phi). \quad (2.211)$$

Now consider the modified hamiltonian

$$H = H' + \frac{qB}{\mu c} S_z = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} H' + \frac{q\hbar B}{2\mu c} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.212)$$

If this spin coupling modifies the energies to  $E'_{nm} + \Delta E$ , suppose that the new energy eigenfunctions are  $\begin{pmatrix} \alpha u_{nlm}(\mathbf{r}) \\ \beta u_{nlm}(\mathbf{r}) \end{pmatrix}$ , with

$$\left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} H' + \frac{q\hbar B}{2\mu c} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right\} \begin{pmatrix} \alpha u_{nlm}(\mathbf{r}) \\ \beta u_{nlm}(\mathbf{r}) \end{pmatrix} = (E'_{nm} + \Delta E) \begin{pmatrix} \alpha u_{nlm}(\mathbf{r}) \\ \beta u_{nlm}(\mathbf{r}) \end{pmatrix}.$$

Hence

$$\frac{q\hbar B}{2\mu c} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} u_{nlm}(\mathbf{r}) = \Delta E \begin{pmatrix} \alpha \\ \beta \end{pmatrix} u_{nlm}(\mathbf{r}).$$

Since the matrices have no effect on the  $u_{nlm}(\mathbf{r})$ , these can be cancelled to give

$$\left( \frac{q\hbar B}{2\mu c} - \Delta E \right) \alpha = 0 \quad \text{and} \quad \left( -\frac{q\hbar B}{2\mu c} - \Delta E \right) \beta = 0$$

from which it follows that

$$\begin{vmatrix} q\hbar B/(2\mu c) - \Delta E & 0 \\ 0 & -q\hbar B/(2\mu c) - \Delta E \end{vmatrix} = 0$$

which has the solution

$$\Delta E = \pm \frac{q\hbar B}{2\mu c}.$$

Considering the positive and negative solutions separately, we have

$$\begin{aligned} \Delta E = +\frac{q\hbar B}{2\mu c} &\Rightarrow \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \Delta E = -\frac{q\hbar B}{2\mu c} &\Rightarrow \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \end{aligned}$$

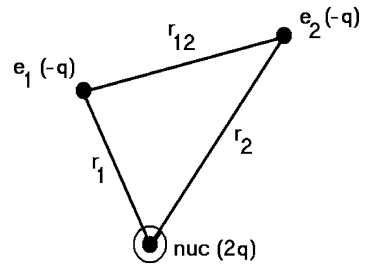
Hence the (already split) energy eigenvalues are further split into

$$E_{nm} + \frac{q\hbar B}{2\mu c} \quad \text{and} \quad E_{nm} - \frac{q\hbar B}{2\mu c}$$

with corresponding eigenfunctions

$$\begin{pmatrix} u_{nlm}(\mathbf{r}) \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ u_{nlm}(\mathbf{r}) \end{pmatrix}.$$

**Fig. 2.11** The helium atom showing the nucleus with charge  $2q$ , and two identical electrons  $e_1$  and  $e_2$  with charges  $-q$ .



## 2.12 Systems of identical particles: BE and FD statistics

We now consider a system of  $N$  identical particles, in which we can specify the positions of the particles, but we cannot identify which particle is at which point. Let  $H(1, 2, \dots, N)$  be the Hamiltonian operator of the system, and let  $P_{ij}$  be the permutation operator which interchanges the two particles  $i$  and  $j$ . This permutation operator has the properties that

$$(P_{ij})^2 = 1, \quad P_{ij}(fg) = (P_{ij}f)(P_{ij}g) \quad (2.213)$$

where  $f$  and  $g$  are any two functions of the particles  $1, 2, \dots, N$ . The fact that the particles are identical means that a permutation of the particles leaves the Hamiltonian unchanged:

$$P_{ij}H(1, 2, \dots, N) = H(1, 2, \dots, N). \quad (2.214)$$

For example, the helium atom shown in Fig. 2.11 has two identical electrons orbiting a nucleus. The Hamiltonian operator for this system is

$$H = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - 2q^2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{q^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (2.215)$$

and is clearly symmetric under the interchange of labels 1 and 2.

### 2.12.1 Symmetric and antisymmetric wave functions

In what follows, we will write  $H$  and  $\psi$  as shorthand to denote  $H(1, 2, \dots, N)$  and the solution  $\psi(1, 2, \dots, N)$  of the TISE respectively. Now

$$H(1, 2, \dots, N)\psi(1, 2, \dots, N) = E\psi(1, 2, \dots, N). \quad (2.216)$$

Hence applying the operator  $P_{ij}$  to both sides, we get

$$P_{ij}(H\psi) = P_{ij}(E\psi) = E(P_{ij}\psi)$$

giving

$$E(P_{ij}\psi) = (P_{ij}H)P_{ij}\psi = H(P_{ij}\psi).$$

Hence

$$H(P_{ij}\psi) = E(P_{ij}\psi),$$

which shows that  $P_{ij}\psi$  is also an eigenfunction of  $H$  corresponding to the eigenvalue  $E$ . One possible special case which follows from this result is that

$$P_{ij}\psi = \lambda_{ij}\psi$$

for some scalar quantity  $\lambda_{ij}$ . Hence

$$\psi = (P_{ij})^2\psi = P_{ij}(\lambda_{ij}\psi) = \lambda_{ij}P_{ij}\psi = \lambda_{ij}^2\psi$$

giving

$$\lambda_{ij}^2 = 1, \quad \text{or} \quad \lambda_{ij} = \pm 1.$$

Hence

$$P_{ij}\psi = \pm\psi. \tag{2.217}$$

This equation shows that the wave function for a system of identical particles can be either an even or an odd function of the particle coordinates under a permutation of two particles. Particles whose wave function is symmetric satisfy *Bose-Einstein* statistics, and are called *bosons*—for example,  $\pi$ -mesons and photons. Particles whose wave function is antisymmetric satisfy *Fermi-Dirac* statistics, and are called *fermions*—for example, electrons, protons and neutrons.

Equation (2.217) also shows that  $\psi$  is an eigenfunction of the permutation operator  $P_{ij}$  with eigenvalues  $\pm 1$ . Further, for any function  $f \equiv f(1, 2, \dots, N)$ , we have

$$\begin{aligned} [P_{ij}, H]f &= P_{ij}(Hf) - HP_{ij}f = (P_{ij}H)(P_{ij}f) - HP_{ij}f \\ &= HP_{ij}f - HP_{ij}f = 0, \end{aligned}$$

showing that  $[P_{ij}, H] = 0$ . Hence

$$\frac{d}{dt}\langle P_{ij} \rangle = \frac{1}{i\hbar}\langle [P_{ij}, H] \rangle = 0, \tag{2.218}$$

indicating that the even or odd characteristic of the wave function  $\psi$  is preserved in time—fermions cannot flip over to become bosons, and vice versa.

### 2.12.2 The Pauli exclusion principle

Suppose that the particles are fermions, and therefore have antisymmetric wave functions under the action of the operator  $P_{ij}$ . Further, suppose that the particles

$i$  and  $j$  are in the same state. Then

$$\psi = P_{ij}\psi = -\psi$$

Hence

$$\psi = 0, \quad \text{or} \quad |\psi|^2 = 0,$$

showing that there is a zero probability of finding two fermions in the same state. The two  $z$ -components of spin angular momentum for the electron are  $\pm\hbar/2$ . Recall from Sect. 2.10.4 in the case of the hydrogen atom that the TISE

$$Hu_{nlm} = E_n u_{nlm}$$

provided an energy level  $E_n$  which was  $n^2$ -fold degenerate. That is, there were  $n^2$  distinct quantum states corresponding to the energy  $E_n$ . More generally for a system with  $N$  identical electrons, the state will be specified by the function  $u_{nlm\dots pq\dots\pm\frac{1}{2}}$  corresponding to the energy level  $E_n$ . Such a collection of states forms an *energy shell*, and the quantum states  $nlm\dots pq\dots$  (that is, excluding the  $\pm 1/2$ ) form an *orbit* within that shell. The exclusion principle then asserts that if two electrons are in the same orbit, then they must have opposite spins. Once a shell is full, any other electron must go into a different shell, and this rule gives rise to the periodic table of elements.

Later, in Chapter 3 on the treatment of quantum states in statistical mechanics, we will need to sum over the particle numbers of various states. For fermions, the sum will therefore only involve the particle numbers 0 and 1. However, there is no such restriction in the case of bosons, and particle numbers in a state will range from 0 to infinity.

### 2.12.3 Non-interacting identical particles

When the identical particles are non-interacting, the Hamiltonian  $H(1, 2, \dots, N)$  splits up into a sum of  $N$  separate terms, each one corresponding to a separate particle:

$$H(1, 2, \dots, N) = H(1) + H(2) + \dots + H(N). \quad (2.219)$$

For example, if the interaction term in Equation (2.215) for the Hamiltonian of the helium atom is ignored, then it can be written

$$H = \left( -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{2q^2}{r_1} \right) + \left( -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2q^2}{r_2} \right).$$

The TISE corresponding to the  $k$ th term in the Hamiltonian is then

$$H(k)\psi_{\alpha_k}(k) = E_{\alpha_k}(k)\psi_{\alpha_k}(k), \quad (k = 1, \dots, N; \alpha_k = 0, 1, 2, \dots), \quad (2.220)$$



and the total energy will be

$$E = \sum_{k=1}^N E_{\alpha_k}(k),$$

with the eigenfunction corresponding to this energy being

$$\psi_{\alpha_1 \alpha_2 \dots \alpha_N}(1, 2, \dots, N) = \prod_{k=1}^N \psi_{\alpha_k}(k). \quad (2.221)$$

In fact, since the particles are identical, any permutation of the particles will give an eigenfunction corresponding to this energy, and so will any linear combination of the  $N!$  possible permutations. This leads us to consider the function

$$\psi_{\alpha_1 \beta_2 \dots \gamma_N}(1, 2, \dots, N) \equiv \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\alpha_1}(1) & \psi_{\alpha_1}(2) & \dots & \psi_{\alpha_N}(N) \\ \psi_{\beta_1}(1) & \psi_{\beta_1}(2) & \dots & \psi_{\beta_N}(N) \\ \dots & \dots & \dots & \dots \\ \psi_{\gamma_1}(1) & \psi_{\gamma_1}(2) & \dots & \psi_{\gamma_N}(N) \end{vmatrix}. \quad (2.222)$$

An interchange of any two coordinates in the determinant will interchange two columns, and hence change the sign of the function. Further, if any two coordinate numbers are identical then two columns will be equal, and so the function will be zero. Again, the action of the Hamiltonian in Equation (2.219) will produce the equation

$$H\psi_{\alpha_1 \beta_2 \dots \gamma_N} = (E_{\alpha_1} + E_{\beta_2} + \dots + E_{\gamma_N})\psi_{\alpha_1 \beta_2 \dots \gamma_N}.$$

Hence the function  $\psi_{\alpha_1 \beta_2 \dots \gamma_N}$  given by the determinant in Equation (2.222) is the wave function of  $N$  non-interacting fermions. If the individual functions  $\psi_{\alpha_k}(k)$  are normalised, then the factor  $1/\sqrt{N!}$  provides the correct normalisation factor.

## 2.13 The Schrödinger equation in device modelling

A number of separate modelling equations are used to model semiconductor devices. These will be described fully in Chapter 6. One of these equations is the *Poisson equation* which must be solved for the electrostatic potential  $\psi$ . The minimum of the conduction band is  $E_c$  where

$$E_c = E_h - q\psi. \quad (2.223)$$

Here  $q$  is the magnitude of the electron charge, and  $E_h$  (measured in eV) is the abrupt conduction band discontinuity at the interface between different material layers. With a change of notation, Equation (2.16) is written

$$-\frac{\hbar^2}{2} \nabla \cdot \left( \frac{1}{m} \nabla \xi_k \right) + (V_{xc} + E_c) \xi_k = \lambda_k \xi_k \quad (2.224)$$

in which the quantities  $\xi_k$  are the energy eigenfunctions and the  $\lambda_k$ , measured in eV, are the energy eigenvalues. The quantity  $V_{xc}$  is the *exchange correlation energy*, measured in eV, which arises from the Coulomb repulsion between electrons, and will be described more fully in Sect. 6.8. The calculation of the normalisation factors in the solutions  $\xi_k$  will depend on the numbers of spatial degrees of freedom allowed to the electrons. In particular,

- For the one dimensional solution,  $\int dy |\xi_k(y)|^2 = 1$ . In this case,  $\xi_k(y)$  has dimension  $m^{-\frac{1}{2}}$ .
- For the two dimensional solution,  $\int dx \int dy |\xi_k(x, y)|^2 = 1$ . In this case,  $\xi_k(x, y)$  has dimension  $m^{-1}$ .

## Problems

**Problem 2.1.** Normalise the solutions

$$u(x) = \begin{cases} A \sin kx + B \cos kx & \text{for } |x| \leq a \\ C e^{-k_1 x} + D e^{k_1 x} & \text{for } |x| \geq a \end{cases}$$

given in Equation (2.44) for the finite square well potential.

**Problem 2.2.** Investigate the case of a particle approaching the finite square well potential given in Sect 2.5.6 from the left hand side with energy  $E > V_0$ . Obtain the reflection coefficient.

**Problem 2.3.** Prove in the case  $E > 0$  for the  $\delta$ -function potential given by

$$V(x) = V_0 \delta(x)$$

that the reflection coefficient is

$$R = \frac{|E|}{|E| + |E_0|}.$$

**Problem 2.4.** Calculate the spherical harmonic function  $Y_{13}(\theta, \phi)$ .

**Problem 2.5.** If the hamiltonian  $H$  is independent of time  $t$ , show that

$$\mathbf{p} = \frac{im}{\hbar} [H, \mathbf{r}].$$

**Problem 2.6.** Use the result in Problem 2.5 to show that

$$\frac{d}{dt} \langle x^2 \rangle = \frac{1}{m} (\langle x p_x \rangle + \langle p_x x \rangle).$$

**Problem 2.7.** A linear harmonic oscillator ( $m, \mu$ ) is in the  $n$ th energy state. Obtain an expression for the probability that the particle will be found outside its classical limits along the  $x$ -axis in terms of the quantity

$$I_n(a) \equiv \frac{1}{2^n \pi^{\frac{1}{2}} n!} \int_{-a}^a H_n(\xi)^2 e^{-\xi^2} d\xi.$$

Calculate this value for the groundstate, given that  $I_0(1) = 0.84$ .

**Problem 2.8.** For the linear harmonic oscillator in the  $n$ th energy state, calculate  $\langle x \rangle$ ,  $\langle x^2 - \langle x \rangle^2 \rangle$ ,  $\langle p_x \rangle$  and  $\langle p_x^2 - \langle p_x \rangle^2 \rangle$ .

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