13

Wave Mechanics

The wave mechanics of Schrödinger (1926) and the equivalent matrix formulation by Heisenberg (1926) are the basis of what is known as 'modern physics'. Without exception they have been successful in replacing or including classical mechanics over the whole range of physics at atomic and molecular levels; these in turn govern the larger scale macroscopic properties. Very high energy phenomena in the physics of elementary particles still, however, present many problems.

In this chapter we shall be concerned only with Schrödinger's wave mechanics and in the way it displays the dual wave–particle nature of matter. This dual nature was first established for electromagnetic radiation but the parallel attempt to establish the wave nature of material particles is the basic history of twentieth century physics.

Origins of Modern Quantum Theory

In the nineteenth century interference and diffraction experiments together with classical electromagnetic theory had confirmed the wave nature of light beyond all doubt but in 1901, in order to explain the experimental curves of black body radiation, Planck postulated that electromagnetic oscillators of frequency ν had discrete energies $nh\nu$ where n was an integer and h was a constant (p. 252). A quarter of a century was to elapse before this was formally derived from the new quantum mechanics.

X-rays had been found by Roentgen in 1895, their wave-like properties were displayed by the diffraction experiments of von Laue in 1912, and their electromagnetic nature was soon proved. A much longer time was required to reconcile a wave nature with the negatively charged particles which J. J. Thomson found in his cathode ray experiments of 1897. It was not until 1927 that interference effects from reflected or scattered electrons were obtained by Davisson and Germer whilst in 1928 G. P. Thomson (the son of J. J.) produced concentric ring diffraction patterns by firing electrons through a thin foil.

In the meantime, in 1906, Einstein had used Planck's idea to explain the photoelectric effect where light falling on a given surface caused electrons to be ejected. Einstein considered the light beam as a stream of individual photons, or quanta of light, each of

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energy $h\nu$. Collisions between these quanta and electrons in the target material gave the electrons sufficient energy to escape.

In 1912 the alpha particle scattering experiments of Rutherford led to his proposal that the atom consisted of a small positively charged nucleus surrounded by enough negative electrons to leave the atom electrically neutral. This atom was the model used by Bohr and Sommerfeld in their 'old quantum theory', a mixture of classical mechanics and quantum postulates, attempting to explain, amongst other things, the regularity of spectroscopic series from radiating atoms. Electrons were required to orbit the nucleus at definite energy levels (like planets round the Sun), and radiation at a fixed frequency ν was given out when an electron moved from a higher to a lower energy orbit with an energy difference $\Delta E = h\nu$. These orbits were required to be stable or 'stationary' orbits with quantized, that is, allowed values of energy and angular momentum. The fact that classical electromagnetic theory had shown that an accelerating charge (electron in an orbit) was itself a source of radiation remained an unresolved difficulty.

By 1920 Einstein had provided two of the vital tools necessary for further progress (a) that a quantum of radiation has energy $E = h\nu$, and (b) that a particle of momentum $p = mv$ and rest mass m_0 has a relativistic energy E where $E^2 = p^2c^2 + (m_0c^2)^2$.

This relation established the equivalence of matter and energy; a stationary particle $v = 0$ has an energy $E = m_0c^2$ where c is the velocity of light.

The time was now ripe for the final steps leading to the modern quantum theory. The first of these was provided by Compton (1922–23) and the second by de Broglie in 1924.

Compton fired X-rays of a known frequency at a thin foil and observed that the frequency ν of the scattered radiation was independent of the foil material. This implied that the scattering was the result of collisions between X-ray quanta of energy $h\nu$ and the electrons in the target material. In addition to scattering at the incident frequency a lower frequency of scattered radiation was always found which depended only on the mass of the scattering particles (electrons) and the angle of scattering. Compton showed that these results were consistent if momentum and energy were conserved in an elastic collision between two 'particles', the electron and an X-ray of energy $h\nu$, a rest mass $m_0 = 0$ and (from Einstein's relativistic energy equation), a momentum

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda},$$

where $c = \nu\lambda$.

De Broglie in 1924 proposed that if the dual wave-particle nature of electromagnetic fields required a particle momentum of $p = h/\lambda$, it was possible that a wavelength λ of a 'matter' field could be associated with **any** particle of momentum $p = mv$ to give the relation $p = h/\lambda$. His argument was as follows.

If the phase velocity of such a 'matter' wave obeys the usual relation

$$v_{\mathrm{p}} = \nu\lambda$$

where ν is the frequency, the assumption that any particle has a momentum $p = h/\lambda$ together with Einstein's expression $E = h\nu$ yields $v_{\mathrm{p}} = E/p$.

The theory of relativity gives, for a particle of rest mass m_0 and velocity v an energy $E = mc^2$ and a momentum $p = mv$, where

$$m = m_0\left(1 - \frac{v^2}{c^2}\right)^{-1/2}$$

is the particle mass at velocity v. For such a particle the phase velocity

$$v_{\mathrm{p}} = \frac{E}{p} = \frac{c^2}{v}$$

that is,

$$vv_{\mathrm{p}} = c^2$$

(an expression we met earlier for the wave guides of p. 243).

This gives a phase velocity $v_{\mathrm{p}} > c$ for a particle velocity $v < c$. However, the energy in the de Broglie wave (or particle) travels with the group velocity

$$v_{\mathrm{g}} = \frac{\partial\omega}{\partial k}$$

which, for

$$E = h\nu = \frac{h}{2\pi}\omega$$

and

$$p = \frac{h}{\lambda} = \frac{h}{2\pi}k$$

gives

$$v_{\mathrm{g}} = \frac{\partial\omega}{\partial k} = \frac{\partial E}{\partial p}$$

Such a particle with relativistic energy E where

$$E^2 = p^2c^2 + (m_0c^2)^2$$

has

$$2E\frac{\partial E}{\partial p} = 2pc^2$$

or

$$v_{\mathrm{g}} = \frac{\partial E}{\partial p} = \frac{pc^2}{E} = \frac{vc^2}{c^2} = v$$

so that *the group velocity of de Broglie matter wave corresponds to the particle velocity v.*

Even the ‘old quantum theory’ of Bohr–Sommerfeld gained something from de Broglie’s hypothesis. Their postulate that the angular momentum of stationary orbits was restricted to integral (quantum) numbers of the unit angular momentum h was shown, for the circular orbit of radius r, to yield

$$2\pi rp = nh$$

or

$$2\pi r = \frac{nh}{p} = n\lambda$$

so that the circumference of a stationary orbit was a standing wave system and contained an integral number n of λ, the de Broglie wavelength.

Within three years, however, such quantum numbers ceased to be assumptions. They were the natural outcome of the new quantum theory of Schrödinger and Heisenberg.

Heisenberg’s Uncertainty Principle

Although, as we shall see, Schrödinger’s equation takes the form of a standing wave equation, the fitting of an integral number of de Broglie standing waves around a Bohr orbit presents a fundamental difficulty. The azimuthal symmetry of such a pattern, Figure 13.1,

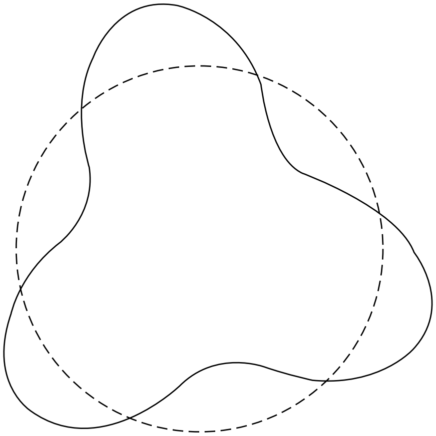

Figure 13.1 Integral number of de Broglie standing waves $\lambda = h/p$ around a circular Bohr orbit does not allow the exact position of the electron to be specified at a particular time

representing an electron in an orbit, does not allow the exact position of the electron to be specified at a particular time. This dilemma was resolved by Heisenberg on the basis of the Bandwidth Theorem we first met on p. 134.

There, a group of waves with a group velocity v_g and a frequency range $\Delta\nu$ superposed effectively only for a time Δt where

$$\Delta\nu\,\Delta t \approx 1$$

Similarly, a group in the wave number range Δk superposed in space over a distance Δx where

$$\Delta x\,\Delta k \approx 2\pi$$

But the velocity of the de Broglie matter wave is essentially a group velocity with a momentum

$$p = \frac{h}{\lambda} = \frac{h}{2\pi}k = \hbar k$$

where

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

so

$$\Delta p = \hbar\,\Delta k$$

and the Bandwidth Theorem becomes Heisenberg's Uncertainty Principle

$$\Delta x\,\Delta p \approx h$$

Since

$$E = h\nu = \frac{h}{2\pi}\omega = \hbar\omega$$

it follows that

$$\frac{\Delta E}{\Delta\nu} = \Delta E\,\Delta t \approx h$$

and

$$\Delta E \approx \hbar\Delta\omega$$

are also expressions of Heisenberg's Uncertainty Principle.

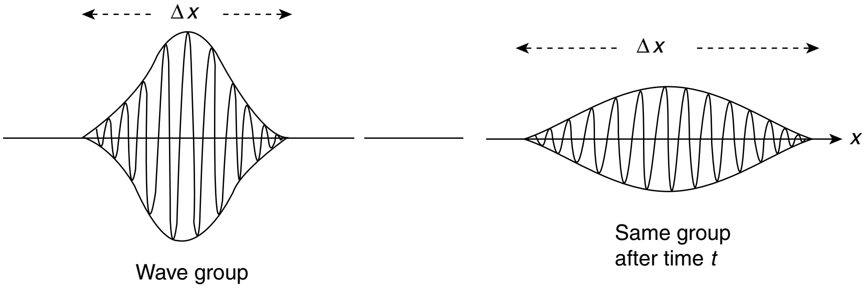

Figure 13.2 A wave group representing a particle showing dispersion after time t. The square of the wave amplitude at any point represents the probability of the particle being in that position, and the dispersion represents the increasing uncertainty of the particle position with time (Heisenberg's Uncertainty Principle)

This relation sets a fundamental limit on the ultimate precision with which we can know the position x of a particle and the x component of its momentum. If Figure 13.2 shows a wave group representing the particle, the range Δx shows the uncertainty of the position of the particle in the range of space over which it could be found, with the probability of its being at a particular place given by the square of the wave amplitude of that position. The relation

$$\Delta x \, \Delta p \approx h$$

means that the velocity of the particle $(p = mv)$ is also uncertain, the more accurate the knowledge of the particle position, the less certain that of the value of its velocity. If the particle is 'observed' at some later time, dispersion of the group will have increased the range Δx and decreased the amplitude. The uncertainty of the position has increased and the probability of its being at any one place has become less. But this is because of the original uncertainty of its velocity, through Δp, which makes an accurate forecast of its position after time t even more unlikely.

The shape of the wave group above is often taken as a Gaussian curve written $\Psi(x, t)$ with a width Δx at $t = 0$ where the value $\Psi(x, t)$ is e^{-1} of its maximum value (see p. 289).

$P(xt)$ defines the probability density of finding the particle at a position Δx, i.e. within the range x and $x + \Delta x$.

The position x and momentum p_x of a particle are conjugate parameters, so the representation of the particle in momentum space $\Phi(p_x, t)$ is the Fourier transform of $\Psi(x, t)$ and $\Phi(p_x, t)$ is also a Gaussian curve with a width Δp_x where $\Phi(p_x t)$ is e^{-1} of its maximum value.

If the group velocity of the wave packet is $v_g = p_0/m$ a rigorous treatment of the time development of these functions leads to the conclusion that $P(xt)$ falls to e^{-1} of its maximum value at the points where

$$x - v_g t = \pm \Delta x$$

where

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

and hence increases with time.

If the time is sufficiently small so that

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

the second term in the bracket is negligible and the wave packet propagates with only a very small change in its width.

As an example, a Gaussian wave packet for an electron localized at time $t = 0$ to within a distance of $10^{-10}m$ (atomic dimensions) with $\Delta p_x = \hbar/\Delta x \approx 10^{-24}\mathrm{kg \cdot m \cdot s^{-1}}$ will have spread to twice its size at time $t = t_1\sqrt{3} \approx 10^{-16}\mathrm{s}$.

An example of the relation

$$\Delta E\,\Delta t \approx h$$

may be found in considering the time spent by an electron in an atomic orbit. In a stable orbit this time Δt is long and the energy uncertainty ΔE is small so the energy levels of stable orbits are well defined. When an electron changes energy levels and radiation is emitted the time in the orbit may be short and the energy levels ill defined so that the term ΔE contributes to the breadth of a spectral line.

(Problems 13.1, 13.2, 13.3, 13.4, 13.5, 13.6, 13.7, 13.8, 13.9, 13.10)

Schrödinger's Wave Equation

The old quantum theory had sought to establish rules for the existence of discrete frequencies and energy levels. An integral number of de Broglie half wavelengths could be fitted around a circular Bohr orbit. Both of these facts are consistent with the classical standing wave systems we examined in Chapters 5 and 9 when waves travelling between rigid boundaries were perfectly reflected.

In Chapter 5 we saw that the transverse displacement $y(xt)$ of a string of length l with both ends fixed obeys the wave equation

$$\frac{\partial^2 y}{\partial x^2} - \frac{1}{v_\mathrm{p}^2}\frac{\partial^2 y}{\partial t^2} = 0$$

where v_p is the wave velocity.

The x and t dependence could be separated in the solution for standing waves to give

$$y(x, t) = A\sin\frac{\omega_n x}{v_\mathrm{p}}\sin\omega_n t$$

where n could take the integral values $n = 1, 2, 3$, etc. to give the discrete *eigenfrequencies*,

$$\omega_n = \frac{n\pi v_{\mathrm{p}}}{l}$$

The solution $y(x, t)$ corresponding to a given ω_n is called an *eigenfunction* or a *wave function*.

In developing the Schrödinger wave equation which applies to particle behaviour we use arguments below which in no way constitute a proof because wave mechanics cannot be derived from classical mechanics. Wave mechanics is based on certain postulates the validity of which can be confirmed only by the accuracy of the predicted results.

From the preceding sections we have the representation of a particle as a matter wave with energy $E = \hbar\omega$, momentum $\mathbf{p} = \hbar\mathbf{k}$ and velocity $v_{\mathrm{g}} = \partial\omega/\partial k$.

Wave mechanics uses the notation

$$\Psi(x, t) = \Psi_0\,\mathrm{e}^{-\mathrm{i}(\omega t - kx)} = \Psi_0\,\mathrm{e}^{\mathrm{i}(px - Et)/\hbar}$$

to define the amplitude of a matter wave at a point x at time t. The physical significance of ψ is amplified on p. 422 but for the moment we note the reversed sign of the exponential index which follows the convention used in all books on quantum mechanics. This merely introduces a π rad phase difference from the notation consistently used in the earlier chapters of this book but the new convention will be used throughout this chapter to avoid confusion with other texts and attention will be carefully drawn to any possible ambiguity.

In classical mechanics the total energy E of a particle of mass m and momentum $\mathbf{p}$ in a conservative field of potential V is given by

$$E = p^2/2m + V$$

Differentiating $\Psi(x, t)$ gives

$$\frac{\partial^2}{\partial x^2}\Psi(x, t) = \frac{-p^2}{\hbar^2}\Psi(x, t)$$

and inserting this value of p^2 in the classical energy equation above gives

$$\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x, t) + (E - V)\Psi(x, t) = 0$$

If we now express $\Psi(x, t) = \psi(x)\,\mathrm{e}^{-\mathrm{i}\omega t}$ we may cancel the common $\mathrm{e}^{-\mathrm{i}\omega t}$ factor from the equation above to obtain the *time independent* Schrödinger wave equation

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

This *time independent* wave equation will give states of *constant frequency*; that is, of *constant energy*, and these are the only states we shall consider in this book.

Note that this equation has the same form as the standing wave equation we first met on p. 124.

States which are not of constant energy require the time dependence to be retained in Schrödinger's equation. We do this by using the fact that

$$\frac{\partial}{\partial t}\Psi(x,t) = \frac{-\mathrm{i}E}{\hbar}\Psi(x,t)$$

and inserting this value of E in the classical energy equation. This gives the *time dependent* Schrödinger wave equation

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

One-dimensional Infinite Potential Well

Consider as a first example the case of a particle constrained to move in a region between $x = 0$ and $x = a$ where the potential $V = 0$. At $x = 0$ and $x = a$ the potential walls are infinitely high as shown in Figure 13.3. This is an idealized form of the potential seen by an electron in the low energy levels near the nucleus of an atom.

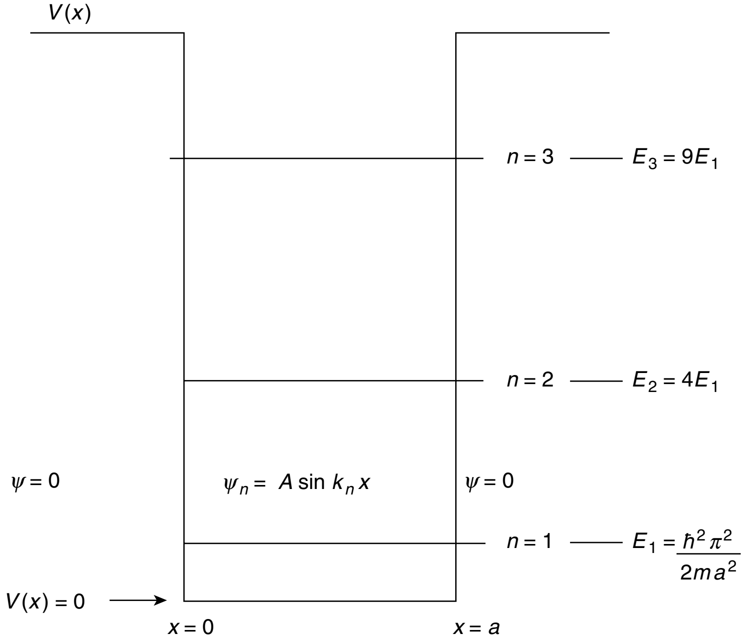

Figure 13.3 An infinitely deep potential well showing allowed energy levels E_n for a particle constrained to move within it with wave function $\psi_n = A\sin k_n x$ where $k_n^2 = 2mE/\hbar^2$ and m is the particle mass

Since $V(x) = 0$ for $0 < x < a$ Schrödinger's equation becomes

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2mE}{\hbar^2}\psi = 0$$

which may be written, as on p. 124, in the form

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0$$

with

$$k^2 = \frac{2mE}{\hbar^2}$$

The boundary conditions are that $\psi(x) = 0$ at $x = 0$ and $x = a$ where $V(x)$ becomes infinite, whilst the other terms in the equation remain finite. The particle must lie within the well and classically, whatever the value of its energy E it will rebound elastically off the potential 'walls'. When moving to the right the particle behaviour may be represented by a wave function of the form $\mathrm{e}^{+\mathrm{i}kx}$ which satisfies Schrödinger's equation, and when moving to the left by a wave function of the form

$$\mathrm{e}^{-\mathrm{i}kx}$$

But, as with the waves on the string, perfect reflection which reverses the amplitude allows $\psi_n(x)$, the solution of Schrödinger's equation, to represent a standing wave system at ω_n; expressed in the form

$$\begin{aligned}\psi_n(x) &= C\,\mathrm{e}^{\mathrm{i}k_n x} - C\,\mathrm{e}^{-\mathrm{i}k_n x}\\ &= A \sin k_n x\end{aligned}$$

where

$$A = \frac{C}{2\mathrm{i}}$$

The boundary condition $\psi_n(x) = 0$ at $x = a$ gives $k_n a = n\pi$ for $n = 1, 2, 3$, etc. i.e. $k_n = n\pi/a$.

Hence

$$k_n^2 = \frac{2mE_n}{\hbar^2} = \frac{n^2\pi^2}{a^2}$$

giving energy eigenvalues

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

Thus, we see that discrete energy values governed by the quantum number n arise naturally from the application of boundary conditions to the wave function solutions of Schrödinger's equation. Values of the particle momentum are also quantized since

$$p = \frac{h}{\lambda} = \hbar k = \frac{n\pi\hbar}{a}$$

It is evident that in an infinite potential well, an electron or particle cannot have an arbitrary energy but must take only the quantized values E_n. This restriction will hold whenever Schrödinger's equation is solved for a potential $V(x)$ which imposes boundary conditions constraining the particle to move in a limited region.

The wave functions $\psi_n(x)$ for $n = 1, 2, 3$ are plotted in Figure 13.4 showing them to be identical with the allowed amplitude functions for standing waves on a vibrating string with fixed ends. Note that the interval between allowed energy states decreases as either the mass of the particle or the dimensions of the potential box increase relative to h. For particles of large mass and systems of large dimensions the allowed energy states form, for all practical purposes, a continuum and are no longer quantized. Thus, in passing from atomic to much larger dimensions the results of quantum mechanics approach those of classical physics.

We see that the minimum value of the energy of the particle in the potential well is not zero but

$$E_1 = \frac{\hbar^2\pi^2}{2ma^2}$$

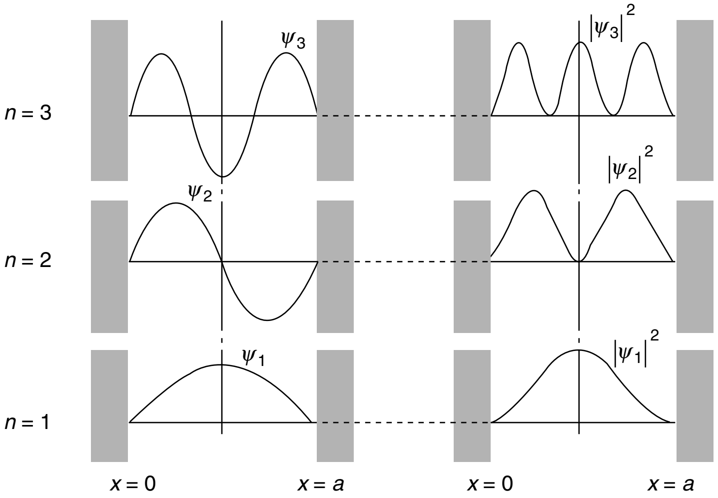

Figure 13.4 Wave functions $\psi_n(x)$ and probability densities $|\psi_n(x)|^2$ for the first three allowed energy levels in an infinitely deep potential well of width a

This minimum energy is related to Heisenberg's Uncertainty Principle

$$\Delta x \, \Delta p \approx h$$

The uncertainty in the position of the particle is obviously $\Delta x = a$ and the particle momentum p may be in either the positive or negative x direction giving an uncertainty

$$\Delta p = 2p$$

Thus

$$\Delta x \, \Delta p = a \cdot 2p \approx h$$

or

$$p \approx \frac{h}{2a}$$

Now, for $V(x) = 0$

$$E = \frac{p^2}{2m} \approx \frac{h^2}{8ma^2} \approx \frac{\hbar^2 \pi^2}{2ma^2}$$

This is an example of the so-called *zero point* energy. We shall meet others.

(Problem 13.11)

Significance of the Amplitude $\psi_n(x)$ of the Wave Function

In Figure 13.4 the amplitude $\psi_n(x)$ of the wave function is plotted for the values $n = 1, 2, 3$ together with the values

$$|\psi_n(x)|^2$$

In the waves we have met so far, the amplitude, or rather the amplitude squared, has been a measure of the intensity of the wave. At a position of high amplitude, the wave was more intense—more energy was localized there. Here we have expressed the motion of a particle confined to a small region of space in terms of its associated matter wave. The amplitude of the wave function $\psi(x)$ varies from point to point within the small region in which the particle is to be found. Outside the infinite well $\psi(x)$ is zero. The intensity of the matter wave is written

$$|\psi(x)|^2 = \psi^*(x)\psi(x)$$

where the complex conjugate $\psi^*(x)$ indicates that $\psi(x)$ may sometimes be complex. Since the matter field describes the motion of the particle we may say that the regions of space in which the particle is more likely to be found are those in which the intensity $|\psi(x)|^2$ is large, or, more formally

> 'the probability of finding the particle described by the wave function $\psi(x)$ in the interval dx around the point x is $|\psi(x)|^2\,\mathrm{d}x$'.

The probability per unit length of finding the particle at x is

$$P(x) = |\psi(x)|^2$$

In three dimensions a wave function would be of the form $\psi(x, y, z)$ and the probability of finding the particle in the unit volume element surrounding the point xyz is

$$P(xyz) = |\psi(xyz)|^2$$

The probability of finding the particle within a finite volume V is obviously

$$P_V = \int_V |\psi(xyz)|^2\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$$

Now the particle must always be somewhere in space so, in extending the integral over all space, the probability becomes a certainty; that is, it equals unity, or

$$\int_{\text{all space}} |\psi(xyz)|^2\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = 1$$

This process of integrating over all possible locations to give unity is called *normalization* and it always imposes restrictions on the form of $\psi(x, y, z)$ which must tend to zero as x, y or z tends to infinity.

Normalization determines the value of the constant A in our wave function

$$\psi_n(x) = A\sin\frac{n\pi x}{a}$$

for the case of the infinite potential well.

There

$$\begin{aligned}\int_{-\infty}^{\infty} |\psi_n(x)|^2\,\mathrm{d}x &= \int_0^a |\psi_n(x)|^2\,\mathrm{d}x \\ &= A^2\int_0^a \sin^2\frac{n\pi x}{a}\,\mathrm{d}x = A^2\frac{a}{2} = 1\end{aligned}$$

Hence

$$A = \sqrt{\frac{2}{a}}$$

and the *normalized* wave function

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

(Problem 13.12)

Particle in a Three-dimensional Box

Suppose the particle is confined to a rectangular volume *abc* at the bottom of an infinitely deep potential well $(V = 0)$ where a, b and c are the lengths of the sides of the rectangular box.

The energy of the particle is then

$$E = \frac{p^2}{2m} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$$

where the momentum components are

$$p_x = n_1 \frac{\pi\hbar}{a}$$
$$p_y = n_2 \frac{\pi\hbar}{b}$$
$$p_z = n_3 \frac{\pi\hbar}{c}$$

and n_1, n_2 and n_3 are integers.

The energy levels allowed in the box are therefore given by

$$E = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)$$

and solutions for the space part of the wave function may be written

$$\psi(x, y, z) = A \sin \frac{n_1\pi x}{a} \sin \frac{n_2\pi y}{b} \sin \frac{n_3\pi z}{c}$$

in accordance with the three-dimensional normal mode solution of p. 249.

If the box is cubical so that $a = b = c$ the allowed energy levels become

$$E = \frac{\pi^2\hbar^2}{2ma^2}(n_1^2 + n_2^2 + n_3^2) = \frac{\pi^2\hbar^2}{2ma^2}k^2$$

where $k^2 = n_1^2 + n_2^2 + n_3^2$ with wave functions

$$\psi(xyz) = A \sin \frac{n_1\pi x}{a} \sin \frac{n_2\pi y}{a} \sin \frac{n_3\pi z}{a}$$

Table 13.1

Energy	n_1, n_2, n_3 Combinations	Degeneracy
$3E_1$	(1, 1, 1)	1
$6E_1$	(2, 1, 1) (1, 2, 1) (1, 1, 2)	3
$9E_1$	(2, 2, 1) (2, 1, 2) (1, 2, 2)	3
$11E_1$	(3, 1, 1) (1, 3, 1) (1, 1, 3)	3
$12E_1$	(2, 2, 2)	1
$14E_1$	(1, 2, 3) (3, 2, 1) (2, 3, 1) (1, 3, 2) (2, 1, 3) (3, 1, 2)	6

We saw, however, on p. 250 that combinations of different n values can give the same k value; that is, the same energy value. When n_1, n_2 and n_3 are permuted without changing the k value, the wave function is also changed so that a certain energy level may be associated with several different wave functions or dynamical states. The energy level is said to be *degenerate*, the *order of degeneracy* being defined by the number of different or independent wave functions associated with the given energy.

In the case of the cubic potential box, the lowest energy level is $3E_1$, i.e.

$$(n_1 = n_2 = n_3 = 1)$$

where

$$E_1 = \frac{\pi^2\hbar^2}{2ma^2}$$

The next energy level is given by $6E_1$, with a degeneracy of 3 where the n values are given by (2, 1, 1) (1, 2, 1) and (1, 1, 2). Higher energy values with degeneracy orders are shown in Table 13.1 above.

(Problem 13.13)

Number of Energy States in Interval E to $E + \mathrm{d}E$

As long as the dimensions of the cubical box above are small the energy levels remain distinct. However, when the volume increases, as is the case for free electrons in a metal, successive energy levels become so close that an almost continuous spectrum is formed.

If we wish to find how many energy levels may be contained in the small energy range dE when the potential box is very large, we have only to apply the result of p. 251 where we found that the number of possible normal modes of oscillation *per unit volume* of an enclosure in the frequency range ν to $\nu + \mathrm{d}\nu$ is given by

$$\mathrm{d}n = \frac{4\pi\nu^2\mathrm{d}\nu}{c^3}$$

There we stressed that the result was independent of any particular system and we applied it to Planck's Radiation Law and Debye's Theory of Specific Heats. Here we use it with

$$E = \frac{p^2}{2m} = h\nu \quad \text{and} \quad p = \frac{E}{c} = \frac{h\nu}{c}$$

$\Big($so that

$$\mathrm{d}E = \frac{p}{m}\,\mathrm{d}p = h\,\mathrm{d}\nu$$

and

$$\mathrm{d}p = \frac{h\,\mathrm{d}\nu}{c}\Big)$$

to give the number of states *per unit volume* in the energy interval dE as

$$\mathrm{d}n(E) = \frac{4\pi(2m^3)^{1/2}E^{1/2}}{h^3}\,\mathrm{d}E$$

This may be applied directly to determine how free electrons in a metal may distribute themselves in a band of energies from zero to some value E. Each energy level can accommodate two electrons (with opposing spins) according to Pauli's Principle so the total number of electrons *per unit volume* in the energy range zero to E is

$$\begin{aligned} n = \int \mathrm{d}n(E) &= \frac{2\cdot 4\pi(2m_{\mathrm{e}}^3)^{1/2}}{h^3}\int_0^E E^{1/2}\,\mathrm{d}E \\ &= \frac{16\pi(2m_{\mathrm{e}}^3)^{1/2}}{3h^3}E^{3/2} \end{aligned}$$

where m_{e} is the electron mass.

If the metal is in its ground state the available electrons will occupy the lowest possible energy levels, and if the total number of electrons *per unit volume* n_0 is less than the total number of energy levels in the band, then the electrons will occupy all energy states up to a maximum energy E_{F} called the Fermi Energy which is given by

$$n_0 = \frac{16\pi(2m_{\mathrm{e}}^3)^{1/2}E_{\mathrm{F}}^{3/2}}{3h^3}$$

Typical values of E_{F} are of the order of 5 eV $(1\,\mathrm{eV} = 1.6\times 10^{-19}\,\mathrm{J})$.

(Problems 13.14, 13.15)

The Potential Step

The standing wave system of the infinite potential well where the wave function

$$\psi_n(x)$$

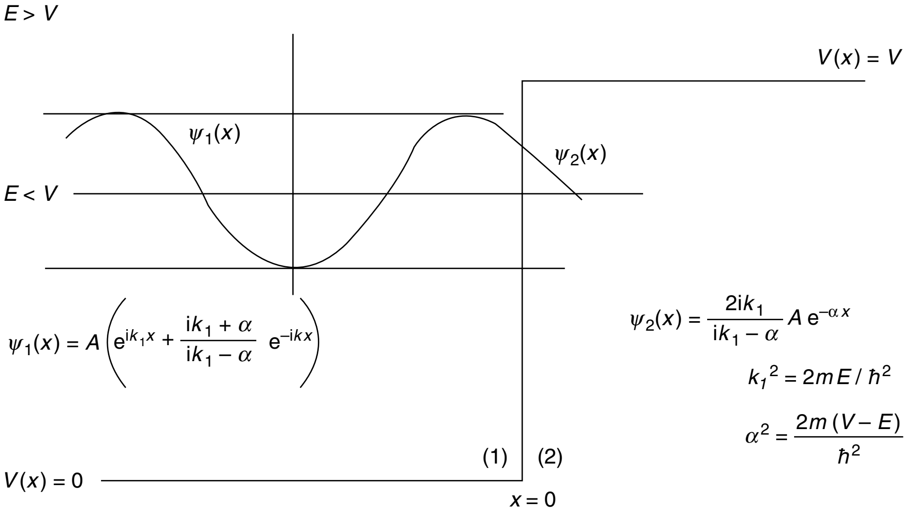

Figure 13.5 Wave functions $\psi_1(x)$ and $\psi_2(x)$ for a particle mass m, energy $E < V$ at a potential step $V(x) = V$

is finite in the region $V(x) = 0$ but zero at all other points is unique in the formal correspondence it presents between classical and quantum mechanical results. The quantum effects become evident when we consider the general case of the potential step of finite height V in Figure 13.5 which is an idealized form of the very steep potential gradient of a conservative force

$$F(x) = -\frac{\partial V}{\partial x}$$

Such a potential step would be seen by a free electron near the surface of a metal.

It is necessary to consider separately the two cases where the total particle energy E is (a) less than the potential energy V, and (b) greater than V, where

$$E = \frac{p^2}{2m} + V(x)$$

(a) $E < V$

When E is less than V, the region $x > 0$ of Figure 13.5 is forbidden to the particle by classical mechanics for the kinetic energy

$$\frac{p^2}{2m}$$

would then have a negative value.

In finding the complete solution for $\psi(x)$ for the potential step we must solve Schrödinger's equation for the separate regions of Figure 13.5, $x < 0$ (region 1) and $x > 0$ (region 2).

In region 1, $V(x) = 0$ and we have

$$\frac{\partial^2 \psi_1(x)}{\partial x^2} + \frac{2mE}{\hbar^2}\psi_1(x) = 0$$

with a solution

$$\psi_1(x) = A\,\mathrm{e}^{\mathrm{i}k_1 x} + B\,\mathrm{e}^{-\mathrm{i}k_1 x}$$

where

$$k_1^2 = \frac{2mE}{\hbar^2}$$

The term $A\,\mathrm{e}^{\mathrm{i}k_1 x}$ (with the sign convention of this chapter) is the wave representation of an incident particle moving to the right, and $B\,\mathrm{e}^{-\mathrm{i}k_1 x}$ represents a reflected particle moving to the left.

In region 2, $V(x) = V$ and Schrödinger's equation becomes

$$\frac{\partial^2 \psi_2(x)}{\partial x^2} + \frac{2m(E - V)}{\hbar^2}\psi_2(x) = 0$$

or

$$\frac{\partial^2 \psi_2(x)}{\partial x^2} - \alpha^2 \psi_2(x) = 0$$

where

$$\alpha^2 = \frac{2m(V - E)}{\hbar^2}$$

This equation has the solution

$$\psi_2(x) = C\,\mathrm{e}^{-\alpha x} + D\,\mathrm{e}^{\alpha x}$$

Now the probability of finding the particle in region 2 where it is classically forbidden depends on the square of the wave function amplitude $|\psi_2(x)|^2$ with the condition that for any wave function to be normalized (i.e. for

$$\int |\psi_2(x)|^2\, \mathrm{d}x = 1\Bigg)$$

the wave function $\psi_2(x) \to 0$ as $x \to \infty$.

This forbids the second term $D\,\mathrm{e}^{\alpha x}$ which increases with x but still leaves

$$\psi_2(x) = C\,\mathrm{e}^{-\alpha x}$$

to give a finite probability of finding the particle beyond the potential step, a probability which decreases exponentially with distance. This is a profound departure from classical behaviour.

At the boundary $x = 0$, $\psi(x)$ must be finite to give a finite probability of finding the particle there, but there is a finite discontinuity in $V(x)$. In these circumstances Schrödinger's equation asserts that the second derivative

$$\frac{\partial^2\psi(x)}{\partial x^2}$$

at $x = 0$ is finite, which means that both $\psi(x)$ and $(\partial\psi(x)/\partial x)$ are continuous at $x = 0$.

These are the boundary conditions which allow the separate solutions

$$\psi_1(x) \quad \text{and} \quad \psi_2(x)$$

for the wave function, to be matched across the boundary of the two regions.

The continuity of $\psi(x)$ at $x = 0$ gives $\psi_1(x) = \psi_2(x)$ or $A + B = C$ whilst

$$\frac{\partial\psi_1(x)}{\partial x} = \frac{\partial\psi_2(x)}{\partial x}$$

at $x = 0$ gives

$$\mathrm{i}k_1(A - B) = -\alpha C = -\alpha(A + B)$$

Thus

$$B = \left(\frac{\mathrm{i}k_1 + \alpha}{\mathrm{i}k_1 - \alpha}\right)A$$

and

$$C = \frac{2\mathrm{i}k_1}{\mathrm{i}k_1 - \alpha}A$$

The wave functions for the separate regions then become

$$\psi_1(x) = A\left(\mathrm{e}^{\mathrm{i}k_1 x} + \frac{\mathrm{i}k_1 + \alpha}{\mathrm{i}k_1 - \alpha}\,\mathrm{e}^{-\mathrm{i}k_1 x}\right)$$

and

$$\psi_2(x) = \frac{2\mathrm{i}k_1}{\mathrm{i}k_1 - \alpha}A\,\mathrm{e}^{-\alpha x}$$

and these are shown in Figure 13.5. Note particularly that the intensity of the incident part of the wave function

$$|\psi_1(x)|^2 = |A|^2$$

whilst the reflected intensity is

$$|B|^2 = \left|\frac{\mathrm{i}k_1 + \alpha}{\mathrm{i}k_1 - \alpha} A\right|^2 = |A|^2$$

Thus, for any energy $E < V$ we have total reflection as in the classical case, even for those particles which penetrate the classically forbidden region $x > 0$ where $\psi_2(x)$ is finite.

In region 2 the probability of finding the particle is

$$\begin{aligned} P(x) &= |\psi_2(x)|^2 = |C\,\mathrm{e}^{-\alpha x}|^2 \\ &= \left|\frac{2\mathrm{i}k_1}{\mathrm{i}k_1 - \alpha} A\,\mathrm{e}^{-\alpha x}\right|^2 = \frac{4k_1^2}{k_1^2 + \alpha^2} A^2\,\mathrm{e}^{-2\alpha x} \end{aligned}$$

Since the exponential coefficient α depends on $V(x)$ the greater the value $V(x)$ the faster the wave function $\psi_2(x)$ goes to zero in region 2 for a given total energy $E < V$.

When $V(x) \to \infty$, as in the case of the infinite potential well, $\psi_2(x)$ becomes zero, as we have seen; and there is no penetration into the classically forbidden region.

Several important physical phenomena may be explained on the assumption that a particle with $E < V$ meeting a potential step of finite height V and *finite width b* has a wave function $\psi_2(x)$ which is still finite at $x = b$, making it possible for the particle to tunnel through the potential barrier (Figure 13.6). The probability that the particle will penetrate the barrier to $x = b$ is given by

$$P(x) = |\psi_2(x)|^2 \propto \mathrm{e}^{-2\alpha x}$$

and beyond this barrier the particle will propagate in region 3 with a wave function $\psi_3(x)$ of reduced amplitude. The boundary conditions must then be applied at $x = b$ to match $\psi_2(x)$ to $\psi_3(x)$.

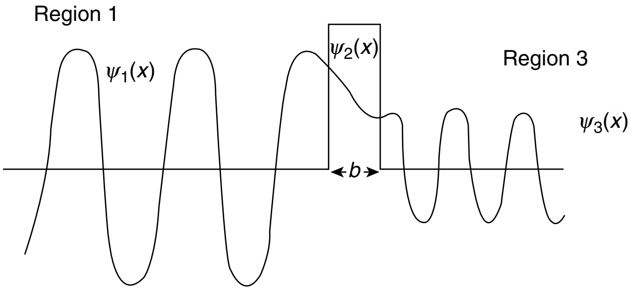

Figure 13.6 Narrow potential barrier of width b penetrated by a particle represented by $\psi_1(x)$ leaving a finite amplitude $\psi_3(x)$ as a measure of the reduced probability of finding the particle in region 3

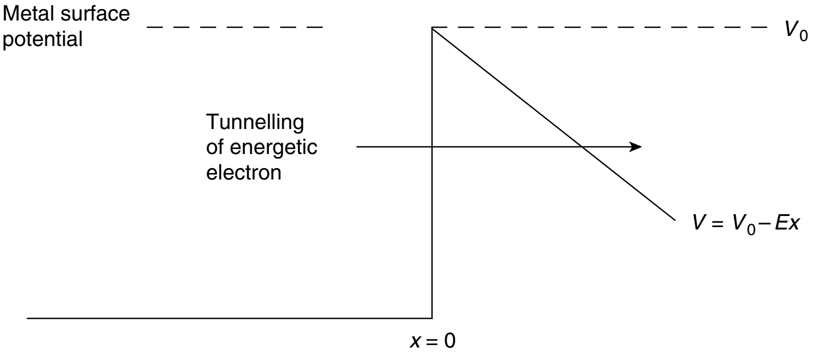

Figure 13.7 Application of an electric field E to the surface of a metal at potential V_0 reduces the potential to $V = V_0 - Ex$ forming a barrier of finite width which may be penetrated by an energetic electron near the metal surface

This quantum 'tunnel effect' is the basis of the explanation of the radioactive decay of the nucleus. In addition the potential step seen by a free electron near the surface of a metal may be distorted, as shown in Figure 13.7, by the application of an external electric field, to form a barrier of finite width. The most energetic electrons near the surface of the metal can leak through the barrier in a process known as *field electron* emission.

Another example results from the two possible positions of the single nitrogen atom with respect to the three hydrogen atoms in the ammonia molecule NH_3. These positions are shown as N and N' in Figure 13.8 together with the potential barrier presented to the nitrogen atom as it moves to and fro between N and N'. This penetration occurs at a frequency of 2.3786×10^{10} Hz for the ground state of NH_3 and its high definition is used as an atomic clock to fix standards of time.

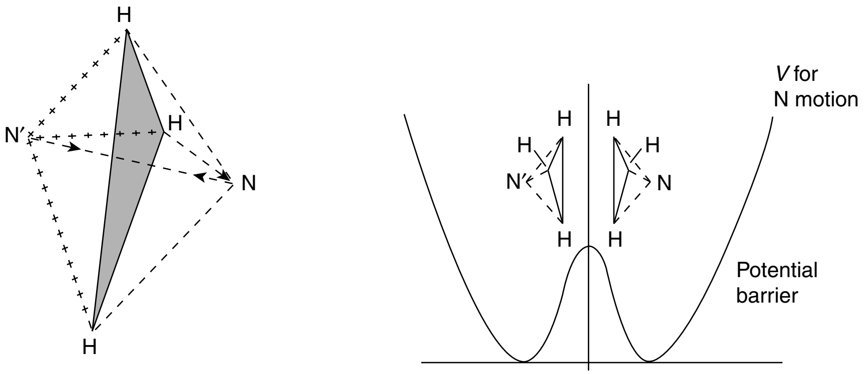

Figure 13.8 The two possible configurations N and N' of the nitrogen atom with respect to the triangular hydrogen base in the ammonia molecule NH_3 and the finite potential barrier penetrated by the nitrogen atom at a frequency of $>10^{10}$ Hz in the NH_3 ground state

(Problem 13.16)

(b) $E > V$

In the region $x < 0$ in Figure 13.5 $V(x) = 0$ and Schrödinger's equation is

$$\frac{\partial^2 \psi_1(x)}{\partial x^2} + \frac{2mE}{\hbar^2}\psi_1(x) = 0$$

or

$$\frac{\partial^2 \psi_1}{\partial x^2} + k_1^2 \psi_1 = 0$$

with

$$k_1^2 = \frac{2mE}{\hbar^2}$$

having a solution

$$\psi_1(x) = A\,\mathrm{e}^{\mathrm{i}k_1 x} + B\,\mathrm{e}^{-\mathrm{i}k_1 x}$$

with both incident and reflected terms.

The momentum of the particle is p_1 where $p_1^2/2m = E$.

In the region $x > 0$, $V(x) = V$ and Schrödinger's equation is

$$\frac{\partial^2 \psi_2(x)}{\partial x^2} + \frac{2m(E - V)}{\hbar^2}\psi_2(x) = 0$$

or

$$\frac{\partial^2 \psi_2}{\partial x^2} + k_2^2 \psi_2 = 0$$

where

$$k_2^2 = \frac{2m(E - V)}{\hbar^2}$$

and the particle momentum p_2 is given by $p_2^2/2m = (E - V)$.

In the wave function solution for this region we consider only the right-going or transmitted term since there is nothing beyond $x = 0$ to cause a reflection, so

$$\psi_2(x) = C\,\mathrm{e}^{\mathrm{i}k_2 x}$$

Now the wave number k is related to the de Broglie wavelength of the particle and we see that k changes when the potential V changes; that is, when the particle experiences a change in the force acting on it. Such a particle therefore reacts to a changing potential as light reacts to changing refractive index. As the potential V increases for $E > V$ the momentum p and wave number $k(p = \hbar k)$ decrease and the wavelength λ increases.

At $x = 0$ the conditions for continuity give

$$\psi_1(x) = \psi_2(x)$$

or

$$A + B = C$$

and

$$\frac{\partial \psi_1(x)}{\partial x} = \frac{\partial \psi_2(x)}{\partial x}$$

or

$$k_1(A - B) = k_2 C$$

These two equations give

$$B = \frac{(k_1 - k_2)}{(k_1 + k_2)} A$$

and

$$C = \frac{2k_1}{k_1 + k_2} A$$

Since B is not zero, some reflection takes place at $x = 0$ even though the energy $E > V$. This is clearly not classical behaviour. If many particles form an incident beam at $x = 0$ and each particle has velocity

$$v_1 = \frac{p_1}{m} = \frac{\hbar k_1}{m}$$

then the velocity of transmitted particles will be

$$v_2 = \frac{p_2}{m} = \frac{\hbar k_2}{m}$$

The incident flux of particles; that is, the number crossing unit area per unit time, may be seen as the product of the velocity and the intensity; that is

$$v_1 |A|^2$$

The reflected flux is

$$v_1|B|^2$$

and the transmitted flux is

$$v_2\,|\,C\,|^2$$

Thus, the reflection coefficient, the ratio of reflected to incident flux is

$$R = \frac{v_1\,|\,B\,|^2}{v_1\,|\,A\,|^2} = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2}$$

and the transmission coefficient, the ratio of transmitted to incident flux is

$$T = \frac{v_2\,|\,C\,|^2}{v_1\,|\,A\,|^2} = \frac{k_2}{k_1}\,\frac{(2k_1)^2}{(k_1 + k_2)^2} = \frac{4k_1k_2}{(k_1 + k_2)^2}$$

results which are similar to those for our classical waves in earlier chapters.

Note that $R + T = 1$ showing that the number of particles is conserved.

We have chosen here to apply R and T to a number of particles forming a beam. These coefficients, when applied to identical particles forming the beam, measure the average probability that an individual particle will be reflected or transmitted.

(Problem 13.17)

The Square Potential Well

Let us consider a particle with energy $E < V$ moving in the square potential well of width a in Figure 13.9. Within the well the potential is zero, and the value $V$of the height of the well

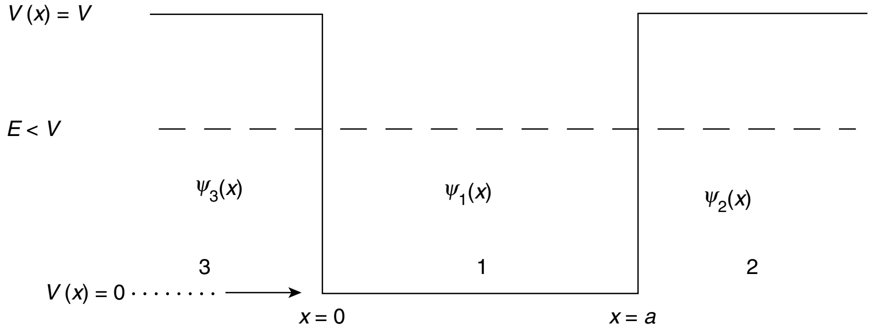

Figure 13.9 A particle with energy $E < V(V =$ the finite height of a square potential well of width a) may take only the energy values E satisfying the equation

$$\tan a\sqrt{\frac{2mE}{\hbar^2}} = \frac{2\sqrt{E(V-E)}}{2E - V}$$

The wave functions in the three regions are matched at the boundaries $x = 0$ and $x = a$ by the conditions that $\psi(x)$ and $\partial\psi(x)/\partial x$ are continuous is finite. This potential approximates that of a finite range force which has no influence beyond a limited distance. Outside the range of the force the potential may be considered constant. From our discussion of the infinitely deep potential well $(V = \infty)$ and of the potential step we can expect our wave function representation to have the form of an integral number of de Broglie half wavelengths within the well, plus an exponentially decaying penetration into the wall on either side.

Writing Schrödinger's equation for each of the three regions, we have for region $1 (0 < x \leq a)$

$$\frac{\partial^2 \psi_1(x)}{\partial x^2} + \frac{2mE}{\hbar^2} \psi_1(x) = 0$$

with a solution, for $k_1^2 = 2mE/\hbar^2$ of

$$\begin{aligned} \psi_1(x) &= A\,\mathrm{e}^{\mathrm{i}k_1 x} + B\,\mathrm{e}^{-\mathrm{i}k_1 x} \\ &= A(\cos k_1 x + \mathrm{i}\sin k_1 x) + B(\cos k_1 x - \mathrm{i}\sin k_1 x) \\ &= A_1 \cos k_1 x + B_1 \sin k_1 x \end{aligned}$$

where $A_1 = A + B$ and $B_1 = \mathrm{i}(A - B)$.

In region $2 (x \geq a)$

$$\frac{\partial^2 \psi_2(x)}{\partial x^2} + \frac{2m(E - V)}{\hbar^2} \psi_2(x) = 0$$

has the solution

$$\psi_2(x) = A_2\,\mathrm{e}^{\alpha x} + B_2\,\mathrm{e}^{-\alpha x}$$

where

$$\alpha^2 = \frac{2m}{\hbar^2}(V - E)$$

In region 3, $(x < 0)$

$$\frac{\partial^2 \psi_3(x)}{\partial x^2} + \frac{2m(E - V)}{\hbar^2} \psi_3(x) = 0$$

has the solution

$$\psi_3(x) = A_3\,\mathrm{e}^{\alpha x} + B_3\,\mathrm{e}^{-\alpha x}$$

For $\psi(x)$ to remain finite as $x \to \pm\infty$ (normalization condition) A_2 and B_3 must be zero, and the boundary conditions $\psi(x)$ and $\partial\psi(x)/\partial x$ continuous, must be satisfied at $x = 0$ and $x = a$.

At $x = 0$,

$$\psi_1(x) = \psi_3(x) \quad \text{and} \quad \frac{\partial \psi_1(x)}{\partial x} = \frac{\partial \psi_3(x)}{\partial x}$$

give

$$A_1 = A_3 \tag{13.1}$$

and

$$k_1 B_1 = \alpha A_3 \tag{13.2}$$

whilst at $x = a$

$$\psi_1(x) = \psi_2(x) \quad \text{and} \quad \frac{\partial \psi_1(x)}{\partial x} = \frac{\partial \psi_2(x)}{\partial x}$$

give

$$A_1 \cos k_1 a + B_1 \sin k_1 a = B_2 \, \mathrm{e}^{-\alpha a} \tag{13.3}$$

and

$$-k_1 A_1 \sin k_1 a + k_1 B_1 \cos k_1 a = -\alpha B_2 \, \mathrm{e}^{-\alpha a} \tag{13.4}$$

In order to satisfy equations (13.1), (13.2), (13.3) and (13.4) some conditions must be imposed on k and α; that is, on the value of E, so only certain values of E are allowed.

Equations (13.1) and (13.2) give

$$\frac{A_1}{B_1} = \frac{k_1}{\alpha}$$

and this equation with equations (13.3) and (13.4) yields

$$\tan k_1 a = \frac{2 k_1 \alpha}{k_1^2 - \alpha^2}$$

or

$$\tan a \sqrt{\frac{2mE}{\hbar^2}} = \frac{2\sqrt{E(V - E)}}{2E - V}$$

Only those values of E which satisfy this relation are allowed energy states, but these values must be found by numerical or graphical methods.

The wave functions for the first three allowed energy values are shown in Figure 13.10 and their general behaviour may be clarified by considering Schrödinger's equation in the form

$$\frac{\partial^2 \psi}{\partial x^2} \Big/ \psi = -(+\text{ve constant})(E - V)$$

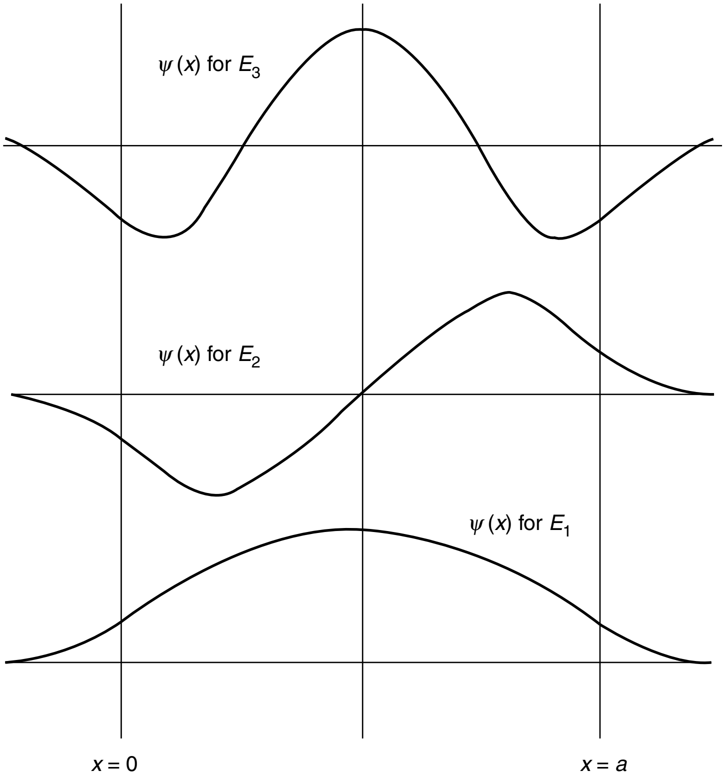

Figure 13.10 Wave functions for a particle in a square potential well with the lowest three allowed energies E_1, E_2, E_3. Note the exponential decay of $\psi(x)$ outside the box

Now $\partial^2\psi/\partial x^2$ is the rate of change of the slope; that is, the curvature of the wave function and when $E > V$ both sides of the equation are negative and the ψ curve must everywhere keep its concave side towards the x axis as it always does, for example, in sine and cosine curves. The curvature increases with E so we shall expect more de Broglie half wavelengths in the higher energy levels. This is consistent with the argument that an increase in E increases the wave number k and reduces the de Broglie wavelength λ.

In the lowest energy level the ψ curve is always without a node, the next level always has one node, the third two nodes, etc. but the zeros will not be quite equally spaced and the ψ amplitude will not be uniform across the well. In particular it will increase near the potential walls as the particle is slowed down to give a higher probability of the particle being found there. Where $E < V$ the ratio

$$\frac{\partial^2\psi/\partial x^2}{\psi}$$

will be positive and the ψ curve must keep its convex side towards the axis as in exponential curves. The classical boundary $E = V$ must always mark the division where the character of the ψ curve changes from one form to the other and the two parts of the curve will only match for certain values of E.

The Harmonic Oscillator

As a final example to illustrate the fitting of ψ curves into a potential well we shall consider the potential curve $V = \frac{1}{2}sx^2$ of the harmonic oscillator in Figure 13.11. The calculation of the ψ curves is too complicated for this chapter but their essential features confirm what we may expect from our earlier examples. Moreover, by purely classical arguments we shall obtain a very good approximation to the wave mechanical results.

In 1901 Planck had postulated that the energy of such an oscillator could have the values $E = nh\nu$ where n was an integer and ν was the frequency. Schrödinger was able to derive this result in 1926 but one essential difference arises from the Uncertainty Principle which requires a minimum energy level or *zero point energy* of $\frac{1}{2}h\nu$.

For a classical oscillator the minimum energy $E = 0$, point 0 in Figure 13.11 gives the precise and simultaneous values $x = 0$ and $p = 0$; that is, a zero oscillation. The Uncertainty Principle forbids this. If a_0 is the smallest amplitude of the oscillator compatible with the Uncertainty Principle, then

$$a_0 \sim \tfrac{1}{2}\Delta x$$

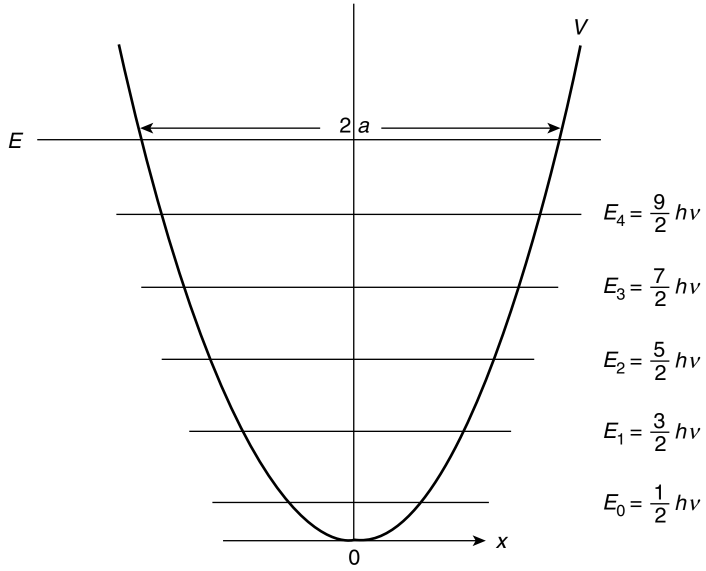

Figure 13.11 Potential energy curve V of a harmonic oscillator with allowed energy levels $E_n = (n + \frac{1}{2})h\nu$. The energy E (with oscillator amplitude a) is shown in the text to define an average value of the de Broglie wavelength $\lambda = h/(\frac{4}{3}mE)^{1/2}$

If p_0 is the maximum momentum of the oscillator with amplitude a_0 it may be either in the positive or negative direction so

$$p_0 \sim \tfrac{1}{2}\Delta p$$

The energy of a classical oscillator is given by

$$\begin{aligned} E &= \tfrac{1}{2}m\omega^2 a_0^2 = \tfrac{1}{2}\omega(a_0)(m\omega a_0) = \tfrac{1}{2}\omega a_0 p_0 \\ &\approx \tfrac{1}{8}\omega\Delta x\Delta p \approx \tfrac{1}{8}h\omega \approx \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}h\nu \end{aligned}$$

All other energy levels will therefore take integral steps of $h\nu$ above this zero point energy.

Let us consider the energy level of the oscillator which has an amplitude a so that

$$E = \frac{p^2}{2m} + V = \frac{p^2}{2m} + \frac{1}{2}sx^2 = \frac{1}{2}sa^2 = \frac{1}{2}m\omega^2 a^2$$

so that

$$2a = \frac{2}{\omega}\sqrt{\frac{2E}{m}}$$

The value of the kinetic energy of the oscillator averaged over the distance $2a$ between $\pm a$ may be written

$$\frac{\int_{-a}^{a} p^2/2m\,\mathrm{d}x}{\int_{-a}^{a}\mathrm{d}x} = \frac{1}{2a}\int_{-a}^{a}\left(E - \frac{1}{2}m\omega^2 x^2\right)\mathrm{d}x = E - \frac{1}{6}m\omega^2 a^2 = \frac{2}{3}E$$

because

$$E = \tfrac{1}{2}m\omega^2 a^2$$

Thus, the average value of the kinetic energy

$$\frac{p^2}{2m} = \frac{2}{3}E$$

giving

$$p = \frac{h}{\lambda} = \sqrt{\frac{4mE}{3}}$$

This gives an average value for the de Broglie wavelength of

$$\lambda = \frac{h}{\sqrt{\dfrac{4mE}{3}}}$$

and we expect n half wavelengths to fit into the length $2a$ at energy E where

$$2a = \frac{2}{\omega}\sqrt{\frac{2E}{m}}$$

Thus

$$n\frac{\lambda}{2} = \frac{nh}{2\sqrt{4mE/3}} = \frac{2}{\omega}\sqrt{\frac{2E}{m}}$$

Writing $\omega = 2\pi\nu$ we have

$$E = \frac{\pi}{4}\sqrt{\frac{3}{2}}nh\nu = 0.96\,nh\nu$$

which is a fairly close approximation to $nh\nu$. The correct result, however, must take into account the zero point energy of $\frac{1}{2}h\nu$ and the energy levels are given by

$$E = (n + \tfrac{1}{2})h\nu, \quad n = 0, 1, 2, 3, \text{etc.}$$

The ψ curves for the first four energy levels are plotted in Figure 13.12 together with those for $|\psi|^2$.

We see that whilst a classical oscillator may never exceed its maximum amplitude a particle obeying a wave mechanical description has a finite probability of being found beyond this limit.

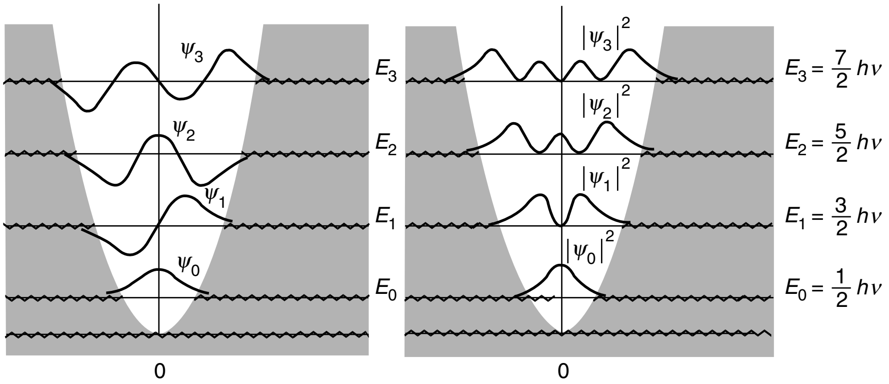

Figure 13.12 Wave functions $\psi(x)$ and probability densities $|\psi(x)|^2$ for the first four energy levels of the harmonic oscillator

(Problems 13.18, 13.19)

Electron Waves in a Solid

Bloch Functions and the Kronig–Penney Model

When electrons move through a solid, e.g. a metal, they meet a series of potential barriers generated by the atoms or ions located at the centre of the valleys between successive barriers. Figure 13.13 shows such a one-dimensional lattice array of ions. The electron wave function is derived via Bloch functions and the electron behaviour is demonstrated using the Kronig–Penney Model which replaces Figure 13.13 in the first instance with a periodic series of potential wells of finite depth as shown in Figure 13.14. An exact but unwieldy solution can be found for the situation described by Figure 13.14, but Kronig and Penney, by deepening the wells and reducing their separation, were able to show how the electrons behaved and to demonstrate the restrictions imposed on their motion.

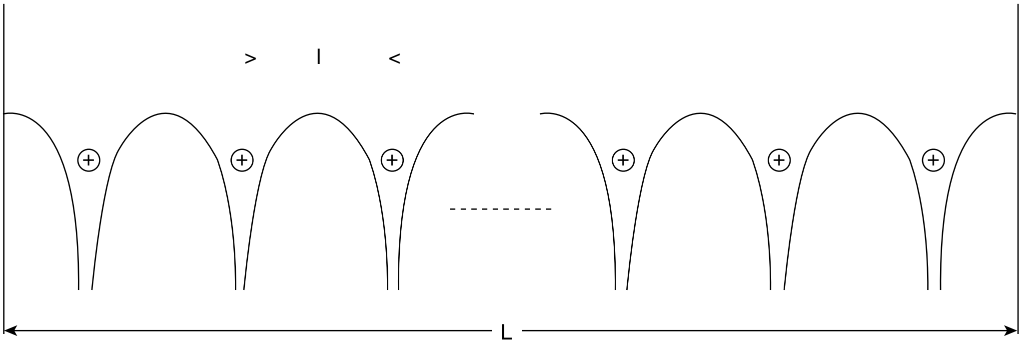

Figure 13.13 A one-dimensonal periodic array of poterntial barriers formed by ions or atoms located along a crystal lattice

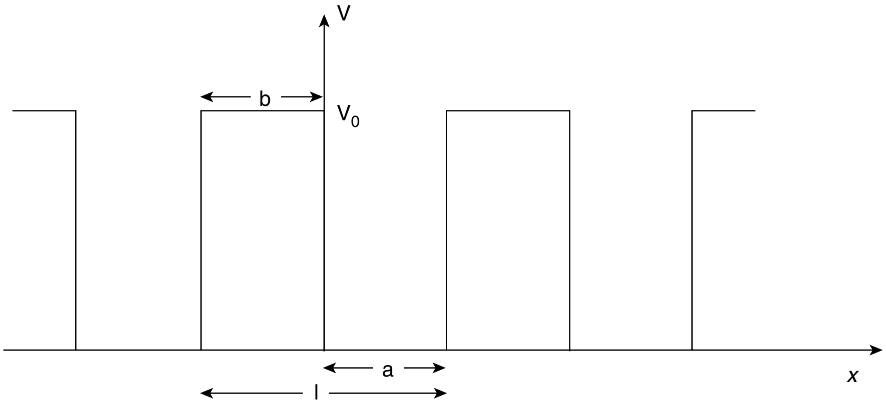

Figure 13.14 A series of finite potential wells used by Kronig and Penney as a first approximation of Figure 13.13

In Figure 13.14 the space between the potential wells is a, the well thickness is b and its height is V_0. The problem is similar to that described on p. 435 where the total energy of the electron is $E - V_0$ so the wave equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0$$

Now, $V(x)$ is periodic so $V_x = V(x + l)$ where $l = a + b$. Evidently, since the probability of finding an electron at x or at $x + l$ is the same, we have

$$|\psi(x)|^2 = |\psi(x + l)|^2$$

Hence, we may write $\psi(x + l) = \gamma\psi(x)$ where $\gamma\gamma^* = |\gamma|^2 = 1$ (γ^* is the complex conjugate of γ).

At this stage we could write $\gamma = e^{ikx}$, but this does not define k well enough to satisfy the boundary conditions at each end of the crystal. For periodic functions the conventional method to meet the boundary conditions is to form a ring of circumference of length $L = Nl$ where L is the length of the crystal and N is the number of atoms along its length. Note that in Figure 13.13 the potential barriers at each end of the crystal add l to its length.

Proceeding along the crystal (or around the ring) we have

$$\psi(x + 2l) = \psi(x + l + l) = \gamma\psi(x + l) = \gamma^2(\psi)$$

or for r integral steps

$$\psi(x + rl) = \gamma^r\psi(x) \qquad r = (0, 1, 2, 3 \ldots N - 1)$$

Now $r = 0$ and $r = N$ are identical positions (one complete circuit of the ring), so

$$\psi(x + Nl) = \gamma^N\psi(x) = \psi(x)$$

that is

$$\gamma^N = 1$$

We may now write

$$\gamma = \mathrm{e}^{i2\pi r/N} \qquad (r = 0, 1, 2, 3 \ldots)$$

so that

$$\psi(x + l) = \gamma\psi(x) = e^{i2\pi r/N}\psi(x)$$

The Bloch function $\mu_k(x)$ is defined by

$$\psi(x) = \mu_k(x)\mathrm{e}^{ikx}$$

where

$$\mu_k(x) = \mu_k(x + l)$$

Here, $k = 2\pi r/lN$ and $\mu_k(x)$ has the periodicity of the potential. Since r changes by units as we move along the crystal each step of r/N (for N large) is so small that $k = 2\pi r/lN$ may be considered as varying continuously.

The Bloch functions satisfy all conditions because

$$\psi(x + l) = e^{ik(x+l)}\mu_k(x + l) = e^{ikl}e^{ikx}\mu_k(x) = e^{i\frac{2\pi r}{N}}\psi(x) = \gamma\psi(x)$$

The wave equations of Figure 13.14 are

$$\frac{\partial^2\psi_1}{\partial x^2} + \alpha^2\psi_1 = 0 \qquad 0 < x < a \tag{13.5}$$

and

$$\frac{\partial^2\psi_2}{\partial x^2} - \beta^2\psi_2 = 0 \qquad -b < x < 0 \tag{13.6}$$

where

$$\alpha^2 = \frac{2mE}{\hbar^2} \quad \text{and} \quad \beta^2 = \frac{2m}{\hbar^2}(V_0 - E)$$

with

$$V(x) = V(x + l) \quad \text{and } l = a + b$$

The Bloch function $\mu_k(x) = \mu_k(x + l)$ where $l = a + b$, so for $x = -b$ we have $\mu_x(a) = \mu_k(-b)$, which is evident from Figure 13.14.

Earlier examples in this chapter have shown that the boundary conditions require $\psi(x)$ and its first derivative to be continuous across any potential change.

Applying $\psi(x) = \mu_k(x)e^{ikx}$ to equations (13.5) and (13.6), we have

$$\begin{aligned} \mu_1(x) &= Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x} \qquad 0 < x < a \\ \mu_2(x) &= Ce^{(\beta-ik)x} + De^{-(\beta+ik)x} \qquad -b < x < 0 \end{aligned}$$

so that the boundary conditions are

$$\mu_1(0) = \mu_2(0) \qquad \text{with} \qquad \left(\frac{\partial\mu_1}{\partial x}\right)_{x=0} = \left(\frac{\partial\mu_2}{\partial x}\right)_{x=0}$$

and

$$\mu_1(a) = \mu_2(-b) \qquad \text{with} \qquad \left(\frac{\partial\mu_1}{\partial x}\right)_{x=a} = \left(\frac{\partial\mu_2}{\partial x}\right)_{x=-b}$$

which give four homogenous equations.

Remember that

$$\mu(x) = \mu(x + l)$$

As with the rectangular well on p. 435 these boundary conditions determine the permitted values of E (via α and β). Here, the boundary conditions require either $A = B = C = D = 0$ or the determinant of their coefficients to be zero. Equating the determinant of the coefficients to zero gives the unwieldy expression

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sin \alpha a \sinh \beta b + \cos \alpha a \cosh \beta b = \cos k(a + b) \tag{13.7}$$

Kronig and Penney simplified this equation by allowing V_0 to tend to infinity as b approached zero in such a way that $V_0 b$ remained constant. This has two important implications. First, the potential wells become very deep so that Figure 13.14 approximates Figure 13.13. Second, their separation is narrowed so that $l = a + b \approx a$ and we may rewrite equation(13.7) as

$$V_0 b\left(\frac{ma}{\hbar^2}\right) \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \tag{13.8}$$

The values of $\alpha = (2mE/\hbar^2)^{\frac{1}{2}}$ which satisfy this equation determine the permitted energy values and wave functions of the electrons.

Note that when $V_0 \rightarrow \infty$ equation (13.8) requires $\sin \alpha a = 0$ to remain valid, leaving

$$\alpha = \pm \frac{n\pi}{a} \qquad (n = 1, 2, 3 \ldots)$$

or

$$E = \frac{\pi^2 \hbar^2 n^2}{2ma^2}$$

which are the quantized energies of the tightly bound electron in the infinitely deep potential of p. 420.

At the other extreme when $V_0 = 0$ equation (13.8) gives

$$\alpha = k = \left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}$$

which allows E to take any positive value. This gives a free particle solution to the wave equation (graphed as the dotted parabola in Figure 13.16).

Between these two extreme values of V_0 the permitted values of the energy E are displayed on the graph in Figure 13.15 where the left-hand side of equation (13.8) is plotted against αa where αa is written w and $V_0 b(\frac{ma}{\hbar^2})$ is written K.

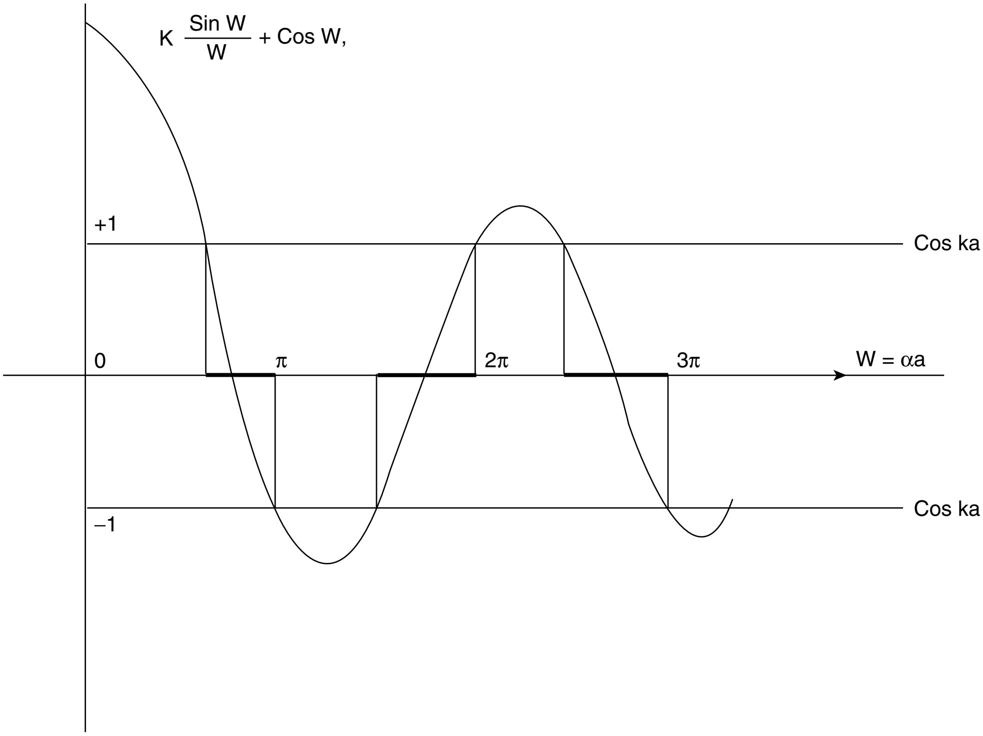

Figure 13.15 Allowed electron energy values are denoted by heavy horizontal lines which define the Brillouin zones. These occur when the left-hand side of equation (13.8) has values between ± 1. The curve is symmetric about the axis $w = 0$.

Now the limits of cos ka in equation (13.8) are ± 1 and these determine the allowed values of $w = \alpha a$ indicated by the heavy horizontal line on the w or αa axis. These in turn denote the permitted ranges or bands of energy values which the electron may take. The bands increase with $w = \alpha a$ and between the bands are gaps where electron energies are forbidden. The limits of each energy band are defined by $\cos ka = \pm 1$ that is

$$k = \pm \frac{n\pi}{a} \qquad (n = 1, 2, 3, \ldots)$$

and the regions in k space defining the energy bands are known as Brillouin zones. The band for $n = 1$ is called the first Brillouin zone, $n = 2$ is the second Brillouin zone and so on. Figure 13.15 can be displayed as the energy E versus k graph in Figure 13.16 where the dotted parabola defines the free electron energy $E = \frac{\hbar^2}{2m}k^2$ and the heavy lines at the k boundaries denote the permitted electron energies in a given band. The cosine curves joining the zone boundaries are justified by Figure 5.15, which shows that no new information is gained by extending the k range beyond $-\pi/a \leq k \leq \pi/a$. This limited range of k values defines the reduced zone scheme.

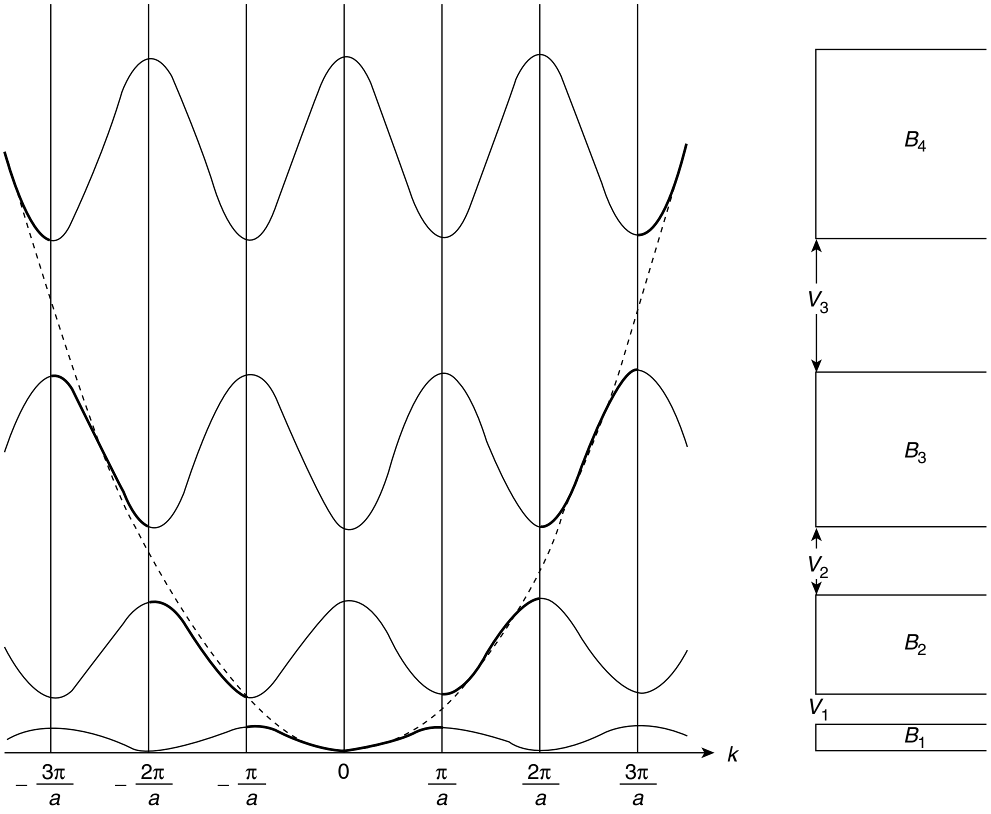

Figure 13.16 Figure 13.15 displayed as allowed electron energies versus k. The dotted parabola defines the free electron energy $E = \hbar^2 k^2/2m$ and the allowed energy bands are the Brillouin zones B_i. V_1, V_2, V_3 are the energy gaps between the zones. The cosine curves joining the zone boundaries are justified by Figure 5.15, i.e. all relevant information is contained in the region $\frac{-\pi}{a} \le k \le \frac{\pi}{a}$

The number of energy states (excluding spin) in each zone is determined by

$$k = \frac{2\pi r}{lN} = \frac{2\pi r}{aN} \qquad (r = 0, 1, 2, 3 \ldots N - 1)$$

for each k value represents an allowed energy state. Each value of r gives a different value of k; there are N such values. Hence, in this range

$$-\frac{\pi}{a} \le k \le \frac{\pi}{a} \text{ i.e.} \frac{2\pi}{a} = \frac{2\pi r}{Na} \qquad \text{where } a \approx l$$

the number of energy levels is equal to the number of atoms.

As $a + b = l \to \infty$ each band contracts to a single level which is N-fold degenerate since the electron can be bound to any one of the atoms. For finite values of l this degeneracy is removed and each discrete atomic level spreads into a band of N levels.

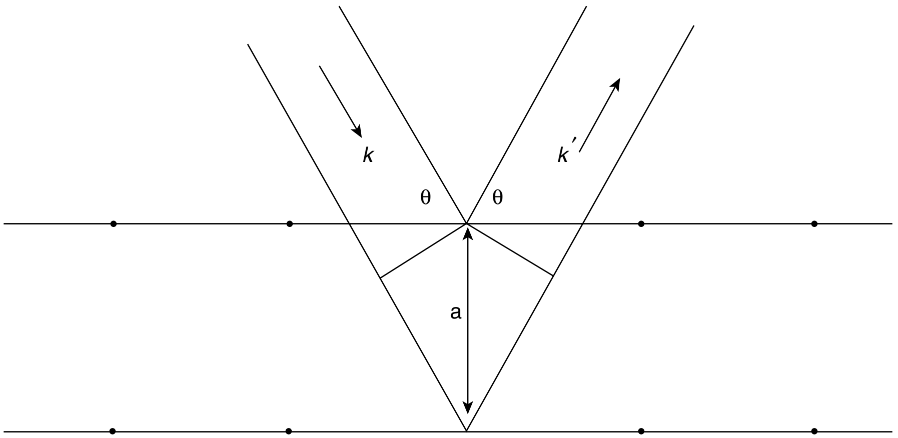

Figure 13.17 Elastic Bragg reflection occurs when electron waves are scattered by atoms in planes separated by a distance a. Principal maxima are formed when $2a \sin = n\lambda$

Only free electrons will escape interaction with the ions in the crystal lattice; almost free electrons will experience weak coupling to the lattice. Coupling which is strong enough to reflect electron waves may be seen in terms of Bragg reflection, Figure 13.17. Here, waves reflected by successive planes in a crystal which are separated by a distance a reinforce to give maxima on reflection when $2a \sin\theta = n\lambda$.

When $\theta = \pi/2$ and the coupling is strong enough the electron waves will be reflected from successive ions, Figure 13.18, giving a path difference of $2a$. Reflection maxima occur for

$$2a = \pm n\lambda = \pm n\frac{2\pi}{k}, \qquad \text{i.e. } k = \pm\frac{n\pi}{a}$$

Thus, Bragg reflections define the Brillouin zone boundaries.

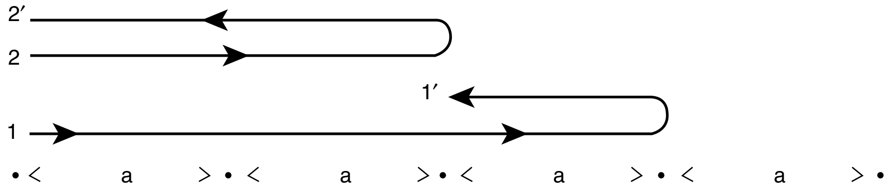

Figure 13.18 When $\theta = \pi/2$ in Figure 13.17 Bragg scattering by electron--ion interactions gives principal maxima when electron waves are reflected from ions separated by multiples of a. The condition $2a = n\lambda$ defines the Brillouin zone boundaries for $n = 1, 2, 3$, etc.

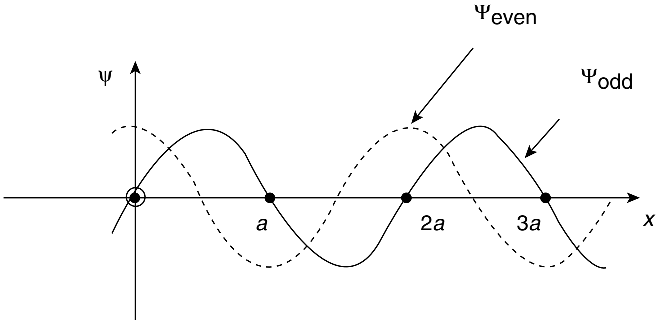

Figure 13.19 The wave function ψ (even) has an anti-node at an ion (atom) site. The anti-node for ψ (odd) is located midway between sites. This governs the energy of interaction, which is different for the two ψ values

Wave functions of electrons can be represented by travelling waves in both directions, i.e. by $\mathrm{e}^{\pm ikx}$ and for $k = \pm n\pi/a$ standing waves will be formed by the sum or difference of, e.g.

$$\mathrm{e}^{i\pi x/a} \quad \text{and} \quad \mathrm{e}^{-i\pi x/a}$$

The sum of these terms creates

$$\psi_{\rm even} = \cos\frac{\pi x}{a}$$

and their difference gives

$$\psi_{\rm odd} = \sin\frac{\pi x}{a}$$

The energies associated with these two wave functions will differ when they interact with the ions. $\psi_{\rm even} = \cos\pi x/a$ has anti-nodes (maxima) at the site of each ion so the electron–ion interaction is attractive and the energy corresponding to $\psi_{\rm even}$ is lowered. $\psi_{\rm odd} = \sin\pi x/a$ has its anti-node midway between ion sites where the potential is repulsive, Figure 13.19. The calculation of these energy shifts requires knowledge of the effective potential, but it can be shown that for $\psi_{\rm even}$ the energy change at a given V_n in Figure 13.16, where V_n is the energy gap between bands, is $\Delta E = -\frac{1}{2}V_n$ and for $\psi_{\rm odd}$ the energy change is $\Delta E = \frac{1}{2}V_n$ (see Problem 13.21). Note that the band widths and gaps increase with n.

The band structure may also be demonstrated by considering the effect of tunnelling. Two widely separated equivalent potential wells may each contain a single electron occupying identical energy levels. When the potential well separation becomes small enough for the tunnelling of Figure 13.6 to be possible this symmetry is destroyed because the wave function of an electron spreads right across both wells and their separating potential barrier, Figure 13.20. There is a finite probability of finding an electron at any

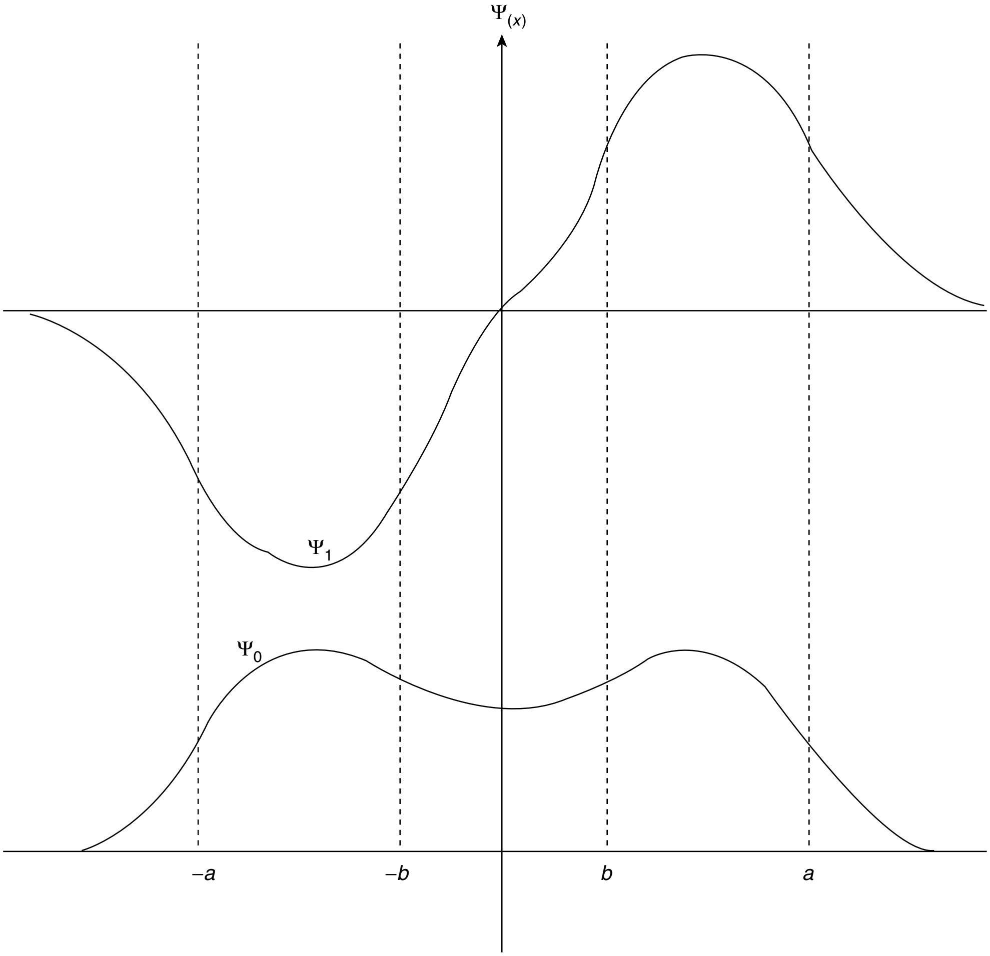

Figure 13.20 When an electron can tunnel between two potential wells (a, b) and − (a, b) it cannot exist in a single energy state. The higher of the two resulting energy states has a greater curvature

point x of its wave function $\psi(x)$ so the two electrons cannot occupy the same energy level and the single state splits into two. The lowest lying energy levels split into a narrow band of very closely spaced states since the barrier to tunnelling is very large for electrons in these levels. Higher energy levels have a wider spread and it is even possible for bands to overlap. The band structure helps to explain the difference between electrical conductors and insulators.

Once an energy level is occupied by an electron it cannot accept another electron. However, in a metal only the lower energy levels in a band or Brillouin zone are occupied and an applied electric field can accelerate electrons which move to occupy higher available energy states within the band. Insulators have completely filled energy bands so the electrons cannot move under the influence of an electric field – there are no empty neighbouring states.

However, a very strong electric field can cause an electron to jump from the top of a band across a gap to occupy an empty level immediately above the gap, so the insulator breaks down. A spark can jump across an air gap between two terminals; lightning is such a spark on a much larger scale. A semiconductor is basically an insulator with a very narrow forbidden gap where even a small energy change will switch the insulator into a conductor.

Phonons

Pages 135 and 162 showed that the elastic field in a crystal could sustain transverse and longitudinal modes of vibration along a chain of atoms acting as a series of coupled oscillators. In a normal mode of angular frequency ω_i every atom performed simple harmonic oscillations of ω_i. On p. 440 we saw that the energy of such oscillations at atomic and sub-atomic levels was quantized with values of $(n + 1/2)\hbar\omega$.

The concept of photons as quanta of energy $\hbar\omega$ associated with an electromagnetic field allows the analogy of *phonons* as quanta of energy associated with the elastic field. In a normal mode of angular frequency ω_i the energy of a phonon is $\hbar\omega_i$ so phonons can be seen as exciting a mode to an energy state $(n + \frac{1}{2})\hbar\omega_i$. When $n = 0$ the mode ω_i is left with the zero-point energy $\frac{1}{2}\hbar\omega_i$. A more detailed calculation of Debye's theory of specific heats (page 253) takes account of this quantization.

Normal modes are plane waves extending throughout the crystal and phonons are not localized particles. The uncertainty principle prevents an exact determination of a phonon position and it exists as a localized wave packet of combined modes with a small spread of frequency and wavelength and a group velocity $\mathrm{d}\omega/\mathrm{k}$. The number of phonons, like that of photons, is not conserved. They are created and absorbed by collisions and, like photons, they obey Bose–Einstein statistics (appendix 1). However, unlike photons, they exist only within the crystal. They contribute to the crystal momentum but do not carry momentum. This is evident from Figure 5.15 where a lattice vibration has a wave number $k = k \pm \frac{m\pi}{a}$ $(m = 1, 2, 3, \ldots)$ so $\hbar k$ has no precise meaning. Indeed, when the mode oscillations are purely harmonic the equilibrium position is zero so phonon momentum is zero.

Phonon–phonon collisions are usually three-phonon processes in which both transverse and longitudinal waves are involved. They are characterized by energy conservation

$$\hbar\omega_1 = \hbar\omega_2 + \hbar\omega_3$$

and by phonon wave vector conservation

$$\mathbf{q}_1 = \mathbf{q}_2 + \mathbf{q}_3$$

A phonon of wave vector $\mathbf{q}_1$ can separate into two phonons with wave vectors $\mathbf{q}_2$ and $\mathbf{q}_3$. Alternatively, $\mathbf{q}_2$ can absorb $\mathbf{q}_3$ to form $\mathbf{q}_1$. Phonon–phonon collisions play a role in the thermal conductivity of a crystal; neutron interactions with the crystal lattice also involve the concept of phonons.

When particles, as waves, interact with crystal structures they create diffraction patterns when the particle wavelength is of the order of atomic separation within the crystal, typically $\sim 2 \times 10^{-10}$ m. The waves of X-rays striking a crystal create principal maxima on reflection to satisfy Braggs Law (p. 447) when the path difference

$$2a \sin\theta = n\lambda$$

where a is the separation between the reflecting (diffracting) planes. If k is normal to the particle wave fronts before striking the crystal and $\mathbf{k}'$ is normal to the wave front leaving the crystal the condition $|\mathbf{k}| = |\mathbf{k}'|$ defines the scattering as elastic, so Bragg scattering is elastic. Knowing the plane separation of a nickel crystal, determined by X-rays, Davisson and Germer were able to find the wavelength of electrons by Bragg elastic scattering (see Problem 13.20).

Neutrons with $\lambda \sim 2 \times 10^{-10}$ m have been used in non-elastic scattering experiments where $|\mathbf{k}| \neq |\mathbf{k}'|$ to probe the structure of crystals, that is, the atomic arrangements and separation. Where X-rays interact chiefly with electrons surrounding the nucleus of an atom, uncharged neutrons interact much more strongly with its nucleus; lattice vibrations are set up so phonons play a role in the scattering.

Non-elastic scattering may be seen in terms of Figure 13.21 where waves in the wave front normal to $\mathbf{k}$ are scattered by atoms 1 and 2 in a row where the atomic separation is a. The phase lag of the wave incident on atom 2 is $\frac{2\pi}{\lambda} a \sin\theta$ with respect to that striking atom 1, but after scattering it leads the wave scattered by atom 1 by a phase $\frac{2\pi}{\lambda'} a \sin\phi$. A diffraction maximum occurs when the phase difference

$$\frac{2\pi}{\lambda} a \sin\theta - \frac{2\pi}{\lambda'} a \sin\phi = ka \sin\theta - k'a \sin\phi = l2\pi \, (l = 1, 2, 3, \ldots)$$

i.e.

$$\mathbf{a}(\mathbf{k} - \mathbf{k}') = l2\pi$$

or

$$\mathbf{k} - \mathbf{k}' = l\frac{2\pi}{a}$$

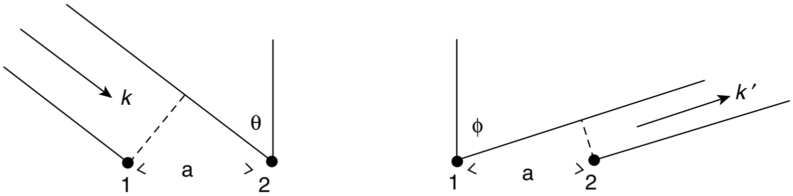

Figure 13.21 When electrons are scattered from atoms separation a, in the same plane, the scattering may be inelastic, i.e. $|\mathbf{k}| \neq |\mathbf{k}'|$. Here, the electron of wave number $k = 2\pi/\lambda$ strikes atom 1 ahead in phase of that striking atom 2 by $2\pi/\lambda \, a \sin\theta$, but after scattering it lags that from atom 2 by a phase difference $\frac{2\pi}{\lambda'} a \sin\phi$. Note that λ need not $= \lambda'$

Note that $\mathbf{k}-\mathbf{k}'$ is a vector in diffraction space and λ' need not equal λ. This is true for every row of lattice points in the x direction.

The expression $l2\pi/a$ represents a series of planes in k space with a separation $2\pi/a$. Crystal planes in a second dimension with separation b would form another series of planes $m\frac{2\pi}{b}$ (m $= 1, 2, 3, \ldots$) with separation $\frac{2\pi}{b}$ in $\mathbf{k}$ space having lines of intersection with the series l. A set of crystal planes in a third dimension with separation c would form a final set of planes $n\frac{2\pi}{c}(n = 1, 2, 3, \ldots)$ with separation $2\pi/c$ in $\mathbf{k}$ space. These three sets of planes would meet in points (l, m, n) in $\mathbf{k}$ space to form the *reciprocal lattice*. In three dimensions the diffracted vector $k-k'$ would end on a reciprocal lattice point l, m, n. There is no requirement for the directions a, b and c in the crystal to be mutually perpendicular, but a symmetry exists between the crystal lattice and its reciprocal in that planes in the one are perpendicular to rows of points in the other and the plane spacing in one is 2π times the reciprocal of the point spacing in the other.

When neutrons are diffracted from a crystal lattice in which a phonon of wave vector $\mathbf{q}$ and frequency ω is already excited, more than one diffraction maximum can appear. This first maximum will result from Bragg elastic scattering, i.e. $|\mathbf{k}| = |\mathbf{k}'|$.

A second maximum occurs in a vector direction

$$\mathbf{g} = \mathbf{k} - \mathbf{k}' + \mathbf{q}$$

or

$$\mathbf{k}' = \mathbf{k} + \mathbf{q} - \mathbf{g}$$

This suggests that a neutron of wave vector $\mathbf{k}$ has absorbed a phonon of wave vector $\mathbf{q}$ to become a neutron of wave vector $\mathbf{k}'$. In the scattering, because the neutron is initially outside the crystal, the crystal plus the phonon receives a momentum

$$\hbar(\mathbf{k} - \mathbf{k}') = \hbar(\mathbf{g} - \mathbf{q})$$

Conventionally, the momentum $\hbar\mathbf{g}$ is associated with the whole lattice while $\hbar\mathbf{q}$ (associated with the absorbed phonon) is known as the crystal or quasi-momentum of the phonon because it acts as a momentum when absorbed by the neutron.

In pure phonon–phonon collisions two processes may occur. The three phonons involved may begin and end in the same Brillouin Zone. this is called a normal process. In some cases, however, the third phonon may finish outside the Brillouin zone. This is known as the Umklapp process. This occurs when a phonon is Bragg reflected (at the edge of a Brillouin zone) at the same time as it absorbs another phonon. We know, however, that a phonon of wave vector $\mathbf{q}$ is identical with a phonon of wave vector $\mathbf{q} \pm \frac{2\pi}{a}$, so the third phonon may be considered as remaining within the Brillouin zone. Umklapp processes play a role in the thermal conductivity of a crystal in the following way.

When the crystal lattice vibrations are purely harmonic the separation between adjacent atoms during vibrations contributes an energy term $\propto (x_i - x_{i\pm1})^2$, where x_i is the displacement of an atom from its equilibrium position. In this case a phonon may travel along hundreds of atoms without hindrance. However, with increasing energy, i.e. temperature, vibrations become anharmonic and cubic terms replace the squared term above because separate normal modes become coupled. Effectively, a cubic term describes the emission of a phonon by another phonon or the decay of a phonon into two phonons and the energies of individual phonons are changed. The phonons constitute a gas where the phonons have approximately constant speed (unlike in a real gas), but have a larger number density and energy density at the hot end of the crystal. Heat flow is primarily by phonon flow with phonons being created at the hot end and destroyed at the cold end. The thermal resistance in an insulator is produced by collisions which reverse the group velocity of the phonons, and the Umklapp process involving high-energy phonons at Bragg reflection on the edge of the Brillouin zone is significant here.

(Problems 13.20, 13.21)

Problem 13.1

The energy of an electron mass m charge e circling a proton at radius r is

$$E = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$$

where p is its momentum.

Use Heisenberg's Uncertainty Principle in the form $\Delta p \Delta r \approx \hbar$ to show that the minimum energy (H_2 atom ground state) is

$$E_0 = \frac{-me^4}{8\varepsilon_0^2 h^2}$$

at a Bohr radius

$$r = \frac{\varepsilon_0 h^2}{\pi m e^2}$$

Problem 13.2

The observation of a particle annihilates its mass m and its rest mass energy is converted to radiation. Use the relations $\Delta p \, \Delta x \approx h$ and $E = pc$ for photons to show that the short wavelength limit on length measurement is the Compton wavelength

$$\lambda = \frac{h}{mc}$$

Show that this is 2.42×10^{-12} m for an electron.

Problem 13.3

When x and p vary simple harmonically it can be shown that the averaged values of the squares of the uncertainties satisfy the relation

$$(\overline{\Delta x^2})(\overline{\Delta p^2}) \approx \frac{\hbar^2}{4}$$

If the energy of a simple harmonic oscillation at frequency ω is written

$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

show that its minimum energy is $\frac{1}{2}h\nu$.

Problem 13.4

An electron of momentum p and wavelength $\lambda = h/p$ passes through a slit of width Δx. Its diffraction as a wave may be regarded in terms of a change of its momentum Δp in a direction parallel to the plane of the slit (its total momentum remaining constant). Show that the approximate position of the first minimum of the diffraction pattern is in accordance with Heisenberg's uncertainty principle. (Note that the variation of the intensity of the principal maximum in the pattern is a direct measure of the probability of the electron arriving at a point on the screen.)

Problem 13.5

A beam of electrons with a de Broglie wavelength of 10^{-5} m passes through a slit 10^{-4} m wide. Show that the angular spread due to diffraction is $5°47'$.

Problem 13.6

Show that the de Broglie wavelength of an electron accelerated across a potential difference V is given by

$$\lambda = h/(2m_e eV)^{1/2} = 1.29 \times 10^{-9} V^{-1/2}\,\mathrm{m}$$

where V is measured in volts.

Problem 13.7

If atoms in a crystal are separated by 3×10^{-10} m (3 Å) show that an accelerating voltage of $\sim 3\,\mathrm{kV}$ would be required to produce electrons diffracted by the crystal.

Problem 13.8

Electromagnetic radiation consists of photons of zero rest mass. Show that the average momentum per unit volume associated with an electromagnetic wave of electric field amplitude E_0 is given by

$$p = \tfrac{1}{2}\varepsilon_0 E_0^2/c$$

(Verify the dimensions of this relation.)

Problem 13.9

Show that the average momentum carried by an electromagnetic wave develops a radiation pressure

$$P = cp = \tfrac{1}{2}\varepsilon_0 E_0^2$$

when the wave is normally incident on a *perfect absorber* and a pressure

$$P = 2cp = \varepsilon_0 E_0^2$$

when the wave is normally incident on a *perfect reflector.* (Radiation incident from all directions within a solid angle of 2π will introduce a factor of $1/3$ in the expressions above.)

Problem 13.10

If the radiation energy from the sun incident upon the perfectly absorbing surface of the earth is $1.4\ \mathrm{W\ m^{-2}}$ and the radiation comes from all directions within a solid angle of 2π show that the radiation pressure is about 10^{-11} of the atmospheric pressure.

Problem 13.11

In a carbon molecule the two atoms oscillate with a frequency of 6.43×10^{-11} Hz. Show that the zero point energy is 1.34×10^{-3} eV ($1\,\mathrm{eV} = 1.6 \times 10^{-19}$ J).

Problem 13.12

A particle of mass m moves in an infinitely deep square well potential of width $2a$ defined by

$$\begin{aligned} V(x) &= 0 \quad && -a \le x \le +a \\ V(x) &= \infty && |x| > a \end{aligned}$$

If it is described by the wave function

$$\begin{aligned} \psi(x) &= \frac{1}{\sqrt{a}}\left(1 - \frac{\pi^2 x^2}{8a^2}\right) \quad && \text{for } |x| \le a \\ &= 0 && |x| > a \end{aligned}$$

show by calculating $\int_{-a}^{a} |\psi(x)|^2\,\mathrm{d}x$ that the probability of finding it in the box is 0.96.

Show that in its normalized ground state, it is represented by $\psi(x) = (1/\sqrt{a})\cos(\pi x/2a)$ and expand this in powers of $\pi x/2a$ to compare it with the wave function above.

Problem 13.13

Show that the normalization constant for the wave function

$$\psi(xyz) = A \sin\frac{n_1 \pi x}{a} \sin\frac{n_2 \pi y}{b} \sin\frac{n_3 \pi z}{c}$$

describing an electron in a volume abc at the bottom of a deep potential well is equal to $(8/abc)^{1/2}$.

Problem 13.14

A total of N electrons occupy a volume V in a solid at a very low temperature between the energy levels 0 to E_F the Fermi energy.

Show that their total energy

$$\begin{aligned} U &= \int E\,\mathrm{d}n = \int_0^{E_\mathrm{F}} E\,\frac{\mathrm{d}n}{\mathrm{d}E}\,\mathrm{d}E \\ &= \frac{3}{5} N E_\mathrm{F} \end{aligned}$$

giving an average energy per electron of $\frac{3}{5}E_\mathrm{F}$.

Problem 13.15

Copper has one conduction electron per atom, a density of 9 and an atomic weight of 64. Show that n_0, the number of free electrons per unit volume is $\approx 8 \times 10^{28}\,\mathrm{m}^{-3}$ and that the value of its Fermi energy level is about 7 eV $(1\,\mathrm{eV} = 1.6 \times 10^{-19}\,\mathrm{J})$.

Problem 13.16

The probability of a particle of mass m penetrating a distance x into a classically forbidden region is proportional to $\mathrm{e}^{-2\alpha x}$ where

$$\alpha^2 = 2m(V - E)/\hbar^2$$

If x is $2 \times 10^{-10}\,\mathrm{m}$ (2 Å) and $(V - E)$ is 1 eV $(1.6 \times 10^{-19}\,\mathrm{J})$ show that

$$\begin{aligned} \mathrm{e}^{-2\alpha x} &= 0.1 \text{ for an electron} \\ &= 10^{-43} \text{ for a proton} \end{aligned}$$

Problem 13.17

A particle of total energy E travels in a positive x direction in a region where the potential energy $V = 0$. The potential suddenly drops to a very large negative value. Show that, quantum mechanically, the amplitude of the reflected wave tends to unity and that of the transmitted wave to zero. Note that this implies non-classical total reflection.

Problem 13.18

Show that Schrödinger's equation for a one dimensional simple harmonic oscillator of frequency ω is given by

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}m\omega^2x^2\right]\psi = 0$$

and verify that if $a^2 = m\omega/\hbar$ then

$$\psi_0(x) = (a/\sqrt{\pi})^{1/2}\,\mathrm{e}^{-a^2x^2/2}$$

and

$$\psi_1(x) = (a/2\sqrt{\pi})^{1/2}2ax\,\mathrm{e}^{-a^2x^2/2}$$

are respectively the normalized wave functions for $E_0 = \frac{1}{2}\hbar\omega$ (zero point energy) and $E_1 = \frac{3}{2}\hbar\omega$.

Problem 13.19

The normalized wave function for a one-dimensional harmonic oscillator with energy $E_n = (n + \frac{1}{2})\hbar\omega$ is

$$\psi_n = N_nH_n(ax)\,\mathrm{e}^{-a^2x^2/2},$$

where

$$\begin{aligned} N_n &= (a/\pi^{1/2}2^n n!)^{1/2} \\ a^2 &= m\omega/\hbar \end{aligned}$$

and

$$H(y) = (-1)^n \, e^{y^2} \frac{d^n}{dy^n} e^{-y^2}$$

Verify that $\psi_0(x)$ and $\psi_1(x)$ of Problem 13.18 satisfy the expression for ψ_n and calculate $\psi_2(x)$ and $\psi_3(x)$.

Problem 13.20

Davisson and Germer (1927) fired electrons with an energy of 54 eV at a nickel crystal which had an atomic plane separation of 0.91×10^{-10} m (0.91 Å). Bragg reflection gave a diffraction maximum at 65°. Calculate the reflected electron momentum p and the kinetic energy to show that the difference between the incident and scattered kinetic energies was within 3.9%.

Problem 13.21

The perturbed energies of ψ (odd) and ψ (even) due to electron–ion interactions are given by

$$\Delta E = \frac{\int \psi^* V \psi \, dx}{\int \psi^* \psi \, dx} \qquad \text{where } \psi^* \text{ is the complex conjugate of } \psi$$

If the zero of energy is taken as the mean value of the potential then the potential may be written as a Fourier series in the form

$$V = -\sum_{n=1}^{\infty} V_n \cos 2\pi n x / a$$

where the V_n are the potential gaps in Figure 13.16. They are positive numbers for a potential with strong negative peaks at the lattice sites. For travelling waves $\psi = e^{\pm ikx}$ so $\psi^*\psi = 1$, which gives $\Delta E = 0$ in the above expression except for $\psi = \sin kx$ or $\cos kx$ when $k = n\pi/a$ where a is the periodicity of the lattice.

Show that for $\psi = \sin ka$

$$\begin{aligned} \Delta E &= -\sum_{n-1}^{\infty} \frac{\int \sin^2 kx V_n \cos \frac{2\pi n x}{a} dx}{\int \sin^2 kx dx} \\ &= \frac{1}{2} V_n \quad \text{for} \quad k = n\pi/a \end{aligned}$$

Show that $\psi = \cos kx$ in the above expression gives $\Delta E = -\frac{1}{2} V_n$ for $k = n\pi/a$

Summary of Important Results

De Broglie Wavelength $\lambda = h/p$

Heisenberg's Uncertainty Principle (Bandwidth Theorem)

$$\Delta x \, \Delta p \approx h$$
$$\Delta E \, \Delta t \approx h$$

determines zero point energy.

Schrödinger's time independent wave equation

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{2m(E-V)}{\hbar^2}\psi(x) = 0$$
$$\psi(x) = A\,\mathrm{e}^{\mathrm{i}kx} + B\,\mathrm{e}^{-\mathrm{i}kx},$$

where

$$k^2 = \frac{2m(E-V)}{\hbar^2} \quad E > V$$
$$\psi(x) = C\,\mathrm{e}^{\alpha x} + D\,\mathrm{e}^{-\alpha x},$$

where

$$\alpha^2 = \frac{2m(V-E)}{\hbar^2} \quad V > E$$

Probability per unit length of finding a particle at x

$$P(x) = |\psi(x)|^2$$

Normalization

$$\int |\psi(xyz)|^2\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = 1$$

all space

Harmonic oscillator

Energy levels $E_n = (n + \frac{1}{2})h\nu$