

## 1.8 COMPTON EFFECT

In 1921, Prof. A.H. Compton discovered that when a monochromatic beam of high frequency radiation (e.g., X-rays and  $\gamma$ -rays) is scattered by a substance, the scattered radiation contains the radiation of greater wavelength (or lower frequency) along with the radiation of the incident wavelength (or frequency). The radiation of unchanged wavelength in the scattered light are called *unmodified radiations* while the radiations of greater wavelength are called *modified radiations*. The phenomenon is called *Compton effect*.

### Compton's Experimental Arrangement

The concept of a photon as a concentrated packet of energy travelling with the speed of light was confirmed by Compton in 1923. He allowed X-rays of monochromatic wavelength  $\lambda$  to fall on a graphite block and measured the intensity of scattered X-rays at different angles. The scattered X-rays are found to have two wavelengths—the original wavelength  $\lambda$  and another wavelength  $\lambda'$ ,  $\lambda'$  being greater than  $\lambda$ . The schematic experimental arrangement is shown in Fig. 1.10 (a).

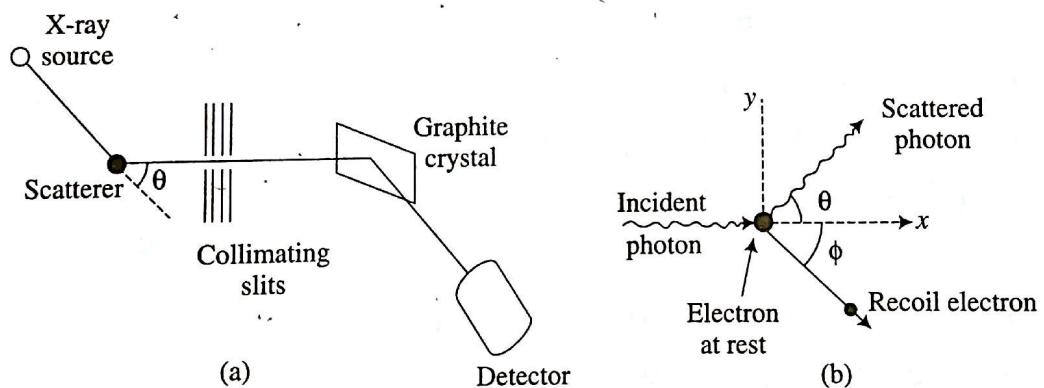


Fig. 1.10 (a) Experimental arrangement and (b) Scattering process in Compton effect.

### Explanation

The effect was explained on the basis of quantum theory of light. The wave picture predicts scattered radiation having the same wavelength though less energetic than the incident radiation. However, the quantum theory, i.e., the photon concept leads to exact result, as discussed below.

Compton analyzed the scattering process as a particle like collision between a single photon of energy  $h\nu$  and an electron which is assumed to be at rest. During collision, the incident photon transfers some of its energy to the electron which is almost free. Hence, the scattered photon must have a lower energy  $h\nu'$  ( $\nu' < \nu$ ). This implies a higher wavelength  $\lambda'$ . The scattering process is illustrated in Fig. 1.10 (b).

Resolving the momenta of the incident photon, scattered photon and electron into  $x$  and  $y$  components and applying the law of conservation of momentum, we have

$$\frac{h\nu}{c} = \frac{h\nu'}{c} \cos \theta + p_e \cos \phi \quad \dots(1.12)$$

$$0 = \frac{h\nu'}{c} \sin \theta - p_e \sin \phi \quad \dots(1.13)$$

where  $p_e$  is the momentum of the electron after scattering. Conservation of energy gives

$$h\nu = h\nu' + k_e$$

or

$$k_e = h(\nu - \nu') \quad \dots(1.14)$$

where  $k_e$  is the kinetic energy of scattered electron. Eqs. (1.12) and (1.13) can be written as

$$p_e c \cos \phi = h\nu - h\nu' \cos \theta \quad \dots(1.15)$$

$$p_e c \sin \phi = h\nu' \sin \theta \quad \dots(1.16)$$

Squaring and adding, we get

$$p_e^2 c^2 = h^2 \nu^2 + h^2 \nu'^2 - 2h^2 \nu \nu' \cos \theta \quad \dots(1.17)$$

Denoting the rest mass of electron by  $m_0$ , from Eq. (1.14), we have

$$k_e + m_0 c^2 = h(\nu - \nu') + m_0 c^2 \quad \dots(1.18)$$

From the theory of relativity, the energy of the recoiling electron is

$$E_e = (c^2 p_e^2 + m_0^2 c^4)^{\frac{1}{2}} \quad \dots(1.19)$$

Since left-hand side of Eq. (1.18) is the total energy  $E_e$  of the recoiling electron.

$\therefore$  From Eq. (1.18) and using Eg. (1.19), we have

$$(c^2 p_e^2 + m_0^2 c^4)^{\frac{1}{2}} = h(\nu - \nu') + m_0 c^2 \quad \dots(1.20)$$

Squaring Eq. (1.20) and using Eq. (1.17), we get

$$h^2 \nu^2 + h^2 \nu'^2 - 2h^2 \nu \nu' \cos \theta = h^2 (\nu - \nu')^2 + 2h(\nu - \nu') m_0 c^2$$

$$\text{or } h^2 \nu \nu' \cos \theta - h^2 \nu \nu' + h(\nu - \nu') m_0 c^2 = 0 \quad \dots(1.21)$$

Since  $\nu = c/\lambda$  and  $\nu' = c/\lambda'$ , Eq. (1.21) reduces to

$$\frac{h^2 c^2}{\lambda \lambda'} \cos \theta - \frac{h^2 c^2}{\lambda \lambda'} + h(c/\lambda - c/\lambda') m_0 c^2 = 0$$

Multiplying both sides by  $\lambda\lambda'$  and rearranging, we have

$$h(1 - \cos \theta) = c(\lambda' - \lambda)m_0$$

$$(\lambda' - \lambda) = \frac{h}{m_0 c}(1 - \cos \theta) \quad \dots(1.22)$$

or,

$$\Delta\lambda = \frac{h}{m_0 c}(1 - \cos \theta) \quad \dots(1.22a)$$

This is the expression for the *Compton shift*.

Since the right-hand side of Eq. (1.22) is always positive,  $\lambda'$  is always greater than  $\lambda$ . The change in wavelength depends upon angle of scattering. The quantity  $(h/m_0 c)$  is referred as *Compton wavelength* of the electron. Substituting the values,

$$\frac{h}{m_0 c} = \frac{6.6 \times 10^{-34}}{9 \times 10^{-31} \times 3 \times 10^8} m = 0.02426 \text{ \AA}^\circ.$$

The maximum value of  $(1 - \cos \theta)$  (for  $\theta = 180^\circ$ ) is 2. Therefore, the maximum possible change in wavelength is  $0.04852 \text{ \AA}$  or  $0.05 \text{ \AA}$  approximately. It follows from Eq. (1.22) that the Compton effect can most readily be detected for radiation of wavelength not greater than a few angstrom units. For example, for  $\lambda = 5 \text{ \AA}$ , the maximum change in wavelength is 1% while for  $\lambda = 1 \text{ \AA}$  the effect is 5%. For visible light (taking  $\lambda \approx 5000 \text{ \AA}$ ), the maximum wavelength change ( $\approx 0.05 \text{ \AA}$ ) is only about 0.001% of the incident wavelength which is undetectable. Hence, *Compton effect cannot be observed for visible light rays*.

Further, it is assumed that the electron is so loosely bound to the atom that it can be regarded as free, which is not true and the electron is tightly bound to the atom and the atom as a whole recoils due to Compton scattering. Therefore, in conservation relations instead of  $m_0$ , the rest mass of  $M_0$  of the atom should be used. For an aluminium target  $M_0 \approx 27 \frac{m_H}{m_o} \times m_o = 27 \times 1840 m_o$ , where  $m_H$  is the mass of the hydrogen atom. Then

$$\frac{h}{m_0 c} = \frac{2.246 \times 10^{-12}}{27 \times 1840} \approx 4.9 \times 10^{-17} \text{ m} \approx 4.9 \times 10^{-7} \text{ \AA}$$

Thus, for an incident wavelength of the order of a few  $\text{\AA}$ , when electron is bound to the atom, the change in wavelength is negligible for all  $\theta$ . This explains the presence of unmodified radiation.

### Direction of Recoil Electron

Dividing Eq.(1.16) by Eq. (1.15), we get

$$\tan \phi = \frac{hv' \sin \theta}{hv - hv' \cos \theta} = \frac{\frac{c}{\lambda'} \sin \theta}{\frac{c}{\lambda} - \frac{c}{\lambda'} \cos \theta}$$

$$\tan \phi = \frac{\lambda \sin \theta}{(\lambda' - \lambda \cos \theta)} \quad \dots(1.23)$$

### Kinetic Energy of the Recoil Electron

The kinetic energy of the recoil electron is given by

$$k_e = (m - m_o)c^2 \quad \dots(1.24)$$

$$k_e = h\nu - h\nu' \quad \dots(1.25)$$

Also,

$$k_e = \frac{hc}{\lambda} - \frac{hc}{\lambda'} = hc \left( \frac{\lambda' - \lambda}{\lambda \lambda'} \right) \quad \dots(1.26)$$

or

From Eq. (1.22), we have

$$\lambda' = \lambda + \frac{h}{m_o c} (1 - \cos \theta)$$

$$\frac{c}{v'} = \frac{c}{v} + \frac{h}{m_o c} (1 - \cos \theta)$$

$$\frac{1}{v'} = \frac{1}{v} \left[ 1 + \frac{h\nu}{m_o c^2} (1 - \cos \theta) \right]$$

$$v' = \frac{v}{1 + \frac{h\nu}{m_o c^2} (1 - \cos \theta)} = \frac{v}{1 + x (1 - \cos \theta)} \quad \dots(1.27)$$

where,

$$x = \frac{h\nu}{m_o c^2}$$

Substituting value of  $v'$  from Eq. (1.27) in Eq. (1.25), the kinetic energy of the recoil electron is

$$\begin{aligned} k_e &= h\nu - h \left[ \frac{v}{1 + x (1 - \cos \theta)} \right] \\ &= h\nu \left[ 1 - \frac{1}{1 + x (1 - \cos \theta)} \right] \\ k_e &= h\nu \left[ \frac{x (1 - \cos \theta)}{1 + x (1 - \cos \theta)} \right] \end{aligned} \quad \dots(1.28)$$

where,

$$x = \frac{h\nu}{m_o c^2}$$

### Variation in Compton shift as $\theta$ varies from $0^\circ$ to $180^\circ$

The change in wavelength  $\Delta\lambda (= \lambda' - \lambda)$  changes from zero to twice the Compton wavelength as  $\theta$  changes from  $0^\circ$  to  $180^\circ$ . We have

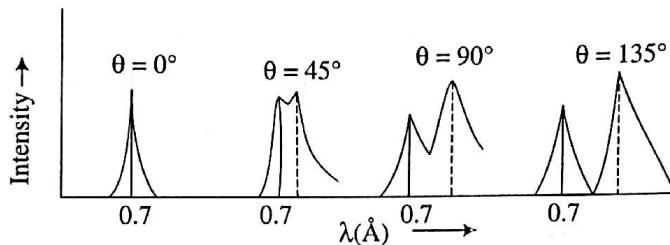
$$\lambda' - \lambda = \frac{h}{m_e c} (1 - \cos \theta)$$

$$\text{For } \theta = 0^\circ, \lambda' - \lambda = \Delta\lambda = \frac{h}{m_o c} (0) = 0$$

$$\text{For } \theta = 90^\circ, \lambda' - \lambda = \Delta\lambda = \frac{h}{m_o c} (1 - 0) = \frac{h}{m_o c}$$

$$\text{For } \theta = 180^\circ, \lambda' - \lambda = \Delta \lambda = \frac{h}{m_o c} (1 - (-1)) = \frac{2h}{m_o c}.$$

This is illustrated in Fig. 1.11.



**Fig. 1.11** Variation of  $\lambda'$  with  $\theta$  in Compton experiment. Solid vertical line corresponds to  $\lambda$  and dotted line that to  $\lambda'$ .

### Example 1.13

*X-rays of wavelength 0.15 nm are scattered from a block of carbon. Calculate wavelength of X-rays scattered at*



### Solution.

Compton wavelength  $\lambda'$  of scattered wave is given by

$$\lambda' = \lambda + \frac{h}{m_o c} (1 - \cos \theta)$$

- (i) For  $\theta = 0^\circ$ ,  $\cos \theta = 1 \quad \therefore \quad \lambda' = \lambda = 0.15 \text{ nm}$   
(ii) For  $\theta = 90^\circ$ ,  $\cos 90^\circ = 0$

$$\begin{aligned}\therefore \lambda' &= \lambda + \frac{2h}{m_o c} \\&= 0.15 + \frac{6.626 \times 10^{-34} \text{ Js}}{(9.1 \times 10^{-31} \text{ kg})(3 \times 10^8 \text{ ms}^{-1})} \\&= 0.15 + 2.4 \times 10^{-12} \text{ m} \\&= 0.1524 \text{ nm}\end{aligned}$$

- (iii) For  $\theta = 180^\circ$ ,  $\cos 180^\circ = -1$

∴

$$\begin{aligned}\lambda' &= \lambda + \frac{2h}{m_o c} \\ &= 0.15 + 2 \times 2.4 \times 10^{-12} \\ &= 0.155 \text{ nm}\end{aligned}$$

**Example 1.14**

X-rays with wavelength  $\lambda = 1.00 \text{ \AA}$  are scattered from a carbon block. The scattered radiations are viewed at right angles to the direction of incident beam. Calculate

- (i) the Compton shift  $\Delta\lambda$  in  $\text{\AA}$ ,
- (ii) wavelength of scattered radiation, and
- (iii) the energy imparted to the recoiling electron in Joules.

Given:  $m_o$  (rest mass of  $e^-$ ) =  $9.1 \times 10^{-31} \text{ kg}$ ,  $c = 3 \times 10^8 \text{ m/s}$ ,  $h = 6.6 \times 10^{-30} \text{ Js}$

**Solution.**

- (i) Compton shift  $\Delta\lambda$  is given by

$$\begin{aligned}\Delta\lambda &= \lambda' - \lambda = \frac{h}{m_o c} (1 - \cos \theta) \\ &= \frac{6.6 \times 10^{-34}}{9.1 \times 10^{-31} \times 3 \times 10^8} (1 - \cos 90^\circ) \\ &= 2.417 \times 10^{-12} (1 - 0) \\ &= 0.02417 \text{ \AA}\end{aligned}$$

- (ii) Wavelength of scattered radiation

$$\begin{aligned}\lambda' &= \lambda + \Delta\lambda = (1 + 0.02417) \text{ \AA} \\ &= 1.02417 \text{ \AA}\end{aligned}$$

- (iii) Energy of the recoiled electron

$$k_e = h\nu \left[ \frac{x(1 - \cos \theta)}{1 + x(1 - \cos \theta)} \right] s$$

where

$$x = \frac{h\nu}{c^2}$$

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8}{1 \times 10^{-10}} = 3 \times 10^{18} \text{ s}^{-1}$$

$$x = \frac{6.6 \times 10^{-34} \times 3 \times 10^{18}}{9.1 \times 10^{-31} \times (3 \times 10^8)^2} = 0.024$$

$$\therefore k_e = 6.6 \times 10^{-34} \times 3 \times 10^{18} \times \left[ \frac{0.024 \times 1}{1 + (0.024 \times 1)} \right]$$

$$= 4.64 \times 10^{-14} \text{ Joules}$$

$\Rightarrow$  Energy imparted to the recoiled electron is  $4.64 \times 10^{-14}$  Joules.

### Example 1.15

In Compton scattering  $\theta$  and  $\Delta\lambda$ , i.e., angle of scattering and Compton shift are related as

$$\Delta\lambda = \frac{h}{m_o c} (1 - \cos \theta)$$

if incident photon has wavelength  $2.0 \times 10^{-10}$  m and  $\phi = 90^\circ$ . Calculate the angle at which the recoil electron appears.

### Solution.

$$\tan \theta = \frac{\lambda \sin \theta}{\lambda' - \lambda \cos \theta}$$

$$= \frac{2 \times 10^{-10} \sin 90^\circ}{2.204 \times 10^{-10} - 2 \times 10^{-10} \cos 90^\circ} = \frac{2}{2.024} = 0.9980$$

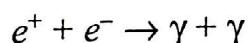
$$\theta = \tan^{-1} (0.9980) = 44^\circ 57'$$

## 1.9 PAIR PRODUCTION AND ANNIHILATION

When  $\gamma$ -ray photon passes close to an atomic nucleus and it possess energy greater than 1.02 MeV, it gets converted into electron-positron pair. This process is termed *pair production* and in this process basically electromagnetic energy gets converted into matter. This phenomenon was observed by Anderson in 1932.

This process is possible only when the incident photon energy exceeds the rest mass energies of both electron and positron (i.e., photon energy  $> 0.51$  eV +  $0.51$  eV, rest mass energy of both electron and positron is  $0.51$  eV). The corresponding maximum photon wavelength is 1.2 pm. This phenomenon occurs mainly in the nuclear field. Both charge and momentum are conserved in this process, however, the presence of nucleus is necessary for the conservation of momentum which carries away most of the photon momentum for the process to occur. Because of its relatively enormous mass, the nucleus absorbs only a negligible fraction of photon energy.

The inverse of pair production occurs when a positron is near an electron and the two come together under the influence of their opposite electric charges. Both the particles vanish simultaneously with lost mass converting into energy of the two photons. The process, termed *pair annihilation*, can be represented as follows.



The directions of the photons are such that both energy and linear momentum are conserved and no nucleus or other particle is needed for pair annihilation.

## 1.10 DUAL NATURE OF RADIATION: DE-BROGLIE WAVES-MATTER WAVES

Light waves show interference, diffraction and polarisation. These phenomena can be explained only on the basis of wave nature of light. On the other hand, photoelectric effect, Compton effect, Raman effect, etc. can be explained only on the basis of particle nature of electromagnetic radiations.

Thus, in some physical phenomena, electromagnetic radiations exhibit wave nature while in some other phenomena it exhibits particle nature. In other words, electromagnetic radiations exhibit *dual nature*.

In 1924, Louis de Broglie suggested that matter, like radiations, have dual nature, i.e., molecules, atoms, electrons, protons, etc. exhibit wave-like behaviour under certain conditions. He put forward the following arguments to defend his duality principle:

1. The entire energy in the universe is in the form of matter and electromagnetic radiation.
2. *The nature loves symmetry. As the radiation has got dual nature, the matter should also possess dual nature.*

Thus, according to de-Broglie, a wave is associated with every moving material particle. These waves, associated with moving material particles, are called *de-Broglie waves or matter waves*. Wavelength is an essential feature of any wave. The expression for wavelength of de Broglie waves is derived below.

According to quantum theory of radiation, the energy ( $E$ ) of a photon of radiation of frequency  $\nu$  is given by

$$E = h\nu \quad \dots(1.29)$$

where,  $h$  is Planck's constant.

The relativistic energy of a particle of rest mass  $m_0$  is given by

$$E = \sqrt{m_0^2 c^4 + p^2 c^2}$$

For a photon, rest mass  $m_0 = 0$

$$E = pc \quad \dots(1.30)$$

From Eqs. (1.29) and (1.30), we have

$$pc = h\nu$$

$$\text{or } p = \frac{h\nu}{c}$$

$$\text{or, } p = \frac{h\nu}{\nu\lambda}$$

$$\text{or, } p = \frac{h}{\lambda}$$

$$\therefore \text{de-Broglie wavelength, } \lambda = \frac{h}{p} \quad \dots(1.31)$$

de-Broglie asserted that this is a general formula applicable to any moving particle having momentum.

For a particle having mass  $m$  and moving with velocity  $v$ ,

$$p = mv$$

...(1.32)

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

This is known as *de-Broglie equation*.

From Eq. (1.32), the following conclusions can be drawn about the matter waves.

(i) Lighter is the material particle, longer is its associated de-Broglie wavelength.

(ii) The faster the particle moves, smaller is its de Broglie wavelength.

(iii) de-Broglie wavelength of a particle is not dependent on its charge.

It should be remembered that matter waves are not electromagnetic in nature. Electromagnetic waves are produced by accelerating charges only.

If the velocity of the particle ( $v$ ) is comparable to the velocity of light ( $c$ ), then mass of the particle is given by

$$m = \frac{m_o}{\sqrt{1 - \frac{v^2}{c^2}}}$$

Therefore, de-Broglie relation in such a case is given by

$$\lambda = \frac{h}{\frac{m_o}{\sqrt{1 - \frac{v^2}{c^2}}} v}$$

$$\lambda = \frac{h \sqrt{1 - \frac{v^2}{c^2}}}{m_o v}$$

...(1.33)

## 1.11 DE-BROGLIE WAVELENGTH OF ELECTRON

Consider an electron of mass  $m$  and charge  $e$ . Let  $v$  be the velocity acquired by it when it is accelerated through a potential difference of  $V$  volt.

Kinetic energy gained by the electron =  $\frac{1}{2}mv^2$

Work done on the electron =  $eV$

Applying law of conservation of energy, we have

$$\frac{1}{2}mv^2 = eV$$

or,

$$v = \sqrt{\frac{2eV}{m}}$$

...(1.34)

de-Broglie wavelength of the electron is given by

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

Substituting for  $v$  from Eq. (1.34), we get

$$\lambda = \frac{h}{m\sqrt{\frac{2eV}{m}}} = \frac{h}{\sqrt{2meV}} \quad \dots(1.35)$$

Putting  $h = 6.62 \times 10^{-34} \text{ Js}$ ,  $m = 9.1 \times 10^{-31} \text{ kg}$ ,  $e = 1.6 \times 10^{-19} \text{ C}$ , we get

$$\begin{aligned} \lambda &= \frac{6.62 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times V}} \\ &= \frac{12.27 \times 10^{-34}}{\sqrt{V}} \text{ m} \\ &\checkmark = \frac{12.27}{\sqrt{V}} \text{ Å} \end{aligned}$$

Suppose,  $V = 100$  volt, then de-Broglie wavelength

$$\lambda = \frac{12.27}{\sqrt{100}} \text{ Å} = 1.227 \text{ Å}$$

This is of the order of the wavelength of  $X$ -rays ( $\approx 1 \text{ Å}$ ). However, the two wavelengths are quite different in nature.

### 1.13 WAVE PACKET: GROUP VELOCITY AND PHASE (OR WAVE) VELOCITY

According to de-Broglie hypothesis a moving material particle has a wavelength  $\lambda = \frac{h}{mv}$  associated with it, where  $m$  is the mass of the particle and  $v$  its velocity. If  $E$  is the energy of the particle, then the frequency  $\nu$  is given by

$$\nu = \frac{E}{h} = \frac{mc^2}{h} \quad (\therefore E = mc^2 - \text{Einstein's mass energy relation})$$

Also, frequency

$$\nu = \frac{\nu}{\lambda} \quad \text{or} \quad \nu = v\lambda$$

$\therefore$

$$\nu = \frac{mc^2}{h} \frac{h}{mv} = \frac{c^2}{v} = c \times \frac{c}{v}$$

As

$$\frac{c}{v} > 1 \Rightarrow \nu > c$$

That is, the wave associated with the particle would travel faster than the particle itself for which the speed of light is the ultimate. This implies that the material particle cannot be equivalent to a single wave train. The paradox was resolved by Schrodinger by postulating that a moving material particle is equivalent to a wave packet rather than a single wave.

A wave packet consists of a group of waves, each of slightly different velocity and wavelength, with such phases and amplitudes that they interfere, constructively over only a small region of space where the particle can be located, outside of which they produce destructive interference so that the amplitude reduces to zero. Such a wave packet is shown in Fig. 1.14. Such a packet moves with a velocity, called the group velocity. The individual wave forming the packet possess an average velocity, called the phase (or wave) velocity.

Suppose, we are looking at waves of the sea in front of us as they are propagating from the left to right-hand side. In order to measure the velocity of a specific wave, we would have to move in the same direction as the wave. When the wave looks stationary, our velocity is the same as that of the phase velocity of the wave.

If a wave is represented by  $A \cos(kx - \omega t)$ , where  $A$  is its amplitude,  $k$  the wave number,  $x$  the direction of propagation,  $\omega$  the angular frequency and  $t$  the time, then following condition must be satisfied at this phase velocity because the wave looks stationary:

$$kx - \omega t = \text{constant}$$

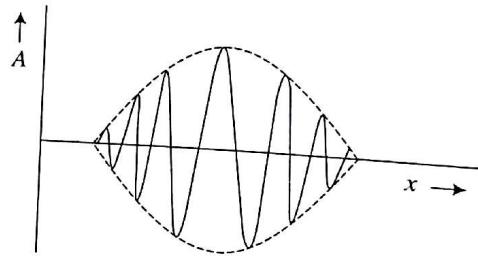


Fig. 1.14 A wave packet.

...(1.36)

Differentiating, we get

$$\frac{dk}{dt} x + k \frac{dx}{dt} - \frac{d\omega}{dt} t - \omega = 0 \quad \dots(1.37)$$

If we assume that  $x$  and  $k$  are independent of time, the above equation becomes

$$k \frac{dx}{dt} - \omega = 0$$

or,

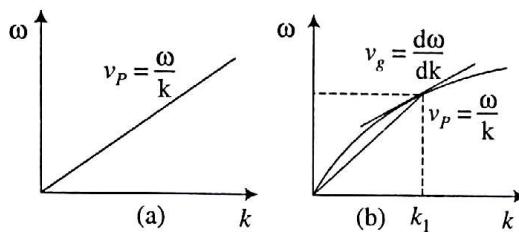
$$\frac{dx}{dt} = \frac{\omega}{k} = v_p \quad \dots(1.38)$$

where  $v_p$  is the phase velocity. Also,

$$v_p = \frac{\omega}{k} = \frac{2\pi v}{2\pi/\lambda} = v\lambda \quad \dots(1.39)$$

where  $\lambda$  is wavelength.

If the phase velocity is independent of frequency, a linear relation between  $\omega$  and  $k$  is obtained as shown in Fig. 1.15 (a). However, an electron wave in a crystal does not meet this condition and the  $\omega$  and  $k$  relationship becomes non-linear as shown in Fig. 1.15 (b). If we focus on a wave with a wave number of  $k_1$ , we can define the velocity of this wave as



**Fig. 1.15** (a) A linear  $\omega$  versus  $k$  relationship and (b) A non-linear  $\omega$  versus  $k$  relationship.

$$v_g = \frac{d\omega}{dk} \quad \dots(1.40)$$

where  $v_g$  is the group velocity. As  $E = \hbar\omega$  also

$$v_g = \frac{1}{\hbar} \frac{dE(k)}{dk} \quad \dots(1.41)$$

**Group velocity equals the particle velocity.** For a particle having total energy  $E$  and potential energy  $V$ , we have kinetic energy

$$\frac{1}{2} mv^2 = E - V$$

$$\text{or, } v = \sqrt{\frac{2(E - V)}{m}} \quad \dots(1.42)$$

According to de Broglie relation,

$$\lambda = \frac{h}{mv} = \frac{h}{m\sqrt{\frac{2(E - V)}{m}}}$$

or

$$\lambda = \frac{h}{m} \sqrt{\frac{m}{2(E-V)}} \quad \dots(1.43)$$

Group velocity

$$v_g = \frac{d\omega}{dk} = \frac{d(2\pi\nu)}{d(2\pi/\lambda)} = \frac{d\nu}{d\left(\frac{1}{\lambda}\right)}$$

or,

$$\begin{aligned} \frac{1}{v_g} &= \frac{d\left(\frac{1}{\lambda}\right)}{d\nu} = \frac{d}{d\nu} \left[ \frac{m}{h} \sqrt{\frac{2(E-V)}{m}} \right] \\ &= \frac{1}{h} \frac{d}{d\nu} \sqrt{2m(h\nu - V)} \\ &= \frac{1}{h} \frac{1}{2} [2m(h\nu - V)]^{-1/2} (2mh) \end{aligned}$$

 $\Rightarrow$ 

$$\frac{1}{v_g} = \frac{m}{\sqrt{2m(E-V)}} = \frac{1}{v} \quad \dots(1.44)$$

Thus, from Eqs. (1.42) and (1.44), we get

$$v_g = v$$

Hence, the motion of a material particle is equivalent to a group of waves or wave packet.

### Relation Between Phase Velocity and Group Velocity

For a dispersive medium, there is variation of phase velocity with wavelength.

Phase velocity

$$v_p = \frac{\omega}{k}$$

Group velocity

$$v_g = \frac{d\omega}{dk}$$

$$= \frac{d\omega}{d\left(\frac{2\pi}{\lambda}\right)} = -\frac{\lambda^2}{2\pi} \frac{d\omega}{d\lambda}$$

$$= -\frac{\lambda^2}{2\pi} \frac{d}{d\lambda} \left( \frac{2\pi v_p}{\lambda} \right) \quad \left( \because \omega = v_p k = \frac{2\pi}{\lambda} v_p \right)$$

$$= -\lambda^2 \left( \frac{-v_p}{\lambda^2} + \frac{1}{\lambda} \frac{dv_p}{d\lambda} \right)$$

$$v_g = v_p - \lambda \frac{dv_p}{d\lambda}$$

or

 $\dots(1.45)$

Thus, the group velocity is smaller than the wave velocity. However, for a non-dispersive medium,

$$\frac{dv_p}{d\lambda} = 0 \text{ and thus } v_g = v_p.$$

### 1.14 UNCERTAINTY PRINCIPLE

According to Heisenberg's uncertainty principle, *it is impossible to measure both the exact position and exact momentum of an object at the same time.*

The limits of accuracy with which the position and momentum of particle can be obtained are specified by the uncertainty principle as

$$\Delta x \cdot \Delta p_x \geq h/4\pi \quad \dots(1.46)$$

or,  $\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2} \left( \text{as } \hbar = \frac{h}{2\pi} \right) \quad \dots(1.47)$

where,  $\Delta x$  is uncertainty in position of an object at some instant,  $\Delta p_x$  is uncertainty in the  $x$  component of the momentum at that instant. This equation states that the product of the uncertainty  $\Delta x$  in the position of an object at some instant and uncertainty  $\Delta p_x$  in its  $x$  component of the momentum at the same instant is equal to or greater than  $h/4\pi$ .

If we arrange matter so that  $\Delta x$  is small, corresponding to a narrow wave group, then  $\Delta p$  will be large. If we reduce  $\Delta p$  in some way, a broad wave group is inevitable and  $\Delta x$  will be large.

These uncertainties are not due to inaccurate apparatus but due to the inherent character in the nature of the quantities involved. Any instrumental or statistical uncertainty that arise during a measurement only increase the product  $\Delta x \Delta p_x$ . Since we cannot measure accurately both, where a particle is and what is its momentum, we cannot say anything definite about where it will be in future and how fast it will be moving then. We cannot know the future for sure because we cannot know the present for sure, but we can say that particle is more likely to be in one place than another and that its momentum is more likely to have a certain value than other.

Another equally useful form of uncertainty relation is in terms of energy and time,

$$\Delta E \Delta t \geq \hbar \quad \dots(1.48)$$

A more precise calculation based on the nature of wave groups gives

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2} \quad \dots(1.49)$$

It implies that the product of uncertainty  $\Delta E$  in an energy measurement and the uncertainty  $\Delta t$  in the time at which the measurement is made is equal to or greater than  $\frac{\hbar}{2}$ .

In terms of angular momentum  $J$  and angle  $\theta$ , the uncertainty principle is expressed as

$$\Delta J \cdot \Delta \theta \geq \frac{\hbar}{2} \quad \dots(1.50)$$

To gain further insight into the uncertainty relation and to understand the uncertainty principle better, a famous thought experiment single slit diffraction experiment is discussed below.

### Single Slit Diffraction Experiment

Consider a beam of electrons travelling in the direction shown in Fig. 1.16. The slit  $AB$  of width  $\Delta x$  is perpendicular to the path of the electrons. Before entering the slit, the electron has a definite momentum  $p = mv$ . After passing through the slit the electron gets diffracted and acquires a momentum  $p \sin \theta$ . The angular deflection  $\theta$  depends upon the component of the momentum parallel to the slit, i.e.,  $\Delta p = p \sin \theta = p\theta$ , for small angular deflection.

The angle  $\theta_0$  in figure corresponds to the direction of first minimum of the diffraction pattern is

$$\theta_0 = \lambda/\Delta x \text{ for small value of } \theta_0.$$

$$\begin{aligned} \Rightarrow \quad \Delta x &= \frac{\lambda}{\theta_0} \\ \therefore \quad \Delta p \cdot \Delta x &= p\theta \frac{\lambda}{\theta_0} \\ &= p\lambda \times \frac{\theta}{\theta_0} \end{aligned}$$

But  $p\lambda = h$  and taking  $\theta \approx \theta_0$

$$\Delta p \cdot \Delta x \sim h \left( \frac{\theta_0}{\theta_0} \right) \sim h$$

The probable deflection  $\theta$  of the electron is less than  $\theta_0$  and according to Heisenberg, the uncertainty relation is given by:

$$\Delta p \cdot \Delta x \geq \frac{\hbar}{2}$$

### Applications

**(1) Non-existence of electrons and existence of protons and neutrons in nucleus:** The radius of the nucleus of any atom is of the order of  $10^{-14}$  m. If an electron is confined inside the nucleus, then uncertainty in the position  $\Delta x$  of the electron is equal to the diameter of the nucleus. That is,  $\Delta x \approx 2 \times 10^{-14}$  m.

Using the uncertainty relation, the uncertainty in the momentum of the electron is given by

$$\Delta p_x \geq \frac{h}{2 \pi \Delta x} \geq \frac{1.055 \times 10^{-34}}{2 \times 10^{-14}}$$

$$\Delta p_x \geq 0.527 \times 10^{-20} \text{ Ns}$$

It means that the momentum component  $p_x$  and hence the magnitude of the total momentum  $|p|$  of the electron in the nucleus must be at least of the order of magnitude, i.e.,

$$|\bar{p}| \sim p_x \sim \Delta p_x \sim 0.527 \times 10^{-20} \text{ Ns}$$

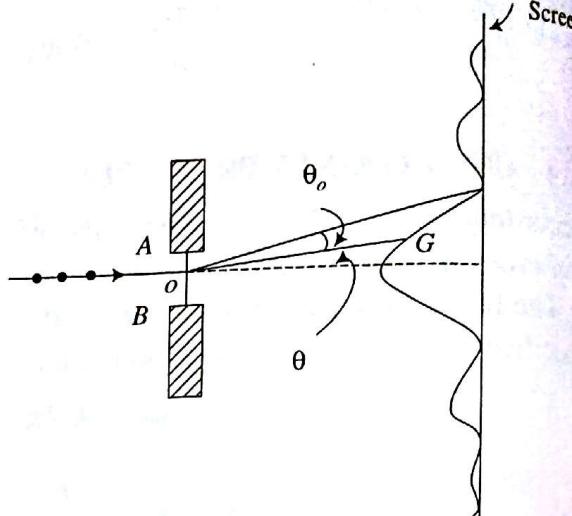


Fig. 1.16

Now the mass of the electron is  $9.1 \times 10^{-31}$  kg, the order of magnitude of the momentum ( $0.527 \times 10^{-20}$  kg m/s) is relativistic and so

$$E^2 = p^2 c^2 + m_o^2 c^4$$

Neglecting  $m_o^2 c^4$  ( $\approx 0.511$  MeV) as it is much smaller than first term.

$$E = pc = (0.527 \times 10^{-20}) \times (3 \times 10^8) \text{ Joule}$$

$$= \frac{0.527 \times 3 \times 10^{-12}}{1.6 \times 10^{-19}} \text{ eV}$$

$$\approx 10 \text{ MeV}$$

Thus, if the electron exists inside the nucleus their energy must be of the order of 10 MeV. The electrons emitted during  $\beta -$  decay in radioactive nuclei have energy of 3 to 4 MeV. Hence, in general, an electron cannot exist inside the nucleus.

For protons and neutrons, mass  $m_o \approx 1.67 \times 10^{-27}$  kg

$$|v| = \frac{|\bar{p}|}{m_0} \sim 3 \times 10^6 \text{ m/s}$$

$$\therefore K.E. = \frac{p^2}{2m_0} = \frac{(0.527 \times 10^{-20})^2}{2 \times 1.67 \times 10^{-27}} \text{ J} \approx 52 \text{ keV}$$

Since the energy is less than the energies carried by these particles emitted by nucleus, protons and neutrons can exist inside the nucleus.

### Binding Energy of an Electron in an Atom

In an atom, an electron is under the influence of electrostatic potential of the positively charged nucleus. It is confined within a linear dimension equal to the diameter of the electronic orbit. The uncertainty  $\Delta x$  is of the order of  $2R$ ,  $R$  being the radius of the orbit and corresponding uncertainty in the momentum component  $\Delta p_x$  is given by

$$\Delta p_x \geq \frac{h}{4\pi 2 R}$$

It shows that the momentum of an electron in an atomic orbit is at least

$$|\bar{p}| \sim p_x \sim \Delta p_x \sim \frac{h}{4\pi 2 R} \sim 0.527 \times 10^{-24} \text{ kg ms}^{-1}$$

This is non-relativistic momentum for an electron.

$$\therefore K.E. = \frac{p^2}{2m_o} = \left( \frac{h}{4\pi 2 R} \right)^2 \frac{1}{2m_o} = \frac{h^2}{64\pi^2 m_o R^2}$$

P.E. of an electron

$$V = -\frac{Ze^2}{4\pi\epsilon_o R}$$

$$\therefore E = K.E. + V = \frac{h^2}{64\pi^2 m_o R^2} - \frac{Ze^2}{4\pi\epsilon_0 R} \\ = \left[ \frac{10^{-20}}{R^2} - \frac{15 \times 10^{-10} Z}{R^2} \right] \text{eV}$$

Taking

$$R = 10^{-10} \text{ m}$$

$$E = (1 - 15 Z) \text{eV}$$

Binding energy of outermost electron in H and He are  $-13.6 \text{ eV}$  and  $-24.6 \text{ eV}$  respectively so the value of binding energy derived on the basis of uncertainty principle is acceptable as these are comparable in magnitudes.

(iv) **Finite width of spectral lines:** We know  $\Delta E, \Delta t \approx h$

Since life time of electron in an excited state is finite ( $\approx 10^{-8} \text{ sec}$ ), so the energy levels of an atom

$$\Delta E = \frac{h}{\Delta t} \text{ must have a finite width}$$

It implies that excited levels must have a finite energy spread. Radiation given out by electron jump cannot be truly monochromatic. Thus, the spectral lines must have a natural finite width.

(v) **Strength of Nuclear force:** We know, nuclear radius,  $r_o \approx 1.2 \times 10^{-13} \text{ cm}$   
From uncertainty principle

$$p \sim \frac{\hbar}{r_o}$$

$$K.E. = \frac{p^2}{2m} \approx \frac{\hbar^2}{2mr_o^2} \approx 10 \text{ MeV}$$

( $M$  – Mass of proton)

Since the nucleus is bound so binding energy should be greater than kinetic energy with negative sign. So the binding energy of a nucleus is of the order of  $10 \text{ MeV}$ .

### Example 1.16

Calculate the minimum uncertainty in the momentum of a  ${}^4\text{He}$  atom confined to  $0.40 \text{ nm}$ .  
**Solution.**

We know that  ${}^4\text{He}$  atom is somewhere in the  $0.40 \text{ nm}$  region, therefore,  $\Delta x = 0.40 \text{ nm}$ . According to uncertainty relation

$$\Delta p_x \geq \frac{\hbar}{\Delta x}$$

For minimum uncertainty

$$\Delta p_x = \frac{\hbar}{\Delta x} = \frac{6.626 \times 10^{-34} \text{ Js}}{2\pi \times 0.40 \times 10^{-9} \text{ m}} \\ = 2.64 \times 10^{-25} \text{ kg m/s}$$

**Example 1.17**

An electron moves in the x-direction with a speed of  $4 \times 10^6 \text{ m/s}$ . We can measure its speed to a precision of 1%. With what precision can its position simultaneously be measured?

**Solution.**

The momentum of the electron

$$\begin{aligned} p = mv &= (9.1 \times 10^{-31} \text{ kg}) (4 \times 10^6 \text{ ms}^{-1}) \\ &= 3.64 \times 10^{-24} \text{ kg ms}^{-1} \end{aligned}$$

$$\Delta p = \frac{3.64 \times 10^{-24}}{100} \text{ kg ms}^{-1} = 3.64 \times 10^{-26} \text{ kg ms}^{-1}$$

$$\begin{aligned} \Delta x &= \frac{\hbar}{2 \Delta p} = \frac{1.05 \times 10^{-34} \text{ Js}}{2 \times 3.64 \times 10^{-26}} \text{ kg ms}^{-1} \\ &= 1.44 \times 10^{-9} \text{ m} = 1.44 \text{ nm} \end{aligned}$$

**Example 1.18**

The average lifetime of an excited atomic state is  $10^{-8} \text{ s}$ . If the wavelength of the spectral line associated with a transition from this state is  $4000 \text{ \AA}$ , what is the width of this line?

**Solution.**

Average lifetime is  $10^{-8} \text{ s}$

$$\Rightarrow \Delta t = 10^{-8} \text{ sec.}$$

$$E = h\nu = \frac{hc}{\lambda} \text{ or } |\Delta E| = \frac{hc}{\lambda^2} \Delta \lambda$$

$$(\Delta E) \cdot (\Delta t) \approx \frac{\hbar}{2} \text{ or } \frac{hc}{\lambda^2} (\Delta \lambda) (\Delta t) \approx \hbar/2$$

$$\begin{aligned} \Delta \lambda &= \frac{\lambda^2}{4\pi c(\Delta t)} = \frac{(4000 \times 10^{-10} \text{ m})^2}{4\pi (3 \times 10^8 \text{ ms}^{-1}) 10^{-8} \text{ s}} \\ &= 4.24 \times 10^{-15} \text{ m.} \end{aligned}$$

**Example 1.19**

The average lifetime of an excited atom is about  $10^{-8}$  second. What is the order of natural width ( $\Delta\nu$ ) of the line emitted by the atom?

**Solution.**

The order of natural line width is

$$\Delta\nu = \frac{1}{2\pi\Delta t} = \frac{10^8}{2\pi} \text{ Hz} = 1.6 \times 10^7 \text{ Hz.}$$

**Example 1.20**

*The radius of an atomic nucleus is typically  $5 \times 10^{-15} \text{ m}$ . What is the lowest limit of the energy that an electron must have to be in the atomic nucleus?*

**Solution.**

The uncertainty in the electron's position is  $\Delta x = 5 \times 10^{-15} \text{ m}$

$$\therefore \Delta p \geq \frac{\hbar}{\Delta x} = \frac{6.626 \times 10^{-34} \text{ Js}}{2\pi \times 5 \times 10^{-15} \text{ m}} = 2.11 \times 10^{-20} \text{ kgm/sec}$$

The momentum would also be of the same order if this is the uncertainty in it. This suggests that the kinetic energy of the electron is far greater than its rest energy and we can write

$$k.e. = pc \quad \text{so that}$$

$$\begin{aligned} k.e. &= pc \geq (2.11 \times 10^{-20} \text{ kg ms}^{-1}) \times (3 \times 10^8 \text{ ms}^{-1}) \\ &\geq 6.33 \times 10^{-12} \text{ J} \\ &\geq 39 \text{ MeV} \end{aligned}$$

Thus, the *k.e.* of an electron must exceed 39 MeV for it to be a nuclear constituent. Experiments indicate that the electrons in an atom have only a fraction of this energy. Thus, we can conclude that electrons are not present in the atomic nuclei.

**Example 1.21**

*The position  $x$  of a 0.01 g pellet has been carefully measured and is known within  $\pm 0.5 \mu\text{m}$ . What is the minimum uncertainty in its momentum?*

**Solution.**

If  $x$  is known within  $\pm 0.5 \text{ cm}$ , the spread  $\pm \Delta x$  in the position is certainly no longer than  $0.5 \mu\text{m}$ :  
 $\Delta x \leq 0.5 \mu\text{m}$

According to the uncertainty relation, this implies that the momentum is uncertain by an amount

$$\Delta p \geq \frac{\hbar}{2\Delta x} \geq \frac{10^{-34} \text{ Js}}{10^{-6} \text{ m}} = 10^{-28} \text{ kg m/s}$$

**Example 1.22**

*Many excited states of atoms are unstable and decay by emission of a photon in a time of order  $\Delta t = 10^{-8} \text{ s}$ . What is the minimum uncertainty in the energy of such an atomic state?*

**Solution.**

According to the uncertainty relation, minimum uncertainty in energy is  $\Delta E \approx \frac{\hbar}{2\Delta t} = \frac{\hbar c}{2c\Delta t}$

$$\begin{aligned} &= \frac{200 \text{ eV} \cdot \text{nm}}{2 \times (3 \times 10^{17} \text{ nm/s}) \times (10^{-8} \text{ s})} \\ &= 3 \times 10^{-8} \text{ eV} \end{aligned}$$

**Example 1.23**

An electron is known to be somewhere in an interval of total width  $a \approx 0.1 \text{ nm}$  (the size of a small atom). What is minimum uncertainty in its velocity?

**Solution.**

If electron is certainly inside an interval of  $\Delta x \leq a/2$

[Since  $\Delta x$  is the spread from central value to either side.]

According to uncertainty principle

$$\Delta p \geq \frac{\hbar}{2\Delta x} \geq \frac{\hbar}{a}$$

$$\Rightarrow \Delta v = \frac{\Delta p}{m} \geq \frac{\hbar}{am}$$

$$\begin{aligned} \Delta v &\geq \frac{\hbar c^2}{amc^2} = \frac{200 \text{ eV} \cdot \text{nm}}{(0.1 \text{ nm}) \times (0.5 \times 10^6 \text{ eV})} c \\ &= \frac{c}{250} = 10^6 \text{ m/s} \end{aligned}$$

**Example 1.24**

The uncertainty in the location of a particle moving with a velocity of  $7.28 \times 10^7 \text{ m/s}$  is two times its de-Broglie wavelength. Find out the uncertainty in measuring the velocity.

**Solution.**

de-Broglie wavelength

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

Given:

$$\Delta x = 2 \lambda = \frac{2h}{mv}$$

According to uncertainty principle  $\Delta x \Delta p \approx \hbar$

$$\Delta x \cdot m \Delta v \approx \hbar \Rightarrow \frac{2h}{mv} m \Delta v \approx \frac{h}{2\pi}$$

or

$$\Delta v \approx \frac{v}{4\pi} = \frac{7.28 \times 10^7}{4 \times 3.14} = 5.79 \times 10^6 \text{ m/s}$$

### 1.15 WAVE FUNCTION

In water, wave that varies periodically is the height of the water surface. In sound waves, it is pressure. In light waves, electric and magnetic fields vary. What in the case of matter waves? It is wave function  $\psi$  (psi). The value of the wave function associated with a moving body at the particular point  $x, y, z$  in space at the time  $t$  is related to the likelihood of finding the body at the time.

The wave function  $\psi$  has no direct physical significance. For the simple reason that  $\psi$  cannot be interpreted by an experiment. The probability that something be at a certain place at a given time must lie between 0 and 1. But the amplitude of any wave is negative as often as it is positive, and a negative probability, say  $-0.2$ , is meaningless. Hence,  $\psi$  by itself cannot be an observable quantity.

This objection does not apply to  $|\psi|^2$ , the square of the absolute value of the function, which is known as probability density.

The probability of experimentally finding the body described by the wave function  $\psi$  at the point  $x, y, z$  at the time  $t$  is proportional to the value of  $|\psi|^2$  there at  $t$ .

A large value of  $|\psi|^2$  means the strong possibility of the body's presence, while a small value of  $|\psi|^2$  means the slight possibility of its presence. This interpretation was formulated by Born in 1926.

The quantity with which quantum mechanics is concerned is the wave function  $\psi$  of a body. While  $\psi$  itself has no physical interpretation, the square of its absolute amplitude  $|\psi|^2$  evaluated at a particular place at a particular time is proportional to the probability of finding the body there at that time. The linear momentum, angular momentum and energy of the body are other quantities that can be obtained from  $\psi$ .

Wave functions are usually complex with both real and imaginary parts. A probability, however, must be a positive real quantity. The probability density  $|\psi|^2$  for a complex  $\psi$  is therefore taken as the product  $\psi^* \psi$  of  $\psi$  and its complex conjugate  $\psi^*$ . The complex conjugate of any function is obtained by replacing  $i (= \sqrt{-1})$  by  $-i$ , wherever it appears in the function.

Wave function  $\psi = A + iB$ , where  $A$  and  $B$  are real function.

The complex conjugate  $\psi^*$  of  $\psi$  is  $= A - iB$  and so  $\psi^* \psi = A^2 - i^2 B^2 = A^2 + B^2$   
Thus,  $\psi^* \psi$  is always a positive real quantity.

Since  $|\psi|^2$  is proportional to the probability density  $P$  of finding the body described by  $\psi$ , the integral of  $|\psi|^2$  over all space must be finite—the body is somewhere, after all. If  $\int_{-\infty}^{\infty} |\psi|^2 dv = 0$ , the particle does not exist, and integral cannot be  $\infty$ . Furthermore,  $|\psi|^2$  cannot be negative or complex because of the way it is defined. Integral must be finite quantity if  $\psi$  is to describe properly a real body.

It is convenient to have  $|\psi|^2$  equal to the probability density  $P$  of finding the particle described by  $\psi$ , rather than merely be proportional to  $P$ . If  $|\psi|^2$  is equal to  $P$ , then it must be true that

$$\int_{-\infty}^{\infty} |\psi|^2 z dv = 1 \text{ (Normalization)} \quad \dots(1.51)$$

Since if the particle exists somewhere at all times

$$\int_{-\infty}^{\infty} P dv = 1 \quad \dots(1.52)$$

A wave function that obeys Eq. (1.51) is said to be *normalized*. Every acceptable wave function can be normalized by multiplying it by an appropriate constant.

Besides being normalizable,  $\psi$  must be single valued, since  $P$  can have only one value at a particular place and time, and continuous. Momentum considerations require that the partial derivatives  $\frac{\partial \psi}{\partial x}$ ,  $\frac{\partial \psi}{\partial y}$ ,  $\frac{\partial \psi}{\partial z}$ , be finite, continuous, and single-valued. Thus, for a wave function to be correct wave function, it must satisfy the following conditions.

1.  $\psi$  must be continuous and single-valued everywhere.

2.  $\frac{\partial \psi}{\partial x}$ ,  $\frac{\partial \psi}{\partial y}$ ,  $\frac{\partial \psi}{\partial z}$  must be continuous and single-valued everywhere.

3.  $\psi$  must be normalizable, which means that  $\psi$  must go to 0 as  $x \rightarrow \pm \infty$ ,  $y \rightarrow \pm \infty$ ,  $z \rightarrow \pm \infty$  in order that  $\int |\psi|^2 dv$  over all space be a finite constant.

The above rules are not always obeyed by the wave functions of particles in model situations that only approximate actual ones. For instance, the wave functions of a particle in a box with infinitely hard walls do not have continuous derivatives at the walls, since  $\psi = 0$  outside the box. But in the real world, where walls are never infinitely hard, there is no sharp change in  $\psi$  at the walls and the derivatives are continuous.

Given a normalized and otherwise acceptable wave function  $\psi$ , the probability that the particle it describes will be in a certain region is simply the integral of the probability density  $|\psi|^2$  over that region. Thus, for a particle restricted to motion in the  $x$ -direction, the probability of finding it between  $x_1$  and  $x_2$  is given by

$$P_{x_1 x_2} = \int_{x_1}^{x_2} |\psi|^2 dx \quad \dots(1.53)$$

## 1.16 BRA-KET NOTATION IN QUANTUM MECHANICS

Initially Werner Heisenberg, Max Planck and others formulated matrix representation in quantum mechanics, sometimes also called matrix mechanics. In matrix mechanics, a quantum state is represented by a quantum state vector and the physical quantities, such as position and momentum of a particle, are represented by matrices.

Later Paul Dirac developed bra-ket notation, which is concise and convenient of describing quantum states in matrix mechanics. He introduced and defined the symbol  $|i\rangle$  to represent a quantum state  $i$ . This is called a *ket* or a *ket vector*.

Dirac notation uses a ket vector  $|i\rangle$  to describe a quantum state instead of a wave function  $\psi_i$ , which is the basis of Schrödinger's notation. The complex conjugate of the wave function  $\psi_i^*$  is

represented by a bra vector  $\langle i |$ . The inner product of two complex functions can be described by the bra-ket notation as

$$\int \psi_i^* \psi_j dv = \langle \psi_i | \psi_j \rangle = \langle i | j \rangle \quad \dots(1.54)$$

If a wave function is normalized, the following must hold

$$\int \psi \psi^* dv = \int |\psi|^2 dv = \langle \psi | \psi \rangle = 1 \quad \dots(1.55)$$

A physical quantity or an action to determine physical quantities (measurements) is represented by  $A$  instead of a linear operator

$$A \psi = A|\psi\rangle \quad \dots(1.56)$$

The Schrödinger equation for a stationary (time independent) state is represented by

$$H_{ij}|\psi_i\rangle = E_i|\psi_i\rangle \quad \dots(1.57)$$

where  $H_{ij}$  is a Hamiltonian matrix. In matrix mechanics, a set of eigenvalues  $E_i$  can be obtained through the diagonalization of the Hamiltonian matrix instead of solving the Schrödinger equation. The principle of superposition is expressed as: if the two vectors  $|\psi_1\rangle$  and  $|\psi_2\rangle$  satisfy the Schrödinger equation above, then a new vector  $c_1|\psi_1\rangle + c_2|\psi_2\rangle$  also satisfies the same Schrödinger equation. In this state, the probability of observing an energy to be  $E_1$  is  $c_1 c_1^*$  and probability of observing the energy to be  $E_2$  is  $c_2 c_2^*$ .

### 1.17 EXPECTATION VALUES

Once Schrödinger equation has been solved for a particle in a given physical situation, the resulting wave function  $\psi(x, y, z, t)$  contains all information about the particle that is permitted by the uncertainty principle. Except for these variables that are quantized this information is in the form of probabilities and not specific numbers.

As an example, let us calculate the expectation value  $\langle x \rangle$  of the position of a particle confined to the  $x$ -axis that is described by the wave function  $\psi(x, t)$ . This is the value of  $x$  we would obtain if we measured the positions of large number of particles described by the same wave function at some instant  $t$  and then averaged the results.

What is the average position  $\bar{x}$  of a number of identical particles distributed along the  $x$  axis in such a way that there are  $N_1$  particles at  $x_1$ ,  $N_2$  particles at  $x_2$ , and so on? The average position in this case is the same as the centre of mass of the distribution, and so

$$\bar{x} = \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + \dots}{N_1 + N_2 + N_3} = \frac{\sum x_i N_i}{\sum N_i}$$

When we are dealing with a single particle, we must replace the number  $N_i$  of particles at  $x_i$  by the probability  $P_i$  that the particle be found in an interval  $dx$  at  $x_i$ . This probability is

$$P_i = |\psi_i|^2 dx \quad \dots(1.58)$$

where  $\psi_i$  is the particle wave function evaluated at  $x = x_i$ . Making this substitution and changing the summations to integrals, we see that the expectation value of the position of the single particle is

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x |\psi|^2 dx}{\int_{-\infty}^{\infty} |\psi|^2 dx} \quad \dots(1.59)$$

If  $\psi$  is a normalized wave function, the denominator of Eq. (1.59) equals the probability that the particle exists somewhere between  $x = -\infty$  and  $x = \infty$  and therefore has the value 1. In this case

$$\text{Expectation value for position } \langle x \rangle = \int_{-\infty}^{\infty} x |\psi|^2 dx \quad \dots(1.60)$$

This formula states that  $\langle x \rangle$  is located at the centre of mass (so to speak) of  $|\psi|^2$ . If  $|\psi|^2$  is plotted versus  $x$  on a graph and the area enclosed by the curve and the  $x$ -axis is cut out, the balance point will be at  $\langle x \rangle$ .

The same procedure as that followed above can be used to obtain the expectation value  $\langle G(x) \rangle$  of any quantity for instance, potential energy  $U(x)$  – that is, a function of the position  $x$  of a particle described by a wave function  $\psi$ . The result is

$$\text{Expectation value } \langle G(x) \rangle = \int_{-\infty}^{\infty} G(x) |\psi|^2 dx \quad \dots(1.61)$$

The expectation value  $\langle p \rangle$  of momentum cannot be calculated this way because, according to the uncertainty principles, no such function as  $p(x)$  can exist. If we specify  $x$  so that  $\Delta x = 0$ , we cannot specify a corresponding  $p$  since  $\Delta x \Delta p \geq \frac{\hbar}{2}$ .

The same problem occurs for the expectation value  $\langle E \rangle$  for energy.

## 1.18 OPERATORS IN QUANTUM MECHANICS

In quantum mechanics, physical quantities or actions undertaken to determine physical quantities (measurements) are represented by linear operators. We may define *an operator as a rule by which, given any function, we can find another function*. Thus, we can define an operator  $P$  as: multiply the function by an independent variable, i.e.,  $Pf(x) = xf(x)$ . Similarly, we can define an operator  $Q$  as the differentiation w.r.t. the independent variable, i.e.,  $Qf(x) = f'(x)$ . The result obtained by the action of  $P$  followed by  $Q$  is different from that obtained by the action of  $Q$  followed by  $P$  as shown below.

$$PQ f(x) = P[Qf(x)] = xf''(x) \quad \dots(1.62)$$

$$QP f(x) = Q[Pf(x)] = xf'(x) + f(x) \quad \dots(1.63)$$

For the two operators  $\alpha$  and  $\beta$ , if  $\alpha\beta = \beta\alpha$ ,  $\alpha$  and  $\beta$  are said to **commute** or be **commutable**. In this sense, the operators  $P$  and  $Q$  are not commutable.

A measurement changes the state of a particle represented by a wavefunction (i.e., an operator operating on the wave function). Suppose, we measure the physical quantities  $a$  and  $b$  of an electron by continuous measurements  $A$  and  $B$ . The result obtained by carrying out first measurement  $A$

followed by the measurement  $B$  is different from that obtained by conducting first measurement followed by measurement  $A$ , because each of the measurements changes the wave function. This can be represented mathematically using operators acting on the wave function as

$$AB \psi \neq BA \psi \quad \dots(1.64)$$

This equation indicates that the operators  $A$  and  $B$  are not commutable. In this case, measurements change the wave function and the two physical quantities corresponding to the operators  $A$  and  $B$  cannot be determined precisely at the same time due to the laws defined by uncertainty principle. On the other hand, if the operators  $A$  and  $B$  are commutable, we can determine the two physical constants at the same time without the restrictions of the uncertainty principle.

Following are the operators corresponding to some important physical quantities:

Physical quantities	Symbol	Operator
Position	$q$ (or $r$ )	$q$ (or $x, y, z; r$ )
Energy	$E$	$i\hbar \frac{\partial}{\partial t}$
Kinetic energy	$T$	$-\hbar^2 \frac{\nabla^2}{2m}$
Momentum	$p$	$-i\hbar \nabla$ $(-i\hbar \frac{\partial}{\partial x}, -i\hbar \frac{\partial}{\partial y}, -i\hbar \frac{\partial}{\partial z}, \text{ for } x, y$ and $z$ -components respectively)
Velocity	$v$	$-\frac{i\hbar}{m} \nabla$ $\left( \frac{-i\hbar}{m} \frac{\partial}{\partial x}, \frac{-i\hbar}{m} \frac{\partial}{\partial y}, \frac{-i\hbar}{m} \frac{\partial}{\partial z} \right)$
Hamiltonian	$H$	$i\hbar \frac{\partial}{\partial t}$

For example, Schrödinger equation

$$H \psi = E \psi$$

can be expressed as

$$H \psi = i\hbar \frac{\partial \psi}{\partial t} \text{ or } (H) \psi = \left( i\hbar \frac{\partial}{\partial t} \right) \psi$$

where  $\hbar = \frac{h}{2\pi}$  and  $h$  is Planck's constant.

Similarly, if  $P$  and  $Q$  are the position and momentum operators respectively, the  $PQ \psi$  can be represented as

$$PQ \psi = -i\hbar \frac{\partial}{\partial q} (q \psi) = -i\hbar \psi - i\hbar q \frac{\partial \psi}{\partial q} \quad \dots(1.65)$$

Similarly,

$$QP \psi = q \left( -i\hbar \frac{\partial \psi}{\partial q} \right) = -i\hbar q \frac{\partial \psi}{\partial q} \quad \dots(1.66)$$

Thus, we see that

$$(PQ - QP) \psi = -i\hbar \psi \neq 0 \quad \dots(1.67)$$

## 1.19 SCHRÖDINGER EQUATION: TIME DEPENDENT FORM

In quantum mechanics the wave function  $\psi$  corresponds to the wave variable  $y$  of wave motion in general. However,  $\psi$ , unlike  $y$ , is not itself a measurable quantity and may therefore be complex. For this reason, we assume that  $\psi$  for a particle moving freely in the  $+x$  direction is specified by

$$\psi = A e^{-i\omega(t-x/v)} \quad \dots(1.68)$$

Replacing  $\omega$  by  $2\pi\nu$  and  $v$  by  $\lambda\nu$ , we get

$$\psi = A e^{-2\pi i \left( vt - \frac{x}{\lambda} \right)} \quad \dots(1.69)$$

This is convenient since we already know that what  $v$  and  $\lambda$  are in terms of the total energy  $E$  and momentum  $p$  of the particle being described by  $\psi$  because

$$E = h\nu = 2\pi\hbar\nu \text{ and } \lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$$

$$\therefore \text{For free particle} \Rightarrow \psi = A e^{-(i/\hbar)(Et - px)} \quad \dots(1.70)$$

Equation (1.70) describes the wave equivalent of an unrestricted particle of total energy  $E$  and momentum  $p$  moving in the  $+x$  direction.

The expression for the wave function  $\psi$  given by Eq. (1.70) is correct only for freely moving particles. However, we are most interested in situations where the motion of a particle is subjected to various restrictions. An important concern, for example, is an electron bound to an atom by the electric field of its nucleus. What we must now do is to obtain the fundamental differential equation for  $\psi$ , which we can then solve for  $\psi$  in a specific situation. This equation, called Schrödinger equation, can be arrived at in various ways, but it cannot be rigorously derived from existing physical principles. The equation represents something new. What will be done here is to show one route to the wave equation for  $\psi$  and then to discuss the significance of the result.

We begin by differentiating Eq. (1.70) for  $\psi$  twice w.r.t.  $x$ , giving

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{p^2}{\hbar^2} \psi \Rightarrow p^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \quad \dots(1.71)$$

Differentiating Eq. (1.70) w.r.t.  $t$  gives

$$\frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar} \psi \Rightarrow E\psi = -\frac{\hbar}{i} \frac{\partial \psi}{\partial t} \quad \dots(1.72)$$

At speeds small compared with that of light, the total energy  $E$  of a particle is the sum of its kinetic energy  $\frac{p^2}{2m}$  and its potential energy  $U$ , where  $U$  is in general a function of position  $x$  and time  $t$ , i.e.,

$$E = \frac{p^2}{2m} + U(x, t) \quad \dots(1.73)$$

The function  $U$  represents the influence of the rest of the universe on the particle, of course, only a small part of the universe interacts with the particle to any extent. For instance, in the case of the electron in a hydrogen atom, only the electric field of the nucleus must be taken into account.

Multiplying both sides of Eq. (1.73) by  $\psi$ , we get

$$E\psi = \frac{p^2\psi}{2m} + U\psi \quad \dots(1.74)$$

Substituting for  $E\psi$  and  $p^2\psi$  from Eq. (1.72) and (1.71), we get *time dependent form of Schrödinger equation* in one dimension

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi \quad \dots(1.75)$$

In 3-D, the time-dependent form of Schrödinger equation is

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi \quad \dots(1.76)$$

where the particle's potential energy  $U$  is some function of  $x, y, z$  and  $t$ .

Any restrictions that may be present on the particle's motion will affect the potential energy function  $U$ . Once  $U$  is known, Schrödinger equation may be solved for the wave function  $\psi$  of the particle, from which its probability density  $|\psi|^2$  may be determined for a specific  $x, y, z, t$ .

Schrödinger equation is a basic principle itself and cannot be derived from other basic principles of physics.

Schrödinger equation is remarkably accurate in predicting the results of experiments for atomic and subatomic particles.

## 1.20 SCHRÖDINGER'S EQUATION: STEADY STATE FORM (TIME INDEPENDENT)

In many situations, the potential energy of a particle does not depend on time explicitly, the forces that act on it, and hence  $U$ , vary with the position of the particle only. When this is true, Schrödinger equation may be simplified by removing all reference to  $t$ .

One-dimensional wave function  $\psi$  of an unrestricted particle may be expressed as

$$\Psi(t) = A e^{-(i/\hbar)(Et - px)} = A e^{-i(E/\hbar)t} e^{+(ip/\hbar)x} = \Psi e^{-(iE/\hbar)t} \quad \dots(1.77)$$

where  $\Psi$  is the product of a time-dependent function  $e^{-(iE/\hbar)t}$  and a position dependent function  $\psi$ . As it happens, the time variations of all wave functions of particles acted on by stationary forces have the same form as that of an unrestricted particle.

Substituting the  $\Psi$  of Eq. (1.77) into the time-dependent form of Schrödinger equation

$$\left( i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + v\Psi \right), \text{ we find that}$$

$$E\Psi e^{-(iE/\hbar)t} = -\frac{\hbar^2}{2m} e^{-(iE/\hbar)t} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi e^{-(iE/\hbar)t}$$

Dividing throughout by the common exponential factor gives

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - U) \Psi = 0 \quad \dots(1.78)$$

Equation (1.78) is the *steady state form of Schrödinger's equation*. In 3-D the corresponding Schrödinger equation is

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - U) \Psi = 0 \quad \dots(1.79)$$

$$\text{As, } \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2 \Rightarrow \nabla^2 \Psi + \frac{2m}{\hbar^2} (E - U) \Psi = 0 \quad \dots(1.80)$$

An important property of Schrödinger's steady state equation is that, if it has one or more solutions for a given system, each of these wave functions corresponds to a specific value of the energy  $E$ . Thus, *energy quantization appears in wave (or quantum) mechanics as a natural element of the theory*, and energy quantization in the physical world is revealed as a universal phenomenon characteristic of all stable systems.

## 1.21 EIGENVALUES AND EIGENFUNCTIONS

The values of energy  $E_n$  for which Schrödinger's steady state equation can be solved are called *Eigenvalues* and the corresponding wave function  $\psi_n$  are called *Eigenfunctions*. (These terms come from the German Eigenwert meaning proper or characteristic value and Eigenfunction meaning proper or characteristic function). The discrete energy levels of the hydrogen atom

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_o^2\hbar^2} \left( \frac{1}{n^2} \right), \quad n = 1, 2, 3, \dots \quad \dots(1.81)$$

are an example of a set of eigenvalues.

An important example of a dynamical variable other than total energy that is found to be quantized in stable systems is angular momentum  $L$ . In the case of the hydrogen atom, the eigenvalues of the magnitude of the total angular momentum are specified by

$$L = \sqrt{l(l+1)\hbar} \quad l = 0, 1, 2, \dots, (n-1) \quad \dots(1.82)$$

## 1.22 DEGENERATE AND NON-DEGENERATE EIGENFUNCTIONS

When  $H\Psi_n = E_n\Psi_n$  is solved, corresponding to each eigenvalue there is only one eigenfunction. In such a situation, the eigenfunction is known as **degenerate**.

**Eigenfunction:** However, there are situations when corresponding to a single eigenvalue, there are a number of eigenfunctions, then these eigenfunctions are known as *degenerate eigenfunctions*.

In quantum mechanics, there are situations when the eigenvalue depends on principal quantum number  $n$  ( $E_n$ ), however, eigenfunction also depends upon orbital quantum number  $l$  and magnetic quantum number  $m$  ( $\psi_{nlm}$ ). As for each  $n$ ,  $l$  can vary from 0 to  $n - 1$  and for each of these  $l$  values,  $m$  can vary from  $-l$  to  $+l$  ( $2l + 1$  values). This leads to degeneracy. The total degeneracy is

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

For  $n = 2$ ,  $l = 0, m = 0; l = 1, m = 0; l = 1, m = \pm 1$ , giving four wave functions, i.e., system becomes fourfold degenerate. Similarly, you can work out for  $n = 3$ , system becomes nine fold degenerate and for  $n = 4$ , the system becomes sixteen fold degenerate, and so on.

### 1.23 PARTICLE IN A BOX

The simplest quantum-mechanical problem is that of a particle in a box with infinitely hard walls. We may specify the particle's motion by saying that it is restricted to travel along the  $x$ -axis between  $x = 0$  and  $x = L$  by infinitely hard walls (Fig. 1.17). A particle does not lose energy when it collides with such walls, so that its total energy stays constant. From a formal point of view the potential energy  $U$  of the particle is infinite on both sides of the box, while  $U$  is a constant-say zero for convenience, inside the box. Because the particle cannot have an infinite amount of energy, it cannot exist outside the box and so its wave function  $\psi$  is 0 for  $x \leq 0$  and  $x \geq L$ . Our task is to find what  $\psi$  is within the box, namely, between  $x = 0$  and  $x = L$ .

Within the box Schrödinger equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad \dots(1.83)$$

Since  $U = 0$  inside the box. (The total derivative  $\frac{d^2\psi}{dx^2}$  is the same as the partial derivative  $\frac{\partial^2 \psi}{\partial x^2}$  because  $\psi$  is a function only of  $x$  in this problem) Equation (1.83) has the general solution

$$\psi = A \sin \frac{\sqrt{2mE}}{\hbar} x + B \cos \frac{\sqrt{2mE}}{\hbar} x \quad \dots(1.84)$$

which we can verify by substitution back into (1.83),  $A$  and  $B$  are constants to be evaluated.

This solution is subject to the boundary conditions that  $\psi = 0$  for  $x = 0$  and for  $x = L$ . Since  $\cos 0 = 1$ , the second term cannot describe the particle because it does not vanish at  $x = 0$ . Hence, we conclude that  $B = 0$ . Since  $\sin 0 = 0$ , the sine term always yields  $\psi = 0$  at  $x = 0$ , as required, but

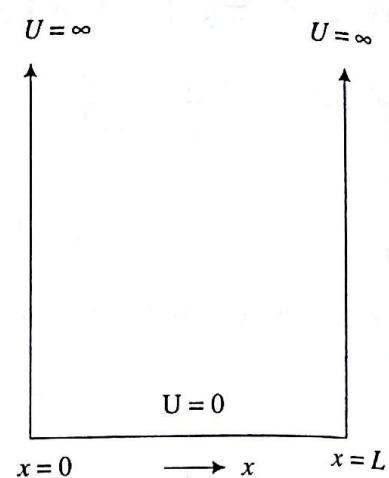


Fig. 1.17 A potential well with infinitely high barriers a box with infinitely hard walls

$$\frac{\sqrt{2mE}}{\hbar} L = n\pi, \quad n = 1, 2, 3, \dots \quad \dots(1.85)$$

This is because the sines of the angles  $\pi, 2\pi, 3\pi, \dots$  are all 0. From Eq. (1.85) it is clear that the energy of the particle can have only certain values which are the eigenvalues. These eigenvalues, constituting the energy levels of the system, are found by solving Eq. (1.85) for  $E_n$ , which gives

$$\frac{\sqrt{E_n}}{\hbar} = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, \quad n = 1, 2, 3, \dots \quad \dots(1.86)$$

### Wave Functions of A Particle in a Box

The wave functions of a particle in a box whose energies are  $E_n$ , from Eq. (1.84) with  $B = 0$ , are

$$\psi_n = A \sin \frac{\sqrt{2mE_n}}{\hbar} x \quad \dots(1.87)$$

Substituting Eq. (1.86) for  $E_n$  gives

$$\psi_n = A \sin \frac{\sqrt{2m \frac{n^2 \pi^2 \hbar^2}{2mL^2}}}{\hbar} x = A \sin \frac{n\pi x}{L} \quad \dots(1.88)$$

For the eigenfunctions corresponding to the energy eigenvalues  $E_n$ .

These eigenfunctions meet all the requirements. For each quantum number  $n$ ,  $\psi_n$  is a finite, single-valued function of  $x$ , and  $\psi_n$  and  $\frac{\partial \psi_n}{\partial x}$  are continuous (except at the ends of the box).

Furthermore, the integral of  $|\psi_n|^2$  over all space is finite, as we can see by integrating  $|\psi_n|^2$  from  $x = 0$  to  $x = L$  (since the particle is confined within these limits). With the help of the trigonometric identity

$$\sin^2 \theta = \frac{1}{2} (1 - \cos 2\theta)$$

we find that

$$\begin{aligned} \int_{-\infty}^{\infty} |\psi_n|^2 dx &= \int_0^L |\psi_n|^2 dx = A^2 \int_0^L \sin^2 \left( \frac{n\pi x}{L} \right) dx = \frac{A^2}{2} \left[ \int_0^L dx - \int_0^L \cos \left( \frac{2n\pi x}{L} \right) dx \right] \\ &= \frac{A^2}{2} \left[ x - \left( \frac{L}{2n\pi} \right) \sin \frac{2n\pi x}{L} \right]_0^L = A^2 \left( \frac{L}{2} \right) \end{aligned} \quad \dots(1.89)$$

To normalize  $\Psi$  we must assign a value to  $A$  such that  $|\psi_n|^2 dx$  is equal to the probability  $Pdx$  of finding the particle between  $x$  and  $x + dx$ , rather than merely proportional to  $Pdx$ . If  $|\psi_n|^2 dx$  is equal  $Pdx$ , then it must be true that

$$\int_{-\infty}^{\infty} |\psi|^2 dx = 1 \quad \dots(1.90)$$

Comparing Eqs. (1.89) and (1.90), we see that the wave function of a particle in a box are

normalized if

$$A = \sqrt{\frac{2}{L}} \quad \dots(1.91)$$

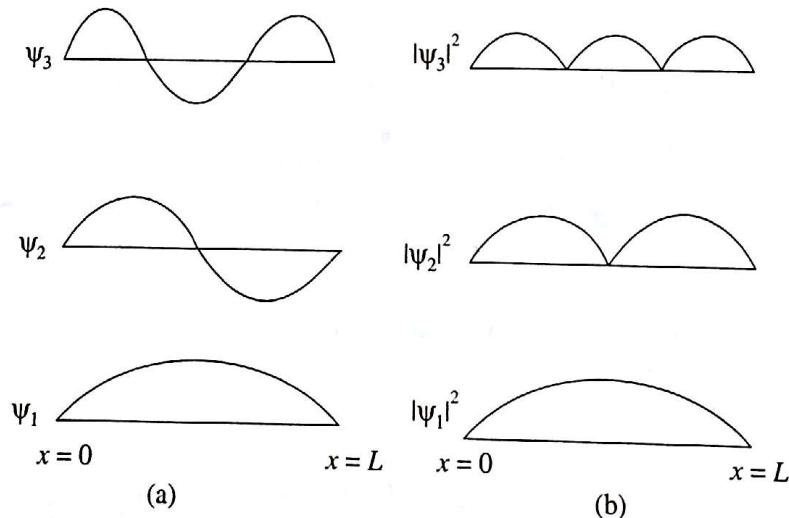
The normalized wave functions of the particle are therefore

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}, \quad n = 1, 2, 3, \dots \dots \quad \dots(1.92)$$

The normalized wave function  $\psi_1$ ,  $\psi_2$  and  $\psi_3$  together with the probability density  $|\psi_1|^2$ ,  $|\psi_2|^2$  and  $|\psi_3|^2$  are plotted in Fig. 1.18. Although  $\psi_n$  may be negative as well as positive,  $|\psi_n|^2$  is always +ve and since  $\psi_n$  is normalized, its value at a given  $x$  is equal to the probability density of finding particle there. In every case  $|\psi_n|^2 = 0$  at  $x = 0$  and  $x = L$ , the boundaries of the box.

At a particular place in the box the probability of the particle being present may be very different for different quantum numbers. For instance,  $|\psi_1|^2$  has its maximum value of  $\frac{2}{L}$  in the middle of the box, while a particle in the next higher state of  $n = 2$  is never there.

The wave function shown in Fig. 1.18(a) resemble the possible vibrations of a string fixed at both ends. This follows from the fact that waves in a stretched string and the wave representing a moving particle are described by equations of the same form, so that when identical restrictions are placed upon each kind of wave, and therefore the formal results are identical.



**Fig. 1.18** (a) Wave functions and (b) Probability densities.

## 1.24 SIMPLE HARMONIC OSCILLATOR

Simple harmonic oscillator is of fundamental importance in physics because there are many quantum systems which can be approximated by harmonic oscillators. For example, the variation of diatomic molecules and motions of atoms in a crystal lattice can be treated to a first approximation as the motion of particles in harmonic fields. We know that the potential energy  $U(x)$  of a harmonic oscillator of mass  $m$  is given by

$$U(x) = \frac{1}{2} kx^2 \quad \dots(1.93)$$

where  $k (= m \omega^2)$  is the force (or spring) constant defined as the force per unit displacement. The Schrödinger equation for this system can be written as.

$$\frac{d^2 \Psi}{dx^2} + \frac{2m}{\hbar^2} \left( E - \frac{k}{2} x^2 \right) \Psi = 0 \quad \dots(1.94)$$

The solution of the Schrödinger equation yields the following wave functions

$$\begin{aligned} \Psi_n &= A_n H_n(z) e^{-z^2/2} \\ &= A_n H_n \left[ \left( \frac{mk}{\hbar} \right)^{\frac{1}{4}} x \right] \exp \left[ -\frac{1}{2} \left( \frac{mk}{\hbar^2} \right)^{\frac{1}{2}} x^2 \right] \end{aligned} \quad \dots(1.95)$$

and eigenvalues

$$\begin{aligned} E_n &= \hbar \sqrt{\frac{k}{m}} \left( n + \frac{1}{2} \right) \\ &= \left( n + \frac{1}{2} \right) \hbar \omega, \quad n = 0, 1, 2, \dots \end{aligned} \quad \dots(1.96)$$

where  $A_n$  and  $H_n(z)$  (Hermite polynomials) are given by

$$A_n = \left[ \frac{(mk/\hbar)^{\frac{1}{2}}}{2^n n! \pi^{\frac{1}{2}}} \right]^{\frac{1}{2}}$$

$$H_n(z) = (-1)^n \exp(z^2) \frac{d^n}{dz^n} \exp(-z^2) \quad \dots(1.97)$$

The first four energy levels, corresponding wave functions  $\Psi_n(x)$  and probability densities  $|\Psi_n(x)|^2$  are shown in Fig. 1.19 (b) and (c) respectively. It is important to note from the figures that  $\Psi_n(x)$  and  $|\Psi_n(x)|^2$  have a finite value outside the classically allowed region. The probability density oscillates between the turning points and decreases exponentially beyond the turning points. The figure clearly indicates the penetration of the particle into the region outside the classical turning points.

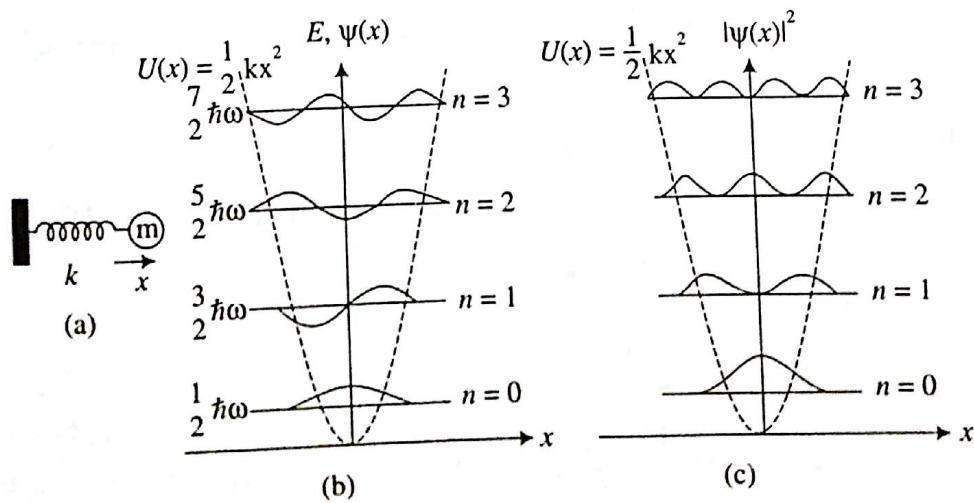


Fig. 1.19 (a) Harmonic oscillator, (b) energy levels and corresponding wave function, and (c) corresponding probability densities.

The energy levels (given by Eq. 1.96) are equally spaced, as shown in Fig. 1.19 (b). For the ground state ( $n = 0$ ), from Eq.(1.96), we have

$$E_0 = \frac{1}{2} \hbar \omega$$

~~Thus, the oscillator will have this energy even at absolute zero. This energy is referred to as zero point energy. This is in contradiction with Planck oscillator for which  $E_n = n \hbar \omega$  and so for  $n=0$ ,  $E_0 = 0$ .~~

It is important to realize that the existence of zero point energy is in accordance with the uncertainty principle. The laws of quantum mechanics do not permit the harmonic oscillator to have zero energy and the smallest allowed energy is the zero point energy. If the oscillator has zero energy, it will also have zero momentum and therefore can be located exactly at the position of minimum potential energy, which will not be in accordance with the uncertainty principle. Hence, the necessary uncertainties in position and momentum give rise to the zero point energy.

A comparison of energy values ( $E_n = \left(n + \frac{1}{2}\right) \hbar \omega$  vs  $E_n = n \hbar \omega$ ) makes it evident that the quantum mechanical values are higher by  $\frac{1}{2} \hbar \omega$ . Also, since  $H_0(z) = 1$ , the ground state wave function can be shown to be

$$\Psi_0 = \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} \exp\left(-\frac{m\omega x^2}{2\hbar}\right) \quad \dots(1.98)$$

### Example 1.25

The strongest vibrational bond of CO molecule occurs at  $6.43 \times 10^{13}$  Hz. If the reduced mass of CO is  $1.1385 \times 10^{-26}$  kg, calculate (i) the force constant and (ii) the zero point energy of the CO bond.

### Solution.

Due to the vibrational motion of the C and O atoms, the C – O bond stretches, then contracts and so on, i.e., undergo simple harmonic motion.

(i) We know  $v_o = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ , where  $\mu$  is the reduced mass.

∴ force constant  $k = 4\pi^2 v_o^2 \mu$

$$= 4 \times (3.14)^2 (6.43 \times 10^{13})^2 (1.1385 \times 10^{-26})$$

$$= 1860 \text{ Nm}^{-1}$$

(ii) Zero point energy  $E_0 = \frac{1}{2} h v_o$

$$= \frac{1}{2} \times 6.62 \times 10^{-34} \times 6.43 \times 10^{13} \text{ J}$$

$$= 21.3 \times 10^{-21} \text{ J}$$

$$= \frac{21.3 \times 10^{-21}}{1.6 \times 10^{-19}} \text{ eV}$$
$$= 0.133 \text{ eV.}$$