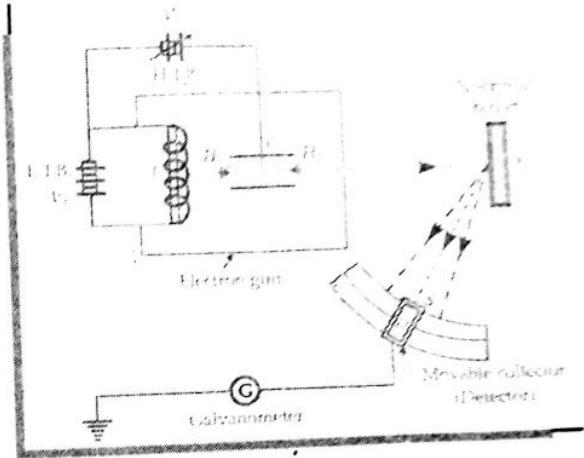


## Chapter 7



# Quantum Theory

*"In a sense, the difference between classical and quantum mechanics can be seen to be due to the fact that classical mechanics took to superficial a view of the world : it dealt with appearances. However, quantum mechanics accepts that appearances are the manifestation of a deeper structure (the wavefunction, the amplitude of the state, not the state itself), and that all calculations must be carried out on this substructure."*

Peter Atkins

### Outline

- Spectral Distribution in Black Body Radiation
- Failure of Classical Theory for Explaining the Black Body Radiation
- Planck's Quantum Theory (Discovery of Planck's Constant) ✓
- The Planck's Law of Energy Distribution in Black Body Radiation
- The Photoelectric Effect ✓
- The Compton Effect ✓
- Wave-Particle Dualism
- de-Broglie's Hypothesis ✓
- Characteristics of Matter Waves ✓
- Phase Velocity and Group Velocity
- Experimental Study of Matter Waves
- Heisenberg's Uncertainty Principle ✓
- Wave Function ✓
- Schrödinger Wave Equation ✓
- Applications of Schrödinger's Wave Equation ✓

**Q**uantum theory or quantum mechanics is a branch of Physics which deals with the laws of particles or bodies on the atomic and subatomic scales. Classical mechanics is an approximation of quantum mechanics. Before understanding the laws of quantum mechanics, it is necessary to know about (i) evolution of mechanics, (ii) the need for new mechanics, (iii) formulation of quantum mechanics and (iv) the difference between classical mechanics and quantum mechanics.

### Evolution of Mechanics

Mechanics, the oldest of the physical sciences, is the study of the motion of the objects. Such motion is made up of the changes in the relative positions of the bodies and their parts, in space in the course of time.

The beginning of Physics date back to prehistoric times. Stone age and other huge rock structures prehistoric people built, indicate that they had some knowledge of mechanics. Such knowledge would have been necessary for them to transport huge rocks and to place them to top of one another. The first people to leave written records of their discoveries and inventions were Sumerians, Babylonians and Egyptians. During the 1100's and 1200's there was also increasing interest in scientific observation and experiments. Robert Grosseteste, Roger Bacon, Leonardo da Vinci, Saint Albertus Magnus, Saint Thomas Aquinas, Aristotle etc., contributed a number of measuring techniques. The work of Galileo, Kepler and Descartes reflects a change in attitude that occurred during the Renaissance (Renaissance is the name given to the period in Europe that extended from about the early 1300's to about 1600). In 1687, Newton showed how both the motions of heavenly bodies and motion of objects on or near the surface of the earth could be explained by four simple laws in his work "*Mathematical Principles of Natural Philosophy*". These laws of gravitation are the basis of the most elementary principles of classical mechanics.

Newtonian mechanics, Maxwell's electromagnetic theory and thermodynamics guided the growth of science and engineering during the years spanning 17th and 19th centuries. These theories explained almost all the scientific results of those times and it seems nothing more could be added. The above theories which are successfully realms of macroscopic world are regarded as classical mechanics. Lagrange's equations, Hamilton's equations and Hamilton's principle are also fundamental principles of classical mechanics because they are consistent with each other and with Newton's laws of motion.

### Need for New Mechanics

The early 1900's brought revolutionary developments in Physics. Scientists looked for inconsistencies in the classical Physics of Newton and others and discovered new interpretations of observed events.

In principle, the properties of bulk matter must be deducible from the properties of electrons and atomic nuclei of which it is composed. However it is found that the observed properties of matter can not be explained on the assumption that the particles obey the laws of classical mechanics. For example, black body radiation, the photoelectric effect, the emission of sharp spectral lines from atoms could not be explained with frame work of classical Physics.

As physicists sought new ways to solve these puzzles another revolutionary work took place in Physics between 1900 and 1930. A new theory called *Quantum (Wave) Mechanics* was highly successful in explaining the behaviour of atoms, molecules and nuclei.

Eugene Wigner, one of the early workers of quantum mechanics wrote,

*"The discovery of quantum mechanics was nearly a total surprise. It describes the physical world in a way that was fundamentally new. It seemed to many of us a miracle".*

### Formulation of Quantum Mechanics

The development of quantum mechanics took place in two stages :

I Stage	II Stage
<p>It began with Max Planck's presentation at a meeting of the German Physical Society on Dec. 14, 1900 of his hypothesis that <i>radiation is emitted or absorbed by matter in discrete packets called quanta</i>. The ideas of quanta which he brought forth in his publication gave birth to a new subject called <i>quantum mechanics</i>. The theory based on this hypothesis consisted of a mixture of classical and non-classical concepts and was not completely satisfactory.</p>	<p>In this stage i.e., quantum mechanics began from two different view points. In 1913, the Danish physicist Niel Bohr explained in terms of quanta, how atoms absorb and radiate energy. A particular form of this mechanics known as <i>Matrix mechanics</i> introduced by Werner Heisenberg in 1925.</p>

Another form of quantum mechanics is called **Wave Mechanics**, developed by Erwin Schrödinger in 1926. In this mechanics earlier ideas of classical wave theory are combined with Louis de Broglie's wave-particle relationship. The mathematical theories of wave mechanics and matrix mechanics appear to be different, but in fact they are equivalent. The combined ideas of Schrödinger and Heisenberg have since been developed as the field of quantum mechanics.

### Difference between Classical Mechanics and Quantum Mechanics

The fundamental difference between classical mechanics and quantum mechanics lies in what they describe. In general mechanics, the future history of a particle is completely determined by its initial position and momentum together with the forces that act upon it. In every day life these quantities can all be determined well enough for the predictions of Newtonian mechanics to agree with what we find.

Quantum mechanics also arrives at relationships between observable quantities, but the uncertainty principle suggests that the nature of observable quantities, but in the atomic realm. Cause of effect are still related in quantum mechanics, but what they concern needs careful interpretation. In quantum mechanics the kind of certainty about the future characteristic of classical mechanics is impossible because the initial state of a particle cannot be established with sufficient accuracy. The more we know about the position of a particle now, the less we know about its momentum and hence about its position later.

The quantities whose relationships in quantum mechanics explore the probabilities. Instead of asserting, for example, that the radius of the electron's orbit in a ground state hydrogen atom is always exactly  $5.3 \times 10^{-11}$  m, as the Bohr theory does, quantum mechanics states that this is **most probable** radius. In a suitable experiment most trials will yield a different value, either larger or smaller, but the value most likely to be found will be  $5.3 \times 10^{-11}$  m.

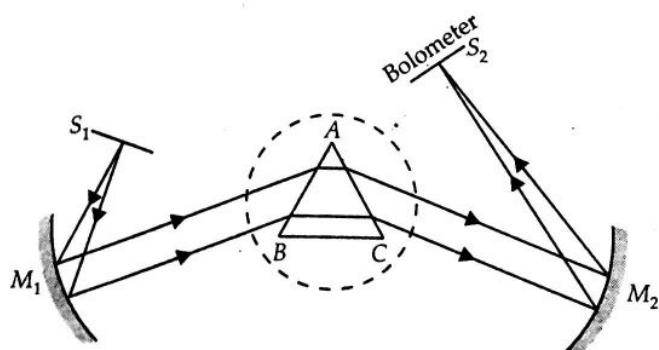
Quantum mechanics might seem a poor substitute for classical mechanics. However, classical mechanics turns out to be just an approximate version of quantum mechanics. The quantities of classical mechanics are illusory and their apparent agreement with experiment occurs because ordinary objects consist of so many individual atoms that departures from average behaviour are unnoticeable. Instead of two sets of physical principles, one for the macroworld and one for microworld, there is only the single set included in quantum mechanics.

### 7.1 SPECTRAL DISTRIBUTION IN BLACK BODY RADIATION

To understand the development of quantum mechanics, we begin with a brief account of black body radiation which could not be explained by classical mechanics.

Lummer and Pringsheim investigated the distribution of energy among the radiation emitted by black body at different temperatures.

Experimental arrangement of Lummer and Pringsheim is shown in Fig. 7.1. Their black body was an electrically heated one whose temperature was measured by a thermocouple.



**Fig. 7.1** Experimental arrangement of black body radiation.

The radiations from the black body pass through the slit  $S_1$  and fall on the reflector  $M_1$ , after being reflected, the parallel beam of radiation falls on a rocksalt or fluorspar

prism  $ABC$  placed on the turn table of the spectrometer. The emergent light is focussed by the reflector (concave mirror)  $M_2$  on a line bolometer placed behind the slit  $S_2$ . The bolometer is connected to a sensitive galvanometer. The turn table is rotated slowly so that different parts of the radiation spectrum successively fall on the bolometer and the corresponding deflections in galvanometer connected in the bolometer circuit are read. The intensity of each line is proportional to the deflection in the galvanometer. Then a curve (Fig. 7.2) is drawn between intensity and the wavelength. Then the body is heated to different temperatures and the curves are drawn for various temperatures.

### Salient Features

- ❖ The energy is not distributed in the radiation spectrum of a black body.
- ❖ At a given temperature, the intensity of radiations increases with increase of wavelength and becomes maximum at a particular wavelength. By further increasing the wavelength, the intensity of heat radiations decreases.
- ❖ An increase in temperature causes a decrease in  $\lambda_m$ , where  $\lambda_m$  the wavelength for which the energy emitted is maximum.
- ❖ It is in accordance to famous Wein's law,

$$\lambda_m T = \text{constant} = 0.2896 \times 10^{-2} \text{ mK}$$

- ❖ An increase in temperature causes increase in energy emission for all wavelengths.
- ❖ The area under each curve represents the total energy emitted by the body at a particular temperature for the range of the wavelengths considered. This area increases with increase of temperature. It is found that area is directly proportional to the fourth power of absolute temperature i.e.,  $E \propto T^4$  which is Stefan's law.

## 7.2 FAILURE OF CLASSICAL THEORY FOR EXPLAINING THE BLACK BODY RADIATION

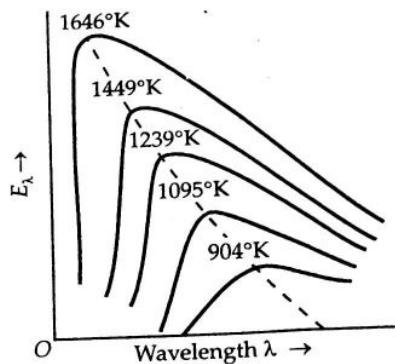
The spectral distribution in black body radiation could not be explained by classical methods which assume that the energy changes of radiation takes place continuously. A summary of several classical developments in radiation theory is given below :

### 7.2.1 Wein's Law

In order to find the distribution of energy of black body radiation among different wavelengths, Wein obtained thermodynamically the following two relations :

$$(a) \lambda_m T = \text{constant} = 0.2896 \times 10^{-2} \text{ mK}$$

$$(b) E_m T^{-5} = \text{a constant} \quad \text{or} \quad E_m \propto T^5$$



**Fig. 7.2** Curve between intensity and wavelength for black body radiation.

The first of these laws show that  $\lambda_m$ , the wavelength for which the emitted energy is maximum, decreases with increase in temperature while second law gives the direct variation of emissive power with the fifth power of absolute temperature.

The combination of two laws gives the general relation for energy density ( $E_\lambda d\lambda$ ) emitted by a black body at a temperature  $T$  within wavelength range  $\lambda$  and  $(\lambda + d\lambda)$  to be form

$$E_\lambda d\lambda = \frac{A}{\lambda^5} f(\lambda, T) d\lambda \quad \dots(1)$$

The Wien's law, however, holds good in the region of shorter wavelengths. For longer wavelengths, it gives values of  $E_\lambda$  lower than the experimental values.

### 7.2.2 Rayleigh-Jean's law

Rayleigh and Jean applied the principle of equipartition of energy to the modes of free vibrations, which might be assigned to radiation. Thus they considered the classical result for average energy per mode of vibration as  $\bar{E} = k_B T$  and showed that energy density within frequency range  $v$  and  $(v + dv)$  is given by

$$E_v dv = \frac{8\pi v^2}{c^3} dv \times k_B T$$

In terms of wavelength  $\left(\lambda = \frac{c}{v}\right)$ , Rayleigh Jean's law may be written as

$$E_\lambda d\lambda = \frac{8\pi}{c^3} \left(\frac{c}{\lambda}\right)^2 \left(\frac{c}{\lambda^2} d\lambda\right) k_B T$$

$$\Rightarrow E_\lambda d\lambda = \frac{8\pi k_B T}{\lambda^4} d\lambda \quad \dots(2)$$

This law agrees well with the experimental results at low frequencies but near the maximum in the spectrum and at higher frequencies it is in violet disagreement. According to this law [Eq. (2)], the energy density  $E_\lambda$  will continuously increase with decrease in  $\lambda$  and approaches infinity when  $\lambda$  tends to zero.

The integral that represents total energy density for all wavelengths from 0 to  $\infty$  is given by

$$\begin{aligned} E &= \int_0^\infty E_\lambda d\lambda \\ &= \int_0^\infty \frac{8\pi k_B T}{\lambda^4} d\lambda \\ &= 8\pi k_B T \left[ -\frac{1}{3\lambda^3} \right]_0^\infty = \infty \quad \Rightarrow \quad E = \infty \end{aligned} \quad \dots(3)$$

Thus according to Rayleigh-Jean's law, almost all the energy should be confined in vibrations of very small wavelengths. It is known as *ultraviolet catastrophe* and is contrary to experimental results.

### 7.3 PLANCK'S QUANTUM THEORY (DISCOVERY OF PLANCK'S CONSTANT)

The failure of Rayleigh-Jeans law to explain the spectral energy curves of black body radiation indicated that the fundamental assumption of classical physics that energy can be absorbed or emitted by the atomic oscillators continuously in any amount requires modification.

**NOTE**

Planck was awarded the Nobel Prize for Physics in 1918 for his work on black body radiation.

On 18th December, 1900, Max Planck put forward the quantum theory to explain the experimentally observed spectrum of black body radiation. He assumed that the atoms of the walls of a black body behave like simple harmonic oscillators and each oscillator has got a characteristic frequency of oscillator.

He made the following revolutionary assumptions regarding the way in which radiation is emitted or absorbed by atoms.

- A simple harmonic oscillator can take only those energy values  $E$  which are given by the relation

$$E = nh\nu \quad \dots(4)$$

where  $n = 1, 2, 3, \dots$  is called the quantum number,  $\nu$  is the frequency of oscillation and  $h = 6.62 \times 10^{-34}$  Js is the universal Planck's constant.

Thus a system can exist only in certain discrete energy states given by Eq. (4). Such states are called *quantum states*. Here  $h\nu$  is the basic unit of energy and is called, the *quantum*. It may be treated as atom of energy. Thus, the *energy may be regarded as having an atomic nature*.

- The oscillators do not absorb or radiate energy continuously but only when the oscillator jumps from one energy level to another.
- The oscillator emit or absorb in bundles of size  $h\nu$  i.e., the *radiation emitted or absorbed* is quantised.

### 7.4 THE PLANCK'S LAW OF ENERGY DISTRIBUTION IN BLACK BODY RADIATION

It is seen that both Wein's formula and Rayleigh-Jean's formula were obtained making certain fundamental assumptions and using well known tested physical principle. But we have already seen that these results are not satisfactory and sometime give absurd conclusions. It is natural to suspect in such circumstances that the fundamental assumption made by these genius workers are at fault. The suspicion first occurred to Planck, who in 1901 proposed a new theory for radiation emitted by black body radiator, which is known as **Quantum Theory of Radiation**. He linked the radiation and the molecules of the black body by resonators of molecular dimension. These resonators serve as media between radiation and molecular dimension. We know that these resonators are excited states of the molecules. Planck assumed that these resonators are excited states of the molecule. Planck assumed that these resonators or linear oscillators can vibrate only with integral values of energy i.e.,  $0, E, 2E, 3E, \dots nE$  etc. where  $E$  represent the elementary quanta. Thus a particular molecule can emit energy in the form of quantum. Planck further

said that the energy of these quanta is inversely proportional to wavelength of radiation emitted by linear oscillator

$$E \propto \frac{1}{\lambda} \quad \dots(5)$$

or  $E \propto v$   $\dots(6)$

or  $E = h\nu$   $\dots(7)$

where  $h$  is known as the Planck's constant.

According to law of probability, the number of resonators (modes of vibration) with zero energy  $E$  will be proportional to  $\exp(-E/k_B T)$ , where  $k_B$  = Boltzmann's constant. Let the number of resonators with zero energy be  $N$ . The number of resonators with energy  $E$  will be  $N \exp(-E/k_B T)$ ; with energy  $2E$  will be  $N \exp(-2E/k_B T)$ , with energy  $3E$  will be  $N \exp(-3E/k_B T)$  and so on. The total number of resonators or modes of vibration for linear oscillators ( $M$ ) will be

$$\begin{aligned} i.e., \quad M &= N + N \exp(-E/k_B T) + N \exp(-2E/k_B T) + \dots + N \exp(-nE/k_B T) + \dots \\ &= \frac{N}{1 - \exp(-E/k_B T)} \end{aligned} \quad \dots(8)$$

and the total energy ( $W$ ) possessed by them is

$$W = N[0 + E \exp(-E/k_B T) + 2E \exp(-2E/k_B T) + \dots + \dots \infty] \quad \dots(i)$$

Equation (i) may be written as

$$\exp(-E/k_B T)W = N[E \exp(-2E/k_B T) + 2E \exp(-3E/k_B T) + \dots \infty] \quad \dots(ii)$$

On subtraction of Eq. (ii) from Eq. (i), we get

$$\begin{aligned} [1 - \exp(-E/k_B T)]W &= N[E \exp(-E/k_B T) + E \exp(-2E/k_B T) + E \exp(-3E/k_B T) + \dots \infty] \\ &= NE \exp(-E/k_B T)[1 + \exp(-E/k_B T) + \exp(-2E/k_B T) + \dots \infty] \\ &= \frac{NE \exp(-E/k_B T)}{1 - \exp(-E/k_B T)} \end{aligned}$$

$$\text{or } W = \frac{NE \exp(-E/k_B T)}{[1 - \exp(-E/k_B T)]^2} \quad \dots(9)$$

Putting value of  $N$  from Eq. (8),

$N = M[1 - \exp(-E/k_B T)]$  in Eq. (9), we obtain

$$W = \frac{ME \exp(-E/k_B T)}{[1 - \exp(-E/k_B T)]} \quad \dots(10)$$

The average energy ( $\bar{E}$ ) per mode of vibration is then given by expression

$$\bar{E} = \frac{W}{M} = \frac{E}{\exp(E/k_B T) - 1} \quad \dots(11)$$

The number of modes of vibration per unit volume lying between the wavelength range  $\lambda$  and  $(\lambda + d\lambda)$  is  $8\pi\lambda^{-4}d\lambda$ . Hence multiplying this by  $\bar{E}$ , one gets the average energy density of radiation lying in the wavelength range  $\lambda$  and  $(\lambda + d\lambda)$  as

$$\begin{aligned} E_\lambda d\lambda &= \frac{8\pi}{\lambda^4} d\lambda \cdot \bar{E} \\ &= \frac{8\pi}{\lambda^4} d\lambda \cdot \frac{E}{[\exp(E/k_B T) - 1]} \end{aligned} \quad \dots(12)$$

Putting  $E = h\nu = hc/\lambda$ , one gets

$$\begin{aligned} E_\lambda d\lambda &= \frac{8\pi hc}{\lambda^4} \frac{1}{\left[\exp\left(\frac{hc}{\lambda k_B T}\right) - 1\right]} d\lambda \\ \text{or} \quad E_\lambda d\lambda &= 8\pi hc \lambda^{-5} \left[\exp\left(\frac{hc}{\lambda k_B T}\right) - 1\right]^{-1} d\lambda \end{aligned} \quad \dots(13)$$

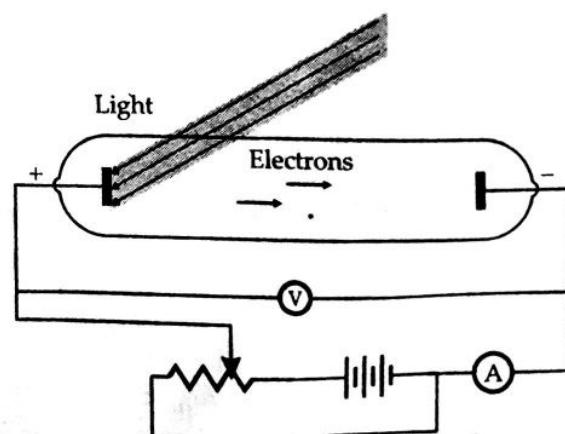
This is Planck's law for the energy distribution in a black body radiation. The law has been verified by numerous workers and has been found to be perfectly true.

### 7.5 THE PHOTOELECTRIC EFFECT

*For the quantum development, Einstein used Planck's hypothesis to explain the photoelectric effect successfully.*

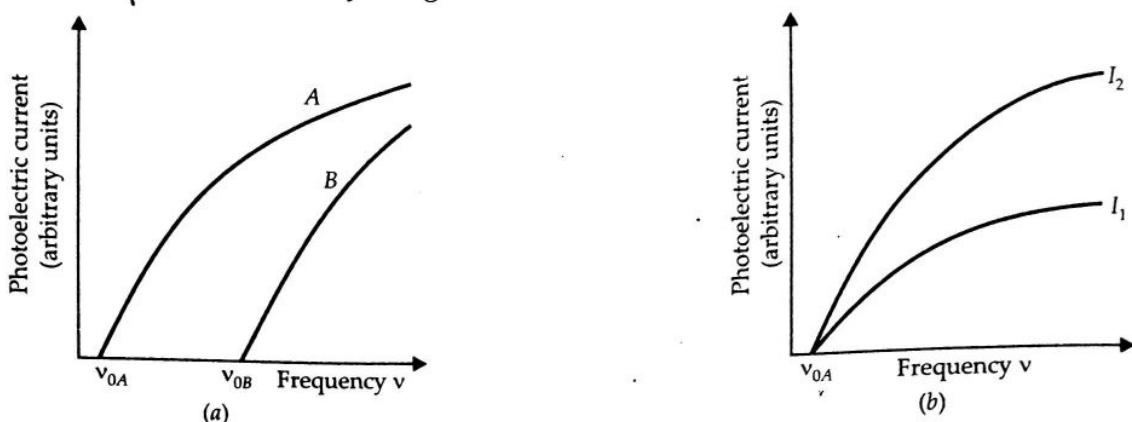
In 1887, Hertz, while working on electromagnetic waves, discovered that the air in a spark gap become a better conductor when it was illuminated by ultraviolet rays. Further investigations by him showed that zinc acquired a positive charge when it was irradiated with ultraviolet rays, i.e., it lost negative charges. In 1900, Leonard showed that the ejected particles were electrons. A series of such experiments revealed that electrons are emitted from a metal surface when light of sufficiently high frequency falls upon it. This phenomenon is known as the **photoelectric effect**.

Figure 7.3 shows a schematic diagram of the apparatus that was employed in some of these experiments. A evacuated tube contains two electrodes connected to an external circuit like that shown schematically. The anode is made up of the metal plate whose surface is to be irradiated. Some of the photoelectrons that emerge from the irradiated surface have sufficient energy to reach the cathode despite its negative polarity and they constitute the current that is measured by the ammeter in the circuit.



**Fig. 7.3** Schematic diagram of the apparatus for photoelectric effect.

As the collecting voltage  $V$ , which retards the electrons, is increased, fewer and fewer electrons get to the cathode and current drops. Ultimately when  $V$  equals or exceeds a certain value  $V_0$  of the order of a few volts, no further electrons strike the cathode and the current ceases. Figures 7.4(a) and (b) show the experimental curves corresponding to this effect when the intensity of light and connecting voltage  $V$  are kept constant.



**Fig. 7.4** (a) Variation of the photoelectric current (in arbitrary units) as a function of frequency for two materials  $A$  and  $B$ . The intensity of light and the collecting voltage are kept constant.  
 (b) Variation of the photoelectric current (in arbitrary units) as a function of frequency for a single material at two values of the intensity ; of the intensities,  $I_2$  is greater than  $I_1$ .

Note that photoelectrons emission occurs only when the frequency of the falling radiation is higher than some threshold frequency  $v_0$ . It was found that for  $v < v_0$ , no emission takes place, no matter how intense the radiation is. The value of  $v_0$  depends upon the material of the surface irradiated. It was also determined that for a given frequency  $v (> v_0)$ , the kinetic energy of the emitted photoelectrons has values between zero and a definite maximum value  $E_{\max}$ . For any given metal,  $E_{\max}$  is proportional to  $(v - v_0)$  and is independent of the intensity of the falling light. Further, when electromagnetic waves fall on the material, emission of photoelectrons starts instantaneously (within  $10^{-9}$  s), no matter how weak or strong the falling light is. All these features of the photoelectric effect could not be explained by classical electromagnetic theory of light on the basis of its wave nature.

In 1905, Einstein proposed a simple but revolutionary explanation for the photoelectric effect. Einstein extended Planck's postulate of the quanta of energy of the electromagnetic field. He viewed the photoelectric phenomenon as a collision between a photon (a quantum of the energy of an electromagnetic field) and a bound electron. In the collision, the photon is completely absorbed and the energy of the bound electron is increased by  $h\nu$ . Since the electrons are bound in the metal their initial energy  $E$  is negative and the largest value of  $E$  is  $-W$ , where  $W$  is work function of the metal. Hence, to escape from the metal, the electron has to use at least an energy equal to  $W$ . Thus, the maximum kinetic energy of the photoelectrons will be

$$E_{\max} = \frac{1}{2}mv_{\max}^2 = h\nu - W \quad \dots(14)$$

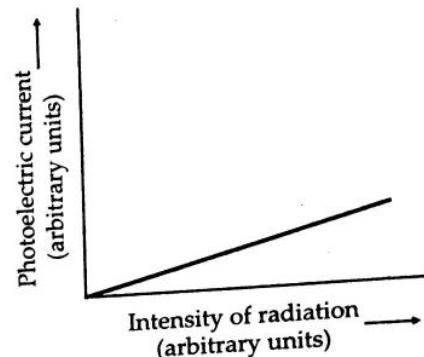
If we take  $W = h\nu_0$ , Eq. (14) may be written as

$$\frac{1}{2}mv_{\max}^2 = h(v - v_0) \quad \dots(15)$$

## QUANTUM THEORY

The implications of Eqs. (14) and (15) are :

- (i) Since  $v_{\max}$  has to be positive, no emission can take place for  $v < v_0$ .
- (ii)  $E_{\max}$  is proportional to  $(v - v_0)$ .
- (iii) An increase in the radiation intensity  $v$  corresponds to an increase in the number of photons. Since each one of them has the same energy  $hv$ , there is no increase in the energy of the photoelectrons. Only the number of emitted electrons and hence the photoelectric current increases (Fig. 7.5).
- (iv) Since the effect is produced by mechanical collisions between electrons and photons, the energy transfer from photons to the electrons is instantaneous. Consequently the time lag is very small.
- (v) Since work function  $W (= hv_0)$  is a characteristic property of the emitting surface,  $v_0$  is independent of the intensity of incident radiation.



**Fig. 7.5** Variation of the photoelectric current with the intensity of radiation of frequency  $v (> v_0)$  at a constant collecting voltage.

In this way, Einstein's quantum theory explained each and every aspect of photoelectric effect with brilliant success and so the absorption of light in the form of packets or quanta was firmly established.

**Example 7.1** The work function of potassium is 2.2 eV. When ultraviolet light of wavelength 3,500 Å falls on a potassium surface, what is the maximum energy in electron volts of the photoelectron ?

**Solution.** From equation,  $E_{\max} = hv - hv_0$

Since  $hv_0$  is already expressed in electron volts, we need only compute the quantum energy  $hv$  of 3500 Å light i.e.,

$$hv = \frac{hc}{\lambda}$$

$$= \frac{6.63 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ m/s} \times 10^{10} \text{ Å/m}}{3500 \text{ Å}} = 5.7 \times 10^{-19} \text{ J.}$$

To convert this energy from joules to electron volts, we recall that

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

and so  $hv = \frac{5.7 \times 10^{-19} \text{ J}}{1.6 \times 10^{-19} \text{ J}} = 3.6 \text{ eV}$

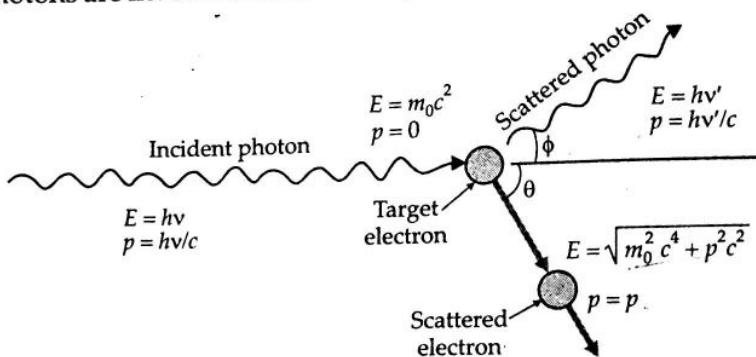
Hence the maximum photoelectron energy is

$$E_{\max} = hv - hv_0 = 3.6 \text{ eV} - 2.2 \text{ eV} = 1.4 \text{ eV.}$$

## 7.6 THE COMPTON EFFECT

The quantum theory of light postulates that photons behave like particles except for the absence of rest mass. If this is true, then it should be possible for us to treat collisions between photons and say, electrons in the same manner as billiard-ball collisions are treated in elementary mechanics.

Figure 7.6 shows how such a collision might be represented, with an X-ray photon striking an electron (assumed to be at rest in the laboratory coordinate system) and being scattered away from its original direction of motion while the electron receives an impulse and begins to move. In the collision the photon may be regarded as having lost an amount of energy that is the same as the kinetic energy  $K$  gained by the electron, though actually separate photons are involved. If the initial photon actually separate photons are involved.



**Fig. 7.6** The Compton Effect.

If the initial photon has the frequency  $\nu$  associated with it, the scattered photon has the lower frequency  $\nu'$ , where

$$\text{Loss in photon energy} = \text{Gain in electron energy}$$

$$\Rightarrow h\nu - h\nu' = K \quad \dots(16)$$

We know that,

$$E = \sqrt{(m_0^2 c^4 + p^2 c^2)} \quad \dots(17)$$

So that, since the photon has no rest mass, its total energy is

$$E = pc$$

$$\text{Since } E = h\nu \quad \dots(18)$$

For a photon, its momentum is

$$p = \frac{E}{c} = \frac{h\nu}{c} \quad \dots(19)$$

Momentum, unlike energy, is a vector quantity, incorporating direction as well as magnitude and the collision momentum must be conserved in each of two mutually perpendicular directions. (When more than two bodies participate in a collision, of course, momentum must be observed in each of three mutually perpendicular directions.) The direction we choose here are that of the original photon and one  $\perp$  to it in the plane

containing the electron and the scattered photon (Fig. 7.6). The initial photon momentum is  $h\nu/c$ , the scattered photon momentum is  $h\nu'/c$ , and the initial and final electron momenta are respectively 0 and  $p$ . In the original photon direction,

Initial momentum = final momentum

$$\frac{h\nu}{c} + 0 = \frac{h\nu'}{c} \cos \phi + p \cos \theta \quad \dots(20)$$

and perpendicular to this direction

Initial momentum = final momentum

$$0 = \frac{h\nu'}{c} \sin \phi - p \sin \theta \quad \dots(21)$$

The angle  $\phi$  is that between the directions of the initial and scattered photons, and  $\theta$  is that between the directions of the initial photon and recoil electron. From Eqs. (16), (20) and (21), we obtain a formula relating the wavelength difference initial and scattered photons with the angle  $\phi$  between their directions, both of which are readily measurable quantities.

Multiplying Eqs. (20) and (21) by  $c$  and rewrite them

$$pc \cos \theta = h\nu - h\nu' \cos \phi$$

$$pc \sin \theta = h\nu' \sin \phi$$

By squaring each of these equations and adding new ones together, the angle  $\theta$  is eliminated, leaving

$$p^2 c^2 = (h\nu)^2 - 2(h\nu)(h\nu') \cos \phi + (h\nu')^2 \quad \dots(22)$$

Next we equate the two expressions for the total energy of a particle

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

or  $(K + m_0 c^2)^2 = m_0^2 c^4 + p^2 c^2$

or  $p^2 c^2 = K^2 + 2m_0 c^2 K$

$\therefore K = h\nu - h\nu'$

We have,  $p^2 c^2 = (h\nu)^2 - 2(h\nu)(h\nu') + (h\nu')^2 + 2m_0 c^2 (h\nu - h\nu')$  ... (23)

Substituting this value of  $p^2 c^2$  in Eq. (22), we finally obtain

$$2m_0 c^2 (h\nu - h\nu') = 2(h\nu)(h\nu') (1 - \cos \theta) \quad \dots(24)$$

This relationship is simpler when expressed in terms of wavelength rather than frequency. Dividing by  $2h^2 c^2$

$$\frac{m_0 c}{h} \left( \frac{\nu}{c} - \frac{\nu'}{c} \right) = \frac{\nu \nu'}{c c} (1 - \cos \phi)$$

and so, since  $v/c = 1/\lambda$  and  $v'/c = 1/\lambda'$

$$\frac{m_0 c}{h} \left( \frac{1}{\lambda} - \frac{1}{\lambda'} \right) = \frac{(1 - \cos \phi)}{\lambda \lambda'}$$

or

$$\lambda' - \lambda = \frac{h}{m_0 c} (1 - \cos \phi) \quad \dots(25)$$

Equation (25) was derived by **Arthur H. Compton** in the early 1920s, and the phenomenon it describes, which he was the first to observe, is known as **compton effect**.

Equation (25) may also be written as

$$\Delta\lambda = \frac{h}{m_0 c} (1 - \cos \phi)$$

Here  $\Delta\lambda$  is known as Compton shift.

### 7.6.1 Compton Wavelength

The quantity  $(h/m_0 c)$  has dimensions of length, and is known as the *Compton wavelength of the electron*.

$$\begin{aligned} \frac{h}{m_0 c} &= \frac{6.63 \times 10^{-34} \text{ J.s}}{9.1 \times 10^{-31} \text{ kg} \times 3 \times 10^8 \text{ m/s}} \\ &= 0.242 \times 10^{-10} \text{ m} = 0.0242 \text{ Å} \end{aligned}$$

Thus the Compton shift  $\Delta\lambda = 0.0242 (1 - \cos \phi) \text{ Å}$

It shows that the change in wavelength (Compton shift) neither depend on the incident wavelength nor the scattering material, but depends on the angle of scattering.

Maximum change in wavelength in a Compton scattering experiment occurs for  $\phi = 90^\circ$

$\therefore$  At  $\phi = 90^\circ$ ;  $\Delta\lambda = 0.0242 \text{ Å}$ .

### 7.6.2 Presence of Unmodified Radiation

Compton theory holds for the free (or loosely-bound) electrons of the atom. If the photon collides with an electron tightly bound to the atom, then whole atom recoils. As the mass of the atom is much large, so the Compton shift  $\frac{h}{m_0 c} (1 - \cos \phi)$ , ( $m_0$  = mass of the atom) is negligible. This explains the presence of unmodified radiation. In the heavier elements in which most of the electrons are tightly bound, the modified radiation is too weak. The Compton effect presents the strongest evidence in favour of the Planck's quantum theory of radiation.

### 7.6.3 Experimental Verification

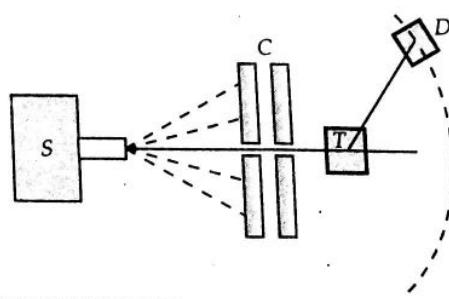
An experimental arrangement for Compton effect consist of a source(S) of X-rays with a single known wavelength. This beam is made to pass through a set of collimators (C) and

then incident on a target ( $T$ ). The wavelength and intensity of the scattered radiation is determined by placing a detector ( $D$ ) at various scattering angle ( $\phi$ ). This experimental set up is shown in Fig. 7.7.

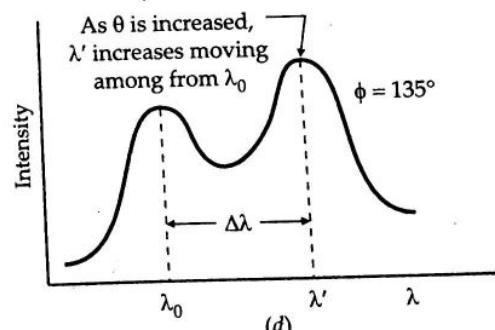
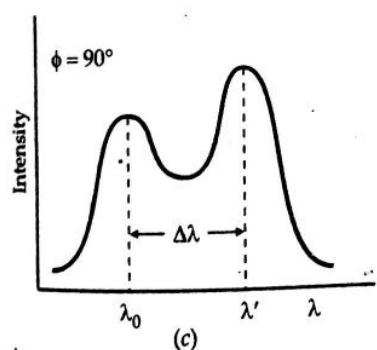
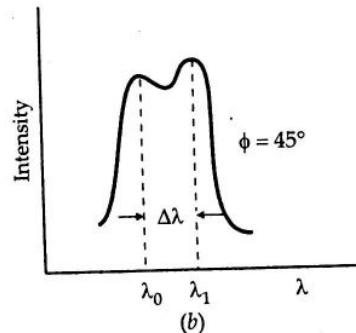
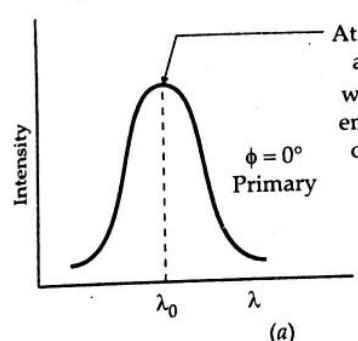
Compton found that X-rays were scattered in different directions. Measuring the wavelength of the scattered radiation, it is found that it consists of two components :

One having the same wavelength as the incident radiation but the wavelength of the second component is slightly longer. The magnitude of shift depends upon the scattering angle.

A graph of intensity versus wavelength for both components at several different angles is shown in Fig. 7.8.



**Fig. 7.7** Compton effect experimental set up.



**Fig. 7.8** Compton's data.

The increase of wavelength of the X-rays is immediately observed. This wavelength increases with the angle of scattering.

For  $\phi = 90^\circ$ ,  $\Delta\lambda = 0.0242 \text{ \AA}$ . This is agreement with the theoretical data.

#### 7.6.4 Can Compton Shift be Observed with Proton

If the proton collides with a proton, the Compton shift  $\frac{h}{m_0 c} (1 - \cos \phi)$  will be negligibly small as the rest mass  $m_0$  of the proton is much larger ( $10^7$  times) than electron. Therefore Compton shift can not be observed with proton.

### 7.6.5 No Observation of Compton Effect with Visible Light

Instead of using X-ray ( $\lambda = 1 \text{ \AA}$ ), if we use light in the visible range ( $\lambda = 400 - 750 \text{ nm}$ ), the wavelength shift ( $\Delta\lambda$ ) will not be perceptible. In case the photon energy ( $hc/\lambda$ ) is so small that it is not even larger than the binding energy of the loosely-bound electrons in the scatterer. Therefore, there is almost no change of detecting any wavelength shift.

The energy of a visible light photon of wavelength 600 nm or ( $6.00 \times 10^{-7} \text{ m}$ ) is

$$E = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{6.00 \times 10^{-7} \times 1.6 \times 10^{-19}} \text{ eV} = 2 \text{ eV (approximately)}$$

The energy of an X-ray photon is a few thousand times greater than that of visible light photon.

The binding energy of an electron in hydrogen atom is 13.6 eV. Therefore, these electrons can be regarded as free electrons, when X-rays or gamma rays are incident on them. These electrons cannot be regarded as free for visible or ultraviolet radiation. For these radiations, the entire atom takes part in Compton scattering. The values of Compton wavelength ( $\lambda_c$ ) for a single electron and an entire carbon atom are  $2.4 \times 10^{-2} \text{ \AA}$  and  $1.1 \times 10^{-6} \text{ \AA}$  respectively when visible light of 6000 Å wavelength is used, detection of Compton shift is possible only if the optical instrument has a resolving power

$$\frac{\lambda}{\Delta\lambda} = \frac{6000 \text{ \AA}}{1.1 \times 10^{-6} \text{ \AA}} = 5 \times 10^9$$

which is much beyond the limit of resolution of these instruments.

Therefore, it is impossible to observe Compton effect with visible light.

### 7.6.6 Comparison of Photoelectric Effect and Compton Effect

We compare photoelectric effect and Compton effect in following manners :

<b>Photoelectric Effect</b>	<b>Compton Effect</b>
<ul style="list-style-type: none"> <li>■ In photoelectric effect, the emission of a photo-electron takes place when the incident photon has greater energy than the work function of the material.</li> <li>■ In photoelectric effect, the total energy of the photon is absorbed by the system and no photon comes out. The momentum and energy remains conserved in this process. Due to emission of electron from the atoms positive ions are created.</li> <li>■ The total energy (and momentum) of the system (photon and the atom) before collision must be equal to the total energy (and momentum) of the system (ion and the photoelectron) after interaction. In this process the ion recoils after the emission of photoelectron.</li> </ul>	<ul style="list-style-type: none"> <li>■ In Compton effect, the incident photon is not completely absorbed. A part of energy is imparted to the electron and it comes out with smaller energy.</li> <li>■ It is essentially an interaction between the incident photon and the electron. Here, the scattering of photon takes place by free electron which is assumed to be at rest before collision.</li> <li>■ The total energy (and momentum) of the system (photon and the electron) before collision must be equal to the total energy (and momentum) of the system (photon and the electron) after collision. In this process the electron recoils after the scattering of photon.</li> </ul>

**Example 7.2.** In Compton experiment the wavelength of X-ray radiation scattered at an angle of  $45^\circ$  is  $0.022\text{ \AA}$ . Calculate the wavelength of the incident X-rays.

**Solution.** Given :  $\lambda' = 0.022\text{ \AA}$ ,  $\phi = 45^\circ$ ,  $\lambda_c = 0.0242\text{ \AA}$

We know Compton formula

$$\begin{aligned}\lambda' - \lambda &= \lambda_c(1 - \cos \phi) \\ \lambda &= \lambda' - \lambda_c(1 - \cos \phi) \\ &= [0.022 - 0.0242(1 - \cos 45^\circ)]\text{ \AA} \\ &= \left[0.022 - 0.0242\left(1 - \frac{1}{\sqrt{2}}\right)\right]\text{ \AA} \\ &= [0.022 - 0.0242 \times 0.293]\text{ \AA} = 0.0149\text{ \AA} = 0.015\text{ \AA}\end{aligned}$$

**Example 7.3.** Calculate the maximum shift in the wavelength of incident photons of wavelength  $1\text{ \AA}$  and  $10\text{ \AA}$  due to Compton scattering. What conclusion do you draw from this calculation.

**Solution.** Given :  $\lambda_1 = 1\text{ \AA}$  and  $\lambda_2 = 10\text{ \AA}$

We know Compton shift is given by

$$\Delta\lambda = \frac{h}{m_0 c} (1 - \cos \phi)$$

or

$$\Delta\lambda = 0.0242(1 - \cos \phi)\text{ \AA}$$

we also know that for maximum value of  $\Delta\lambda$ ,  $\phi = \pi$ , then

$$(\Delta\lambda)_{\max} = 0.0242(1 - \cos \pi)\text{ \AA} = 0.0484\text{ \AA}$$

$\therefore$  Maximum percentage change in wavelength

$$\frac{(\Delta\lambda)_{\max}}{\lambda} \times 100$$

The for  $\lambda_1 = 1\text{ \AA}$ , the maximum % change in wavelength

$$= \frac{0.0484}{1} \times 100 = 4.84\%$$

and for  $\lambda_2 = 10\text{ \AA}$ , the maximum % change in wavelength

$$= \frac{0.0484}{10} \times 100 = 0.484\%$$

i.e.,

$$\lambda = 10\text{ \AA}$$

**Conclusion :**

1. If wavelength of incident photon is high i.e.,  $\lambda = 10\text{ \AA}$ , then the value of maximum % change in  $\lambda$  is low. So it is difficult to detect this change.
2. If wavelength of incident photon is low i.e.,  $\lambda = 1\text{ \AA}$ , the value of maximum % change in  $\lambda$  is higher than (1) and this change is detectable.

Hence Compton effect can be experienced only the photons whose wavelength is smaller or equal to  $1\text{ \AA}$ .

### 7.6.7 Kinetic Energy of the Recoil Electron

Let  $\nu$  and  $\nu'$  be the frequencies of the incident photon and the scattered photon. The electron is assumed to be at rest before collision. The kinetic energy of the electron after collision is given by

$$\begin{aligned} E_k &= h\nu - h\nu' = h\nu \left[ 1 - \frac{\nu'}{\nu} \right] \\ &= h\nu \left( 1 - \frac{\lambda}{\lambda'} \right) = h\nu \left( \frac{\lambda' - \lambda}{\lambda'} \right) = h\nu \frac{\Delta\lambda}{\lambda' + \Delta\lambda} \end{aligned}$$

For Compton scattering, we have

$$\Delta\lambda = \frac{h}{m_0 c} (1 - \cos \phi)$$

Here  $\phi$  is the angle of scattering for the photon and  $m_0$  is the rest mass of the electron.

Hence, the kinetic energy of recoil electron is

$$\begin{aligned} E_k &= h\nu \frac{\Delta\lambda}{\lambda + \Delta\lambda} = \frac{h\nu \frac{h(1 - \cos \phi)}{m_0 c}}{\left( \lambda + \frac{h(1 - \cos \phi)}{m_0 c} \right)} \\ E_k &= \frac{h\nu \alpha(1 - \cos \phi)}{1 + \alpha(1 - \cos \phi)} \quad \dots(26) \end{aligned}$$

where

$$\alpha = \frac{h}{m_0 c \lambda} = \frac{h\nu}{m_0 c^2}$$

**Example 7.4.** Show that the value of energy which a proton must have so that it may transfer half of its energy to an electron at rest is about 256 KeV in a Compton scattering experiment.

**Solution.** Given : Energy transferred to an electron = Half of the energy of the incident photon  $h\nu' = \frac{1}{2} h\nu$

$$\Rightarrow \lambda' = 2\lambda$$

The Compton shift

$$\Delta\lambda = \lambda' - \lambda = 2\lambda - \lambda = \frac{h}{m_0 c} (1 - \cos \phi)$$

$\lambda$  should be maximum for minimum energy i.e.,  $\phi = 180^\circ$

$$\lambda_{\max} = \frac{h}{m_0 c} (1 - \cos \phi) = \frac{2h}{m_0 c} = \frac{2 \times 6.63 \times 10^{-34}}{9.1 \times 10^{-31} \times 3 \times 10^8} = 0.0484 \text{ \AA}$$

∴ Minimum energy of incident photon

$$E_{\min} = \frac{h}{\lambda_{\max}}$$

$$E_{\max} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{0.0484 \times 10^{-10} \times 1.6 \times 10^{-19}} \text{ eV} \approx 256 \text{ keV.}$$

### 7.7 WAVE-PARTICLE DUALISM

- ❖ Light is a wave : It spreads out over space.
- ❖ Light is also a particle (photon) that is at a point.

Phenomena such as the photoelectric effect and the compton effect offer iron-clad evidence that when light and matter interact, the light behaves as wave if it were composed of particles having energy  $h\nu$  and momentum  $h/\lambda$ . But the phenomena of interference, diffraction and polarisation, radiant energy exhibit wave nature. Therefore electromagnetic radiation exhibits the dual property as **wave and particle**. In visible region, it is possible to observe both the particle characteristics and the wave characteristic of light. At higher frequencies, the momentum and energy of the photon increases. Consequently, the particle nature of light becomes more evident than its wave nature. For example, absorption of an X-ray photon is easily detected as a single event but wave effects are difficult to observe. X-rays are also diffracted by a crystal. Since diffraction is a wave phenomenon, X-rays also behave as waves.

In 1923, in his doctoral dissertation, Louis de Broglie postulated that *because photons have both wave and particle characteristics perhaps all forms of matter have both properties.* According to de Broglie, electrons just like light, have a dual particle-wave nature. Accompanying every electron in a wave (not an electromagnetic wave).

Louis de Broglie's hypothesis was based on the following facts :

- (i) In universe, whole of the energy is in the form of radiation and matter. So both the forms of energy should possess similar characteristics.
- (ii) Nature is symmetrical in many ways. As radiation has dual nature, matter should also possess dual nature.
- (iii) Ordinarily, periodicity is associated only with the wave phenomena like interference and diffraction, the patterns being governed by integral multiple of wavelength or *half wavelength*. But some intrinsic properties are associated with electrons in Bohr orbit.
- (iv) Einstein in 1905 established a relation between mass and energy,  $E = mc^2$ . He said that both mass and energy were interconvertible. When energy  $E$  exhibits a dual aspect, mass namely matter also should exhibit a duality.

According to de Broglie, *a moving particle behaves sometimes as a wave and sometimes as a particle or a wave associated with moving particle.* The waves associated with material particles are called **matter waves** or **de Broglie waves**. They are seen with particles like electrons, protons, neutrons etc. The wavelength of matter waves is called **de Broglie wavelength** and is given by

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

...(27)

where  $h$  = Planck's constant.

It can be seen that a microscopic particle is essentially represented by a matter wave with its wavelength given by de Broglie relation. How do we describe the motion of such a particle or a system of such particles ? Clearly, we can not make use of Newton's laws of

motion for this purpose. So a new theoretical description is needed for the motion of quantum mechanical particles. The new theory should be consistent with wave nature of particles. It should also reduce to Newtonian mechanics for macroscopic particles. Recall this condition is similar to the special theory of relativity which reduces to Newtonian mechanics at velocities much smaller than the velocity of light.

### 7.8 DE-BROGLIE'S HYPOTHESIS

**A moving body behaves in certain ways as though it has a wave nature.**

The dual nature of light possessing both wave and particle properties is clearly illustrated by combining Planck's relation for energy of a photon,  $E = h\nu$  with Einstein mass energy relation  $E = mc^2$ .

Considering the photon to be a particle of mass  $m$  moving with it is given by Einstein's mass-energy relation as

$$E = mc^2 \quad \dots(28)$$

According to Planck's hypothesis, energy of photon of frequency  $\nu$  is given by

$$E = h\nu \quad \dots(29)$$

$$\therefore h\nu = mc^2$$

or

$$mc = \frac{h\nu}{c}$$

Momentum of photon,  $p = mc$

$$\therefore p = \frac{h\nu}{c}$$

$$= \frac{h}{c/\nu} = \frac{h}{\lambda} \quad \left[ \because \frac{c}{\nu} = \lambda \right] \quad \dots(30)$$

As the matter also possesses dual nature, therefore, wavelength of the wave associated with a matter particle of mass  $m$  moving with velocity  $v$  is

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \dots(31)$$

This is called **de-Broglie wave relation**. Hence, de-Broglie wavelength depends upon the mass of particle and its velocity.

#### 7.8.1 de-Broglie Wavelength of an Electron

Consider an electron of mass  $m$  is under the potential difference of  $V$  volts. Its kinetic energy is  $\frac{1}{2}mv^2$ .

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

$$\text{or} \quad v = \sqrt{\left(\frac{2eV}{m}\right)} = \sqrt{\left(\frac{2E}{m}\right)} \quad \dots(32)$$

**NOTE**

150 V is enough to produce electrons of wavelength 1 Å in contrast with X-rays which require about 12,000 V for 1 Å. Electrons generated by de-Broglie waves are of short wavelengths and are quite useful for certain types of diffraction experiments. Because of the smallness of  $h$ , only for particles of atomic or nuclear size will the

If  $\lambda$  is the de-Broglie wavelength associated with an electron, then

$$\lambda = \frac{h}{mv} = \frac{h}{m\sqrt{\frac{2eV}{m}}} = \frac{h}{\sqrt{2meV}} = \frac{h}{\sqrt{2mE}} \quad \dots(33)$$

Substituting the value of  $h$ ,  $m$  and  $e$  in Eq. (33), we get

$$\lambda = \frac{12.28}{\sqrt{V}} \text{ Å} \quad \dots(34)$$

function be observable.

### **7.8.2 Relativistic Corrections in the Formula**

In Newtonian Physics, mass is not a variable quantity while according to the theory of relativity, it is a variable quantity.

On account of the relativistic increase in the mass of the high velocity electrons, the necessary correction in Eq. (34) may be made. The relativistic mass is given by

$$m = \frac{m_0}{\sqrt{\left(1 - \frac{v^2}{c^2}\right)}} \quad \dots(35)$$

where  $m_0$  is the rest mass of the particle,  $v$  is its velocity and  $c$  the velocity of light.

Applying relativistic equation for kinetic energy  $K$ , viz

$$K = (m - m_0)c^2, \text{ we have}$$

$$(m - m_0)c^2 = Ve \quad \text{or} \quad (m - m_0) = \frac{Ve}{c^2}$$

$$\text{or} \quad m = m_0 + \frac{Ve}{c^2} = m_0 \left(1 + \frac{Ve}{m_0 c^2}\right) \quad \text{or} \quad m^{1/2} = m_0^{1/2} \left(1 + \frac{Ve}{m_0 c^2}\right)^{1/2}$$

Substituting the value of  $m^{1/2}$  in Eq. (33), above, we get

$$\lambda = \frac{h}{\sqrt{2Vem_0}} \left(1 + \frac{Ve}{m_0 c^2}\right)^{-1/2} \quad \dots(36)$$

For the wavelength of electrons of known energy,

$$\text{Now, } \frac{h}{\sqrt{2Vem_0}} = \frac{12.28}{\sqrt{V}} \text{ Å} \quad \dots(37)$$

Substitution in the above gives

$$\lambda = \frac{12.28}{\sqrt{V}} \left(1 + \frac{Ve}{m_0 c^2}\right)^{-1/2} \text{ Å} \quad \dots(38)$$

**Example 7.5.** What is speed of a particle whose de-Broglie wavelength and Compton wavelength are equal. [PTU, June 2002 (4 marks)]

**Solution.** Let  $m$  and  $v$  be the mass and velocity of a particle, then de-Broglie wavelength is given by

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

Also the Compton wavelength for that particular particle is

$$\lambda_c = \frac{h}{m_0 c}$$

where  $m_0$  = rest mass of particle,  $c$  = velocity of light  
As per question  $\lambda_d = \lambda_c \Rightarrow \frac{h}{mv} = \frac{h}{m_0 c}$  or  $mv = m_0 c$

But  $m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$  or  $\frac{mv}{\sqrt{1 - \frac{v^2}{c^2}}} = m_0 c$   
or  $\frac{v^2}{c^2} = 1 - \frac{v^2}{c^2}$  or  $\frac{2v^2}{c^2} = 1$  or  $v = \frac{c}{\sqrt{2}}$

**Example 7.6.** Calculate the de-Broglie wavelength of

- (i) a particle accelerated by a potential difference of 30,000 V, and
- (ii) an electron moving with a velocity of 0.01  $c$ , where  $c$  is the speed of light.

**Solution.** (i) The de-Broglie wavelength is given by

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mE}} \quad \left[ \because E = \frac{1}{2}mv^2 \text{ so that } mv = \sqrt{2mE} \right]$$

Given :  $E = Ve = 1.6 \times 10^{-19}$  V Joule

mass of electron =  $9.1 \times 10^{-31}$  kg

and Planck's constant ( $h$ ) =  $6.63 \times 10^{-34}$  Js

$$\therefore \lambda = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} V}} = \frac{12.28 \times 10^{-10}}{\sqrt{V}}$$

$$= \frac{12.28}{\sqrt{V}} \text{ Å} = \frac{12.28}{173.2} \times 10^{-10} = 7.09 \times 10^{-12} \text{ m}$$

(ii) The de-Broglie wavelength is given by

$$\begin{aligned} \lambda &= \frac{h}{mv} = \frac{h}{m \times (0.01c)} \\ &= \frac{6.63 \times 10^{-34}}{9.1 \times 10^{-31} \times 0.01 \times 3 \times 10^8} \text{ m} = \frac{6.63 \times 10^{-11}}{9.1 \times 0.03} \text{ m} = 2.43 \times 10^{-10} \text{ m} = 2.43 \text{ Å} \end{aligned}$$

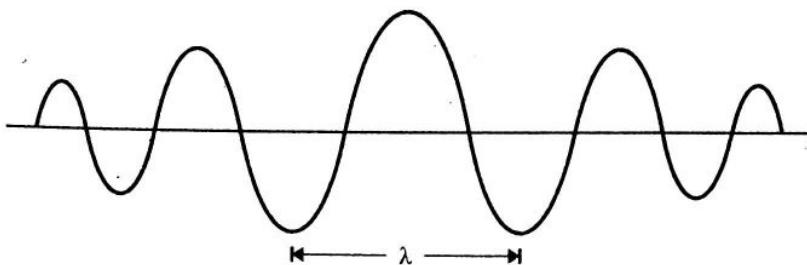
**Example 7.7.** Calculate the de-Broglie wavelength of virus particle of mass  $1.0 \times 10^{-15}$  kg moving at a speed of 2.0 mm/s.

**Solution.** Given  $m = 1.0 \times 10^{-15}$  kg,  $v = 2.0 \times 10^{-3}$  m/s  
The de-Broglie wavelength is given by

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}}{1.0 \times 10^{-15} \times 2.0 \times 10^{-3}} = 3.315 \times 10^{-16} \text{ m}$$

### 7.9 CHARACTERISTICS OF MATTER WAVES

1. The de-Broglie wavelength of a particle of mass  $m$  moving with a velocity  $v$  is given by  $\lambda = \frac{h}{\sqrt{2meV}}$ . Larger the mass, shorter will be the de-Broglie wavelength.
2. de-Broglie waves are **pilot waves** i.e., these waves guide the particle.
3. de-Broglie waves are not electromagnetic waves.
4. Matter waves can not be observed. It is a wave model to describe and to study matter.
5. de-Broglie waves are called **probability waves**. The amplitude of the wave reveals the probability of finding a particle in space at a particular instant. A large wave amplitude means a large probability to find the particle at that position as visualised in Fig. 7.9.



**Fig. 7.9** Matter wave as probability wave.

6. The matter wave consists of a group of waves. The velocity of the group is different from that of the individual components of the wave. But it can be shown that the particle velocity  $v$  is same as that of the de-Broglie groups associated with the particles. If the wave velocity and particle velocity are different, then the particle would soon be in the region where the amplitude of the wave is negligible and the wave would not have given the correct indication of the particle.
7. The phase velocity of the matter waves depends on the wavelength, even if the particle is moving in vacuum. But in vacuum all electromagnetic waves travel with the same velocity and is independent of the wavelength.

### 7.10 PHASE VELOCITY AND GROUP VELOCITY

To understand the difference between phase and group velocity of waves, consider the following analogy :

A group of people, say city marathon runners, start from the starting at the same time. Initially it would appear that all of them are running at the same speed. As time passes, group speeds out (disperses) simply because each runner in the group is running with different speed. If we think of phase velocity to be like the speed of individual runner, then the group velocity is the speed of entire group as a whole. Obviously and most often, individual runners can run faster than a group as a whole. To stretch this analogy, we note that the phase velocity of waves are typically larger than the group velocity of waves. However, this really depends on the properties of the medium.

The phase velocity and group velocity are described on next sections.

### 7.10.1 Phase Velocity

According to de-Broglie, the matter wave consists of a group of waves or a wavepacket. The velocity with which each individual wave travels is called phase velocity or wave velocity.

The de-Broglie wave velocity or phase velocity is given by

or

$$v_p = v\lambda = 2\pi v \cdot \frac{\lambda}{2\pi}$$

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

$$\left[ \because k = \frac{2\pi}{\lambda} \right]$$

A plane simple harmonic wave travelling in the positive  $x$ -direction is given by

$$y = A \sin \omega \left( t - \frac{x}{v} \right) \quad \dots(39)$$

where  $A$  is amplitude,  $v$  the velocity of propagation of wave and  $\omega$  the angular frequency  $= 2\pi\nu$ .

The wave velocity is also phase velocity. The reason for this follows. In Eq. (39), the phase  $\phi$  of the wave at position  $x$  and at time  $t$  is

$$\phi(x, t) = \omega \left( t - \frac{x}{v} \right) \quad \dots(40)$$

Differentiating this equation with respect to  $t$ , we get

$$\frac{d\phi}{dt} = \omega \left( 1 - \frac{1}{v} \frac{dx}{dt} \right)$$

For a point of constant phase,

$$\frac{d\phi}{dt} = 0$$

$$\therefore 1 - \frac{1}{v} \left( \frac{dx}{dt} \right)_\phi = 0 \quad \text{or} \quad \left( \frac{dx}{dt} \right)_\phi = v \quad \dots(41)$$

$\left( \frac{dx}{dt} \right)_\phi$  is the velocity with which the displacement of a given phase moves forward.

Therefore, this quantity is called phase velocity and it is usually represented by  $v_p$  or  $v_\phi$ . Thus the velocity of propagation or the velocity of a wave is the velocity with which a displacement of a given phase moves forward. Replacing  $v$  by  $v_p$  in Eq. (39) and rewriting,

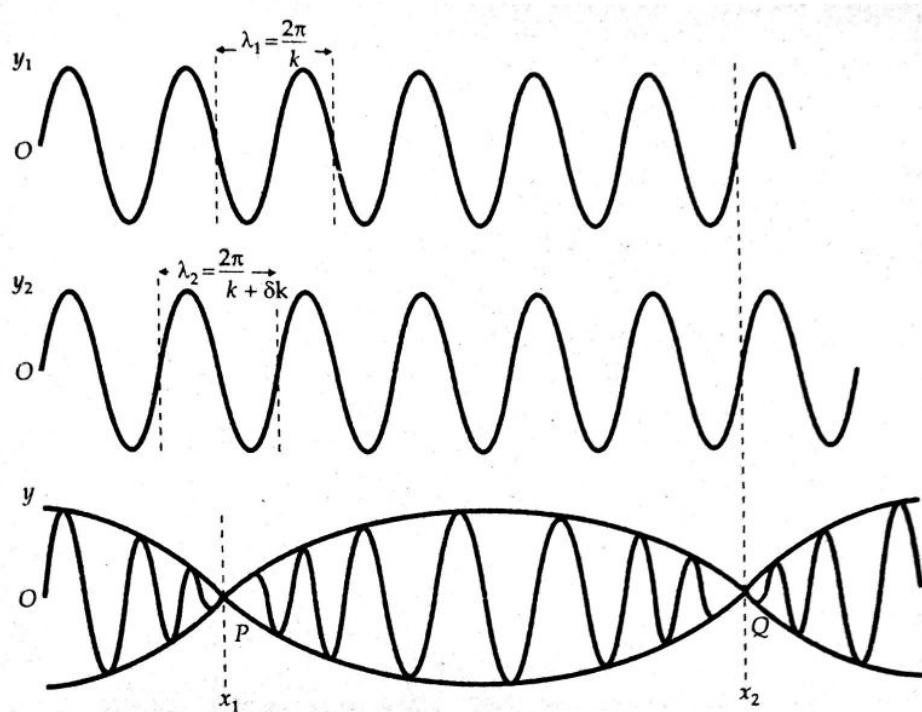
$$y = A \sin \omega \left( t - \frac{x}{v_p} \right) = A \sin \left( \omega t - \frac{\omega x}{v_p} \right) = A \sin (\omega t - kx) \quad \dots(42)$$

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

The quantity  $k$  is called the propagation constant, or the phase constant or the propagation number of the wave.

### 7.10.2 Group Velocity and Wave Packets

When plane waves of slightly different wavelengths travel simultaneously in the same direction along a straight line, through a dispersive medium, (i.e., a medium in which the phase velocity  $v_p = \frac{\omega}{k}$  of a wave depends on its wavelength) successive groups of the waves are produced (Fig. 7.10).



**Fig. 7.10** Successive groups of wave.

These wave groups are called **wave packets**. Each wave group travels with a velocity is called **group velocity**. "The velocity with which the resultant envelope of the group of waves travels is called group velocity", denoted by  $v_g$ . The velocity of the group is different from that of the individual components of the wave. The group velocity is different from the phase velocity of a wave.

The velocity with which resultant envelope moves is called group velocity and the velocity with which a point like  $P$  on the wave moves is called phase velocity.

### Expression for Group Velocity

Let two plane simple harmonic waves of the same amplitude  $A$ , but of slightly different wavelengths travelling simultaneously in the +ve  $x$ -direction in a dispersive medium be represented by

$$y_1 = A \sin(\omega t - kx) \quad \dots(43)$$

$$y_2 = A \sin[(\omega + \Delta\omega)t - (k + \Delta k)x] \quad \dots(44)$$

where  $y_1$  and  $y_2$  are instantaneous displacements,  $\omega$  and  $\omega + \Delta\omega$  are the angular velocities,  $k$  and  $k + \Delta k$  are the wave propagation vectors or constants.

The resultant displacement  $y$  at time  $t$  and at position  $x$  is given by

$$y = y_1 + y_2 = A \sin(\omega t - kx) + A \sin[(\omega + \Delta\omega)t - (k + \Delta k)x]$$

We know,

$$\sin A + \sin B = 2 \cos\left(\frac{A-B}{2}\right) \sin\left(\frac{A+B}{2}\right)$$

Making use of this equation, we get

$$y = 2A \cos\left[\left(\frac{\Delta\omega}{2}\right)t - \left(\frac{\Delta k}{2}\right)x\right] \sin\left[\left(\frac{2\omega + \Delta\omega}{2}\right)t - \left(\frac{2k + \Delta k}{2}\right)x\right] \quad \dots(45)$$

Since  $\Delta\omega$  and  $\Delta k$  are small compared with  $\omega$  and  $k$  respectively  $2\omega + \Delta\omega = 2\omega$  and  $2k + \Delta k = 2k$ .

Then,  $y = 2A \cos\left[\left(\frac{\Delta\omega}{2}\right)t - \left(\frac{\Delta k}{2}\right)x\right] \sin(\omega t - kx) \quad \dots(46)$

This is analytical expression for the group of waves i.e., the wave packet formed by the two waves. The above equation is in the form of  $y = A \sin(\omega t - kx)$ . Hence the amplitude of the resultant wave is

$$R = 2A \cos\left[\left(\frac{\Delta\omega}{2}\right)t - \left(\frac{\Delta k}{2}\right)x\right] \quad \dots(47)$$

The sine factor represents a carrier wave which travels with the velocity,  $v_p = \frac{\omega}{k}$ .

From Eq. (47), it is seen that the amplitude of the resultant wave varies according to the cosine term with the circular frequency  $\frac{\Delta\omega}{2}$ .

The group velocity  $v_g$  is the velocity with which the maximum amplitude moves. At  $x=0$  and  $t=0$ , the maximum amplitude is given by

$$R_{\max} = 2A \quad \dots(48)$$

The group velocity is given by

$$v_g = \lim_{\Delta k \rightarrow 0} \frac{(\Delta\omega/2)}{(\Delta k/2)} = \lim_{\Delta k \rightarrow 0} \frac{\Delta\omega}{\Delta k} = \frac{d\omega}{dk} \quad \dots(49)$$

Hence

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

### 7.10.3 Relation Between Group Velocity and Phase Velocity

Phase velocity  $v_p = \frac{\omega}{k}$  ...(50)

Group velocity  $v_g = \frac{d\omega}{dk}$  ...(51)

where  $\omega$  is the angular frequency of the wave and  $k$  is the wave vector.  
From Eq. (50), we have

$$\omega = v_p k$$

$$\therefore v_g = \frac{d}{dk}(v_p k) = v_p + k \frac{dv_p}{dk}$$

or  $v_g = v_p + k \frac{dv_p}{d\lambda} \frac{d\lambda}{dk}$  ...(52)

We know that propagation constant  $k = \frac{2\pi}{\lambda}$

$$\left( \because \lambda = \frac{2\pi}{k} \right)$$

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

...(53)

Equation (52) becomes,

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

$$v_g = v_p - \frac{2\pi}{k} \frac{dv_p}{d\lambda}$$

or  $v_g = v_p - \lambda \frac{dv_p}{d\lambda} \quad \left[ \because \lambda = \frac{2\pi}{k} \right] \quad \dots(54)$

Equation (54) shows that  $v_g$  is less than  $v_p$  when the medium is dispersive i.e., when  $v_p$  is a function of  $\lambda$ . For light wave in vacuum, there is no dispersion. Hence  $\frac{dv_p}{d\lambda} = 0$ , so that  $v_g = v_p = c$  (velocity of light in vacuum). This is true for elastic waves in a homogenous.

#### ~~7.10.4 Relation between Group Velocity and Particle Velocity~~

We know that

Group velocity,  $v_g = \frac{d\omega}{dk}$  ... (55)

Angular frequency  $\omega = 2\pi\nu = 2\pi \frac{E}{h}$  ... (56)

Differentiating,  $d\omega = \left( \frac{2\pi}{h} \right) dE$  ... (57)

Propagation constant  $k = \frac{2\pi}{\lambda} = 2\pi \cdot \frac{p}{h}$  ... (58)

For matter waves,  $\lambda = \frac{h}{p}$  ... (59)

where  $p$  = momentum of the particle.

Differentiating Eq. (59),

$$dk = \left( \frac{2\pi}{h} \right) dp \quad \dots(60)$$

Dividing Eq. (57) by Eq. (60), we get

$$\frac{d\omega}{dk} = \frac{\left( \frac{2\pi}{h} \right) dE}{\left( \frac{2\pi}{h} \right) dp} = \frac{dE}{dp} \quad \Rightarrow \quad \frac{d\omega}{dk} = \frac{dE}{dp} \quad \dots(61)$$

We also know that

$$E = \frac{1}{2} mv^2 = \frac{1}{2} \frac{m^2 v^2}{m} = \frac{1}{2} \frac{p^2}{m}$$

or  $dE = \frac{1}{2} \frac{2p}{m} dp = \frac{p}{m} dp$

or  $\frac{dE}{dp} = \frac{p}{m}$  ... (62)

Since,  $p = mv_{\text{particle}}$ ,

$$\frac{dE}{dp} = \frac{mv_{\text{particle}}}{m} = v_{\text{particle}}$$
 ... (63)

From Eqs. (55), (61) and (63), we have

$$v_g = v_{\text{particle}}$$
 ... (64)

Hence the group velocity of the wave packet is the same as the particle velocity.

### 7.10.5 Relation Between Velocity of Light ( $c$ ), Group Velocity ( $v_g$ ) & Phase Velocity ( $v_p$ )

Phase velocity of the wave is given by,

$$v_p = \frac{\omega}{k}$$
 ... (65)

Substituting the values of  $\omega = 2\pi\nu = \frac{2\pi E}{h}$  and  $k = \frac{2\pi}{\lambda} = 2\pi \frac{p}{h}$ , we have

$$v_p = \frac{2\pi E/h}{2\pi p/h} = \frac{E}{p} \frac{mc^2}{mv_{\text{particle}}} = \frac{c^2}{v_{\text{particle}}}$$
 ... (66)

$\therefore v_g = v_{\text{particle}}$ , we have

$$v_p = \frac{c^2}{v_g} \quad \text{or} \quad v_p v_g = c^2$$
 ... (67)

This is relation of velocity of light with phase velocity and group velocity.

### 7.10.6 Relation between $v_g$ and $v_p$ for a Non-relativistic Free particle

According to de-Broglie hypothesis,

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

Total energy  $E = \frac{1}{2} mv_g^2$

Also,  $E = h\nu$

$$\nu = \frac{E}{h} = \frac{mv_g^2}{2h}$$

$\therefore$  Phase velocity,

$$v_p = v \cdot \lambda = \frac{mv_g^2}{2h} \times \frac{h}{mv_g} = \frac{v_g}{2}$$

$$v_p = \frac{v_g}{2} \quad \dots(68)$$

Hence for a non-relativistic free particle, the phase velocity is half of the group velocity.

### 7.10.7 Expression for de-Broglie Wavelength in terms of Group Velocity and Phase Velocity

According to de-Broglie, a material particle in motion is associated with a system of plane waves, the superposition of a system of plane wave of slight different frequencies form a wave packet.

The group velocity of wave packet is given by

$$v_g = \frac{d\omega}{dk} \quad \dots(69)$$

We know that,  $\omega = 2\pi v$  and  $k = \frac{2\pi}{\lambda}$

Differentiating the above equations, we have

$$d\omega = 2\pi dv \text{ and } dk = 2\pi d\left(\frac{1}{\lambda}\right)$$

Substituting the value of  $d\omega$  and  $dk$  in Eq. (69), we get

$$v_g = \frac{2\pi dv}{2\pi d\left(\frac{1}{\lambda}\right)} = \frac{dv}{d\left(\frac{1}{\lambda}\right)} \quad \dots(70)$$

Since the particle velocity is equal to group velocity, we can write

$$v_{\text{particle}} = \frac{dv}{d\left(\frac{1}{\lambda}\right)} \text{ or } d\left(\frac{1}{\lambda}\right) = \frac{dv}{v_{\text{particle}}} \quad \dots(71)$$

Let  $E$  be the total energy and  $V$  the potential energy of the particle of mass  $m$ . If  $v$  is the velocity, then the total energy of the particle is given by

$$E = \frac{1}{2} mv_{\text{particle}}^2 + V \quad \dots(72)$$

The relationship between the energy  $E$  of a photon and the frequency  $v$  of the associated electromagnetic wave is given by the Planck-Eisntein equation :

$$E = h\nu \quad \dots(73)$$

Comparing Eqs. (72) and (73), we get

$$h\nu = \frac{1}{2} mv_{\text{particle}}^2 + V \quad \dots(74)$$

Let the particle be moving under a constant electric potential i.e.,  $V$  is a constant quantity.

Differentiating Eq. (74),

$$\begin{aligned} h dv &= \frac{1}{2} m \cdot 2 v_{\text{particle}} dv \\ &= m v_{\text{particle}} dv \end{aligned} \quad \dots(75)$$

Substituting the value of  $dv$  from Eq. (75) in Eq. (71), we get

$$d\left(\frac{1}{\lambda}\right) = \frac{m}{h} \frac{v_{\text{particle}}}{v_{\text{particle}}} dv = \left(\frac{m}{h}\right) dv$$

Integrating,  $\int d\left(\frac{1}{\lambda}\right) = \int \left(\frac{m}{h}\right) dv$

$$\frac{1}{\lambda} = \left(\frac{m}{h}\right)v + C \quad \dots(76)$$

where  $C$  = constant of integration and let  $C$  is zero.

$$\frac{1}{\lambda} = \frac{mv}{h} = \frac{p}{h} \quad [\because p = \text{momentum} = mv]$$

or  $\lambda = \frac{h}{p} = \frac{h}{mv}$  ... (77)

Equation (77) represents the wave-particle relation for photons and is called de-Broglie equation.

**Example 7.8.** An electron has a de-Broglie wavelength of 2 pm. Find its kinetic energy and phase and group velocities of its de-Broglie waves. Rest mass energy of electron = 511 keV.

**Solution.** Given  $\lambda = 2 \text{ pm} = 2 \times 10^{-12} \text{ m}$ ,  $E_0 = 511 \text{ keV}$ .

According to Einstein's mass-energy relation

$$\text{Rest mass energy} = m_0 c^2 \quad \text{or} \quad 511 \text{ keV} = m_0 c^2$$

$$\begin{aligned} \therefore \text{Rest mass of electron } m_0 &= \frac{511 \text{ keV}}{c^2} \\ &= \frac{511 \times 10^3 \text{ eV}}{(3 \times 10^8)^2} = 9.1 \times 10^{-31} \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Kinetic energy of the electron} &= \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} \\ &= \frac{(6.63 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31} \times (2 \times 10^{-12})^2} \text{ J} \end{aligned}$$

$$\therefore \frac{1}{2} mv^2 = 6.038 \times 10^{-14} \text{ J.}$$

or  $v^2 = \frac{2 \times 6.038 \times 10^{-14}}{9.1 \times 10^{-31}} = 1.327 \times 10^{17} \text{ m}^2/\text{s}^2$

$\therefore$  Particle velocity  $v_{\text{particle}} = \sqrt{1.327 \times 10^{17}} = 3.64 \times 10^8 \text{ m/s}$

$\because$  The particle velocity ( $v_{\text{particle}}$ ) is equal to  $v_g$  (group velocity).

i.e.,  $v_{\text{particle}} = v_g$

$$v_g = 3.64 \times 10^8 \text{ m/s}$$

$$\text{Phase velocity } v_p = \frac{c^2}{v_g} = \frac{(3 \times 10^8)^2}{3.64 \times 10^8} = 2.47 \times 10^8 \text{ m/s}$$

**Example 7.9.** The phase velocity of ripples on a liquid surface is  $\sqrt{\left(\frac{2\pi S}{\lambda\rho}\right)}$ , where  $S$  is the surface tension and  $\rho$  the density of the liquid. Find the group velocity of the ripples.

**Solution.** Since phase velocity  $v_p = \sqrt{\frac{2\pi S}{\lambda\rho}}$

$$\therefore v_p^2 = \frac{2\pi S}{\lambda\rho} \quad \text{or} \quad \lambda = \frac{2\pi S}{v_p^2 \rho}$$

As wave number,

$$k = \frac{2\pi}{\lambda} = \frac{\omega}{v_p} \quad (\text{where } \omega \text{ is angular velocity})$$

$$k = \frac{2\pi}{2\pi S} v_p^2 \rho = \frac{v_p^2 \rho}{S}$$

We know that group velocity is given by

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

$$\text{As } k = \frac{v_p^2 \rho}{S} = \frac{\omega^2 \rho}{k^2 S}$$

$$k^3 = \frac{\omega^2 \rho}{S}$$

$$\omega^2 = \frac{k^3 S}{\rho}, \quad \omega = \sqrt{\frac{S}{\rho}} k^{3/2}$$

$$v_g = \frac{d\omega}{dk} = \sqrt{\frac{S}{\rho}} \frac{3}{2} k^{1/2}$$

$$= \frac{3}{2} \sqrt{\left(\frac{Sk}{\rho}\right)} = \frac{3}{2} \sqrt{\frac{S}{\rho} \frac{v_p^2 \rho}{S}}$$

$$v_g = \frac{3}{2} v_p$$

## 7.11 EXPERIMENTAL STUDY OF MATTER WAVES

*An experiment that confirms the existence of de-Broglie waves.*

A wave effect with no analog in the behaviour of Newtonian particles is diffraction. In 1927, Clinton Davisson and Lester Germer in U.S.A. and G.P. Thomson in England independently confirmed de-Broglie's hypotheses by demonstrating that electron beams are diffracted when they are scattered by a regular arrays of crystals. It was found that there was considerable difference between X-rays and short waves produced by electrons in that the scattering coefficient of the electrons by atoms of the target substance is much higher than that of X-rays. In fact, atom scatter electrons much more efficiently for the energy involved and hence are preferred for structure investigations than X-rays. Electrons do not penetrate matter so well as X-rays, so that electron diffraction effect results from penetration only to small depths in the material. Evidently, surface would not be investigated by X-rays diffraction, because the patterns obtained are characteristic of the bulk material. Note that diffraction of electrons by gases required much shorter exposures than for X-rays diffraction. This is because of the relatively higher scattering coefficient of electrons by atoms.

### 7.11.1 Davisson and Germer's Experiment

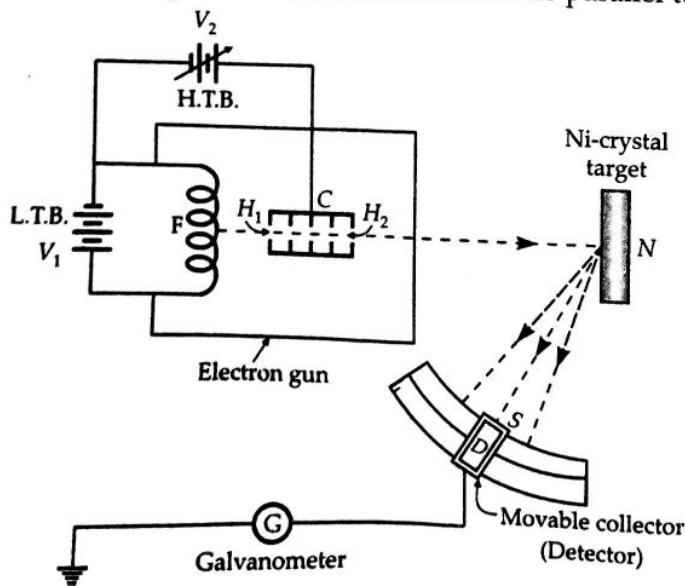
Davisson and Germer in 1927 designed an apparatus to determine the wavelength associated with electrons.

The experimental arrangement used by Davisson and Germer is as visualised in Fig. 7.11. It consists of an electron gun which comprises of a tungsten filament  $F$  coated with zinc oxide heated by a low tension battery (L.T.B.)  $V_1$  produces electrons. These electrons are accelerated by applying suitable potential from a high tension battery (H.T.B.)  $V_2$ . The accelerated electrons are collimated into a fine beam by allowing them to pass through pin holes  $H_1$  and  $H_2$  provided in the cylinder  $C$ .

The collimated beam of electrons falls on a large single crystal of nickel  $N$ . The crystal is capable of rotation about an axis parallel to the axis of the incident beam. The electrons

are now scattered in all directions by the atoms of the crystal. The scattered electrons are collected by a Faraday chamber ( $D$ ), called the collector. The collector also rotates about the sensitive galvanometer  $G$  whose deflection is proportional to the intensity of the electron beam entering the collector.

It is possible that secondary electrons, produced by the impact of primary electrons on the nickel target may also enter the Faraday's chamber ( $D$ ). This is prevented surrounding the collector by shielding chamber  $S$ , to which a retarding potential is applied. This potential is about nine-tenth of the accelerating voltage.



**Fig. 7.11** Davisson and Germer experimental arrangement.

If a beam of electron incidents on the crystal, turned at any arbitrary azimuth and the distribution of the scattered beam is measured as a function of the colatitude – the angle between the incident beam and the beam entering the collector.

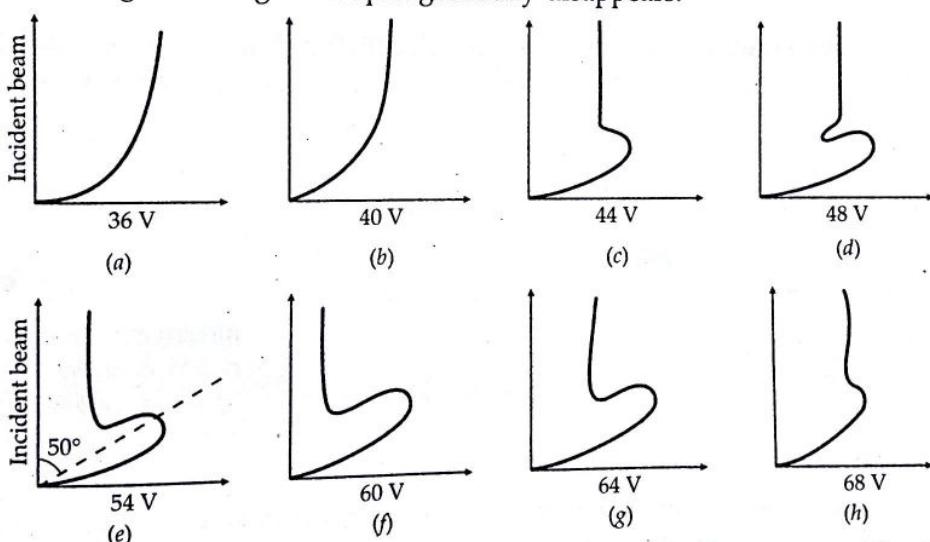
The whole instrument is kept in an evacuated chamber. The nickel crystal belongs to face-centered cubic (f.c.c.) type and it is so cut as to present a smooth reflection surface parallel to the lattice plane  $\langle 111 \rangle$ .

This experiment can be performed by

- ❖ Normal incidence method and
- ❖ Oblique incident method.

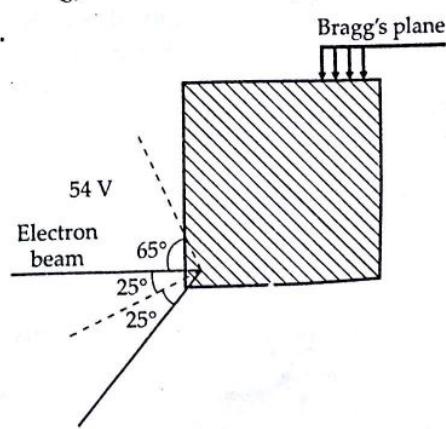
#### (i) Normal Incidence Method

In this method voltage  $V_2$  applied to the accelerating cylinder  $C$  is maintained at different constant value namely 36, 40, 44, 48, 54, 60, 64 and 68 V. If now the crystal is turned to the azimuth, the distribution curve for 44 V electrons [(Fig. 7.12c)] shows a slight hump at about colatitude  $60^\circ$ . With increasing voltage this hump moves upward and develops into a spur which becomes most prominent at 54 V [Fig. 7.12e] at which the colatitude of the spur is  $50^\circ$ . At higher voltages the spur gradually disappears.



**Fig. 7.12** Results of the Davisson-Germer Experiment.

The intensity of the scattered beam is found to be maximum in a direction at  $50^\circ$  to the incident radiation as visualized in Fig. 7.13. This is due to the constructive interference of electron waves scattered in this direction from the regularly spaced parallel planes in the crystal, which are rich in atoms.



**Fig. 7.13** Normal Incidence Method.

If the electron behaves as wave then according to Bragg's equation for maxima in the diffraction pattern

$$2d \sin \theta = n\lambda \quad \dots(78)$$

where  $d$  is the interplaner distance for the  $\langle 111 \rangle$  plane and  $n$  is the order of diffraction. For normal incident method, we have

$$2d \sin \theta = n\lambda \quad \dots(79)$$

For nickel,  $d = 0.91 \text{ \AA}$ , distance between the Bragg planes, then

$$2 \times 0.91 \times 10^{-10} \sin 65^\circ = 1 \times \lambda$$

or

$$\lambda = 1.65 \text{ \AA} \quad \dots(80)$$

Considering the electron to be a charged particle, the wavelength of the electron wave is given by

$$\lambda_e = \frac{12.28}{\sqrt{V}} \text{ \AA} \quad \dots(81)$$

$$\text{Since, } V = 54 \text{ V} \quad \lambda_e = \frac{12.28}{\sqrt{54}} \text{ \AA} = 1.66 \text{ \AA} \quad \dots(82)$$

The electron wavelength therefore agrees well with the observed wavelength of  $1.66 \text{ \AA}$ . The Davisson-Germer experiment thus directly verifies to de-Broglie hypothesis of the wave nature of moving bodies.

$$\frac{1}{\lambda} = \frac{n}{2d \sin \theta} = \frac{p}{h} = \frac{\sqrt{2 m E}}{h} = \frac{\sqrt{2 m eV}}{h} \quad \dots(83)$$

Electron wavelength	Bragg's Law	de-Broglie relationship	Acceleration through voltage $V$
---------------------	-------------	-------------------------	----------------------------------

$$\frac{1}{\lambda} = \frac{n}{2d \sin \theta} = 0.815 \sqrt{V}$$

 **NOTE**  
Interatomic distance for nickel is  $2.15 \text{ \AA}$ . Thus

$$d = 2.15 \sin 25^\circ = 0.91 \text{ \AA}$$

### (ii) Oblique Incidence Method

In this method the accelerating voltage  $V_2$  is maintained at a constant value and the galvanometer deflection at various glancing angles of incidence is noted. A graph of glancing angle and galvanometer deflection is shown in Fig. 7.14. It shows the various orders of maxima (humps).

Consider one such hump at  $31^\circ$  which occurs for  $60 \text{ V}$  accelerating potential. Another hump occurs at  $62^\circ$ .

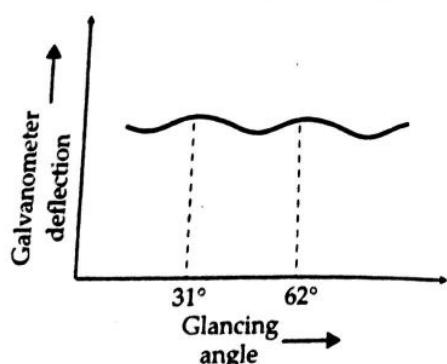
According to Bragg's law, we have

$$2d \sin \theta_1 = n\lambda_e \quad \dots(84)$$

and  $2d \sin \theta_2 = (n+1)\lambda_e \quad \dots(85)$

Subtracting Eq. (84) from Eq. (85), we have

$$2d(\sin \theta_2 - \sin \theta_1) = \lambda_e \quad \dots(86)$$



**Fig. 7.14** Graph between glancing angle and galvanometer deflection.

Substituting the value of  $d$ ,  $\theta_1$  and  $\theta_2$  in Eq. (86), we get

$$\begin{aligned}\lambda_e &= 2 \times 2.15 (\sin 62^\circ - \sin 31^\circ) \text{ Å} = 4.30 \times 0.3679 \text{ Å} \\ &= 2 \times 2.15 (0.8829 - 0.5150) \text{ Å} = 4.30 \times 0.3679 \text{ Å} \\ \lambda_e &= 1.582 \text{ Å}\end{aligned}\quad \dots(87)$$

We know,  $\lambda = \frac{h}{\sqrt{2meV}} = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times 60}} = 1.55 \text{ Å}$

This is in excellent agreement with observed value.

**Example 7.10.** An electron initially at rest is accelerated through a potential difference of 5000 V. Compute (i) momentum, (ii) the de-Broglie wavelength, and (iii) the wave propagation vector of the electron. Also calculate the Bragg's angle for the first order reflection from the  $\langle 1 1 1 \rangle$  planes of nickel which are 2.04 Å apart.

**Solution.** (i) Let  $v$  be the velocity of the electron then its K.E.

$$\frac{1}{2}mv^2 = Ve = 5000 \text{ eV} = 5000 \times 1.6 \times 10^{-19} \text{ J}$$

$$\therefore (mv)^2 = 2m \times 5000 \times 1.6 \times 10^{-19} \text{ J.}$$

and momentum of the electron

$$\begin{aligned}mv &= \sqrt{(2m \times 5000 \times 1.6 \times 10^{-19} \text{ J})} \\ &= \sqrt{2 \times 9.1 \times 10^{-31} \text{ kg} \times 5000 \times 1.6 \times 10^{-19} \text{ J}} \quad [\because m = 9.1 \times 10^{-31} \text{ kg}] \\ &= \sqrt{9.1 \times 1.6 \times 10^{-46} \text{ kg ms}^{-1}} \\ &= 10^{-23} \sqrt{9.1 \times 1.6} \text{ kg ms}^{-1} = 3.818 \times 10^{-23} \text{ kg ms}^{-1}\end{aligned}$$

(ii) The de-Broglie wavelength of the electron

$$\begin{aligned}\lambda &= \frac{h}{mv} = \frac{6.625 \times 10^{-34} \text{ Js}}{3.818 \times 10^{-23} \text{ kg ms}^{-1}} \\ &= 1.729 \times 10^{-11} \text{ m} = 0.1729 \text{ Å}\end{aligned}$$

(iii) Here wave propagation vector or angular wave number is given by

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{1.729 \times 10^{-11} \text{ m}} = 36.34 \times 10^{10} \text{ m}^{-1}$$

(iv) Let  $\theta$  be the Bragg's angle for the first order reflection from  $\langle 1 1 1 \rangle$  plane of nickel (face centered cubic lattice). Here  $d = 2.04 \text{ Å}$ ;  $n = 1$  and  $\lambda = 0.1729 \text{ Å}$

Now, by Bragg's equation,

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

$$2 \times 2.04 \text{ Å} \sin \theta = 1 \times 0.1729 \text{ Å}$$

or

$$\sin \theta = \frac{0.1729}{2 \times 2.04} = \frac{0.1729}{4.08} = 0.04237$$

$$\theta = 2^\circ 25'$$

## 7.12 HEISENBERG'S UNCERTAINTY PRINCIPLE

*We can not know the future because we can not know the present.*

The new fundamental principle of indeterminacy also called *uncertainty principle* has been derived from the theoretical investigation of the wave probability associated with matter. We know that an electron in motion is associated with a wave whose wavelength is given by de-Broglie relation. It can be considered as a *wave packet* formed by the superposition of a large number of waves of wavelengths slightly different from the wavelength of the associated wave. (The amplitude of the wave packet is zero everywhere in space except only over a region in which the particle (electron) is located). Since a wave packet is of finite width there will be uncertainty in specifying the position of electron. According to de-Broglie's theory, the momentum of the electron will also be uncertain. Therefore, in general, it is not possible to determine position of the electron. If the momentum of electron is known, then by the de-Broglie relation, the wavelength of the associated wave has a unique value i.e., the associated wave is monochromatic. In such a case the wave packet has infinite length and hence the position of electron may be anywhere between minus infinity to plus infinity. On the basis of these considerations, Werner Heisenberg in 1927, enunciated the principle of **Unbestimmtheit**. This term has been translated as uncertainty, indeterminacy or indefiniteness.

### **7.12.1 Statement of Heisenberg's Uncertainty Principle**

Heisenberg was first, who pointed out the inherent relation in specifying the position and momentum of a particle regarded as a wave which is known as the **uncertainty principle**.

Heisenberg uncertainty principle states that

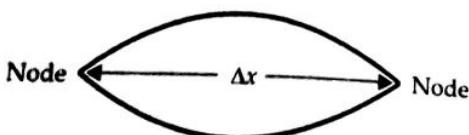
*"In any simultaneous determination of the position and momentum of the particle, the product of the uncertainty  $\Delta x$  (or possible error) in the x-coordinate of a particle, in motion and uncertainty  $\Delta p_x$  in the x-component of momentum is of the order of or greater than  $\hbar (= 1.054 \times 10^{-34} \text{ Js})$ "*

$$\Delta x \cdot \Delta p_x \geq \hbar$$

In other words, it is physically impossible to measure simultaneously the exact position and exact linear momentum of the particle.

### **7.12.2 Proof of Heisenberg's Uncertainty Principle**

Consider a particle moving along x-axis. It is considered as a wave packet. The envelope of the wave packet moves with a velocity equal to particle velocity. The wave packet moves with a velocity of equal to particle velocity. The wavelength is equivalent of the position of the particle. When the wave packet extends over a finite distance  $\Delta x$  along the axis of motion, then the two points at which the amplitude of the wave packet becomes zero successively will be separated by a distance  $\Delta x$  as shown in Fig. 7.15.



**Fig. 7.15** Spatial extension of wave packet.

The points at which the amplitude of the wave packet becomes zero are called nodes. Due to the wave nature of matter, any measurement made to find the position of the particle will have a minimum error equal to the distance ( $\Delta x$ ) between two successive nodes. Thus there is uncertainty in the position of the particle between two successive nodes.

The amplitude of the wave packet is given by

$$R = 2A \cos \left[ \left( \frac{\Delta\omega}{2} \right) t - \left( \frac{\Delta k}{2} \right) x \right] \quad \dots(88)$$

At nodes the, amplitude of the wave packet is zero. Hence

$$0 = 2A \cos \left[ \left( \frac{\Delta\omega}{2} \right) t - \left( \frac{\Delta k}{2} \right) x \right]$$

Since  $2A \neq 0$ .

Then

$$\cos \left[ \left( \frac{\Delta\omega}{2} \right) t - \left( \frac{\Delta k}{2} \right) x \right] = 0$$

or  $\left( \frac{\Delta\omega}{2} \right) t - \left( \frac{\Delta k}{2} \right) x = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, \dots, (2n+1)\frac{\pi}{2}$

If  $x_1$  and  $x_2$  are the two positions of two consecutive nodes, then

$$\left( \frac{\Delta\omega}{2} \right) t - \left( \frac{\Delta k}{2} \right) x_1 = (2n+1)\frac{\pi}{2} \quad \dots(89)$$

and  $\left( \frac{\Delta\omega}{2} \right) t - \left( \frac{\Delta k}{2} \right) x_2 = (2n+1)\frac{\pi}{2} + \pi = (2n+3)\frac{\pi}{2} \quad \dots(90)$

Subtracting Eq. (62) from Eq. (63), we get

$$\begin{aligned} \frac{\Delta k}{2}(x_2 - x_1) &= \pi \\ \text{or } (x_2 - x_1) &= \frac{2\pi}{\Delta k} \quad \text{or} \quad \Delta x = \frac{2\pi}{\Delta k} \end{aligned} \quad \dots(91)$$

This is the fundamental error in the measurement of the position of the particle.

We know that propagation constant,

$$k = \frac{2\pi}{\lambda} = 2\pi \frac{p_x}{h} \quad \left[ \because \lambda = \frac{h}{p_x} \right] \quad \dots(92)$$

If  $\Delta p_x$  is the momentum of the particle along  $x$ -axis and  $h$  is Planck's constant, then

$$\Delta k = 2\pi \left( \frac{\Delta p_x}{h} \right) \quad \dots(93)$$

where  $\Delta p_x$  is fundamental error in the measurement of the momentum of particle.

Substituting the value of  $\Delta k$  from Eq. (93) in the Eq. (91), we get

$$\Delta x = \frac{2\pi}{2\pi(\Delta p_x/h)} = \frac{h}{\Delta p_x} \quad \dots(94)$$

According to Fourier analysis, the width  $\Delta x$  of a single wave represents the superposition of waves whose propagation constants vary in the range  $\Delta k$ .

It is given by

$$\Delta x = \frac{1}{\Delta k} \quad \text{or} \quad \Delta k = \frac{1}{\Delta x} \quad \dots(95)$$

Equation (95) is obeyed for superposition of only two wave trains. Hence Eq. (94) is also valid for a superposition of wave trains. Comparing Eqs. (93) and (95), we get

$$\frac{1}{\Delta x} = 2\pi \left( \frac{\Delta p_x}{\hbar} \right)$$

or

$$\Delta x \Delta p_x = \frac{\hbar}{2\pi} = \hbar \approx h \quad \dots(96)$$

If wave packets have shapes different from that visualised in Fig. 7.14, then the sign of equality is replaced by the sign  $\geq$

$$\Delta x \Delta p_x \geq h$$

Hence it proves the uncertainty principle.

### 7.12.3 Uncertainty Principle in Terms of Energy and Time

Let us consider a photon of energy  $E$  and momentum  $p (= E/c)$ . Let it cover the distance  $x$  in time  $t$  with speed  $c$ , then we have

$$x = ct \quad \dots(97)$$

In terms of uncertainty, this relation can be written as

$$\Delta x = c \Delta t \quad \dots(98)$$

Also, the uncertainty in momentum of the photon is

$$\Delta p = \frac{\Delta E}{c} \quad \dots(99)$$

According to Heisenberg's uncertainty principle, we know that

$$\Delta p \Delta x = \frac{\hbar}{2} \quad \dots(100)$$

Using Eqs. (98), (99) and (100), we get

$$\frac{\Delta E}{c} c \Delta t = \frac{\hbar}{2}$$

or

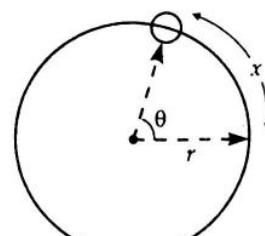
$$\Delta E \Delta t \approx \frac{\hbar}{2} \quad \dots(101)$$

This is uncertainty principle in terms of energy and time.

### 7.12.4 Uncertainty Principle in Terms of Angular Momentum and Angular Displacement

Let us consider, the motion of an electron having momentum  $p$  in an atomic orbit of radius  $r$  as shown in Fig. 7.16.

Let  $\theta$  be its angular displacement corresponding to linear displacement  $x$ .



**Fig. 7.16** Motion of an electron in an atomic orbit.

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Fig. 7

Then, we have

$$\theta = \frac{x}{r} \quad \left[ \because \text{angle} = \frac{\text{arc}}{\text{radius}} \right]$$

In terms of uncertainty, this relation can be written as

$$\Delta\theta = \frac{\Delta x}{r}$$

or

$$\Delta x = r\Delta\theta \quad \dots(102)$$

The angular momentum of electron is given by

$$L = mv r = pr \quad [\because p = mv]$$

i.e.,

$$\Delta L = \Delta pr$$

i.e.,

$$\Delta p = \frac{\Delta L}{r} \quad \dots(103)$$

According to Heisenberg's uncertainty principle, we know that

$$\Delta p \Delta x \approx \frac{\hbar}{2} \quad \dots(104)$$

Using Eqs. (102), (103) and (104), we get

$$\frac{\Delta L}{r} r \Delta\theta \approx \frac{\hbar}{2}$$

or

$$\Delta L \Delta\theta \approx \frac{\hbar}{2} \quad \dots(105)$$

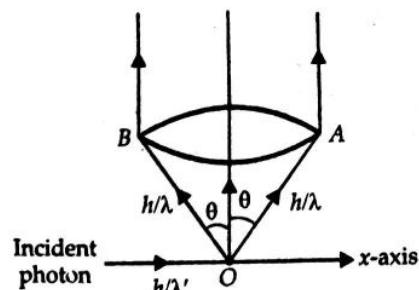
This is the uncertainty principle in terms of angular momentum and angular displacement.

#### 7.12.5 Experimental Proof of the Uncertainty Principle

The validity of Heisenberg's uncertainty principle may be illustrated by following hypothesis experiment.

##### (i) Determination of Position of a Particle by a Microscope

Let us consider a process, where a particle, say an electron, is being observed by a microscope (Fig. 7.17). The minimum distance between two points which can be distinguished as separate by the microscope is given by



**Fig. 7.17** Position of a particle by a Microscope

$$\Delta x = \frac{\lambda}{2 \sin \theta} \quad \dots(106)$$

Hence it represents the error or uncertainty in the measurement of position of the particle.

Now in order that the electron may be seen through the microscope, the incident photon must be scattered by the electron into the microscope objective. During scattering the electron recoils and suffers a change in

momentum. Let the incident photon has a wavelength  $\lambda'$  and hence a momentum  $h/\lambda'$ . It will scatter into the microscope with increased wavelength  $\lambda$  anywhere between OA and OB. In case it enters along OA, its momentum along x-axis is given by  $\frac{h}{\lambda'} \sin \theta$ . Hence the loss of momentum of the photon or the momentum imparted to the electron in the x-direction.

$$= \frac{h}{\lambda'} - \frac{h}{\lambda} \sin \theta \quad \dots(107)$$

If the scattered photon enters the microscope along OB, then the momentum imparted to the electron along x-direction

$$\begin{aligned} &= \frac{h}{\lambda'} - \left( -\frac{h}{\lambda} \sin \theta \right) \\ &= \frac{h}{\lambda'} + \frac{h}{\lambda} \sin \theta \end{aligned} \quad \dots(108)$$

The momentum imparted to the electron can thus have any value between those given by Eqs. (107) and (108). Thus the error or the uncertainty in the measurement of momentum of the electron.

$$\begin{aligned} \Delta p &= \left( \frac{h}{\lambda'} + \frac{h}{\lambda} \sin \theta \right) - \left( \frac{h}{\lambda'} - \frac{h}{\lambda} \sin \theta \right) \\ &= \frac{2h}{\lambda} \sin \theta \end{aligned} \quad \dots(109)$$

Multiplying Eqs. (106) and (109),

$$\Delta p \cdot \Delta x = \frac{\lambda}{2 \sin \theta} \cdot \frac{2h}{\lambda} \sin \theta = h \Rightarrow \Delta p \cdot \Delta x = h \quad \dots(110)$$

This is in accordance with Heisenberg's uncertainty principle.

### (ii) Diffraction of an Electron Beam by a Single Slit

Consider a narrow beam of electrons of momentum  $p$  passing through a narrow slit of width  $\Delta y$  (Fig. 7.18). Since the electron must pass through the slit, the width of the slit,  $\Delta y$  is a measure of uncertainty in the position of electron. Diffraction will occur and the diffraction pattern will be produced on screen as shown in Fig. 7.18. If we assume that the screen is enough far away relative to the width of the slit, the first minimum of the Fraunhofer diffraction pattern is obtained by putting  $n=1$  in the equation ( $d \sin \theta = n\lambda$ ) describing the diffraction pattern due to single slit.

Thus,  $\Delta y \sin \theta = \lambda$

$$\text{or } \Delta y = \frac{\lambda}{\sin \theta} \quad \dots(111)$$

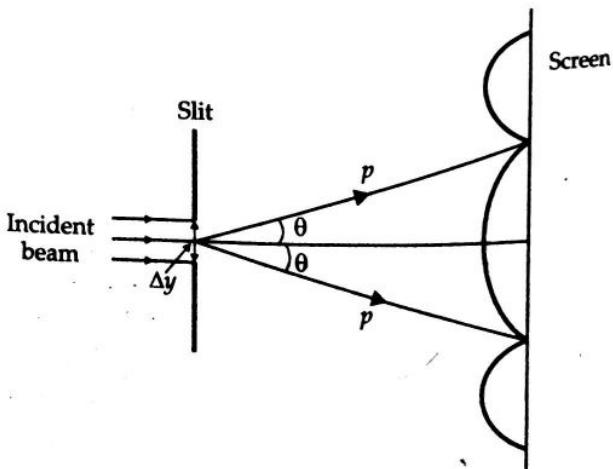


Fig. 7.18 Diffraction by a single slit.

The moving electrons in the beginning have no component of momentum along  $y$ -axis, since they are moving along  $x$ -axis. But at the slit, they deviate from their original path to form a pattern on the screen and hence have a component of momentum  $p \sin \theta$  in the  $y$ -direction. Now as the electron may be anywhere within the pattern from angle  $-\theta$  to  $+\theta$ , the  $y$ -component of momentum of electron may lie anywhere between  $p \sin \theta$  and  $-p \sin \theta$ . Obviously, the uncertainty in the  $y$ -component of the momentum of electron is

$$\begin{aligned}\Delta p_y &= p \sin \theta - (-p \sin \theta) = 2p \sin \theta \\ &= 2 \frac{\hbar}{\lambda} \sin \theta\end{aligned}\quad \dots(112)$$

Multiplying Eqs. (111) and (112), we have

$$\Delta y \Delta p_y = \frac{\lambda}{\sin \theta} \cdot \frac{2\hbar}{\lambda} \sin \theta = 2\hbar \Rightarrow \Delta y \Delta p_y = 2\hbar$$

which is good agreement with uncertainty principle.

#### 7.12.6 Applications of Heisenberg's Uncertainty Principle

Many phenomena can be understood in terms of the uncertainty principle. A few of them are discussed here.

##### (i) Non-existing of Free Electrons in the Nucleus

According to theory of relativity, energy of a particle is given by the relation

$$E = mc^2 = \frac{m_0 c^2}{\sqrt{1 - \frac{v^2}{c^2}}} \quad \dots(113)$$

where  $m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$  is called relativistic mass and  $m_0 c^2$  is called rest energy of particle

(electron) whose mass at rest is  $m_0$ .

Squaring Eq. (113), we get

$$E^2 = \frac{m_0^2 c^4}{\left(1 - \frac{v^2}{c^2}\right)} = \frac{m_0^2 c^6}{c^2 - v^2} \quad \dots(114)$$

We know the momentum  $p = mv$

$$= \frac{m_0 v}{\sqrt{1 - \frac{v^2}{c^2}}} \quad \dots(115)$$

Squaring, we get

$$p^2 = \frac{m_0^2 v^2}{\left(1 - \frac{v^2}{c^2}\right)} = \frac{m_0^2 v^2 c^2}{(c^2 - v^2)} \quad \dots(116)$$

Multiplying, Eq. (116) by  $c^2$ , we get

$$p^2 c^2 = \frac{m_0^2 v^2 c^4}{(c^2 - v^2)} \quad \dots(117)$$

Subtracting Eq. (117) from Eq. (113), we get

$$\begin{aligned} E^2 - p^2 c^2 &= \frac{m_0^2 c^6}{c^2 - v^2} - \frac{m_0^2 v^2 c^4}{c^2 - v^2} \\ &= \frac{m_0^2 c^4 (c^2 - v^2)}{c^2 - v^2} = m_0^2 c^4 \end{aligned}$$

or

$$E^2 = p^2 c^2 + m_0^2 c^4 \quad \dots(118)$$

According to Heisenberg's uncertainty principle,

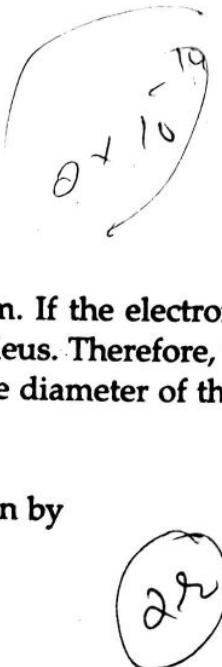
$$\Delta x \Delta p_x = \frac{h}{2\pi} \quad \dots(119)$$

The diameter of the nucleus is of the order of  $10^{-14}$  m. If the electron exists in the nucleus, it can be anywhere within the diameter of the nucleus. Therefore, the maximum uncertainty  $\Delta x$  in the position of electron is the same as the diameter of the nucleus.

i.e.,  $\Delta x = 10^{-14}$  m

$\therefore$  The minimum uncertainty in the momentum is given by

$$\begin{aligned} \Delta p_x &= \frac{h}{2\pi\Delta x} \\ &= \frac{6.63 \times 10^{-34}}{2\pi \times 10^{-14}} = \frac{6.63 \times 10^{-20}}{2\pi} \\ &= 1.055 \times 10^{-20} \text{ kg m/sec.} \end{aligned}$$



It means that if electron exists in the nucleus, its minimum momentum must be

$$p_{\min} = 1.055 \times 10^{-20} \text{ kg m/s}$$

For the electron of the minimum momentum, the minimum energy is given by

$$\begin{aligned} E_{\min}^2 &= p_{\min}^2 c^2 + m_0^2 c^4 \\ &= (1.055 \times 10^{-20} \times 3 \times 10^8)^2 + (9.1 \times 10^{-31})^2 (3 \times 10^8)^4 \\ &= (3 \times 10^8)^2 [1.113 \times 10^{-40} + 7.4692 \times 10^{-44}] \end{aligned}$$

Since the second term in the bracket is much smaller than the first, it can be neglected, then,

$$\begin{aligned} E_{\min} &= 3 \times 10^8 \sqrt{1.113 \times 10^{-40}} \text{ J} \\ &= 3 \times 10^8 \times 1.055 \times 10^{-20} \text{ J} = 3.1649 \times 10^{-12} \text{ J} \\ \text{or } E_{\min} &= \frac{3.1649 \times 10^{-12}}{1.6 \times 10^{-19}} \text{ eV} \approx 20 \text{ MeV.} \end{aligned}$$

Thus, if a free electron exists in the nucleus it must have a minimum energy of about 20 MeV.

The maximum K.E. which a  $\beta$ -particle, emitted from radioactive nuclei is of the order of 4 MeV. Therefore, this clearly shows that electrons can not be present within the nucleus.

### (ii) Spectral Lines have a Finite Width

The average period that takes between the excitation of an atom and the time it radiates is  $10^{-8}$  s. Thus the photon energy is uncertain by the amount

$$\Delta E = \frac{h}{\Delta t} = \frac{6.6 \times 10^{-34} \text{ Js}}{10^{-8} \text{ s}} = 6.6 \times 10^{-26} \text{ J}$$

It means that excited energy levels have a finite energy spread. Thus when atoms fall back an excited level to ground level, the radiations emitted are not truly monochromatic.

Thus the energy levels of the atom must have a finite width or in other words the spectral lines can never be sharp but have a natural finite width.

### (iii) Radius of Bohr's First Orbit

If  $\Delta x$  and  $\Delta p$  are the uncertainty in determining the position and momentum of electron in Bohr's first orbit.

$$\text{Then, } \underbrace{\Delta x \Delta p}_{\approx \hbar} \quad \text{or} \quad \underbrace{\Delta p}_{\approx \frac{\hbar}{\Delta x}}$$

Now kinetic energy,

$$K = \frac{1}{2} mv^2 = \frac{m^2 v^2}{2m} = \frac{p^2}{2m}$$

Therefore, uncertainty in K.E.

$$\Delta K = \frac{(\Delta p)^2}{2m} = \frac{\hbar^2}{2m(\Delta x)^2} \quad \text{where } \hbar = \frac{h}{2\pi}$$

Then uncertainty in P.E. of same electron,

$$\Delta V = \frac{1}{4\pi\epsilon_0} \frac{(Ze)(-e)}{\Delta x} = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{\Delta x}$$

Therefore, uncertainty in total energy,

$$\Delta E = \Delta K + \Delta V = \frac{\hbar^2}{2m(\Delta x)^2} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{\Delta x}$$

The value of energy  $E$  in fundamental state is minimum and the uncertainty in energy will be minimum when

$$\begin{aligned} & \frac{d(\Delta E)}{d(\Delta x)} = 0 \\ \text{i.e., } & -\frac{\hbar^2}{m(\Delta x)^3} + \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{(\Delta x)^2} = 0 \\ \Rightarrow & \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{(\Delta x)^2} = \frac{\hbar^2}{m(\Delta x)^3} \\ \therefore & \Delta x = 4\pi\epsilon_0 \cdot \frac{\hbar^2}{mZe^2} \end{aligned}$$

Therefore, radius of first Bohr orbit,

$$\begin{aligned} r = \Delta x &= 4\pi\epsilon_0 \frac{\hbar^2}{mZe^2} = 4\pi\epsilon_0 \frac{\left(\frac{\hbar}{2\pi}\right)^2}{mZe^2} \\ r &= \frac{\epsilon_0 \hbar^2}{\pi m Ze^2} \end{aligned} \quad \dots(120)$$

#### (iv) Zero Point Energy of a Simple Harmonic Oscillator

Consider a particle of mass  $m$  executing simple harmonic motion with angular frequency  $\omega$ . Let  $x$  be the displacement of the particle from its mean position and  $p$  is its momentum. The expression for its total energy at this position is

$$E = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \quad \dots(121)$$

Let  $a$  be the amplitude of oscillation, i.e.,  $x_{\max} = a$ . The separation between two extreme positions on its path is  $2a$ .

Hence, the maximum uncertainty in position is given by

$$(\Delta x)_{\max} = 2a$$

The minimum uncertainty in momentum is given by

$$(\Delta p_x)_{\max} = \frac{\hbar}{(\Delta x)_{\max}} = \frac{\hbar}{2a}$$

The momentum ( $p$ ) of the oscillator cannot be smaller than  $(\Delta p_x)_{\max}$ . Then we have

$$p_{\min} = \frac{\hbar}{2a}$$

For a macroscopic body in simple harmonic motion, it is observed that the kinetic energy ( $K$ ) reaches its lowest value when the potential energy ( $U$ ) attains its maximum value. So the total energy ( $E$ ) can be expressed as,

$$\begin{aligned} E &= (K)_{\min} + (U)_{\max} \\ &= \frac{p_{\min}^2}{2m} + \frac{1}{2} m\omega^2 x_{\max}^2 = \frac{1}{2m} \left( \frac{\hbar}{2a} \right)^2 + \frac{1}{2} m\omega^2 a^2 \\ \text{or } E &= \frac{\hbar^2}{8ma^2} + \frac{1}{2} m\omega^2 a^2 \end{aligned} \quad \dots(122)$$

Equation (122) expresses the total energy as a function of amplitude  $a$ . The total energy has its minimum value at a certain value of  $a$ . Let  $a = \alpha$  be the amplitude of the oscillator when its total energy remains its minimum value. The following conditions must be satisfied :

$$(i) \left( \frac{dE}{da} \right)_{a=\alpha} = 0 \quad \text{and} \quad (ii) \left( \frac{d^2E}{da^2} \right)_{a=\alpha} > 0$$

Applying condition (i), we get

$$\alpha^2 = \frac{\hbar}{2m\omega} \quad \dots(123)$$

It can be easily shown that this value satisfies condition (ii).

Substituting  $a^2 = \alpha^2 = \frac{\hbar}{2m\omega}$  in Eq. (122), the lowest possible value of total energy ( $E_{\min}$ ) is obtained as

$$E_{\min} = \frac{1}{2} \hbar \omega = \frac{1}{2} \frac{\hbar}{2\pi} 2\pi\nu = \frac{1}{2} h\nu \quad \dots(124)$$

Advanced quantum mechanical calculations show that the total energy is given by

$$E_n = \left( n + \frac{1}{2} \right) h\nu \quad \dots(125)$$

where  $n = 0, 1, 2, 3, \dots$

This is correct expression for the total energy of a simple harmonic oscillator.

For  $n=0$ , the system has the minimum energy, which is  $E_0 = \frac{1}{2} h\nu$ . This value is known as the zero point energy of a simple harmonic oscillator.

**Example 7.11.** Find the smallest possible uncertainty in position of the electron moving with velocity  $3 \times 10^7$  m/s (Given  $\hbar = 6.63 \times 10^{-34}$  Js,  $m_0 = 9.1 \times 10^{-31}$  kg).

**Solution.** Given  $v = 3 \times 10^7$  m/s

Let  $\Delta x_{\min}$  be the minimum uncertainty in position of the electron and  $\Delta p$  the maximum uncertainty in the momentum of the electron.

Thus we have,

$$\Delta x_{\min} \cdot \Delta p_{\max} = \frac{h}{2\pi} \quad \dots(i)$$

or

$$\Delta p_{\max} = p = mv$$

$$\Delta p_{\max} = \frac{m_0 v}{\sqrt{\left(1 - \frac{v^2}{c^2}\right)}} \quad \dots(ii)$$

$$\Delta x_{\min} = \frac{h \sqrt{\left(1 - \frac{v^2}{c^2}\right)}}{2\pi m_0 v}$$

$$\begin{aligned} &= \frac{6.63 \times 10^{-34}}{2 \times 3.14 \times 9.1 \times 10^{-31}} \sqrt{1 - \left(\frac{3 \times 10^7}{3 \times 10^8}\right)^2} \text{ m} \\ &= 0.03867 \times 0.9949 \times 10^{-10} \text{ m} = 3.8 \times 10^{-12} \text{ m} \end{aligned}$$

**Example 7.12.** A microscope, using photons, is employed to locate an electron in an atom within a distance of  $0.2 \text{ \AA}$ . What is the uncertainty in the momentum of the electron located in this way?

**Solution.** Given  $\Delta x = 0.2 \text{ \AA} = 2 \times 10^{-11} \text{ m}$ ;  $\Delta p = ?$

Since we know that the uncertainty principle

$$\Delta x \Delta p \approx \frac{h}{2\pi} \quad \text{or} \quad \Delta p = \frac{h}{2\pi \Delta x}$$

$$\therefore \Delta p = \frac{6.626 \times 10^{-34}}{2 \times 3.14 \times (0.2 \times 10^{-10})} = 5.27 \times 10^{-24} \text{ kg ms}^{-1}$$

Hence uncertainty in momentum ( $\Delta p$ ) =  $5.27 \times 10^{-24} \text{ kg ms}^{-1}$

### 7.13 WAVE FUNCTION

As we know, the height of water surface varies periodically in water waves, the pressure of gas varies periodically in sound waves and the electric and magnetic fields vary periodically in light waves but what is the quantity which varies periodically in case of matter waves?

Answer is **wave function**, the quantity whose variations make up the matter waves. So the amplitude of matter wave is described by wave function, represented by a Greek letter  $\psi$  consists of real and imaginary parts :

$$\psi = A + iB$$

Conjugate of  $\psi$  is  $\psi^* = A - iB$   
and  $|\psi^*|^2 = |\psi|^2 = A^2 + B^2$   $[\because i^2 = -1]$

$|\psi|^2$  at a particular place at a particular time is proportional to the probability of finding the particle there at that time.

$$\therefore \text{Probability density} = |\psi|^2 = \psi^* \psi$$

Let us assume that wavefunction  $\psi$  is specified in  $x$ -direction by a wave equation

$$\psi = Ae^{-i\omega(t-\frac{x}{v})}$$

where  $\omega = 2\pi v$  and  $v = \lambda$

$$\therefore \psi = Ae^{-2\pi(vt-\frac{x}{\lambda})} \quad \dots(126)$$

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

Putting the values of  $E$  and  $\lambda$  in Eq. (126), we get

$$\psi = Ae^{-\frac{i}{\hbar}(Et-px)} \quad \dots(127)$$

Equation (127) is the wave equation for a free particle.

Partially differentiate Eq. (127) with respect to  $t$ , we get

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= -\frac{iE}{\hbar} Ae^{-\frac{i}{\hbar}(Et-px)} \\ &= -\frac{iE}{\hbar} \psi \end{aligned}$$

$$\text{or } E\psi = i\hbar \frac{\partial \psi}{\partial t} \quad [i^2 = -1] \quad \dots(128)$$

$$\text{Here Energy operator } E = i\hbar \frac{\partial}{\partial t} \quad \dots(129)$$

Now, partially differentiate Eq. (127), with respect to  $x$ , we get

$$\frac{\partial \psi}{\partial x} = \frac{ip}{\hbar} Ae^{-\frac{i}{\hbar}(Et-px)}$$

$$\text{or } \frac{\partial \psi}{\partial x} = \frac{ip}{\hbar} \psi$$

$$\text{or } p\psi = \frac{\hbar}{i} \frac{\partial \psi}{\partial x} \quad \dots(130)$$

$$\text{Hence, Momentum operator } p = \frac{\hbar}{i} \frac{\partial}{\partial x} = -i\hbar \frac{\partial}{\partial x} \quad \dots(131)$$

An operator tells us what operation to carry out on the quantity that follows it.

The operator  $i\hbar \frac{\partial}{\partial t}$  (as Eq. (129)) instructs us to take partial derivative of what comes after it with respect to  $t$  and multiply the result by  $i\hbar$ .

From Eq. (129), consider the eigen-value equation.

$$i\hbar \frac{\partial \psi}{\partial t} = E\psi$$

Hence,  $\psi$  is said to be *eigen function* of the operator  $i\hbar \frac{\partial}{\partial t}$  and  $E$  is called the corresponding *energy eigen value*.

### 7.13.1 Requirements that are Imposed on a Physically Acceptable Wave Function or Properties of the Wave Function

1.  $\psi$  must be single valued, finite and continuous for all values of  $x$ .
2.  $\frac{\partial \psi}{\partial x}$ ,  $\frac{\partial \psi}{\partial y}$  and  $\frac{\partial \psi}{\partial z}$  must be finite and continuous for all values of  $x$ ,  $y$  and  $z$  respectively, except at those points where  $V \rightarrow \infty$ . At these points  $\frac{\partial \psi}{\partial x}$ ,  $\frac{\partial \psi}{\partial y}$  and  $\frac{\partial \psi}{\partial z}$  have a finite discontinuity but  $\psi$  remains continuous.
3.  $\psi$  must be normalised, which means that  $\psi$  must go to zero as  $x \rightarrow \pm\infty$ ,  $y \rightarrow \pm\infty$ ,  $z \rightarrow \pm\infty$  in order that  $\int |\psi|^2 dV$  overall space be a finite constant.

If  $\int_{-\infty}^{+\infty} |\psi|^2 dV = 0$  i.e., the particle does not exist but  $|\psi|^2$  overall space must be finite i.e., the body is to be somewhere.

$$\therefore \int_{-\infty}^{+\infty} |\psi|^2 dV \neq 0, \infty, -ve \text{ or complex } [\text{which is not possible}]$$

Therefore only possibility left is that integral be a finite quantity.

### Normalization

Normalization condition is

$$\therefore \int_{-\infty}^{+\infty} |\psi|^2 dV = 1 \quad \dots(132)$$

[Wave functions which satisfy this condition [Eq. (132)] are said to be normalized]

As  $|\psi|^2 = \psi \psi^* \psi = \text{probability density} = P$

Therefore, probability between the limits  $x_1$  and  $x_2$  is given as in one-dimensional case.

**Probability**

$$P_{x_1 x_2} = \int_{x_1}^{x_2} |\psi|^2 dx$$

...(133)

**Expectation Value**

To correlate experiment and theory we define the expectation value of any parameter :

$$\langle x \rangle = \frac{\int_{-\infty}^{+\infty} x |\psi|^2 dx}{\int_{-\infty}^{+\infty} |\psi|^2 dx} = \frac{\int_{-\infty}^{+\infty} \psi^* x \psi dx}{\int_{-\infty}^{+\infty} \psi^* \psi dx}$$

If  $\psi$  is a normalised wave function, then  $\int_{-\infty}^{+\infty} \psi^* \psi dx = 1$ .

$$\therefore \langle x \rangle = \int_{-\infty}^{+\infty} x |\psi|^2 dx$$

...(134)

**Orthogonal Wave Functions**

If  $\psi_a$  and  $\psi_b$  are the wave functions such that

$$\int \psi_a^* \psi_b dV = 0 \quad \text{or} \quad \int \psi_b^* \psi_a dV = 0 \quad \text{for } a \neq b. \quad \dots(135)$$

then the wave functions  $\psi_a$  and  $\psi_b$  are known as **orthogonal** to each other. The wave functions which satisfy normalisation condition i.e.,

$$\int \psi_a^* \psi_a dV = 1 \quad \dots(136)$$

and orthogonality condition Eq. (135) are called **orthonormal functions** and condition for orthonormality is

$$\int \psi_a^* \psi_b dV = \delta_{ab} \quad \dots(137)$$

where  $\delta_{ab}$  = kronecker delta function, it is defined as

$$\begin{aligned} \delta_{ab} &= 0 & \text{if } a \neq b \\ &= 1 & \text{if } a = b \end{aligned}$$

**Example 7.13.** A particle limited to the x-axis has the wave function  $\psi = ax$  between  $x = 0$  and  $x = 1$ ,  $\psi = 0$  elsewhere. Find (a) the probability that particle can be found between  $x = 0.45$  and  $x = 0.55$ .  
(b) The expectation value  $\langle x \rangle$  of the particle's position.

**Solution.** (a) The probability is

$$\int_{x_1}^{x_2} |\psi|^2 dx = a^2 \int_{0.45}^{0.55} x^2 dx = a^2 \left[ \frac{x^3}{3} \right]_{0.45}^{0.55} = 0.0251 a^2$$

(b) The expectation value is

$$\langle x \rangle = \int_0^1 x |\psi|^2 dx = a^2 \int_0^1 x^3 dx = a^2 \left[ \frac{x^4}{4} \right]_0^1 = \frac{a^2}{4}$$

**Example 7.14.** The wave function of a particle is given by

$$\psi(x) = Ce^{-\alpha^2 x^2}, \quad -\infty < x < \infty$$

where  $C$  and  $\alpha$  are some constants. Calculate the probability of finding the particle in the region  $0 < x < \infty$ .

**Solution.** The probability of finding the particle in the region  $0 < x < \infty$  is

$$P = \int_0^\infty |\psi(x)|^2 dx = \int_0^\infty C^2 e^{-2\alpha^2 x^2} dx$$

$$[\text{Also from standard integral } \int_0^\infty e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{2}}]$$

$$\text{We get, } P = C^2 \int_0^\infty e^{-2\alpha^2 x^2} dx = \frac{1}{2} C^2 \sqrt{\left(\frac{\pi}{2\alpha^2}\right)}$$

Applying normalising condition i.e.,

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \int_{-\infty}^{\infty} C^2 e^{-2\alpha^2 x^2} dx = 1$$

$$\Rightarrow C^2 \sqrt{\frac{\pi}{2\alpha^2}} = 1$$

$$\text{Which gives } C^2 = \sqrt{\frac{2\alpha^2}{\pi}}$$

$$\therefore P = \sqrt{\frac{2\alpha^2}{\pi}} \frac{1}{2} \sqrt{\frac{\pi}{2\alpha^2}} = \frac{1}{2}$$

**Example 7.15.** Show that functions  $\psi_0 = \left(\frac{b}{4}\right)^{1/4} \exp\left(-\frac{bx^2}{2}\right)$  and  $\psi_1 = \left(\frac{4b^3}{4}\right)^{1/4} \exp\left(-\frac{bx^2}{2}\right)x$  are normalised over the interval  $-\infty < x < \infty$ .

$$\text{Solution. (a)} \int_{-\infty}^{\infty} \psi_0 \psi_0^* dx = \int_{-\infty}^{\infty} \left(\frac{b}{4}\right)^{1/2} \exp(-bx^2) dx$$

$$\text{Let } xb^{1/2} = y; \quad dx = \frac{dy}{\sqrt{b}}$$

$$\text{Now, } \int_{-\infty}^{+\infty} \psi_0 \psi_0^* dx = \int_{-\infty}^{\infty} |\psi_0|^2 dx = 2 \left( \frac{b}{\pi} \right)^{1/2} \int_0^{\infty} \exp(-bx^2) dx \\ = 2 \left( \frac{b}{\pi} \right)^{1/2} \int_0^{\infty} \frac{\exp(-y^2)}{\sqrt{b}} dy = 2 \left( \frac{b}{\pi} \right)^{1/2} \cdot \frac{1}{2} \left( \frac{\pi}{4b} \right)^{1/2} = 1$$

$$(b) \quad \int_{-\infty}^{\infty} \psi_1 \psi_1^* dx = 2 \left( \frac{4b^3}{\pi} \right)^{1/2} \int_0^{\infty} x^2 \exp(-bx^2) dx \quad \left[ \because \int_0^{\infty} x^2 \exp(-\alpha x^2) dx = \frac{1}{4} \sqrt{\frac{\pi}{\alpha^3}} \right]$$

$$\text{We get, } \int_0^{\infty} |\psi|^2 dx = 2 \left( \frac{4b^3}{\pi} \right)^{1/2} \left[ \frac{\pi}{16b^3} \right]^{1/2} = 1$$

### ~~7.13.2 Postulates of Quantum Mechanics~~

#### (i) Description of the System

Every particle (or a system of particles) is represented by a "wave function", which is a function of space coordinates and time. The wave function determines all that can be known about the system it represents.

#### (ii) Time Evolution of a System

The time dependent Schrödinger equation for one-dimensional motion of a particle of mass  $m$  moving in a potential  $V(x, t)$  is given by

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x, t)\psi(x, t) \quad \dots(138)$$

#### (iii) Probabilistic Interpretation of the Wave function

If at any instant  $t$ , a measurement is made to locate the object represented by the wave function  $\psi(x, t)$ , then the probability  $P(x, t)dx$  that the object will be found between  $x$  and  $(x+dx)$ .

$$P(x, t)dx = \psi^*(x, t)\psi(x, t)dx = |\psi(x, t)|^2 dx \quad \dots(139)$$

#### (iv) Description of Physical Quantities

Every physical observable is associated with an operator which acts on the wave function.

#### (v) The Measurement Postulate

The average of the measured value of  $x$  is given by

$$\langle x \rangle = \frac{\int \psi^* x \psi dV}{\int \psi^* \psi dV} = \frac{(\psi, x\psi)}{(\psi, \psi)} \quad \dots(140)$$

$\langle x \rangle$  is known as the expectation value of  $x$ .

### 7.13.3 Physical Significance of Wave Function ( $\psi$ )

$\psi$  can not be interpreted in terms of an experiment. The probability that something be in certain place at a given time must lie between 0 (the object is not definitely there) and 1 (the

object is definitely there). An intermediate probability, say 0.2 means, there is a 20% chance of finding the object. But the amplitude of a wave can be negative as well as positive and negative probability is meaningless. Hence  $\psi$  by itself cannot be an observed quantity. 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. As long as  $|\psi|^2$  is not actually zero somewhere, there is a definite change however small, of detecting it there.

### 7.14 SCHRÖDINGER WAVE EQUATION

So far, we have made a lot of progress concerning the properties and interpretation of the wave function but as yet we have had very little to say about how the wavefunction may be derived in a general situation, that is to say, we do not have on hand a "wave equation" for a wave function. There is no true derivation of this equation, but its form can be motivated by physical and mathematical arguments at a wide variety of levels of sophistication. Here, we will offer a simple derivation based on what we have learned so far about the wavefunction.

The Schrödinger equation has *two forms*, one in which time explicitly appears, and so describes how the wave function of a particle will evolve in time. In general, the wave function behaves like a wave, and so the equation is often referred to as **time dependent Schrödinger wave equation**. The other is the equation in which the time dependence has been "removed" and hence is known as the **time independent Schrödinger's wave equation** and is found to describe amongst other things, what the energies are of the particle.

These are not two separate independent equations – the time independent equation can be derived readily from time dependent equation.

#### 7.14.1 Schrödinger's Time Dependent Wave Equation

Let us assume that  $\psi$  for a particle moving freely in positive  $x$ -direction is

$$\psi = Ae^{-i\omega\left(t-\frac{x}{v}\right)} \quad \dots(141)$$

as

$$\omega = 2\pi v \quad v = v\lambda$$

$$\psi = Ae^{-2\pi i\left(vt-\frac{x}{\lambda}\right)} \quad \dots(142)$$

As  $E = hv = 2\pi\hbar v$  and  $\lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$

$\therefore$  For a free particle wave equation becomes

$$\psi = Ae^{-\frac{i}{\hbar}(Et-px)} \quad \dots(143)$$

As it is calculated in article 7.13 at pages .

$$E\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \text{and} \quad p\psi = \frac{\hbar}{i} \frac{\partial \psi}{\partial x} \quad \dots(a)$$

As total energy,  $E = \text{Kinetic energy (K)} + \text{Potential energy (V)}$  ... (144)

$$\text{Now, K.E.} = \frac{p^2}{2m}$$

$\therefore$  Equation (143) in terms of wave function  $\psi$  can be written as

$$E\psi = \left( \frac{p^2}{2m} \right) \psi + V\psi \quad \dots (145)$$

Putting the values of  $E\psi$  and  $P\psi$  from Eq. (a) in Eq. (145), we have

$$i\hbar \frac{\partial \psi}{\partial t} = \left( \frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 \frac{1}{2m} \psi + V\psi$$

or

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi \quad \dots (146)$$

Equation (146) is Schrödinger's time dependent wave equation in one-dimension.

The time dependent Schrödinger's equation in three-dimensional form,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \left[ \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right] + V\psi \quad \dots (147)$$

or

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \quad \left[ \because \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad \dots (148)$$

or

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \dots (149)$$

or

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi = i\hbar \frac{\partial \psi}{\partial t} \quad \dots (150)$$

Equation (150) contains time and hence is called time dependent Schrödinger equation.

The operator  $\left( -\frac{\hbar^2}{2m} \nabla^2 + V \right)$  is called Hamiltonian and is represented by  $H$ ; while operator  $i\hbar \frac{\partial}{\partial t}$ , operated on  $\psi$ , gives  $E$  which may be seen by Eq. (147). Equation (150) may be written as

$$H\psi = E\psi$$

The above forms of the Schrödinger's equation describe the motion of a non-relativistic material particle.

#### 7.14.2 Schrödinger's Time Independent Wave Equation

Again consider Eq. (141),

$$\psi = A e^{-\frac{i}{\hbar}(Et - px)} = A e^{-\frac{i}{\hbar}Et} \cdot e^{\frac{i}{\hbar}px}$$

or

$$\psi = \psi_0 e^{-\frac{i}{\hbar}Et} \quad \dots (151)$$

Differentiate partially with respect to  $t$ , we get

$$\frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar} \psi_0 e^{-\frac{iEt}{\hbar}} \quad \dots(152)$$

Equation (151), partially differentiated with respect to  $x$  twice, we get

and  $\frac{\partial^2 \psi}{\partial x^2} = +\frac{\partial^2 \psi_0}{\partial x^2} e^{-\frac{iEt}{\hbar}}$  ... (153)

Putting Eqs. (151), (152) and (153) in Eq. (150), we get

$$\begin{aligned} i\hbar \frac{\partial \psi}{\partial t} &= -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi \\ i\hbar \left(-\frac{iE}{\hbar}\right) \psi_0 e^{-\frac{iEt}{\hbar}} &= -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_0}{\partial x^2} e^{-\frac{iEt}{\hbar}} + V\psi_0 e^{-\frac{iEt}{\hbar}} \\ \Rightarrow E\psi_0 &= -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_0}{\partial x^2} + V\psi_0 \end{aligned} \quad \dots(154)$$

or  $\frac{\partial^2 \psi_0}{\partial x^2} + \frac{2m}{\hbar^2}(E-V)\psi_0 = 0$  ... (155)

This is Schrodinger's time independent wave equation in one-dimension.

In three-dimensional case, Eq. (155) will be of the form as

$$\nabla^2 \psi_0 + \frac{2m}{\hbar^2}(E-V)\psi_0 = 0 \quad \dots(156)$$

where  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

### 7.14.3 Eigen Values and Eigen Functions

Consider an operator, which has a special property such that when it is operating on a function it produces a constant multiplied by that function. Then the function is said to be an *Eigen function*. The various possible values of the constant value are said to be *Eigen values*. The equation is said to be an *Eigen value equation*.

Consider the equation

$$\frac{d^2}{dt^2} (\sin \omega t) = -\omega^2 (\sin \omega t)$$

where  $\frac{d^2}{dt^2}$  is the operator,  $\sin \omega t$  is the function and  $-\omega^2$  is the constant value. Similarly, the

equation  $H\psi = E\psi$  has a special property. The Hamiltonian operator,  $H$  operating on the wave function produces another wave function  $\psi$  multiplied by a constant  $E$ . Such equation is called *eigen value equation*. The wave function  $\psi_1, \psi_2$  and  $\psi_3$  are called *eigen functions* and the energy value  $E_1, E_2, E_3$ , are called *eigen values*.

## 7.15 APPLICATIONS OF SCHRÖDINGER'S WAVE EQUATION

### 7.15.1 The Free Particle

When a particle is not subjected to any external force, so that it moves in a region in which its potential energy is constant, it is said to be a free particle. Such a particle has a definite value of total energy and definite value of momentum. But the position of the particle is completely unknown.

Suppose a particle of mass  $m$  is in motion along the  $x$ -axis. Suppose no force is acting on the particles so that the potential energy of the particle is constant. For convenience, the constant potential energy is taken to be zero i.e.,  $V=0$ .

Hence Schrödinger equation becomes,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad \dots(157)$$

$$\text{or } \frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{\hbar^2} E \psi = 0 \quad \dots(158)$$

Multiplying by  $\frac{\hbar^2}{8\pi^2 m}$  throughout, we get

$$\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2 \psi}{\partial x^2} + E \psi = 0 \quad \text{or} \quad \frac{-\hbar^2}{8\pi^2 m} \frac{\partial^2 \psi}{\partial x^2} = E \psi \quad \dots(159)$$

Since the particle is moving freely with zero potential energy its total energy  $E$  is the kinetic energy, given by

$$E = \frac{p_x^2}{2m} \quad \dots(160)$$

where  $p_x$  is the momentum of the particle,

Rewriting Eq. (159),

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{\hbar^2} E \psi = 0 \quad \text{or} \quad \frac{\partial^2 \psi}{\partial x^2} + K^2 \psi = 0 \quad \dots(161)$$

$$\text{where } K^2 = \frac{8\pi^2 m E}{\hbar^2}$$

So that,

$$E = \frac{K^2 \hbar^2}{8\pi^2 m} \quad \dots(162)$$

In this case energy  $E$  is not quantised. Hence when a particle is not bound in a system it does not have quantised energy state.

### 7.15.2 Particle in Box (Infinite Square Well Potential)

Consider a particle moving inside a box along the  $x$ -direction. The particle is bouncing back and forth between the walls of the box  $a$  is the width of the box as shown in Fig. 7.19.

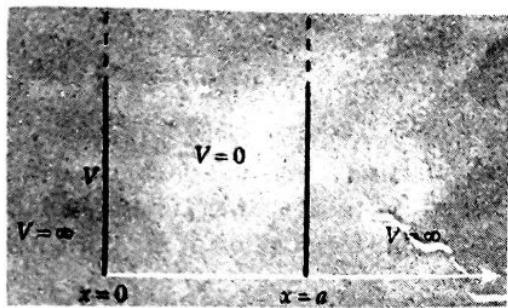


Fig. 7.19 Particle in box.

The potential energy  $V$  of the particle is infinite on both sides of the box.

$$V = 0 \text{ for } 0 < x < a$$

$$V = \infty \text{ for } x \leq 0 \text{ and } x \geq a$$

The particle can not exist outside the box, so its wave function  $\psi$  is 0 for  $x \leq 0$  and  $x \geq a$ .

Within the box, the Schrödinger's equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad [:\ V \text{ is 0 for the free particle}] \quad \dots(163)$$

$$\Rightarrow \frac{d^2\psi}{dx^2} + K^2\psi = 0 \quad \text{where } K = \sqrt{\frac{2mE}{\hbar}} \quad \dots(164)$$

The general solution of this equation is

$$\psi = A\sin Kx + B\cos Kx$$

Using boundary conditions

$$\psi = 0 \text{ at } x = 0$$

$$0 = A\sin 0 + B$$

$$B = 0$$

and

$$\psi = 0 \text{ at } x = a$$

$$0 = A\sin Ka$$

$$\sin n\pi = \sin Ka$$

$$K = \frac{n\pi}{a}$$

Wave function,  $\psi_n(x) = A\sin \frac{n\pi x}{a}$  where  $n = 1, 2, 3, \dots$  ... (165)

Energy level,  $E_n = \frac{K^2 \hbar^2}{2m} \quad \left[ \hbar = \frac{h}{2\pi} \right]$

$\therefore$  Eigen value  $E_n = \left(\frac{n\pi}{a}\right)^2 \left(\frac{h}{2\pi}\right)^2 \frac{1}{2m}$

$$E_n = \frac{n^2 h^2}{8ma^2} \quad \text{where } n = 1, 2, 3, 4, \dots \quad \dots(166)$$

Therefore, it is clear from Eq. (166) that inside an infinitely deep potential well (or in an infinite square well), the particle cannot have an arbitrary energy, but can have only certain discrete energy corresponding to  $n = 1, 2, 3, \dots$ . Each permitted energy level energy is called *eigen-value* of the particle and constitutes the energy level of the system. The wave function  $\psi$  corresponding to each eigen value are called *eigen functions*.

To find eigen-functions of the particle using Eq. (165) and applying normalisation condition,

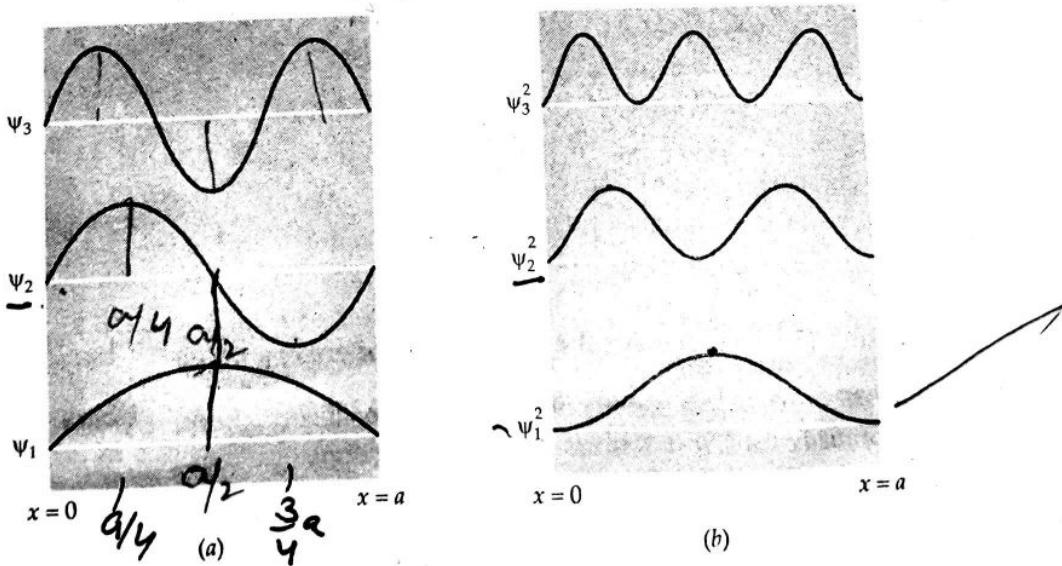
$$\begin{aligned} & \int_{-\infty}^{+\infty} |\psi_n(x)|^2 dx = 1 \\ \Rightarrow & \int_0^a |\psi_n(x)|^2 dx = 1 \\ \Rightarrow & A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1 \\ \Rightarrow & \frac{A^2}{2} \int_0^a \left[1 - \cos\left(\frac{2n\pi x}{a}\right)\right] dx = 1 \\ \Rightarrow & \frac{A^2}{2} \left[ \int_0^a dx - \int_0^a \cos\left(\frac{2n\pi x}{a}\right) dx \right] = 1 \\ \Rightarrow & \frac{A^2}{2} [a] = 1 \quad \Rightarrow \quad A = \sqrt{\left(\frac{2}{a}\right)} \end{aligned}$$

$\therefore$  Eigen function

$$\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \quad \text{where } n = 1, 2, 3, \dots \quad \text{...(167)}$$

*Sin (y)*

Although  $\psi_n$  may be negative as well as positive,  $|\psi_n|^2$  is always positive and since  $\psi_n$  is normalised, its square value at a given  $x$  is equal to the probability of finding the particle. The first three eigen functions  $\psi_1, \psi_2, \psi_3$  together with probability densities  $|\psi_1|^2, |\psi_2|^2, |\psi_3|^2$  are shown in Figs. 7.20(a) and (b) respectively.



**Fig. 7.20** Wave-functions and probability densities of a particle confined to a box with rigid walls.

$$\frac{a - a_1}{2}$$

### 7.15.3 Particle in 3-D Box

The Schrödinger equation for 3-D can be written as

$$\nabla^2 \psi + \frac{2mE}{\hbar^2} \psi = 0 \quad \dots(168)$$

or  $\frac{d^2 \psi}{dx^2} + \frac{d^2 \psi}{dy^2} + \frac{d^2 \psi}{dz^2} + \frac{2mE}{\hbar^2} \psi = 0$

Solution of Eq. (168) will be product of wave function of  $x$ ,  $y$ ,  $z$  directions wave function, i.e.,

$$\psi = X(x) Y(y) Z(z) \quad \dots(169)$$

Since  $X(x) = \sqrt{\frac{2}{L_x}} \sin K_x x = \sqrt{\frac{2}{L_x}} \sin \frac{n_x \pi x}{L_x}$

$$Y(y) = \sqrt{\frac{2}{L_y}} \sin K_y y = \sqrt{\frac{2}{L_y}} \sin \frac{n_y \pi y}{L_y}$$

$$Z(z) = \sqrt{\frac{2}{L_z}} \sin K_z z = \sqrt{\frac{2}{L_z}} \sin \frac{n_z \pi z}{L_z}$$

$$\psi = \sqrt{\frac{2}{L_x}} \sqrt{\frac{2}{L_y}} \sqrt{\frac{2}{L_z}} \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z} \quad \dots(170)$$

where  $K^2 = K_x^2 + K_y^2 + K_z^2 = \frac{2mE}{\hbar^2}$

Then energy  $E = \frac{\hbar^2 (K_x^2 + K_y^2 + K_z^2)}{2m}$

$$E = \frac{\hbar^2}{2m} \left[ \frac{\pi^2 n_x^2}{L_x^2} + \frac{\pi^2 n_y^2}{L_y^2} + \frac{\pi^2 n_z^2}{L_z^2} \right]$$

$$= \frac{\pi^2 \hbar^2}{2m} \left[ \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right] \quad \dots(171)$$

Equation (171) represents the eigen value of energy in 3D.

**Example 7.16.** A particle is moving in a one-dimensional box (of infinite height) of width 2.5 nm at the centre of the box when it is in its state of least energy.

**Solution.** Since we know that,

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

When the particle is in least energy state ( $n=1$ ), the wave function becomes

$$\psi_1(x) = \sqrt{\left(\frac{2}{a}\right)} \left[ \sin \frac{\pi x}{a} \right]$$

At the centre of the box,  $x = \frac{a}{2}$ , the probability of finding the particle at midpoint of the box is

$$|\psi_1(x)|^2 = \left(\frac{2}{a}\right) \left[ \sin^2 \frac{\pi x}{a} \right]$$

The probability 'P' in the interval  $\Delta x$  is given by

$$P = |\psi_1(x)|^2 (\Delta x) = \left(\frac{2}{a}\right) \Delta x \text{ at } x = \frac{a}{2}.$$

With (i)  $a = 2.5 \text{ nm}$       (ii)  $\Delta x = 0.5 \text{ nm}$

Thus,  $P = \left(\frac{2}{a}\right) \Delta x = \frac{2}{2.5} \times (0.5) = 0.4$

$$P = 0.4$$

**Example 7.17.** Find the energy of an electron moving in one dimension in an infinitely high potential box of width  $1 \text{ \AA}$ .

**Solution.** The eigen value of energy,  $E_n = \frac{n^2 h^2}{8ma^2}$

when the particle is in the least energy state ( $n=1$ ), the energy,

$$E_1 = \frac{h^2}{8ma^2}$$

with (i)  $h = 6.62 \times 10^{-34} \text{ Js}$     (ii)  $m = 9.1 \times 10^{-31} \text{ kg}$     (iii)  $a = 1 \times 10^{-10} \text{ m}$

i.e.,  $E_1 = \frac{(6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (1 \times 10^{-10})^2}$

$$= \frac{6.62}{8 \times 9.1} \times 10^{-68} \times 10^{+51}$$

$$= \frac{6.62}{72.8} \times 10^{-17} = \frac{6620}{728} \times 10^{-19} \text{ J}$$

$$= 9.093 \times 10^{-19} \text{ J} = 5.68 \text{ eV}$$

Assume that the potentials are constant in time and that are also constant for prescribed region of space.

**Example 7.18.** Determine the expectation value of position of a particle in one-dimensional box.

**Solution.** Given :  $\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ , limit range = 0 to  $a$

We know expectation value of any function  $x$  is given by

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\psi|^2 dx$$

Then for one-dimensional box

$$\begin{aligned}\langle x \rangle &= \int_0^a x \cdot \frac{2}{a} \sin^2 \frac{n\pi x}{a} dx = \frac{2}{a} \int_0^a \frac{x}{2} (1 - \cos 2x) dx \quad [\cos 2x = 1 - 2 \sin^2 x] \\ &= \frac{1}{a} \int_0^a (x - x \cos 2x) dx = \frac{2}{a} \left[ \int_0^a x dx - \int_0^a x \cos 2x dx \right] \\ &= \frac{1}{a} \left\{ \left[ \frac{x^2}{2} \right]_{x=0}^{x=a} - \left[ \frac{x \sin 2x}{2} \right]_{x=0}^{x=a} - \left[ \cos 2x \cdot \frac{x^2}{2} \right]_{x=0}^{x=a} \right\} \\ &= \frac{1}{a} \times \frac{a^2}{2} = \frac{a}{2}\end{aligned}$$

**Example 7.19.** Find the probability that a particle trapped in a box 'L' wide can be found between 0.30 L and 0.65 L for the first excited state. [PTU, June 2004 (4 marks)]

**Solution.** Since we know that for the particle in box

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

∴ The probability to find the particle between  $x_1$  and  $x_2$  is

$$\begin{aligned}P &= \int_{x_1}^{x_2} \left| \psi_n(x) \right|^2 dx = \frac{2}{L} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L} dx \\ &= \left[ \frac{x}{L} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{L} \right]_{x_1}^{x_2}\end{aligned}$$

Given,  $x_1 = 0.30 L$  and  $x_2 = 0.65 L$ ,  $n = 2$  (for first excited state).

$$\begin{aligned}P &= \left[ \frac{0.65 L}{L} - \frac{1}{2n\pi} \sin \frac{2 \times 2 \times \pi \times 0.65 L}{L} - \frac{0.30 L}{L} + \frac{1}{2n\pi} \sin \frac{2 \times 2 \times \pi \times 0.30 L}{L} \right] \\ &= \left[ 0.35 - \frac{1}{2n\pi} (\sin 2.60\pi - \sin 1.2\pi) \right]\end{aligned}$$

## Formulae at a Glance

1. Wein's Law  $\lambda_m T = \text{constant}$  and  $E_m T^{-5} = \text{constant}$  where  $\lambda_m$  = wavelength for which emitted energy is maximum.

2. Rayleigh-Jean's Law

$$E_\lambda d\lambda = \frac{8\pi k_B T}{\lambda^4} d\lambda$$

3. Planck's law for the energy distribution in black body radiation

$$E_\lambda d\lambda = 8\pi h c \lambda^{-5} \left[ \exp\left(\frac{hc}{\lambda k_B T}\right) - 1 \right] d\lambda$$

4. Einstein's photoelectric equation

$$E_{\max} = \frac{1}{2} m v_{\max}^2 = h\nu - W$$

$$\text{or } \frac{1}{2} m v_{\max}^2 = h\nu - h\nu_0$$

5. Compton shift

$$\lambda - \lambda' = \frac{h}{m_0 c} (1 - \cos \phi)$$

6. Compton wavelength

$$\frac{h}{m_0 c} = 0.0242 \text{ \AA}$$

7. Kinetic energy of recoil electron

$$E_k = \frac{h\nu\alpha(1-\cos\phi)}{1+\alpha(1-\cos\phi)}$$

where

$$\alpha = \frac{h}{m_0 c \lambda} = \frac{h\nu}{m_0 c^2}$$

8. Dual Nature of Matter,

$$\text{The wavelength } (\lambda) = \frac{h}{p}$$

$$= \frac{\text{Planck's constant}}{\text{momentum}}$$

9. de Broglie wavelength of an electron

$$\lambda = \frac{h}{\sqrt{2mE}} = \frac{12.28}{\sqrt{V}} \text{ \AA}$$

10. Phase Velocity,

$$v_p = \frac{\omega}{k} = \frac{\text{Angular frequency } (2\pi\nu)}{\text{Propagation constant}}$$

11. Group Velocity,  $v_g = \frac{d\omega}{dk}$

12. Relation between  $v_p$  and  $v_g$ .

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

13. Relation between  $v_g$  and particle velocity  $v_{\text{particle}}$

$$v_g = v_{\text{particle}} = \frac{dE}{dp}$$

14. Relation between velocity of light ( $c$ ),  $v_g$  and  $v_p$

$$v_p v_g = c^2$$

15. In Davisson and Germer experiment,

$$(i) 2d \sin \theta = n\lambda$$

$$\Rightarrow \lambda = 1.65 \text{ \AA};$$

$d$  = interplanar distance

$$(ii) \lambda_e = \frac{12.28}{\sqrt{V}} \text{ \AA} = 1.66 \text{ \AA}. \quad (\text{at } V = 54 \text{ V})$$

16. Heisenberg's uncertainty principle,

$$(i) \Delta x \Delta p_x \approx \frac{h}{2\pi} = \hbar$$

$$\Delta y \Delta p_y \approx \frac{h}{2\pi} = \hbar \quad \Delta x \Delta p_x \geq \hbar$$

$$\Delta z \Delta p_z \approx \frac{h}{2\pi} = \hbar$$

$$(ii) \Delta E \cdot \Delta t \geq \hbar \quad E = \text{energy}$$

$$(iii) \Delta L \Delta \theta \geq \frac{h}{2\pi} \quad L = \text{angular momentum}$$

$\Delta \theta$  = angular change

17. Experimental Proof of Uncertainty principle :

(i) Det. of position of particle by a microscope

$$\Delta x = \frac{\lambda}{2 \sin \theta}; \quad \Delta p_x = \frac{2h}{\lambda} \sin \theta$$

$$\Delta p_x \cdot \Delta x = \frac{2h}{\lambda} \sin \theta \cdot \frac{\lambda}{2 \sin \theta} = h$$

(ii) Diffraction of an electron beam by a single slit

$$\Delta y \sin \theta = \lambda$$

$$\Delta y = \frac{\lambda}{\sin \theta}$$

$$\Delta p_y = p \sin \theta - (-p \sin \theta) = 2p \sin \theta = 2 \frac{h}{\lambda} \sin \theta$$

$$\Delta y \Delta p_y = \frac{\lambda}{\sin \theta} \cdot \frac{2h}{\lambda} \sin \theta = 2h$$

**18. Applications of Uncertainty Principle**

(i) Non-existence of free electrons in the nucleus

$$E^2 = p^2 c^2 + m_0^2 c^4,$$

$$\Delta x \Delta p_x = \hbar$$

(ii) Spectral lines have a finite width

$$\Delta E = \frac{\hbar}{\Delta t} = 6.6 \times 10^{-26} \text{ J}$$

(iii) Radius of Bohr's first orbit

$$\Delta x \Delta p \approx \hbar$$

$$r = \Delta x = \frac{\varepsilon_0 \hbar^2}{\pi m Z e^2} = \frac{\varepsilon_0 h^2}{\pi m z e^2}$$

**19. Wave equation for a free particle**

$$\psi = A e^{\frac{-i}{\hbar}(Et - px)}$$

where  $\psi$  = wave function,  $E$  = Energy, $p$  = momentum20. Energy operator,  $E = i\hbar \frac{\partial}{\partial t}$ **21. Momentum operator,**

$$p = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

$$22. i\hbar \frac{\partial \psi}{\partial t} = E\psi$$

 $\psi$  = Eigen function of the operator  $i\hbar \frac{\partial}{\partial t}$  $E$  = energy eigen value**23. Normalisation**

$$\int_{-\infty}^{\infty} |\psi|^2 dV = 1$$

As  $|\psi|^2 = \psi^* \psi$  = Probability density =  $P$ 

$$24. \text{Probability } P_{x_1 x_2} = \int_{x_1}^{x_2} |\psi|^2 dx$$

**25. Expectation value**

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x \psi^* \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx}$$

For normalised function the

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1.$$

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi|^2 dx$$

**26. Orthogonal wave function**

$$\int \psi_a^* \psi_b dV = 0$$

$$\text{or } \int \psi_b^* \psi_a dV = 0 \text{ for } a \neq b$$

**27. Orthonormality**

$$\begin{aligned} \int \psi_a^* \psi_b dV &= \delta_{ab} \\ \delta_{ab} &= 0 \quad \text{if } a \neq b \\ &= 1 \quad \text{if } a = b \end{aligned}$$

**28. Schrödinger's time dependent wave equation**

For 1-D,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi$$

For 3-D,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$H\psi = E\psi.$$

**29. Schrödinger's time independent wave equation**

$$\text{For (1-D), } \frac{\partial^2 \psi_0}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \psi_0 = 0$$

$$\text{For (3-D), } \nabla^2 \psi_0 + \frac{2m}{\hbar^2} (E - V) \psi_0 = 0$$

**30. Schrödinger's wave equation for free particle ( $V = 0$ )**

$$\nabla^2 \psi + \frac{2m}{\hbar^2} E \psi = 0 \Rightarrow E = \frac{K^2 \hbar^2}{8\pi^2 m}$$

**31. Particle in box**

$$(i) \text{Eigenvalue } E_n = \frac{n^2 \hbar^2}{8ma^2}$$

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

where  $a$  is the width of the box.

(b) Now substituting  $\psi = a\psi_1 + b\psi_2$  in the given equation

$$i\hbar \left( a \frac{\partial \psi_1}{\partial t} + b \frac{\partial \psi_2}{\partial t} \right) = -\frac{\hbar^2}{2m} \left( a \frac{\partial^2 \psi_1}{\partial x^2} + b \frac{\partial^2 \psi_2}{\partial x^2} \right) + V a \psi_1 + V b \psi_2$$

or  $a \left( i\hbar \frac{\partial \psi_1}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \psi_1}{\partial x^2} - V \psi_1 \right) + b \left( i\hbar \frac{\partial \psi_2}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \psi_2}{\partial x^2} - V \psi_2 \right) = 0 \quad \dots(ii)$

Since  $\psi_1$  and  $\psi_2$  satisfy the given equation, the Eq. (ii) is identically zero. Hence  $\psi$  satisfies the given equation.

## Conceptual Questions

**1. Explain how the wave nature of particles gives rise to uncertainty principle.**

**Ans.** Wave nature of a particle requires that the particle is to be represented by means of a wave group or a wave packet. A wave group is obtain by a superposition of a large number of monochromatic waves with slightly varying frequencies or wave vectors. The wave group has a finite spatial extent which implies that the position of a particle cannot be pin-pointed, it must have some uncertainty. Again the momentum  $p$  of a particle is related to the wave vector  $k$  by  $p = \frac{hk}{2\pi}$ . Since a wave group is made up of several waves of slightly varying wave vector, it is clear that a wave group has a certain spread  $\Delta k$  in wave vector. This means that momentum of the particle is not definite but has an uncertainty  $\Delta p = \hbar \Delta k$ . We know that a narrow wave group has a broader range of wave-vector. So smaller position uncertainty is associated with large momentum uncertainty. Thus the wave nature of particle gives rise to the uncertainty principle.

**2. What do you mean by matter waves ?**

**Ans.** Because of such a dual nature of radiation, Louis de-Broglie of France in 1924, put forward bold hypothesis that since nature loves symmetry, if the radiation behaves as particle under certain circumstances and as a waves under certain other circumstances, then one can even expect that entities which ordinary behaves as particles to exhibit properties attributable to only waves under appropriate circumstances and he termed them as matter waves.

**3. What is de-Broglie wavelength ?**

**Ans.** The wavelength of matter waves is called de-Broglie wavelength and is given by

$$\lambda = \frac{h}{p}, \quad \text{where } h = \text{Planck's constant.}$$

**4. What is meant by travelling waves ?**

**Ans.** The wave motion associated with the oscillating mass under such a condition, has a close resemblance to the progressive motion of waves, caused in water by some disturbance, or to those set up in a rope by trying it at one end, and oscillating it at the free end. Such progressive waves are called travelling waves.

**5. What do you understand by (i) phase velocity and (ii) group velocity ?**

**Ans.** (i) *Phase velocity.* If a point is imagined to be marked on a travelling wave, then it becomes a representative point for a particular phase of the wave, the velocity with which it is transported owing to the motion of the wave, is called the phase velocity.

(ii) *Group velocity.* Group velocity is the velocity with which the envelope enclosing a wave group called wave packet, formed due to superposition of two or more travelling waves of slightly different wavelengths, is transported. It is the velocity with which the energy transmission occurs in a wave.

**6. Write statement of Heisenberg's uncertainty principle.**

**Ans.** In any simultaneous determination of the position and momentum of the particle, the product of the corresponding uncertainty inherently present in the measurement is equal to, or greater than  $(\hbar / 2\pi)$ .

**7. What was the aim of Davisson-Germer experiment ?**

**Ans.** Davisson and Germer in 1927 designed an apparatus to determine the wavelength associated with electrons.

**8. What is importance of uncertainty principle ?**

[PTU, May 2011 (2 marks)]

**Ans.** According to new quantum mechanics

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

if  $\Delta x = 0$ , then

$$\Delta p_x = \frac{\hbar}{2\Delta x} = \infty$$

This means, if the position of a moving particle is determined accurately in simultaneous measurement, then the uncertainty in momentum will be infinite, i.e.,

$$\Delta x = \frac{\hbar}{2\Delta p_x} = \infty \text{ if } \Delta p_x = 0$$

Thus in any simultaneous measurement of position and momentum the accuracy is limited by the uncertainty relation.

From the relation

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \quad \text{or} \quad \Delta x (\Delta m v_m) \geq \frac{\hbar}{2} \quad \text{or} \quad \Delta x \Delta v_x \geq \frac{\hbar}{2m}$$

where  $v_x$  is the velocity of the particle along  $x$ -direction.

Since  $\frac{\hbar}{2m} \rightarrow 0$ ,  $\Delta x \Delta v_x \rightarrow 0$  for such particle, the position and velocity can be determined almost accurately.

If mass =  $\infty$ , i.e., heavy bodies,  $\hbar / 2m = 0$ , then position and momentum of such bodies can be determined with perfect accuracy. This is limiting case of classical mechanics.

Hence

Classical mechanics gives correct result for macroscopic bodies, but quantum mechanics is true for microscopic bodies like electron and proton etc.

**9. What is a wave function ?**

**Ans.** In quantum mechanics every physical system is represented by means of function which implicitly contains all the information about the system. This function is known as the wave function of the system. For a single particle the wave function is a function of its position  $r$  and time  $t$ .

10. What is physical significance of the wave function?

**Ans.** In classical mechanics, the square of a wave amplitude associated with electromagnetic radiation is interpreted as a measure of radiation intensity. This suggests that we should make a similar interpretation for de Broglie waves associated with electron or any particle. Hence, if we consider a system of electrons, and if  $\psi$

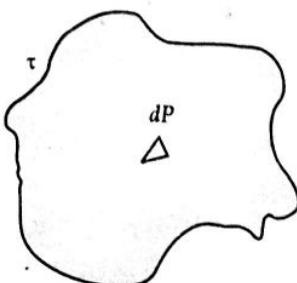


Fig. 4.21 Presence of electron in a certain region.

is the wave function associated with the system, then  $|\psi|^2$  may be regarded as a measure of density of electrons. Also, if  $\tau$  is a volume inside which, an electron is known to be present as shown in Fig. 4.21, but where exactly the electron is situated inside volume  $\tau$  is not known, and if  $\psi$  is the wave function associated with the electron, then the probability of finding the electron in a certain element of volume  $d\tau$  of  $\tau$  is given equal to the  $|\psi|^2 d\tau$ . For this reason  $|\psi|^2$  is called the probability function. This interpretation was first given by Max Born in 1926.

Since the electron must be somewhere inside the volume  $\tau$ , the integration of  $|\psi|^2$  over the whole volume  $\tau$  must be unity, so that  $\int |\psi|^2 d\tau = 1$

In a quantum mechanics it is postulated that the state of a system is completely characterised by a wave function.

11. What is Born's probability interpretation of wave function?

[PTU, Dec. 2010 (2 marks)]

**Ans.** Max Born proposed that the wave function  $\psi$  for a beam of particles be interpreted in this same way. That is, its square  $\psi^2$  is a direct measure of the average density of particles in the beam. In a problem like the structure of hydrogen atom, there is electron only present what is meaning of the average density of particles? For such cases Born proposed that we should interpret the square of the wave function  $\psi^2$  at any point as the probability (per unit volume) that the particle will be at that point. Specifically, if  $dV$  is a volume element located at a point whose coordinates are  $(x, y, z)$ , then the probability that the particle will be found in that small volume element in time  $t$ , is proportional to  $\psi^2 dV$ . By analogy with ordinary mass density (a mass per unit volume), we call the square of the wave function  $\psi^2$  a probability density i.e., the probability per unit volume.

12. What are the properties of the wave function?

**Ans.**  $\diamond$   $\psi(x)$  must be single valued, finite and continuous for all values of  $x$ .

$\diamond$   $\frac{d\psi(x)}{dt}$  must be finite and continuous for all values of  $x$ , except at those point where  $V \rightarrow \infty$ . At

these points  $\frac{d\psi(x)}{dt}$  has a finite discontinuity but  $\psi$  remains continuous.

$\diamond$  For bound state and probability of finding the particle between  $x$  and  $(x + dx)$ , i.e.,  $|\psi|^2 dx$  must vanish as  $|x| \rightarrow \infty$ .

Hence  $|\psi(x)| \rightarrow 0$  as  $|x| \rightarrow \infty$  i.e.,  $\psi(x)$  is a square integrable wave function.

**13. Why the wave function  $\psi$  itself has no direct physical significance ?**

**Ans.**  $\psi$  cannot be interpreted in terms of an experiment. The probability that something be in a certain place at a given time must be lie between 0 (the object is definitely there) and 1 (the object is definitely there). An intermediate probability, say 0.2 means that there is a 20% chance of finding the object. But the amplitude of a wave can be negative as well as positive and negative probability is meaningless. Hence  $\psi$  by itself cannot be an observable quantity.

**14. What is zero point energy ?**

**Ans.** The possible energies of a particle in a box of length ' $a$ ' is given by

$$E_n = \frac{n^2 h^2}{8ma^2} \quad (\text{where } n = 1, 2, 3, \dots)$$

$$\text{If } n = 1, \text{ then } E_1 = \frac{h^2}{8ma^2}$$

This is the energy of the ground state of particle. Since, the particle in a box cannot be at rest, its minimum energy is positive and is often called the zero point energy.

**15. What are eigenvalues and eigenfunctions ?**

$$\text{Ans. From equation, } E_n = \frac{n^2 h^2}{8ma^2} \quad (\text{where } n = 1, 2, 3, 4, \dots)$$

It is clear that inside an infinitely deep potential well (or in an infinite square well), the particle cannot have an arbitrary energy, but can have only certain discrete energy corresponding to  $n = 1, 2, 3, 4, \dots$ . Each permitted energy level energy is called eigenvalue of the particle and constitutes the energy level of the system. The wave function  $\psi$  corresponding to each eigenvalue are called eigenfunctions.

**16. Is Schrödinger equation is linear in the wavefunction  $\psi$  ? What is meaning of it ?**

**Ans.** Yes, Schrödinger equation is linear in wave function  $\psi$ . By this we mean that the equation has terms that contain  $\psi$  and its derivatives but no terms independent of  $\psi$  or that involves higher power of  $\psi$  or its derivatives.

**17. Why  $n = 0$  state is not allowed for particle confined to an infinite potential box ?**

[PTU, May 2010 (2 marks)]

**Ans.** We know  $E_n = \frac{n^2 h^2}{8ma^2}$ , if  $n = 0$ , then the value of  $k$  will be zero. If  $k$  is zero, then momentum and kinetic energy will be zero. The existing particle will be at rest, which is impossible. If  $k = 0$ , then  $\psi_n(x) = A \sin kx$  will be zero, which means the probability density will be zero i.e., the particle will not be in box.

**18. What is expectation value ?**

**Ans.** In quantum mechanics a physical system is represented by means of a wave function. So the physical variables like the position, momentum and energy of the system do not have definite values, instead they have a probable value. Thus results of two successive measurements of the position of a particle may not yield the same value. The average value of a physical variable is called its expectation value. This may be obtained by a large number of independent measurements on the same system or by a single measurement on each of the large number of identical systems.

19. Which of the following functions are acceptable wave functions?

(a)  $\psi = \frac{1}{x}$ ; (b)  $\psi = \frac{1}{1+x^2}$ ; (c)  $\psi = x^n$ ; (d)  $\psi = \sin x$

(b)  $\psi = e^x$ ; (f)  $\psi = e^{-x}$ ; (g)  $\psi = e^{-x^2}$ ; (h)  $\psi = \frac{1}{1+x}$

**Ans.** (a) As  $x \rightarrow 0$ ,  $\psi \rightarrow \infty$ .

Hence  $\psi$  is not an acceptable wave function.

(b) As  $x \rightarrow \pm\infty$ ,  $\psi \rightarrow 0$ .

Hence  $\psi$  is an acceptable wave function.

(c) As  $x \rightarrow \pm\infty$ ,  $\psi \rightarrow \pm\infty$ .

Hence  $\psi$  is not acceptable wave function.

(d) Here,  $\psi$  oscillates between +1 and -1, hence it is acceptable.

(e) As  $x \rightarrow \infty$ ,  $\psi \rightarrow \infty$ .

Hence  $\psi$  is not an acceptable wave function.

(f) As  $x \rightarrow -\infty$ ,  $\psi \rightarrow \infty$ .

Hence  $\psi$  is not an acceptable wave function.

(g) As  $x \rightarrow \pm\infty$ ,  $\psi \rightarrow 0$ .

Hence  $\psi$  is an acceptable wave function.

(h) As  $x \rightarrow -1$ ,  $\psi \rightarrow \infty$ .

Hence  $\psi$  is not an acceptable wave function.

## EXERCISES

### Theoretical Questions

- What is Compton effect? Also give the expression for  $\Delta\lambda$ . [PTU, Jan. 2003 (2 marks)]
- Discuss Compton scattering and derive a relation for change in wavelength of scattered waves. [PTU, Jan. 2003 (6 marks)]
- Obtain an expression for shift in wavelength of the scattered photon by Compton scattering.
- Explain how Compton scattering confirms the quantum nature of radiation.
- Explain the Compton effect and its physical significance.
- Explain Compton scattering. Derive an expression for Compton shift. Give its experimental verification.
- Describe Compton effect. Derive an expression for Compton shift. How does it support the particle nature of light. [PTU, June 2005 (2 marks)]
- What is Compton effect.
- Differentiate between photoelectric effect and Compton effect and calculate the expression for Compton shift. [PTU, Dec. 2009 (8 marks)]
- Discuss de Broglie hypothesis. [PTU, Dec. 2010 (2 marks)]
- What is Compton effect?
- What is de-Broglie hypothesis. [PTU, Dec. 2010 (2 marks)]
- Discuss de Broglie hypothesis. [PTU, Jan. 2003 (2 marks)]
- Explain de-Broglie concept of matter waves. [PTU, May 2006 (2 marks)]