



Quantum Theory

(1) NEED OF QUANTUM MECHANICS

Classical mechanics explained successfully the motion of objects which are either directly observable or can be made observable by simple instruments like microscope. However when attempt was made to explain mechanics of subatomic particles like electron, proton, neutron etc., the classical mechanics failed drastically. A few examples, where classical mechanics were inadequate to give explanation of observed facts are described below :

(i) **Stability of atom.** On the basis of classical physics, the atomic model was proposed by Rutherford, which assumes the atom to be consisting of a positively charged nucleus in the centre and negatively charged electrons are revolving around the nucleus in a circular orbit. However the classical theory of electromagnetic radiation says that whenever a charged particle undergoes accelerated motion, it emits electromagnetic radiation. Thus an electron (being a charged particle) must emit energy continuously as its motion is accelerated. As a result, the orbital radius should decrease continuously and ultimately electron would fall into nucleus. Hence an atom would collapse ultimately. But as all of us know that atom is a stable entity. Thus stability of atom could not be established by classical physics. Later on the stability was explained by Bohr's old quantum theory of atom.

(ii) **Optical Spectra.** When any substance is raised to a high temperature or subjected to electric discharge, it emits light (electromagnetic) waves of various frequencies. When various frequencies are resolved on a screen in a definite order using diffraction grating, then the pattern formed on screen is called optical spectra. According to classical physics the optical spectra should extend over a wide range of frequencies and it should be of continuous nature. However it was observed that optical spectrum consists only of certain discrete frequencies. Moreover these optical lines were found to be in certain groups (e.g. Lyman, Balmer, Paschen, Brackett, Pfund series of Hydrogen atom). Thus optical spectra could not be explained by classical physics.

(iii) **Specific Heat of Solids.** The specific heat of any substance is defined as the amount of heat required to raise the temp. of 1 g of substance through 1°C . According to old physics, the molar specific heat of all the solids is independent of the temperature of solid and is given as

$$C = 3R \quad (\text{This relation is called Dulong Petit Law})$$

where $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ is gas constant.

However experimentally it was observed that the specific heat of solids is constant only at temperatures more than certain specific temperature T_D (called Debye Temperature). For temperature less than T_D the specific heat is found to change with temperature roughly as

$$C \propto T^3 \quad (\text{This is called Debye's } T^3 \text{ law}).$$

Hence this observation was not explained by classical physics. Later on Einstein's theory and Debye's Quantum theory of specific heats explained this observation successfully.

(iv) **Photoelectric Effect.** When a photon of light falls on the metal surface and if frequency of light is more than certain minimum frequency called Threshold frequency, then electrons are ejected from metal surface. This effect is called photoelectric effect. According to classical theory (wave theory) of light, there should be no threshold frequency, the photoelectric current should increase with increase in frequency of light and kinetic energy of ejected electron should increase with increase in intensity of light. Further there must be a finite delay between the incidence of photons and ejection of electrons from metal surface. However experimental observations about this effect were totally contradictory. i.e. photoelectric effect is instantaneous, the photoelectric current depends upon the intensity instead of frequency of light (provided frequency is more than threshold frequency) and kinetic energy of electrons ejected from the metal surface depends upon the frequency of the incident radiation. Thus classical mechanics failed to explain photoelectric effect. These observations were successfully explained later on by Einstein's theory of photoelectric emission, which in fact is based on Planck's Quantum Theory of Radiation.

Conclusion

There were a lot of other observations which were not explained by classical mechanics, like Black Body Radiation, Compton Effect, Theory of alpha decay from radioactive nuclei etc. Hence we conclude that classical mechanics is inadequate to discuss the subatomic phenomenon. Thus there is a need to introduce a new theory, which can deal with motion of microscope or subatomic particles. "The branch of physics dealing with motion of subatomic particles is called Quantum Mechanics."

(2) DUAL NATURE OF MATTER (MATTER WAVES)

There are certain properties of electromagnetic radiations which can be explained by assuming light as wave. e.g. interference, diffraction, polarisation etc. While certain other properties like photoelectric effect, Compton effect and Black body radiation could be explained by assuming particle character of radiation. Thus radiations possess Dual Character. Wave character of radiations is observed when interaction takes place between two different kinds of radiations and particle character is observed during interaction of radiation with matter.

Louis De Broglie came forward and with a revolutionary idea in 1926. He proposed that, our universe is made of matter and radiation. Just as radiations have Dual Character, matter should also possess dual character as nature loves symmetry. "The waves associated with material particles are called Matter waves and the wavelength of matter wave is called de Broglie Wavelength."

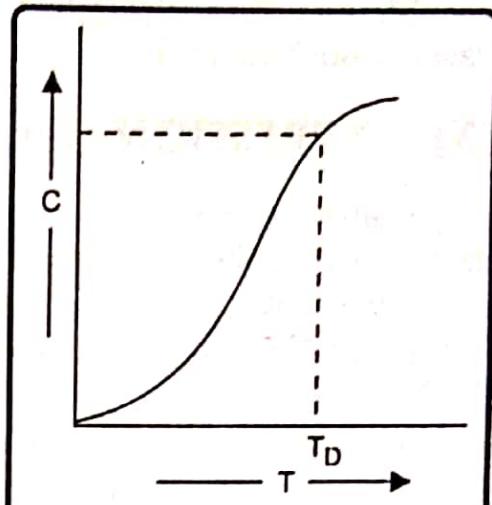


Fig. 1.

Matter wave is also called Pilot or Guide Wave. These are non-electromagnetic and can travel through vacuum.

(3) EXPRESSION FOR de BROGLIE WAVELENGTH OF A PARTICLE

Consider a material particle such as an electron or a proton as a standing wave system in the region of space occupied by the particle. We know that a wave motion is always associated with a periodic change in some quantity (e.g. in case of sound propagation, pressure of air changes periodically). Let ψ be a quantity, which undergoes a periodic change, giving rise to matter waves.

We consider a frame of reference S' attached with the particle i.e. particle appears to be at rest in S'. Let ν' is the frequency of wave associated with particle and A is amplitude of the wave function ψ . Then value of ψ at any time t' in frame S' is given by standard equation of standing wave as

$$\psi = A \sin(2\pi \nu' t') \quad \dots(1)$$

If m_0 = rest mass of the particle then by equivalence of Einstein's mass energy relation and Planck's formula, we have

$$E = m_0 C^2 = h\nu'$$

So that

$$\nu' = \frac{m_0 C^2}{h} \quad \dots(2)$$

Consider a frame S fixed in the laboratory and let the particle (and hence frame S') is moving along +X axis with velocity V. Then by Lorentz transformation, we have

$$t' = \frac{t - \frac{V}{C^2} x}{\sqrt{1 - V^2/C^2}} \quad \dots(3)$$

So that wave function w.r.t. S is given as

$$\psi = A \sin \left[2\pi \left(\frac{\nu'}{\sqrt{1 - V^2/C^2}} \right) \left(t - \frac{Vx}{C^2} \right) \right] \quad \dots(4)$$

Note that equation (1) represents standing wave while equation (4) represents a progressive wave.

Moreover if u is phase (or wave) velocity of a progressive wave. Then standard equation of progressive wave moving along +X-axis is given by

$$\psi = A \sin \left[2\pi \nu \left(t - \frac{x}{u} \right) \right] \quad \dots(5)$$

where ν is frequency of wave. Comparing equations (4) and (5), we see that effective frequency in frame S is given as

$$\nu = \frac{\nu'}{\sqrt{1 - V^2/C^2}} \quad \dots(6)$$

and phase velocity of matter wave is given as

$$\frac{1}{u} = \frac{V}{C^2} \quad \text{or} \quad u = \frac{C^2}{V} \quad \dots(7)$$

Put value of ν' from (2) in equation (6) we get

$$\begin{aligned} \nu &= \frac{m_0 C^2}{h \sqrt{1 - V^2/C^2}} \\ &= \frac{m C^2}{h} \quad \dots(8) \left(\because m = \frac{m_0}{\sqrt{1 - V^2/C^2}} \right) \end{aligned}$$

Let λ = wavelength of the de Broglie wave associated with the particle as observed in laboratory frame S.

Then

$$\lambda = \frac{\text{Velocity of Wave}}{\text{Frequency}}$$

$$= \frac{u}{\nu} = \frac{C^2/V}{mc^2/h}$$

$$\boxed{\lambda = \frac{h}{mV}} \quad \dots(9)$$

Equation (9) gives expression for wavelength of the matter wave associated with the particle. The relation has been derived using Lorentz Transformation. Hence it is valid at low as well as high speed. The method of obtaining expression for λ indicates that a material particle in motion involves two different velocities, one of which refers to the mechanical motion of particle, represented by V and other refers to the propagation of the associated wave and is represented by u .

Further $\lambda \propto \frac{1}{m}$ also Planck's constant h appears in the numerator in equation (9). Because of very small value of h , the value of λ is very small for particles of macroscopic world. Hence if λ is to be observed practically, then we must consider particles of very small mass. Thus obvious choice would be subatomic particles like electron, proton & neutron.

(4) de-Broglie WAVELENGTH OF AN ELECTRON ACCELERATED BY A POTENTIAL DIFFERENCE

(i) Non Relativistic Case. Let q = charge on electron and V = accelerating voltage.

If v is velocity acquired by the electron which is very small compared to velocity of electron, then, then the non-relativistic formula for kinetic energy may be employed. Thus

$$\begin{aligned} qV &= \frac{1}{2} mv^2 \\ v &= \sqrt{\frac{2qV}{m}} \quad \dots(10) \end{aligned}$$

Thus de Broglie wavelength is given by

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mqV}} \quad (\text{Using (10)})$$

For an electron $m = 9.1 \times 10^{-31} \text{ kg}$, $q = 1.6 \times 10^{-19} \text{ C}$

Thus above expression becomes (in units of Å)

$$\lambda = \frac{12.27}{\sqrt{V}} \text{ Å} \quad \dots(11)$$

(ii) **Relativistic Case.** If the velocity acquired by electron is comparable to speed of light then kinetic energy is no longer given by $\frac{1}{2}mv^2$. Instead we use relativistic expressions for total energy (E) and kinetic energy (T). These are

$$E = \sqrt{p^2C^2 + m_0^2C^4} \quad \dots(12)$$

and

$$E = T + m_0C^2 \quad \dots(13)$$

From (12) and (13) we get

$$(T + m_0C^2)^2 = p^2C^2 + m_0^2C^4$$

$$T^2 + m_0^2C^4 + 2Tm_0C^2 = p^2C^2 + m_0^2C^4$$

$$T^2 + 2Tm_0C^2 = p^2C^2 \quad \dots(14)$$

But the kinetic energy is also given as work done during accelerating the electron
i.e.

$$T = qV$$

Put in (14)

$$\Rightarrow q^2V^2 + 2(qV)m_0C^2 = p^2C^2$$

$$\text{or} \quad 2m_0qVC^2 \left(1 + \frac{qV}{2m_0C^2} \right) = p^2C^2$$

$$\Rightarrow p = \sqrt{2m_0qV \left(1 + \frac{qV}{2m_0C^2} \right)} \quad \dots(15)$$

Hence de Broglie wavelength of electron is given as

$$\lambda = \frac{h}{\sqrt{2m_0qV \left(1 + \frac{qV}{2m_0C^2} \right)}} \quad \dots(16)$$

This relation is valid for any charged particle accelerated through potential difference V. The only difference is that values of m_0 and q should be used corresponding to that particle.

(5) de-Broglie WAVELENGTH OF THERMAL NEUTRONS

Neutrons cannot be accelerated by potential difference. Let T is temp. of neutron, then its kinetic energy is given as thermal kinetic energy, which is

$$\frac{1}{2}mv^2 = \frac{3}{2}kT \quad \text{where } m = \text{mass of neutron}$$

$$\text{Hence } v = \sqrt{\frac{3kT}{m}}$$

Thus de-Broglie wavelength is given by

$$\lambda = \frac{h}{mv} = \frac{h}{m \sqrt{\frac{3kT}{m}}}$$

$$\lambda = \frac{h}{\sqrt{3mkT}}$$

...(17)

(6) DAVISSON AND GERMER EXPERIMENT : EXPERIMENTAL VERIFICATION OF MATTER WAVES

In 1927, an experiment was performed by American Scientists Davisson and Germer and it was found that electron beam shows diffraction phenomenon, which is characteristic of waves only. Thus wave nature of electrons and hence matter was verified.

The experimental arrangement is shown in the figure (2). Electrons are produced thermally by a cathode gun, which are then accelerated by a battery whose voltage 'V' can be adjusted using a Rheostat. The accelerated electrons come out as a narrow beam through hole H on the other end of evacuated tube. The electron beam strikes on a single crystal of nickel and scattering takes place along all directions. These scattered electrons can be detected by using detector cum counter and intensity of detected electrons is proportional to detector current. The detector is capable of rotating about the crystal so that electron beam scattered at any angle can be detected.

A graph was plotted between detector current and accelerating voltage (V) for scattering angle $\phi = 50^\circ$. The shape of graph is as shown in fig. (3). The detector current showed a peak when accelerating voltage is 54V. Since Intensity is determined by current. So we can say that intensity of electrons shows maxima & minima just as in case of diffraction of waves. This observation implies that diffraction of de-Broglie waves associated with electrons is responsible for non-uniform distribution of current or intensity, proving the wave nature.

Mathematical Treatment.

Let ϕ = angle of scattering

θ = angle of glance

From figure $\theta + \phi + \theta = 180^\circ$

$$\Rightarrow \theta = \frac{180^\circ - \phi}{2}$$

$$\text{For } \phi = 50^\circ, \text{ we have } \theta = \frac{180^\circ - 50^\circ}{2} = 65^\circ$$

d = Spacing between crystal planes of nickel crystal

$$= 0.91 \text{ \AA}$$

According to Bragg's law of diffraction

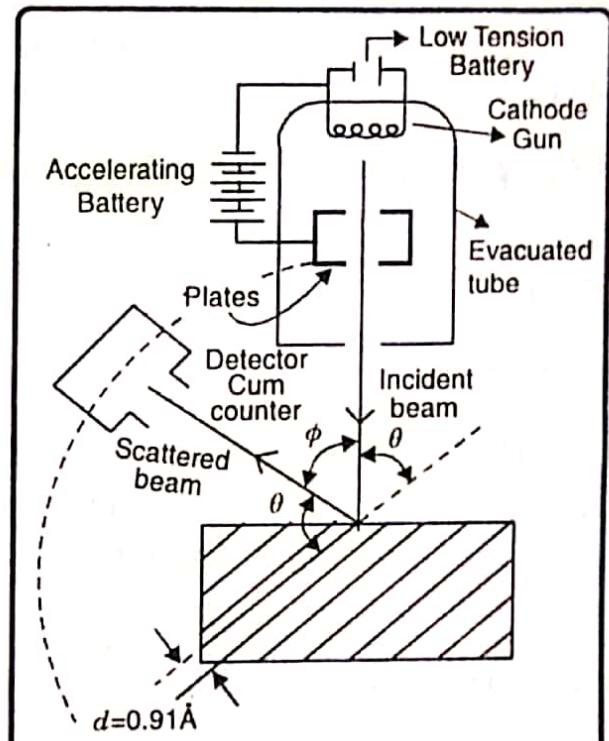


Fig. 2.

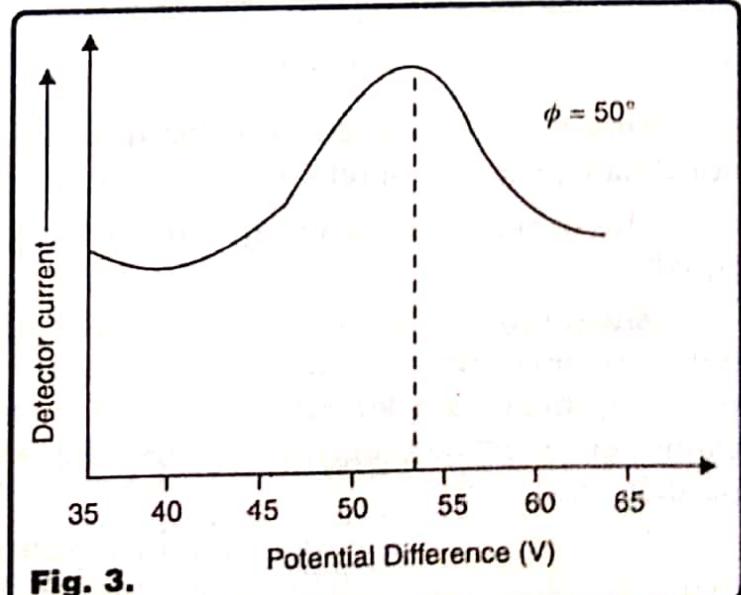


Fig. 3.

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

For First Order Diffraction $n = 1$

$$\Rightarrow \lambda = 2d \sin \theta = 2 \times 0.91 \text{ \AA} \times \sin 65^\circ = 1.65 \text{ \AA}$$

Thus according to Bragg's law the wavelength of electrons when accelerated by a potential difference of 54 V should be 1.65 \AA.

According to de Broglie formula, the wavelength of such electrons should be

$$\lambda = \frac{12.27 \text{ \AA}}{\sqrt{V}} = \frac{12.27 \text{ \AA}}{\sqrt{54}} = 1.67 \text{ \AA}$$

Within experimental errors, the two results agree well with each other. Hence wave nature of electrons is confirmed and is in accordance with de-Broglie Hypothesis.

(7) NATURE OF de-Broglie WAVE ASSOCIATED WITH A PARTICLE

In section (8), we found that the velocity with which a wave associated with a particle is given by

$$u = \text{Phase velocity or wave velocity} = \frac{C^2}{V}$$

Here V is velocity of particle in laboratory frame of reference

$$C = \text{Velocity of light}$$

Since C is always greater than V (\therefore no material particle can travel faster than speed of light)

so we have

$$u = \frac{C^2}{V} \\ = C \left(\frac{C}{V} \right) \quad \dots(18)$$

or

$$u > C \quad (\because \frac{C}{V} > 1)$$

Thus wave associated with a particle can travel faster than speed of light (this fact does not violate postulate of relativity?).

This observation poses a question before us "Are phase velocity u and particle velocity V equal"?

Answer to above question is obviously 'no' as no particle can travel faster than speed of light. However particle and wave character of a mass are inseparable. Assume that a monochromatic (single) wave is associated with particle. Then wave and particle character cannot be associated together because single wave can travel faster than speed of light and particle cannot do so.

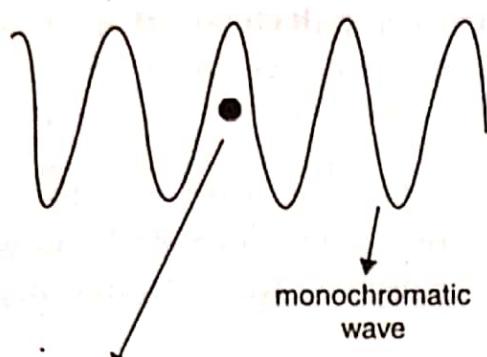
Thus we can conclude that a wave packet or a wave group (i.e. collection of infinitely many single waves) must be associated with the particle instead of a single wave. In a wave packet every component wave can travel faster than speed of light but different component waves forming the wave packet will have different directions of their velocity and different phases. These component waves will superimpose in such a way that the average velocity of component waves is less than speed of light and wave packet as well as particle must travel with this average velocity. This is shown in figure (4).

It should be noted that a photon of electromagnetic radiation has zero rest mass and it always travels with speed of light. Thus

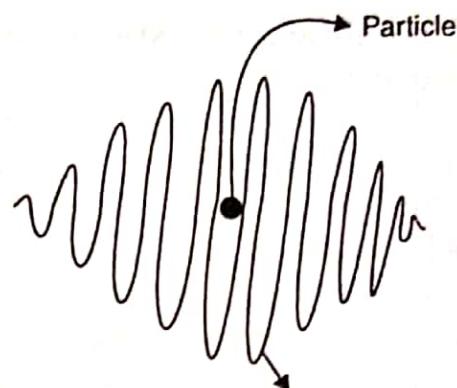
$$V = C$$

Put in (18) we get

$$u = C$$



(Not possible)
(a)



Wave packet
(Possible)
(b)

Fig. 4.

Thus for a photon, there is always a monochromatic wave associated with it and for it phase and particle velocity both are equal and have value equal to speed of light.

(8) FORMATION OF WAVE PACKET AND GROUP VELOCITY

As we have discussed above, a wave packet or a wave group is formed by superposition of infinitely many monochromatic waves and the average of velocities of component waves (by taking into account phase relation & direction velocity) is equal to group velocity. In a wave packet the waves interfere in such a way that the waves interfere constructively over a small region of space and destructively elsewhere. Thus a wave packet is limited in region of space although the component waves forming it are infinitely long. However mathematical treatment of handling superposition infinitely many waves involves Fourier Transforms, which is beyond the scope of this book. We shall discuss elementary idea about formation of wave packet.

Let two waves y_1 and y_2 having same amplitude A and slightly different angular frequencies (or wavelengths) ω , and $\omega + d\omega$, superimpose to form wave packet. Then y_1 and y_2 can be represented as

$$y_1 = A \sin(\omega t - kx) \quad \dots(19)$$

and

$$y_2 = A \sin((\omega + d\omega)t - (k + dk)x) \quad \dots(20)$$

Here k and $k + dk$ represent propagation vector of first and 2nd wave respectively. The resultant displacement at position x is given by superposition principle as

$$\begin{aligned} y &= y_2 + y_1 \\ y &= A \sin((\omega + d\omega)t - (k + dk)x) + A \sin(\omega t - kx) \\ &= A [\sin((\omega + d\omega)t - (k + dk)x) + \sin(\omega t - kx)] \\ &= 2A \sin\left(\left(\omega + \frac{d\omega}{2}\right)t - \left(k + \frac{dk}{2}\right)x\right) \cos\left(\frac{d\omega}{2}t - \left(\frac{dk}{2}\right)x\right) \end{aligned} \quad \dots(21)$$

However the quantities $\frac{d\omega}{2}$ and $\frac{dk}{2}$ are very small in comparison to ω and k respectively, then we can neglect these in first factor.

$$\therefore y \approx 2A \sin(\omega t - kx) \cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right)$$

$$= R \sin(\omega t - kx) \quad \dots(22)$$

where $R = 2A \cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right) \quad \dots(23)$

Thus (22) indicates that when two waves superimpose at position x then resultant is also a wave of frequency ω , propagation vector k and amplitude R . However major difference between (22) and (23) is that amplitude A of component wave is constant while amplitude R of the resultant wave is varying with time as well as space. Further frequency and propagation velocity y is same as that of y_1 . Hence we can visualise a wave packet to be a wave y_1 whose amplitude is modulated by wave y_2 . So wave y_2 is called modulating wave. In general if wave packet is formed by N waves y_1, y_2, \dots, y_N , then y_1 will be a resultant progressive wave which is modulated by all remaining waves y_2, y_3, \dots, y_{N-1} .

The phase velocity of each component wave (as well as of resultant wave packet) is

$$u = v\lambda = \frac{2\pi\nu}{2\pi/\lambda}$$

or $u = \frac{\omega}{k} \quad \dots(24)$

While the group velocity is the average of velocities of component waves forming the wave packet & from the expression for phase velocity, we can write group velocity V_g as

$$V_g = \text{average of phase velocities}$$

$$= \frac{\text{Change in } \omega}{\text{Change in } k} = \frac{(\omega + d\omega) - (\omega)}{(k + dk) - k}$$

$$\Rightarrow V_g = \frac{d\omega}{dk} \quad \dots(25)$$

Note. If velocity is defined as

$$V = \frac{x}{t}$$

\therefore average velocity is given by

$$V_{av} = \frac{x_2 - x_1}{t_2 - t_1}$$

Thus group velocity is equal to the derivative of ω with respect to k .

(a) Relation between group velocity and phase velocity

From (24), we have $\omega = uk$

Thus $V_g = \frac{d\omega}{dk} = \frac{d}{dk}(uk)$

$$V_g = u(1) + k \frac{du}{dk}$$

$$= u + \left(\frac{2\pi}{\lambda}\right) \times \frac{du}{d\lambda} \times \frac{d\lambda}{dk} \quad (\because k = 2\pi/\lambda)$$

$$= u + \left(\frac{2\pi}{\lambda}\right) \frac{du}{d\lambda} \left(\frac{-\lambda^2}{2\pi}\right) \quad \left(\because \frac{dk}{d\lambda} = \frac{-2\pi}{\lambda^2}\right)$$

$$V_g = u - \lambda \frac{du}{d\lambda} \quad \dots(26)$$

Equation (26) gives relation between group and phase velocities. This is called dispersion relation.

If $\frac{du}{d\lambda}$ is +ve i.e. phase velocity increases with increase in wavelength, such medium is called dispersive medium. In this case of course $V_g < u$, the dispersion taking place in this manner is called Normal Dispersion.

If $\frac{du}{d\lambda}$ is zero i.e. phase velocity is independent of wavelength, then such a medium is called non-dispersive medium and $V_g = u$ in this case.

If $\frac{du}{d\lambda}$ is -ve i.e. phase velocity increases with decrease in wavelength, then medium is again dispersive and dispersion of this kind is called Anamalous Dispersion.

Of course in this case $V_g > u$ i.e. group velocity is more than the phase velocity. This situation is practically unrealistic.

(b) Relation between group velocity and particle velocity

We can write relation (25) as

$$\begin{aligned} V_g &= \frac{d\omega}{dk} \\ &= \frac{d(2\pi\nu)}{d\left(\frac{2\pi}{\lambda}\right)} = \frac{d(\nu)}{d\left(\frac{1}{\lambda}\right)} \\ &= \frac{d(h\nu)}{d\left(\frac{h}{\lambda}\right)} = \frac{dE}{dp} \end{aligned} \quad \dots(27)$$

where $E = h\nu$ = total energy of particle.

$p = \frac{h}{\lambda}$ = linear momentum of particle.

(i) If particle is moving non relativistically. In this case the expression for the total energy of particle (assuming that it is free) is given by

E = Kinetic Energy

$$\begin{aligned} &= \frac{p^2}{2m} \\ \therefore \frac{dE}{dp} &= \frac{2p}{2m} = \frac{p}{m} = \frac{mV}{m} \\ &= V = \text{particle velocity} \end{aligned}$$

Put in (28) \Rightarrow

$$V_g = V$$

..(28)

Thus group velocity and particle velocity are equal.

(ii) If particle is moving non-relativistically. Let m_0 is the rest mass of the particle then total energy is given as

$$\begin{aligned} E &= mc^2 = \frac{m_0 C^2}{\sqrt{1 - V^2/C^2}} \\ \therefore \frac{dE}{dV} &= m_0 C^2 \left\{ \left(-\frac{1}{2}\right) \left(1 - \frac{V^2}{C^2}\right)^{-3/2} \left(\frac{-2V}{C^2}\right) \right\} \end{aligned}$$

$$= \frac{m_0 V}{(1 - V^2/C^2)^{3/2}} \quad \dots(29)$$

The linear momentum of the particle is given by

$$\begin{aligned} p &= mV = \frac{m_0 V}{\sqrt{1 - V^2/C^2}} \\ \frac{dp}{dV} &= m_0 \left\{ \frac{1}{\sqrt{1 - V^2/C^2}} + V \left(-\frac{1}{2} \right) \left(1 - \frac{V^2}{C^2} \right)^{-3/2} \left(\frac{-2V}{C^2} \right) \right\} \\ &= m_0 \left\{ \frac{1}{\sqrt{1 - V^2/C^2}} + \frac{\left(\frac{V^2}{C^2} \right)}{\left(1 - V^2/C^2 \right)^{3/2}} \right\} = m_0 \left\{ \frac{1 - \frac{V^2}{C^2} + V^2/C^2}{\left(1 - V^2/C^2 \right)^{3/2}} \right\} \\ &= \frac{m_0}{\left(1 - V^2/C^2 \right)^{3/2}} \end{aligned} \quad \dots(30)$$

Hence group velocity is given by

$$\begin{aligned} V_g &= \frac{dE}{dp} = \frac{\frac{dE}{dV}}{\frac{dp}{dV}} = \frac{m_0 V}{(1 - V^2/C^2)^{3/2}} \times \frac{(1 - V^2/C^2)^{3/2}}{m_0} \\ \Rightarrow V_g &= V \end{aligned} \quad \dots(31)$$

Thus whether particle is moving relativistically or non-relativistically, its velocity is always equal to group velocity.

Example 1. Prove that for a non-relativistic particle, the phase velocity is half of the group velocity.

Solution. For a non-relativistic free particle total energy = Kinetic energy.

$$\Rightarrow E = \frac{1}{2} mV^2 = \frac{p^2}{2m}$$

$$\text{Thus } V_g = \frac{dE}{dp} = \frac{2p}{2m} = \frac{mV}{m} = V \quad \dots(i)$$

where V = particle velocity

Also phase velocity is given by

$$\begin{aligned} u &= v\lambda \\ &= (hv) \times \frac{\lambda}{h} \\ &= \frac{E}{p} \quad (\because E = hv \text{ & } \frac{h}{\lambda} = p) \\ &= \frac{p^2/2m}{p} = \frac{p}{2m} = \frac{mV}{2m} = \frac{V}{2} \end{aligned} \quad \dots(ii)$$

From (i) & (ii) we get $u = \frac{V_g}{2}$

Example 2. Calculate the velocity and de Broglie wave length of a proton energy 10^5 eV. Given that: mass of proton $= 1.66 \times 10^{-34}$ g; Planck's constant $= 6.6 \times 10^{-27}$ erg sec and charge on electron $= 4.8 \times 10^{-10}$ e.s.u.

Solution. The energy of proton $= 10^5$ eV

$$\text{or } \frac{1}{2} mV^2 = 10^5 \times 1.6 \times 10^{-19} \text{ Joule}$$

$$\text{or } \frac{1}{2} \times 1.66 \times 10^{-24} V^2 = 10^5 \times 1.6 \times 10^{-19} \times 10^7 \text{ erg}$$

$$\Rightarrow V = 4.47 \times 10^8 \text{ cms}^{-1}$$

de Broglie wavelength is given by

$$\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-27}}{1.66 \times 10^{-24} \times 4.47 \times 10^8} = 9.3 \times 10^{-8} \text{ cm}$$

Example 3. Calculate the wavelength of thermal neutrons at 27°C , assuming that energy of a particle at absolute temperature T is of the order of kT , where k is Boltzmann constant.

Solution. The de-Broglie wavelength is given as

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

Given Thermal Energy $= E = kT$

$$\therefore \lambda = \frac{h}{\sqrt{2mkT}} \\ = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.38 \times 10^{-23} \times 300}} \\ = 1.77 \times 10^{-10} \text{ m} = 1.77 \text{ Å}$$

Example 4. Find the de Broglie wavelength of the electron in third orbit of Helium ion He^+ .

Solution. The energy of electron in one electron atoms or ions is

$$E_n = -\frac{13.6 Z^2}{n^2} \text{ eV}$$

For He^+ ion in 3rd orbit, $Z = 2$, $n = 3$

$$\therefore |E_3| = \frac{13.6 \times (2)^2}{(3)^2} = 13.6 \times \frac{4}{9} \times 1.6 \times 10^{-19} \text{ J} = 9.67 \times 10^{-19} \text{ J}$$

The de Broglie wavelength of electron is given as

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_3}} \\ = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 9.67 \times 10^{-19}}} = \frac{6.625 \times 10^{-34}}{\sqrt{176}}$$

$$= \frac{6.625 \times 10^{-34}}{13.26 \times 10^{-20}} = 0.4996 \times 10^{-14} \text{ m} = 4.996 \times 10^{-13} \text{ m}$$

Exercise 1. What voltage must be applied to an electron source to produce electrons of wavelength 0.4 \AA . Given that charge on electron $= 1.6 \times 10^{-19} \text{ C}$, mass of electron $= 9 \times 10^{-31} \text{ kg}$. [Ans. 960 Volt]

Exercise 2. An electron and a proton has same de Broglie wavelength. Calculate the ratio of velocity of electron to that of proton. [Ans. 1838]

Exercise 3. An electron and a photon have same de Broglie wavelength, if the energy of electron is $9 \times 10^{-14} \text{ J}$, calculate the energy of photon. Given mass of electron $= 9 \times 10^{-31} \text{ kg}$. [Ans. $3.74 \times 10^{-14} \text{ J}$]

Exercise 4. Find the ratio of de-Broglie wavelength for electrons in the second and third Bohr orbits in hydrogen atom. [Ans. 2/3]

(9) WAVE MECHANICAL TREATMENT OF PARTICLE DYNAMICS

We are now well aware of the fact that a particle has a wave associated with it. Old physics treats motion of particle based on Newton's Laws. However it was proposed by Schroedinger that if motion of wave packet associated with a particle is considered then it would exactly describe the motion of particle itself.

"The study of particle motion through the motion of wave packet associated with it is called Wave Mechanical Treatment."

Obviously in wave mechanical treatment the equation of motion of the associated wave packet must be a wave equation. Further we know that in all wave motions (sound, light etc.) there is some physical quantity which changes both with respect to time and space e.g. in sound waves, their propagation is possible by change in pressure of air. Similarly propagation of light takes place due to variation of electric and magnetic fields. Similarly there must be quantity, which should change with respect to space and time and causes the motion of wave packet. This quantity is called wave function.

"Thus a wave function in case of matter waves is a mathematical function (complex or real), whose variation with respect to space and time generates wave packet associated with particle". It is generally denoted by symbol ψ .

The equation of motion of a wavepacket associated with a particle is called Schrödinger Equation.

(10) TIME INDEPENDENT SCHRÖDINGER EQUATION

Consider a particle of mass m and (x, y, z) be the co-ordinates of the particle at any instant ' t '. Let ψ be the instantaneous value of wave function at time t .

(ψ plays same role in wave mechanical treatment as is played by 'displacement' in a progressive wave). In 3-dimensions, the differential equation of a progressive wave is given by

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{1}{u^2} \frac{\partial^2 \psi}{\partial t^2} \quad \dots(32)$$

where u is phase velocity.

Let the wave function of particle in three dimensions is of the form

$$\psi(x, y, z) = Ae^{-i(\omega t - \vec{k} \cdot \vec{r})} \quad \dots(33)$$

Here A is a constant, ω is angular frequency, \vec{k} is propagation vector and \vec{r} is position vector of the point (x, y, z) , i.e.

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k} \quad \dots(34)$$

$$\text{and } \vec{k} = k_x\hat{i} + k_y\hat{j} + k_z\hat{k} \quad \dots(35)$$

$$\therefore \vec{k} \cdot \vec{r} = k_x x + k_y y + k_z z \quad \dots(36)$$

Now

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= \frac{\partial}{\partial t} [Ae^{-i(\omega t - \vec{k} \cdot \vec{r})}] \\ &= Ae^{-i(\omega t - \vec{k} \cdot \vec{r})} \times \frac{\partial}{\partial t} (-i\omega t) \\ &= -i\omega (A e^{-i(\omega t - \vec{k} \cdot \vec{r})}) \\ &= -i\omega \psi \end{aligned} \quad \dots(37)$$

$$\begin{aligned} \frac{\partial^2 \psi}{\partial t^2} &= \frac{\partial}{\partial t} (-i\omega \psi) = -i\omega \frac{\partial \psi}{\partial t} \\ &= -i\omega (-i\omega \psi) \quad (\text{using (37)}) \\ &= \omega^2 \psi \end{aligned} \quad \dots(38)$$

Put value from (38) in (32), we get

$$\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{-\omega^2}{u^2} \psi$$

$$\text{or } \frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{\omega^2}{u^2} \psi = 0 \quad \dots(39)$$

But

$$\omega = \text{angular frequency} = 2\pi\nu$$

$$u = \text{wave velocity} = v\lambda$$

$$\therefore \frac{\omega}{u} = \frac{2\pi\nu}{v\lambda} = \frac{2\pi}{\lambda} = k \quad \dots(40)$$

Here v and λ is the frequency and wavelength of de-Broglie wave respectively. Put value from (40) in (39), we get

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

$$\text{or } \nabla^2 \psi + k^2 \psi = 0 \quad \dots(41)$$

Equation (41) is called Dirac equation. It is valid at low as well as high velocities.

Suppose that particle is moving non relativistically (i.e. its speed is very small as compared to speed of light), then kinetic energy of particle is given by the following non relativistic expression :

$$\text{KE} = \frac{p^2}{2m} \quad \dots(42)$$

where p = linear momentum of particle
 m = mass of particle

According to de-Broglie, the wavelength of matter wave is given as

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

$$\Rightarrow p = \frac{h}{\lambda} = \left(\frac{h}{2\pi}\right) \left(\frac{2\pi}{\lambda}\right)$$

$$= \hbar k \quad \dots(43)$$

where $\frac{2\pi}{\lambda} = k$ = propagation constant

and $\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34} \text{ Js}$

\hbar is called Planck's reduced constant.

Put value from (43) in (42), we get

$$\text{KE} = \frac{\hbar^2 k^2}{2m} \quad \dots(44)$$

If U is potential energy of particle and E is total energy of particle, then

$$E = \text{KE} + U = \frac{\hbar^2 k^2}{2m} + U$$

$$\Rightarrow k^2 = \frac{2m}{\hbar^2} (E - U) \quad \dots(45)$$

Put this value in (41), we get

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad \dots(46)$$

Equation (46) is called time independent schrodinger equation for a restricted particle or particle subjected to an external force.

Case I. If the particle is free, then no external force is acting on it and potential energy of particle will be zero.

$$\text{i.e.} \quad U = 0$$

Put in (46), we get

$$\nabla^2 \psi + \frac{2m}{\hbar^2} E \psi = 0 \quad \dots(47)$$

Equation (47) is called time independent schrodinger equation for a free particle.

Case II. If particle is moving in one dimension (say X-axis) only, then

$$\begin{aligned} \nabla^2 \psi &= \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \\ &= \frac{\partial^2 \psi}{\partial x^2} = \frac{d^2 \psi}{dx^2} \end{aligned} \quad \dots(48)$$

Put this value in (46), we get

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad \dots(49)$$

Equation (49) is one dimensional time independent schrodinger equation for a restricted particle.

Put value from (48) in (47), we get

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad \dots(50)$$

Equation (50) is one dimensional time independent equation for a free particle.

(11) TIME DEPENDENT SCHRODINGER EQUATION

The three dimensional wave function of particle is given as

$$\psi(x, y, z) = A e^{-i(\omega t - \vec{k} \cdot \vec{r})} \quad \dots(51)$$

where symbols have their usual meanings.

From (51), we have

$$\begin{aligned} \frac{\partial \psi}{\partial x} &= \frac{\partial}{\partial x} [A e^{-i(\omega t - \vec{k} \cdot \vec{r})}] \\ &= A e^{-i(\omega t - \vec{k} \cdot \vec{r})} \times \frac{\partial}{\partial x} [i \vec{k} \cdot \vec{r}] \\ &= i \psi \times \frac{\partial}{\partial x} (k_x x + k_y y + k_z z) \\ &= i \psi (k_x + 0 + 0) = i k_x \psi \end{aligned} \quad \dots(52)$$

$$\begin{aligned} \therefore \frac{\partial^2 \psi}{\partial x^2} &= i k_x \frac{\partial \psi}{\partial x} \\ &= i k_x (i k_x \psi) \text{ (using (52))} \\ &= -k_x^2 \psi \end{aligned} \quad \dots(53)$$

Similarly

$$\frac{\partial^2 \psi}{\partial y^2} = -k_y^2 \psi \quad \dots(54)$$

and

$$\frac{\partial^2 \psi}{\partial z^2} = -k_z^2 \psi \quad \dots(55)$$

$$\therefore \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = - (k_x^2 + k_y^2 + k_z^2) \psi$$

$$\text{or } \nabla^2 \psi = -k^2 \psi \quad (\because \vec{k} = k_x \hat{i} + k_y \hat{j} + k_z \hat{k} \quad \therefore k^2 = k_x^2 + k_y^2 + k_z^2)$$

$$\text{or } \nabla^2 \psi = -\frac{p^2}{\hbar^2} \psi \quad \dots(55) \quad (\because p = \hbar k, \text{ see eq. (43)})$$

Again from (51), we get

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= \frac{\partial}{\partial t} [A e^{-(\omega t - \vec{k} \cdot \vec{r})}] \\ &= A e^{-i(\omega t - \vec{k} \cdot \vec{r})} \times \frac{\partial}{\partial t} (-i\omega t) \\ &= -i\omega \psi \end{aligned} \quad \dots(56)$$

But according to Planck's theory of light, the energy E of a wave packet is given as

$$E = h\nu = \left(\frac{h}{2\pi}\right)(2\pi\nu)$$

$$\Rightarrow E = \hbar\omega \quad \dots(57)$$

Put this value in (57), we get

$$\frac{\partial\psi}{\partial t} = -i\frac{E}{\lambda}\psi$$

$$\text{or} \quad i\hbar\frac{\partial\psi}{\partial t} = E\psi \quad \dots(58)$$

Now if a particle of mass m , and having potential energy U is moving non relativistically, then its total energy is given as

$$E = \frac{p^2}{2m} + U$$

Multiply both sides by ψ , we get

$$E\psi = \frac{p^2\psi}{2m} + U\psi$$

Put values from (55) and (58), we get

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m}\nabla^2\psi + U\psi \quad \dots(59)$$

Equation (59) is called time dependent Schrodinger equation for a restricted particle.

If particle is free then $U = 0$, Put in (59), we get

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m}\nabla^2\psi \quad \dots(60)$$

Equation (60) is called time dependent Schrodinger equation for a free particle.

Case I. If particle is moving in one dimension (say along X-axis) only, then $\nabla^2\psi = \frac{d^2\psi}{dx^2}$.

Put this value in (59), we get

$$i\hbar\frac{d\psi}{dt} = \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U\psi \quad \dots(61)$$

Equation (61) is one dimensional time dependent Schrodinger equation for a restricted particle.

For a free particle $U = 0$. Put in (61)

$$i\hbar\frac{d\psi}{dt} = \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} \quad \dots(62)$$

Equation (61) is called one dimensional time dependent Schrodinger equation for a free particle.

(12) PHYSICAL SIGNIFICANCE OF WAVE FUNCTION

The significance of the wave function ψ was given by Max. Born. According to him the wave function acquires significant through square of its magnitude.

"The square of magnitude of wave function $|\psi|^2 = \psi\psi^*$ represents the probability density of the particle in the state represented by ψ ". Here ψ^* means complex conjugate of ψ .

Thus if $dP(x, y, z)$ is probability of finding the particle in a small volume dV considered around point (x, y, z) then according to Max Born, the probability density $\frac{dP}{dV}$ is directly proportional to $|\psi|^2$.

$$\text{i.e. } \left(\frac{dP}{dV} \right) \propto |\psi|^2 \quad \text{or} \quad \frac{dP}{dV} = N |\psi|^2 \quad \dots(63)$$

Here 'N' is called Normalisation constant. Its value can be found by applying boundary conditions that must be satisfied by the wave function.

In one dimensional case probability density means probability per unit length and 2-dimensions, it means probability per unit area.

(13) NORMALISATION OF A WAVE FUNCTION

We have just studied that probability density is proportional to square of magnitude of wave function. Thus probability of finding the particle in a small region of volume dV around point (x, y, z) is given by

$$dP = N |\psi|^2 dV$$

Thus total probability of finding the particle in whole of universe is given as

$$\begin{aligned} P &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dP \\ &= N \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\psi|^2 dx dy dz \end{aligned} \quad \dots(64)$$

(where $dV = dx dy dz$)

However particle must be present some where in the universe thus total probability of finding the particle in whole of the universe must be exactly unity.

$$\text{i.e. } P = 1$$

$$\text{or } N \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\psi|^2 dx dy dz = 1 \quad \dots(65)$$

Equation (65) is called Normalisation condition and the value of N can be found from above equation.

If value of N comes out to be unity then

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\psi|^2 dx dy dz = 1 \quad \dots(66)$$

A wave function is said to be normalised if its normalisation constant is unity (i.e. probability density is exactly equal to $|\psi|^2$ instead of being proportional to it) and it satisfies equation (66).

If wave function is not normalised, then value of N will not be unity. However we can find value of N using equation (49) and then we can redefine our wave function as

$$\Psi = \sqrt{N} \psi \quad \dots(67)$$

So that new wave function Ψ is normalised. This process of finding normalisation constant and then redefining the wave function is called Normalisation of wave function. We know that if a function ψ satisfies a linear differential equation then any scalar multiple of ψ also satisfies that equation. Thus the redefined wave function will also satisfy Schrödinger Equation and the results would be unaltered in doing so.

Importance of Normalisation. Normalisation of a wave function ensures that the particle is present in the universe (or in the region under study) so that making calculations and finding various parameters using such function will not go in vain.

(14) ORTHOGONAL WAVE FUNCTIONS

Consider two different wave functions ψ_m & ψ_n such that both satisfy Schrödinger equation. If these functions are such that the integral $\int \psi_m^* \psi_n dV$ or $\int \psi_m \psi_n^* dV$ vanishes over the entire space, then these are called orthogonal wave functions i.e.

$$\int \psi_m^* \psi_n dV = \int \psi_m \psi_n^* dV = 0 \quad \dots(68)$$

For $m \neq n$

Also if wave functions ψ_m and ψ_n are simultaneously normalised, then

$$\int \psi_m^* \psi_m dV = 1 = \int \psi_n^* \psi_n dV \quad \dots(69)$$

The set of wave functions, which are both normalised as well as orthogonal are called Orthonormal Wave Functions. Equations (68) and (69) can be collectively written as follows

$$\int \psi_m^* \psi_n dV = \begin{cases} 0 & \text{if } m \neq n \\ 1 & \text{if } m = n \end{cases} \quad \dots(70)$$

Note that whenever we do not specify limits of integration, then it means integration is over the whole universe.

Importance of Orthogonal Wave Functions. If we have a complete set of orthogonal wave functions, then, any other wave function, which is a solution of Schrödinger Equation, can be expanded as a series combination of complete set of orthogonal wave functions.

(15) OPERATORS

An operator is in general a procedure, which when applied to a function, changes it to a new function. An operator is generally denoted by Symbol \hat{A} . Some examples are given below:

(1) Let \hat{A} = Take square root of (. . .)

Thus $\hat{A}(2) = \text{Take square root of } (2) = \sqrt{2} = 1.414$

Similarly $\hat{A}(4) = 2$

(ii) Let $\hat{A} = \text{Take derivative with respect to } 'x' \text{ of } (\dots)$
 $= \frac{d}{dx}$

$$\text{Thus } \hat{A}(\sin x) = \frac{d}{dx}(\sin x) = \cos x \text{ & } \hat{A}(\tan x) = \sec^2 x$$

Properties of Operators

(a) An operator is said to be linear if for functions $\psi_1, \psi_2, \dots, \psi_n$ and scalars C_1, C_2, \dots, C_n , the following condition is satisfied :

$$\hat{A}(C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + \dots + C_n\psi_n) = C_1\hat{A}\psi_1 + C_2\hat{A}\psi_2 + \dots + C_n\hat{A}\psi_n$$

Examples. If $\hat{A} = \frac{d}{dx}$

$$\begin{aligned} \text{then } \hat{A}(C_1\psi_1(x) + C_2\psi_2(x) + \dots + C_n\psi_n(x)) \\ &= \frac{d}{dx}(C_1\psi_1(x) + C_2\psi_2(x) + \dots + C_n\psi_n(x)) \\ &= C_1 \frac{d}{dx}\psi_1(x) + C_2 \frac{d}{dx}\psi_2(x) + \dots + C_n \frac{d}{dx}\psi_n(x) \\ &= C_1\hat{A}\psi_1 + C_2\hat{A}\psi_2 + \dots + C_n\hat{A}\psi_n \end{aligned}$$

Thus differentiation operator is a linear operator.

Similarly the operation integration is a linear operation.

Consider $\hat{A} = \text{Square root of } (\dots)$

Consider $\psi_1 = 9, \psi_2 = 16$

$$\text{Now } \hat{A}(\psi_1 + \psi_2) = \sqrt{9 + 16} = 5$$

$$\text{And } \hat{A}(\psi_1) + \hat{A}(\psi_2) = \sqrt{9} + \sqrt{16} = 3 + 4 = 7$$

$$\text{Clearly } \hat{A}(\psi_1 + \psi_2) \neq \hat{A}\psi_1 + \hat{A}\psi_2$$

Thus operation of taking root of function is non-linear.

(b) If an operator is such that when it is applied on a function, then it gives us as a result, same function multiplied with a scalar, then such an operator is called eigen value operator. i.e. if

$$\hat{A}\psi = \alpha\psi \quad \dots(71)$$

Where α is some scalar then the operator \hat{A} is called Eigen operator. The above equation is called eigen value equation, the scalar α obtained in the process is called eigen value and the wave function ψ satisfying eigen function.

Note that an operator may be eigen operator for one function & may not be so for some other function. e.g. consider $\hat{A} = \frac{d^2}{dx^2}$

$$\therefore \hat{A}\sin(ax) = -a^2 \sin(ax)$$

$\therefore \hat{A} = \frac{d^2}{dx^2}$ is eigen operator for function $\sin ax$ having eigen value $-a^2$.

$$\text{Now } \hat{A}(x)^n = n(n-1)x^{n-2}$$

Clearly this is not an eigen value equation. Hence the operator $\frac{d^2}{dx^2}$ is not eigen operator for a polynomial function. Similarly $\frac{d^2}{dx^2}$ is not an eigen operator for function $\tan x$.

(c) **Hermitian Operators.** An operator \hat{A} is said to be Hermitian, if for any two wave functions ψ_1 & ψ_2 the following condition is satisfied by \hat{A} :

$$\int \psi_1^* \hat{A} \psi_2 dV = \int \psi_1 (\hat{A} \psi_2)^* dV \quad \dots(72)$$

Importance of Hermitian operators arises from the fact that their eigen waves are real as proved below :

Suppose we consider a single wave function ψ such that when a Hermitian operator operates on it, we get eigen value α .

$$\text{i.e. } \hat{A}\psi = \alpha\psi \quad \dots(73)$$

Take complex conjugate of equation (73), we get

$$(\hat{A}\psi)^* = \alpha^* \psi^* \quad \dots(74)$$

Since \hat{A} is assumed to be Hermitian operator, hence it satisfies equation (72). By putting $\psi_1 = \psi_2 = \psi$, we get

$$\int \psi^* \hat{A} \psi dV = \int \psi (\hat{A}\psi)^* dV$$

$$\text{or } \int \psi^* \alpha\psi dV = \int \psi \alpha^* \psi^* dV$$

$$\text{or } \alpha \int \psi^* \psi dV = \alpha^* \int \psi \psi^* dV$$

$$\text{or } (\alpha - \alpha^*) \int \psi^* \psi dV = 0 \quad \dots(75)$$

But $\int \psi^* \psi dV$ is proportional to total probability of finding the particle in whole universe and hence it cannot be zero. Thus (68) implies

$$\alpha - \alpha^* = 0 \quad \text{or} \quad \alpha = \alpha^*$$

Hence α is a real number. Thus eigen values of Hermitian operators are real.

Importance of Operators. In classical physics, if we know about position and momentum of a particle, then all other physical quantities like energy, velocity, force acting etc. can be determined. Thus we say that we know the state of a particle if its position and momentum are known.

However, in quantum mechanics, the wave mechanical approach is used and for that we solve Schrödinger equation for each problem. The solution gives us the value of the wave function ψ . However we are interested in measurable quantities like position, momentum,

energy of the particle and these quantities can be very well obtained from the wave function by operating it by a suitable Hermitian operator.

"Thus operators in quantum mechanics help us to determine measurable quantities from the wave function". Since if we know ψ , then we can know position, momentum and energy of particle, so wave function is also called state of particle.

(16) EXAMPLES OF HERMITIAN OPERATORS

There are a number of hermitian operators, which are used in quantum mechanics to determine various quantities associated with particle like position, energy, momentum etc. A few of these are explained below :

(a) Linear Momentum Operator. The three dimensional wave function of a particle is given as

$$\psi(x, y, z) = A e^{-i(\omega t - \vec{k} \cdot \vec{r})} \quad \dots(76)$$

Consider an operator \hat{p}_x defined as follows

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad \dots(77)$$

$$\begin{aligned} \therefore \hat{p}_x \psi &= -i\hbar \frac{\partial}{\partial x} \psi \\ &= -i\hbar \frac{\partial}{\partial x} [A e^{-i(\omega t - \vec{k} \cdot \vec{r})}] \\ &= [-i\hbar A e^{-i(\omega t - \vec{k} \cdot \vec{r})}] \frac{\partial}{\partial x} (i \vec{k} \cdot \vec{r}) \end{aligned}$$

$$\begin{aligned} &= \hbar \psi \frac{\partial}{\partial x} (k_x x + k_y y + k_z z) \\ &= \hbar \psi (k_x + 0 + 0) \\ &= \hbar p_x \psi \end{aligned}$$

$$\Rightarrow \hat{p}_x \psi = p_x \psi \quad \dots(78)$$

$$(\because \vec{p} = \hbar \vec{k} \therefore p_x = \hbar k_x, p_y = \hbar k_y \text{ and } p_z = \hbar k_z)$$

Here $p_x = \hbar k_x$ is X-component of linear momentum of the particle.

From (78) we see that when operator \hat{p}_x is applied on wavefunction ψ , then we get x-component of linear momentum multiplied with wave function. Thus \hat{p}_x is linear momentum operator for X-component of linear momentum. Similarly operator for Y and Z component of linear momentum are given as follows :

$$\hat{p}_y = -i\hbar \frac{\partial}{\partial y} \quad \dots(79)$$

$$\hat{p}_z = -i\hbar \frac{\partial}{\partial z} \quad \dots(80)$$

Let \hat{p} is operator for total linear momentum of particle.

Then

$$\hat{p} = \hat{p}_x \hat{i} + \hat{p}_y \hat{j} + \hat{p}_z \hat{k}$$

$$= -i\hbar \left(\hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \right)$$

or

$$\hat{p} = i\hbar \vec{\nabla} \quad \dots(81)$$

Equation (81) gives operator for total linear momentum of particle.

(b) **Hamiltonian Operator:** The wave function of particle in three dimensions is given as:

$$\psi(x, y, z) \equiv A e^{-i(\omega t - \vec{k} \cdot \vec{r})} \quad \dots(82)$$

$$\therefore \frac{\partial^2 \psi}{\partial x^2} = -k_x^2 \psi \quad \dots(83)$$

$$\frac{\partial^2 \psi}{\partial y^2} = -k_y^2 \psi \quad \dots(84)$$

$$\frac{\partial^2 \psi}{\partial z^2} = -k_z^2 \psi \quad \dots(85)$$

(See equation (53), (54), (55))

$$\therefore \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = - (k_x^2 + k_y^2 + k_z^2) \psi$$

$$\text{or} \quad \nabla^2 \psi = -k^2 \psi = -\frac{p^2}{\hbar^2} \psi \quad (\because p = \hbar k) \quad \dots(86)$$

$$\Rightarrow \frac{-\hbar^2}{2m} \nabla^2 \psi = \frac{p^2}{2m} \psi$$

From (86), we see that if we operate the operator $\frac{-\hbar^2}{2m} \nabla^2$ on wave function ψ of a non relativistic particle, then we get kinetic energy of particle multiplied with wave function. Thus the operator

$$\hat{K} = \frac{-\hbar^2}{2m} \nabla^2 \quad \dots(87)$$

is called kinetic energy operator.

The potential energy operator of particle is the potential energy itself.

i.e.

$$\hat{U} = U$$

The operator for total energy is called Hamiltonian operator. It is denoted by \hat{H} and it is equal to sum of kinetic energy operator and potential energy operator.

i.e.

$$\hat{H} = \hat{K} + \hat{U}$$

or

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U \quad \dots(88)$$

Thus

$$\begin{aligned} \hat{H} \psi &= -\frac{\hbar^2}{2m} \nabla^2 \psi + U \psi \\ &= \frac{p^2}{2m} \psi + U \psi \quad (\text{using (86)}) \end{aligned} \quad \dots(89)$$

$$\begin{aligned}
 &= \left(\frac{p^2}{2m} + U \right) \psi \\
 \hat{H} \psi &= E \psi
 \end{aligned} \tag{90}$$

This verifies that when \hat{H} is applied on wave function, then we get total energy of particle multiplied with wave function.

Again we have

$$\begin{aligned}
 i\hbar \frac{\partial \psi}{\partial t} &= i\hbar \frac{\partial}{\partial t} [\Lambda e^{-i(\omega t - \vec{k} \cdot \vec{r})}] \\
 &= i\hbar \Lambda e^{-i(\omega t - \vec{k} \cdot \vec{r})} \times \frac{\partial}{\partial t} (-i\omega t) \\
 &= i\hbar \psi (-i\omega) \\
 &= \hbar \omega \psi \\
 \therefore i\hbar \frac{\partial \psi}{\partial t} &= E \psi
 \end{aligned} \tag{91} \text{ [using (57)]}$$

Thus when operator $i\hbar \frac{\partial}{\partial t}$ is applied to wave function ψ , then we get total energy of particle multiplied with wave function. Thus operator $i\hbar \frac{\partial}{\partial t}$ is also Hamiltonian operator. i.e.

$$\hat{H} = i\hbar \frac{\partial}{\partial t} \tag{92}$$

Note that if we put values from (91) and (89) in (59), we can write Schrodinger equation in operator form as follows :

$$\begin{aligned}
 E\psi &= \hat{H}\psi \\
 \text{or} \quad \hat{H}\psi &= E\psi
 \end{aligned} \tag{93}$$

This is time dependent Schrodinger equation for a non relativistic particle.

Note. Just like potential energy, the operator for position co-ordinate of particle is the position co-ordinate it self.

$$\begin{aligned}
 \hat{x} &= x \\
 \hat{y} &= y \\
 \hat{z} &= z
 \end{aligned} \tag{94}$$

Example 5. Derive time independent Schrodinger equation from time dependent equation.

Solution. Time dependent Schrodinger wave equation is given as

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + U\psi = i\hbar \frac{\partial \psi}{\partial t} \tag{i}$$

The wave function of particle is given as

$$\begin{aligned}
 \psi(x, y, z, t) &= A e^{-i(\omega t - \vec{k} \cdot \vec{r})} \\
 &= (A e^{i\vec{k} \cdot \vec{r}}) e^{-i\omega t}
 \end{aligned}$$

This equation tells that complete wave function $\psi(x, y, z, t)$ is equal to product of two new wave functions viz., $\phi(x, y, z)$ depending only upon space variables (x, y, z) and $\phi_o(t)$ depending only upon time i.e.

$$\psi(x, y, z, t) = \phi(x, y, z) \phi_o(t) \quad \dots(ii)$$

Put this value in (i), we get

$$\begin{aligned} \frac{-\hbar^2}{2m} \nabla^2 (\phi \phi_o) + U \phi \phi_o &= i \hbar \frac{\partial}{\partial t} (\phi \phi_o) \\ \Rightarrow \frac{-\hbar^2}{2m} \phi_o \nabla^2 \phi + U \phi \phi_o &= i \hbar \phi \frac{\partial}{\partial t} \phi_o \end{aligned}$$

Dividing both sides by $\phi \phi_o$, we get

$$\frac{-\hbar^2}{2m \phi} \nabla^2 \phi + U = \frac{i \hbar}{\phi_o} \frac{\partial \phi_o}{\partial t} \quad \dots(iii)$$

In equation (ii) we see that left hand side depends only on space variables (x, y, z) and right hand side only on time (t) . Thus this equation can be satisfied only if each side is equal to a constant of motion (i.e. some quantity which does not change with time and position). Hence that constant must be equal to total energy (E) of particle, which is always conserved. Thus equating each side of (iii) to total energy E separately, we get

$$\begin{aligned} \frac{i \hbar}{\phi_o} \frac{\partial \phi_o}{\partial t} &= E \\ \Rightarrow i \hbar \frac{\partial \phi_o}{\partial t} &= E \phi_o \end{aligned} \quad \dots(iv)$$

Equation (iv) gives time evolution of wave function.

Similarly equation left hand side of (iii) to total energy, we get

$$\frac{-\hbar^2}{2m \phi} \nabla^2 \phi + U = E$$

Multiply sides by $\frac{-2m\phi}{\hbar^2}$, we get

$$\begin{aligned} \nabla^2 \phi - \frac{2m}{\hbar^2} U \phi &= -\frac{2m}{\hbar^2} E \phi \\ \Rightarrow \nabla^2 \phi + \frac{2m}{\hbar^2} (E - U) \phi &= 0 \end{aligned} \quad \dots(v)$$

Equation (v) is time independent Schrodinger equation.

Example 6. Derive time dependent Schrodinger equation from time independent equation.

Solution. Time independent equation is given as

$$\begin{aligned} \nabla^2 \psi + \frac{2m}{\hbar^2} (E - U) \psi &= 0 \\ \Rightarrow \frac{2mE}{\hbar^2} \psi &= -\nabla^2 \psi + \frac{2m}{\hbar^2} U \psi \\ \Rightarrow E \psi &= -\frac{\hbar^2}{2m} \nabla^2 \psi + U \psi \end{aligned} \quad \dots(i)$$

The three dimensional wave function is given as

$$\psi(x, y, z, t) = A e^{-i(\omega t - \vec{k} \cdot \vec{r})} \quad \dots(ii)$$

$$\therefore \frac{\partial \psi}{\partial t} = [A e^{-i(\omega t - \vec{k} \cdot \vec{r})}] \times (-i\omega) = -i\omega \psi$$

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

Put value from (iii) in (i), we get

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + U\psi$$

which is time dependent Schrodinger equation.

(20) APPLICATIONS OF SCHRONDINGER EQUATION

(a) Particle in one dimensional box. Consider a single particle of mass 'm' is moving in a one dimensional region along X-axis specified by the limits $x = 0$ & $x = L$ where L is length of region. We can call this region as one dimensional box.

For simplicity, we may assume that particle is moving non-relativistically and the potential energy of particle is zero inside the box and infinity elsewhere.

i.e. potential energy $U(x)$ is of the form

$$U(x) = \begin{cases} 0 & ; \text{ if } 0 \leq x \leq L \\ \infty & ; \text{ Elsewhere} \end{cases} \quad \dots(96)$$

This kind of choice of potential energy ensures that particle will never go out of the box classically.

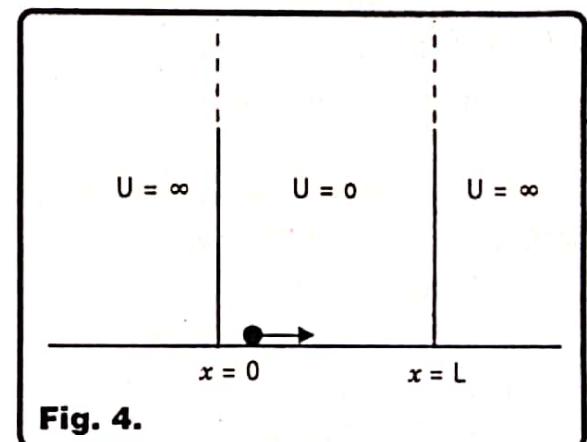


Fig. 4.

The one dimensional time independent Schrödinger equation is given by

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad \dots(97)$$

Here we have converted partial derivatives into exact because equation now contains only one variable, that is x co-ordinate.

Inside the box $U = 0$, so that above equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0$$

or

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \dots(98)$$

where

$$k = \frac{\sqrt{2mE}}{\hbar} \quad \dots(99)$$

quantity k has dimensions reciprocal of length & it is called propagation constant of the wave associated with particle. (It is easy to verify from (99) that $k = 2\pi/\lambda$).

Equation (98) is a second order linear differential equation, whose solution is of the form

$$\psi(x) = A \sin kx + B \cos kx \quad \dots(100)$$

Here A & B are constants of integration. For finding their value, we make use of boundary conditions on ψ , that are essential for ψ to be well behaved.

We know that particle is confined only within the box, thus probability of finding the particle outside the box must be zero. This is possible only if value of wave function ψ outside the box is identically zero. Inside the box the probability of finding the particle at some points may or may not be zero (of course it must be exactly one for whole region of box), thus wave of ψ at different points inside box may be zero or non zero. However the wave function must be continuous everywhere from $-\infty$ to $+\infty$. The condition of continuity can be fulfilled only if at the end points $x = 0$ and $x = L$, the wave function is identically zero.

Thus we must have (for ψ to be a well behaved function)

$$\psi(x) = 0 \quad \text{whenever} \quad x = 0 \text{ or } x = L$$

Putting first boundary condition in (100), we get

$$0 = A(0) + B(1) \quad \text{or} \quad B = 0$$

Thus wave function becomes $\psi(x) = A \sin kx$... (101)

Putting second boundary condition in (101), we get

$$0 = A \sin(kL)$$

But A cannot be zero since in that case, wave function becomes identically zero everywhere, which means particle is present nowhere, which is absurd.

Hence we must have

$$\sin(kL) = 0 \quad \text{or} \quad kL = 0, \pm\pi, \pm 2\pi, \pm 3\pi, \dots$$

However the case $kL = 0, -\pi, -2\pi, -3\pi, \dots$ are not acceptable to us because zero or negative length of box is meaningless.

Hence we get

$$kL = \pi, 2\pi, 3\pi, \dots \quad \text{or} \quad kL = n\pi \quad \dots (102)$$

where $n = 1, 2, 3, 4, \dots$ n is Quantum number

Substituting value of k from (99), we get

$$\left(\frac{\sqrt{2mE_n}}{\hbar} \right) L = n\pi$$

We have put subscript n to total energy E because total energy E now depends on Quantum number n

$$\text{or} \quad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad \dots (103)$$

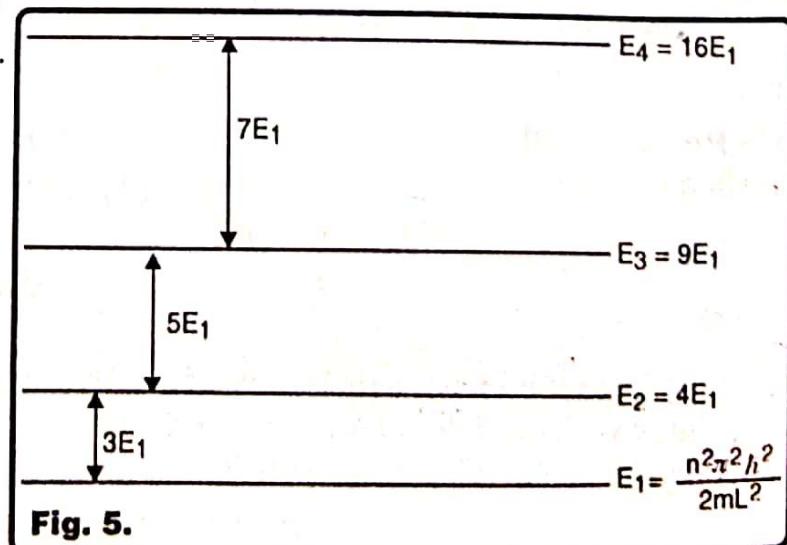
Equation (103) gives energy eigen values of a particle confined to move in a one dimensional box of length L .

Since minimum allowed value of n is one, thus minimum energy of particle in box is

$$E_{\min} = E_1 = \frac{\pi^2\hbar^2}{2mL^2} \quad \dots (104)$$

Thus equation (103) can be rewritten as

$$E_n = n^2 E_1 \quad \dots (105)$$



This equation shows that whenever a particle is confined to move in a bounded region then its total energy is quantised, i.e. total energy is always integral multiple of minimum value of energy E_1 (called one Quantum). This result is different from classical physics according to which energy values taken by particle are continuous i.e. any value of energy is possible.

The discrete energy level spectrum of particle in a one dimensional box is shown in fig. (5). The energy difference between two consecutive energy levels is given by

$$\Delta E_n = E_n - E_{n-1}$$

$$= n^2 E_1 - (n-1)^2 E_1 = (n^2 - n^2 - 1 + 2n) E_1 = (2n-1) E_1$$

Thus ΔE_n depends on n hence the energy gap between energy states goes on increasing with increase in quantum number n . Thus energy levels of particle in a box are unevenly spaced. The state E_1 is called Ground State and E_2, E_3, \dots etc. called First, 2nd, excited states respectively.

We now turn our attention to finding the value of second constant of integration A . For that we assert that wave function $\psi(x)$ is normalised. Thus we must have

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1 \quad \text{or} \quad \int_0^L |\psi(x)|^2 dx = 1 \quad \left(\because \psi(x) = 0 \text{ for } -\infty < x \leq 0 \text{ and } L \leq x < \infty \right)$$

$$\text{or} \quad A^2 \int_0^L \sin^2(kx) dx = 1 \quad \text{or} \quad \frac{A^2}{2} \int_0^L [1 - \cos(2kx)] dx = 1$$

$$\text{or} \quad \frac{A^2}{2} \int_0^L \left[1 - \cos\left(\frac{2n\pi}{L}x\right) \right] dx = 1 \quad (\because kL = n\pi)$$

$$\text{or} \quad A = \sqrt{\frac{2}{L}} \quad \dots(106)$$

Thus complete normalised wave function of particle in 1-D box is given by

$$\psi(x) = A \sin kx$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad \dots(107)$$

(Using (102) & (106))

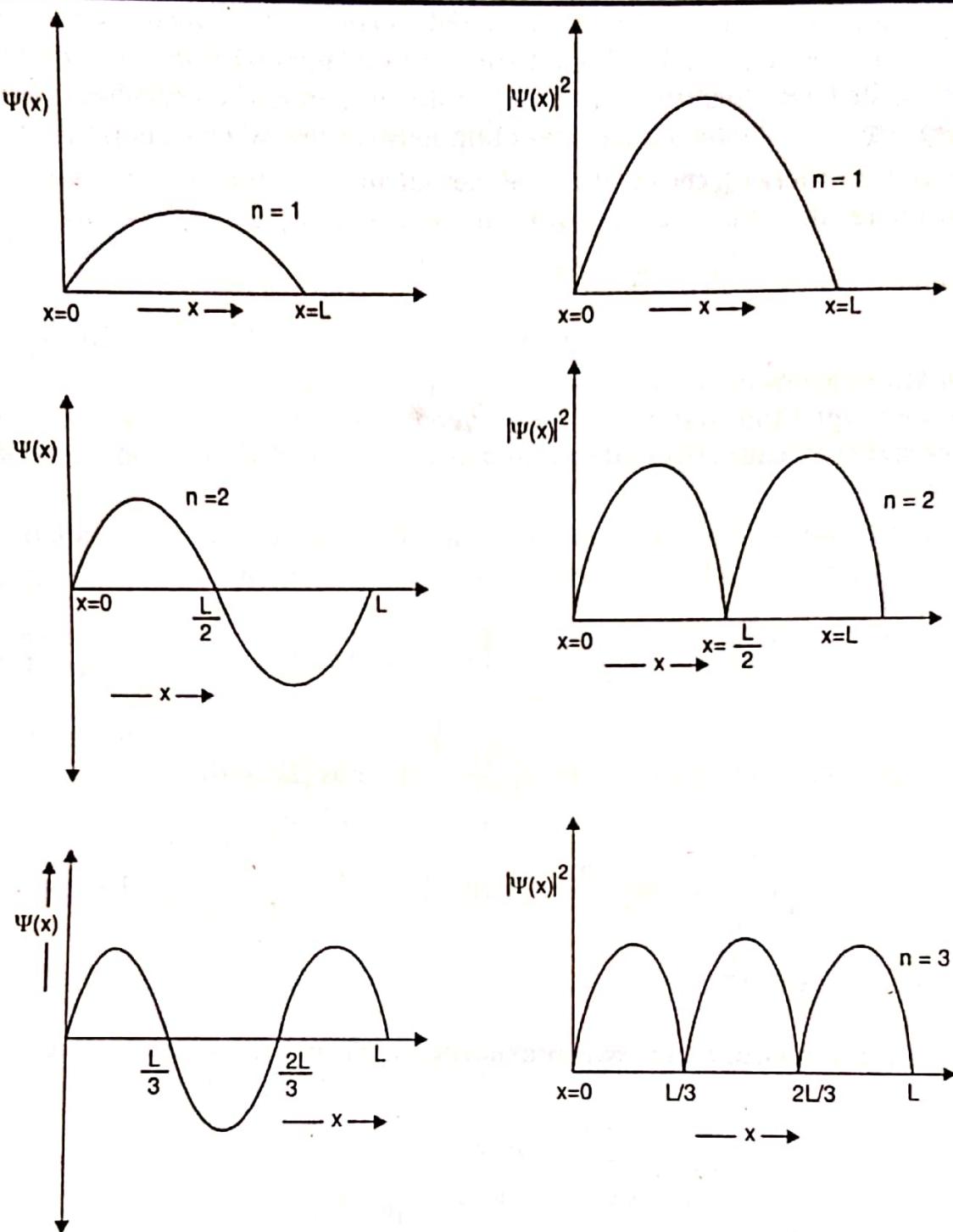
The graph of wave function versus x and probability density versus x for first few Quantum numbers is shown next page.

Remark. 1. If we assume that potential energy of particle inside box is not zero but a constant quantity U (say), then our results would get modified as follows :

$$k = \sqrt{\frac{2m(E-U)}{\hbar}}$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} + U, \quad kL = n\pi$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \quad [\text{one may easily verify these results}]$$

**Fig. 6.**

Here also we see that minimum value of $n = 1$ so that $E - U = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$ is never zero. But $E - U$ represents kinetic energy of particle. So we arrive at very interesting conclusion.

"Whenever a particle is bounded in a region, it can never be at rest".

If we consider an atom to be a one dimensional box and electron to be a particle confined within it, then we can now easily recognise that electron inside atom can never be at rest, otherwise it will fall into nucleus. Thus the condition imposed on electron to revolve around nucleus in Rutherford Model appears here naturally. Hence results of classical and quantum mechanics are apparent. Note that we have just given idea on the above results & the mathematical results derived above should not be used to solve problems of motion of electron in atom. Because in actual practice the motion of electron in atom is 3 dimensional.

2. If we assume that particle is moving freely in whole universe then no Quantum condition is obtained even with Schroedinger Equation. Thus particle can take any value of energy in that case and energy spectrum becomes continuous. Thus for motion of particle in unbounded region (macroscopic world) the classical and Quantum physics agree with each other.

(b) **Particle in a 3-dimensional box.** Consider a cuboid of edges a, b, c having one of the corners as origin. A particle of mass m is confined to move in this box. The potential energy of particle $U(x, y, z)$ is assumed zero everywhere inside the box and infinity elsewhere.

Thus

$$U(x, y, z) = \begin{cases} 0 & ; \quad \text{if } 0 \leq x \leq a \\ \infty & ; \quad \text{elsewhere} \end{cases} \quad \dots(108)$$

The 3-dimensional time independent Schroedinger equation is given as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad \dots(109)$$

Since potential energy $V(x, y, z)$ is independent of the time t , hence we can carry out separation of variables method to solve this equation.

We assert that the overall wavefunction ψ is equal to product of 3 wave functions $P(x), Q(y), R(z)$ i.e.

$$\psi(x, y, z) = P(x) Q(y) R(z) \quad \dots(110)$$

Put (110) in (109), we get

$$QR \frac{\partial^2 P}{\partial x^2} + PR \frac{\partial^2 Q}{\partial y^2} + PQ \frac{\partial^2 R}{\partial z^2} + \frac{2mE}{\hbar^2} - PQR = 0 \quad (\because U=0 \text{ inside the box})$$

Divide both sides by PQR we get

$$\frac{1}{P} \frac{\partial^2 P}{\partial x^2} + \frac{1}{Q} \frac{\partial^2 Q}{\partial y^2} + \frac{1}{R} \frac{\partial^2 R}{\partial z^2} + \frac{2m}{\hbar^2} (E) = 0$$

or

$$-\frac{1}{P} \frac{\partial^2 P}{\partial x^2} = \frac{1}{Q} \frac{\partial^2 Q}{\partial y^2} + \frac{1}{R} \frac{\partial^2 R}{\partial z^2} + k^2 \quad \dots(11)$$

where

$$k = \frac{\sqrt{2mE}}{\hbar} \quad \dots(112)$$

The left hand side of this equation depends only on x -coordinate while right side only on y and z -co-ordinates. This equation can be satisfied only if each side is equal to some constant k_x^2 (say). Hence we can write

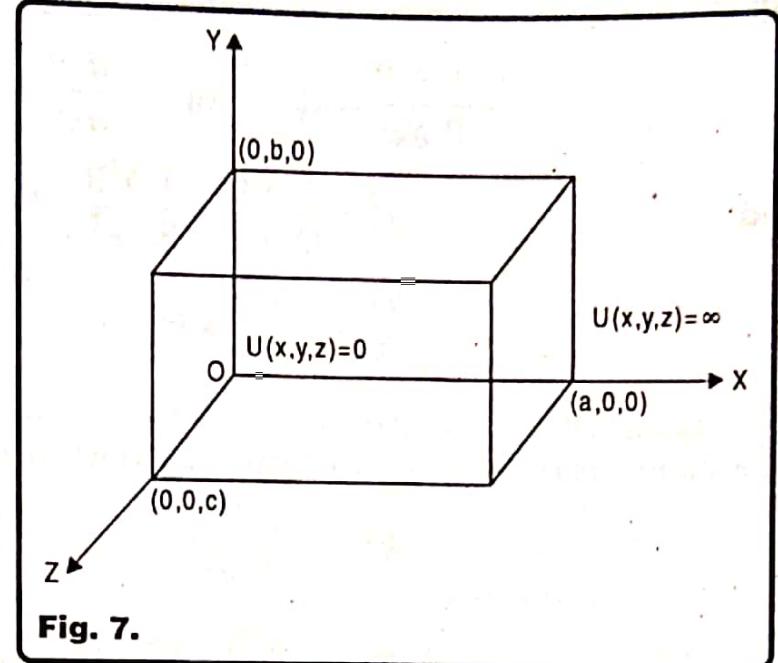


Fig. 7.

$$-\frac{1}{P} \frac{\partial^2 P}{\partial x^2} = k_x^2 \quad \text{or} \quad \frac{d^2 P}{dx^2} + k_x^2 P = 0 \quad \dots(113)$$

and

$$k_x^2 = \frac{1}{Q} \frac{\partial^2 Q}{\partial y^2} + \frac{1}{R} \frac{\partial^2 R}{\partial z^2} + k^2$$

or

$$\frac{-1}{Q} \frac{\partial^2 Q}{\partial y^2} = \frac{1}{R} \frac{\partial^2 R}{\partial z^2} + k^2 - k_x^2 \quad \dots(114)$$

Again LHS of (114) depends only on y -coordinate and RHS on z co-ordinate, hence each side should be equal to some constant k_y^2 (say) so we can write (114) as

$$k_y^2 = -\frac{1}{Q} \frac{\partial^2 Q}{\partial y^2} \quad \text{or} \quad \frac{d^2 Q}{dy^2} + k_y^2 Q = 0 \quad \dots(115)$$

and

$$k_y^2 = \frac{1}{R} \frac{\partial^2 R}{\partial z^2} + k^2 - k_x^2 \quad \text{or} \quad \frac{d^2 R}{dz^2} + k_z^2 R = 0 \quad \dots(116)$$

where we have put

$$k_z^2 = k^2 - k_x^2 - k_y^2$$

or

$$k^2 = k_x^2 + k_y^2 + k_z^2 \quad \dots(117)$$

In equations (113), (115) and (116), we have changed partial derivatives into exact, because variables have been separated.

Equation (113) represents one dimensional particle in a box along X-axis and we have already solved it. Hence its solution is given by

$$P(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \quad \dots(118)$$

where

$$k_x a = n_x \pi ; n_x = 1, 2, 3, \dots$$

Similarly solution of (115) is

$$Q(y) = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \quad \dots(119)$$

where

$$k_y b = n_y \pi \quad \dots(120)$$

$$n_y = 1, 2, 3, \dots$$

Similarly solution of (116) is given as

$$R(z) = \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right) \quad \dots(121)$$

where

$$k_z c = n_z \pi \quad \dots(122)$$

$$n_z = 1, 2, 3, \dots$$

Thus normalized wave function is given by

$$\begin{aligned} \psi(x, y, z) &= P(x) Q(y) R(z) \\ &= \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) \end{aligned} \quad \dots(123)$$

The energy eigen values are given by

$$E_n = \frac{k^2 \hbar^2}{2m}$$

(See equation (102))

$$= (k_x^2 + k_y^2 + k_z^2) \frac{\hbar^2}{2m}$$

(using (107))

Substitute, various values, we get

$$E_n = \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \frac{\pi^2 \hbar^2}{2m}$$

...(124)

This equation gives energy eigen values of particle in 3-dimensional box. Clearly, the energy values are quantised.

The minimum energy (Ground State) is obtained when $n_x = n_y = n_z = 1$. Thus

$$E_{\min} = E_1 = \left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \right) \frac{\pi^2 \hbar^2}{2m}$$

Next higher energy levels are obtained when (n_x, n_y, n_z) attains values $(1, 1, 2)$ or $(1, 2, 1)$ or $(2, 1, 1)$ depending upon values of a, b, c .

(c) One Dimensional Harmonic Oscillator. Consider a particle of mass m , having natural frequency of vibration ω along one dimension (say X-axis). Classically the potential energy of harmonic oscillator is given by the familiar expression

$$U(x) = \frac{1}{2} m \omega^2 x^2 \quad \dots(125)$$

The one dimensional time independent Schrödinger equation is given as

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad \dots(126)$$

Substitute value of V from (125) we get

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} m \omega^2 x^2 \right) \quad \dots(127)$$

This equation represents Schrödinger equation for a harmonic oscillator. Here x has units of length and E has units of energy. To solve this equation we define unit of length as

$\sqrt{\frac{\hbar}{m\omega}}$ (It is easy to verify that dimensions of $\sqrt{\frac{\hbar}{m\omega}}$ is of length) and unit of energy as $\frac{1}{2} \hbar\omega$.

Thus in these units let y and λ are numerical values of x and E respectively. Then, we can write

$x = (\text{numerical value}) \times \text{unit}$, $E = \text{numerical value} \times \text{unit}$

or

$$x = y \sqrt{\frac{\hbar}{m\omega}} \quad \dots(128)$$

and

$$E = \lambda \frac{\hbar\omega}{2} \quad \dots(129)$$

Clearly y and λ are dimensionless quantities.

From equation (128) we get

$$\frac{dx}{dy} = \sqrt{\frac{\hbar}{m\omega}} \quad \dots(130)$$

Now by chain rule $\frac{d\psi}{dx} = \frac{d\psi}{dy} \cdot \frac{dy}{dx} = \sqrt{\frac{m\omega}{\hbar}} \frac{d\psi}{dy}$ (using 130)

$$\begin{aligned} \text{Thus } \frac{d^2\psi}{dx^2} &= \frac{d}{dx} \left(\frac{d\psi}{dx} \right) = \frac{d}{dx} \left(\sqrt{\frac{m\omega}{\hbar}} \frac{d\psi}{dy} \right) = \sqrt{\frac{m\omega}{\hbar}} \frac{d}{dx} \left(\frac{d\psi}{dy} \right) \\ &= \sqrt{\frac{m\omega}{\hbar}} \frac{d}{dy} \left(\frac{d\psi}{dy} \right) \frac{dy}{dx} = \frac{m\omega}{\hbar} \frac{d^2\psi}{dy^2} \end{aligned} \quad \dots(131)$$

Put values from (128), (129) and (131) in (127), we get

$$\frac{m\omega}{\hbar} \frac{d^2\psi}{dy^2} + \frac{2m}{\hbar^2} \left(\lambda \frac{\hbar\omega}{2} - \frac{1}{2} m\omega^2 \times y^2 \frac{\hbar}{m\omega} \right) = 0$$

or

$$\frac{d^2\psi}{dy^2} + (\lambda - y^2) \psi = 0 \quad \dots(132)$$

This is a linear differential equation of second order with variable coefficients. Its solution can be obtained by series method. The solution is found to be of the form

$$\psi(y) = A e^{-y^2/2} \phi(y) \quad \dots(133)$$

where $\phi(y)$ is an infinite series function and it is given as

$$\phi(y) = \sum_{\substack{l=0, 2, 4, 6, \dots \\ \text{or } l=1, 3, 5, 7, \dots}} a_l y^l \quad \dots(134)$$

The coefficients a_l are related to each other by the following Recurring relation

$$a_{l+2} = \frac{2l+1-\lambda}{(l+2)(l+1)} a_l \quad \dots(135)$$

Now we know that wave function must vanish at $y \rightarrow \pm \infty$. However the function $\psi(y)$ is found to diverge as y increases. This is because of the fact that $\phi(y)$ is diverging. Hence this wave function as such is not a well behaved wave function. To overcome this problem, we notice that if we somehow restrict the number of terms in $\phi(y)$ from ∞ to finite then $\phi(y)$ & hence $\psi(y)$ will become converging (any series containing finite number of terms is converging). Now we carefully analyse equation (135). If one coefficient a_l is zero then next coefficient a_{l+2} will also be zero because of (135). If we change l to $l+2$ we see that

$$a_{l+4} = \frac{2l+3-\lambda}{(l+4)(l+3)} a_{l+2}$$

Since a_{l+2} is zero so a_{l+4} is also zero. Thus in general all expansion coefficients $a_{l+2}, a_{l+4}, a_{l+6}, \dots$ will become identically zero if at least one coefficient a_l is zero. In that case $\phi(y)$ will become a polynomial of finite degree and will converge.

From (135) we see that at least one coefficient will become zero if λ is some odd integer of the form

$$\lambda = 2n + 1 \quad \dots(136)$$

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

When condition (136) is imposed on $\psi(y)$, then it becomes well behaved function. Since λ is numerical value of energy of oscillator, hence the total energy of oscillator is thus given by

$$E_n = \lambda \frac{\hbar\omega}{2} = (2n+1) \frac{\hbar\omega}{2} = \left(n + \frac{1}{2} \right) \hbar\omega \quad \dots(137)$$

This equation gives the total energy of the oscillator. Clearly the energy is quantised. The minimum allowed value of quantum number n is zero. Thus minimum energy of harmonic oscillator is given by

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

This energy is called Zero Point Energy. Clearly the energy of harmonic oscillator can never be zero according to quantum mechanics. This result is different from classical mechanics according to which the minimum energy of harmonic oscillator is zero.

The difference between adjacent energy levels is given by

$$\Delta E_n = E_n - E_{n-1} = \left(n + \frac{1}{2}\right) \hbar \omega - \left(n - \frac{1}{2}\right) \hbar \omega = \hbar \omega$$

Thus $\Delta E_n = \Delta E = \hbar \omega$... (138)

Thus energy levels of harmonic oscillator are evenly spaced.

Let us now turn our attention to equation (134). If the quantum condition (136) is used in this equation then $\phi(y)$ will contain finite number of terms & it will be a polynomial of degree

n ($\because \lambda = 2n + 1 \Rightarrow a_{l+2} = \frac{2(l-n)}{(l+2)(l+1)} a_l$. So when $l = n$ then $a_{l+2} = a_{l+4}, \dots$ all will be zero). So polynomial will be of the form

$$\phi(y) = a_0 + a_2 y^2 + a_4 y^4 + \dots + a_n y^n \quad (\text{when } n \text{ is even})$$

or $\phi(y) = a_1 + a_3 y^3 + a_5 y^5 + \dots + a_n y^n \quad (\text{when } n \text{ is odd})$

To evaluate coefficients a_l , we define this polynomial in such a way that coefficient of highest degree term must be equal to 2^n (where n = degree of polynomial). With this condition, polynomial $\phi(y)$ becomes a special kind of polynomial and is called Hermite polynomial of degree n and is denoted as $H_n(y)$.

Thus the eigen functions of linear harmonic oscillator are given by

$$\psi_n(y) = A e^{-y^2/2} H_n(y) \quad \dots (139)$$

To find the constant A , we assert that wave function $\psi_n(x)$ are normalised i.e.

$$\int_{-\infty}^{\infty} \psi_n \psi_n^* dy = 1$$

This equation gives us on solving, the value of A as

$$A = \frac{1}{\sqrt{2^n \cdot n! \sqrt{\pi}}} \quad \dots (140)$$

Hence normalised eigen functions of Harmonic oscillator are

$$\psi_n(y) \frac{1}{\sqrt{2^n (n!) \sqrt{\pi}}} e^{-y^2/2} H_n(y) \quad \dots (141)$$

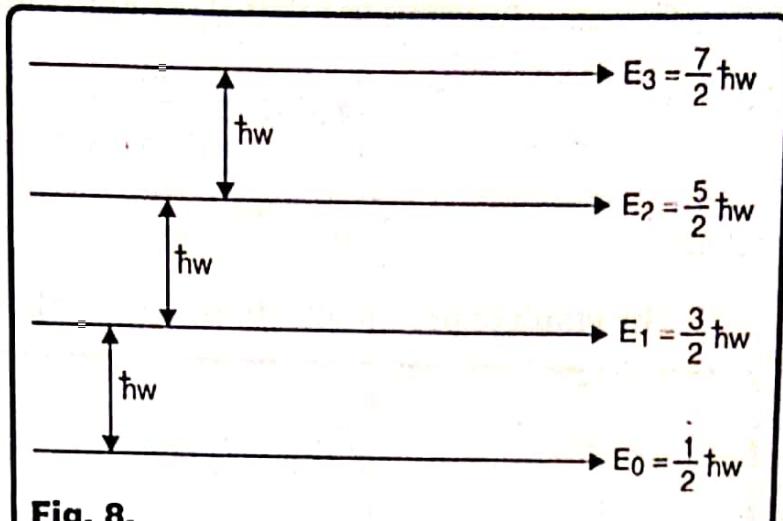


Fig. 8.

The wave function in original variable x are given by the result

$$\psi_n(x) \frac{\sqrt{a}}{\sqrt{2^n (n!) \sqrt{\pi}}} e^{-\alpha^2 x^2/2} H_n(\alpha x) \quad \dots(142)$$

where

$$\alpha = \frac{m\omega}{\hbar} \quad \dots(143)$$

The graph of probability density for various values of n are shown in figure (9)

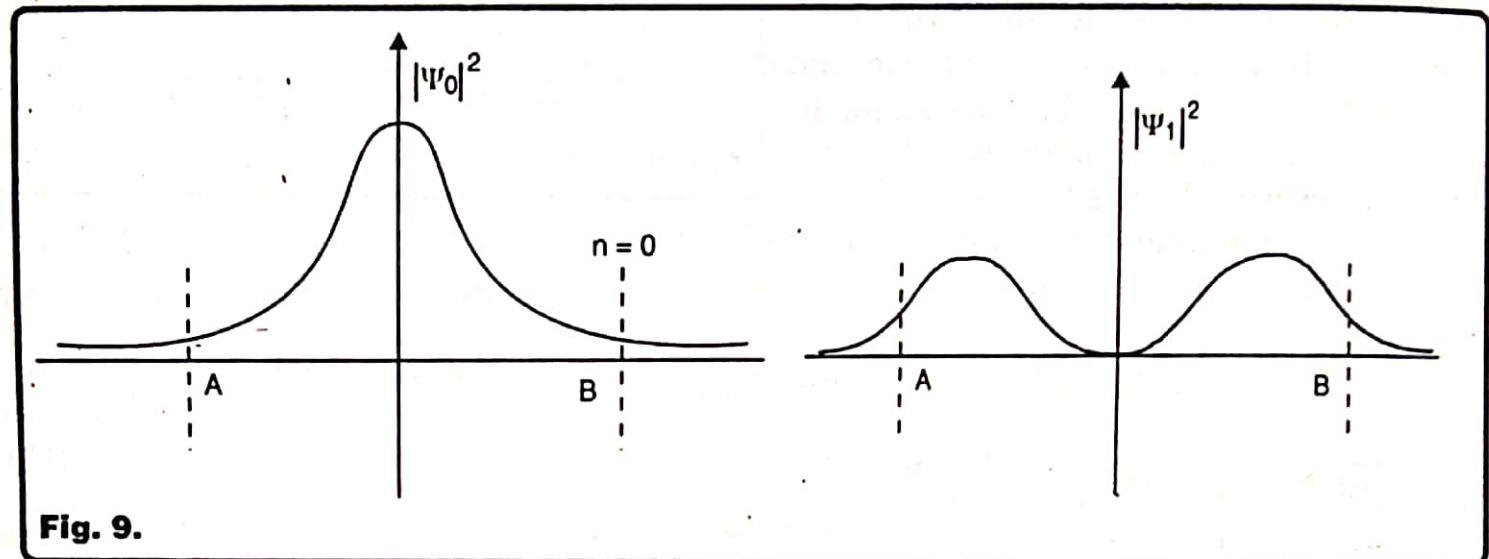


Fig. 9.

Here A and B represent classical extreme limits of oscillator. From these graphs we conclude that there are finite chances that particle may go beyond extreme limits. This result is also in contrast to classical physics, according to which particle can never go beyond extreme limit.

Remark. 1. If the harmonic oscillator is three dimensional, then its energy eigen values are given as $E_n = (n + 3/2) \hbar\omega$ and wave function is given by

$$\psi(x, y, z) = \left(\sqrt{\frac{\alpha^3}{2^n n_x! n_y! n_z! \sqrt{\pi}}} \right) \cdot \left(e^{-\frac{\alpha^2}{2}(x^2 + y^2 + z^2)} \right) \\ (H_{nx}(\alpha x) H_{ny}(\alpha y) H_{nz}(\alpha z))$$

where $\lambda_x = 2n_x + 1, \lambda_y = 2n_y + 1, \lambda_z = 2n_z + 1$

2. The expression for Hermite polynomial is given by $H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n} (e^{-y^2})$

Example 7. Show that wave functions of particle in a box are orthonormal.

Solution. The wave functions of particle in a box are given as

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

$$(i) \text{ Normalisation : } \int_{-\infty}^{\infty} |\psi_n|^2 dx = \frac{2}{L} \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{1}{L} \int_0^L \left[1 - \cos\left(\frac{2n\pi}{L}x\right) \right] dx = \frac{1}{L} [L - 0] = 1$$

Thus wave functions are normalised.

(ii) **Orthogonality.** Consider two different wave functions ψ_m & ψ_n ($m \neq n$) then

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_m^* \psi_n dx &= \frac{2}{L} \int_0^L \sin\left(\frac{m\pi}{L}x\right) \sin\left(\frac{n\pi}{L}x\right) dx \\ &= \frac{1}{L} \int_0^L \left[\cos\left(\frac{(m-n)}{L}\pi x\right) - \cos\left(\frac{(m+n)}{L}\pi x\right) \right] dx \\ &= \frac{1}{L} \left[\frac{L}{(m-n)\pi} \left[\sin\left(\frac{(m-n)}{L}\pi x\right) \right]_0^L - \frac{L}{m+n} \left[\sin\left(\frac{(m+n)}{L}\pi x\right) \right]_0^L \right] \\ &= \frac{1}{L} [(0 - 0) - (0 - 0)] = 0 \end{aligned}$$

Thus wave functions are orthogonal. Combining both results, we see that, wave functions are both orthogonal as well as normalised.

Example 8. Locate the points at which probability of finding the particle is either maximum or minimum, when it is confined to move in a box of length L .

Solution.

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

Let

$p(x)$ = probability density at x

$$= |\psi(x)|^2 = \frac{2}{L} \sin^2\left(\frac{n\pi}{L}x\right)$$

Now

$$\frac{dp}{dx} = \frac{2}{L} \times 2 \sin\left(\frac{n\pi}{L}x\right) \times \cos\left(\frac{n\pi}{L}x\right) \times \frac{n\pi}{L} = \frac{2n\pi}{L^2} \sin\left(\frac{2n\pi}{L}x\right)$$

and

$$\frac{d^2p}{dx^2} = \frac{2n\pi}{L^2} \times \cos\left(\frac{2n\pi}{L}x\right) \times \frac{2n\pi}{L} = \frac{4n^2\pi^2}{L^3} \cos\left(\frac{2n\pi}{L}x\right) \quad \dots(i)$$

p will be maximum or minimum when $\frac{dp}{dx} = 0$

$$i.e. \quad \sin\left(\frac{2n\pi}{L}x\right) = 0$$

or

$$\frac{2n\pi}{L}x = 0, \pi, 2\pi, 3\pi, 4\pi, \dots$$

or

$$x = 0, \frac{L}{2n}, \frac{2L}{2n}, \frac{3L}{2n}, \frac{4L}{2n}, \dots \leq L \quad (\because x \text{ cannot be more than } L)$$

Now p will be minimum at those points, where $\frac{d^2p}{dx^2}$ is +ve

From (i) we see that $\cos\left(\frac{2n\pi}{L}x\right)$ is positive wherever $x = 0, \frac{L}{2n}, \frac{2L}{2n}, \frac{3L}{2n}, \dots \leq L$ etc.

Thus probability of finding particle is minimum at these points.

From (i) we see that $\frac{d^2 p}{dn^2}$ is -ve when $\cos\left(\frac{2n\pi}{L}x\right)$ is -ve and for this x can be $\frac{L}{2n}, \frac{3L}{2n}, \frac{5L}{2n}, \dots \leq L$

Hence probability of finding particle is minimum at these points. For example in the ground state $n = 1$.

So probability of finding particle is minimum when $x = 0, L$ and it is maximum at point $x = \frac{L}{2}$.

Example 9. A particle is confined to move in a box of length L along X-axis. Find the probability of finding the particle in the region $0 \leq x \leq \frac{L}{4}$. Hence find this probability for (i) Ground state (ii) First excited state.

Solution. The probability to find particle in a specified region is given by

$$P(a \leq x \leq b) = \int_a^b |\psi|^2 dx \quad [\text{Provided } \psi \text{ is normalised wave function}]$$

$$\begin{aligned} \text{Thus } P\left(0 \leq x \leq \frac{L}{4}\right) &= \frac{2}{L} \int_0^{\frac{L}{4}} \sin^2\left(\frac{n\pi}{L}x\right) dx \\ &= \frac{1}{L} \int_0^{\frac{L}{4}} \left[1 - \cos\left(\frac{2n\pi}{L}x\right)\right] dx = \frac{1}{L} \left[x - \frac{L}{2n\pi} \sin\left(\frac{2n\pi}{L}x\right)\right]_0^{\frac{L}{4}} \\ &= \frac{1}{L} \left[\left(\frac{L}{4} - \frac{L}{2n\pi} \sin\left(\frac{n\pi}{2}\right)\right) - \{0\}\right] = \frac{1}{4} - \frac{1}{2n\pi} \sin\left(\frac{n\pi}{2}\right) \end{aligned}$$

(i) In the ground state $n = 1$

$$\therefore P\left(0 \leq x \leq \frac{L}{4}\right) = \frac{1}{4} - \frac{1}{2\pi} \times \sin\left(\frac{n\pi}{2}\right) = \frac{1}{4} - \frac{1}{2\pi} = \left(\frac{\pi - 2}{4\pi}\right) \text{ Ans.}$$

(ii) In the first excited state $n = 2$

$$P\left(0 \leq x \leq \frac{L}{4}\right) = \frac{1}{4} - \frac{1}{4\pi} \sin(\pi) = \frac{1}{4} \text{ Ans.}$$

Example 10. Find the ground state energy of an electron confined to a one dimensional box of width 1\AA .

Solution. The ground state energy of particle is given by

$$\begin{aligned} E_1 &= \frac{\pi^2 \hbar^2}{2mL^2} = \frac{(3.142)^2 \times (1.054 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31} \times (1 \times 10^{-10})^2} \\ &= 0.6026 \times 10^{-17} \text{ J} = 37.6 \text{ eV} \end{aligned}$$

Example 11. Find the energy of electron contained in a box of dimension 1\AA such that its wave function has 5 nodes in the box.

Solution. In the n th ground state the wave function of particle has $n + 1$ nodes (node is the point where the value of wave function is zero).

$$\text{Given number of nodes} = n + 1 = 5$$

$$\text{Hence } n = 4$$

Thus energy of electron is given by

$$E_4 = (4)^2 \frac{\pi^2 \hbar^2}{2mL^2} = 16 \times 37.6 \text{ eV} = 601.6 \text{ eV}$$

Example 12. A wave function in one dimension is given as

$$\psi(x) = \begin{cases} Ae^{-\alpha x} & ; \text{ for } x > 0 \\ Ae^{\alpha x} & ; \text{ for } x < 0 \end{cases}$$

Normalise this function.

Solution. Function is normalised if $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$

i.e.

$$\int_{-\infty}^0 |\psi|^2 dx + \int_0^{\infty} |\psi|^2 dx = 1$$

or

$$A^2 \left[\int_{-\infty}^{\infty} e^{2\alpha x} dx + \int_0^{\infty} e^{-2\alpha x} dx \right] = 1$$

or

$$A^2 \left[\left(\frac{1}{2\alpha} \right) [e^0 - e^{-\infty}] + \left(\frac{1}{-2\alpha} \right) [e^{-\infty} - e^0] \right] = 1$$

or

$$A^2 \left[\frac{1}{\alpha} \right] = 1 \quad \text{or} \quad A = \sqrt{\alpha}$$

Hence normalised wave function is given by

$$\psi(x) = \begin{cases} \sqrt{\alpha} e^{-\alpha x} & ; \text{ for } x > 0 \\ \sqrt{\alpha} e^{\alpha x} & ; \text{ for } x < 0 \end{cases}$$

Example 13. At a certain time, the normalised wave function of a particle moving along x -axis has the form given by

$$\psi(x) = \begin{cases} x + \beta & \text{for } -\beta < x < 0 \\ -x + \beta & \text{for } 0 < x < \beta \\ 0 & \text{elsewhere} \end{cases}$$

Find value of β and probability that particle's position lies between $x = \beta/2$ and $x = \beta$.

Solution. Since $\psi(x)$ is normalised wave function

$$\therefore \int_{-\beta}^{\beta} |\psi(x)|^2 dx = 1$$

$$\Rightarrow \int_{-\beta}^0 (x + \beta)^2 dx + \int_0^{\beta} (-x + \beta)^2 dx = 0$$

$$\begin{aligned}
 & \Rightarrow \int_{-\beta}^0 x^2 dx + \beta^2 \int_0^\beta dx + 2\beta \int_{-\beta}^0 x dx + \int_0^\beta x^2 dx + \beta^2 \int_0^\beta dx - 2\beta \int_0^\beta x dx = 1 \\
 & \Rightarrow \left(\frac{x^3}{3} \right)_{-\beta}^0 + \beta^2 (x) \Big|_0^\beta + 2\beta \left(\frac{x^2}{2} \right) \Big|_{-\beta}^0 + \left(\frac{x^3}{3} \right) \Big|_0^\beta + \beta^2 (x) \Big|_0^\beta - 2\beta \left(\frac{x^2}{2} \right) \Big|_0^\beta = 1 \\
 & \Rightarrow \frac{2\beta^3}{3} + 2\beta^3 - 2\beta^3 = 1 \\
 & \Rightarrow \frac{2\beta^3}{3} = 1 \quad \therefore \quad \beta = \left(\frac{3}{2} \right)^{1/3}
 \end{aligned}$$

Now probability of particle lying in $\beta/2$ to β is given by

$$\begin{aligned}
 P\left(\frac{\beta}{2} \leq x \leq \beta\right) &= \int_{\beta/2}^{\beta} |\psi(x)|^2 dx = \int_{\beta/2}^{\beta} (-x + \beta)^2 dx \\
 &= \int_{\beta/2}^{\beta} x^2 dx + \beta^2 \int_{\beta/2}^{\beta} dx - 2\beta \int_{\beta/2}^{\beta} x dx \\
 &= \left(\frac{x^3}{3} \right)_{\beta/2}^{\beta} + \beta^2 (x) \Big|_{\beta/2}^{\beta} - 2\beta \left(\frac{x^2}{2} \right) \Big|_{\beta/2}^{\beta} \\
 &= \frac{\beta^3}{3} - \frac{\beta^3}{24} + \beta^2 \left(\beta - \frac{\beta}{2} \right) - \beta \left(\beta^2 - \frac{\beta^2}{4} \right) \\
 &= \frac{7\beta^3}{24} + \frac{\beta^3}{2} - \frac{3}{4}\beta^3 = \left(\frac{7+12-18}{24} \right) \beta^3 \\
 &= \frac{\beta^3}{24} = \frac{1}{24} \times \frac{3}{2} = \frac{1}{16}
 \end{aligned}$$

Exercise 5. Show that the wave function $\psi(x, t) = A \cos(kx - \omega t)$ does not satisfy Schrödinger equation. [Hint : The wave function is time dependent].

Exercise 6. A particle is described by the wave function

$$\psi(x) = \begin{cases} \sqrt{3}x & ; \quad 0 < x < 1 \\ 0 & ; \text{ Elsewhere} \end{cases}$$

Find probability of finding the particle in the interval $(0, \frac{1}{2})$. [Ans. $\frac{1}{8}$]

Exercise 7. A wave function is given as

$$\psi(x) = \frac{B}{\sqrt{x^2 + a^2}} ; -\infty < x < \infty$$

Normalise this wave function.

$$\text{Ans. } \psi(x) = \frac{a}{\sqrt{\pi(x^2 + a^2)}}$$

Exercise 8. Calculate the probability of finding the particle between $\frac{L}{4} \leq x \leq \frac{3L}{4}$ for
 (i) ground state (ii) first excited state.

$$\left[\text{Ans. (i)} \frac{\pi - 2}{2\pi} \quad \text{(ii)} \frac{1}{2} \right]$$

(21) UNCERTAINTY PRINCIPLE

The wave nature of particle has a lot of implications. One immediate implication is that no measurement can be 100% accurate. It is because of the fact that due to wave nature of matter, a particle is always in disturbed state in the wave packet associated with it. Hence it is almost impossible to locate the position and momentum of a particle with 100% accuracy. The two variables which cannot be measured simultaneously with complete accuracy are called Conjugate Variables. Heisenberg put forward a principle which gives the lowest possible value of uncertainty product. According to him

"The product of uncertainty in position of particle in certain direction and the uncertainty in component of linear momentum of particle in same direction can never be less than $\frac{\hbar}{2}$ or $\frac{h}{4\pi}$." Where h = Planck's constant

$$\text{i.e. } \Delta x \Delta p_x \geq \frac{\hbar}{2} \quad \dots(144)$$

Here Δx and Δp_x are uncertainty in position along X-axis and component of linear momentum along X-axis respectively.

The proof of this relation is beyond the scope of this book. At the most we can verify this relation for various problems. Before that we will write other forms of uncertainty principle.

(i) position momentum uncertainty for other variables is also of the above form i.e.
 $\Delta y \Delta p_y \geq \frac{\hbar}{2}$ and $\Delta z \Delta p_z \geq \frac{\hbar}{2}$

(ii) Just as position and corresponding component of linear momentum are conjugate, in the same way energy and momentum are conjugate variables.

Consider a particle of mass m moving unrelativistically along X-axis then $E = \frac{p_x^2}{2m}$

So that $\Delta E = \frac{2p_x}{2m} (\Delta p_x)$

$$= \frac{mV_x}{m} \Delta p_x = \frac{\Delta x}{\Delta t} \Delta p_x \quad \left(\because V_x = \frac{\Delta x}{\Delta t} \right)$$

$$\Rightarrow \Delta x \Delta p_x = \Delta E \Delta t$$

Put in (144), we get

$$\Delta E \Delta t \geq \frac{\hbar}{2} \quad \dots(145)$$

This relation gives energy time uncertainty.

(iii) If we put $E = h\nu = 2\pi \hbar \nu$

then $\Delta E = 2\pi \hbar \Delta \nu$

Put in (145), we get

$$2\pi \hbar \Delta\nu \Delta t \geq \frac{\hbar}{2} \quad \text{or} \quad \Delta\nu \Delta t \geq \frac{1}{4\pi}$$

This is frequency time uncertainty. In Electronics, the function generators used for producing various audio and radio frequency waves obey the relation.

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

(iv) Let a particle describe an arc of length Δx in small time Δt and of radius r then from figure (10)

$$\Delta x = r\Delta\theta$$

$$\text{and} \quad \Delta x \Delta p_x = (\Delta\theta) (r\Delta p_x) = \Delta\theta \Delta L$$

where $\Delta L = r \Delta p_x$ is uncertainty in angular momentum

Put in (144), we get

$$\Delta\theta \Delta L \geq \frac{\hbar}{2} \quad \dots(146)$$

This equation gives uncertainty relation between angular momentum and angular displacement.

(22) CALCULATION OF UNCERTAINTY

For calculating uncertainty in any measurable quantity, we must have knowledge of Expectation Value and Wave function.

The expectation value or average value of any quantity ' f ' is defined as follows :

$$\langle f \rangle = \frac{\int_{-\infty}^{\infty} \psi^* \hat{f} \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx} \quad \dots(147)$$

where \hat{f} is an operator for the quantity f .

Now uncertainty in a quantity is nothing but the standard deviation, with which we all are familiar. e.g. uncertainty in position is given as

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

Similarly uncertainty in momentum is defined as

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$$

Let us now calculate the uncertainty product for particle in a one dimensional box.

The wave function is given as $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$

$$\int_{-\infty}^{\infty} \psi^* x \psi dx$$

$$\text{Thus} \quad \langle x \rangle = \frac{\int_{-\infty}^{\infty} \psi^* x \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx}$$

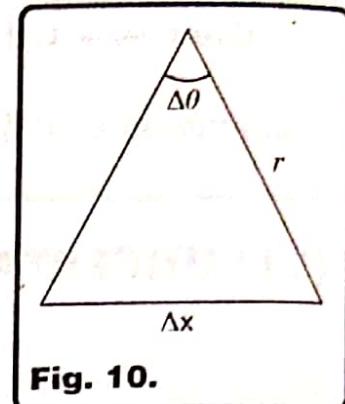


Fig. 10.

$$= \frac{2}{L} \int_0^L x \sin^2 \left(\frac{n\pi x}{L} \right) dx \quad (\because \int_0^L \psi^* \psi dx = 1 \text{ as wave function is normalised})$$

$$= \frac{2}{L} \int_0^L x \left[\frac{1 - \cos \left(\frac{2n\pi}{L} x \right)}{2} \right] dx$$

$$= \frac{1}{L} \left[\int_0^L x dx - \int_0^L x \cos \left(\frac{2n\pi}{L} x \right) dx \right] = \frac{1}{L} \left[\frac{L^2}{2} - 0 \right] = \frac{L}{2}$$

$$\langle x^2 \rangle = \frac{\int_{-\infty}^{\infty} x^2 \psi^* \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx} = \frac{2}{L} \int_0^L x^2 \sin^2 \left(\frac{2n\pi}{L} x \right) dx$$

$$= \frac{1}{L} \int_0^L x^2 \left(1 - \cos \left(\frac{2n\pi}{L} x \right) \right) dx$$

$$= \frac{1}{L} \left[\int_0^0 x^2 dx - \int_0^L x^2 \cos \left(\frac{2n\pi}{L} x \right) dx \right]$$

$$= \frac{1}{L} \left[\frac{L^3}{3} - \frac{L^3}{2n^2\pi^2} \right] = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$$

$$\langle p \rangle = \frac{\int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx}$$

$$= \frac{2}{L} \int_0^L \sin \left(\frac{n\pi}{L} x \right) \left(-i\hbar \frac{\partial}{\partial x} \sin \left(\frac{n\pi}{L} x \right) \right) dx$$

$$= -i\hbar \times \frac{L}{n\pi} \times \frac{2}{L} \int_0^L \sin \left(\frac{n\pi}{L} x \right) \cos \left(\frac{n\pi}{L} x \right) dx$$

$$= \frac{-i\hbar}{n\pi} \int_0^L \sin \left(\frac{2n\pi}{L} x \right) dx = 0$$

$$\langle p^2 \rangle = \frac{\int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right)^2 \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx}$$

Now

and

$$\begin{aligned}
 &= \hbar^2 \times \frac{2}{L} \int_0^L \sin\left(\frac{n\pi}{L}x\right) \left[\frac{d^2}{dx^2} \left(\sin\left(\frac{2\pi}{L}x\right) \right) \right] dx \\
 &= -\hbar^2 \times \frac{2}{L} \times \left(\frac{n^2\pi^2}{L^2} \right) \times \int_0^L \sin\left(\frac{n\pi}{L}x\right) \left[-\sin\left(\frac{n\pi}{L}x\right) \right] dx \\
 &= \frac{n^2\pi^2\hbar^2}{L^3} \int_0^L \left(1 - \cos\left(\frac{2n\pi}{L}x\right) \right) dx \\
 &= \frac{n^2\pi^2\hbar^2}{L^3} [L - 0] = \frac{n^2\pi^2\hbar^2}{L^2}
 \end{aligned}$$

Thus

$$\begin{aligned}
 (\Delta x)^2 &= \langle x^2 \rangle - \langle x \rangle^2 \\
 &= \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - \left(\frac{L}{2} \right)^2 = \frac{L^2}{12} - \frac{L^2}{2n^2\pi^2}
 \end{aligned}$$

and

$$\begin{aligned}
 (\Delta p)^2 &= \langle p^2 \rangle - \langle p \rangle^2 \\
 &= \frac{n^2\pi^2\hbar^2}{L} - 0 = \frac{n^2\pi^2\hbar^2}{L^2}
 \end{aligned}$$

Now $(\Delta x \Delta p)^2 = \left(\frac{L^2}{12} - \frac{L^2}{2n^2\pi^2} \right) \left(\frac{n^2\pi^2\hbar^2}{L^2} \right)^2 = \left(\frac{n^2\pi^2}{12} - \frac{1}{2} \right) \hbar^2$

Hence $(\Delta x \Delta p) = \hbar \left(\frac{n^2\pi^2}{12} - \frac{1}{2} \right)^{\frac{1}{2}}$... (148)

Since minimum value of n is 1. Hence minimum value of uncertainty product is $\hbar \left(\frac{\pi^2}{12} - \frac{1}{2} \right)^{1/2} = 0.57 \hbar$

Clearly $0.57 \hbar > \frac{\hbar}{2}$. Hence condition (113) is valid. Thus uncertainty principle is verified for particle in a box.

(23) VERIFICATION UNCERTAINTY PRINCIPLE FOR SINGLE SLIT EXPERIMENT

Fig. (11) shows Schematic diagram of a single slit experiment. The width of slit is d and lies along Y-axis. A beam of monochromatic radiations is incident on the slit.

Initially beam of photons is travelling along X-axis. Thus we know the y -component of linear momentum of photon exactly because $p_y = 0$ for each photon and $p_y = 0 \Rightarrow \Delta p_y = 0$

However we do not know position of a particular photon along Y-axis i.e. it may be present anywhere between $-\infty$ to $+\infty$ along Y-axis. Hence uncertainty in position along Y-axis is ∞ , i.e. $\Delta y = \infty$. This result is in accordance with uncertainty principle i.e. when $\Delta p_y = 0$ then $\Delta y = \infty$.

Now beam of light falls on slit and diffraction pattern is formed on the screen. Now we can say with confidence that any photon which falls on screen must have come through a distance

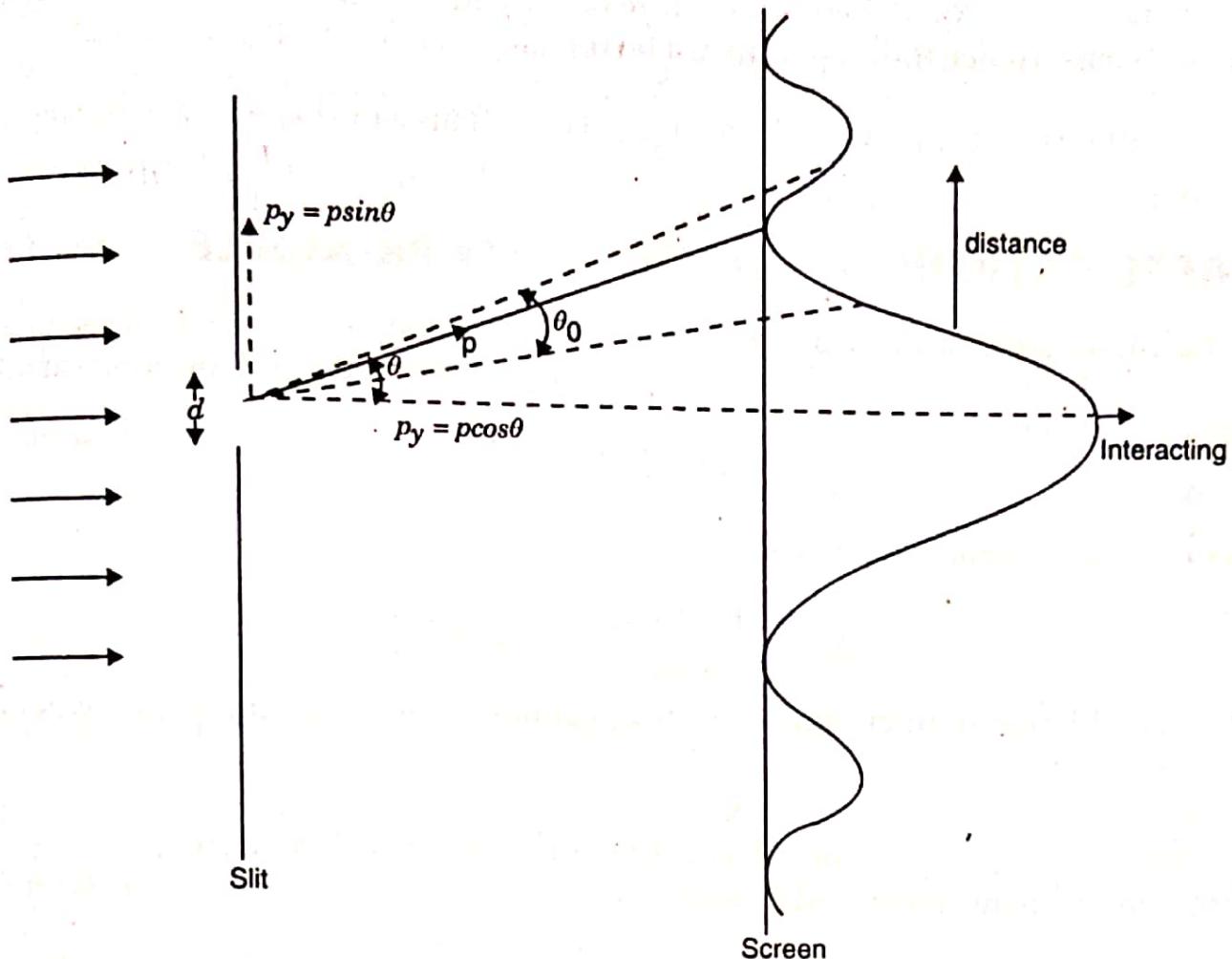


Fig. 11.

d equal to width of slit. Hence after striking the slit, the uncertainty in position of photon reduces from ∞ to $\Delta y = d$.

But to obey uncertainty principle, the photon must suffer a change in direction of motion (i.e. it diffracts) so that uncertainty in linear momentum along Y-axis increases from 0 to some higher value.

Let θ is angle of diffraction.

Thus $p_y = p \sin \theta$ = linear momentum acquired by photon along Y-axis due to diffraction.

Hence uncertainty in linear momentum along Y-axis becomes $\Delta p_y \approx p_y = p \sin \theta$

$$\text{Thus } (\Delta y) (\Delta p_y) \approx (d) (p \sin \theta)$$

$$= (d) \left(\frac{h}{\lambda} \theta \right) \quad (\because p = \frac{h}{\lambda} \text{ and for small angles } \sin \theta \approx \theta)$$

$$= \frac{h\theta}{\left(\frac{\lambda}{d}\right)} = \frac{h\theta}{\theta_0} \quad (\text{where } \theta_0 = \frac{\lambda}{d} = \text{angular fringe width})$$

But $\theta \geq \theta_0$ for single slit experiment.

If we take $\theta \approx \theta_0$ then $\Delta y \Delta p_y \approx h$... (149)

Since $h > \frac{\hbar}{2}$. Hence equation (144) is again verified.

Conclusion. (i) We see that condition (144) is never violated. However the value of uncertainty product $\Delta x \Delta p_x$ depends on nature of wave function i.e. its value is different for different problems. Hence these values must be remembered for solving numericals.

(ii) The value of $\Delta x \Delta p_x$ is exactly equal to $\frac{\hbar}{2}$ for a Gaussian shaped wave packet (wave function graph) only.

(24) APPLICATIONS OF UNCERTAINTY PRINCIPLE

(i) **Non Existence of electrons in the nucleus.** The size of nucleus is of the order of $10^{-14} m$. Let an electron exists inside the nucleus, then uncertainty in its position cannot be more than size of nucleus.

Thus

$$\Delta x \approx 10^{-14} m$$

By uncertainty principle $\Delta p_x \approx \frac{\hbar}{2\Delta x}$

or
$$\Delta p_x \approx \frac{1.054 \times 10^{-34}}{2 \times 10^{-14}} = 5.27 \times 10^{-21} \text{ kg m/s}$$

The actual linear momentum of electron cannot be less than uncertainty in linear momentum

Thus

$$p_x \geq \Delta p_x$$

Let us take $p_x = \Delta p_x = \text{minimum linear momentum possessed by electron}$

\therefore Minimum energy possessed by electron is

$$E = \frac{p_x^2}{2m} = \frac{(5.27 \times 10^{-21})^2}{2 \times 9.1 \times 10^{-31}} = 1.54 \times 10^{11} \text{ J} = 96.4 \text{ MeV}$$

Thus to remain inside the nucleus, the minimum energy of the electron should be ≈ 96.4 MeV. However experimentally it is found that no electron possesses energy more than 5 MeV. Thus electrons do not exist inside the nucleus.

(ii) **Minimum Energy of particle in a box.** Let a particle of mass m is restricted to move in a one dimensional box of length L . According to uncertainty principle $\Delta x \Delta p_x \approx \hbar$

or

$$\Delta p_x \approx \frac{\hbar}{\Delta x} = \frac{\hbar}{L} \quad (\text{Taking } \Delta x \approx L = \text{maximum uncertainty in } x \text{ so that } \Delta p_x = \text{minimum uncertainty in linear momentum})$$

Thus $p_x = \text{linear momentum of particle must not be less than } \Delta p_x$

Hence minimum value of p_x is $p_x \approx \Delta p_x = \frac{\hbar}{L}$

Thus minimum energy is $E = \frac{p_x^2}{2m} = \frac{\hbar^2}{2mL^2}$. This energy is non zero. Thus particle in a box cannot possess zero energy.

(iii) **The radius of first Bohr's Orbit.** According to uncertainty principle

$$\Delta x \Delta p_x \approx \hbar \Rightarrow \Delta p_x \approx \frac{\hbar}{\Delta x}$$

The uncertainty in kinetic energy is

$$\Delta KE \approx \frac{\Delta p_x^2}{2m} = \frac{\hbar^2}{2m(\Delta x)^2}$$

The uncertainty in potential energy is $\Delta V = -\frac{1}{4\pi\epsilon_0} \frac{(Ze^2)}{\Delta x}$

The uncertainty in total energy is given by

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

We take $\Delta x \approx r$ = radius of orbit

$$\therefore \Delta E = \frac{\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \quad \dots(150)$$

The uncertainty in total energy will be minimum when $\frac{d}{dr} (\Delta E) = 0$

$$0 = \frac{\hbar^2}{2m} \left(\frac{-2}{r^3} \right) - \frac{Ze^2}{4\pi\epsilon_0} \left(\frac{-1}{r^2} \right)$$

$$\text{or } r = \frac{\hbar^2(4\pi\epsilon_0)}{mZe^2} \quad \dots(151)$$

For Hydrogen atom $Z = 1$

$$\Rightarrow r = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.53 \text{ Å} \text{ which is radius of first orbit of Hydrogen atom.}$$

Put value of r in equation (150), we get

$$E_{\min} = \frac{\hbar^2 m^2 e^4}{2m(4\pi\epsilon_0)^2 \hbar^4} - \frac{e^2}{\hbar^2 (4\pi\epsilon_0)^2} me^2 = -\frac{me^4}{32\pi^2 \epsilon_0^2 \hbar^2} = -13.6 \text{ eV}$$

This value is same, as calculated by using Bohr's theory.

(iv) **Minimum Energy of a Harmonic Oscillator.** The total energy of Harmonic oscillator is

$$E = KE + PE$$

Thus minimum energy is equal to minimum uncertainty in energy.

$$\therefore E_{\min} \approx \Delta E$$

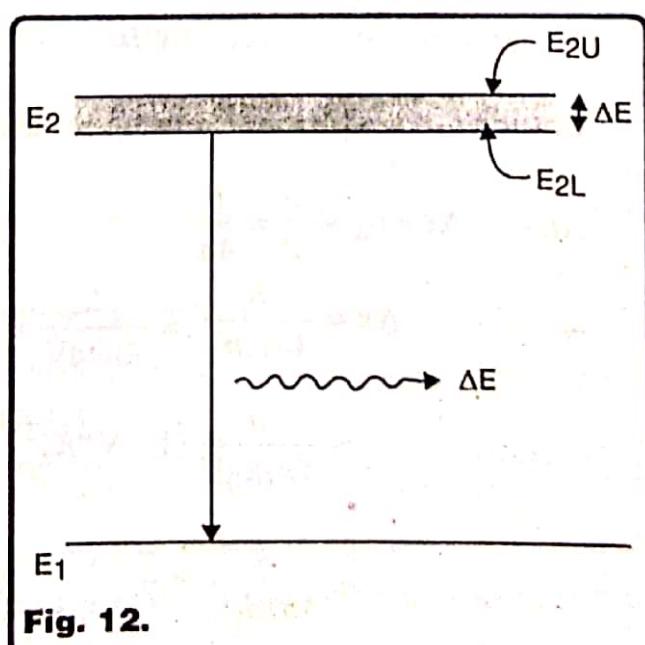
$$\begin{aligned} &= \frac{(\Delta p_x)^2}{2m} + \frac{1}{2} m\omega^2 (\Delta x)^2 \\ &= \frac{\hbar^2}{2m(\Delta x)^2} + \frac{1}{2} m\omega^2 (\Delta x)^2 \\ &\quad (\because \Delta p_x \Delta x \approx \hbar) \end{aligned}$$

$$\text{or } E_{\min} = \frac{\hbar^2}{2mr^2} + \frac{1}{2} m\omega^2 r^2$$

where $\Delta x \approx r$ = amplitude of the oscillations.

(v) **Finite width of Spectral Lines.** Let an electron make downward transition from energy level E_2 to ground state energy level E_1 .

The life time of excited state is approximately 10^{-6} s .



This means when electron is excited to level E_2 then it can make downward transition anytime within the span of 10^{-6} s (i.e. it may or may not stay in E_2 for 10^{-6} s). Hence there is an uncertainty of the order of $\Delta t \approx 10^{-6}$ s in the decay time of electron.

It means the energy of emitted photon is also uncertain by an amount

$$\Delta E \approx \frac{\hbar}{\Delta t} \quad (\because \Delta E \Delta t \approx \hbar)$$

$$= \frac{1.054 \times 10^{-34}}{10^{-6}} = 1.054 \times 10^{-28} \text{ J}$$

This means that the emitted photon is not monochromatic. We can visualise this effect by assuming that the excited energy level is not a sharp line but instead it has finite width $\Delta E = E_{2U} - E_{2L}$ when an electron jumps down from E_{2L} to E_1 then its decay time is having no uncertainty. While if electron starts from E_{2V} i.e. upper edge of E_2 then uncertainty in decay time is 10^{-6} s. Thus corresponding the spectral line on the screen due to emitted photon will not correspond to one unique frequency but it will show a spread of roughly $\Delta V = \frac{1}{\Delta t} = 10^6$ Hz = 1 MHz around central frequency. Thus spectral lines are of finite width.

Example 14. An electron has a speed of 500 m/s, correct upto 0.01% with what minimum accuracy, can you locate the electron?

Solution. $\Delta V_x = \frac{0.01}{100} \times 500 = 0.05 \text{ m/s}$

$$\Delta p_x = m \Delta V_x = 9.1 \times 10^{-31} \times 0.05 = 4.55 \times 10^{-32} \text{ kg m/s}$$

$$\Delta x \approx \frac{\hbar}{\Delta p_x} = \frac{1.054 \times 10^{-34}}{4.55 \times 10^{-32}} = 2.316 \times 10^{-3} \text{ m} = 2.316 \text{ mm}$$

Example 15. Show that for a particle moving with velocity V , the minimum uncertainty in its position is given by

$$\Delta x = \frac{\lambda_c}{4\pi} \left(\frac{C^2}{V^2} - 1 \right)^{1/2}$$

where λ_c is its compton wavelength.

Solution. Compton wavelength is given as $\lambda_c = \frac{h}{m_0 C}$

$$\text{Now } \Delta x \Delta p_x \approx \frac{\hbar}{2} = \frac{h}{4\pi}$$

$$\Rightarrow \Delta x = \frac{h}{4\pi \Delta p_x} = \frac{h}{4\pi m V} \quad (\text{taking } \Delta p_x \approx p_x = mV)$$

$$= \frac{h}{4\pi m_0 V} \left(1 - V^2/C^2 \right)^{1/2} \quad \left(\because m = \frac{m_0}{\sqrt{1 - V^2/C^2}} \right)$$

$$= \frac{h}{4\pi m_0 C} \times \frac{V}{C} \left(\frac{C^2}{V^2} - 1 \right)^{1/2} = \frac{h}{4\pi m_0 C} \left(\frac{C^2}{V^2} - 1 \right)^{1/2} = \frac{\lambda_c}{4\pi} \left(\frac{C^2}{V^2} - 1 \right)^{1/2}$$

Example 16. Show that fractional energy difference $\Delta E/E$ between two adjacent levels of a particle in a box is given by $(2n+1)/n^2$.

Solution. We know

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

$$\frac{\Delta E}{E} = \frac{E_{n+1} - E_n}{E_n} = \frac{\left(\frac{\pi^2 \hbar^2}{2mL^2}\right)((n+1)^2 - n^2)}{\frac{\pi^2 \hbar^2}{2mL^2} \cdot (n)^2}$$

$$\Rightarrow \frac{\Delta E}{E} = \frac{2n+1}{n^2} \text{ Ans.}$$

Exercise 9. Calculate the minimum uncertainty in the position of an electron, moving with velocity $0.8 C$ where C is velocity of light. [Ans. 0.018 \AA]

Exercise 10. Show that if the angular momentum of an electron is $2\hbar$ having 5% error, then the uncertainty in angular orbital position of the particle cannot be specified at all.

Exercise 11. A particle is described by a wave function $\psi(x) = \frac{1+ix}{1+ix^2}$. Calculate the expectation of position of particle. [Ans. 0]

Exercise 12. Show that for a free particle, the uncertainty relation can be written as

$$\Delta x \Delta \lambda \leq \frac{\lambda^2}{2\pi}$$

where Δx is uncertainty in location for the wave and $\Delta \lambda$ is the simultaneous uncertainty in the wavelength.

SHORT ANSWER TYPE QUESTIONS

Q. 1. Why we cannot observe wave nature of matter in daily life ?

Ans. Since value of Planck's constant \hbar is very small, so wave nature of matter cannot be observed in daily life.

Q. 2. Can de Broglie waves be electromagnetic ?

Ans. No. It is because of the fact that electromagnetic waves are originated when a charged particle moves under acceleration. However, de-Broglie waves are associated even with neutral particles and particles moving without acceleration.

Q. 3. Can any type of wave travel faster than speed of light ?

Ans. Yes, matter waves can travel faster than speed of light.

Q. 4. What are limitations of Schrödinger Equation ?

Ans. (i) This equation is valid only in non relativistic case (i.e. when particle is moving with small velocity in comparison to speed of light).

(ii) This equation does not include the spin motion of the particle. The spin motion of particle has to be introduced arbitrarily to explain fine and hyperfine spectrum of substances.

(iii) The equation cannot be solved exactly in most of the problems. Infact, we have to resort to approximation when a complex problem is solved using this equation.

Q. 5. What is a free particle ?

Ans. A particle, on which no forces are acting is called free particle.

Q. 6. An electron and a photon have same de-Broglie wavelength. Which one will have more energy.

Ans. Given

$$\lambda_e = \lambda_p$$

$$\Rightarrow \frac{h}{p_e} = \frac{h}{p_p}$$

$$\Rightarrow p_e = p_p$$

Now Energy of photon is given as

$$\begin{aligned} E_p &= \sqrt{p_p^2 C^2 + m_{op}^2 C^4} \\ &= \sqrt{p_p^2 C^2} \end{aligned}$$

... (1) ($\because m_{op} = 0$)

Energy of Electron is given as

$$\begin{aligned} E_e &= \sqrt{p_e^2 C^2 + m_{oe}^2 C^4} \\ &= \sqrt{p_p^2 C^2 + m_{oe}^2 C^4} \end{aligned}$$

... (2) ($\because p_e = p_p$)

from (1) and (2) we see that $E_e \gg E_p$.

Thus electron will have more energy.

Q. 7. Can a single wave be associated with a particle ?

Ans. A single wave cannot be associated with a particle due to the fact that a de-Broglie wave can travel faster than speed of light, while no particle can travel faster than speed of light.

Q. 8. What is zero point energy of a harmonic oscillator ?

Ans. It is the ground state energy of a harmonic oscillator. It is given as $E_0 = \frac{1}{2} \hbar w_0$.

Q. 9. Can $\psi(x) = x^3$ be a wave function in quantum mechanics ?

Ans. As x approaches $\pm \infty$, $\psi(x)$ must approach to zero. We see that $\psi(x)$ does not obey this condition. Hence, it is not an acceptable wave function in quantum mechanics.

Q. 10. Why the quantum number $n=0$ is not possible for particle in a one dimensional box ?

Ans. The normalised wave function of particle in one dimensional box is given as

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right); \text{ when } 0 \leq x \leq L$$

and $\psi(x) = 0$, otherwise

If we put $n=0$

$$\therefore \psi(x) = 0; \text{ for all values of } x$$

This means that wave function is zero every where in the universe. Since probability of finding the particle is proportional to $[\psi(x)]^2$, so it will also be zero in whole universe. This means particle is not located anywhere in the universe, which is not acceptable. Hence $n=0$ is not allowed.

QUESTIONS

1. What is group velocity and phase velocity ? Show that the group velocity of particle is equal to the velocity of the particle.
2. What are the various conditions for acceptability of the wave function.
3. Define the term expectation value for the energy E of a particle in a box.
4. What is uncertainty principle ?
5. Give Born's interpretation of wave function.
6. Write Schroedinger wave equation for the particle in a box and solve it to obtain the eigen waves and eigen functions.
7. Explain Briefly Uncertainty principle.
8. Differentiate between group and phase velocities.
9. Determine the energy levels and the corresponding eigen functions of a particle moving in a potential of the form

$$V(x) = \infty \text{ for } x < 0, \text{ for } x > a = 0 \text{ for } 0 < x < a$$
10. Explain Compton Effect. Find the change in wavelength of an X-ray photon scattered through an angle 45° .
11. What is the significance of a wave function ?
12. Explain the meaning of phase velocity and group velocity. Show that the group velocity of a wave packet associated with a moving particle is same as that of velocity of particle.
13. Is it possible to observe compton scattering of visible light ? Explain.
14. Can every physical system be described by the time independent Schroedinger Equation? Comment.
15. Show that energy lost by a photon of frequency ν in compton interaction with a stationary electron (rest mass m_0) is given by

$$\frac{h\nu \alpha (1 - \cos \theta)}{1 + \alpha (1 - \cos \theta)}$$

where $\alpha = \frac{h\nu}{m_0 c^2}$ and θ is the angle of scattering of the photon. Also obtain an expression

for the maximum kinetic energy of the recoil electron.

16. How do you explain zero point energy of a harmonic oscillator ?
17. Obtain normalised wave functions of particle in a box. Represent them graphically.
18. What is the importance of Hermitian Operators.
19. Find an expression for wavelength of de-Broglie wave associated with a particle.
20. Find a relation between angle of scattering and angle of recoil in case of Compton Effect.
21. Show that first five Hermite polynomials are given as

$$H_0(y) = 1, H_1(y) = 2y, H_2(y) = 4y^2 - 2, H_3(y) = 8y^3 - 12y, H_4(y) = 16y^4 - 48y^2 + 12.$$

