15.6 de BROGLIE WAVES: MATTER WAVES

In 1924, Louis deBroglie proposed in his doctoral dissertation that there was a fundamental relation between waves and particles. Therefore, the energy of the photon according to special theory of relativity is given by

$$E = h\nu \tag{i}$$

and momentum p is

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{ii}$$

Here, it can be noted that E and p are the characteristics of the partricles, and ν and λ are the characteristics of the waves. From above relations, we see that these sets of quantities are related to each other by the Planck's constant h. deBroglie also suggested that the dual nature of electromagnetic radiation may be extended to material particles such as electrons, protons, neutrons etc. It means that a moving particle, whatever its nature be, has wave properties associated with it. The waves associated with these particles are known as matter waves or deBroglie waves. The difference between the electromagnetic radiation and elementary particles is that in the case of photons, $m_0 = 0$ and $v = c$ but in the case of material particles $m_0 \neq 0$ and $v < c$. deBroglie gave the following hypothesis which is applicable to all matters, radiation and particles.

(1) If there is a particle of momentum p, its motion is associated with a wave of wavelength

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

(2) If there is a wave of wavelength λ, the square of the amplitude of the wave at any point in space is proportional to the probability of observing, at that point in space, a particle of momentum

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

The dual nature of matter can be proved if we could show that a beam of particles also exhibits the phenomenon of diffraction pattern just like the electromagnetic waves show the phenomena of diffraction and interference.

15.6.1 Demonstration of Matter Waves: Davisson-Germer Experiment on Electron Diffraction

The Davisson-Germer experiment was conducted in 1927 which confirmed the deBroglie hypothesis, according to which particles of matter (such as electrons) have wave properties. This demonstration of the wave particle duality was important historically in the establishment of quantum mechanics and of the Schröedinger equation. The experimental setup is shown in Fig. 15.8(a). Here the electrons from a heated filament or electron gun were accelerated by a voltage V and allowed to fall on the surface of nickel target. *Davisson* and *Germer* measured the intensity of the scattered electrons as a function of the angle ϕ and plotted it in the form of polar diagram. Fig. 15.8(b) shows the results from the accelerating voltage of 54 V. For this case, there is an intense scattering or a pronounced

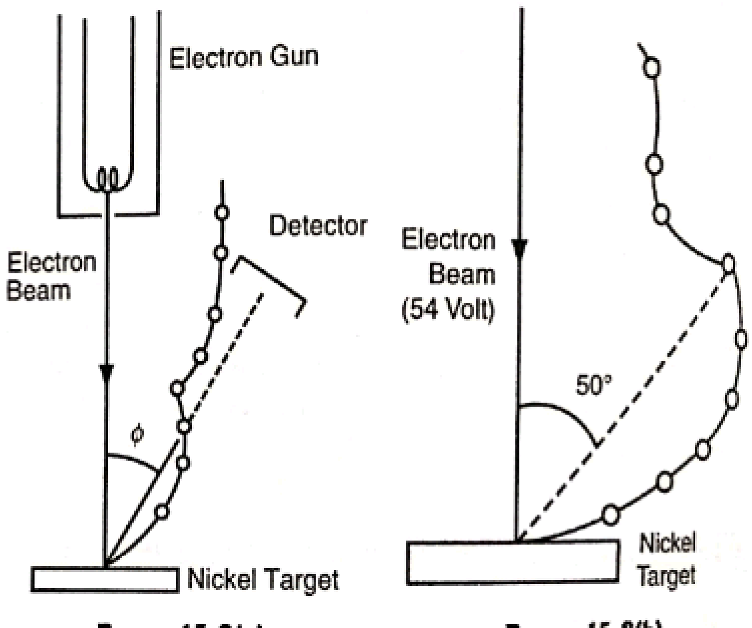

FIGURE 15.8(a) **FIGURE 15.8(b)**

peak at an angle of $\theta = 50°$. Such deflection can be explained by assuming that the electron beam has a wave associated with it. This situation is similar to the Bragg's diffraction. So the waves associated with the electron beam were satisfying Bragg's law, which caused a diffraction peak. In order to prove this, consider Fig. 15.9 that shows atomic planes in Ni crystal. Here $\theta = 50°$, $\phi = (180 - 50)/2 = 65°$, $d = 0.91$ Å. Hence, for $n = 1$, Bragg's law $n\lambda = 2d \sin\theta$ gives

$$\lambda = 2d\sin\theta = 2 \times 0.91 \times \sin 65° = 1.65 \text{ Å} \qquad (i)$$

Since Bragg's law basically talks about the diffraction of X-rays, this experiment enables us to treat the electrons as waves and the wavelength associated with the electrons should be 1.65 Å, if they are scattered at $\theta = 50°$.

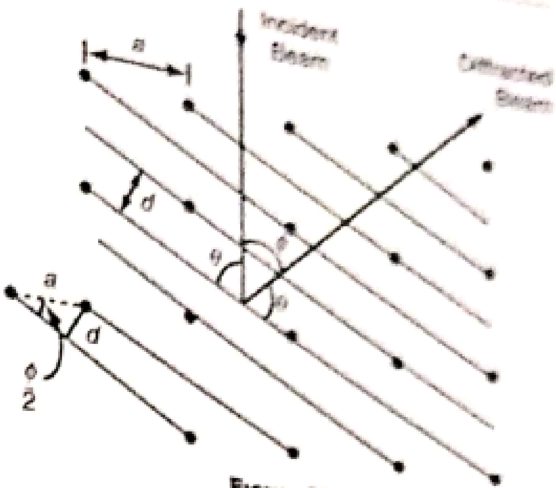

FIGURE 15.9

Now, we apply deBroglie's hypothesis. Since the electron of mass m gains the velocity v when it gets accelerated through a potential difference of V, we write the following relation for the energy for the nonrelativistic motion of the electron

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

So the deBroglie wavelength associated with the electron is given by

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}$$

$$\text{or} \quad \lambda = \sqrt{\frac{150}{V}}\text{Å}$$

Therefore, deBroglie wavelength associated with the electron that is accelerated by 54 V is given as

$$\lambda = \sqrt{\frac{150}{V}}\text{Å} = \sqrt{\frac{150}{54}}\text{Å} = 1.67\text{Å} \qquad (ii)$$

A comparison of Eq. (i) with Eq. (ii) shows that the value of the wavelength λ is the same in both the cases. It means there is a wave called deBroglie wave associated with the electrons. Therefore, this confirms the deBroglie hypothesis.

Similar... So... 0.00079%. ... Compton scattering.
X-rays are approp...

15.8 PHASE AND GROUP VELOCITIES: de BROGLIE WAVES

LO6

Phase Velocity

Waves have already been discussed in Chapter 1. However, here we will discuss phase and group velocities in the context of deBroglie waves. We can write the deBroglie wave travelling along the $+x$ direction as

$$y = a \sin(\omega t - kx) \tag{i}$$

where a is the amplitude, $\omega\ (=2\pi\nu)$ is the angular frequency and $k\ (=2\pi/\lambda)$ is the propagation constant of the wave. By the definition, the ratio of angular frequency ω to the propagation constant k is the phase (or wave) velocity. If we represent the phase velocity by u, then

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

$(\omega t - kx)$ is called the phase of the wave motion. It means the particle of the constant phase travels such that $(\omega t - kx)$ = constant.

$$\text{or} \quad \frac{d}{dt}(\omega t - kx) = 0$$

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

$$\text{or} \quad \frac{dx}{dt} = u = \frac{\omega}{k} \tag{ii}$$

where $u = \dfrac{dx}{dt}$ is the phase (or wave) velocity. Thus the wave velocity is the velocity of planes of constant phase which advances through the medium. We can write the phase velocity $u = \nu\lambda$ and for an electromagnetic wave $E = h\nu$, or $\nu = E/h$

According to deBroglie $\lambda = \dfrac{h}{p} = \dfrac{h}{mv}$

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

$$u = \frac{c^2}{v} \tag{iii}$$

Since $c >> v$, Eq. (iii) implies that the phase velocity of deBroglie wave associated with the particle moving with velocity v is greater than c, the velocity of light.

Group Velocity

As we have seen, the phase velocity of a wave associated with a particle comes out to be greater than the velocity of light. This difficulty can be overcome by assuming that each moving particle is associated with a

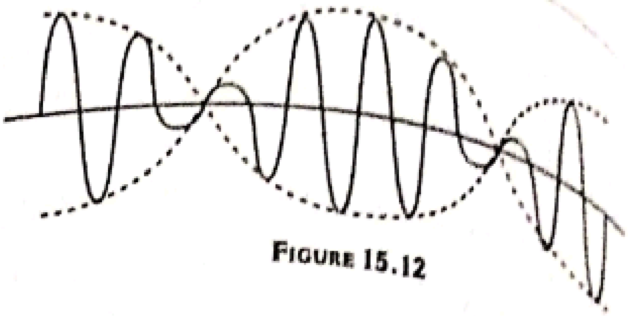

FIGURE 15.12

group of waves or a wave packet rather than a single wave. In this context, deBroglie waves are represented by a wave packet and hence we have *group velocity* associated with them. In order to realize the concept of group velocity, we consider the combination of two waves, resultant of which is shown in Fig. 15.12. The two waves are represented by the following relations

$$y_1 = a \sin(\omega_1 t - k_1 x) \quad \text{(i)}$$

and $$y_2 = a \sin(\omega_2 t - k_2 x) \quad \text{(ii)}$$

Their superposition gives

$$y = y_1 + y_2 = a\,[\sin(\omega_1 t - k_1 x) + \sin(\omega_2 t - k_2 x)]$$

or $$y = 2a \sin\left[\frac{(\omega_1+\omega_2)t}{2} - \frac{(k_1+k_2)x}{2}\right]\cos\left[\frac{(\omega_1-\omega_2)t}{2} - \frac{(k_1-k_2)x}{2}\right]$$

$$\therefore \quad y = 2a\cos\left[\frac{(\omega_1-\omega_2)t}{2} - \frac{(k_1-k_2)x}{2}\right]\sin(\omega t - kx) \quad \text{(iii)}$$

where $$\omega = \frac{\omega_1+\omega_2}{2},\ k = \frac{k_1+k_2}{2}$$

Eq. (iii) can be re-written as

$$y = 2a\cos\left[\frac{(\Delta\omega)t}{2} - \frac{(\Delta k)x}{2}\right]\sin(\omega t - kx) \quad \text{(iv)}$$

where $\Delta\omega = \omega_1 - \omega_2$ and $\Delta k = k_1 - k_2$.

The resultant wave Eq. (iv) has two parts.

(i) A wave of frequency ω, propagation constant k and the velocity u, given by

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

which is the phase velocity or wave velocity.

(ii) Another wave of frequency $\Delta\omega/2$, propagation constant $\Delta k/2$ and the velocity $G = \frac{\Delta\omega}{\Delta k}$. This velocity is the velocity of envelope of the group of waves, i.e., it is the velocity of the wave packet (shown by dotted lines) and is known as group velocity.

For the waves having small difference in their frequencies and wave numbers, we can write

$$G = \frac{\Delta\omega}{\Delta k} = \frac{\partial\omega}{\partial k} = \frac{\partial(2\pi\nu)}{\partial(2\pi/\lambda)} = \frac{\partial\nu}{\partial(1/\lambda)} = -\lambda^2\frac{\partial\nu}{\partial\lambda}$$

$$G = -\frac{\lambda^2}{2\pi}\frac{\partial\omega}{\partial\lambda}$$

This is the expression for the group velocity.

15.8.1 Relation between Group Velocity and Phase Velocity

If u be the phase (wave) velocity, then the group velocity can be written as

$$G = \frac{d\omega}{dk} = \frac{d}{dk}(uk) \quad \left[u = \frac{\omega}{k}\right]$$

or $$G = u + k\frac{du}{dk}$$

But $$k = \frac{2\pi}{\lambda} \Rightarrow dk = -\frac{2\pi}{\lambda^2}d\lambda \text{ and } \frac{k}{dk} = -\frac{\lambda}{d\lambda}$$

Therefore, the group velocity is given by

$$G = u + \left(-\frac{\lambda}{d\lambda}\right)du$$

or $$G = u - \lambda\frac{du}{d\lambda}$$

This relation shows that the group velocity G is less than the phase velocity u in a dispersive medium where u is a function of k or λ. However, in a non-dispersive medium, the velocity u is independent of k, i.e., the wave of all wavelength travel with the same speed, i.e., $\frac{du}{d\lambda} = 0$. Then $\mathbf{G} = \mathbf{u}$. This is true for electromagnetic waves in vacuum and the elastic waves in homogenous medium.

15.8.2 Relation between Group Velocity and Particle Velocity

Consider a material particle of rest mass m_0. Let its mass be m when it moves with velocity v. Then its total energy E is given by

$$E = mc^2 = \frac{m_o c^2}{\sqrt{1 - v^2/c^2}}$$

Its momentum is given by

$$p = mv = \frac{m_o v}{\sqrt{1 - v^2/c^2}}$$

The frequency of the associated deBroglie wave is given by

$$\nu = \frac{E}{h} = \frac{m_o c^2}{\sqrt{1 - v^2/c^2}}\frac{1}{h}$$

$$\omega = 2\pi\nu = \frac{2\pi m_0 c^2}{h\sqrt{1 - v^2/c^2}}$$

or $$\frac{d\omega}{dv} = \frac{2\pi m_0 c^2}{h(1 - v^2/c^2)^{3/2}}\left[-\frac{1}{2}\times\left(-\frac{2v}{c^2}\right)\right]$$

$$\text{or} \quad \frac{d\omega}{dv} = \frac{2\pi m_0 v}{h(1 - v^2/c^2)^{3/2}}$$

The wavelength of the associated deBroglie wave is given by

$$\lambda = \frac{h}{p} = \frac{h(1 - v^2/c^2)^{1/2}}{m_0 v}$$

Hence propagation constant

$$k = \frac{2\pi}{\lambda} = \frac{2\pi m_0 v}{h(1 - v^2/c^2)^{1/2}}$$

$$\text{or} \quad \frac{dk}{dv} = \frac{2\pi m_0}{h} \frac{\left(1 - \frac{v^2}{c^2}\right)^{1/2} - v\frac{1}{2}\left(1 - \frac{v^2}{c^2}\right)^{-1/2}\left(-\frac{2v}{c^2}\right)}{\left(1 - \frac{v^2}{c^2}\right)}$$

$$\text{or} \quad \frac{dk}{dv} = \frac{2\pi m_0}{h}\left[\left(1 - \frac{v^2}{c^2}\right)^{-1/2} + \frac{v^2}{c^2}\left(1 - \frac{v^2}{c^2}\right)^{-3/2}\right]$$

$$= \frac{2\pi m_0}{h}\left(1 - \frac{v^2}{c^2}\right)^{-3/2}\left[1 - \frac{v^2}{c^2} + \frac{v^2}{c^2}\right]$$

$$= \frac{2\pi m_0}{h}\left(1 - \frac{v^2}{c^2}\right)^{-3/2}$$

$$\frac{dk}{dv} = \frac{2\pi m_0}{h(1 - v^2/c^2)^{3/2}}$$

Since the group velocity

$$G = \frac{d\omega}{dk} = \frac{d\omega/dv}{dk/dv}$$

$$G = \frac{\dfrac{2\pi m_0 v}{h(1 - v^2/c^2)^{3/2}}}{\dfrac{2\pi m_0}{h(1 - v^2/c^2)^{3/2}}} = v$$

$\boldsymbol{G = v}$ = the particle velocity

Thus the wave group associated with the moving material particle travels with the same velocity as the particle. It proves that a material particle in motion is equivalent to group of waves or a wave packet.

16.1 HEISENBERG UNCERTAINTY PRINCIPLE

LO1

Heisenberg uncertainty principle is perhaps the best known result of the wave particle duality, i.e., the concept of waves or wave packet associated with a moving particle. According to Heisenberg uncertainty principle it is impossible to determine simultaneously the exact position and momentum (or velocity) of a small moving particle like electron.

As discussed earlier, the quantity $|\psi(x, t)|^2\Delta x$ represents the probability that the particle is within the region between x and $x + \Delta x$. It means there is an uncertainty in the location of the position of the particle and Δx is a measure of the uncertainty. The uncertainty in the position would be less if Δx is smaller, i.e., if the wave packet is very narrow. The narrow wave packet means the range of wavelength $\Delta\lambda$ between λ and $\lambda + \Delta\lambda$ is smaller or the range of wave numbers Δk between k and $k + \Delta k$ is larger. So Δx is inversely proportional to Δk, i.e.,

$$\Delta x \propto \frac{1}{\Delta k}$$

We may approximate this as $\Delta x\Delta k \approx 1$. Taking $\hbar = \frac{h}{2\pi}$, we get $p = \frac{h}{\lambda} = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar k, \Delta k = \frac{\Delta p}{\hbar}$. Therefore

$$\Delta x\Delta p \approx \hbar$$

The above relation represents the lowest limit of accuracy. Therefore, we can write more generally.

$$\Delta x\Delta p \geq \hbar$$

The principle of uncertainty can also be represented in terms of energy E and time t. Since $\frac{\Delta p}{\Delta t} = \Delta F$, we can write

$$\Delta p = \Delta F \cdot \Delta t$$

Putting this value of Δp in the expression $\Delta x\Delta p \geq \hbar$ we obtain

$$\Delta x \times (\Delta F \times \Delta t) \geq \hbar$$

or

$$[\Delta F \times \Delta x]\, \Delta t \geq \hbar$$

$$\Delta E\, \Delta t \geq \hbar$$

The principle of uncertainty can also be expressed in terms of angular momentum and angle. Suppose we have a particle at a particular angular position θ and its angular momentum is L_θ. Then the limits in the uncertainties $\Delta\theta$ and ΔL_θ are given by the relation $\Delta\theta\Delta L_\theta \geq \hbar$.

16.1.1 Mathematical Proof

Heisenberg's uncertainty principle can be proved on the basis of deBroglie's wave concept that a material particle in motion is equivalent to a group of waves or wave packet, the group velocity G being equal to the particle velocity v. Consider a simple case of wave packet which is formed by the superposition of two simple harmonic plane waves of equal amplitudes a and having nearly equal frequencies ω_1 and ω_2. The two waves can be represented by the equations.

$$y_1 = a \sin(\omega_1 t - k_1 x)$$

$$y_2 = a \sin(\omega_2 t - k_2 x)$$

where k_1 and k_2 are their propagation constants and $\frac{\omega_1}{k_1}$ and $\frac{\omega_2}{k_2}$ are their respective phase velocities. The resultant wave due to superposition of these wave is given by

$$y = y_1 + y_2$$

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

where $\omega = (\omega_1 + \omega_2)/2$, $k = (k_1 + k_2)/2$, $\Delta\omega = \omega_1 - \omega_2$ and $\Delta k = k_1 - k_2$. (i)

The resultant wave is shown in Fig. 16.1. The envelope (loop) of this wave travels with the group velocity G, given by

$$G = \frac{\Delta\omega}{\Delta k} = \frac{\omega_1 - \omega_2}{k_1 - k_2}$$

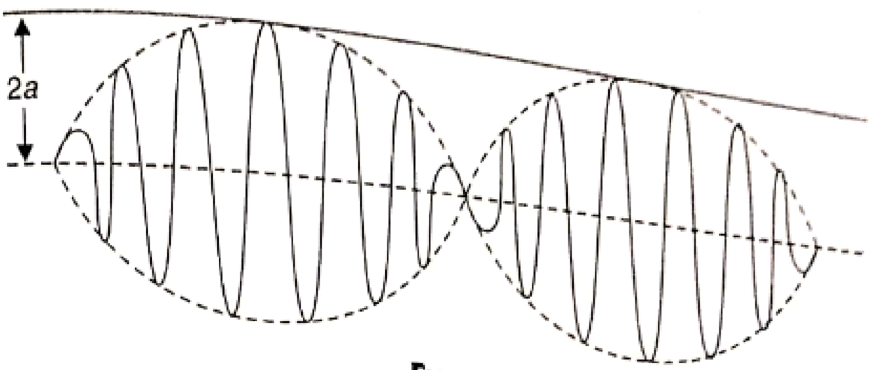

Figure 16.1

Since the group velocity of deBroglie wave group associated with the moving particle is equal to the particle velocity, the loop so formed is equivalent to the position of the particle. Then the particle may be anywhere within the loop. Now the condition of the formation of node from Eq. (i) is given by

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

or

$$\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x = \frac{\pi}{2}, \frac{3\pi}{2}, \ldots, \frac{(2n+1)\pi}{2} \qquad \text{(ii)}$$

where $n = 0, 1, 2, \ldots..$

If x_1 and x_2 be the values of positions of two consecutive nodes, then from above equation by putting n and $(n+1)$, we get

$$\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x_1 = \frac{(2n+1)\pi}{2} \qquad \text{(iii)}$$

and

$$\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x_2 = \frac{(2n+3)\pi}{2} \qquad \text{(iv)}$$

From Eqs. (iii) and (iv), we have

$$\frac{\Delta k}{2}(x_1 - x_2) = \pi$$

$$\frac{\Delta k}{2}\Delta x = \pi$$

or

$$\Delta x = \frac{2\pi}{\Delta k}$$ (v)

or

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

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

where Δp is the error (uncertainty) in the measurement of momentum p. Therefore, from Eq. (v)

$$\Delta x = \frac{2\pi h}{2\pi \Delta p} = \frac{h}{\Delta p}$$

or
$$\Delta p \Delta x = h$$

However, more accurate measurements show that the product of uncertainties in momentum (Δp) and the position (Δx) cannot be less than $h/2\pi$. Therefore

or $\quad \Delta p \Delta x \geq \hbar$

This is the Heisenberg's uncertainty principle.

16.1.2 Applications

Some important applications of uncertainty principle are discussed below.

16.1.2.1 Non-Existence of Electron in the Nucleus

The radius of the nucleus of an atom is of the order of 10^{-14} m. If an electron is confined within the nucleus, the uncertainty in its position must not be greater than 10^{-14} m. According to uncertainty principle for the lowest limit of accuracy

$$\Delta x \Delta p = \frac{h}{2\pi} \tag{i}$$

where Δx is uncertainty in the position and Δp is the uncertainty in the momentum.

From Eq. (i),

$$\Delta p = \frac{h}{2\pi \Delta x} = \frac{6.625 \times 10^{-34}}{2 \times 3.14 \times 2 \times 10^{-14}} \quad \text{(as } \Delta x = \text{diameter of nucleus)}$$

$$\Delta p = 5.275 \times 10^{-21} \text{ kg m/sec}$$

This is the uncertainty in momentum of the electron. It means the momentum of the electron would not be less than Δp, rather it could be comparable to Δp. Thus

$$p = 5.275 \cdot 10^{-21} \text{ kg m/sec}$$

The kinetic energy of the electron can be obtained in terms of momentum as

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

$$= \frac{(5.275\times10^{-21})^2}{2\times9.1\times10^{-31}}\text{ J}$$

$$= \frac{(5.275\times10^{-21})^2}{2\times9.1\times10^{-31}\times1.6\times10^{-19}}\text{ eV}$$

$$= 95.55\times10^{6}\text{ eV}$$

$$\approx 96\text{ MeV}$$

From the above result, it is clear that the electrons inside the nucleus may exist only when it possesses the energy of the order of 96 MeV. However, the maximum possible kinetic energy of an electron emitted by radioactive nuclei has been found about 4 MeV. Hence, it is concluded that the electron cannot reside inside the nucleus.

16.1.2.2 Radius of Bohr's First Orbit

If Δx and Δp be the uncertainties in determining the position and momentum of the electron in the first orbit, then from the uncertainty principle

$$\Delta x\Delta p \approx \hbar$$

or

$$\Delta p \approx \frac{\hbar}{\Delta x} \qquad \text{(i)}$$

The uncertainty in kinetic energy (K.E.) of electron may be written as

$$\Delta T = \frac{(\Delta p)^2}{2\,m} \qquad \left[\text{K.E.} = T = \frac{p^2}{2m}\right] \qquad \text{(ii)}$$

From Eqs. (i) and (ii), we have

$$\Delta T = \frac{1}{2m}\left[\frac{\hbar}{\Delta x}\right]^2$$

and the uncertainty in the potential energy of the same electron is given by

$$\Delta V = \frac{1}{4\pi\varepsilon_0}\frac{(Ze)(-e)}{\Delta x} \qquad \left[\because\; V = \frac{1}{4\pi\varepsilon_0}\frac{(Ze)(-e)}{x}\right]$$

The uncertainty in the total energy of electron together with Ze as the nucleus charge

$$\Delta E = \Delta T + \Delta V$$

$$= \frac{\hbar^2}{2m(\Delta x)^2} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{\Delta x}$$

The condition for this uncertainty in the energy to be minimum is

$$\frac{d(\Delta E)}{d(\Delta x)} = 0$$

or

$$-\frac{\hbar^2}{m(\Delta x)^3} + \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{(\Delta x)^2} = 0$$

$$\Delta x = \frac{\hbar^2(4\pi\varepsilon_0)}{mZe^2}$$

Hence, the radius of first orbit

$$r = \Delta x = \frac{\hbar^2 (4\pi\varepsilon_0)}{mZe^2}$$

or

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

This is the radius of first Bohr's orbit.

16.1.2.3 Energy of a Particle in a Box or Infinite Potential Well

Let us consider a particle having mass m in infinite potential well of width L. The maximum uncertainty in the position of the particle may be

$$(\Delta x)_{max} = L$$

From the uncertainty principle

$$\Delta x \Delta p = \hbar$$

or

$$\Delta p = \frac{\hbar}{\Delta x} = \frac{\hbar}{L}$$

Kinetic energy

$$T = \frac{p^2}{2m} = \frac{\hbar^2}{2mL^2}$$

$$T = \frac{\hbar^2}{2mL^2}$$

This is the minimum kinetic energy of the particle in an infinite potential well of width L.

16.1.2.4 Ground State Energy of Linear Harmonic Oscillator

The total energy E of a linear harmonic oscillator is the sum of its kinetic energy (K.E.) and potential energy (P.E.).

$$E = \text{K.E} + \text{P.E.}$$

$$E = \frac{p^2}{2m} + \frac{1}{2}kx^2 \tag{i}$$

Let a particle of mass m executes a simple harmonic motion along x-axis. The maximum uncertainty in the determination of its position can be taken as Δx. From the uncertainty relation, the uncertainty in momentum is then given by

$$\Delta p = \frac{\hbar}{2\Delta x} \quad \left[\text{Taking } \Delta p \Delta x = \frac{\hbar}{2} \text{ for more accuracy}\right] \tag{ii}$$

For maximum uncertainties $\Delta p = p$ and $\Delta x = x$

Hence, the total energy E of the oscillator becomes

$$E = \frac{(\Delta p)^2}{2m} + \frac{1}{2}k(\Delta x)^2$$

or

$$E = \left(\frac{\hbar}{2}\right)^2 \cdot \frac{1}{2m(\Delta x)^2} + \frac{1}{2}k(\Delta x)^2$$

or

$$E = \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}k(\Delta x)^2 \tag{iii}$$

For a minimum value of energy,

$$\frac{\partial E}{\partial(\Delta x)} = 0$$

Then we get

$$-\frac{\hbar^2}{4m(\Delta x)^3} + k(\Delta x) = 0$$

$$(\Delta x)^4 = \frac{\hbar^2}{4mk}$$

or

$$(\Delta x) = \left(\frac{\hbar^2}{4mk}\right)^{1/4} \qquad \text{(iv)}$$

or

Substituting value of Δx in Eq. (iii) from Eq. (iv), we get

$$E_{\min} = \frac{\hbar^2}{8m}\left(\frac{4mk}{\hbar^2}\right)^{1/2} + \frac{1}{2}k\left(\frac{\hbar^2}{4mk}\right)^{1/2}$$

$$E_{\min} = \frac{\hbar}{2}\left(\frac{k}{m}\right)^{1/2}$$

But $\sqrt{\frac{k}{m}} = \omega =$ angular frequency. Therefore, the minimum energy of harmonic oscillator is expressed by the following relation

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

Here it would be worth mentioning that the energy comes out to be $E_{\min} = \hbar\omega$ if we use $\Delta p \Delta x = \hbar$ (less accuracy).

16.2 WAVE FUNCTION AND ITS PHYSICAL SIGNIFICANCE

Waves in general are associated with quantities that vary periodically. In case of matter waves, the quantity that varies periodically is called *wave function*. The wave function, represented by ψ, associated with the matter waves has no direct physical significance. It is not an observable quantity. However, the value of the wave function is related to the probability of finding the particle at a given place at a given time. The square of the absolute magnitude of the wave function of a body evaluated at a particular time at a particular place is proportional to the probability of finding the particle at that place at that instant.

The wave functions are usually complex. The probability in such a case is taken as $\psi^*\psi$, i.e., the product of the wave function with its complex conjugate, ψ^* being the complex conjugate. Since the probability of finding a particle somewhere is finite, we have the total probability over all space equal to unity. That is

$$\int_{-\infty}^{\infty} \psi^* \psi \, dV = 1 \qquad \text{(i)}$$

where $dV = dxdydz$.

Equation (i) is called the normalisation condition and a wave function that obeys this equation is said to be normalised. Further, ψ must be a single valued since the probability can have only one value at a particular place and time. Besides being normalisable, a further condition that ψ must obey is that it and its partial derivatives $\frac{\partial\psi}{\partial x}$, $\frac{\partial\psi}{\partial y}$ and $\frac{\partial\psi}{\partial z}$ be continuous everywhere.

The important characteristics of the wave function are as follows.

(i) ψ must be finite, continuous and single valued everywhere.

(ii) $\frac{\partial\psi}{\partial x}$, $\frac{\partial\psi}{\partial y}$ and $\frac{\partial\psi}{\partial z}$ must be finite, continuous and single valued.

(iii) ψ must be normalisable.

16.3 TIME INDEPENDENT SCHRÖDINGER EQUATION

LO2

Consider a system of stationary waves associated with a moving particle. The waves are said to be stationary w.r.t the particle. If the position coordinates of the particle are (x, y, z) and ψ be the periodic displacement for the matter waves at any instant of time t, then we can represent the motion of the wave by a differential equation as follows.

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=\frac{1}{u^2}\frac{\partial^2\psi}{\partial t^2} \tag{i}$$

where u is the velocity of wave associated with the particle. The solution of Eq. (i) gives ψ as a periodic displacement in terms of time, i.e.,

$$\psi(x, y, z, t) = \psi_0(x, y, z)e^{-i\omega t} \tag{ii}$$

where ψ_0 is the amplitude of the particle wave at the point (x, y, z) which is independent of time (t). It is a function of (x, y, z), i.e., the position r and not of time t. Here,

$$r = x\hat{i} + y\hat{j} + z\hat{k} \tag{iii}$$

Eq. (ii) may be expressed as

$$\psi(r, t) = \psi_0(r)e^{-i\omega t} \tag{iv}$$

Differentiating Eq. (iv) twice with respect to t, we get

$$\frac{\partial^2\psi}{\partial t^2} = -\omega^2\psi_0(r)e^{-i\omega t}$$

or

$$\frac{\partial^2\psi}{\partial t^2} = -\omega^2\psi \tag{v}$$

Substituting the value of $\frac{\partial^2\psi}{\partial t^2}$ from this equation in Eq. (i), we get

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{\omega^2}{u^2}\psi = 0 \tag{vi}$$

where $\omega = 2\pi\nu = 2\pi(u/\lambda)$ [as $u = \lambda\nu$]

so that

$$\frac{\omega}{u} = \frac{2\pi}{\lambda} \tag{vii}$$

Also

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \nabla^2 \psi \tag{viii}$$

where ∇^2 is known as Laplacian operator. Using Eqs. (vi), (vii) and (viii), we have

$$\nabla^2 \psi + \frac{4\pi^2}{\lambda^2} \psi = 0 \tag{ix}$$

Also from the deBroglie wave concept

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

Using this relation in Eq. (ix) gives

$$\nabla^2 \psi + \frac{4\pi^2 m^2 v^2}{h^2} \psi = 0 \tag{x}$$

Here it can be noted that the velocity of particle v has been introduced in the wave equation.

If E and V are respectively the total energy and potential energy of the particle then its kinetic energy is given by

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

$$m^2 v^2 = 2m(E - V) \tag{xi}$$

The use of Eq. (xi) in Eq. (x) gives rise to

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0 \tag{xii}$$

or

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

This is the time independent Schrödinger equation, where the quantity ψ is known as *wave function.*

For a freely moving or free particle $V = 0$. Therefore, Eq. (xii) becomes

$$\nabla^2 \psi + \frac{2mE}{\hbar^2} \psi = 0 \tag{xiii}$$

This is called time independent Schrödinger equation for a free particle.

LO3

16.4 TIME DEPENDENT SCHRÖDINGER EQUATION

In order to obtain a time dependent Schrödinger equation, we eliminate the total energy E from time independent Schrödinger equation. For this we differentiate Eq. (iv) w.r.t. t and obtain

$$\frac{\partial\psi}{\partial t} = -i\omega\psi_0(r)e^{-i\omega t}$$

$$= i(2\pi\nu)\psi_0(r)e^{-i\omega t}$$

$$= -2\pi\nu i\psi = -2\pi i\frac{E}{h}\psi = -\frac{iE}{\hbar}\times\frac{i}{i}\psi$$

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

or
$$E\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad \text{(xiv)}$$

Substituting the value of Eψ from Eq. (xiv) in Eq. (xii), we have

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left[i\hbar\frac{\partial\psi}{\partial t} - V\psi\right] = 0$$

or
$$\nabla^2\psi = -\frac{2m}{\hbar^2}\left[i\hbar\frac{\partial\psi}{\partial t} - V\psi\right]$$

or
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad \text{(xv)}$$

This equation is known as *Schrödinger's time dependent wave equation*. The operator $\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)$ is called *Hamilitonian operator* and is represented by H. If we see the RHS of Eq. (xv) and keep in mind Eq. (xiv), we notice that the operator $i\hbar\frac{\partial}{\partial t}$ operating on ψ gives E. Hence, Schrödinger equation can be written in operator form, as below

$$H\psi = E\psi$$

16.5 OPERATORS

LO3

In a physical system, there is a quantum mechanical operator that is associated with each measurable parameter. In quantum mechanics, we deal with waves (wave function) rather than discrete particles whose motion and dynamics can be described with the deterministic equations of Newtonian physics. Generally an operator is anything that is capable of doing something to a function. There is an operator corresponding to every observable quantity. However, the choice of operator is arbitrary in quantum mechanics. When an operator operates on a wave function it must give observable quantity times the wave function. It is a must condition for an operator.

If we consider an operator represented by A corresponding to the observable quantity a, then

$$A\psi = a\psi$$

Wave function that satisfies the above equation is called *eigen function* and corresponding observable quantity is called *eigen value* and the equation is called eigen value equation. Some of those operators are tabled below.

Classical Quantity	Quantum Mechanical Operator
Position x, y, z,	x, y, z
Momentum p	$-i\hbar\vec{\nabla}$
Momentum components p_x, p_y, p_z	$-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z}$
Energy E	$i\hbar\frac{\partial}{\partial t}$
Hamiltonian (Time independent)	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(r)$
Kinetic energy	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}$

16.6 APPLICATIONS OF SCHRÖDINGER EQUATION

LO4

In classical mechanics, based on Newton's second law of motion ($\vec{F}=m\vec{a}$) we make a mathematical prediction of the path, a given system will take following set of known initial conditions. The analogue of Newton's law is Schrödinger equation in quantum mechanics for a quantum system such as atoms, molecules and subatomic particles. The subatomic particles may be free, bound or localized. Schrödinger equation describes the time evolution of the system's wave function.

Schrödinger's equation is extremely useful for investigating various quantum mechanical problems. With the help of this equation and boundary conditions, the expression for the wave function is obtained. Then the probability of finding the particle is calculated by using the wave function. In the following subsections, we discuss different quantum mechanical problems, viz. particle in a box, one-dimensional harmonic oscillator, step potential and step barrier.

16.6.1 Particle in a Box (Infinite Potential Well)

The simplest quantum mechanical problem is that of a particle trapped in a box with infinitely hard walls. Infinitely hard walls means the particle does not loose energy when it collides with such walls, i.e., its total energy remains constant. A physical example of this problem could be a molecule which is strictly confined in a box.

Let us consider a particle restricted to move along the x-axis between $x = 0$ and $x = L$, by ideally reflecting, infinitely high walls of the infinite potential well, as shown in Fig. 16.2. Suppose that the potential energy V of the particle is zero inside the box, but rises to infinity outside, that is,

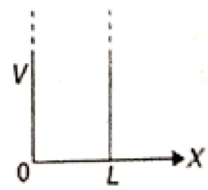

FIGURE 16.2

$$V=0 \quad \text{for} \quad 0 \le x \le L$$
$$V=\infty \quad \text{for} \quad x<0 \quad \text{and} \quad x>L$$

In such a case, the particle is said to be moving in an infinitely deep potential well. In order to evaluate the wave function ψ in the potential well, Schoredinger equation for the particle within the well ($V = 0$) is written as

$$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 mE}{h^2}\psi=0 \qquad \text{(i)}$$

we put $\frac{8\pi^2 mE}{h^2} = k^2$ in the above equation for getting

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

The general solution of this differential equation is

$$\psi(x) = A \sin kx + B \cos kx \tag{iii}$$

where A and B are constants.

Applying the boundary condition $\psi(x) = 0$ at $x = 0$, which means the probability of finding particle at the wall $x = 0$ is zero, we obtain

$$A \sin(0) + B \cos(0) = 0 \quad \Rightarrow \quad B = 0$$

Again, we have $\psi(x) = 0$ at $x = L$, then

$$A \sin kL + B \cos kL = 0 \quad \Rightarrow \quad A \sin kL = 0$$

The above equation is satisfied when

$$kL = n\pi$$

or
$$k = \frac{n\pi}{L} \qquad \text{where } n = 1, 2, 3, \ldots$$

or
$$k^2 = \frac{n^2\pi^2}{L^2} \tag{iv}$$

or
$$\frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{L^2} \tag{v}$$

or in general we can write Eq. (v) as

$$E_n = \frac{n^2 h^2}{8mL^2} \qquad \text{where } n = 1, 2, 3, \ldots$$

Thus, it can be concluded that in an infinite potential well the particle cannot have an arbitrary energy, but can take only certain discrete energy values corresponding to $n = 1, 2, 3, \ldots$. These are called the *eigen values* of the particle in the well and constitutes the energy levels of the system. The integer n corresponding to the energy level E_n is called its *quantum number*, as shown in Fig. 16.3.

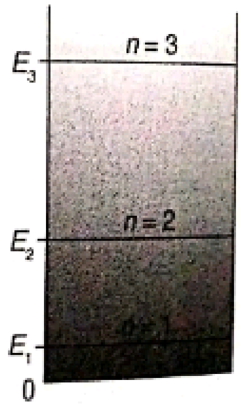

FIGURE 16.3

We can also calculate the momentum p of the particle or the eigen values of the momentum, as follows,

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

$$p = \hbar k = \frac{n\pi\hbar}{L}$$

The wave function (or eigen function) is given by Eq. (iii) along with the use of expression for k.

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

To find the value of A, we use the normalisation condition.

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = 1$$

As mentioned earlier, the above expression simply says that the probability of finding the particle is 1. In the present case, the particle is within the box i.e., between $0 < x < L$. So the normalisation condition becomes

$$A^2 \int_0^L \sin^2 \frac{n\pi x}{L} \, dx = 1$$

$$A^2 \left(\frac{L}{2}\right) = 1 \quad \text{or} \quad A = \sqrt{\frac{2}{L}}$$

The normalised eigen wave function of the particle is, therefore, given by

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

The first three eigen functions ψ_1, ψ_2, ψ_3 together with the probability densities $|\psi_1|^2$, $|\psi_2|^2$, $|\psi_3|^2$, are shown in Figs. 16.4(a) and (b), respectively.

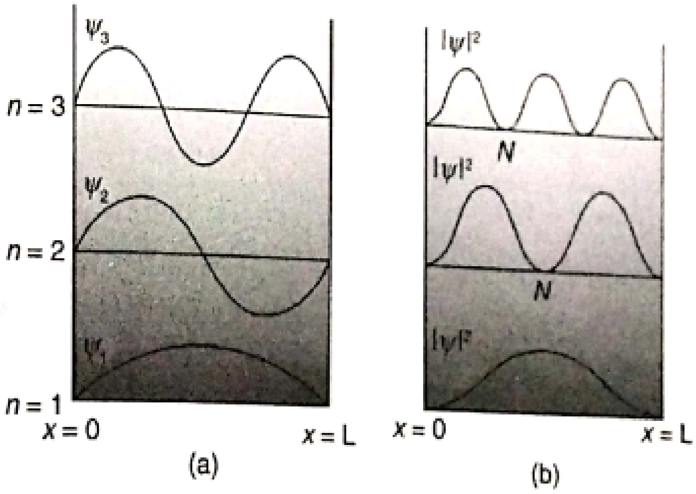

Figure 16.4

Classical mechanics predicts the same probability for the particle being anywhere in the well. Wave mechanics, on the other hand, predicts that the probability is different at different points and there are points (nodes) where the particle is never found. Further, at a particular point, the probability of finding the particle is different for different energy states. For example, a particle in the lowest energy state ($n = 1$) is more likely to be in the middle of the box, while in the next energy state ($n = 2$) it is never there since $|\psi_2|^2$ is zero there. It is $|\psi_n|^2$ which provides the probability of finding the particle within the potential well.

16.6.2 Finite Potential Step

A physical example of this quantum mechanical problem can be thought as the neutron which is trying to escape nucleus. The potential function of a potential step may be represented as

$$\begin{aligned} V(x) &= 0 && \text{for} \quad x < 0 \text{ region I} \\ V(x) &= V_0 && \text{for} \quad x > 0 \text{ region II} \end{aligned} \qquad \text{(i)}$$

We consider that a particle of energy E is incident from left on the potential step of height V_0 as shown in Fig. 16.5. Further, we assume that the energy of the incident particle is greater than the step barrier height i.e., $E > V_0$. Since $E > V_0$, according to classical theory there should be no reflection at the boundary of the step potential barrier. However, quantum mechanically this is not true. It means that there will be some reflection from the boundary of the potential step.

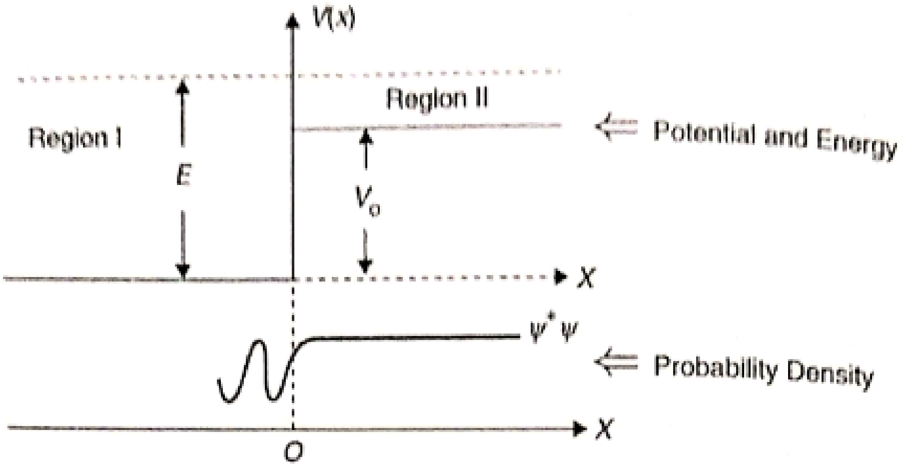

FIGURE 16.5

The wavelength of the particle suddenly changes from region I to region II and is given as follows

$$\lambda_1 = \frac{h}{p_1} = \frac{h}{\sqrt{2mE}} \tag{ii}$$

and

$$\lambda_2 = \frac{h}{p_2} = \frac{h}{\sqrt{2m(E - V_0)}} \tag{iii}$$

Hence, a small part of the wave associated with the particle is reflected due to this change in wavelength and the rest part is transmitted. This can be proved with the solution of Schrödinger wave equations for two regions. The Schrödinger equation for region I is written as

$$\frac{d^2\psi_1(x)}{dx^2} + \frac{2mE}{\hbar^2}\psi_1(x) = 0 \tag{iv}$$

Schrödinger equation for region II is written as

$$\frac{d^2\psi_2(x)}{dx^2} + \frac{2m(E - V_0)}{\hbar^2}\psi_2(x) = 0 \tag{v}$$

The solutions of Eqs. (iv) and (v) are written as

$$\psi_1(x) = A_1 e^{ik_1 x} + A_2 e^{-ik_1 x} \tag{vi}$$

$$\psi_2(x) = A_3 e^{ik_2 x} + A_4 e^{-ik_2 x} \tag{vii}$$

where $\psi_1(x)$ and $\psi_2(x)$ are the wave functions of region I and II and A_1, A_2, A_3 and A_4 are constants. k_1 and k_2 are defined as follows

$$k_1 = \frac{\sqrt{2mE}}{\hbar} \quad \text{and} \quad k_2 = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

The first term in Eq. (vi) represents the wave travelling in the positive x direction in the first region and second term represents the reflected part of the incident wave travelling in the negative x direction in region I. In Eq. (vii), first term represents the transmitted part of the incident particle wave travelling in the direction of positive x axis in region II. The second term of Eq. (vii) has no meaning, because the reflection of the particle cannot take place in region II. So, considering this, Eq. (vii) can be written as

$$\psi_2(x) = A_3 e^{ik_2 x} \tag{viii}$$

The boundary condition at $x = 0$ is defined as

$$\psi_1(0) = \psi_2(0), \tag{ix}$$

which means the wave function is continuous at the boundary. Also the derivative of ψ should be continuous at the boundary, i.e.,

$$\left.\frac{d\psi_1(x)}{dx}\right|_{x=0} = \left.\frac{d\psi_2(x)}{dx}\right|_{x=0} \tag{x}$$

Using these boundary conditions, we get

$$A_1 + A_2 = A_3 \tag{xi}$$

and

$$ik_1(A_1 e^{ik_1 x} - A_2 e^{-ik_1 x})\big|_{x=0} = ik_2 A_3 e^{ik_2 x}\big|_{x=0}$$

or

$$ik_1(A_1 - A_2) = ik_2 A_3 \tag{xii}$$

Solving Eq. (xi) and (xii), we get

$$\frac{A_2}{A_1} = \frac{k_1 - k_2}{k_1 + k_2} \tag{xiii}$$

and

$$\frac{A_3}{A_1} = \frac{2k_1}{k_1 + k_2} \tag{xiv}$$

Since the reflection and transmission of the particle takes place, the problem can be investigated based on the reflection and transmission coefficients. Further, the coefficient A_1 is related to the wave function ψ_1, i.e., of the incident particle and A_3 is related to the wave function ψ_3, i.e., of the transmitted particle. It means the reflection and transmission coefficients can be defined as follows.

Reflection coefficient = Reflected intensity/Incident intensity
= (Reflected amplitude)^2/(Incident amplitude)^2 (xv)

Transmission coefficient = Transmitted intensity/Incident intensity
= (Transmitted amplitude)^2/(Incident amplitude)^2 (xvi)

The reflection coefficient is

$$R = \frac{|A_2|^2}{|A_1|^2} = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2 \neq 0 \tag{xvii}$$

and transmission coefficient is

$$T = \frac{|A_3|^2}{|A_1|^2} = \left(\frac{2k_1}{k_1 + k_2}\right)^2 \neq 1 \tag{xviii}$$

From the above results we see that the reflection coefficient (R) is not zero and the transmission probability (T) is not unity in the quantum mechanical treatment of the particle behaviour in the finite potential step problem. However, classically the reflection coefficient should be zero and transmission coefficient should be equal to unity.

16.6.3 Finite Potential Barrier

A physical example of this quantum mechanical problem can be thought as the α particle which is trying to escape Coulomb barrier. For this case, the potential function is defined as

$V(x) = 0$	for $x < 0$	Region I
$V(x) = V_0$	for $0 < x < a$	Region II
$V(x) = 0$	for $x > a$	Region III

The potential barrier is considered between $x = 0$ and $x = a$, as shown in Fig. 16.6. Here, we suppose that a particle incident on the barrier has energy E which is less than the barrier height V_0, i.e., $E < V_0$. Classically, when $E < V_0$, the particle can never penetrate the potential barrier and appear in region III. It means the particle is always reflected from the barrier. Therefore, the transmission coefficient is zero. However, quantum mechanically this is not true and there is some probability for a particle penetrate the barrier. It means a fraction of the particles incident from the left will cross the barrier and appear in region III.

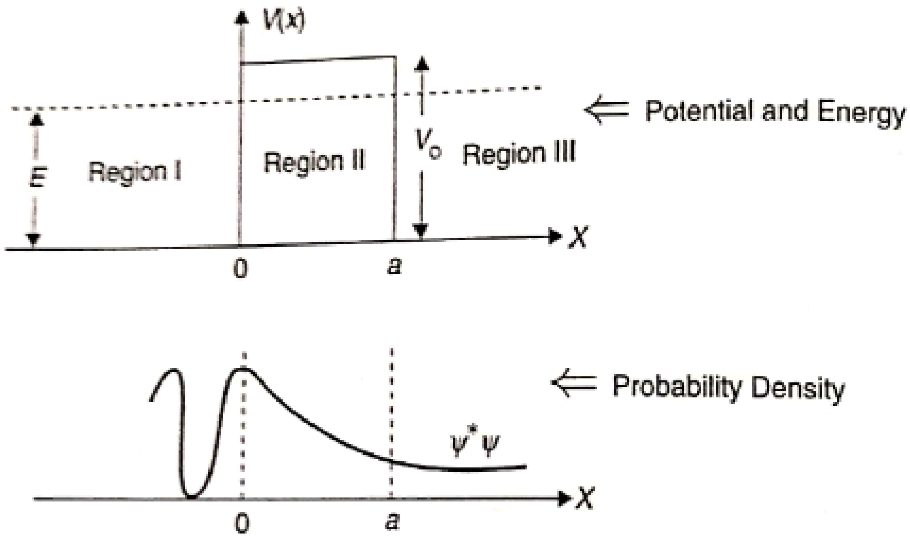

Figure 16.6

Schrödinger wave equations for the regions I and III are as follows

$$\frac{d^2\psi_1(x)}{dx^2} + \frac{2mE}{\hbar^2}\psi_1(x) = 0 \tag{ii}$$

and

$$\frac{d^2\psi_3(x)}{dx^2} + \frac{2mE}{\hbar^2}\psi_3(x) = 0 \tag{iii}$$

where $\psi_1(x)$ and $\psi_3(x)$ are the wave function of region I and III. The solutions of these equations are

$$\psi_1(x) = A_1 e^{ik_1 x} + A_2 e^{-ik_1 x} \tag{iv}$$

and

$$\psi_3(x) = A_3 e^{ik_1 x} + A_4 e^{-ik_1 x} \tag{v}$$

where $k_1 = \dfrac{\sqrt{2mE}}{\hbar} = \dfrac{p}{\hbar} = \dfrac{2\pi}{\lambda}$ and A_1, A_2, A_3 and A_4 are constants. The solution for ψ_1 is a combination of reflected and transmitted wave in region I. But in the region III, the reflected part of the wave is zero ($A_4 =$ 0) and the transmitted wave is traveling in the positive x direction. So the solution in region III becomes

$$\psi_3(x) = A_3 e^{ik_1 x}$$

Now, the Schrödinger equation for region II is written as

$$\frac{d^2\psi_2(x)}{dx^2} + \frac{2m(E - V_0)}{\hbar^2}\psi_2(x) = 0 \qquad \text{(vi)}$$

But as we know that $E < V_0$ then it will be convenient to write this equation in the form

$$\frac{d^2\psi_2(x)}{dx^2} - \frac{2m(V_0 - E)}{\hbar^2}\psi_2(x) = 0 \qquad \text{(vii)}$$

where ψ_2 is the wave function of region II. The solution of above equation is

$$\psi_2(x) = A_5 e^{-ik_2 x} + A_6 e^{ik_2 x} \qquad \text{(viii)}$$

where

$$k_2 = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \qquad \text{(ix)}$$

In order to calculate the transmission probability T, we must apply the boundary conditions to wave function ψ_1, ψ_2 and ψ_3. These boundary conditions at the left hand (at $x = 0$) or at the right hand wall (at $x = a$) of the barrier are defined as

Boundary conditions at $x = 0$ are

$$\psi_1(0) = \psi_2(0) \qquad \text{(x)}$$

and

$$\frac{\partial\psi_1(0)}{\partial x} = \frac{\partial\psi_2(0)}{\partial x} \qquad \text{(xi)}$$

At $x = a$ are

$$\psi_2(a) = \psi_3(a) \qquad \text{(xii)}$$

and

$$\frac{\partial\psi_2(a)}{\partial x} = \frac{\partial\psi_3(a)}{\partial x} \qquad \text{(xiii)}$$

The above boundary conditions along with the use of wave functions ψ_1, ψ_2 and ψ_3 yield

$$A_1 + A_2 = A_5 + A_6 \qquad \text{(xiv)}$$

$$ik_1A_1 - ik_1A_2 = -k_2A_5 + k_2A_6 \qquad \text{(xv)}$$

$$A_5 e^{-k_2 a} + A_6 e^{k_2 a} = A_3 e^{ik_1 a} \qquad \text{(xvi)}$$

$$-k_2A_5 e^{-k_2 a} + k_2A_6 e^{k_2 a} = ik_1A_3 e^{ik_1 a} \qquad \text{(xvii)}$$

Solving Eqs. (xiv) and (xv), we get

$$A_1 = \frac{(ik_1 - k_2)}{2ik_1}A_5 + \frac{(ik_1 + k_2)}{2ik_1}A_6 \qquad \text{(xviii)}$$

and solving Eqs. (xvi) and (xvii), we get

$$A_6 = \frac{(k_2 + ik_1)e^{ik_1 a}}{2k_2 e^{k_2 a}} A_3 \tag{xix}$$

and
$$A_5 = \frac{(k_2 - ik_1)e^{ik_1 a}}{2k_2 e^{-k_2 a}} A_3 \tag{xx}$$

Substituting these values in Eq. (xviii), we get

$$\frac{A_1}{A_3} = \left[\frac{1}{2} + \frac{i}{4}\left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\right] e^{(ik_1 + k_2)a} + \left[\frac{1}{2} - \frac{i}{4}\left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\right] e^{(ik_1 - k_2)a} \tag{xxi}$$

As we assumed, the potential barrier to be much higher than the energy of the incident particles. In this condition $k_2/k_1 >> k_1/k_2$ and hence

$$\frac{k_2}{k_1} - \frac{k_1}{k_2} \approx \frac{k_2}{k_1} \tag{xxii}$$

Further we assume that the potential barrier wide enough so that for ψ_2 gets severely weakened between $x =$ 0 and $x = a$. This means $k_2 a >> 1$, i.e.,

$$e^{k_2 a} >> e^{-k_2 a} \tag{xxiii}$$

So Eq. (xxi) is approximated by

$$\frac{A_1}{A_3} = \left(\frac{1}{2} + \frac{ik_2}{4k_1}\right) e^{(ik_1 + k_2)a} \tag{xxiv}$$

The complex conjugate of this is written as

$$\left(\frac{A_1}{A_3}\right)^* = \left(\frac{1}{2} - \frac{ik_2}{4k_1}\right) e^{(-ik_1 + k_2)a} \tag{xxv}$$

On multiplying Eqs. (xxiv) and (xxv), we get

$$\text{So, } \frac{A_1 A_1^*}{A_3 A_3^*} = \left(\frac{1}{4} + \frac{k_2^2}{16k_1^2}\right) e^{2k_2 a} \tag{xxvi}$$

Since the coefficient A_1 is related to the wave function ψ_1, i.e., of the incident particle and A_3 is related to the wavelength of ψ_3, of the transmitted particle, the transmission probability is equivalent to

$$T = \frac{A_3 A_3^*}{A_1 A_1^*} = \left(\frac{A_1 A_1^*}{A_3 A_3^*}\right)^{-1} = \left(\frac{16}{4 + (k_2/k_1)^2}\right) e^{-2k_2 a} \tag{xxvii}$$

From the definitions of k_1 and k_2 we see that

$$\left(\frac{k_2}{k_1}\right)^2 = \frac{2m(V_0 - E)/\hbar^2}{2mE/\hbar^2} = \frac{V_0}{E} - 1 \tag{xxviii}$$

With this it can be seen that the quantity in the bracket varies slowly with E and V_0 than the variation of exponential term. So the approximated transmission probability is

$$T = e^{-k_2 a}$$

(xxix)

16.6.4 One-Dimensional Harmonic Oscillator

A physical example of this quantum mechanical problem can be thought as an atom of vibrating diatomic molecule. In general, a particle undergoing simple harmonic motion in one dimension is called one dimensional harmonic oscillator. The potential and total energy of such a system is shown in Fig. 16.7 where the probability density is also shown. In such a motion, the restoring force F is proportional to the particle's displacement x from the equilibrium position, i.e.,

$$F = -kx \tag{i}$$

where k is force constant. The potential energy V can be written as

$$V = \frac{1}{2}kx^2$$

Then, the Schrödinger's equation for the oscillator with $V = \frac{1}{2}kx^2$ is

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

Putting $\hbar = \frac{h}{2\pi}$, $\frac{8\pi^2 mE}{h^2} = \alpha$ and $\left(\frac{4\pi^2 mk}{h^2}\right)^{1/2} = \beta$ in the above equation, we obtain

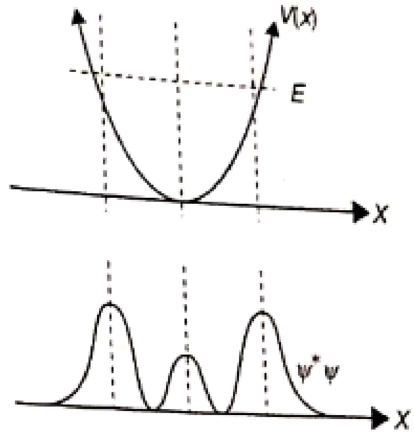

FIGURE 16.7

$$\frac{d^2\psi}{dx^2} + (\alpha - \beta^2 x^2)\psi = 0 \tag{ii}$$

Now we introduce a dimension less independent variable as $\xi = \sqrt{\beta}x$. Thus Eq. (ii) becomes.

$$\beta\frac{d^2\psi}{d\xi^2} + \left[\alpha - \beta^2\frac{\xi^2}{\beta}\right]\psi = 0$$

$$\frac{d^2\psi}{d\xi^2} + \left[\frac{\alpha}{\beta} - \xi^2\right]\psi = 0 \tag{iii}$$

The solution of this equation is

$$\psi = CUe^{-\xi^2/2} \tag{iv}$$

where U is a function of ξ. Then Eq. (iii) takes the form

$$\frac{d^2U}{d\xi^2} - 2\xi\frac{dU}{d\xi} + \left[\frac{\alpha}{\beta} - 1\right]U = 0$$

If we replace $\frac{\alpha}{\beta} - 1$ by $2n$, this equation becomes Hermite differential equation. Then function $U(\xi)$ may be replaced with Hermite polynomial H. So, we get

$$\frac{d^2H}{d\xi^2} - 2\xi\frac{dH}{d\xi} + 2nH = 0$$

Thus, the solution of Eq. (iii) is obtained by replacing U by Hermite polynomial H in Eq. (iv). Hence, we get

$$\psi = CHe^{-\xi^2/2}$$

In general, $\psi_n(\xi) = CH_n(\xi)e^{-\xi^2/2}$, where $n = 0, 1, 2, \ldots$

Eigen Values of Energy

Since $\frac{\alpha}{\beta} - 1 = 2n$

$$\Rightarrow \quad \frac{\alpha}{\beta} = 2n + 1 \quad \Rightarrow \quad \alpha = (2n+1)\beta \quad \Rightarrow \quad \frac{8\pi^2 mE}{h^2} = (2n+1)\sqrt{\frac{4\pi^2 mk}{h^2}}$$

This restriction gives a corresponding restriction on E, i.e.,

$$E = \left(n + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{m}}$$

But $\frac{1}{2\pi}\sqrt{\frac{k}{m}} = \nu$ is the frequency of oscillations. Hence, the energy can be written in terms of ν as

$$E = \left(n + \frac{1}{2}\right)h\nu$$

Thus, in general, the oscillator has finite, unambiguous and continuous solutions at values of E given by

$$E_n = \left(n + \frac{1}{2}\right)h\nu \qquad \text{(v)}$$

Following conclusions can be drawn from equation (v)

The particle executing simple harmonic motion can have only

(i) discrete energy levels that are equidistant and are separated by $h\nu$, as shown in Fig. 16.8

(ii) The energy levels are non-degenerate.

(iii) For $n = 0$, $E_0 = \frac{1}{2}h\nu$. It means the minimum energy is not zero.

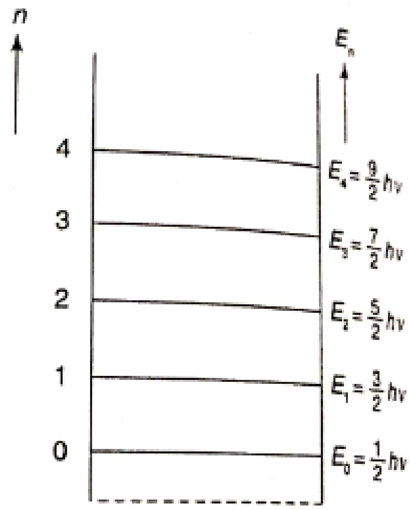

Figure 16.8

Solved Examples

Example 1 The position and momentum of a 1.0 keV electron are simultaneously measured. If the position is located within 1 Å, what is the percentage of uncertainty in momentum?

Solution Given $\Delta x = 1.0 \times 10^{-10}$ m and $E = 1000 \times 1.6 \times 10^{-19}$ J $= 1.6 \times 10^{-16}$ J.

Heisenberg's uncertainty principle says

$$\Delta x \Delta p = \frac{\hbar}{2} \quad \text{and} \quad p = \sqrt{2mE}$$

$$p = \sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-16}}$$

$$= 1.71 \times 10^{-23} \text{ kg m/sec}$$

and

$$\Delta p = \frac{\hbar}{2\Delta x} = \frac{h}{2 \times 2\pi \times \Delta x} = \frac{6.62 \times 10^{-34}}{2 \times 2 \times 3.14 \times 1.0 \times 10^{-10}}$$

$$= 5.27 \times 10^{-25} \text{ kmg/sec}$$

Percentage of uncertainty in momentum

$$= \frac{\Delta p}{p} \times 100 = \frac{5.27 \times 10^{-25}}{1.71 \times 10^{-23}} \times 100$$

$$= \mathbf{3.1\%}$$

Example 2 The uncertainty in the location of a particle is equal to its deBroglie wavelength. Calculate the uncertainty in its velocity.

Solution Given $\Delta x = \frac{h}{p}$.

$$\Delta x \Delta p = \frac{\hbar}{2} = \frac{h}{4\pi}$$

$$\Delta p = \Delta(mv) = \frac{h}{4\pi}\frac{1}{\Delta x} = \frac{h}{4\pi}\frac{p}{h} = \frac{mv}{4\pi}$$

$$m\Delta v = \frac{mv}{4\pi}$$

$$\Delta v = \frac{v}{4\pi}$$

Example 3 The position and momentum of 0.5 keV electron are simultaneously determined. If its position is located within 0.2 nm, what is the percentage uncertainty in its momentum?

Solution Given $E = 0.5\times10^{3}\times1.6\times10^{-19} = 0.8\times10^{-16}$ J and $\Delta x = 0.2\times10^{-9}$ m.

Now

$$\Delta x \Delta p = \frac{\hbar}{2} \text{ and momentum } p = \sqrt{2mE}$$

$$p = \sqrt{2\times9.1\times10^{-31}\times0.8\times10^{-16}} = 12.06\times10^{-24}$$

$$p = 1.21\times10^{-23}\ \text{kg m/sec}$$

$$\Delta p = \frac{\hbar}{2}\frac{1}{\Delta x} = \frac{h}{4\pi}\frac{1}{0.2\times10^{-9}}$$

$$\Delta p = \frac{6.62\times10^{-34}}{4\times3.14\times0.2\times10^{-9}} = 2.635\times10^{-25}\ \text{kg m/sec}$$

∴ Percentage uncertainty in momentum

$$\frac{\Delta p}{p}\times100 = \frac{2.635\times10^{-25}}{1.21\times10^{-23}}\times100$$

$$= \frac{2.635\times10^{-23}}{1.21\times10^{-23}} = \mathbf{2.18\%}$$

Example 4 Wavelengths can be determined with accuracies of one part in 10^6. What is the uncertainty in the position of a 1 Å X-ray photon when its wavelength is simultaneously measured?

Solution Given $\lambda = 10^{-10}$ m.

By uncertainty principle,

$$\Delta x \Delta p = \frac{\hbar}{2} = \frac{h}{4\pi}$$

and

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

By differentiating

$$p\Delta\lambda + \lambda\Delta p = 0$$

or

$$\Delta p = \frac{p\Delta\lambda}{\lambda} = \frac{h\Delta\lambda}{\lambda^2} \qquad \left[\because\ p = \frac{h}{\lambda}\right]$$

By using Eqs. (i) and (ii), we get

$$\Delta x \frac{h\Delta\lambda}{\lambda^2} = \frac{h}{4\pi}$$

or

$$\Delta x \Delta\lambda = \frac{\lambda^2}{4\pi}$$

Wavelength can be measured with accuracy of one part in 10^6, it means the uncertainty in wavelength is

$$\frac{\Delta\lambda}{\lambda} = \frac{1}{10^6} = 10^{-6}$$

By putting this value in Eq. (iii), then

$$\Delta x \frac{\Delta\lambda}{\lambda} = \frac{\lambda}{4\pi} \quad \text{or} \quad \Delta x \times 10^{-6} = \frac{\lambda}{4\pi}$$

or

$$\Delta x = \frac{10^6 \times \lambda}{4\pi} = \frac{10^6 \times 10^{-10}}{4 \times 3.14} = \mathbf{7.96\ \mu m}$$

Example 5 Calculate the uncertainty in measurement of momentum of an electron if the uncertainty in locating it is 1 Å.

Solution Given $\Delta x = 1.0 \times 10^{-10}$ m.

Formula used is

$$\Delta x \Delta p = \frac{\hbar}{2} = \frac{h}{4\pi}$$

$$\Delta p = \frac{h}{4\pi}\frac{1}{\Delta x} = \frac{6.62 \times 10^{-34}}{4 \times 3.14} \times \frac{1}{10^{-10}}$$

$$\Delta p = \mathbf{5.27 \times 10^{-25}\ kgm/sec}$$

Example 6 An electron has a momentum 5.4×10^{-26} kg m/sec with an accuracy of 0.05%. Find the minimum uncertainty in the location of the electron.

Solution Given $p = 5.4 \times 10^{-26}$ kg m/sec.

The uncertainty in the measurement of momentum

$$\Delta = \frac{5.4 \times 10^{-26} \times 0.05}{100}$$

$$= 2.7 \times 10^{-29} \text{ kg m/sec}$$

$$\Delta x \Delta p = \frac{\hbar}{2} = \frac{h}{4\pi}$$

$\therefore$

$$\Delta x = \frac{h}{4\pi}\frac{1}{\Delta p} = \frac{6.62 \times 10^{-34}}{4 \times 3.14} \times \frac{1}{2.7 \times 10^{-29}}$$

$$= 1.952 \times 10^{-6} \text{ m}$$

$$= \mathbf{1.952\ \mu m}$$

Example 7 A hydrogen atom is 0.53 Å in radius. Use uncertainty principle to estimate the minimum energy an electron can have in this atom.

Solution Given $\Delta x_{max} = 0.53$ Å

Heisenberg's uncertainty principle

$$\Delta x \Delta p = \frac{\hbar}{2} = \frac{h}{4\pi}$$

$$(\Delta x)_{max}(\Delta p)_{min} = \frac{h}{4\pi} \quad \text{(i)}$$

$$(\text{K.E.})_{min} = \frac{p_{min}^2}{2m} = \frac{(\Delta p)_{min}^2}{2m} \quad [\because p_{min} = \Delta p_{min}]$$

and

$$(\Delta p)_{min} = \frac{h}{4\pi}\frac{1}{\Delta x} = \frac{6.62 \times 10^{-34}}{4 \times 3.14}\frac{1}{0.53 \times 10^{-10}}$$

$$= 0.9945 \times 10^{-24}$$

$$= 9.945 \times 10^{-25} \text{ kg m/sec}$$

and

$$(\text{K.E.})_{min} = \frac{(\Delta p)_{min}^2}{2m} = \frac{(9.945 \times 10^{-25})^2}{2 \times 9.1 \times 10^{-31}}$$

$$= \mathbf{5.434 \times 10^{-19}\ J}$$

Example 8 The speed of an electron is measured to be 5.0×10^3 m/sec to an accuracy of 0.003%. Find the uncertainty in determining the position of this electron.

Solution Given $v = 5.0 \times 10^3$ m/sec.

Formula used is

$$\Delta x \Delta p = \frac{\hbar}{2} = \frac{h}{4\pi}$$

$$\Delta v = v \times \frac{0.003}{100} = 5.0 \times 10^3 \times \frac{0.003}{100} = 0.15 \text{ m/sec}$$

$$\Delta p = m\Delta v = 9.1 \times 10^{-31} \times 0.15 = 1.365 \times 10^{-31} \text{ kg m/sec}$$

and

$$\Delta x = \frac{6.62 \times 10^{-34}}{4 \times 3.14}\frac{1}{\Delta p} = \frac{6.62 \times 10^{-34}}{4 \times 3.14}\frac{1}{1.365 \times 10^{-31}}$$

$$= \mathbf{3.861 \times 10^{-4}\ m}$$

Example 9 An electron has speed of 6.6×10^4 m/sec with an accuracy of 0.01%. Calculate the uncertainty in position of an electron. Given mass of an electron as 9.1×10^{-31} kg and Planck's constant h as 6.6×10^{-34} J sec.

Solution Given $v = 6.6 \times 10^4$ m/sec and $\Delta v = 6.6 \times 10^4 \times \frac{0.01}{100}$ m/sec

$$= 6.6 \text{ m/sec.}$$

Formula used is

$$\Delta x \Delta p = \frac{\hbar}{2} = \frac{h}{4\pi} \quad \text{or} \quad \Delta x = \frac{h}{4\pi}\frac{1}{\Delta p}$$

$$\Delta p = m\Delta v = 9.1 \times 10^{-31} \times 6.6$$

or

$$\Delta x = \frac{h}{4\pi}\frac{1}{\Delta p} = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 6.6}$$

$$\Delta x = \mathbf{8.75 \times 10^{-6}\ m}$$

Example 10 Calculate the smallest possible uncertainty in the position of an electron moving with a velocity 3×10^7 m/sec.

Solution Given $v = 3 \times 10^7$ m/sec

Formula used is

$$\Delta x \Delta p = \frac{\hbar}{2} = \frac{h}{4\pi}$$

$$\Delta p_{max} = p = mv = \frac{m_0 v}{\sqrt{1 - v^2/c^2}}$$

$$\Delta x = \frac{h}{4\pi}\frac{1}{\Delta p} = \frac{h}{4\pi}\left[\frac{\sqrt{1 - v^2/c^2}}{m_0 v}\right]$$

$$= \frac{6.62 \times 10^{-34}}{4 \times 3.14}\left[\frac{\sqrt{1 - \left(\frac{3 \times 10^7}{3 \times 10^8}\right)^2}}{9.1 \times 10^{-31} \times 3 \times 10^7}\right]$$

$$= \mathbf{1.92 \times 10^{-12}\ m}$$

Example 11 If an excited state of hydrogen atom has a life-time of 2.5×10^{-14} sec, what is the minimum error with which the energy of this state can be measured? Given $h = 6.62 \times 10^{-34}$ J sec.

Solution Given $\Delta t = 2.5 \times 10^{-14}$ sec.

Formula used is

$$\Delta E \Delta t = \frac{\hbar}{2} = \frac{h}{4\pi}$$

$$\Delta E = \frac{h}{4\pi}\frac{1}{\Delta t} = \frac{6.62 \times 10^{-34}}{4 \times 3.14} \times \frac{1}{2.5 \times 10^{-14}} = 0.211 \times 10^{-20}\ \text{J}$$

$$\Delta E = \mathbf{2.11 \times 10^{-21}\ J}$$

Example 12 An excited atom has an average life-time of 10^{-8} sec. During this time period it emits a photon and returns to the ground state. What is the minimum uncertainty in the frequency of this photon?

Solution Given $\Delta t = 10^{-8}$ sec.

Formula used is

$$\Delta E \Delta t = \frac{\hbar}{2} = \frac{h}{4\pi}$$

As $E = h\nu$ or $\Delta E = \Delta(h\nu) = h\Delta\nu$

or $$h\Delta\nu\Delta t = \frac{h}{4\pi} \quad \text{or} \quad \Delta\nu\Delta t = \frac{1}{4\pi}$$

or $$\Delta\nu = \frac{1}{4\pi}\frac{1}{\Delta t} = \frac{1}{4 \times 3.14} \times \frac{1}{10^{-8}}$$

$$\Delta\nu = \mathbf{7.96 \times 10^6\ sec}$$

Example 13 Compare the uncertainties in velocity of a proton and an electron contained in a 20 Å box.

Solution Given $\Delta x = 2.0 \times 10^{-9}$ m.

Formula used is

$$\Delta p \Delta x = \frac{\hbar}{2} = \frac{h}{4\pi} \quad \text{or} \quad \Delta p = \frac{h}{4\pi\Delta x}$$

As uncertainty in momentum for electron and proton does not depend upon mass, we have

$$\Delta p = \Delta(mv) = m\Delta v \quad \text{or} \quad \Delta v = \frac{\Delta p}{m}$$

As $\Delta p_p = \Delta p_e$

$$\Delta v_p = \frac{\Delta p_p}{m_p}$$

$$\Delta v_e = \frac{\Delta p_e}{m_e}$$

and

$$\frac{\Delta v_p}{\Delta v_e} = \frac{\Delta p_p}{\Delta p_e}\frac{m_e}{m_p} = \frac{m_e}{m_p} \qquad [\because \Delta p_p = \Delta p_e]$$

$$= \frac{9.1 \times 10^{-31}}{1.67 \times 10^{-27}} = \mathbf{5.45 \times 10^{-4}}$$

Example 14 Find the energy of an electron moving in one dimension in an infinitely high potential box of width 1.0 Å. Given $m = 9.1 \times 10^{-31}$ kg and $h = 6.62 \times 10^{-34}$ J sec.

Solution Given $l = 1.0 \times 10^{-10}$ m, $m = 9.1 \times 10^{-31}$ kg and $h = 6.62 \times 10^{-34}$ J sec.

Formula used is

$$E_n = \frac{n^2h^2}{8mL^2}$$

$$= \frac{n^2(6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (1.0 \times 10^{-10})^2}$$

$$= 0.602 \times 10^{-17} n^2\ \text{J}$$

for $n = 1$, $$E_1 = 6.02 \times 10^{-18}\ \text{J}$$

and for $n = 2$, $$E_2 = 6.02 \times 10^{-18} \times 4\ \text{J}$$
$$= 2.408 \times 10^{-17}\ \text{J}$$
$$= \mathbf{2.41 \times 10^{-17}\ J}$$

Example 15 Calculate the energy difference between the ground state and the first excited state for an electron in a box of length 1.0 Å.

Solution Given $L = 1.0 \times 10^{-10}$ m.

Formula used is

$$E_n = \frac{n^2h^2}{8mL^2}$$

Put $n = 1$ for ground state and $n = 2$ for first excited state

$$E_2 - E_1 = \frac{h^2}{8mL^2}[2^2 - 1^2] = \frac{(6.62 \times 10^{-34})^2 \times 3}{8 \times 9.1 \times 10^{-31} \times (1.0 \times 10^{-10})^2}$$

$$= \mathbf{1.81 \times 10^{-17}\,J}$$

Example 16 Compute the energy of the lowest three levels for an electron in a square well of width 3 Å.

Solution Given $L = 3 \times 10^{-10}$ m.

Formula used is

$$E_n = \frac{n^2h^2}{8mL^2}$$

Put $n = 1, 2, 3$ for first three levels, then

$$E_1 = \frac{h^2}{8mL^2} = \frac{(6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (3 \times 10^{-10})^2}$$

$$= 6.688 \times 10^{-19}\,J$$

$$= \mathbf{6.7 \times 10^{-19}\,J}$$

$$E_2 = 4E_1 = \mathbf{2.68 \times 10^{-18}\,J} \quad \text{and}$$

$$E_3 = 9E_1 = \mathbf{6.03 \times 10^{-18}\,J}$$

Example 17 An electron is bound in one-dimensional potential box which has a width 2.5×10^{-10} m. Assuming the height of the box to be infinite, calculate the lowest two permitted energy values of the electron.

Solution Given $L = 2.5 \times 10^{-10}$ m.

Formula used is

$$E_n = \frac{n^2h^2}{8mL^2}$$

For lowest two permitted energy values of electrons, put $n = 1$ and 2. Then

for $n = 1$,

$$E_1 = \frac{h^2}{8mL^2} = \frac{(6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (2.5 \times 10^{-10})^2}$$

$$= \mathbf{9.63 \times 10^{-19}\,J}$$

for $n = 2$,

and

$$E_2 = \frac{(2)^2 \times (6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (2.5 \times 10^{-10})^2}$$

$$= \mathbf{3.853 \times 10^{-18}\,J}$$

Properties of wave function

① ψ should be well behaved.

· ψ must be single valued & continuous everyone.

② Differentiation of ψ $\left(\frac{d\psi}{dx}, \frac{d\psi}{dy}, \frac{d\psi}{dz}\right)$ must also be continuous & single valued everywhere and finite.

③ ψ must be normalized

has 2 condition

(i) $\psi \rightarrow 0$ when $x = \pm\infty, y = \pm\infty, z = \pm\infty$

*(ii) $\int_{-\infty}^{\infty} \psi \psi^* dV = 1$

Postulates of Quantum Mechanics

① Wave function - Explained above

② Operators - To every physical quantity there exist a corresponding operator in Quantum Mechanics with the help of which physical quantity can be extracted from wave function.

Physical Quantity	Symbol	Operator
① Coordinates	x, y, z, t	x, y, z, t
② Functions ~~of~~ coordinate	$f(x, y, z)$	$f(x, y, z)$
③ Momentum	P_x, P_y, P_z	$-i\hbar \frac{d}{dx}$, $-i\hbar \frac{d}{dy}$, $-i\hbar \frac{d}{dz}$

	$\vec{P} = \hat{i}P_x + \hat{j}P_y + \hat{k}P_z$	$-i\hbar\vec{\nabla}$ $\vec{\nabla}$ = inverse of delta known as laplacian operator $\nabla = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$
(4) Energy	E	$i\hbar\frac{d}{dt}$
(5) P.E. (Potential energy)	$V(r)$	$V(r)$
(6) K.E. (Kinetic energy)	$\frac{P^2}{2m}$	$\frac{-\hbar^2}{2m}\left[\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right]$

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③ Eigen Value Equation

$$(A-\lambda I)X = 0$$
$$(A-\lambda)X = 0$$
$$AX = \lambda X$$

Eigen value equation is used to calculate the observables or physical quantity corresponding whose operators acts on the wave function giving eigen value as operator. If $\hat{A}$ be the operator corresponding to observable A then the observable can be calculated as

$$\hat{A}\psi = A\psi$$

where A is the information or physical quantity
$\hat{A}$ is the operator which is operating on ψ in LHS
∴ we can't cancel ψ from both sides.

④ Expectation value or Average value

If a system in a state is represented by wave function ψ, the average or expected value of observable whose operator is $\hat{A}$ is calculated as Denoted by $\langle A \rangle$

$$\langle A \rangle = \frac{\int_{-\infty}^{\infty} \psi^* \hat{A} \psi \, dr}{\int_{-\infty}^{\infty} \psi \psi^* \, dr}$$

$\int_{-\infty}^{\infty} \psi \psi^* \, dr$ is Normalisation condition

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⑤ Time development Quantum system

The wave function $\psi(r,t)$ of a system evolves in time according to time dependent Schrodinger equation.

$$i\hbar \frac{\partial}{\partial t} \psi(r,t) = H\psi(r,t)$$

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

where H = Hamiltonian operator which is independent of time.

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Schrodinger time independent Wave Equation

Consider a particle of mass m moving with velocity v. If ψ be wave function of the wave associated with particle then the wave must satisfy the classical wave equation.

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=\frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2} \quad -(1)$$

$$\vec{\nabla}=\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}$$

Squaring both sides

$$\nabla^2=\left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)\left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$$

$$\hat{i}\cdot\hat{i}=\hat{j}\cdot\hat{j}=\hat{k}\cdot\hat{k}=1$$
$$\hat{i}\cdot\hat{j}=\hat{j}\cdot\hat{k}=\hat{k}\cdot\hat{i}=0$$

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

$$\nabla^2\psi=\frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2} \quad -(2)$$

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$$\psi = A e^{i(kr - \omega t)}$$ Solution of wave

$$\psi = \psi_0(r)\, e^{-i\omega t} \quad -③$$

where $\psi_0(r) = \psi_0 = A e^{ikr}$ (independent of time)

$\psi_0(r)$ is time independent or space dependent part of solution.

If eq. ③ is the solution of wave, then it should satisfy eq. ②

Diff eq. ③ w.r.t. t

$$\frac{\partial \psi}{\partial t} = -i\omega \psi_0 e^{-i\omega t}$$

Diff again w.r.t. t

$$\frac{\partial^2 \psi}{\partial t^2} = i^2 \omega^2 \psi_0 e^{-i\omega t}$$

$i^2 = -1$ $\qquad$ $\psi_0 e^{-i\omega t} = \psi$

$$\boxed{\frac{\partial^2 \psi}{\partial t^2} = -\omega^2 \psi} \quad -④$$

Substitute eq. ④ in eq. ②

$$\nabla^2 \psi = \frac{1}{v^2}(-\omega^2 \psi)$$

$$\left(\frac{\omega}{v}\right)^2 = \left(\frac{2\pi\nu}{v}\right)^2 = \left(\frac{2\pi}{\lambda}\right)^2 = \frac{4\pi^2}{\lambda^2} \qquad \left(\frac{\nu}{v} = \frac{1}{\lambda}\right)$$

$$\boxed{\nabla^2 \psi = -\frac{4\pi^2}{\lambda^2}\psi} \quad -⑤$$

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where λ is de broglie wavelength

$$\lambda = \frac{h}{mv} \qquad \lambda^2 = \frac{h^2}{m^2v^2}$$

&

$$\nabla^2\psi = -4\pi^2 \frac{m^2v^2}{h^2}\psi$$

$$\hbar = \frac{h}{2\pi} \Rightarrow \hbar^2 = \frac{h^2}{4\pi^2} \Rightarrow \frac{1}{\hbar^2} = \frac{4\pi^2}{h^2}$$

$$\boxed{\nabla^2\psi = \frac{-m^2v^2}{\hbar^2}\psi} \quad — ⑦$$

If V be the potential energy of the particle then the total energy is given by

$$E = KE + PE = KE + V(r)$$

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

$$mv^2 = 2(E - V) \qquad E = \text{Total energy}$$

Multiply both sides by m

$$\boxed{m^2v^2 = 2m(E - V)} \quad — ⑧$$

Substitute eq. ⑧ in eq. ⑦

$$\boxed{\nabla^2\psi = \frac{-2m(E-V)}{\hbar^2}\psi} \leftarrow \text{Schroodinger Eq.}$$

or $$\boxed{\frac{-\hbar^2}{2m}\nabla^2\psi = (E-V)\psi} \quad -(9)$$

If particle is free $\Rightarrow V=0$

$\Rightarrow$ Schrodinger Eq. is

$$\boxed{\frac{-\hbar^2}{2m}\nabla^2\psi = E\psi}$$

This is time independent eq.

Time dependent Schrodinger Wave Equation

Upto eq. 9 we will do the same

Consider a particle of mass m moving with velocit v. If ψ be the wave function of the wave associated with particle then the wave must satisfy the classical wave equation.

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=\frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2} \quad -(1)$$

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

where $\vec{\nabla}=\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}$

$$\boxed{\nabla^2 \psi = \frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2}} \quad - (2)$$

$$\psi = A e^{i(kr - \omega t)}$$

$$\psi(r, t) = \psi_0(r) e^{-i\omega t} \quad - (3)$$

where $\psi_0(r) = \psi_0 = A e^{ikr}$

$\psi_0(r)$ is space dependent part of solution

Diff eq. (3) wrt t

$$\frac{\partial \psi}{\partial t} = -i\omega \psi_0 e^{-i\omega t}$$

Diff again wrt t

$$\frac{\partial^2 \psi}{\partial t^2} = i^2 \omega^2 \psi_0 e^{-i\omega t} = -\omega^2 \psi \quad - (4)$$

Substitute eq. (4) in eq. (2)

$$\nabla^2 \psi = \frac{1}{v^2}\left(-\omega^2 \psi\right)$$

$$\left(\frac{\omega}{v}\right)^2 = \left(\frac{2\pi\nu}{v}\right)^2 = \left(\frac{2\pi}{\lambda}\right)^2 = \frac{4\pi^2}{\lambda^2}$$

$$\boxed{\nabla^2 \psi = -\frac{4\pi^2}{\lambda^2} \psi} \quad - (5)$$

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where λ is de broglie wavelength

$$\lambda = \frac{h}{mv} \qquad \lambda^2 = \frac{h^2}{m^2v^2} \quad -(6)$$

Use eq. (6) in eq. (5)

$$\nabla^2 \psi = -\frac{4\pi^2 m^2v^2}{h^2} \psi$$

$$\hbar = \frac{h}{2\pi} \Rightarrow \hbar^2 = \frac{h^2}{4\pi^2} \Rightarrow \frac{1}{\hbar^2} = \frac{4\pi^2}{h^2}$$

$$\boxed{\nabla^2 \psi = -\frac{m^2v^2}{\hbar^2} \psi} \quad -(7)$$

If V be the potential energy of the particle then the total energy is given by

$$E = KE + V(r) = \frac{1}{2}mv^2 + V$$

$$mv^2 = 2(E - V)$$

Multiply both sides by m

$$\boxed{m^2v^2 = 2m(E - V)} \quad -(8)$$

Substitute eq. (8) in (7)

$$\boxed{\nabla^2 \psi = -\frac{2m(E-V)}{\hbar^2} \psi} \leftarrow \text{Schrodinger Eq.}$$

or $$\boxed{\frac{\hbar^2}{2m}\nabla^2\psi = (E-V)\psi} \quad -(9)$$

$$\boxed{\frac{\hbar^2}{2m}\nabla^2\psi = E\psi - V\psi} \quad -(10)$$

$$\psi = \psi_0 e^{-i\omega t}$$

Diff w.r.t t

$$\frac{\partial\psi}{\partial t} = -i\omega\psi_0 e^{-i\omega t} = -i\omega\psi$$

$$\frac{\partial\psi}{\partial t} = -i2\pi\nu\psi$$

Multiply both sides by h

$$h\frac{\partial\psi}{\partial t} = -i2\pi h\nu\psi$$

$E = h\nu$ = Energy of photon

$$h\frac{\partial\psi}{\partial t} = -i2\pi E\psi$$

Multiply both sides by iota (i)

$$i\frac{h}{2\pi}\frac{\partial\psi}{\partial t} = -i^2 E\psi$$

$$i\hbar\frac{\partial\psi}{\partial t} = E\psi \qquad \hbar = \frac{h}{2\pi}$$

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

$$\boxed{E = i\hbar\frac{\partial}{\partial t}} \quad -(11)$$

Substitute eq. 11 in 10

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

$$\boxed{\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t}}$$ Time dependent Schrodinger eq.

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V\right]\psi = i\hbar\frac{\partial}{\partial t}\psi$$

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V$$ = Hamiltonian Operator

$$\boxed{\hat{H}\psi = i\hbar\frac{\partial}{\partial t}\psi}$$

Easy Method (Just for Remembering)

$$\hat{H}\psi = E\psi$$

$$\hat{H} = KE + PE$$

$$KE = \frac{p^2}{2m}$$ $$PE = V(r) = V$$

$$p = -i\hbar\vec{\nabla}$$ $$p^2 = -\hbar^2\nabla^2$$

$$KE = \frac{-\hbar^2}{2m}\nabla^2$$

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$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V$$

$$\boxed{\left(\frac{-\hbar^2}{2m}\nabla^2 + V\right)\psi = \cancel{i\hbar\frac{\partial}{\partial t}}E\psi}$$ Time independent Schrodinger eq.

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

$$\boxed{\left(\frac{-\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\frac{\partial}{\partial t}\psi}$$ Time dependent Schrodinger eq.