Quantum Mechanics

Prerequisite:

Concepts from Dual nature of radiation and matter (12^{th})

de Broglie Hypothesis:

- Just like radiation, matter also possesses wave as well as particle nature.
- Matter exhibit wave nature in some instances and particle nature in another instances. Particle and wave nature are not exhibited at a same time.
- The waves associated with moving microscopic particles are called as de Broglie's waves or Matter waves.
- The de Broglie's wavelength is given by

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

Conclusions from de Broglie's equations:

1) $\lambda \rightarrow \infty$ when the velocity of the particle is zero. It means that matter waves are detectable only for moving particles.
2) Lighter the particle, smaller the value of mass m and hence the longer is the wavelength of the matter wave associated with it. Therefore, wave behavior of micro-particles will be significant whereas waves associated with macro-bodies can never be detected.
3) The smaller the velocity of the micro-particle, the longer is the wavelength of the matter wave associated with it.

Derivation of de Broglie's equation:

The energy of mass less particle like photon is given by

$$E = mc^2 = mc \times c = pc \qquad (1)$$

By Planck's quantum theory, the energy of the photon is given by

$$E = h\nu \qquad (2)$$

From equation (1) and (2), we can write

$$pc = h\nu$$

$$p = \frac{h\nu}{c} \qquad (3)$$

But,

$$c/\nu = \lambda$$

Putting this in equation (3), we get

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

$$\lambda = \frac{h}{p} \qquad (4)$$

For material particle, p = mv hence equation (4) becomes

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

de Broglie's wavelength in terms of Kinetic Energy E:

The kinetic energy of the free particle is given by

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

Multiplying and dividing RHS by mass m, we get

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

$$p = \sqrt{2mE}$$

Putting this in equation (4), we get

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

de Broglie's wavelength in terms of potential difference:

When particle such as electron is accelerated through Potential Difference V, its kinetic energy is given by

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

$$\frac{m^2v^2}{2m} = \frac{p^2}{2m} = eV$$

$$p = \sqrt{2meV}$$

Putting this in equation (4), we get

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

For an electron,

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

$$\lambda = \frac{12.27}{\sqrt{V}}\ \text{Å}$$

De Broglie wavelength associated with particles in thermal equilibrium:

If particles are in thermal equilibrium at temperature T, then their kinetic energy is given by

$$\frac{1}{2}\,mv^2 = \frac{3}{2}kT$$

$$\frac{m^2v^2}{2m} = \frac{p^2}{2m} = \frac{3}{2}kT$$

$$p = \sqrt{3mkT}$$

Putting this in equation (4), we get

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

Concept of Phase and Group Velocity:

Phase Velocity / Wave velocity:

Definition:

The velocity with which a particular phase of the wave propagates in the medium is called phase velocity.

The equation of a wave travelling in +X axis direction s given by

$$y = A\sin(\omega t - kx)$$

Here, ω is angular frequency and k is propagation constant.

The phase velocity v_p is given by

$$v_p = \nu\lambda$$

$$v_p = 2\pi\nu \times \frac{\lambda}{2\pi}$$

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

Where, $\omega = 2\pi\nu$ and $k = \frac{2\pi}{\lambda}$

Show that phase velocity is greater than the velocity of light.

The phase velocity of a wave is given by

$$v_p = \nu\lambda \qquad (1)$$

Using Planck's quantum theory, we can write

$$E = h\nu$$

$$\nu = \frac{E}{h} \qquad (2)$$

And using de Broglie's equation, we can write

$$\lambda = \frac{h}{p} \qquad (3)$$

Substituting equations 2 and 3 in 1, we get

$$v_p = \nu\lambda = \frac{E}{h} \times \frac{h}{p} = \frac{E}{p} \qquad (4)$$

Using Einstein's mass energy relation $E = m\,c^2$ in equation (4), we get

$$v_p = \frac{m\,c^2}{p} \qquad (5)$$

When the atomic particle velocity is non-relativistic, the total energy $E = mc^2$ and momentum $p = mv$.

$$v_p = \frac{m\,c^2}{mv} = \frac{c^2}{v}$$

$$v_p = \left(\frac{c}{v}\right)c \qquad (6)$$

As the particle velocity is always less than velocity of light, $\frac{c}{v} > 1$and hence we can write

$$v_p > c$$

When the atomic particle velocity is relativistic.

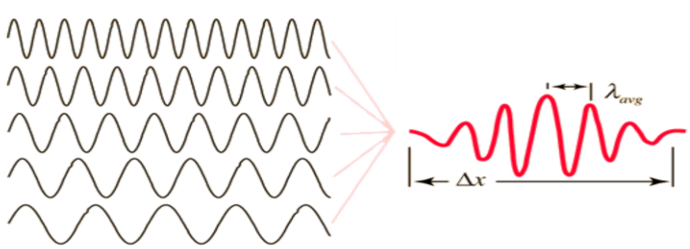
$$\upsilon_p = \frac{E}{p} = \left[\frac{m_o^2c^4 + p^2c^2}{p^2}\right]^{1/2}$$

$$= c\left[\frac{m_o^2c^2}{p^2} + 1\right]^{1/2} = c\left[\frac{m_o^2c^2\lambda^2}{h^2} + 1\right]^{1/2}$$

Group Velocity:

Wave packet/ wave group:

- A wave packet consists of a group of harmonic waves with slightly different wavelengths.
- These harmonic waves superimpose to give a wave packet as shown in following figure.



Definition of Group velocity:

The velocity with which the wave packet propagates through the medium is called group velocity.

Expression for the Group Velocity:

Let us consider two harmonic waves with slightly different wavelengths. The displacement of the first wave is given by

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

$$y_2 = A\sin[(\omega + d\omega)t - (k + dk)x]$$

The superposition of these two waves is given by

$$y = y_1 + y_2$$

$$y = A\sin(\omega t - kx) + A\sin[(\omega + d\omega)t - (k + dk)x]$$

Using $\sin C + \sin D = 2\sin\frac{C+D}{2}\cos\frac{C-D}{2}$, we get

$$y = 2A\sin\left(\frac{2\omega + d\omega}{2}\,t - \frac{2k + dk}{2}x\right)\cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right)$$

As dw and dk are very small compared to w and k, we can write

$$2\omega + d\omega = 2\omega$$

$$2k + dk = 2k$$

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

The sin term in his equation represents a wave with angular frequency w and propagation constant k.

The cosine term modulates this wave with angular frequency dw/2 and propagation constant dk/2 to produce wave groups.

The velocity of the wave groups is given by

$$v_g = \frac{d\omega}{dk} \qquad (1)$$

This velocity is known as group velocity.

We know that

$$\omega = 2\pi\nu$$

And

$$k = 2\pi/\lambda$$

Putting these in equation ,1 we get

$$v_g = \frac{d(2\pi\nu)}{d(2\pi/\lambda)}$$

$$v_g = \frac{2\pi d(\nu)}{2\pi\, d(1/\lambda)}$$

$$v_g = -\lambda^2\frac{d\nu}{d\lambda}$$

Show that the particle velocity is equal to the group velocity in matter waves.

The group velocity of the matter waves is given by

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

This equation can be written as

$$v_g = \frac{d\omega}{dE} \times \frac{dE}{dp} \times \frac{dp}{dk} \qquad (1)$$

We know that

$$\omega = 2\pi\nu$$

$$\omega = 2\pi\left(\frac{E}{h}\right) = \frac{E}{\hbar} \qquad (2)$$

Where $\nu = E/h$ and $\hbar = h/2\pi$

Differentiating equation 2 w.r.t. E , we get

$$\frac{d\omega}{dE} = \frac{1}{\hbar} \qquad (3)$$

Using de Brogli's equation, we can write

$$p = \frac{h}{\lambda} \qquad (4)$$

but

$$k = \frac{2\pi}{\lambda} \quad \rightarrow \lambda = \frac{2\pi}{k}$$

Putting value of λ in equation (4), we get

$$p = \frac{h}{2\pi} k = \hbar k \qquad (5)$$

Differentiating equation 5 w.r.t. k , we get

$$\frac{dp}{dk} = \hbar \qquad (6)$$

Putting equations (3) and (6) in (1), we get

$$v_g = \frac{1}{\hbar} \times \frac{dE}{dp} \times \hbar$$

i.e.

$$v_g = \frac{dE}{dp} \qquad (7)$$

For a particle,

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

And

$$\frac{dE}{dp} = \frac{d\left(\frac{p^2}{2m}\right)}{dp} = \frac{2p}{2m} = \frac{p}{m} \qquad (8)$$

Substituting equation 8 in 7, we get

$$v_g = \frac{dE}{dp} = \frac{p}{m} = \frac{mv}{m}$$

$$v_g = v$$

Relation between phase velocity and group velocity

The velocity of the individual component wave of the wave packet is given by

$$v_p = \nu\lambda$$

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

$$\omega = k\,v_p \qquad (1)$$

The group velocity is given by

$$v_g = \frac{d\omega}{dk} \qquad (2)$$

Putting equation 1 in 2 , we get

$$v_g = \frac{d(k\,v_p)}{dk}$$

$$v_g = v_p + k\frac{d\,v_p}{dk} \qquad (3)$$

But

$$k = \frac{2\pi}{\lambda} \qquad (4)$$

And

$$dk = -\lambda^{-2}\,2\pi\,d\lambda \qquad (5)$$

Putting 4 and 5 in 3, we get

$$v_g = v_p + \frac{2\pi}{\lambda}\frac{d\,v_p}{-\lambda^{-2}\,2\pi\,d\lambda}$$

$$v_g = v_p - \left(\frac{2\pi}{\lambda} \times \frac{d\,v_p}{-\lambda^{-2}\,2\pi\,d\lambda}\right)$$

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

Properties of matter waves:

- Matter waves are produced by the motion of the particles and are independent of the charge. Therefore, they are neither electromagnetic nor acoustic waves but are new kind of waves.
- They can travel through vacuum and do not require any material medium for their propagation.
- The smaller the velocity of the particle, the longer is the wavelength of the matter wave associated with it.

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

- The lighter the particle, the longer is the wavelength of the matter wave associated with it.
- The velocity of matter waves depends on the velocity of the material particle and is not a constant quantity.
- The velocity of matter waves is greater than the velocity of light.

$$v_p = \frac{c^2}{v}$$

- They exhibit diffraction phenomenon as any other waves.
- The wave and particle properties are not exhibited simultaneously.

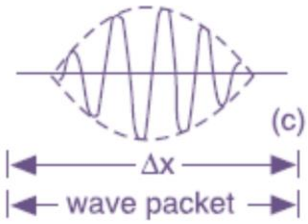
Heisenberg uncertainty principle:

Statement:

"It is not possible to know simultaneously and with exactness both the position and the momentum of a microparticle".

$$\boldsymbol{\Delta x\,\Delta p \geq \frac{\hbar}{2}}$$

Explanation:



- Schrödinger postulated that a moving microparticle is equivalent to a wave packet. A wave packet spreads over a region of space. Therefore, it is difficult to locate the exact position of the microparticle.
- Although the particle is somewhere within the wave packet, it is impossible to know where exactly the particle is at a given instant.
- If the linear spread of the wave packet is Δx, the particle would be located somewhere within the region Δx.
- The probability of finding the particle is a maximum at the centre of the wave packet and falls off to zero at its ends. Therefore, there is an **uncertainty** Δx in the position of the particle. As a result, the momentum of the particle at that instant cannot be determined precisely.
- It means that the location and momentum of a microparticle cannot be **simultaneously** determined with certainty. Any attempt to determine these variables will lead to uncertainties in each of the variables.

Heisenberg uncertainty principle applied to angular momentum and angular position:

We know that angular position is given by

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

And angular momentum is given by

$$\Delta L = r\Delta p$$

Substituting these values in Heisenberg's equation, we get

$$\boldsymbol{\Delta\theta\ \Delta L \geq \frac{\hbar}{2}}$$

Heisenberg uncertainty principle applied to energy and time:

The kinetic energy of a particle can be written as

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

The uncertainty in energy is given by

$$\Delta E = \frac{1}{2} m\ 2v\ \Delta v$$

$$\Delta E = v\ (m\ \ \Delta v)$$

$$\Delta E = v\Delta p \qquad (1)$$

But,

$$v = \frac{\Delta x}{\Delta t} \qquad (2)$$

Putting equation (2) in (1), we get

$$\Delta E = \frac{\Delta x}{\Delta t} \Delta p$$

$$\Delta E\ \Delta t = \Delta x\ \Delta p$$

But according to Heisenberg's uncertainty principle,

$$\Delta E\ \Delta t = \Delta x\ \Delta p\ \geq\ \hbar/2$$

Hence, we can write

$$\mathbf{\Delta E\ \Delta t \geq\ \hbar/2}$$

Prove that electrons cannot be present in the nucleus:

- The radiation emitted by radioactive nuclei consists of alpha, beta and gamma-rays, out of which beta-rays are identified to be electrons.
- We apply uncertainty principle to find whether electrons are coming out of the nucleus.

Proof:

The radius of the nucleus is of the order of 10^{-14} m. Therefore, if electrons were to be in the nucleus, the maximum uncertainty Δx in the position of the electron is equal to the diameter of the nucleus

$$\Delta x = 2\ \times \text{radius of nucleus}$$

$$\Delta x = 2\ \times\ 10^{-14}$$

The minimum uncertainty in momentum is given by

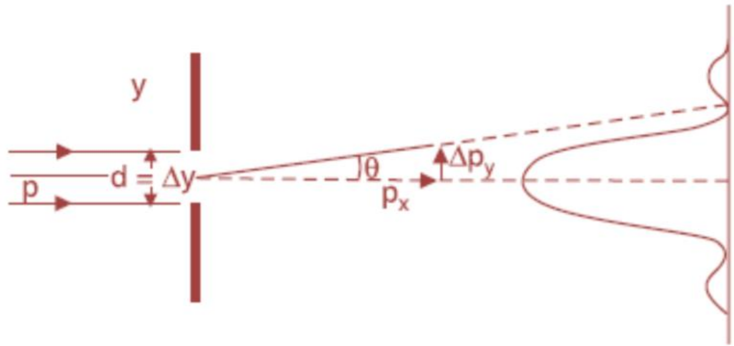
$$\Delta p = \frac{\hbar}{\Delta x} = \frac{1.04 \times 10^{-34}\ J.s}{2 \times 10^{-14}\ m} = 5.2 \times 10^{-21}\ \text{kg-m/s}.$$

The minimum energy of the electron in the nucleus is then given by

$$E_{min} = p_{min}\, c = (5.2 \times 10^{-21}\ \text{kg-m/s})(3 \times 10^{8}\ \text{m/s}) = 1.56 \times 10^{-12}\ \text{J} = 9.7\ \text{MeV}.$$

If an electron exists within the nucleus, it must have a minimum energy of about 10 MeV. But the experimental measurements showed that the maximum kinetic energies of b-particles were of the order of 4 MeV only. Hence electrons are not present in the nucleus.

Thought Experiment: Treating electron as a wave:



- We assume that an electron has wave character.
- When beam of electrons is incident on slit the diffraction pattern is formed on the screen as shown in above figure.
- It is not known that from which position of slit electron is coming out. Hence, the uncertainty in the position along y axis is $d = \Delta y$

Let

θ = diffraction angle

d= Δy = slit width or uncertainty in the position of an electron along y direction

Δp_y= uncertainty in the momentum of an electron along y direction when it leaves slit

p_x= momentum of an electron along x direction

According to the theory of diffraction at a single slit, the angle θ and uncertainty in position Δy is given by

$$\sin\theta = \frac{\lambda}{d}$$

$$sin\,\theta = \frac{\lambda}{\Delta y} \qquad (1)$$

$$\Delta y = \frac{\lambda}{\sin\theta}$$

The uncertainty in the momentum of the electron parallel to *y*-axis is given by

$$\Delta p_y = p\sin\theta \qquad (2)$$

According to de Broglie's equation and from equation (1), equation 2 can be written as

$$\Delta p_y = \frac{h}{\lambda} \times \frac{\lambda}{\Delta y}$$

$$\Delta y \, \Delta p_y \approx h$$

$$\Delta y \, \Delta p_y \geq h$$

Question: Prove Heisenberg's uncertainty principle treating electron as a wave. [4M]

Concept of wave function:

- Waves represent the propagation of a disturbance in a medium.
- The quantity whose periodic vibrations make up matter waves is denoted by mathematical function $\psi(x, y, z, t)$ and $\psi(x, y, z, t)$ is called as wave function.
- ψ describes the wave as a function of position and time. However, it has no direct physical significance, as it is not an observable quantity. Ψ is a complex-valued function.
- According to Heisenberg uncertainty principle, we can only know the probable value in a measurement. The probability cannot be negative. Hence ψ cannot be a measure of the presence of the particle at the location (x, y, z). But it is certain that it is in some way an index of the presence of the particle at around (x, y, z, t).

Physical Significance of wave function ψ / Probability Interpretation of Wave Function given by Max Born:

- Ψ is a complex-valued function.
- Although it contains all the information regarding position of particle at a particular time, we cannot extract that information directly because of complex nature of ψ. Hence, ψ has no direct physical significance.
- However, if we convert ψ in real number we can extract information from it.
- The product $\psi\psi^* = |\psi|^2$ is a real quantity.
- According to Max Born, the square of the magnitude of the wave function $|\psi|^2$ evaluated in a particular region represents the probability of finding the particle in that region.

$$P \propto |\psi(x, y, z, t)|^2 \, dV$$

  - Since the particle is certainly somewhere in the space, the probability $P = 1$ and the integral of $|\psi|^2 \, dV$ over the entire space must be equal to unity.

$$\int_{-\infty}^{+\infty} |\psi|^2 \, dV = 1$$

  - To conclude, ψ has no physical significance but $|\psi|^2$ gives the probability of finding the atomic particle in a particular region.

Normalization condition:

The process of constructing ψ_N from ψ such that it satisfies $\psi_N = \psi/N$ is called normalization.

$$\psi_N = \frac{\psi}{N}$$

$$N^2 = \frac{1}{\int_{-\infty}^{+\infty} |\psi|^2 \, dV}$$

Here, N is finite, positive and real quantity

Well behaved Wave function:

- Ψ function must be finite
- ψ function must be single–valued
- ψ function must be continuous
- ψ function must be normalized

8.8.1 Schrödinger's Time independent wave Equation:

Consider a system of stationary waves associated with a moving particle. Let (x, y, z) be the position co-ordinates of the particle and ψ, the periodic displacement for the matter wave at any time t.

The classical differential equation of the wave motion is given by

$$\frac{\partial^2\psi}{\partial t^2} = v^2\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = v^2\nabla^2\psi \dots\dots\dots\dots (8.10)$$

where v = wave velocity

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \text{Laplacian operator}$$

The solution of equation (8.10) gives ψ as a periodic displacement in terms of time t i.e.

$$\psi(x, y, z, t) = \psi_0(x, y, z)e^{-i\omega t} \dots\dots\dots. (8.11)$$

where ψ_0 is the amplitude of the particle wave at the point (x, y, z) which is independent of time (t) and a function of (x, y, z) i.e. the position r.

Equation (8.11) can also be expressed as

$$\psi(\overline{r}, t) = \psi_0(\overline{r})e^{-i\omega t} \dots\dots\dots\dots (8.12)$$

Differentiating equation (8.12) twice we get

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

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

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

$$\frac{\partial^2\psi}{\partial t^2} = -\omega^2\psi \dots\dots\dots\dots.. (8.13)$$

Substituting the value of $\frac{\partial^2\psi}{\partial t^2}$ from equation (8.13) in equation (8.10) we have

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{\omega^2}{v^2}\psi = 0 \dots\dots\dots (8.14)$$

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

$$\therefore \frac{\omega}{v} = \frac{2\pi}{\lambda}$$

Substituting the value of $\frac{\omega}{v} = \frac{2\pi}{\lambda}$ in equation (8.14)

We have

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{4\pi^2}{\lambda^2}\psi=0$$

Using Laplacian operator we have

$$\nabla^2\psi+\frac{4\pi^2}{\lambda^2}\psi=0 \dots\dots\dots\dots\dots (8.15)$$

From de Broglie relation $\lambda=\frac{h}{mv}$ in equation (8.15) we have

$$\nabla^2\psi+\frac{4\pi^2}{h^2}m^2v^2\psi=0 \dots\dots\dots\dots (8.16)$$

Let E and V be the total and potential energies of the particle respectively then

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

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

$$\Rightarrow m^2v^2=2m(E-V) \dots\dots\dots (8.17)$$

From equation (8.16) & (8.17) we have

$$\nabla^2\psi+\frac{4\pi^2}{h^2}2m(E-V)\psi=0$$

$$\Rightarrow \nabla^2\psi+\frac{8\pi^2m}{h^2}(E-V)\psi=0 \dots\dots\dots\dots. (8.18)$$

Equation (8.18) is known as Schrödinger time independent wave equation in three dimensions

Putting $\hbar=h/2\pi$ in equation (8.18) the Schrödinger equation can be also written as

$$\Rightarrow \nabla^2\psi+\frac{2\,m}{\hbar^2}(E-V)\psi=0 \dots\dots\dots\dots\dots (8.19)$$

For free particle $V=0$, so Schrödinger wave equation for a free particle can be written as

$$\Rightarrow \nabla^2\psi+\frac{2\,mE}{\hbar^2}\psi=0 \dots\dots\dots\dots\dots\dots (8.20)$$

8.8.2 Schrödinger's Time dependent wave Equation

The Schrödinger's time independent wave equation is given by

$$\nabla^2\psi + \frac{2\,m}{\hbar^2}(E - V)\psi = 0 \;\ldots\ldots\ldots\; (8.19)$$

Schrödinger's time dependent wave equation may be obtained by eliminating E from time independent wave equation (8.19).

Consider a system of stationary waves associated with a moving particle. Let (x, y, z) be the position co-ordinates of the particle and ψ, the wave displacement of the matter wave at time t.

The classical differential equation of the wave motion is given by

$$\frac{\partial^2\psi}{\partial t^2} = v\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = v^2\nabla^2\psi \;\ldots\ldots\ldots\ldots\; (8.10)$$

where v = wave velocity

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \text{Laplacian operator}$$

The solution of equation (8.10) is given by

$$\psi(x, y, z, t) = \psi_0(x, y, z)e^{-i\omega t} \;\ldots\ldots\ldots\; (8.11)$$

$$\psi(\overline{r}, t) = \psi_0(\overline{r})e^{-i\omega t} \;\ldots\ldots\ldots\; (8.12)$$

Differentiating equation (8.11) w.r. to t. we get (8.12)

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

$$= -i\,2\pi\left(\frac{E}{h}\right)\psi \qquad [E = hv]$$

$$= -i\frac{2\pi}{h}E\psi \qquad \left[\hbar = \frac{h}{2\pi}\right]$$

$$= -i\left(\frac{E}{\hbar}\right)\psi = -\frac{i}{\hbar}E\psi$$

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

$$-\frac{i\,\hbar}{i \times i}\frac{\partial\psi}{\partial t} = E\psi \qquad [i^2 = -1]$$

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

$$E\psi = i\,\hbar\frac{\partial\psi}{\partial t} \;\ldots\ldots\ldots\ldots\; (8.21)$$

From equation (8.19) Schrödinger time independent wave equation is

$$\nabla^2\psi + \frac{2\,m}{\hbar^2}[E\psi - V\psi] = 0$$

$$\nabla^2\psi = -\frac{2\,m}{\hbar^2}[E\psi - V\psi]$$

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

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\,\hbar\frac{\partial\psi}{\partial t} \;\ldots\ldots\ldots\ldots\ldots\; (8.22)$$

The equation is known as time dependent Schrödinger wave equation

Equation (8.22) can also be written as

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

$$\Rightarrow H\psi = E\psi \dots\dots\dots\dots\dots (8.23)$$

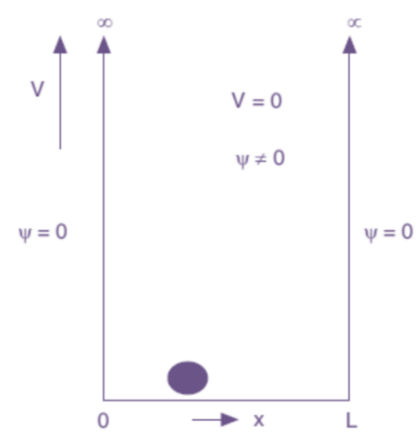
where $H = \left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]$ = Hamilton Operator

and $E = i\,\hbar\frac{\partial}{\partial t}$ = Energy Operator

The function ψ is called an Eigen function and the Scalar quantity E is called Eigen Value.

Applications of Schrodingers equation:

1) Particle in a Rigid Box (infinite potential well)



Let us consider a particle of mass m that is restricted to move along the x-axis between x=0 and x=L inside a infinite potential well. Particle is free to move along either direction between 0 to L.

The walls of the well act as ideal reflecting barriers so that particle cannot leave the well.

The potential inside and outside of the well can be given as

$$V = 0 \qquad for\ 0 < x < L$$

$$V = \infty \qquad for\ 0 > x > L$$

As particle cannot leave the well, wavefunction ψ has zero value outside and some certain value inside the potential well.

We have schrodinger's time indepedndet equation in one dimension as

$$\frac{d^2\psi}{dt^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad (1)$$

For particle in a region $0 < x < L$, equation (1) becomes

$$\frac{d^2\psi}{dt^2} + \frac{8\pi^2 m}{h^2}E\psi = 0$$

$$\frac{d^2\psi}{dt^2} + K^2\psi = 0 \qquad (2)$$

Where

$$K^2 = \frac{8\pi^2 m}{h^2} E \qquad (3)$$

The general solution differential equation (2) is given as

$$\psi = A \sin Kx + B cos\, Kx \qquad (4)$$

Here, A and B are constants and can be calculated using boundary conditions.

The first Boundary condition is

$$\psi = 0 \qquad at \quad x = 0$$

Putting this in equation (4), we get

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

i.e.

$$B = 0$$

Hence, equation (4) can be written as

$$\psi = A \sin Kx \qquad (5)$$

The second boundary condition is

$$\psi = 0 \qquad at \quad x = L$$

Putting this in equation (5), we get

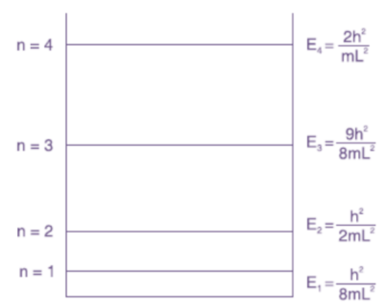
$$0 = A \sin KL$$

i.e.

$0 = \sin KL$

$$KL = n\pi$$

$$K = \frac{n\pi}{L} \qquad (6)$$



Squaring equation (6) and equating it with equation (3), we get

$$\left(\frac{n\pi}{L}\right)^2 = \frac{8\pi^2 m}{h^2} E$$

$$E = \frac{n^2 h^2}{8mL^2} \qquad (7)$$

Here, n=1,2,3, ….

This is the expression of energy or eigen value for a particle in a Rigid box.

Substituting equation (6) in equation(7), we get

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

This is the expression of the wave function or eigen function for a particle in a box.

Normalization of Wavefunction:

We have a wave function for a particle in infinite potential well as

$$\psi = A \sin\left(\frac{n\pi}{L}x\right) \qquad (1)$$

The complx conjugate of this wave function is

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

To normalize this wave funciton, we use condition

$$\int_0^L \psi\psi^*\, dx = 1 \qquad (3)$$

Putting 1 and 2 in equation 3, we get

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

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

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

$$\frac{A^2}{2}\left[\mathrm{x} - \frac{\sin 2\left(\frac{n\pi}{L}x\right)}{2\left(\frac{n\pi}{L}\right)}\right]_0^L = 1$$

Putting upper and lower limits, we get

$$\frac{A^2}{2}L = 1$$

i.e.

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

Putting this value in equation (1), we get normalized wave function

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