"Quantum Theory" (By Ranjan)

* Need and Origin of Quantum Concepts:

Optical Phenomenon such as interference, diffraction etc could be explained by wave theory of light. But this theory failed to explain photo electric effect, compton effect emission and absorption of radiation

A complete theory should be able to predict, on theoretical grounds the energy level of any particular atom.

In 1913 Bohr model of hydrogen atom was step towards it. But it combined classical principles with new ideas that were inconsistent with classical theory and it raised many questions. More drastic departures from classical concepts were needed.

A succesful drastic departure is 'Quantum theory', Besides waves that sometimes act like particles, quantum theory extends the concept of wave-particle duality to include particles that sometimes show behaviour of waves.

Quantum theory is the Key to understanding atoms and molecules.

In 1924, French physicist Prince Louis de Broglie gave a hypothesis known as 'De Broglie hypothesis"

Wave particle Duality :→

Acc. to Einstein, energy of light is concentrated in small region. This represents the smallest quantity of energy known as photon. This photon is energy particle. Hence light shows ~~that~~ wave nature as well as particle nature. This nature of light is known as dual nature & property is known as wave-particle duality.

In 1924, Louis de Broglie introduced a idea that matter (e^-) should also posses dual nature. He connected wavelength of e^- wave and momentum of the particle by

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

λ is wavelength

h = plank's constant $= 6.62 \times 10^{-34}$ Js

p = momentum of particle

Matter waves:

In 1924 Louis de-Broglie proposed that matter also possesses dual character like light. His concept about dual nature of matter was based on:

1. Matter and light both are forms of energy & each of them can be transformed into each other.

2. Both are governed by space time symmetries of theory of relativity.

"A moving matter particle is surrounded by wave whose wavelength depends upon the mass of particle and its velocity. The wave associated with matter particles are known as matter waves or de-Broglie waves"

Consider a photon whose energy is

$$E = h\nu = \frac{hc}{\lambda} \longrightarrow (1)$$

$h = 6.62 \times 10^{-34}\ Js$, λ = wavelength

ν = frequency

c = velocity of light

If mass of particle is converted in to energy, the energy is given by :

$$E = mc^2 \rightarrow (2)$$

Equating (1) & (2) :-

$$\Rightarrow mc^2 = \frac{hc}{\lambda}$$

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

$$\boxed{\lambda = \frac{h}{p}} \quad , \quad p = mc$$

This is wavelength of de-Broglie waves, p is momentum associated with photon

If in place of photon, a material particle of 'm' mass is moving with velocity 'v'

$$p = mv$$

$$\therefore \text{wavelength} \quad \boxed{\lambda = \frac{h}{mv}}$$

This is called de-Broglie wavelength

(i) Now we know

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

$\Rightarrow mv = p$

$$E = \frac{p^2}{2m}, \quad p = \sqrt{2mE}$$

$\Rightarrow \lambda$ becomes;

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

$$\boxed{\lambda = \frac{h}{\sqrt{2mE}}} \rightarrow A$$

For Gases :→

$$E = \frac{3}{2}KT, \quad K = 1.38 \times 10^{-23} J/K$$

T = absolute temp.

$\therefore$ A can be written as

$$\boxed{\lambda = \frac{h}{\sqrt{3mKT}}}$$

(iii) Suppose an e^- accelerates through potential 'V'

Work done by electric field = Gain in K.E

$$eV = \frac{1}{2}mv^2 \; ; \; e = 1.6 \times 10^{-19} C$$

$$\Rightarrow m^2v^2 = 2meV, \quad mv = \sqrt{2meV}$$

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

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

Properties of wave matter :→

1. The debroglie wavelength of wave associated with moving light particle is greater than wavelength associated with heavier particle.

2. The de-Broglie wavelength of wave associated with slow moving particle is greater than wavelength associated with fast moving particle.

3. For particle at rest, i.e $V = 0$ de-Broglie wavelength becomes ∞, i.e wave becomes indeterminate and vice-versa

4. The de broglie wavelength is independent of charge of particle

5. The velocity of matter wave is greater than velocity of electromagnetic wave.

$$V_P = c^2/v$$

6. The velocity of matter wave is not constant like the radiations which move with const. velocity equal to velocity of light. The velocity of matter waves depends upon the velocity of material particle.

7. The wave and particle aspects of matter never appear simultaneously in same experiment.

8. De broglie waves are not e-m waves.

Group & Phase velocity

Acc. to de Broglie, wave of wavelength 'λ'

$$\lambda = \frac{h}{mv}$$, m = mass of particle
v = velocity " "

Energy, $E = h\nu$

$$\nu = \frac{E}{h}$$

Acc. to Einstein's mass energy relationship

$$E = mc^2$$

$$\nu = \frac{mc^2}{h}$$

$$c = \nu\lambda$$

The de Broglie wave velocity, v_p

$$= \nu\lambda$$

$$\Rightarrow v_p = \left(\frac{mc^2}{h}\right)\left(\frac{h}{mv}\right)$$

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

Because particle velocity 'v' must be less than velocity of light 'c'. the de-Broglie waves always travel faster than light. This apparently brings us in conflict with theory of relativity. To understand this result, we must look into distinction b/w phase velocity and group velocity.

Mathematically, A wave packet (group) is formed by superposition of two waves. Consider a string stretched along x-axis vibrating along y-axis. The amplitude of vibration 'A' for both waves, $d\omega$ be diff. b/w their angular freq. & dk be diff. b/w their propogation

These two wave trains can be represented by:

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

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

∴ Acc. to superposition principle,

$$y = y_1 + y_2 = A\left[\cos\{(\omega + d\omega)t - (k+dk)x\} + \cos(\omega t - kx)\right]$$

Since $\cos\theta + \cos\phi = 2\cos\left(\frac{\theta+\phi}{2}\right)\cos\left(\frac{\theta-\phi}{2}\right)$

$$\therefore \quad y = 2A\cos\left[\frac{(2\omega + d\omega)}{2}t - \left(\frac{2k+dk}{2}\right)x\right]$$

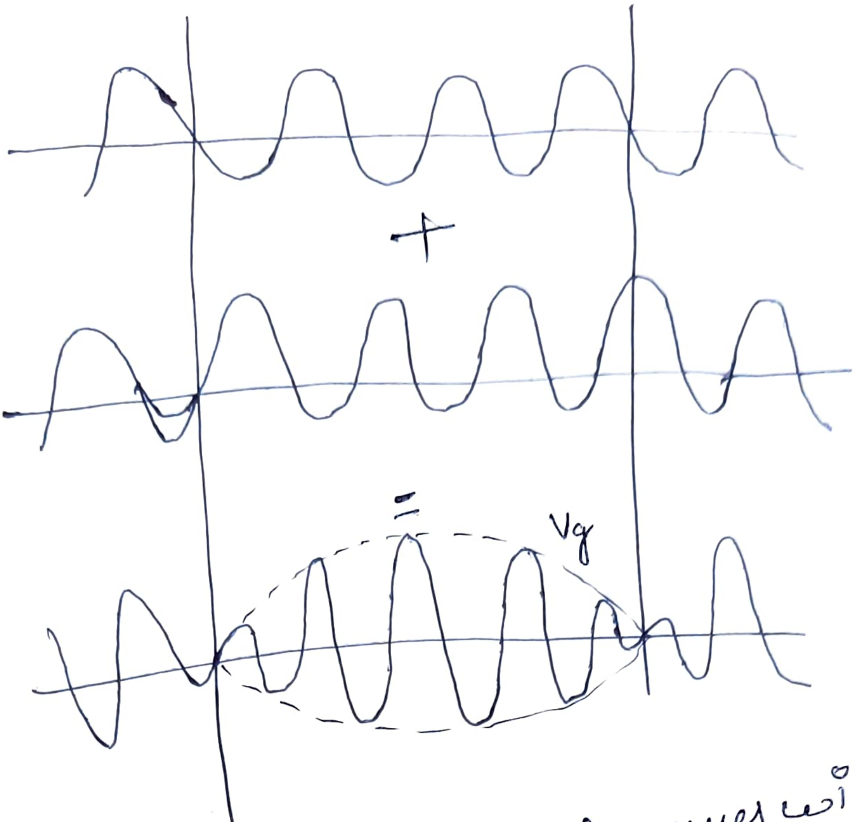
$$\times \cos\left[\frac{d\omega}{2}t - \frac{dk}{2}x\right]$$

Since $d\omega$ and dk are very-2 small,

$$\frac{2\omega + d\omega}{2} = \omega, \quad \frac{2k+dk}{2} = k$$

Hence, $y = 2A\cos(\omega t - kx)\cos\left[\frac{d\omega}{2}t - \frac{dkx}{2}\right]$

This eqn represents eqn of motion of wave of angular freq. 'ω' & propogation const. 'k' that has superimposed upon it modulation freq. $\frac{d\omega}{2}$ and propogation $\frac{dk}{2}$.



(Superposition of waves with diff. freq.)

Let phase velocity V_p,

$$V_p = \nu\lambda = \frac{2\pi\nu}{2\pi/\lambda} = \frac{\omega}{K}$$

Group velocity, $V_g = \frac{d\omega/2}{dK/2} = \frac{d\omega}{dK}$

Since, $V_p = \frac{\omega}{K}$

$$\omega = V_p K$$

$$V_g = \frac{d\omega}{dK} = \frac{d(V_p K)}{dK}.$$

$$V_g = V_p + K\frac{dV_p}{dK} = V_p + \frac{2\pi}{\lambda}\frac{dV_p}{d\left(\frac{2\pi}{\lambda}\right)}$$

$$\boxed{V_g = V_p - \lambda\frac{dV_p}{d\lambda}}$$

Depending upon $\frac{dV_P}{d\lambda}$,

(i) when $\frac{dV_P}{d\lambda} = 0$; $V_g = V_P$

The medium in which this happens.
Known as non-dispersive medium.

(ii) when $\frac{dV_P}{d\lambda} > 0$, $V_g < V_P$

The medium in which this happens,
Known as dispersive medium.

In dispersive medium, $\frac{dV_P}{d\lambda}$ = +ve

Group velocity is less than phase velocity.
$(V_g < V_P)$

Group velocity & Particle Velocity are Equal :-

Angular frequency, $\omega = 2\pi\nu = \frac{2\pi E}{h} = \frac{2\pi mc^2}{h}$

Particle moving with velocity 'v'

$$\omega = \frac{2\pi m_0 c^2}{h\sqrt{1-\frac{v^2}{c^2}}}$$, m_0 rest mass of particle.

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

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

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

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

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

$$v_g = \frac{d\omega/dv}{dk/dv} = \frac{2\pi m_0 v}{h\left(1-\frac{v^2}{c^2}\right)^{3/2}} \cdot \frac{h\left(1-\frac{v^2}{c^2}\right)^{3/2}}{2 m_0 \pi}$$

$$\Rightarrow \boxed{v_g = v}$$

Thus, de-Broglie wave group associated with a moving particle travels with same velocity as that of particle.

The phase velocity or wave velocity v_p of de-Broglie wave evidently has no physical significance in itself.

Heisenberg's uncertainity Principle:

Acc. to this principle, It is impossible to determine the exact position and momentum of a particle simultaneously.

We know, Group velocity of wave packet,

$$V_g = \frac{\Delta\omega}{\Delta K}$$

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

$\Rightarrow \partial\omega = 2\pi \Delta\nu$

Also, $K = \frac{2\pi}{\lambda}$

$\lambda = \frac{h}{p} \Rightarrow K = \frac{2\pi p}{h}$

$\Rightarrow \Delta K = \frac{2\pi}{h} \Delta p$

$\Rightarrow \Delta K = \frac{2\pi}{h} \Delta p$

$\Rightarrow V_g = \frac{\Delta\omega}{\Delta K} = \frac{2\pi \Delta\nu h}{2\pi \Delta p}$

$\Rightarrow V_g = \frac{h\Delta\nu}{\Delta p} \longrightarrow (1)$

Also, $V_g = \frac{\Delta x}{\Delta t}$

where Δt is least time required for one complete wave packet to cross the refrence point.

The freq. ΔV is related to Δt,

$$\Delta t \geq \frac{1}{\Delta V} \longrightarrow (2)$$

$$\therefore \frac{\Delta x}{\Delta t} = \frac{h \Delta V}{\Delta p}$$

$$\text{or} \quad \Delta x \cdot \Delta p = h \Delta V \Delta t \rightarrow (3)$$

From eq.^{n} (2) $\Rightarrow$

$$\Delta t \cdot \Delta V \geq 1$$

$\therefore$ $\Delta x \cdot \Delta p \geq h$, More sophisticated derivation,

Also, $\boxed{\Delta x \cdot \Delta p = \frac{h}{2\pi}}$

Due to small value of h, uncertainity has no relavance in the macroscopic world.

$$E = hV$$

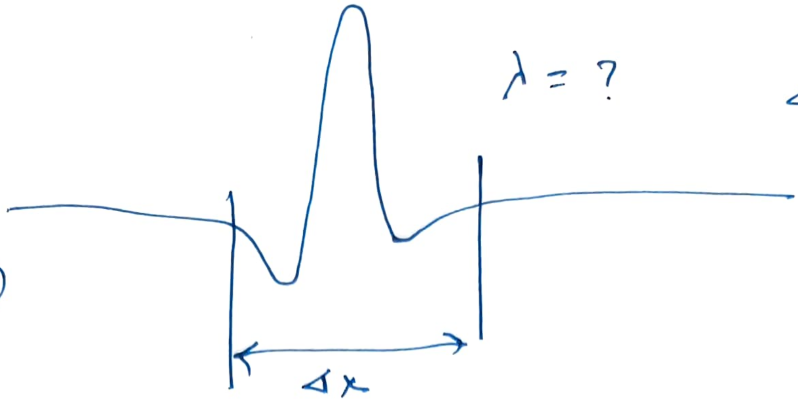
$$V = \frac{E}{h}$$

From eq. (2), $\Delta t \cdot \Delta V \geq 1$

$$\Delta\left(\frac{E}{h}\right) \cdot \Delta t \geq 1 \quad \text{or} \quad \Delta E \cdot \Delta t \geq h$$

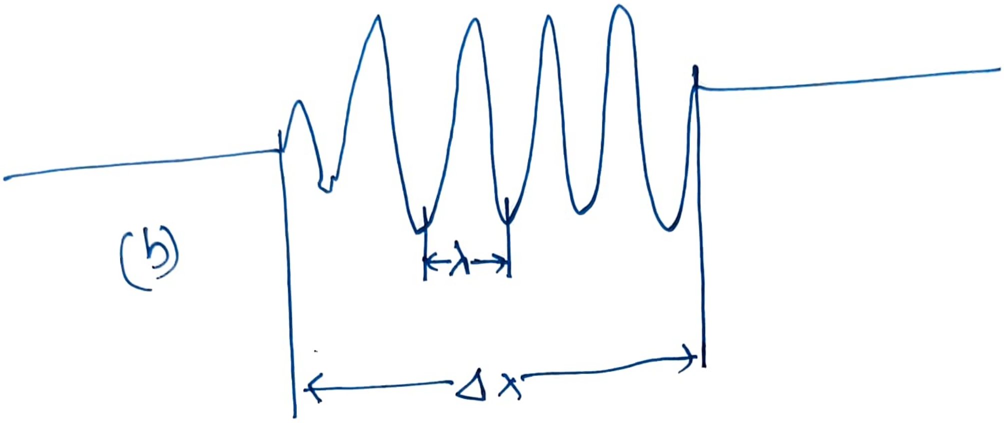
A more sophisticated derivation

$$\boxed{\Delta E \cdot \Delta t \geq \frac{h}{2\pi}}$$



(a)

Δx small
Δp large



(b)

Δw large
Δp large

According to quantum free electron theory:

- The energy values of the free electrons are discontinuous because of which their energy values are discrete.
- The free electrons obey the Pauli's exclusion principle. Hence no two electrons can possess same energy.
- The distribution of energy among the free electrons is according to Fermi- Dirac statistics, which imposes a severe restriction on the possible ways in which the electrons absorb energy from an external source.

Basics of Quantum Theory

de-Broglie Wave Concepts

- The universe is made of Radiation (light) and matter (Particles).The light exhibits the dual nature i.e. it can behave both as a wave and as a particle. The phenomena of diffraction and interference can only be explained with the concept that light travels in the form of waves. The phenomena of photoelectric effect, Compton effect and black body radiation can only be explained with the concept of quantum theory of light. It means to say that light possesses particle nature. Hence, it is concluded that light exhibits the dual nature namely wave nature and particle nature.
- Since the nature loves symmetry was suggested by Louis deBroglie. de Broglie suggested that an electron or any other material particle must exhibit wave like properties in addition to particle nature. *The waves associated with a moving material particle are called matter waves, pilot waves or de Broglie waves.*

De-Broglie Wavelength

- de-Broglie formulated an equation relating the momentum (p) of the electron and the wavelength (λ) associated with it, called de-Broglie wave equation.
- $\lambda =$ **h/mv=h / p** where h - is the planck's constant.

Relation between de-Broglie Wavelength and Energy

Consider an electron with charge ***e***, mass ***m*** and velocity ***v*** is under the influence of an electric potential **V**. The energy acquired by electron is given by,

$$E = eV = \frac{1}{2}mv^2 = \frac{p^2}{2m} \qquad (1)$$

Here $\boldsymbol{p}$ is the momentum of the electron. From (1), we can write

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

The expression for de-Broglie wavelength is given by,

$$\lambda = \frac{h}{mv} = \frac{h}{p} = \frac{h}{\sqrt{2meV}} = \frac{h}{\sqrt{2mE}} \tag{3}$$

Wave Function

- A variable quantity which characterizes de-Broglie waves is known as Wave function and is denoted by the symbol $\boldsymbol{\psi}$.
- The value of the wave function associated with a moving particle at a point (x, y, z) and at a time '*t*' gives the probability of finding the particle at that time and at that point.

Physical significance of ψ

- The wave function $\boldsymbol{\psi}$ enables all possible information about the particle. $\boldsymbol{\psi}$ is a complex quantity and has no direct physical meaning. It is only a mathematical tool in order to represent the variable physical quantities in quantum mechanics.
- Born suggested that, the value of wave function associated with a moving particle at the position co-ordinates (x,y,z) in space, and at the time instant '*t*' is related in finding the particle at certain location and certain period of time 't'.
- If $\boldsymbol{\psi}$ represents the probability of finding the particle, then it can have two cases.

  Case 1: certainty of its Presence: +ve probability

  Case 2: certainty of its absence: - ve probability, but –ve probability is meaningless.

  Hence the wave function $\boldsymbol{\psi}$ is complex number and is of the form $a+ib$
- Even though $\boldsymbol{\psi}$ has no physical meaning, the square of its absolute magnitude $|\boldsymbol{\psi}|^2$ gives a definite meaning and is obtained by multiplying the complex number with its complex conjugate then $|\boldsymbol{\psi}|^2$ represents the probability density '*P*' of locating the particle at a place at a given instant of time. And has real and positive solutions.

  $\boldsymbol{\psi(x,y,z,t)=a+ib}$

  $\boldsymbol{\psi^*(x,y,z,t)=a-ib}$

  $P= \psi\psi^*=|\psi|^2=a^2+b^2 \;\; as\; i^2=-1$

  where '*P*' is called the probability density of the wave function.
- If the particle is moving in a volume '*V*', then the probability of finding the particle in a

volume element dv, surrounding the point x,y,z and at instant 't' is Pdv

$\int|\psi|^2 dv = 1$ *if particle is present*

$\int|\psi 2| dv = 0$ if particle does not exist

This is called normalization condition.

Schrödinger Wave Equations

- Schrödinger describes the wave nature of a particle in mathematical form and is known as Schrödinger wave equation. Schrödinger wave equation plays the role of Newton's laws and conservation of energy in classical mechanics i.e. it predicts the future behavior of a dynamic system. It is a wave equation in terms of wave function which predicts analytically and preciously the probability of events or outcomes. Schrödinger wave equation are of two types:
  1. Time dependent wave equation and
  2. Time independent wave equation.

  To obtain these two equations, Schrödinger connected the expression of de-Broglie wavelength into classical wave equation for a moving particle. The obtained equations are applicable for both microscopic and macroscopic particles.

Schrödinger Time Dependent Wave Equation

To explain the wave function, let us consider a particle of mass m moving along the positive x-direction having accurately known momentum p and total energy E. The position of the particle is completely undetermined.

Let wave associated with such a particle be a plane, continuous harmonic wave travelling in the positive x-direction. The wavelength of the wave is

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

$$\therefore p = \frac{h}{\lambda} = \frac{h}{2\pi} \cdot \frac{2\pi}{\lambda} = \hbar k$$

where

$$\hbar = \frac{h}{2\pi}, k = \frac{2\pi}{\lambda}$$

Now,

$$E = h\upsilon = \frac{h}{2\pi}.2\pi\upsilon = \hbar\omega, \qquad where\,\omega = 2\pi\upsilon$$

or

$$\omega = \frac{E}{\hbar}$$

Let the plane wave be represented by a complex variable quantity $\boldsymbol{\psi}$ called the wave function of the particle and is given by

$$\Psi = Ae^{i(kx-\omega t)} \tag{1}$$

Putting $\qquad \omega = 2\pi\upsilon$ and $k = \frac{2\pi}{\lambda}$

$$\psi = Ae^{i(\frac{2\pi x}{\lambda}-2\pi\upsilon t)} = Ae^{-2\pi i(\upsilon t-\frac{x}{\lambda})} \tag{2}$$

As $\qquad E = h\upsilon = 2\pi\hbar\upsilon$ and $\lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$

or $\qquad \frac{E}{\hbar} = 2\pi\upsilon$

Therefore, for a free particle wave equation becomes

$$\Psi = Ae^{\frac{-i}{\hbar}(Et-px)} \tag{3}$$

Differentiate equation (3) w.r.t. ***t***, we get

$$\frac{\partial\psi}{\partial t} = -\frac{i}{\hbar}EAe^{\frac{-i}{\hbar}(Et-px)}$$

$$EAe^{\frac{-i}{\hbar}(Et-px)} = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}$$

$$\Rightarrow E\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{4}$$

Differentiate equation (3) w.r.t. ***x***, we get

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

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

$$\Rightarrow p\psi = \frac{\hbar}{i}\frac{\partial\psi}{\partial x} \tag{5}$$

As total energy, E= Kinetic energy (*K*) +Potential energy (*V*)

Now, Kinetic Energy $= \dfrac{p^2}{2m}$

Equation (5) in terms of wave function $\boldsymbol{\psi}$ can be written as,

$$E\psi = \left(\frac{p^2}{2m}\right)\psi + V\psi \tag{6}$$

Putting the values of $E\psi$ and $p\psi$ from (4) and (5), we have

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

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi \tag{7}$$

Equation (7) is called Schrödinger time dependent wave equation in one-dimension. The Schrödinger time dependent wave equation in three-dimensional form is written as,

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right] + V\psi \tag{8}$$

or

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi \tag{9}$$

$$\left[\because \vec{\nabla} = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right] \quad \text{and} \quad \left[\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]$$

or

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{10}$$

Equation (10) contains time and hence is called time dependent Schrödinger wave equation.

The operator $\left(-\dfrac{\hbar^2}{2m}\nabla^2 + V\right)$ is called *Hamiltonian* and is represented by ***H***.

Schrödinger Time Independent Wave Equation

Again consider equation (3), the we have

$$\Psi = Ae^{\frac{-i}{\hbar}(Et-px)} = Ae^{\frac{-i}{\hbar}Et}e^{\frac{i}{\hbar}px}$$

or

$$\Psi = \psi_0 e^{\frac{-i}{\hbar}Et} \tag{11}$$

Where $\psi_0 = Ae^{\frac{i}{\hbar}px}$

Differentiate (11) partially w.r.t. ***t***, we get

$$\frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar}\psi_0 e^{\frac{-i}{\hbar}Et} \tag{12}$$

Differentiate (11) partially w.r.t. ***x*** twice, we get

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial^2 \psi_0}{\partial x^2} e^{-\frac{i}{\hbar}Et} \tag{13}$$

Putting equations (11), (12) and (13) in equation (7) $i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi$, we get

$$i\hbar\left(-\frac{iE}{\hbar}\right)\psi_0 e^{-\frac{i}{\hbar}Et} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi_0}{\partial x^2} e^{-\frac{i}{\hbar}Et} + V\psi_0 e^{-\frac{i}{\hbar}Et}$$

or
$$E\psi_0 = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi_0}{\partial x^2} + V\psi_0$$

or
$$\frac{\partial^2 \psi_0}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi_0 = 0 \tag{14}$$

This is time independent Schrödinger wave equation in one-dimension.

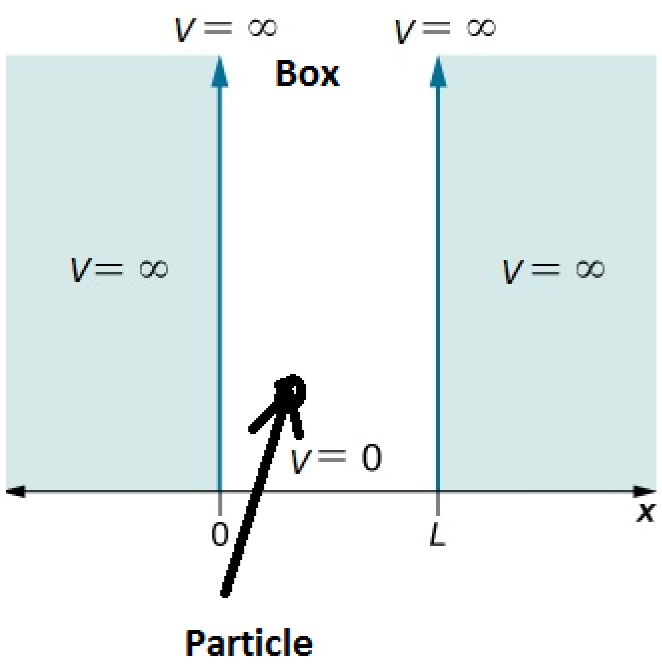
In three-dimensional, it will be of the form as

$$\nabla^2 \psi_0 + \frac{2m}{\hbar^2}(E - V)\psi_0 = 0 \tag{15}$$

where, $\left[\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]$ is called the Laplacian operator.

Particle in one dimensional Box

- The wave nature of a moving particle leads to some remarkable consequences when the particle is restricted to a certain region of space instead of being able to move freely *i.e.* when a particle bounces back and forth between the walls of a box.
- The Schrodinger wave equation will be applied to study the motion of a particle in 1-D box to show how quantum numbers, discrete values of energy and zero point energy arise.
- From wave point of view, a particle trapped in a box is like a standing wave in a string stretched between the box's walls.
- Consider a particle of mass 'm' moving freely along x- axis and is confined between $x=0$ and $x= L$ by infinitely two hard walls, so that the particle has no chance of penetrating them and bouncing back and forth between the walls of a 1-D box.
- If the particle does not lose energy when it collides with such walls, then the total energy remains constant.



- This box can be represented by a potential well of width 'L', where V is uniform inside the box throughout the length 'L' i.e V= 0 inside the box or convenience and with potential walls of infinite height at x=0 and x=L, so that the P.E. 'V' of a particle is infinitely high V=∞ on both sides of the box.

Boundary Conditions

The boundary conditions are

$V(x)=0, \psi(x)=1 \qquad when\ 0<x<L \qquad (1)$

$V(x)=\infty, \psi(x)=0 \qquad when\ 0\geq x\geq L \qquad (2)$

Where $\psi(x)$ is the wave function and it gives the probability of finding the particle inside the box.

The Schrodinger wave equation for the particle in the potential well can be written as

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

$$\hbar = \frac{h}{2\pi}$$

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

As $V=0$ for a free particle, above equation reduces to,

$$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}E\psi = 0 \qquad (3)$$

In the simplest form equation (3) can be written as

$$\frac{\partial^2\psi}{\partial x^2}+k^2\psi = 0 \qquad (4)$$

Where $\boldsymbol{k}$ is the propagation constant and is give by

$$k=\sqrt{\frac{8\pi^2 mE}{h^2}} \qquad (5)$$

The general solution of equation (4) is

$$\psi(x) = A\sin kx + B\cos kx \qquad (6)$$

Where A and B are arbitrary constants and value of these constants can be obtained by applying the boundary conditions. Substituting equation (1) in (6), we get

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

Putting B=0 in (6)

$$\psi(x) = A\sin kx \qquad (7)$$

Substituting equation (2) in (7), we get

$$0 = A\sin k(L)$$

$$\Rightarrow A = 0 \, or \sin kL = 0$$

But

$$A \neq 0$$

As already B=0, and if A=0, there is no solution at all. Therefore,

$$\sin kL = 0$$

$$i.e. kL = n\pi$$

$$k = \frac{n\pi}{L} \qquad (8)$$

where n= 1, 2, 3, 4,…….. . and so on.

But

$$n \neq 0$$

Because if n=0, k=0, E=0 everywhere inside the box and moving particle can not have zero energy.

From (8)

$$k^2 = \left(\frac{n\pi}{L}\right)^2$$

From (5)

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

$$E = \frac{n^2 h^2}{8mL^2} \qquad (9)$$

Zero point energy

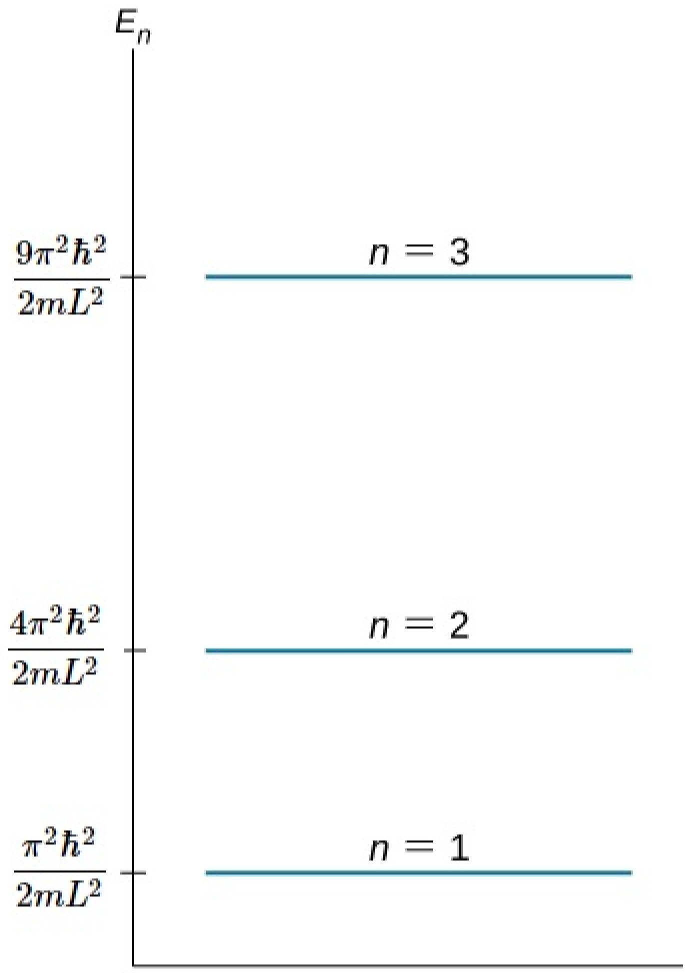
The lowest energy of the particle is given by putting n= 1 in equation (9) *i.e.*

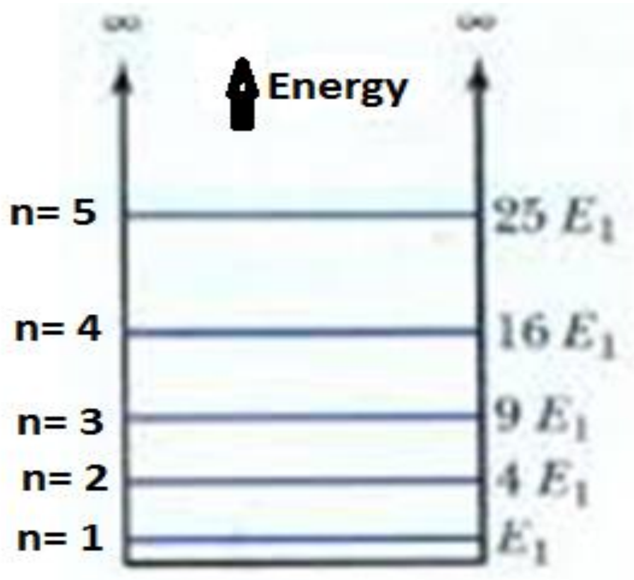
$$E_1 = \frac{h^2}{8mL^2} \qquad (10)$$

$E_0 = 0$ is not allowed. The particle can never be at rest. The lowest energy is E_1. This is the minimum energy that the particle will be having in its lowest state or ground state. This is also called Ground state energy or Zero point energy of the system. Other levels are called excited states.

We can write

$$E_n = n^2 E_1$$


E_n
$\frac{9\pi^2\hbar^2}{2mL^2}$
$n = 3$
$\frac{4\pi^2\hbar^2}{2mL^2}$
$n = 2$
$\frac{\pi^2\hbar^2}{2mL^2}$
$n = 1$


∞
∞
Energy
n= 5
$25\ E_1$
n= 4
$16\ E_1$
n= 3
$9\ E_1$
n= 2
$4\ E_1$
n= 1
E_1

Wave Functions

The wave functions ψ_n corresponding to E_n are called Eigen functions of the particle. The integer 'n' corresponding to energy E_n are quantum number of the energy level E_n. Putting (8) in (7),

$$\psi_n = A\sin\frac{n\pi x}{L} \tag{11}$$

Normalization of Wave function

According to the normalization condition, the total probability of finding the particle somewhere inside the box must be unity.

$$\int_0^L p_x dx = \int_0^L |\psi_n|^2 dx = 1 \tag{12}$$

From (11) and (12),

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

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

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

The second term of the integrand expression becomes zero at both the limits. So,

$$\left(\frac{A}{2}\right)^2 [x]_0^L = 1$$

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

$$A = \sqrt{\frac{2}{L}} \tag{13}$$

Hence, the normalized wave function is

$$\psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \tag{14}$$

The plots below show ψ_n versus x and $|\psi_n|^2$ versus x for n=1, 2, and 3etc. Note that although ψ_n can be positive or negative, $|\psi_n|^2$ is always positive.

$|\psi_n|^2$ is zero at the boundaries, satisfying our boundary conditions. In addition, $|\psi_n|^2$ is zero at other points. The number of zero points depends on the quantum number n. Only certain wavelengths for particle are allowed.