

# Classical Physics.

Classical Physics deals with heavy mass with small velocity so that to describes the very high velocity (nearly equal to velocity of light). We need new physics which are called quantum physics. Furthermore, the failure of Classical physics to explain black body radiation, photo-electric effect, atomic stability and atomic spectroscopy is the necessity of quantum physics.

**Black body:** a black body is an object that absorbs all incident electromagnetic radiations that falls on it. No radiation passes through it and none is reflected. Despite the name, black bodies are not actually black as they radiate energy as well.

## Black Body Radiation

It is a thermal electromagnetic radiation within or surrounding a body in thermodynamics equilibrium with its environment, or emitted by a black body. It has a specific spectrum and intensity that depends only on the body's temperature but independent of the material of the body.

For experimental purpose, a black body is a metallic cavity with small hole as shown in figure (a). Any radiation entering from the small hole has a very small probability of being reflected out. Due to multiple reflection by the inner walls of the cavity, the radiation is eventually absorbed by the atoms in turn, will radiate electromagnetic waves into the cavity and some of it will leave out through the hole.

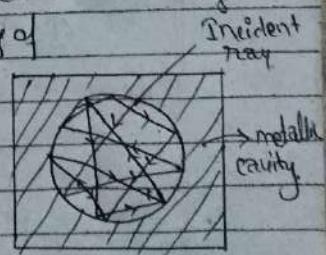
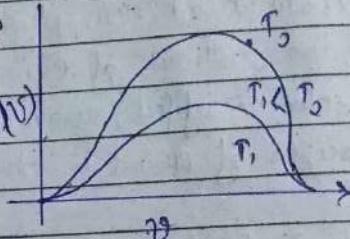


fig (a)

## Characteristic of spectrum of black body.

The observed variation of the spectral intensity  $I(\nu)$  (power per unit area per unit frequency)  $I(\nu)$  of black body radiation as a function of frequency ( $\nu$ ) is shown in figure (b).



1. The intensity reaches a maximum at some frequency  $\nu_{\text{max}}$  ( $\nu_{\text{max}} \propto T$ )
2. The frequency  $\nu_{\text{max}}$  as well as the height of the peak increases with temperature.
3. The spectrum is continuous with a broad maximum.
4. The spectrum shifts towards higher frequency as the temperature increases.
5. The integral of  $I(\nu)$  over all  $\nu$  is called  $I_T$ , represents the energy emitted per unit time per area, regardless of the frequency and it is found to increase with the forth power of the temperature. This empirical fact is known as the Stefan Boltzmann Law ie :

$$I_T = \int_0^\infty I(\nu) d\nu = \sigma T^4 \text{ where}$$

$$\text{the Stefan's constant } (\sigma) = 5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4$$

## Atomic Structure:

The definition of atomic structure is the positively charged nucleus and the negatively charged electrons circling around it, with an atom. For the study of atomic structure different scientist proposed various types of theory, these theory we have called atomic theory. Eg:

i. J.J. Thomson atomic model

ii. Rutherford Atomic model

iii. Bohr's Atomic model.

iv. Sommerfeld's Atomic model.

v. Vector Atomic Model.

## Atom :

An atom is the smallest constituent of ordinary matter that has the properties of a chemical element. Every solid, liquid, gas and plasma composed of neutral atom or ionized atom. Atoms are extremely small, typically size are around 100 picometers (a ten billionth of meter).

## Bohr's Atomic Model.

A model of Hydrogen atom was proposed by Bohr in 1911. He assumed basically Rutherford nuclear model of the atom & tried to overcome the defects of his (Rutherford) model. He proposed the following two postulates:

- (i) An electron can not revolve round the nucleus in all possible orbits as suggested by the classical theory. The electron can revolve round the nucleus only in those allowed or permissible orbits for which the angular momentum of the electron is an integral

multiple of  $h/2\pi$ , where  $h$  is Planck's constant having value  $6.64 \times 10^{-34} \text{ Js}$ . These orbits are called stationary orbits and an electron revolving in these orbits does not radiate energy.

For an electron of mass  $m$  and  $v$  is the velocity of the electron in an orbit of radius  $r$ , then angular momentum

$$L = mv \times r$$

$$= mvr \times r$$

$$\frac{nh}{2\pi} = mvr^2$$

where  $n$  is the integer having value  $1, 2, 3, \dots$  which is called principal quantum number. This eqn is called Bohr's quantization condition.

1. An atom radiates energy only when an electron jumps from a stationary orbit of higher energy to one of lower energy. If the electrons jump an initial orbit of energy  $E_i$  to a final orbit of energy  $E_f$  ( $E_f < E_i$ ), a photon of frequency  $\nu = \frac{E_i - E_f}{h}$  is emitted.

### Bohr's Theory of Hydrogen spectrum:

Based on above two postulates, Bohr derived the formula for the radius of the stationary orbits and the total energy of electron in the orbit.

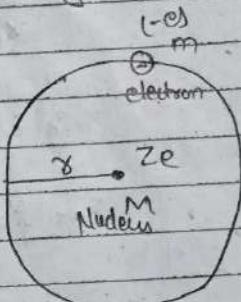
Let us consider an atom of hydrogen ( $Z=1$ ) whose nucleus has a positive charge  $Ze$  and mass  $M$  and electron of charge

(-e) and mass m move around the nucleus in an orbit of radius r as shown in figure

Since,  $M \gg m$ , the nucleus is stationary.

The electrostatic force bet'n the nucleus and the electron

$$= \frac{1}{4\pi\epsilon_0} \frac{(ze)(-e)}{r^2} \quad \text{--- (1)}$$



The centrifugal force between nucleus and electron is  $\frac{mv^2}{r}$  --- (2)

fig (1).

The system will be stable if  $\frac{mv^2}{r} = \frac{ze^2}{4\pi\epsilon_0 r^2}$  --- (3)

$$v^2 = \frac{ze^2}{4\pi\epsilon_0 rm}$$

From 1<sup>st</sup> postulate of Bohr's.

$$\frac{n\hbar}{2\pi} = mv\gamma$$

$$2\pi$$

$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$

We have,

$$\frac{n^2 h^2}{4\pi^2 m^2 r^2} = \frac{1}{4\pi\epsilon_0} \frac{ze^2}{rm} \quad [v^2 = \gamma^2]$$

1<sup>st</sup> postulate

force eq<sup>n</sup>  
(Electro = centri<sup>2</sup>)

$$r_n = \frac{n^2 h^2 e_0}{m \pi^2 c^2} \quad \text{--- (1)}$$

This is the expression for the radius of the Bohr's orbit.

For first orbit radius,

$$n=1$$

$$r_1 = \frac{1^2 \times (6.625 \times 10^{-34})^2 \times (8.85 \times 10^{-12})}{\pi \times (1.6 \times 10^{-19})^2 \times (9.11 \times 10^{-31})}$$

$$= 0.53 \text{ nm}$$

$$r_1 = 0.53 \text{ Å}$$

$$r_0 = 0.53 \times 2^2 \text{ Å}$$

$$r_n = 0.53 \times n^2$$

$$\boxed{r_n = r_0 n^2}$$

$$r_0 = \text{first radius} = 0.53 \text{ Å}$$

The radius of the  $n^{\text{th}}$  permissible orbit

$= r_0 n^2$ , where  $r_0$  is Bohr's radius having value  $0.53 \text{ Å}$ .

Velocity of the electron.

Putting the value of  $r$  in velocity expression,

$$v = nh$$

$$v_n = \frac{2\pi m}{e^2} \left( \frac{1}{2 e_0 n h} \right)$$

$$\Rightarrow \boxed{v_n \propto \frac{1}{n}}$$

which shows that the velocity of the electron closer to the nucleus move with higher velocity than those lying far away.

### Calculation of total energy:

The total energy of the electron in any orbit is the sum of its kinetic energies and potential energies. The potential energy of the electron is considered to be zero when it is at an infinite distance from the nucleus. P.E. of an electron is given by the work done in bringing the electron from infinity to that orbit. This amount of work done is obtained by integrating the electrostatic force of  $\frac{k e^2}{r}$  of attraction between the nucleus and the electron from the limits  $-\infty$  to  $r$ .

$$\text{P.E. of the electron} = \int_{-\infty}^r \frac{Ze^2}{4\pi\epsilon_0 r^2} dr = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\text{K.E. of the electron} = \frac{1}{2} \frac{mv^2}{r} = \frac{1}{2} \left( \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right)$$

Total energy of the electron in the  $n^{th}$  orbit.

$$E_n = PE + KE \\ = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{Ze^2}{8\pi\epsilon_0 r} = -\frac{Ze^2}{8\pi\epsilon_0 r}$$

Putting the value of  $r$  then

$$E_n = \frac{-me^4 z^2}{8\epsilon_0 n^2 h^2} = \left( \frac{-me^4 z^2}{8\epsilon_0 h^2} \right) \cdot \frac{1}{n^2}$$

As the value of  $n$  increases,  $E_n$  decreases. Hence, the outer orbits have greater energy than the inner orbits.

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

## Bohr's Interpretation of Hydrogen Atom.

If an electron jumps from an outer initial point  $n_1$  of higher energy to an inner orbit of  $n_2$  of lower energy, the frequency of radiation emitted is given by,

$$\nu = (\epsilon_{n_2} - \epsilon_{n_1}) / h$$

$$= \left\{ \frac{-me^4}{8E_0^2 h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \right\} / h$$

$$= \left\{ \frac{3me^4}{8E_0^2 h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \right\} / h$$

The wave number  $\bar{\nu}$  of a radiation is defined as the reciprocal of its wavelength  $\lambda$  in the vacuum gives the number of waves contained in unit length in vacuum.

$$\bar{\nu} = \frac{1}{\lambda} = \frac{c}{\lambda}$$

$$\bar{\nu} = \frac{me^4}{8E_0^2 ch^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\bar{\nu} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where 'R' is called Rydberg constant having value  $= \frac{me^4}{8E_0^2 ch^2}$

## Spectral Series of Hydrogen Atom

### I) Lyman Series

When an electron jumps from second, third, ... orbit to the first orbit of the atom, this series is called Lyman series which lies in the UV region.

Here,  $n_1 = 1$  and  $n_2 = 2, 3, 4, 5, 6, \dots$

$$\text{So, that, } \bar{V} = R \left( \frac{1}{1^2} - \frac{1}{n^2} \right) \text{ where } n = 2, 3, \dots, n$$

### II) Balmer Series

When an electron jumps from third, forth, fifth, ... orbit to the second orbit of the atom, this series is called Balmer series.

$$\text{So that, wave number } \bar{V} = R \left[ \frac{1}{2^2} - \frac{1}{n^2} \right] \text{ where } n = 3, 4, 5, \dots, n^{\text{th}}$$

This series lies in the visible region of the spectrum. The first series ( $n=3$ ) to second orbit also called  $H_{\alpha}$  line, similarly second series ( $n=4$ ) to second orbit is called  $H_{\beta}$  & so on.

### III) Paschen Series

Paschen series in the infrared region are given by  $n_1 = 3$  &  $n_2 = 5, 6, \dots, n^{\text{th}}$ . The wave number in Paschen series is,

$$\bar{V} = R \left[ \frac{1}{3^2} - \frac{1}{n^2} \right] \text{ where } n = 4, 5, 6, \dots, n^{\text{th}}$$

### IV) Brackett Series

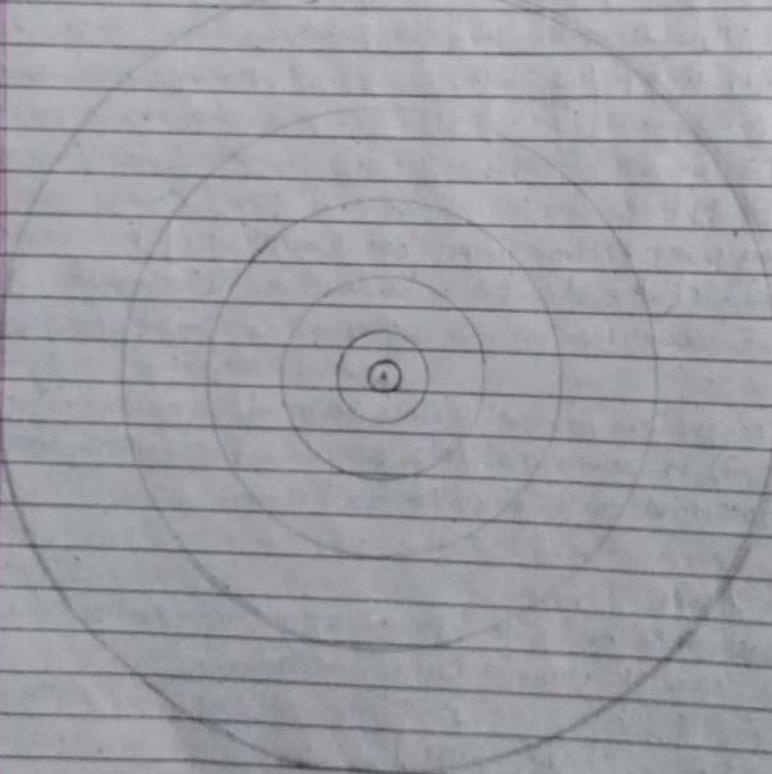
If  $n_1 = 4$  &  $n_2 = 5, 6, 7, 8, \dots, n^{\text{th}}$  orbits, we get the Brackett series, lies in the very far infrared region of the hydrogen spectrum.

$$\bar{V} = R \left[ \frac{1}{4^2} - \frac{1}{n^2} \right] \text{ where } n = 5, 6, 7, \dots$$

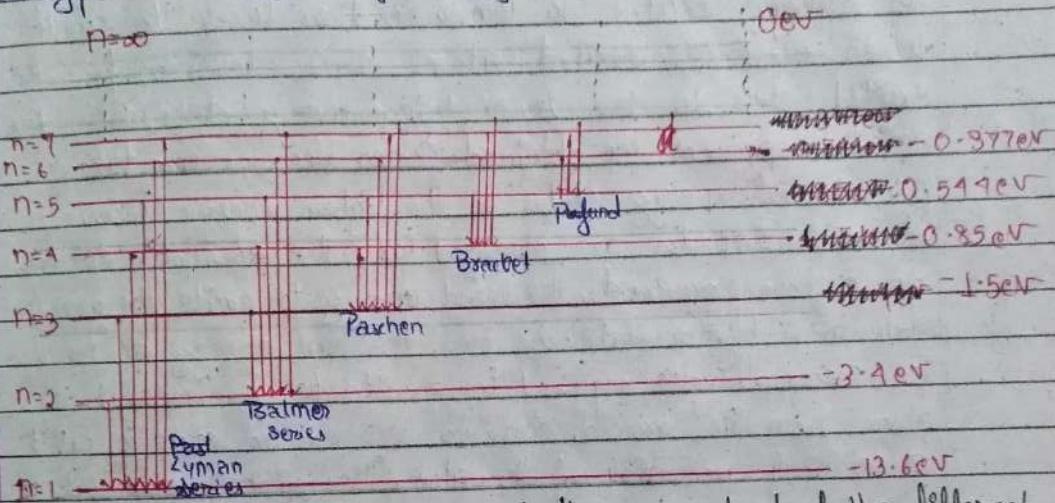
### ✓ P-fund series

When an electron jumps from any orbit  $n$  of  $6, 7, 8, \dots n^{th}$  to the  $5^{th}$  orbit of the atom, is called P-fund series. It also lies in the very far infrared region of hydrogen spectrum.

$$\bar{V} = R \left[ \frac{1}{5^2} - \frac{1}{n^2} \right] \text{ where } n = 6, 7, 8, \dots n^{th}$$



## Energy level Diagram of Hydrogen atom.



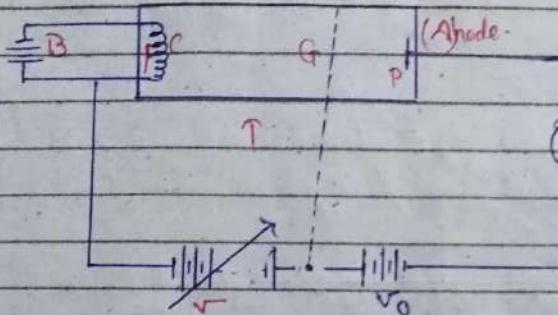
The horizontal line represent the energy levels of the different orbit of the hydrogen atom. The transition of electron different orbit of the hydrogen atom. The transition of electron from one state to another state is indicated by vertical lines with arrows. The ground state has the least energy. As the principal quantum number ' $n$ ' increases energy becomes less negative (i.e. the energy increased). When ' $n$ ' approach infinite energy approach zero. So zero level is the maximum energy state. For large value of ' $n$ ' the energy level are so close that they constitute as energy continuous.

Energy spectrum are two types depend on the transforming of energy excited to lower and or lower to excited. When less than excited atoms make transition from the excited state, to the lower lying energy state, then the emission spectrum. When electrons are taken from lower energy states to the higher energy states, absorption spectra are obtained. For the absorption spectra, an electron required the least energy to excite the ground state to a higher state. So that, the least energy expressed in electron volts required to excite the free neutral atom from its ground state to the excited state is called a critical potential of the atom. The critical potential are two types

- i. excitation potential
- ii. ionization potential

1. The minimum accelerating potential required to energies an electron which on collision can be excite an atomic called the excitation potentials of that atom. The energy required to raise the an atom from its ground state to an excited state is called excitation energy of an atom.
2. The minimum accelerating potential required to energize an electron which can ionize the atom is called the ionization potential of that atom. The minimum energy required to remove an electron from the atom to a infinite distance far away from its nucleus is called ionization energy. Generally, the ground state energy is equal to ionization energy.

## Experimental Determination of critical potential. (Frank and Hertz Experiment.)

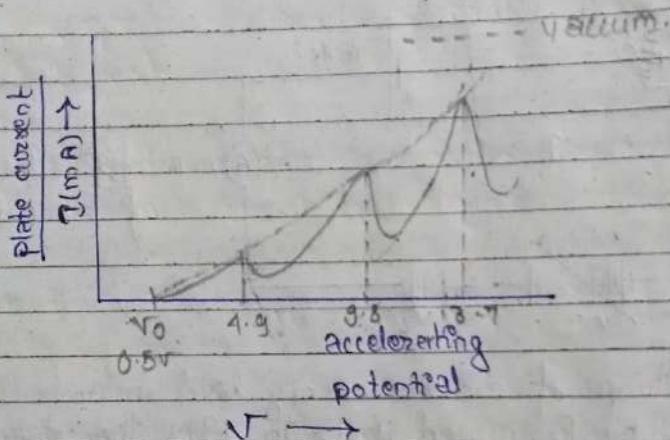


**Fig 1** Schematic Diagram of Frank & Hertz Experiment.

The existence of discrete energy level in atom was demonstrated directly by Frank and Hertz in 1914. They studied the excitation and ionization of atoms of mercury, Helium, Ne, etc. & found that the atoms of different element absorb different but definite energy i.e. the energy state in atoms are quantized in nature.

A schematic diagram of the experimental setup is shown in fig (1). The mercury vapour is filled in a glass tube (T) at a pressure of about 1 mm of Hg. Electrons are produced by heating the filament 'F' by a low tension battery 'B'. These electrons are accelerated towards a grid 'G' by a p.d. 'V' between F & G. 'V' can be varied between 0 to 60V by an arrangement of potentiometer. 'P' is the collector plate which is kept at a slightly negative potential ( $V_0$ ) with respect to 'G'. Thus, only those electron from 'G' can go to 'P' which has k.e. ' $P_1$ ' which is greater than potential diff. ' $V_0$ '. The milliammeter measures the plate current keeping  $V_0$  constant.

$V$  is gradually increased from 0 to upwards. A plot of collector current (Plate current) against the accelerating potential ' $V$ ' is shown in fig.(ii).



Explanation of graph :-

In the absence of any vapour, i.e. vacuum,  $I-V$  characteristics are shown by dotted lines.

There is no collector current for  $V < 0.5V$ . Above this value the collector current increases continuously. When the accelerating reaches a value 4.9 volt, current becomes maximum and then suddenly dips to a minimum value. Again, the plate current increases gradually till another maximum is reached. When the p.d. is just 9.8V, then suddenly current again dips steeply to a minimum so that every 4.9V significant decrease in the collector current occurs.

The fact that there is no drop in current  $V = 4.9V$ , indicates that the electrons do not lose energy through collision until they have 4.9 eV of K.E.. When the electrons collide with

a heavy atom such as Hg, there are two possible kinds of collisions:-

• Elastics & In elastic. In the case of elastic collision, the total energy of both particles before and after the collision is same. The requirement that the total energy & momentum be conserved leads to the fact that the K.E. of the light particle (electron) is hardly changed, the velocity is slightly reversed, so they will eventually be able to overcome the small retarding voltage,  $V$  and contribute to the plate current. No drop in the current will be caused by this kind of collision. In the case of inelastic collision, the external kinetic E. of the colliding particles (e & Hg) becomes internal energy of mercury atoms, absorb energy & gets excited. Some of the electrons may loose enough energy to prevent them from reaching the plate by retarding potential  $V$  i.e. drop in the current should occur for any value of  $V_0$ , so that the 1<sup>st</sup> excited state of Hg' (the smallest amount of energy that the mercury can absorb) is 4.9 eV, above the ground state.  $\therefore 2 \times 4.9 \text{ eV} = 9.8 \text{ eV}$  is the 2<sup>nd</sup> excited state and so on.

### Limitations of Frank and Hertz Experiment.

- Frank and Hertz observed the critical potential, but is not able to distinguish ionization & ionization potential.
- This method is not applicable for strong electro-negative gases like O<sub>2</sub> & F<sub>2</sub> because these gases attract electron strongly.  
The actual value of critical potential is slightly less than the observed value.

## Limitations of Bohr Atom Model.

1. Bohr's theory could explain the spectral lines of Hydrogen but couldn't explain the spectra of multi-electron atoms (other than hydrogen).
2. Bohr's theory doesn't give explanation, why only circular orbits are possible around the nucleus.
3. Bohr's theory doesn't give explanation about the relative intensities of spectral lines.
4. Bohr's theory doesn't account for the wave nature of electron.

# Black Body

Black body radiation. Explain by quantum theory

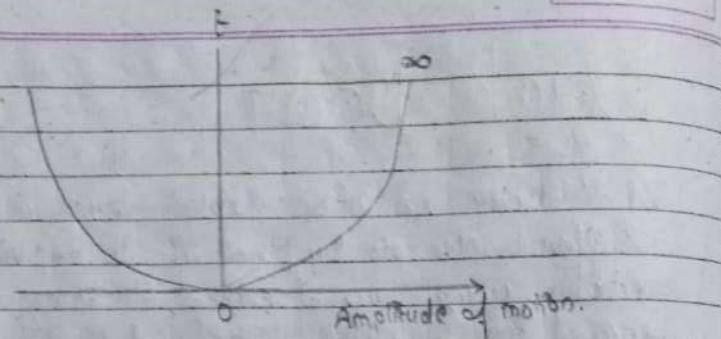
- Different attempts by physicist to explain the black body spectrum using law of classical electromagnetism & thermodynamics proved was unsuccessful. The quantum idea introduced by Planck to explain the spectrum of black body i.e. to find the empirical mathematical expression for  $I(\lambda)$  that would fit the experimental data is also called the Planck's theory, was further expanded by Albert Einstein i.e. light incident on a metal will cause electron to be ejected from the metal surface is called photoelectric effect, give theoretical and experimental support to describe black body radiation by quantum mechanically.

## 1. Planck's Theory

The Planck's theory introduced quantum ideas to explain the distribution of energy in the spectrum of a black body. From his hypothesis, "A system undergoing harmonic motion with frequency ( $\nu$ ) can only have and therefore can only emit energy given by  $(E = nh\nu)$ , where  $n = 1, 2, 3 \dots$ "

$$\& h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ Js}^{-1}$$

We know that, the energy of a harmonic oscillator is proportional to the amplitude of motion. In classical treatment, such as an oscillatory spring, <sup>this</sup> amplitude may vary continuously from 0 to  $\infty$  which is shown in fig (1).



In contrast, Planck postulate that atomic oscillators can have only discrete energy levels as shown in fig (2) which was the main discrepancy, in

black body radiation did not successfully describe by classical theory. By Planck's hypothesis, an oscillator (such as the atoms in the walls of the cavity) can take only certain values of the energy, when they loose that energy (by emitting electro-magnetic radiation). They loose it in multiple of  $\hbar\nu$ . These small quantity of energy are called quanta (singular). He derives  $I(\nu)$  that match the experimental data which expression is

$$I(\nu) = \frac{2\pi h\nu^3}{c^2} \left\{ \exp\left(\frac{h\nu}{k_B T}\right) - 1 \right\}$$

$$\Rightarrow \frac{2\pi h\nu^3}{c^2} \left( e^{\frac{h\nu}{k_B T}} - 1 \right)$$

where,  $c$  is velocity of light,  $k_B$  is Boltzmann constant,  $\nu$  is frequency of electromagnetic wave and  $T$  is absolute temperature of black body.

## 2. Photoelectric effect:

The experimental fact of Albert Einstein's photoelectric effect also helps to explain spectrum of black body radiation. He stated that, "whenever light of electromagnetic radiation (such as X-ray, UV-ray, Y-ray, visible & infrared light, etc.) fall on a small metal plate, when illuminated by light of suitable wavelength is called photoelectric effect. The electrons emitted are known as photoelectrons."

### Experimental fact:

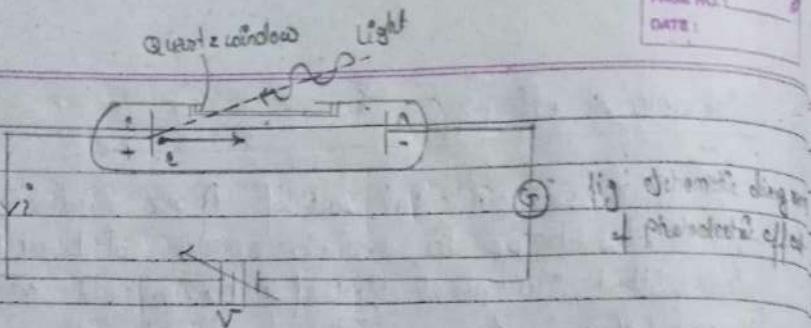
When a photon of light of frequency ( $\nu$ ) is incident on a metal, the energy is completely transferred to a free electron in the metal. A part of energy is acquired by the electron is used to pull out the electron from the surface of metal and rest of it is utilized in imparting kinetic energy to the emitted electron.

$$\text{ie. } h\nu = h\nu_0 + \frac{1}{2}mv^2 \quad \dots \quad (1)$$

$$\Rightarrow h\nu = \phi + \frac{1}{2}mv^2$$

which is the relation is known as Einstein photoelectric equation.

where  $\nu_0$  is the threshold frequency which just ejects an electron from the metal,  $\phi$  is the light frequency of incident on metal,  $v$  is the velocity of imparted/rejected electron. This eqn (1) is full agreement with existing data. This cannot be explained by classical theory.



Einstein was able to explain the photoelectric effect by proposing a theory about the nature of electromagnetic radiations that was dramatically different from the classical theory based on continuous electromagnetism. According to him, the energy of an electromagnetic wave of frequency ( $\nu$ ) is not continuously distributed over the entire wavefront but instead it is localized in small bundles called photons.

### Duality (Dual Nature of Light)

Wave + Particle

(Continuous)      (Discrete)

The phenomenon of interference, diffraction & polarization of light can only be explained on the basis of wave theory of light. So that these phenomenon allows that light possess wave nature. But, certain phenomena such as photoelectric effect, Compton effect, and discrete emission and absorption of radiation can only be explained on the basis of quantum theory (particle nature). According to this theory, light propagates in a small packets or quanta and hence behave like particle. This shows that light possess particle nature also. In conclusion we can say that light(radiation) possess dual (wave & particle) nature which is called duality.

## De-Broglie's Hypothesis

In 1925, Louis De-Broglie assumed that existence of a natural symmetry in nature & propose the dual character exhibited by photons should equally apply to all material particles. Accordingly, he hypothesized, "the motion of a particle is governed by the wave propagation properties of a wave, the wavelength ' $\lambda$ ' and frequency ' $\nu$ ' of a matter wave associated with a particle of momentum ' $p$ ' and energy ' $E$ '.

i.e.

$$\lambda = \frac{h}{p} \quad \text{and} \quad E = h\nu$$

where,  $h$  is Planck's constant,  $m$  is the mass of particle or matter &  $\nu$  is the velocity of this particle.

The wave associated with a moving particle are called De-Broglie wave or matter wave and the wavelength ' $\lambda$ ' associated with matter waves is called De-Broglie wavelength. It concludes that greater the momentum, there will be shorter wavelength or higher the frequency and vice versa.

Proof:

According to Planck's theory;

$$E = h\nu \quad \dots \dots \quad (1)$$

where,  $E$  is the energy of photon and  $\nu$  is frequency of photon.

If photon is considered as a particle of mass ' $m$ ' moving with velocity of light ' $c$ ', then according to Einstein's mass-energy relation,

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

We know,

Equating (1) and (2),

$$h\nu = mc^2$$

$$\text{or, } h \cdot c = mc^2$$

$\lambda$

$$\text{or, } \frac{h}{\lambda} = mc - \dots \quad (3)$$

 $\lambda$ 

Again, we know, momentum of photon is

$$p = mc$$

Putting value of  $mc$  in eqn (3),

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

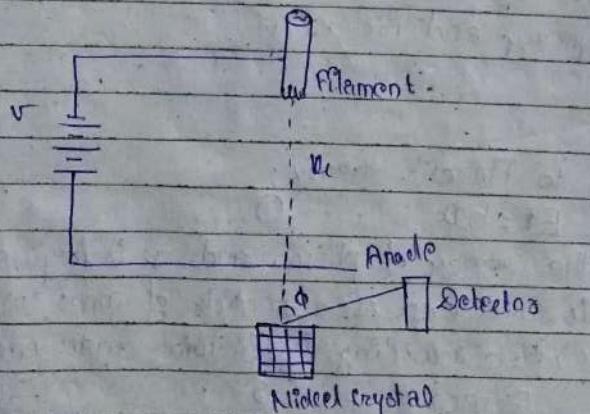
 $\lambda$ 

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

Hence, proved,

Experimental Verification of De-Broglie's Hypothesis:

For the experimental verification of De-Broglie hypothesis, Davisson and Germer in 1927 AD perform a experiment choose a particle of mass (namely) such as electron which is shown in fig (1).



fig(1) Schematic diagram of apparatus setup by Davisson & Germer.

where a beam of electron strikes a single crystal of Nickel with a kinetic energy  $eV$ . The beam strikes a single crystal

of nickel and intensity of scattered beam can be measured for different angle  $\phi$  and various voltage  $V$ . If the propagation of beam is particle like while rotating the electron for observing the variation in intensity of a certain value of potential 54V and angle  $50^\circ$  is maximum as shown in figure (2)

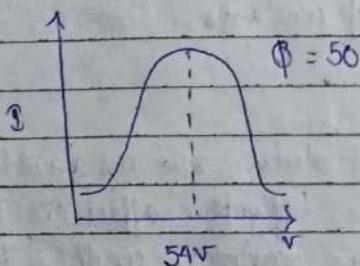


fig (2)

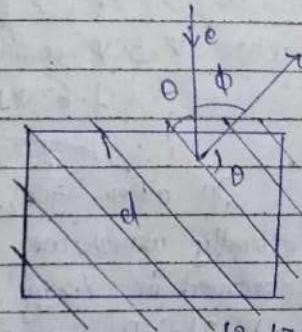


fig (3):

It concludes that if the propagation of the beam is like a particle then any incoming angle will observe the same number of particles rebounding at a similar angle regardless of their velocity & potential through which they have been accelerated as shown in fig (3).

It concludes that in uniform intensity of different value of  $\phi$  produces the diffraction of electrons as a wave and is the direct experimental elements of de-Broglie hypothesis.

Let us consider an electron of mass 'm' is accelerated with velocity 'v' by the accelerating potential 'V'. Then,

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

$$\text{i.e. } v = \sqrt{\frac{2eV}{m}}$$

We know,

From de-Broglie hypothesis,

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

$$= \frac{h}{m \cdot 2eV/m} = \frac{h}{2meV}$$

when  $V = 54V$ , using st values of constants,

$$\lambda = 1.67 \times 10^{-10} m$$

On other hand, if the incoming electron are not particles but are actually waves, we would expect a diffraction effect like the one observed in X-ray when the Bragg's scattering condition is satisfied  $n\lambda = 2d \sin \theta$ . For nickel,  $d = 0.91 \text{ \AA}$ .

For calculating  $\theta$ , from fig ③

$$\phi + \theta + 40^\circ = 180^\circ$$

When  $\phi = 50^\circ$ , then  $\theta = 65^\circ$ .

For 1<sup>st</sup> order diffraction,

$$\lambda = 0.2 \times 0.91 \times 10^{-10} \times \sin 65^\circ \\ = 1.65 \times 10^{-10} m$$

This is good agreement between the predicted de-Broglie wavelength for electron for this energy and wavelength calculated by X-ray diffraction experiment. So, this experiment confirm de-Broglie hypothesis, particle have wave properties so there is certain wavelength which is calculated by  $\lambda = \frac{h}{mv}$ .

## Heisenberg Uncertainty Principle:

Statement:

It is impossible to specify precisely and simultaneously the values of both members of particular pairs (canonically conjugated) of physical variables that describes the behaviour of an atomic system.

According to him, the position and momentum, energy and time, and angular position and angular momentum are canonically conjugate variables, which cannot be determined simultaneously to any desired degree of accuracy. If a position ( $x$ ) has an uncertainty ( $\Delta x$ ) and the corresponding momentum component ( $p$ ) has uncertainty ( $\Delta p$ ) then, uncertainties are found to be related in general by an  $\geq$  inequality

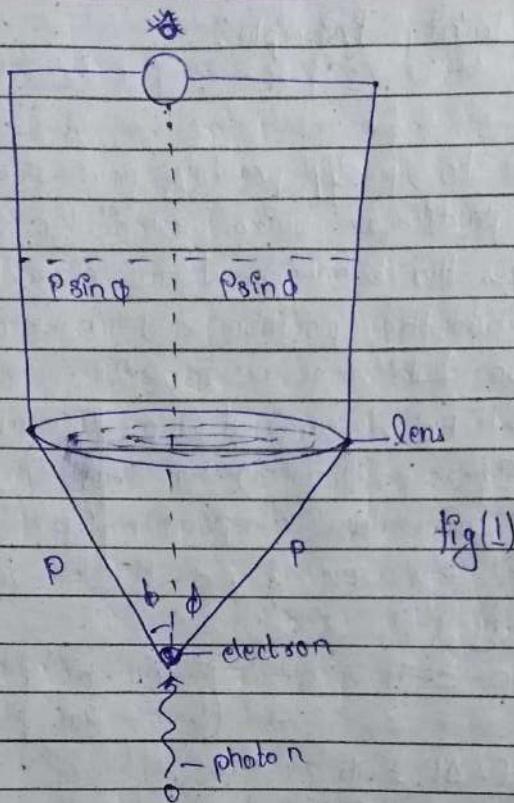
$$\text{i.e. } \Delta x \cdot \Delta p \geq \hbar \quad [ \frac{\pi \cdot h}{2\pi} ]$$

Similarly,  $\Delta E \cdot \Delta t \geq \hbar$   
 $\Delta L \cdot \Delta \theta \geq \hbar$

### Physical Origin of Uncertainty Principle

The uncertainty principle is a direct consequence of the De-Broglie's hypothesis. Bohr's purpose is a 'thought' experiment which illustrate the physical origin of uncertainty principle.

Suppose that to determine the position of an electron with a hypothetical microscope. To see electron, it must ~~be~~ shine light on the electron; it is ~~at~~ the scattered photons that the eye ~~safely~~ sees. Any photon scattered by the electron with an angle equal to  $2\theta$  will be focused by the microscopic lens and will be detected by the eye as shown in fig (1).



It is clear that the collision of photons with the electron will change the momentum of electron. A photon may enter the objective lens anywhere within the range  $-\phi$  to  $\phi$ . This implies that  $x$ -component of momentum of this photon could have any value between  $-p \sin \phi$  to  $+p \sin \phi$ , where,  $p$  is the magnitude of momentum of the photon. We conclude that the uncertainty of the  $x$ -component of the momentum of photon is,

$$\Delta p_x (\text{photon}) = p \sin \phi + p \sin \phi \\ = 2p \sin \phi \quad - \quad (1)$$

## Conservation of the linear momentum.

Conservation of the linear momentum necessitates that if photon acquires a certain momentum in the  $\hat{x}$  direction, the electron must acquire the same amount of momentum in the opposite direction. This means that the uncertainty in the momentum of the electron also has the same magnitude.

$$\text{i.e. } \Delta p_{x(\text{electron})} = \Delta p_{x(\text{photon})} = \frac{2p \sin \phi}{\lambda} \quad \text{--- (ii)}$$

We know that, momentum of the photon is given by de Broglie hypothesis

$$p_{\text{photon}} = \frac{h}{\lambda}$$

then,

$$\Delta p_{x(\text{electron})} = \frac{2h \sin \phi}{\lambda} \quad \text{--- (iii)}$$

Thus, we see that in the process of locating the electron, we have introduced an uncertainty in its momentum.

According to eqn (iii), we could reduce the uncertainty in momentum in two ways,

- a) By reducing the angle  $\phi$  subtended by the lens by making the aperture of the lens small.
- b) By using the photon of longer wavelength.

These

Unfortunately, these two factors lead to an increase in the uncertainty of the position of the electron. It illustrates that the measuring process itself introduce an uncertainty.

Major particle

# Matter Wave and Uncertainty Principle

(Relation between matter wave and Uncertainty Principle)

The propagation of a particle is governed by a wave function  $\psi(x, t)$ . Let us write the specific mathematical form of the wave function  $\psi(x, t)$  at a common type of wave, the sinusoidal wave represented by the

$$\psi(x, t) = A \sin(Kx - \omega t) \quad \dots \dots (1)$$

where,  $A$  = amplitude same for all point in space.

$t$  = time period ,  $x$  = position.

$\lambda = \frac{2\pi}{K}$  ;  $K \rightarrow$  wave propagating vector  
 $\& \lambda \rightarrow$  wave length.

$$2\pi \times \frac{\omega}{2\pi} = \omega ; \omega \rightarrow \text{frequency}.$$

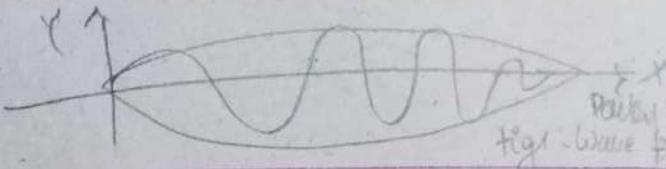
The wave travels towards increasing value of  $x$  with a velocity ( $v$ ) =  $\omega \times \lambda$

$$= \omega \times \frac{2\pi}{K} = \frac{\omega}{k}$$

$$\therefore v = \frac{\omega}{k} \quad \dots \dots (1)$$

Since the particle has well defined momentum and energy. Here, the amplitude of the wave is same & values of  $x$ . The particle can be found with equal probability at any point in space, i.e. the particle is completely unlocalized i.e.  $\Delta x = \infty$ .

$$\text{i.e. } \Delta x = \infty$$



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However, well-defined ' $\lambda$ ' implies a well defined momentum of the particle i.e.  $\Delta p \rightarrow 0$ . This is in agreement with uncertainty principle. Thus, although the wave function of the equation can be used to describe a particle of well defined momentum and energy, the wave packet is a complete fails of localization. Let us calculate the velocity of particle and wave. We have, from de-Broglie's relation,

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

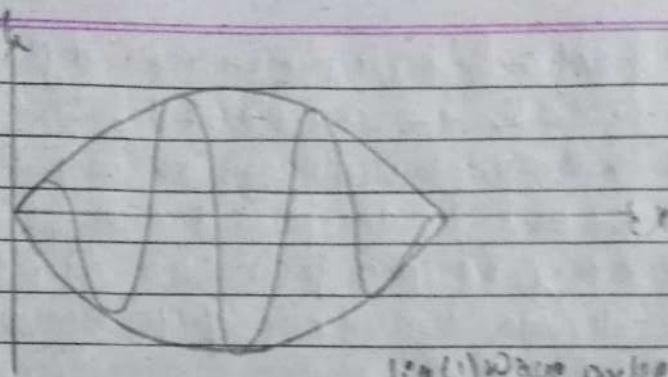
$$\text{and, } E = h\nu$$

We know, velocity of wave,  $v_{\text{wave}} = \nu \times \lambda$

$$\begin{aligned} &= \frac{E}{h} \times \frac{h}{mv} : \text{Energy} \\ &= \frac{1}{2} mv_{\text{particle}}^2 : \text{Energy} \\ \Rightarrow v_{\text{wave}} &= \frac{1}{2} v_{\text{particle}} \quad \dots \text{(iii)} \end{aligned}$$

The velocity of the wave is half the velocity of particle (this shows that the velocity of wave is not same as the velocity of particle i.e. in guides) because the amplitude of the wave is same everywhere in space. However, this condition could not be acceptable in the case of a partially localized particle.

To describe a particle i.e. partially localized in amplitude i.e. different from zero only over a small region of space where there is a chance of finding the particle which is as shown in figure (1).



fig(1) Wave packet.

Mathematically, such a wave packet is obtained by adding / mixing together of infinitely large number of sinusoidal travelling wave of slightly different wavelength and frequency described by  $\psi(x,t) = \int_{-\infty}^{\infty} A(k,\omega) \sin(kx - \omega t) dk \quad \text{eqn(4)}$

Thus the amplitude become a function of wavelength and frequency. The wavelength associated with eqn(4) is called matter wave. In this case, the wave packets doesn't have the well defined wavelength and the particle associated with it will not have a well defined momentum, this proves the uncertainty principle.

### Phase velocity.

The rate at which phase of the wave propagate in space is known as phase velocity.

1 (OR)

It is the velocity of particular phase in the wave.

(OR)

The phase velocity of a monochromatic wave  $\lambda \& f_{\text{wave}}$  is the velocity with which a definite phase of wave such as crest or trough is propagated in the medium.

An equation of plane progressive wave with amplitude 'a' in constant phase ( $kx - \omega t$ ) is given by:

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

$$\text{where, } \omega = 2\pi\nu \quad \& \quad K = \frac{2\pi}{\lambda}$$

We know that,

For constant phase,

$$kx - \omega t = \text{constant}$$

Differentiating w.r.t. to  $t$ ,

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

$$\frac{dx}{dt} = \frac{\omega}{K} = \frac{\text{Velocity}}{\text{Phase}}$$

which is the required relation for phase velocity.

Phase velocity of De-Broglie wave:

According to De-Broglie's hypothesis, a material particle in motion have a wave associated with it has a wavelength of

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

$$\& E = h\nu$$

$$\text{or, } \nu = \frac{E}{h} \quad \dots \quad (ii)$$

According to Einstein mass-energy relation,

$$E = mc^2$$

Then eqn (ii) becomes

$$\nu = \frac{mc^2}{h} \quad \dots \quad (iii)$$

The De-Broglie wavelength,  $\lambda_p$  is given that,

$$\lambda_p = h/\lambda$$

$$= \frac{mc^2}{h} \times \frac{h}{mv}$$

$$= \frac{c^2}{v} \quad \text{--- (iv)}$$

According to Einstein theory of relativity, the speed of light 'c' in vacuum is maximum that can be attained by a particle in nature. But eqn (iv) implies that De-Broglie wave must be greater than 'c' which is unexpected result. Furthermore according to this result, the De-Broglie wave associated with the particle would travel faster than the particle itself. Thus leaving the particle far behind. Hence it is clear that material particle can't be equivalent to a single wave train. To remove this difficulty the concept of group wave is needed.

Schrodinger postulated that material particle in motion is equivalent to a wave packet rather than a single wave train.

### (Group velocity)

In order to describe a localized variable, we must use a wave particle, we must mix two travelling waves that differ slightly in wavelength and frequency

$$\Psi_1 = A \sin(kx - \omega t)$$

$$\Psi_2 = A \sin((k + \Delta k)x - (\omega + \Delta \omega)t)$$

wavelength      frequency

where  $\Delta K \ll K$  &  $\Delta \omega \ll \omega$

The resulting of  $\psi_1$  &  $\psi_2$  is represented by,

$$\begin{aligned}\psi(x, t) &= \psi_1 + \psi_2 \\ &= A [\sin(kx - \omega t) + \sin((k + \Delta k)x - (\omega + \Delta \omega)t)] \\ &= 2A \cos\left(\frac{\Delta K}{2}x - \frac{\Delta \omega}{2}t\right) \sin(kx - \omega t) \quad \dots \quad (1)\end{aligned}$$

where we have used the approximation  $(2k + \Delta k) \rightarrow 2k$  &  $(2\omega + \Delta \omega) \rightarrow 2\omega$

The resulting wave is the product of two travelling waves. The first term of eqn(1) defines a wave having a much larger wavelength and much smaller frequency. Similarly second term represents a wave having roughly the same frequency and wavelength as the original wave.

A snapshot of  $\psi$  is shown in fig(1) where it does not have a single wave packet but rather a series of wave-packets.

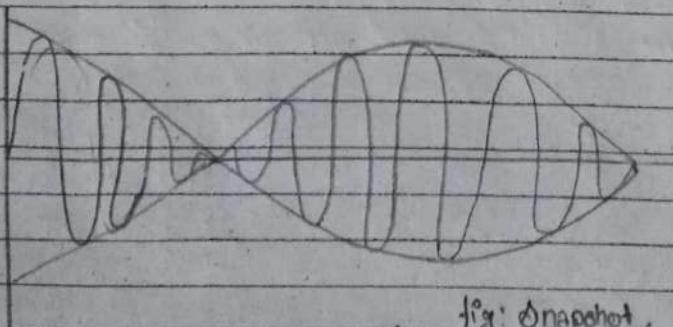


fig: Snapshot.

The velocity of waves inside the envelope is the same as the velocity of the individual wave.

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

Similarly, the wave packets travel with velocity, called the group velocity ( $v_g$ ).

$$v_g = \frac{\Delta\omega/2}{\Delta k/2} = \frac{\Delta\omega}{\Delta k}$$

which is required relation for group velocity.

# Method of Quantum Mechanics

Schrodinger's wave eqn (S.W.F.)

A differential eq whose soln yield the possible wave function that can be associated with a particle in a given physical situation. This eqn is known as Schrodinger eqn which tell us how the wave function changes as the result of the force acting on the particle.

The Schrodinger theory of Quantum Mechanics.

This is the fundamental mech. theory of quantum mechanics which is importantly <sup>same</sup> as the 2nd law of Newton law of motion in the classical mechanics. There are two types of Schrodinger wave eqn:

i. Time dependent Schrodinger wave eqn,

ii. Time independent Schrodinger wave eqn.

Time dependent Schrodinger's wave eqn,

If a particle has a well defined energy and momentum we can use a sinusoidal travelling wave i.e either

$$\text{i.e. } \Psi = A \sin(\omega t - kx)$$

$$\text{i.e. } \Psi = A \cos(\omega t - kx)$$

$$\text{i.e. } \Psi = A \sin(Kx - \omega t)$$

$$\Psi = A \cos(Kx - \omega t)$$

or linear combination of both. As we have seen, if we want to describe a free particle which is partially localized, we could use a wave packet. The Schrodinger

Theory tells us how to obtain the wave function  $\psi(x, t)$  associated with a particle when we specify the force acting on the particle by giving the potential energy associated with the force. Now, the wave function  $\psi$  is function of space & time, the equation contains derivatives w.r.t.  $x, y, z$  and w.r.t. time 't' but we will primarily concern in  $x$  direction only. The total energy of particle,

$$E = P.E. + K.E.$$

$$E = E_p + \frac{P^2}{2m} \quad \dots \dots \dots (i)$$

Multiplying by  $\psi$  in eqn (i),

$$E \cdot \psi = E_p \cdot \psi + \frac{P^2}{2m} \cdot \psi \quad \dots \dots \dots (ii)$$

From  $\Rightarrow$  the relation of energy, and momentum ' $P$ ' with the operators form,

$$E = i\hbar \frac{d}{dt} \quad \text{and} \quad P = i\hbar \frac{d}{dx}$$

Substituting  $E$  and  $P$  in eqn (ii) we get,

$$i\hbar \frac{d}{dt} \psi = E_p \cdot \psi + \left( i\hbar \frac{d}{dx} \right)^2 \cdot \frac{\psi}{2m}$$

$$\frac{i\hbar d\psi}{dt} = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + E_p \psi = \frac{d}{dt} \frac{i\hbar d\psi}{dx}$$

$$+ \frac{i\hbar d\psi}{dt}$$

This is the one dimensional time dependent Schrodinger wave equation. If the potential energy  $E_p$  is known, this eqn

can be solved in principle find the solution will give the possible wave function that we can associate with the particle.

Time-Independent Schrödinger Wave Eqn

The S.I.E. in one dimensional is a partial differential eqn that involves time 't' and position 'x' as the independent variables. Using separation of variable method, let us try to find a solution i.e. a product of two functions (time & position)

$$\psi(x, t) = X(x) \Gamma(t) \quad \text{--- (1)}$$

Let us substitute the value of eqn(1) into time-dependent eqn of motion

$$-\frac{\hbar^2}{2m} \Gamma(t) \frac{\partial^2 X(x)}{\partial x^2} + E_p(x) X(x) \Gamma(t) = i\hbar X(x) \frac{d\Gamma(t)}{dt} \quad \text{--- (II)}$$

Divide through by  $\Gamma(t) X(x)$  we get,

$$-\frac{\hbar^2}{2m} \frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} + E_p(x) = i\hbar \frac{d\Gamma(t)}{\Gamma(t) dt} \quad \text{--- (III)}$$

The right side of the eqn(3) is dependent only time & the left side only dependent on position only so that we can equate both sides with any quantity ( $C$ ).

$$i\hbar \frac{d\Gamma(t)}{\Gamma(t) dt} = C \quad \text{--- (4)}$$

$$-\frac{\hbar^2}{2m} \frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} + E_p(x) = C \quad \text{--- (5)}$$

From eqn (4),

$$\frac{\partial \Gamma(t)}{\Gamma(t)} = -i \cdot C_r dt \quad \dots \dots (6)$$

Integrating eqn,

$$\Gamma(t) = e^{-\frac{i}{\hbar} C_r t} \dots \dots (7)$$

Let us operate on the wave function  $\Psi(x, t)$  with the energy operator  $i\hbar \frac{\partial}{\partial t}$ .

$$E \Psi_{\text{in}} = i\hbar \frac{\partial}{\partial t} \Psi(x, t)$$

$$E \Psi_{\text{in}, t} = i\hbar \frac{\partial}{\partial t} (\chi_{\text{in}} \Gamma(t))$$

$$E \Psi(x, t) = i\hbar \frac{\partial}{\partial t} (\chi_{\text{in}} d\Gamma(t))$$

$$E \Psi(x, t) = i\hbar \chi_{\text{in}} \frac{\partial}{\partial t} (e^{iGt/\hbar})$$

$$E \Psi(x, t) = i\hbar \chi_{\text{in}} \left( -\frac{iG}{\hbar} \right) \cdot e^{\frac{iGt}{\hbar}}$$

$$E \Psi(x, t) = G \chi_{\text{in}} \Gamma(t)$$

$$E \Psi(x, t) = G \Psi(x, t) \dots \dots (8)$$

Comparing eqn (7) with  $i\hbar \frac{\partial \Psi}{\partial t} = E \Psi$

we get,  $E = G$  the separation  $G_r$  is the total energy of the system.

Thus, the time dependent part of the wave function  $\Psi(x, t)$  is  $\Gamma(t) = e^{-\frac{iET}{\hbar}} \rightarrow (g)$  (Replacing  $G$  by  $E$ )

To find the space-dependent part of the wave function, we have to solve the differential equation (5), where  $G$  is now becomes,  $E$ ,

$$-\frac{\hbar^2}{2m} \frac{d^2 \chi(x)}{dx^2} + E_p(x) \chi(x) = E \chi(x) \quad \text{--- (1)}$$

which is called the time independent S.W.F. For a given  $E_p(x)$  the eq<sup>n</sup> has to be solved to find the possible  $\chi(x)$ 's that can be associated with the system.

### Application :

- ① For a free particle.

Let us consider a free particle moving along  $x$ -axis with definite momentum ( $p = mv$ ) and definite energy ( $E = \frac{1}{2}mv^2$ ). If no other force act on the particle i.e. ( $F=0$ ), the potential energy, ( $E_p = \text{constant}$ ) which can be assumed zero. i.e.  $E_p=0$ .

The time dependent S.W.F. is

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + E_p = i\hbar \frac{d\psi}{dt}$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = i\hbar \frac{d\psi}{dt} \quad \text{--- (1)}$$

The solution would be in the form of travelling wave with linear coefficient of sine and cosine.

$$\text{i.e. } \psi = A \cos(kx - \omega t) + B \sin(kx - \omega t) \quad \text{--- (2)}$$

This can be written in another form

$$\psi = A e^{i(kx - \omega t)} \quad \text{--- (3)}$$

$\therefore$  We have,

$$\frac{\partial^2 \Psi}{\partial x^2} = (ik)^2 A e^{i(kx - \omega t)} = k^2 \Psi$$

$$\frac{\partial \Psi}{\partial t} = -i\omega \Psi$$

Substituting these values in eqn (1), we get,

$$\text{or, } -\frac{\hbar^2}{2m} (ik)^2 A e^{i(kx - \omega t)} = i\hbar \cdot -i\omega$$

We get,

$$\frac{\hbar \omega}{2m} = k^2 \frac{\hbar^2}{2m} \quad \dots \dots \quad (4)$$

From de Broglie's hypothesis,

$$E = \hbar v = \hbar \omega \quad \Rightarrow \frac{E}{\hbar \omega} = 1$$

$$E = \hbar \omega$$

$$\text{and, } p = \frac{\hbar}{\lambda} = \frac{\hbar}{2\pi/k} = \frac{\hbar \cdot k}{2\pi}$$

then,

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

$$\frac{\hbar \omega}{2m} = \frac{k^2 \hbar^2}{2m} \quad \dots \dots \quad (5)$$

which is similar to the result obtained in S.I.D.E.

## Physical significance of $\psi$ (wave function):

The wave function  $\psi(x, t) = A e^{i(kx - \omega t)}$  is not a real because it has an imaginary component. So that, wave function,  $\psi$  itself has no physical meaning but if it is  $|\psi|^2$ , that has a physical significance. When  $\psi^*$  is a complex function of  $\psi$ , we can write by mathematical definition,

$$\begin{aligned} |\psi|^2 &= \psi^* \cdot \psi \\ &= (A)^* e^{-i(kx - \omega t)} \cdot (A) e^{i(kx - \omega t)} \\ &= A^* A \\ &= |A|^2 \end{aligned}$$

This result is a real quantity.

$$\text{i.e. } |\psi|^2 = A^2$$

which it must be because an imaginary probability is not defined mathematically. In this equation, the probability of finding the particle at any point in space is given by

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

and therefore  $|\psi|^2$  is considered a probability density and when properly normalized, that must have both real and positive for a normalized wave function.

For 1 dimensional,

$$\begin{aligned} \text{Probability (P)} &= \int |\psi|^2 dx \\ &= 1 \end{aligned}$$

For 3 dimensional,

$$P = \iiint |\psi|^2 dx dy dz$$

## Second application of Schrodinger Wave equation

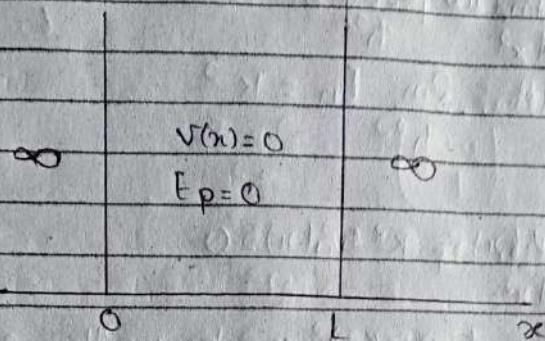


fig: Infinite potential well

let us consider an electron of mass 'm' confined within a 1 dimensional line in a crystal of length 'l' bounded by infinite potential wall at the end of length  $x$  as shown in fig above. Then, the potential for this  $\Rightarrow$  free particle in one dimensional is given by,

$$E_{pl(n)} = 0 \quad ; \quad 0 < x < l$$

$$E_p(x) = \infty \quad ; \quad x \geq l \quad \& \quad x \leq 0$$

Now, the wave function  $\psi_n(x)$  of the electron is the solution of Schrodinger eqn. Therefore, Schrodinger equation for electron in one dimensional case can be written as,

$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + E_{pl(n)} \right) \psi_n(x) = E_n \psi_n(x)$$

$$\text{or, } \frac{d^2 \psi_n}{dx^2} - \frac{2m E_{pl(n)}}{\hbar^2} \psi_n(x) = - \frac{2m E_n \psi_n(x)}{\hbar^2}$$

$$\text{or, } \frac{d^2 \psi_n}{dx^2} - \frac{2m E_p(x)}{\hbar^2} \psi_n(x) + \frac{2m E_n \psi_n(x)}{\hbar^2} = 0$$

For,  $0 < n \leq 1$ ,  $F_{pl}(x) = 0$

$$\frac{d^2\psi_n(x)}{dx^2} + \frac{2m}{\hbar^2} E_n \psi_n(x) = 0 \quad \dots \dots \quad (1)$$

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

Then,

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

The solution of eqn (2) can be written as,

$$\psi_n(x) = A \sin kx + B \cos kx \quad \dots \dots \quad (3)$$

Applying the boundary condition,

$$\text{at } x=0, \psi_n(0) = 0 \quad \dots \dots \quad (A)$$

$$\text{at } x=1, \psi_n(1) = 0 \quad \dots \dots \quad (B)$$

By applying first boundary condition,

$$\psi_n(x) = A \sin kx + B \cos kx$$

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

$$\Rightarrow B = 0$$

Applying another boundary condition,

$$\psi_n(1) = A \sin kL + B \cos kL$$

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

Since,  $A \neq 0$  so,  $\sin kL = 0 = \sin n\pi$   
 $\Rightarrow k = \frac{n\pi}{L}$

Now, eqn (3) becomes,

$$\begin{aligned}\psi_n(x) &= A \sin Kx + B \cos Kx \\ &= A \sin \frac{n\pi}{L} x\end{aligned}$$

To determine the value of A, let us normalized the wave function in the region  $0 < x < L$ , then

$$\text{normalize } \int_0^L \psi_n^2 dx = 1 \Rightarrow \int_0^L A^2 \sin^2 n\pi x \cdot A^2 \sin^2 n\pi x dx = 1$$

$$\Rightarrow \int_0^L |A|^2 \sin^2 n\pi x dx = 1 \Rightarrow |A|^2 \int_0^L (1 - \cos^2 n\pi x) dx = 1$$

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

$$\Rightarrow |A|^2 \cdot L = 1 \Rightarrow |A| = 1$$

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

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

∴ the complete wave function is  $\psi_n(x) = \sqrt{\frac{2}{L}} \sin n\pi x$  --- (4)

Now, the complete solution of the particle is

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

For the energy Eigen value, we have the relation  
 Above  $\frac{e^2}{2} = \frac{2mE_n}{\hbar^2}$  and  $k = \frac{n\pi}{L}$

so that,

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

for all members of  
and,  $L > 0$  implies  
L being

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

$E_n \propto n^2$

Hence, this relation shows that energy of electron is proportional to square of the state of electron. If we plot a graph in between  $E_n$  with  $n$  as shown in fig 2.

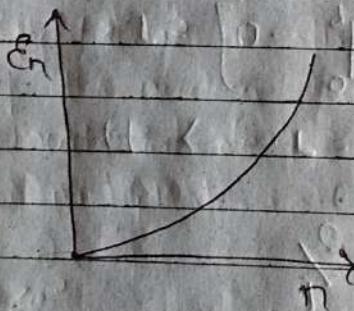


fig (2)

We have, normalized wave function  $\psi_n(n) =$

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

For different level of  $n$ , we have the wave functions at different states.

For  $n=0$  (ground state),

$$\Psi_0(x) = \sqrt{\frac{2}{L}} \sin 0 = 0$$

at  $x=0$ ,  $\Psi_0(0)=0$

$x=L$ ,  $\Psi_0(L)=0$ .

and, for  $n=1$ ,

$$\Psi_1(x) = \sqrt{\frac{2}{L}} \sin \frac{1\pi x}{L} = 0 \text{ at } x=0.$$

$$\Psi_1(L) = \sqrt{\frac{2}{L}} \sin \frac{1\pi L}{L} = 0 \text{ at } x=L.$$

$$\Psi_1\left(\frac{L}{2}\right) = \sqrt{\frac{2}{L}} \sin \frac{1\pi L/2}{L} = \sqrt{\frac{2}{L}}, \text{ at } x=\frac{L}{2} \text{ is maximum}$$

Thus the wave function is maximum as  $x=\frac{L}{2}$ . Similarly, for  $n=2, 3, \dots$  get such types of nature of wave as shown in figure 3.

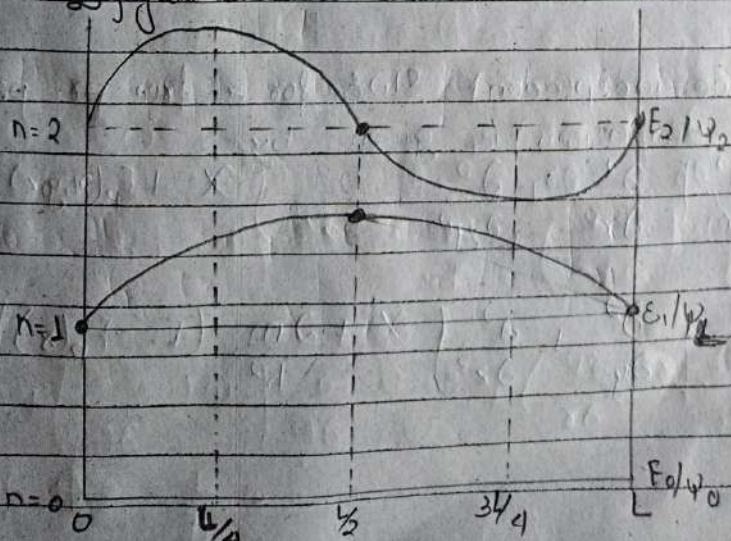


fig : Energy levels  
and corresponding  
wave function

## Solution of Schrodinger wave eqn for Hydrogen atom

According to the Bohr's Atom model of the hydrogen, potential energy of the electron in the electric field of a nucleus is given as,

$$\begin{aligned} E &= \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} \\ &= \frac{1}{4\pi\epsilon_0} \frac{(-e)(e)}{r} \\ &= \frac{-e^2}{4\pi r} = - (1) \end{aligned}$$



where  $r = (x^2 + y^2 + z^2)^{1/2}$  is the distance between the electron and the proton. If the nucleus has more than a single positive charge, we must include the additional charge in the coulomb energy by multiplying the term  $Z$ , called the atomic number,

$$E_p = \frac{-Ze^2}{4\pi r} \quad \dots \quad (2)$$

The time-independent SWE for a free pt particle moving in three dimensions is given by

$$\frac{-\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) X + E_p(x, y, z) X = E X$$

$$\left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] X + 2m (E - E_p(x)) X = 0$$

$$= R(r) \Theta(\theta) \Phi(\phi)$$

$$\begin{aligned} F(r, \theta, \phi) &= X(r) Y(\theta) \\ Y(\theta, m, n) &= L_m(\theta) M(m, n) \end{aligned}$$

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Eqn (3) is a partial differential eqn and  $F_p$  is a function of  $x, y, z$ . It is difficult to solve in the Cartesian  $(x, y, z)$  coordinate, so that it is easy to solve converting Cartesian  $(x, y, z)$  to spherical polar  $(r, \theta, \phi)$  and transform as follows.

$$\left. \begin{array}{l} x = r \sin \theta \cos \phi \\ y = r \sin \theta \sin \phi \\ z = r \cos \theta \end{array} \right\} \rightarrow (1)$$

Hence the expression of  $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  becomes

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \chi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \chi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \chi}{\partial \phi^2}$$

Therefore the schrodinger eqn becomes,

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \chi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \chi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \chi}{\partial \phi^2} + \frac{2U}{\hbar^2} (E - E_p) \chi = 0 \quad (5)$$

$$\text{where, } U = \frac{m_p m_e}{m_p + m_e}$$

is called reduced mass.

Eqn (5) can be solved by separation of variable method. We

$$\chi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \quad (6)$$

where,  $R$  be the function of position only,  
 $\Theta$  be function of  $\theta$  only &  $\Phi$  function of  $\phi$

Putting their value in eqn (5)

$$\frac{1}{\alpha^2} \frac{\partial}{\partial \alpha} \left( \alpha^2 \frac{\partial (R \Theta \Phi)}{\partial \alpha} \right) + \frac{1}{\alpha^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial (R \Theta \Phi)}{\partial \theta} \right) + \\ + \frac{1}{\alpha^2 \sin^2 \theta} \left( \frac{\partial^2 (R \Theta \Phi)}{\partial \phi^2} \right) + \frac{2\mu (E - E_p)}{\hbar^2}$$

$$\text{or, } \frac{1}{\alpha^2} \frac{\partial}{\partial \alpha} \left( \alpha^2 \frac{\partial R}{\partial \alpha} \right) + \cancel{\frac{\partial}{\partial \alpha} R \Theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) \\ + \cancel{\frac{\partial}{\partial \theta} R \Theta} \left( \frac{\partial^2 \Phi}{\partial \phi^2} \right) + \frac{2\mu (E - E_p) R \Theta \Phi}{\hbar^2} = 0$$

Dividing by  $R \Theta \Phi$ ,

$$\text{or, } \frac{1}{R \alpha^2} \frac{\partial}{\partial \alpha} \left( \frac{\partial^2 R}{\partial \alpha^2} \right) + \frac{1}{\alpha^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) \\ + \frac{1}{\Phi \alpha^2 \sin^2 \theta} \left( \frac{\partial^2 \Phi}{\partial \phi^2} \right) + \frac{2\mu (E - E_p)}{\hbar^2} = 0$$

Multiplying by  $\alpha^2 \sin^2 \theta$  on both sides.

$$\text{or, } \frac{1}{R} \frac{\sin^2 \theta}{\alpha^2} \frac{\partial}{\partial \alpha} \left( \frac{\partial^2 R}{\partial \alpha^2} \right) + \frac{1}{\Theta} \frac{\sin \theta}{\alpha^2} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) \\ + \frac{1}{\Phi} \left( \frac{\partial^2 \Phi}{\partial \phi^2} \right) + \frac{2\mu \alpha^2 \sin^2 \theta}{\hbar^2} (E - E_p) = 0$$

$$\text{or, } \frac{1}{R} \frac{\sin^2 \theta}{\alpha^2} \frac{\partial}{\partial \alpha} \left( \frac{\partial^2 R}{\partial \alpha^2} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{2\mu \alpha^2 \sin^2 \theta}{\hbar^2} \\ = - \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2}$$

The right side of above eqn (7) is a function of  $\Phi$  only and left side of above eqn is function of ' $\theta$ ' and  $\phi$ .

The only way above eqn can be valid when both sides of equation are equal to same constant. For a convenience let us suppose this constant is  $m_1^2$ .

$$\text{so that, } -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_1^2 \quad \dots \quad (8)$$

Then,

$$\frac{m_1^2}{R} = \sin^2 \theta \frac{\partial}{\partial \theta} \left( \frac{r^2 dR}{d\theta} \right) + \sin \theta \frac{d}{\theta} \left( \sin \theta \frac{d\theta}{d\theta} \right) + \frac{2\mu}{h^2} r^2 \sin^2 \theta (E - E_p)$$

$$\therefore \text{R.H.S.} \quad \dots \quad (9)$$

Dividing eqn (8) by  $\sin^2 \theta$ , we get,

$$\frac{m_1^2}{\sin^2 \theta} = \frac{1}{R} \frac{d}{d\theta} \left( \frac{r^2 dR}{d\theta} \right) + \frac{1}{\sin \theta (\theta)} \frac{d}{d\theta} \left( \sin \theta \frac{d\theta}{d\theta} \right) + \frac{2\mu}{h^2} \frac{r^2 \sin^2 \theta (E - E_p)}{\sin^2 \theta}$$

$$\frac{1}{R} \frac{d}{d\theta} \left( \frac{r^2 dR}{d\theta} \right) + \frac{2\mu r^2 (E - E_p)}{h^2} = \frac{m_1^2}{\sin^2 \theta} - \frac{1}{\sin \theta (\theta)} \frac{d}{d\theta} \left( \sin \theta \frac{d\theta}{d\theta} \right) \quad \dots \quad (10)$$

The R.H.S. of eqn (10) is the function of  $\theta$  only and the L.H.S. of eqn (10) is the function of ' $\theta$ ' only. The only way above eqn can be valid when both sides of equation are equal to same constant. For a convenience let us suppose this constant is  $l(l+1)$ .

$$\frac{1}{R} \frac{d}{d\theta} \left( \frac{r^2 dR}{d\theta} \right) + \frac{2\mu r^2 (E - E_p)}{h^2} = l(l+1) \quad \dots \quad (11)$$

$$\frac{m_1^2}{\sin^2 \theta} - \frac{1}{\sin \theta (\theta)} \frac{d}{d\theta} \left( \sin \theta \frac{d\theta}{d\theta} \right) = l(l+1) \quad \dots \quad (12)$$

where  $l$  is an integer.

$\theta \rightarrow$  azimuthal eqn  
 $\theta \rightarrow$  polar eqn  
 $r \rightarrow$  radial eqn  
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(1) When we solve the azimuthal eqn (eqn 3), we get the solution of  $\Phi$ ,

$$\Phi = A_c e^{im_l \theta}$$

where,  $A$  = normalization constant &

$m_l$  = magnetic orbital quantum number.

The solution of  $\Phi$  are single valued, for those value of  $m_l$   
 $m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm n$ .

(2) When we solve the polar equation, eqn (11)(12), we find the soln of  $\Theta$ , we find that the only solution that we find value of  $\Theta$ , everywhere for those values of  $\theta$   
 $\theta = 0, \pi/2, \pi, 3\pi/2, \dots, (n-1)\pi$   
 and  $\theta \geq |m_l|$   
 where  $\theta$  is the orbital quantum number.

(3) Finally, we solve the radial equation, eqn (11), for  $R$ , we find that the only solution for  $R$  that remain finite everywhere for those which

$$E_n = -Z^2 c^2 m \frac{1}{8 \epsilon_0^2 h^2 n^2}$$

where  $n$  is the principle quantum number and  
 $n \geq 1+1$

## Significance of the different Quantum Number.

1. The most important result of the solution of the SIE of H-atom is the fact that the energy of the atom is quantized. Because of the energy depends only on the quantum number  $n$ , called principle quantum number, which determines the discrete set of negative (attractive force) value for bound state. So, that, the principle quantum number ( $n$ ) describes the quantization of energy of H-atom.
2. The quantum number  $l$  is called the orbital quantum number because  $l$  determine the magnitude of the angular momentum  $L$  of the atom, the states for which  $l=0$  are called s states,  $l=1$  are called p-states,  $l=2$  is called d-states,  $l=3$  are called f-states.
3. The quantum number  $m_l$  is called the magnetic orbital quantum number because it determine the orientation of angular momentum  $L$  in a magnetic field;  $|m_l| \leq l$ . It can be show that if an atom is placed in magnetic field directed along the z-direction, the z-component of angular momentum  $l$  of the atom is given by  $l_z = m_l \hbar$ .

$$\chi_{R\Theta\Phi} = \chi_{n, l, m_l}$$

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| Principal Quantum No. | Orbital Qu. No. | Magnetic orbital Qu. No. |
|-----------------------|-----------------|--------------------------|
|-----------------------|-----------------|--------------------------|

For eg:  $n=1$        $l=0 \rightarrow s$  state       $m_l=0$       ] only one state

$n=2$        $l=0 \rightarrow s$  state       $m_l=0 \rightarrow 1$       ] 2 states  
 $l=1 \rightarrow p$  state       $m_l=0, \pm 1, -1 \rightarrow 3$

$n=3$        $l=0 \rightarrow s$  state       $m_l=0 \rightarrow 1$       ] 3 states  
 $l=1 \rightarrow p$  state       $m_l=0, \pm 1 \rightarrow 3$   
 $l=2 \rightarrow d$  state       $m_l=0, \pm 1, \pm 2 \rightarrow 5$

Degenerate state:  $(\chi_{n, l, m_l})$

only one state       $\chi_{100}$

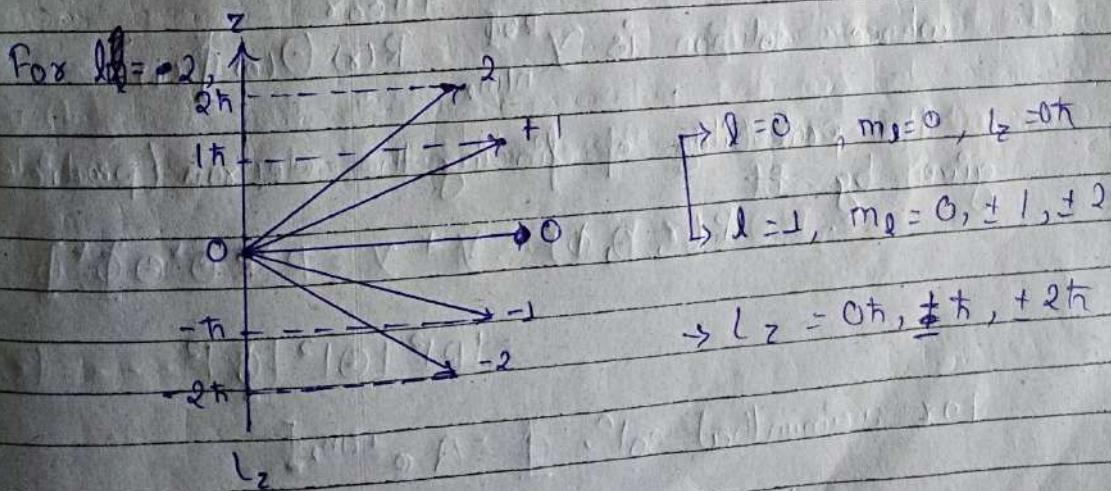
3 states       $\chi_{200}, \chi_{210}, \chi_{211}, \chi_{21-1}$

9 states       $\chi_{300}, \chi_{310}, \chi_{311}, \chi_{31-1}, \chi_{320}, \chi_{321},$   
 $\chi_{32-1}, \chi_{322}, \chi_{32-2}, \chi_4$

Thus, the wave function is written as with different quantum numbers as in subscript,  $\psi_{n_1 n_2 \dots}$ . Because for a given principle quantum number 'n', the other two numbers can take a several value. This means that, it is possible for the electron to have a quite different characteristics while maintaining the same energy. While the state X having the same energy but different values for the quantum numbers, 'l' & 'm<sub>l</sub>' are called degenerate state. The degree of degeneracy depends on the principal quantum number 'n'.

### Space Quantization

In an atom, angular momentum, 'l' cannot have any arbitrary orientation with respect to Z-axis but rather it can have only certain discrete orientation. This fixed orientation, <sup>is</sup> known as space quantization.



## Atomic wave function.

(Probability density of electron).

The sol<sup>n</sup> of spherical polar coordinate of S.W.F. is the atomic wave function in quantum mechanics. This wave function describes the wave like behaviour of electron. either one electron or pair of electron and it also can be used to calculate the probability of finding an electron of an atom in any specific region around the atoms of nucleus.

The SWF in spherical polar coordinate system is given by

$$+\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \chi}{\partial r^2} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \chi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left( \frac{\partial^2 \chi}{\partial \phi^2} \right) + (E - E_p(r)) \chi = 0 \quad \dots \dots \quad (1)$$

where,  $E_p(r) = -e^2$

$4\pi \epsilon_0 r$

whose solution is  $\chi_{nml}^{R\Theta\Phi} = R(r) \Theta(\theta) \Phi(\phi) \quad \dots \dots \quad (2)$

The probability of finding the electron (particle) is given by

$$P(r, \theta, \phi) = \chi^* \chi = R^* R \Theta^* \Theta \Phi^* \Phi$$

$$= |R|^2 |\Theta|^2 |\Phi|^2 \dots \dots \quad (3)$$

For azimuthal sol<sup>n</sup>,  $\Phi = A e^{\pm im\phi}$

then,  $\Phi^* = A^* e^{\mp im\phi}$

then for normalization  $\int_0^{2\pi} \Phi^* \Phi d\phi = 1$

or,  $A^* A \int_0^{2\pi} \Phi^* \Phi d\phi = 1$

$\Rightarrow |A| = \frac{1}{\sqrt{2\pi}}$

From eqn (3), substituting value of  $|\Phi|^2$ .

$$P(r, \theta, \phi) = \frac{1}{\sqrt{2\pi}} |R(r)|^2 |Y(\theta, \phi)|^2 \quad \dots \text{--- (4)}$$

The eqn (4) show that the probability density is independent of azimuthal co-ordinate  $\Phi(\phi)$ . Thus the probability depends upon the radial probability  $|R(r)|^2$  and polar probability  $|Y(\theta, \phi)|^2$  that is electron distribution is symmetric about z-axis, and there is equal probability of electron to exist in element space.

### 1. Radial probability :

The radial probability density  $P(r)$  is the probability of finding the electron between  $r$  and  $r+dr$ . We get this by integrating the probability density per unit volume  $X^* X$  over the volume enclosed by the spherical shells with radius  $r$  and  $r+dr$  respectively. As we can see  $P(r)$  varies with the distance from the nucleus  $r$  with a maximum at certain  $r$  values depends on the particular wave function.

$$P(r) dr = |X^* X|^2 dr$$

In spherical coordinate  $dr = r^2 \sin \theta d\theta d\phi d\theta d\phi$

$$P(r) dr = |X|^2 r^2 \sin \theta d\theta d\phi dr$$

Then the probability of finding the electron of any loc. with radial co-ordinates between  $r$  &  $r+dr$  is obtained.

$$P(r) dr = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta |X|^2 r^2 dr$$

$$P(r) dr = \frac{1}{\pi r_0^3} \left( e^{-\frac{2r}{r_0}} \right) 4\pi r^2 dr$$

(where,  $4\pi r^2$  is the volume of sphere &  $r_0$  = Bohr's radius)

$$\text{Now, let } |X(100)|^2 = \frac{1}{\pi r_0^3} \left( e^{-\frac{2r}{r_0}} \right)$$

$$\text{then, } P(r) dr = |X_{100}|^2 4\pi r^2 dr$$

#### 11. Polar probability

To find the polar probability, the value of  $\Theta$  varies with polar angle  $\Theta$ . Therefore  $|(\Theta)|^2$  measure the polar prob density.

$$\text{i.e. } P(\Theta) = |(\Theta)|^2 = (\Theta)^2 \cdot \Theta$$