

Quantum Mechanics

①

Introduction—

Classical mechanics— Towards the end of the 19th century, physicists were greatly satisfied that they were able to explain most of the phenomena on the basis of Newton's laws of motion and Maxwell's electromagnetic wave theory. According to this theory energy is emitted or absorbed continuously.

The Newton's laws of motion were used to explain the phenomena related to motion eg. trajectories of planets, falling stones etc. and Maxwell's theory was used to explain the phenomena related to energy transfer.

The branch of science based on Newton's laws of motion and Maxwell's electromagnetic wave theory to explain phenomena related to motion & energy is known as classical mechanics or Newtonian mechanics.

Failure of classical mechanics—

During the latter of the nineteenth century, a number of experimental observations were reported which could not be explained on the basis of the classical theory.

A few phenomena for which the classical mechanics fails to give a satisfactory explanation are— (2)

1. The spectral distribution of energy in Black-body radiation.
2. Photoelectric effect
3. Variation of heat capacity of monoatomic solids with temperature.
4. The discrete spectra emitted by excited atoms i.e. Atomic & Molecular spectra.

Classical mechanics was able to explain phenomena related to large size objects [macroscopic particles].

However, it fails when applied to small particles such as electrons, atoms, molecules etc [microscopic particles].

eg. according to classical mechanics, it should be possible to determine simultaneously the position and velocity [or momentum] of a moving particle but this is contradicted by the Heisenberg's uncertainty principle.

Similarly, classical mechanics assumes that the energy is emitted or absorbed continuously whereas quantum mechanics assumes [postulates] that energy is emitted or absorbed discontinuously in the form of packets of energy, called quanta, further, the concept of quantum numbers was introduced arbitrarily to

explain the atomic spectra.
Max Planck was the first to suggest a new theory based on the quantum behaviour of energy. when applied to various problems, it was able to account for the experimental observations and hence led to the new theory, named, the quantum theory.

Black-Body Radiation

Classical Theory of Radiation Prior to Max Planck [1901], light was considered to be electromagnetic wave whose energy was proportional to the square of the amplitude of the wave, and was considered to be independent of the frequency of the radiation. This classical theory of radiation was able to explain optical phenomena such as diffraction and scattering. However, when applied to the black-body radiation, this theory could not explain the relative intensities of radiations emitted from a black-body when heated to a higher temperature.

According to classical theory of radiation,

Energy \propto [amplitude]²
and independent of ν [frequency of radiation]

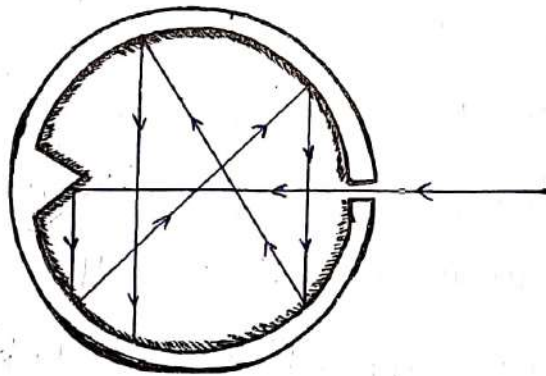
According to Planck-
 $E \propto \nu$
or $E = h\nu$
where ν - frequency of light.

Radiations
emitted by a
Black Body

A black body is one which can absorb all types of radiation that falls upon it. or (4)

"A body which completely absorbs the radiant energy falling on it is called a perfectly black-body."

Experimentally, such a body is best represented by a hollow container with a very small hole in the wall. This hollow sphere blackened on the inside and having a small hole for the entry of the radiation.



When such a body is heated, it emits radiations of all types of wavelengths. The origin of radiations from a heated body is the rapid vibrating particles [known as oscillators] composing the body.

According to Maxwell's electromagnetic theory, these oscillators emit radiant energy in the form of electromagnetic waves.

The frequency of the wave emitted from an oscillator is equal to the frequency of the latter. (5)

At low temperatures, the emission is mainly in the infra-red region, but as the temperature is raised, the wave length at which most of the light is emitted shifts towards the blue region of the spectrum.

The intensity of the emitted radiation depends on the temperature of the container as well as on the wave length of the radiation.

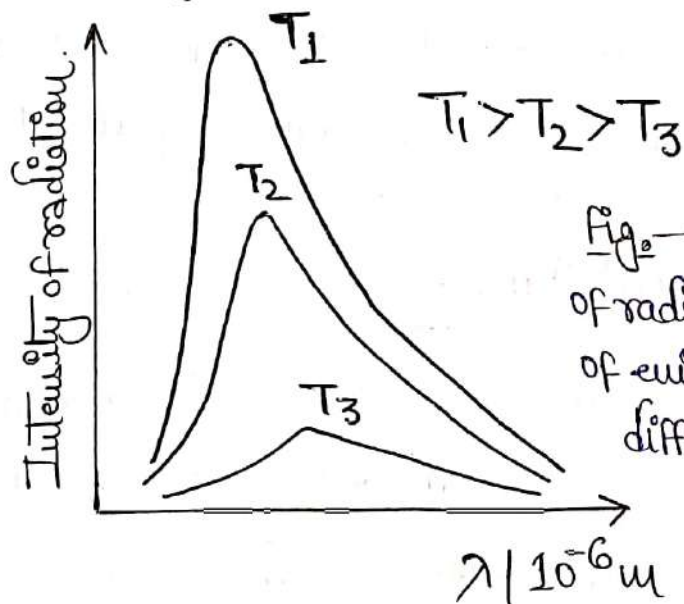


Fig. - Variation of intensity of radiation with the wave length of emitted radiations at three different temperatures.

i.e. μm .

Two fundamental laws of Black-Body Radiations -

Based on the classical theory, attempts were made to explain qualitatively and quantitatively the nature of the curves. Two fundamental laws regarding the nature of the curves were established. These are described below.

Stefan-Boltzmann Law -

6

According to this, the intensity E of total radiation [the area under the curve] is proportional to the fourth power of the Kelvin temperature T ; i.e.

$$E = \sigma' T^4 = \left[\frac{4\sigma}{c} \right] T^4$$

where σ is a constant, known as the Stefan's constant. Its value is found to be 5.672×10^{-8} $\text{Jm}^{-2}\text{s}^{-1}\text{K}^{-4}$ subsequently, this law was derived by Boltzmann using thermodynamic principles.

Wien's displacement law -

According to this law, the wavelength λ at the maximum of the spectral distribution is inversely proportional to the temperature T . Thus,

$$\lambda_{\text{max}} T = \text{constant.}$$

Other results observed from the Black-Body Radiation curve -

(i) At a particular temperature, the distribution of energy is not uniform among the various wavelengths of the radiation emitted by the black body.

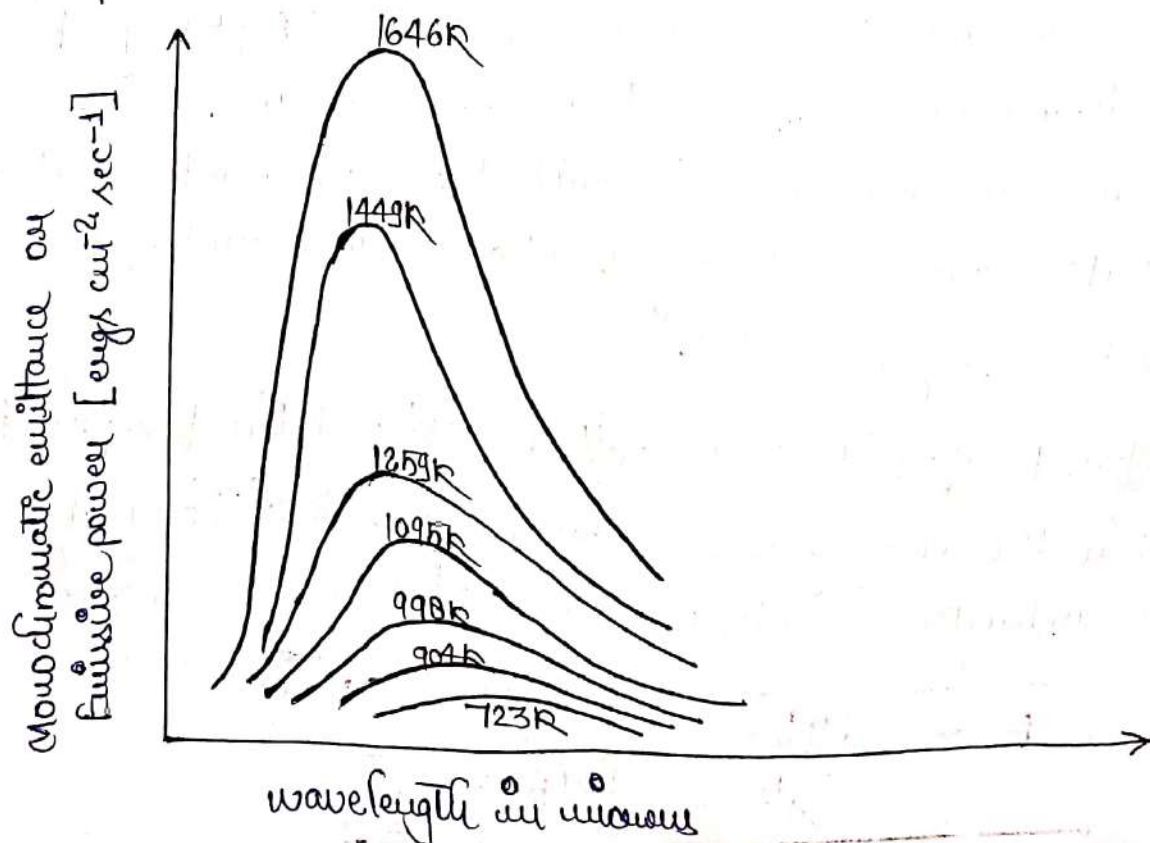
(ii) For each temperature, there is a wavelength λ at which the energy radiated is maximum. (7)

(iii) With increase in temperature, the maximum shifts higher but towards lower wavelength. This means that with increase in temperature, E_m increases but the corresponding λ_m decreases.

(iv) Higher the temperature, more pronounced is the maximum.

(v) The area under the curve for a particular temperature gives the total energy emitted by the black-body per unit area per second for the complete spectrum i.e. corresponding to all the wavelengths at that particular temperature [from $\lambda=0$ to $\lambda=\infty$].

(vi) The area under the curve increases with increase of temperature.



Planck's radiation law - Max Planck in 1900 put forward a bold assumption that the oscillator of black body can not have any amount of energy but has a discrete energy equal to the integral multiple of some minimum energy, E . i.e.

$$E_i = nE$$

where, E_i - is the energy of the i th oscillator and n is an integer.

Planck ^{thus} summed up his result as under -

"Energy is emitted or absorbed not continuously but discontinuously in the form of packets of energy called quanta. The energy of each quantum is given by the relation, $E = h\nu$, where ν is the frequency of the radiation and h is called Planck's constant.

Thus the total energy emitted or absorbed is either unit quantum i.e. $h\nu$ or a whole number multiple of $h\nu$ i.e. equal to $nh\nu$."

Based upon these concepts, Planck's deduced expression for the energy E_λ radiated by a black body at wavelength λ , which is as under -

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/RT\lambda} - 1}$$

$$E_{\lambda} = \frac{8\pi^5 h c}{\lambda^5} \cdot \frac{1}{[e^{\beta E} - 1]}$$

$$\because \beta = \frac{1}{RT} \quad \& \quad E = h\nu$$

$$\& \quad \nu = \frac{c}{\lambda}$$

(9)

This expression is called Planck's radiation law.

It can be seen that both Wien's law as well as Rayleigh-Jeans law are simply particular cases of Planck's radiation law.

(i) At low values of λ — λT is small.

$$\because \frac{hc}{RT\lambda} \gg 1$$

so that 1 in the denominator in above equation can be neglected. This gives —

$$E_{\lambda} = \frac{8\pi^5 h c}{\lambda^5} e^{-hc/RT\lambda}$$

which is Wien's law.

(ii) At high values of λ — λT is large.

$e^{hc/RT\lambda}$ may be expanded by the exponential theorem

$$e^x = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \dots$$

$$\text{i.e. } e^{\frac{hc}{RT\lambda}} = 1 + \frac{hc}{RT\lambda} + \dots$$

so the Planck's radiation law equation reduces to form

$$E_{\lambda} = \frac{8\pi^5 h c}{\lambda^5} \times \frac{RT\lambda}{hc}$$

$$E_{\lambda} = \frac{8\pi^5}{\lambda^4} \cdot RT$$

which is Rayleigh-Jeans law.

Summary of Planck's Contribution

Planck's contribution may be summarized as follows—

(10)

(i) In order that the Planck's equation may be reduced to the Wien's equation only in the low wavelength region, Planck assumed that the energy of the oscillator is directly proportional to its frequency with h as the constant of proportionality. This constant is called Planck's constant and it has to have a finite value.

The value of h cannot be zero since this would lead to the classical theory of continuous energy distribution.

(ii) In order that the Planck's equation may be reduced to Rayleigh and Jean's equation only in longer wavelength region, Planck assumed that the oscillator in a black-body can exchange energy only by discrete amounts, i.e. the oscillator can't radiate or absorb any amount of energy but can do so only in small lumps or bundles called quanta.

The Photoelectric Effect

When a beam of light with frequency equal to or greater

than a particular value [called threshold frequency] is allowed to strike the surface of a metal, e^- s are ejected instantaneously from the surface of the metal. This effect is called photoelectric effect.

The Planck's statement that the oscillators in a black-body radiate energy in elementary discrete units was extended by Einstein to the extent that the radiation field itself is quantized, consisting of light quanta called photons. Thus, Einstein considered the light wave to be corpuscular in nature with each photon carrying an energy equal to $h\nu$. With the corpuscular nature of light, he was successful in interpreting the photoelectric effect.

Characteristics of photoelectric Effect

In the photoelectric effect, the electrons are emitted instantaneously from a clean metal plate in vacuum when a beam of light falls on it.

The following characteristics are observed — (12)

- The e^- are emitted instantaneously from a given metal plate when it is irradiated with radiation of frequency equal to or greater than some minimum frequency, called the threshold frequency.
- The kinetic energy of the emitted e^- depends on the frequency of the incident radiation and not on its intensity. The kinetic energy of e^- increases linearly with increase in the frequency of the incident radiation.
- The number of e^- emitted is proportional to the intensity of the incident radiation.

Energy requirement for the emission of Electrons

The e^- in a metal possesses potential energy [PE] which must be supplied before an e^- can be removed from the metal. This energy is known as

the work function, is the ionisation energy [IE] of the metal. If the emitted e^- carries some kinetic energy [KE], the total energy supplied to the e^- is equal to the sum of its potential energy and kinetic energy.

$$E_T = h\nu = KE + PE$$

(13)

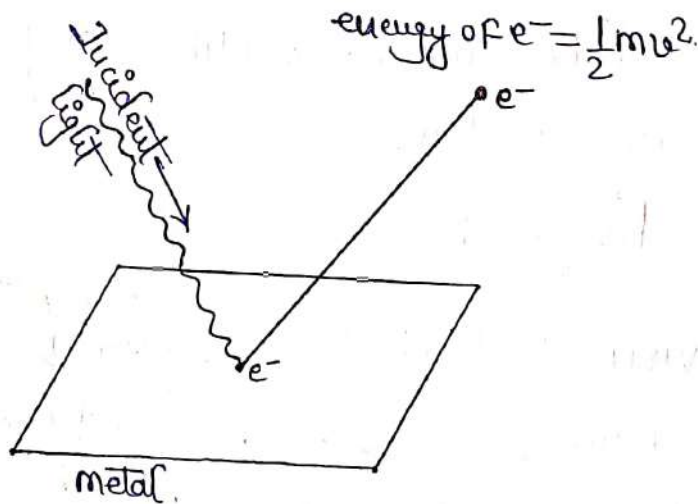
Failure of classical theory to explain photoelectric effect

In the classical theory, the energy of the light beam depends on its intensity. Thus, a continuous exposure of the metal

with light causes the e^- to gain more and more energy from the light and ultimately a stage would be reached when it has acquired sufficient energy to cause its ionization. Hence, it is expected that there might exist a time interval between the exposure of the metal and the emission of e^- .

This time interval may be decreased by increasing the intensity of the light. Thus, the classical theory of light can not explain the characteristics of photoelectric effect.

Photoelectric Effect



Einstein
Explanation of
Photoelectric
Effect

According to Einstein, the characteristics of the photoelectric effect can be explained by employing Planck's idea of quantization of energy. Thus, light may be considered to be made up of discrete particles called photons. Each photon carries an energy equal to $h\nu$. When this photon collides with the e^- of the metal, the e^- acquires energy equal to the energy of the photon. Thus, the energy of the emitted e^- is given by-

$$h\nu = KE + PE = \frac{1}{2}mv^2 + IE \quad \text{--- (i)}$$

If the incident radiation is of threshold frequency, the e^- will be emitted without any kinetic energy. In this case, we have

$$h\nu_0 = IE \quad \text{--- (ii)}$$

It is obvious that if the frequency of the light is smaller than ν_0 , the e^- will not acquire sufficient energy to cause its ionisation.

From the above equation (i), it follows that the kinetic energy of e^- depends on the frequency of incident radiation and not on the intensity of light.

By the term intensity of light, we mean the number of quanta striking the metal per unit time. This will have an effect only on the number of e^- s emitted and not on their kinetic energy. Thus the number of e^- s emitted increases with increase in the intensity of light.

Kinetic Energy of Emitted Electrons

Combining eqⁿ (i) and (ii), we have

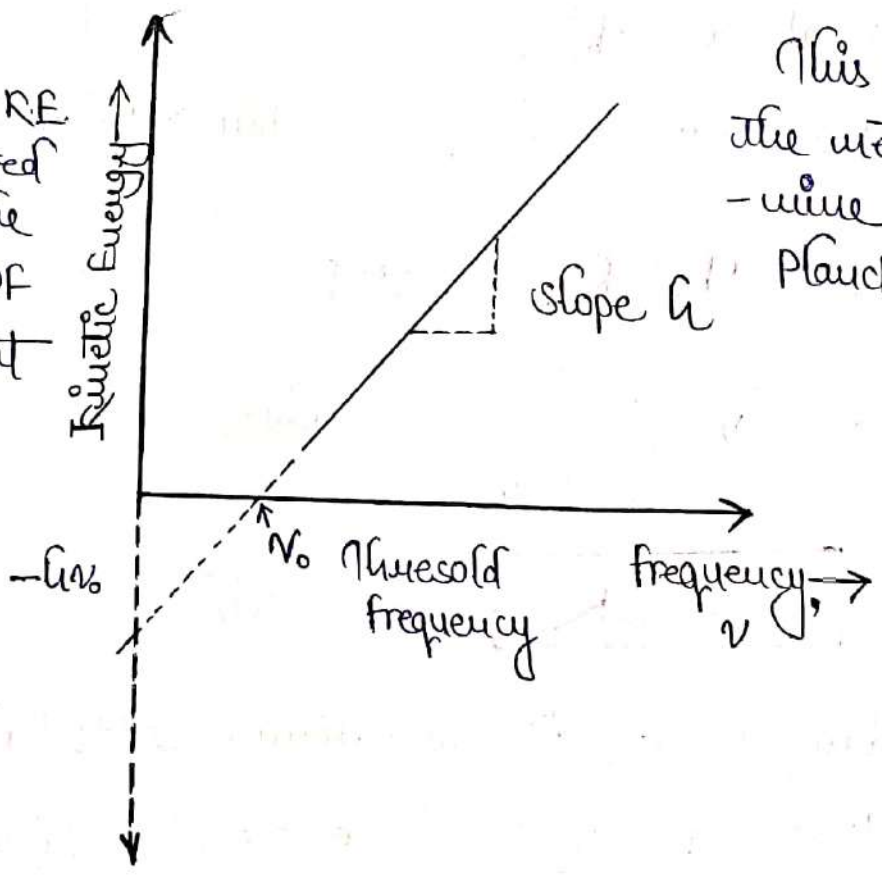


$$h\nu = KE + h\nu_0$$

$$KE = h\nu - h\nu_0$$

$$y = mx + c$$

Variation of KE of the emitted e^- s with the frequency of the incident radiation.



This provides one of the methods to determine the value of Planck's constant.

Heat Capacity

(6)

Heat capacity
Based on the
Law of Equipartition
of Energy.

Einstein also showed that the problem of variation of heat capacity of monatomic solids with temperature can be resolved by employing Planck's idea of quantization.

The monatomic solid may be considered a collection of oscillators with three vibrational degree of freedom. On the basis of the classical law of equipartition of energy, each oscillator of such a solid possesses an average energy equal to $3kT$.

Thus, for one mole of oscillators, the molar energy is

$$E = N_A [3kT] = 3RT \quad \text{--- (i)}$$

Since, $C_V = \left[\frac{\partial E}{\partial T} \right]_V$, we have

$$\boxed{C_V = 3R} \quad \text{--- (ii)}$$

According to Eq. (ii), monatomic solids have a constant heat capacity equal to $3R$ [a value which was obtained empirically by Dulong and Petit].

Experimentally, it is found that this value of heat capacity is observed only at high temperatures.

At low temperature, the value is found to be less than $3R$ and the values approach zero as $T \rightarrow 0$.

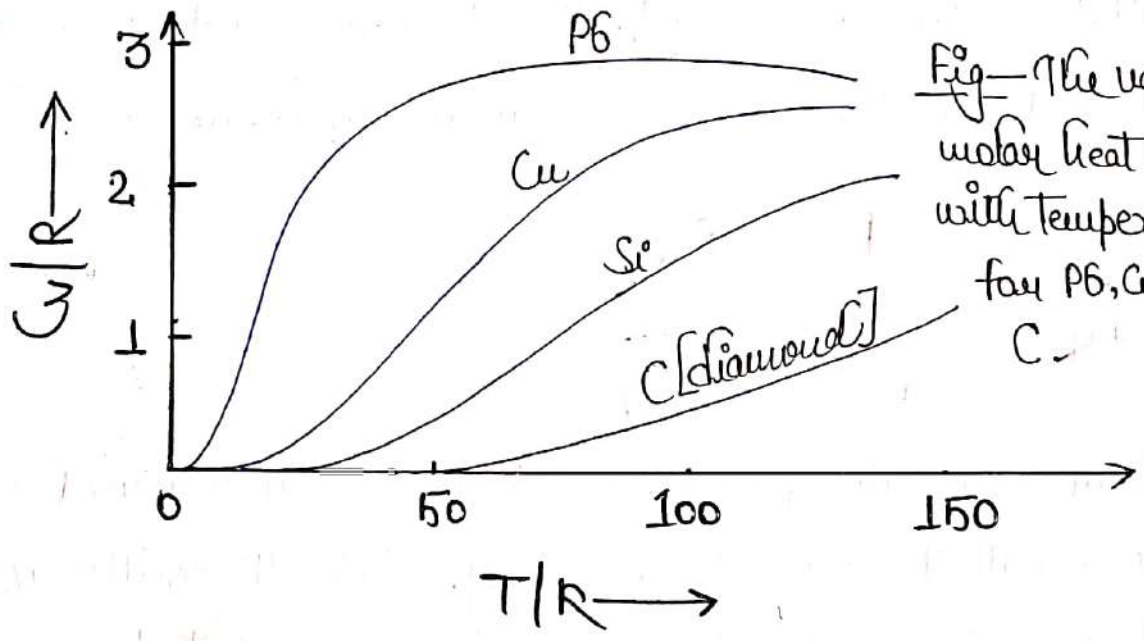


Fig - The variation of molar heat capacity with temperature for Pb, Cu, Si and C.

Disagreement with Experimental fact

According to the classical theory, the heat capacity of a monatomic solid should be independent of temperature.

This conclusion, however, does not agree with the experimental findings, according to which the heat capacity decreases with the decrease in temperature.

Einstein
Explanation of
Variation of Heat
Capacity

By employing Planck's idea of quantization, Einstein was able to explain the variation of heat capacity with temperature. He assumed that the oscillator can have vibrational energy which is an integral multiple of some minimum value, i.e.

$$E = n E_0$$

or

$$v = n v_0$$

where v is the frequency of the oscillator and v_0 is the smallest allowed frequency. Thus all oscillators are not vibrating with the same frequency but have values which are simply an integral multiple of the smallest frequency v_0 . The number of oscillators possessing the frequency v can be determined from Boltzmann law.

$$\frac{N_{upper}}{N_{lower}} = e^{\frac{-\Delta E}{RT}}$$

The average energy of the oscillators is given by-

$$\bar{E} = \frac{E_0}{e^{E_0/RT} - 1}$$

Substituting $E = h\nu_0$, we get.

(19)

$$\bar{E} = \frac{h\nu_0}{e^{\frac{h\nu_0}{RT}} - 1}$$

The molar energy of a solid is,

$$E = N_A [3\bar{E}] = N_A \cdot \left[3 \cdot \frac{h\nu_0}{e^{\frac{h\nu_0}{RT}} - 1} \right]$$

and the corresponding value of molar heat capacity is-

$$C_V = \left[\frac{\partial E}{\partial T} \right]_V = 3N_A R \left[\frac{h\nu_0}{RT} \right]^2 \frac{e^{\frac{h\nu_0}{RT}}}{\left[e^{\frac{h\nu_0}{RT}} - 1 \right]^2} \quad \text{--- 1}$$

This eqⁿ is known as Einstein equation.

Limiting value
of C_V at Lower
Temperature

At low temperatures, we have

$$h\nu_0 \gg RT$$

and thus $e^{\frac{h\nu_0}{RT}} \gg 1$.

Under these conditions, eqⁿ (1) [Einstein eqⁿ] will reduce to,

$$C_V = 3N_A R \left[\frac{h\nu_0}{RT} \right]^2 \frac{h\nu_0}{RT}$$

On decreasing the temperature, the exponential factor decreases much faster than the corresponding increase in the factor $\left[\frac{h\nu_0}{RT} \right]^2$. Consequently, C_V decreases with decrease in temperature. Einstein suggested that the above decrease is basically due to the lesser absorption

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of energy by the oscillators at low temperatures.

This is so because the oscillators can absorb energy in units of $h\nu_0$ and the value of RT is much smaller as compared to $h\nu_0$.

The value of ν_0 is different for different solids. The temperature at which the decrease in heat capacity becomes important depends upon the value of ν_0 of the solid. If we assume the oscillators to be harmonic, then,

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k_f}{m}}$$

where, k_f - Hook's law constant of the oscillator
 m - its mass.

Limiting value of C_v at Higher Temperatures

$$h\nu_0 \ll RT$$

Then from eqn (1) [Einstein eqn].

$$C_v = 3N_A R \left(\frac{h\nu_0}{RT}\right)^2 \frac{e^{h\nu_0/RT}}{[e^{h\nu_0/RT} - 1]^2}$$

Expanding the exponential factor, we have-

$$\therefore e^x = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \dots$$

$$C_v = 3N_A R \left[\frac{h\nu_0}{RT}\right]^2 \left[\frac{1 + \frac{h\nu_0}{RT} + \left(\frac{h\nu_0}{RT}\right)^2 + \dots}{\left[1 + \frac{h\nu_0}{RT} + \left(\frac{h\nu_0}{RT}\right)^2 + \dots\right]^2} \right]$$

$$\text{or } C_V = 3N_A R \left[\frac{\left(\frac{h\nu_0}{RT}\right)^2 + \left(\frac{h\nu_0}{RT}\right)^3 + \dots}{\left[\left(\frac{h\nu_0}{RT}\right) + \left(\frac{h\nu_0}{RT}\right)^2 + \dots\right]^2} \right] \quad (21)$$

At sufficiently high values of T , $\frac{h\nu_0}{RT}$ is very small and the terms with powers higher than two can be neglected.

Thus, we have -

$$C_V = 3N_A R = 3R$$

The Bohr Model of Atom

To overcome the drawback of Rutherford's model of atom and to explain the line spectrum of hydrogen Niels Bohr, a Danish physicist in 1913 proposed a new model of atom based upon Planck's quantum theory. This new model is called Bohr's model of atom.

X

Rutherford Model of Hydrogen Atom In the Rutherford model of the atom, e^- revolve around the nucleus in such a way that the Coulombic attraction of the e^- by the nucleus is balanced by the

Centrifugal force which tends to pull the e^- and nucleus apart, i.e. (22)

|attractive [centripetal] force| = Centrifugal force.

$$\frac{(Ze)(e)}{(4\pi\epsilon_0)r^2} = \frac{mv^2}{r} \quad \text{--- (i)}$$

where — e^- elementary charge

r — any distance of e^- from the nucleus.

All other symbols have their usual meanings.

For a given value of r , the velocity with which an e^- moves in the orbit can be calculated from eqn (i).
Since r can vary in a continuous manner, the velocity of the e^- can also vary in a continuous manner.

Instability of Rutherford Model of Hydrogen Atom

The model of atom in which the e^- s move in orbits around positively charged nucleus would

have to be reconciled with the principles of classical electrodynamics, according to which a negative charge revolving around a positive charge experiences a continuous acceleration and thereby should radiate continuous energy.

(23)

By losing ^{energy} continuously, the e^- would come nearer and nearer to the nucleus and eventually, would fall in the nucleus. Thus, it gives rise to an unstable atom — a conclusion which contradicts the experimental observations (as atom is quite stable) and moreover, such a model would give rise to continuous spectra instead of the experimentally determined discrete spectra.

Bolr Model of H-atom

Bolr resolved the above problem by introducing Planck's idea of quantization of energy. The first thing which Bolr concluded was that the classical electrodynamics did not adequately represent systems of atomic dimensions and, therefore, it has to be set aside. His model of atomic structure involved the following postulates.

— The electron in an atom can revolve around the nucleus only in certain allowed circular orbits without losing any energy.

— The e^- can jump from one of the allowed orbits to another and can thereby gain or lose energy equivalent to the difference in the energy of the two involved orbits. Thus, when it jumps from a higher energy orbit to a state of lower energy,

The e^- loses energy which appears in the form of radiation of frequency ν such that $h\nu$ is equal to the difference in the energies of the two states. (24)

Bohr showed that the allowed stationary orbits can be generated by imposing the quantum restriction on the classical expression given by eqⁿ (i) of the Rutherford's model.

The quantum restriction proposed by Bohr was that the angular momentum of the revolving e^- is an integral multiple of the basic unit of $\frac{h}{2\pi}$ i.e.

$$mvr = n \frac{h}{2\pi} \quad \text{--- (ii)}$$

where — n — no. of quanta of angular momentum and is known as the quantum number.
 n can have only integral values 1, 2, 3,

Radius of Stationary Orbits

The allowed stationary orbits can be obtained by eliminating v from eqⁿ

(i) & (ii), we get,

$$mvr = n \frac{h}{2\pi}$$

$$r = \frac{nh}{2\pi mv}$$

substituting this value in eqⁿ (i) —

$$\frac{ze^2}{(4\pi\epsilon_0)r^2} = \frac{m}{r} \left(\frac{nh}{2\pi m r} \right)^2 = \frac{n^2 h^2}{4\pi^2 m r^3}$$

(25)

$$\frac{ze^2}{4\pi\epsilon_0} = \frac{n^2 h^2}{4\pi^2 m r}$$

$$r = \frac{n^2 h^2}{4\pi^2 m \times z e^2} \times 4\pi\epsilon_0$$

$$r = \frac{n^2}{z} \times \frac{h^2 \epsilon_0}{\pi m \times e^2} = \frac{n^2}{z} a_0$$

$$a_0 = \frac{h^2 \epsilon_0}{\pi m e^2} = 0.529 \times 10^{-10} \text{ m} = 0.529 \text{ \AA}$$

$$r = \frac{n^2}{z} a_0$$

where a_0 — Bohr radius

Comment on the Radii of Bohr Orbits It follows that only certain orbits are allowed since the quantum number n can have only integral values 1, 2, 3, ...

The smallest Bohr radius for a hydrogen atom is equal to a_0 , since $n=1$ and $z=1$. The radii of other orbits are simply n^2 times the value of a_0 . Thus, the second orbit has a radius which is four times that of the first orbit, the 3rd

9 times, # 4th orbit, 16 times and so on.

(26)

Energy of e⁻ in a stationary orbit

The total energy of the e⁻ in any orbit consists of two terms, viz., energy due to its motion

[kinetic energy, represented by the symbol T] and energy by virtue of its position relative to the nucleus [potential energy, represented as V]. Thus, we have—

$$E = T + V \quad \text{--- (i)}$$

$$= \frac{1}{2} m v^2 - \frac{z e^2}{(4\pi\epsilon_0) r} \quad \text{--- (ii)}$$

from eqⁿ (i), we have

$$m v^2 = \frac{z e^2}{(4\pi\epsilon_0) r}$$

Substituting this in eqⁿ (ii), we have—

$$E = \frac{1}{2} \frac{z e^2}{(4\pi\epsilon_0) r} - \frac{z e^2}{(4\pi\epsilon_0) r} = -\frac{1}{2} \frac{z e^2}{(4\pi\epsilon_0) r}$$

Substituting the expression of (ii) in above eqⁿ—

$$E = \frac{-1}{2} \frac{z e^2}{4\pi\epsilon_0} \times \frac{z \times \pi \times m \times e^2}{v^2 \times r^2 \times \epsilon_0}$$

$$E = \frac{-1}{2 n^2} \times \frac{m z^2 e^4}{4\pi^2 \epsilon_0^2}$$

$$E = -\frac{1}{n^2} \left[\frac{mz^2e^4}{\hbar^2 \epsilon_0^2} \right]$$

(27)

General energy formula

$$E_n = -\frac{1}{n^2} \left[\frac{2\pi^2 m z^2 e^4}{\hbar^2 (4\pi\epsilon_0)^2} \right] \quad \text{--- (ii)}$$

Comment on Energies Since n can have only integral values, it follows that the total energy of the e^-

is also quantized. The negative sign in above eqn (ii) [energy formula] tells that the e^- is bound to the nucleus. The e^- has a minimum energy when it occupies the lowest allowed orbit (i.e. $n=1$) and its energy increases as n becomes larger and larger. The e^- can have zero value of maximum energy when $n=\infty$. The zero energy means that the e^- is no longer bound to the nucleus.

Energy Expression for the Spectral Lines

Now according to the Bohr ^(2B) postulates, the atom can emit radiations only when the e^- jumps from an

orbit of higher energy to one of lower energy. This amounts to a jump from an orbit of higher quantum number $[n_2]$ to the orbit of lower quantum number $[n_1]$. The energy difference would be—

$$\begin{aligned}\Delta E &= E_{n_2} - E_{n_1} \\ &= \frac{2\pi^2 m z^2 e^4}{h^2 (4\pi\epsilon_0)^2} \left[-\frac{1}{n_2^2} + \frac{1}{n_1^2} \right] \\ &= \frac{2\pi^2 m z^2 e^4}{h^2 (4\pi\epsilon_0)^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]\end{aligned}$$

for the hydrogen atom, $z=1$, and thus,

$$\Delta E = \frac{2\pi^2 m e^4}{h^2 (4\pi\epsilon_0)^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$\because \Delta E = h\nu$ Writing this in the frequency unit, we have

$$\nu = \frac{\Delta E}{h} = \frac{2\pi^2 m e^4}{h \cdot h^2 (4\pi\epsilon_0)^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\nu = \frac{2\pi^2 m e^4}{h^3 (4\pi\epsilon_0)^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

(29)

$$\nu = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where R_H - Rydberg constant ; $R_H = \frac{2\pi^2 m e^4}{h^3 (4\pi\epsilon_0)^2}$

This eqn is known as Ritz equation.

Calculated value
of Rydberg
constant

Bohr's theory identifies the Rydberg constant with the other fundamental constants, the value of which is calculated in the following.

$$\begin{aligned} R_H &= \frac{2\pi^2 m}{h^3} \times \frac{e^4}{(4\pi\epsilon_0)^2} \\ &= \frac{2(3.1416)^2 \times (9.1095 \times 10^{-31} \text{ kg})}{(6.626 \times 10^{-34} \text{ Js})^3} \\ &\quad \times \left[\frac{(1.6022 \times 10^{-19} \text{ C})^4}{\{4(3.1416)(8.8542 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})\}^2} \right] \\ R_H &= 3.2902 \times 10^{15} \text{ s}^{-1} \end{aligned}$$

$$R_H = 3.2902 \times 10^{15} \text{ s}^{-1}$$

(30)

In terms of wave number, we have-

$$R_\infty = \frac{3.2902 \times 10^{15} \text{ s}^{-1}}{2.9979 \times 10^8 \text{ m s}^{-1}}$$

$$R_\infty = 1.0972 \times 10^7 \text{ m}^{-1}$$

$$\text{m}^{-1} = (100 \text{ cm})^{-1}$$

$$= 10^{-2} \text{ cm}^{-1}$$

$$R_\infty = 1.0972 \times 10^5 \text{ cm}^{-1}$$

The value of R_∞ is very close to the experimental value of $1.09737 \times 10^5 \text{ cm}^{-1}$.

Spectral Series
shown by
Hydrogen atom

The spectral series of atomic hydrogen are known. These are-

+

$$\nu = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\because \nu = c/\lambda$$

$$c/\lambda = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

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

$$\frac{1}{\lambda} = \frac{R_H}{c} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\bar{\nu} = R_{\infty} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ cm}^{-1}$$

(31)

where $R_{\infty} = 1.0972 \times 10^5 \text{ cm}^{-1}$
Rydberg constant.

$$\bar{\nu} = R_{\infty} \left[\frac{1}{1^2} - \frac{1}{n^2} \right] \quad \text{Lyman Series} \quad \text{UV region}$$

$$n = 2, 3, 4, \dots$$

$$\bar{\nu} = R_{\infty} \left[\frac{1}{2^2} - \frac{1}{n^2} \right] \quad \text{Balmer Series} \quad \text{UV-visible region}$$

$$n = 3, 4, 5, \dots$$

$$\bar{\nu} = R_{\infty} \left[\frac{1}{3^2} - \frac{1}{n^2} \right] \quad \text{Paschen Series} \quad \text{IR-region}$$

$$n = 4, 5, 6, \dots$$

$$\bar{\nu} = R_{\infty} \left[\frac{1}{4^2} - \frac{1}{n^2} \right] \quad \text{Brackett Series} \quad \text{IR-region}$$

$$n = 5, 6, 7, \dots$$

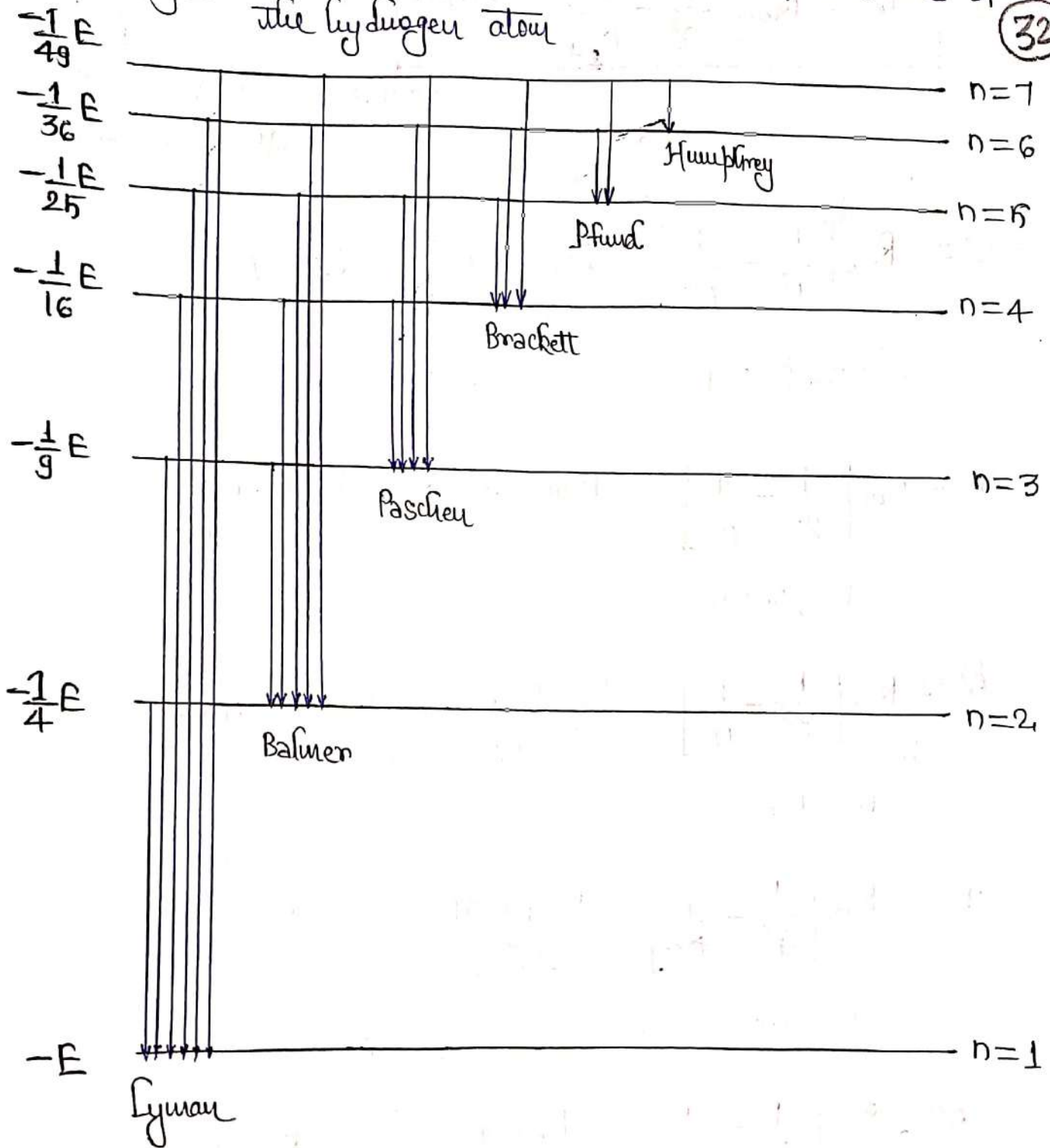
$$\bar{\nu} = R_{\infty} \left[\frac{1}{5^2} - \frac{1}{n^2} \right] \quad \text{Pfund Series} \quad \text{IR-region}$$

$$n = 6, 7, 8, \dots$$

$$\bar{\nu} = R_{\infty} \left[\frac{1}{6^2} - \frac{1}{n^2} \right] \quad \text{Humphrey Series} \quad \text{IR-region}$$

$$n = 7, 8, 9, \dots$$

fig — representation of the observed spectral lines of the hydrogen atom (32)



① No. of lines in Hydrogen spectrum —

$$= \sum (n_2 - n_1) = \sum \Delta n$$

eg. —] $n_1=1$ & $n_2=3$ — then $\sum (n_2 - n_1) = \sum \Delta n = \sum (3-1)$
 $= \sum 2 = 2+1 = 3$.

No. of lines = 3.

6] $n_1=1, n_2=4$; calculate the no. of lines.

(33)

$$\sum (n_2 - n_1) = \sum (4 - 1) = \sum 3$$

$$= 3 + 2 + 1 = 6$$

$$\text{No. of lines} = 6$$

(ii) No. of fine lines in Hydrogen atom spectrum —

$$= n_1 \times n_2$$

$$\text{IF } n_1=3, n_2=4$$

$$\text{No. of lines} = 4 \times 3$$

$$= 12$$

(iii) Increasing order of Energy in Orbits —

$$E_1 < E_2 < E_3 < E_4 \dots \dots$$

Limitations of

Bohr's Theory

The Bohr's Theory was abandoned 12 years after its formulation in

favour of the present quantum theory of atomic structure.

— Bohr by introducing quantization of angular momentum was able to explain the spectral lines of hydrogen atom. His theory can very well account for the spectral lines for the hydrogenic species — species containing only one e^- such as He^+ , Li^{2+} , Be^{3+} . Bohr's theory, however, completely failed when applied to atoms containing more than one e^- .

- 34
- Besides these, Bohr's theory provides no explanation for the relative intensities of the various spectral lines.
 - This theory also can't explain the splitting of spectral lines in the presence of a magnetic field [Zeeman effect] and an Electrical field [Stark effect].
 - According to Bohr's model of atom, the e^- move along certain circular paths in one plane. Thus, it gives a flat model of atom. But now it is well established that the atom is three dimensional and not flat.

Wave particle duality : de-Broglie hypothesis

Electromagnetic radiations which were considered to have wave characteristics, also possess particle characteristics.

The converse of the above aspect, viz, all material particles, whether big or small, possess the wave characteristics, was proposed by de-Broglie.

The relation connecting the characteristics of wave and particle nature of radiation may be derived as follows— (35)

Both the wave and particle nature of the radiation are associated with the energy according to the following relations.

Planck's relation $E = h\nu = \frac{hc}{\lambda}$ — (i)

Einstein's relation $E = mc^2$ — (ii)

On equating eqⁿ (i) & (ii), we get—

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

or

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

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

— (iii)

According to eqⁿ (iii), the characteristics particle nature (ie. mass m) and wave nature [i.e. wavelength λ] are inversely related to each other. Now c in eqⁿ (iii) is the velocity of the photon, and thus mc may be considered to be the momentum p of the light photon. Thus, we have—

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

— (iv)

for ordinary material particles, de-Broglie suggested that c may be considered to be equivalent to v (i.e. their velocities) and thus eqn (iv) [$\lambda = \frac{h}{p}$] is also applicable to the material particles.

If the mass of a particle is small, as in the case of sub-atomic particles, the wavelength is significant, i.e. for them wave nature is expected. for a particle of larger mass, the wavelength is too small to be of any practical significance.

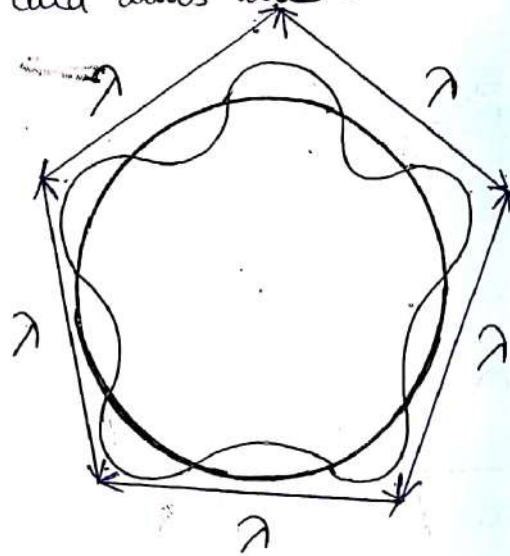
Application of the de-Broglie Relation to Hydrogen Atom

The stationary Bohr's orbit can be readily explained on the basis of the wave nature of e^-

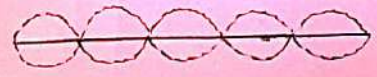
if it is assumed that the wave in any of the orbits is the stationary wave, i.e. the position of its maxima and minima do not change with time. for this to occur, the length of the circular orbit must be an integral multiple of the wavelength, i.e.

$2\pi r = n\lambda$; where $n = 1, 2, \dots$
—(v)

If the above condition is not satisfied, the positions of the maxima would change each time the e^- went around the nucleus and thus the wave would not be stationary.



Stationary wave—
when two progressive waves of same amplitude and wave-length travelling along a straight line in opposite direction superimpose on each other, stationary waves are formed.



Introducing de-Broglie's relation in eqⁿ (i) — we get.

$$2\pi r = n \left[\frac{h}{p} \right]$$

or $pr = L = n \left[\frac{h}{2\pi} \right] \quad \text{--- (ii)}$

a relation which was introduced by Bohr while describing his theory of atomic structure.

X Formula for the wavelength, λ calculation for an e^- accelerated through a certain potential difference, V .

The kinetic energy of the e^- would be given by the relation—

$$\frac{1}{2} mv^2 = eV \quad \text{--- (i)}$$

and thus its momentum is,

$$p = mv \quad \text{--- (ii)}$$

On multiplying and dividing with m in eqn (i), we get

$$\frac{1}{2m} (mv)^2 = eV \quad (30)$$

Now from eqn (ii) -

$$\frac{1}{2m} p^2 = eV$$

$$p^2 = 2meV$$

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

*
eg: What is the speed and de-Broglie wavelength of an e^- that has been accelerated by a potential difference of 500V?

Solution - Since $\frac{1}{2}mv^2 = eV$; we have

$$v = \left[\frac{2eV}{m} \right]^{1/2}$$
$$= \left[\frac{2(1.602 \times 10^{-19} \text{ C})(500\text{V})}{9.109 \times 10^{-31} \text{ kg}} \right]^{1/2}$$

$$v = 1.326 \times 10^7 \text{ m/s} \quad \underline{\text{Ans.}}$$

Now,

$$\lambda = \frac{h}{[2meV]^{1/2}}$$
$$= \frac{6.626 \times 10^{-34} \text{ Js}}{[2(9.109 \times 10^{-31} \text{ kg})(1.602 \times 10^{-19} \text{ C})(500\text{V})]^{1/2}}$$
$$\lambda = 0.55 \text{ \AA} \quad \underline{\text{Ans.}}$$

The Compton Effect The particle nature of the radiation, i.e. that the radiation consisted of (39)

packets of energy called photons, was confirmed to be correct with the experiments performed by A. H. Compton in 1923. He found that if monochromatic X-rays [i.e. X-rays consisting of a single wavelength] are allowed to hit a material of low atomic weight eg. graphite, the scattered radiations contained not only wavelengths of that of the incident X-rays but also contained radiations of higher wavelength [or lower frequency and hence lower energy]. This effect is called Compton effect.

As the scattering is produced by e^- s, it was suggested that it must be due to interaction [collision] between the X-ray photon and the individual e^- of the target that must have resulted in the increase of the wavelength of the scattered X-rays.

If wavelength of incident X-rays = λ

& Energy of incident X-rays = $h\nu$

Then by de-Broglie relation, its momentum will be h/λ .

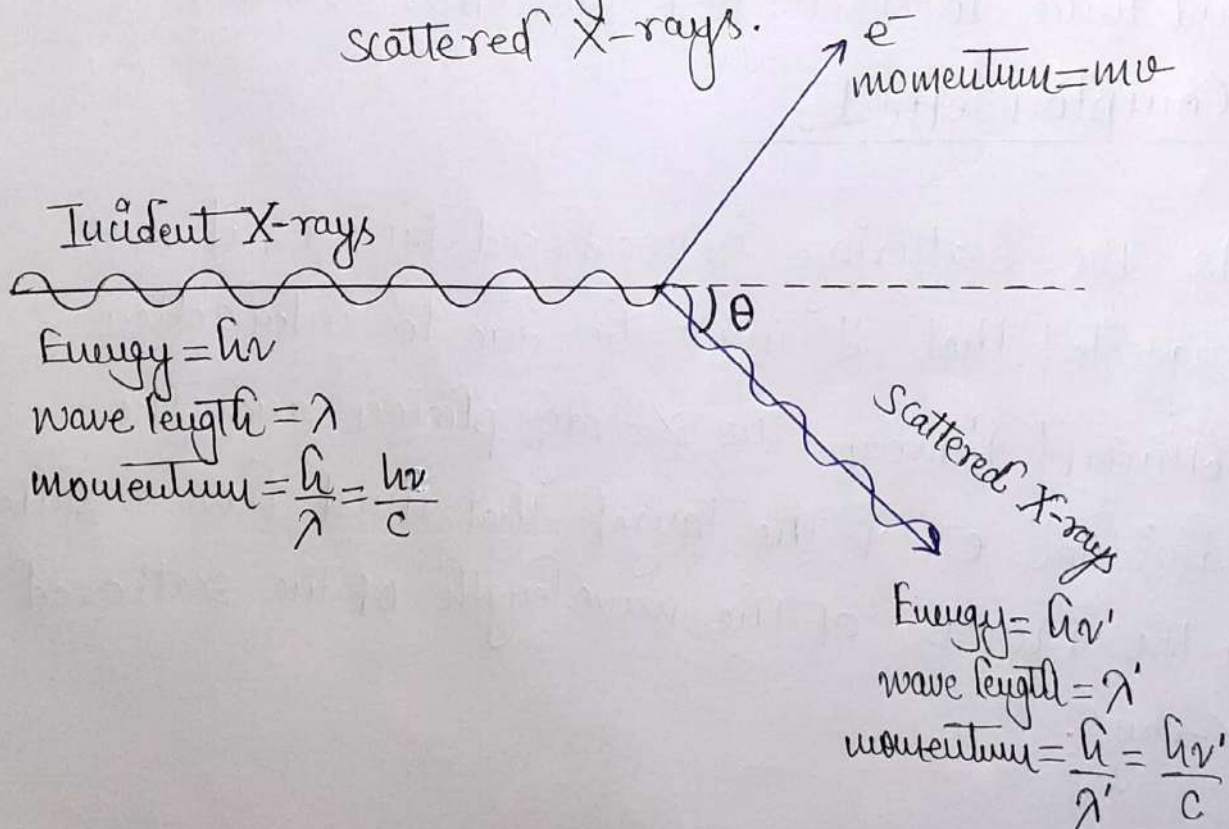
If wavelength & Energy of scattered X-ray photon is λ' & $h\nu'$ and then its momentum will be h/λ' . (40)

If mv is momentum of the e^- after collision, where m is the rest mass of the e^- and v is its velocity, then by applying the laws of conservation of energy and momentum, it can be deduced that the increase in wavelength $[\Delta\lambda = \lambda' - \lambda]$ is given by

$$\Delta\lambda = \lambda' - \lambda = \frac{2h}{mc} \sin^2 \frac{\theta}{2}$$

where - $\Delta\lambda$ - Compton shift.

θ - angle between the incident and the scattered X-rays.



Heisenberg's Uncertainty principle -

In 1927, Werner Heisenberg pointed out that one can not measure accurately both the position and velocity (momentum) of microscopic particle.

On the basis of this observation Heisenberg put forward a principle, known as the Heisenberg's Uncertainty principle. According to this principle -

"It is not possible to determine precisely both the position and the momentum (velocity) of small moving particles with accuracy."

mathematical expression for the uncertainty principle is -

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

where - h - Planck's constant [6.626×10^{-34} Js]

Δx - uncertainty in position

Δp - uncertainty in momentum

$$\because p = mv$$

$$\Delta p = m \Delta v$$

then uncertainty principle can be write as.

$$\Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

(42)

where Δv - uncertainty in velocity.

(i) if Δx is small i.e. the position of particle is measured accurately, then Δp would be large and thus the uncertainty in momentum will be large.

(ii) On the other hand, if Δp is small the momentum of the particle can be measured accurately and the uncertainty in the position (i.e. Δx) will be large.

* Schrodinger Wave Equation—

Erwin Schrodinger (1926) proposed a simple idea that if the e^- behaves like a wave, it should obey the classical eqⁿ of wave motion.

On substituting de-Broglie wave length (given by the relation $\lambda = \frac{h}{mv}$) into classical wave eqⁿ.

Schrodinger obtained an eqⁿ that describes the three-dimensional wave motion of the electron.

This eqⁿ popularly known as Schrodinger wave eqⁿ can be written in its simplest form as—

Shielding for $d e^-$ — $(1s)^2 (2s2p)^8 (3s3p)^8 (3d)^{10} (4s)^2$.

30

$$S = 9 \times 0.35 + 10 \times 1$$

$$S = 21.15$$

$$Z^* = Z - S$$

$$= 30 - 21.15$$

$$Z^* = \underline{\underline{8.85}}$$

X

43

Hamiltonian Operator —

from Schrodinger wave equation,

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

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

$$\text{or } \frac{-h^2}{8\pi^2 m} \nabla^2 \psi + V\psi = E\psi$$

$$\text{or } \left[\frac{-h^2}{8\pi^2 m} \nabla^2 + V \right] \psi = E\psi$$

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

Another form of Schrodinger wave Eqⁿ.

where — \hat{H} — Hamiltonian operator

$$\hat{H} = \frac{-h^2}{8\pi^2 m} \nabla^2 + V$$

ψ - Eigen function.

E - Eigen value.

44

$\hat{H}\psi = E\psi$ - also called eigen value equation.

or

$$\left(\begin{array}{c} \text{Energy} \\ \text{operator} \end{array} \right) \left(\begin{array}{c} \text{wave} \\ \text{function} \end{array} \right) = \left(\begin{array}{c} \text{Energy} \end{array} \right) \left(\begin{array}{c} \text{wave} \\ \text{function} \end{array} \right)$$

This result can be generalised as it is equally applicable to all other observables, i.e. measurable properties of a system. Thus in general, we can write -

$$\left[\begin{array}{c} \text{Operator corresponding} \\ \text{to an observable} \end{array} \right] \left[\begin{array}{c} \text{wave} \\ \text{function} \end{array} \right] = \left[\begin{array}{c} \text{value of} \\ \text{observable} \end{array} \right] \times \left[\begin{array}{c} \text{wave} \\ \text{function} \end{array} \right]$$