

Chapter  $\Rightarrow$  12

# ATOMS

Atom Model  $\Rightarrow$  Propose theory to describe the structure of an atom.

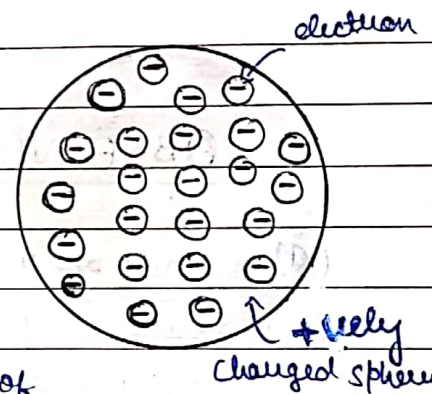
## THOMSON'S ATOM MODEL

In 1898, J.J. Thomson proposed that an atom is a sphere of positively charged matter with electrons embedded in it. The +ve charge is uniformly distributed over the entire atom.

Thomson's atomic model is also known as **plum pudding model**.

Drawbacks of Thomson's Model  $\Rightarrow$

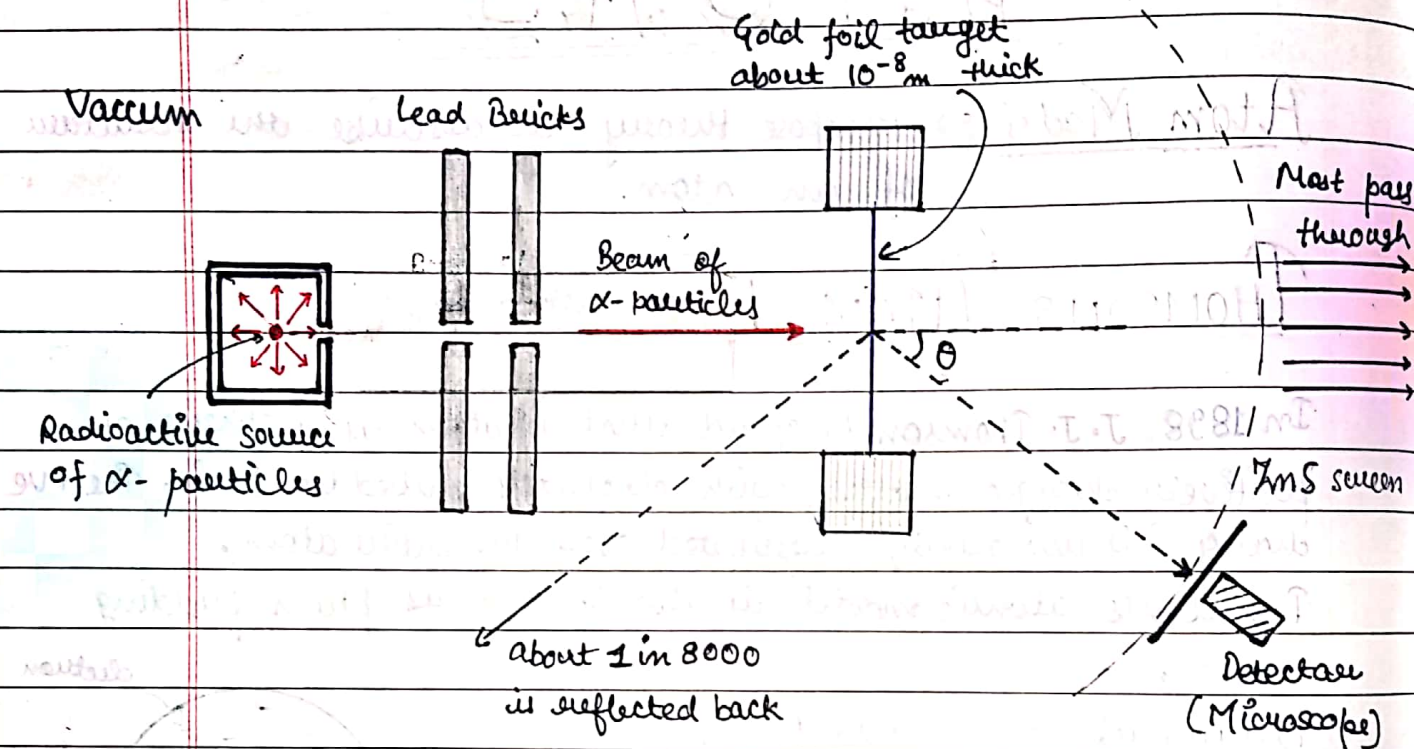
- (1) It could not explain the origin the origin of several spectral series in the case of hydrogen and other atoms.
- (2) It failed to explain the large angle scattering of  $\alpha$ -particles in Rutherford's experiment.



## RUTHERFORD'S ALPHA PARTICLE SCATTERING EXPERIMENT [GEIGER - MARS DEN EXPERIMENT]

$\alpha$ -particle is a helium ion [ $\text{He}^{2+}$ ] and its mass is nearly 4 times the mass of proton.

The  $\alpha$  particle from a radioactive source [ ${}_{83}^{214}\text{Bi}$ ] which is enclosed in a thick lead block with narrow opening are collimated into a narrow beam with the help of a lead plate having a narrow slit. The beam is then allowed to fall on a thin gold foil (of thickness  $2.1 \times 10^{-7} \text{ m}$ ). The  $\alpha$ -particles scattered in different directions are observed with the help of a rotatable detector which consists of a zinc sulphide screen and a microscope. The whole apparatus is enclosed in a vacuum chamber.



### OBSERVATIONS :-

- Most of the  $\alpha$ -particles pass straight through gold foil.
- Different  $\alpha$ -particles underwent different amount of deflections.
- Very small no. of  $\alpha$ -particles reverse their paths (about 1 in 8000).

Not in syllabus.

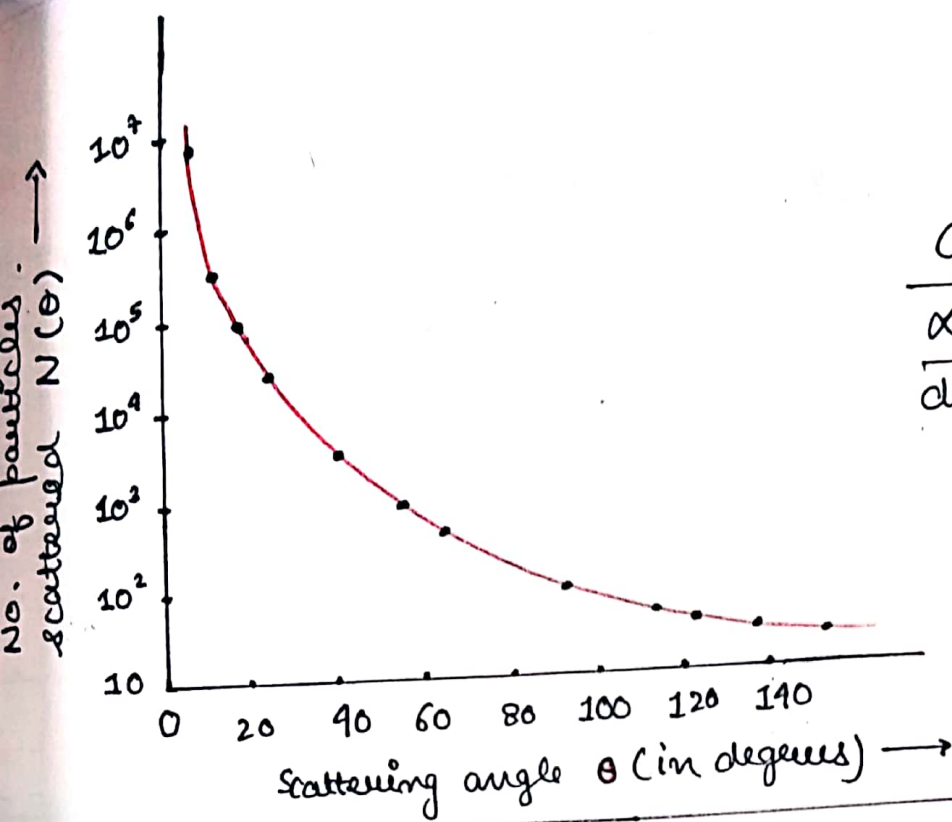
### Distance of Closest Approach: Estimation of Nuclear size -

As the  $\alpha$ -particle approaches the +ve nucleus, it experiences Coulombic repulsion and its kinetic energy gets progressively converted into electrical energy.

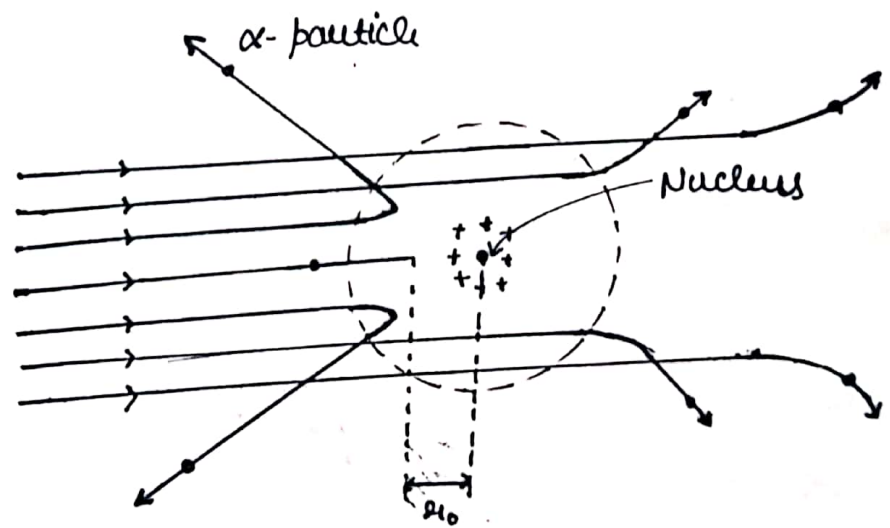
'The minimum distance from the nucleus at which the  $\alpha$ -particle stops and then begins to retrace its path, is called the distance of closest approach.'

Denoted by  $\Rightarrow r_0$

$\alpha$ -particle



Graph of the total no. of  $\alpha$ -particles scattered at different angles  $\theta$ .



Scattering of  $\alpha$ -particles on the Rutherford Model

# RUTHERFORD'S MODEL OF AN ATOM

## [Classical / Planetary Atom Model]

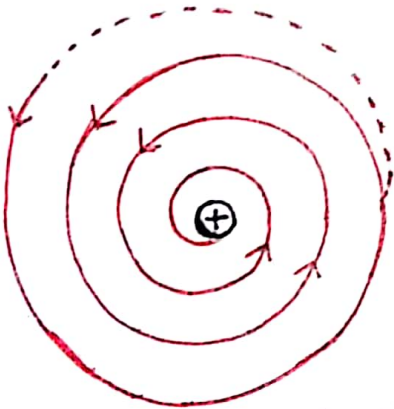
On the basis of the  $\alpha$ -particle scattering experiment, Rutherford proposed the following model of an atom:→

- (1) Atom may be regarded as a sphere of diameter  $10^{-10}$  m.
- (2) Whole of the +ve charge and almost the entire mass of the atom is concentrated in a small central core (diameter  $\approx 10^{-15}$  m) called nucleus.
- (3) The nucleus is surrounded by electrons leaving plenty of empty space in the atom.
- (4) As atom is electrically neutral, therefore total +ve charge on the nucleus  $\approx$  total -ve charge of electrons in atom.
- (5) Electrons in the atom revolve around the nucleus in circular orbits. The required centripetal force to them is provided by electrostatic force of attraction between  $e^-$  and nucleus.

"The butterfly counts not months but moments, and has time enough."—Rabindranath Tagor

## Drawbacks of Rutherford's Atom Model :->

- (1) If Rutherford's atom model is true, then revolving electron should continuously emit energy and hence the radius of its path should go on decreasing and ultimately it should fall into the nucleus but it does not happen. Thus, Rutherford's Atom Model could not explain the stability of the atom.
- (2) If Rutherford's atom model is true then electron can revolve in the orbits of all possible radii and hence it should emit a continuous energy spectrum. However, atoms like hydrogen possess a discrete line spectrum.



Spiral Path of an accelerated  $e^-$

ing through a potential difference of  $2 \times 10^6$  V  
 atomic no. of silver is 47. Calculate (i) the  
 - the time of falling on the foil (ii) the K.E.  
 a distance of  $5 \times 10^{-14}$  m from the nucleus  
 distance from nucleus of Ag to which  $\alpha$ -particle

$$V = 2e \times 2 \times 10^6$$

$$\text{particle} = 2 \times 1.6 \times 10^{-19} \times 2 \times 10^6 = 6.4 \times 10^{-13} \text{ J}$$

# BOHR'S ATOMIC MODEL

Bohr retained all essential features of Rutherford's Atom Model but to overcome its drawbacks he introduced a concept of stationary orbits.

## POSTULATES :-

(1) In a hydrogen atom -vely charged  $e^-$  revolves in a circular orbit around the heavy +vely charged nucleus. The required centripetal force is provided by the attractive force exerted by the nucleus on it.

(2) Bohr's Quantisation Condition :-

Electron can revolve around the nucleus only in those circular orbits in which angular momentum of an  $e^-$  is an integral multiple of  $\frac{h}{2\pi}$ .

$$L = mvr = n \left( \frac{h}{2\pi} \right) \quad n = 1, 2, 3, \dots$$

$r \Rightarrow$  radius of permitted orbits  $\rightarrow$  Principle Quantum Number

While revolving in such an orbit electron can not radiate energy and hence such orbits are called stationary or non-radiating orbits.

(3) Bohr's Frequency Condition :-

Energy is radiated when  $e^-$  jumps from higher to lower energy orbits and energy is absorbed when it jumps from lower to higher energy orbits.

Let  $E_i$  is the energy associated with the orbit of principle quantum number  $n_i$ .

$E_f$  is the energy associated with the orbit of principle quantum number  $n_f$ .

then,  $E = E_i - E_f$  (let  $n_i > n_f$ )

$$h\nu = E_i - E_f$$

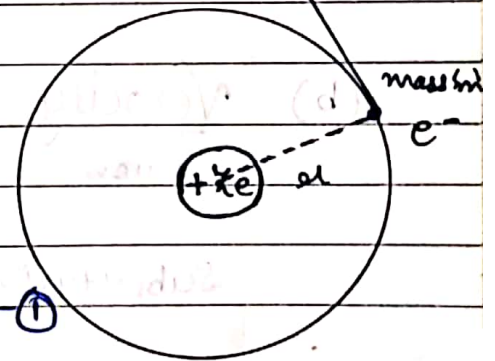
## BOHR'S THEORY OF HYDROGEN ATOM

In hydrogen like atom let an electron [charge ' $-e$ '] revolves around a nucleus [charge ' $+Ze$ '] in a circular orbit of radius ' $r$ ' with velocity ' $v$ '. Its mass be ' $m$ ' of  $e^-$ .

### 1) Radius of Orbit

Electrostatic force on  $e^-$  due to nucleus

$$F_e = \frac{k(Ze)(e)}{r^2} \therefore F_e = \frac{kZe^2}{r^2} \quad (1)$$



Centripetal force on  $e^-$  to move in circular path

$$F_c = \frac{mv^2}{r} \quad (2)$$

As centripetal force is provided to  $e^-$  by electrostatic force

$$\therefore F_e = F_c$$

$$\frac{mv^2}{r} = \frac{kZe^2}{r^2}$$

$$mv^2 = \frac{kZe^2}{r} \quad (3)$$

Using Bohr's Quantisation Condition

$$mvr = \frac{nh}{2\pi} \quad \text{or } v = \frac{nh}{2\pi mr}$$

$$\therefore v = \frac{nh}{2\pi m r} \quad (4)$$

from (3) and (4)

$$m \left[ \frac{nh}{2\pi m r} \right]^2 = \frac{kZe^2}{r}$$

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

$$\therefore r = \frac{n^2 h^2}{4\pi^2 m k Z e^2} \quad \text{--- (5)}$$

$$r = 0.53 \frac{n^2 \text{ \AA}}{Z} \quad \text{ie., } r \propto n^2 \quad \text{--- (6)}$$

Clearly, the radii of the permitted orbits are proportional to  $n^2$  & increase in the ratio 1:4:9:16:-----

(b) Velocity of electron  $\rightarrow$

from eq<sup>n</sup> (4)  $v = \frac{nh}{2\pi m r}$

Substituting value of  $r$  from eq<sup>n</sup> (5) in above eq<sup>n</sup>

$$v = \frac{nh}{2\pi m \left[ \frac{n^2 h^2}{4\pi^2 m k Z e^2} \right]}$$

$$v = \frac{2\pi k Z e^2}{nh} \quad \text{--- (7)}$$

$n = 1, 2, 3, \dots$

For hydrogen atom,  $Z = 1$ ,  $\therefore$  from eq<sup>n</sup> (7)

$$v = \frac{2\pi k e^2}{nh} = \frac{2\pi k e^2}{ch} \left[ \frac{c}{n} \right] \quad \left[ c \Rightarrow \text{speed of light} \right]$$

$$\therefore v = \alpha \cdot \frac{c}{n} \quad \text{--- (8)}$$

Here,  $\alpha = \frac{2\pi k e^2}{ch}$  = Dimensionless constant

[Fine Structure Constant =  $\frac{1}{137}$ ]



∴ from eq<sup>n</sup> (8)

$$v = \frac{1}{137} \frac{c}{n} \quad (9)$$

$$v = \frac{2.19 \times 10^6}{n} \text{ m/s}$$

for  $n = 1$

$$v = \frac{c}{137} \quad (10)$$

Clearly, velocity ( $v$ )  $\propto \frac{1}{n}$

(c) Energy of electron  $\Rightarrow$  It includes both kinetic energy and potential electrostatic potential energy of the two charges.

(i) Kinetic Energy  $\Rightarrow$  From eq<sup>n</sup> (3)  $mv^2 = \frac{kZe^2}{a}$

$$\therefore \frac{1}{2} mv^2 = \frac{1}{2} \frac{kZe^2}{a}$$

$$\text{K.E.} \quad E_k = \frac{kZe^2}{2a} \quad (11)$$

(ii) Potential Energy  $\Rightarrow$  P.E. of electron in  $n^{\text{th}}$  orbit is

$$U = k \frac{q_1 q_2}{a} = k \frac{(Ze)(-e)}{a}$$

$$U = -\frac{kZe^2}{a} \quad (12)$$

$$U = -2E_k$$

(iii) Total energy of electron  $\Rightarrow E = \text{K.E.} + \text{P.E.}$

$$E = \frac{kZe^2}{2a} - \frac{kZe^2}{a}$$

$$E_n = -\frac{kZe^2}{2a} \quad (13)$$

$$E_n = -E_k$$

from eq<sup>n</sup> (5) substitute the value of  $a$  in above eq<sup>n</sup>, we

$$E_n = -\frac{kZe^2}{2a}$$

$$= -\frac{kZe^2}{2 \cdot \frac{n^2 h^2}{4\pi^2 m k Z e^2}}$$

$$E_n = -\frac{2\pi^2 m k^2 Z^2 e^4}{n^2 h^2} \quad (14)$$

$$n = 1, 2, 3, 4, \dots$$

$$E_n = - (\text{const}) \frac{Z^2}{n^2}$$

$$\text{or, } E_n = -13.6 \frac{Z^2}{n^2} \text{ (eV)} \quad (15)$$

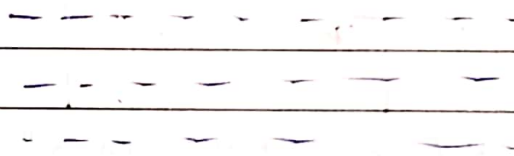
Clearly,

$$E_1 = -13.6 Z^2$$

$$E_2 = -13.6 \frac{Z^2}{4} = \frac{1}{4} E_1$$

$$E_3 = -13.6 \frac{Z^2}{9} = \frac{1}{9} E_1$$

$$E_4 = -13.6 \frac{Z^2}{16} = \frac{1}{16} E_1$$



$$E_\infty = 0$$

from above result, it is clear that  $e^-$  can have only some definite values of energies while revolving in orbits  $n = 1, 2, 3, 4, \dots$

It is called Energy Quantisation.

## SPECTRAL SERIES OF HYDROGEN ATOM

'When an  $e^-$  jumps from higher energy level to lower energy, the difference of the energies of the two levels is emitted as radiation of particular wavelength known as Spectral Lines.'

$$\text{as } E_n = - \frac{2\pi^2 m k^2 Z^2 e^4}{n^2 h^2} \quad (1)$$

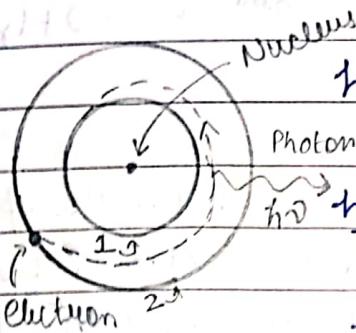
If  $e^-$  jumps from orbit with Principle Quantum number  $n_i$  to an orbit with principle Quantum no.  $n_f$  then,

Energy radiated is given as -

$$E = E_i - E_f$$

$$h\nu = -\frac{2\pi^2 m k^2 e^4}{n_i^2 h^2} - \left[ -\frac{2\pi^2 m k^2 e^4}{n_f^2 h^2} \right]$$

$$h\nu = -\frac{2\pi^2 m k^2 e^4}{n_i^2 h^2} + \frac{2\pi^2 m k^2 e^4}{n_f^2 h^2}$$



$$\frac{hc}{\lambda} = \frac{2\pi^2 k^2 m e^4}{h^2} \left[ \frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \quad (d)$$

$$\frac{1}{\lambda} = \frac{2\pi^2 k^2 m e^4}{ch^3} \left[ \frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \quad (2)$$

$\frac{2\pi^2 k^2 m e^4}{h^3 c}$  = a constant called **RYDBERG CONSTANT**  
 $[R_H] = 1.097 \times 10^7 \text{ m}^{-1}$   
 $\approx 1.1 \times 10^7 \text{ m}^{-1}$

∴ eq<sup>n</sup> (2) can be written as

$$\frac{1}{\lambda} = R_H \left[ \frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \quad (3)$$

Here,  $\frac{1}{\lambda} = \bar{\nu}$  represents **WAVE NUMBER** i.e., no. of waves of wavelength  $\lambda$  in 1m.

eq<sup>n</sup> (3) gives the wavelength of the spectral lines emitted when electron jumps from the orbit of principle quantum no. ' $n_i$ ' to the orbit of principle quantum no. ' $n_f$ '.

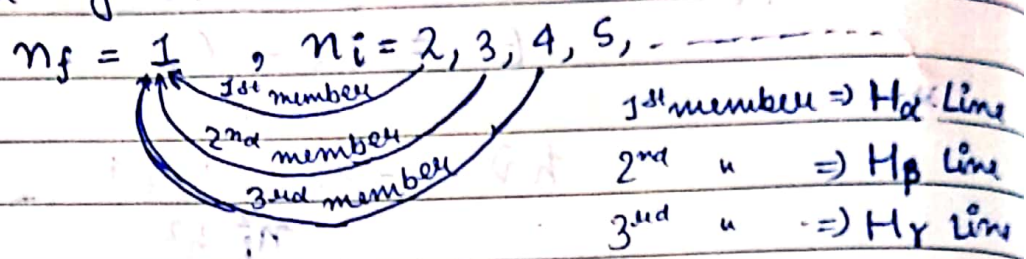
For the transition of electron b/w two different energy levels, the spectral lines of the different wavelengths are obtained which are found to fall into a number of the spectral series as discussed below:→

(a) **LYMAN SERIES** :→ 'It is the series in which the spectral lines correspond to the transition of electron from some higher energy orbit to lower energy orbit corresponding to  $n_f = 1$ .'

1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> member all same for all series as per the series  
 (H $\alpha$ ) (H $\beta$ ) (H $\gamma$ ) Balmer 1<sup>st</sup> memb.  $\Rightarrow$  3  $\rightarrow$  2  
 2<sup>nd</sup> memb.  $\Rightarrow$  4  $\rightarrow$  2  
 3<sup>rd</sup> memb.  $\Rightarrow$  5  $\rightarrow$  2 and so on for other series

Date \_\_\_/\_\_\_/\_\_\_

i.e., for Lyman Series



This series lies in Ultraviolet region.

(b) BALMER SERIES  $\Rightarrow$  'It is the series in which the spectral lines correspond to the transition of electron from some higher energy orbit to lower energy orbit corresponding to  $n_f = 2$ .'

i.e., for Balmer series

$n_f = 2$ ,  $n_i = 3, 4, 5, 6, 7, \dots$

This series lies in Visible region.

(c) PASCHEN SERIES  $\Rightarrow$  'It is the series in which the spectral lines correspond to the transition of electrons from some higher energy orbit to lower energy orbit corresponding to  $n_f = 3$ .'

i.e., for Paschen Series,

$n_f = 3$ ,  $n_i = 4, 5, 6, 7, 8, \dots$

This series lies in Infra-Red Region.

(d) BRACKETT SERIES  $\Rightarrow$  'It is the series in which the spectral lines correspond to the transition of electrons from some higher energy orbit to lower energy orbit corresponding to  $n_f = 4$ .'

i.e., for Brackett Series,

$n_f = 4$ ,  $n_i = 5, 6, 7, 8, 9, \dots$

This series lies in Infra-Red Region.

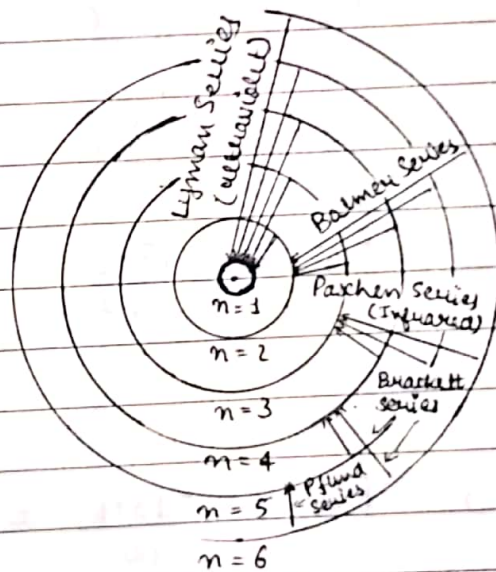
2) **PFUND SERIES**  $\Rightarrow$  'It is the series in which the spectral lines correspond to the transition of electrons from some higher energy orbit to lower energy orbit corresponding to  $n_f = 5$ '

i.e., four Pfund series,

$$n_f = 5, \quad n_i = 6, 7, 8, 9, \dots$$

This series lies in <sup>Far</sup> Infra-Red region.

Spectral series of Hydrogen atom



## ENERGY LEVEL DIAGRAM OF HYDROGEN ATOM

The energy of electron in  $n^{\text{th}}$  orbit is given by

$$E_n = - \frac{2\pi^2 m e^4 k^2}{n^2 h^2} \quad \text{--- (1)}$$

For hydrogen  $Z=1$ , therefore substituting the values of all constants

$$E_n = - \frac{21.76 \times 10^{-19} \text{ J}}{n^2}$$

or  $E_n = - \frac{21.76 \times 10^{-19} \text{ eV}}{n^2 \times 1.6 \times 10^{-19}}$

$$E_n = - \frac{13.6 \text{ eV}}{n^2} \quad \text{--- (2)}$$

for  $n = 1$ ,  $E_1 = \frac{-13.6}{1^2} = -13.6 \text{ eV}$

for  $n = 2$ ,  $E_2 = \frac{-13.6}{2^2} = -3.4 \text{ eV}$

for  $n = 3$ ,  $E_3 = \frac{-13.6}{3^2} = -1.51 \text{ eV}$

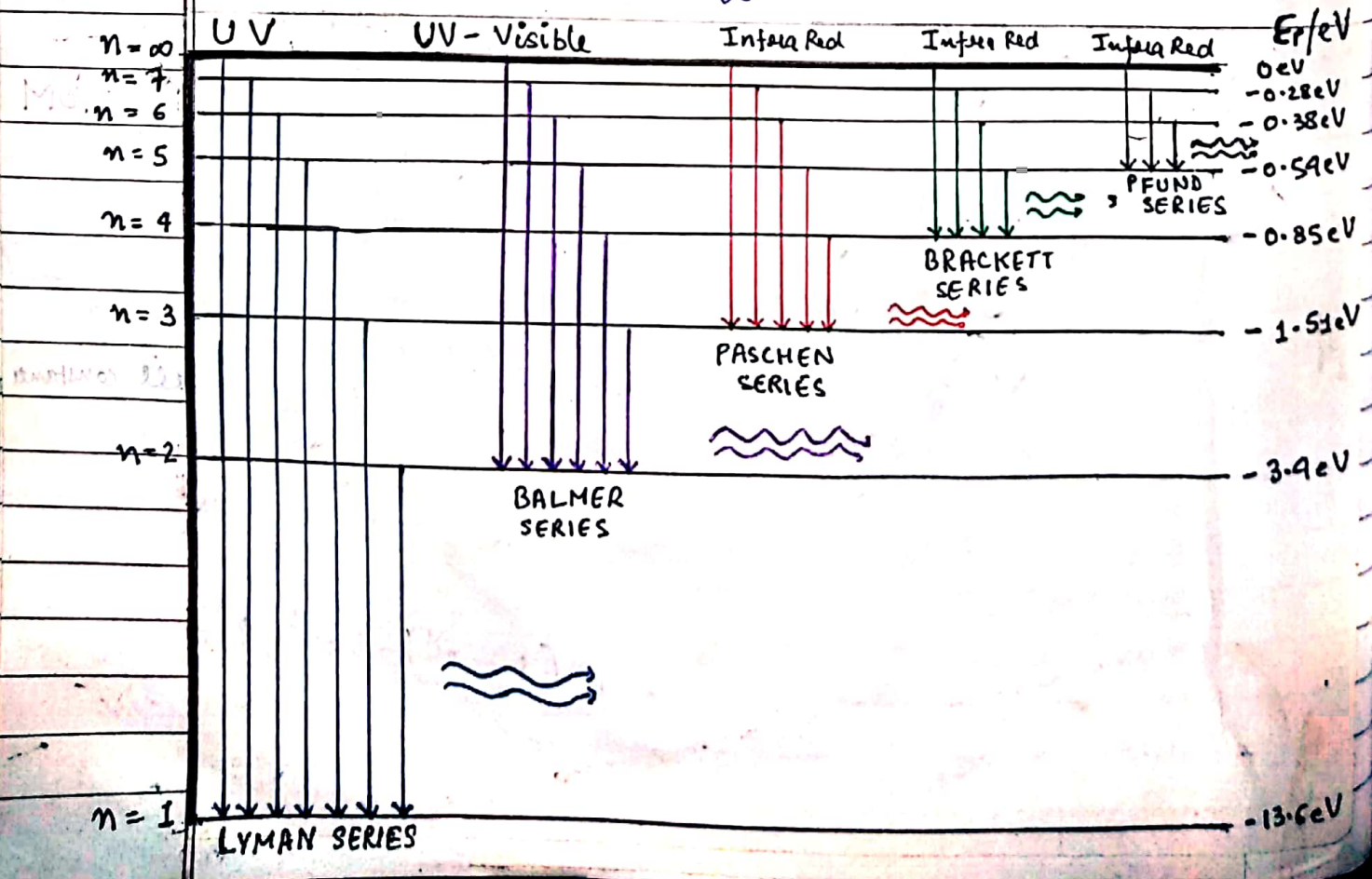
for  $n = 4$ ,  $E_4 = \frac{-13.6}{4^2} = -0.85 \text{ eV}$

for  $n = 5$ ,  $E_5 = \frac{-13.6}{5^2} = -0.54 \text{ eV}$

for  $n = 6$ ,  $E_6 = \frac{-13.6}{6^2} = -0.38 \text{ eV}$

for  $n = 7$ ,  $E_7 = \frac{-13.6}{7^2} = -0.28 \text{ eV}$

for  $n = \infty$ ,  $E_{\infty} = \frac{-13.6}{\infty} = 0$



EXCITATION  $\Rightarrow$  'The process of absorption of energy by an electron so as to raise it from a lower energy level to some higher energy level is called excitation.'

EXCITATION ENERGY  $\Rightarrow$  'The energy required to raise an electron from its ground state to an excited state is called excitation energy.'

EXCITATION POTENTIAL  $\Rightarrow$  'The potential difference through which an electron in an atom has to be accelerated to just raise it from its ground state to the excited state is called excitation potential for that state.'

For e.g. Energy required to raise an  $e^-$  from  $n=1$  to  $n=2$  orbit and  $n_1$  to  $n_3$  for hydrogen atom.

$$n_1 \text{ to } n_2 = E_2 - E_1 = -3.4 - (-13.6) = 10.2 \text{ eV (1}^{\text{st}} \text{ excitation energy)}$$

$$n_1 \text{ to } n_3 = E_3 - E_1 = -1.51 - (-13.6) = 12.09 \text{ eV (2}^{\text{nd}} \text{ excitation energy)}$$

For hydrogen atom:-

$$1^{\text{st}} \text{ excitation Potential (} n_1 \text{ to } n_2) = -3.4 - (-13.6) = 10.2 \text{ V}$$

$$2^{\text{nd}} \text{ excitation Potential (} n_1 \text{ to } n_3) = -1.51 - (-13.6) = 12.09 \text{ V}$$

IONISATION  $\Rightarrow$  'The process of knocking an electron out of the atom (to take  $e^-$  from its ground state to the outermost orbit  $n=\infty$ ) is called ionisation.'

IONISATION ENERGY  $\Rightarrow$  'The energy required to eject an  $e^-$  out of the atom is called ionisation energy.'

For e.g. In hydrogen atom Ionisation energy = Energy required to raise an  $e^-$  from  $n=1$  to  $n=\infty$

$$= E_{\infty} - E_1 = 0 - (-13.6) = 13.6 \text{ eV}$$

IONISATION POTENTIAL  $\Rightarrow$  'The potential through which an electron in an atom has to be accelerated to knock an electron out of the atom is called ionisation potential.'

$$\text{Ionisation Potential of hydrogen atom} = 0 - (-13.6) = 13.6 \text{ V}$$

### LIMITATIONS OF BOHR'S THEORY $\Rightarrow$

- (1) Applicable only to hydrogen like atoms only i.e., atoms having only 1 electron.
- (2) Failed to explain the fine structure of spectral line. (in hydrogen spectrum, certain spectral lines are not single lines but a group of closed lines with slightly different frequencies)
- (3) Bohr's theory does not tell about the relative intensities of spectral lines.
- (4) Contradictory to Heisenberg's Uncertainty Principle.
- (5) It considers electron as a particle but it exhibits the wave nature also.
- (6) It does not tell the further splitting of spectral lines in a magnetic field (Zeeman effect) or in an electric field (Stark effect).

Q  $\Rightarrow$  Calculate kinetic energy and Potential energy of electron in the 1<sup>st</sup> orbit of Hydrogen atom.

Sol<sup>n</sup> as 
$$r = 0.53 \frac{n^2}{Z}$$

for Hydrogen atom  $Z = 1$  and  $n = 1 \therefore r = 0.53 \text{ \AA}$

$$K.E. \text{ of } e^- = \frac{kZe^2}{2r} = \frac{9 \times 10^9 \times 1 \times (1.6 \times 10^{-19})^2}{2 \times 0.53 \times 10^{-10}}$$

$$= \frac{9 \times 10^9 \times 1.6 \times 10^{-19}}{1.06 \times 10^{-10}} \text{ eV}$$

$$\boxed{E_k = 13.58 \text{ eV}}$$