

Atomic Structure : Old view -

In older days, the philosophers' views regarding structure of matter was that every matter is composed of tiny particles. They had no experimental proof in support of this view. In 1803, Dalton pronounced his atomic theory.

According to this theory, matter is constituted of tiny particles, called 'atoms'. According to Dalton, atoms could not be divided by any physical or chemical process.

In 1897, Sir J.J. Thomson discovered electron and almost at the same time Becquerel discovered radioactivity. Then it was proved by experiments that there are negatively-charged particles in the atom of every element.

At that times there was no knowledge about the distribution of electrons, the positive charge and the mass inside the atom.

Thomson's Model of Atom

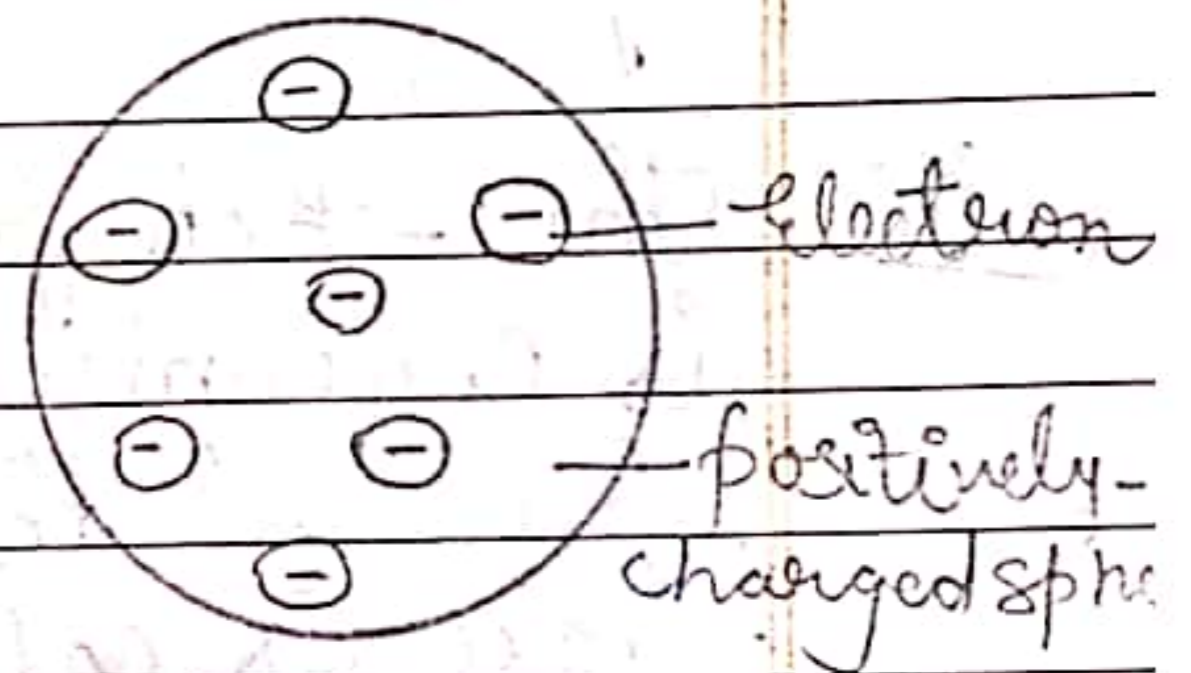
In 1904, J.J. Thomson for the first time suggested a model for the atom, called

the 'Thomson's atomic model'. According to this model, an atom is a positively-charged sphere of radius 10^{-10} m , in which mass and positive charge of atom are uniformly distributed.

The phenomena of thermionic emission, photoelectric emission and ionisation were explained on the basis of this model.

The emission of spectra from atoms could not be explained from this model.

Thomson's model could not predict any reason for the scattering of α -particles demonstrated later on by Rutherford.

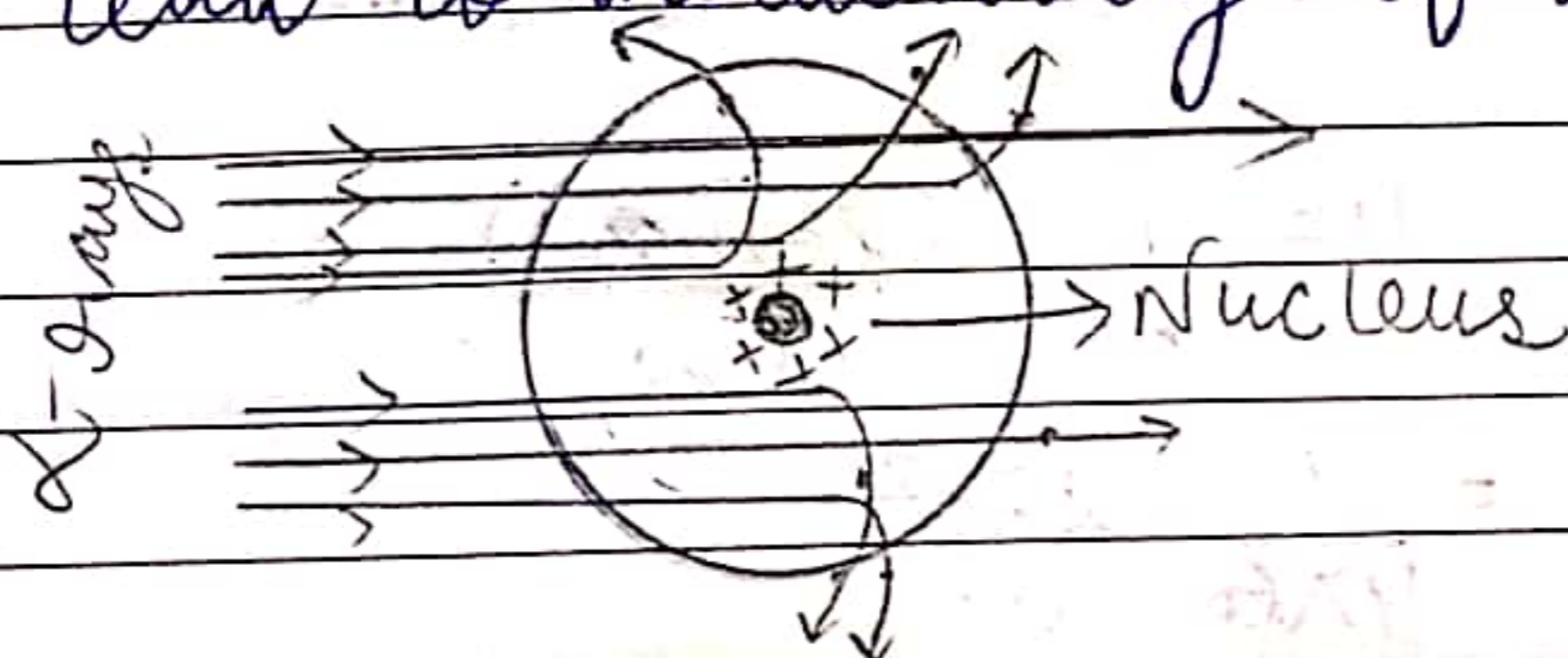


Thomson's Model

α -particle Scattering Experiment

In 1906, Rutherford observed that when a sharp beam of α -particles falls upon a photographic plate in vacuum, a sharp image is obtained.

In 1909 Geiger and Marsden made a series of measurement on the scattering of α -particles which lead to the discovery of atomic nucleus.



It was found that although most of the particles scattering through angle of the order of 1° or less, but a small number, say about 1 in every 10,000, scattered through 90° or even 180°

i Atoms ~~are~~ are mostly hollow inside.

ii The whole of the +ve charge of atom must be concentrated in a very small space.

iii The whole positive charge in the atom is concentrated in an extremely small space at the centre of the atom. This place is called the nucleus.

Distance of Closest Approach (Estimation of the Size of Nucleus)

We can estimate the size of the nucleus by the scattering of α -particles. The particles are emitted with k.e. from the radioactive source. The particle which goes straight (head on) towards the nucleus reaches closest to the nucleus.

$$U = \frac{1}{4\pi\epsilon_0} \frac{(Ze)(Ze)}{r_0}$$
$$= \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_0}$$

$$K = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_0}$$

$$\left[r_0 = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{K} \right]$$

Rutherford's Model of Atom

In this model the total negative charge of the electrons is equal to the positive charge of the nucleus, the atom as a whole being electrically neutral. Rutherford assumed that the electrons in the atom are not stationary, but are revolving around the nucleus in different orbits, and the necessary centripetal force is provided by the electrostatic force of attraction b/w the electron & the nucleus.

Drawbacks of Rutherford's Model

Regarding stability of atom - electromagnetic waves should be continuously radiated by the revolving electrons. Due to this continuous loss of energy of the electrons, the radii of their orbits should be continuously decreasing and ultimately the electrons should fall into the nucleus. Thus atom cannot remain stable.

Regarding explanation of line-spectrum - Due to continuously changing radii of the circular orbits

of electrons, the frequency of revolution of the electrons must also be changing. As a result, electrons will radiate electromagnetic waves of all frequencies. i.e. the spectrum of these waves will be 'Continuous' in nature. But experimentally the atomic spectra are not continuous, they have many sharp lines and each spectral line corresponds to a particular frequency. So an atom should radiate waves of some definite frequencies only, not of all frequencies, thus, Rutherford model was unable to explain the line spectrum.

Bohr's model of atom

In 1913 Prof. Niels Bohr proposed the following three postulates.

i Electrons can revolve only in those orbits in which their angular momentum is an integral multiple of $\frac{h}{2\pi}$.

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

This equation is called 'Bohr's quantization condition'.

ii When the while revolving in stable orbits, the electrons do not radiate energy in

spite of their acceleration towards in the centre of the orbit. Hence atom remains stable.

iii) When the atom receives energy from outside then one of its outer electrons leaves its orbit and goes to some higher orbit. This state of the atom is called 'excited state'. The electron in the higher orbit stays only for 10^{-8} second & returns back to a lower orbit. While returning back, the electron radiates energy in the form of electromagnetic waves.

$$h\nu = E_2 - E_1$$

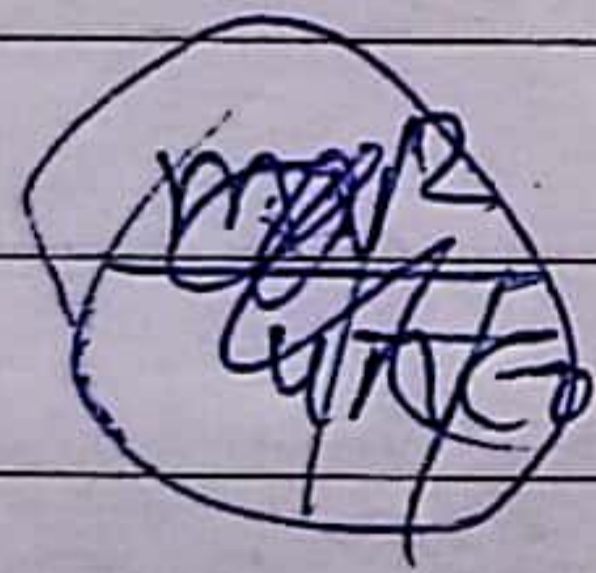
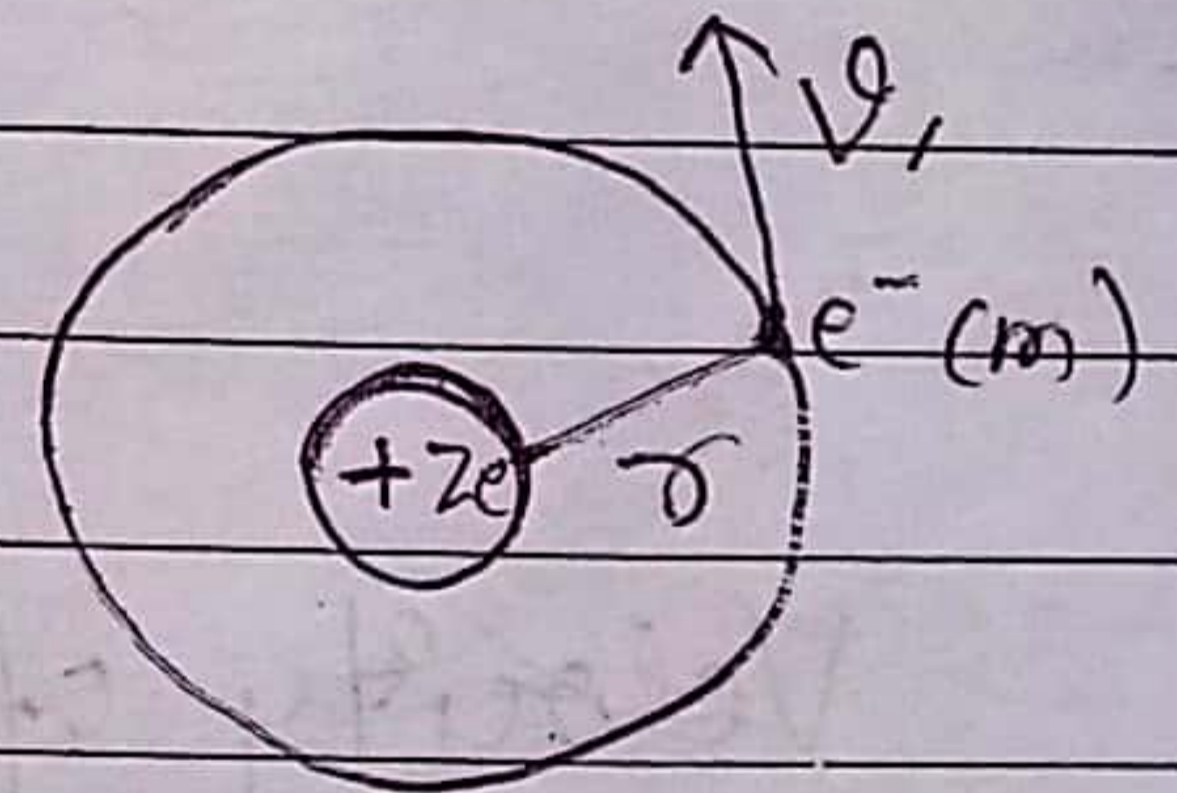
$$\left[\nu = \frac{E_2 - E_1}{h} \right]$$

This equation is called Bhor's frequency condition.

Radius of orbit

Electric force b/w e^- & nucleus = Centripital force]

$$\frac{1}{4\pi\epsilon_0} \frac{Ze \times e}{r^2} = \frac{mv^2}{r}$$



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

According to Bohr's atomic model.

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

$$\frac{(2)^2 \div (1)}{m^2 v^2 r^2} = \frac{n^2 h^2}{4\pi^2} \times \frac{1}{4\pi^2 \frac{ze^2}{r}}$$

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

$$r = \left(\frac{h^2 z e^2}{\pi m e^2} \right) \times \frac{n^2}{z} \quad (3)$$

$[r \propto n^2]$

★ Ex - The radius of 2nd orbit of H atom is 0.80 \AA then what will be the radius of 4th orbit of H atom?

Ans

$$\frac{r_2}{r_4} = \frac{(2)^2}{(4)^2}$$

$$\frac{r_2}{r_4} = \frac{4}{16}$$

$$r_4 = 4r_2$$

$$r_4 = 4 \times 0.80$$

$$r_4 = 3.20 \text{ \AA}$$

Velocity of e^- in stationary orbit

Putting the value of v in eq - (2)

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

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$$v = \left(\frac{e^2}{2 h c} \right) \cdot \frac{z}{n}$$

$$\left[v \propto \frac{1}{n} \right]$$

Energy of electron in stationary orbit

$$v_1 \rightarrow v_2 \quad u = \frac{1}{4 \pi \epsilon_0} \frac{q_1 q_2}{r}$$

K.E. of e^- in stationary orbit

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

$$\frac{1}{2} m \times \left(\frac{e^2 z}{2 h c n} \right)^2 = \frac{1}{8} m \times \frac{e^4 z^2}{4 h^2 c^2 n^2}$$

$$K.E. = \frac{1}{8} \frac{m e^4 z^2}{h^2 c^2 n^2} \quad \text{--- (1)}$$

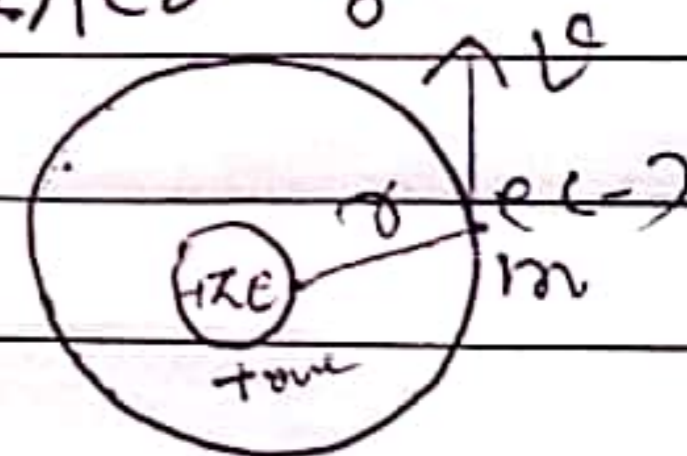
The electrical P.E. of e^-

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

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

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

$$P.E. = - \frac{1}{4} \frac{m e^4 z^2}{h^2 c^2 n^2} \quad \text{--- (2)}$$



For H atom

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

If e^- transmit from n_2 higher energy level to n_1 lower energy level

According to Bohr model .

$$E_{n_2} - E_{n_1} = h\nu$$

$$-\frac{Rhc}{n_2^2} - \left(-\frac{Rhc}{n_1^2}\right) = \frac{hc}{\lambda}$$

$$\therefore \nu = \frac{c}{\lambda}$$

$$\frac{Rhc}{n_1^2} - \frac{Rhc}{n_2^2} = \frac{hc}{\lambda}$$

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

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The value of Rydberg constant is

$$R = \frac{me^4}{8\epsilon_0^2 h^3} = \frac{(9.11 \times 10^{-31} \text{ kg}) \times (1.60 \times 10^{-19} \text{ C})^4}{8 \times (8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})^2 \times (3.00 \times 10^8 \text{ m/s}) \times (6.63 \times 10^{-34} \text{ Js})^3}$$
$$= \underline{1.090 \times 10^7 \text{ m}^{-1}}$$

Discrete Energy levels of Atom

i) when $E = 0$ to 4.86 eV, then $E' = E$, Thus
 $(E - E') = 0$.

ii) when $E = 4.86$ eV, then $E' = 4.86$ eV or zero.
 $(E - E') = 0$ or 4.86 eV.

iii) when $E > 4.86$ eV, then $E' = E$ or $(E - 4.86)$ eV.
 $(E - E') = 0$ or 4.86 eV.

iv When $E = 6.67 \text{ eV}$, then $E' = 6.67 \text{ or } (6.67 - 4.86) \text{ eV}$
or \circ
 $(E - E') = 0 \text{ or } 4.86 \text{ eV or } 6.67 \text{ eV}$.

v When $E > 6.67 \text{ eV}$, then $E' = E \text{ or } (E - 4.86 \text{ eV}) \text{ or}$
 $(E - 6.67 \text{ eV})$.
 $(E - E') = 0 \text{ or } 4.86 \text{ eV or } 6.67 \text{ eV}$

vi When the energy of the entering electrons was increased to 10.4 eV .

Excitation and Ionisation Potentials

The minimum accelerating potential required to energise an electron which, on collision, can excite an atom is called the 'excitation potential' of that atom, similarly, the minimum accelerating potential required to energise an electron which can ionise an atom is called the 'ionisation potential' of that atom.

Absorption of Light

Atoms not only emit light, but if they get light photons of appropriate energy, they also absorb them.

white light has photons of all energies.

The number of the emission transitions is larger than the number of absorption transitions.

Hydrogen Spectrum

Hydrogen spectrum was studied systematically by Balmer. It consists of discrete bright lines on a dark background. These lines are called $H_\alpha, H_\beta, H_\gamma, H_\delta, \dots$ lines.

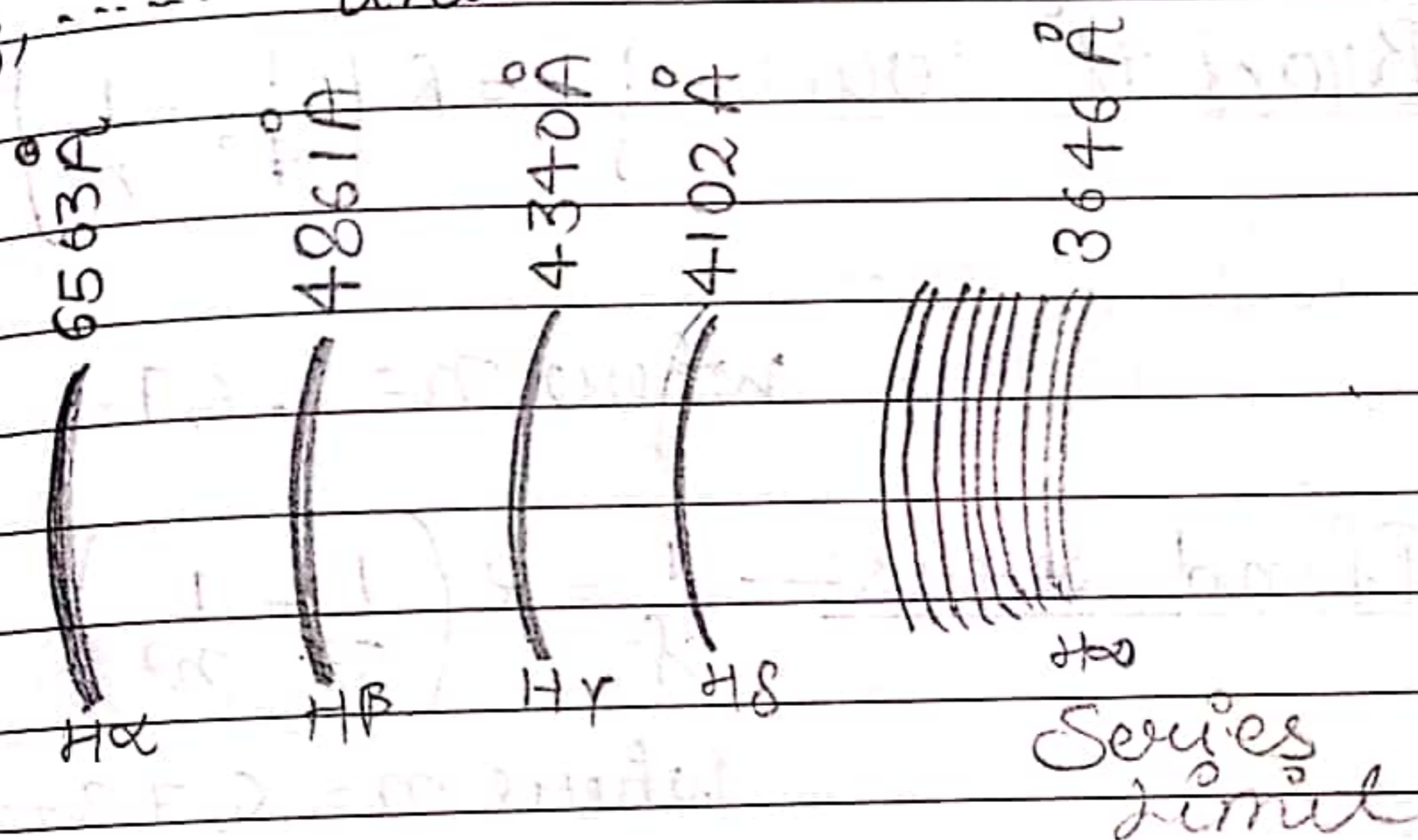


Fig - Balmer Series of Hydrogen

The lines of Balmer series are found in visible part of the spectrum.

Other series were found in the invisible parts of the spectrum.

i) For Lyman series - $\frac{1}{\lambda} = R \left(\frac{1}{1^2} - \frac{1}{n^2} \right)$

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

ii For Balmer Series - $\frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$

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

iii For Paschen Series - $\frac{1}{\lambda} = R \left(\frac{1}{3^2} - \frac{1}{n^2} \right)$

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

iv For Brackett Series - $\frac{1}{\lambda} = R \left(\frac{1}{4^2} - \frac{1}{n^2} \right)$

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

v For Pfund Series - $\frac{1}{\lambda} = R \left(\frac{1}{5^2} - \frac{1}{n^2} \right)$

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

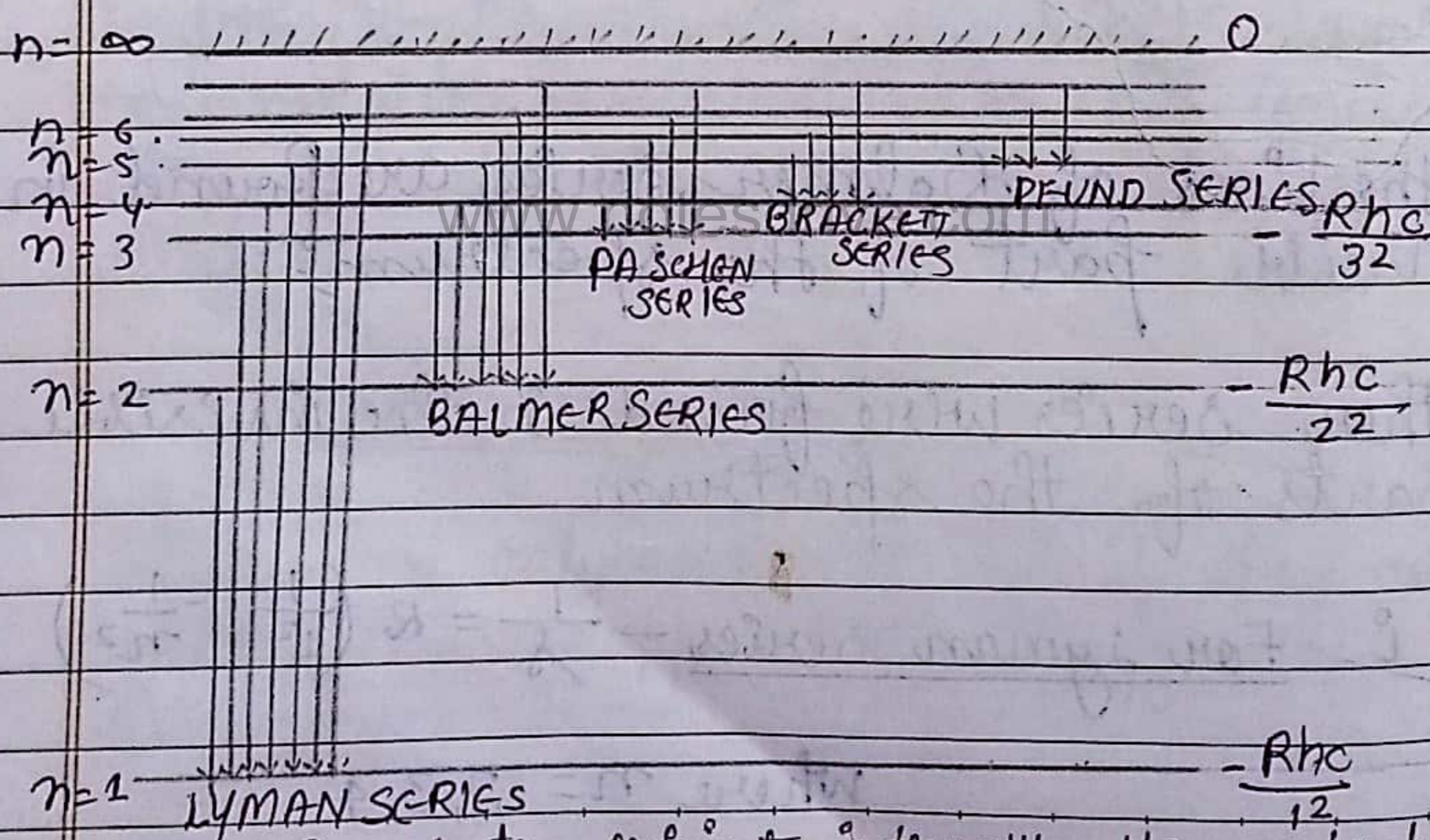


Fig - line spectra originate in transitions b/w energy levels.

i. Lyman Series - when an atom comes down from some higher energy level to the first energy level. (1916) It lies in ultra violet region

* The longest wavelength of this series (for $n=2$) is 1216 Å and shortest wavelength (for $n=\infty$) is 1912 Å

ii. Balmer Series - when an atom comes down from some higher energy level to the second energy level. (In 1885) lies in visual region

* The longest wavelength of this series (for $n=3$) is 6563 Å and the shortest wavelength (for $n=\infty$) is 3646 Å.

iii. Paschen Series - when an atom comes down from some higher energy level to the third energy level. lies in infrared region

iv. Brackett Series - when an atom comes down from some higher energy level to the fourth energy level. lies in infrared region

v. Pfund Series - when an atom comes down from some higher energy level to the fifth energy level. (infrared region)

* only Lyman series is found in the absorption spectrum of hydrogen atom

Sun has Balmer series also, besides the Lyman Series.

uses of Rydberg Constant

- i Determination of ionisation energy.
- ii Determination of wavelengths.

Limitations of Bohr's Theory

- i It explains the spectra of one-electron atoms only. It fails to explain the spectra of multi electron atoms.
- ii Can't explain about Zeeman effect & Stark effect.
- iii The theory does not explain the distribution of electrons in different orbits.
- iv It gives no information about the wave-nature of electron.

Angle of Scattering

Angle by which a particular particle gets deviated from its original path around the nucleus is called angle of scattering.

Impact parameter

perpendicular distance of the velocity vector of a particle from the central line of the nucleus of the atom.

$$b = \frac{1}{4\pi\epsilon_0} \cdot \frac{Ze^2 \cot \theta / 2}{K}$$

De-Broglie's Hypothesis

The electrons having a wavelength $\lambda = \frac{h}{mv}$ gave an explanation for Bohr's quantised orbits by bringing in the wave-particle duality. The orbits correspond to circular standing waves in which the circumference of the orbit equals a whole number of wavelengths.