unit - 2

Atomic Structure

☆ Dalton atomic Theory →

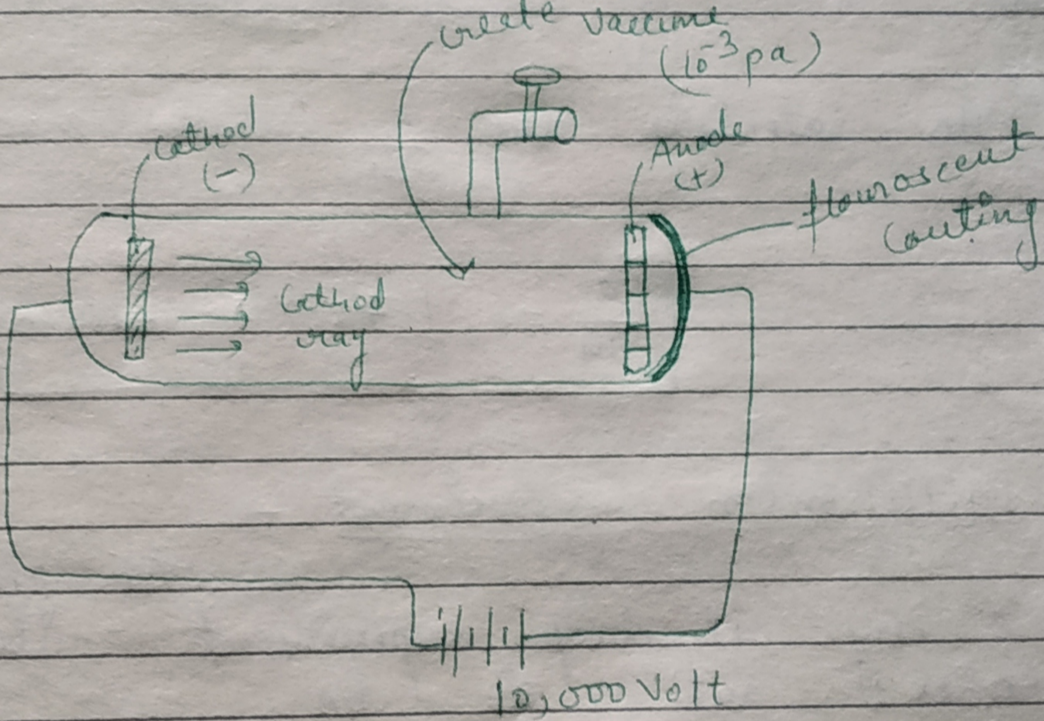
Acco. to dalton smallest fundamental particles is atom which can't be subdivided.

The term atom comes from the greek words A-tomio which means non-divisible.

→ acco. to dalton's atom is electrically neutral fundamental particle.

☆ Disconvery of electron - (by (J.J. Thomson)) →

→ e^- is discovered by cathod rays discharge tube.



→ Anode used is a perparated anode (Hole in Anode).

* Characteristic of Cathode rays –

→ (i) They are (−)tively charge
(ii) They travel in straight line
(iii) They possess K.E
(iv) They are made up of small particle
(v) They are deflected in E. magnetic feild
(vi) They produce X-rays
(vii) Cathod ray particles are known as e^-'s
(viii) Cathod rays remain Same when using different electrode & different gases
So e^- is a fundmental particle

→ He calculate the $\frac{e}{m}$ (charge/mass ratio of e^-)

$$\boxed{\frac{e}{m} = 1.75 \times 10^{11} \text{ Coulumbs}}$$

* Millikonson Experiment →

M. gives charge on e^- by oil drop experiment method which Comes out to be

$$\text{charge on } e^- = 1.6 \times 10^{-19}\ C$$
$$\text{mass of } e^- = 9.1 \times 10^{-31}\ kg$$

(A) Discovery of Proton (by {E. goldstein})

→ protons produce by Anode rays / Canal rays.

→ They use low pressure in compare to e^- experme (10^{-1} mm)

→ perporated cathode is used.

→ coloured rays observed.

→ They are positively charge (Anode rays)

→ Anode rays are made up of gases ions

→ Anode ray depends upon nature of gas taken.

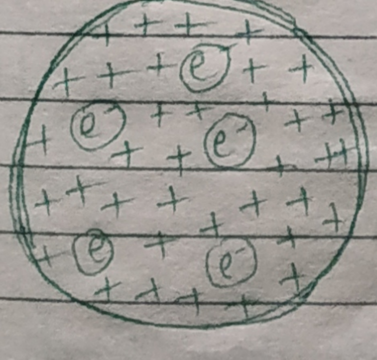
→ $\frac{e}{m}$ depends upon nature of gas.

$$\boxed{\text{charge on proton} = 1.6 \times 10^{-19}\,C}$$

$$\boxed{\text{mass on proton} = 1.605 \times 10^{-27}\,kg}$$

Proton mass is 1837 times of e^- mass.

A J.J Thomson Model of atom →



(i) Atom is spherical & positively charge

(ii) e^- are embeded

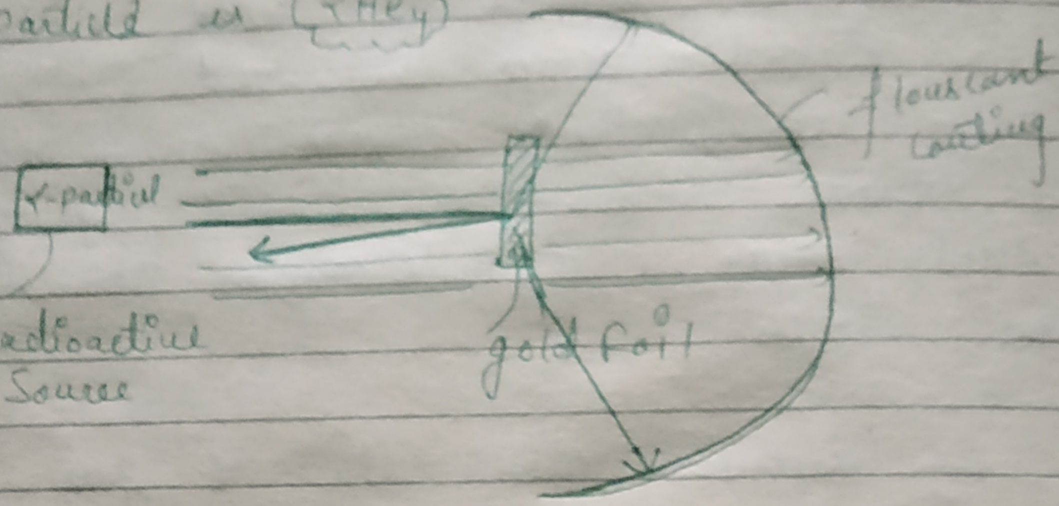
(iii) plum pudding / watermelon model

(iv) atom is electrically neutral.

Failar of J.J Thomson — mass is uniformly distributed.

★ Rutherford Model → (α-particle scattering model).

α-particle is ${}_2He^4$



Observations → ① 99.9 α-particles passed undeviated.
② Some of α-particle particle deviated by small angle
③ Very few (1 in 20000) which return on its path deflected nearly 180° angle

→ Rutterford Said that most of the part of atom is empty.

→ Whole mass of atom is concentrated at centre called nucleous.

→ no. of e^- = no. of Protons
→ Size of nucleous is very... very small in comparision to atom

10^{5} 10^{-10}, 10^{-15}

Imp

→ e^- revolve in close circular around the nucleous due to electrostatic force of attraction & centripetal force.

$$\boxed{F_e = F_c}$$

Failure/drawback → He connot explain stability of atom

→ Maxwell Theory → The accelerated charge particle emits radiations & loose their energy

→ He connot explain lines of spectrum/descreate spectrum.

☆ Bohr - Model -

→ Postulates → ① Atom has a centre called Nucleous.

② electron revolves only in fixed circular orbits $\bar{c}$ fixed energy & fixed velocity.

③ Quantisation Condition - e^- revolve only in those circular orbits for which the angular momentum (L) is integral multiple of $\frac{h}{2\pi}$

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

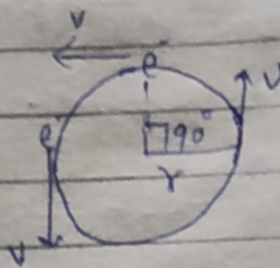
angular momentum

n = integer

n = 1, 2, 3, 4 - - -

$\boxed{n = \text{shell no.}}$

angular momentum $\vec{L} = \vec{r} \times \vec{p} \rightarrow$ momentum



$$\vec{L} = \vec{r} \times m\vec{v}$$

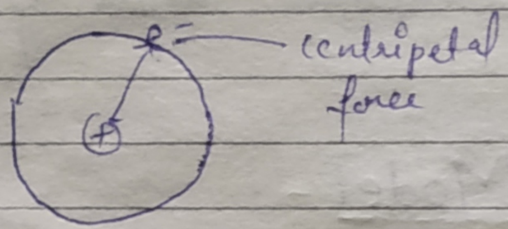
$$r m v \sin\theta = m v r \sin\theta (90°)$$

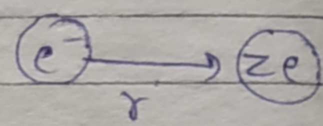
$$\boxed{L = mvr}$$

$$\boxed{mvr = \frac{nh}{2\pi}} \text{ --- (1)}$$

plank's constant
$h \Rightarrow 6.6 \times 10^{-34}$ sec.

(4) While revolving the electrostatic force b/w e^- & nucleus provide centripetal force..





$$F_e = F_c$$

$$\boxed{F = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r^2} = \frac{mv^2}{r}}$$

centripetal force

'Proton in nucleus = atomic no. = Z

$$\boxed{\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} = \frac{mv^2}{r}} \text{ --- (2)}$$

(5) While revolving in a particular orbital an e^- neither gain energy nor loses energy
Energy of an orbital / shell is fixed.

shell $\rightarrow$ stationary energy levels.

$n=1 \rightarrow K$
$n=2 \rightarrow L$
$n=3 \rightarrow M$
$n=4 \rightarrow N$

(6) Calculation $\rightarrow$ r, v, K.E, P.E Total energy.

$$mvr = \frac{nh}{2\pi} \quad \text{—(i)}$$

$$\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

Square equ^n (1) & ÷ equ^n —(2)

$$\frac{\frac{n^2h^2}{4\pi^{\cancel{2}}} = \cancel{m^2}\cancel{v^2}r^{\cancel{2}}}{\frac{Ze^2}{4\pi\varepsilon_0 r^{\cancel{2}}} = \frac{\cancel{m}v^2}{r}} \Rightarrow \frac{n^2h^2}{\pi m} = \frac{\varepsilon_0 r}{Ze^2}$$

$$\Rightarrow \boxed{r = \frac{n^2h^2\varepsilon_0}{\pi m Z e^2}}$$

$$r = \left(\frac{h^2\varepsilon_0}{\pi m e^2}\right) \times \frac{n^2}{Z}$$

$$\boxed{r = 0.53 \times \frac{n^2}{Z} \, A^\circ}$$

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Q=① find radius of 1^{st}, 2^{nd}, 3^{rd} shell of H-atom $(Z=1)$

Ans -

$$r_1 = 0.53 \times \frac{1}{1} \ A^\circ$$

$$r_2 = 0.53 \times \frac{4}{1} \ A^\circ$$

$$r_3 = 0.53 \times 9 \ A^\circ$$

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

Q=② Which of the fallowing will have same radius as 1^{st} shell of H atom

$0.53 \times \frac{1}{1}$

(a) $n=2$ Li $(z=3)$
(b) $n=2$ $Be(z=4)$
(c) $n=2$ He $(Z=2)$
(d) $n=3$ $He(z=2)$

Bohr model is valid only single e^- species.

$H \rightarrow 1e$
$He \rightarrow 2e$ $\quad He^{+}$

$Li \rightarrow 3e^-$ $\quad Li^{++}$

$Be \rightarrow 4e^-$ $\quad Be^{+++}$

valid only single e species.

(2) Velocity →

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

$$r = \frac{n^2h^2\varepsilon_0}{\pi m Z e^2}$$

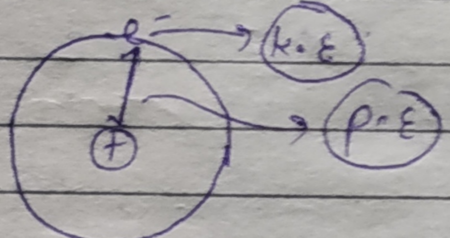
put the value of 'r'

$$\Rightarrow \cancel{m}v\left(\frac{\cancel{n^2}\cancel{h^2}\varepsilon_0}{\cancel{\pi}\cancel{m}Ze^2}\right) = \frac{\cancel{n}h}{2\cancel{\pi}}$$

$$\Rightarrow \boxed{V_n = \frac{Ze^2}{2h\varepsilon_0 n}}$$

$$v_n = \underbrace{\left(\frac{e^2}{2h\varepsilon_0}\right)}_{\text{constant}} \times \frac{Z}{n} \Rightarrow \boxed{v_n = 2.18 \times 10^6 \frac{Z}{n} \ m/s}$$

(3) Energy →



$$k.E = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{Ze^2}{2h\varepsilon_0 n}\right)^2$$

$$k.E = \frac{1}{2}\frac{mZ^2e^4}{4h^2\varepsilon_0^2 n^2} \Rightarrow \frac{1}{8}\frac{mZ^2e^4}{h^2\varepsilon_0^2 n^2}$$

$$K.E = \left(\frac{me^4}{8h^2\varepsilon_0^2}\right) \times \frac{z^2}{n^2}$$

$$\boxed{K.E = 13.6 \times \frac{z^2}{n^2} \text{ e.v.}}$$ (electron volt)

Potential energy →

$$q_1 \xrightarrow{r} q_2$$

$$P.E = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{ze^2}{r}$$

put the value of 'r'

$$\Rightarrow \frac{1}{4\cancel{\pi}\varepsilon_0}\frac{ze^2 \times \cancel{\pi} mze^2}{n^2h^2\varepsilon_0}$$

$$\Rightarrow (-)\frac{mz^2e^4}{4n^2h^2\varepsilon_0^2}$$

multiply & divided by (2)

$$P.E = \left(-\frac{me^4}{8h^2\varepsilon_0^2}\right) \times \frac{z^2}{n^2} \times 2$$

$$\Downarrow$$

$$13.6$$

~~P.E~~ =

$$\boxed{P.E = -2 \times 13.6 \times \frac{z^2}{n^2} \text{ eV}}$$

Total energy → P.E + K.E

$$\Rightarrow -2 \times 13.6 \times \frac{z^2}{n^2} + 13.6 \times \frac{z^2}{n^2}$$

$$\Rightarrow \boxed{T.E \Rightarrow -13.6 \times \frac{z^2}{n^2}\ eV}$$

→ Total energy of electron in n^{th} shell of H-atom.

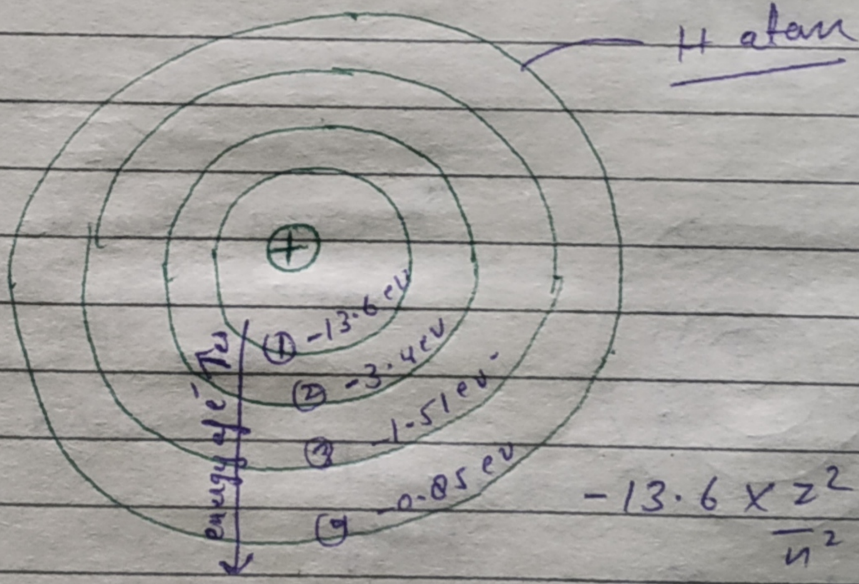
$$T.E = -13.6 \times \frac{z^2}{n^2}\ eV \quad -13.6 \times \frac{1}{n^2}\ eV$$

$n=1$ $\quad T.E \Rightarrow -13.6\ eV$

$n=2$ $\quad T.E \Rightarrow -13.6 \times \frac{1}{4} \Rightarrow -3.4\ eV$

$n=3$ $\quad T.E \Rightarrow -13.6 \times \frac{1}{9} \Rightarrow -1.51\ eV$

$n=4$ $\quad T.E \Rightarrow -13.6 \times \frac{1}{16} \Rightarrow -0.85\ eV$



$$-13.6 \times \frac{z^2}{n^2}\ eV$$

$n \to \infty$

$\boxed{T.E \Rightarrow 0}$ → e^- is free from nucleus

ionisa^n occurs

* " e^- can accept energy & can lose energy "

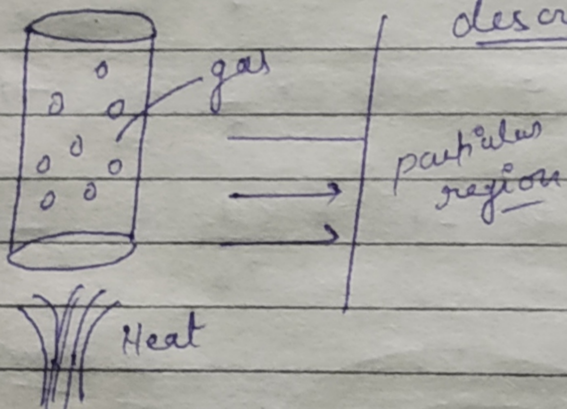
→ If e^- accepts an energy it jumps to higher energy level → excitation of e^-

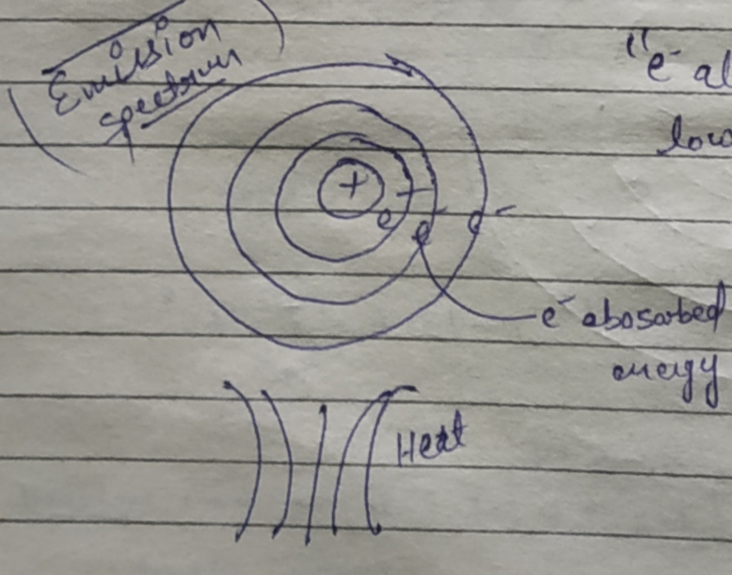
→ If e^- loses energy it ~~recedes~~ recedes back to lower energy level → dexcitation of e^-

→ An e^- gain or lose only those energy which are equal to difference in two energy level.

Atomic Spectrum →

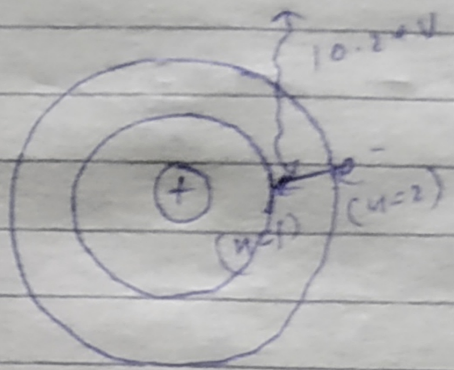
descreate/lines spectrum





" e^- always tries to remain in lowest energy level so e^- return back energy is emitted → in forms of radiation/visible light

Q = An e^- in H-atom jumps from $n=2$ to $n=1$ find the energy & wavelength of emitted radiation.



$$\Delta E = E_2 - E_1$$

$$\Delta E = -\frac{13.6}{4} - 13.6$$

$$\Delta E = 13.6 - 3.4$$

$$\Delta E = 10.2 \text{ eV}$$

planck const

$E = \frac{hc}{\lambda}$ → speed of light

λ → wavelength.

energy of wave

shortcut →. $\boxed{E = \frac{12375}{\lambda}}$ A°

eV

$$10.2 = \frac{12375}{\lambda}$$

$$\Rightarrow \lambda = \frac{12375}{10.2} A^\circ$$

e^- jump $n = n_2$ to $n = n_1$

$$\Delta E = E_{n_2} - E_{n_1}$$

$$\Rightarrow \frac{hc}{\lambda} = \frac{-13.6 \times Z^2}{n_2^2} + \frac{13.6 \times Z^2}{n_1^2}$$

$$\Rightarrow \frac{\cancel{h}c}{\lambda} = \cancel{h}c \frac{13.6}{hc} Z^2 \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

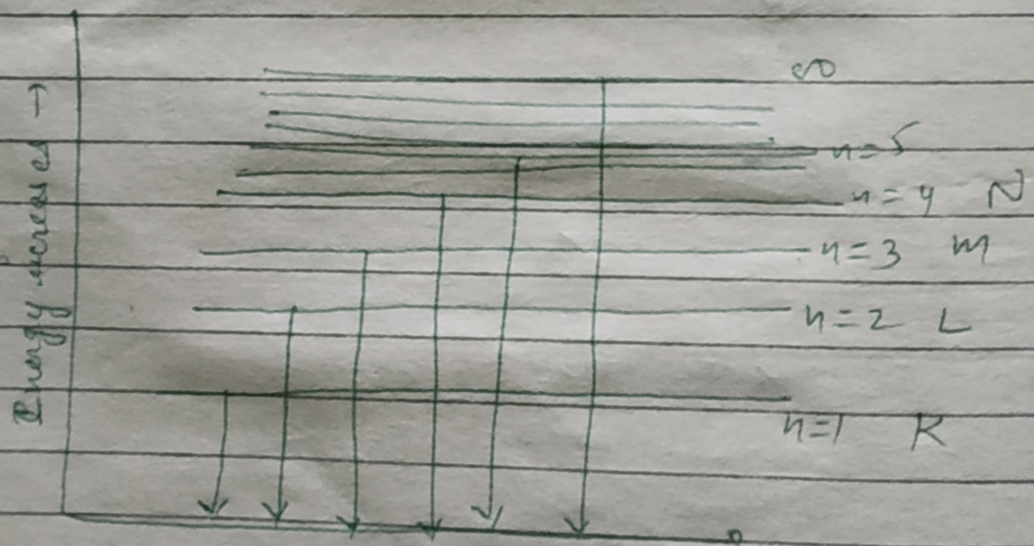
$$\Rightarrow \frac{1}{\lambda} = \frac{13.6}{hc} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

R

$$\Rightarrow \boxed{\frac{1}{\lambda} = R Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)}$$

R ⇒ Rydberg constant

$R = 1.09 \times 10^{-7}\ m^{-1}$



Lyman series

Calculate λ when e^- dexcite from $n=2$, to $n=1$

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$\frac{1}{\lambda} = R(1)^2\left(1 - \frac{1}{4}\right)$$

$$\boxed{\frac{1}{R} \Rightarrow 911 A^\circ}$$

$$\frac{1}{\lambda} = R\left(\frac{3}{4}\right)$$

$$\lambda = \frac{4}{3R} \Rightarrow \lambda = \frac{4}{3} \times \frac{1}{R}$$

$$\Rightarrow \lambda = \frac{4}{3} \times 911 A^\circ$$

$$\lambda = 4 \times 304$$

$$\boxed{\lambda = 1216 A^\circ}$$

$\Rightarrow$ $n=2$, to $n=1$ $\rightarrow$ first line of lyman series
$n=\infty$ to $n=1$ $\rightarrow$ last line of lyman series

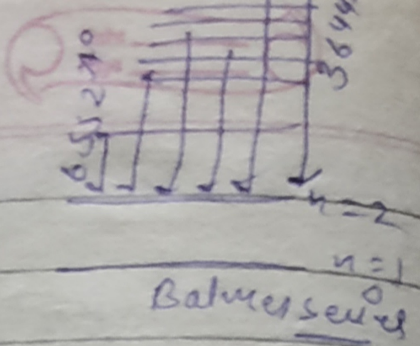
for lyman series $\rightarrow$ $n_1 = 1$

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$$

shortest wavelength $= 911 A^\circ$
(largest transition)

longest wavelength $= 1216 A^\circ$
(shortest transition)

② Balmer Series → $\boxed{n=2}$



Shortest wavelength. & Longest wavelength
$\infty - 2$ $\quad\quad$ $3 \rightarrow 2$

$$\frac{1}{\lambda} = R(Z)^2\left(\frac{1}{2^2} - \cancel{\frac{1}{\infty^2}}\right) \rightarrow 0$$

$$\frac{1}{\lambda} = R\left(\frac{1}{4}\right)$$

$$\lambda = \frac{4}{R} = 4 \times \frac{1}{R} = 4 \times 911 A^{\circ}$$

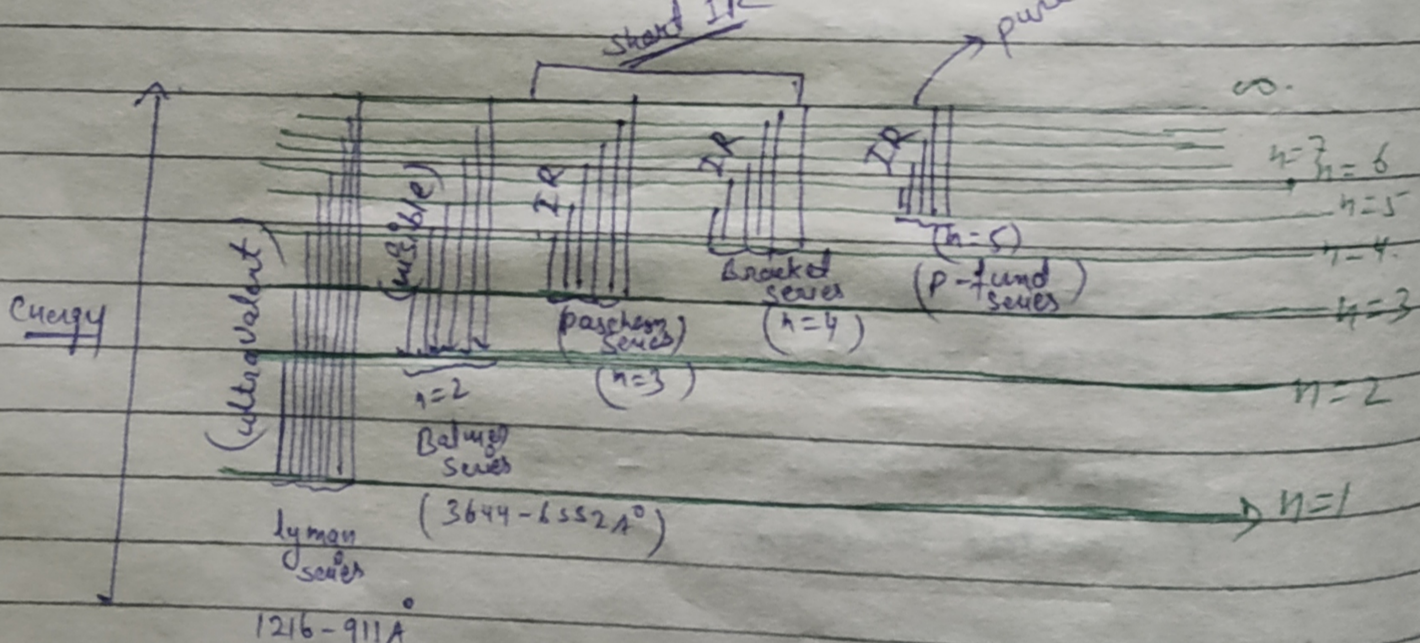
$$\boxed{\lambda = 3644}$$

$\Downarrow$

Shortest Wavelength.

Longest wavelength $\Rightarrow$ 6552 A°

Hydrogen lines Spectrum –



$$\boxed{\text{No. of spectral lines} = \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}}$$

$n=5$ to $n=1$ $\Rightarrow$ $\frac{(5-1)(5-1+1)}{2} = \frac{4 \times 5}{2}$ $\frac{20}{2}$

$= 10$

Drowback of Bohr Model $\Rightarrow$

(i) Only valid for single e^- species.
like, H, He^+, Li^{++}, Be^{+++}

(ii) Bohr consider e^- as a particle not as a wave.

(iii) He determines smaltaneously momentum & position of e^- $\left\{ \begin{array}{l} r = 0.53 \times \frac{n^2}{Z} A^\circ \\ v = 2.18 \times 10^6 \frac{Z}{n} \end{array} \right.$ $m \rightarrow$ ~~unkn~~ Known. $\}$.

(iv) He does not explain the splitting of spectral lines in magnetic feild (Zeiman effect) & in electric feild (stark effect)

(v) He does not explain ultrafine spectrum.

Quantum Machenical Model of atom -

De-broglei - Acco. to debroglei every particle which have mass must posess a wave associated $\bar{c}$ it known as matter wave.

→ The Wavelength (λ) of this matter wave is given by -

$$\boxed{\lambda = \frac{h}{p} = \frac{h}{mv}} \quad \text{— (i)}$$

as we ~~known~~ know wavelength (λ) $\propto \frac{1}{mass}$; $\lambda \propto \frac{1}{m}$

So λ is very small for heavier object so we can't be measurable.

Q= Calculate the wave length (λ) of wave associated $\bar{c}$ a moving e^-

Ans → $\lambda = \frac{h}{mv} \Rightarrow \lambda = \frac{6.6 \times 10^{-34}}{9.1 \times 10^{-31} kg \times 2.18 \times 10^{6}}$

$$\lambda = 0.33 \times 10^{-9} m$$

$$\boxed{\lambda = 3.3 \, \mathring{A}}$$

- We know that $K.E = \frac{1}{2} mv^2$

$$\Rightarrow \cancel{mv = \frac{2 \times K.E}{v}}$$

$$\Rightarrow \boxed{v = \sqrt{\frac{2 \cdot K.E}{m}}} \quad \text{— (2)}$$

So, by eq. (1) $\lambda = \frac{h}{m \cdot \sqrt{\frac{2 \cdot KE}{m}}} \Rightarrow \boxed{\lambda = \frac{h}{\sqrt{2mKE}}}$

$$\boxed{\lambda = \frac{h}{\sqrt{2m\,K.E}}}$$

★ Hiesenberg uncertainity Principle –

Acco. to Hiesenberg ~~the~~ one connil determine aquarately & simultaneously the position & momentum of a particle

The uncertainity is given by –

$$\boxed{\underbrace{\Delta x}_{\text{uncertainity in position}} \times \underbrace{\Delta p}_{\text{momentum}} \geq \frac{h}{4\pi}}$$

→ uncertainity is always equal to or greater than equal $\frac{h}{4\pi}$

$$\boxed{\text{uncertainity} \geq \frac{h}{4\pi}}$$

To overcome these drawbacks of Bohr model the new model suggested by scientists named as quantum machenical model.

Schrondinger :-

Wave equⁿ for e^- probability.

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

$$\psi^2 = e^- \text{ finding probability}$$

→ Solution to schrondiger e^- wave equⁿ gives
3 Variable → represent position of e^-
↓
3 - quantum numbers
$\boxed{n \; l \; m \; s}$

→ Those ~~possible~~ position where probability of e^- finding is maximum.

Quantum Numbers - (l m n s)

n = principle Quantum no.
l = Azimuthal " "
m = magnetic " "
s = Spin " "

→ tell us the e^- probability highest loca of e^-

Orbitals → 3-D space in which the probability of finding e^- is maximum.

n → principle Quantum no. → it define the size of the atom & have denote the shell no. $n = 1, 2, 3, 4 \text{ — — . } \infty$

n does not equal to zero

$n \neq 0$

② l- Azimuthal quantum no. →

it define the shape of the orbital.

l	name		shape
0	s	→	spherical
1	p	→	dumble shape
2	d	→	double dumble
3	f	→	complicated & fold structure
4	g		

↳ sub-shell

→

→ $0 \leq l < n-1$

③ Magnetic Quantum no. →

it define the Orientation of orbitals

→ no. of orbitals-

$-l \leq m \leq +l$

l		m
0	s	0
1	p	-1 0 +1
2	d	-2 -1 0 +1 +2
3	f	-3 -2 -1 0 +1 +2 +3

$M = (2l+1) \Rightarrow$ no. of orbital

no. of e^- in a shell $= 2n^2$

No. of orbital in a shell $= n^2$
no. of orbital in a subshell $= 2l+1$
no. of e^- in a orbital $= 2n^2$
no. of subshell in a shell = no. of shell
no. of e^- in a subshell $= 2(2l+1)$

* Pauli's Exclusion Principle –

Acco. to pauli's no. of 2e⁻ of a atom have same set of 4 quantum no. / only 2e⁻ of opposite spin can be present in an orbital $\boxed{\uparrow\downarrow}$

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* Afbau's Principle - not a name of any scientis

e^- is filled first in lower energy State then higher energy state.

if $(n+l)$ is same then $n\uparrow$ $E\uparrow$

$$\boxed{\text{Energy} \propto (n+l)}$$

$(n+l)$	1s	2s	2p	3s	3p	3d	4s	4p
	(1+0)	(2+0)	(2+1)	(3+0)	(3+1)	(3+2)	(4+0)	(4+1)
	1	2	3	3	4	5	4	5

Exception - we can't apply afbau's principle on single e^- species like, H, He^+, Li^{++}, Be^{+++}

Hund's Rule - pairing will not start untill all the orbital will have e^-