

## DISCOVERY OF ELECTRONS

On applying very high voltage (10,000 V to 20,000 V) and very low pressure in discharge tube or Cathode ray tube.

Discharge tube glow with green light and also glowing behind anode.

It means some invisible rays produced at cathode strike behind the anode and produce fluorescence.

These rays are termed as Cathode rays.

Gases ionise at high voltage



- Cathode rays is the beam of negatively charged particles which were termed as NEGATRON by JJ Thomson.
- Name electron was given by STRONEY.

### PROPERTIES OF CATHODE RAYS

- Cathode rays travel in straight line.
- On placing an object in Cathode rays path, same sized images are obtained.
- On placing a pin wheel in path of cathode rays, it rotates. Which proves Particle Nature and Energy ( $E_k$ ) of rays.

- Cathode rays produce Shining on Zinc Sulphide ( $\text{ZnS}$ ) which prove that Cathode rays have

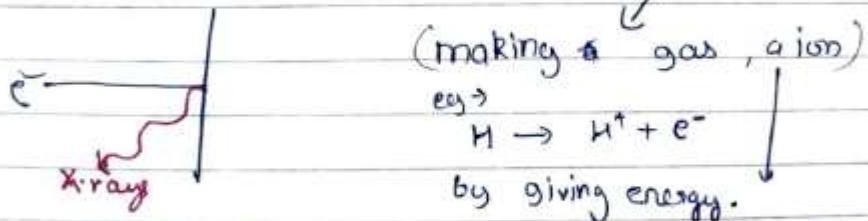
## Kinetic Energy.

- Cathode rays can deflect from its path by electric field.



In electric field, rays deflect towards positive plate which proves Cathode rays is a beam of negatively charged particle.

- Cathode rays can penetrate thin metal foil.
- Cathode rays can ionise the gaseous molecules.



- Cathode rays strike on metal to form X-Rays (high frequency & energy EM rays.). Hence Cathode rays can produce X-rays when incident on metal surface.

Thompson calculated  $e/m$  ratio.

$\frac{e}{m} \Rightarrow$  Specific Charge

$$= -1.7588 \times 10^11 \text{ C/kg}$$

Specific Charge ( $e/m$  ratio) for

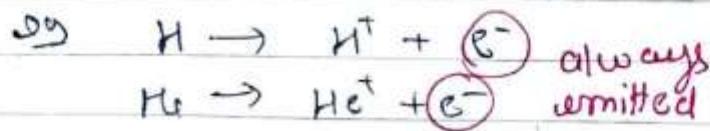
Cathode rays DOES NOT

depend on Nature of gas

filled in discharged tube.

~~cathode rays~~  $\rightarrow e^-$  beam

take any  
gas

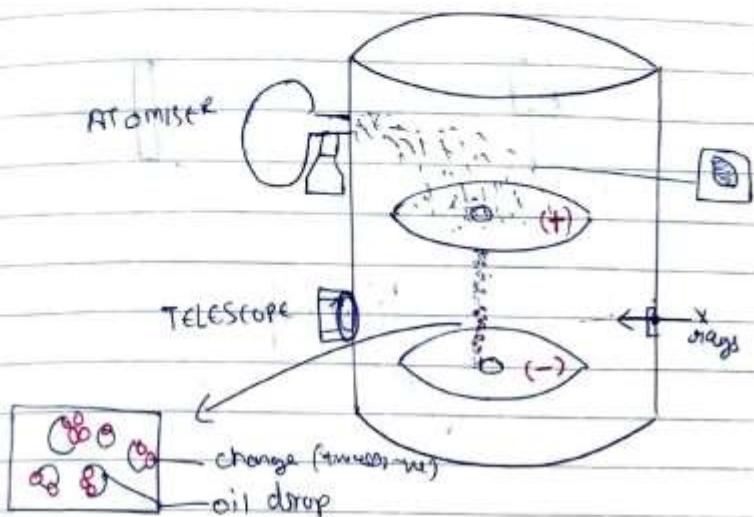


no

always emitted

X-rays is electrically neutral, not deflected in electric or magnetic field.

### Milikan's Oil drop Experiment



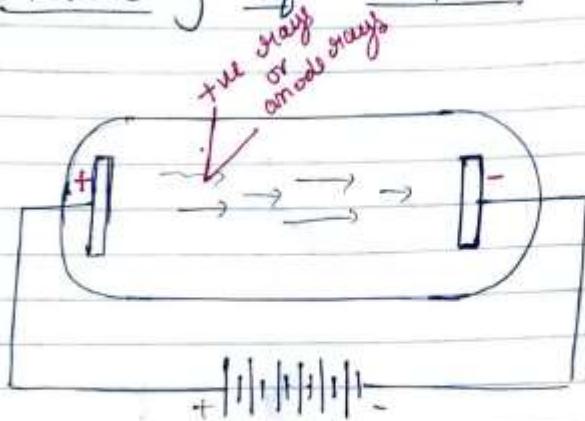
It (This experiment) proved that charge on electron was found  $1.6 \times 10^{-19} C$ .

$$m_e = \frac{e}{c/m} = \frac{1.6 \times 10^{-19} C}{1.7588 \times 10^{11} C/kg}$$

$$= 9.1 \times 10^{-31} kg$$

# Mass of  $1 e^-$  is  $\frac{1}{1837}$  times that of mass of Hydrogen atom.

## Discovery of Proton.



- High Potential  
Very Low Pressure

Goldstein repeat the J J Thompson experiment and found that some rays also travel from anode towards cathode. They were termed as anode rays.

Anode rays are the beam of positively charged ions produced by IONISATION of gaseous molecules or atoms.

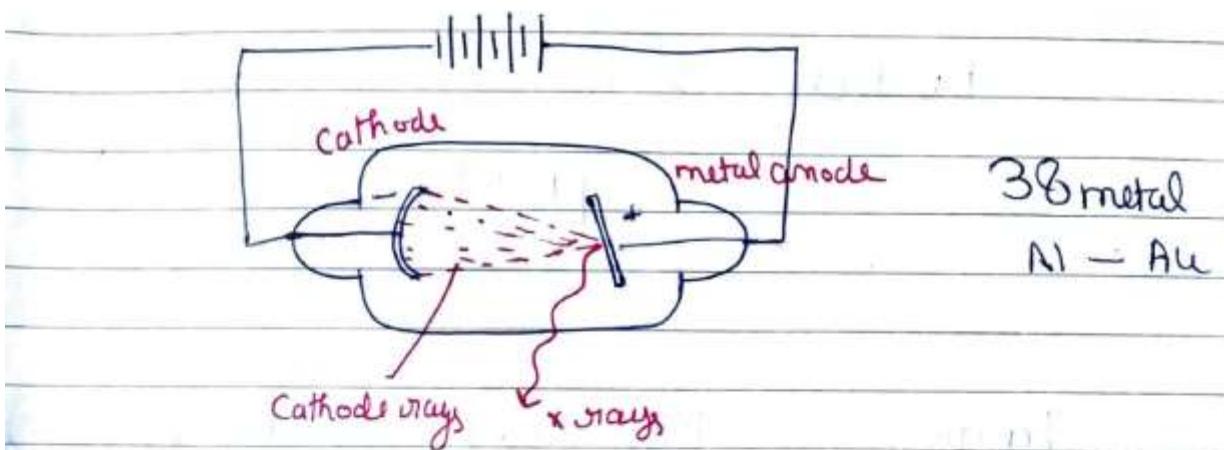
When Hydrogen gas was filled in a discharged tube then positive rays were termed as beam of proton.

name given by  
Rutherford,

e/m ratio for positive rays  
DEPENDS ON Nature of Gas filled  
in discharged tube

In electric field positive rays  
deflected towards negative plate.

## MOSELEY EXPERIMENT



$$\sqrt{V} = a(z - b)$$

Moseley relation

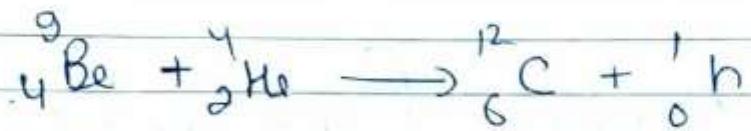
$Z$  = Serial no. of metal used as anode (at.n)

$V$  = frequency of emitted rays.

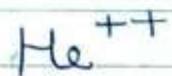
$a, b$  = Moseley constant

## DISCOVERY OF NEUTRON

Neutron was discovered by James Chadwick by bombardment of  $\alpha$ -particle on Beryllium particles.



$\alpha$ -Particle  $\rightarrow$  nucleus of He



## In term Units

mass of  $p^+$  = 1 unit mass

mass of

Charge on  $p^+$  = 1 unit charge

	<u>mass</u>	<u>charge</u>
$e^-$	0 unit	- 1 unit

$p^+$	1 unit	+ 1 unit
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$n^0$	1 unit	0 unit
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## Symbol

$A \rightarrow$  Mass no (no of  $p^+$ s + no of  $n_0$ )

~~$A$~~   
 ~~$Z$~~

$\hookrightarrow$  atomic number

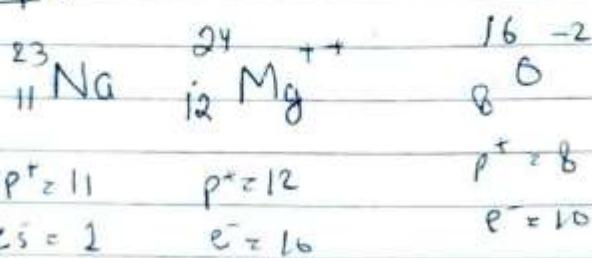
no of  $p^+$ s

||

no of  $e^-$  (when neutral)

$$\text{no of } N_0 = A - Z$$

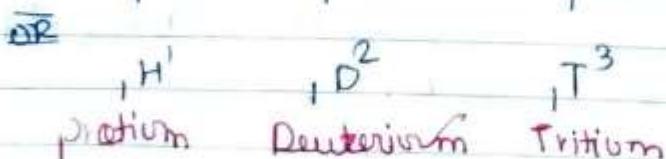
examples:-



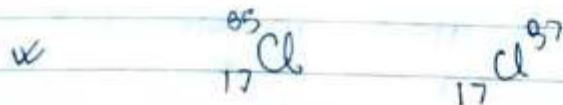
## ISOTOPES

The species having same atomic no but different mass no.

examples:-



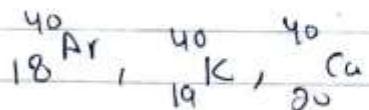
Protium    Deuterium    Tritium



## W ISOBARS

The species having same mass no.  
but different atomic no.

Ex:-



## W ISOELECTRONIC

Same No of electrons.

example

	$\text{O}^{-2}$	$\text{F}^{-}$	$\text{Ne}$	$\text{Na}^{+}$	$\text{Mg}^{++}$
no of electron	10	10	10	10	10

eg

	$\text{CO}$	$\text{CN}^{-}$	$\text{N}_2$
no of electron	6+8 = 14	6+7+1 = 14	7+7 = 14

## W ISOPROTOMIC

Same no of Protons

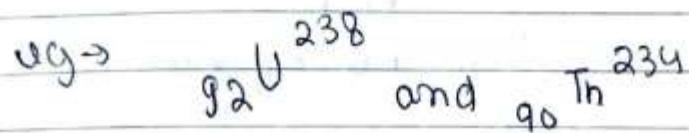
ISO NEUTRONIC or ISOTONES

Same no of neutrons

## ✓ ISODIAPHERES

Same difference between no of  
neutrons and protons.

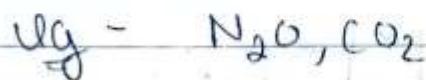
$$(n_0^! - p^+)$$



$$n(p^+) = 92 \quad 90$$

$$\cancel{n}(n_0^!) = 238 - 92 \quad 234 - 90 \\ = 146 \quad 144$$

$$n^o - p^+ = 146 - 92 \quad 144 - 90 \\ = 54 \quad = 54$$



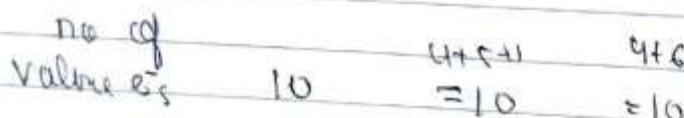
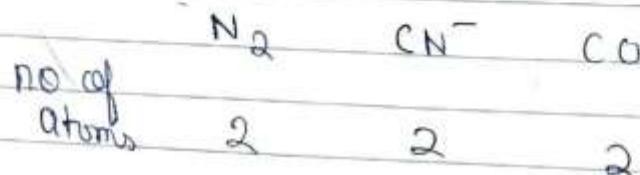
# USE  $(A - Z)$  to calculate  
the difference.

## ISOSTERS

Same no of atoms and same no of valence electrons

Isoesters = Same no of atoms  
and

Same no of Valences

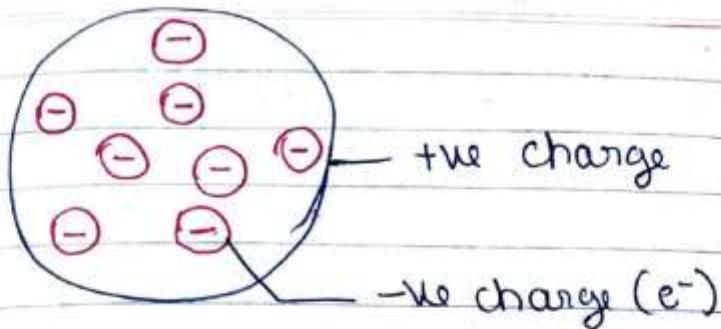


## ATOMIC MODEL

(i) Plum Pudding model

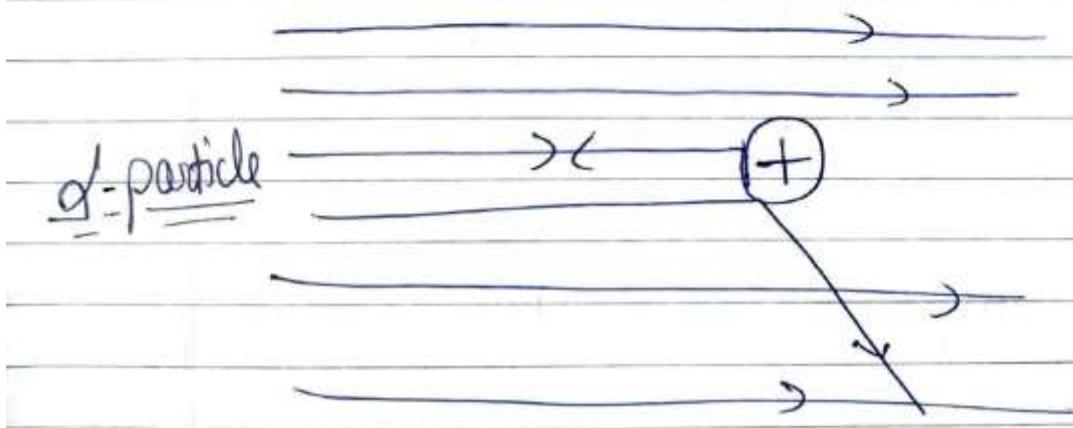
also called :- water melon

By:- JJ Thomson



According to this model  
 negatively charged electrons are  
 submerged uniformly in  
 positively charged electrons.

## RUTHERFORD EXPERIMENT



# RUTHERFORD EXPERIMENT

Observation :-

- Most of  $\alpha$  particles passed undeflected
- Few  $\alpha$  particles deflected by an angle.
- Very few (1 out of 20,000) revert back on its path.

Conclusion :-

- Most of  $\alpha$  particles passed undeflected which shows that most part of atom are empty.
- Some  $\alpha$  particles were deflected by an angle which shows positive charge on atom.
- Very few  $\alpha$  particles revert back which shows that there is presence of hard part in atom due to which it revert back.

• no of particle deflected  $\propto \frac{1}{\sin^4(\frac{\theta}{2})}$

$$\propto \frac{K}{\sin^4(\frac{\theta}{2})}$$

• no of particles deflected  $\propto \frac{1}{\frac{1}{2}mv^2}$

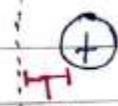
$$\propto (ze)^2$$

charge  
atomic no

distance of closest approach

$\alpha$  particle  $\rightarrow$

$$\frac{1}{2}mv^2_{\max}$$



$$KE = PE$$

at  $r_0$  distance

$$KE = 1 PE$$

$$\frac{1}{2} m_\alpha V_{max}^2 = \frac{K q_1 q_2}{r_1} \quad PE = -\frac{K q_1 q_2}{r}$$

$$= K \frac{(2Q)(2e)}{r_0}$$

$$= K \frac{2Ze^2}{r_0}$$

$$r_0 = \frac{K 4Ze^2}{M_\alpha V_{max}^2}$$

$$r_0 = K \frac{2Ze^2}{(KE)_{max}}$$

$r_0$  = distance of closest approach

$K$  = Constant =  $9 \times 10^9 \text{ N m}^2 \text{ C}^{-2}$

$M_\alpha$  = mass of  $\alpha$  particle

$Z$  = atomic no

Ques) Find the distance of closest approach if  $\alpha$  particle (with 5J energy) bombarded on aluminium metal.

$$2.9 \times 10^9 \times 13 \times (1.6 \times 10^{-14})$$

5

## Rutherford Model

- Atom is an spherical shape in which electrons revolve around the nucleus situated at centre of the atom.
- Nucleus is very small in order of  $10^{-13}$  cm diameter having diameter  $10^{-8}$  cm.

- o Electrons revolve around the nucleus under electrostatic attractive force b/w the nucleus and electrons.

## Drawback

According to classical model (Maxwell) When a charged body revolve under another charged body then it lose energy. That is why radius of circle path in which  $e^-$  revolve continuously

decreases and after all it falls on nuclei.

- Rutherford model couldn't explain the ~~discrete~~ stability of atom.
- Rutherford model could not explain the line spectrum of atom.

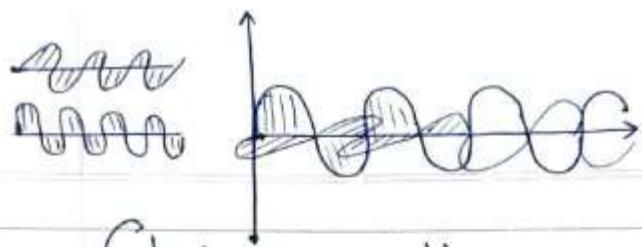
## RADIUS OF THE NUCLEUS

$$R = R_0 A^{1/3}$$

$\downarrow$        $\downarrow$  mass no  
Radius of      constant  
nucleus       $1.33 \times 10^{-13} \text{ m}$

## ELECTROMAGNETIC RADIATION

These are the waves produced by varying electric field and magnetic field which are perpendicular to each other and also in the direction  $\perp$  to both of them.



Electromagnetic wave can be produced by movement of charged particle in magnetic field or movement of a magnet in electric field.

# There is no requirement of medium to propagate EM radiations.

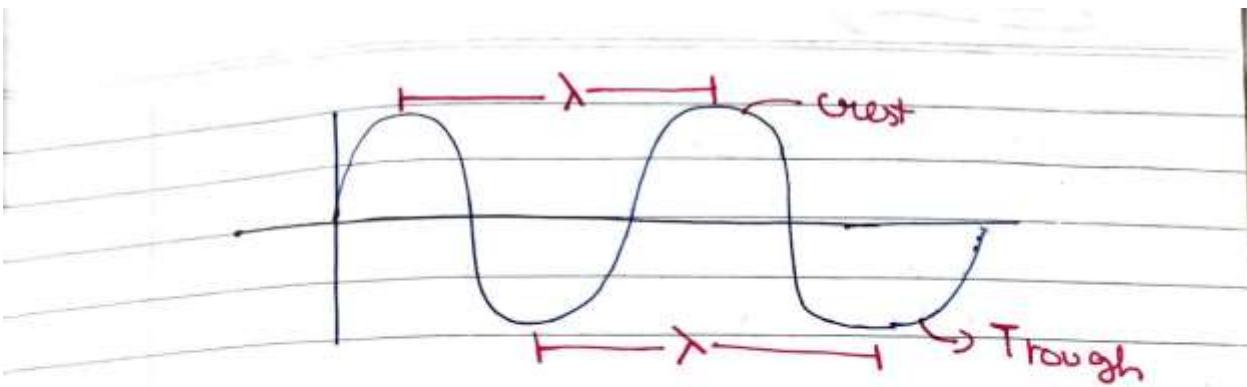
# Electromagnetic radiation travels with velocity of light.

# These rays do not deflect in electric and magnetic field.

## CHARACTERISTICS OF EM radiation

### • Wavelength ( $\lambda$ )

Distance b/w two consecutive Troughs or Crests.



Unit of length  $\rightarrow \text{m}$

- Frequency ( $v$ )

It is no of wave passing  
through a given point in  
one second.

Unit  $\rightarrow$  Hertz (Hz)

Cycle per Second

$$v = \frac{c}{\lambda}$$

- Wave number ( $\bar{v}$ )

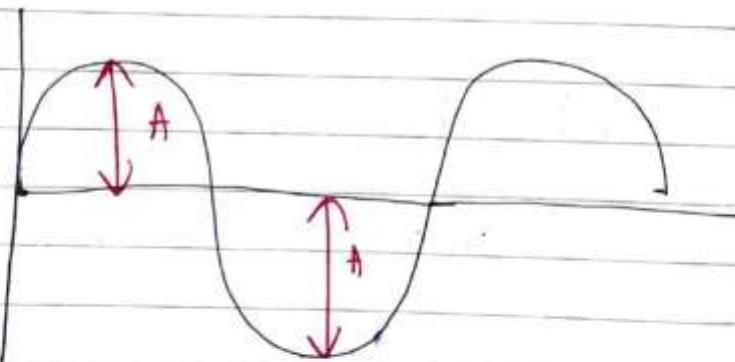
It is the no. of waves in unit cycles.

$$\boxed{\bar{v} = \frac{1}{\lambda}}$$

unit -  $\text{cm}^{-1}$   
 $\text{m}^{-1}$   
 $\text{A}^{-1}$

Apt

- Amplitude



Height of Crest and depth of trough.

unit  $\rightarrow$  cm

# Velocity

The distance travelled by wave  
in one second.

$$C = V \lambda$$

for white light :-

Cosmic Xrays Visible IR Micro Radio

$\lambda \uparrow$   $V \downarrow$   $E \downarrow$

# Particle Nature of Electromagnetic Radiation

(Planck Quantum Theory)

EM radiation explain many of wave phenomena but failed to explain the following:-

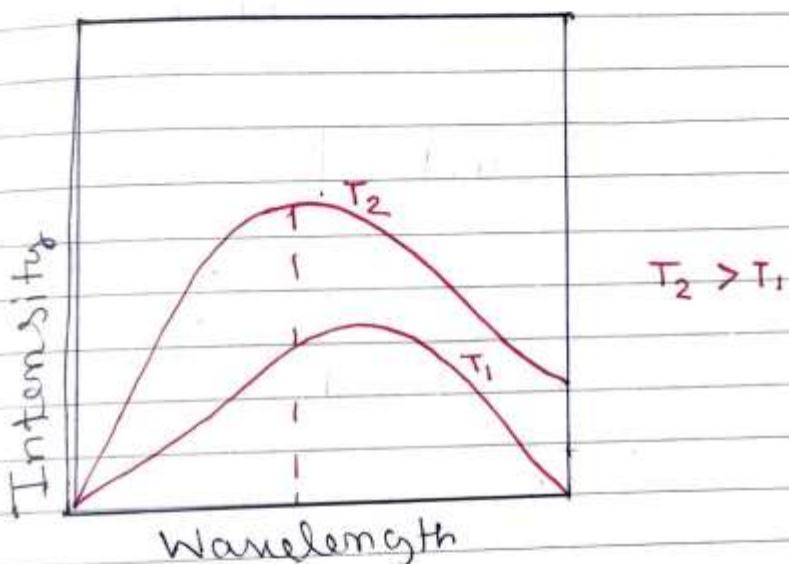
- Blackbody Radiation
- Photoelectric Effect
- Heat Capacity of Solids

## ⇒ Black body radiation

Emission and absorption over a wide range of wavelength from hot body which include change in colour with temperature.



The substance which can emit or absorb a wide range of wavelength is termed as blackbody and the radiation associated with it is called Blackbody radiation.



### Planck Theory

According to this theory energy cannot be absorbed or released continuously but can be released in form of small packets termed as quanta (sing: Quantum)

In case of light, it is called photon.

According to Planck, energy is released or absorbed from source in quantised manner.

$$E = h\nu$$
 (Energy of one photon / quantum)

$$E = nh\nu$$

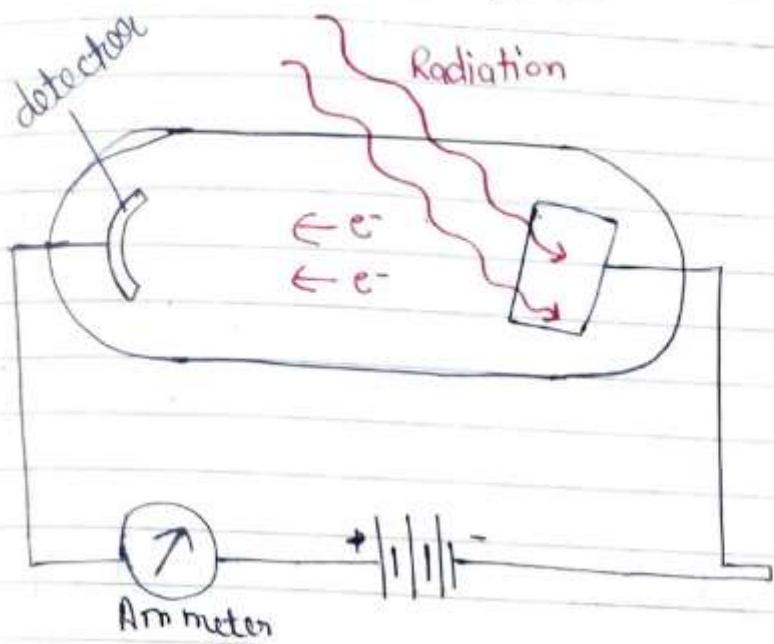
$$n = 1, 2, 3, 4, \dots$$

$$\begin{aligned}h &= \text{Planck's Constant} \\&= 6.63 \times 10^{-34} \text{ J-s}\end{aligned}$$

Ques Find the no of photons of 4000 Å wavelength which produce 1 J energy.

$$E = n \frac{\nu c}{\lambda}$$

## Photoelectric Effect



On incident of radiation on a metal surface, electric current is produced due to ejection of  $e^-$  from the metal surface, this is turned as photoelectric effect.

$$KE = E_{\text{incident}} - E_{\text{threshold}}$$

$$\frac{1}{2}mv^2_{(\text{max})} = h\nu - \omega_0$$

$$\begin{aligned}\frac{1}{2}mv_{\max}^2 &= h\nu - \omega_0 \\ &= h\nu - h\nu_0 \\ &= h\left(\frac{c}{\lambda} - \frac{c}{\lambda_0}\right)\end{aligned}$$

$$\boxed{\frac{1}{2}mv_{\max}^2 = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)}$$

## # Work Function and Threshold Energy

Minimum Energy required to just free an electron from a metal surface is termed as Work function.

Threshold or Work function depends upon nature of element, i.e., for different elements, it may have different value while atoms of same element will have same value.

## Threshold frequency -

The 'minimum' frequency of radiation which is required to just free an electron from metal surface.

incident  
radiation

## Threshold Wavelength ( $\lambda_0$ )

Maximum wavelength of incident radiation which is required to just free an electron from metal surface.

Ques A metal have work function 1.5 J.  
= If a photon with 5 J energy is incident on metal surface, then find the velocity of ejected electron.

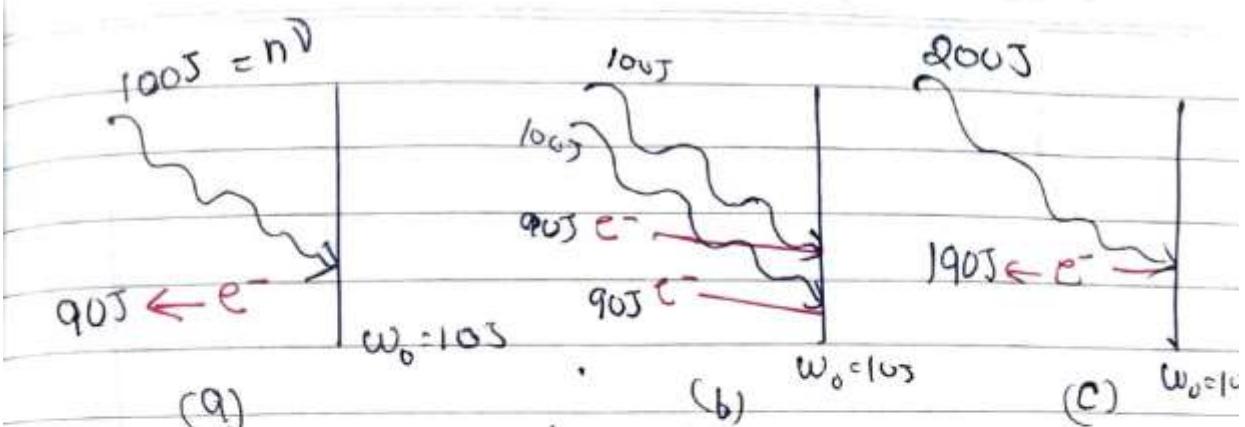
$$\frac{1}{2}mv^2 = 5 - 1.5$$

$$v = \sqrt{\frac{3.5 \times 2}{9.1 \times 10^{-31}}}$$

$$\# V_{\max} = \sqrt{\frac{2hc}{m_e} \left( \frac{1}{\lambda} - \frac{1}{\lambda_0} \right)}$$

## Rules for photoelectric Effect :-

- One electron can absorb one photon. Some energy of photon is used to just free  $e^-$  from metal surface and remaining energy provide KE for ejected electron.
- Photoelectric effect is shown when incident radiation have energy  $>$  the threshold energy or work function.
- On increasing intensity of incident radiation, number of ejected  $e^-$  increases but KE of each electron remains unaffected.
- On increasing frequency of incident radiation, no of ejected  $e^-$  REMAIN SAME but KE of ejected electron increases.

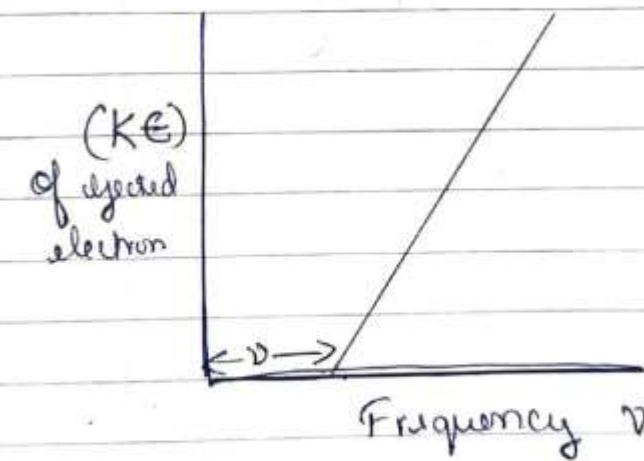


increasing intensity by increasing no. of modulations.

### Graph

(a) No of  $e^-$  ejected Vs Frequency  
(drawn afterwards)

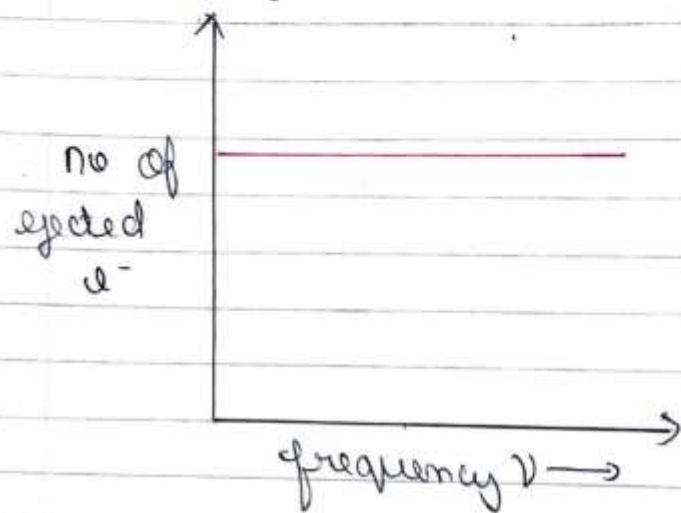
(b) KE of ejected  $e^-$  Vs Frequency



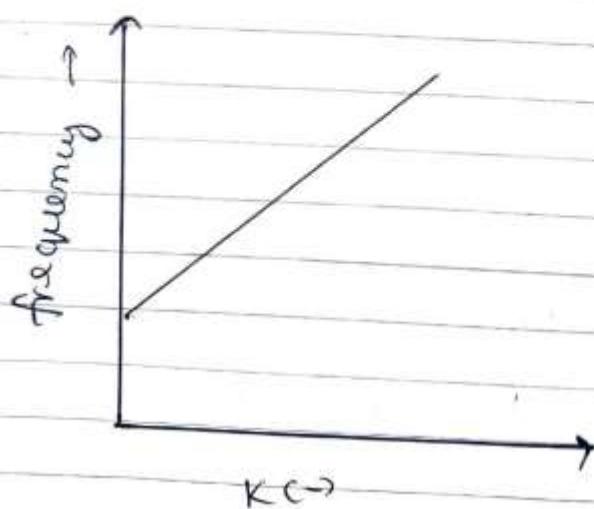
$$KE = hV - w_0$$

$$y = mx + c$$

(a) No of ejected  $\alpha^-$  Vs Frequency



(c)  $(KE)$  vs Frequency



## STOPPING Potential

The minimum potential applied by which the velocity of ejected  $e^-$  becomes 0 is known as Stopping potential

$$\frac{1}{2} mv^2 = eV_0$$

$e \rightarrow$  magnitude of electric charge

$V_0 \rightarrow$  Stopping potential

## BOHR'S ATOMIC MODEL

According to this model, atom is spherical in shape in which a nucleus is present at the centre of sphere.

Electrons revolved around the nucleus under electrostatic force of attraction b/w nucleus and electron in definite path-

termed as  $\rightarrow$  stationary  $\downarrow$  Orbit or shell

- These path will be stationary orbit in which revolving electron have angular momentum

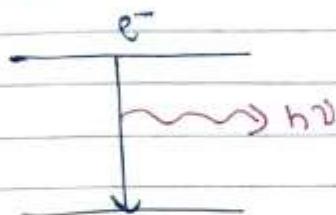
either  $\frac{h}{2\pi}$  or whole multiple of this value

$$\text{angular momentum} = \frac{nh}{2\pi}$$

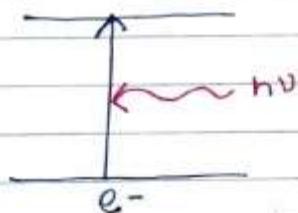
$$n = 1, 2, 3, \dots$$

- During revolution in these stationary orbits, electrons have constant energy, i.e. electron neither lose energy or absorb energy during revolution in a definite orbit.
- Energy absorption or emission takes place when electron jumps from one energy level to another energy level.
- When electron jumps from higher energy level to lower energy level then energy is

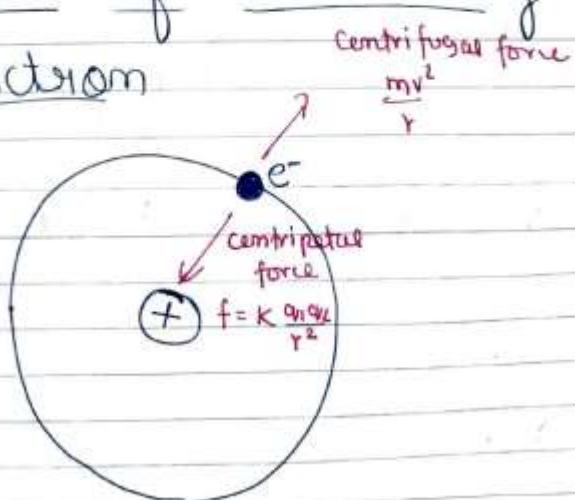
released.

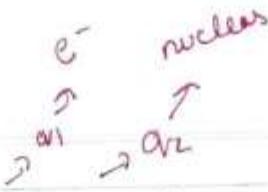


When electron jumps from lower energy level to higher energy level then energy is absorbed.



Calculation of Radius of Orbit of revolving electron





$$\frac{mv^2}{r} = k(e) (ze)$$

$$v^2 = \frac{kze^2}{mr} \quad \leftarrow \textcircled{1}$$

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

$$v = \frac{n\hbar}{2\pi mr}$$

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

[putting this value in eqn. ①]

$$\frac{n^2 \cancel{\hbar^2}}{4\pi^2 m^2 r^2} = \frac{kze^2}{mr}$$

$$r = \underbrace{\frac{\hbar^2}{4\pi^2 K me^2}}_{\text{constant}} \left( \frac{n^2}{z} \right) \text{ a}$$

$$r = \cancel{m} \frac{\hbar^2}{4\pi^2 K me^2} = 0.529$$

$$\delta r = 0.529 \frac{n^2}{Z} \text{ Å}$$

$$0.529 \text{ Å} = a_0 \text{ or } R_0$$

for H atom

$$r_1 = 0.529 \times \frac{1^2}{1} = 0.529 \text{ Å} = a_0$$

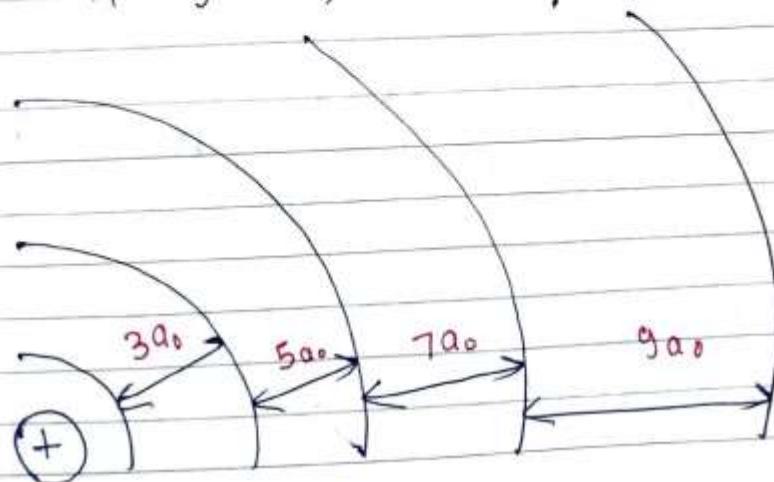
$$r_2 = 0.529 \times \frac{2^2}{1} = 0.529 \dots = 4a_0$$

$$r_3 = 0.529 \times \frac{3^2}{1} = 9a_0$$

$$r_4 = 0.529 \times \frac{4^2}{1} = 16a_0$$

- $\delta r_4 > \delta r_3 > \delta r_2 > \delta r_1$

- $\delta r_4 - \delta r_3 > \delta r_3 - \delta r_2 > \delta r_2 - \delta r_1$



$$\frac{r_1}{r_2} = \left(\frac{n_1}{n_2}\right)^2 \left(\frac{z_2}{z_1}\right)$$

Calculation of Velocity of moving electron

$$\frac{mv^2}{r} = \frac{Kze^2}{vr^2}$$

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

$$v(mv_0) = Kze^2$$

$$v \cdot \frac{nh}{2\pi} = Kze^2$$

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

$$v = 2.19 \times 10^8 \times \frac{z}{n} \text{ cm/s}$$

$$V_1 = 2.19 \times 10^8 \times \frac{1}{1} = V_1$$

$$V_2 = 2.19 \times 10^8 \times \frac{1}{2} = \frac{V_1}{2}$$

$$V_3 = 2.19 \times 10^8 \times \frac{1}{3} = \frac{V_1}{3}$$

$$\boxed{\frac{V_L}{V_2} = \frac{Z_1}{Z_2} \times \frac{n_2}{n_1}}$$

## ENERGY CALCULATION

$$P_E = -K \frac{q_1 q_2}{r}$$

$$\boxed{P_E = -K \frac{(ze)e}{r}}$$

$$\frac{mv^2}{r} = K \frac{ze^2}{r^2}$$

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

$$PE = -mv^2$$

$$\frac{1}{2}mv^2 = k \frac{ze^2}{2r}$$

$$KE = k \frac{ze^2}{2r}$$

$$E_{\text{Total}} = E_{\text{kinetic}} + E_{\text{potencial}}$$

$$= k \frac{ze^2}{2r} + \left( -k \frac{ze^2}{r} \right)$$

$$E_T = -k \frac{ze^2}{2r}$$

$$E_T = -\frac{kze^2}{2} \times \frac{4\pi^2 m k z e^2}{n^2 h^2}$$

$$E_T = \frac{2\pi^2 k^2 m e^4}{h^2} \left(\frac{z}{n}\right)^2$$

$$E_T = -13.6 \times \frac{z^2}{n^2} \text{ ev per atom}$$

## KNOWLEDGE BOX

In case of composite system  
Mass can be used as reduced mass

$$\text{reduced mass } \mu = \frac{m_e m_n}{m_p + m_e}$$

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M} = \frac{M+m}{Mm}$$

$$N = \frac{m M}{m+M}$$

$$\mu = \frac{m_e m_n}{m_n + m_e}$$

$\because m_n \gg m_e$

$$m_n + m_e \approx m_n$$

$$\approx \frac{m_e m_n}{m_n}$$

$$\approx m_e$$

$$E_T = -13.6 \times \frac{Z^2}{n^2} \text{ ev per atom}$$

$$E_T = -313.6 \frac{Z^2}{n^2} \text{ Kcal/mol}$$

$$E_t = -1312 \frac{Z^2}{n^2} \text{ kJ/mol}$$

For Hydrogen atom

$$E_1 = -13.6 \times \frac{1^2}{1^2} = -13.6 \text{ eV/atom}$$

$$E_2 = -13.6 \times \frac{1^2}{2^2} = -3.4 \text{ eV/atom}$$

$$E_3 = -13.6 \times \frac{1^2}{3^2} = -1.51 \text{ eV/atom}$$

$$E_4 = -13.6 \times \frac{1}{4^2} = -0.85$$

$$-0.85 \longrightarrow n=4$$

$$-1.51 \text{ eV} \longrightarrow n=3$$

$$-3.4 \text{ eV} \longrightarrow n=2$$

$$-13.6 \text{ eV/atom} \longrightarrow n=1$$

$$E_4 > E_3 > E_2 > E_1$$

$$E_4 - E_3 < E_3 - E_2 < E_2 - E_1$$

at infinity

$$K\epsilon = 0 \quad P\epsilon = 0 \quad E_T \approx 0$$

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

$$E_n \propto \frac{n^2}{Z^2} \quad (\text{due to } (-) \text{ sign})$$

Also use this formula for  
case.

$$\frac{E_1}{E_2} = \left(\frac{Z_1}{Z_2}\right)^2 \left(\frac{n_2}{n_1}\right)^2$$

if  $P\epsilon = -2$   $K\epsilon = x$

$$E_T = -x$$

Good relation

$$E_T = -KE = \frac{RE}{2}$$

If energy of revolving electron of  
2<sup>nd</sup> orbit  $\text{He}^+$  is  $E$  find the  
energy in 3<sup>rd</sup> orbit of  $\text{Li}^{2+}$

$$\frac{E}{E_2} = \left(\frac{2}{3}\right)^2 \times \left(\frac{3}{2}\right)^2$$

$$E = E_2$$

### IONIZATION ENERGY

The amount of energy required to transit an electron from ground state up to infinite.

$$IE = E_{\infty} - E_{\text{g.s.}}$$

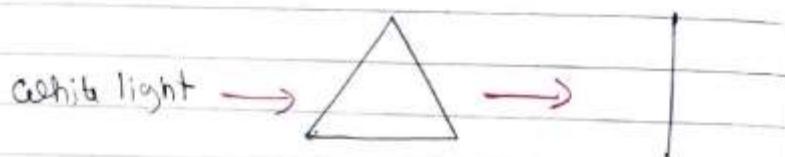
$$= 0 - (-13.6 \text{ eV})$$

$$= 13.6 \text{ eV}$$

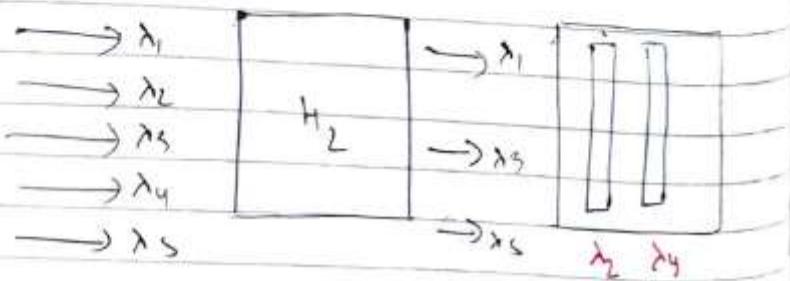
# Spectrum

The image obtained on screen when white light or radiation pass through a prism is termed as spectrum.

When interradiation by a source is observed on screen through prism then Emmision spectrum



If interradiation is passed through a gas and then emergent radiation is observed on screen through prism then it is absorption spectrum



### Emission Spectrum

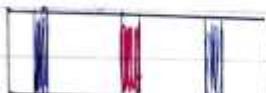
- It is observed by emitted radiation of the source.
- It is observed on dark background.
- It forms both continuous and discontinuous spectrum.

### Absorption Spectrum

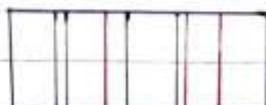
- It is observed by absorbed radiation of the source.
- It is observed at light background



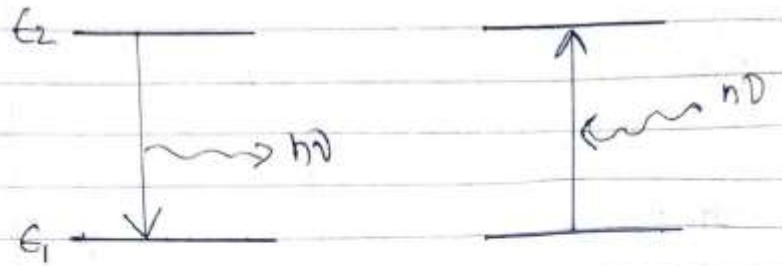
Continuous spectrum



Discontinuous (band spectrum)



Discontinuous (line spectrum)



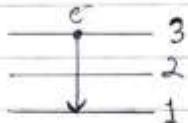
Emission Spectrum

Absorption Spectrum

Jumping Energy Calculation

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

Example Problem



$$\Delta E = \epsilon_3 - \epsilon_1$$

$$= (-1.51 \text{ eV}) - (-13.6 \text{ eV})$$

$$= 12.09 \text{ eV}$$

to calculate frequency, simply  
use this

$$h\nu = \frac{hc}{\lambda}$$

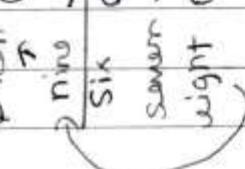
$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

## Calculation of Wave number ( $\bar{\nu}$ )

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

$R$  = Rydberg Constant

$$= 109678 \text{ cm}^{-1}$$

$z$  = atomic no 

$n_1$  = lower\* energy level

$n_2$  = higher\* energy level

if suppose it goes from  $n = 3$  to  
 $n = 6$  then  $n_1 = 3$ ,  $n_2 = 6$   
lower      higher

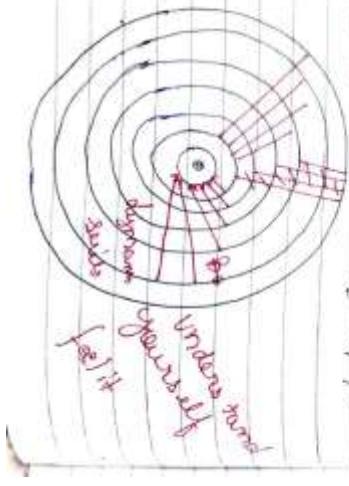
if suppose it goes from  $n = 13$  to  
 $n = 31$ , then  $n_1 = 13$ ,  $n_2 = 31$   
lower      higher

Ritz  
formula =

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

H - Spectrum (U-B-P-B-P-H)

- 1 Lyman Series  $n_1=1$   $n_2=2, 3, 4, \dots, \infty$
- 2 Balmer Series  $n_1=2$   $n_2=3, 4, 5, \dots, \infty$
- 3 Paschen Series  $n_1=3$   $n_2=4, 5, 6, \dots, \infty$
- 4 Bragiotti Series  $n_1=4$   $n_2=5, 6, 7, \dots, \infty$
- 5 Pfund Series  $n_1=5$   $n_2=6, 7, 8, \dots, \infty$
- 6 Humphreys  $n_1=6$   $n_2=7, 8, 9, \dots, \infty$



$$\frac{n_2}{n_1}$$

$n+1 \rightarrow n$  1<sup>st</sup> line  $E_{\min}$   $V_{\min}$   $\lambda_{\max}$

$n+2 \rightarrow n$  2<sup>nd</sup> line

$n+3 \rightarrow n$  3<sup>rd</sup> line

$n+4 \rightarrow n$  4<sup>th</sup> line

$\infty \rightarrow n$  limiting  $E_{\max}$   $V_{\max}$   $\lambda_{\min}$

$$\text{no of Spectral lines} = \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

if  $n_1$  = Ground State  
↓

$$\text{no of Spectral lines} = n \left( \frac{n-1}{2} \right)$$

~~2~~  $\rightarrow \frac{(5-1)(5-1+1)}{2}$

## LIMITATION OF BOHR Model

- o Bohr model is only applicable for single electron species, i.e., H atom & H-like ions (having single electron)
- o On analysis of spectral lines of H atom it is found that each spectral line also consists of

many fine lines, it is termed as fine spectrum. Bohr's model cannot explain the fine spectrum.

Bohr's model does not explain the splitting of spectral lines in electric field (Stark Effect) and also in magnetic field (Zeeman effect).

STARK → Electric field

ZEEMAN → Magnetic field

- Bohr's model is not the agreement of Heisenberg's Uncertainty Principle.
- In Bohr's model path of electron in an atom is Circular.

## • Separation Energy

If electron is already present in excited state then energy required to transit an electron from excited state to infinite is termed as Separation Energy.

$$SE = E_{\infty} - E_{\text{excited state}}$$

if e<sup>-</sup> present in 2<sup>nd</sup> excited state-

$$\Rightarrow SE = E_{\infty} - C_0 - (-1.051 \text{ eV})^3$$

$$= 1.51 \text{ eV}$$

## • EXCITATION ENERGY

Energy required to transit an electron from ground state or any excited state to other excited state is called excitation energy.

## • Orbital frequency

No. of revolution by an electron in an orbit in unit second is called orbital frequency.

$$\text{Orbital frequency } \nu = \frac{\text{Velocity } (v)}{\text{Circumference } (2\pi r)}$$

$$= 6.66 \times 10^{15} \times \frac{Z^2}{h^3} \text{ Hz}$$

## TIME PERIOD

Time required to complete one revolution in an orbit by an electron is called Time period.

$$\text{Time period} = \frac{2\pi r}{v}$$

$$= 1.5 \times 10^{-16} \times \frac{n^3}{z} \text{ sec}$$

# Dual nature of $e^-$

(De-Broglie wavelength)

Microscopic particle moving with very high speed can behave as both particle and wave.

as wave nature

as particle nature

$$E = h\nu$$

$$E = mc^2$$

$$\Rightarrow h\nu = mc^2$$

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

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

$$\lambda = \frac{c}{f^{-1}m}$$

if velocity = v

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

De Broglie Wavelength)

De broglie equation is the a gyement  
of Bohr's model

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

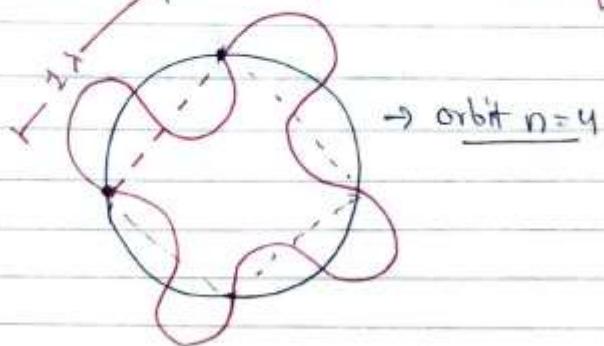
$$\lambda = \frac{h}{\sqrt{2m\kappa E}}$$

$$\lambda = \frac{h}{\sqrt{2meV}}$$

NOTE: For macroscopic bodies wavelength  
is too short which is not  
observable. No -

$$\text{angular } P = n \frac{h}{2\pi}$$

- No of waves made by an  $e^-$  in a shell is equal to no of shell.



$4\lambda$  or 4 wavelength  
= no of waves in a shell

Proof:

$$\begin{aligned} \text{no of waves} &= \frac{2\pi \omega}{\lambda} \\ \text{of a shell} \end{aligned}$$

$$= \frac{2\pi \omega}{n/mv}$$

$$= \frac{2\pi}{n} \times mv \nu$$

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

$$= n$$

## The Heisenberg Uncertainty Principle

According to this theory it is impossible to measure the position and momentum of a moving electron simultaneously with 100% accuracy.

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

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

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

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

$\Delta x$  = uncertainty in measurement of position

$$\Delta p =$$

This theory is not applicable for moving static bodies.

$$E_T = (KE)_e + (KE)_N + (PE)_{\text{atom}}$$
$$= (KE)_e + (PE)_{\text{atom}}$$

for  $e^-$

$$\lambda = \frac{12.27}{\sqrt{V}} \text{ Å}^\circ$$

$$\text{for } p^+ \quad \lambda = \frac{0.286}{\sqrt{V}} \text{ Å}$$

for  $\alpha$

$$\lambda = \frac{0.101}{\sqrt{V}} \text{ Å}$$

for  $n^\circ$

$$\lambda = \frac{0.286}{\sqrt{E} (\rho V)} \text{ Å}$$

for gas

$$\lambda = \frac{h}{m v_{\text{rms}}} = \frac{h}{\sqrt{3 m k T}}$$

$$K \rightarrow \text{Boltzmann Constant}$$
$$= 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$$

$m$  = mass of one gas particle (molecule/atom)

$V_{rms}$  = Root mean square velocity

$T$  = Temperature in Kelvin

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{4\pi}$$

$\Delta x$  → wavelength in  
Energy in excited state

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{4\pi} \quad \Delta t \rightarrow \text{uncertainty in time of electron reside in excited state.}$$

$$\Delta \theta \cdot \Delta \phi \geq \frac{\hbar}{4\pi} \quad \Delta \theta = \text{Uncertainty in angular displacement}$$

$\Delta \theta = \text{Uncertainty in angular momentum}$

## Wave Mechanical Theory

(Quantum model)

This model was proposed by Schrodinger and Heisenberg independently.

## Schrodinger equation

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m(E-V)}{\hbar^2} \Psi = 0$$

m → mass of electron

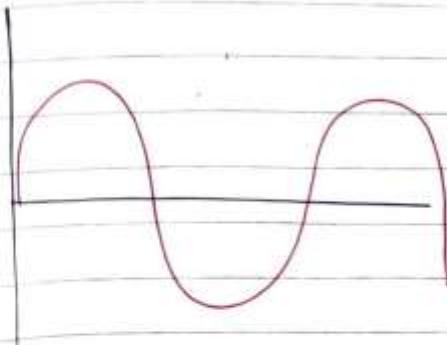
E → Total electron energy

V → Total Potential Energy

$\Psi$  → wave function of wave  
of associated with movement  
of e<sup>-</sup>

$\partial$  → Partial differentiation

$\Psi \rightarrow$  wave amplitude

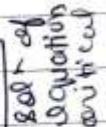


$\psi^2 =$  probability of finding of  
 $e^-$  at a point.

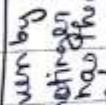
## Quantum numbers

Quantum numbers addresses an electron in an atom

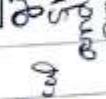
(i) Principal Quantum no & 'n'



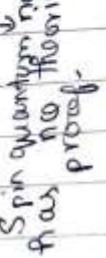
(ii) Azimuthal quantum no m. 'l'



(iii) Magnetic quantum no 'm'



(iv) Spin quantum no 's'



Orbit

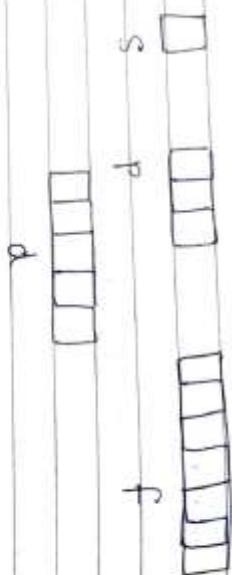


Subshell

s, p, f, d, g



Orbitals



## # Principal Quantum No

Inform about orbit & on shell no.

for given value of  $n$

- (a) no of electron (Maximum) which can accommodate in an orbital shell.

$$2n^2$$

when  $n \in \mathbb{N}$

examples

$$n=1 \quad 2 \times 1^2 = 2$$

$$n=2 \quad 2 \times 2^2 = 8$$

$$n=3 \quad 2 \times 3^2 = 18$$

$$n=4 \quad 2 \times 4^2 = 32$$

- (b) No of Suborbit =  $n$

1<sup>st</sup> Orbit  $n=1$  No of Suborbits = 1  
s

2<sup>nd</sup> Orbit  $n=2$  " " " = 2  
s p

(c) no of Orbital =  $n^2$

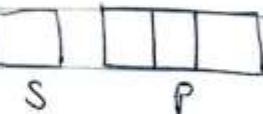
$n=1$

1



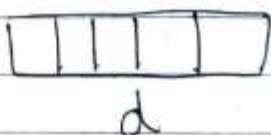
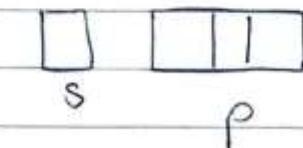
$n=2$

$2^2=4$



$n=3$

$3^2=9$



# Azimuthal Quantum no

or

Subsidiary Quantum no

OR

Secondary quantum no

w Information about shape of Sub orbits

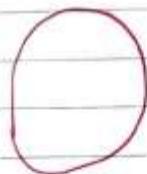
s - Suborbit  $l=0$

p - Suborbit  $l=1$

d - Suborbit  $l=2$

f - Suborbit  $l=3$

\*  $l=0$  S-Suborbit



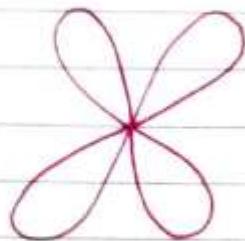
Spherical

\*  $l=1$  p-Suborbit



dumbbell shaped

$l=2$  d - Suborbit



double dumble

For given 'n'

Value of  $l = 0$  to  $(n-1)$

$n=1$   $l = 0$  to  $(1-1) = 0$  s-orbital

$n=2$   $l = 0$  to  $(2-1) = 1$   
0, 1  
s, p

$n=3$   $l = 0$  to  $(3-1) = 2$   
0, 1, 2  
s p d

for given  $l$  no of electrons :-

no of electrons which can be accommodated in a subshell.

$$= 2(2l+1)$$

example

Suborbital

s             $l=0$              $2(2 \cdot 0 + 1) = 2$

p             $l=1$              $2(2+1) = 6$

d             $l=2$              $2(5) = 10$

for given  $l$

no of orbitals in a suborbit

$$= (2l+1)$$

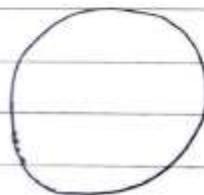
		no of orbitals
s	$l=0$	$" = 2(0)+1 = 1$
p	$l=1$	$" = 2(1)+1 = 3$
d	$l=2$	$" = 2(2)+1 = 5$
f	$l=3$	$" = 2(3)+1 = 7$

## # Magnetic Quantum Number "m"

informs about the orientation of orbitals.

S- Suborbital

no of  
orbital = 1



P-Suborbital

no of  
orbital = 3

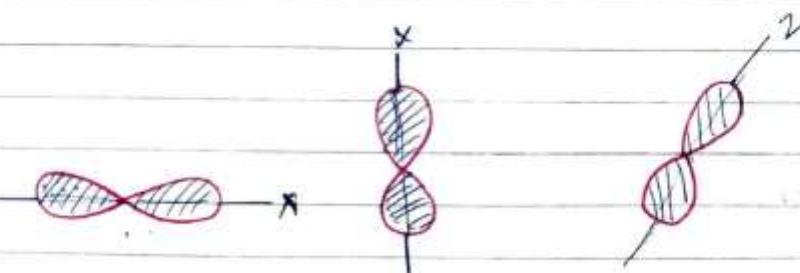
$l=1$

$m = -1 \ 0 \ 1$

$p_x$

$p_y$

$p_z$

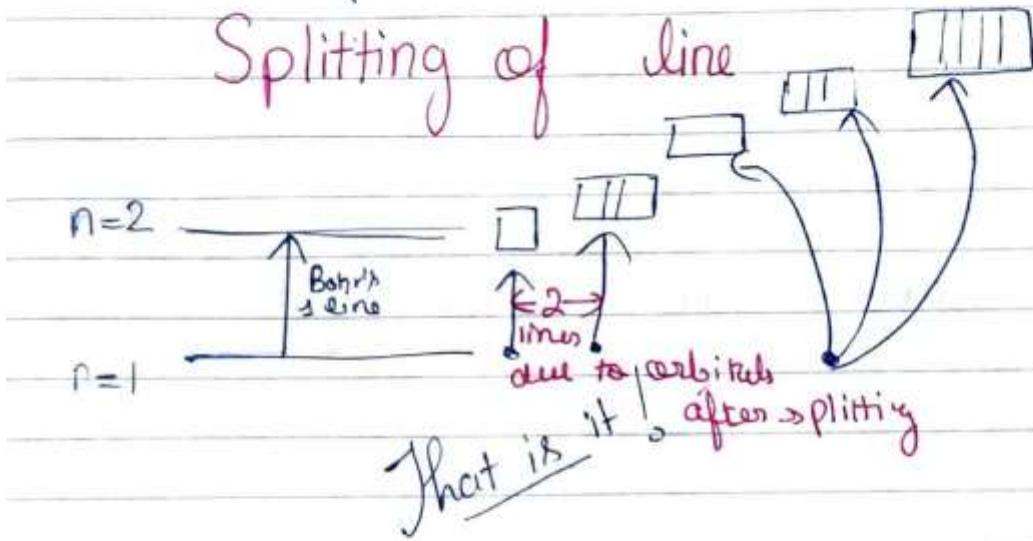


## Orbital

Orbital is the region in which probability of finding the electron is maximum.

Extended the  
ZEEMAN EFFECT  
OR  
STARK EFFECT

Splitting of line



Magnetic Quantum number explain  
zeeman effect

$l = 2$  no of orbitals = 5

						$d_{xy}$	$d_{yz}$	$d_{zx}$
$m =$	-2	-1	0	1	2	$d_{x^2-y^2}$	$d_{z^2}$	

$d_{xy} = \pm 2$  then  $d_{x^2-y^2} = \pm 2$

$$d_{yz} = \pm 1 \quad d_{z^2} = \pm 1$$

$$d_{x^2} = 0$$

for given  $l$

values of  $m = -l$  to  $+l$

S  $l = 0$

$m = 0$

P  $l = 1$

-1 to +1

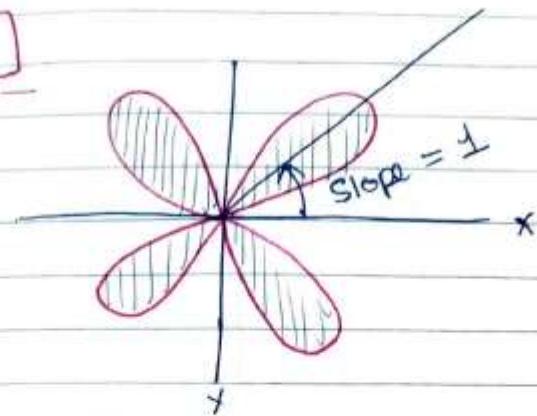
-1, 0, +1

D  $l = 2$   
 $m = -2$

$m = -2$  to +2

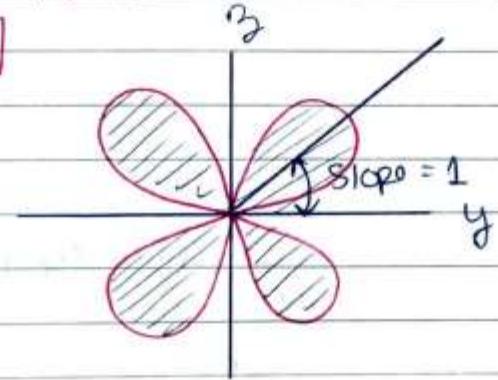
-2, -1, 0, 1, 2

$d_{xy}$

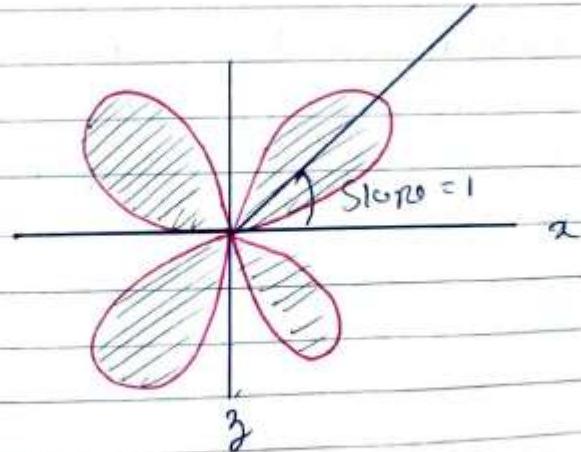


Maximum electron density is present between the x and y axis at  $45^\circ$ .

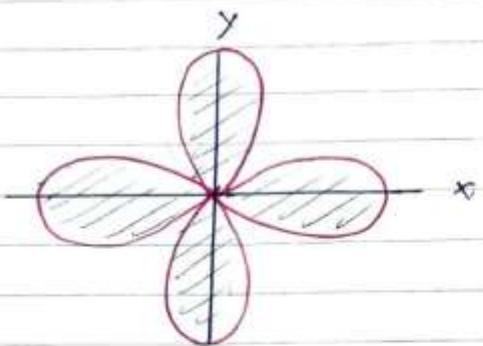
$d_{yz}$



$d_{zx}$

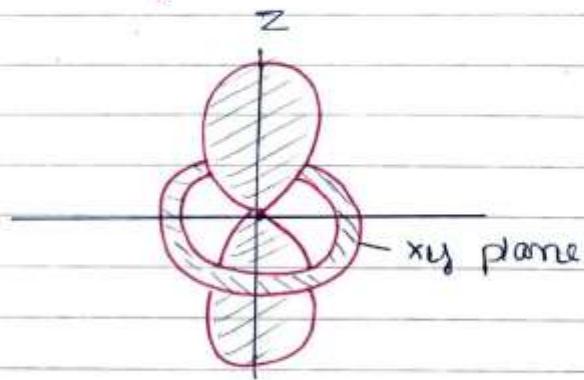


$|d_{x^2-y^2}|$



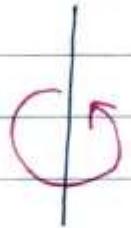
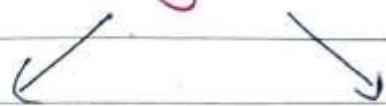
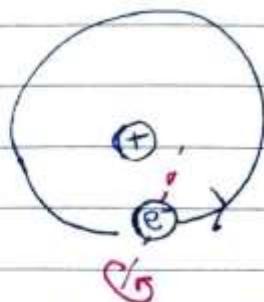
Electron density present on the  
x and y axis.

$|d_{z^2}|$



Maximum electron density present  
in z axis but some electron  
density is also present in xy plane

# # Spin Quantum No 'S'



clockwise



anticlockwise



$$S = +\frac{1}{2} \quad -\frac{1}{2}$$

THIS QUANTUM NO HAS  
NO THEORITICAL PROOF BUT  
IS FOR CONVENTION ONLY. !!

*new symbol*  $\hbar$   $\rightarrow$  h-dirac

$$\psi \quad \text{angular orbital momentum} = \boxed{\sqrt{l(l+1)} \frac{h}{2\pi}}$$

$$= \sqrt{l(l+1)} \hbar$$

$$\hbar = \frac{h}{2\pi}$$

angular orbital momentum for  
an electron present in

- S orbital =  $\sqrt{0(0+1)} \hbar = 0$
- p orbital =  $\sqrt{1(1+1)} \hbar = \frac{\sqrt{2}h}{2\pi}$
- d orbital =  $\sqrt{2(2+1)} \hbar = \frac{\sqrt{6}h}{2\pi}$

$\psi$  Spin Orbital Angular Momentum

$$\mu_s = \boxed{\sqrt{s(s+1)} \frac{h}{2\pi}}$$

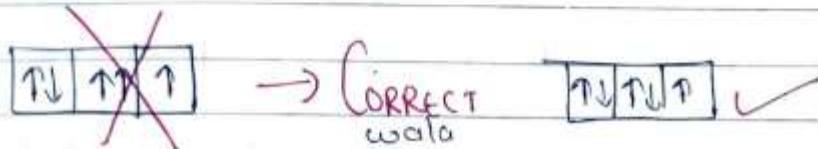
$$s = 1/2$$

$$\mu_s = \sqrt{\frac{1}{2}(\frac{1}{2}+1)} \hbar = \sqrt{\frac{3}{4}} \frac{h}{2\pi}$$

# ELECTRONIC CONFIGURATION

## ⇒ Pauli exclusion Principle

If it is impossible to have the value of all 4 quantum number similar for any two electrons in an atom.

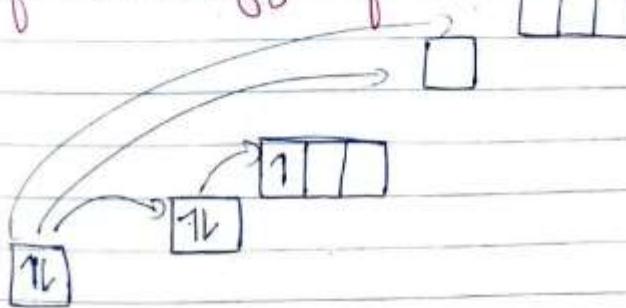


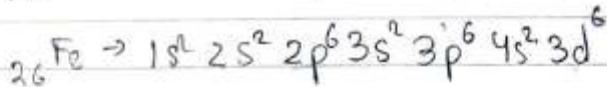
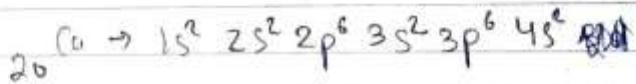
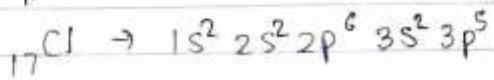
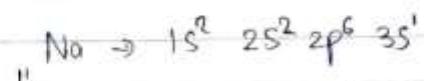
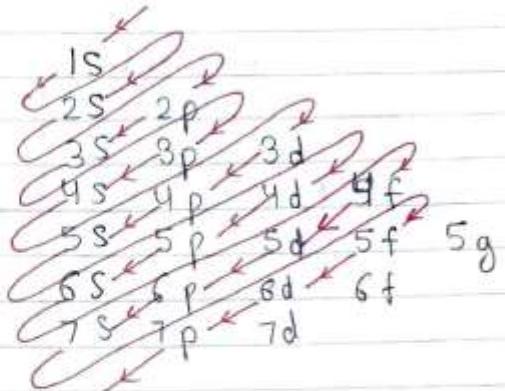
According to the rule no two electrons with same spin will be present in orbital.

# An orbital cannot have more than two electron

## ⇒ Aufbau rule

Filling of electrons occur according to increasing energy of energy of orbital.





$(N+l)$  rule

$(N+l) \uparrow$        $\epsilon \uparrow$

Rule I

$3^{\frac{1}{2}}d$        $4^{\frac{1}{2}}s$

$$\begin{array}{ccc} n+l & 3+2 & 4+0 \\ & = 5 & = 4 \end{array}$$

The Orbital having lowest  $(n+l)$  value will be filled first.

If  $(n+l)$  value will be same for different orbital then the orbital with minimum  $n$  value will be filled first.

### Hund's Rule

Pairing of electrons occur when each orbital with similar energy occupied by one electron.

## Important point

All three orbitals of p subshell are equal in shape, energy and size but different in orientation.

All orbitals of d subshells are similar in energy.

## # Degeneracy

Equal in energy

e.g:-

degeneracy in p subshell  $\Rightarrow$



$$d = 5$$

$$f = 7$$

## $\Psi$ for Hydrogen atom

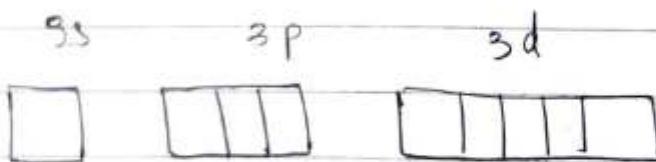
$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$$

due to presence of only one electron in Hydrogen atom, energy only depends on attraction between

Electron and nucleus which directly depends on principal quantum no.  $\rightarrow (n)$

Ques:  $\rightarrow$

degeneracy of 3<sup>rd</sup> orbit in H atom.



$$= 9$$

- Orbital of same subshell of different orbit are similar in shape but different in size and energy.

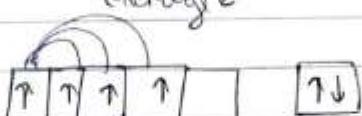
Ans

Size- 1s < 2s < 3s

2p < 3p < 4p

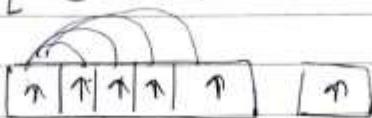
## EXCEPTIONS

~~Coupi<sup>t</sup>~~ Wronus Cr.  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$   
~~24~~ exchange



unsymmetrical

~~Coupi<sup>t</sup>~~ Cr.  $[Ar] 3d^5 4s^1$   
~~24~~



symmetrical

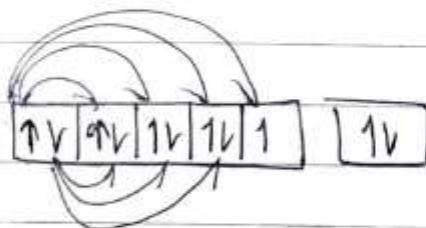
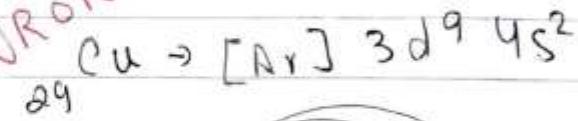
### REASON:-

~~also~~ ~~1st~~ Second Configuration is stable:-  
Due to following reason

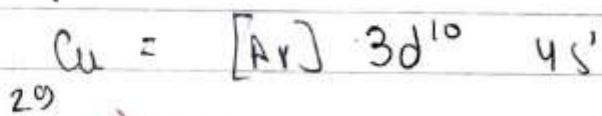
- 1 First configuration has unsymmetrical filling of electrons while second one has symmetrical filling. Since symmetrical filling is more stable, 2<sup>nd</sup> config. is more stable.
- 2 Electron can exchange position having same energy and same spin. In this process, energy is released which is termed as exchange energy.

Greater the exchange energy, greater will be the energy of system. Since in first configuration, there were only 3 chance of exchange of an  $e^-$  with other  $e^-$ . while in 2<sup>nd</sup> config., there is four chance to exchange.

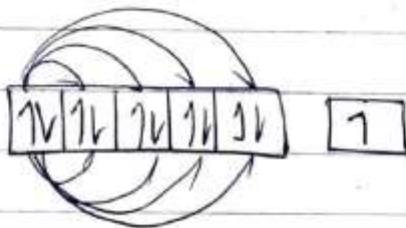
~~Cast<sup>2</sup>  
copper~~  
~~WRONG~~



wrong symmetrical

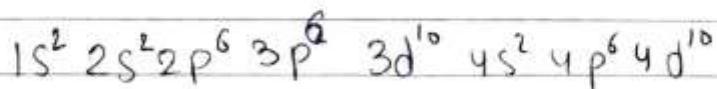
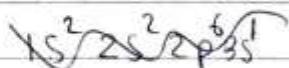
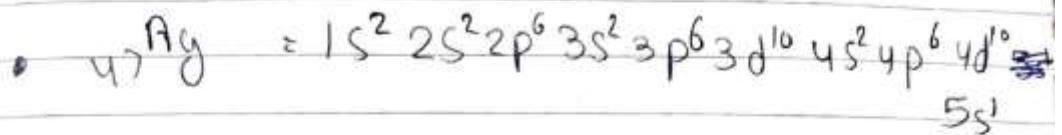


~~Correct~~



Symmetrical

## ψ Other Unique configuration

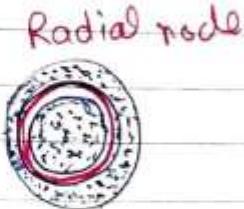


## Node and Nodal Plane

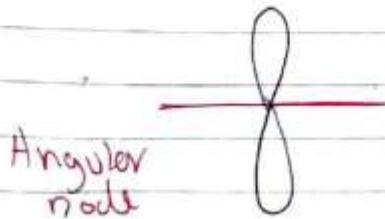
The point at which probability of finding an e<sup>-</sup> is zero.

\* radial node =  $n - l - 1$

\* angular node =  $l$   
 (or Nodal plane)



\* Total nodes =  $n - 1$

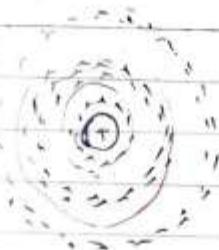


for 1s

$$\text{no of radial nodes} = 1 - 0 - 1 = 0$$

for 2s

$$\text{no of } " " = 2 - 0 - 1 = 0$$



### Nodal Plane

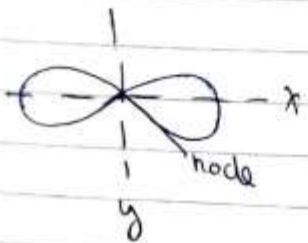
1)



nodal plane = 0  
(angular node)

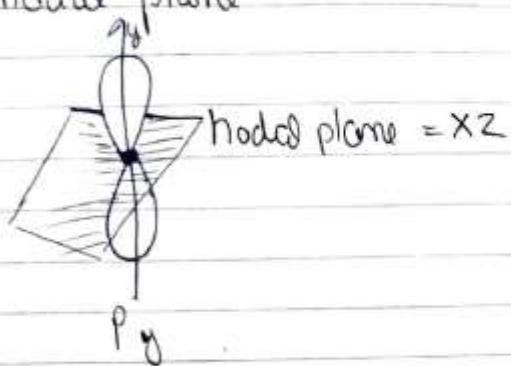
S-Orbital

2)

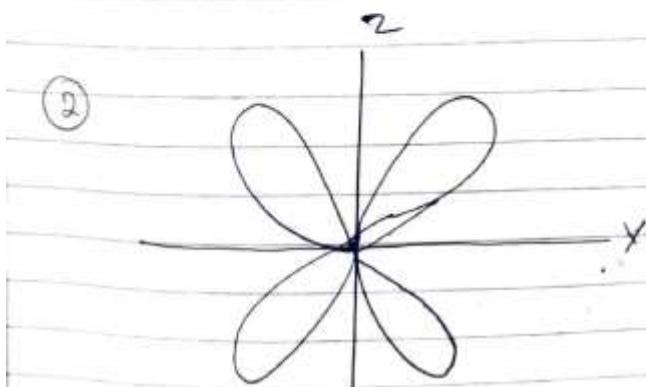
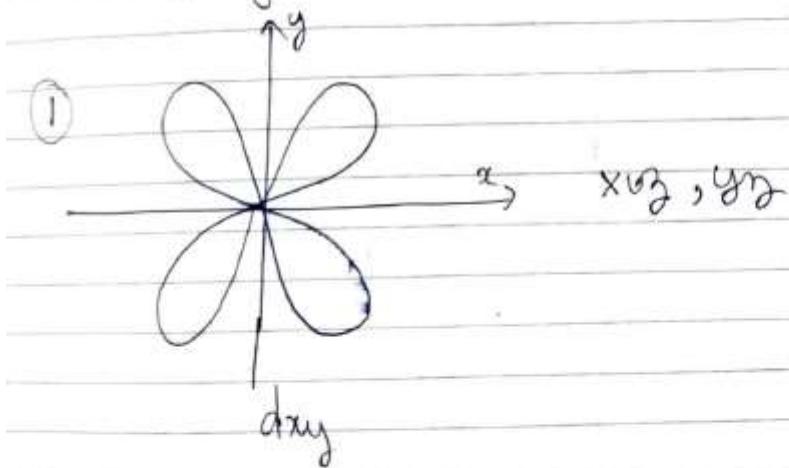


nodal plane = yz

$P_2 = xy$  nodal plane



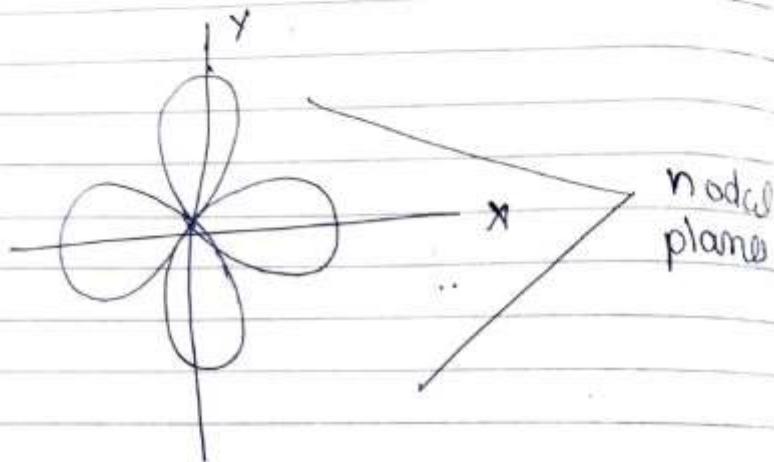
No of Nodal plane = 1  
(angular node)



$d_{yz}$

nodal plane  $yz$  and  $z^2$

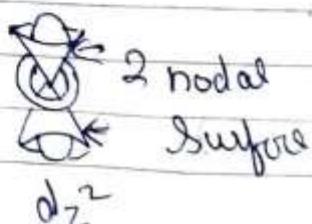
- $d_{zx}$  nodal plane  
 $yz$  and  $xy$



Nodal plane passing through  
x and y axis at  $45^\circ$   
from any axis

$d_{z^2}$

No nodal plane but Surface



Spin only magnetic moment

$$mm = \sqrt{4s(s+1)} BM$$

↓  
Bohr's Magneton

$$S = \sum_{i=1}^{i=n} s$$

$$N = 1s^2 2s^2 2p^3$$



$$S = 5 \times \left( +\frac{1}{2} \right) + 2 \left( -\frac{1}{2} \right)$$

$$= \frac{3}{2}$$

$$mm = \sqrt{4 \times \frac{3}{2} \left( \frac{3}{2} + 1 \right)} = \sqrt{15}$$

$$mm = \sqrt{n(n+2)} BM$$

$n \rightarrow$  no of unpaired e<sup>-</sup>

Trick

$$M.M - 0.8 = X \rightarrow$$

round off  $X$  to nearest integer

It gives no of unpaired electron

$$n=1 \quad M.M = \sqrt{1(1+2)} = \sqrt{3} \approx 1.73$$

$$n=2 \quad = \sqrt{2(2+2)} = \sqrt{8} = 2.82$$

Paramagnetic

reactive nature

due to presence of unpaired  $e^-$   
weakly attracted in magnetic field.

no of electron unpaired  $\propto$  paramagnetic nature

Diamagnetic

if all  $e^-$  present in paired form  
Repelled in magnetic field

## Dependence of Energy of

$e^-$  in multielectron atom

depends on both  $n$  and  $l$  value unlike hydrogen atom because there are two types of interaction present:-

- Attraction b/w nucleus and Electron of atom.
- Repulsion b/w concerned  $e^-$  and rest of  $e^-$  present in the atom.

## $\Psi$ SHIELDING EFFECT (SCREENING EFFECT)

Due to presence of inner electrons in multielectron atom resultant attraction force by the nucleus on outermost electron decreases because inner electrons repel the outer electron, that is, inner electron shield the outer electron from the attraction of nucleus. This effect is termed as Shielding effect.

## Effective nuclear Charge

$$Z_{\text{eff}} = Z - \sigma \quad \begin{matrix} \rightarrow \text{Screening Constant} \\ \downarrow \\ \text{atomic number} \end{matrix}$$

Shielding constant

order of Shielding

$$s > p > d > f$$

Rule: Calculation of  $\sigma$  (Slater's rule)

I If an electron is present in 's' or 'p' orbital (Suborbit) then each electron present in same shell that of electron under consideration contributes 0.35 towards shielding of <sup>1</sup>st <sub>8</sub>shell

II Each electron present in  $(n-1)$  shell contributes 0.85 towards shielding.

III Each electron present in  $(n-1)$  on lower orbit contributes one towards shielding.

no contribution of outer shells

Example.

$$(I) {}_{17}Cl = 1s^2 \underbrace{2s^2}_{(n-2)} \underbrace{2p^6}_{(n-1)} \underbrace{3s^2}_{\text{17th}} \underbrace{3p^1}_{\text{17th}}$$

(1s)  $\rightarrow$  one electron  
(2s)  $\rightarrow$  one electron  
(2p)  $\rightarrow$  one electron  
will not contribute

$$\sigma = 1 \times 2 + 0.85 \times 5 + 0.35 \times 6$$

$$= 2 + 6.8 + 2.1$$

$$= 10.9$$

$$Z_{\text{eff.}} = 17 - 10.9 \\ = 6.1$$

$$(II) {}_{19}K = 1s^2 \underbrace{2s^2}_{(n-2)} \underbrace{2p^6}_{(n-1)} \underbrace{3s^2 3p^6 4s^1}_{\text{n}^{th}} \rightarrow -1e$$

$$\sigma = 1 \times 10 + 0.85 \times 8 + 0.35 \times 0$$

$$(III) {}_{29}Cu = 1s^2 \underbrace{2s^2}_{(n-2)} \underbrace{2p^6}_{(n-1)} \underbrace{3s^2}_{(n-1)} \underbrace{3p^6}_{(n-1)} \underbrace{3d^{10}}_{(n-1)} \underbrace{4s^1}_{\text{n}^{th}}$$

$$\sigma = 10 \times 1 + 18 \times 0.85 + 0.35 \times 0$$

$$n^{th} = 0.35$$

$$(n-1) = 0.85$$

$$(n-2) \dots = 1$$

If electron is present in d or f orbital then each electron present in that group except considered electron contribute 0.35 in shielding.

Other electrons present in lower group contribute by one for each electron.

99

1s    2s 2p    3s 3p    3d    4s 4p    4d 4f

~~aw~~  ${}_{19}Cu = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

$$\sigma = 1 \times 8 + 0.35 \times 9$$

## Spin Multiplicity

$$= 2 \sum s + 1$$

↙ Singlet State

$$\boxed{1} \quad \text{spin multiplicity} = 2(+\frac{1}{2} - \frac{1}{2}) + 1 \\ = 1$$

↙ Triplet State

$$\begin{matrix} 1 \\ 1 \\ 1 \end{matrix} \quad \text{Spin multiplicity} = 2(+\frac{1}{2} + \frac{1}{2}) + 1 \\ = 3$$

Out Spin multiplicity of N

$$N = 1s^2 2s^2 2p^3$$

$$\boxed{1} \boxed{1} \boxed{111}$$

$$\text{Spin multiplicity} = 2(\frac{1}{2} \times 3) + 1 \\ = 4$$