ENGINEERING CHEMISTRY

1st SEM

CIVIL ENGG.

Under SCTE&VT,Odisha

PREPARED BY

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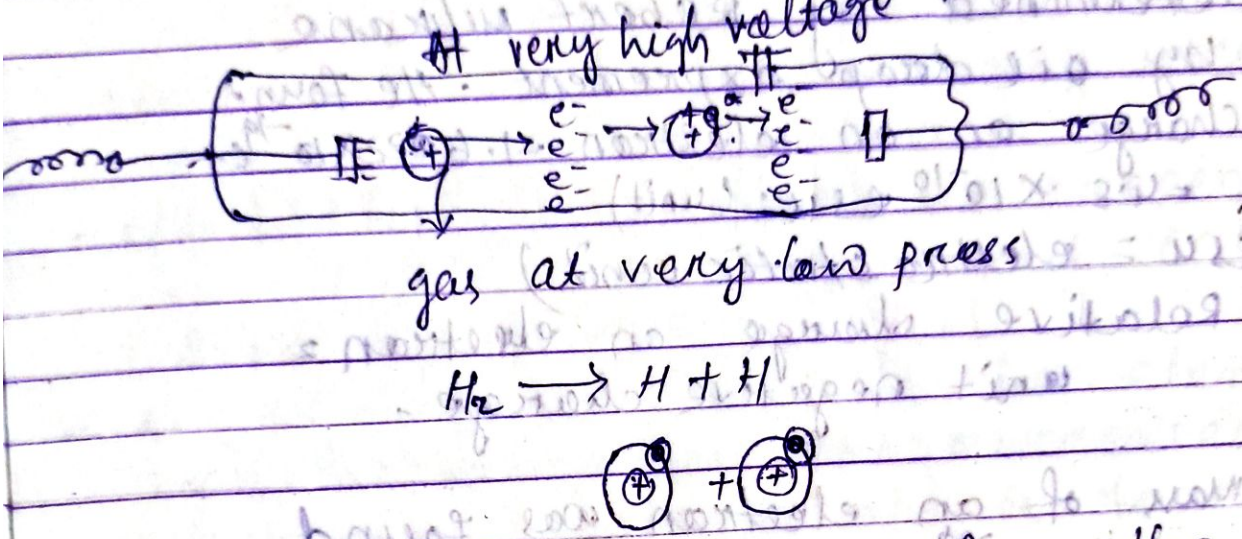
KALINGA NAGAR POLYTECHNIC.

TARAPUR,JAJPUR ROAD

STRUCTURE OF ATOM

- There are 3 fundamental particle of atom.
. electron, neutron, proton.

Electron:-
It was 1st discovered by J.J. Thomson in cathode ray experiment.

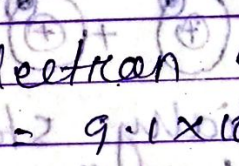


- Cathode ray initially starts from the atom collides to the atom, the flow of the cathode ray continue. This is flow of -vely charged particles. This particles are called as electron by Goldy.
- when cathode ray strikes against
① metal - produces heating effect.
② Flourescent screen - Produce flourescence
③ with spin wheel - gives mechanical effect.
④ with photo graphic plate - fogged.
⑤ Against heavy metal anti-cathode - produce x-ray.

Specific charge (e/m)
Determined by J.J Thomson.

He found its value

- A specific charge (e/m) for cathode ray is independent to the nature of the cathode material and gas used in discharged tube.
- Absolute charge of electron was determined by Robert Millikan by oil drop experiment. He found charge on an electron $= 1.6022 \times 10^{-19} C$.
$= 4.8 \times 10^{-10}$ esu. (unit)
(esu = electrostatic unit)
- Relative charge on electron = unit negative charge.



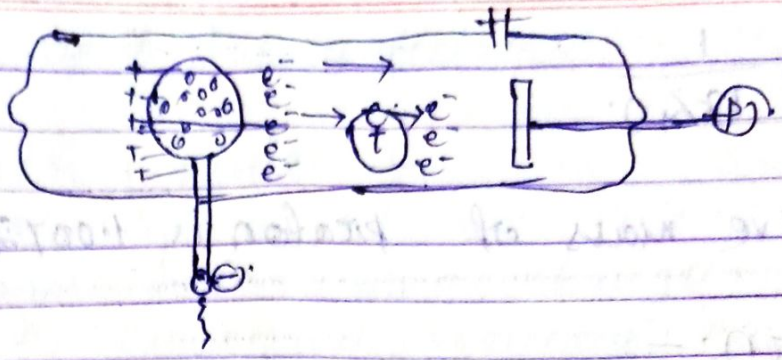
- Mass of an electron was found $9.1 \times 10^{-31} kg = 9.1 \times 10^{-28} g$
- On increasing the velocity of electron, mass of electron increases called reduced mass of e⁻ (m')

$$m' = \frac{m_{rest}}{\sqrt{1-(v/c)^2}}$$

- If velocity of electron becomes equal to velocity of light, then reduced mass become infinity.

Proton:—

It was discovered by E. Goldstein during canal ray or positive ray expt.



All the properties of canal ray / +ve ray except following properties.

- +ve ray cannot produce x-ray when strike against heavy metal.
- Specific charge on proton e/m - depends on the nature of gas used in discharged tube.
- As the atomic mass of the element (gas) increase then e/m decreases. Therefore maximum e/m is found in case of H.

$$\boxed{e/m = +9.579 \times 10^4 \ C/g}$$

- Absolute charge on proton $+1.6022 \times 10^{-19} C$ (or) $+4.8 \times 10^{-10}$ esu.
- Absolute mass of proton.

$= 1.672 \times 10^{-24} g$

$= 1.672 \times 10^{-27} kg$

$$\frac{(e/M)_e}{(e/M)_p} = 1840:1$$

$\frac{M_e}{M_p} = \frac{1}{1840}$

Relative mass of proton is 1.0072 amu

Neutron:-

- Discovered by James Chadwick by bombarding α-ray on Be plate.

$$^{9}_{4}Be + ^{4}_{2}He^{2+} \rightarrow ^{12}_{6}C + ^{1}_{0}n$$

- Due to chargless particle neutron was discovered at last.
- Absolute mass of neutron $= 1.675 \times 10^{-24}$ gm
  $= 1.675 \times 10^{-27}$ kg
- Neutron is the heaviest fundamental particle.
- Its relative mass is 1.00866 amu
- But specific and relative charge is 0.
- Compare

- Specific charge of α, p, e, n

	α	p	e	n
e/M	$\frac{2}{4}$	$\frac{1}{1}$	$\frac{1}{1/1840}$	$0/1$

e/M order: $n < \alpha < p < e$

- Neutron, Proton, Nucleus & electron all spin in their nuclear axis. Therefore in case of clock wise

spin $+1/2$ and $+$ on anticlockwise $-1/2$

· Plums Pudding Model :—

- Atom is spherical and entire sphere is formed with +ve charge & e^- are embonded around the center like raisin in the plums · pudding & seeds in watermelon.
- This model only explains electrically neutral nature of atom · but failed to explain α- scattering experiment.

α- scattering experiment :—

- On the basis of α- scattering experiment Rutherford propose of nuclear model of atom.
- 99% inner part of the atom is hollow.
- All massive particle, (proton & neutrons) are concentrated at the centre of the atom in very small volume. This is called Nucleus of the atom.

$$\frac{\text{Diameter of Atom}}{\text{Diameter of Nucleus}} = \frac{R_{atom}}{R_{nucleus}} = \frac{10^{-8}\,cm}{10^{-13}\,cm} = \frac{10^{-10}\,m}{10^{-15}\,m} = 10^5$$

$$\boxed{R_{atom} = 10^5 \times R_{nucleus}}$$

$$V = \frac{4}{3}\pi R^3 \;,\quad \frac{\text{Vol. of atom}}{\text{Vol. of Nucleus}} = \frac{R_{atom}^3}{R_{nucleus}^3} = (10^5)^3 = 10^{15}$$

$$\boxed{\text{size of atom} = 10^{15} \times \text{size of nucleus}}$$

Defects:-
- According to Maxwell clark theory of electromagnetic radiation when e revolves around the nuclus releases electromagnetic wave continually. Radius of curvature decreases, electron falls at its nucleus. But this doesn't happen.
- Electron if releases energy continu. atomic spectrum should be continuo
- Atomic spectrum is found discontinuous spectrum.

Electromagnetic waves:-
waves having no particle associate with electric field & magnetic fiel & 1's to each other, & ⊥ to the direction of propagation. Having constant velocity. 3×10^8 m/sec, needs no medium to propagate are called electro-magnetic waves.
- These have same velocity but frequency & wavelength are differ

Electromagnetic Spectrum:
when EM waves having no particle are arranged in increasing order of wave length & decreasing order of frequency & energy a series of waves obtain called electromagnetic spectru

Cosmic Ray.
Gamma ray
x- ray
U.V ray
visible ray
I.R rays.
Microwaves.
Radiowaves.

Radha ne Mira ko Invite kiya. Ultra. Ret. X-ray Game Co

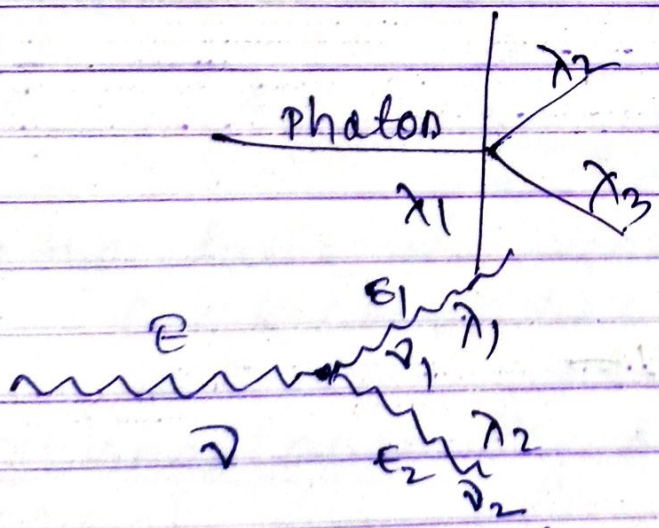
$\lambda\lambda - \nu_1 = E_1$.

$\lambda = c/\nu$, $c = \lambda \times \nu$

$\nu = c/\lambda$ $E = h \cdot \nu$

$E = h \cdot c/\lambda$

$h = 6.625 \times 10^{-34}$ (J.sec)



$\Rightarrow \frac{1}{\lambda_1} = \frac{1}{\lambda_2} + \frac{1}{\lambda_3}$

Acc. to law of conservat^n of energy.

$E = E_1 + E_2$

$h\nu = h\nu_1 + h\nu_2$

$\nu = \nu_1 + \nu_2$

$\frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$

$\frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$

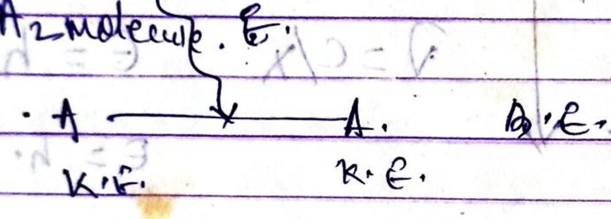
$$\frac{1}{\lambda} = \frac{\lambda_1 + \lambda_2}{\lambda_1 \cdot \lambda_2}$$

$$\boxed{\lambda = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}}$$

$$E_1 = h\nu_1 = h\, c/\lambda_1$$

$$E_2 = h\nu_2 = h\, c/\lambda_2.$$

$$\boxed{\frac{E_1}{E_2} = \frac{\nu_1}{\nu_2} = \frac{\lambda_2}{\lambda_1}}$$

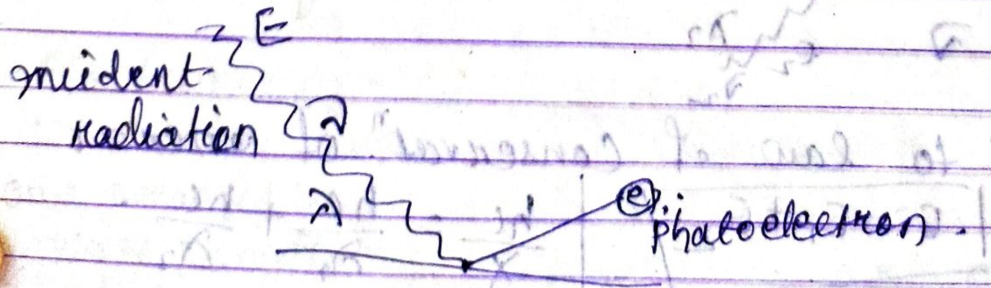


$E = B.E + 2K.E.$

$2K.E = E - B.E.$

$$\boxed{K.E = \frac{E - B.E}{2}}$$

Photo electric effect:-



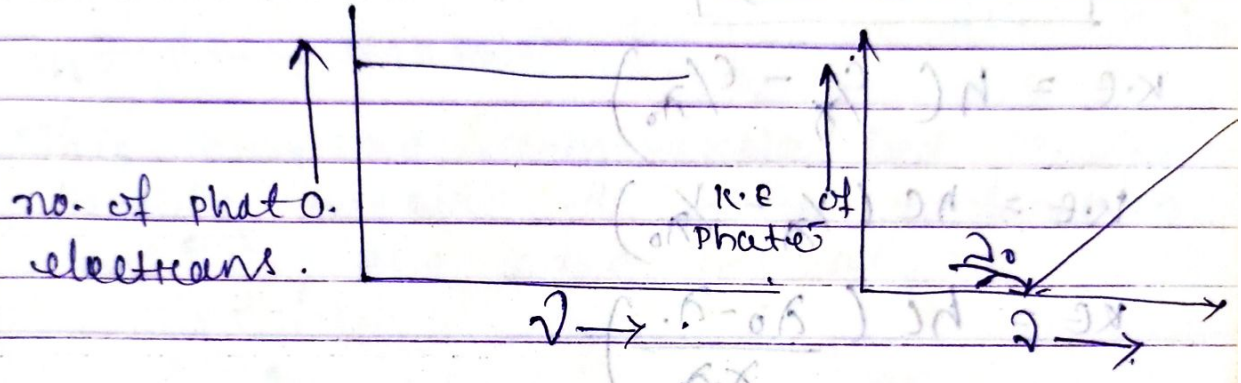
(V)

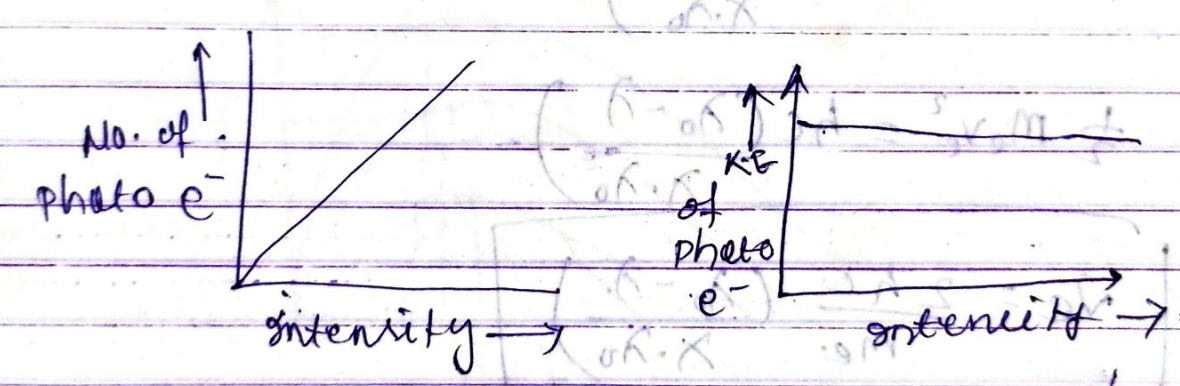
Threshold frequency (ν_0)

Minimum frequency of incident radiation which can eject electron.

(2) Work function (W_0) = Minimum energy of incident radiation which can eject e⁻.

$$\boxed{W_0 = h\nu_0}$$





- On the basis of work function (Q)

$Cs < K < Na < Li < Zn < Cu < Ag < Fe \approx W$ (Pt)

Explanation:- By Einstein)

Case-1

$E < W_0$

$\nu < \nu_0$

no photoelectric effect.

Case-2 $E = W_0$

$\nu = \nu_0$

Photoelectron is ejected with zero K.E.

Case-III $E > \omega_0$
$\nu > \nu_0$

Photoelectron is ejected with some K.E.

$E = \omega_0 + KE$

$KE = E - \omega_0$

$K.E = h\nu - h\nu_0$

$\boxed{K.E = h(\nu - \nu_0)}$

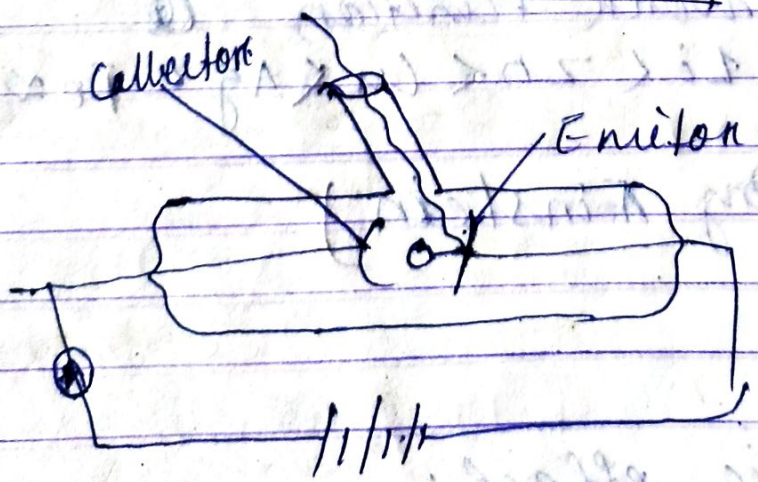
$K.E = h\left(\frac{c}{\lambda} - \frac{c}{\lambda_0}\right)$

$K.E = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$

$KE = hc\left(\frac{\lambda_0 - \lambda}{\lambda \cdot \lambda_0}\right)$

$\frac{1}{2} m_e v_e^2 = hc\left(\frac{\lambda_0 - \lambda}{\lambda \cdot \lambda_0}\right)$

$$\boxed{v_e = \frac{2hc}{m_e}\left(\frac{\lambda_0 - \lambda}{\lambda \cdot \lambda_0}\right)}$$



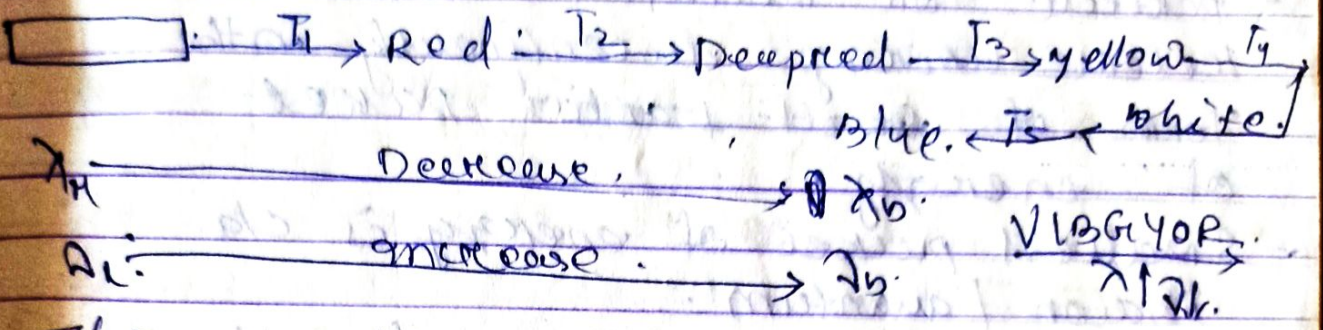
Stopping potential = $e \cdot V$

Therefore $KE = e \cdot V$

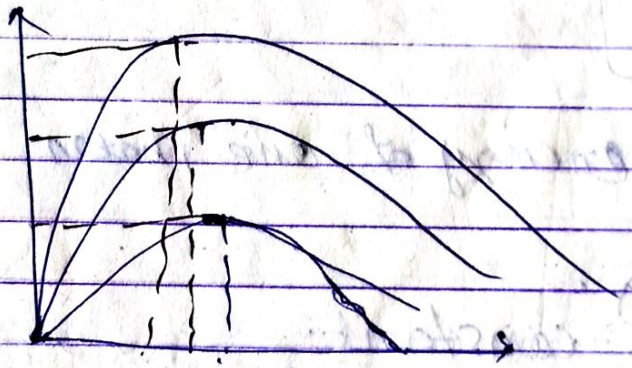
$\boxed{\frac{1}{2} m_e v_0^2 = eV}$

Black body radiation :-

The ideal body which can absorb or emit radiation of all types of frequency.



This can be only explained by the particle nature of radiation not only by the wave nature.



Important points :-

Wave natures of radiation only explains interference of light & diffraction of light.

- Following effects can only explained if we consider particle nature of radiation.
  1. Black body effect.
  2. Photo electric effect.
  3. Compton effet.

(iv) Variation of heat capacity on increasing temp.
(v) Discontinuous spectrum of fusion.

Planks quantum theory:
- particle or oscilator, absob or release energy discontinously in the form of small packet of energy.
- Smallest packet of energy is called photon / quantum.
- Energy of quantum is directly proportional to frequency.

$E \propto \nu$

$$E = h\nu$$

This is energy of one photon one quantum.

$E = hc/\lambda$.

h = planks constant.

$= 6.625 \times 10^{-34}$ J sec.

$$E = \frac{hc}{\lambda}$$ — meter/sec $= 3 \times 10^8$ m/s
— meter.

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

$1 A^\circ = 10^{-10}$ m.

The energy absorbed or emitted is integral multiple of $h\nu$

$$\boxed{\Delta E = n h\nu} \quad , n = 1, 2, 3, 4 \cdots$$

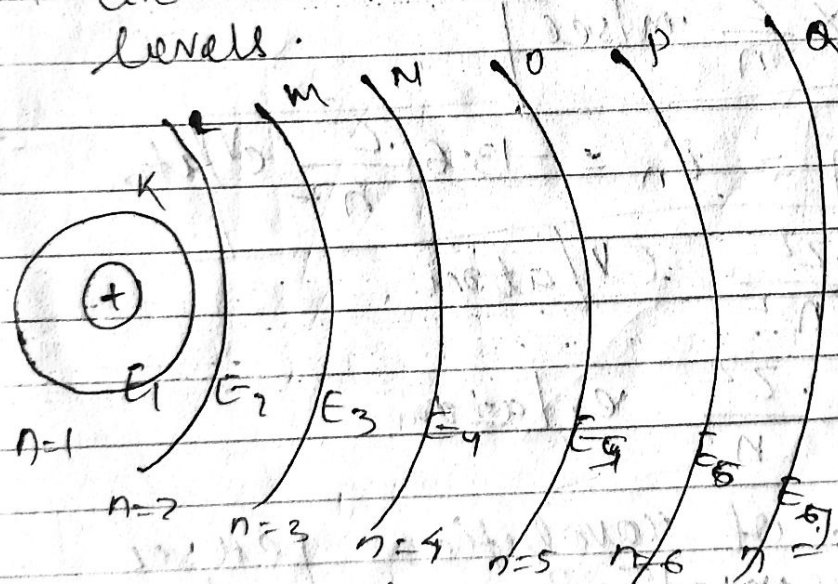
This is called quantisation of energy

$$\text{No. of photons} = \frac{\text{Total energy (J)}}{\text{Energy of photon (J)}}$$

Energy of 1 mol photon $= \boxed{N_A \cdot h\nu}$

Bohr's atomic theory :—

① Electrons are revolving around the nucleus in circular path called shells or energy levels.



② Energy of constant cells are also called stationary orbits.

$$E_1 < E_2 < E_3 < E_4 < E_5 \cdots$$

$$(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) > \cdots$$

- When electron jumps from one orbit to another orbit it absorbs or releases energy.

$$\Delta E = E_2 - E_1$$

- Angular momentum of e in nth orbit i.e.

$$m_e v_e r_n = \frac{nh}{2\pi}$$

No of orbit = n. 1st, 2nd, 3rd

$$r_n = 0.53 \frac{n^2}{Z} \text{ Å}$$

$$v_n = 2.19 \times \frac{Z}{n} \times 10^6 \text{ m/sec}$$

Total energy $= E_n = -13.6 \frac{Z^2}{n^2}$ eV/atom.

P.E $= -27.2 \frac{Z^2}{n^2}$ eV/atom.

K.E $= +13.6 \frac{Z^2}{n^2}$ ev/atom.

- f_n = no. of revolution per sec

$$f_n = 6.6 \times 10^{15} \frac{Z^2}{n^3} \text{ sec}^{-1}$$

$$T_n = 1.5 \times 10^{-16} \frac{n^3}{Z^2}$$

Total energy $= \frac{-kze^2}{2r_n}$

$$k = \frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \text{ Nm}^2.$$

$$P.E = \frac{-kze^2}{r_n}, \quad K.E = \frac{kze^2}{2r_n}$$

Limitations on Bohr's theory:—

(1) This theory only explains - mono electronic atom and ion spectrum.

(2) This theory cannot explain zeemann's effect and stark effect.

Zeemann's effect:—

When spectrum taken under electric field line spectrum is converted into fine line spectrum.

stark effect:—

when a spectrum is obtained under electric field line spectrum converted into fine line spectrum.

H- spectrum:

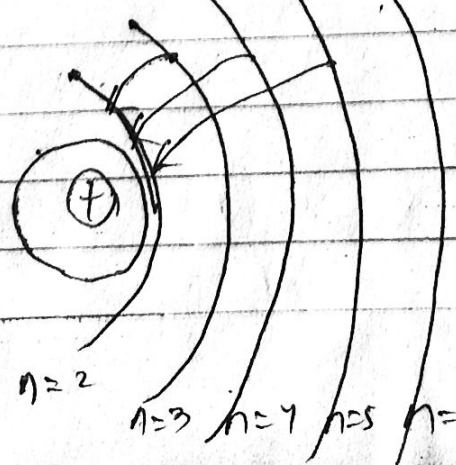
Balmer eqn $= \bar{\nu} = \frac{1}{\lambda} = R_H \left[\frac{1}{2^2} - \frac{1}{n^2}\right]$ — (1).

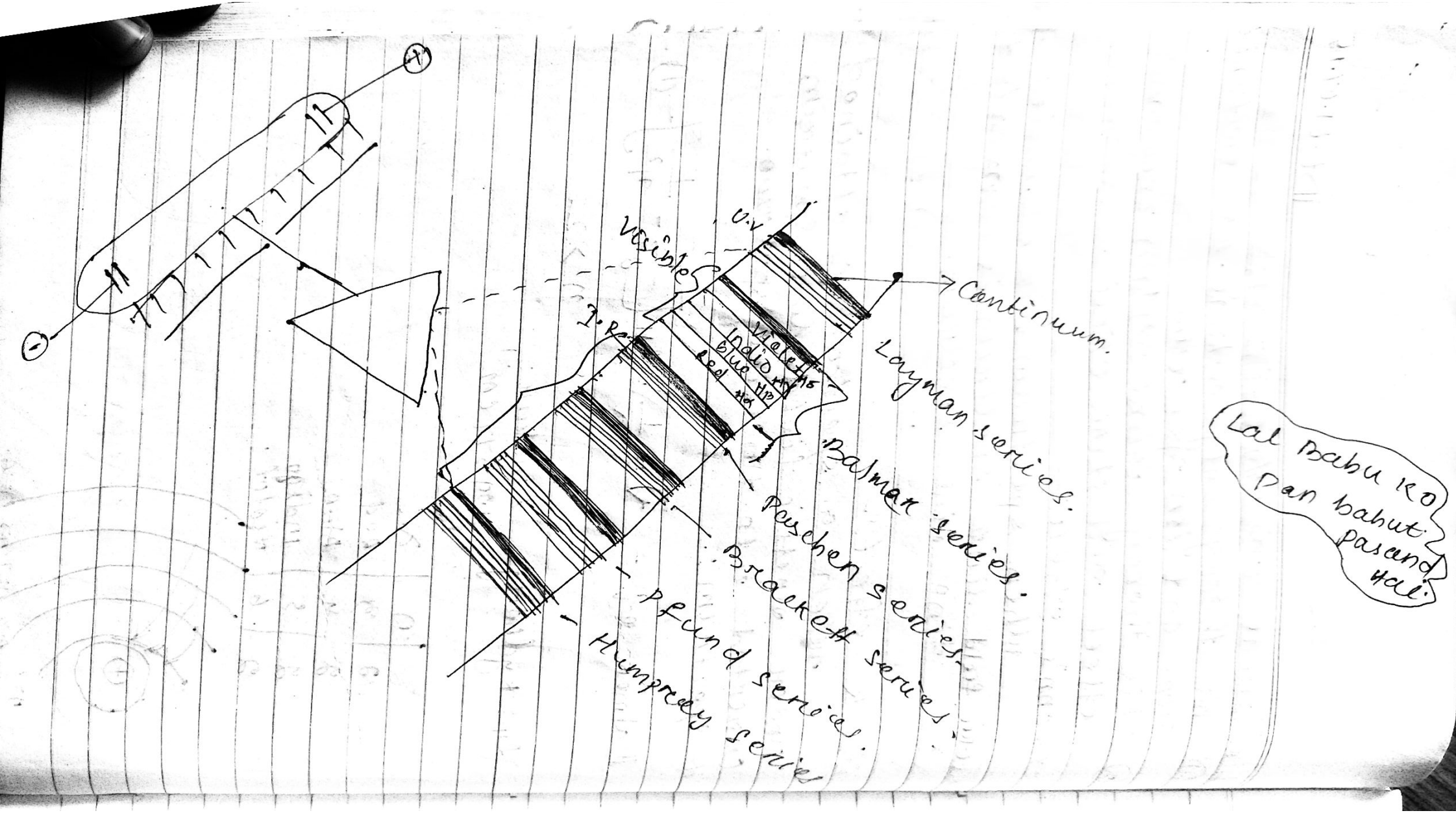
$n > 2$

R_H = Rydberg's constant.

$= 109677\ cm^{-1}$

	n	λ.
2	3	Red
2	4	Blue
2	5	Indigo
2	6	violet.





Lal babu ko
pan bahut
pasand
hai.

(2) Ritz Principle of Combination:-

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

(3) Bohr's equation:-

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

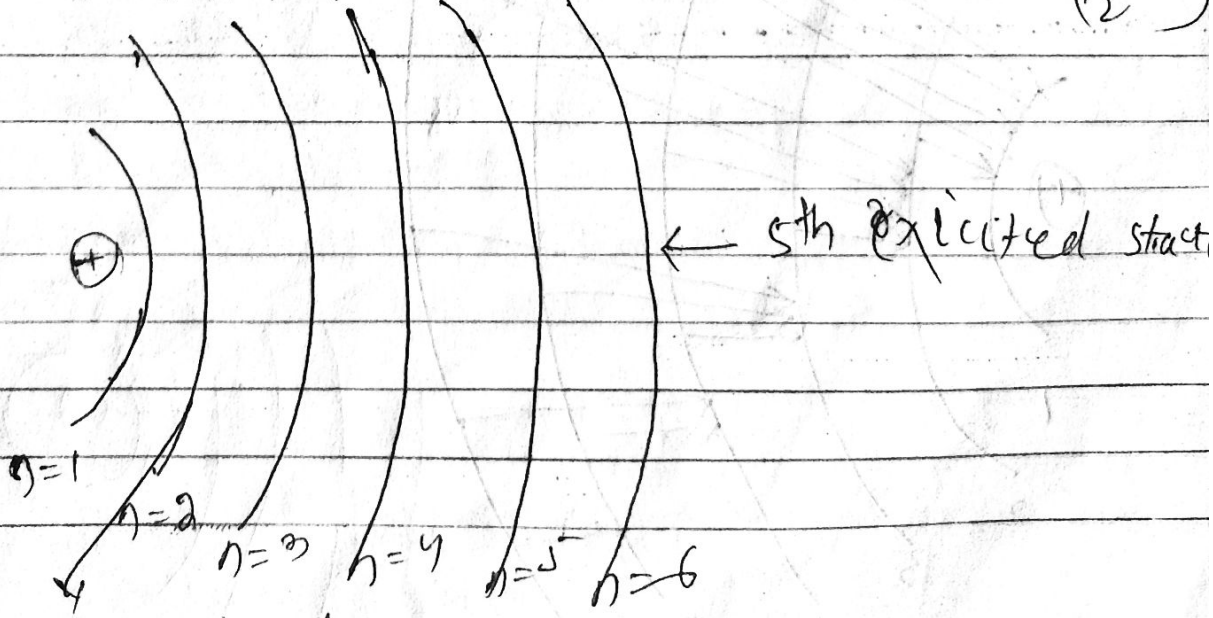
n_1	n_2		
1	2, 3, - - - ∞	Lyman series	U.V.
2	3, 4, - - - ∞	Balmer series	visible region
3	4, 5, - - - ∞	Paschen	near I.R
4	5, 6, 7 - - ∞	Brackett	middle I.R
5	6, 7, - - - ∞	pfund	Far I.R
6	7, 18, - - - ∞	Humphrey	V. Far I.R

No. of lines in spectrum.

(1) Total lines $= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

(2) No. of lines in particular series $= (n_2 - n_1)$

(3) In Balmer series, No. of lines $= (n_2 - 2)$



for e^- :

$h = 6.625 \times 10^{-34}$ J·sec.

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

$e = 1.6 \times 10^{-19}$ C.

$$\lambda = \frac{12.26 \times 10^{-10}}{\sqrt{V_{volt.}}} \text{ meter}$$

$$\boxed{\lambda = \frac{12.26}{\sqrt{V_{volt.}}} \text{ Å}} \quad \text{— (8)}$$

- 1st time De-broglie wave eqn was confirmed by Davison & Germer.

- No. of e⁻ waves on an orbit :-

From Bohr's theory :-

$$m_e v_e r_n = \frac{nh}{2\pi}$$

$$m_e v_e = \frac{nh}{2\pi r_n} \quad \text{— (4)}$$

From de broglie wave eqn.

$$\lambda = \frac{h}{m_e v_e}$$

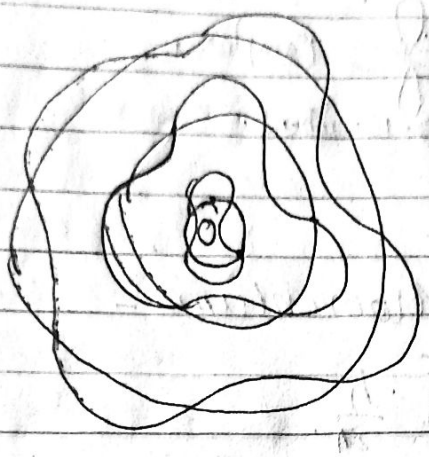
$$\therefore m_e v_e = \frac{h}{\lambda} \quad \text{— (5)}$$

$$\frac{mv}{2\pi r_n} = \frac{h}{\lambda}$$

$$n\lambda = 2\pi r_n \quad \text{---} (3)$$

$2\pi r_n$ ← circumference of n^{th} orbit.

λ = wavelength of e^- wave.



No. of orbit.	No. of e^- wave.
1	1
2	2
3	3
4	4

No. which characterised position, shape, size, energy, orientation & spin of an electron are c/a quantum no.

- Principal quantum no. (n) - (Bohr)
  - Q.NO. characterised no. of shells, radius, velocity of e^-, angular momentum of e^-, etc.

n = 1 2 3 4 5 - - - -

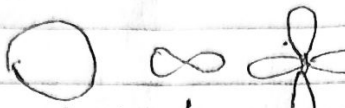
Shell : K L M N O - - - -

Azimuthal quantum no.:- (l) - (Sommerfield)
Eliptical shell or sub shell.

$l = 0 - - - (n-1)$

This characterises shell, subshell, shape of orbital,

l :	0	1	2	3	4 - - -
subshell =	s	p	d	f	g - - -



spherical ⊥ D. Dumbell.
Dumbell

Orbital angular momentum:-

$$\sqrt{l(l+1)} \cdot \frac{h}{2\pi}$$

$$= \sqrt{l(l+1)} \cdot \hbar \quad (\hbar\text{- direc})$$

eg:- for e^- in 3d-subshell.

$$O.A.M = \sqrt{2(2+1)} \cdot \hbar$$

$$= \sqrt{6}\,\hbar$$

No. of orbitals in a subshell:-

$$= \sum_{i=0}^{l} (2l+1)$$

In d-subshell no. of orbitals.

$$= 2 \times 2 + 1 = 5$$

No. of e^- in subshell

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

in d-subshell $= 2 \cdot (2 \times 2 + 1) = 10.$

Magnetic Quantum no:- (m)

- Proposed by Linde to explain zeeman's effect and stark effect.
- This characterised the orientation.

$m = -l ---- 0 --- +l$.

$l = 0 \rightarrow s$, $m = 0$.

$l = 1 \rightarrow p$, $m = -1 \quad 0 \quad +1$

$P_x \quad P_z \quad P_y$

$L = 2 \rightarrow d$, $m = -2, -1, 0, 1, +2$.

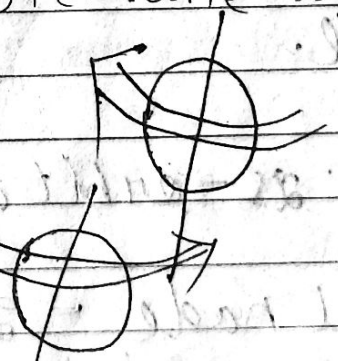
$= d_{xy}, d_{yz}, d_{z^2}, d_{xz}, d_{x^2-y^2}$

Spin q.no.

(s) - Goudemith, uhlenbeus & Gerlach to explain double line spectrum

$s = +1/2 \uparrow$

$s = -1/2 \downarrow$



Spin angular Momentum:-

$= \sqrt{s(s+1)}\,\hbar$

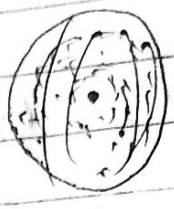
$\therefore$ Always $s = +1/2$

Orbital :-

3d space around the Nucleus where there is max^m probability (90-95 %) of finding an electron is called orbital.

① 4 types of orbital.

s-orbital :-



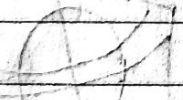
- spherical in shape.

Node / Nodal :-

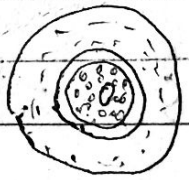
The plane / space where e⁻ density / probability is zero called Node.

(i) Radial node or spherical node.
= (n-l-1)

(ii) Angular node / ~~spherical~~ nodal plane.
= l.

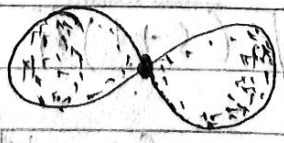


(iii) for 2s-orbital :-

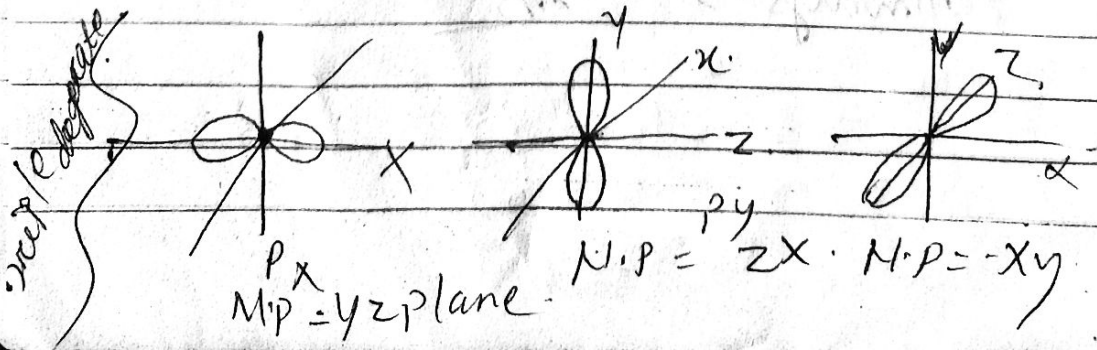


Radial node = 2-0-1 = 1
Ang. node = 0.

② p-orbital :-

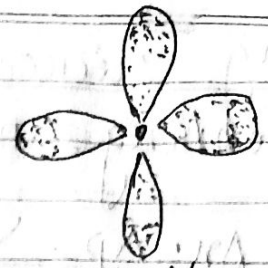


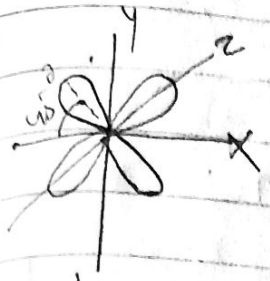
It is of 3 types.



d-orbital .. Double dumbell

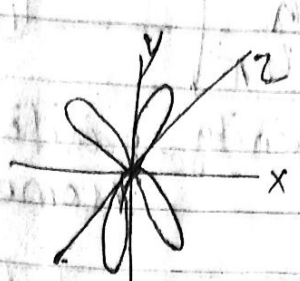
5 - types.





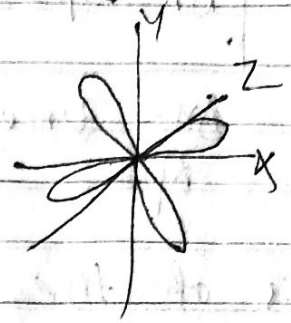
d_{xy}

N.P = (ZX, YZ)



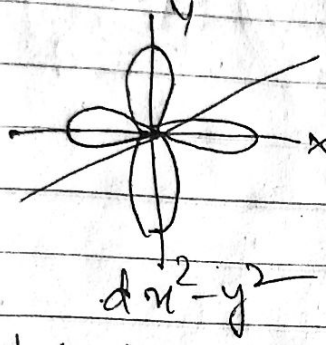
d_{yz}

N.P = (XY, ZX)



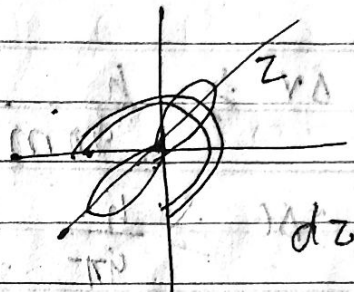
d_{zx}

N.P = (YZ, XY)



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

2 nodal planes bet^n axes.



d_{z^2}

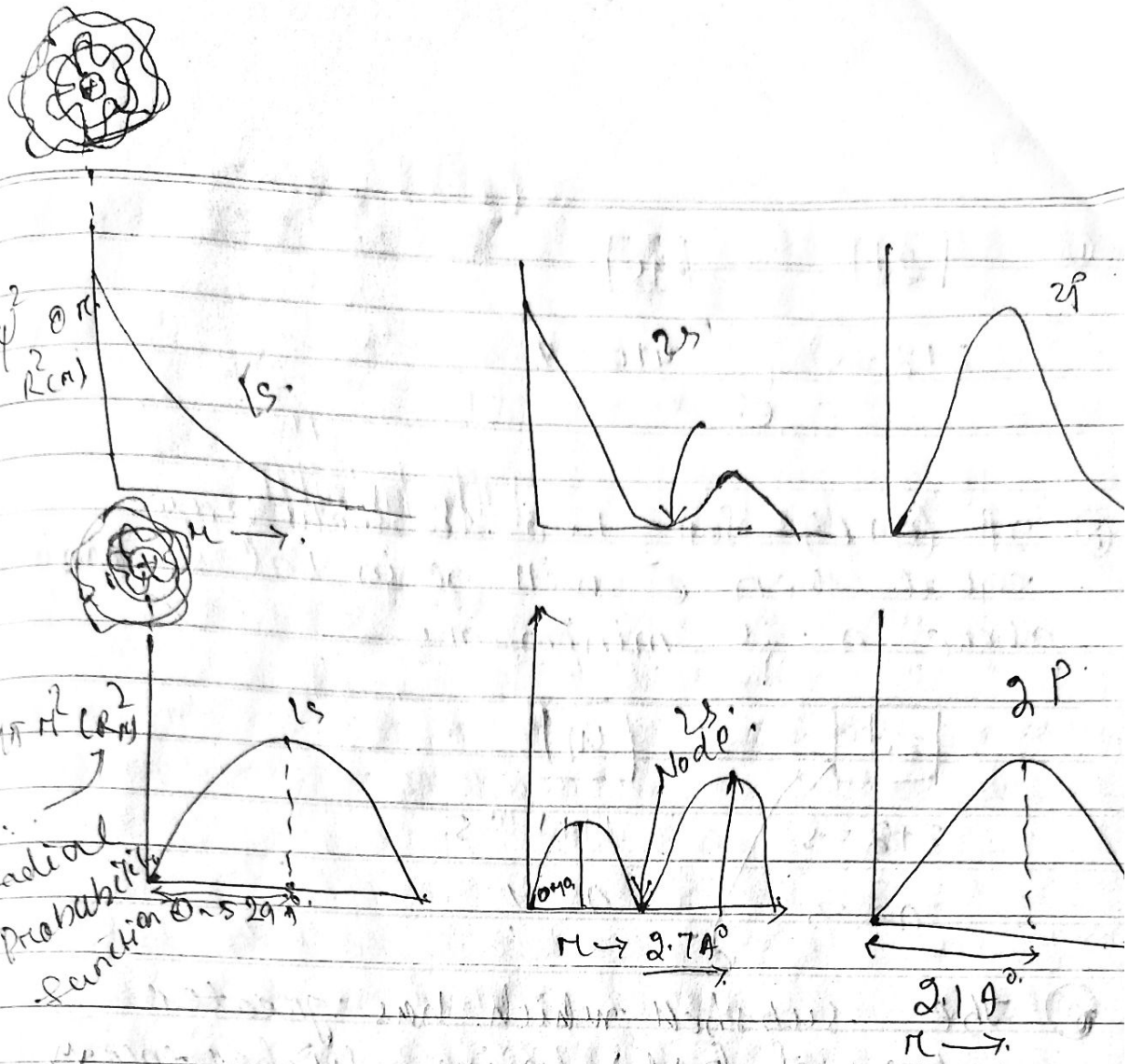
No. nodal plane
Having two conical nodes
(Dough Nut) Plane
(Baby Soother)

f - orbitals.

7 types of f orbital.
- Triple dumbell or Complex shape.

Dt. 23.07.15

Heisenberg Uncertainity Principle :-
It is impasible to determine exact position and exact velocity or momentum of an electron or



No. of peaks = $(n-l)$

No. of minima = $(n-l-1)$

27.07.15

Electronic Configuration :-

Subshell wise configuration :-

Aufbau Principle :-

- e^- has tendency to occupy that subshell which has lowest energy state

- $K < L < M < N < \cdots$

  $s < p < d < f < \cdots$

$(n+l)$ Rules :-

e^- will go in that substance where $(n+l)$ is minimum.

(1) [3d] [4s]

3+2 = 5 4+0 = 4

e^-

(2) If (n+l) for two subshells are equal then e will go in that subshell where n is minimum.

[3d] [4p]

3+2 = 5 4+1 = 5

n = 3 n = 4

e^-

(3) The subshell which has greater value of (n+l) having higher energy state. But if (n+l) have equal then which has higher value of n will have greater energy state.

1s

2s 2p

3s 3p 3d

4s 4p 4d 4f

5s 5p 5d 5f

6s 6p 6d 6f

7s 7p 7d 7f

Subshell
s = 2
p = 6
d = 10
f = 14

[Fe] [26] = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

$Fe^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

$Fe^{3+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

BM $[35] = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$

$\rightarrow 4p^6$.

- Aufbau principle is violated in 2 cases.

(1) for mono electronic atom or ions.

$H[1] \rightarrow 1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$

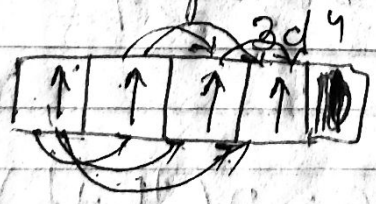
- If an element has d^4 electrons & becomes d^5 & if it has d^9 then it is d^{10} because half filled and give more stable electronic configur.

$Cr[24] = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

$Cu[29] = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

Half & Completely filled subshell will be more stable.

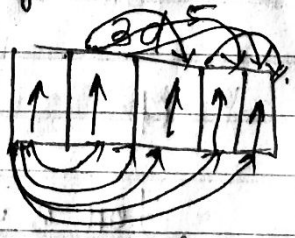
- more symmetric arrangement
- lower energy state due to higher exchange energy.



No. of exchange = 6

$= \frac{4(4-1)}{2} + 0$

$= \frac{4 \times 3}{2} = 6$



No. of exchange = 10.

Higher exchange energy lower energy state (more stable)

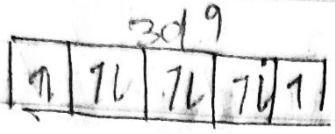
$\frac{5(5-1)}{2} = 10.$

No. of exchange = $\frac{c(c-1)}{2} + \frac{A(A-1)}{2}$

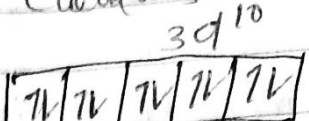
c = No. of clockwise e⁻

A = No. of Anti clockwise e⁻

eg



No. of exchange = $\frac{5(5-1)}{2} + \frac{4(4-1)}{2}$ = 16

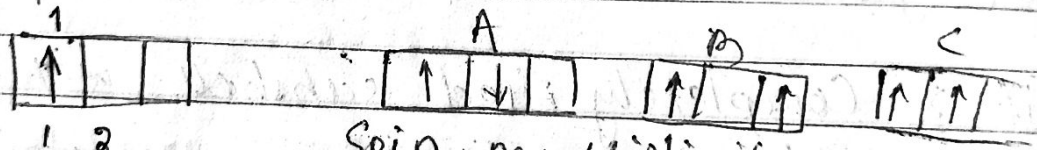


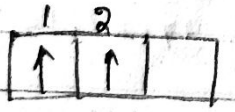
$= \frac{5(5-1)}{2} + \frac{5(5-1)}{2}$

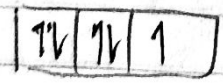
$= 10 + 10 = 20$

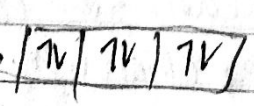
Orbital wise Configuration:-
(Hunds rule of max^m multiplicat^y)

- In case of degenerate orbital ist one filled singly with same spin after then pairing take place with antiparallel spin.









Spin multiplicity.

$(S) = 2(\sum s + 1)$

for A = $S = 2(\frac{+1}{2} - \frac{1}{2}) + 1$

$= 1$

for B = $S = 2(\frac{+1}{2} + \frac{1}{2}) + 1$

$= 3$

for C = $S = 2(+\frac{1}{2} + \frac{1}{2}) + 1$

$= 3$

Angular multiplicity - $L = \Sigma m$. $\{m = +1, 0, -1\}$

For B = $L = +1 + 0 - 1 = 0$

For C = $L = 1$

Max^M the value of spin multiplicity & angular multiplicity will be more correct configuration orbital wise.

Pauli's exclusion principle:-

No two electrons in an atom can have same values of all quantum nos.

He [2] = $1s^2$

$n = 1$	$n = 1$
$l = 0$	$l = 0$
$m = 0$	$m = 0$
$s = +1/2$	$s = -1/2$

Calculation of magnetic moment:-

- By spin only formula:-

- Mag. moment, $\mu = \sqrt{n(n+2)}$ B.M.

n = no. of unpaired e^- in d-orbital

$Fe^{3+} = 3d^5 = \sqrt{5(5+2)} = \sqrt{35}$ B.M.

$= 5.91$ B.M.

$3d^3 = \sqrt{3(3+2)} = \sqrt{15}$ B.M $= 3.9$ B.M.

⇒ Before decimal no. indicate unpaired e^-.

- which rule violate.
valid.

3s 3d — Aufbau principle