ATOMIC STRUCTURE

7.01.2022

Discovery of electron, Proton, neutron, Atomic number, Isotopes, Isobars.

John Dalton :- Smallest particle is atom (1803 - 1808) "Indivisible".

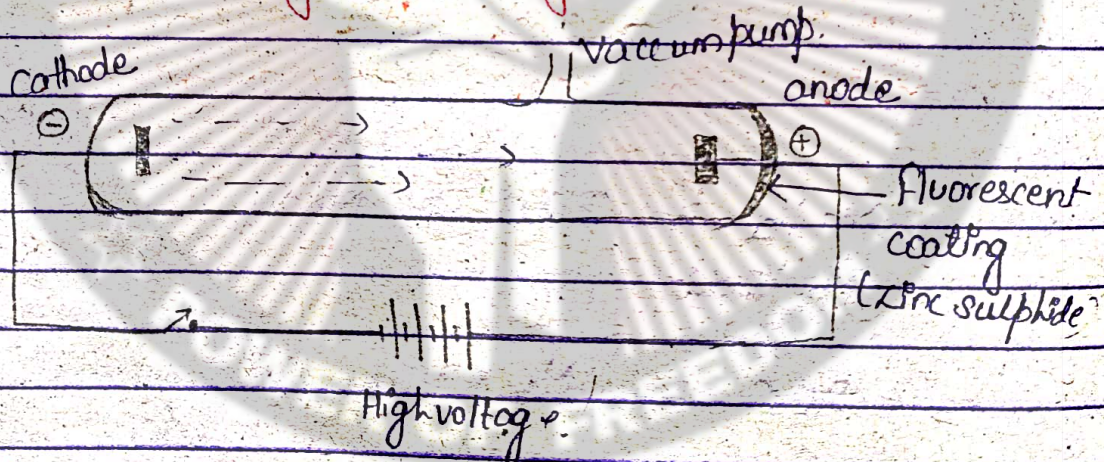
1. * Discovery of electron - Cathode ray Tube.

Davy, Michael Faraday, Stoney

* Electrons :- J. J. Thomson

→ Michael Faraday showed that if electricity is passed through a solution of an electrolyte chemical reactions occured at the electrodes which resulted in the liberation and deposition of matter at the electrodes.

* Cathode Ray Discharge Tube Experiment :-



Characteristics of Electrons :-

1) They travel in a straight path as they cast shadow on the wall opp. to the cathode.

* Stoney – electrons. – meaning – amber – a material which becomes electrically charged when rubbed with wool or silk.

ii) They produce a green glow when they strike the zinc sulphide screen/fluorescent screen.

iii) Cathode rays posses kinetic Energy as when a pin wheel is placed it rotates.

iv) They are deflected by electric and magnetic field. as these are deflected towards the positively charged plate. So, the particles are negatively charged.

v) They are made up of small particles.

vi) They produce X-rays as when the cathode rays strike with a heavy atoms X-rays are produced.

* On changing the gas or the electrode material The properties(em) of cathode rays remains same.

* J.J Thomson measured the ratio of electrical charge (e) to the mass of electron (m).

$$\frac{e}{m} = 1.75 \times 10^{11} \text{ C/kg}$$

$$m = \frac{m_0}{\sqrt{1-\left(\frac{v}{c}\right)^2}}$$

where, m = mass of moving particle
m_0 = mass of particle at rest
v = velocity of particle
c = velocity of light.

1. Millikan Oil drop Experiment.

Charge of electron(e) = 1.6×10^{-19} C.

mass of electron = 9.1×10^{-31} kg.

2. **PROTON** : (E. Goldstein) - Anode Rays / Canal Rays

Anode ⟶ Cathode

(1) They are +vely charged.

(2) Origin - gaseous ion.

(3) They depend upon nature of gas taken.

(4) Anode rays are not protons, In case of hydrogen Anode rays are made up of Protons, and In this case only charge/mass ratio is highest.

Discharge tube ⟶ Gas Pressure - 10^{-1} mm

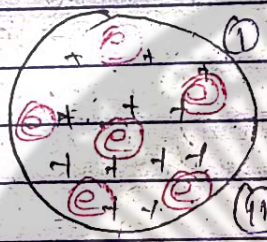
⟶ Perforate Cathode

coloured rays ⟶ + ⟶ (Flourescent material)

* J. J. Thompson – first Atomic Model.

↓

Subatomic particles



(i) Atom is a sphere of positive charge.

(ii) e^- are embeded

(iii) Plum pudding / watermelon

(iv) Atom is electrically ~~not~~ Neutral.

~~Rutherford~~.

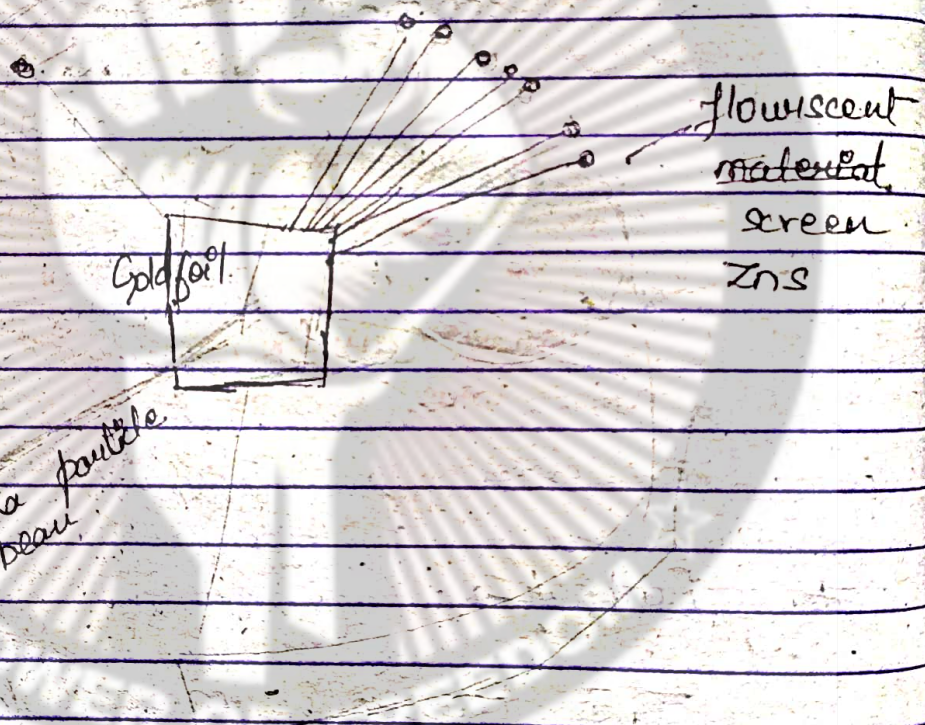
J. J. Thomson's model failed because it couldn't explain the sphere of positive charge. Theory and e^- are embeded.

#3. Rutherford : α particle Scattering Experiment.

α → +2 charge
→ 4 times mass of proton. 4 amu

It is nucleus of He.

2p 2n 2e⁻ nikal lo 2e⁻ तो +2 charge होगा और 4 amu



Observations :-

i) Nearly 99.9% α particles passed undeviated.

ii) Some of the α particles were deflected

by small Angles

(5) (6) very few (1 in 20,000) α particle returns backs - deflected.

Conclusion :- Rutherford Model of Atom - 1890's

(i) He said that +ve charge is not spread. It is concentered ~~on~~ at ~~center~~ very small space. — Nucleus

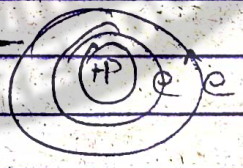
(ii) +ve charge (Proton) is heavy (Nucleus). Since α particle is already heavy as it returned back or there is something heavy in ~~the~~ nucleus atom.

(iii) Most part of the atom is empty.

(iv) No. of Protons = No. of electrons (Neutral Atom).

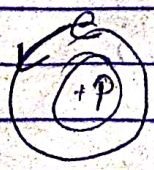
(v) The size of nucleus is very very small compared to size of atom.

(vi) Most Imp. e⁻ revolve in closed circular orbits around the nucleus. —



electrons use electrostatic force of attraction with proton in circular motion

$F_{electro\ static} = F_{centripetal}$.



There is a change in velocity as electron moves then there is a acceleration & has force ie centripetal force

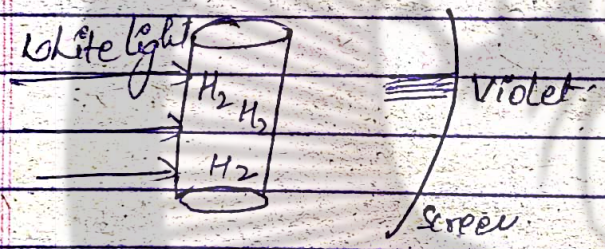
Failure of Rutherford Model.

(1) Maxwell Theory. - Any accelerated charge particles emits radiation & loses energy.

Acc to this Theory, e^- will collide with nucleus. Atom is destroyed.

He cannot explain stability of Atom.

(2) He cannot explain line Spectrum or Discrete Spectrum of Atom.



4. # Bohr's Atomic Model.

(i) Atom has a centre called Nucleus.

(ii) Electron revolves only in fixed circular orbit with fixed energy & fixed velocity.

(iii) Quantisation condition :

Electrons revolves on only those circular orbits for which the [angular momentum (L)] is Integral multiple of $\frac{h}{2\pi}$.

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

n = Integral multiple. = Shell number.

n = 1 = K

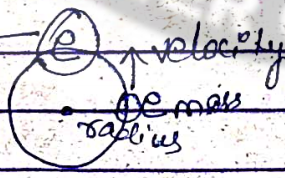
n = 2 = L

n = 3 = M

n = 4 = N.

(iv) Angular momentum :

$\vec{L} = \vec{r} \times \vec{P}$ → Momentum



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

$= r\,mv\sin\theta$

$= mvr\sin 90^\circ = mvr$.

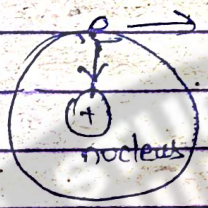
$$\boxed{L = mvr}$$

$$\boxed{mvr = \frac{nh}{2\pi}}$$ ——(1) Bohr's quantisation conditions

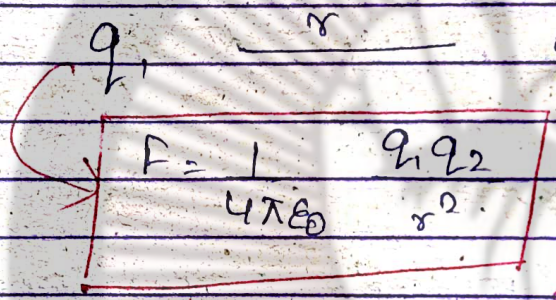
h = Planck's constant

$h = 6.636 \times 10^{-34}$ Js

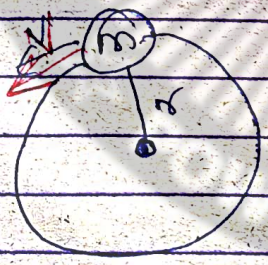
(iv) While revolving the electrostatic force between e^- and nucleus provides centripetal force.



Electrostatic force = Centripetal force.



If both charges are opp. then force is attractive & if both charges are equal then force is Repulsive.



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

Centripetal force = $\frac{mv^2}{r}$

Now in an atom,

No. of protons in nucleus = Atomic no

$F_e = F_c$

$$\frac{1}{4\pi\varepsilon_0} \frac{ze^2}{r^2} = \frac{mv^2}{r} \quad \text{---- (ii)}$$

$$\frac{1}{4\pi\varepsilon_0}\frac{ze^2}{r^2} = \frac{mv^2}{r} \quad \text{---(ii)}$$

(v) While revolving in a particular orbit, an e^- neither gains energy nor loses energy.

Energy of an orbit / shell is fixed.

Shells → stationary energy level

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

Till the time, the electron remains in any one of the stationary orbits, it does not lose energy. Such a state is called ground or normal state.

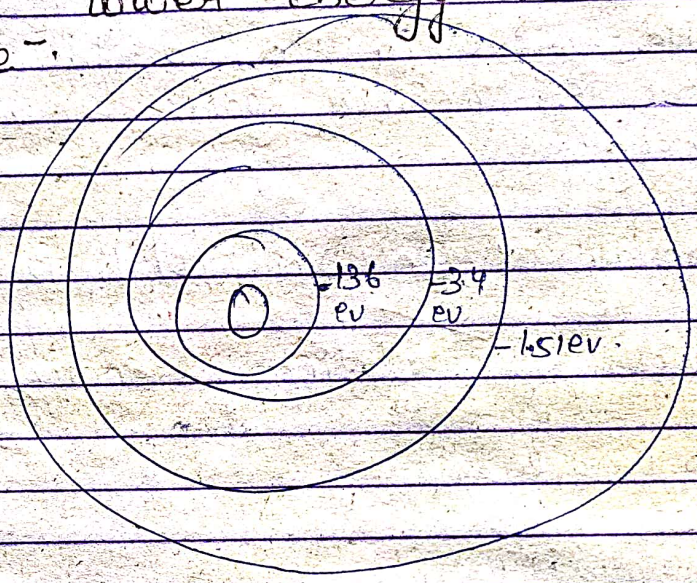
Each stationary orbit is associated with a definite amount of energy.

(vi) electron can accept energy & can lose energy.

If an e^- accepts an energy, it jumps to higher energy level -

excitation of e^-

If an e^- loses energy, it recedes back to lower energy level. - deexcitation of e^-.



If it takes energy it becomes excited

$$E_1 + \Delta E = E_2$$
$$E_1 + \Delta E = E_3$$

An e^- gains or loses only those energy which are equal to difference in two energy levels.

$$\Delta E = E_{high} - E_{low} = h\nu.$$

Energy is absorbed when e^- jumps from inner to outer orbit and is emitted when it moves from outer to an inner orbit.

Atomic no. $_{Z}X^{A}$

No. of neutron :- Mass no. - Atomic no.

Atomic Spectrum:

5.4 Isotopes, Isobars, Isotones & Isoelectronic

#1. Isotopes :- It is derived from two Greek words "Isos" and "topos" which means "the same place". Isotopes are the atoms of same elements having identical atomic number but different mass number. The difference is due to the difference in number of neutrons.

The chemical properties of atoms are controlled by the number of electrons. Thus, Isotopes of an element show same chemical behaviour, but have different physical properties (B.P. M.P. mass, density, freezing point etc.)

Isotopes of hydrogen.

Isotope	formula	Mass number	Atomic no./ No. of Protons	No. of neutrons.
Protium	$_{1}^{1}H$ (H)	1	1	0
Deuterium	$_{1}^{2}H$ (D)	2	1	1
Tritium	$_{1}^{3}H$ (T)	3	1	2
Carbon-12	$_{6}^{12}C$	12	6	6
Carbon-13	$_{6}^{13}C$	13	6	7
Carbon-14	$_{6}^{14}C$	14	6	8

Ar - 2,8,8
K - 2,8,8,1
Ca - 2,8,8,2

2. Isobars :-

Atoms of different elements having different atomic numbers but same mass numbers are called Isobars.

Eg :-

	$^{40}_{18}Ar^{2+}$	$^{40}_{19}K^{+}$	$^{40}_{20}Ca$
no. of electron	18	19	20
mass no. — no. of Proton	18	19	20
mass no. — no. of neutron	22	21	20

3. Isotones :-

Atoms of different elements which contain same number of neutrons are called Isotones.

eg :- $^{36}_{16}S$, $^{37}_{17}Cl$, $^{38}_{18}Ar$, $^{39}_{19}K$, $^{40}_{20}Ca$

4. Isoelectronic :-

The species containing the same number of electrons are called Isoelectronic. eg.

O^{2-} , F^{-} , Na^{+} , Mg^{+2} , Al^{+3} , Ne , etc.
10 , 10 , 10 , 10 , 10 , 10

Mass number = Total number of protons and neutrons in an atom.

Atomic number = Total number of protons.

Mass number ← A

Atomic no. ← Z

$^{A}_{Z}X$

Number of neutrons = Mass no. − Atomic no.

Quantum Numbers.

(Quantum numbers may be defined as a set of four Identification numbers which are needed to have full information about various electrons present in an atom. i.e. to know about their location, energy, shape, orientation and spin.)

The names given to these quantum numbers are:

i) ~~Azimuth~~ Principal quantum number. (n)
ii) Azimuthal quantum number. (l)
iii) Magnetic quantum number. (m)
iv) Spin quantum number. (s)

I. Principal Quantum number (n):

It describes the average distance of the electron from the nucleus.

$n \neq 0$, $n = 1$ to (any Integer)

- Size of orbital. $n = 1, 2, 3, 4, 5, 6, 7$ – K, L, M, N, O, P, Q.
- Energy of orbital. $\xrightarrow[\text{Energy Increases}]{\text{Size Increase}}$

$$E_n^{th} = -13.6 \times \frac{Z^2}{n^2} \text{ e.v.}$$

Z = Atomic no.
n = Shell no.

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

$$E_n = -1312 \frac{Z^2}{n^2} \text{ KJ per mol.}$$

- maximum no. of electrons which can be present in principle energy shell is $2n^2$.

1st shell - $2 \times (1)^2 = 2$ electrons
2nd shell = $2 \times (2)^2 = 8$ electrons
3rd shell = $2 \times (3)^2 = 18$ electrons and
4th shell = $2 \times (4)^2 = 32$ electrons.
No elements possess more than 32 elect

- Angular momentum can also be calculated.

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

2. Azimuthal Quantum number (l) / Angular momentum Quantum number :-

→ Shape of orbital

l	subshell Name	Shape
0	s	spherical — ◯
1	p	dumb-bell — ∞
2	d	double-dumbbell — ⧖
3	f	complicated structure 8 fold structure

For any given value of 'n' the value of l will be from 0 to $(n-1)$

$0 \leq l \leq n-1$

Principle Quantum no. n	Azimuthal Quantum no. l	Subshell	Designated as
1	0	s	1s
2	0	s	2s
	1	p	2p
3	0	s	3s
	1	p	3p
	2	d	3d
4	0	s	4s
	1	p	4p
	2	d	4d
	3	f	4f

- Orbital Angular momentum of an e⁻

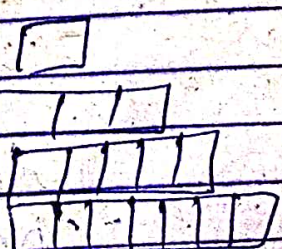
$$= \frac{h}{2\pi}\sqrt{l(l+1)}$$

3. Magnetic Quantum Number (m) :-

It represents the orientation of orbitals around the nucleus. For given l value, m can be $-l$ to l including 0.

$$-l \leq m \leq +l$$

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



no. of orbitals in a given subshell $= (2l+1)$

n → shell → size of orbital
l → subshell → shape of "
m → no. of orbital → orientation of orbital

n	l $0 \le l \le (n-1)$	m $-l \le m \le +l$
1	0 s	0 [ ] 1s
2	0 s	0 [ ] 2s
	1 p	−1, 0, +1 [Px] [Py] [Pz] 2p
3	0 s	0 [ ] 3s
	1 p	−1, 0, +1 [ ] [ ] [ ] 3p
	2 d	−2, −1, 0, 1, 2 [dxy] [dyz] [dz²] [dxz] [dx²−y²] 3d

Q. How many subshells and orbitals are present in n = 3 ?

~~l = 0, 1, 2~~
~~s p d.~~

l = 0 − 0 3s
1 − −1, 0, +1 3p
2 − −2, −1, 0, 1, 2 3d

no. of subshells = 3.
no. of orbitals in a shell = $9 = 3^2 = n^2$.

4d⁶ — n = 4, l = 2, m = 5, s = ±½/+½ — l = 0, 1, 2, 3 = s, p, d, f — (2l+1), 2×2+1, (4+1), 5

No. of orbitals in a subshell = $2l+1$.

Q Find no. of orbitals in $n=2$.

no. of orbitals in a shell = n^2

$= 4$.

4. Spin Quantum number (s) :-

s = e^- rotates about it's own axis.

$s = +\frac{1}{2}$ — clockwise (↑)

$s = -1/2$ = Anticlockwise, (↓)

Total spin = $n \times \frac{1}{2}$

n = no. of unpaired electrons.

Conclusion :-

i) The maximum capacity of a main energy shell is equal to $2n^2$ electrons.

ii) The maximum capacity of a subshell is equal to $2(2l+1)$ electrons.

iii) No. of subshell = no. of shell.

iv) No. of orbital in main shell = n^2.

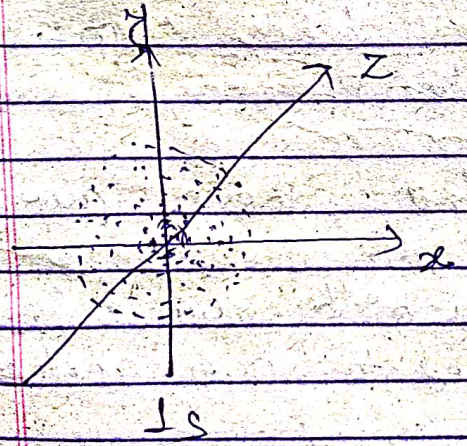
Shapes of Atomic Orbitals.

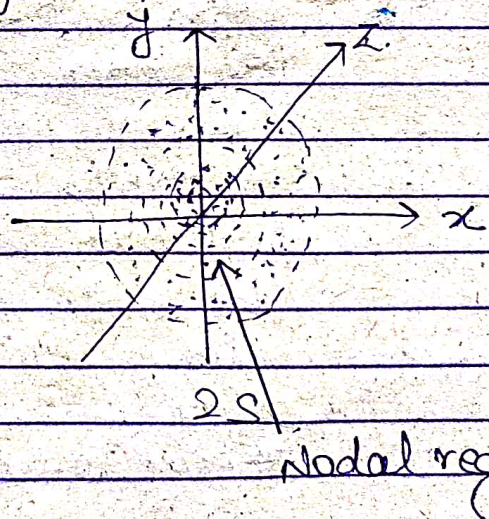
To interpret and visualize an atomic orbital in an atom, the diagrams based on probability density (ψ^2) values should be constructed. For this purpose, the

i) Shape of S- orbital.

a) ~~S- orbitals or~~ On the basis of quantum numbers, for S- orbital l and m values are zero i.e. S-orbital has one orientation

ii) The only shape having one orientation is sphere. Hence, S-orbital is always spherical in shape.





iii) The density of charge cloud is max. at nucleus and decreases with

iv) No. of nodes for 1s orbital = (n-1).

Increase in distance from the nucleus.

iv) The size and energy of s-orbital increases with increase of principal quantum number n, i.e 1s < 2s < 3s < 4s.

v) Diff. between 1s orbital and 2s orbital is that there is a spherical shell within this orbital where probability of finding ele is negligible, i.e almost zero.

b) Shapes of p-orbitals :

i) p-orbitals are dumb-bell shaped.

ii) For p-orbital, $l = 1$ $\therefore m = -1, 0, +1$ i.e three orientation.

iii) For every p-subshell there are 3 p-orbital which are termed as p_x, p_y, p_z which are oriented in 90° angles to one another

iv) These 3-orbitals are equal in energy

v) No. of nodes for np orbital = (n-2)
i.e for 2p orbital no. of nodes = 0
for 3p orbital no. of nodes = 1.

c) Shapes of d-orbitals:

i) For d orbital, $l = 2$

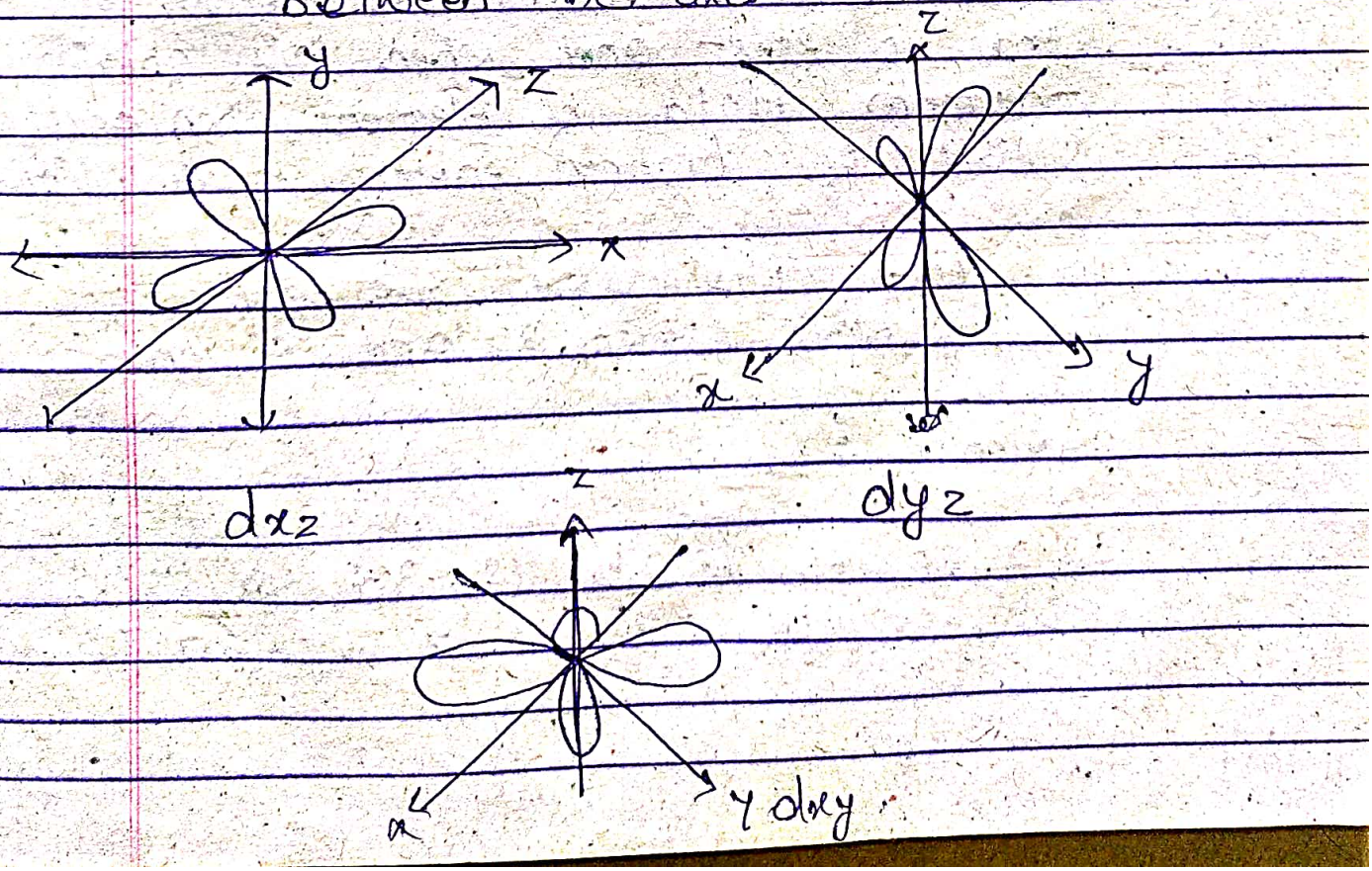
ii) ie there are 5 possible orientation.
$-2, -1, 0, +1, +2$.

iii) 4 of 5 d-orbitals are cloverleaf-shaped and have 4 lobes
5th orbital is similar to p orbital and have additional donut shaped region

iv) On the basis of orientation, d-orbitals are divided into two sets.

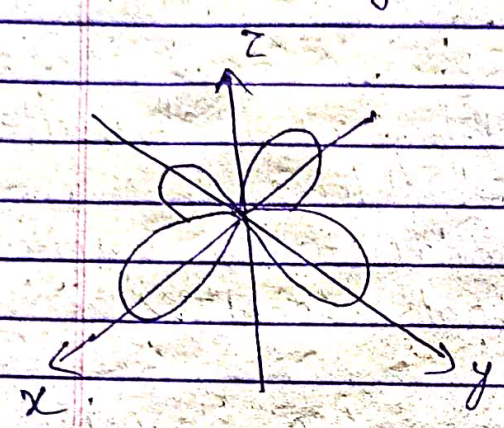
a) Set I : It includes d_{xy}, d_{yz} and d_{xz}

- Max. electron density in the region between the axes.

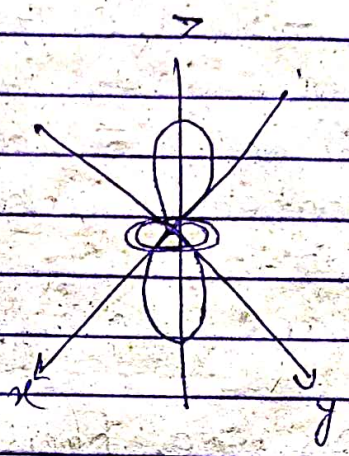


b) Set II : dx^2-y^2 , dz^2.

- Max e^- density in the region along axes.



dx^2-y^2



dz^2

* Afbau Principle :-

1) The subshell with minimum energy is filled up first and when this obtains maximum quota of electrons, then next subshell of higher energy starts filling

for ex- Firstly we are going to fill 1s orbital then 2s and so on.

sequence :

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p.

iii) The subshell with lowest value of $(n+l)$ is filled up first. When two or more subshells have same $(n+l)$ value, then the subshell with lowest value of n is filled first.

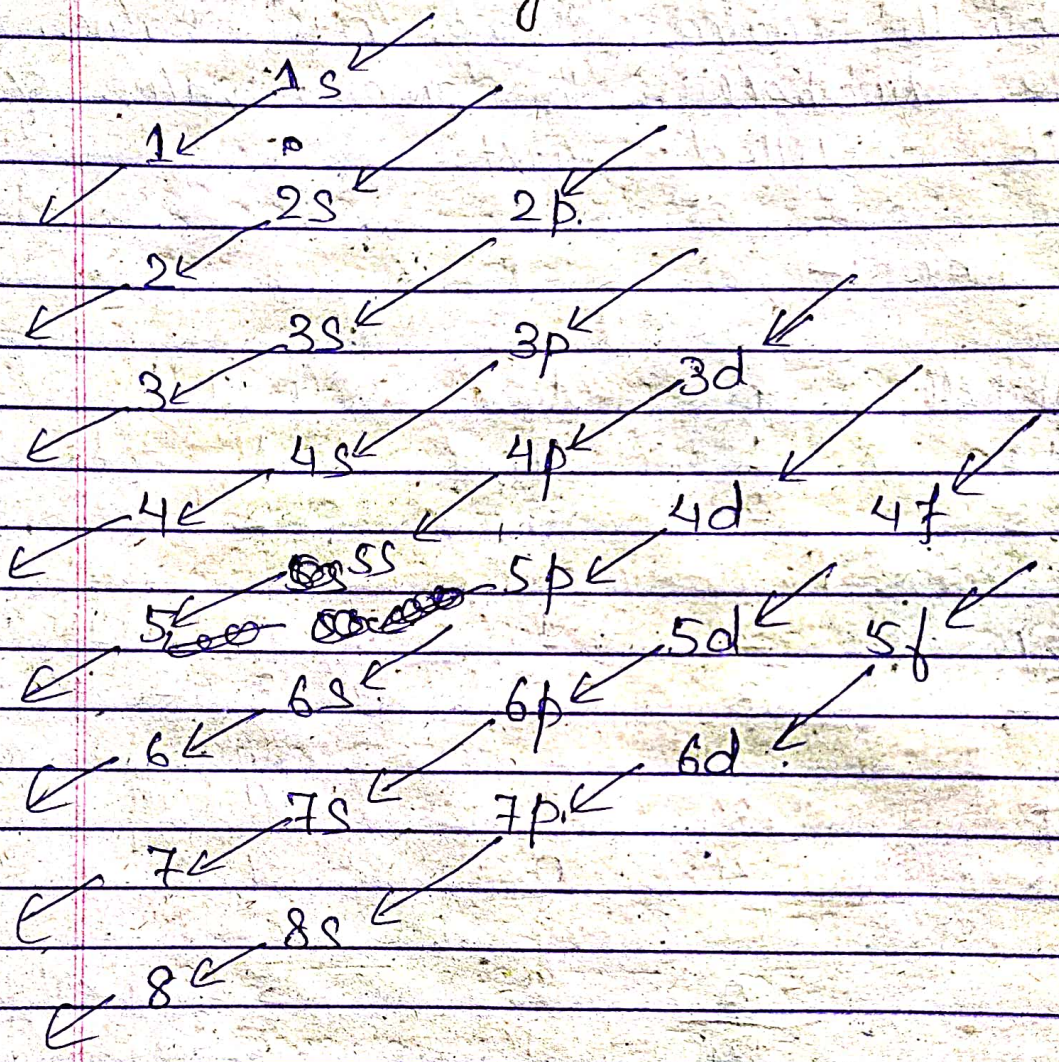
For ex :-

Subshell	n	l	$(n+l)$
1s	1	0	1 - 1st
2s	2	0	2 - 2nd.
2p	2	1	3 - 1st lowest value of n.
3s	3	0	3 - 2nd.
3p	3	1	4 - 1st
4s	4	0	4 - 2nd
3d	3	2	5 - lowest value of n 1st.
4p	4	1	5 2nd
5s	5	0	5 3rd

* Pauli's exclusion Principle

This Principle states that an orbital can have max. two electrons with opposite spins.

Order of filling of various subshell (Aufbau Principle).



This principal states that no two electrons in an atom can have the same set of all the four quantum numbers.

Because the other 3 quantum numbers (Azimuthal, principal, magnetic) can be same but spin quantum number is diff. for diff electrons.

Hund's Rule of Multiplicity

It states that electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electrons with parallel spin.

subshell are first singly filled before they begin to pair.

The rule is based on the fact that electrons being of the same charge repel each other when present in the same orbital.