Dual Nature of Electron

According to Planck,

$$\underset{\text{Energy}}{E} = \underset{\text{planck's const..}}{h}\,\nu \rightarrow \text{frequency of radiation} \quad —— ①$$

einstein's mass energy,

$$\underset{\text{Energy}}{E} = \underset{\text{mass}}{m}\,c^2 \rightarrow \text{speed of light} \quad —— ②$$

comp. ① & ②,

$$mc^2 = h\nu = \frac{hc}{\lambda}$$

$$\underset{\text{wavelength}}{\lambda} = \frac{h}{mc} = \frac{h}{p} = \frac{h}{mv} \quad v \rightarrow \text{velocity}$$

Heinsberg's uncertainity principle :-

The uncertainity principle states that we can't know both the position and speed of particle, such as photon or electron, with perfect accuracy, The more we nail down the particle's position, the less we know about its speed and vice versa.

$$\underset{\substack{\downarrow \\ \text{error in position}}}{\Delta x} . \underset{\substack{\downarrow \\ \text{error in momentum}}}{\Delta p} \geq \frac{h \xrightarrow{} \text{Planck's const.}}{4\pi}$$

$$\Delta x \, \Delta mv \geq \frac{h}{4\pi}$$

or

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

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

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

The uncertainity principle is applicable to any pair of conjugated dynamical variable, such as angular momentum and angular coordinate, energy & time.

Significance of ψ & ψ^2

- ψ is a wave function it refers to the amplitude of e^- wave i.e. probability amplitude. It has got no physical significance.
  The wave fn may be +ve, -ve or imaginary

- $(\psi)^2$ is known as probability density and determine the probability of finding an e^- at a pt. within the atom. This means that ψ^2

1) If zero, the probability of finding an e^- at the point is negligible.
2) $[\psi]^2$ is high, the probability of finding an e^- is present at that place for a long time.
3) $[\psi]^2$ is low, the prob. of finding an e^- is low, i.e. electron is present at that place for shorter time.

Schrodinger wave eq^n

~~Schrodinger eq^n is a linear partial differential eq^n that governs the wave fn of a quantum mechanical system.~~

It is a mathematical exp. describing the energy and position of the electron in space and time, taking ~~into account the matter wave~~

Schrodinger derived an eq^n based on dibroglie dual behaviour of electron and Heinsberg uncertainity princle is known as schrodiger wave eq^n.

total energy of e^- of any particle.

$$E = K.E + P.E.$$

$$E = \frac{1}{2} mv^2 + V \text{ — } ①$$

K.E can also be expressed as

$$\frac{1}{2} mv^2 = \frac{1}{2} m . \frac{mv^2}{m} = \frac{1}{2} \times \frac{(mv)^2}{m}$$

Acc. to dibrogie eq^n.

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

$$\frac{1}{2} mv^2 = \frac{\left(\frac{h}{\lambda}\right)^2}{2m} = \frac{h^2}{2\lambda^2 m} \text{ — } ②$$

Put ② in ①

$$E = \frac{h^2}{2\lambda^2 m} + V$$

$$\frac{h^2}{2\lambda^2 m} = E - V \quad \text{—③}$$

$$\lambda^2 = \frac{h^2}{2m(E-V)} \quad \text{—④}$$

for moving particle like electron in the x-dirn can be expressed as,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 \psi}{\lambda^2} = 0 \quad \text{—⑤}$$

Put value of λ^2 in eq⑤

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} + 4\pi^2 \psi \times \frac{2m}{h^2}(E-V) = 0$$

$$\Rightarrow \boxed{\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0} \quad \text{—⑥}$$

eqn for a particle in x direction.

eq^n of a particle move in x, y, z dir^n.

$$\boxed{\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0} \;//$$

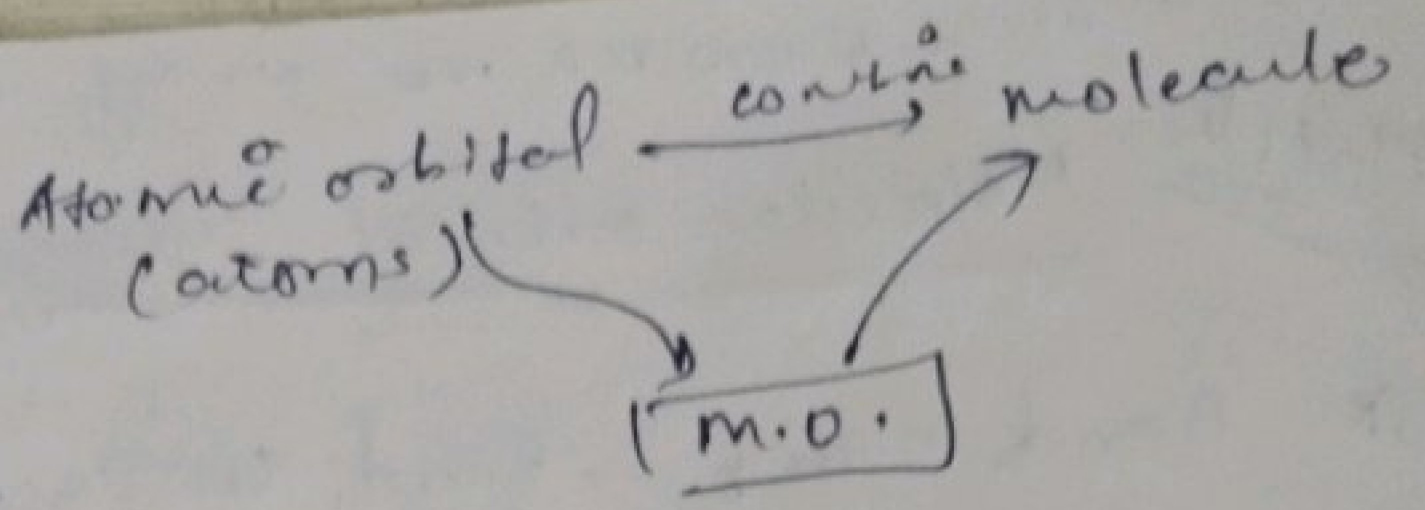
m = mass of e^-

V = P.E. of electron

E = Total energy

$\psi \rightarrow$ wave function

MOT



1) BMO / AMO
↓
2) σ, π / σ*, π*
3) Z ≤ 7 (~~Energy level → σ1s, σ*1s, σ2s, σ*2s,~~ π2px, σ2pz, π2py, π*
↓
atomic no.

Energy level

σ1s, σ*1s, σ2s, σ*2s, π2px π2py, σ2pz, π*2px π*2py, σ*2pz

if Z < 7, σ1s, σ*1s, σ2s, σ*2s, σ2pz, π2px π2py, π*2px π*2py, σ*2pz

4) unpaired e⁻ → Paramagnetic
paired e⁻ → Diamagnetic

5) $$\text{Bond Order} = \frac{N_b - N_a}{2}$$
N_b → no. of e's in b.o.s
N_a → No. of e's in antibonding orbitals

6) $$\text{B.O} \propto \text{stability} \propto \text{B.E} \propto \frac{1}{\text{Bond length}}$$

Molecular Orbital theory was given by Hund & mulliken in 1932

The main ideas of this theory is

1) when two atomic orbitals overlap, they lose their identity and form new orbital. The new orbitals are called moleculer orbitals.

2) molecular orbitals are the energy states of a molecule in which the electrons of the molecule are filled.

3) Only those atomic orbitals can combine to form moleculer orbital which have comparable energies and proper orientation

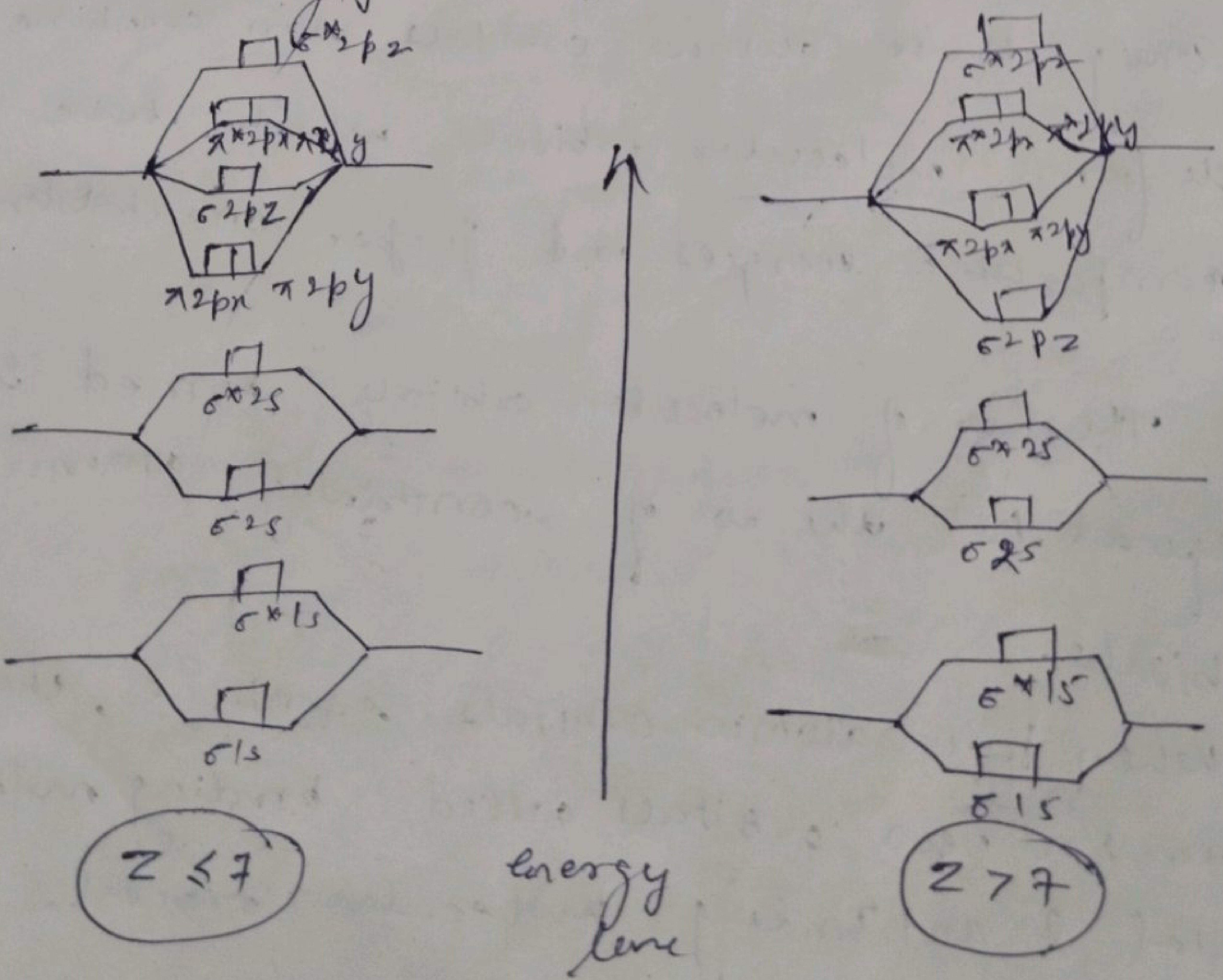
4) The no. of molecular orbitals formed is equal to the no. of combining atomic orbitals.

5) when two atomic orbitals combine, they form two new orbitals called bonding molecul orbital & antibonding moleculer orbital.

6) The bonding molecular orbitals are represented by σ, π etc. where as the antibonding molecular orbitals are represented by σ^*, π^* etc.

7) The filling of molec. orbitals in a molecule takes place in accordance with Aufbau Principle, Pauli's exclusion principle & Hund's rule.

8) Energy level of molecular orbitals.



8) B.M.O. A.B.M.O.

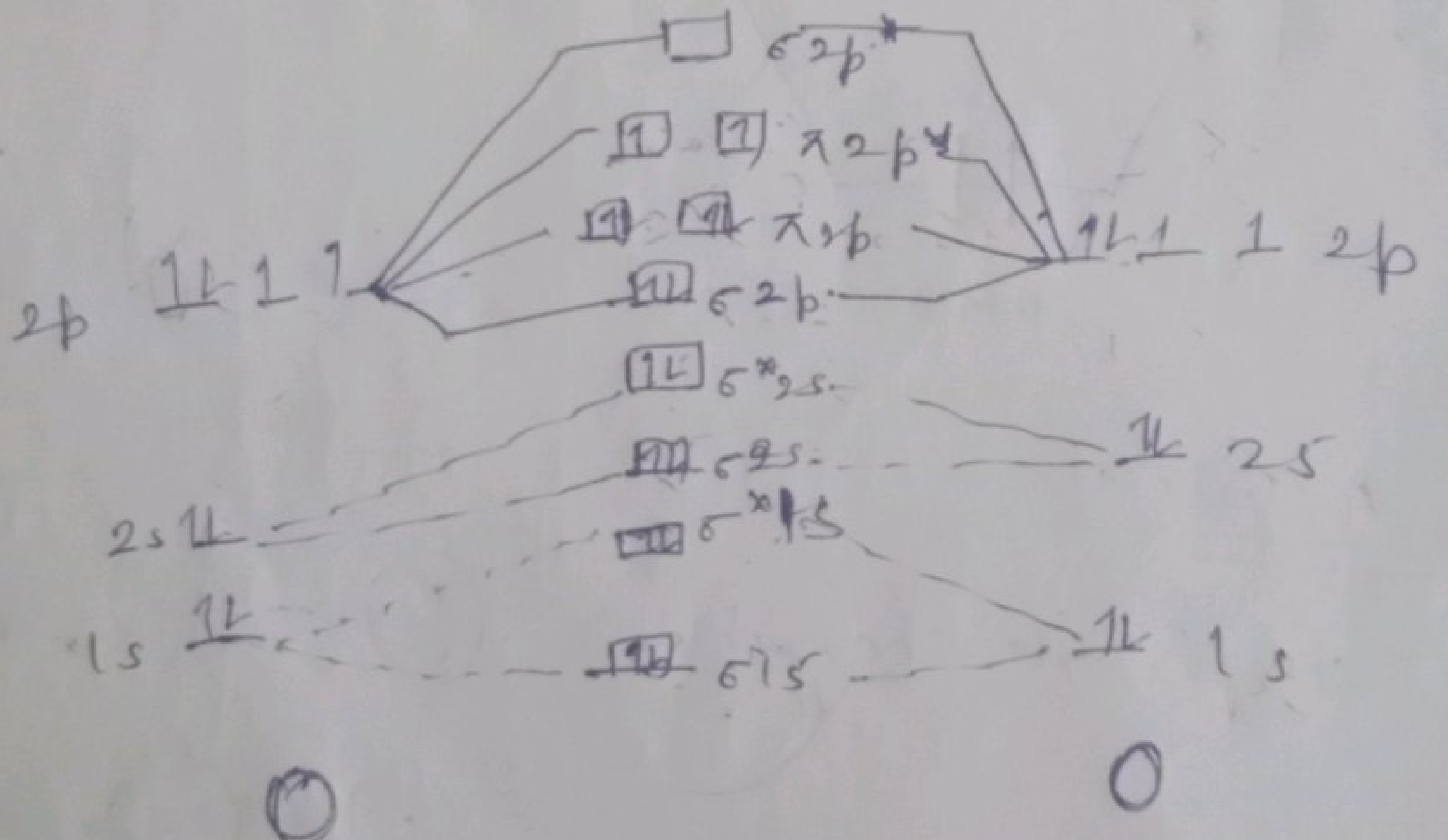
lower energy. higher energy

greater stability less stability

Ex B.O. of O^2 molecule

$O_2 = 8+8 = 16$

$1s^2 2s^2 2p^4$



$$B.O = \frac{1}{2}(Nb - Na) = \frac{1}{2}(10-6)$$

$$= \frac{4}{2} = 2$$

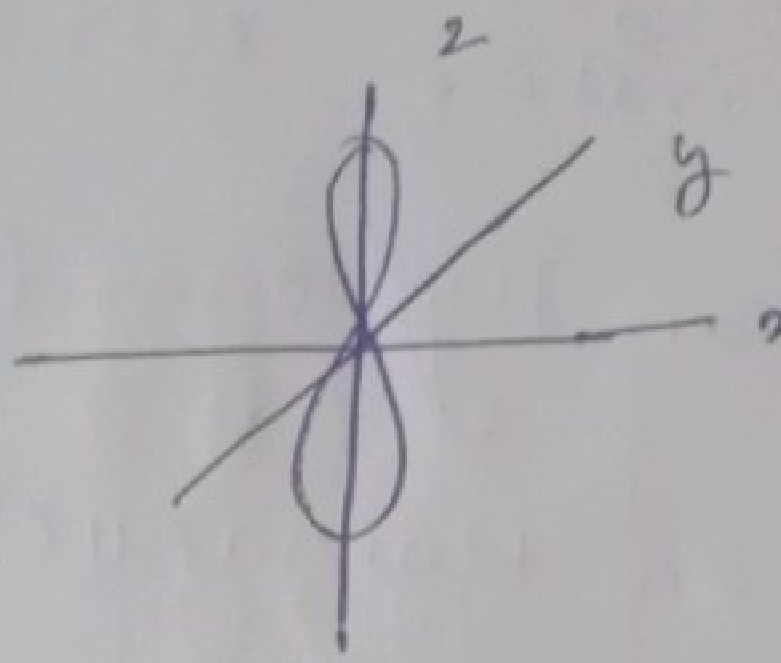
O_2 molecule is double bonded & is paramagnetic due to presence of two unpaired e^-s

shape of orbitals

1) s-orbital

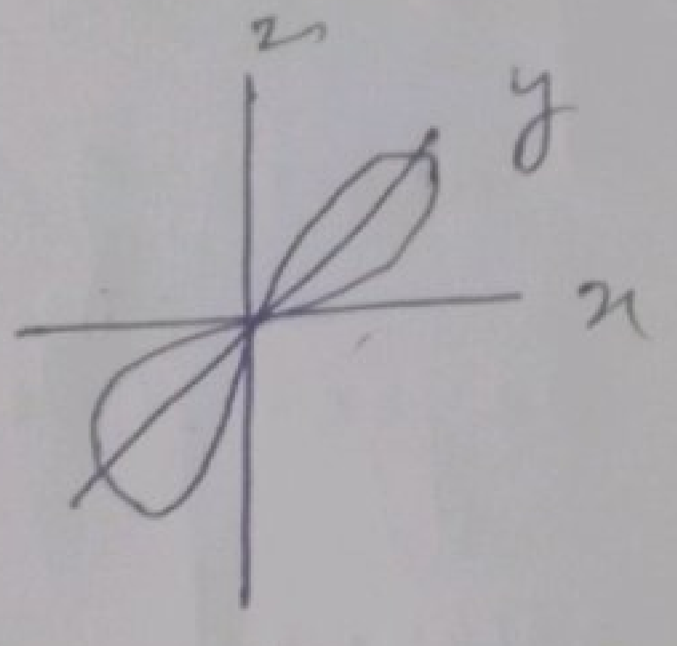
spherical

2) p-orbital

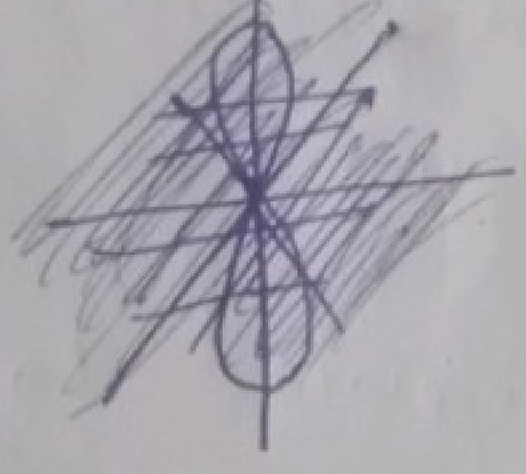


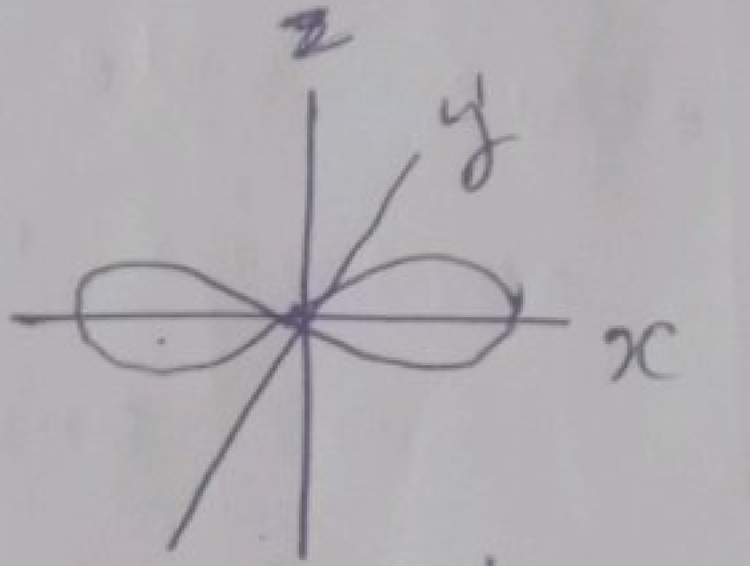
pz

dumble shape



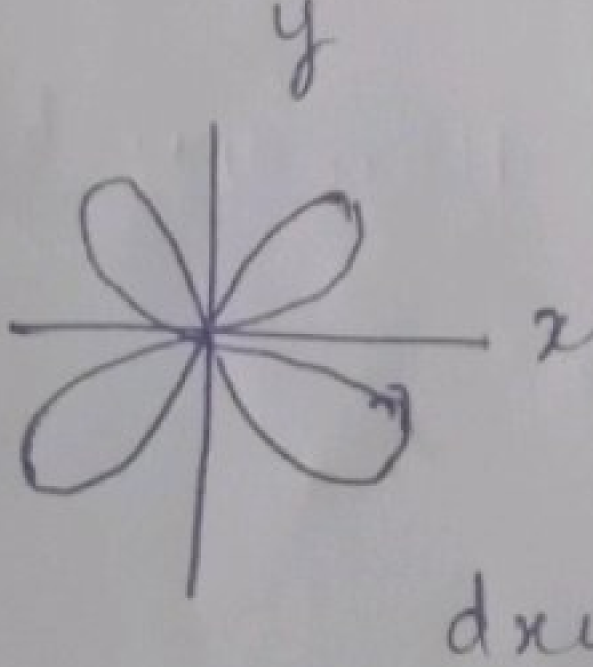
py



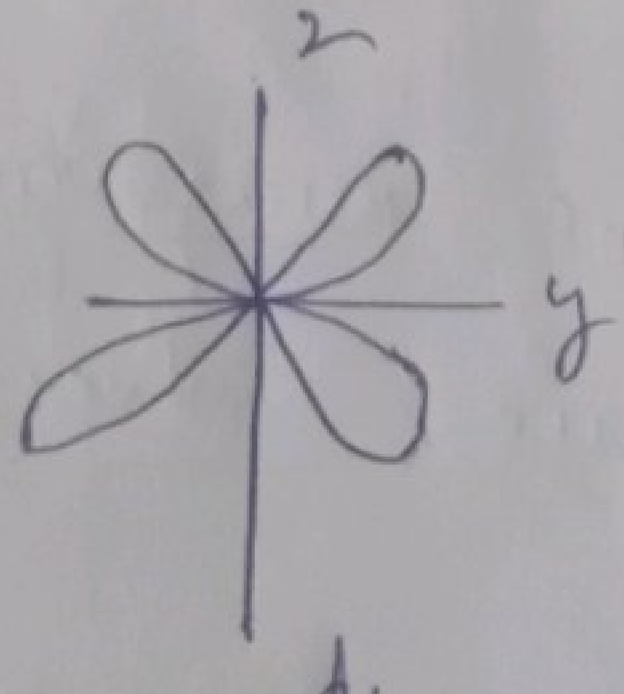


px

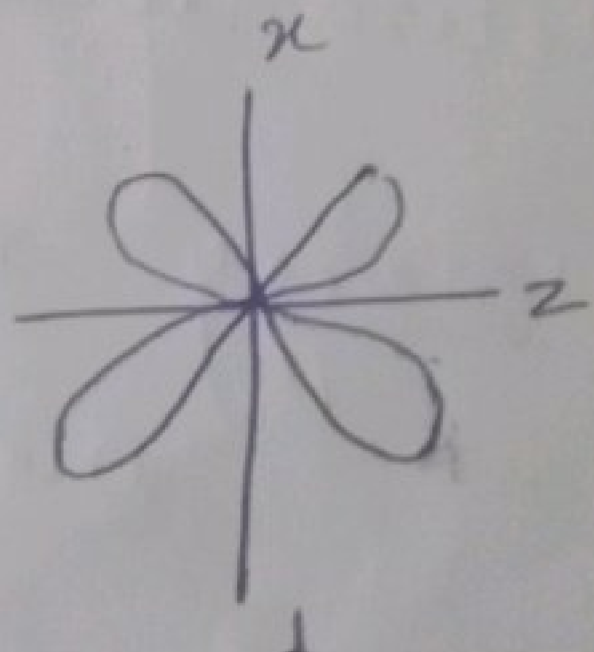
3) z-orbital (double dumble shape)



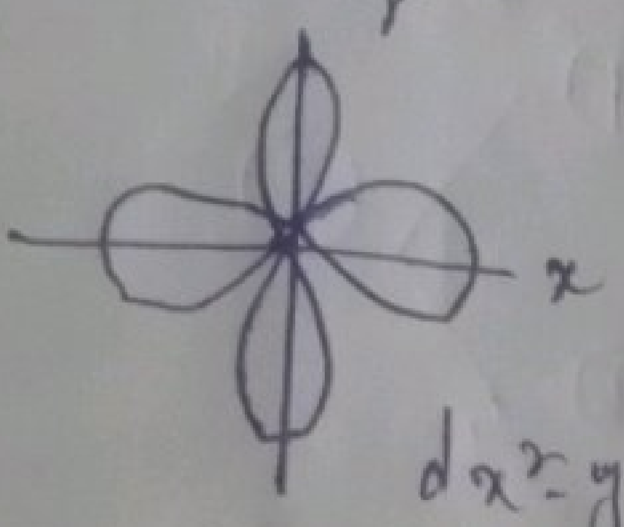
dxy



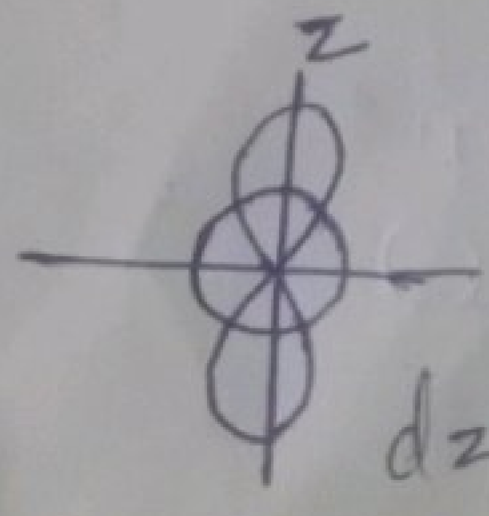
dyz



dzx



dx^2-y^2



dz^2 (Doughnut) shape

Order of Energy

s < p < d < f

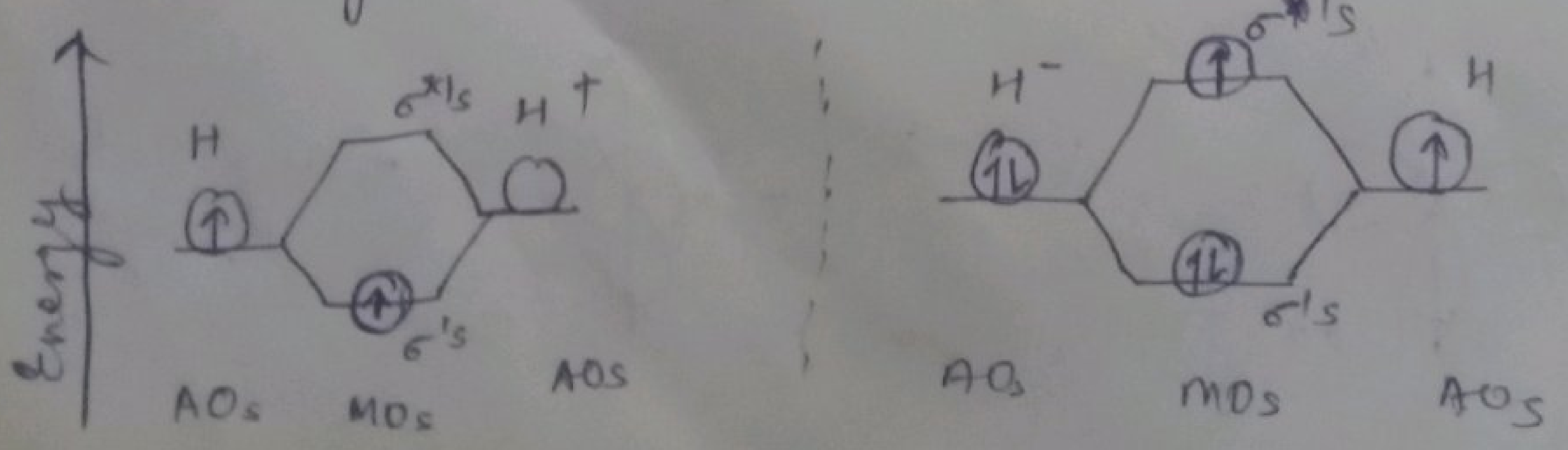
Homonuclear and Heteronuclear Diatomic molecules

If a diatomic molecule contains two atoms of similar elements such as Oxygen (O_2) or Hydrogen (H_2), it is reffred to as Homonuclear.

On the other side, if a diatomic molecule contains two different atoms, such as nitric oxide (NO) or carbon monoxide (CO) it is referred to as Heteronuclear.

Energy level Diagram for Homonuclear Diatomic molecule :-

Ex- Diagram for H_2^+, H_2^-



* B.O. for H_2^+ = $\frac{1}{2}$ (Nb - Na)

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

Hence due to unpaired e⁻ it is paramagnetic.

* B.O for H_2^- = $\frac{1}{2}$ (Nb - Na) $= \frac{1}{2} (2-1) = \frac{1}{2}$

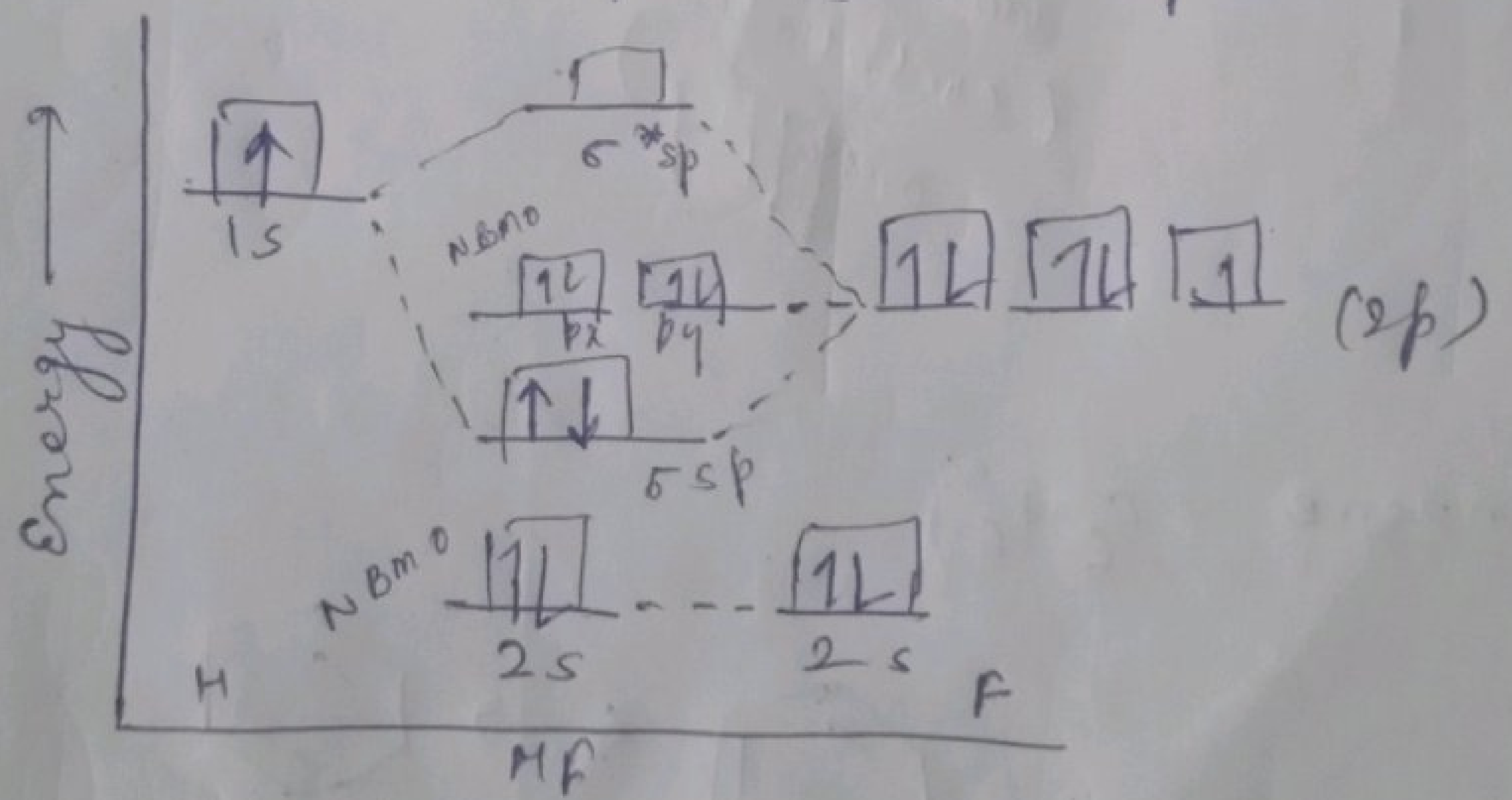
Hence due to one unpaired e⁻ is present in the antibonding orbital it is paramagnet

Energy level diagram for Heteronuclear diatomic molecule :-

* diagram for HF molecule :-

H : $1s^1$
F : $1s^2 2s^2 2p^5$

H & F have more energy gap.



B.O = $\frac{1}{2}$ (Nb - Na) = $\frac{1}{2}$ (2-0) = 1

and due to paired of e⁻s it is diamagnetic behaviour.

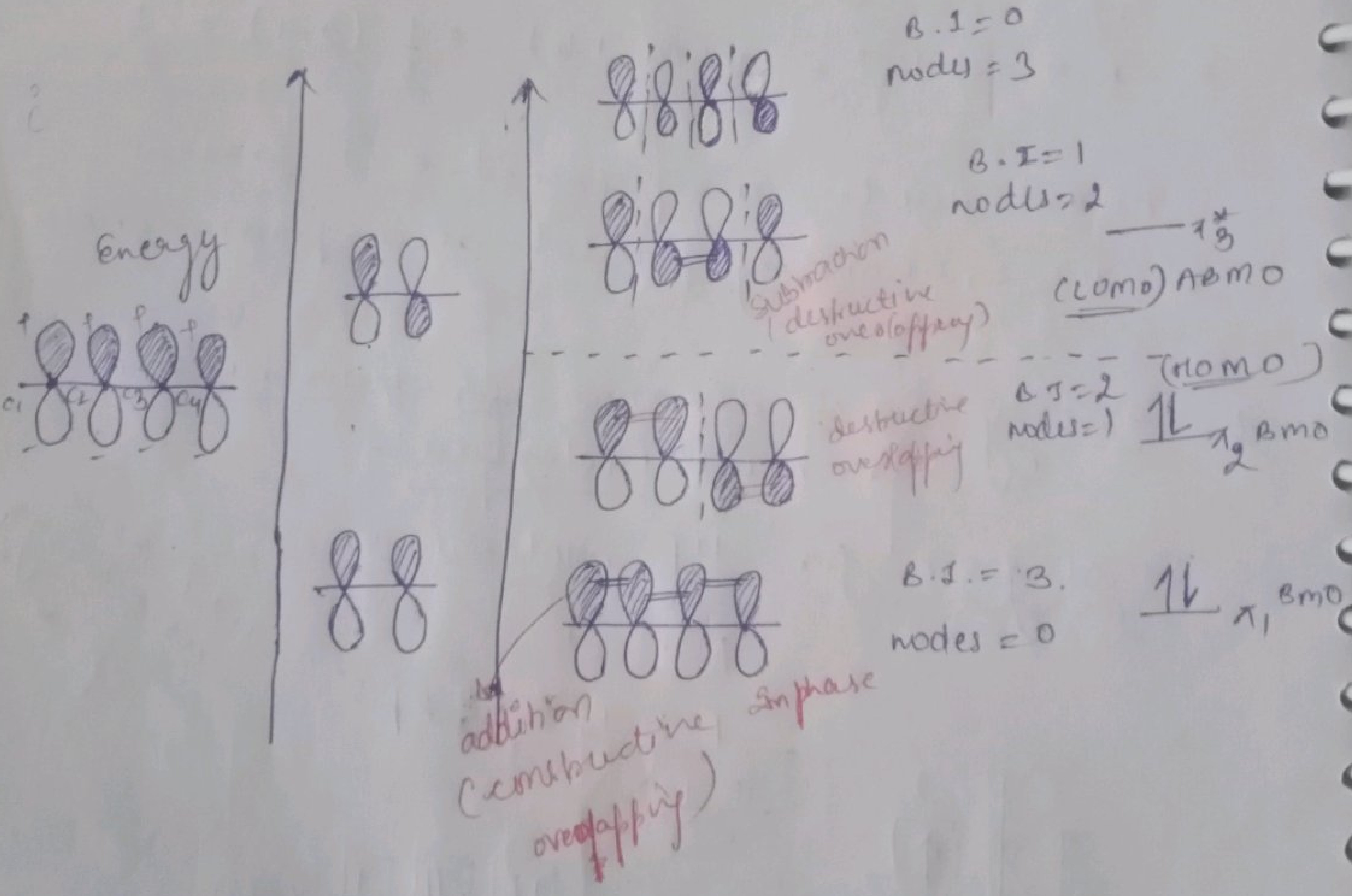
π-molecular Orbital of butadiene

1) Butadiene (C_4H_6)

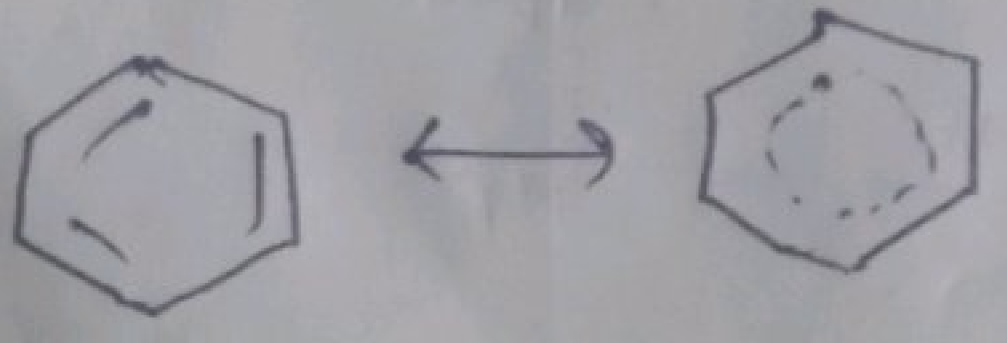
$$\overset{4}{C}H_2 = \overset{3}{C}H - \overset{2}{C}H = \overset{1}{C}H_2$$

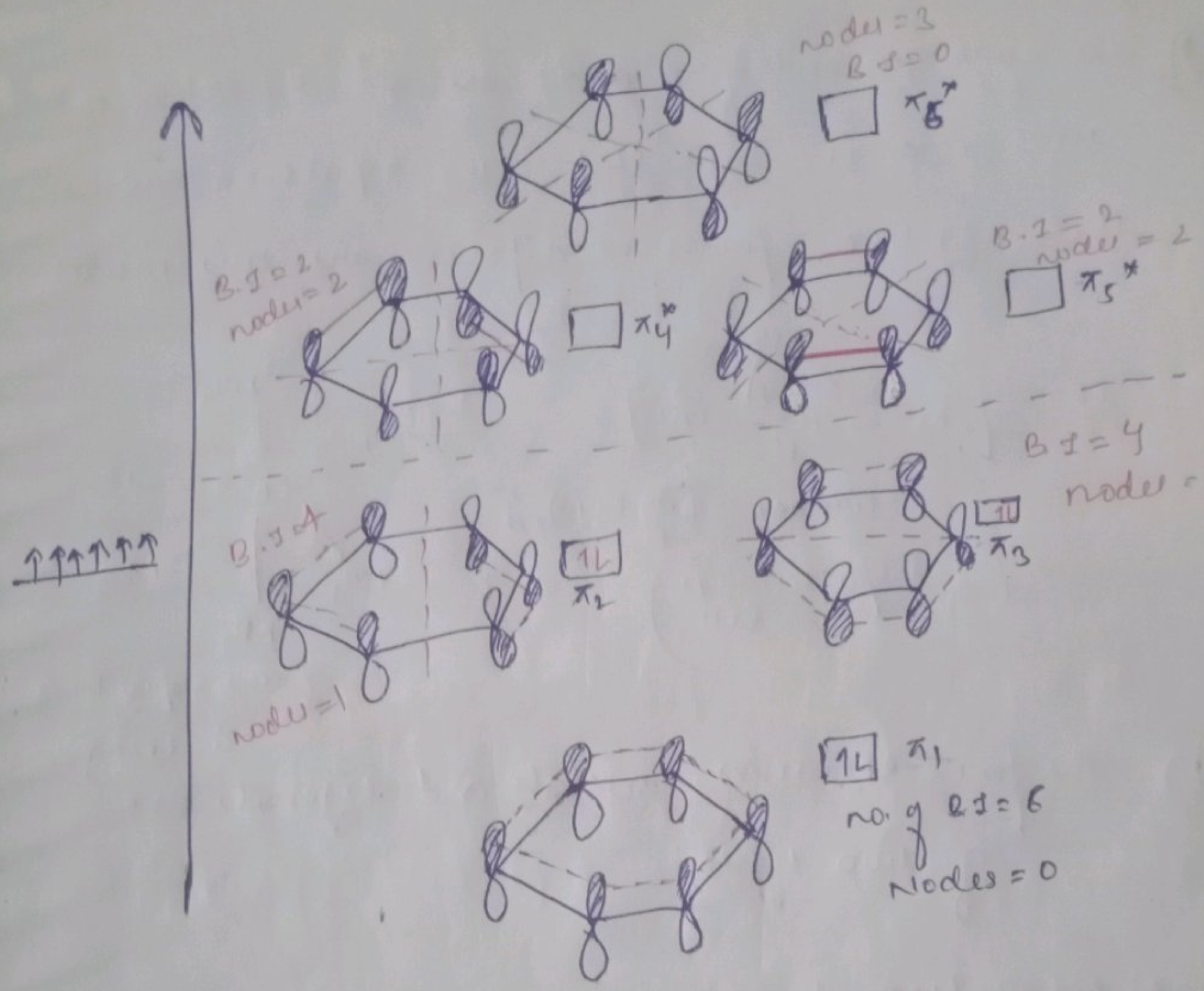
π bonds = 2
= 4π e⁻'s

1, 3, Butadiene



2) **Benzene** (C_6H_6)





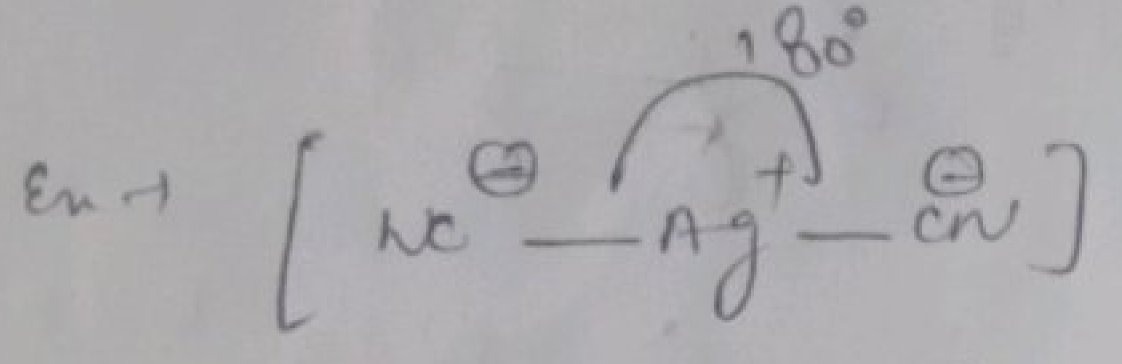
CFT (Crystal field theory)

i) CFT assume that bonds between central metal atom or ion & ligands are purely ionic

- metals → +ve charge or neutral,
- ligands →
  - -ve (F^-, Cl^-, Br^-, OH^-, CN^-) } point charge ligands
  - +ve (NO^+) ——
  - Neutral - (NH_3, H_2O) → point dipole or single dipole

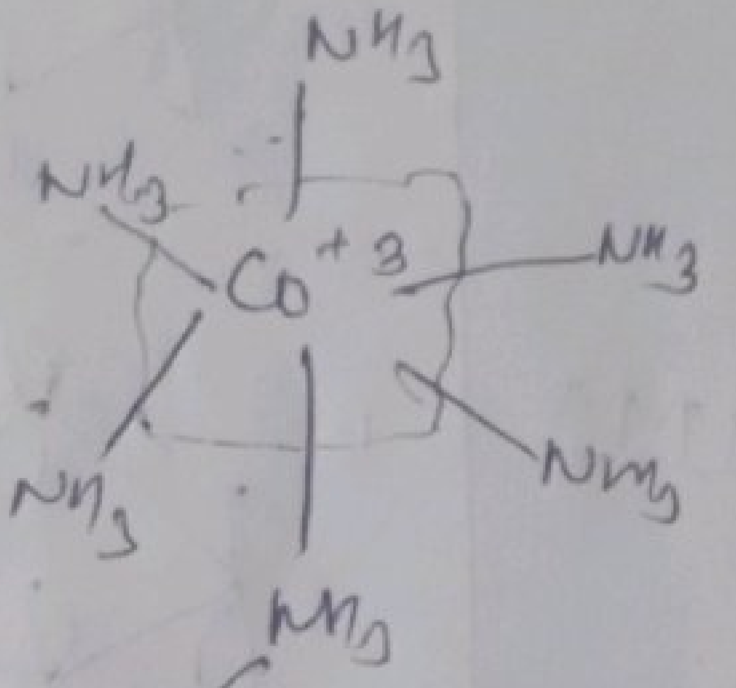
2) The arrangement of ligands around the central metal atom or ion is such that the repulsion b/w these negative points or dipoles are minimum.

Ex→



linear $[Ag(CN)_2]^-$

(repulsion is less)



(The repulsion is less)

3) The force between metals and ligands are of two types!

A) <u>Attraction force</u>:-

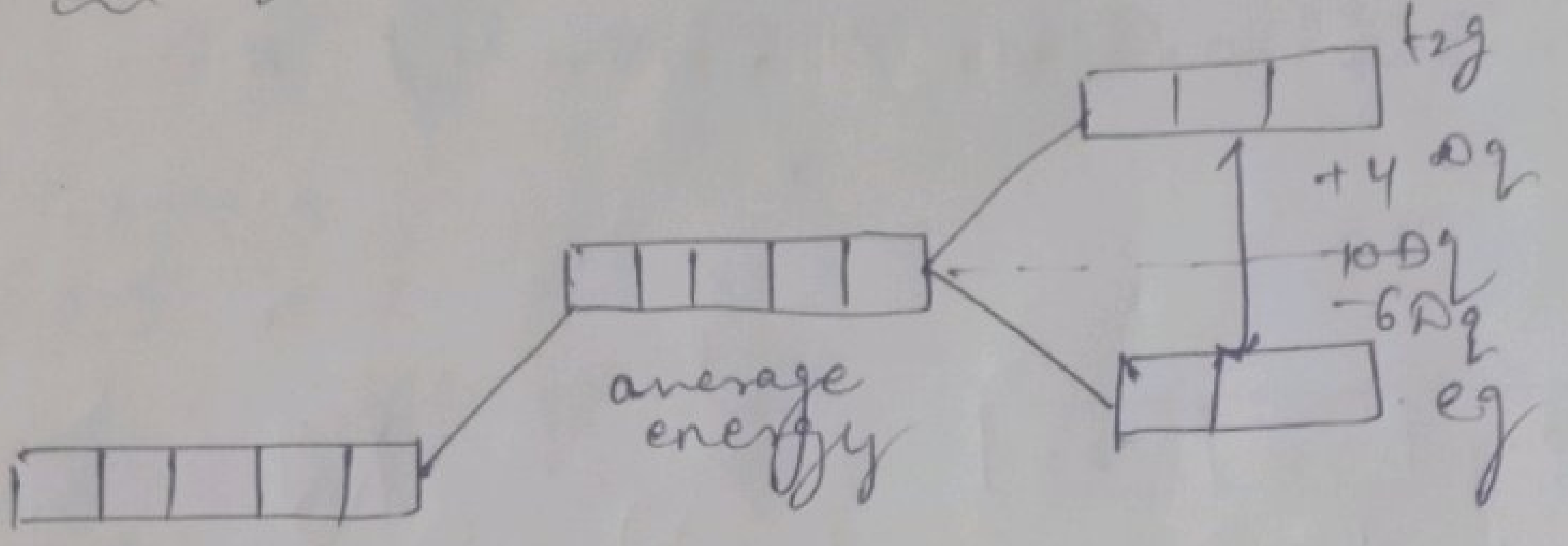
the charge of central metal atom & -ve charge of ligands

B) <u>Repulsion force</u>:-

d-electrons of central metal atom & lone pair electrons of ligands.

4) d-orbitals of central metal atom are divided into two sets depending on their orientation.

B) CFS in tetrahedral complex



Uses of CFT :-

1) It explain high spin and low spin state of co-ordinate compounds.
2) It Explain magnetic properties of complex compounds
3) It explain colour of complex compounds.

splitting of t_{2g} & e_g for $d^1, d^2, d^3, d^4, d^5, d^6$ d^7, d^8, d^9, d^{10} system (Octahedral complex)

	strong field ligand (low spin complex)	weak field ligand (high spin complex)
d^1	$t_{2g}^1\ e_g^0$	$t_{2g}^1\ e_g^0$
d^2	$t_{2g}^2\ e_g^0$	$t_{2g}^2\ e_g^0$
d^3	$t_{2g}^3\ e_g^0$	$t_{2g}^3\ e_g^0$
d^4	$t_{2g}^4\ e_g^0$	$t_{2g}^3\ e_g^1$
d^5	$t_{2g}^5\ e_g^0$	$t_{2g}^3\ e_g^2$

d^6	$t_{2g}^6 e_g^0$	$t_{2g}^4 e_g^2$
d^7	$t_{2g}^6 e_g^1$	$t_{2g}^5 e_g^2$
d^8	$t_{2g}^6 e_g^2$	$t_{2g}^6 e_g^2$
d^9	$t_{2g}^6 e_g^3$	$t_{2g}^6 e_g^3$
d^{10}	$t_{2g}^6 e_g^4$	$t_{2g}^6 e_g^4$

Calculation of CFSE for Oct. coordination :-

$$\boxed{CFSE = -0.4\Delta_0 \times x + 0.6\Delta_0 \times y}$$

where $x \rightarrow$ no. of e's in t_{2g}

$y \rightarrow$ no. of e's in e_g

Ex → for $d^2 = 2 \times (-0.4\Delta_0) = -0.8\Delta_0$

$d^9 = 6 \times (-0.4\Delta_0) + 3 \times (0.6\Delta_0) = -0.6\Delta$

splitting of t_{2g} & e_g for (Tetrahedral complex)

(All tetrahedral are high spin complex)

d^1	e_g	d^5	$e_g^2 t_{2g}^3$
d^2	e_g^2	d^6	$e_g^3 t_{2g}^3$
d^3	$e_g^2 t_{2g}^1$	d^7	$e_g^4 t_{2g}^3$
d^4	$e_g^2 t_{2g}^2$	d^8	$e_g^4 t_{2g}^4$
		d^9	$e_g^4 t_{2g}^5$
		d^{10}	$e_g^4 t_{2g}^6$

CFSE of tetrahedral complex

$$\boxed{CFSE = -0.6\,\Delta t \times x + 0.4\,\Delta t \times y}$$

$x \rightarrow$ electrons in eg

$y \rightarrow$ electrons in t_2g

Conclusion:-

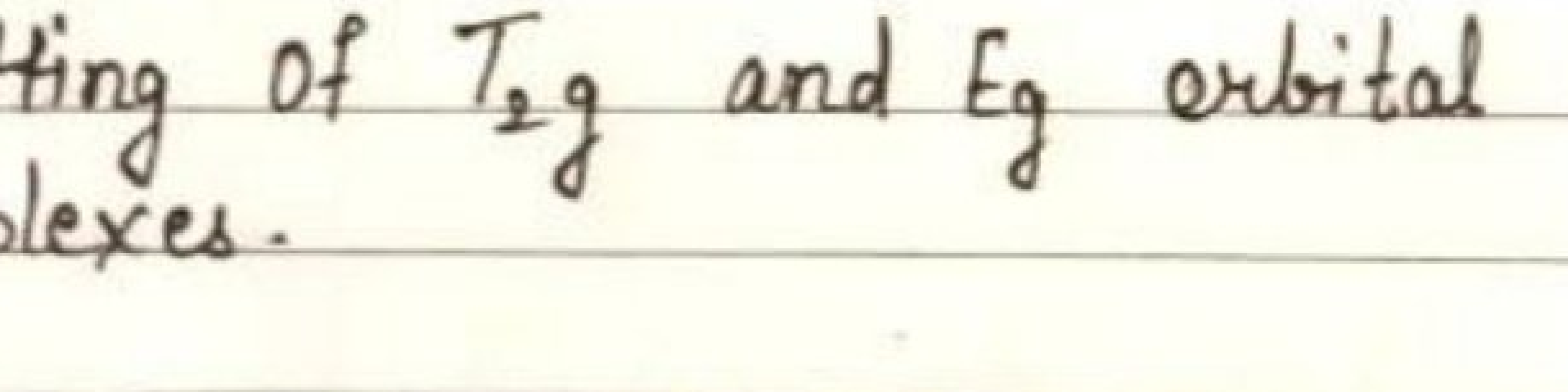
$$\boxed{\Delta t = \frac{4}{9}\Delta o}$$

- Crystal field Theory Splitting of T_2g and Eg orbitals for octahedral complexes for d_1, d_2, d_3 ---------- d_{10}.

d system	Strong field Complexes (Low spin complexes)	Weak field Complexes. (High spin complexes)
d^1	$t_2g^1\ eg^0$	$T_2g^1\ Eg^0$
d^2	$T_2g^2\ Eg^0$	$T_2g^2\ Eg^0$
d^3	$T_2g^3\ Eg^0$	$T_2g^3\ Eg^0$
d^4	$T_2g^4\ Eg^0$	$T_2g^3\ Eg^1$
d^5	$T_2g^5\ Eg^0$	$T_2g^3\ Eg^2$
d^6	$T_2g^6\ Eg^0$	$T_2g^4\ Eg^2$
d^7	$T_2g^6\ Eg^1$	$T_2g^5\ Eg^2$
d^8	$T_2g^6\ Eg^2$	$T_2g^6\ Eg^2$
d^9	$T_2g^6\ Eg^3$	$T_2g^6\ Eg^3$
d^{10}	$T_2g^6\ Eg^4$	$T_2g^6\ Eg^4$

(CFSE) Crystal field Splitting Energy = $(-0.4)\Delta_0 \times x + 0.6\,\Delta_0 \times y$

where x is no. of electrons in T_2g orbital and y is no. of electrons in Eg orbitals.



- Splitting of T_2g and Eg orbital for Tetrahedral complexes.

NOTE:→ All tetrahedral complexes are high spin complexes means (energy gap is less)

~~Weak field Complex.~~
~~High Spin Complex.~~

d system	Weak ~~Strong~~ field Complex. Haigh spin Complex.
d_1	$Eg^1\ T_2g^0$
d^2	$Eg^2\ T_2g^0$
d^3	$Eg^2\ T_2g^1$
d^4	$Eg^2\ T_2g^2$
d^5	$Eg^2\ T_2g^3$
d^6	$Eg^3\ T_2g^3$
d^7	$Eg^4\ T_2g^3$
d^8	$Eg^4\ T_2g^4$
d^9	$Eg^4\ T_2g^5$
d^{10}	$Eg^4\ T_2g^6$

Crystal Field Splitting Energy $= -(0.6)\Delta_t \times x + 0.4\,\Delta_t \times y$.

$$\therefore \quad \boxed{\Delta_t = \frac{4}{9}\Delta_0}$$

- Splitting Of Square Planar Complexes.

Δsp is larger than the pairing energy. So, the square planar complexes are low spin complexes.

- Classification Of Semi-Conductors

Semi-conductors are of two types intrinsic and extrinsic semiconductors.

1. Intrinsic Semi-Conductors.

The pure Semi-conductors are called intrinsic sem-conductors. The ratio of no of electrons and hol is 1:1

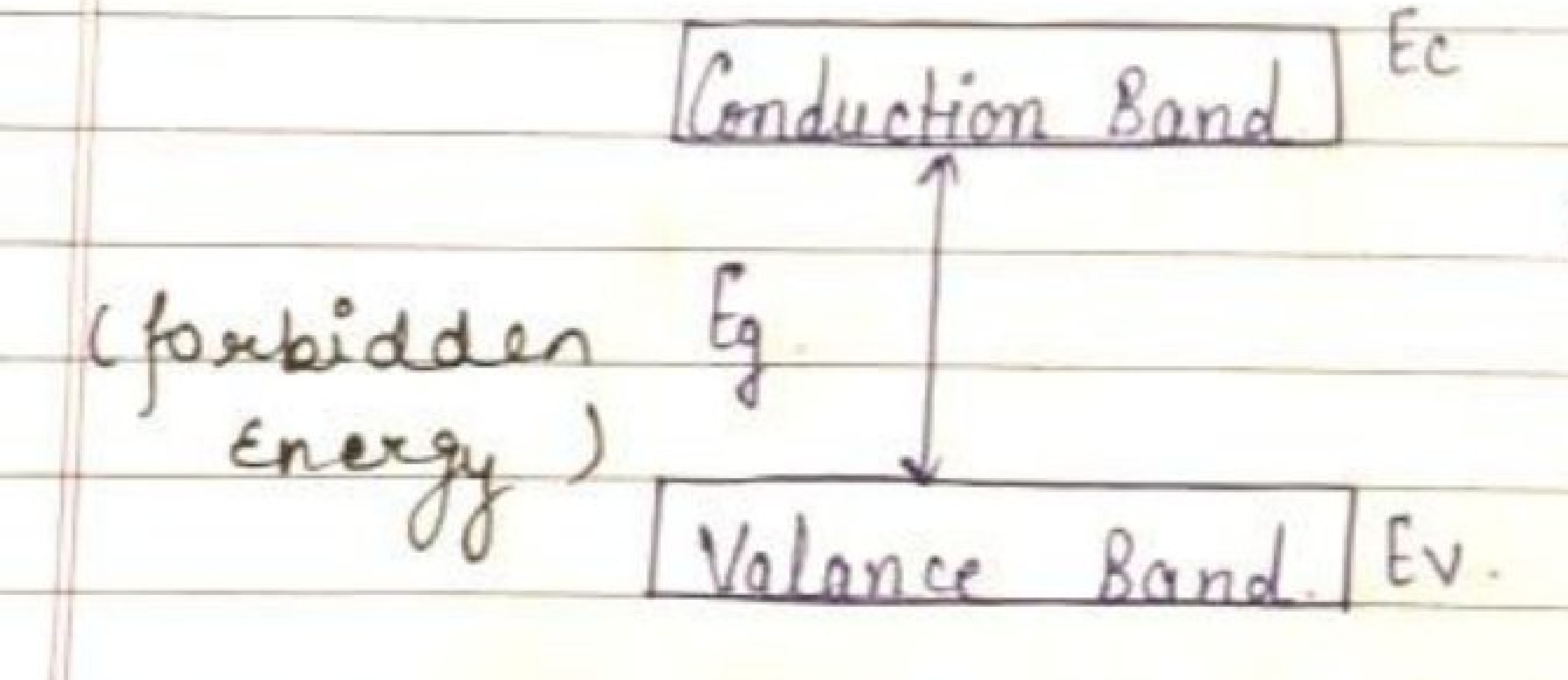
2. Extrinsic Semi-Conductors.

The semi-conductors obtained by adding or dopping the pure semi-conductor with external impurity are called extrinsic semi-conductor.

- Band Theory in Solid.

According to this theory, there exits two energy level termed as bands. The highest energy band filled with valance ~~band~~ electrons is called valance band The lowest energy band next to valance band is called conduction band.

→ The gap between top of valance band and the bottom of conduction band in which no allowed energy levels for electron can exist is called energy band gap.



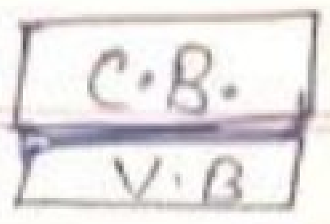
$\mathcal{E}_g = E_c - E_v$.

- Depending on the energy band gap zero, large or small. The solids are classified into the following :→

1. Metals.

a) In this last occupied band called conduction band is partially filled with electrons.

b) Band Gap is approximate zero.



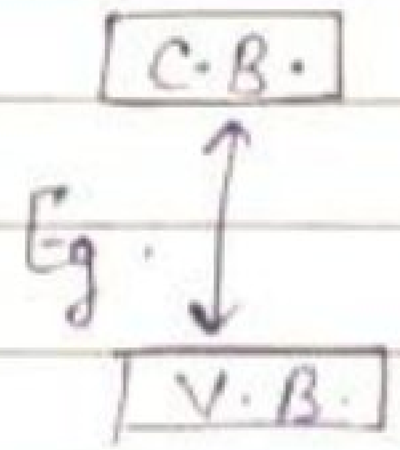
$E_g = 0$.

Here, C.B & V.B overlap to each other

2. Insulators

a) Valance band is completely filled with electrons.
b) No free electrons present in conduction band.
c) Band gap is large. Then, $E_g > 5eV$.

i.e. $1eV = 1.6 \times 10^{-19} J$



3. Semi-Conductors

a) Conduction band is empty, valance band is filled
b) Band Gap is between (0.5 - 0.3 eV)
c) Semi-conductor's conductivity can be increased by dopping process.

- Dopping

It is the process of addition of a desirable impurities in a pure semi-conductor to increase its conductivity. This process is known as Dopping.

- Types Of Extrinsic Semi-Conductor.

Extrinsic Semi-conductor are classified into two parts:

1. n-type Semi-Conductor

A semi-conductor which is obtained by dopping the tetravalent semi-conductors with pentavalent impurities (As, Pb, P, Sb) is called n-type Semi-Conductors.

OR