

# Structure And Bonding Models

## VBT - Valency Bond Theory

It explains the formation of covalent bond.

### Postulates:

- Covalent bond is formed by overlapping of orbitals.
- Orbitals of valence shell in which electrons are in opposite spin take part in overlapping.
- Extent of overlapping decide strength of bond.
- After bond formation also, the spin of  $e^-$ 's is present.
- the overlapping of orbitals is exothermic process that means after bond formation, energy released.
- Valency bond theory give information about directional property of covalent bond.

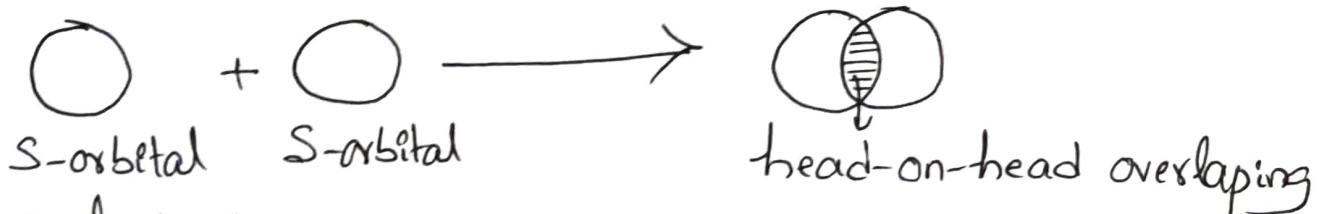
Types of covalent bond.

$\sigma$ ,  $\sigma$ -bond       $\pi$ -bond.

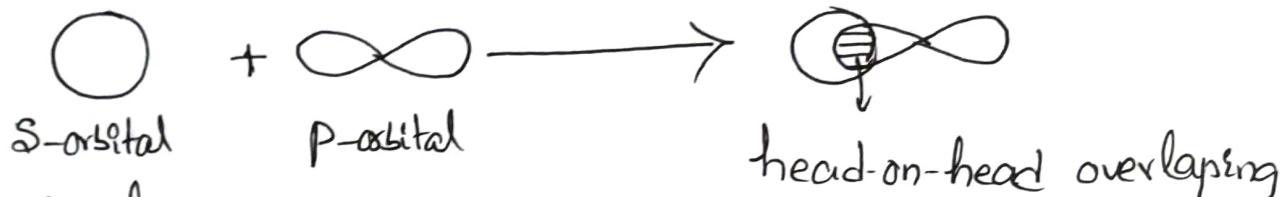
### $\sigma$ -bond :

It is also known as axial overlapping. and is formed by the head-on-head (or) end to end overlapping along the internuclear axis.

$\sigma$ -bond is formed by following overlapping  
S-S overlapping:



S-P overlapping:



P-P Overlapping:

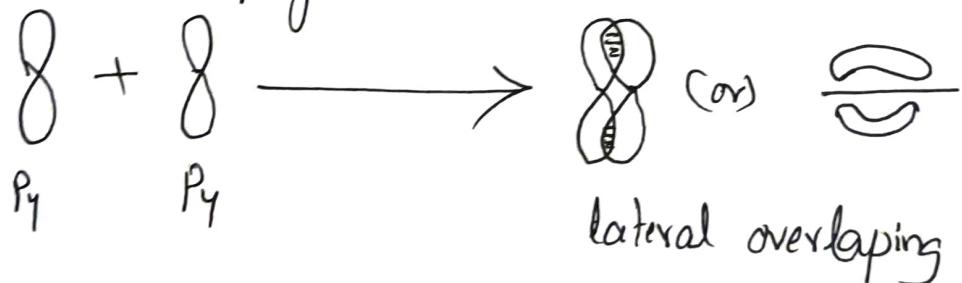


2.  $\pi$ -bond:

$\pi$ -bond is formed by overlapping of orbitals

(or) lateral overlapping of orbitals i.e., right angle to their internuclear axis.

$P_y - P_y$  /  $P_z - P_z$  overlapping:



$\equiv$  bond  $\rightarrow$  1 $\sigma$ , 2 $\pi$

= bond  $\rightarrow$  1 $\sigma$ , 1 $\pi$

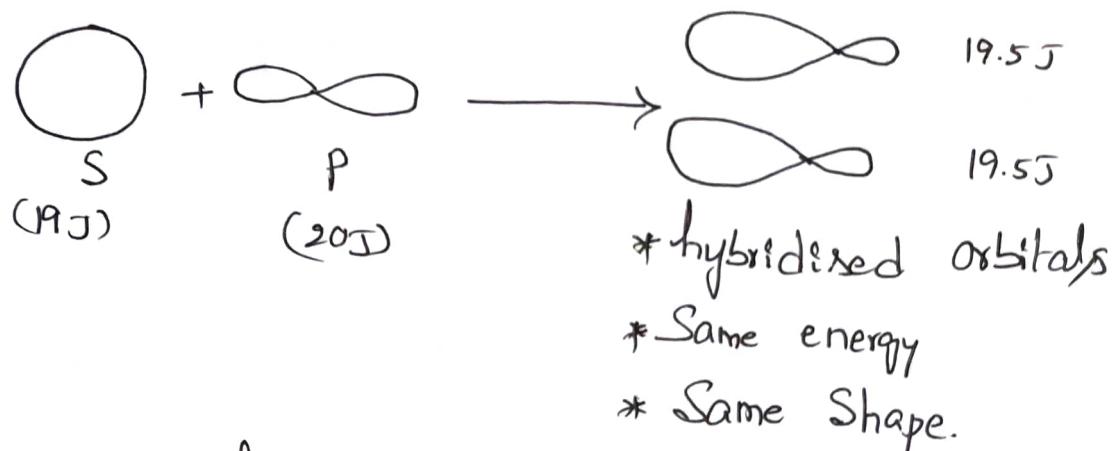
- bond  $\rightarrow$  1 $\sigma$

## Drawbacks of VBT :

- The paramagnetic behaviour of  $O_2$  cannot be explained on the basis of VBT.
- Formation of unielectron bond cannot be explained on the basis of VBT.
- $\textcircled{1} + O \longrightarrow \textcirclearrowleft \textcirclearrowright$
- $\textcircled{\uparrow\downarrow} + O \longrightarrow \textcirclearrowleft \textcirclearrowright$
- fails to explain colors of complexes.
- fails to explain high spin / low spin of molecules.
- fails to explain Magnetic behaviour of molecules.

## Hybridization:

- Hybridisation is a process of mixing of atomic orbitals of central atom in polyatomic molecule.
- In hybridization, atomic orbitals having almost same energy but different shape are mixed and new type of orbitals formed known as hybrid orbitals.



- No. of hybrid orbitals = No. of atomic orbitals participated
- The hybrid orbitals are identical in shape, energy and directional nature.
- In hybridisation, half filled, fully filled, valent orbitals can participate because it is a mixing of orbitals not mixing of electrons.

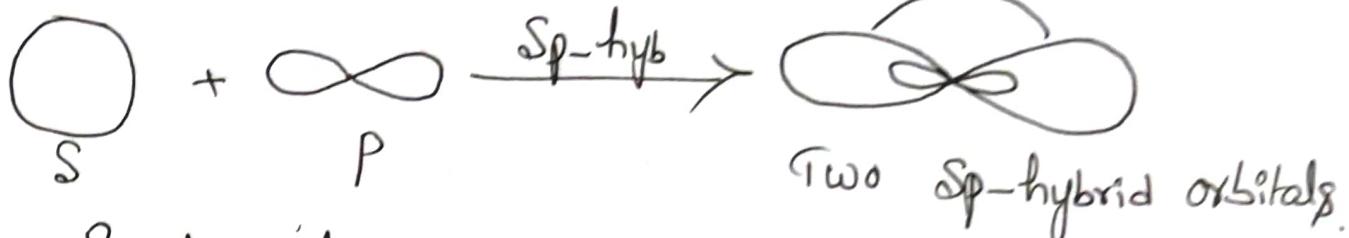
## Types of hybridisation:

- i) Sp-hybridisation
- ii) Sp<sup>2</sup>-hybridisation
- iii) Sp<sup>3</sup>-hybridisation

- iv) Sp<sup>3</sup>d-hyb
- v) Sp<sup>3</sup>d<sup>2</sup>-hyb
- vi) Sp<sup>3</sup>d<sup>3</sup>-hyb

# i) Sp-hybridisation:

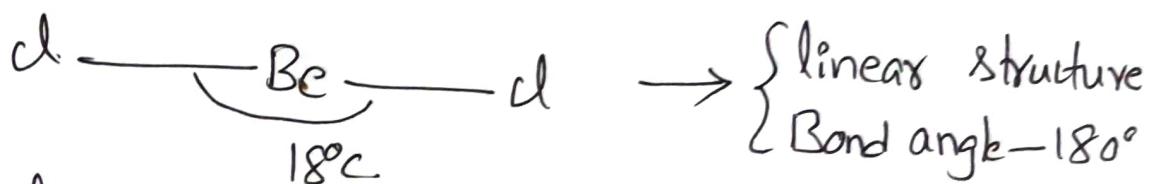
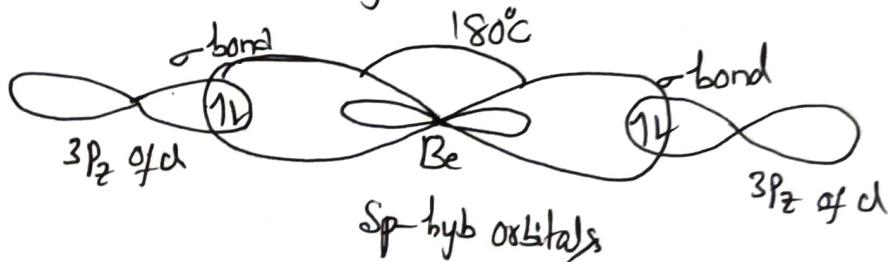
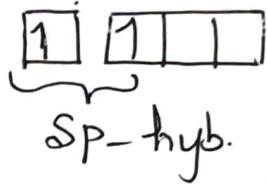
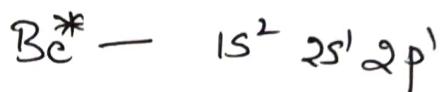
An S-orbital & P-orbital combine to form two new identical orbitals, the process is known as Sp-hybridisation.



→ Bond angle -  $180^\circ$

→ Two Sp-hybrid orbitals are made up of two lobes, in which one lobe is small & one lobe is big in size.

Ex:  $\text{BeCl}_2$

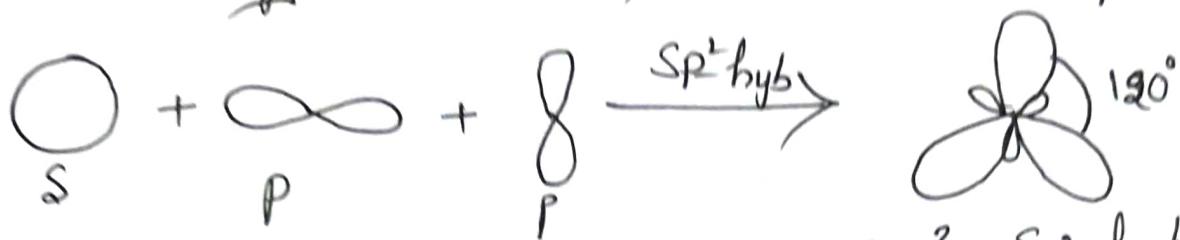


Sp-hybridised orbitals of central atom 'Be'

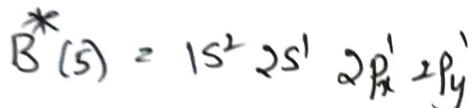
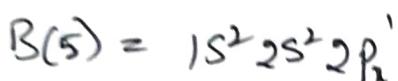
Overlaps with  $3\text{p}_z$  orbital of 'cl' and forms  $2\sigma$ -bonds.

### (ii) $Sp^2$ -hybridisation :

One S-orbital & two p-orbitals combine together to form 3 new identical orbitals having same energy, the process is known as  $Sp^2$ -hybridisation.

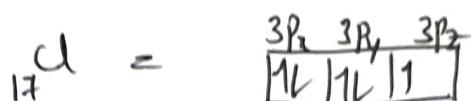


Ex:  $BCl_3$



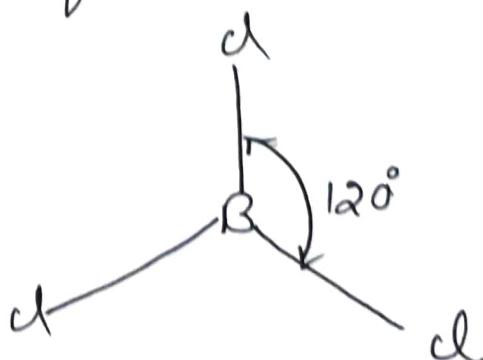
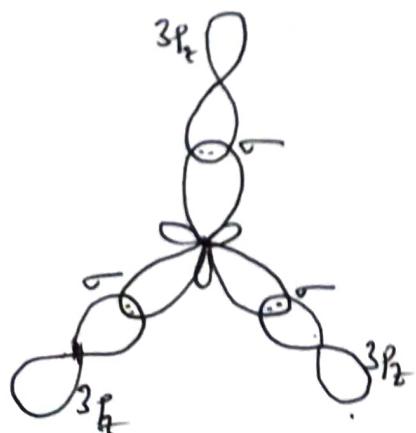
$Sp^2$ -hyb.

forms 3 hybridised  
 $Sp^2$ -orbitals.



chlorin has one  $\ominus$  in  $3P_z$

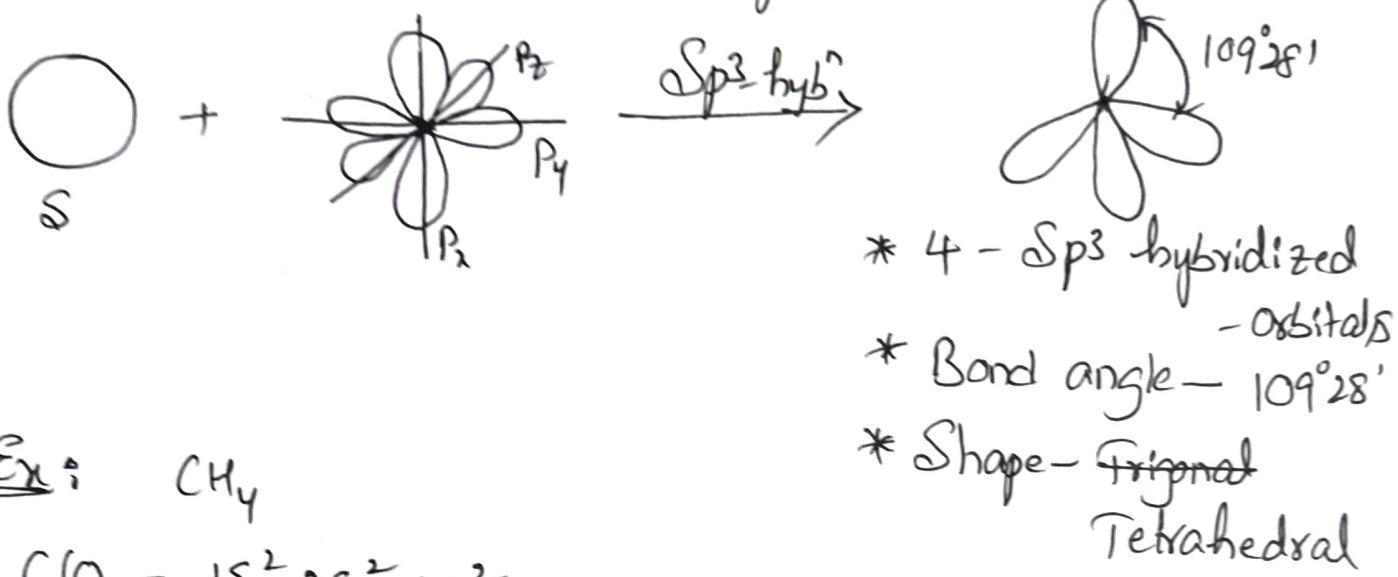
The 3- $Sp^2$ -hybrid orbitals of 'B' overlaps with  $3P_z$  orbital of chlorine and forms three  $\sigma$ -bonds.



Shape - Trigonal planar  
Bond angle -  $120^\circ$

### iii) $Sp^3$ - hybridisation:

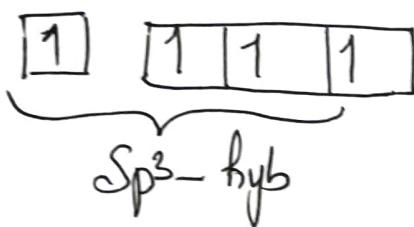
one S-orbital and 3, p-orbitals combine to form 4 new identical orbitals with the same energy, the process is known as  $Sp^3$ -hybridisation.



Ex:  $CH_4$

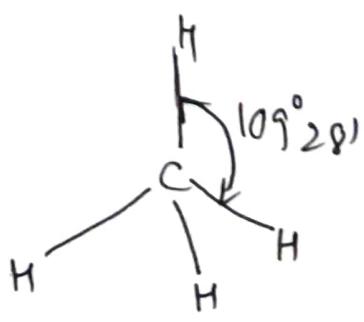
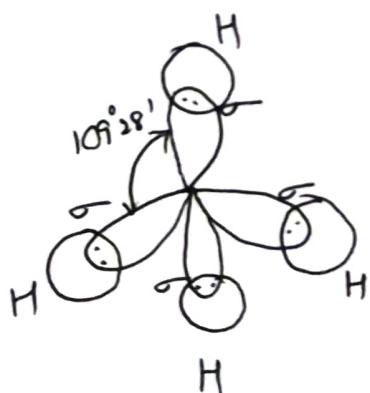
$$C(6) = 1S^2 2S^2 2p^2$$

$$C^*(6) = 1S^2 2S^1 2p'_x 2p'_y 2p'_z$$



$$H(1) = 1S^1$$

four  $Sp^3$  hybrid orbitals of 'C', overlaps with  $1S$ -orbital of 'H' atom. and forms 4  $\sigma$ -bonds.



→ Bond angle  $109^\circ 28'$   
→ Structure -  
Tetrahedral

#### IV) $Sp^3d$ - hybridisation :

one S-orbitals, three p-orbitals and one d-orbital combine with each other form 5 new identical hybridized orbitals with same energy, and the process is known as  $Sp^3d$  hybridisation.



\* 5-  $Sp^3d$  hybridised orbitals.

\* Bond angles -  $120^\circ, 90^\circ$

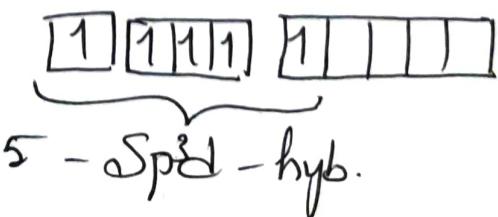
\* Trigonal Bipyramidal shape

→ Out of 5-  $Sp^3d$  hybridised orbitals, 3 hybrid orbitals lie in horizontal plane, inclined at an angle  $120^\circ$  to each other, remaining 2 hybrid orbitals lie in vertical plane at  $90^\circ$  to planar orbitals.

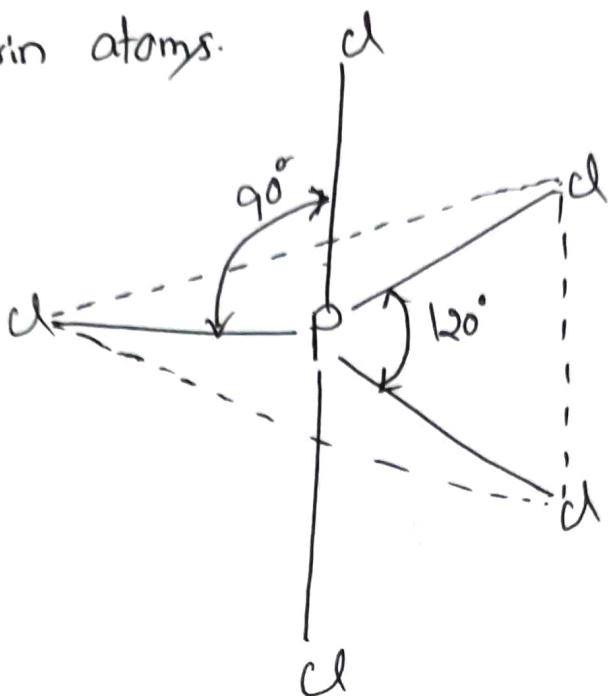
Ex:  $PCl_5$

$$P(1s) = 1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^3$$

$$P^* = 1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^1 \quad 3p^3 \quad 3d^1$$



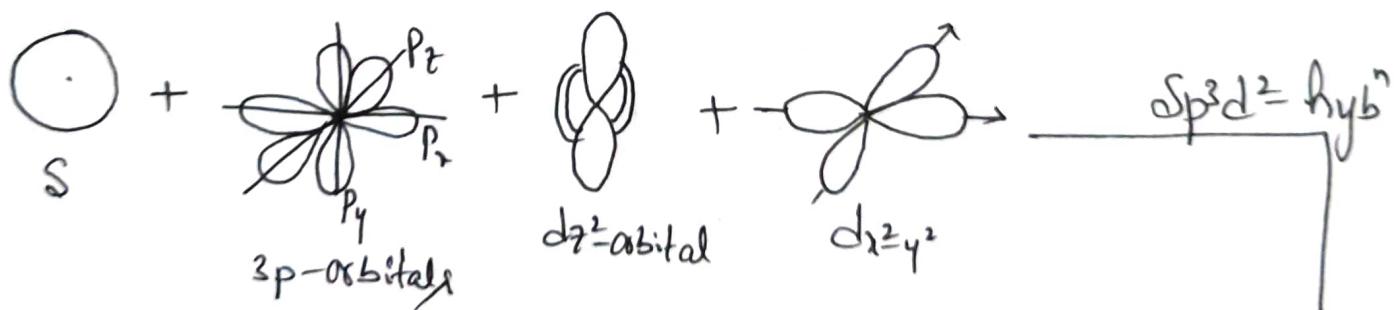
These 5 hybrid orbitals forms 5 covalent bonds with 5 chlorine atoms.



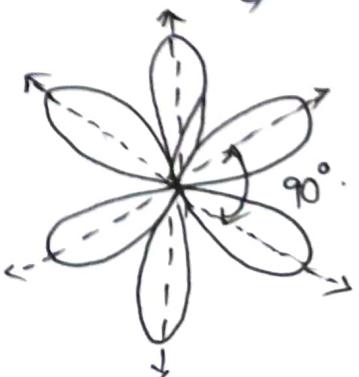
Bond angles -  $120^\circ, 90^\circ$   
Shape - Trigonal  
Bipyramidal.

#### (V) $Sp^3d^2$ - hybridisation:

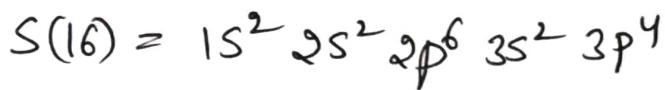
One S-orbital, three p-orbitals and three d-orbitals combine with each other to form 6 new identical hybrid orbitals with the same energy, the process is known as  $Sp^3d^2$ - hybridisation.



- \* 6- $Sp^3d^2$ -hyb. orbitals.
- \* Bond angle -  $90^\circ$
- \* Structure - Octahedral.

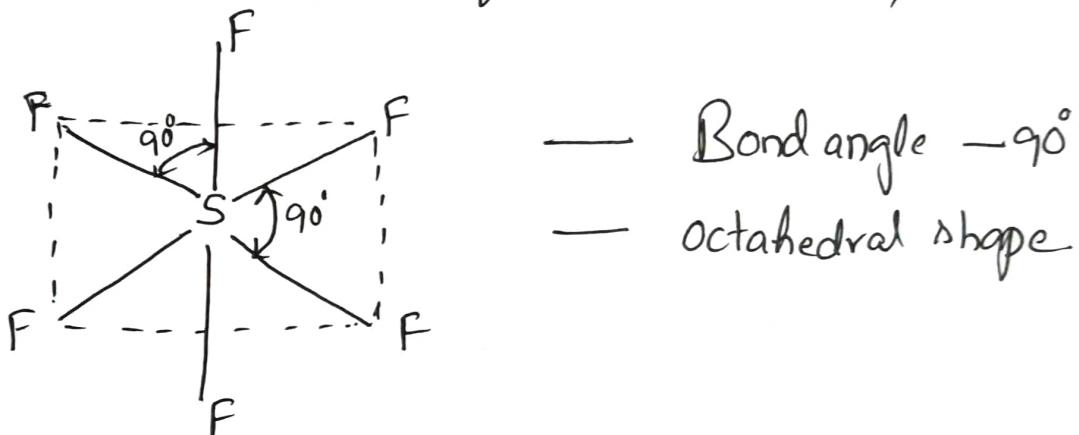


Ex:  $\text{SF}_6$



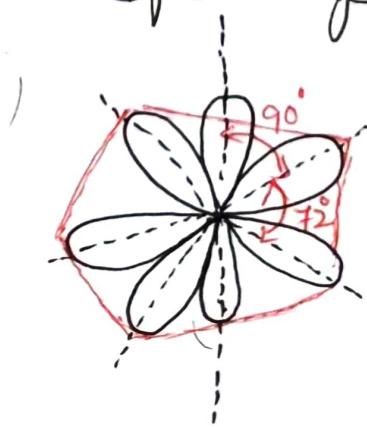
6 -  $\text{sp}^3\text{d}^2$  - hybrid orbitals.

In  $\text{SF}_6$ , 6 -  $\text{sp}^3\text{d}^2$  hybridized orbitals of S overlaps with 6 p-orbitals of F and forms 6  $\sigma$ -bonds.



(vi)  $\text{Sp}^3\text{d}^3$  - hybridization :

One S-orbital three p-orbitals and three d-orbitals combine with each other to form 7  $\text{sp}^3\text{d}^3$  hybrid orbitals with same energy, and the process is known as  $\text{Sp}^3\text{d}^3$  - hybridisation.

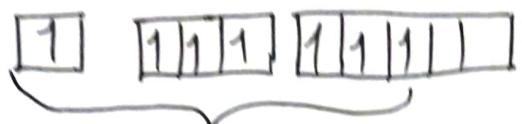


→ 7 new  $\text{sp}^3\text{d}^3$  hybrid orbitals  
→ Bond angles  $90^\circ, 72^\circ$   
→ Shape - Pentagonal Bipyramidal

Ex:  $\text{IF}_7$

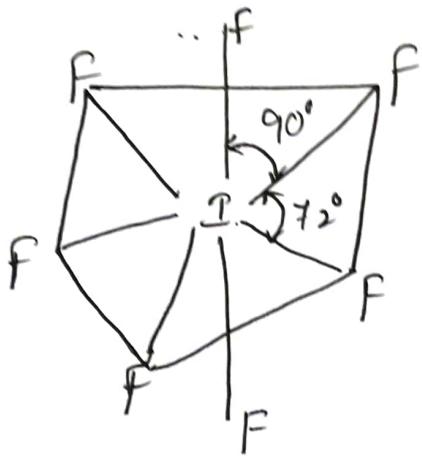
$$\text{I}(5s) = 5s^2 \ 5p^5$$

$$\text{I}^* = 5s^1 \ 5p^3 \ 5d^3$$



$7 - \text{Sp}^3\text{d}^3$  hybrid orbitals.

The formed  $7 - \text{Sp}^3\text{d}^3$  hybrid orbitals of 'I' overlaps with 7 p-orbitals of 'F' atoms and forms  $\sigma$ -bonds.



Shape - Pentagonal Bipyramidal.

Bond angles -  $90^\circ, 72^\circ$ .

## Molecular orbital theory (MOT) :

VB Theory fails to explain the paramagnetic nature of  $O_2$  molecule & it was explained by MOT.

This theory was proposed by Hund & Mullikan.

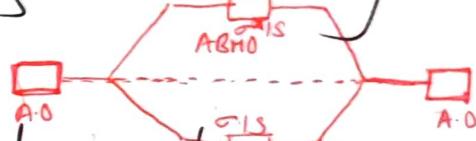
This theory explains,

- \* formation of molecules
- \* magnetic behaviour of molecules
- \* relative bond length, bond strength, bond stability.

### Postulates of MOT :

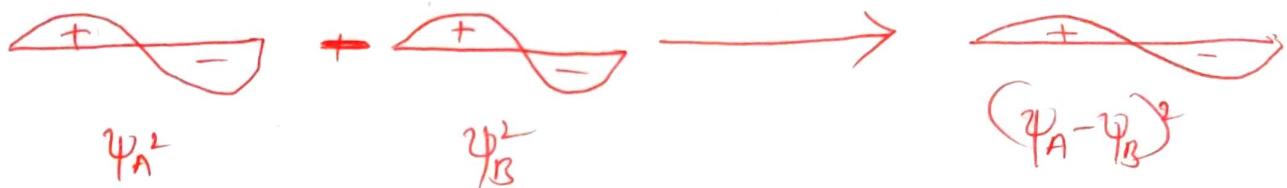
1. All filled or unfilled atomic orbitals of bonding atoms take part in bond formation.
2. Molecular orbitals are formed by L.C.A.O  
(Linear Combination of atomic orbitals)
3. When molecular orbitals are formed then A.O loose their identity.
4. Combining of A.O's is possible when A.O's have similar energy levels.
5. When two A.O's overlaps with each other, two new molecular orbitals are formed which are known as

bonding molecular orbitals (BMO) & antibonding molecular orbitals (ABMO)



Bonding atomic orbitals have lower energy & greater stability while ABMO has higher energy and low stability.  $ABMO > A \cdot O > BMO$ .

→ B.M.O are formed by Constructive addition of wave function.   
A.BMO are formed by destructive addition of wave function.



- No. of combined A.O's = No. of formed M.O's.
- Each M.O. have maximum  $2e^-$ 's with opposite spin and  $e^-$ 's filling in M.O's follows all rules like Aufbau, Hund's & pauli's rules.
- M.O's are defined as 3D space in a molecule at which probability of finding  $e^-$ 's are maximum just like A.O's.
- All Stability of molecule is defined by Bond order (No. of bonds present b/w 2 atoms)

$$B.O = \frac{N_b - N_a}{2}$$

$N_b \rightarrow$  No. of bonding  $e^\ominus$ 's

$N_a \rightarrow$  No. of antibonding  $e^\ominus$ 's

$B.O \propto$  Bond stability

$B.O \propto$  Bond strength

$$B.O \propto \frac{1}{\text{Bond length.}}$$

if  $B.O = 0 \rightarrow$  molecule does not exists.

\* The  $B.O$  and Bond strength are directly proportional with each other. Therefore, higher the  $B.O$ , greater will be the bond strength and greater will be the stability of molecules.

→ Magnetic behaviour :

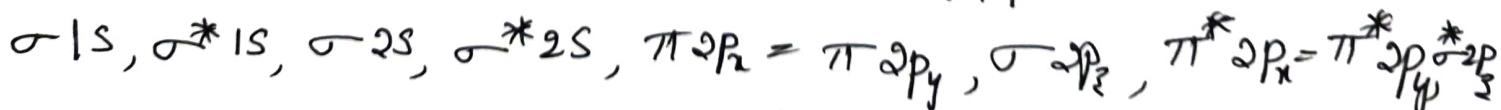
paramagnetic — if unpaired  $e^\ominus$  is present

diamagnetic — if all  $e^\ominus$ 's are paired.

→  $e^\ominus$  Configuration :

(a) Lighter molecules (no. of  $e^\ominus$ 's upto 14)

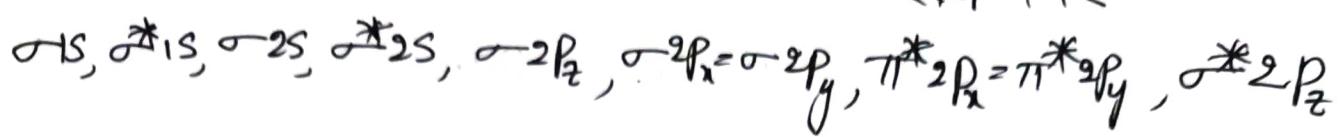
$> 14$



↗ Increasing order of energy

(b) Heavier molecules (no. of e<sup>-</sup>'s more than 14)

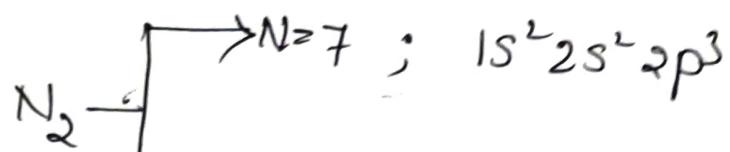
<14<



Energy ↑

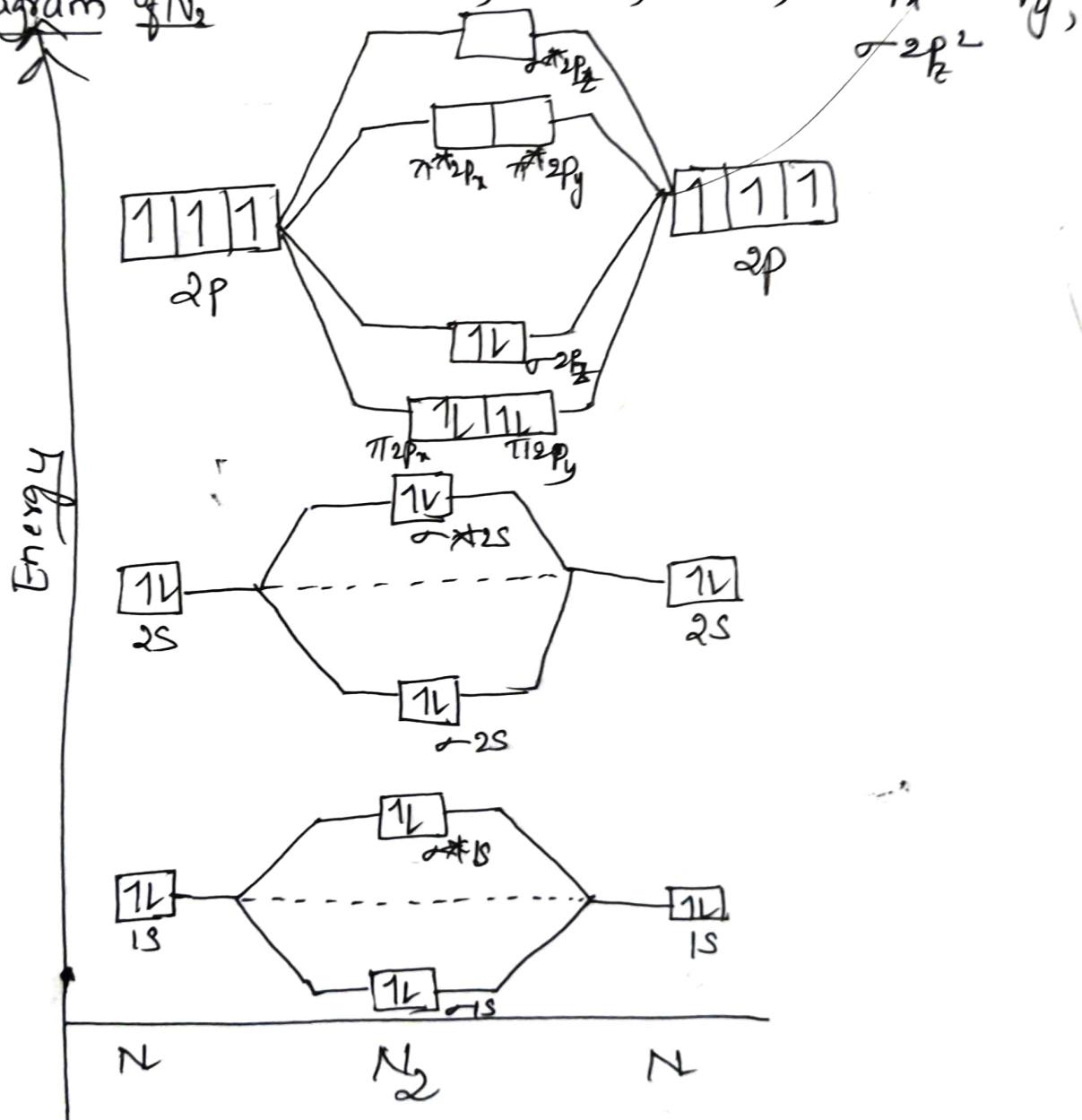
## Energy level diagrams :

N<sub>2</sub> molecule:



\* Configuration  $\text{Total} = 14 \text{ electrons}$   
 $\text{Total} = 18^2$

## M.O. diagram of $N_2$

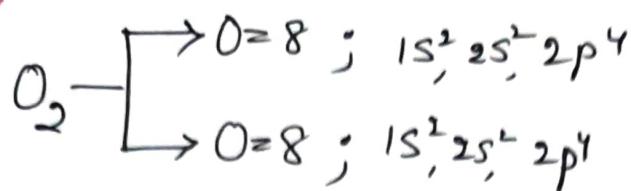


$$* B.O = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = \frac{6}{2} = 3$$

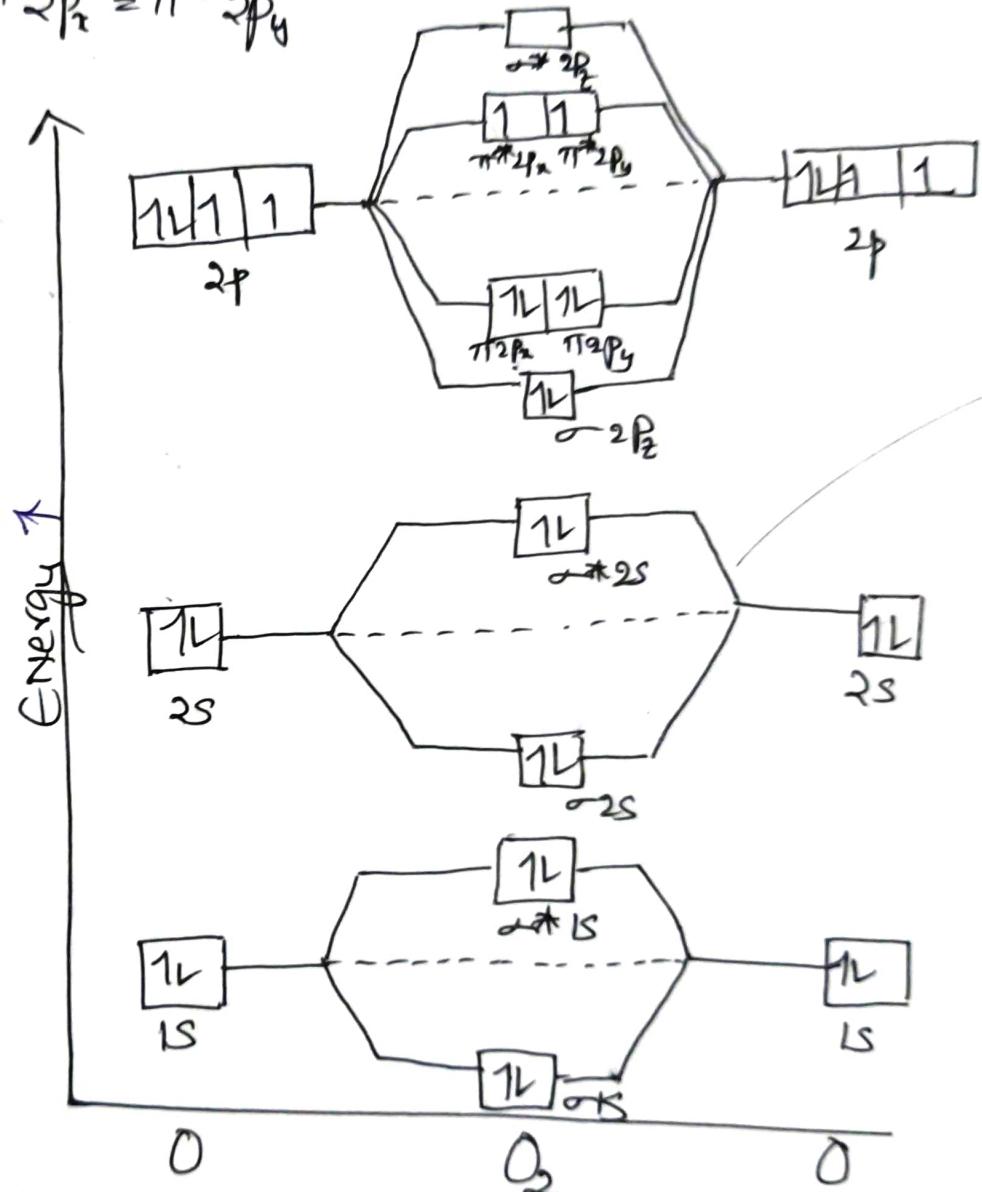
$$N \equiv N$$

\* Magnetic Nature — Since all e<sup>⊖</sup>s are paired  
So diamagnetic.

$O_2$  molecule : No. of  $e^\ominus/\delta = 16$  (heavier)



\* Configuration -  $\sigma 1S^2, \sigma^* 1S^2, \sigma 2S^2, \sigma^* 2S^2, \sigma 2P^2, \pi 2P_x^2 = \pi 2P_y^2,$   
 $\pi^* 2P_z^1 = \pi^* 2P_y^1$



$$* B.D = \frac{N_b - N_a}{2}$$

$$B.D = \frac{10 - 6}{2} = 2$$

\* Magnetic Nature  $\rightarrow O = O$  paramagnetic - because of presence of unpaired  $e^\ominus/\delta$

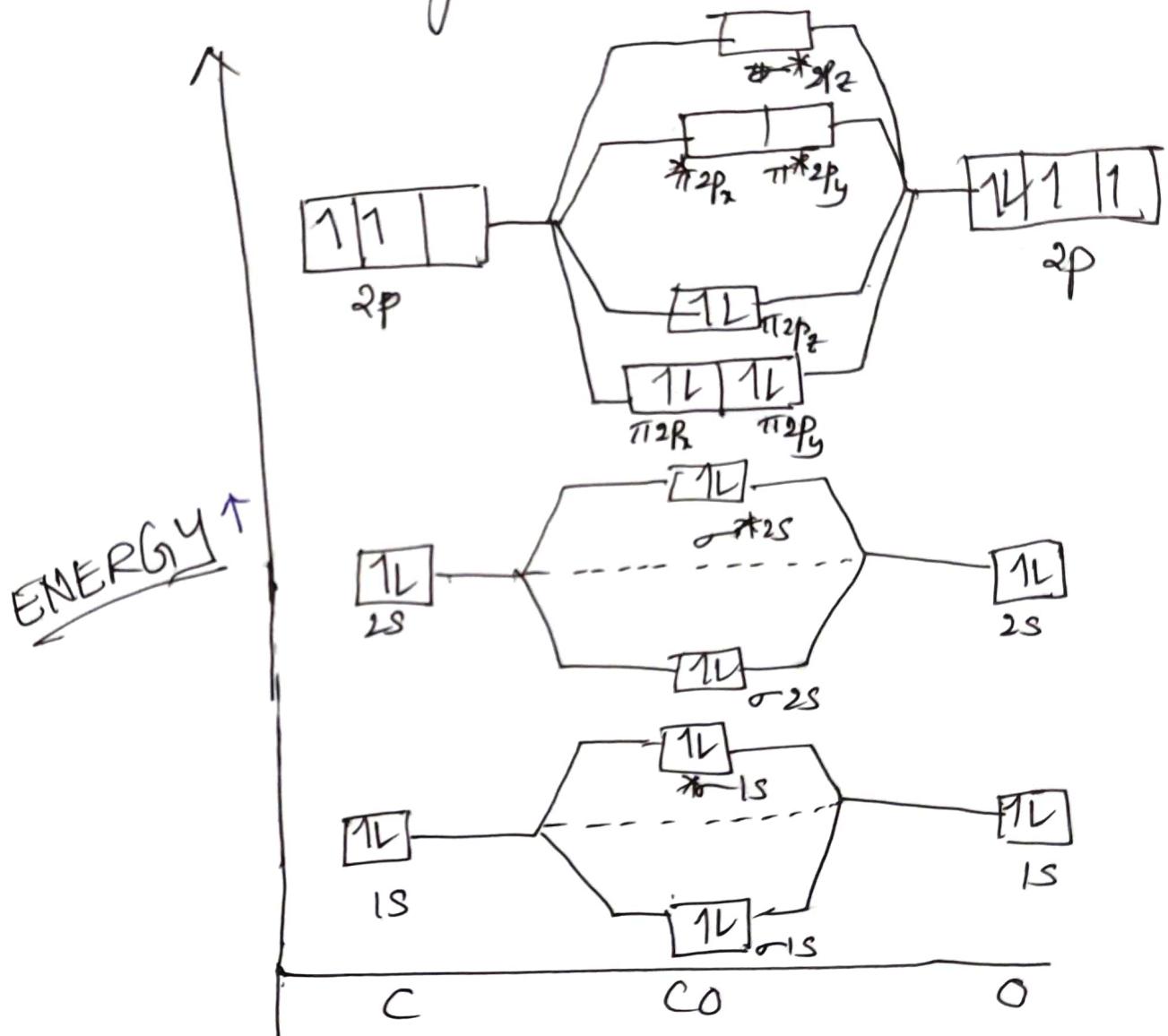
## CO molecule:

$$\text{No. of } e^{\ominus}/\text{atom} = 14$$

CO → C = 6 ;  $1s^2 2s^2 2p^2$

CO → O = 8 ;  $1s^2 2s^2 2p^4$

\* Configuration —  $\sigma 1s^2$ ,  $\sigma^* 1s^2$ ,  $\sigma 2s^2$ ,  $\sigma^* 2s^2$ ,  $\pi 2p_z^2$  =  $\pi^* 2p_y^2$ ,  $\sigma^* p_x^2$ ,  
 $\pi^* 2p_x^2$  =  $\pi 2p_y^2$ ,  $\sigma^* 2p_z$

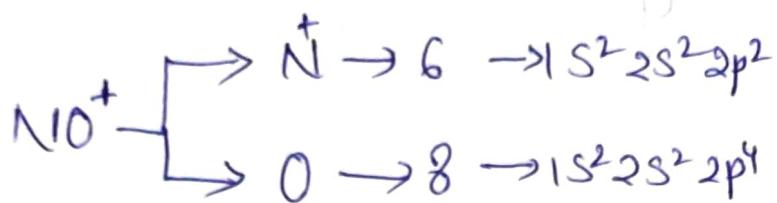


$$* \text{ B.O.} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3. \quad ; \quad C \equiv O$$

\* Magnetic Behaviour → Diamagnetic — Bf doesn't contain lone pair unpaired  $e^{\ominus}$

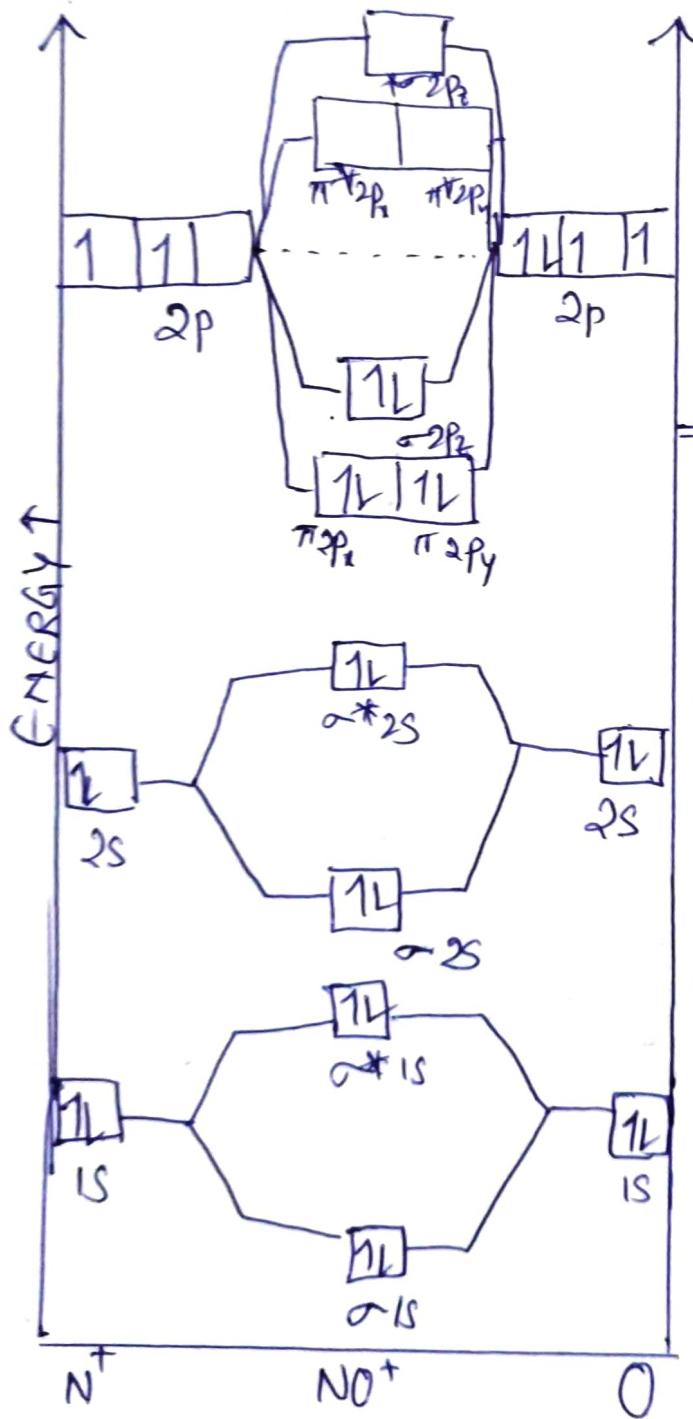
# M.O. diagrams of $\text{NO}^+$ , $\text{NO}$ , $\text{CO}^+$ , $\text{CO}^-$

$\text{NO}^+$ :



Total no. of  $e^\ominus$ s in  $\text{NO}^+$  = 14  $e^\ominus$ s.

M.O. configuration of  $\text{NO}^+$  ion =  $\sigma 1\text{S}^2, \sigma^* 1\text{S}^2, \sigma 2\text{S}^2, \sigma^* 2\text{S}^2, \pi 2\text{p}_x^2 = \pi 2\text{p}_y^2, \sigma 2\text{p}_z^2$



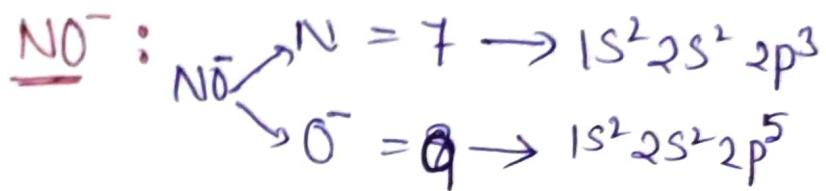
$$\text{B.O.} = \frac{\text{Nb} - \text{Na}}{2}$$

$$= \frac{10 - 4}{2} = \frac{6}{2} = 3$$

$$\Rightarrow \boxed{\text{B.O.} = 3}$$

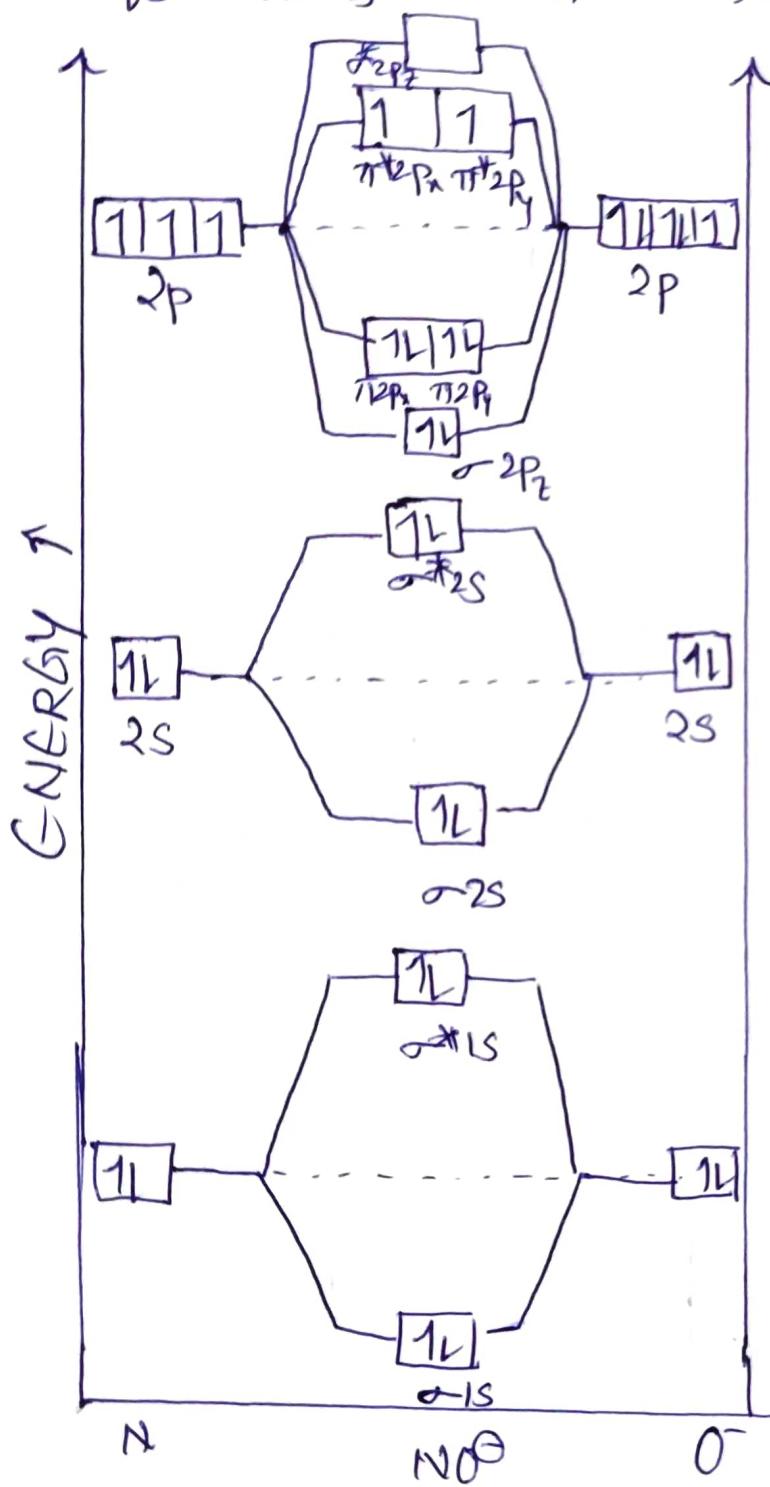
$\Rightarrow$  Magnetic behavior -

Diamagnetic due to the presence of all paired  $e^\ominus$ s  
 $\Rightarrow$  Colourless molecule - due to absence of unpaired  $e^\ominus$ s.  
 $\Rightarrow$  Low spin molecule.



Total no. of e<sup>-</sup>s in NO<sup>-</sup> = 16 e<sup>-</sup>s

M.O. configuration of NO<sup>-</sup> ion =  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \pi 2p_x^2 = \pi 2p_y^2$ ,  $\pi^* 2p_z^1 - \pi^* 2p_y^1$ .



$$\Rightarrow B.O. = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2$$

$$B.O. = 2$$

- ⇒ Magnetic behaviour
  - Paramagnetic in nature due to the presence of unpaired e<sup>-</sup>s in π<sub>2p<sub>x</sub></sub> & π<sub>2p<sub>y</sub></sub>.
- ⇒ Coloured compound
  - Due to the presence of unpaired e<sup>-</sup>s having high spin.