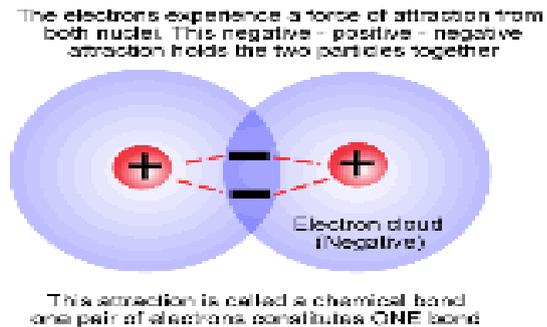


Hybridization in Chemistry

Hybridization in Organic and
Inorganic Compounds.

Chemical Bonding

- *Chemical bonds* are the **GLUE** holding atoms together to form Molecules. Obviously there must be some attractive force to hold them (atoms, molecules, ions, etc.) together.



- These attractive forces must be Chemical in nature and that could only be by the participation of electrons and if electrons are not involved then it will only be a physical bond.
- *“On the nature of Chemical bond” A book written by “Linus Pauling” known as “The Bible of Chemistry”*

What is Chemical Bonding ?

Chemical Bonding is a physical process in which same or different kind of atoms combine together to form molecules of elements or molecule of compounds respectively.

Chemical Bonding is a process in which rearrangement of electrons in atoms take place.

Chemical Bonding is a process in which atom tends to attain stability by - Completing their incomplete octet, this is **Octet Rule (Classical Concept)**

Chemical Bonding is a process in which atom tends to attain stability by Pairing up their unpaired electrons, this is **Duplet Rule (Modern Concept)**

Chemical Bonding is a process in which atom tends to attain stability by having nearest **Inert Gas Configuration i.e., ns np**

Chemical Bonding is a process in which atom tends to attain stability by losing **Potential Energy** and this energy will be used to hold atoms together; more the loss of energy stronger will be the bond between them.

Chemical Bonding is a process in which atom tends to *attain* stability by transferring or sharing of electrons

Types of Bond –

- These can be classified into the following types: *ionic bond, covalent bond (equal or mutual sharing) including coordinate bond (unequal sharing), metallic bond, hydrogen bond and Vander Wall bond.*
- The relative strength of bonds are as follows -
Ionic bond > Covalent bond > Metallic bond > H bond > Vander Wall Force
- **H bond** is neither truly Chemical nor truly physical and Vander Waal bond is a physical bond.
- Among **Vander Waal bonds** the order in decreasing bond strength:
Dipole forces \succ *Debye or Induction forces* \succ *London or Dispersion Forces* ^{*Keesom or*}

Elements and Bonding

<i>Atoms involved in bonding</i>	<i>Types of Bonding</i>
<i>Metal + Non Metal</i>	<i>Ionic</i>
<i>Non Metal + Non Metal</i>	<i>Covalent</i>
<i>Metal + Metal</i>	<i>Metallic Bond</i>
<i>Electron deficient molecule or Ion (Lewis acid) and electron rich molecule or Ion (Lewis base)</i>	<i>Co ordinate or Dative or Bipolar bond</i>
<i>H and Electronegative elements (N, O, F)</i>	<i>Hydrogen Bond</i>

Elements and Bonding

Conditions for ionic bond	Low IE	High EA	High -ve value of LE
Conditions for covalent bond	High IE	Low EA	Low -ve LE

Ionic bond between (Adhesive force)	p + p block elements	M + NM	Low IE + High IE	HEN + HEP Elements	Difference in EN 1.7	P + d block element (LOS)
Covalent bond between (Cohesive force)	s + p block elements	NM + NM (M + M – Metallic bond)	HIE + HIE	HEN + HEN Elements	Difference in EN 1.7	P + d block element (HOS)

Basically forces of attractions are of two types -

- *Primary or Inter atomic Forces of attractions-*

It holds the atoms together in molecules by ionic, covalent or metallic bonds.

- *Secondary Weak or Inter molecular Forces of attraction-*

It holds molecules together in molecular aggregates. These are H-bond and Vander Waal Forces of attraction.

Valence Shell Electron Pair Repulsion Theory

- *Valence Shell Electron Pair Repulsion Theory (VSEPR)* was given by **Sidgwick and Powell** , developed by **Gillespie and Nyholm** to predict the shape of the simple covalent molecules or ions with single covalent bonds only.

Postulates of VSEPR Theory-

- The total number of valence electron pairs decides the shape of the molecule.
- The lone pair of electrons around the central atom are closer to each other, they will repel each other, occupy position in space that minimise repulsion and maximise distance between them and the energy of the molecule will be more.
- If lone pair of electrons are present on central atom the geometry of the molecule will be distorted.
- The strength of the repulsion is strongest in two lone pairs and weakest in two bond pairs.

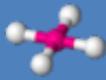
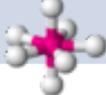
Predicting the Shapes of Molecules:

- The least EN atom must be the central atom.
- The atom which is least in number must be the central atom.
- The total number of valence electrons of the central atom must be counted.
- The total number of electrons shared with the central atom must be counted.

VSEPR – Tabular Study

Total pairs	Bonding electron pairs	Lone pairs	Electron domains (Steric #)	Shape	Ideal bond angle	Example	Image NMR	Electron Diffraction method
2	2	0	2	linear	180°	CO₂		
3	3	0	3	trigonal planar	120°	BF₃		
	2	1	3	bent	120° (119°)	SO₂		
4	4	0	4	tetrahedral	109.5°	CH₄		
	3	1	4	trigonal pyramidal	107.5°	NH₃		
	2	2	4	angular	104.5°	H₂O		
	1	3	4	Linear	180°	HCl		
		dSp²	dx²-y²	Square planar	90°	[Ni(CN) ₄] ²⁻ , [Co(NH ₃) ₄] ²⁺ , [PtCl ₄] ²⁻		
5	5	0	5, sp ³ d(dz ²)	trigonal bipyramidal	90°, 120°, 180°	PF ₅ , PCl ₅		
			dsp³ (dz ²)	TGBP		[Fe(CO) ₅]		
	4	1	5	See saw	180°	SF ₆		

VSEPR – Tabular Study

4					2	6 square planar square planar d^2sp^3 dz^2, dx^2-y^2 Octahedral	$90^\circ, 180^\circ$ 90°	XeF_4, ICl_4^- , XeF_4		
7	0	7	sp^3d^3 dxy, dyz, dxz	pentagonal bipyramidal	$90^\circ, 72^\circ$	I_7				

Limitations of VSEPR-

- Shape of many molecules can't be predicted, so modern theories are given-
- *Valence Bond Theory (VBT)*
- *Molecular Orbital Theory (MOT)*
- This theory fails to explain iso electronic species.
- The VSEPR theory does not shed any light on the compounds of transition metals.
- Another limitation of VSEPR theory is that it predicts that halides of group 2 elements will have a linear structure, whereas their actual structure is a bent one.

Valence bond theory - VBT

- *Introduction* – Valence bond theory - VBT primarily focuses on the formation of individual bonds from the atomic orbitals of the atoms during the formation of a molecule.
- Valence Bond theory was given by *Heitler and London* and was further developed by *Pauling and Slater*.

Postulates of VBT –

- Atomic orbitals of approximately same energy level overlap each other to form covalent bond.
- Atomic orbitals having unpaired electrons can overlap each other.
- Number of half filled atomic orbital is equal to valence of that atom.
- Spin of the electron overlapping each other must be opposite.
- Greater the extent of the overlapping more will be the strength of the bond.

Limitations of VBT –

- According to VBT Oxygen molecule is diamagnetic in nature but as we know Oxygen is paramagnetic in nature but VBT can't explain it.
- Failure to explain the tetra covalence exhibited by carbon.
- No distinction between weak and strong ligands.
- No explanation for the colour exhibited by coordination compounds

Hybridization

- Process of mixing of two or more atomic orbitals of approximately same energy level to form new hybrid orbitals is called *hybridization* .
- Number of hybrid orbitals formed is always equal to the number of atomic orbitals taking part.

Hybridized orbitals and Molecular orbitals

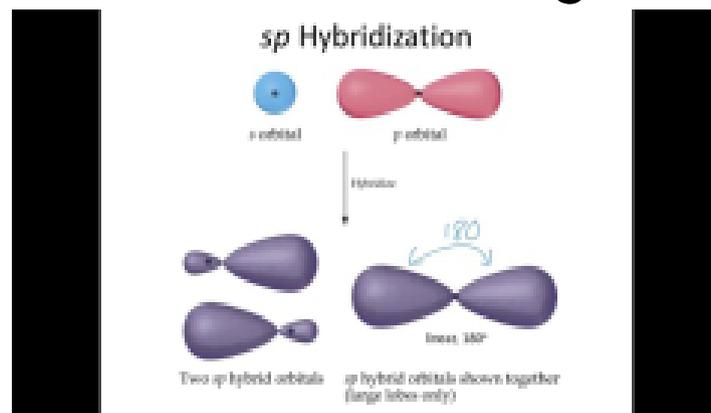
Hybridized orbitals	Molecular orbitals
Formed by excitation of atomic orbitals.	By combination of atomic orbitals.
More stable than atomic orbital.	More or less unstable than atomic orbital.
Greater energy than atomic orbital.	Less or more than atomic orbital.
Always bonding.	Maybe bonding or anti bonding.
Mono centric because made of one atom.	Poly centric because made of more than one atom.

Types of Hybridization -

- ***Sp or Linear or diagonal Hybridization-***
- One s and one p orbital of approximately same energy level in an atom mix to form two new equivalent sp hybridized orbitals.
- Geometry of the molecule will be linear with an angle of 180° .
- Each sp hybridized orbital has an equal amount of s and p character, i.e., 50% s and p character.

Sp or Linear or diagonal Hybridization-

- Be – Atomic Number = 4
- Ground state Electronic Configuration - $1s^2, 2s^2$
- Excited state Electronic Configuration - $1s^2, 2s^1 2p^1$



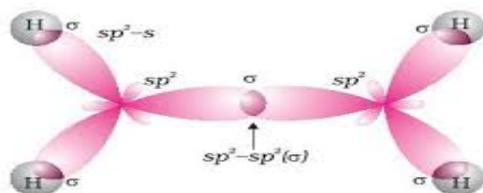
- Shown by Be in BeCl_2 , BeF_2 , and BeH_2 .

Sp or Linear or diagonal Hybridization in Alkynes-

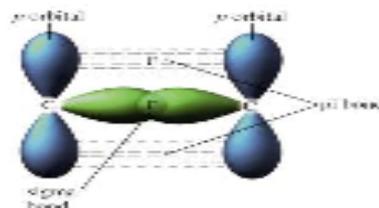
- In alkynes with triple bonds is explained by sp hybridisation. The 2s atomic orbital of C is mixed with only one of the three p orbitals, resulting in two sp hybridized orbitals. So in acetylene (ethyne) (C_2H_2) sp-sp overlap between the two carbon atoms forming a σ bond and two additional π bonds formed by p-p overlap. Its shape will be linear and bond angle will be 180° .

Sp² or Planar Hybridization-

- It is formed when one s and two p orbitals of the same shell of an atom mix to form 3 equivalent sp² Hybridized orbitals.
- Shape of the molecule will be Trigonal planar, bond angle will be 120° and s and p character will be 33% and 67% respectively.



Orbital picture of ethene depicting
σ bonds only



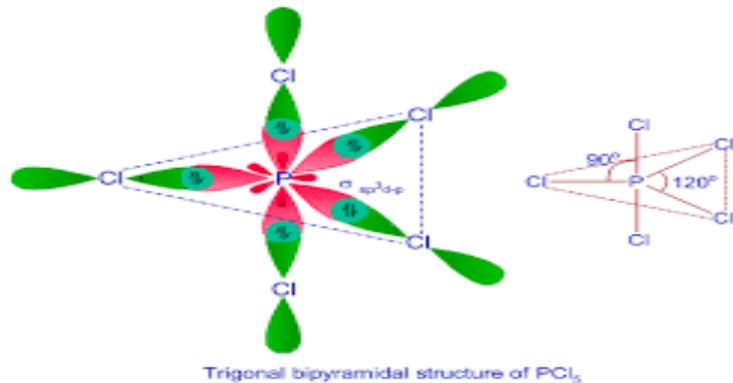
- In Ethene $H_2C=CH_2$, carbon is sp² hybridized, because between 2 carbon atoms 1 sigma and 1 pi bond and each C is further attached with 2 H atom through sigma bond (s-sp² overlap) so three σ bonds are formed per carbon atom.

sp³ or Tetrahedral Hybridization-

- Carbon's ground state configuration is $1s^2 2s^2 2p^2$.
- The carbon atom can also bond to four hydrogen atoms by an excitation (or promotion) of an electron from the doubly occupied 2s orbital to the empty 2p orbital, producing four singly occupied orbitals.
- In CH_4 , four sp^3 hybrid orbitals of C are overlapped by 1s orbitals of Hydrogen, yielding four σ (sigma) bonds (that is, four single covalent bonds) of equal length and strength.

sp^3d hybridization-

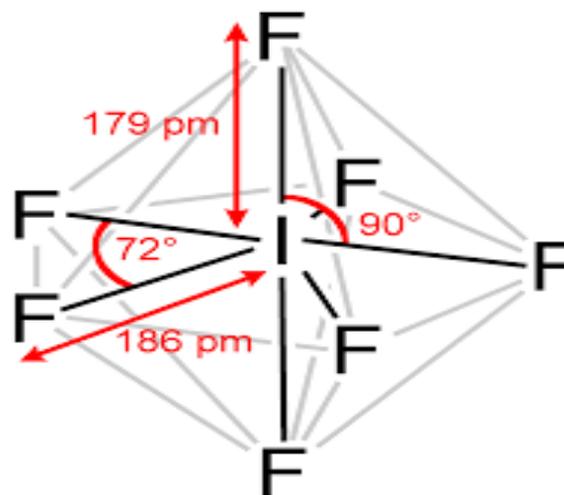
- one s atomic orbital combines with the three p and one d atomic orbitals of the same energy level to form a molecule having Trigonal bipyramidal geometry of bond angle 120° (3 longer equatorial positions) and 90° (2 shorter axial positions).



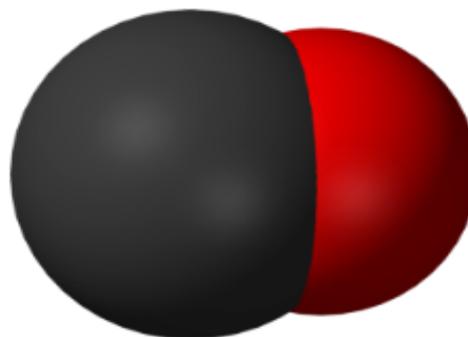
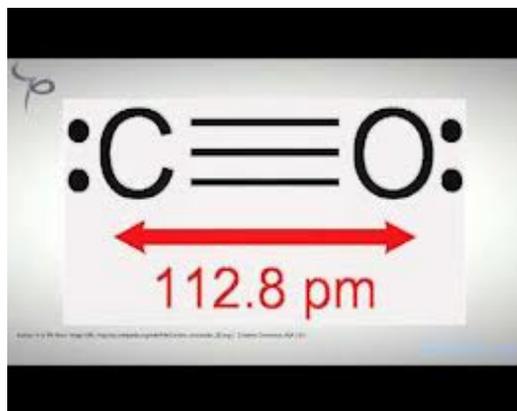
- P in excited state shows sp^3d hybridization in PCl_5 molecule and in ground state shows sp^3 in PCl_3 .

sp^3d^2 and sp^3d^3 hybridization-

- S in SF_6 shows sp^3d^2 hybridization, two d orbitals taking part are dz^2 and dx^2-y^2 and have octahedral geometry.
- I in IF_7 shows sp^3d^3 hybridization, geometry will be pentagonal bipyramidal, bond angles will be 90° and 72° .



Hybridization in CO –



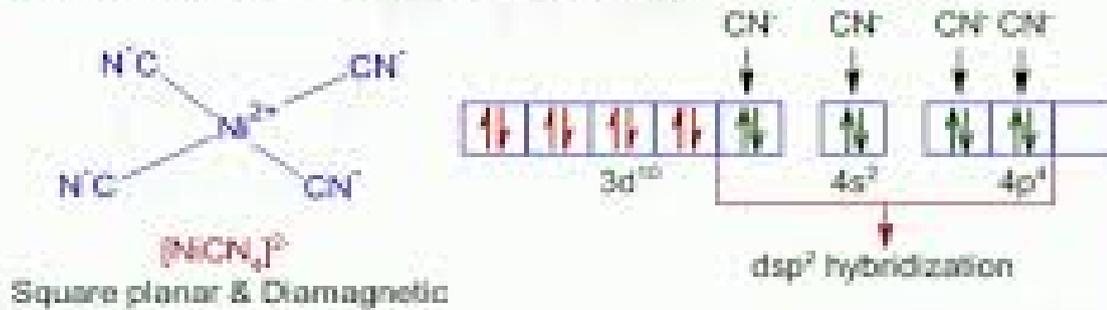
- **Hybridization in CO –**

- C in CO has 1 bond pair and 1 lone pair, so total 2 pairs, hybridization will be sp and geometry will be linear.
- As we know in hybridization only sigma bond will be considered never pi bond.
- O in CO has 1 bond pair and 1 lone pair, so total 2 pairs, hybridization will be sp and geometry will be linear.

dsp² Hybridization



- The empty 4d, 3s and two 4p orbitals undergo dsp² hybridization to make bonds with CN⁻ ligands in square planar geometry. Thus $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic.



Method to calculate Hybridization-

- $X = SA + \frac{1}{2} (G - V - E)$
- X = Number of Hybridized orbitals,
- SA = Number of surrounding atoms,
- G = Number of valence electrons
- V = Valence
- E = Charge
- In IF₅ hybridization shown by I will be
- $X = 5 + \frac{1}{2} (7 - 5 + 0)$
- =6, sp₃d₂
- Number of surrounding atoms to I is 5 so X=5, Number of valence electrons in I is 7 so G=7, valence of I is 5 because attached to 5 mono valent I atoms so V = 5 and charge is 0

H_3PO_4 and ClO_4^- hybridization

- *In HPO_4 hybridization shown by P will be*

- $X = 7 + \frac{1}{2} (5 - 11 + 0)$

- $=4, sp$

- Number of surrounding atoms to P is 7 so $X=7$, Number of valence electrons in P is 5 so $G=5$, valence of P is 11 because attached to 4 divalent O atoms and 3 mono valent H atoms so total $V = 11$ and Charge is 0

- *In ClO_4 hybridization shown by Cl will be*

- $X = 4 + \frac{1}{2} (7 - 8 + 1)$

- $=4, sp$

- Number of surrounding atoms to Cl is 4 so $X=4$, Number of valence electrons in Cl is 7 so $G=7$, valence of Cl is 8 because attached to 4 divalent O atoms so $V = 8$ and charge is -1 so $E = +1$

Odd electron bond

- Odd electron bond containing species
Such as NO, NO₂, ClO₂, Br₃O₈ always show
sp² hybridization, are Paramagnetic in
nature and have fractional Bond order =
1.5 or 2.5 etc.

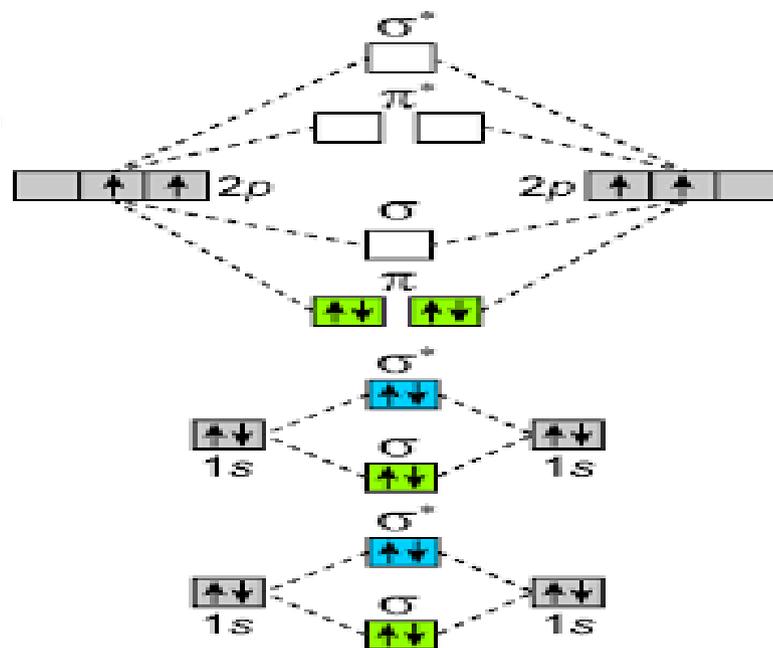
Molecular Orbital Theory (MOT) — was given by ~~H~~und and Mullikan

• Postulates of MOT:

1. Molecular orbital theory asserts that atomic orbitals no longer hold significant meaning after atoms form molecules. Molecular orbital theory holds electrons reside in molecular orbitals that are distributed over the entire molecule.
2. Atomic orbitals of comparable energy and proper symmetry combine together to form molecular orbitals.
3. The total number of orbitals is conserved; the number of molecular orbitals equals the number of original atomic orbitals.
4. When atomic orbitals interact, if added then it results in a bonding orbital and if subtracted then an anti bonding orbital is obtained. Anti bonding orbitals are denoted with an asterisk (*).
$$\psi = \psi \quad \sigma = \psi + \psi \quad \sigma^* = \psi - \psi$$
5. The movement of electrons in a molecular orbital is influenced by all the nuclei of combining atoms.

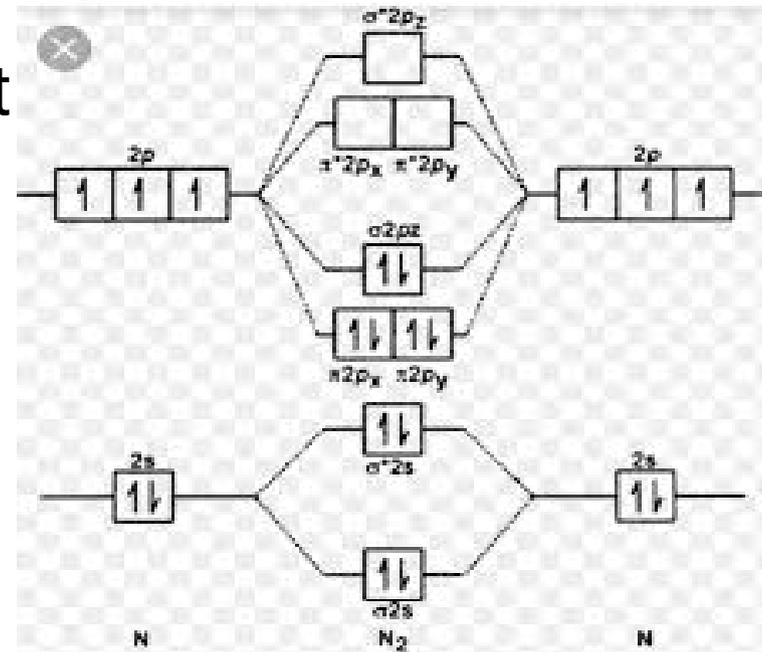
MOT of Different Molecules-

- *MOT of B₂ Molecule-*
- i. Molecular orbital diagram-MOD
- ii. MEC - $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2$
- iii. Bond Order
- iv. Magnetic Nature- Diamagnetic
- v. Stability - stable can exist



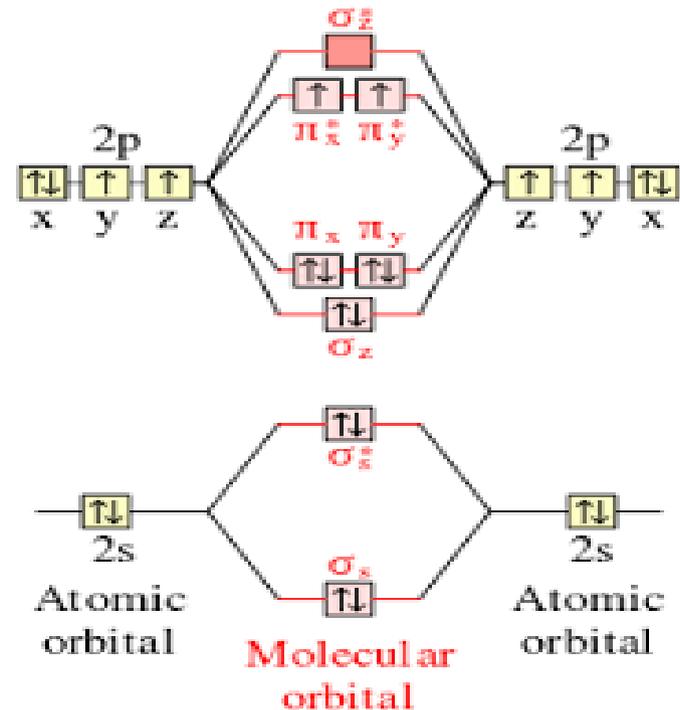
MOT of N₂ Molecule-

- i. Molecular orbital diagram
- ii. MEC - $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2,$
 $\pi^* 2p_x^0 = \pi^* 2p_y^0, \sigma^* 2p_z^0$
- iii. Bond Order = $n_b - n_a / 2 = 10 - 4 / 2 = 3$
- iv. Magnetic Nature- Diamagnet
- v. Stability - stable can exist



MOT of O₂ Molecule-

- i. Molecular orbital diagram
- ii. MEC - $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2,$
 $\pi^* 2p_x^1 = \pi^* 2p_y^1, \sigma^* 2p_z^0$
- iii. Bond Order = $n_b - n_a / 2 = 8 - 2 / 2 = 3$
- iv. Magnetic Nature - Paramagnetic
- v. Stability- stable can exist



Molecule/ion	Total Ion of electrons	Molecule Orbital Configuration	Bond Order	Magnetic Nature
O ₂ ⁺	15	KK(σ_{1s}) ² (σ_{1s}^*) ² (σ_{2s}) ² (π_{2p_x}, π_{2p_y}) ⁴ ($\pi_{2p_z}^*$) ¹	2.5	Paramagnetic
O ₂	16	KK(σ_{1s}) ² (σ_{1s}^*) ² (σ_{2s}) ² (π_{2p_x}, π_{2p_y}) ⁴ ($\pi_{2p_z}^*$) ²	2	Paramagnetic
O ₂ ⁻ (superoxide ion)	17	KK(σ_{1s}) ² (σ_{1s}^*) ² (σ_{2s}) ² (π_{2p_x}, π_{2p_y}) ⁴ ($\pi_{2p_z}^*$) ³	1.5	Paramagnetic
O ₂ ²⁻ (peroxide ion)	18	KK(σ_{1s}) ² (σ_{1s}^*) ² (σ_{2s}) ² (π_{2p_x}, π_{2p_y}) ⁴ ($\pi_{2p_z}^*$) ⁴	1	Diamagnetic

MOT of CO Molecule-

- i. Molecular orbital diagram
- ii. MEC- $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2, \pi^* 2p_x^0 = \pi^* 2p_y^0, \sigma^* 2p_z^0$
- iii. Bond Order = $n_b - n_a / 2, 8 - 2 / 2 = 3$
- iv. Magnetic Nature- Diamagnetic
- v. Stability- stable can exist