

Atomic and molecular structure

Introduction:

Atom:

An atom is the smallest unit of matter and indivisible. They are made up of particles called protons, neutrons and electrons, which are responsible for the mass and charge of atoms.

Orbit: It is a circular path around the nucleus in which an electron revolve.

Orbital: It is a 3D space where the probability of finding an electron is maximum.

Node: It is a space where the probability of finding an electron is zero.

Molecule: Atoms combine to form molecules.

Atomic orbital:

- Atomic orbital is a region in space just outside of the nucleus of the atom, where the probability of finding an electron is high (95%).
(or)
- Atomic orbitals are regions of space in which electrons can be found.
- Two electrons can fit in each orbital and different orbitals have different shapes.
- Atomic orbitals are less stable and mono centric.

Ex: s,p,d and f orbitals

s (spherical shape), p (dumb bell shape)

Molecular orbital:

- Two or more atomic orbitals combine together to form molecular orbitals.
- Molecular orbitals are more stable and polycentric.

Molecular orbital theory:

- Molecular orbital theory was proposed by Friedrich Hund and Mulliken.
- According to molecular orbital theory, molecular orbitals are formed by the Linear Combination (addition or subtraction) of Atomic Orbitals of atoms.
- No. of atomic orbitals are equal to the no. of molecular orbitals formed.
- The electrons are filled into molecular orbitals in the increasing order of orbital energy.
- The combination of atomic orbitals occurs when the combining atomic orbitals have similar energies.

Linear Combination of Atomic Orbitals: (LCAO)

- Consider two atoms A and B, which form a molecule AB.
Let wave function of atom A = ψ_A and wave function of atom B = ψ_B .
- The wave function for the molecular orbitals can be obtained by a linear combination of atomic orbitals ψ_A and ψ_B . i.e addition or subtraction of wave functions of atomic orbitals.

$$\psi_{MO} = \psi_A \pm \psi_B$$

- The above equation forms two molecular orbitals.
1) Bonding molecular orbital 2) Anti bonding molecular orbital

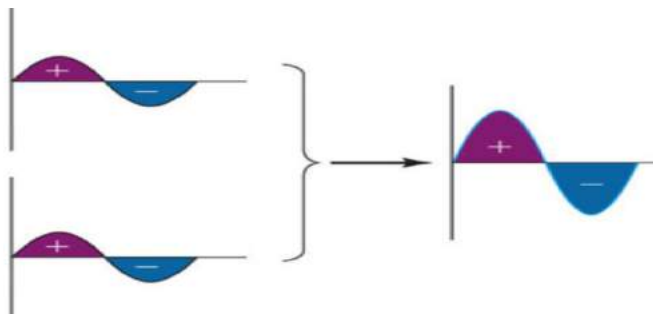
Bonding molecular orbital:

Bonding molecular orbitals are formed by the constructive interference (addition) of wave functions of atomic orbitals.

$$\psi_b = \psi_A + \psi_B$$

ψ_b = Wave function of bonding molecular orbital.

Constructive interference: it occurs when in phase waves meet with each other and form a new wave with greater amplitude.



According to above equation

$$\psi_b = \psi_A + \psi_B$$

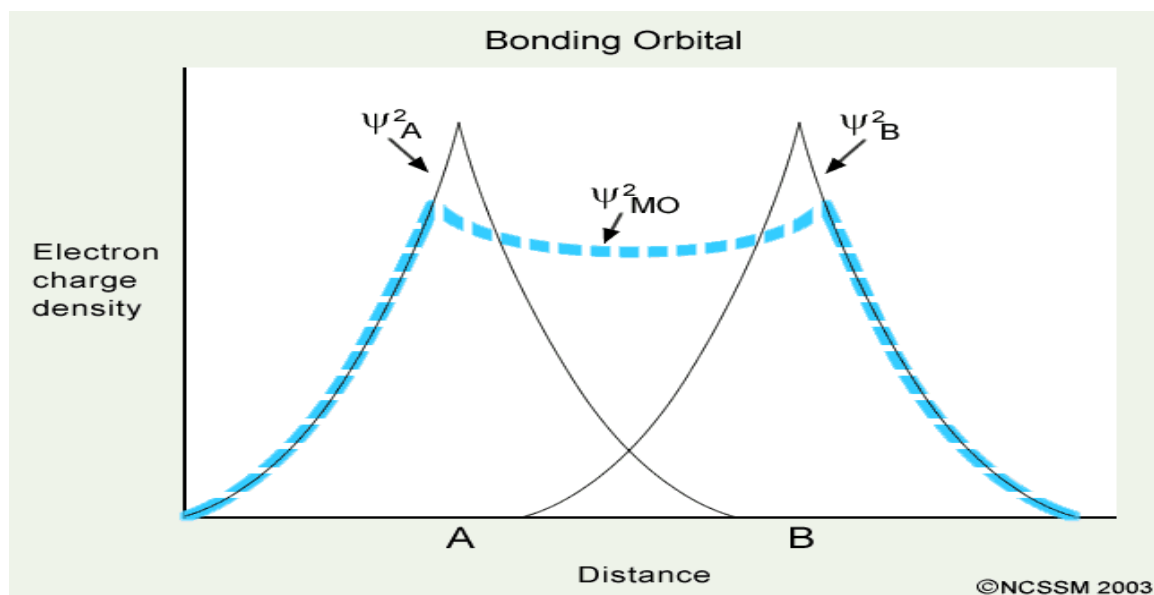
Probability density is given by ψ^2

$$\psi_b^2 = (\psi_A + \psi_B)^2$$

$$\psi_b^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

$$\psi_b^2 > \psi_A^2 + \psi_B^2 \text{ by } 2\psi_A\psi_B$$

Probability of finding an e^- in bonding molecular orbital is greater than atomic orbitals.



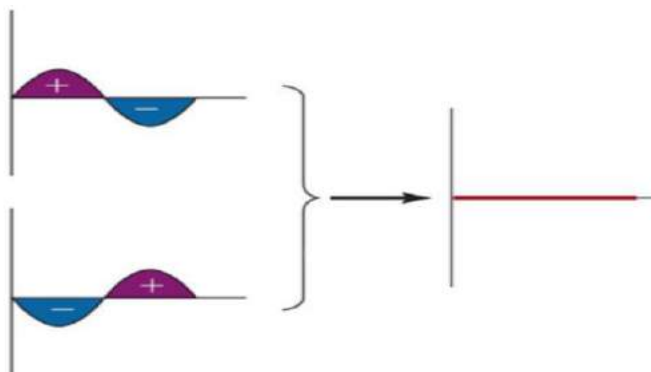
Anti bonding molecular orbital:

Anti bonding molecular orbitals are formed by the destructive interference (subtraction) of wave functions of atomic orbitals.

$$\psi_a = \psi_A - \psi_B$$

ψ_a = Wave function of anti bonding molecular orbital.

Destructive interference: it occurs when out of phase waves meet with each other and form a new wave with lesser or zero amplitude.



According to above equation

$$\psi_a = \psi_A - \psi_B$$

Probability density is given by ψ^2

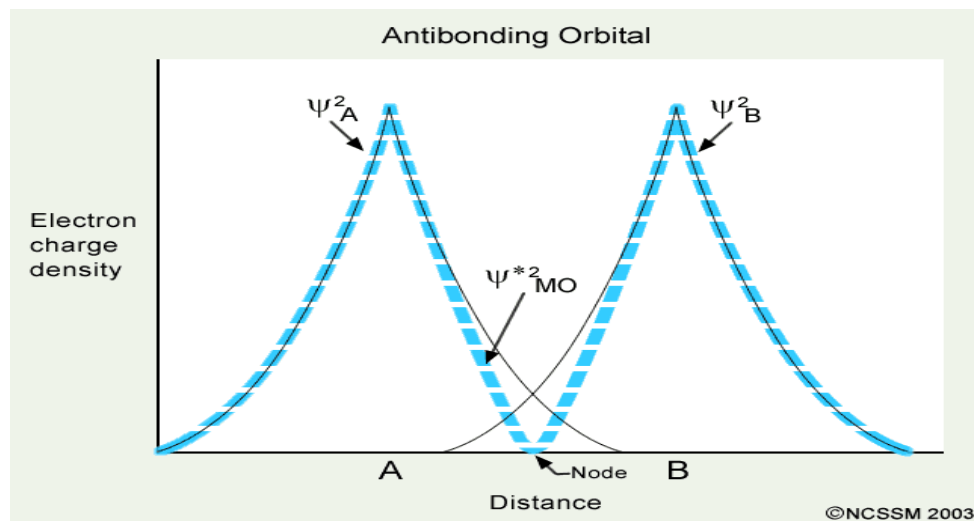
$$\psi_a^2 = (\psi_A - \psi_B)^2$$

$$\psi_a^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$

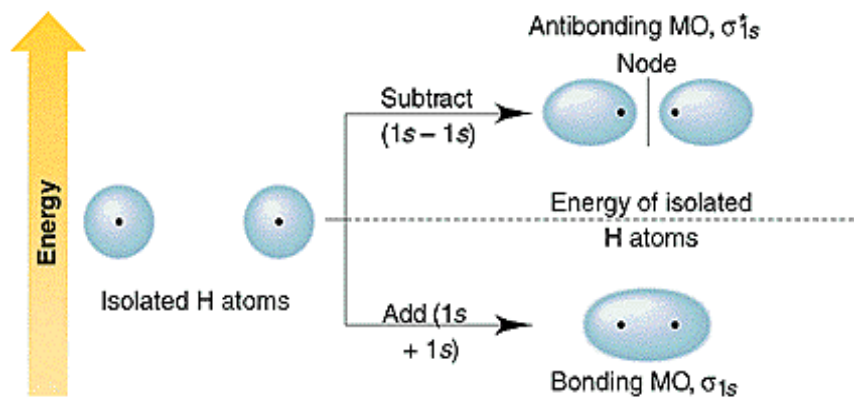
$$\psi_a^2 < \psi_A^2 + \psi_B^2 \text{ by } 2\psi_A\psi_B$$

Probability of finding an e^- s in anti bonding molecular orbital is less than atomic orbitals.

Therefore, combination of two atomic orbitals results in the formation of two molecular orbitals. One is bonding molecular orbital (BMO) whereas other is anti bonding molecular orbital (ABMO).



Ex: Formation of H_2 molecule



- BMO has lower energy and greater stability than AMBO.
- ABMO has higher energy and less stability than BMO.

Energy level diagrams of molecular orbitals:

Order of energy of various molecular orbitals:

- Molecule which contains ≤ 14 e-

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_y = \pi 2p_z) < \sigma 2p_x < (\pi^* 2p_y = \pi^* 2p_z) < \sigma^* 2p_x$$

- Molecule which contains > 14 e-

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < (\pi 2p_y = \pi 2p_z) < (\pi^* 2p_y = \pi^* 2p_z) < \sigma^* 2p_x$$

- Bond order (B.O) = $\frac{\text{no. of e- in BMO} - \text{no. of e- in ABMO}}{2}$

Magnetic behavior:

- Molecules with unpaired electrons are paramagnetic.
- Molecules with paired electrons are diamagnetic.

Energy level diagrams of N₂:

- Nitrogen(N) atomic number = 7
- Electronic configuration: $1s^2 2s^2 2p^3$
- No. Of electrons in N₂ molecule = 14
- Order of energy of various molecular orbitals in N₂ molecule:

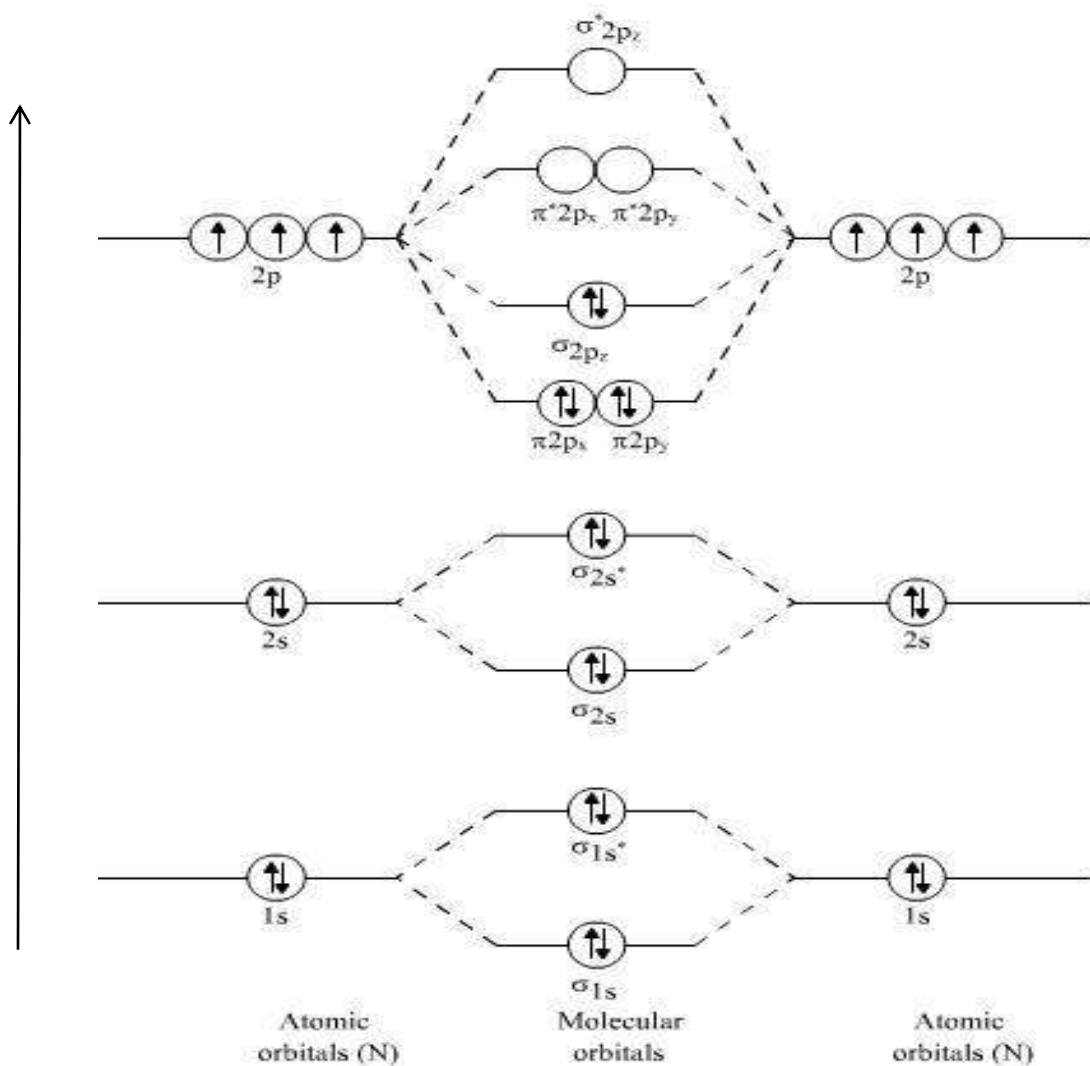
$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_y = \pi 2p_z) < \sigma 2p_x < (\pi^* 2p_y = \pi^* 2p_z) < \sigma^* 2p_x$$

$$\text{bond order (B.O)} = \frac{\text{no. of electrons in BMO} - \text{no. of electrons in ABMO}}{2}$$

$$\text{bond order (B.O)} = \frac{10 - 4}{2}$$

$$\text{bond order (B.O)} = 3$$

- N₂ molecule has paired electrons so, it is a diamagnetic compound.



Energy level diagrams of O₂:

- Oxygen (O) atomic number = 8
- Electronic configuration: $1s^2 2s^2 2p^4$
- No. Of electrons in O₂ molecule = 16
- Order of energy of various molecular orbitals in O₂ molecule:

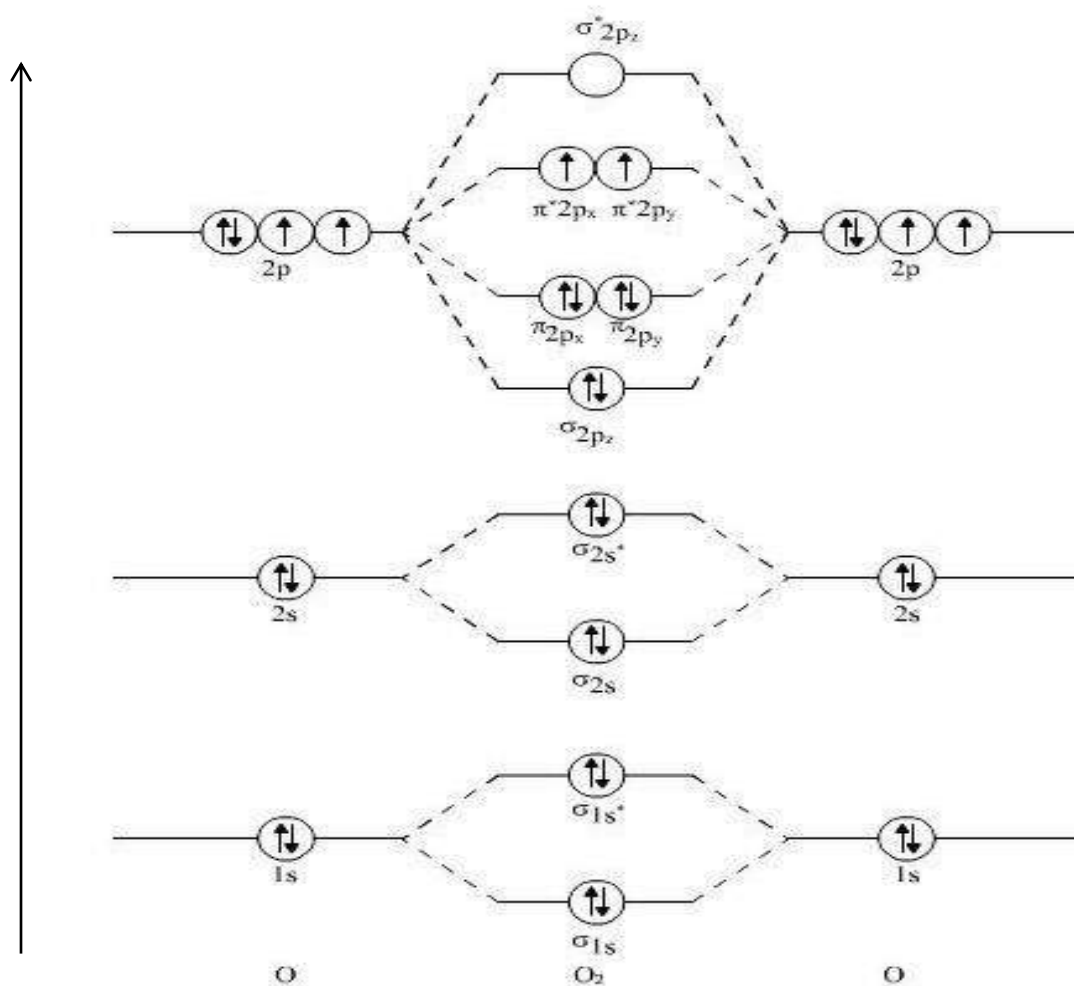
$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < (\pi 2p_y = \pi 2p_z) < (\pi^* 2p_y = \pi^* 2p_z) < \sigma^* 2p_x$$

$$\text{bond order (B.O)} = \frac{\text{no. of electrons in BMO} - \text{no. of electrons in ABMO}}{2}$$

$$\text{bond order (B.O)} = \frac{10 - 6}{2}$$

$$\text{bond order (B.O)} = 2$$

- O₂ molecule has unpaired electrons so, it is a paramagnetic compound.



Energy level diagram of F₂:

- Fluorine ((F) atomic number = 9
- Electronic configuration: 1s² 2s² 2p⁵
- No. Of electrons in F₂ molecule = 18
- Order of energy of various molecular orbitals in F₂ molecule:

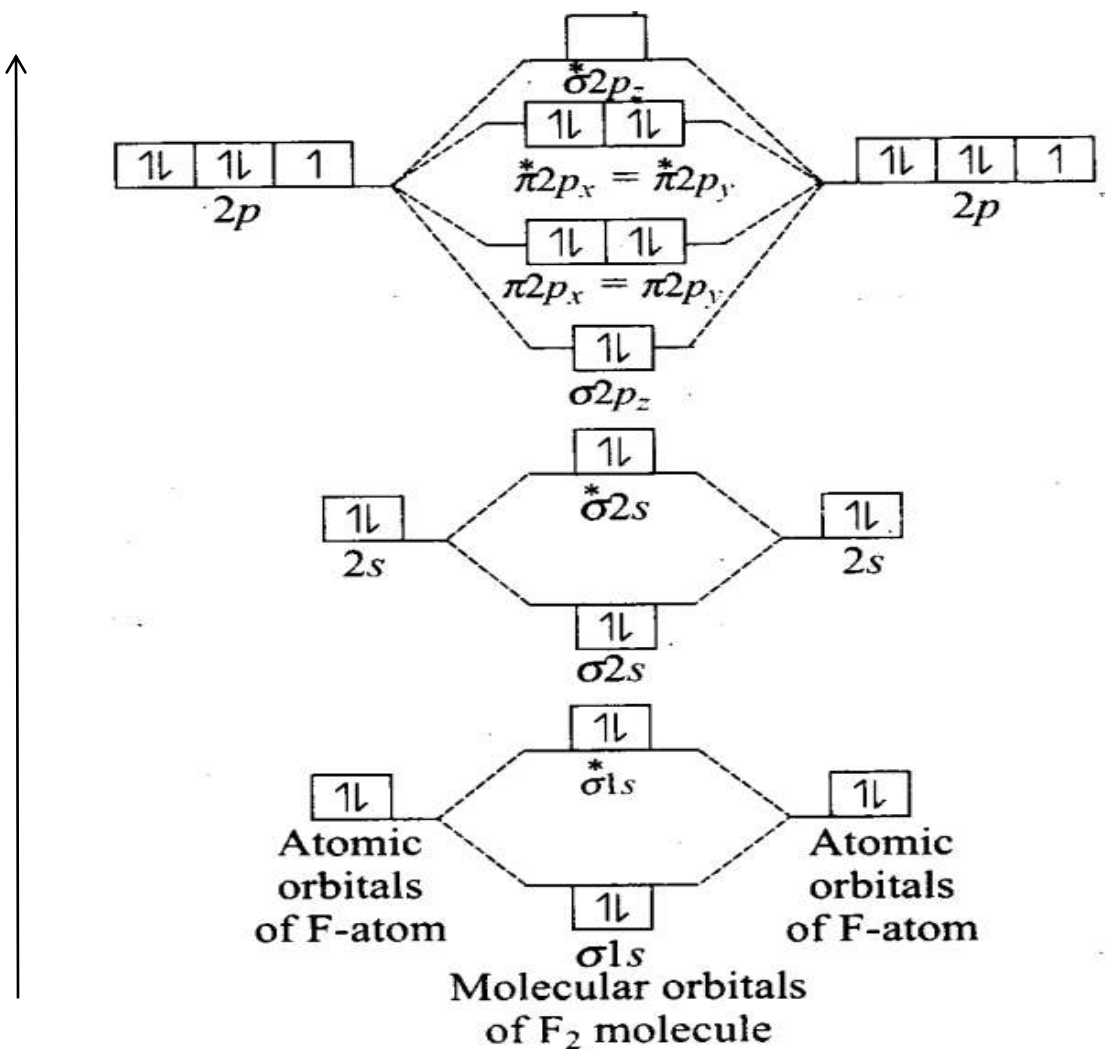
$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < (\pi 2p_y = \pi 2p_z) < (\pi^* 2p_y = \pi^* 2p_z) < \sigma^* 2p_x$$

$$\text{bond order (B.O)} = \frac{\text{no. of electrons in BMO} - \text{no. of electrons in ABMO}}{2}$$

$$\text{bond order (B.O)} = \frac{10 - 8}{2}$$

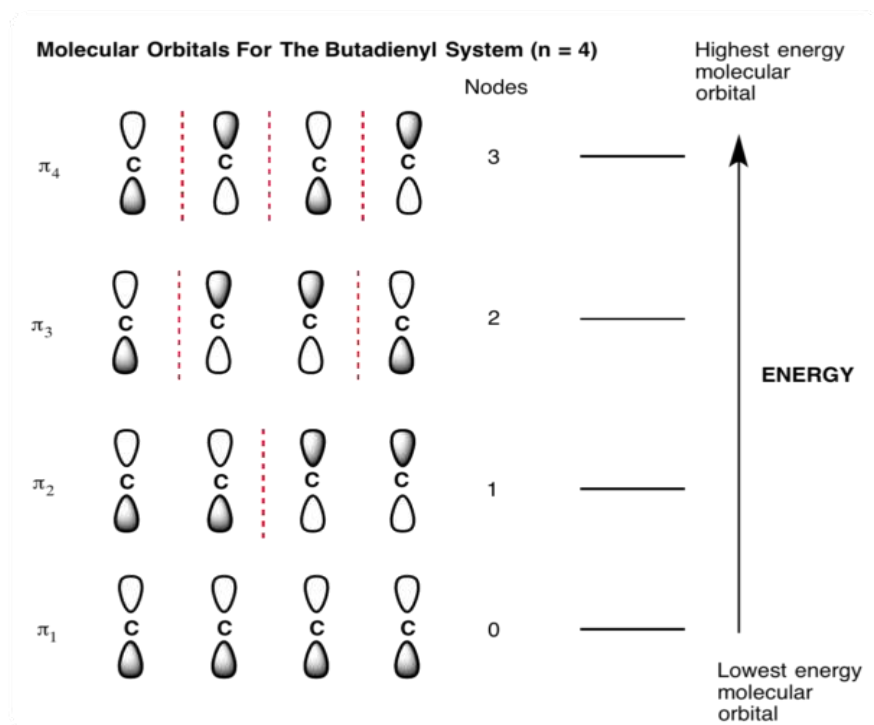
$$\text{bond order (B.O)} = 1$$

- F₂ molecule has paired electrons so, it is a diamagnetic compound.



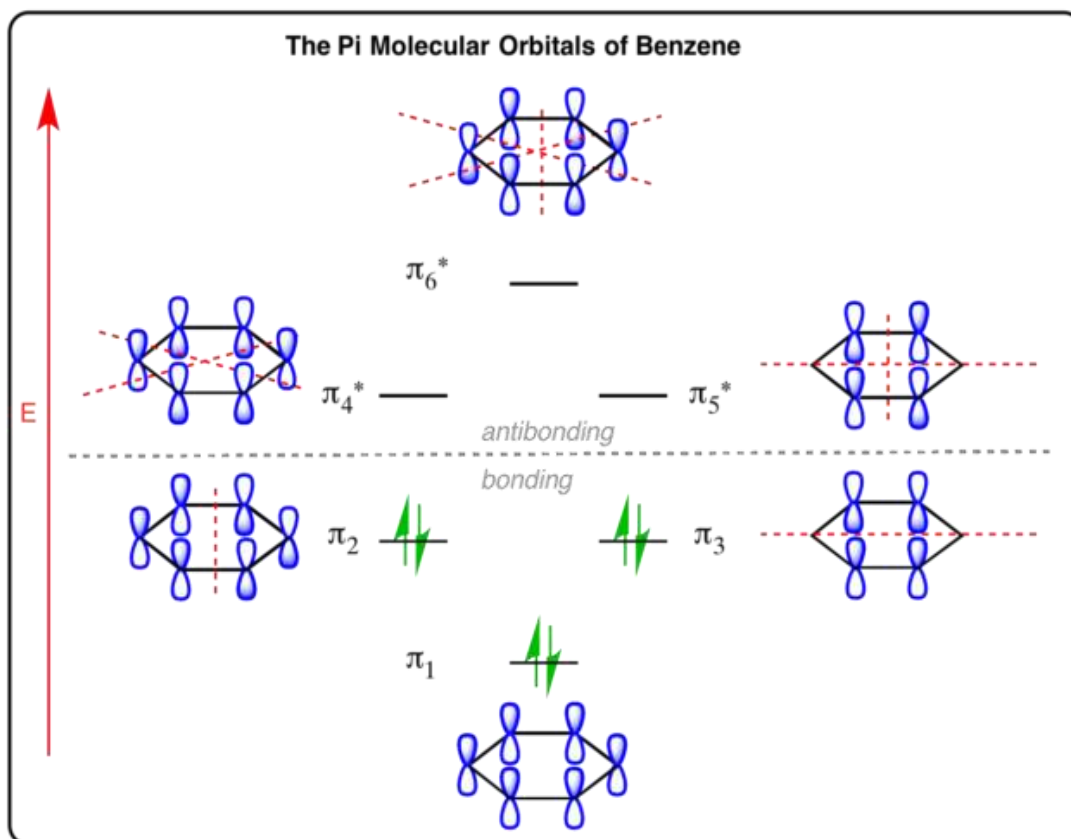
Pi (π) molecular orbitals of 1, 3-butadiene:

- The structure of 1, 3-butadiene is $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
- In this molecule the double bonds are conjugated and the carbon atoms exhibit sp^2 hybridisation.
- This molecule has four carbons in the π system. Each of the four carbons contributes one un-hybridised p- atomic orbitals containing one electron and these un-hybridised p- atomic orbitals combine to produce four π -molecular orbitals π_1 , π_2 , π_3 and π_4 .
- Half of molecular orbitals are bonding molecular orbitals (π_1 and π_2) and another half are anti-bonding molecular orbitals. (π_3^* and π_4^*).



Pi (π) molecular orbital of benzene:

- Benzene is a planar cyclic compound with molecular formula C_6H_6 .
- In this six carbons each carbon is having p_z orbital containing single electron. Hence these six p_z orbitals combine to produce six π molecular orbitals π_1 , π_2 , π_3 , π_4 , π_5 and π_6 .
- In these, 3 molecular orbitals are bonding and 3 molecular orbitals are anti-bonding.



Crystal field theory (CFT):

- CFT was proposed by Hans Bethe and J.H Van vleck.

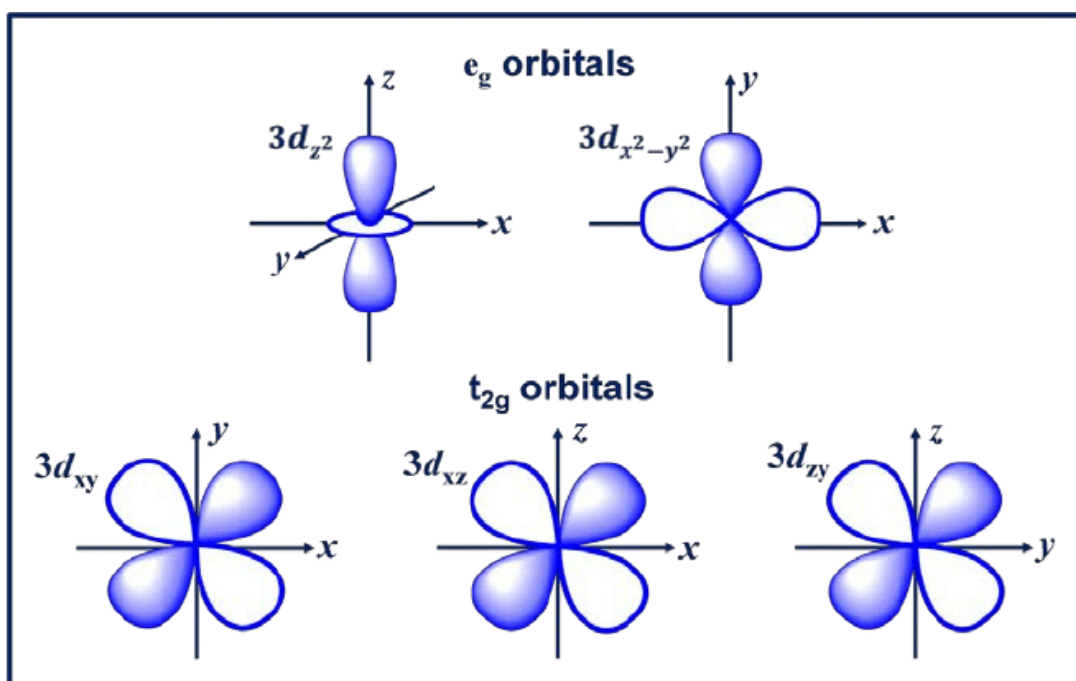
Salient features of CFT:

- CFT regards a complex as a combination of a central metal ion and surrounded by ligands which acts as point charges (or) point dipoles. Ligands contain one or more lone pair of electrons.
- According to this theory the interaction between the metal ion and ligands is purely electrostatic i.e., metal and ligand bonds are 100% ionic.
- Interaction of positive metal ion and negative charged ligands are of two types
- (i)The attractive force arises between positive metal ions and negative end of polar neutral molecules.
- (ii)The repulsive force arises between the lone pair of the ligands and the electron of d-orbital of the metal ion or atom due to this the five degenerate d-orbitals of the metal split into two groups. This splitting is called as crystal field splitting.

Crystal field splitting:

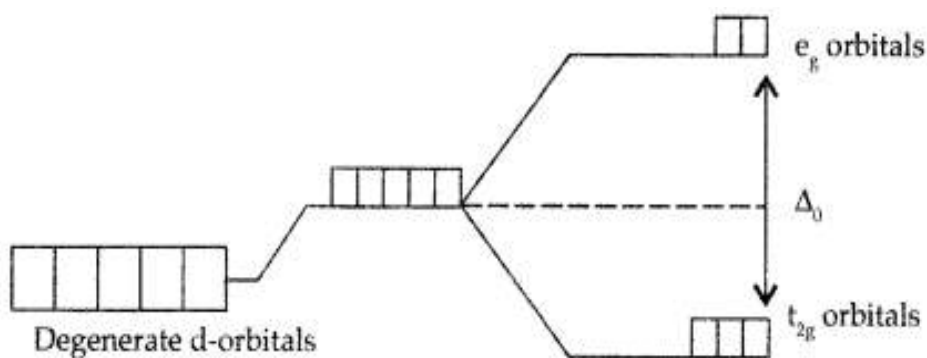
The five d-orbitals of the metal ion, three namely d_{xy} , d_{yz} , d_{zx} have maximum electron density directed between the x,y and z axes. The set of these three orbitals is collectively known as “ t_{2g} ” orbitals.

The d_{z^2} orbital has maximum electron density along the z-axis, while the $d_{x^2-y^2}$ orbital has maximum electron density along the x-axis and y-axis. These two orbitals (d_{z^2} and $d_{x^2-y^2}$) together are known as “ e_g ” orbitals.



Crystal field splitting of d-orbitals in octahedral complexes:

- In an octahedral complex, the co-ordination number is 6.
- The metal ion placed at the center of the octahedron is surrounded by six ligands are placed at the 6 corners of a regular octahedron.
- These six ligands approach the metal ion along the axes of the co-ordinate system.
- Two of the 5 orbitals (e_g orbitals) are oriented along the axes, they will be repelled more than the remaining three d orbitals (t_{2g} orbitals) directed between the approaching ligands.
- Consequently, energy of the two e_g orbitals increase much more than the energy of three t_{2g} orbitals.
- Thus, the 5 d-orbitals split into two groups of different energies.
- The energy gap between t_{2g} and e_g sets is denoted by Δ_o or $10 Dq$.



Splitting of d-orbitals in an octahedral complex

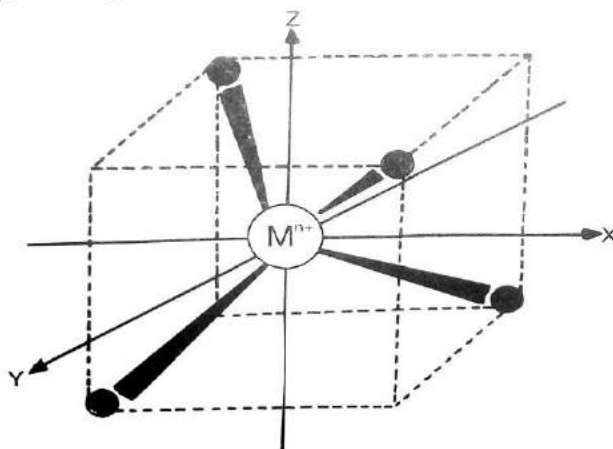
- e_g - The higher energy set of orbitals (d_{z^2} and $d_{x^2-y^2}$).
- t_{2g} - The lower energy set of orbitals (d_{xy} , d_{yz} and d_{xz}).
- Δ_o or $10 Dq$ - The energy separation between the two levels.
- The e_g orbitals are repelled by an amount of 0.6 orbitals.
- The t_{2g} orbitals to be stabilized to the extent of 0.4 Δ_o .

State I: It represents the degeneracy of all the 5 d-orbitals of the free metal ion in the absence of ligands.

State II: It represents hypothetical degeneracy of all the 5 d-orbitals at a higher energy level. When all the ligands approaching the central metal ions are at an equal distance from each of the d-orbitals.

State III: It represents the splitting of d-orbitals in the octahedral crystal field.

Crystal field splitting of d-orbitals in tetrahedral complexes:



- In tetrahedral complexes, the co-ordination number is 4.
- The metal ion is at the center of the tetrahedron and four ligands surrounding it are placed at the 4 corners of the tetrahedron.
- The ligands interact more with t_{2g} set of orbitals lying close to the axes of approaching ligands as compared to the e_g set of orbitals lying between the axes.
- This causes more repulsion, therefore increases in energy of t_{2g} set of orbitals as compared to the e_g set of orbitals.
- In tetrahedral complexes, crystal field splitting is denoted by Δ_t (where 't' is tetrahedral). In tetrahedral complexes d-orbitals do not directly interact with the approaching ligands. The extent of splitting is less than that of octahedral complexes so,

$$\Delta_t < \Delta_o$$

$$\Delta_t = \frac{4}{9} \Delta_o.$$

- This value of Δ_t may also be due to the less number of surrounding ligands which are 4 as compared to 6 in octahedral complexes.

