



UNIT - 1

STRUCTURE AND BONDING MODELS

❖ PLANCK'S QUANTUM THEORY

Black Body: A perfect absorber and a perfect emitter is called black body.

Ex : Sun, Carbon black.

In 1900, Max Planck had studied radiations emitted by hot black bodies and through black body radiations experiments, he showed that light has a dual character, behaving like a particle as well as a wave.

Postulates of Planck's quantum theory:

1. Substances radiate or absorb energy discontinuously in the form of small packets or bundles of energy.
2. These packets of energy are called quanta. In case of light, the quanta (or) Packets are known as a photon.
3. The energy of a quantum or photon is directly proportional to the frequency of the radiation.

Mathematically

$$E \propto \vartheta$$

$$E = h \vartheta$$

Where E = Energy of the photon

ϑ = Frequency of radiation

h = Planck's constant 6.626×10^{-34} erg-sec or 6.626×10^{-34} J-sec.

4. A body can radiate or absorb energy in whole number multiples of a quantum nhv , $2hv$, $3hv$, ..., nhv . where n is the positive integer

Similarly

$$E = \frac{hc}{\lambda} \quad (\text{where } \vartheta = \frac{c}{\lambda})$$

The above equation says that a wave of higher frequency (or) lower wave length will be more energetic and vice versa.

Applications: By the help of Planck's quantum theory

1. We can easily explain the difference between the monochromatic and polychromatic light.
2. It explains the phenomenon of photoelectric effect
3. It explains phenomenon of black body radiation.



❖ DUAL NATURE OF THE MATTER

In 1923, de Broglie, has proposed that every material particle in motion posses both particle and wave nature. According to Niel's Bohr electron is exclusively a particle. But de Broglie's wave theory proposes that every material particle in motion describe a wave.

Similarly electron also moves in the form of wave of wavelength $\lambda = h/mv$. This equation can be derived by combining Planks equation and Einstein equation.

deBroglie's equation : According to de-Broglie, the wavelength associated with a particle of mass m , moving with velocity v is given by the mathematical equation

$$\lambda = \frac{h}{mv} \text{ (or) } \lambda = \frac{h}{P}$$

Whare

λ = Wavelength.

m = mass of the electron.

h = Plank's constant.

P = movement of electron

The above equation is known as DeBroglie's wave equation, which is derived from Plank's quantum theory and Einstein mass - energy relation.

Proof of deBroglie's Equation :

De Broglie first used Einstein's famous equation relating matter and energy:

$$E = mc^2 \quad \dots \dots \dots \quad (1)$$

Where

E = energy, m = mass, c = speed of light

Using Planck's quantum equation:

$$E = h v^9$$

From equations (1) and (2) we get

$$\therefore \frac{hc}{\lambda} = mc^2$$

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

If 'c' is replaced with the velocity of electron 'v' then

$$\lambda = \frac{h}{mv} \text{ (or) } \lambda = \frac{h}{P}$$



Applications of Dual nature of matter:

1. It is used in the construction of an electron microscop
 2. It helps in determining the probability of finding any particle in the configuration space
 3. It is used to explaine the Photoelectric Effect
 4. By using this theory wave length of an electron can be determined in bohr's orbit and relate it with circumference and multiply with a whole number.
 5. It explains the Light dependant resistance.

❖ SCHRODINGER EQUATION

Schrodinger wave equation : Schrodinger wave equation is a mathematical expression describing the energy and probability of finding electron in three dimensional space and time, taking into account the matter wave nature of the electron inside an atom

To determine the electron wave at different places Schrodinger given an equation

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

Where:

m = Mass of the electron

E = Total energy of the electron

V = Potential energy of the

electron

h = Plank's Constant =

6.626×10^{-27} erg-sec or 6.626×10^{-34} J-sec.

x y and z = Cartesian coordinates

Ψ = Wave function

According to Classical wave equation

$$\Psi = A \sin 2\pi \frac{x}{\lambda} \quad \dots \dots \dots \quad (1)$$

Where

Ψ = Wave function

A = Amplitude (or) maximum value of Ψ

λ = Wave length of standing wave

x = Distance of the particle from the nucleus

Partial differentiating Ψ with respect to 'x' we get

$$\frac{\partial \Psi}{\partial x} = A \cos 2\pi \frac{x}{\lambda} \left(\frac{2\pi}{\lambda} \right)$$

$$= 2\pi \frac{A}{\lambda} \cos 2\pi \frac{x}{\lambda}$$

Differentiating again, we get

$$\begin{aligned}\frac{\partial^2 \Psi}{\partial x^2} &= 2\pi \frac{A}{\lambda} \left(-\sin \frac{2\pi x}{\lambda} \right) \frac{2\pi}{\lambda} \\ &= -\frac{4\pi^2 A}{\lambda^2} \left(\sin \frac{2\pi x}{\lambda} \right) \\ &= -\frac{4\pi^2}{\lambda^2} \left(A \sin \frac{2\pi x}{\lambda} \right)\end{aligned}$$

The above equation represents wave motion of particle.

Since electron has a wave as well as particle character, the above equation also represents the wave motion of electron along x-axis.

If the electron is considered to move along x, y and z axis, then

$$\therefore \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{4\pi^2}{r^2} \Psi = 0$$

(or)

$$\nabla^2 \Psi = -\frac{4\pi^2 \psi}{\lambda^2} \dots \dots \dots \quad (4)$$

Where

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2 \quad (\text{The Laplacian operation})$$

Then

$$\frac{4\pi^2\Psi}{j^2} = -\nabla^2\Psi$$

But according to deBroglie's equation



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

Squaring on both sides, we get

From equation (4) and (6), we get

$$\frac{m^2 v^2}{h^2} = -\nabla^2 \Psi \frac{1}{4\pi^2 \Psi}$$

$$\Rightarrow m^2 v^2 = -\nabla^2 \Psi \frac{h^2}{4\pi^2 \Psi}$$

$$\Rightarrow mv^2 = -\nabla^2\Psi \frac{h^2}{4\pi^2 m \Psi}$$

$$\Rightarrow \frac{1}{2}mv^2 = -\nabla^2\Psi \frac{\hbar^2}{8\pi^2m\Psi}$$

$$\Rightarrow K.E = -\nabla^2 \Psi \frac{h^2}{8\pi^2 \Psi_m}$$

$$\nabla^2 \Psi = -\frac{8\pi^2 \Psi m}{h^2} \text{ K.E}$$

Thus

But we know that the total energy (E) of the system is equal to the sum of potential energy (P.E) and kinetic energy (K.E).

$$E = KE + PE$$

$$\Rightarrow K.E = E - P.E$$

Substitute the value of kinetic energy in equation (7) we get

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E - P.E) \Psi = 0$$

$$\therefore \nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0$$

The above equation is known as Schrodinger Wave Equation

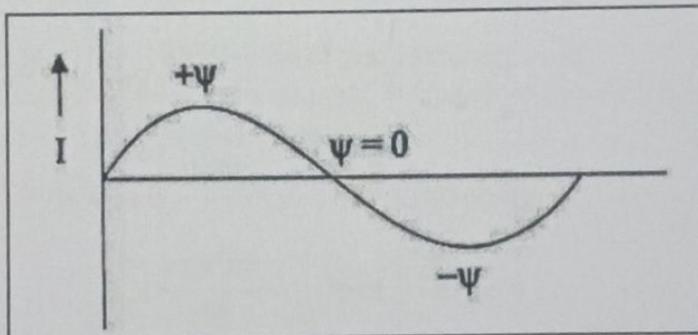
Applications :

1. It's the foundation of wave mechanics.
2. It helps in the studying of atomic structure.
3. It reflects all of the wave-like nature of matter.
4. It can be used to calculate the probability of finding a particle at any given point in space

❖ SIGNIFICANCE OF Ψ AND Ψ^2

Significance of Ψ :

1. It is a wave function which is a solution of the Scrodinger Equation
2. It represents amplitude of wave and describes how this amplitude varies with distance and direction
3. It takes a positive value above the axis and negative value below the axis and become zero while crossing/intercepting the axis.



4. It has no physical significance
5. The Shrodinger wave equation may have different values of Ψ . The significant values of wave function, Ψ , are known as Eigen functions. These functions give significant values of the total energy (E) of the electron. These values are called Eigen values.
6. Each Eigen function corresponds to an atomic and molecular orbital of an atom and a molecule respectively

Significance of Ψ^2 :

1. For light wave, it represents intensity of light
2. For electron waves, it represents intensity of electrons at any point, ie., it represents the probability of finding electron (of specific energy) at different regions in space.
3. It leads to the idea of orbital.
4. If Ψ^2 value is zero, it is called nodal plane.



A	B	AB (MO)
1s	1s	$\sigma 1s$
		$\sigma^* 1s$
2s	2s	$\sigma 2s$
		$\sigma^* 2s$
2p _x	2p _x	$\sigma 2p_x$
		$\sigma^* 2p_x$
2p _y	2p _y	$\Pi 2p_y$
		$\Pi^* 2p_y$
2p _z	2p _z	$\Pi 2p_z$
		$\Pi^* 2p_z$

9. The molecular orbitals are arranged in the increasing order of their energies
- a) The bonding order in Homonuclear Diatomic Molecule: The order of energy levels of the homonuclear MOs in the order of increasing energy is as follows

$$\begin{aligned} \sigma(1s) &< \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_x) < [\pi(2p_y) = \pi(2p_z)] \\ &< [\pi^*(2p_y) = \pi^*(2p_z)] < \sigma^*(2p_x) \end{aligned}$$

- b) The bonding order in Heteronuclear Diatomic Molecule : The order of energy levels of the heteronuclear MOs and also for Boron, carbon and nitrogen molecules in the order of increasing energy is as follows

$$\begin{aligned} \sigma(1s) &< \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < [\pi(2p_y) = \pi(2p_z)] < \sigma(2p_x) \\ &< [\pi^*(2p_y) = \pi^*(2p_z)] < \sigma^*(2p_x) \end{aligned}$$

10. Electrons fill up these orbitals in the same way as atomic orbitals in accordance to the three principles (Pauli Principle Aufbau and Hund's)

- a) Pauli Exclusion Principle : According to Pauli Exclusion Principle, each molecular orbital accommodates a maximum of two electrons in it.
- b) Aufbau Principle : According to Aufbau Principle, Molecular Orbitals are filled in the increasing order of their energy.
- c) Hund's Principle : According to Hund's Principle, equal energy molecular orbitals filled with one electron each and then electrons paired.

11. Shape of molecular orbitals formed depends up on the type of combining orbitals.

12. Relation between electronic configuration and molecular behaviour

- a) Bond Order: The total number of covalent bonds present in between the two atoms of a covalent molecule is called its bond order.

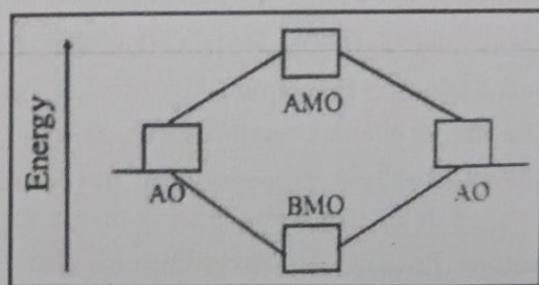
◆ MOLECULAR ORBITAL THEORY

Valence Bond Theory fails to answer certain questions like why He_2 molecule does not exist and why O_2 is paramagnetic. Therefore in 1932 F. Hood and RS. Mulliken came up with theory known as Molecular Orbital Theory to explain questions like above.

Molecular orbital : Molecular orbitals are regions around molecules where electrons are most likely to be found.

Postulates of MOT:

1. All the atomic orbitals of one atom overlap with all the atomic orbitals of other atom to form molecular orbitals as a result, the atomic orbitals loose their identity.
2. The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
3. In molecular orbital electrons are in influence of two or more nuclei.
4. As a set of atomic orbitals combine to form molecular orbitals, the number of molecular orbitals formed are equal to number of atomic orbitals that combined
5. When two atomic orbitals are combined to form two molecular orbitals. These are formed by addition and subtraction by the wave functions respectively .They are
6. Bonding molecular Orbital: The molecular orbital possess lower energy than energy of either of atomic orbitals is called Bonding molecular Orbital (BMO) $[\sigma, \pi]$
7. Anti Bonding molecular Orbital : The molecular orbital possess higher energy than energy of either of atomic orbitals is called Anti Bonding molecular Orbital (ABMO) $[\sigma^*, \pi^*]$



8. Let the atomic orbitals of $1s, 2s, 2p_x, 2p_y, 2p_z$ of atom 'A' overlap with $1s, 2s, 2p_x, 2p_y, 2p_z$ orbitals of another atom 'B' to form the following molecular orbitals.



$$\text{Bond Order} = \frac{1}{2} [\text{No. of Electrons in BO} - \text{No. of Electrons in ABO}]$$

b) Stability:

Case1: If No.of electrons in Bonding orbital > No.electrons in Antibonding electrons then the molecule whould be stable

Case2: If No.of electrons in Bonding orbital \leq to No.electrons in Antibonding electrons then the molecule donot exist.

c) Magnetic Property: If all the electrons in molecular orbitals are paired the molecule is diamagnetic. If some of the electrons are unpaired, the molecule is Paramagnetic

Differences between bonding and anti bondig molecular orbitals

S.No	Bonding Molecular Orbital	Antibonding Molecular orbital
1	The molicular orbital formed by the addition of wave functionsof the atomic orbitals	The molicular orbital formed by the subtraction of wave functionsof the atomic orbitals
2	It may or may not have a node.	It always has a node in between the nuclei of bonded atoms.
3	In this orbital electron density is more in between the nucle	In this orbital electron density is less in between the nuclei.
4	Electrons in this orbital lead to attraction between atoms	Electrons in this orbital lead to repulsion between atoms.
5	It's energy is less than the energy of the atomic orbitals.	It's energy is more than the energy of the atomic orbitals.

Differences between Atomic orbital and molecular orbitals

S.No	Atomic Orbital	Molecular orbital
1	It is the region having the highest probability of finding an electron in an atom.	It is the region having the highest probability of finding an electron in a molecule.
2	Formed by the electron cloud around the atom.	Formed by the fusion of atomic orbitals that have nearly the same energy.
3	The electrons of an atomic orbital are influenced by one positive nucleus.	The electrons of a molecular orbital are influenced by the two or more nuclei
4	They are found in following orbitals: s, p, d, f	They are found in following orbitals: bonding and antibonding
5	Orbitals such as s, p, d, f determines its shape.	The presence of atomic orbitals determines its shape
6	The electronic configuration has no effect on the stability of electron.	The electronic configuration effect the stability of electron

❖ BOND ORDER

Bond Order : The total number of covalent bonds formed between the two bonded atoms in the covalent molecule is called the "bond order".

The bond order (B.O) can be calculated by using the following expression

$$B.O = \frac{1}{2}[N_b - N_a]$$

Where

N_b = Total no. of electrons in bonding molecular orbitals

N_a = Total no. of electrons in anti- bonding molecular orbitals

The value of bond order also refers to existence, stability of molecule and nature of the bond

- a) Zero and less than zero value indicates that the species does not exist.
- b) 1,2 and 3 indicates that the molecule is stable and the two atoms are held together by a single, double and triple bond respectively.
- c) $+\frac{1}{2}$ value indicates that the species exists but it is unstable eg., H_2^+ , He_2^+

Calculation of Bond order of the some of the species

A. Calculation of bond order for homo diatomic molecules:

1. Bond order for H_2 molecule

- a) The H_2 molecule is obtained by two H - atoms
- b) The atomic number of the hydrogen atom = 1
- c) So the total number of electrons in H_2 molecule = $1+1 = 2$
- d) Molecular electronic configuration of H_2 = σ_{1s}^2

We know that

$$B.O = \frac{1}{2}[N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2} [2 - 0] = \frac{1}{2} \times 2 = 1$$

So a single bond is present in between the two hydrogen atoms in H_2 molecule

2. Bond order for He_2 molecule

- a) The He_2 molecule is obtained by two He - atoms
- b) The atomic number of the He atom = 2
- c) The total number of electrons in He_2 molecule = $2+2 = 4$
- d) Molecular electronic configuration of He_2 = $\sigma_{1s}^2 \sigma^*_{1s}^2$

We know that



$$B.O = \frac{1}{2} [N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2} [2 - 2] = \frac{1}{2} \times 0 = 0$$

So the He_2 molecules does not exists

3. Bond order for Li_2 molecule

- a) The Li_2 molecule is obtained by two Li - atoms
- b) The atomic number of the Li atom = 3
- c) The total number of electrons in Li_2 molecule = $3+3 = 6$
- d) Molecular electronic configuration of Li_2 = $\sigma_{1s}^2 \sigma^*_{1s}^2 \sigma_{2s}^2$

We know that

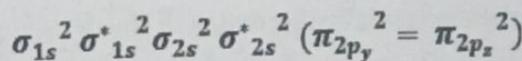
$$B.O = \frac{1}{2} [N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2} [4 - 2] = \frac{1}{2} \times 2 = 1$$

So a single bond is present in between the two Li atoms in Li_2 molecule

4. Bond order for C_2 molecule

- a) The C_2 molecule is obtained by two C - atoms
- b) The atomic number of the Carbon atom = 6
- c) The total number of electrons in C_2 molecule = $6+6 = 12$
- d) Molecular electronic configuration of C_2 is



We know that

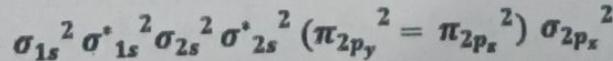
$$B.O = \frac{1}{2} [N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2} [8 - 4] = \frac{1}{2} \times 4 = 2$$

So double bond is present in between the two Carbon atoms in C_2 molecule

5. Bond order for N_2 molecule

- a) The N_2 molecule is obtained by two N - atoms
- b) The atomic number of the Nitrogen atom = 7
- c) The total number of electrons in N_2 molecule = $7+7 = 14$
- d) Molecular electronic configuration of N_2 is



We know that

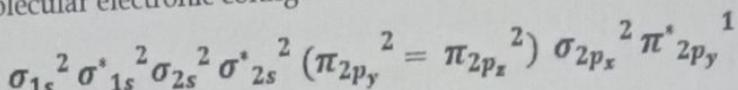
$$B.O = \frac{1}{2} [N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2} [10 - 4] = \frac{1}{2} \times 6 = 3$$

So triple bond is present in between the two Nitrogen atoms in N_2 molecule

6. Bond order for N_2^- molecule

- a) The N_2^- molecule is obtained by N- atom and N⁻ ion
- b) The atomic number of the Nitrogen atom = 7
- c) The total number of electrons in N_2^- molecule = $14 + 1 = 15$
- d) Molecular electronic configuration of N_2^- is



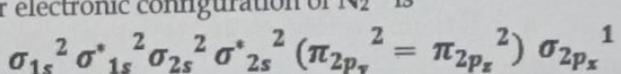
We know that

$$B.O = \frac{1}{2} [N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2} [10 - 5] = \frac{1}{2} \times 5 = 2.5$$

7. Bond order for N_2^+ molecule

- a) The N_2^+ molecule is obtained by N- atom and N⁺ ion
- b) The atomic number of the Nitrogen atom = 7
- c) The total number of electrons in N_2^+ molecule = $14 - 1 = 13$
- d) Molecular electronic configuration of N_2^+ is



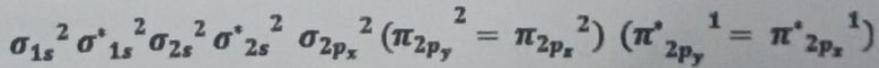
We know that

$$B.O = \frac{1}{2} [N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2} [9 - 4] = \frac{1}{2} \times 5 = 2.5$$

8. Bond order for O_2 molecule

- a) The O_2 molecule is obtained by two O- atoms
- b) The atomic number of the Oxygen atom = 8
- c) The total number of electrons in O_2 molecule = $8 + 8 = 16$
- d) Molecular electronic configuration of O_2 is



We know that

$$B.O = \frac{1}{2} [N_b - N_a]$$

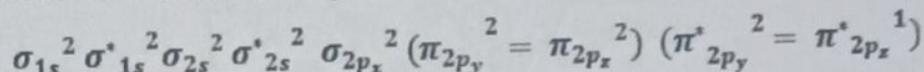
$$\therefore \text{Bond order} = \frac{1}{2} [10 - 6] = \frac{1}{2} \times 4 = 2$$

So double bond is present in between the two Oxygen atoms in O_2 molecule



9. Bond order for O_2^- molecule

- a) The O_2^- molecule is obtained by O- atom and O⁻ ion
- b) The atomic number of the Oxygen atom = 8
- c) The total number of electrons in O_2^- molecule = 16 + 1 = 17
- d) Molecular electronic configuration of O_2^- is



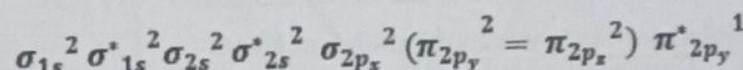
We know that

$$B.O = \frac{1}{2}[N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2}[10 - 7] = \frac{1}{2} \times 3 = 1.5$$

10. Bond order for O_2^+ molecule

- a) The O_2^+ molecule is obtained by O- atom and O⁺ ion
- b) The atomic number of the Oxygen atom = 8
- c) The total number of electrons in O_2^+ molecule = 16 - 1 = 15
- d) Molecular electronic configuration of O_2^+ is



We know that

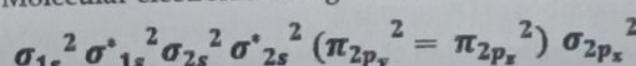
$$B.O = \frac{1}{2}[N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2}[10 - 5] = \frac{1}{2} \times 5 = 2.5$$

B. Calculation of bond order for Hetero diatomic molecules:

1. Bond order for CO molecule

- a) The CO molecule is obtained by one C- atom and one O- atom
- b) The atomic number of the Carbon atom = 6
- c) The atomic number of the Oxygen atom = 8
- d) The total number of electrons in CO molecule = 6 + 8 = 14
- e) Molecular electronic configuration of CO is



We know that

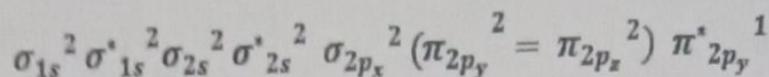
$$B.O = \frac{1}{2}[N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2}[10 - 4] = \frac{1}{2} \times 6 = 3$$

So triple bond is present in between Carbon atom and Oxygen atom in CO molecule

2. Bond order for NO molecule

- a) The NO molecule is obtained by one N- atom and one O - atom
- b) The atomic number of the Carbon atom = 7
- c) The atomic number of the Oxygen atom = 8
- d) The total number of electrons in NO molecule = $7+8 = 15$
- e) Molecular electronic configuration of NO is



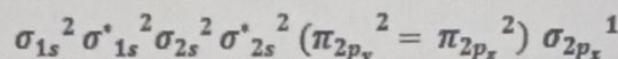
We know that

$$B.O = \frac{1}{2}[N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2}[10-5] = \frac{1}{2} \times 5 = 2.5$$

3. Bond order for CN molecule

- a) The NO molecule is obtained by one N- atom and one O - atom
- b) The atomic number of the Carbon atom = 6
- c) The atomic number of the Nitrogen atom = 7
- d) The total number of electrons in NO molecule = $6+7 = 13$
- e) Molecular electronic configuration of NO is



We know that

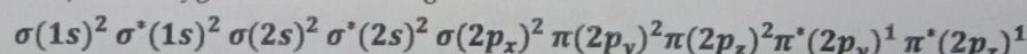
$$B.O = \frac{1}{2}[N_b - N_a]$$

$$\therefore \text{Bond order} = \frac{1}{2}[9-4] = \frac{1}{2} \times 5 = 2.5$$

❖ ENERGY LEVEL DIAGRAMS OF O₂ AND CO:

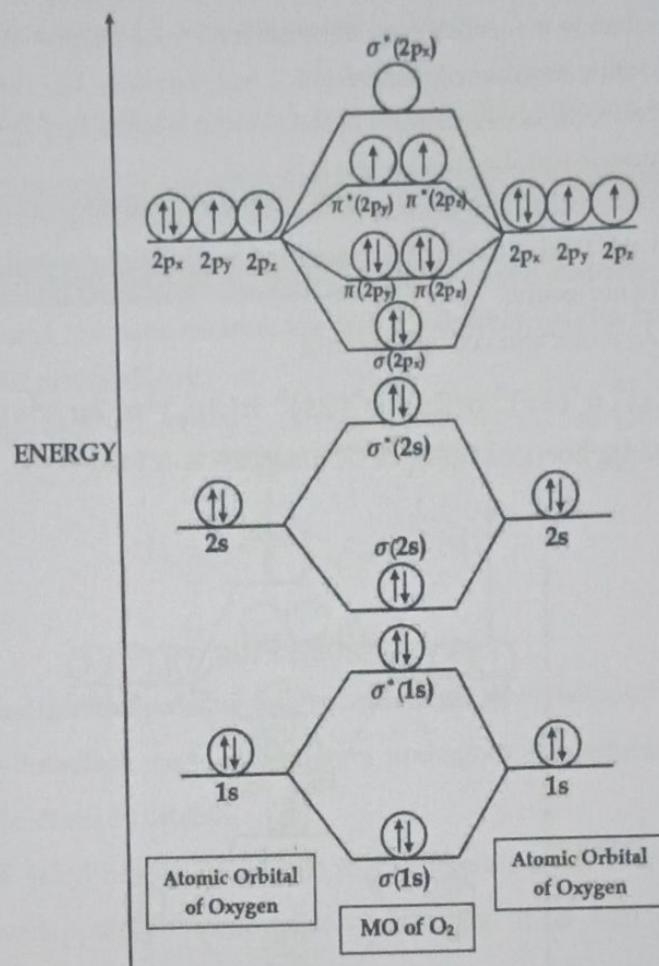
1. Molecular Energy Diagram of O₂ Molecule:

- a) Oxygen molecule is formed from the combination of two O-atoms
- b) The Atomic number of Oxygen is 8
- c) The electronic configuration of the O-atom is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
- d) When the two Oxygen atoms combine, there will be 16 electrons in the O₂ molecule.
- e) The Oxygen molecular configuration is





- f) Molecular Energy Diagram of O₂ molecule is as follows



- g) Bond Order in Oxygen Molecule:

We know that

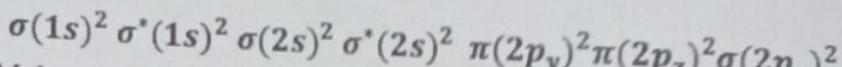
$$\begin{aligned} \text{Bond Order} &= \frac{1}{2} [\text{No. of electrons in BO} - \text{No. of electrons in ABO}] \\ &= \frac{1}{2} [10 - 6] = 2 \end{aligned}$$

That is Oxygen molecule has double bond between two oxygen atoms

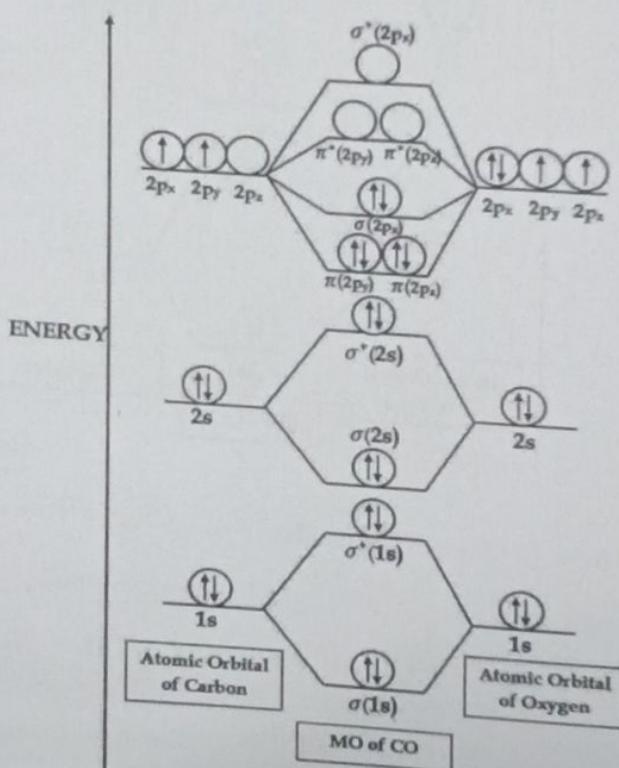
- h) **Magnetic Character:** The configuration shows that two unpaired electrons in Oxygen molecule. Hence O₂ is paramagnetic in nature.
- i) **Stability:** O₂ molecule has 4 antibonding electrons valency shell (more than in N₂ molecule) and hence it should be less stable than nitrogen molecule

2. Molecular Energy Diagram of CO Molecule :

- CO molecule is formed from the combination of Carbon atom and O-atoms
- The Atomic number of Carbon is 6
- The electronic configuration of the C-atom is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$
- The Atomic number of Oxygen is 8
- The electronic configuration of the O-atom is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
- When the Carbon and Oxygen atoms combine, there will be 14 electrons in the CO molecule.
- The CO molecular configuration is



- Molecular Energy Diagram of CO molecule is as follows



i) Bond Order in CO Molecule:

We know that

$$\begin{aligned}
 \text{Bond Order} &= \frac{1}{2} [\text{No. of electrons in BO} - \text{No. of electrons in ABO}] \\
 &= \frac{1}{2} [10 - 4] = 3
 \end{aligned}$$



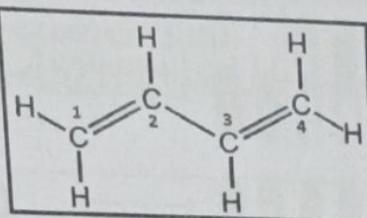
That is CO molecule has triple bond between Carbon and Oxygen atoms

- j) **Magnetic Character:** The configuration shows that no unpaired electrons in CO molecule. Hence CO is diamagnetic in nature.
- k) **Stability:** CO molecule has 2 antibonding electrons valency shell (same in N₂ molecule) and hence it should be more stable than nitrogen molecule

❖ π -MOLECULAR ORBITALS OF BUTADIENE AND BENZENE

1. **π -Molecular Orbital diagram of Butadiene :** The stability of alkenes, alkanes derivatives and aromatic compounds and its derivatives can be explained by using π - molecular orbital theory.

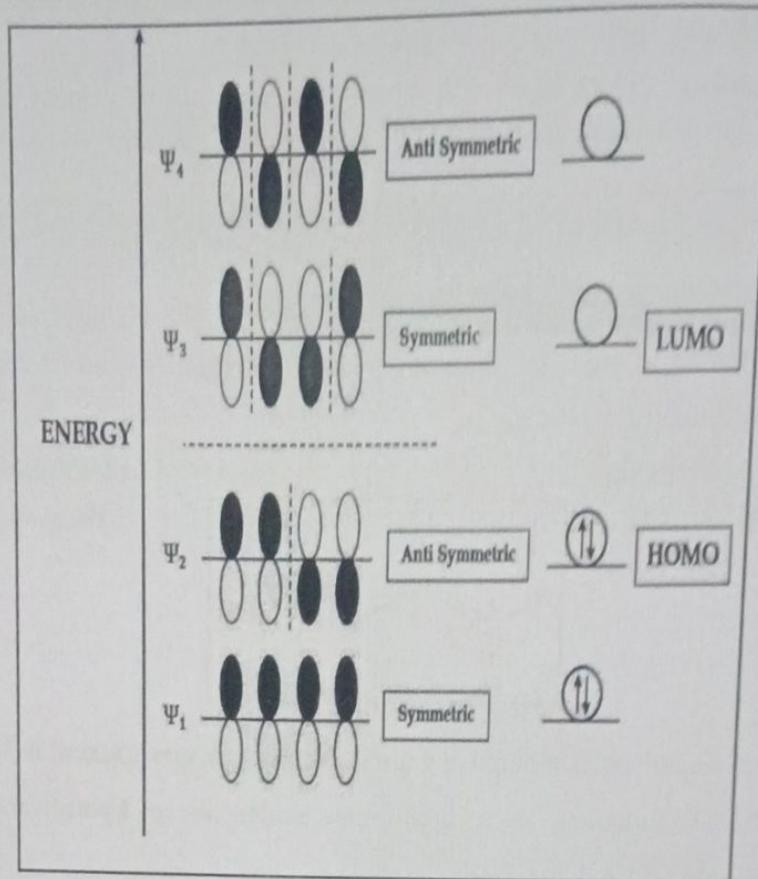
1. The structure



of 1,3 -Butadiene is H₂C = CH₂

2. 1,3 -Butadiene composed of 4 carbon atoms with two adjacent π - bonds .
3. In 1,3 -Butadiene, each carbon atom undergoes sp^2 hybridization and contains 4 unhybridized 2p orbitals.
4. These 4 unhybridized 2p orbitals in 4 different carbon atoms undergoes side by side overlapping to form adjacent π -bonds, it is also called as conjugated π -electrons system .
5. In 1,3 -Butadiene four 2p orbitals combined to form four π - molecular orbitals that are Ψ_1 , Ψ_2 , Ψ_3^* , and Ψ_4^*
6. The diagram contains in-phase and an out-of-phase combination for both the π and π^*
7. Four electrons in four 2p orbitals occupying first two electrons in Ψ_1 molecular orbitals and then remaining two electrons in Ψ_2 molecular orbitals.
8. This molecular orbital diagram Butadiene shows two molecular orbital. They are
 - a) Highest occupied molecular orbital. (HOMO)
 - b) Lowest unoccupied molecular orbital. (LUMO)
9. The highest occupied molecular orbital or HOMO is Ψ_2 . in 1,3-butadiene and the lowest unoccupied orbital or LUMO is Ψ_3

10. The π molecular diagram of 1,3-Butadiene is as follows

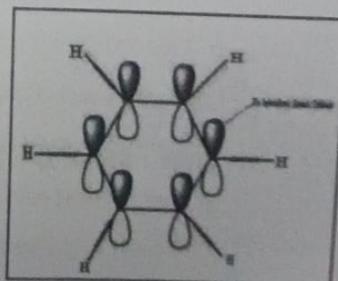


11. Number of Bonding and Ant bonding Interactions in 1,3-butadiene:

S.No	Type of MO	No of Nodal planes	Bonding Interactions (BI)	Anti bonding interactions (ABI)
1	Ψ_1	0	3 BI	0 ABI
2	Ψ_2	1	2 BI	1 ABI
3	Ψ_3	2	1 BI	2 ABI
4	Ψ_4	3	0 BI	3 ABI

2. π -Molecular Orbital diagram of Benzene : The stability of alkenes, alkanes derivatives and aromatic compounds and it's derivatives can be explained by using π - molecular orbital theory.

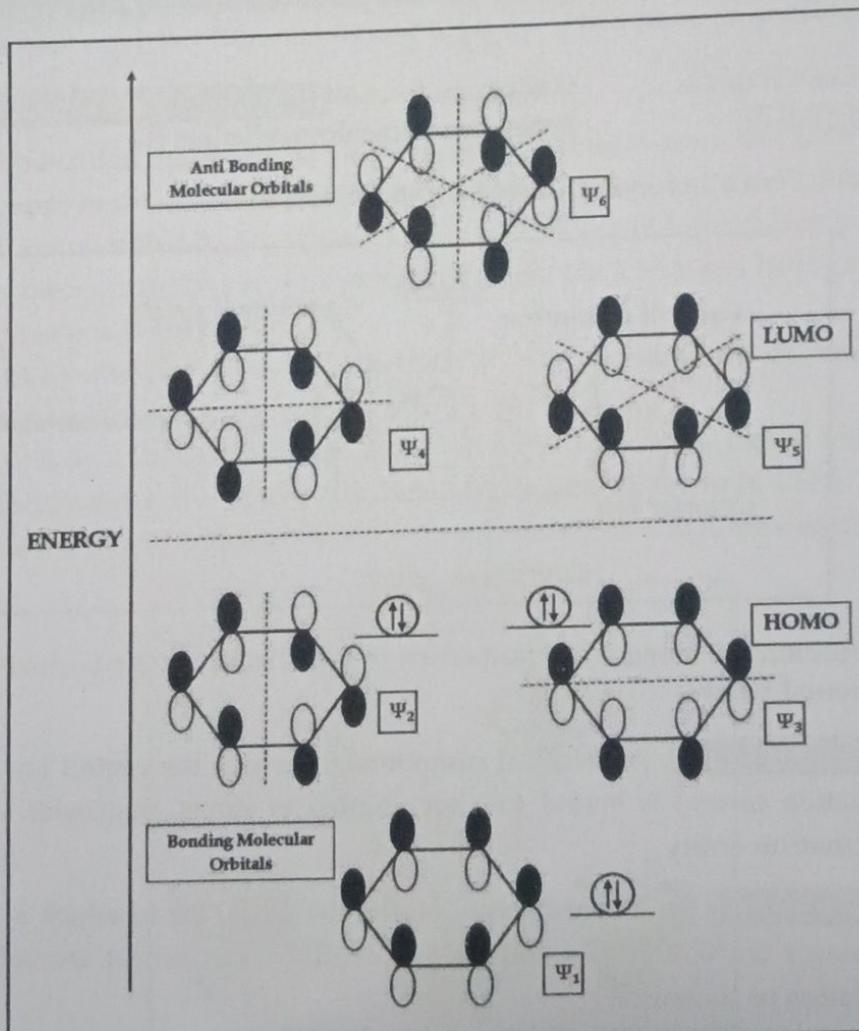
1. Benzene (C_6H_6) has a planar hexagonal structure in which all the six carbon atoms are sp^2 hybridized.
2. Six individual $2p$ - orbitals in 6 different carbon atoms undergo side by side overlapping to form 3 adjacent π - bonds, it is called as conjugated π system.
3. Since benzene consist of Six individual $2p$ - orbitals and hence π system of benzene contains 6





molecular orbitals. That is $\Psi_1, \Psi_2, \Psi_3, \Psi_4, \Psi_5, \Psi_6$.

4. Out of 6 molecular orbitals, three are bonding and remaining three are antibonding molecular orbitals
5. The diagram contains in-phase and an out-of-phase combination for both the π and π^*
6. In out of 6 molecular orbitals, bonding molecular orbitals of Ψ_2, Ψ_3 and anti bonding orbitals of Ψ_4, Ψ_5 are degenerate orbitals.
7. Six electrons in six 2p orbitals occupying first two electrons in Ψ_1 molecular orbitals and then remaining four electrons occupied in Ψ_2 and Ψ_3 molecular orbitals.
8. Ψ_2 and Ψ_3 are Highest occupied molecular orbitals (HOMO) and Ψ_4 and Ψ_5 lowest unoccupied molecular orbitals (LUMO)
9. The π molecular diagram of Benzene is as follows



Number of Bonding and Anti bonding Interactions in benzene:

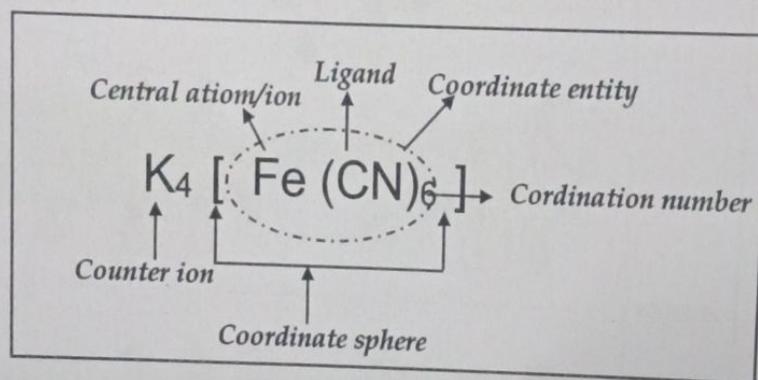
S.No	Type of MO	No of Nodal planes	Bonding Interactions (BI)	Anti bonding interactions (ABI)
1	Ψ_1	0	6 BI	0 ABI
2	Ψ_2	1	4 BI	2 ABI
3	Ψ_3	1	2 BI	0 ABI
4	Ψ_4	2	0 BI	2 ABI
5	Ψ_5	2	2 BI	4 ABI
6	Ψ_6	3	0 BI	26ABI

COORDINATION COMPOUNDS

Coordination compounds: Coordination compounds are chemical compounds that consist of an array of anions or neutral molecules that are bound to a central atom via coordinate covalent bonds (dative bonds). Coordination compounds are also referred to as coordination complexes

Ex: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$: Hexaamminecobalt (III) chloride.
 $\text{K}_2[\text{PdCl}_4]$: Potassium tetrachloropalladate (II)

Important Terms Involving Coordination Compounds:



The definitions of some important terms in the chemistry of coordination compounds can be found below

Coordination Entity: A chemical compound in which the central ion or atom (or the coordination centre) is bound to a set number of atoms, molecules, or ions is called a coordination entity.

Central atom/ion: In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ionions.

In coordination compounds, the central atoms or ions are typically Lewis Acids and can therefore act as electron-pair acceptors.



Ligands : The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. In coordination compounds, the ligands are typically Lewis bases and can therefore act as electron-pair donators

These ligands can either be a simple ion or molecule (such as Cl^- or NH_3) or in the form of relatively large molecules, such as ethane-1,2-diamine ($\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$).

Coordination Sphere : The non-ionizable part of a complex compound which consists of central transition metal ion surrounded by neighbouring atoms or groups enclosed in square bracket. This coordination sphere is usually accompanied by a counter ion

Counter ion : The ionizable groups that attach to charged coordination complexes

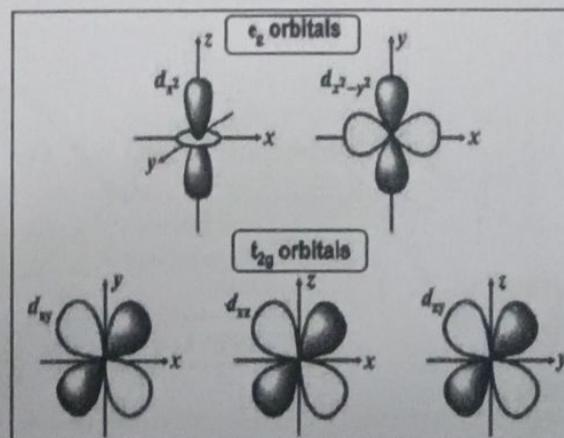
❖ CRYSTAL FIELD THEORY

In order to account for the limitations of VB theory, the CFT was developed by Bethe and Ven Vleck (1929).

Crystal field Theory: Crystal Field Theory (CFT) is a model for the bonding interaction between transition metals and ligands

Postulates (or) Assumption of CFT :

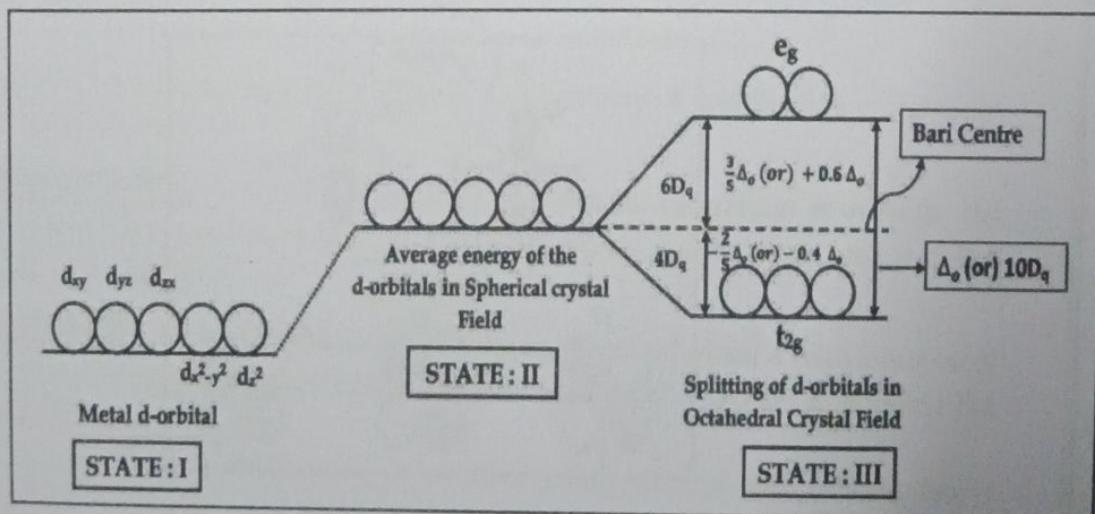
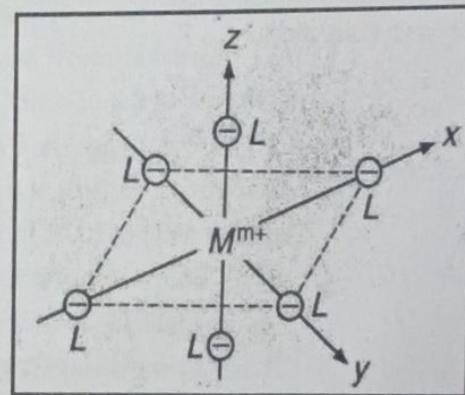
1. The transition metal acts as Central cation. The ligands donate their lone pair of electrons to the vacant orbitals of this cation.
2. CFT assumes that the Central metal Atom (CMA) and Ligands are point charges
3. This theory considers that the interaction between CMA and ligands to be purely Electrostatic ie 100% ionic.
4. When the complex is formed the CMA is surrounded by the oppositely charged ligand molecules.
5. There is no overlapping of the atomic orbitals of CMA and ligand molecules
6. To form a bond, the ligand molecules must approach towards CMA
7. In the absence of external field, the five d-orbitals of CMA are degenerate



8. During the complex formation the ligands surrounded the CMA then
- If symmetrical field is generated between the CMA and Ligands, the degeneracy of d-orbitals remains same
 - If unsymmetrical field is generated between the CMA and Ligands, the degeneracy of d-orbitals is lost. Then the splitting of orbitals takes place into different energies as t_{2g} (d_{xy}, d_{yz}, d_{zx}) and $e_g(d_{x^2-y^2}, d_z^2)$
9. Crystal Field Splitting: The splitting of d-orbitals into two different sets of orbitals in the presence of the repulsive field created by the approaching ligand molecules
10. Magnetic Charector : The magnetic character depends upon the extent of splitting of d-orbitals by a ligand. Greater the splitting of the d-orbital, lesser will be the unpaired electrons and hence lesser will be the magnetic character.
11. Colour : The colour of transition metal complexes is explained on the basis of electronic transitions between various d-orbitals of different energies.

CRYSTAL FIELD SPLITTING IN OCTAHEDRAL GEOMETRY

- In the formation of an Octahedral Complex, the six ligand molecules approach the central metal atom along the axis.
- During the approaching of ligand, the d-orbitals whose lobes lie along the axes will feel more repulsion as compared to other orbitals.
- Therefore the energy of e_g ($d_{x^2-y^2}, d_z^2$) set of orbitals will be increased and the five d-orbitals will split into two different sets
- Crystal field splitting in Octahedral Complex is as follows

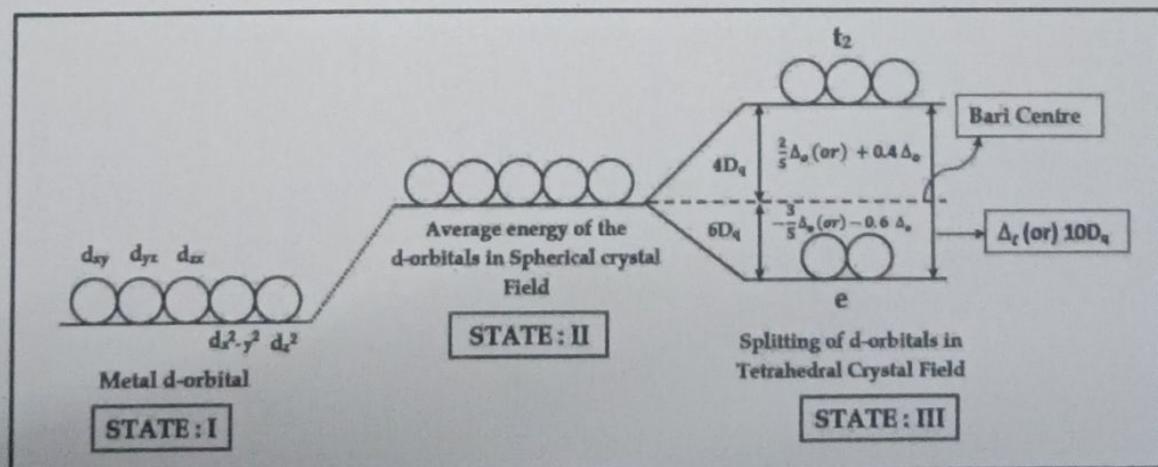
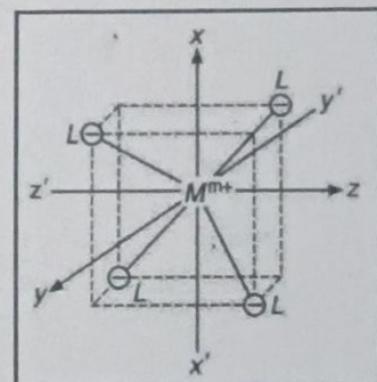




5. State - I : It represents degeneracy of all the five d-orbitals in the isolated central ion.
6. State - II : It represents hypothetical degeneracy of all the orbitals at a higher energy level if all the ligand approaching the central ion.
7. State - III : It represents Crystal field splitting of d-orbitals in Octahedral Crystl field as discussed bove
8. In this splitting the three lower energy orbitals are collectively called as t_{2g} orbitals while the two higher energy orbitals are called e_g orbitals.
9. The energy gap between e_g and t_{2g} is called crystal field splitting energy and it is denoted by Δ_o or Δ_{oct} or $10Dq$, where Δ represent Crystal field splitting energy, "o" in Δ_o is for octahedral.
10. The t_{2g} -orbitals lie at an energy that is $-0.4 \Delta_o$ below the average d-orbital energy.
11. The e_g orbitals lie at an energy that is $+0.6 \Delta_o$ above the average d-orbital energy
12. The magnitude of the CFS (Δ_o) depends upon the field produced by the ligand and charge on the metal ion.

CRYSTAL FIELD SPLITTING IN TETRAHEDRAL GEOMETRY

1. In the formation of a tetrahedral Comlex, the ligand molicules approach the central metal atom from between the axis.
2. During the approaching of ligands, the d-orbitals whose lobes lie between the axes will feel more repulsion as compared to other orbitals.
3. Therefore the energy of t_2 (d_{xy}, d_{yz}, d_{zx}) set of orbitals will be increased and the five d-orbitals will split into two different sets
4. The Cristal field splitting in Tetrahedral Complexes is as follows





5. State - I: It represents degeneracy of all the five d-orbitals in the isolated central ion.
6. State - II: It represents hypothetical degeneracy of all the orbitals at a higher energy level if all the ligands approaching the central ion.
7. State - III : It represents Crystal field splitting of d-orbitals in Tetrahedral Crystl field as discussed bove
8. In this splitting the two lower energy orbitals are collectively called as e - orbitals while the three higher energy orbitals are called t_2 - orbitals.
9. The energy difference exists between these two sets of orbitals is called Crystal field splitting energy and it is represented as Δ_t (The subscripts 't' stans for tetrahedral) or $10D_q$
10. The e - orbitals lie at an energy that is $-0.6 \Delta_o$ below the average d-orbital energy.
11. The t_2 orbitals lie at an energy that is $+0.4 \Delta_o$ above the average d-orbital energy.