

1. Structure and bonding models

Atoms are the smallest part of element that chemically react. In 1808, the 1st atomic theory was proposed by J.J. Thomson. At the end of 19th century it was proved that atoms are divisible into e^- , protons, neutrons.

Many atomic models such as J.J. Thomson's model, Rutherford's model, Bohr's model etc were suggested from time to time.

Electromagnetic radiation: In 1864, Maxwell proposed that an alternative current of high frequency is capable of radiating continuous energy in the form of waves called electro-magnetic waves (or) radiations. They have both electric & magnetic properties. The radiations such as visible, UV, IR, X-ray etc are called electromagnetic radiation. They travel with the speed of light i.e. 3×10^{10} cm/s or 3×10^8 m/s. All the waves have the following characteristics.

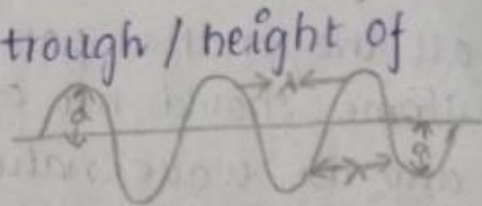
- (1) wavelength
- (2) velocity
- (3) frequency
- (4) Amplitude
- (5) wave number

1) **Wavelength:** The distance between 2 consecutive crest (or) trough of the wave is known as wavelength. Denoted by ' λ ' & expressed in

Angstrom (A°)

$$1 \text{ A}^\circ = 10^{-8} \text{ cm}, 10^{-10} \text{ m}$$

- 2) Frequency: No. of times a wave passes through a fixed point per unit time is known as frequency. Denoted by ' ν ' & expressed in cycles/sec or Hertz (Hz)
- 3) Wave number: - The reciprocal of wavelength is called wave number. Denoted by ' $\bar{\nu}$ ' & expressed in cm^{-1} .
- 4) Amplitude: - The depth of trough / height of crest is called amplitude. Denoted by ' a '.
- 5) Velocity: - Distance travelled by a wave in 1 sec is called velocity. Denoted by ' c ' & expressed in m/s (or) cm/s.



Planck's quantum theory: - In 1900, Max Planck proposed a theory of radiation while analyzing a light emitted by heated object that the emitted light is non-continuous and is in the form of discrete energy packets. These small packets of energy are known as quanta or photon. The energy of photon is directly proportional to frequency of radiation.

$$\text{Mathematically } E \propto \nu$$
$$\Rightarrow E = h\nu$$

where E = energy of photon

$$h = \text{Planck's constant} = 6.625 \times 10^{-34} \text{ Js.}$$

$$= 6.625 \times 10^{-27} \text{ ergs.}$$

ν = frequency of radiation

further the total energy emitted or absorbed by a body is always an integer & multiple of

$h\nu$, i.e. $E = nh\nu$ where $n = 1, 2, 3, \dots$. for eq: $h\nu, 2h\nu, 3h\nu, \dots$.

Similarly $E = \frac{hc}{\lambda}$ ($\because \nu = \frac{c}{\lambda}$)

Dual nature of matter: - The dual concept of matter gave worth to ^{wave} mechanical theory of matter. Radiations have dual nature i.e. wave nature & particle nature.

Debroglie's Equation: - According to debroglie's hypothesis, all the matter particles like e^- , proton, neutrons & atoms should not only have particle nature but also the wave nature.

Debroglie's wave eq. is derived from planck's quantum theory & einstein's mass energy relation.

According to planck's quantum theory, $E = h\nu$
 $\Rightarrow E = \frac{hc}{\lambda}$ ($\because \nu = \frac{c}{\lambda}$) \rightarrow ①

According to Einstein's mass energy relation,
 $E = mc^2 \rightarrow$ ②

Compare ① & ② equations.

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

$$\Rightarrow \lambda = \frac{h}{mc}$$

If c is replaced by velocity of a e^- 'v' then

$$\Rightarrow \lambda = \frac{h}{mv} = \frac{h}{p} \quad (\because p = mv)$$

Heisenberg's uncertainty principle: It states that it is impossible to determine simultaneously both the position & momentum of the particle

like e^- with accuracy.
Mathematically the relation, $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$
(or) the same written as $\Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$

where Δx = uncertainty in position
 Δp = uncertainty in momentum
 m = mass of e^- , h = Planck's constant.

case i:- If the position of particle is known exactly
($\Delta x = 0$) $\Delta x \cdot \Delta v = \frac{h}{4\pi m}$
 $\Rightarrow \Delta v = \frac{h}{4\pi m \Delta x}$
 $\Rightarrow \Delta v = \frac{h}{4\pi m(0)} = \infty$

case ii:- If velocity of a particle is known exactly
($\Delta v = 0$) then $\Delta x \cdot \Delta v = \frac{h}{4\pi m}$
 $\Rightarrow \Delta x = \frac{h}{4\pi m \Delta v}$
 $\Rightarrow \Delta x = \frac{h}{4\pi m(0)} = \infty$ (or) 0

The uncertainty principle gives the wave nature of e^- , only provides the probability of finding the e^- in given space.

Schrodinger's wave equation: In 1926, Erwin Schrodinger develop a new model of the atom. He incorporated the idea of quantization and conclusions of de Broglie's theory and Heisenberg's theory in this model.

In Schrodinger wave eq, e^- are treated as the wave motion in 3 dimensional space around the nucleus having nodes and quantized energy from classical wave mechanic if ψ is

the amplitude or a wave function of a wave moving in a 3 dimensional space with a velocity of 'v' and frequency 'ν', the wave equation is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + 4\pi^2 V^2 \psi = 0 \quad (\because V = PE)$$

According to deBroglie's wave equation

$$\lambda = \frac{h}{mv} \Rightarrow \frac{1}{\lambda} = \frac{mv}{h}$$

Since potential energy, $V = \frac{mv^2}{h}$,

substituting in the above eqⁿ.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + 4\pi^2 \left(\frac{mv}{h}\right)^2 \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + 4\pi^2 \frac{m^2 v^2}{h^2} \psi = 0$$

As $KE = \frac{1}{2}mv^2 \Rightarrow 2KE = mv^2$, substituting in above eqⁿ.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + 4\pi^2 m \frac{(2KE)}{h^2} \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} KE \psi = 0$$

(Since $E = PE + KE$)

$$KE = E - PE$$

$$KE = E - V$$

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

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

$$\nabla^2 \psi + \hat{H} \psi = 0$$

m = mass of e^- ,

V = PE (potential energy)

E = total energy

h = Planck's constant

v = velocity,

x, y, z = cartesian axis

Significances of ψ and ψ^2 :-

→ ψ is the amplitude of wave and its called wave function.

→ It is a positive value above the axis and negative value below the axis and becomes zero while crossing or intercepting the axis.

→ ψ is a state function but it has no physical significance it only represents the amplitude of wave.

→ The square of ψ (ψ^2) gives the propability function which describes the propability of finding an e^- around the nucleus which is maximum.

→ ψ^2 can be interpreted as propability density of dv is definite volume then $\psi^2 dv$ gives the propability of finding the e^- in an region having volume.

Particle in a one dimensional box :-

Consider a particle i.e. constrain to move only in x-direction from $x=0$ to $x=L$. Schrodinger wave equation is in operator form and can be given as $\hat{H}\psi = E\psi \rightarrow (1)$



\hat{H} is Hamiltonian operator.

$$\hat{H} = \frac{-\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} + V$$

Sub \hat{H} in the eqⁿ (1)

$$\Rightarrow \frac{\hbar^2}{8\pi^2 m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = E\psi$$

$$\Rightarrow \frac{\hbar^2}{8\pi^2 m} \frac{\partial^2 \psi}{\partial x^2} + V\psi - E\psi = 0$$

$$\Rightarrow \frac{\hbar^2}{8\pi^2 m} \frac{\partial^2 \psi}{\partial x^2} + (V-E)\psi = 0$$

Multiply by $\frac{8\pi^2 m}{\hbar^2}$

$$\frac{8\pi^2 m}{\hbar^2} \left(\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2 \psi}{\partial x^2} + (V-E)\psi \right) = 0$$

$$\Rightarrow \frac{8\pi^2 m}{\hbar^2} \cdot \frac{\hbar^2}{8\pi^2 m} \frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{\hbar^2} (V-E)\psi = 0$$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{\hbar^2} (V-E)\psi = 0$$

Case i:- Inside the box, $V=0$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{\hbar^2} (E-0)\psi = 0$$

$$\begin{aligned} \because E &= V + KE \\ E - V &= KE \end{aligned}$$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m E}{h^2} \psi = 0$$

Since $k^2 = \frac{2mE}{h^2}$ and replacing $k^2 = \frac{8\pi^2 m E}{h^2}$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0$$

case ii:- Outside the box, $V = \infty$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - \infty) \psi = 0$$

This is possible only when $\psi = 0$.

Wave function can be represented in a trigonometric function.

$$\psi_x = A \sin kx + B \cos kx$$

When $x=0$ then $\psi(x)=0$

$$0 = A \sin k(0) + B \cos k(0)$$

$$0 = B$$

Molecular orbital theory (MOT): Hund's and

Mullikan proposed the MOT. According to this

theory, all the atomic orbitals of the participating atoms gets mixed up to give equal no. of new orbitals called molecular orbitals

(MO).

Linear combination of atomic orbitals (LCAO):

Molecular orbitals of a molecule are

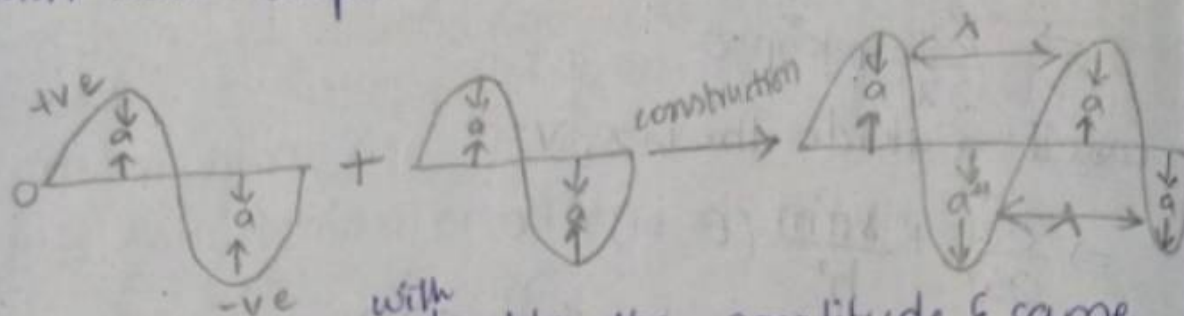
obtained by the linear combination of atomic orbitals of bonded atoms. According to LCAO

method, the LCAO can take place either by adding (constructive) or subtracting (destructive)

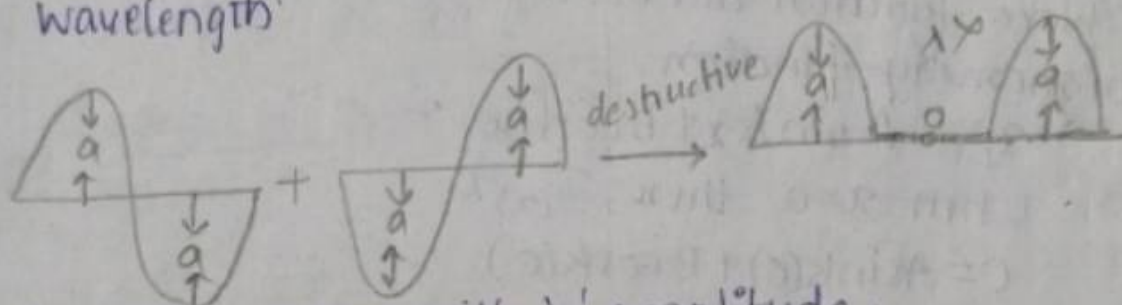
the wave function of the atomic orbitals involved. If two identical waves are added they

combined constructively to produce the wave

with double the amplitude & same wavelength. If they combine destructively, to produce the wave with zero amplitude



Resulting wave with double the amplitude & same wavelength



Resulting wave with '0' amplitude.

The MO formed as a result of constructive interference is known as Bonding molecular orbital (BMO) and the molecular orbital formed as a result of destructive interference are known as Anti-bonding molecular orbital (ABMO).

Characteristics of BMO & ABMO :-

Bonding molecular orbital	Anti-bonding molecular orbital.
1) The probability of finding the e^- in the internuclear region is greater than that of combining atomic orbitals.	1) The probability of finding e^- in the inter nuclear region decreases in the ABMO.

1) The e^- present in BMO result in the attraction between the two atoms.

2) The BMO has lower energy, as a result of attraction & hence has greater stability than that of the combining atomic orbitals.

3) They are formed by the additive effect of the atomic orbitals, so that the amplitude of the new wave is given by

$$\phi = \psi_A + \psi_B$$

4) They are represented by σ , π etc. towards

1) The e^- present in ABMO result in the repulsion between the two atoms.

2) The ABMO have higher energy because of the repulsive forces and lower stability.

3) They are formed by the subtractive effect of atomic orbitals, the amplitude of new wave is given by $\phi = \psi_A - \psi_B$.

4) They are represented by σ^* , π^* etc.

Salient features of molecular orbitals:-

1) The no. of MO produced is equal to the no. of atomic orbitals combined.

2) When 2 AO combine they form two molecular orbitals, one of which is called BMO and the other is called ABMO. These are formed by addition & subtraction of wave function respectively.

3) BMO have energy lower than the combining atomic orbitals while anti bonding MO have higher energy than combining atomic orbitals.

4) Each MO accommodates a maximum of two e^- obeying Pauli's exclusion principle.

5) Electrons enter in the MO of identical energies singling before they pair up obeying Hund's rule.

6) MO are filled to increase energies starting with the orbitals of minimum energy obeying Aufbau's principle.

7) Shapes of MO formed depend on type of combining orbitals.

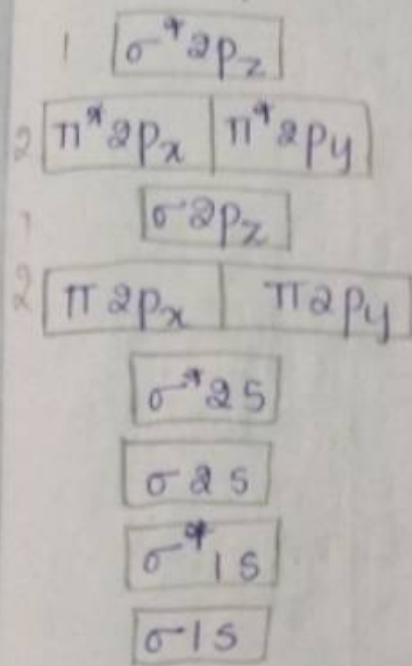
Energy level diagram for Molecular orbitals:

The energy of MO depends on following facts

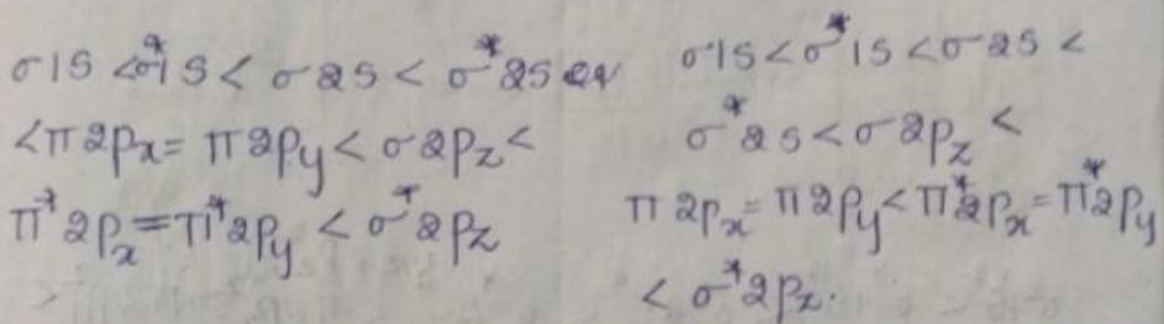
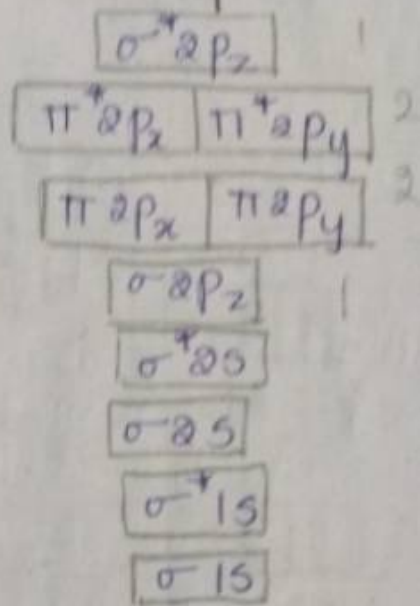
- 1) The energy of σ_{2s} & σ^*_{2s} molecular orbitals formed by the combination of two $2s$ orbitals will be higher than the MO of σ_{1s} and σ^*_{1s} formed by the combination of two $1s$ orbitals.
 - 2) The MO formed by combination of two p orbitals will have higher energy than those formed by two s orbitals.
 - 3) The energy level of these molecular orbitals have been determined experimentally by spectroscopic method by π_{2p_x} , π_{2p_y} are degenerated orbitals similarly $\pi^*_{2p_x}$ & $\pi^*_{2p_y}$.
 - 4) $2p_z$ have maximum energy among six $2p$ orbitals. The energy of σ_{2p_z} is not definite when the energy difference between $2s$ and $2p$ are smaller, σ_{2p_z} molecular orbital lies at higher energy than π_{2p_x} , π_{2p_y} .
- Thus the energy for the orbitals can be given

ies
as follows:

$$\bar{e} \leq 14$$



$$\bar{e} > 14$$



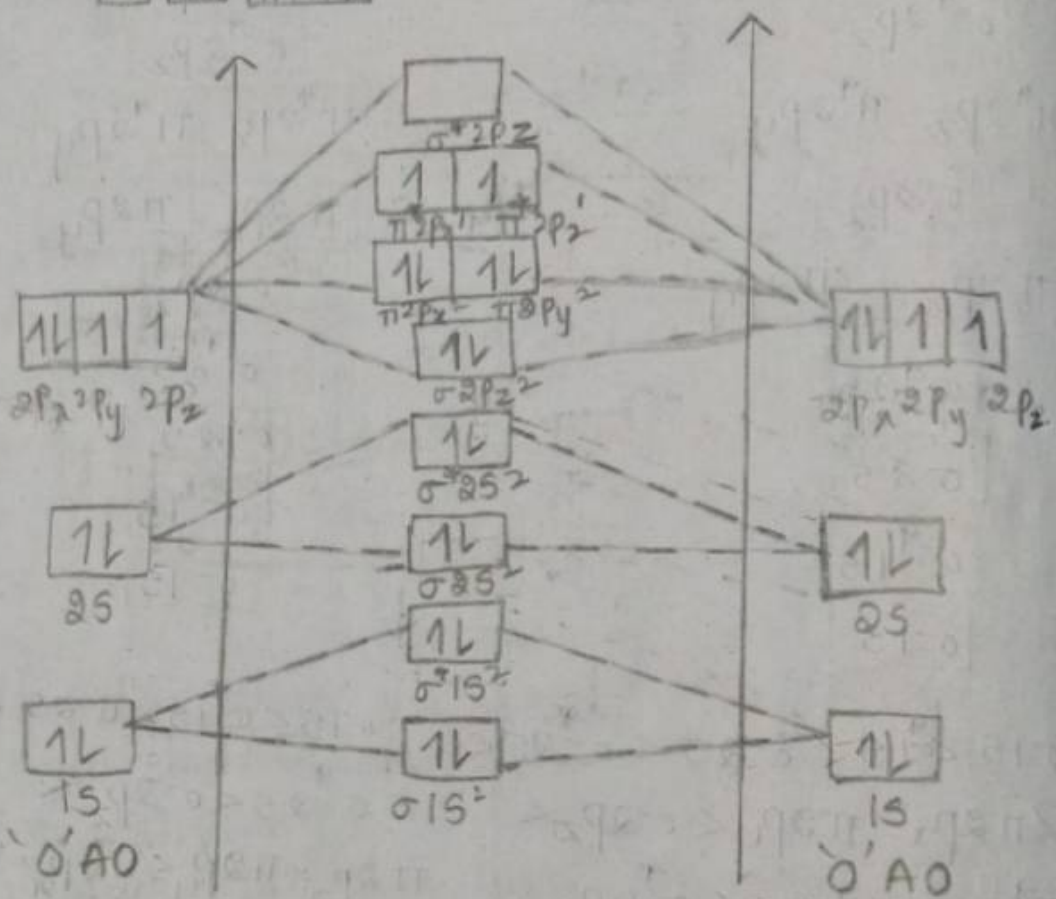
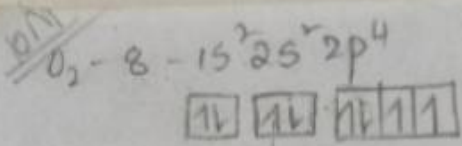
Bond order:- Bond order is defined as $\frac{1}{2}$ of the difference between the no. of e^- present in Bonding & anti bonding orbitals.

Mathematically, bond order = $\frac{1}{2} \left[\begin{matrix} \text{No. of } e^- \\ \text{in bonding} \end{matrix} - \begin{matrix} \text{No. of } e^- \\ \text{in anti} \\ \text{bonding} \end{matrix} \right]$

Bond order = $\frac{1}{2} [N_B - N_A]$

BMO - σ, π

ABMO - σ^*, π^*



$$\sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2p_z}^2 < \pi_{2p_x}^2 = \pi_{2p_y}^2 < \pi_{2p_x}^{*1} = \pi_{2p_y}^{*1}$$

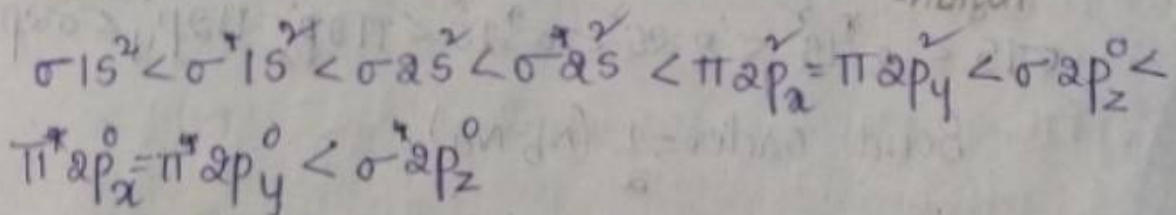
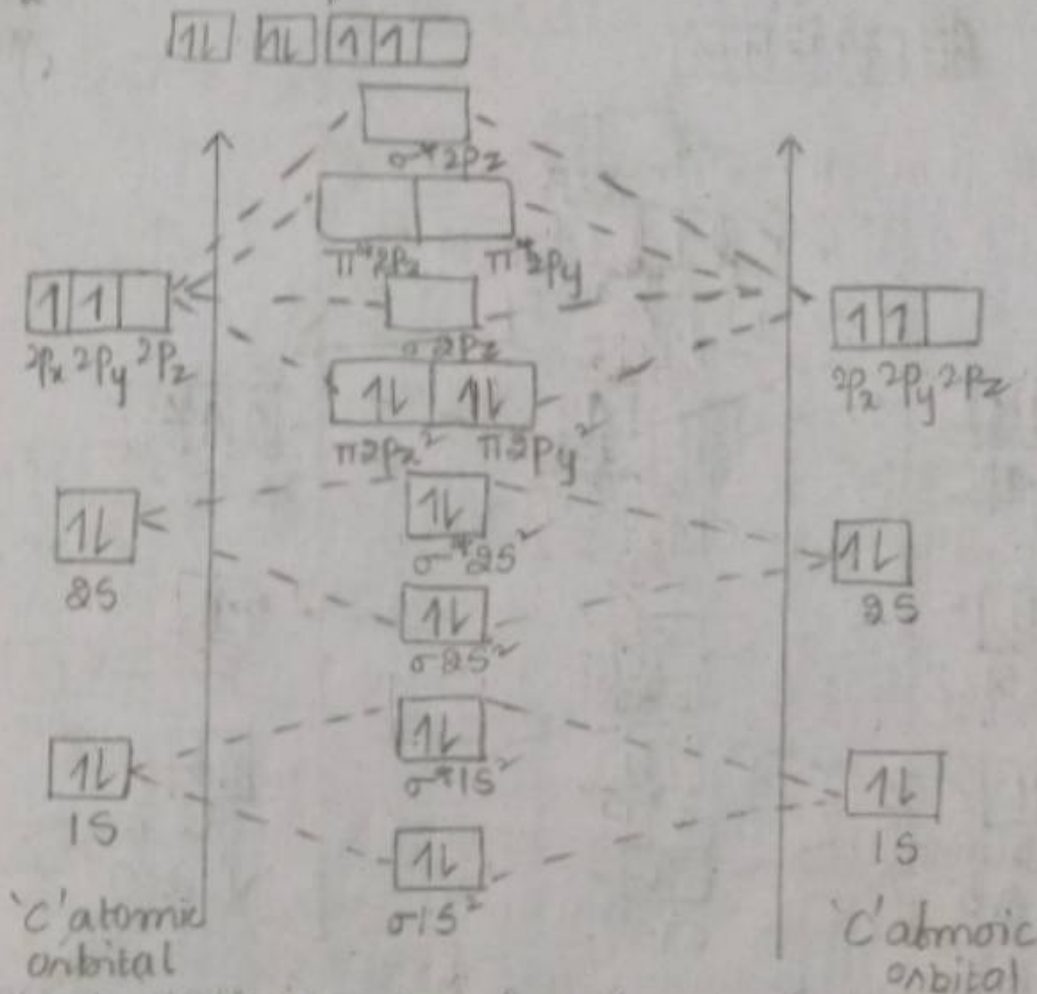
$$\text{Bond order} = \frac{1}{2} [N_b - N_a]$$

$$= \frac{1}{2} [10 - 6] = 2$$

\therefore It is paramagnetic property (as B.O is even)

\therefore The oxygen molecule behaves as paramagnetic molecule.

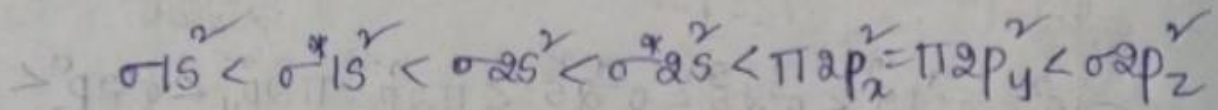
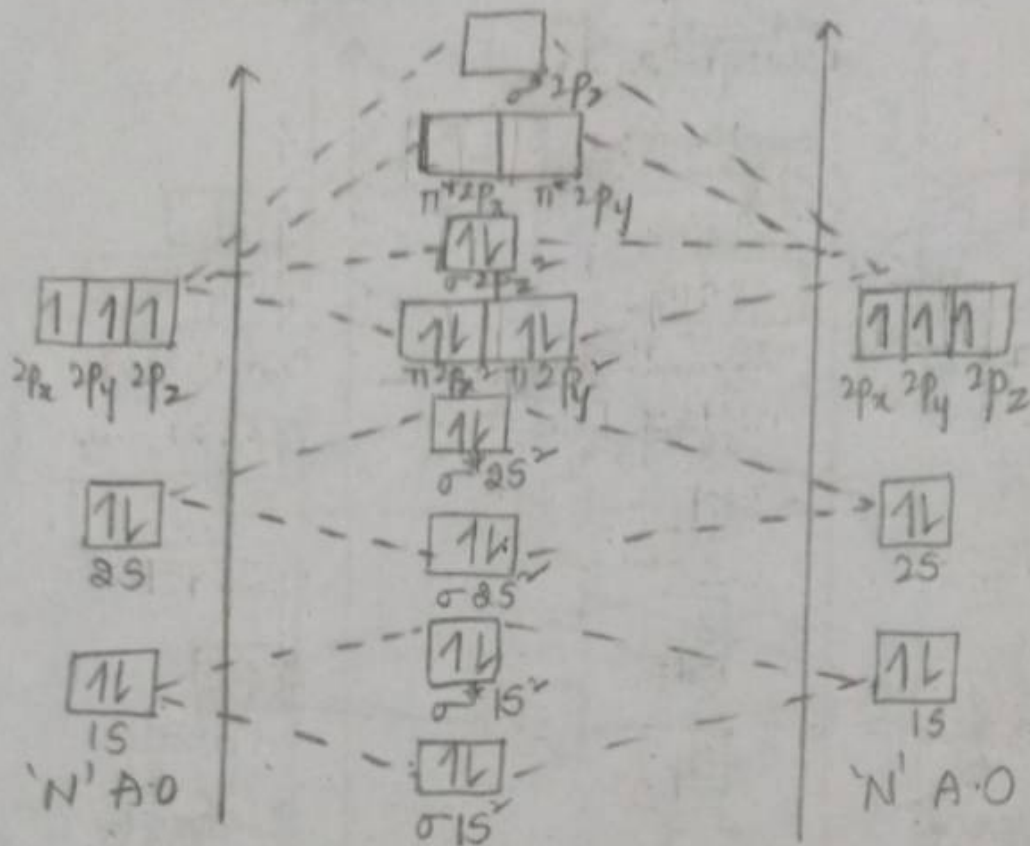
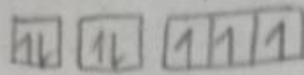
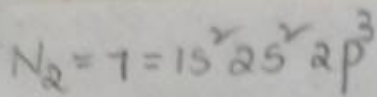
$$C_2 = 6 = 1s^2 2s^2 2p^2$$



$$\text{Bond order} = \frac{1}{2} (N_b - N_a)$$

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

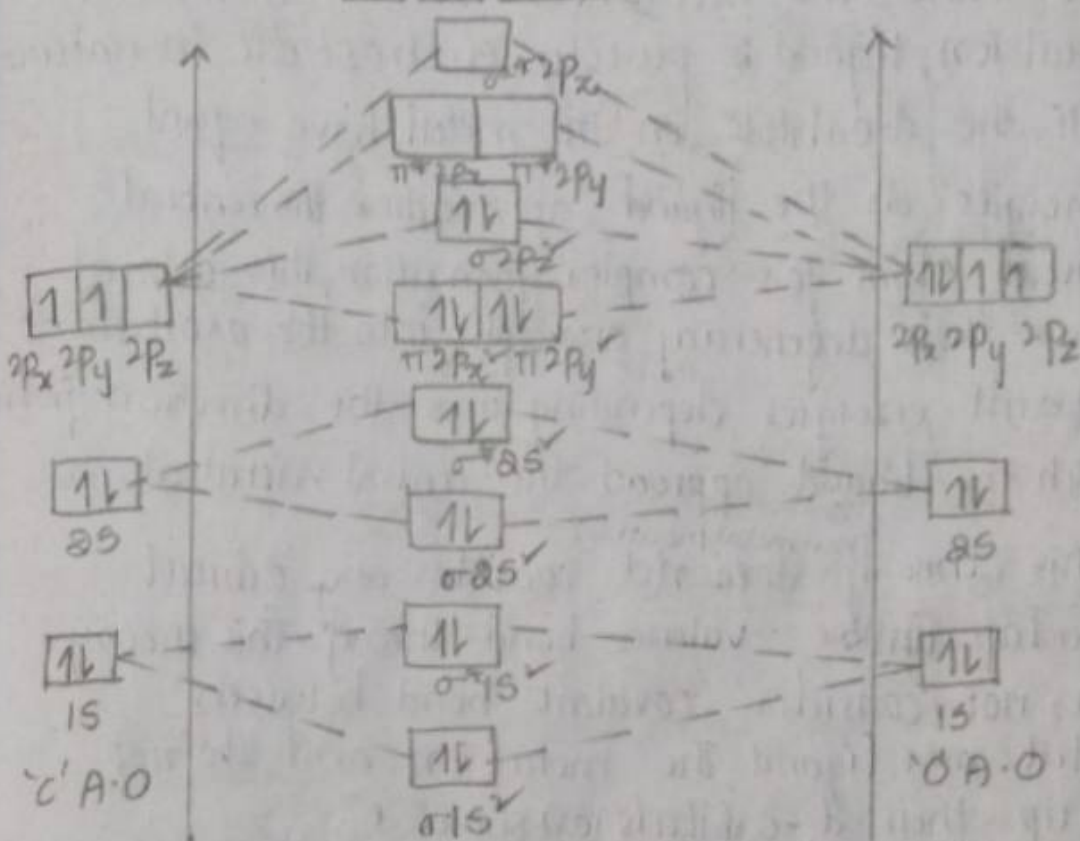
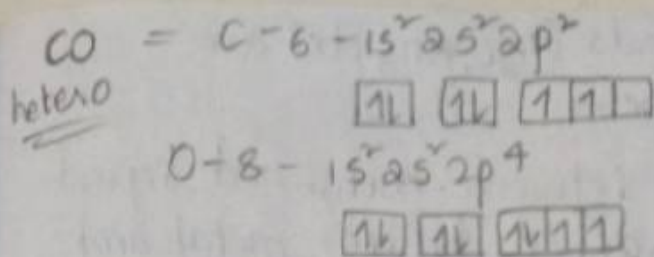
\therefore The carbon molecule behaves paramagnetic molecule because of ~~two~~ unpaired e^- .



$$\text{Bond order} = \frac{1}{2} (N_b - N_a)$$

$$= \frac{1}{2} (10 - 4) = 3$$

∴ The N_2 molecule behaves diamagnetic molecule because of unpaired e.



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

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 4) = 3$$

∴ The CO molecule behaves as diamagnetic molecule because of no unpaired e⁻ in CO, hence it is stable.

Crystal Field Theory:- The main postulates of this theory are.

1. A complex is considered as a combination of central metal ion surrounded by ligands.
2. The ionic ligands are regarded as point charges

where as neutral ligands (H_2O, NH_3 etc) are regarded as point dipoles.

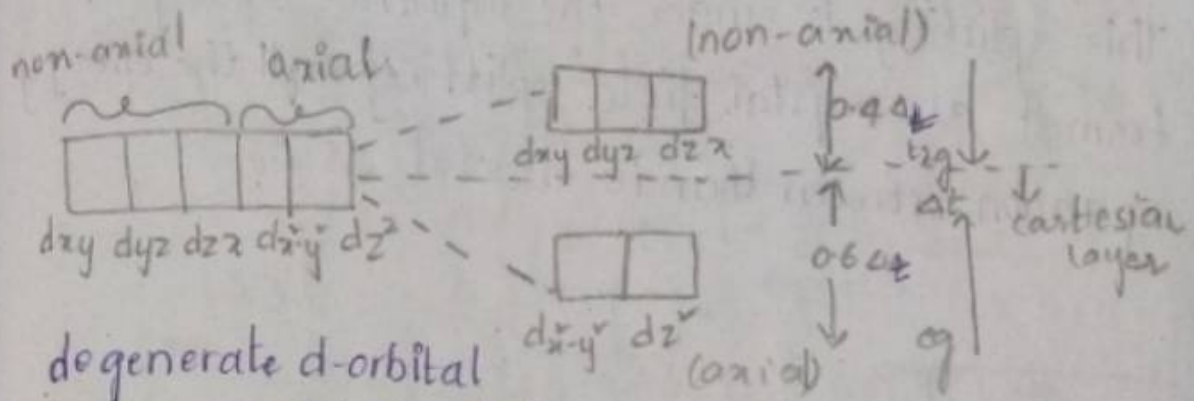
3. There is no overlap between metal and ligand orbital and the interaction between metal and metal ion, ligand is purely electrostatic in nature.

4. All the d-orbitals on the metal have equal energies. As the ligand approaches the central metal atom for complex formation, this orbital loses their degeneracy and split into the orbitals of different energies depending upon the direction from which the ligand approach the central metal atom.

5. This theory ^(non metal/neutral) does not consider any orbital overlap unlike valence bond theory. This theory does not consider covalent bond between metal and ligand. The metal ion and do not mix up their d-orbitals (or) share e^- .

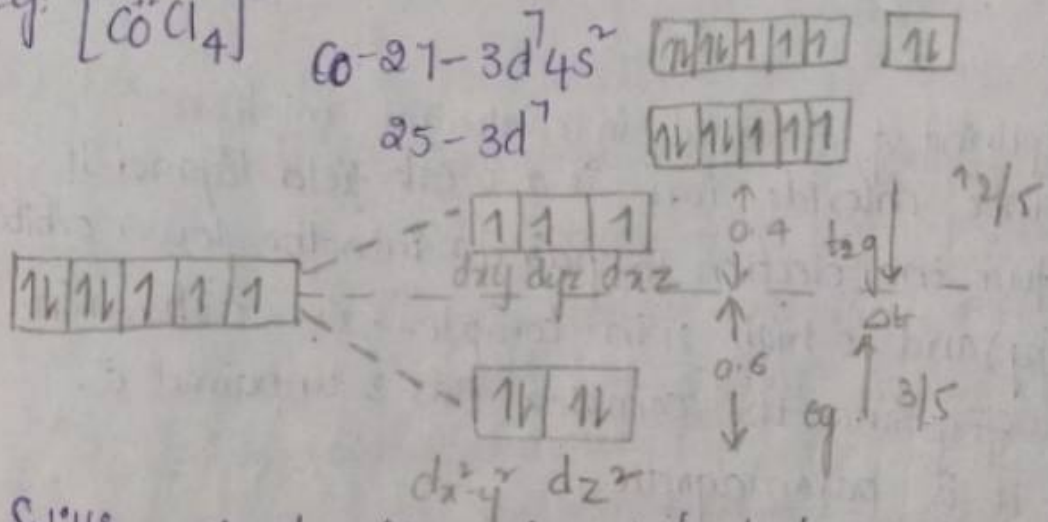
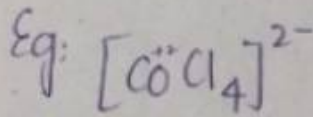
Splitting of d-orbitals in tetrahedral complexes:-

In tetrahedral complex four ligands occupy 4 corners of a cube and the metal ion is in the centre. Here d-orbitals are not pointed directly towards ligands the d_{xy}, d_{yz}, d_{zx} (non-axial orbitals) are closer to ligands than $d_{z^2}, d_{x^2-y^2}$ (axial orbitals). Therefore energy of t_{2g} orbital is more and $\therefore e_g$ orbital is less from the centre. The crystal field splitting in tetrahedral complexes is represented by Δ_t .



degenerate d-orbital
in free metal ion state

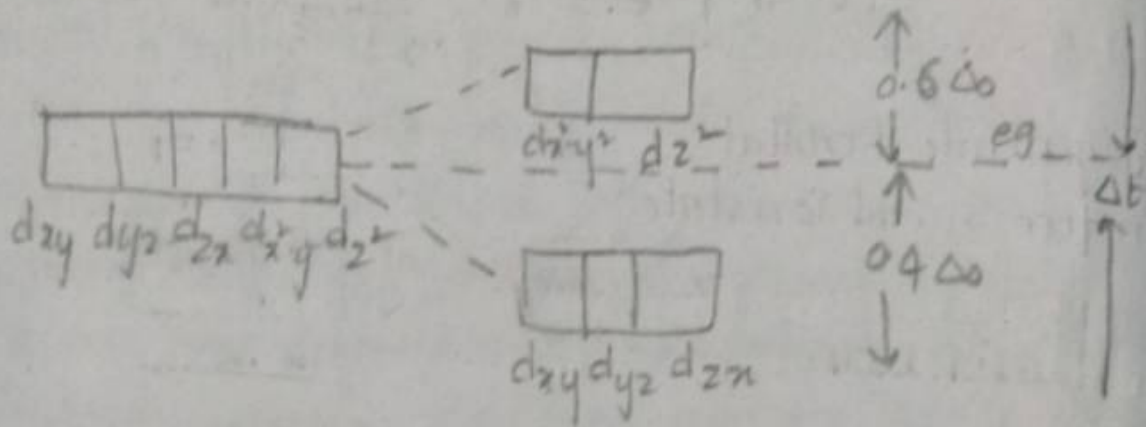
(first fill the e in lower orbital & then after upper orbital pairing)



Splitting of d-orbitals in octahedral complex:-

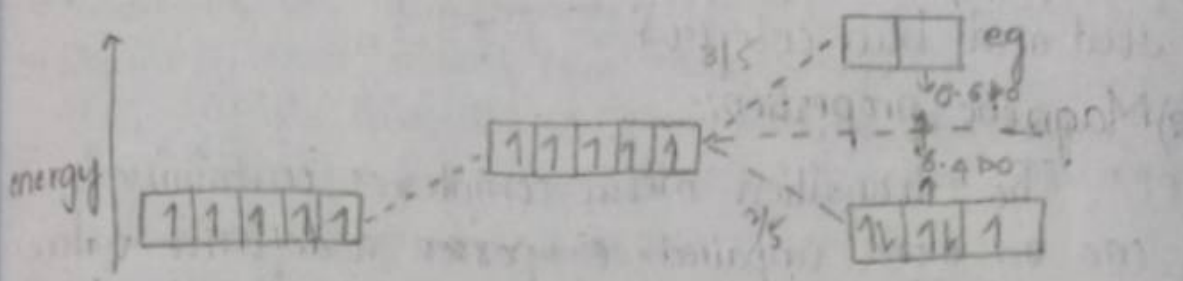
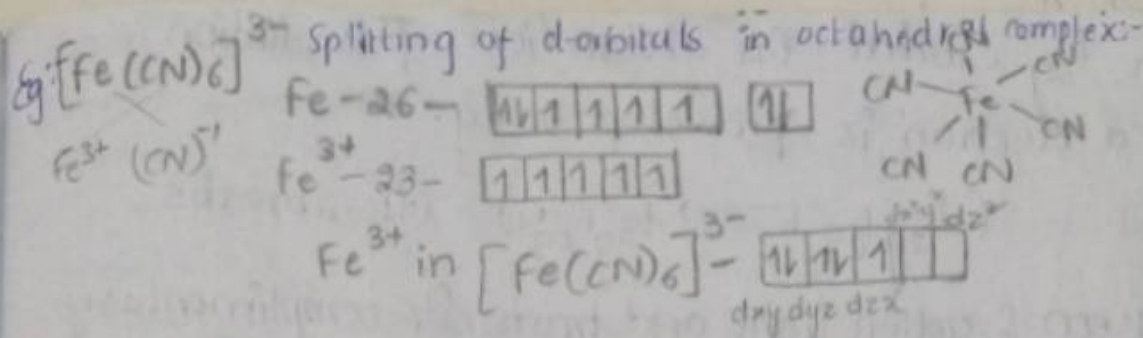
In octahedral complex the ligand approach the metal atom along the axis as result the axial orbitals have greater repulsion (axial orbital) than non-axial orbitals (d_{xy}, d_{yz}, d_{zx}). The degenerate d-orbital split into two discrete sets one with the lower energy and more stable t_{2g} and the other with the higher energy & less stable e_g orbital.

This splitting is under the influence of ligands is termed as crystal field splitting and the energy separation between them is denoted as Δ_0 .



Splitting of d-orbitals in tetrahedral complexes:

Since chloride ion is a weak field ligand. It force the electron to pair up into the lower orbital (eg) and so high spin complex is as shown in fig. Since the complex has 3 unpaired e^- . it is paramagnetic.



In octahedral complex of ferrous cyanide $[\text{Fe}(\text{CN})_6]^{3-}$, the central metal ion Fe^{3+} has the electronic configuration of $3d^5$. Since the cyanide ion $(\text{CN})^{-1}$ is a strong field ligand. Pairing of e^- takes place in the lower energy d-orbital (t_{2g}) and so a low spin complex is formed. Since the complex has 1 unpaired e^- in t_{2g} orbital, it is paramagnetic.

Most of the colours: Most of the transition metal are coloured. The colour of these complexes attributed to be d-d transition between t_{2g} and eg orbitals. The difference in the energy is so small that the absorption of even small amount of light brings excitation from lower to higher energy d orbital.

eg: In the complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, Ti^{3+} has one $d e^-$

in t_{2g} orbital. On absorption of radiation d electron is promoted to e_g .

$(t_{2g}^1 e_g^0 \longrightarrow t_{2g}^0 e_g^1)$ (it absorbs green & yellow light and transmits complimentary red and blue colour)

2) Magnetic properties:-

The transition metal complexes containing one or more unpaired e^- possess a definite value ~~value~~ of magnetic momentum. It is denoted by μ .

The substances having magnetic momentum are attracted by magnetic field. Such substances are called paramagnetic. The substances

having no unpaired e^- have zero magnetic momentum are called diamagnetic.

Eg:- The complex $[Fe(H_2O)_6]^{2+}$ has 4 unpaired e^- and is paramagnetic which is a high-spin complex whereas ferrous $[Fe(CN)_6]^{3+}$ _{hexacyanide} is a low-spin complex has no unpaired e^- and is diamagnetic. The magnetic momentum of co-ordination compounds depends on number of unpaired e^- .

Essay Questions:

- 1) Derive & Explain Schrodinger wave eq along with the significances of ψ & ψ^2 .
- 2) In detail, explain about particle in 1 dimensional box model.
- 3) Explain the characteristics of BMO & ABMO.
- 4) What are the significances MOT.
- 5) Draw a neat energy level diagram for:
a) O_2 b) CO . Give its configuration & B.O.
- 6) Explain the crystal field splitting of tetrahedral and octahedral complexes with an example.
- 7) Give any two applications of CFT colour.

Short questions:

- 1) Given schrodinger wave equation.
- 2) Give the limitations of ψ & ψ^2 .
- 3) Distinguish between BMO & ABMO.
- 4) What is bond order.
- 5) Briefly explain about ψ .
- 6) Expand CFT. (1/2M)

CFSE - crystal
field stabilization of energy.