

Quantum Mechanics:-

* Quantum mechanics is the mathematical description of matter on the atomic scale. In chemistry we are mostly interested in the electrons that give atoms their properties and hold atoms together to form molecules. Thus to describe matter and to predict the properties of molecules, we must use quantum mechanics.

* Quantum mechanics \rightarrow Newton mechanics
classical mechanics \rightarrow Maxwell electro magnetic sound wave theory \rightarrow phenomenon related to motion
classical mechanics:

- Formulated by Sir Isaac Newton (1642-1727)
- It is obeyed by "macroscopic particles" such as planets & rigid bodies.
- To determine simultaneously the position & the velocity of a moving particle.
- Classical mechanics assumes that energy is emitted or observed in a continuous manner but Quantum theory indicates that emission or absorption of energy takes place in an uncontinuous manner in the form of packets called quanta.

* Quantum mechanics obeyed by "microscopic particle" such as electrons, protons, atom and molecules.

- * Classical mechanics failed to provide satisfactory explanation for the black body radiation
Photo electric effect
Atomic and molecular Spectra
Heat capacities of solids.

$$P(\frac{d\sigma}{d\Omega}) = P \Delta$$

Schrodinger Time independent wave equation:

Let us consider a particle of mass 'm' moving with a velocity 'v'. The deBroglie wavelength associated with it is given by,

$$\lambda = \frac{h}{mv} \quad \text{--- (A)}$$

Where $h = \text{Plank's constant} = 6.626 \times 10^{-34} \text{ Js}$

Let ψ be the wave function of the particle along x, y and z coordinate at any time 't'. The classical differential equation of a progressive wave moving with a wave velocity 'v' can be written as

$$\left(\frac{\partial^2 \psi}{\partial t^2} - \frac{\nabla^2 \psi}{v^2} \right) + \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = 0 \quad \text{--- (2)}$$

The solution of the equation (2) is given by

$$\psi = \psi_0 e^{-i\omega t} \quad \text{--- (3)}$$

Where $\psi_0 = \text{Amplitude of the wave at the point } (x, y, z)$

$\omega = \text{Angular frequency of the wave}$

Differentiating eqn (3) with respect to 't'

$$\frac{\partial \psi}{\partial t} = (-i\omega) \psi_0 e^{-i\omega t}$$

Differentiating again w.r.t 't'

$$\frac{\partial^2 \psi}{\partial t^2} = (-i\omega)^2 \psi_0 e^{-i\omega t} = -\omega^2 \psi_0 e^{-i\omega t} \quad \text{--- (4)}$$

Substituting eqn (4) in eqn (2)

$$\nabla^2 \psi = -\left(\frac{\omega^2}{v^2}\right) \psi \quad \text{--- (5)}$$

where ∇^2 = Laplacian operator

$$\text{But } \omega = 2\pi f$$

$$= 2\pi \left(\frac{v}{\lambda}\right) \text{ or } \frac{\omega}{v} = \frac{2\pi}{\lambda}$$

$$\therefore \frac{\omega^2}{v^2} = \frac{4\pi^2}{\lambda^2} \quad \text{--- (6)}$$

Substituting eqn (6) in eqn (5).

$$\nabla^2 \psi = -\left(\frac{4\pi^2}{\lambda^2}\right) \psi \quad \text{--- (7)}$$

Substituting eqn (1) in eqn (7)

$$\nabla^2 \psi = \frac{4\pi^2}{(h/mv)^2} \psi \quad \text{--- (8)}$$

If E is the total energy of the particle,
the potential energy, then total
energy of the particle $\Rightarrow E = PE + KE$

$$E = V + \frac{1}{2}mv^2 \quad \text{--- (9)}$$

$$2(E-V) = mv^2$$

Multiplying both sides by m

$$2m(E-V) = m^2v^2 \quad \text{--- (10)}$$

Substituting eqn (10) in eqn (8)

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E-V) \psi = 0 \quad \text{--- (11)}$$

This equation is known as Schrodinger's
time independent wave equation.

For one dimensional motion, the above equation becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \text{--- (11)}$$

Introducing $\alpha = \frac{h}{2\pi}$ in the above equation

$$\boxed{\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\alpha^2} (E - V) \psi = 0} \quad \text{--- (12)}$$

For three dimension

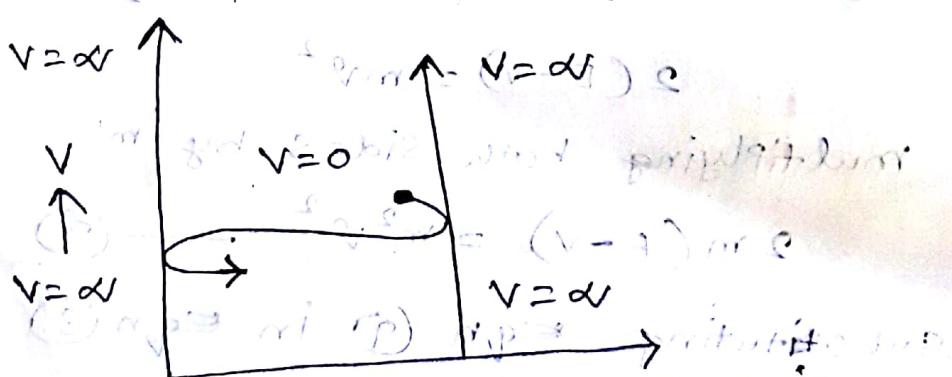
$$\boxed{\nabla^2 \psi + \frac{2m}{\alpha^2} (E - V) \psi = 0}$$

Particle in a box:-

(or)

Application of Schrodinger wave equation to a particle (electron) enclosed in a one-dimensional potential box:-

Let us consider a particle (electron) of mass 'm' moving along x -axis, enclosed in a one dimensional potential box as shown in figure.



Length of the box \rightarrow

Figure 1 Variation of potential energy of an electron in an one dimensional potential box.

Since the walls are of infinite potential the particle does not penetrate out from the box.

Also, the particle is confined between the length 'l' of the box and has elastic collisions with the walls.

Therefore, the potential energy of the electron inside the box is constant and can be taken as zero for simplicity.

∴ we can say that outside the box and on the wall of the box, the potential energy V of the electron is ∞ .

Inside the box the potential energy (V) of the electron is zero.

In other words we can write the boundary conditions as

$$V(x) = 0 \text{ when } 0 < x = l$$

$$V(x) = \infty \text{ when } 0 \geq x \geq l$$

Since the particle cannot exist outside the box the wave function $\psi = 0$ when $0 > x > l$

To find the wave function of the particle within the box of length 'l' let us consider the Schrodinger one dimensional time independent wave equation (i.e)

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} [E - V] \psi = 0$$

Since the potential energy inside the box is zero [$V=0$]. The particle has kinetic energy alone and thus it is named as a free particle (or) free electrons.

∴ For a free particle (electron), the Schrodinger wave equation is given by

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad \text{--- } ①$$

(or)

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0 \quad \text{--- } ②$$

where $k^2 = \frac{2mE}{\hbar^2}$

Equation ② is a second order differential equation, ∴ it should have solution with two arbitrary constants.

∴ The solution for eqn(2) is given by -

$$\psi(x) = A \sin kx + B \cos kx \quad \text{--- } ③$$

Where A and B are called as arbitrary constants, which can be found by applying the boundary conditions.

(i.e), $V(x) = \alpha V$ when $x=0$ and $x=l$

Boundary condition :-

(i) at $x=0$, potential energy $V=\alpha$

∴ There is no change for finding the particle at the walls of the box ∴ $\psi(x)=0$

∴ Equation ③ becomes

$$0 = A \sin 0 + B \cos 0$$

$$0 = 0 + B(1) \therefore B = 0$$

$$\boxed{\therefore B = 0}$$

Boundary Conditions:-

(ii) at $x=l$, potential energy $V=\infty$
 \therefore There is no chance for finding the particle at the walls of the box

$$\text{Given } \psi(x) = 0$$

\therefore equation (3) becomes

$$0 = A \sin kl + B \cos kl$$

since $B=0$ (From I Boundary Condition),

we have, that we have

$$\Rightarrow B=0 = A \sin kl$$

since $A \neq 0$, $\sin kl = 0$.

We know $\sin n\pi = 0$ to general form

Comparing these two equations, we can write $kl=n\pi$, where n is an integer

$$(3) \quad k = \frac{n\pi}{l} \quad (4)$$

Substituting the value of B and k in equation (3) we can write, the wave function associated with the free electron confined in a one dimensional box as

$$\text{envelope } \psi(x) = A \sin \frac{n\pi x}{l} \quad (5)$$

Energy of the Particle (Electron)

we know from $k^2 = \frac{2mE}{h^2}$

$$= \frac{2mE}{(h^2/4\pi^2)}$$

$$\therefore h^2 = \frac{\hbar^2}{4\pi^2}$$

$$\text{Eqn. } k^2 = \frac{8\pi^2 m E}{h^2} \quad (6)$$

Squaring Eqn ④ we get $K^2 = \frac{h^2 \pi^2}{l^2} \rightarrow ⑦$

Equation ⑥ and ⑦ Equating we can write

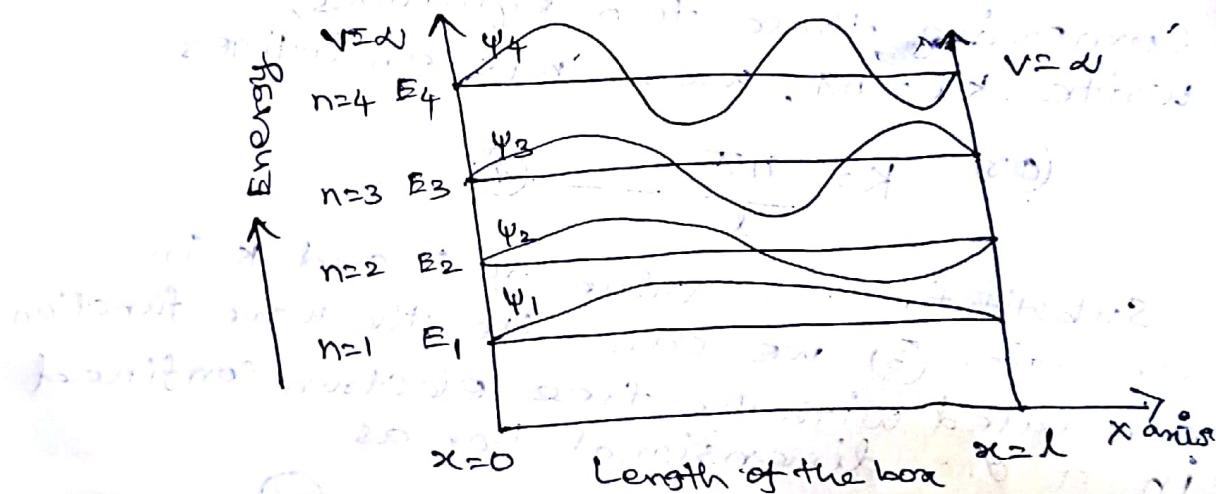
$$\frac{8\pi^2 m E}{h^2} = \frac{h^2 \pi^2}{l^2}$$

∴ The energy of the particle (electron) $E_n = \frac{h^2 l^2}{8ml^2} \rightarrow ⑧$

∴ From eqn ⑧ and ⑤, we can say that for each value of 'n', there is an energy level and the corresponding wave function?

Thus we can say that, each value of E_n is known as Eigen value and the corresponding value of ψ_n is called as Eigenfunction.

Energy levels of an electron:-



For various values of 'n' we get various energy values of the electron given in Fig. 2

The lowest energy value (or) ground state energy value can be got by substituting $n=1$ in eqn ⑧

∴ When $n=1$, we get $E_1 = \frac{h^2}{8ml^2}$

When $n=2$ we get $E_2 = \frac{4h^2}{8ml^2} = 4E_1$

When $n=3$ we get $E_3 = \frac{9\hbar^2}{8ml^2} = 9E_1$

When $n=4$ we get $E_4 = \frac{16\hbar^2}{8ml^2} = 16E_1$

∴ In general, we can write the energy eigen function as

$$E_n = n^2 E_1$$

It is found from the energy levels E_1, E_2, E_3 etc., the energy levels of an electron are discrete.

This is the great success which is achieved in quantum mechanics than classical mechanics, in which energy levels are found to be continuous.

The various energy eigen values and their corresponding eigen functions of an electron in one dimensional box have discrete energy values.

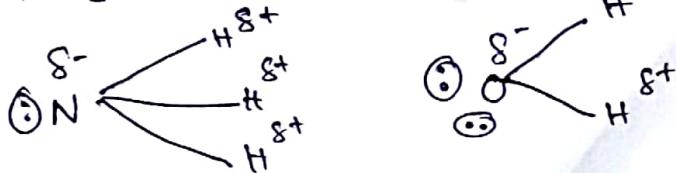
Basic Principles of crystal field theory:- (CFT)

The crystal field theory was given by Brønsted and Van Vleck. This theory was applied originally to ionic crystals and therefore called as crystal field theory.

* According to this crystal field theory, the ligand atoms of the ionic crystals such as Cl^- , F^- or CN^- considered as the negative point charges.

* On the other hand if the ligands are neutral molecules, they are regarded as point dipoles.

Eg: NH_3 and H_2O

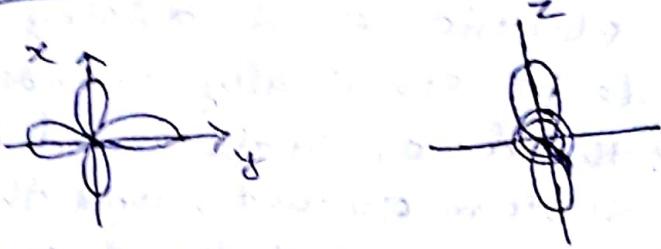


* Salient features of Crystal field theory are:

- 1) A complex is considered to be a combination of central metal ion surrounded by various ligands.
- 2) The interactions between the metal ion and ligands is purely electrostatic (ionic).
- 3) It does not consider only orbital overlap.
- 4) The ligands are either negatively charged ions eg: F^- & CN^- or neutral molecules eg, H_2O & NH_3 .
- 5) The interaction between the electrons of the metal ion and those of the ligand is purely repulsive. It is these repulsive forces that are responsible for causing the splitting of the 'd' orbitals of the metal into two groups t_{2g} & e_g . This effect is known as crystal field splitting.
- 6) The Number of ligands and their arrangement around the central metal ion will determine the crystal field splitting.
- 7) Different crystal fields will have different effects on the relative energies of the five d-orbitals.

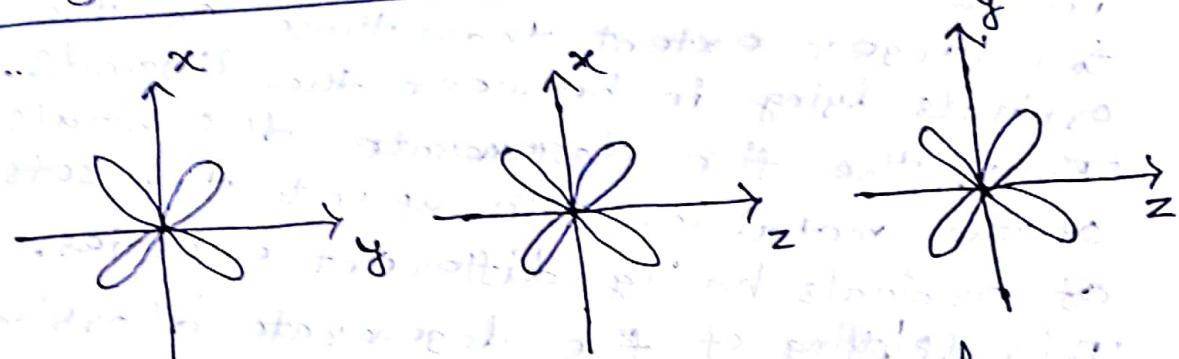
The outcome of crystal field theory is that the degeneracy of the d-orbitals of the central metal ion is when the ligands approach it consequently the d-orbitals split into two groups. To understand this we recollect the shapes of d-orbitals, they are as follows.

eg sets of orbitals:-



$$dx^2-y^2 \text{ and } dz^2$$

t_{2g} sets of orbitals:-



$$d_{xy} \text{ and } d_{xz}$$

* In a free (transition) metal ion all the five d-orbitals are degenerate i.e. the same energy. An electron is free to occupy any five d-orbitals d_{xy} , d_{yz} , d_{xz} , d_{z^2} and $d_{x^2-y^2}$. d_{xy} , d_{yz} , d_{xz} orbitals lie between x , y , and z axes respectively. They are known as t_{2g} set of orbitals (non axial orbitals).

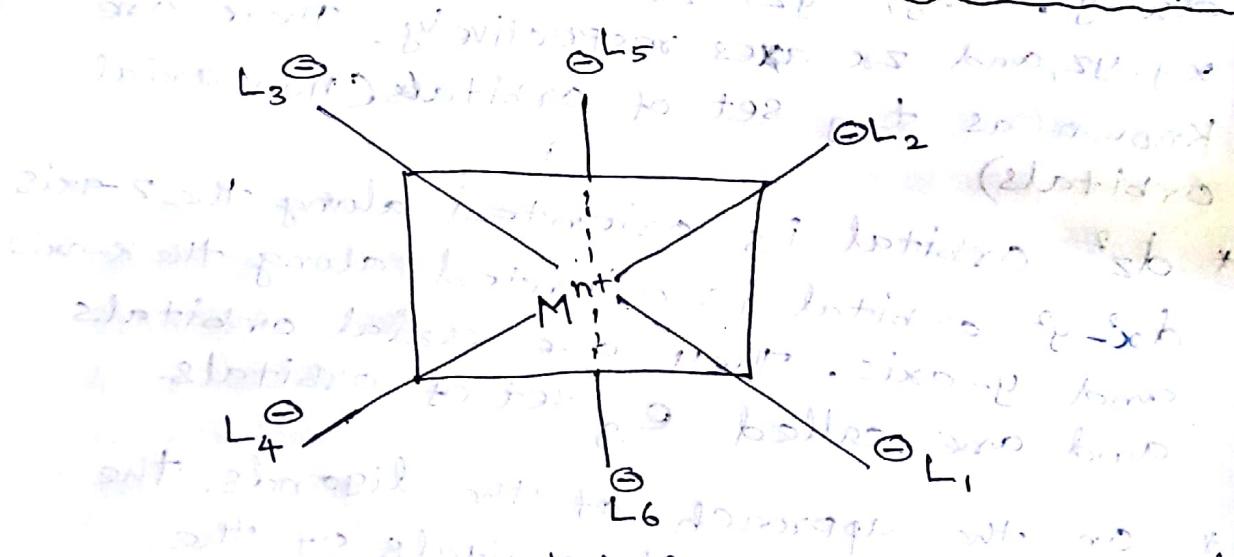
* d_{z^2} orbital is oriented along the z-axis and $d_{x^2-y^2}$ orbital is oriented along the x-axis and y-axis. They are axial orbitals and are called eg set of orbitals.

* On the approach of the ligands, the electrons in the d-orbitals of the central ion are repelled by the ions pairs of the ligands. As a result, the

energy of the entire system will be raised. If the electric field arising from the ligands is spherically symmetrical the energy of the d -orbitals would be raised to the system extent, and they will still be degenerate. But the d -orbitals differ in their orientation. As a result, the energies of the orbitals lying in the direction of the ligands are raised to a larger extent than those of the orbitals lying in between the ligands. Thus, the five degenerate 'd' orbitals of the metal ion split up into two sets of orbitals having different energies. This splitting of five degenerate 'd' orbitals of the metal ion under the influence of approaching ligands, into two sets of orbitals having different energies is called Crystal field splitting (or) energy level splitting.

* The crystal field splitting depends on the numbers and the arrangement of ligands around the central metal ion.

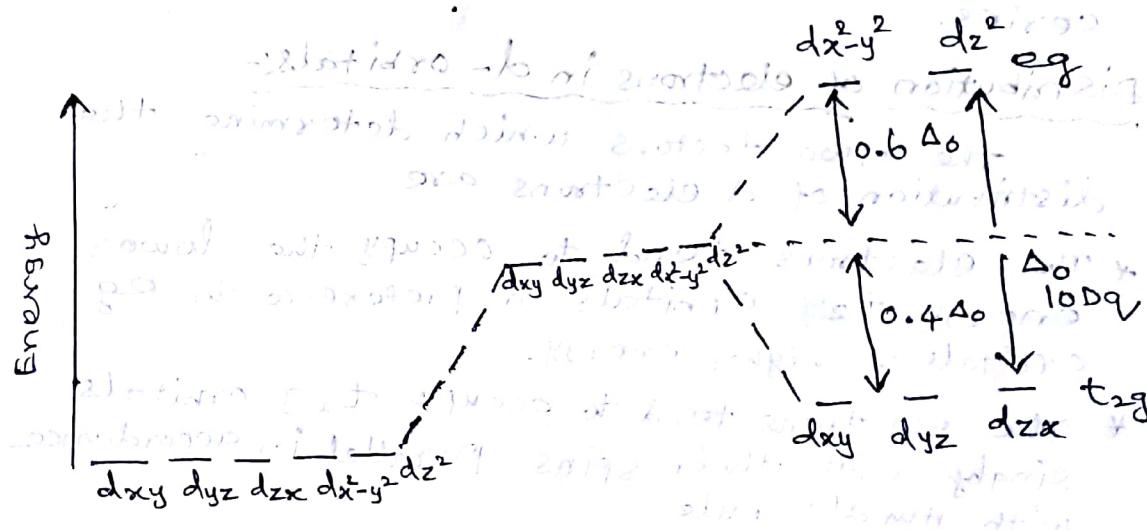
Crystal field splitting in octahedral complexes



In the octahedral complex, the six ligands are arranged octahedrally around a central metal ion. In this arrangement the $d_{x^2-y^2}$ and d_{z^2} orbitals lie along the x, y and z axes

and point directly towards the ligands. so they experience much more repulsion than the remaining 'd' orbitals (d_{xy} , d_{yz} and d_{zx}) which are directed in between the x, y and z axes. consequently the energies of $d_{x^2-y^2}$ and d_{z^2} orbitals are increased much more in comparison to other orbitals.

The energy difference between e_g and t_{2g} sets of orbitals is known as crystal field stabilization energy (CFSE) and this is represented by the symbol Δ_o , where 'o' indicates an octahedral arrangement of ligands. It is measured in terms of a parameter Dq . The magnitude of splitting is arbitrarily set as $10Dq$, i.e., $2Dq$ for each unpaired electron.



Electrons will tend to occupy the lower energy t_{2g} orbitals to achieve stability. Each electron entering the t_{2g} orbitals stabilises the complex by $0.4 \Delta_o$ units and each electron entering the higher energy orbitals (e_g), introduces in the complex, an instability unit of $0.6 \Delta_o$. The greater the amount of CFSE of the complex greater its stability. since $\Delta_o = 10Dq$, each electron entering t_{2g} orbital stabilises by $4Dq$, each electron entering e_g orbital destabilises by $6Dq$.

The magnitude of Δ_o depends upon the following factors.

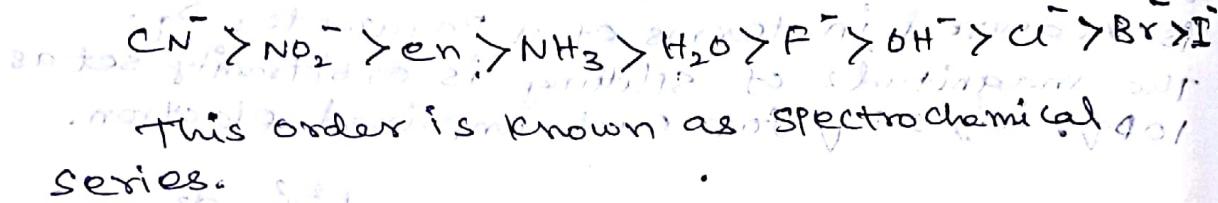
- * size of the metal ion
- * oxidation state of the metal
- * nature of the ligand
- * stereochemistry of the complex.

Strong and weak field ligands:-

Ligands which cause only a small degree of splitting of 'd' orbitals are called weak ligands and those which cause a large splitting are called strong ligands. Strong ligands have higher value of Δ_o .

Spectrochemical series:-

The crystal field splitting ability of the ligands decreases in the order.



Distribution of electrons in d-orbitals:-

The two factors which determine the distribution of d electrons are

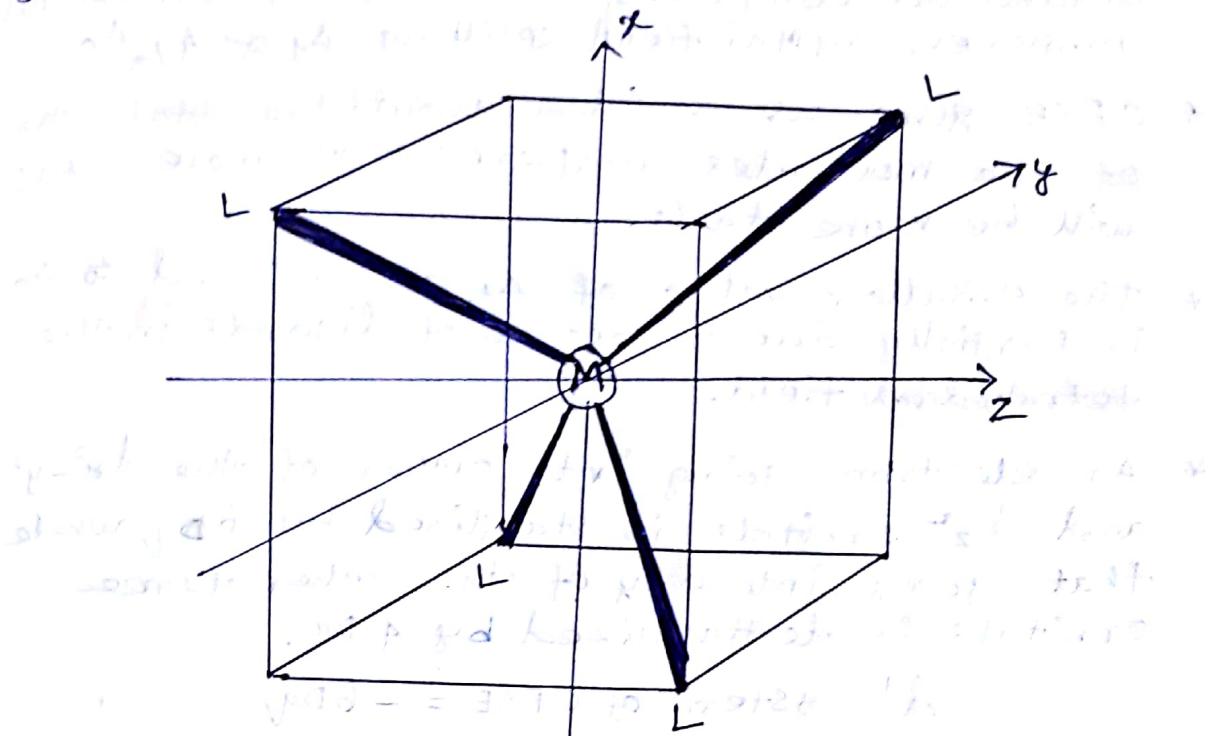
- * The electrons tend to occupy the lower energy t_{2g} orbitals in preference to e_g orbitals of higher energy.
- * The electrons tend to occupy t_{2g} orbitals singly with their spins parallel in accordance with Hund's rule.

The strong ligands force the electrons to pair up in the lower energy t_{2g} set. Thus they reduce the number of unpaired electrons and the resultant spin(s). The complexes formed by strong ligands have the minimum number of unpaired electrons. Such complexes are called low spin or spin paired complexes.

The weak ligands makes the electrons occupy all the five d-orbitals singly and then pairing occurs. Thus weak ligands give higher number of unpaired electrons. The complexes given by weak ligands are called high-spin or spin-free complexes.

Crystal field splitting in tetrahedral complexes:-

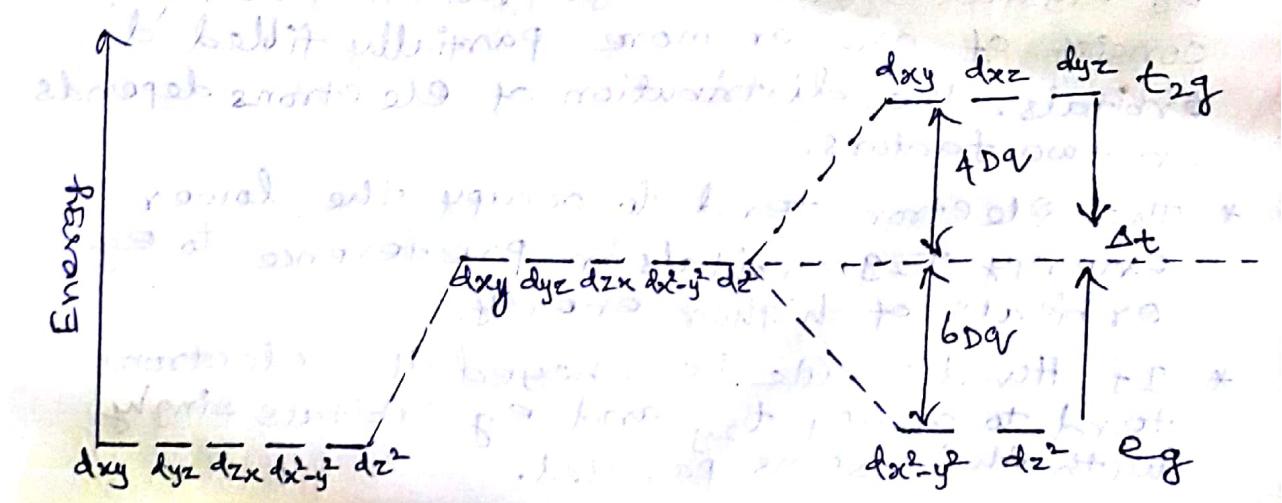
④ The tetrahedral arrangement of a central metal ion surrounded by four ligands is shown in Fig.



we find that in a tetrahedral arrangement no d-orbital point exactly towards the ligand. d_{xy} , d_{yz} and d_{zx} are pointing approximate in the directions of the approaching ligands. $d_{x^2-y^2}$ and d_{z^2} are lying in between approaching ligands.

so the energies of d_{xy} , d_{yz} and d_{zx} increase more than those of $d_{x^2-y^2}$ and d_{z^2} .

thus we find that d' orbital splitting is just the reverse of what happened in octahedral complexes.



- * Thus the crystal field splitting in a tetrahedral complex will be about half the magnitude of that in an octahedral complex. Hence crystal field effects favour the formation of octahedral complexes over that of tetrahedral complexes, crystal field splitting $\Delta_t \approx \frac{1}{2} \Delta_o$
- * CFSE gives us an idea about the stability of the molecules complexes with more CFSE will be more stable.
- * The smaller value of Δ_t as compared to Δ_o is partially due to less no of ligands in the tetrahedral field.
- * An electron going into either of the $d_{x^2-y^2}$ and d_{z^2} orbitals is stabilised by $6Dq$, while that going into any of the other three orbitals is destabilized by $4Dq$.
- d^1 system of CFSE = $-6Dq$
- d^2 system of CFSE = $-12Dq$
- * For d^3 system, both low spin and high spin states are possible. However, no tetrahedral complexes with low spin configuration is formed.
- * At Δ_t low spin, so pairing does not occur & most of the complexes are high spin complex.

Magnetic Properties:-

The magnetic properties of coordination compounds can be interpreted successfully by crystal field theory. Transition metal consist of one or more partially filled 'd' orbitals. The distribution of electrons depends on two factors.

- * The electrons tend to occupy the lower energy t_{2g} orbitals in preference to e_g orbitals of higher energy.
- * If Hund's rule is obeyed the electrons tend to occupy t_{2g} and e_g orbitals singly with their spins parallel.

Magnetic moment calculated by using the formula

$$\boxed{\mu = \sqrt{n(n+2)}}$$

n - no. of unpaired electrons.

Magnetic Properties of octahedral complexes:-

Example:- The magnetic moment of $[\text{FeF}_6]^{3-}$ ion is 5.9 BM while that of $[\text{Fe}(\text{CN})_6]^{3-}$ ion is 1.8 BM. This property can be explained as follows:

Fe^{3+} is the central metal ion in both $[\text{Fe}(\text{F}_6)]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ ions.

The electronic configuration of Fe^{3+} is as follows:



CN^- being a strong ligand forces the electrons to pair up against Hund's rule. Hence a single unpaired electron is present in $[\text{Fe}(\text{CN})_6]^{3-}$ ion. This is in agreement with the magnetic moment value of 1.8 BM.

In the presence of a weak ligand such as F^- no pairing occurs in Fe^{3+} ion.

Hence five unpaired electrons are present in $[\text{Fe}(\text{F}_6)]^{3-}$ ion. This is in agreement with the magnetic moment value of 5.9 BM.

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Molecular orbital theory

- * Molecular orbital was developed by Hund, Mulliken, Hückel.
- * It is used to find bond strength, bond order, magnetic behavior.
- * The atomic orbitals overlap to form new orbitals called molecular orbitals. When two atomic orbitals overlap (or) combine, they lose their identity and form new orbitals. The new orbitals thus formed are called molecular orbitals.
- * Molecular orbitals are the energy states of a molecule in which the electrons of the molecule are filled, just as atomic orbitals are the energy states of an atom in which the electrons of the atoms are filled.
- * A MO gives the electron probability distribution around a group of nuclei just as, AO's give the electron probability distribution around the single nucleus.
- * only those AO's can combine to form MO's which have comparable energies and proper orientation.
For ex:- 1s can combine with 1s and not with 2s.
- * The no. of MO's formed is equal to no. of combining AO's.
- * when two AO's combine, they form two new orbitals called bonding MO's & anti bonding MO's
- * The bonding MO's has lower energy and hence greater stability than the corresponding anti bonding orbitals.
- * The bonding MO's are represented by σ, π, δ whereas the corresponding antibonding MO's are represented by $\sigma^*, \pi^*, \delta^*$.
- * The shape of MO's formed depend upon the type of the combining AO's.
- * The filling of MO's takes place, according to same rules as those of AO's. These are

(i) Aufbau principle:- Mo's are filled in the order of the increasing energies.

(ii) Pauli exclusion principle:- Mo can have maximum of $2e^-$ s and these must have opposite spin.

(iii) Hund's rule of maximum multiplicity:-

For degenerate orbitals pairing takes place only after each orbital is singly occupied.

Bonding & Antibonding Molecular orbitals:-

Bonding

Antibonding

* Bonding molecular orbitals are a type of molecular orbitals that are involved in the formation of a chemical bond.

* Electron density is higher, * Energy is comparatively lower.

* Energy is comparatively lower, * Energy is comparatively higher.

* Electrons contribute to the formation of a bond. * Electrons do not contribute to the formation of a bond.

* Represented without an asterisk mark (*)

* Stability is comparatively higher. * Stability is comparatively lower.

* Geometry of a molecule is represented by the spatial arrangement.

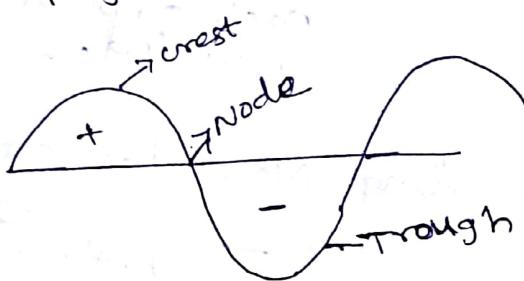
* Geometry of a molecule does not depend on the spatial arrangement.

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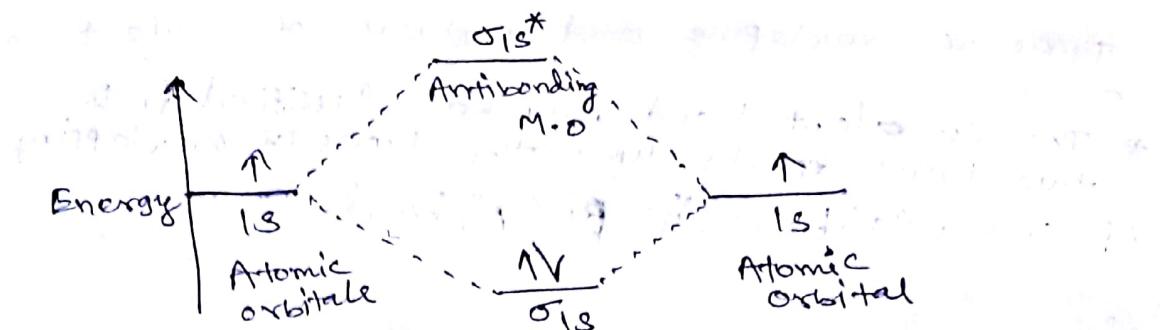
Linear combination of atomic orbitals : (LCAO)

Linear combination of atomic orbitals is an approximate method for representing MO's.

- * In linear combination of atomic orbitals method, the correct molecular orbitals are approximated by combining linearly the atomic orbitals of the atoms that form the molecule.
- * An atomic orbitals may be considered as an electron wave having a crest (+) and a trough (-) as shown in fig.



- * When two combining atoms approach each other, their atomic orbitals of comparable energies combine to form molecular orbitals. During the process of coalescence, there could be two possibilities.
- * If the electron waves of the combining orbitals reinforce each other i.e. crest of one wave overlaps the crest of the other wave, an attractive molecular orbital of low energy is formed. This is called bonding molecular orbital.
- * However, if the electron waves of combining atoms oppose each other i.e., the crest of the one wave overlaps the trough of the other, a repulsive molecular orbital of high energy is obtained. This is called antibonding molecular orbital.
- * Thus by the combination of two atomic orbitals, always, two molecular orbital are formed. The configuration of the ~~mole~~ molecule maybe obtained.
- * The ~~configuration~~ configuration of the molecule may be obtained by placing electrons into these molecular orbitals in accordance to aufbau principle.
- * The molecular orbitals are represented by Greek letters σ (sigma), π (pi), δ (delta) etc... The antibonding molecular orbitals are represented by putting an asterisk (*) over these letters.



conditions of LCAO:-

- * The participating orbitals must have same (or nearly same) energy. For example 1s orbital of one atom cannot combine with 2s orbital of another atom.
- * The corresponding orbitals of both atoms should have same symmetric orientation around the molecular axis. For example although all the three orbitals of 2p have the same energy, 2p_z orbital of one atom can only combine with the 2p_z orbital, not 2p_x or 2p_y of the other atom.
- * The combining atomic orbitals must overlap to the maximum extent. The greater will be the electron overlap, the greater will be the electron density between the nuclei of a molecular orbital.

Overlapping of atomic orbitals:-

When orbitals of two atoms come close to form bonds, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of (phase) and direction of orientation of amplitude of orbital wave function in phase.

positive (or) in Phase overlap:-



Negative (or) out of phase overlap:-



Types of overlapping and Nature of covalent bond

- * The covalent bond may be classified into two types depends upon the types of overlapping.
- (i) sigma (σ) bond (ii) pi (π) bond.

Sigma bond:-

This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called on overlap (or) axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

Molecular orbitals from S-atomic orbitals

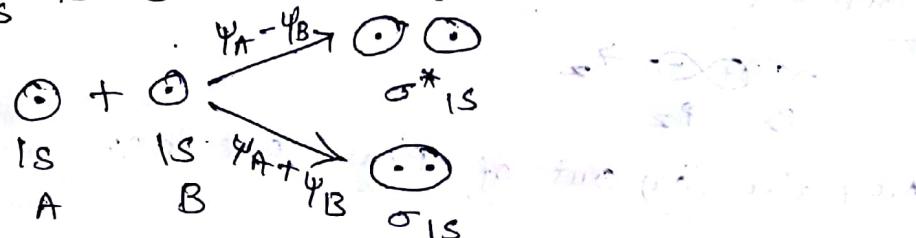
S - S - Overlapping :-

Let ψ_A and ψ_B the wave functions of two S-atomic orbitals. The linear combinations of these orbitals give the following bonding and anti bonding molecular orbitals.

$$\Psi_b = \psi_A + \psi_B$$

$$\Psi_a = \psi_A - \psi_B$$

Ψ_b orbital is obtained when $++$ (crest, crest) regions of both S-atomic orbitals overlap along the internuclear axis, while orbital Ψ_a is obtained when $+-$ (crest, trough) regions of atomic orbitals overlap. If the combining atomic orbitals are $1s$ & $1s$ Ψ_b is designated as σ_{1s} , while Ψ_a is represented by σ^*_{1s} . formation of σ_{1s} & σ^*_{1s} is shown in Fig.



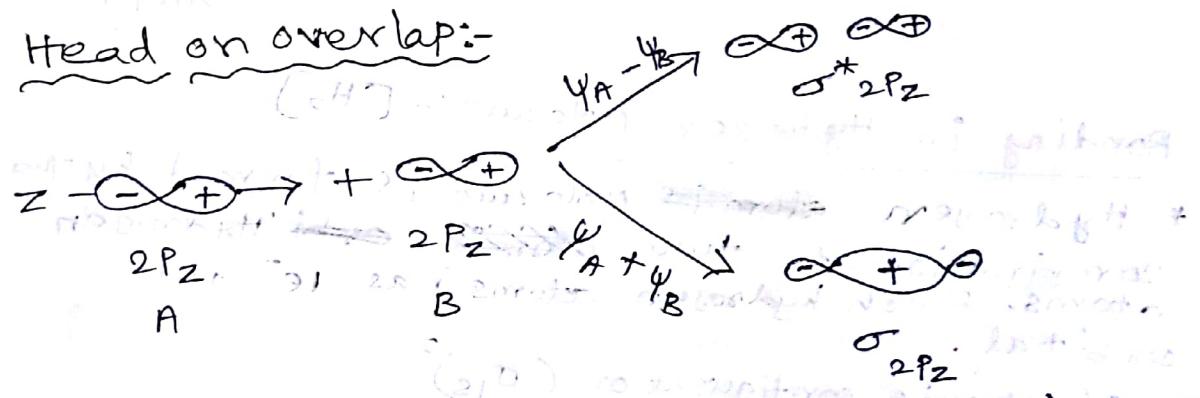
If the combining atomic orbitals are $2s$ & $2s$, the bonding molecular orbital is represented by σ_{2s} and the antibonding molecular orbital by σ^*_{2s} .

Molecular orbitals from p-atomic orbitals:-

p-p overlapping:-

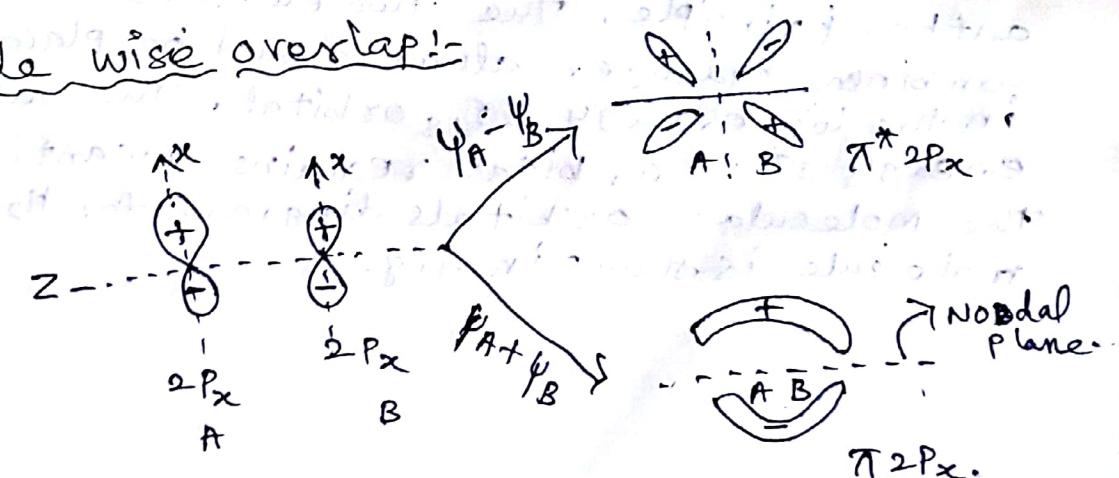
The three p-orbitals are directed along the three coordinate axes (x, y and z axes). If z-axis is taken as the internuclear axis, i.e. the line joining the centres of the nuclei in a diatomic molecule, the overlap of p-orbitals can be either head on or sideways. The head on overlap is overlap along the internuclear axis gives a bonding and an antibonding σ-molecular orbital while the sideways overlap gives four π-molecular orbitals. Two molecular orbitals are obtained by the combination of the two P_z orbitals while the other two are obtained by the combinations of two P_y -orbitals.

Head on overlap:-



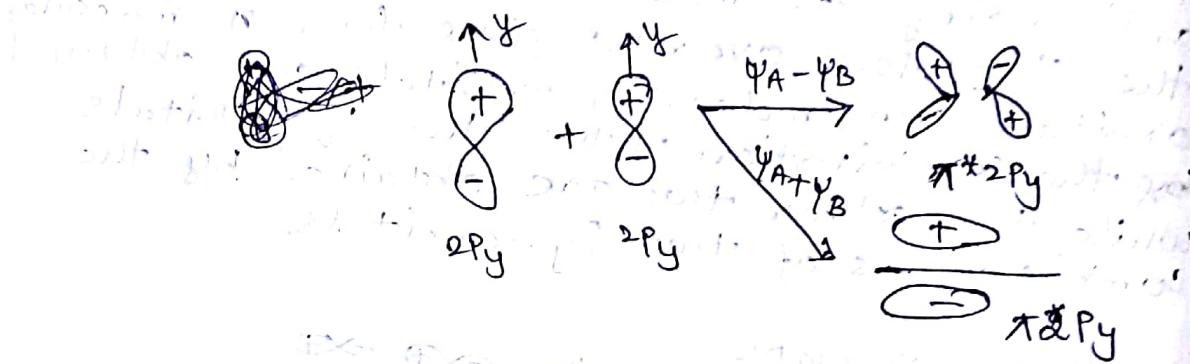
When two $2P_z$ orbitals of the combining atoms overlap in phase (+ +), a sigma bonding molecular orbital $\sigma 2p_z$ is obtained. In case the two $2P_z$ orbitals combine out of phase (+ -), a sigma antibonding molecular orbital $\sigma^* 2p_z$ is obtained.

Side wise overlap:-



When the $2p_x$ orbitals overlap in phase (+ +) a bonding molecular orbital π^2p_x is obtained. In case two $2p_x$ atomic orbitals overlap out of phase (+ -) an antibonding molecular orbital π^*2p_x is obtained.

Similarly addition and subtraction overlap of $2p_y$ orbitals results in the formation of π^2p_y and π^*2p_y orbitals respectively as illustrated in :

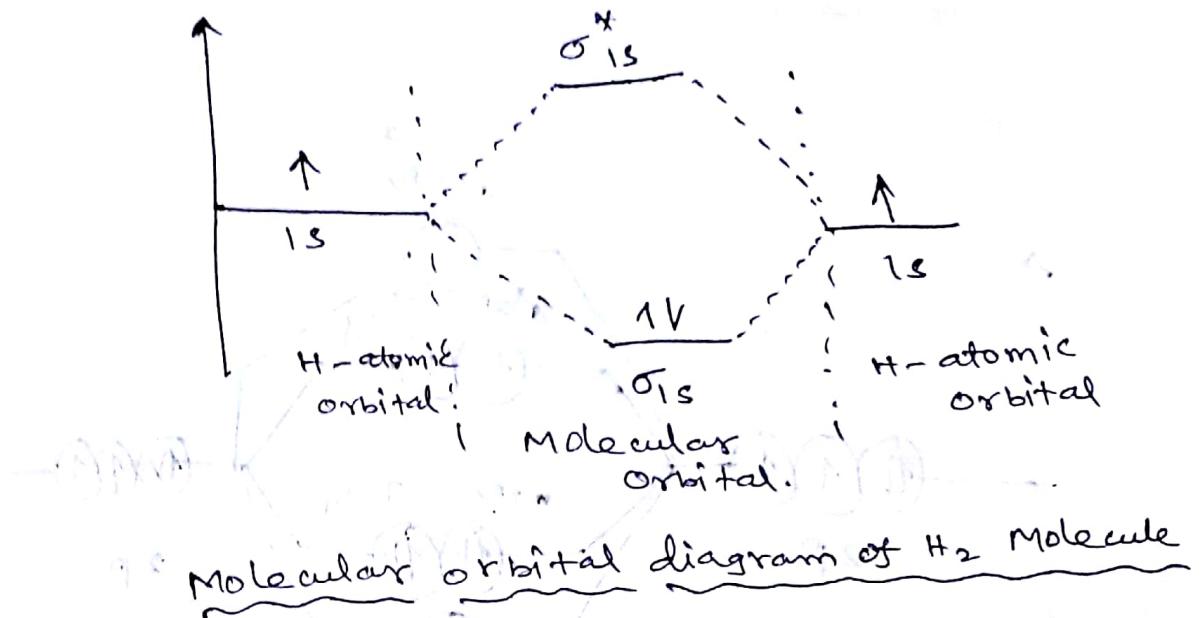


Bonding in Hydrogen molecule :- [H₂]

* Hydrogen ~~molecule~~ molecule is formed by the combination of two ~~atoms~~ ~~hydrogen~~ atoms. Each hydrogen atoms has $1e^-$ in its orbital.

* Electronic configuration (σ_{1s})²

* Hydrogen atom (1s¹) contains only one electron in 1s atomic orbital. H₂ molecule will thus possess two electrons. At a certain internuclear distance, the 1s atomic orbitals of the two combining H-atoms overlap to form σ_{1s} and σ^*_{1s} molecular orbitals. According to aufbau principle, the two electrons of the combining hydrogen atoms should be placed in the low energy σ_{1s} orbital. The high energy σ^*_{1s} orbital remains vacant. The molecular orbital diagram for H₂ molecule is shown in fig.



Molecular orbital diagram of H₂ Molecule

From the above diagram it is clear that
 $N_b = 2$ & $N_a = 0$. Therefore.

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

N_b - No of bonding molecular orbital
 N_a - No of antibonding molecular orbital

Status of bond:- Since the value of bond order is one, the two hydrogen atoms in H₂ molecule may be regarded as being connected by a single bond.

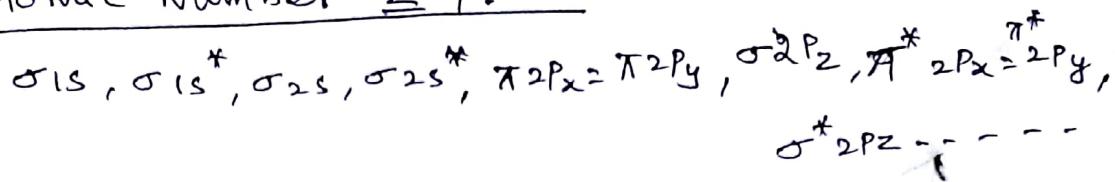
Diamagnetic nature:- H₂ Molecule does not possess any unpaired electron. Hence the molecule is diatomic nature.

Similarly:-

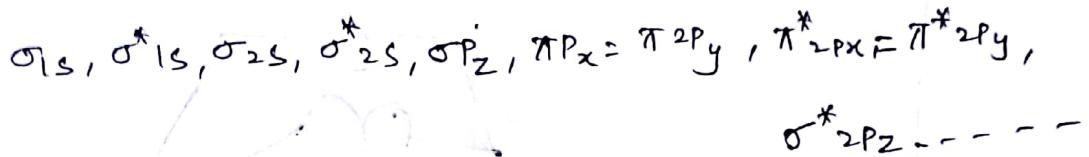
$$* H_2^+ \text{ Bond order} = \frac{N_b - N_a}{2} = \frac{1 - 0}{2} = \gamma_2^+$$

$$* H_2^- \text{ Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 1}{2} = \gamma_2^-$$

Atomic Number ≤ 7 :



Atomic Number > 7 :



Carbon Monoxide Molecule: - (~~O~~ CO)

* The electronic configurations of 'C' and 'O' atoms are $1s^2 2s^2 2p^2$ and $1s^2 2s^2 2p^4$ respectively. There are 4 electrons in the outer shell of carbon and 6 electrons in the outer shell of oxygen. Thus a total of 10 outer electrons are to be accommodated in the molecular orbitals of CO molecule. Because of higher electronegativity of oxygen, its atomic orbitals would be of lower energy than the corresponding atomic orbitals of carbon. Due to this energy difference, the bonding and antibonding molecular orbitals will receive different contributions from atomic orbitals of carbon and oxygen. The bonding molecular orbitals will receive more contribution from atomic orbitals of lower energy. i.e. the atomic orbitals of oxygen and would be closer to it in energy than the antibonding molecular orbitals which would be closer to carbon in energy, as shown in fig.

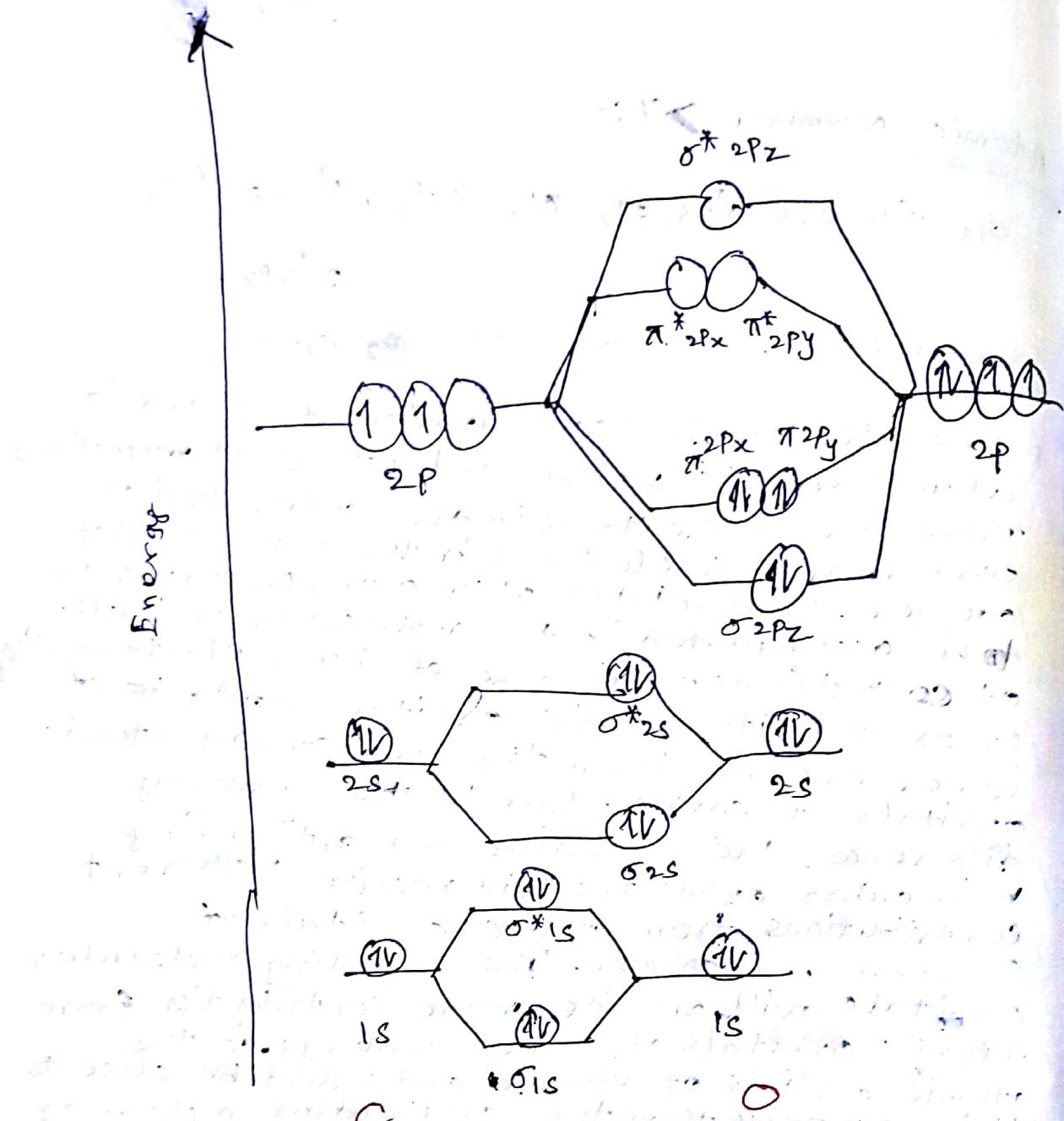
$$\text{Bond order} = \frac{N_b - N_a}{2}$$

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

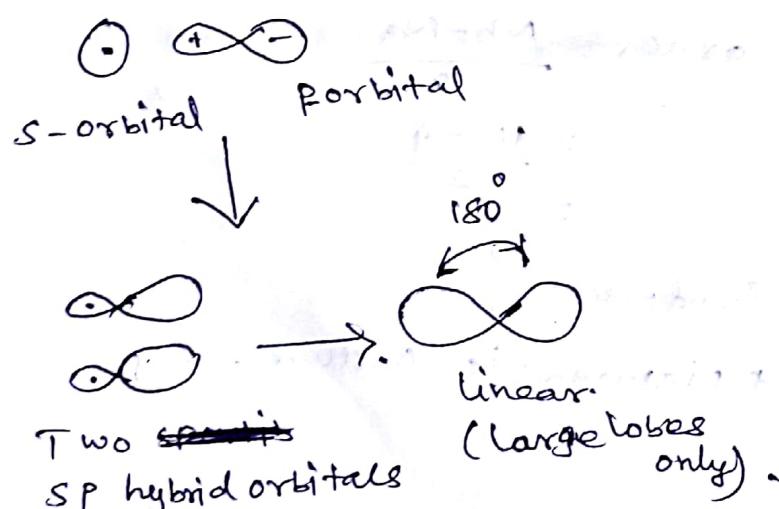
$$= \frac{6}{2}$$

$$\text{Bond order} = 3$$

* Diamagnetic Nature.

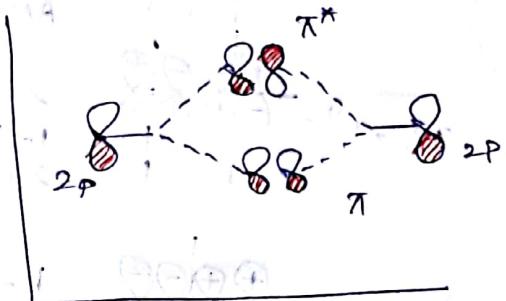
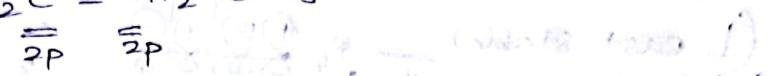
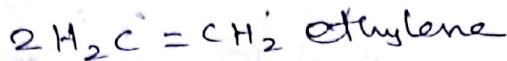


S-P overlapping:-



π -molecular orbitale of Butadiene:-

Since 1,3-butadiene consists of ~~4~~ 4 $2p$ orbitals of each carbon, construct π -molecular orbitals using two ethylene molecule.



* The two Carbon having $2p$ orbitals with same energy level.

* Same energy level.

* There 2 $2p$ orbitals having same sign approach each other to form π (m.o) having lower energy.

* Now one $2p$ orbital change its sign, & combining together to form π^* Antibonding high energy.

* Now combining two M.O.

Possible combinations are,

6-major combinations

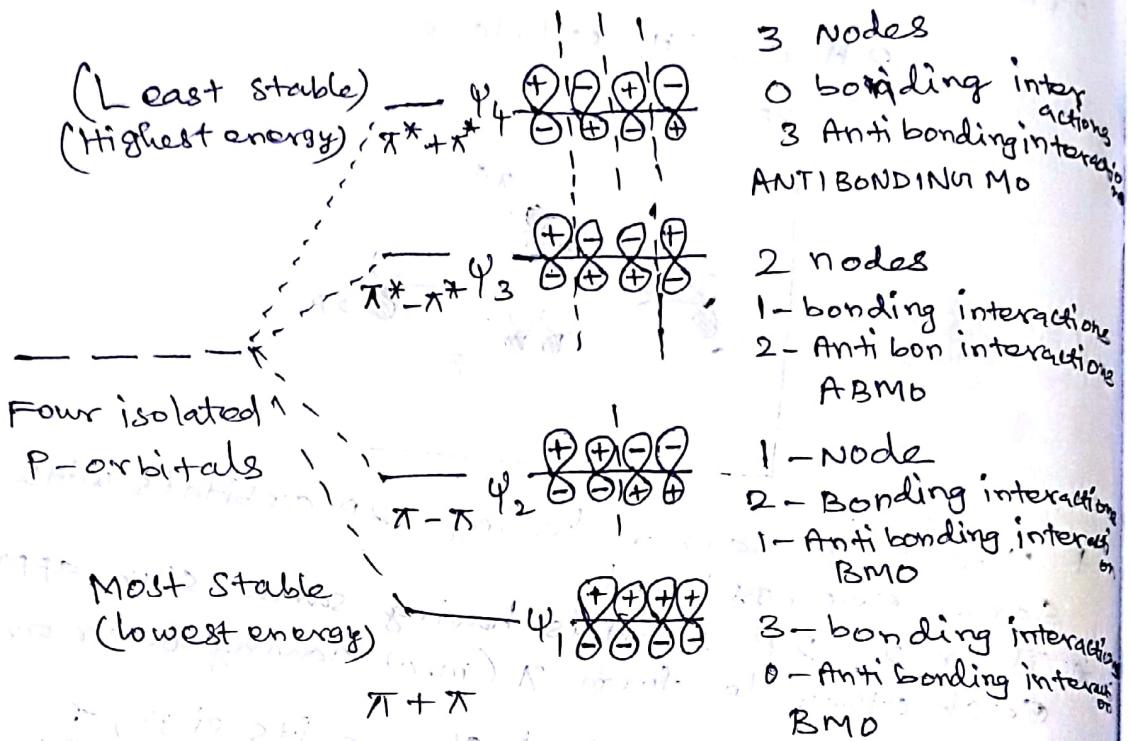
$\pi + \pi$ } These combinations only actively takes place.

$\pi - \pi$ } These are ruled out.

$\pi^* + \pi^*$ } These are ruled out.

$\pi^* - \pi^*$ } These are ruled out.

Intense white light is produced. When it passes through a prism, it splits into various colors due to dispersion. It is due to scattering of light by small particles, dust, water droplets, etc.



3 Nodes
 0 bonding interactions
 3 Anti bonding interactions
 ANTIBONDING MO

2 nodes
 1-bonding interactions
 2-Anti bond interactions
 ABMO

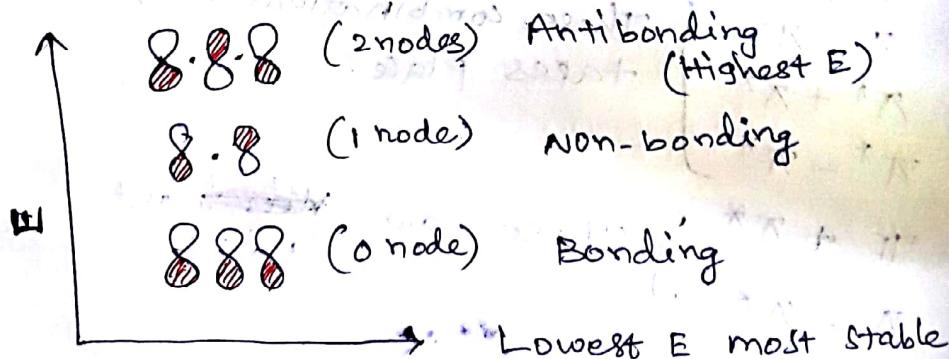
1-node
 2-Bonding interactions
 1-Anti bonding interactions
 BMO

3-bonding interactions
 0-Anti bonding interactions
 BMO

π-Molecular orbitals of Benzene:-

* To construct 6π molecular orbitals of C_6H_6 molecule using π molecular orbital of Propene.

* 3π M.O of C_6H_6 molecules are shown in the energy diagram.



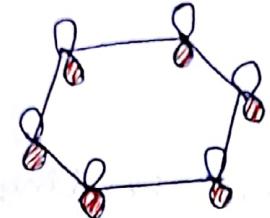
The lowest energy & most stable orbital which contain 0 nodes, it contain, $2e^-$ in the propene molecule within π MO. each one produce another one M.O, totally 6π M.O.

According to No. of nodal plane & energy we construct the energy level diagram.

overlapping take place only in the same energy level bonding.

Bonding :-

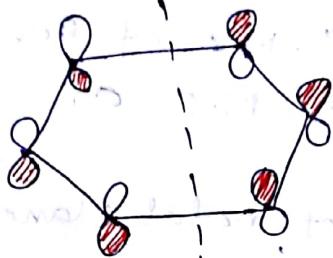
1.



0 nodes, lowest Energy

↑ this combine with (-) sign

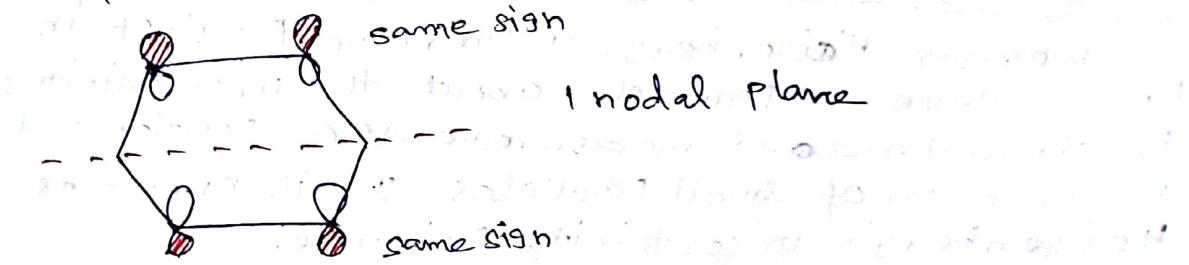
2.



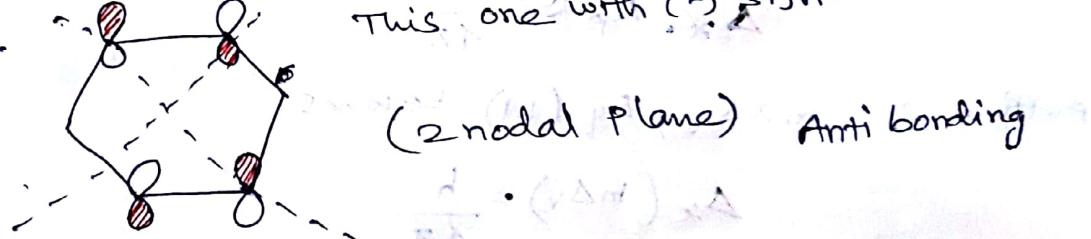
1 node, (bonding, Antibonding)

3.

Non-bonding

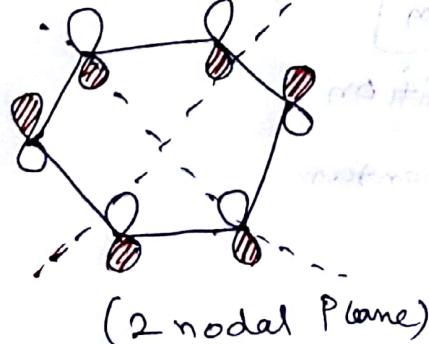


4.



This one with (-) sign.

5.

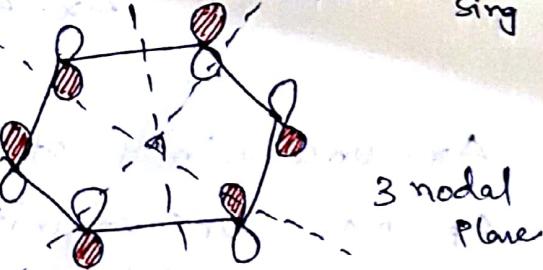


(2 nodal Plane)

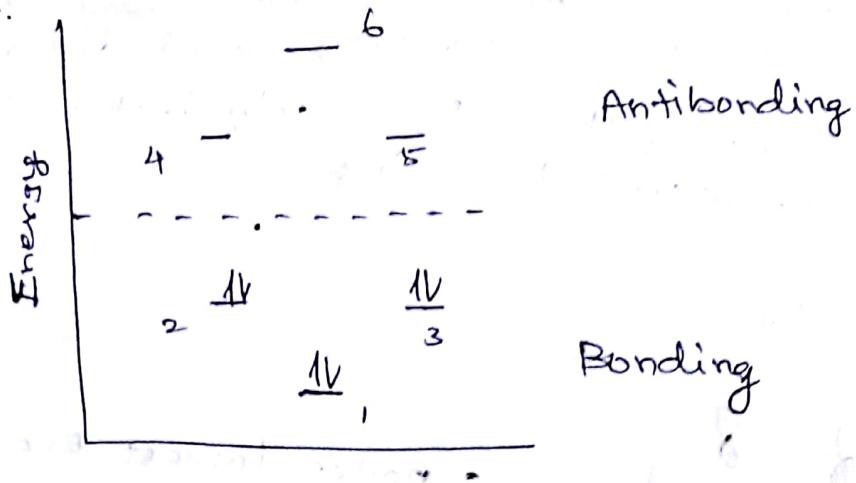
This with (+) sign

This with (-) sign

6.



3 nodal Plane



 3 π bond: so 6 e^- s are bonding
stable orbitals, low energy.

There are 6 different π -M.O of Benzene,
they are built with using 3 π M.O of
Propene molecule.

The maximum number of nodal planes
in benzene is 3.

Heisenberg's Uncertainty Principle

Werner Heisenberg, a German physicist in 1927, gave a principle about the uncertainties in simultaneous measurements of position and momentum of small particles. It is known as Heisenberg's uncertainty principle.

$$\Delta x \cdot \Delta p \approx \frac{h}{4\pi}$$

putting $\Delta p = m \times \Delta v$, Eq (1.1) becomes

$$\Delta x (m \Delta v) \approx \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta v = \frac{h}{4\pi m}$$

Δx - Uncertainty of the position

$\Delta p = m \Delta v$ - Uncertainty momentum

Δv - Uncertainty velocity

h - Planck's constant.

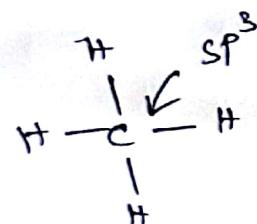
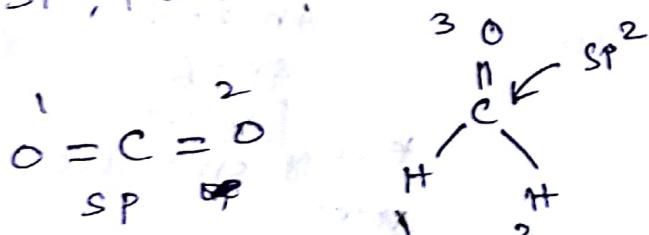
Aromaticity:-

The aromatic compound contain alternate double and single bonds in a cyclic structure and resemble benzene in chemical behaviour. They undergo substitution reaction rather than addition reactions. This characteristic behaviour is called ~~is~~ Aromatic character or Aromaticity.

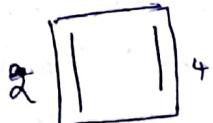
Definition:-

Aromaticity is the property of the sp^2 hybridized planar rings in which the p-orbitals (one on each atom) allow cyclic delocalization of π electrons.

| Aromatic | Antiaromatic | Non-Aromatic |
|--|--------------------------------------|---------------------------------------|
| * Stable | wrstable | Regular |
| * obey Hückle rule $4n+2$ | $4n$ | will not obey hückle rule. |
| * $2, 6, 10, 14, 18 \dots$ π electrons | $4, 8, 12, 16 \dots$ π electrons | $1, 3, 5, 7, 9 \dots$ π electrons |
| * cyclic, conjugated | cyclic conjugated | noncyclic |
| * sp^2 , planar | sp^2 , planar | sp^3 non-planar |



cyclobuta diene :-



~~DIB~~

- * 4π electron
- * planar
- * cyclic
- * conjugated
- * Anti aromatic
- * obey only $4n$ rule.

benzene



$6\pi e^-$

- * Planar
- * cyclic
- * conjugated

* obey $4n+2$ Hückel Rule.

* Aromatic.

$$4n+2 = 6$$

$$4n = 6 - 2$$

$$4n = 4$$

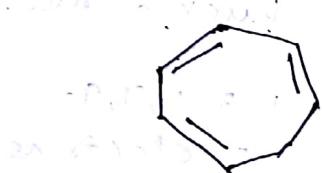
$$\boxed{n=1}$$

Diagram of benzene

Diagram of benzene

Diagram of benzene

cyclohepta triene :-



$6\pi e^-$

- * cyclic
- * planar
- * conjugated is not possible
- * Non aromatic

cyclo octa ~~tetraene~~ tetraene



$8\pi e^-$

- * cyclic
- * planar
- * conjugated double bond.
- * not obey $4n+2$ rule
- * Anti aromatic

$$4n+2 = 8$$

$$4n = 6$$

$$\boxed{n=1.5}$$

* very unstable.

Note:-

cyclooctatetraene

sub shape

* Non aromatic

Anthracene:-



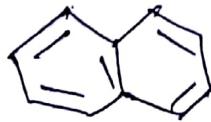
- * ~~14~~ $14\pi e^-$
- * cyclic
- * Planar
- * Conjugated double bond
- * 4n+2 Rule obeyed.

$$4n+2 = 14$$

$$\begin{aligned} 4n &= 12 \\ n &= 3 \end{aligned}$$

* Aromatic

Naphthalene



- * $10\pi e^-$
- * cyclic
- * Planar
- * Conjugated double bond
- * Obey $4n+2$ rule
- * $4n+2 = 10$

$$4n = 8$$

$$\boxed{n=2}$$

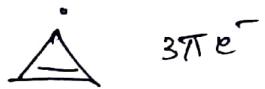
* Aromatic.

Cyclopropenyl Cation



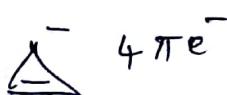
Aromatic

cyclopropenyl Radical



Non aromatic

cyclopropenyl Anion.



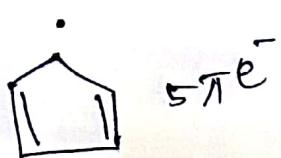
Anti aromatic

cyclopentenyl cation



Anti aromatic

cyclopentenyl Radical



Non-aromatic

cyclopentenyl Anion



Aromatic