

Schrodinger equation

Introduction:-

Necessity of Wave Theory:-

General Introduction about Classical mechanics:-

Classical mechanics describes the motion of macroscopic objects from projectiles to parts of machinery and astronomical objects such as space craft, planets, stars and galaxies. It is known to possible if the present state of an object is known to predict the future state of the object.

The earliest development of classical mechanics is the law of the Newtonian mechanics.

It was developed by Isaac Newton and Gottfried Wilhelm Leibniz in the 17th century to describe the motion of bodies under the influence of the system of forces.

Classical mechanics extremely provides accurate results when studying large objects that are not extremely massive and speeds not approaching the speed of light.

Description of theory:-

Classical mechanics explains the real effect a point particle. The motion of the point particles is characterized by small number of parameters - its position and the force applied on it.

classical mechanics describes the non-zero size particles.

The objects of non-zero size particles are more complicated behaviour than the hypothetical point particles. This is due to the additional degree of freedom. Classical mechanics can able to sense the motions between the force and the energy can interact. It is possible to determine the location in space and speed of the movement of the particle with definite quantity.

Heisenberg Uncertainty principle

According to Heisenberg, uncertainty principle it is impossible to determine simultaneously the exact position and momentum velocity of a minute moving particle like an electron.

Therefore, he postulate that electrons travel in sharp orbits in well defined orbits around the nucleus with well defined velocities.

The principle of Uncertainty

mathematically as

$$\Delta x \cdot \Delta p \geq h$$

In is the measurement of the momentum

Δp is the measurement of the position
of is the velocity

- * Consider a photon incident on a particle. If the particle is reasonable in size, its position and velocity will not be altered by the impact of light photon.
- * It is exactly possible to know the position and velocity of the particle. However if the case is for small minute particle like electron it is impossible to determine it.
- * It will change its position when the light observes it. After the impact of the light observed the original path function can be altered. For an electron moving in a n-dimension, mathematically Heisenberg represented as

$$(\Delta x) \Delta p_x \geq \frac{h}{4\pi}$$

Δx is the Uncertainty with regard to its position
 Δp_x is the Uncertainty corresponds to the momentum

Planck's Hypothesis

Importance of Planck's role of energy quantisation was quickly recognised by Albert Einstein. He intended his idea to all kinds of electromagnetic radiation, and explained other important phenomena of photoelectric effect.

According to this effect when a beam of electromagnetic radiation of particular frequency falls on the metal surface, the latter emits electrons.

this happens because electrons on metal surface absorb energy from light beam and ultimately overcome of the binding energy.

there are two ways to concerning the photo-electron effect:

① Photo-electric emission of electron is possible only with a light of certain minimum frequency & this is called threshold frequency. Vedoes from metal to metal surface

② kinetic energy of the emitted electrons increase on increasing the frequency but remains unaffected on increasing the intensity.

If the light of constant frequency hits an isolated photon of particular frequency with an electron on a metal surface it transfers its energy λ to the electron and also increases the kinetic energy ($\frac{1}{2}mv^2$)

$$[W = h\nu + \frac{1}{2}mv^2]$$

if $\nu < \nu_0$ the photon will not change the sufficient energy to eject the electrons from the metal surface.

De-Broglie Hypothesis:

Einstein had suggested on 1905 the light has dual character as wave and also particle.

De-Broglie suggested (1892-1987) proposed

that matter also has dual character that is de-broglie and particle.

this happens because electrons on metal surface absorb energy from light beam and ultimately overcome of the binding energy.

there are two ways to concerning the photoelectric effect:

- ① Photo-electric emission of electron is possible only with a light of certain minimum frequency. This is called threshold frequency.
- ② Kinetic energy of the emitted electrons increases on increasing the frequency but remains unaffected on increasing the intensity of the light if intensity is less than the depth of the light.
- When a photon of particular frequency hits an electron in a metal, it transfers its energy $\propto \nu$ to the electron and also increases its kinetic energy ($\frac{1}{2}mv^2$)

$$[h\nu = W + \frac{1}{2}mv^2]$$

If $h\nu < W$, the photon will not have the sufficient energy to eject the electrons from the metal surface.

De-Broglie's Hypothesis:-

Einstein had suggested in 1905 that light has dual character as wave and also as a particle.

De-Broglie suggested (1892-1987) proposed that matter also has dual character as a wave and particle.

According to de-Broglie equation the mathematical relation is expressed by

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

λ is the wavelength of the particle of mass m moving with a velocity u .

Schrodinger Wave equation

Derivation:- In 1926 Erwin Schrodinger gave a wave equation

In 1926 Erwin Schrodinger gave a wave equation to describe the behaviour of electron waves in atoms and molecules.

According to Schrodinger, ψ is related to the probability of finding electrons at various places around the nucleus.

Consider a simple wave motion, as that of the vibration of stretched string.

Let y be the amplitude of this vibration at any point whose co-ordinate x at time t . Then the equation can be expressed as

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{u^2} \times \frac{\partial^2 y}{\partial t^2}$$

Where u is the velocity with which wave is propagating. There are two variables x and t in the

above differential equation (1) the

Amplitude y depends upon two variables x and t .

In order to solve the equation it is necessary to separate the two variables

$$y = f(x) g(t) \rightarrow ②$$

Where $f(x)$ is a function of the co-ordinate x only

$g(t)$ is a function of the time t only
Then for stationary waves such as occurs in a stretched string then the function of $g(t)$ is represented by

$$g(t) = A \sin(2\pi ft) \rightarrow ③$$

Where f is the vibrational frequency
 A is a constant known as maximum amplitude
then for stationary waves it is given by

y can be written as

$$y = f(x) A \sin(2\pi ft) \rightarrow ④$$

$$\text{Hence } \frac{\partial^2 y}{\partial t^2} = f(x) A \sin(2\pi ft) \rightarrow ⑤$$

from equation Number ② that

$$\frac{\partial^2 y}{\partial t^2} = -A \omega^2 f(x) g(t) \rightarrow ⑥$$

Combining equation No ④ and ⑥ we have

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{A \omega^2}{f(x)} \rightarrow ⑦$$

As we know the frequency of the vibrations is related to the velocity u by the expression $\nu = \frac{u}{\lambda}$. Therefore λ is the corresponding wavelength. Hence from equation number 8.

$$\frac{\partial^2 f(n)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} f(x) \rightarrow 9$$

Equation 9 is valid for the plane motion in one dimension only, i.e. x and y . In three Cartesian co-ordinates (x, y, z) amplitude $f(n)$ will then be replaced by the amplitude function for the three co-ordinates. Therefore equation 9 can be written as $\Phi(x, y, z)$.

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \Phi \rightarrow 10$$

Incorporating de Broglie idea and relationship:

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2} = -\frac{4\pi^2 m u^2}{\hbar^2} \Phi \rightarrow 11$$

Where m is the mass and u is the velocity of the particle.

The kinetic energy of the particle given by $\frac{1}{2} mu^2$ is equal to the total energy minus the potential energy V of the particle.

$$k.E = \frac{1}{2} mu^2 = E - V \quad mu^2 = 2(E - V) \rightarrow 12$$

Combining the equation no 12 with equation No 11

We get:-

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

Equation is in the well known form of the Schrodinger wave equation. (13)

Application of Schrodinger wave equation in the particle in One Dimensional Box.

Particle in One Dimensional Box:-

Particle in One Dimensional Box, mechanical problem.

* It is the simplest quantum mechanical problem.

Which represents the translational motion.

* Consider a particle of a particle of mass m in one-dimensional box

i.e. confined to move on one-dimensional box

i.e. having infinitely high walls.

of width a , such that the potential is zero everywhere

For the sake of simplicity, let us assume

energy of the particle is zero every where

inside the box.

inside $V(x) = 0 \rightarrow \textcircled{1}$.

A molecule may have three types of motion, viz

* A molecule may have three types of motion, viz translational, rotational and vibrational.

According to classical mechanics, the energy

associated with each of three motion can have any value

continuously i.e. it can have any value

But according to Wave mechanics the

energies are quantized i.e. they are in

discontinuous manner.

Let the particle is not allowed to move outside this box.

This can be achieved by setting the very high potential energy of infinity at the sides of the box.

End the box cannot move outside]
When it is reaching the walls, it cannot go back and penetrate and return to the original level.

Starting with the one dimensional Schrodinger equation

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \rightarrow \textcircled{2}$$

The function ψ depends only on one independent variable viz x -coordinate outside the box.

Then equation $\textcircled{2}$ re-written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - \infty) \psi = 0 \rightarrow \textcircled{3}$$

On Neglecting E to ∞ then equation $\textcircled{3}$ becomes

$$\frac{d^2\psi}{dx^2} = 2x\psi \quad (\text{for})$$

$$\psi = \frac{d^2\psi}{dx^2}$$

that is, $\varphi = 0$ outside the box.
 This means the particle cannot exist outside
 the region in the limit "if $d < l$ ".
 Within the box, the Schrödinger equation for the
 motion of the particle takes the form:

$$\frac{d\varphi}{dx} + \frac{8\pi^2 m}{h^2} E \varphi = 0$$

$$(i.e.) \frac{d\varphi}{dx} + L^2 \varphi = 0$$

$$\text{Where } L^2 = \frac{8\pi^2 m E}{h^2}$$

→ (a)

→ (b)

General equation of (a) is given by

$$\varphi = A \sin(Lx) + B \cos(Lx)$$

A and B are constants, from eq No 6 large
 number of wave functions differ in the values of

A , B and L can be obtained.

But not all the functions acceptable for the
 motion of the particle in the box.

Only those functions which satisfy the boundary
 conditions of $\varphi = 0$ at $x = 0$ and $x = l$ will be

the acceptable wave functions.

Condition:

For $\varphi = 0$ at $x = 0$, eq (b) becomes

$$0 = A \sin(0) + B \cos(0) \quad \text{or}$$

$B = 0$

Condition satisfied only with $B = 0$

$$\therefore \varphi = A \sin(Lx)$$

→ (c)

For $\Psi = 0$ at $n=1$ then the equation No ⑥ become

$$b = A \sin(\lambda) \rightarrow ⑧$$

Condition satisfied only with λ is an integral multiple of π (ie)

$$\lambda d = n\pi \rightarrow ⑨ \Rightarrow \lambda = \frac{n\pi}{d}$$

Here 'b' can have only the integrals of 1, 2, 3 and so on can be eliminated since it leads to $\lambda = 0$ ($\Psi = 0$) everywhere within the box

$$\text{Substitute the value of } \lambda \text{ in eqn } ⑨ \rightarrow ⑩$$

from eq No ⑩

$$L^2 = \frac{8\pi^2 m l^2}{h^2} \quad \text{or} \quad E = \frac{L^2 \cdot h^2}{8\pi^2 m l^2}$$

Substitute the value of L from eq No ⑨

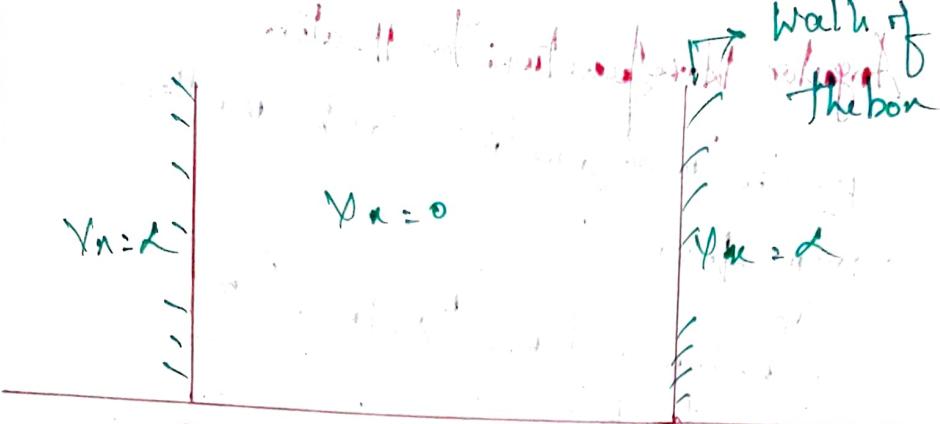
$$E = \frac{h^2}{8m l^2} \left(\frac{h^2}{l^2} \right) \rightarrow ⑪$$

Where h is 1, 2, 3... and $m = h/2\pi$

Where h is the reduced Planck's constant.

and also Strel's constant.

Equation 11 is the expression for the energy of the particle in one dimensional box



Particle in a box with $V_{n+1/2} = 0$ within the box
and $V_{n+1} = d$ outside the box.

Application of the Particle in One-Dimensional Box

The electron in polymeric system may be identified with the system of a particle in One Dimensional Box.

The length of the box is taken to be end to end distance of the molecule. The electronic energy levels can be determined by the following equation

$$E = n^2 \frac{h^2}{8ml^2}$$

The energy difference can be calculated from HOMO to LOMO

$$\Delta E = E_{n+1} - E_n = \frac{(n+1)^2 h^2}{8ml^2} - \frac{n^2 h^2}{8ml^2} = \frac{h^2}{8ml^2} (n+1)^2 - n^2$$

$$(2n+1) \frac{h^2}{8ml^2}$$

Example butadiene molecule - 8.82 nm

$$l = 1 (\text{single bond-length}) + 2 (\text{double bond length}) + 154 \text{ pm}$$

$$= 154 \text{ pm} + 2(135 \text{ pm}) + 154 \text{ pm} = 544 \text{ pm} = 5.44 \times 10^{-10} \text{ m}$$

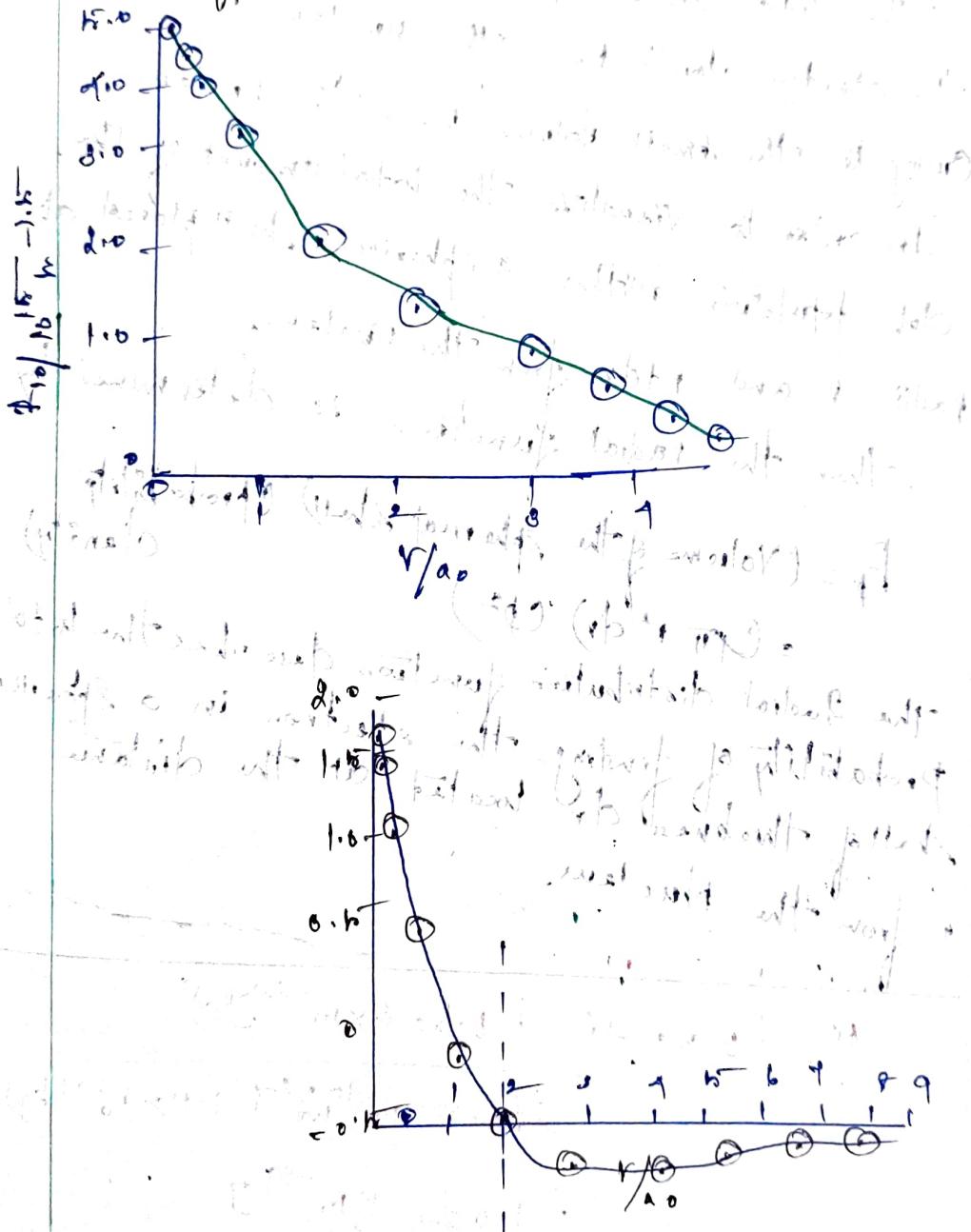
$$h = \text{Number of } e^- \text{, i.e., } \frac{2}{2} = 2$$

Since for 1s orbital

we have

$$U_{n=1, l=0} = \frac{1}{\sqrt{4\pi}} f_{n=1, l=0}$$

so the radial part will have the same form as those of Nucleus.



Radial distribution function for the electron
in 1s and 2s orbitals. (Hydrogen atom)

Though the probability of finding the electron in
s-orbital is maximum near to the nucleus,
the total amount of the dot population (or
the electron cloud) near the nucleus is very small
going to the small volume near the nucleus.

In order to visualize the total amount of the
dot population within a spherical shell placed at
radii r and $r+dr$ from the nucleus,
then the radial function is determined by

$$P_r = \frac{(\text{Volume of the spherical shell}) (\text{Probability density})}{= 4\pi r^2 dr} (Z^2)$$

The radial distribution function describes the total
probability of finding the electron in a spherical
shell of thickness dr located at the distance
from the nucleus.

$$\Delta E = (2 \times 2 + 1) \left(\frac{6.626 \times 10^{-34} \text{ Js}}{8 \times 1.6 \times 10^{-19} \text{ C}^2 \times (9.11 \times 10^{-31} \text{ kg})} \right)^2$$
$$= 9.02 \times 10^{-19} \text{ J}$$

$$\Delta E = \frac{\Delta E}{hc} = \frac{9.02 \times 10^{-19}}{\left(6.626 \times 10^{-34} \text{ Js} \right) \left(2.998 \times 10^8 \text{ m s}^{-1} \right)}$$
$$= 4.57 \times 10^6 \text{ m}^{-1} = 4.57 \times 10^4 \text{ cm}^{-1}$$

Radial Distribution Function and Angular wavefunction

* Radial distribution function can be used to solve the Schrodinger wave equation for the hydrogen atom and also for the related ions H_2^+ and H_3^+ .

* It is the complete equation for the wave equation and helps to reduce the wave function of the Cartesian Co-ordinates x, y and z into Polar Co-ordinates r, θ and ϕ .
Converted into the polar Co-ordinates r, θ and ϕ .

If the Cartesian Co-ordinates are measured from the point A measured from the origin x, y and z in from the point A measured from the origin r, θ, ϕ in in Cartesian Co-ordinates and r, θ, ϕ in Polar Co-ordinates.

Two sets of Co-ordinates are related by the following expression:

$$x = r \cos \theta \sin \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \sin \theta \cos \phi$$

The Schrodinger wave equation is, usually written as

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \left(\frac{1}{r^2} \frac{\partial^2 V}{\partial r^2} + E - V \right) \psi = 0$$

with problem of differentiation with respect to θ and ϕ .

$$\frac{\partial^2 \psi}{\partial \theta^2} + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{\partial^2 \psi}{\partial r^2}$$

is changing into polar Co-ordinates θ and ϕ becomes

$$\frac{1}{r^2} \frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \left(\frac{1}{r^2} \frac{\partial^2 V}{\partial r^2} + E - V \right) \psi = 0$$

The solution of this is of the form

$\Psi = R(r)\Theta(\theta)\Phi(\phi)$ → ①

Where $R(r)$ is a function that depends on the distance from the nucleus, which in turn depends on the Quantum Numbers n and l .

② $\Theta(\theta)$ is a function of θ , which depends on the Quantum numbers l and m .

③ $\Phi(\phi)$ is a function of ϕ , which depends only on the Quantum number m .

Equation ① can be re-written as

$$\Psi = R(r) n.l.m.$$

$R(r)$ is the radial function which depends on the Quantum numbers n and l .

On the Quantum numbers m and l , the angular wave function which depends on the Quantum numbers m and l .

Radial wave function R has no physical meaning.

R^2 represents the probability of finding the electron in a small volume.

point at which it is measured.

If the small radius and a small volume is Δr^2 so the probability of finding the electron

at a distance from the nucleus

P_{distr} is called the Radial Distribution Function.

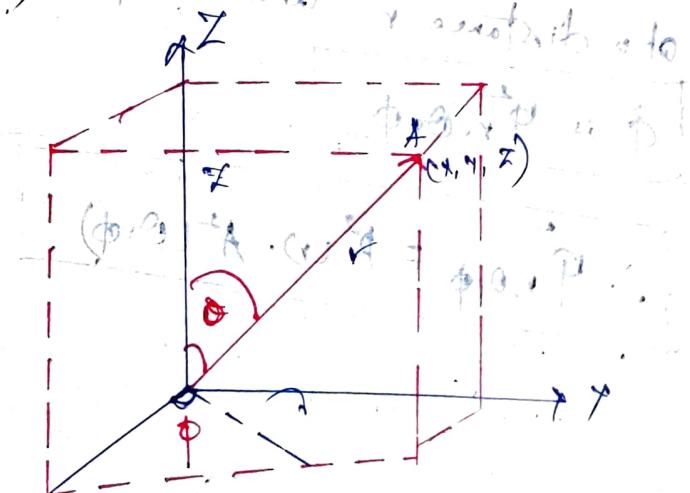
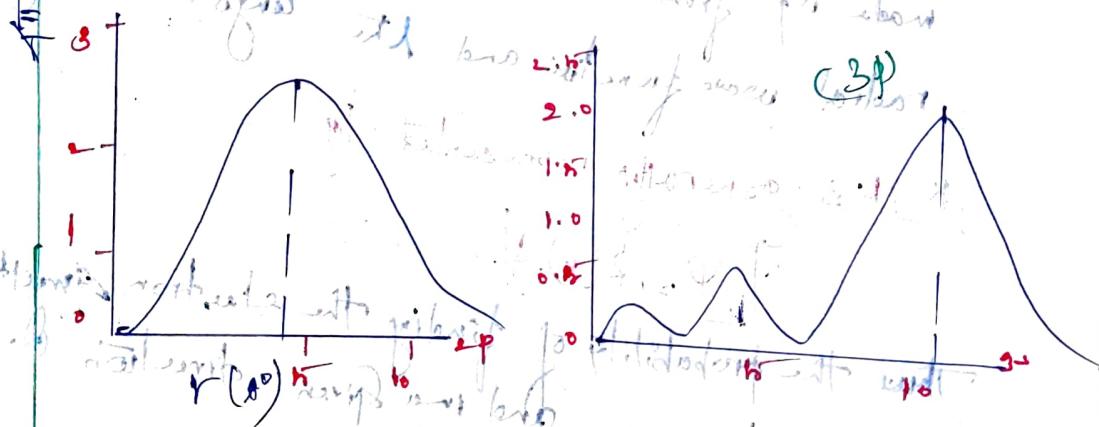
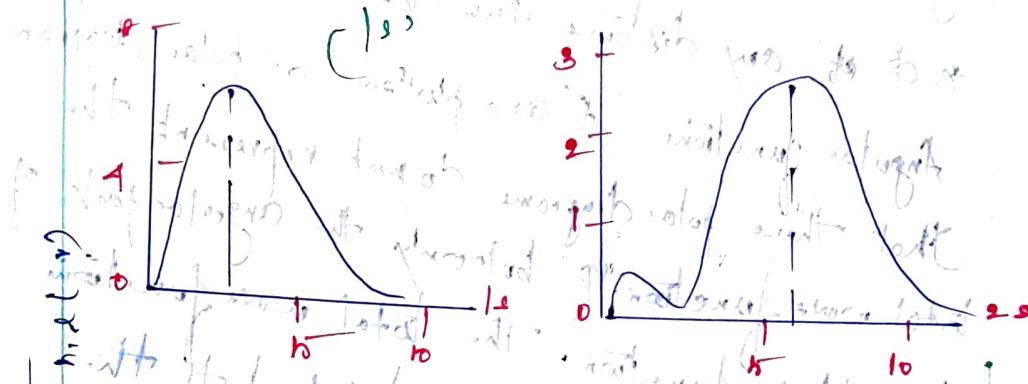
The graphs explained the radial distribution for the hydrogen atom plotted against r . It shows the probability is zero at the nucleus $\alpha(r=0)$ of the principle

$$\alpha_1(r=0)$$

$\alpha_1(r=0)$ as the distance increases, as the principle

If the distance increased, the number increased.

Osmunda cinnamomea (L.) L. (25)



- Relationship between Cartesian and polar coordinates

Angular function

- * Angular function A^2 depends only on the direction and it is independent of the distance from the nucleus (r).
- * A^2 is the probability of finding an electron at a given distance r .
- * ϕ at any distance from the nucleus is only angular function A^2 are plotted as polar diagram.
- * That these polar diagrams do not represent the total wave function Ψ , but only the angular part of the total wave function. The total wave function is made up from the contributions of both the radial wave function and the angular wave function.
- * It is generally represented by

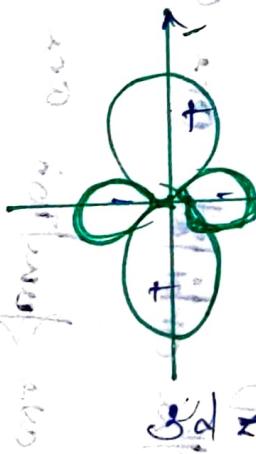
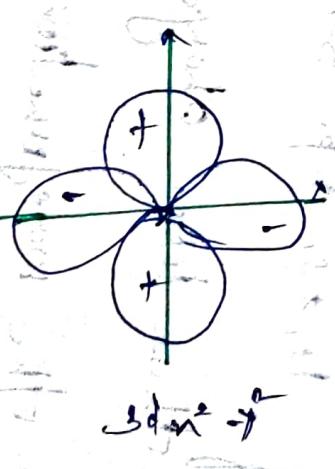
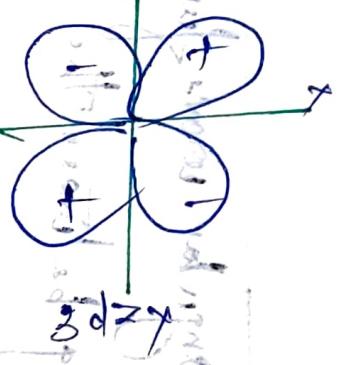
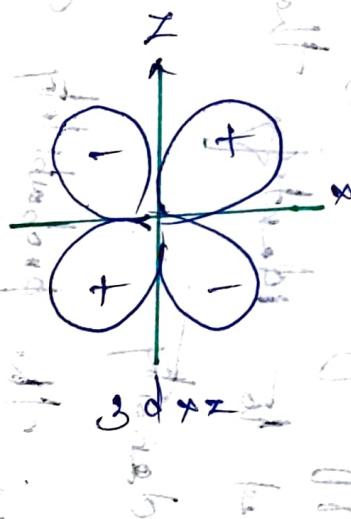
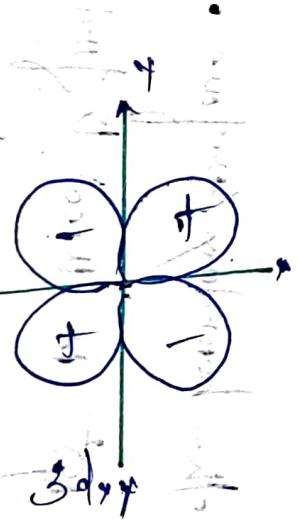
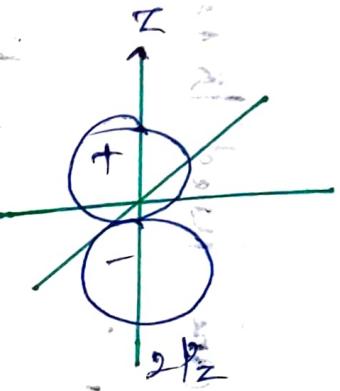
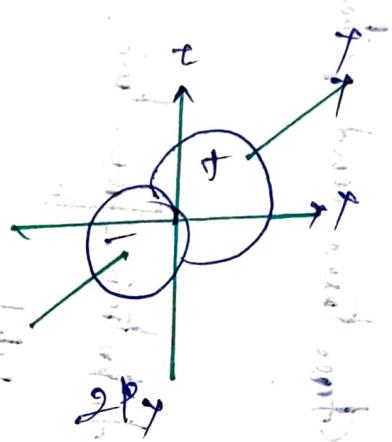
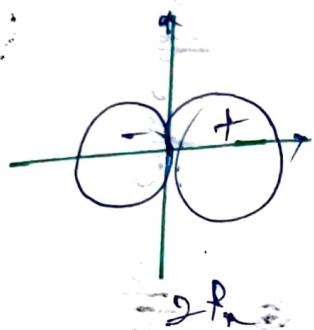
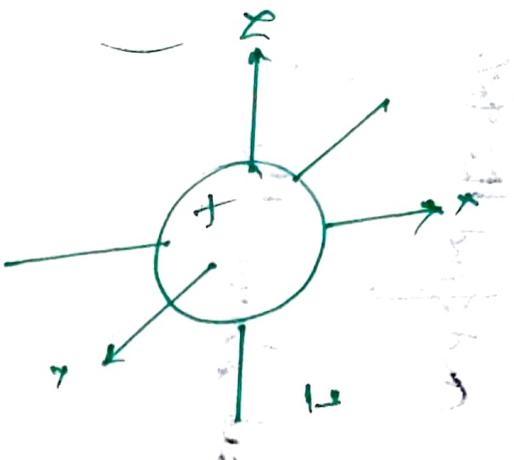
$$\boxed{\Psi = R(r) A(\theta, \phi)}$$

thus the probability of finding the electron simultaneously at a distance r and in a given direction θ .

$$\boxed{P \approx R^2(r) A^2(\theta, \phi)}$$

$$\boxed{\therefore P_{r, \theta, \phi} = R^2(r) A^2(\theta, \phi)}$$

- * Polar diagram represents the angular wave function. Are used to represent the overlapping of the orbitals bonding between the $1s_0$ atoms.
- * Photos of the orbitals are differ from their original structure and shape.
- * Angular wave function are used to identify the structure and shape and find the electron density of the electron distribution function and shown in the diagram of these orbital. Shows the probability distribution function and also s, p, d orbitals.
- * Diagram of $1s, 2s, 2p, 3s, 3p$ represents the boundary surface. The boundary surface is used to find the electron density and sign of this lobes charge.
- * Squared of the wavefunction is used to find the probability of finding the electron.



Molecular orbital theory.

* In General, Valence bond theory (electron pair) theory a molecule is considered to be made up of atoms with one electron in atomic orbitals occupying atomic orbitals.

* In VBT theory electrons in atomic orbitals occupy atomic orbitals. These orbitals may or may not be get hybridized.

* In the molecular orbital theory, the valence electrons are considered to be associated with all the nuclei in the molecule.

* Other the atomic orbitals from different atoms must be combined to produce the molecular orbitals.

In the general phenomena, electrons are able to consider as a particle wave. An electron is considered as a particle wave. An electron is therefore be described as an atom may occupy an atomic orbital or by a wave function occupying an atomic orbital. or by a wave function which is a solution of Schrodinger's wave equation.

which is a solution of Schrodinger's wave equation is called a molecular orbital.

The wave function describing a molecular orbital may be obtained by one of two procedures.

i) Linear combination of atomic orbitals (LCAO)

g) United atom method.

United atom method is based on the idea of a molecule as a single entity with a total number of electrons.

LCAO

Linear combination of atomic orbitals (LCAO)

Linear combination of atomic orbitals (LCAO)

LCAO Method:-

* Consider two atoms A and B which share the atomic orbitals described by the wave equation for wave functions Ψ_A and Ψ_B . When they are approaching each other, their atomic orbitals get overlapped. Then the wave function for the molecule, Ψ_{AB} , can be obtained.

Conjugate orbital Ψ_{AB} can be obtained as a linear combination of the two atomic orbitals

Ψ_A and Ψ_B .

$$\Psi_{(AB)} = N [c_1 \Psi_A + c_2 \Psi_B]$$

* Where N is the normalizing constant; ensure to find the probability of an electron in the nucleus over the whole space of Density.

c_1 and c_2 are constants chosen to give minimum energy for $\Psi_{(AB)}$. If the atoms A and B are similar, then the energy values are similar.

If atoms A and B are equal then the energy values are also equal.

* The probability of finding an electron in a volume of space dV is $\Psi^2 dV$, so the probability density for the combination of the two atoms

$$\text{above is } \Psi_{(AB)}^2 = [c_1^2 \Psi_A^2 + 2 c_1 c_2 \Psi_A \Psi_B + c_2^2 \Psi_B^2]$$

If we examine these three terms, the first term is $C_1 \Psi_{(A)}$ Probability of finding an electron in atom A.

Second term $C_2 \Psi_{(B)}$ Probability of finding an electron in atom B.

Third term $C_3 \Psi_{(C)}$ Probability of finding an electron in atom C.

Middle term $C_1 C_2 \Psi_{(A)} \Psi_{(B)}$ Overlapping of the two atomic orbitals increases and this term is called as the overlap Integral.

S-S combination of orbitals

Consider the Hydrogen atoms of A and B. In the corresponding wave function of atom A and B Ψ_A and Ψ_B are possible.

1) Where the signs of two wave functions are same.

2) Where the signs of two wave functions are different.

One of the wave function is represented by +VE sign.

Other can be represented by -VE sign.

+VE sign represents the wave function are in the same phase and the -VE sign indicates the wave function are in the out of phase.

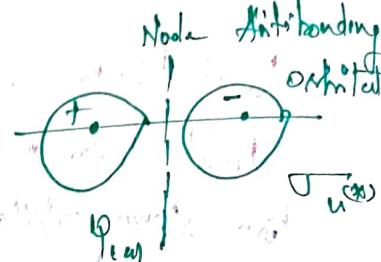
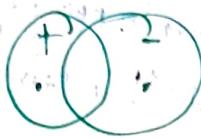
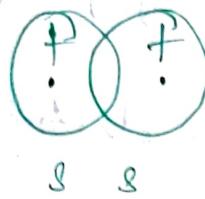
They cancel each other. They are destructive interference.

$$\Psi_{(C)} = N \{ \Psi_{(A)} + \Psi_{(B)} \}$$

$$\text{and } \Psi_{(C)} = N \{ \Psi_{(A)} + [-\Psi_{(B)}] \} = N \{ \Psi_{(A)} - \Psi_{(B)} \}$$

atomic orbitals

molecular orbitals

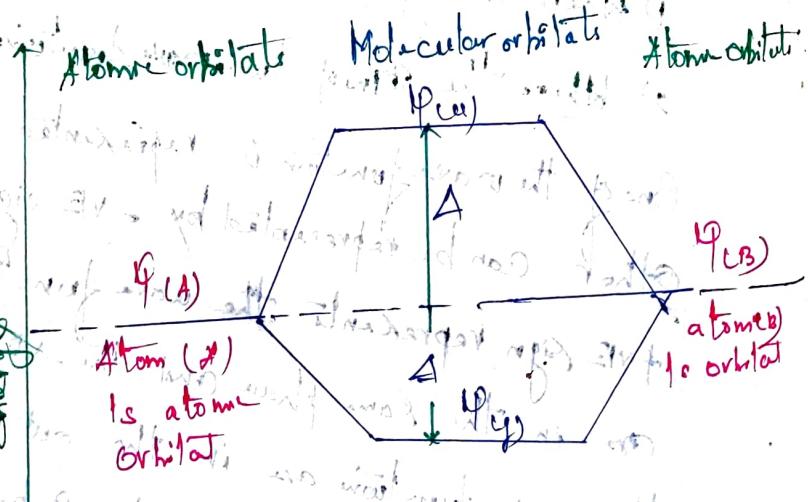


* The molecular orbitals were formed with aligned

as $\psi_{(B)}$, and $\psi_{(B)}$ gerade and ungerade.

Gerade means even, bonding molecular orbital.

Ungerade represents for of antibonding molecular orbital.



Energy levels of atomic and

molecular orbitals

* Energy of the bonding molecular orbital and the antibonding molecular orbital are separated by the distance A . This is known as the stabilization energy.

* The energy of the bonding molecular orbital passes through the distance called the internuclear distance.

* The energy of the bonding molecular orbital are lower than that of the antibonding molecular orbital. Similarly the energy of the antibonding molecular orbital is increased by the A .

S-p Combined two of orbitals:-

* One s-pure orbital and one p-pure orbital combined to form the one atomic orbital.

* New molecular S-p orbital has the same sign as the two atomic orbitals. The electron density between the nuclei.

* When the lobes of the two atomic orbitals are in the different sign they reduced the electron density of the nuclei.

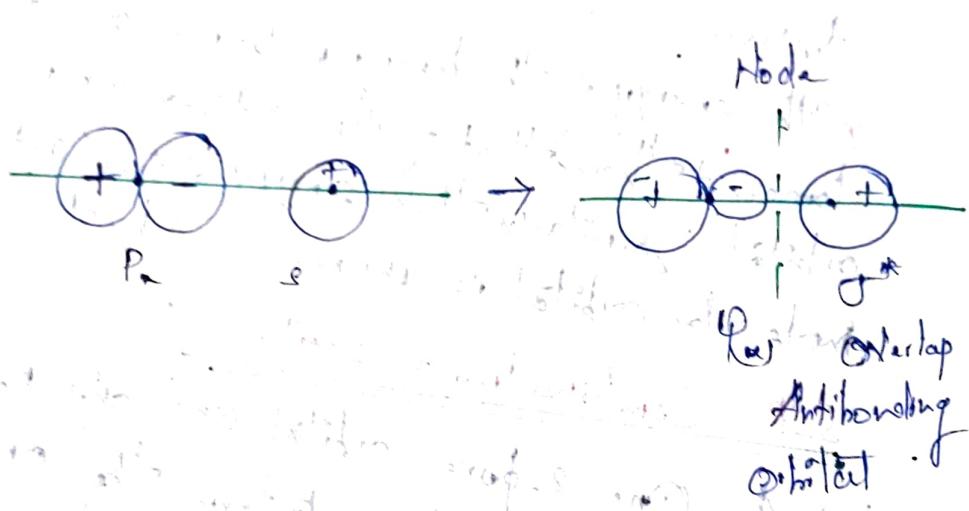
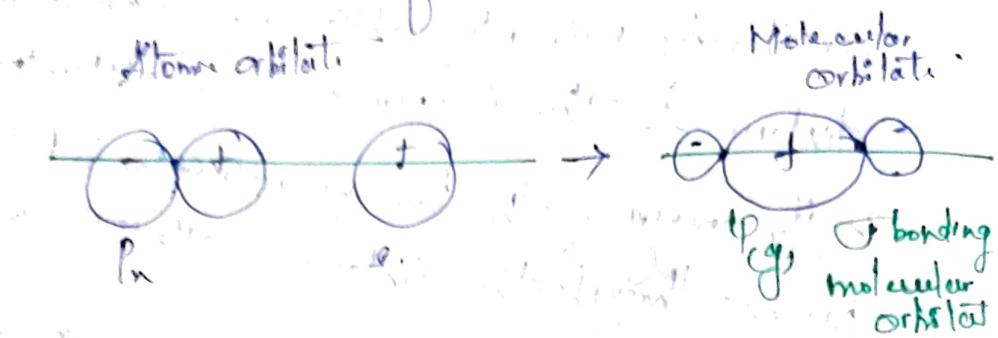
* It is called antibonding orbital.

* It is formed by the overlap of two atomic orbitals.

* It is formed by the overlap of two atomic orbitals.

* It is formed by the overlap of two atomic orbitals.

P-P Combination of atomic orbitals



p-p Combination of orbitals:

- * P-P atomic orbitals are formed from the combination of the two pure p_x and p_y atomic orbitals.
- * These two pure p atomic orbitals are overlapping in two different ways.
- * Both the lobes of the p_x and p_y orbitals pointing along the axis joining the nuclei. Both the bonding Mo and the antibonding Mo are formed.
- * Both the lobes of Pure p_x and p_y atomic orbitals pointing perpendicular to the axis joining the nuclei. Both the antibonding Mo & bonding Mo are being produced.

There are three points of difference between both the molecular orbitals and the atomic orbitals

1) For π overlap the lobes of the atomic orbitals are ~~parallel~~ perpendicular to the line joining the nuclei. Unlike for σ overlap the lobes point along the line joining the two nuclei.

2) For π molecular orbital ψ is zero along the internuclear line and consequently the electron density ρ is also zero.

3) The symmetry of the π molecular orbitals is different from the σ bonding orbitals.

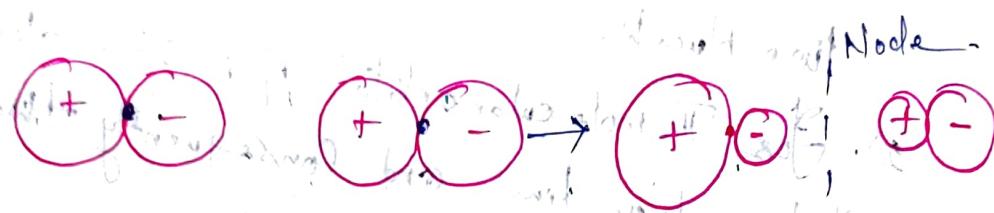
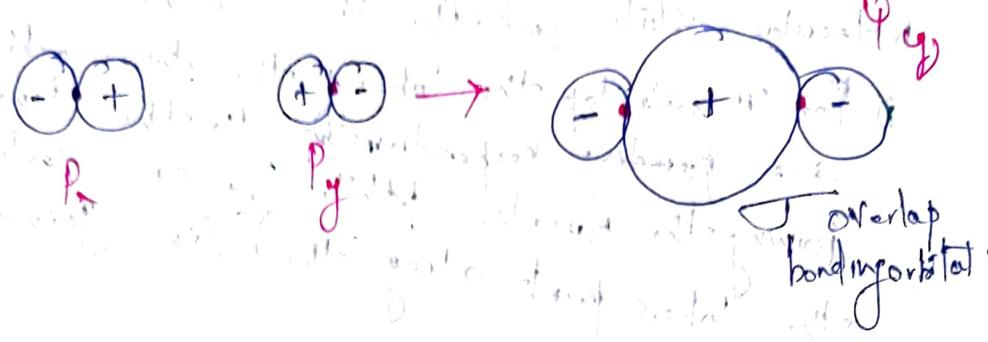
If the bonding molecular orbitals are rotated about the internuclear line a change in the sign of the lobes occurs. Therefore the π bonding orbitals are degenerate whereas all σ bonding orbitals are ~~gerade~~ gerade.

Conversely the Antibonding π Mo is ~~gerade~~ gerade whereas all σ antibonding Mo's are ~~ungerade~~ ungerade.

Antibonding Mo's are ~~ungerade~~ ungerade.

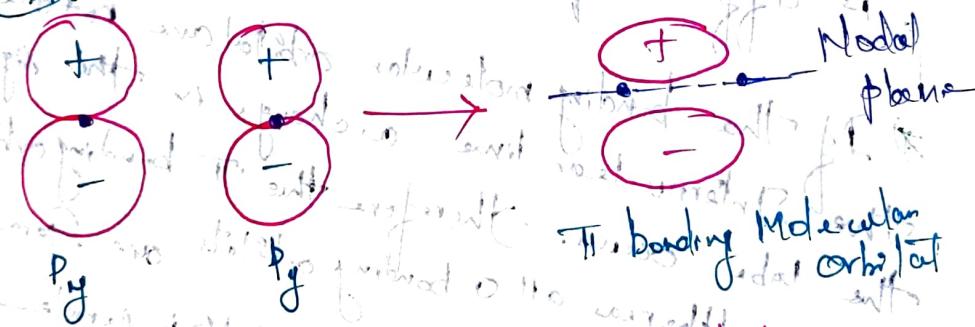
and it is difficult to understand.

Atomic orbitals → Molecular orbitals

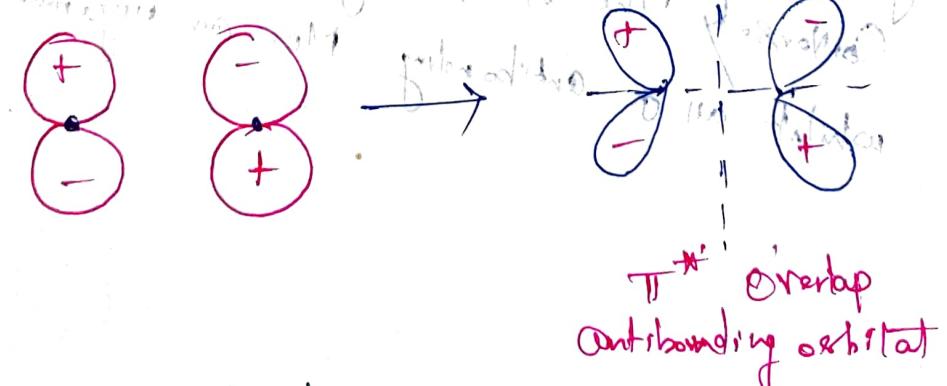


$p-p$ Combination of p_y atomic orbitals

Atomic orbitals



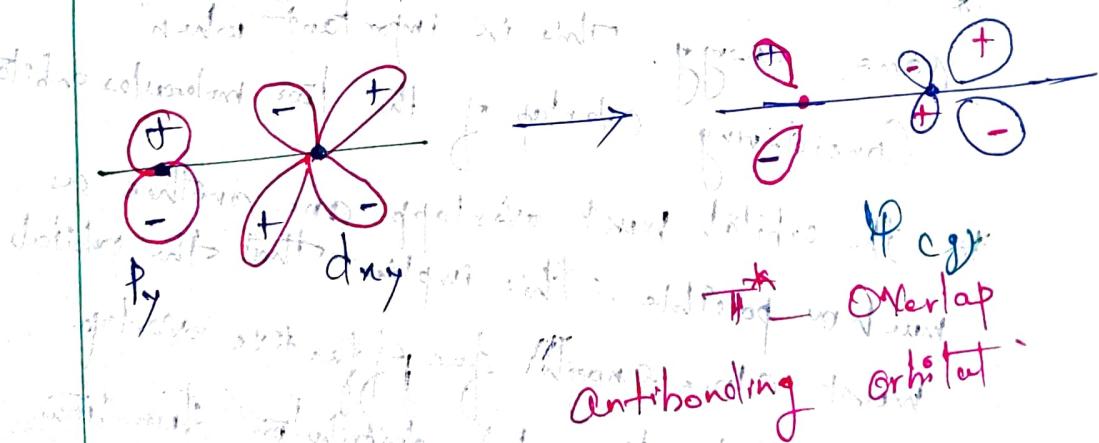
$p-p$ Combinations of giving π bonding



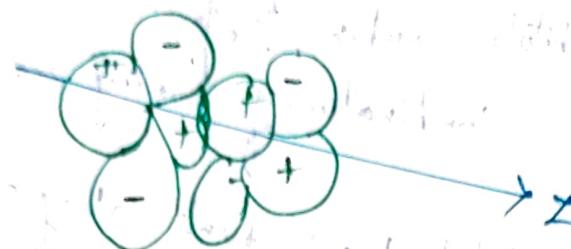
$p-p$ Combinations of giving π bonding

P-d combination of atomic orbitals

- * One pure P atomic orbital and one pure d atomic orbital combine to form p-d molecular orbitals giving the combination of bonding and antibonding orbitals.
- * Since the orbitals do not point along the line joining the two nuclei, overlap must be of the ~~type~~ type in the oxides and the ~~type~~ type of bonding occurs.
- * This type of bonding occurs in the oxides and oxoacids of phosphorous and sulphur. It also occurs in transition metal complexes such as the carbonyls and cyanides.



d-d Combination of atomic orbitals



Two pure atomic one of $3d$ orbitals are overlapping together to form $d-d$ molecular orbitals of bonding and antibonding. These are called δ and δ^* respectively.

Rules for Linear Combination of atomic orbitals

- * When atomic orbitals are combined to form the molecular orbitals, three rules must be considered.
 - * The atomic orbitals must be roughly of the same energy. This is important when considering overlap of the two molecular orbitals.
 - * The orbitals must overlap one another as much as possible. This implies that the orbitals must be close enough for effective overlap.
 - * And that the radial distribution function of the two atoms must be similar at this distance.

* In order to produce bonding and antibonding Mo, either the symmetry of the atomic orbitals must remain unchanged when rotated about the internuclear axis.

Each atomic orbitals are defined by four quantum numbers and they are all have definite energy.

* The principal Quantum Number n has the same significance in the atomic orbital.

* The subsidiary Quantum Number l also has the same significance on in atomic orbitals.

* The magnetic Quantum numbers of atomic orbitals is replaced by a new Quantum number ℓ .

represents as

$\ell = -1, \dots, 0, +1, +2, +3, \dots$

when $\ell = 0$, the orbitals are symmetrical around the axis and are called σ orbitals.

When $\ell = \pm 1$ they are called π orbitals.

and when $\ell = \pm 2$ they are called δ orbitals.

* The spin Quantum number is the same as for atomic orbitals and may have values of $\pm \frac{1}{2}$.

$$\boxed{\pm \frac{1}{2}}$$

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According to Pauli exclusion principle

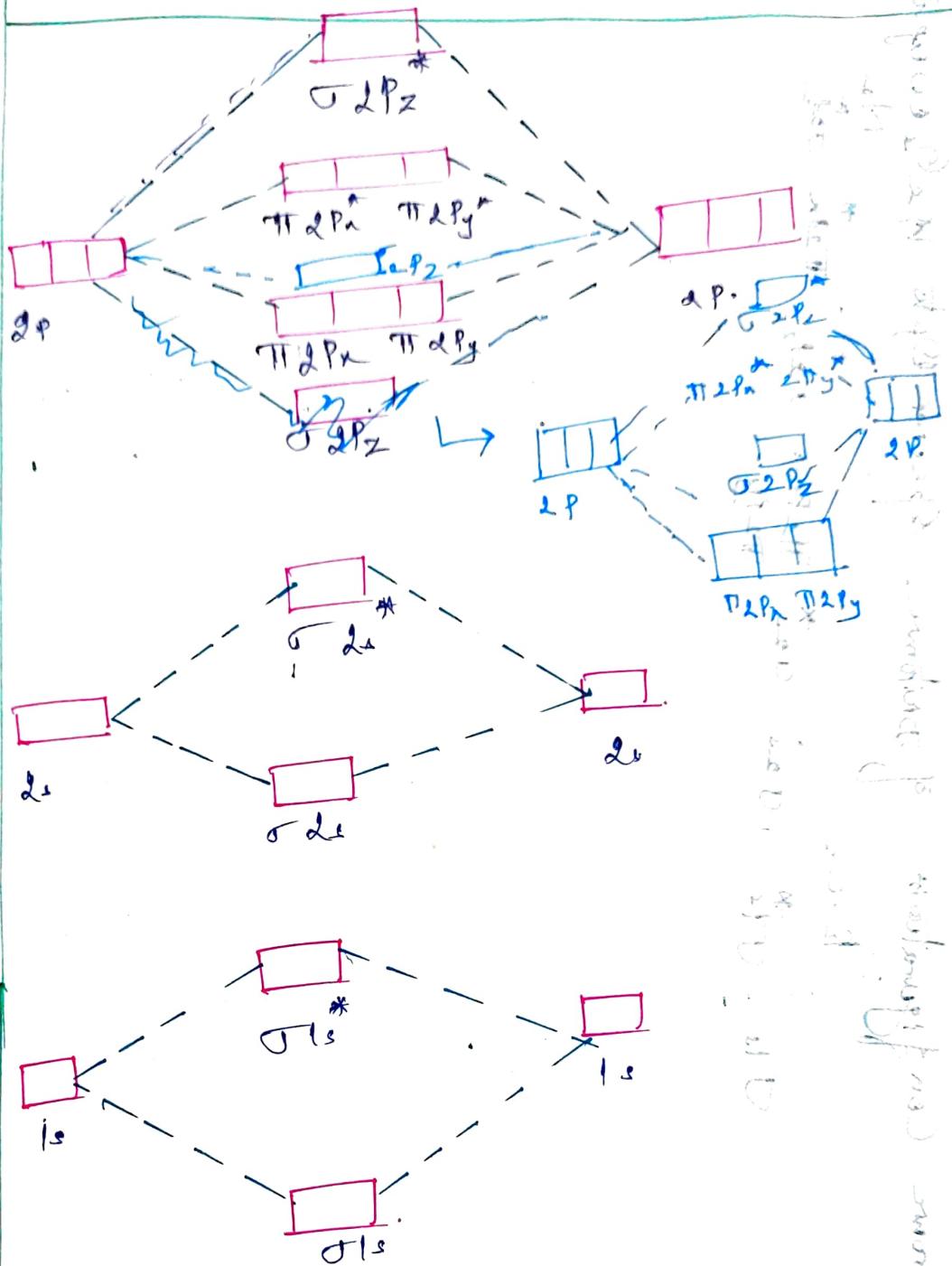
No two electrons can have same quantum numbers in an atom.

all four Quantum Numbers the same. No two electrons in the same molecule can have all

four Quantum numbers the same.

Upto 14 electrons can have all

$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^10$, $4s^2$, $3p^6$, $3d^10$, $4p^6$, $4d^10$, $5s^2$, $4p^6$, $4d^10$, $5p^6$, $5d^10$, $6s^2$, $4f^14$, $5p^6$, $5d^10$, $6p^6$, $6d^10$, $7s^2$, $5f^14$, $6p^6$, $6d^10$, $7p^6$, $7d^10$, $8s^2$, $6f^14$, $7p^6$, $7d^10$, $8p^6$, $8d^10$, $9s^2$, $7f^14$, $8p^6$, $8d^10$, $9p^6$, $9d^10$, $10s^2$, $8f^14$, $9p^6$, $9d^10$, $10p^6$, $10d^10$, $11s^2$, $9f^14$, $10p^6$, $10d^10$, $11p^6$, $11d^10$, $12s^2$, $10f^14$, $11p^6$, $11d^10$, $12p^6$, $12d^10$, $13s^2$, $11f^14$, $12p^6$, $12d^10$, $13p^6$, $13d^10$, $14s^2$, $12f^14$, $13p^6$, $13d^10$, $14p^6$, $14d^10$, $15s^2$, $13f^14$, $14p^6$, $14d^10$, $15p^6$, $15d^10$, $16s^2$, $14f^14$, $15p^6$, $15d^10$, $16p^6$, $16d^10$, $17s^2$, $15f^14$, $16p^6$, $16d^10$, $17p^6$, $17d^10$, $18s^2$, $16f^14$, $17p^6$, $17d^10$, $18p^6$, $18d^10$, $19s^2$, $17f^14$, $18p^6$, $18d^10$, $19p^6$, $19d^10$, $20s^2$, $18f^14$, $19p^6$, $19d^10$, $20p^6$, $20d^10$, $21s^2$, $19f^14$, $20p^6$, $20d^10$, 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Bond order :-

$$\text{B.O.} = \frac{\text{Total No. of } e^- \text{ in } \text{LW-BMO}}{\text{No. of } e^- \text{ in B MO}}$$

$\frac{1}{2}$

1/2
1/2
1/2
1/2

Molecular Constitution	Electron Configuration	No. of Electrons	Total No. of Mon.
H_2	$1s^2$	2	2
H_2^+	$1s$	1	1
H_2^-	$1s^3$	3	1
Li_2	$1s^2 2s$	6	1
Be_2	$1s^2 2s^2$	8	1
B_2	$1s^2 2s^2 2p$	10	1
C_2	$1s^2 2s^2 2p^2$	12	1

Molecular orbital diagram for O_2 molecule

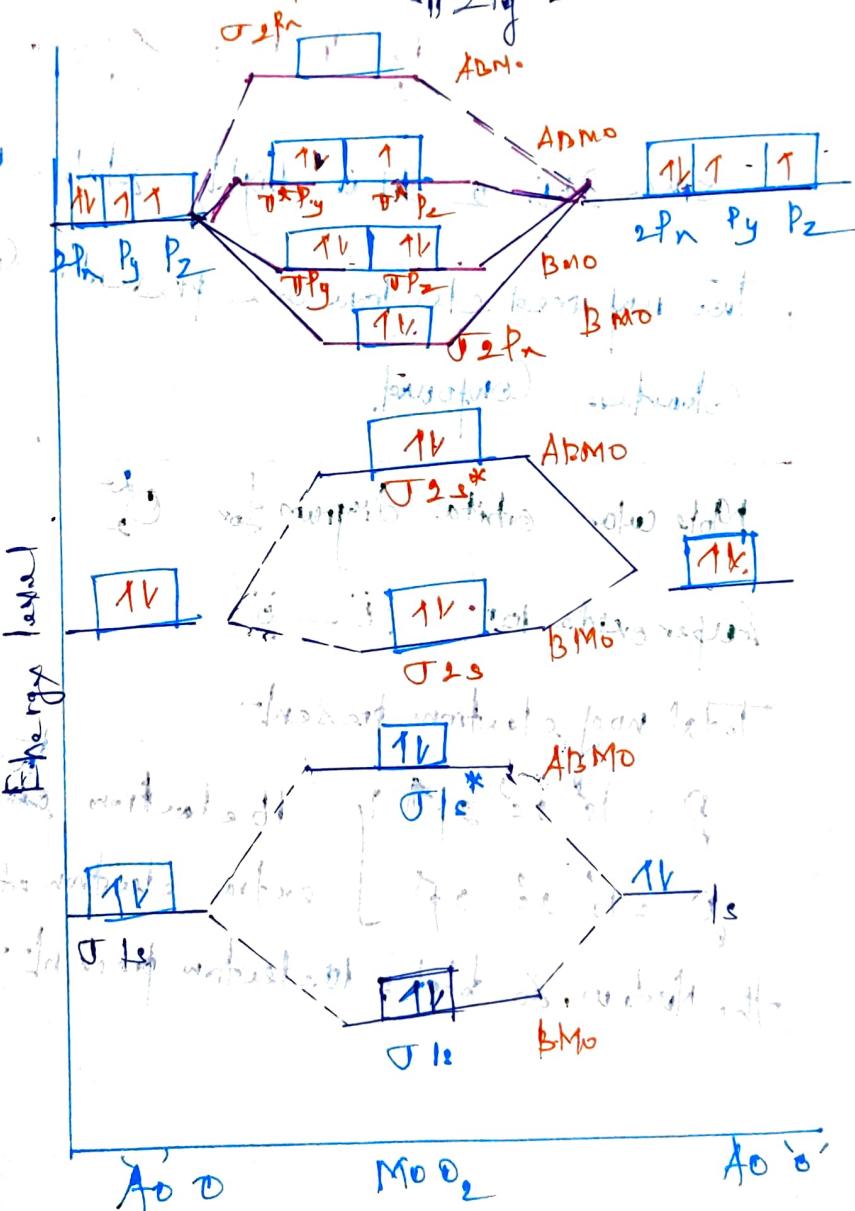
Oxygen electrons & Configuration

$O: -1s^2 2s^2 2p^4$

Number of electrons in O_2 molecule = 16 electrons

Molecular orbital configuration

$\sigma 1s^2 \sigma 1s^2 2p_{\sigma}^2 2p_{\sigma}^2 2p_{\pi}^4 = \pi^2 p_z^2 \pi^2 p_z^2 <$



O_2 molecule is paramagnetic because two unpaired electrons are present in one orbital. One unpaired electron is in π_{p_x} and one in π_{p_y} .

Total No. of Bonding electrons = 6

Total No. of Antibonding electrons = 2

Step 1: $(H_2 - H_2) \rightarrow 1/2 O_2 + 2H_2$
Step 2: Bond Order = $\frac{1}{2}$

$$= \frac{1}{2} (10 - 6) = \frac{1}{2} \times 4 = 2$$

Since it is 2 it is highly stable molecule.

Two unpaired electrons are present so it is

Cobaltic Compound.

Molecular orbital diagram for O_2^{2-}

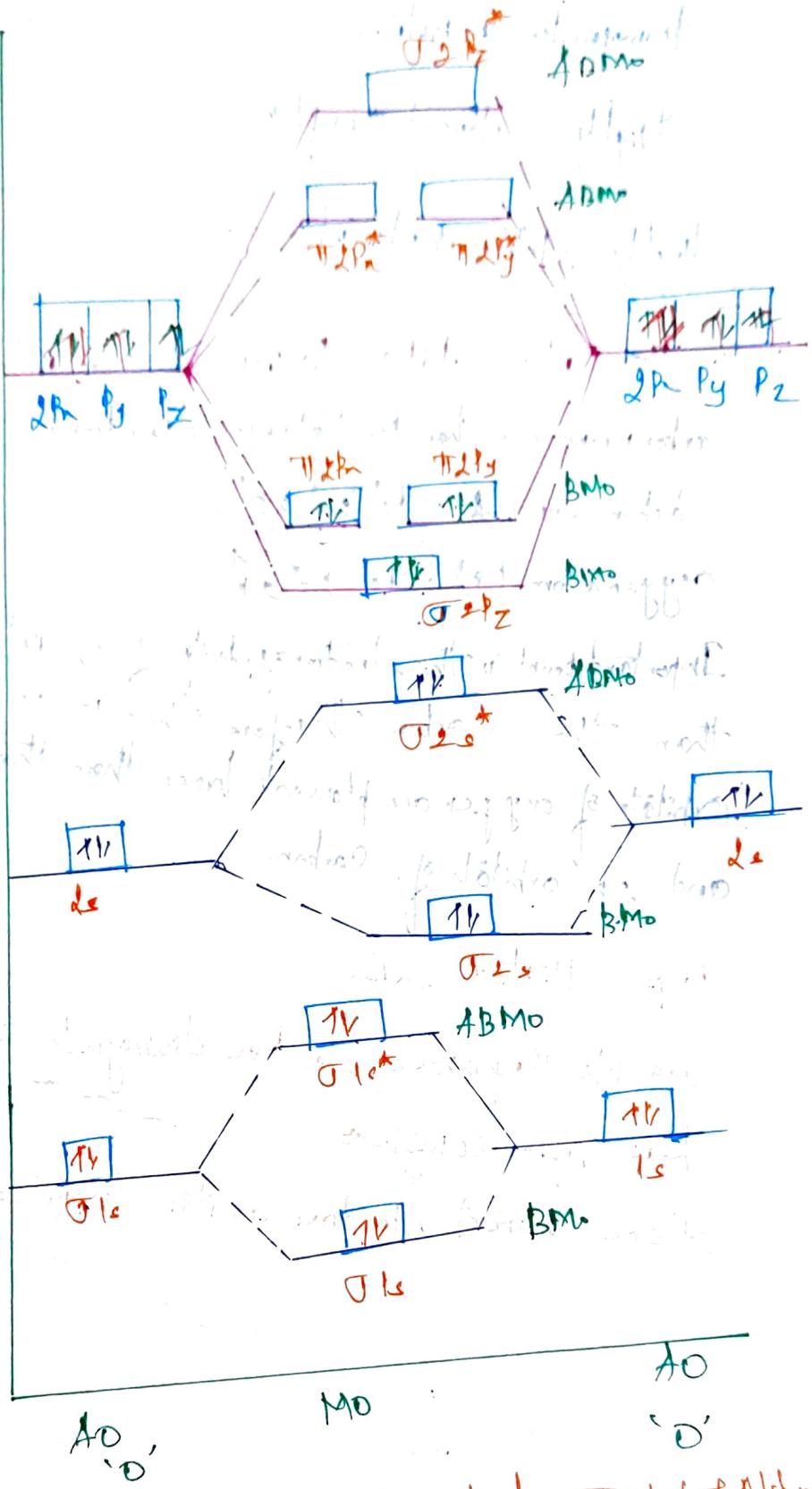
Super oxide ion: $[O - O]^-$

Total no. of electrons present:

$O = 1s^2 2s^2 2p^4$ } 16 electrons one of the

$O = 1s^2 2s^2 3p^5$ } extra electron added to

the Nucleus so total 17 electrons present.



Bond order = $\frac{\text{Total no. of bonding electrons} - \text{Total no. of antibonding electrons}}{2}$

$$= 6 - 4/2 = 6/2 = 3 \quad \boxed{\text{Bond order} = 3}$$

Since it has no unpaired electron so its
diamagnetic in Nature

Highly Coloured Complex

Highly stable molecule

Molecular orbital diagram for CO molecule

Carbon monoxide has ten valence electrons

Carbon atom (C) = $1s^2(2s^2, 2p^2)$

Oxygen atom (O) = $1s^2(2s^2, 2p^4)$

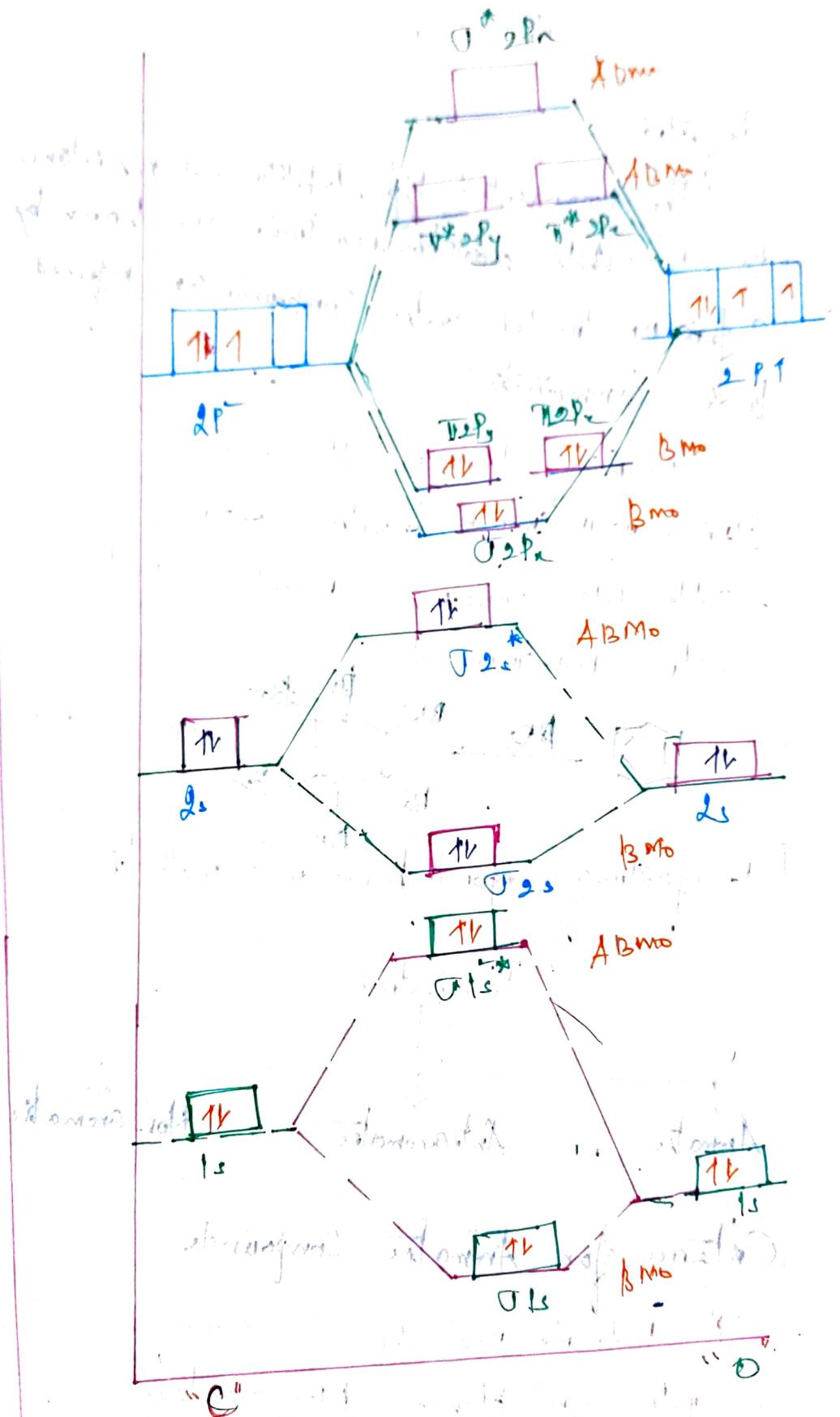
Important point is the electronegativity of oxygen is greater than the carbon. Therefore the $1s$, $2s$, and $2p$ orbitals of oxygen are placed lower than the $1s$, $2s$ and $2p$ orbitals of carbon.

It is Highly enantiomeric

No Unpaired electron diamagnetic in Nature

Low spin complex

All are paired electron so it is Colourless.



$$\text{Bond condr} = \frac{\text{Nb}-\text{Na}}{2} = \frac{6-4}{2} = 3$$

$\text{C}^{\infty} \equiv \text{O}^{\infty}$

Aromaticity:

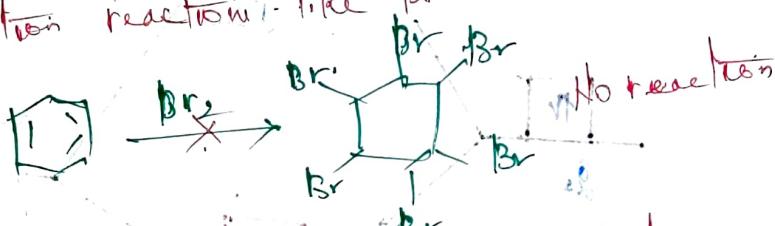
Definition:-

The unexpected high stability and resistance to electrophilic addition reactions are shown by a few unsaturated cyclic compounds are referred to as aromaticity.

Example:- Benzene Well known.

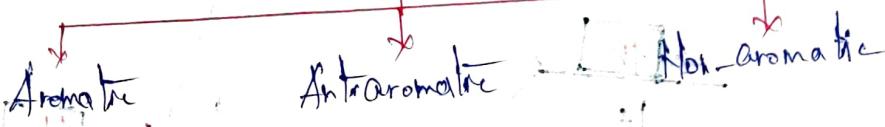
It is a well known aromatic compound.

Highly stable compound and resists electrophilic addition reactions like bromine



Classification of Compounds based on aromaticity

Classification



Criteria for Aromatic Compounds.

The molecule must be

- Cyclic and planar (More compact)
- (p_n + 2)π electrons (Hückel Number) that can be delocalized along the periphery of the ring in a closed loop.

Highly Stable Compounds

Hückel Numbers

(Anti) is the Hückel Number.

Where $n = 0, 1, 2, 3, \dots$.

∴ therefore, 2, 6, 10, 14, 18, are called Hückel Number.

The cyclic planar molecule with a delocalised π electrons is equal to the Hückel Number in a closed loop called aromatic.

Aromatic Compounds

The molecule must be

- cyclic and planar (more or less)

- $n\pi$ electrons that can be delocalised along the periphery of the ring in a closed loop.

- Highly Stable Compound.

Non-Aromatic Compounds

The molecules can be either Aromatic or anti-aromatic.

or Non-planar

Cyclic or Non-cyclic

There may be (Anti) π electrons which may be or may not be in conjugation.

Moderately stable Compounds

Two examples

Benzene

(1) Li

* Cyclic & planar molecule

* 6π electrons ($(n+2)\pi$) π electron system

* Aromatic compound (it is very strong after resonance its shape is unchanged)

(2) Cyclopropenyl cation



* Cyclic & planar molecule (very strong after resonance)

* 2π ($2n+2\pi$) system

* Aromatic (it is very strong after resonance it is modified with groups)

(3) Cyclopropenyl cation



Cyclic & planar

Antiaromatic

2π system

Highly unstable

It loses a proton (H^+)

(4) Cyclopentadienyl cation

6π electrons

($n+2\pi$) system

Cyclic and planar

Highly stable Compound

Aromatic

Compound

Moderately Stable Compounds

Two examples

Benzene

① 

- * Cyclic planar system with 6π electrons ($(n+2)\pi$)
- * Aromatic compound (no σ electrons in ring)

② Cyclohexenyl cation



Cyclic & planar with two single bonds

2π ($n+2$) system

Aromatic



③ Cyclopropenyl cation

Cyclic & planar

Antiaromatic

2π system ($n=1$)

④ Cyclopentadienyl cation

6π electrons

($n+2$) system ($n=2$)

Cyclic & planar



Highly stable compound

Cyclopentadienyl Cation and its Analogues



Unpaired electron

Anti system

Cyclic and planar

Aromaticity Compound must have closed loop with
conjugated double bonds and

Naphthalene

Two sets of 4 electrons (Ante 1) and (Ante 2)



Cyclic planar Anti system has paired electrons

Aromatic Compound, closed system

Highly Stable



Stabilized by delocalization of electrons

Aromatic Compounds

6π electrons - (Ante 1) by stem

Highly Stable

Cyclic and planar

Conjugated system with closed loop with no breaks

Electron rich dyes with substituted groups

Structure of Benzene and Butadiene

barrier to rotation

butadiene



- * From valence bond theory in the $C=C$ bond in the molecule we expect that $C=C$ bond is able to rotate freely as it is a σ bond.
- * But empirically, it was observed that there is a significant barrier to rotation about $C=C$ bond throughout the entire molecule. It is a planar bond throughout the molecule. $C=C$ bond is shorter than $C-C$ single bond (about 140 pm long) though longer than typical $C=C$ double bond (about 135 pm).

Molecular orbital theory accounts for these observations with the concept of delocalization of π -bonds.

The four $2p_{\pi}$ atomic orbitals combine mathematically to form 2π -bond molecular orbitals of increasing energy.

Two π -bonding molecular orbitals of lower in energy than the principle atomic orbitals from which they are formed.

Two of the antibonding π orbitals are higher in energy.

Molecular orbital diagram for isolated H_2 has the lowest energy of interaction and zero bonds than H_2 only. Construction is less loose but still has a higher in energy but still has a lower in energy.

Isolated p-orbitals overlap one node but

π_g second ~~level~~ of orbital has one node but forms π_u one node because it forms two π_u construction

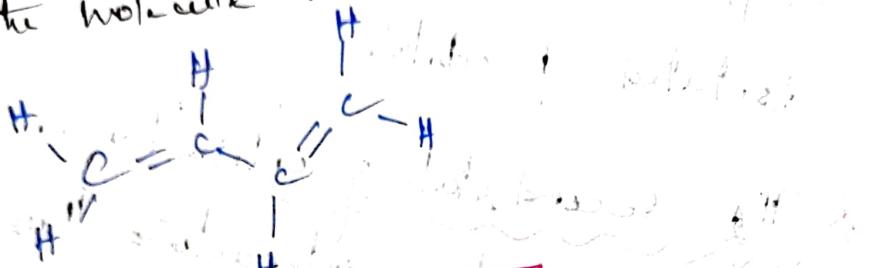
two bonding orbital overlap. One σ bonding orbital has two nodes and

* Two antibonding π_g has two nodes and π_u has two nodes and zero construction

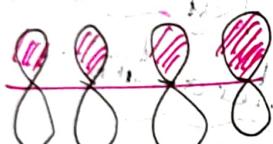
* π_g has three nodes and π_u has two nodes and zero construction. According to the π_g located between the two atoms Ti and Mg . The π_g from the bonding Ti and Mg are placed in the bonding interaction.

* It includes construction in the because Ti has a higher interaction with C_2 and C_2 bonding interaction between molecules of which account for the C_2 between C_2 length and accounts for the barrier to rotation.

XBT shows two π -bonds of isolated another but MOF predicts accurately that another but π bonds are to some extent delocalised over, the π hole of the molecule.



1,3-butadiene



1 1 1 1

(LUMO)



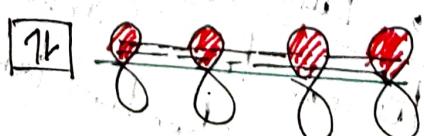
σ bonding



π bonding

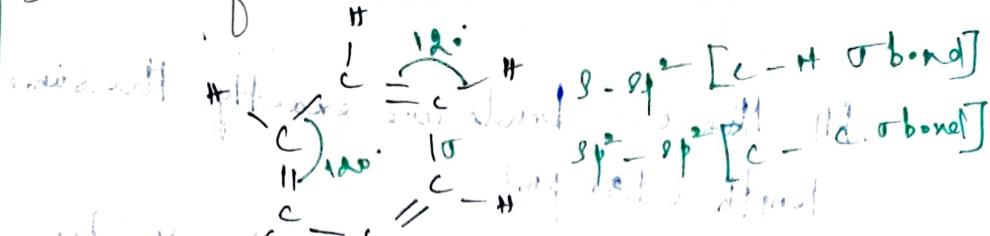


π , bonding



(HOMO)

Structure of Benzene

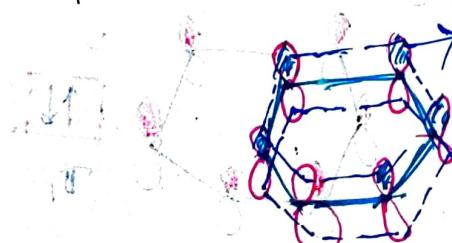


* All 6 carbon atoms in benzene nucleus are sp² hybridized. The sp^2 hybrid orbitals of C atoms overlap with each other with 6σ bonds of H atoms forming $C-C$ and $C-H$ bonds.

* since σ bonds results from overlap of planar sp^2 orbitals all carbons and H atoms in benzene lie in the same plane. All σ bonds in benzene lie in one plane and all bond angles are 120° .

* Each carbon atom in benzene possesses an unhybridized $2p$ -orbital containing one electron.

* The two p orbitals are perpendicular to the plane of σ bonds. The lateral overlap of these p orbitals produces a π -molecular orbital containing one half of the electrons and the other half lies above and the other half lies below the plane of σ bonds.



$\rightarrow \pi$ molecular orbitals

The delocalized electrons are distributed above and below

to the plane

All three π -bonds are exactly the same length (138 pm).

π -bonds in benzene are significantly less reactive than normal π -bonds either isolated or conjugated.

According to Quantum mechanical calculation

tells us that the π -Mol in benzene formed from atomic orbitals of p_z occupy 4 separate energy levels.

π_1 & π_6 has unique energy levels.



Benzene

Atomic orbitals

\uparrow						
p_x	p_y	p_z	p_x	p_y	p_z	p_x

Antibonding

Bonding Mol

Holding

π_1

$\uparrow \downarrow$

π_2

π_3

π_4

π_5

π_6

Bonding

Perpendicular to π
with all four angles
of 120°

$\pi_2 - \pi_3$ and $\pi_4^* - \pi_5^*$ are not at the same energy level they are not degenerate. The degeneracy level.

According to Aufbau principle the electrons is used to fill π_2 in these orbitals and the π_5 are completely filled and the antibonding molecular orbitals are empty. Hence benzene exhibits high stability in nature.

Crystal Field Theory

Postulates

CF developed by Hans Bethe in the year of 1929 to interpret color, magnetic and spectra of the crystals in magnetism etc. the crystals.

The following assumptions are made for CFT:

The central metal ion surrounded by the ligands which have lone pair of electrons. Central metal ion which form complex to the transition metal ion which form complex to the is regarded as positive ion of charge equal to three oxidation state.

Ligands approaching the central metal atom considered as a negative pole (con. Negative charge whose negative point charge directed to the central metal atom) interaction between the ligands and metal atom.

The interactions between the ligands rather than the metal ions are found by electrostatic forces they are lost.

the Covalent bond formation due to the small nature of the ligands.

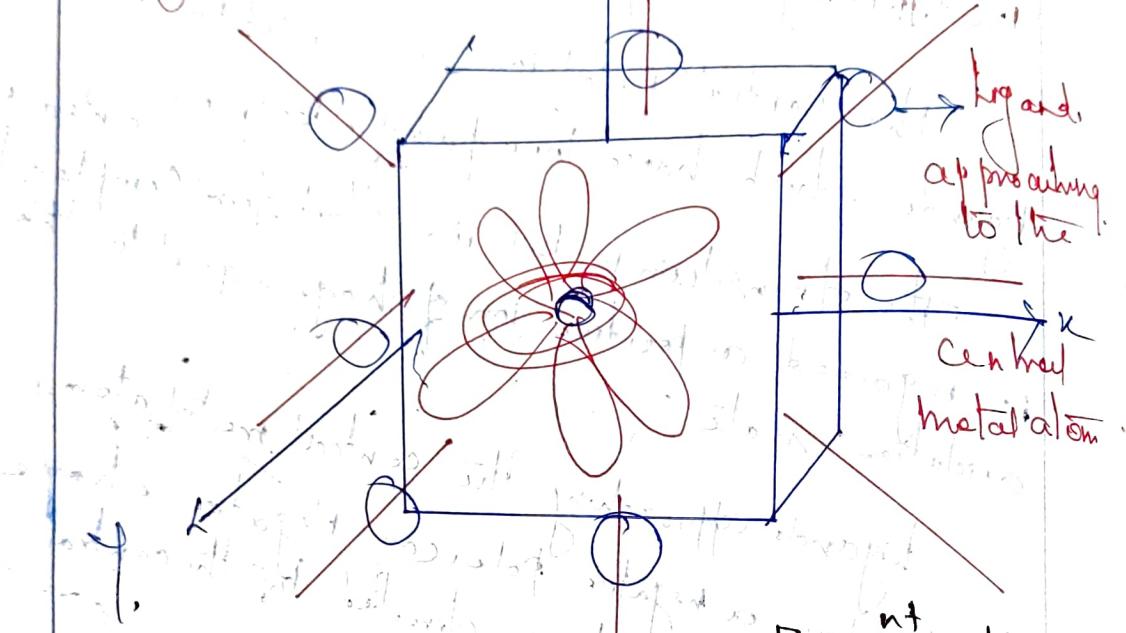
Due to the presence of d-orbitals in free metal ions, the degeneracy of some energy levels is destroyed by the approach of the ligands during the formation of a complex.

There is no interaction between the metal orbitals and the ligand orbitals.

Theory of Crystal Field

Crystal field splitting

Octahedral field



In an octahedral Complex $[M_{\text{b}}]^n$, the metal cation is at the centre of the octahedron and the ligands are at the 6m corners.

All five d orbitals are degenerate in the absence of the ligands. (as for free M^{+}) but when the ligands from each of the three axes approach towards the central metal atom break its degeneracy and raised to the higher energy level.

the electron in the ligands and the electron in the metal exhibits a strong repulsive force between the metal ion and negative end of the ligand.

According to the spectroscopic term theory, d_{xy}, d_{xz}, d_{yz} orbitals are collectively known as t_{2g} orbitals and the d_{z²} and d_{z²} known as e_g orbitals. Orbitals are known as e_g orbitals.

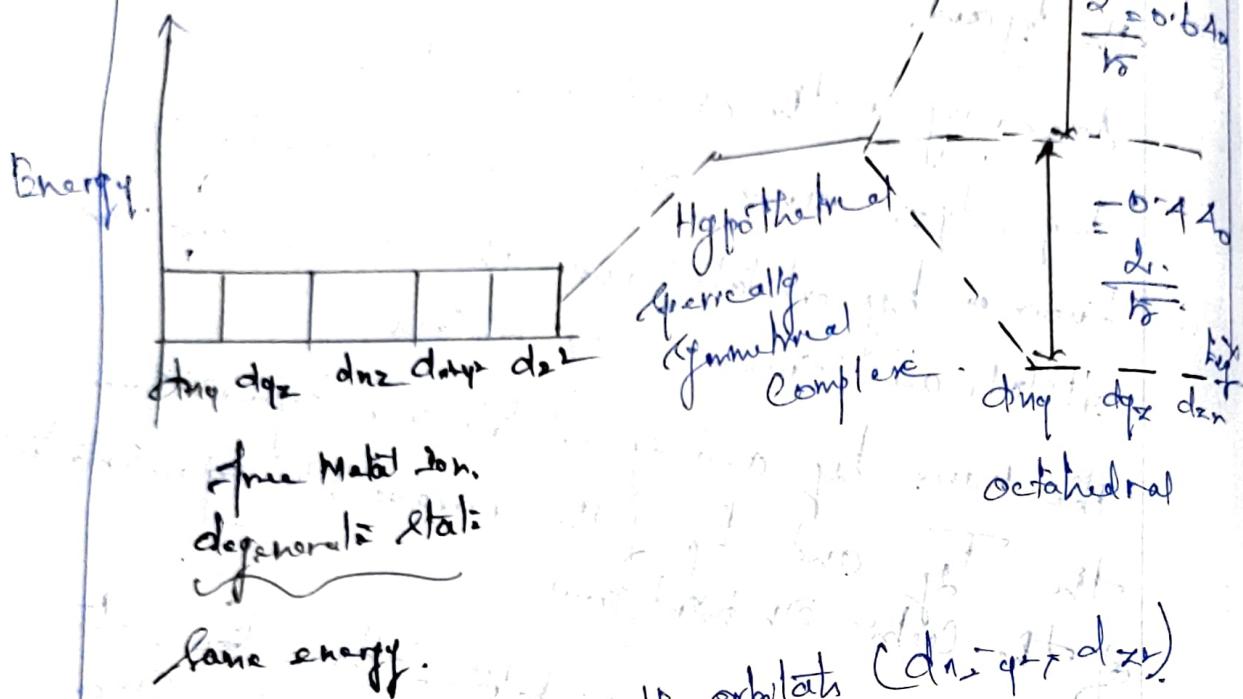
The name t_{2g} and e_g orbitals are originated from the T_{2g} and E_g of the irreducible representation of the C_{3v} Oh point group.

The difference in energy between these two sets of the orbitals (d-orbitals) (t_{2g} and e_g) is given by the symbols. Δo.

It follows that e_g orbitals are located above the average level and t_{2g} orbitals are located below the average level. The difference is called energy gap.

i) Generally called CFSE or barrier.

Orbital field splitting of d-orbitals
in Octahedral Complex



free Metal Ion.
degenerate states

same energy.

e.g. → Higher energy set of the orbitals (d_{5g^2}, d_{4g^2})

e.g. → Lower energy set of the orbitals ($d_{5t_2g}, d_{4t_2g}, d_{3t_2g}$)

A0 → Energy separation between the two levels.

A0 → Energy of separation between the two levels.

e.g. orbitals are repelled by an amount $\approx 0.6 A_0$
and the t_{2g} orbitals are stabilized by an amount $\approx 0.6 A_0$

Calculation for CFSE

$$CFSE = [-0.9 n(t_{2g}) + 0.6 m(e_g)] A_0 \text{ fm}^{-3}$$

$n(t_{2g})$ = No of electrons in t_{2g} orbitals

$n(e_g)$ = Total No of electrons in e_g orbitals

m = Total No of electrons paired.

P = Pairing energy $A_0 = 10Dq$

Field Ligands

Boyle's law.

Do ΔP .

Strong field ligand
(cor)

Spin paired
(cor)

Low spin Complexes

$\text{CF}_3^-, \text{CN}^-$)

Weak field ligand

Spin-free
(cor)

High spin Complexes
(H_2O).

High spin and low spin Complexes
Ligand's orbitals are strongly interact with the metal

Ligand's orbitals are called strong field ligands.
Orbitals are called weak field ligands.
With these, the split. between the t_{2g} and e_g orbitals is large. As a result do it large

orbital is large ligand need to form spin complexes.

Strong field ligand

Do ΔP .

Ligand's orbitals are interact weakly with the metal

Ligand's orbitals are called weak field ligands.

Orbitals are called splitting energy. Do ΔP .

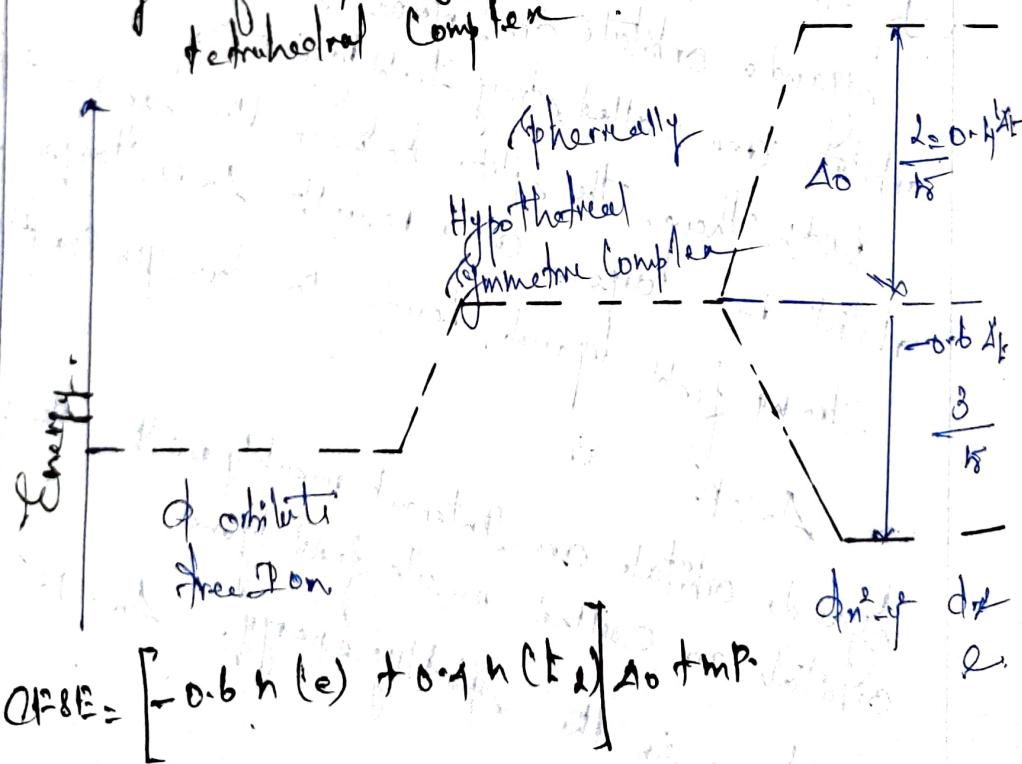
lower in the splitting energy.

Theory of Tetrahedral field : For tetrahedral arrangement, the ligands do not approach directly to the central metal atom of the d-orbitals but they approach toward, to the edges of the d-orbitals.

As a result d-orbitals undergo splitting in the reverse order of an octahedral field. Since t_2 orbitals are nearer to the field, since t_2 orbitals are rather than the e-orbitals t_2 orbitals are higher in energy than e-orbitals.

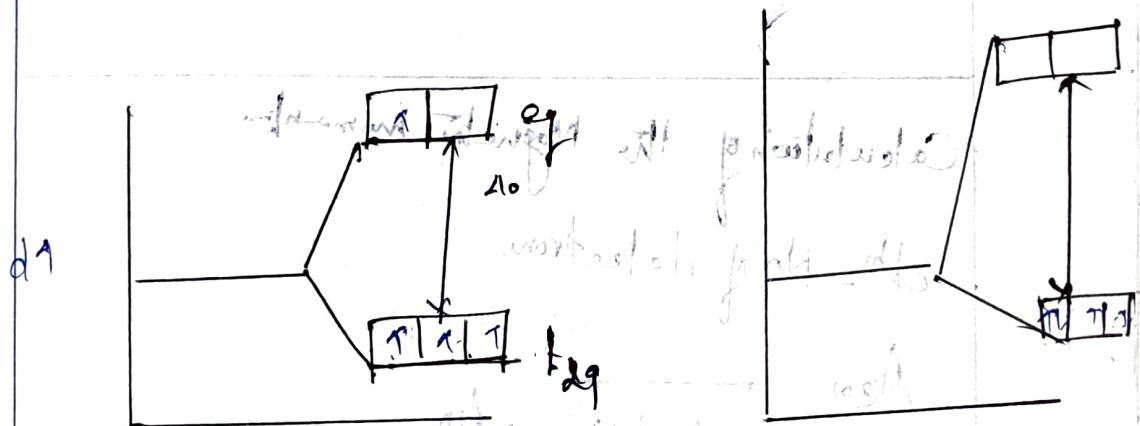
One factor in energy.

Crystal field splitting of d-orbitals in tetrahedral Complex



$$\text{CFSE} = [-0.6 n(e) + 0.1 n(t_2)] \Delta_o \text{ atm.p.}$$

d^n	Weak field \Rightarrow High spin can spin free	CISE value	Strong field \Rightarrow low spin can pair paired	CISE value.
d^1	$t_{2g}^1 e_g^0$ configuration	$0 + 4$ -0.4	$t_{2g}^1 e_g^0$	$+0.4$
d^2	$t_{2g}^2 e_g^0$	-1.2	$t_{2g}^2 e_g^0$	-0.2
d^3	$t_{2g}^3 e_g^0$	-0.6	$t_{2g}^3 e_g^0$	-1.2
d^4	$t_{2g}^4 e_g^1$	0.0	$t_{2g}^4 e_g^1$	$-1.6 + 4P$
d^5	$t_{2g}^5 e_g^1$	$-0.4 + 4P$	$t_{2g}^5 e_g^1$	$-2.0 + 2P$
d^6	$t_{2g}^6 e_g^1$	$-0.8 + 2P$	$t_{2g}^6 e_g^1$	$-2.4 + 3P$
d^7	$t_{2g}^7 e_g^1$	$-1.2 + 3P$	$t_{2g}^7 e_g^1$	$-1.8 + 3P$
d^8	$t_{2g}^8 e_g^2$	$-0.6 + 4P$	$t_{2g}^8 e_g^2$	$-1.2 + 3P$
d^9	$t_{2g}^9 e_g^2$	$-0.6 + 5P$	$t_{2g}^9 e_g^2$	$-0.8 + 4P$
d^{10}	$t_{2g}^{10} e_g^2$	$0.0 + 5P$	$t_{2g}^{10} e_g^2$	$0.0 + 5P$



$d^1 - d^8$ No change in electronic configuration
 $d^9 - d^{10}$ Change in electronic configuration

Electronic Configuration changes from $d^1 - d^7$.
 Electronic system

Q & S Nature

d¹ & getem

$$= [-0.2(1) + 0.6(0)] + (1)p$$

$$d^1 = -0.1$$

$$d^2 = [-0.4(2) + 0.6(0)] + (0)p$$

$$\boxed{d^2 = -0.8}$$

$$d^3 = [-0.4(\cancel{1}) + 0.6(\cancel{1})] + 2(p)$$

$$= -2.0 + 1.2$$

$$\boxed{d^3 = -0.8 + 2p}$$

Calculation of the Magnetic moment

d^h = No of electrons.

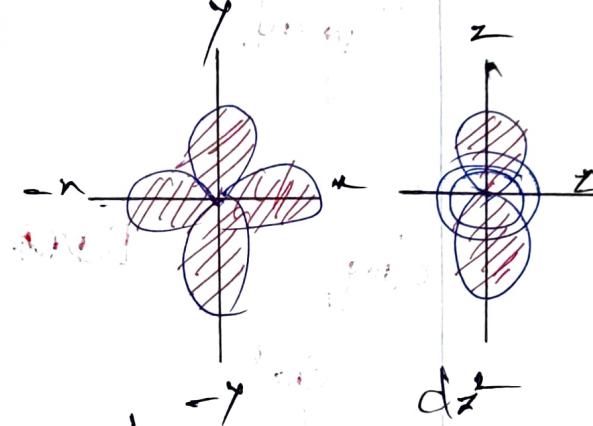
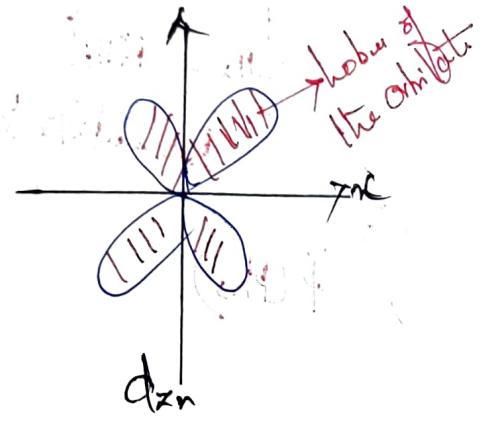
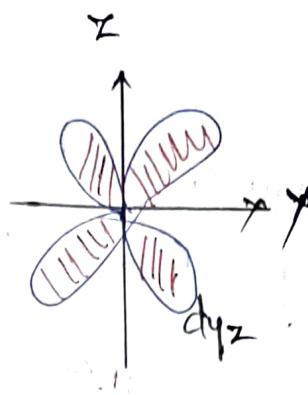
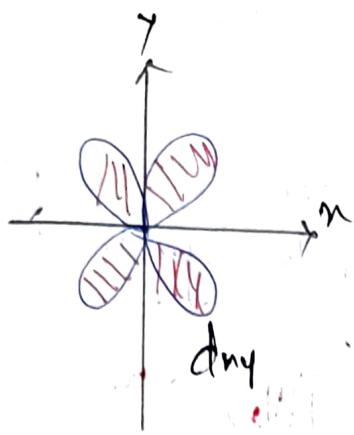
M_{go}

$$M_{eff} = \sqrt{n(n+2)} \cdot \mu_B$$

n = No of Unpaired electron

μ_B (on Bohr magneton)

$$d^1 = \sqrt{1(1+2)} = \sqrt{2} = 1.414$$



Spatial arrangement of the five d-orbitals in the three axes.

How to identify weak ligand and the strong ligand.

Ligands are which the donor atoms are ligands. e.g. oxygen, CO , sulphur are the weak ligands. Halogens, e.g. F^- , Br^- , I^- , Cl^- , OH^- , Se^{2-} . Spherical ligands.

example

F^- , Br^- , I^- , Cl^- , OH^- , Se^{2-} .

Halogens.

If Sulphur is a donor atom it is a weak ligand

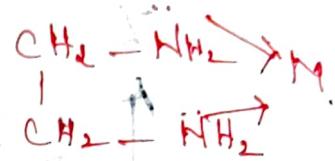
CO_3^{2-}



Ligands in which donor atoms are O/N/P.
they act as a strong field ligand.

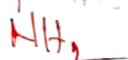


Antidentate
ligand



Adalentate ligand

dtg, EDTA



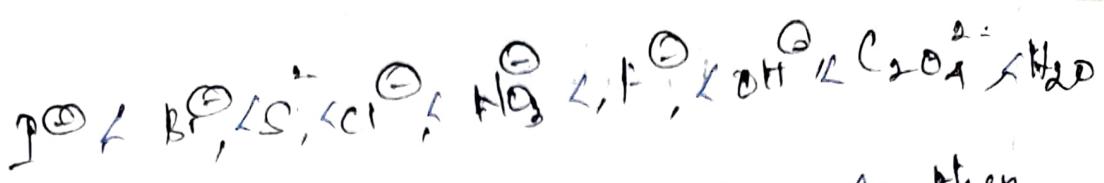
Spectrochemical series.

for a given metal ion, Δ depends upon the magnitude on the ligand.

The Common ligand can be arranged in the ascending order of crystal field splitting:

This series of arrangement is called

Spectrochemical series.



EDTA + NH₃ in pyridine & en 2-phen

Increasing A →
Hydroxide donors.
Hydroxide donors.

Weak Ti
donor. → Strong Ti eng.
Strong Ti eng.

Ligand upto H₂O are weak field ligand or high spin
Complex.
Ligand beyond H₂O are strong field ligand and
tend to relate to low spin Complex.

Example.
Identify the following components of the complex.

- 1) Weak field / strong ligand
- 2) High spin or low spin Complex
- 3) Magnetic moment.
- 4) Magnetic moment.