

Sl

Needs of Quantum mechanics:-

The dynamical properties (position, momentum, kinetic energy) of particles were determined by laws of mechanics. Classical mechanics explains the dynamical properties like large or small. But fails to explain atomic and molecular systems for well-defined set. for Ex: An electron moving around the nucleus. because it has quantisation (discrete) energy. therefore it was need to postulate a new system of mechanics, that is called quantum mechanics.

Planck's theory:-

A hot body radiates energy in small units of wave, not in continuous waves. An each unit of wave is called as quantum (or) photon. The energy of photon is given by. $E = h\nu$

where $h = \text{planck const } 6.626 \times 10^{-34} \text{ JS}$)

$\nu = \text{frequency of emitted radiation.}$

Heisenberg uncertainty principle:-

It was not possible to measure the exact position and momentum simultaneously (for a α particles like electron.) If the position is determined accurately the velocity becomes uncertain and vice versa.

$$\Delta x \cdot \Delta P_x \geq \frac{h}{4\pi}$$



De Broglie equation:-

He says electron has both particles and wave character

Statement:-

The momentum (p) of a particle in motion is inversely proportional to wave length (λ), ^{here} Planck's constant (h) being the constant proportionality.

Derivation:-

According to Einstein's mass energy relationship,

$$E = mc^2 \quad | \begin{array}{l} E \rightarrow \text{Energy} \\ m \rightarrow \text{mass} \\ c \rightarrow \text{velocity of light} \end{array}$$

According to Planck's eq.

$$E = h\nu \quad | \quad h \rightarrow 6.626 \times 10^{-34} \text{ Js}$$

By equating both

$$h\nu = mc^2$$

$\nu \rightarrow \text{frequency of light}$

Here we know $\nu = c/\lambda$

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

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

Subs velocity of electron v in place of c . we get

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

$$\boxed{\lambda = \frac{h}{P}}$$

| movement
 $P = mv$.

This equation is called de Broglie's eq.
Significance:-

It is applicable only for small particles like electron not for large particles.

Schrodinger Equations:

By considering the electron as standing wave around the nucleus in an atom, Schrodinger derived an equation for calculation of probability of finding the electron at various points in an atom. The equation for standing wave is

$$\psi = A \sin \frac{2\pi x}{\lambda}$$

Differentiate the eq ①.

①.

where
 ψ → Wave function
 Amplitude of wave
 x → Displacement
 λ → wavelength
 A → const.

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

$$\frac{d^2\psi}{dx^2} = -A \frac{4\pi^2}{\lambda^2} \sin \frac{2\pi x}{\lambda} \quad \text{--- ②}$$

Subs eq ① in ②

$$\boxed{\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi}$$

The kinetic energy of the particle of mass m and velocity v is given by the equation.

$$KE = \frac{1}{2}(mv^2)$$

$$KE = \frac{m^2 v^2}{2m}$$

According to de Broglie's eq.

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

$$\lambda^2 = \frac{h^2}{m^2 v^2}$$

$$m^2 v^2 = \frac{h^2}{\lambda^2}$$

$$\therefore m^2 v^2 = KE \times 2m.$$

$$KE \times 2m = \frac{h^2}{\lambda^2}$$

$$KE = \frac{h^2}{\lambda^2 2m} \quad \text{--- ③}$$

we know $\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi$

$$\therefore \lambda^2 = -\frac{4\pi^2}{\frac{d^2\psi}{dx^2}} \psi$$

Subs λ^2 to equation ③ we get.

$$KE = -\frac{\hbar^2}{2m} \times \frac{d^2\psi}{dx^2} \times \frac{1}{4\pi^2} \times \frac{1}{\psi}$$

Simplify that

$$KE = -\frac{\hbar^2}{8\pi^2 m \psi} \frac{d^2\psi}{dx^2} \quad \text{--- (4)}$$

The total energy of a particle is the sum of KE and potential energy (PE).

$$E = KE + PE \Rightarrow KE = E - PE.$$

Subs eq (4) in above.

$$-\frac{\hbar^2}{8\pi^2 m \psi} \frac{d^2\psi}{dx^2} = E - PE.$$

$$\frac{d^2\psi}{dx^2} = -\frac{8\pi^2 m}{\hbar^2} \psi (E - PE).$$

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{\hbar^2} (E - PE) \psi = 0.}$$

This is Schrodinger's eq for one dimension.

For particles whose motion is three dimension

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{\hbar^2} (E - PE) \psi = 0}$$

This eq is called Schrodinger wave equation

(00)

$$\boxed{\nabla^2 \psi + \frac{8\pi^2 m}{\hbar^2} (E - PE) \psi = 0}$$

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Particle in a box

Using the Schrodinger equation we solve the particles present in 1D one dimensional box.
 \Rightarrow Three dimensional box.

Particles in One Dimensional box:-

Consider a microscopic particle like electron confined to a one D box with a length is 'a'.

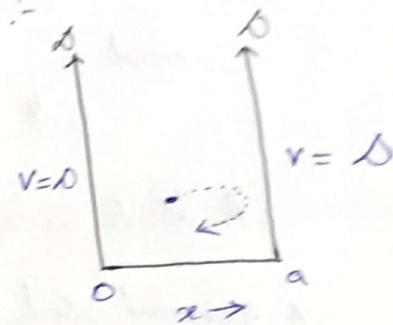
on either side of box has infinite PE. let the mass of particle be 'm' and total energy E. The particles move to and fro motion.

Let the PE(v) inside the box is zero (ie) $v=0$.

$$E = T + V \Rightarrow [E = T]$$

$E \rightarrow$ Total Energy
 $T \rightarrow$ KE
 $V \rightarrow$ PE.

outside the box	inside the box.
$v=0$	$v=0$
$\psi^2 = 0$	$\psi^2 = ?$
$\psi = 0$	$\psi = ?$



Since it is a 1D box. So Schrodinger eq for

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

Since $v=0$.

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E \psi = 0} \quad \text{--- (1)}$$

This is Schrodinger eq for particle in 1D box

we have to solve this eq to find E and ψ .

$$E = ?$$

$$\psi = ?$$

To solve the above eq we rearrange it first.

$$\frac{d^2\psi}{dx^2} = -\frac{8\pi^2 m E}{h^2} \psi$$

Solu for this eq is

$$\psi = A \sin\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} x \quad \text{--- (2)}$$

and

$$\psi = B \cos\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} x \quad \text{--- (3)}$$

A & B are undetermined parameter.

A general solu is the linear combination of (2) & (3)

$$\psi = A \sin\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} x \pm B \cos\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} x$$

Function should be well behaved. To find this we apply the boundary condition.

Consider an infinitesimally small distance away from the wall (outside). $\psi = 0$. The value of ψ should be zero for the function to be continuous at the boundary.

The two boundary condition are

$$1. \psi = 0 \text{ at } x = 0$$

$$2. \psi = 0 \text{ at } x = a.$$

1) First boundary condition :-

$$\psi = 0, \text{ at } x = 0.$$

we know.

$$\psi = A \sin\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} x \pm B \cos\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} x$$

Subs $\psi = 0$, and $x = 0$. we get.

$$0 = 0 \pm B \cos 0$$

$$\boxed{0 = B}$$

$$\begin{cases} \sin 0 = 0 \\ \cos 0 = 1. \end{cases}$$

$$\therefore \psi = A \sin\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} x + 0.$$

$$\boxed{\psi = A \sin\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} x} - \textcircled{5}$$

(ii) Apply the second boundary condition on $\textcircled{5}$

$$\psi = 0 \text{ at } x = a$$

$$\text{we get it } A \sin\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} a = 0.$$

Product of two terms is zero, so at least one term must be zero. If $A = 0$,

$$\psi = A \sin\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} a$$

$$\psi = 0$$

This shows that the probability of finding the particle in 1D box is zero, which is not possible. So A cannot be zero. Then the \sin term must be zero.

$$\therefore \sin\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} a = 0 \quad - \textcircled{6}$$

we know

$$\sin n\pi = 0 \quad - \textcircled{7}.$$

$$\text{so } \textcircled{6} = \textcircled{7}$$

$$\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} a = n\pi$$

Squaring on both sides,

$$\frac{8\pi^2 m E}{h^2} \times a^2 = n^2 \pi^2$$

$$\boxed{E = \frac{n^2 h^2}{8ma^2}} - \textcircled{8}$$

Subs $\textcircled{8}$ in $\textcircled{5}$

$$\psi = A \sin\left(\frac{8\pi^2 m E}{h^2}\right)^{\frac{1}{2}} x$$

$$= A \sin\left(\frac{8\pi^2 m}{h^2} \times \frac{n^2 h^2}{8ma^2}\right)^{\frac{1}{2}} x$$

$$\psi = A \sin\left(\frac{\pi^2 n^2}{a^2}\right)^{\frac{1}{2}} x$$

$$\psi = A \sin \frac{n\pi x}{a}$$

normalised wavefn for particle
where $n = 1, 2, 3, \dots$
 n cannot be zero

ψ is a function of quantum number n .
can have only certain discrete values so ψ is quantised.

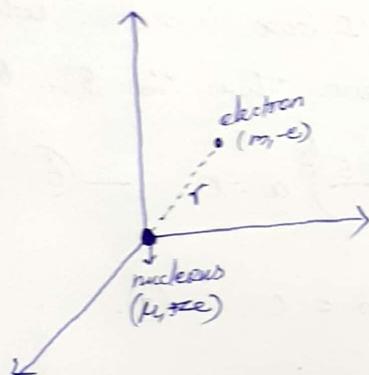
$$\psi_n = A \sin \left(\frac{n\pi x}{a} \right)$$

like a particle in 3D box

$$\psi = \sqrt{\frac{8}{a_x a_y a_z}} \cdot \sin \frac{n_x \pi x}{a_x} \sin \frac{n_y \pi y}{a_y} \sin \frac{n_z \pi z}{a_z}$$

S3

Hydrogen atom:-

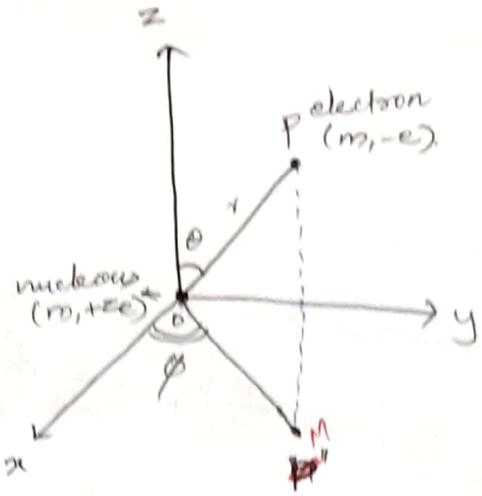


- Hydrogen atom is an one electron system
- It is a two particle system. It has one nucleus and one electron between which coulombic force of attraction is operating.
- Potential energy = $\frac{\text{charge of nucleus} \times \text{charge of electron}}{\text{distance between them}}$

$$V = \frac{(+ze) \times (-e)}{r}$$

$$V = -\frac{ze^2}{r}$$

- potential energy is a function of r only. $V(r)$
- The coordinates of hydrogen atom are represented as follows.



The position of the nucleus coincides with origin 'O'. The nucleus is 1836 times heavier than electron. So the reduced mass of the two particle system is

$$\mu = \frac{mM}{m+M} \quad \text{where } M \rightarrow \text{Mass of nucleus}$$

$m \rightarrow \text{mass of electron}$

$M \ggg m.$

So $\mu = \frac{mM}{M}$

$\boxed{\mu = m}$

So reduced mass of hydrogen atom and mass of electron are almost same.

In the diagram

$OP = r$ (ie) radius vector. The angle that radius vector make with z axis is θ . θ is called zenith angle. Draw projection of radius vector on xy plane (ie) OM. The projection makes an angle ϕ with x axis and ϕ is called the azimuthal angle.

Cartesian coordinates x, y, z are related to the polar coordinates r, θ, ϕ by the below relation.

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned}$$

} Relationship between r, θ, ϕ and x, y, z .

The limits are

$$\gamma = 0 \text{ to } \infty$$

$$\theta = 0 \text{ to } \pi$$

$$\phi = 0 \text{ to } 2\pi$$

(The Schrodinger equation is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m}{h^2} (E - V)$$

we know for hydrogen atom $V = -\frac{ze^2}{r}$

$$\boxed{\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m}{h^2} (E + \frac{ze^2}{r})}$$

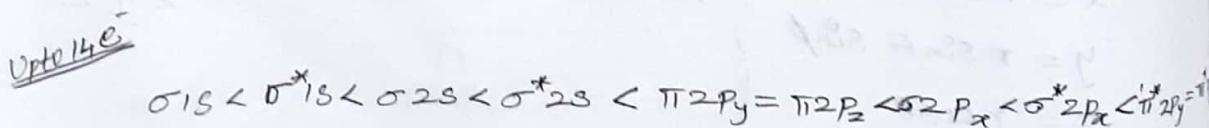
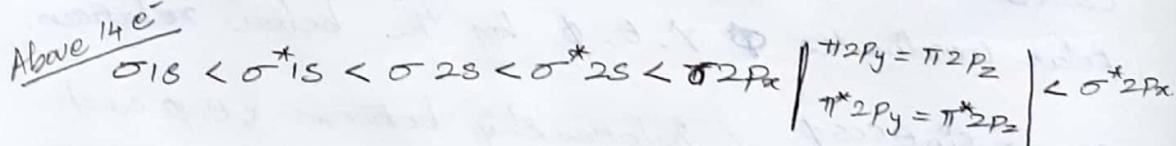
This is Schrodinger equation for hydrogen atom.

S1 Molecular Orbital Theory:

MOT was developed by F. Hund and R.S. Mulliken

Postulates:-

- Atomic Orbitals are of comparable energies combine together to form molecular orbitals. The shape of the molecular orbital depends upon the shape of the combining atomic orbitals.
- The number of MO formed is equal to the number of combining AO's.
- The electron filling in MO is in accordance with Pauli's, Aufbau, and Hund's rules.



- Number of bonds b/w two atoms is called BO. which is directly proportional to the stability of the molecules.

Linear combination of atomic orbitals (LCAO).

we express

~~the~~, $\psi(r, \theta, \phi)$ as a product of three independent functions.

$$\psi(r, \theta, \phi) = \underbrace{R_{nl}(r)}_{\text{Radial part}} \underbrace{Y_{lm}(\theta, \phi)}_{\text{Angular part.}} \quad \text{--- (1)}$$

where

$n \rightarrow$ principle quantum no...

$l \rightarrow$ Azimuthal quantum no...

$m \rightarrow$ magnetic quantum no..

For H atom,

$$R_{nl}(r) \text{ will be } R_{10}(r)$$

we get the radial Eigenfunction.

$$R_{10}(r) = 2 \left(\frac{z}{a_0} \right)^{3/2} e^{-2r/a_0} \quad \text{--- (2)}$$

$$Y_{lm}(\theta, \phi) \text{ will be } Y_{00}(\theta, \phi)$$

we get the angular eigenfunction

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \quad \text{--- (3)}$$

Sub (2) & (3) in (1)

$$\psi_{100}(r, \theta, \phi) = \phi \left(\frac{z}{a_0} \right)^{3/2} e^{-2r/a_0} \cdot \frac{1}{\sqrt{4\pi}}$$

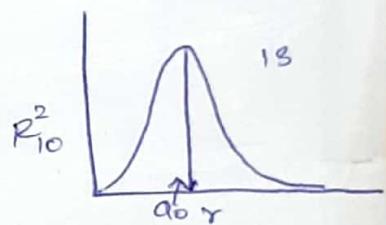
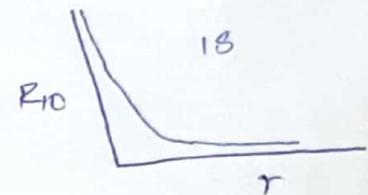
If one atomic unit $a_0 = 1$.

$$\boxed{\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} z^{3/2} e^{-2r}} \quad \text{--- (1)}$$

This is the normalized wave function for H-atom.

$$R_{10}(r) \propto r$$

$$R_{10}^2(r) \propto r$$



Radial distribution

Linear combination of atomic orbitals (LCAO).

It is more Superposition method where constructive interference of two atomic wave fun. produces a bonding MOs whereas destructive interference produces non-Bonding MOs.

Let ψ_A and ψ_B be the wave function of two AOs of atoms A and B. These AOs combine to form two MOs known as bonding ψ_b and anti-bonding ψ_a MOs.

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

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

Conditions for LCAO:-

1) Same energy of combining orbitals:-

The combining AOs must have same (or) nearly same energy. This means that $2p$ orbital of an atom can combine another $2p$ orbital of another atom but $1s$ and $2p$ cannot combine together.

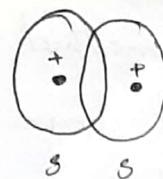
2) Same symmetry about the molecular axis:-

The combining atoms should have same symmetry around the molecular axis for proper combination. Ex:- All the sub-orbitals of $2p$ have same energy but still $2p_z$ orbital of an atom can only combine with a $2p_z$ orbital of another atom but cannot combine with $2p_x$ and $2p_y$ orbital as they have different axis of symmetry.

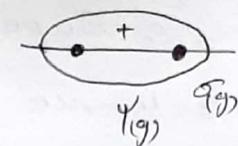
3) Proper overlap between the atomic orbitals:-

Two AOs will combine to form MO's if the overlap is proper. Greater the extent of overlap of orbitals, greater will be the nuclear density between the nuclei of the two atoms.

AO^s

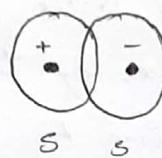


$M O^s$

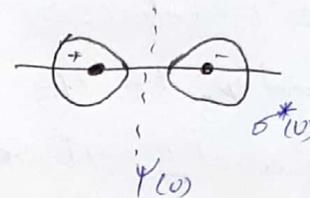


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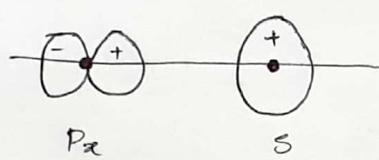


AO (Antibonding
Orbital)

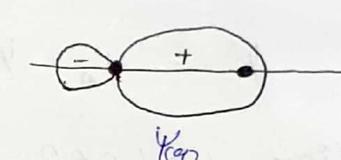
① S-S combination of atomic orbitals.

AO^s

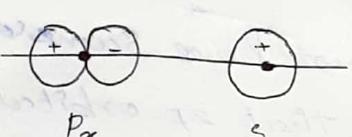
$M O^s$



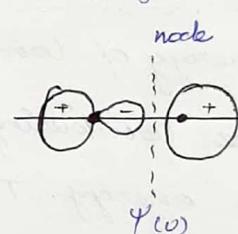
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σ overlap
Banding orbital

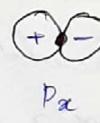
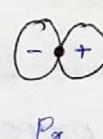


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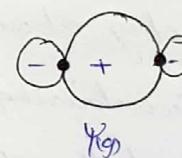


σ^* overlap
Antibonding
orbital

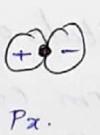
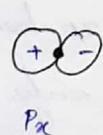
② S-P combination of atomic orbitals.



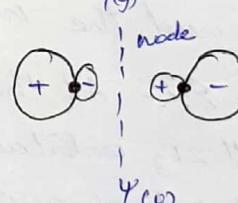
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σ overlap
Banding orbital

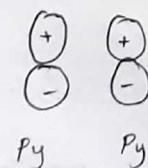


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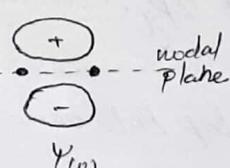


σ^* overlap
antibonding orbital

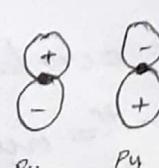
③ P-P combination of AOs.



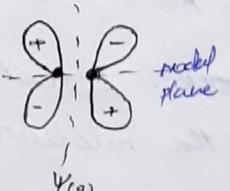
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π -overlap
Banding orbital



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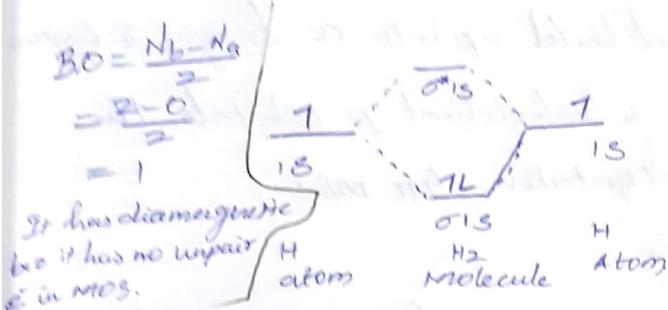


π^* overlap
antibonding orbital

④ P-P combination giving π bonding

Energy level diagrams:-

Homo nuclear diatomic orbital:-



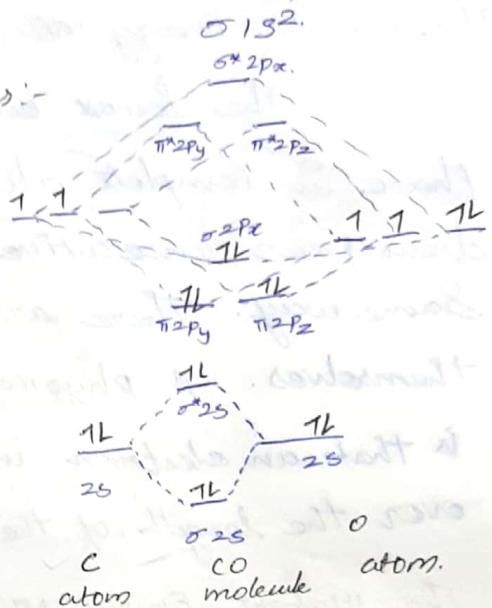
Each atoms have one electron and hence two electron in H_2 molecule. These occupy the lowest energy MO.

Hetero nuclear diatomic molecules:-

Here $C \Rightarrow 2 + 4$
= 6 electron

$O \Rightarrow 2 + 6$
= 8 electron

so CO molecule = 14 e^-



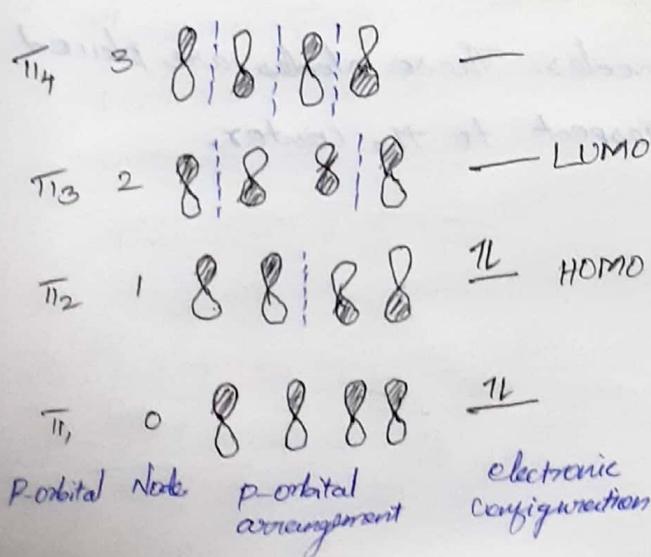
$\sigma 1s^2 < \sigma^* 1s^2 < 2s^2 < 2p^2 < \pi^* 2p_y^2 = 2p_z^2 < 2p_x^2$

Bond order = $\frac{N_b - N_a}{2}$
= $\frac{8 - 2}{2} = 3$

Hence CO is a stable molecule and diamagnetic.

$[C \equiv O]$

Structure and orbital picture of butadiene:-



} orbital diagram of butadiene

Butadiene is composed of 4 carbons with two adjacent π bonds which are conjugated. All four p-orbitals are all aligned with each other, and build up into a larger π system. Since butadiene consists of 4 individual p orbitals, the π -system of butadiene will contain 4 π MOs.

The Lowest-Energy MOs (π_1):-

The lowest energy MO will have p orbital with phase ~~is~~ complete alignment ~~with~~ each other i.e., draw four consecutive p-orbitals all aligned the same way. There are zero nodes bw the p orbitals themselves. A physical interpretation of this orbital is that an electron in this orbital is delocalized over the length of the π system.

The Highest-Energy MOs (π_4):-

Here four p-orbitals should be drawn in alternate phases of each. This creates a π^* system with three nodes.

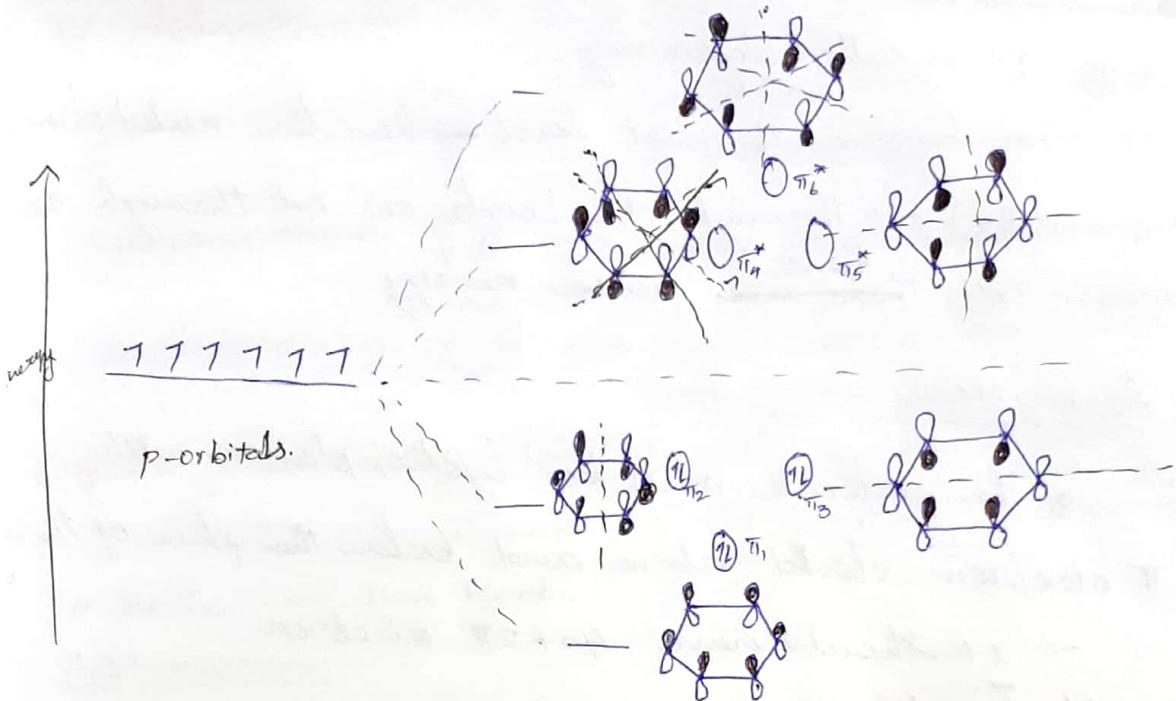
The Second-Lowest-Energy MOs:-

It has one node. According to Schrödinger wave eq, the node placement for this orbital is in the middle.

The Third-Lowest-Energy MOs:-

It has two nodes. These nodes are placed symmetrically with respect to the center.

Structure and orbital picture of benzene



→ The aromatic system of benzene consists of six p-orbitals (atomic orbitals). Benzene must have six molecular orbitals.

→ The lowest-energy molecular orbitals of benzene have zero nodes. The phases of all p-orbitals aligned the same way.

→ The highest energy molecular orbitals have p-orbitals with completely alternating phases. All the p-orbitals position should be alternating phases there is no two adjacent p-orbitals should have lobes with the same phase. There are three nodal planes, which cut through the molecule at various points. This orbital has zero overlap bw adjacent p orbitals and therefore e⁻s in this orbital have the minimum possible delocalization. They are therefore the highest energy.

→ For benzene, draw a system with one nodal plane that cuts through two of the single bonds. We can also draw a ~~so~~ nodal plane through the atoms.

These two molecular orbitals (π_2 and π_3) have the same number of nodal planes, therefore have the same energy. It is called degeneracy.

For benzene; the next level ~~up~~ has two nodal planes (π_4 and π_5) cut through the bonds, or cut through the atoms. Both ~~these are~~ ^{have} same energy.

Aromaticity :-

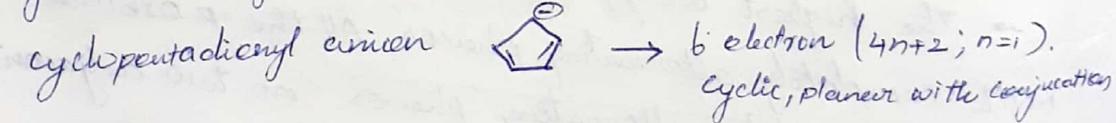
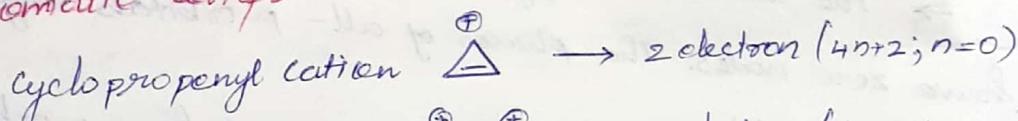
→ The molecule must be cyclic, planar with π electron cloud above and below the plane of the ring.

→ It should have $4n+2\pi$ electrons.

Hückel Rule: (HÜCKEL)

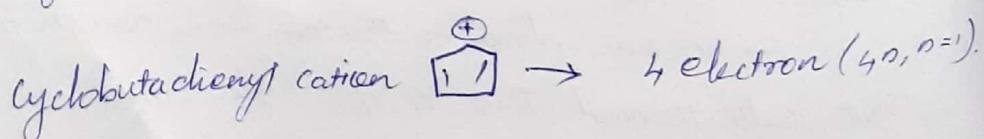
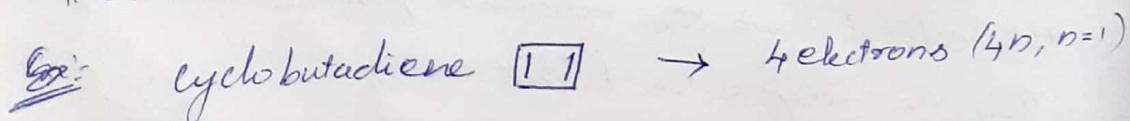
If molecules are aromatic it must satisfy the $4n+2 \pi$ electrons ($n=0, 1, 2, 3\dots$)

Aromatic Compounds :-



Antiaromatic Compounds :-

Anti aromatic compounds satisfy the $4n$ π electrons.



Non aromatic :-

The molecule have non planarity (or) disruption of delocalization. It may contain $4n(0)$ $4n+2 \pi$ electrons.

cyclopropane  \rightarrow 2 electrons $n=0$, The delocalization is interrupted due to sp^3 methyls.

cyclopentadiene  \rightarrow 4 π s. Does not have conjugation.

cycloheptatriene  \rightarrow 6 π s. Does not have conjugation.

Crystal field theory :- (CFT).  [11] anulene & [16], [8] annulene non aromatic bcz it does not have planar structure.

CFT also known as LFT was proposed by

H. Bethe and Van Vleck.

Assumptions:-

\rightarrow The metal-ligand bond is ionic due to electrostatic interaction b/w the metal ion and ligand.

\rightarrow Ligands are treated as point charges in case of anions and dipoles in case of neutral molecules.

\rightarrow The five d-orbitals i.e., d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$, d_{z^2} in an isolated gaseous metal atom/ion are degenerate.

\rightarrow As ligand approach the metal ions, the degeneracy of five d-orbitals is loosed. Because, the σ s in the d-orbitals and ligands repel each other due to electrostatic repulsion and hence, d-electron closer to the ligands will have a higher energy than those further away.

\rightarrow The splitting of d-orbitals depends on the nature of crystal field charge and metal ion.

Advantages:-

CFT successfully explains the structure, colour and magnetic properties of coordination compounds.

Limitations:-

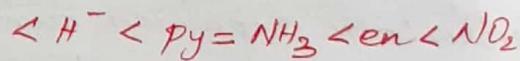
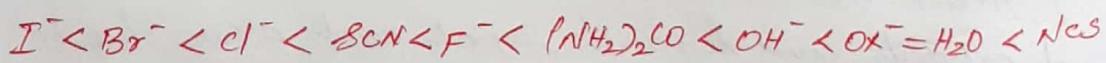
- It is also unable to account satisfactorily for the relative strengths of ligand (e.g) it does not explain why H_2O is stronger ligand than OH^-
- It gives no account of the covalent character of bonding between the ligand and the central atom.

Spectrochemical Series:-

The ligands which has high splitting power is known as strong field ligands and low splitting power is known as weak ligands.

The common ligands can be arranged in the order of their increasing splitting powers to cause 'd' orbitals splitting. This series is called Spectrochemical Series and is given below. The ligands are arranged in the order in which they produce increasing value of σ value (or $\log \kappa_{\text{f}}$)

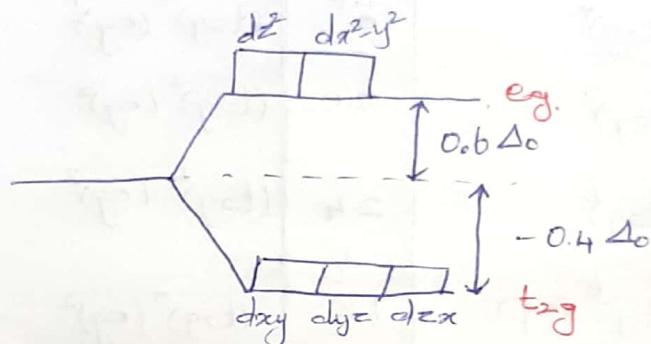
It is given as follows.



- (a) In the above ligand series up to pyridine (py) are weak field ligands. (1) weak field ligands obey Hund's rule (2) It's having maximum number of unpaired electrons in their compound (i.e) Spin free complex (3) It is a high spin complex.

- (1) $\text{NH}_3 < \text{en} < \text{NO}_2 < \text{CN}^- < \text{Cl}$ are strong field ligands
- (1) Strong field ligands does not obey Hund's rule
 - (2) It is having minimum number of unpaired electrons in their compound. i.e. Spin paired complex.
 - (3) It is low spin complex.

CFT splitting of d-orbitals in octahedral complexes



→ CFT divides into 2 groups. The orbital with lobes along the axis called eg orbital (dz^2, dx^2-y^2). The lobes inbetween the axis are called t_{2g} orbitals $d_{xy}, d_{yz}, \& d_{zx}$.

→ The energy gap between t_{2g} & eg sets is denoted by Δ_0 (or) $10Dq$. and this is known as CFSE.

$$\boxed{\text{CFSE} = (-0.4x + 0.6y) \Delta_0 + mp.}$$

Where
 $x \rightarrow$ no. of e⁻ present in t_{2g} orbital.

$y \rightarrow$ No. of e⁻ present in eg orbital

$m \rightarrow$ Tot. no. of paired e⁻s

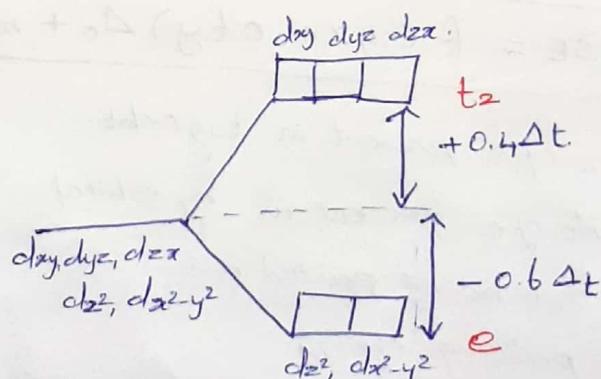
$p \rightarrow$ pairing energy

- In oh. complexes, the six ligands approach the central metal ion along the coordination axis is the axis $d_{x^2-y^2}$ and d_{z^2} orbitals. The set of orbitals has higher energy than t_{2g} orbitals.
- In case of free metal ion all five d-orbitals are degenerate. Once the ligand approach to the central metal ion it loses their degeneracy, and split in to t_{2g} and eg.
- Since the lobes of eg orbital lie in towards the approaching ligand, but in t_{2g} orbital lobes are directed in space b/w the approaching ligand so it goes to lower energy.
- The attraction b/w central metal atom and ligand in the complex are negligible.
- The ligands are considered as point charge

Octahedral field (oh).

d^n	Example	Strong field $\Delta_0 > \mu$		weak field $\Delta_0 < \mu$	
		configuration low spin	CFSE (Δ_0)	configuration High spin	CFSE (Δ_0)
d^0	Sc^{3+}	$(t_{2g})^0 (eg)^0$	0	$(t_{2g})^0 (eg)^0$	0
d^1	Ti^{3+}	$(t_{2g})^1$	0.4	$(t_{2g})^1$	0.4
d^2	V^{3+}	$(t_{2g})^2$	0.8	$(t_{2g})^2$	0.8
d^3	Cr^{3+}, V^{2+}	$(t_{2g})^3$	1.2	$(t_{2g})^3$	1.2
d^4	Mn^{3+}, Cr^{2+}	$(t_{2g})^4$	1.6	$(t_{2g})^3 (eg)^1$	0.6
d^5	Fe^{3+}, Mn^{2+}	$(t_{2g})^5$	2.0	$(t_{2g})^3 (eg)^2$	0
d^6	Co^{3+}, Fe^{2+}	$(t_{2g})^6$	2.4	$(t_{2g})^4 (eg)^2$	0.4
d^7	Co^{2+}	$(t_{2g})^6 (eg)^1$	1.8	$(t_{2g})^5 (eg)^2$	0.8
d^8	Ni^{2+}	$(t_{2g})^6 (eg)^2$	1.2	$(t_{2g})^6 (eg)^2$	1.2
d^9	Cu^{2+}	$(t_{2g})^6 (eg)^3$	0.6	$(t_{2g})^6 (eg)^3$	0.6
d^{10}	Zn^{2+}, Cu^{+}	$(t_{2g})^6 (eg)^4$	0	$(t_{2g})^6 (eg)^4$	0

CFT splitting of d-orbitals in tetrahedral complex:



→ In T_d complexes for ligand approach the metal ion in b_{1g} the axis. so the orbital with lobes lies in blw the axis are reflected more than the d orbitals which has lobes lie in the axis.

→ so that t_2 orbitals lie $0.4 \Delta t$ above the hypothetical degenerate energy level and e orbital lie $0.6 \Delta t$ below the level.

$$\text{CFSE} = (0.6x + 0.4y) \Delta t + mP.$$

$x \rightarrow$ No. of e^- present in e orbital

$y \rightarrow$ No. of e^- present in t_2 orbital.

Magnetic properties :-

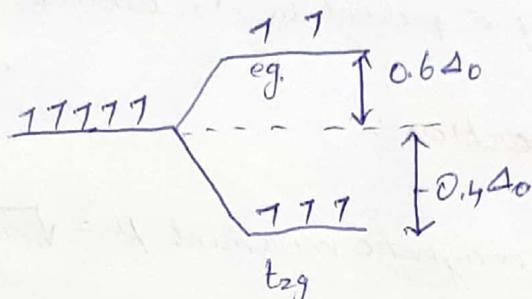
Spin only magnetic moment $\mu = \sqrt{n(n+2)}$.

Tetrahedral field (Td).

System	Example	Weak field		Strong field	
		Configuration (high spin)	CFSE	Configuration (low spin)	CFSE
d^0	Sc^{3+}	$e^0 t_2^0$	0	$e^0 t_2^0$	0
d^1	Ti^{3+}	$e^1 t_2^0$	0.6	$e^1 t_2^0$	0.6
d^2	V^{3+}	$e^2 t_2^0$	1.2	$e^2 t_2^0$	1.2
d^3	Cr^{3+}, V^{2+}	e^2, t_2^1	0.8	$e^3 t_2^0$	1.2
d^4	Mn^{3+}, Cr^{2+}	e^2, t_2^2	0.4	$e^4 t_2^0$	2.4
d^5	Fe^{3+}, Mn^{2+}	$e^2 t_2^3$	0.0	$e^2 t_2^1$	2.0
d^6	Co^{2+}, Fe^{2+}	$e^3 t_2^3$	0.6	$e^4 t_2^2$	1.6
d^7	Co^{2+}	$e^4 t_2^3$	1.2	$e^4 t_2^3$	1.2
d^8	Ni^{2+}	$e^4 t_2^4$	0.8	$e^4 t_2^4$	0.8
d^9	Cu^{2+}	$e^4 t_2^5$	0.4	$e^4 t_2^5$	0.4
d^{10}	Zn^{2+}, Cu^+	$e^4 t_2^6$	0	$e^4 t_2^6$	0

Calculate CFSE for $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

Electronic configuration of Mn^{2+} is $t_{2g}^3 e_g^3$.
Here H_2O is weak field ligand. So it forms a high spin complex.



$$\text{CFSE} = [-0.4x + 0.6y] \Delta_o + mP$$

$$x = 3 \quad y = 2 \quad m = 0$$

$$\begin{aligned} \text{CFSE} &= [-0.4 \times 3 + 0.6 \times 2] + 0P \\ &= [-1.2 + 1.2] + 0 = 0 \end{aligned}$$

Pureparamagnetism:-

P.m. Subs are weakly attracted by a mag. field. They are magnetised in a mag. field in same direction. They lose their magnetism in absence of mag. field. It has due presence of unpaired e⁻s. O₂, Cu²⁺, Fe³⁺, Cr³⁺

Diamagnetism:-

D.M. are weakly repelled by a mag. field. They are weakly magnetised in a mag. field in opposite direction. It has paired e⁻s. Pairing of electrons cancels their mag. moments and they lose their mag. character.

Ex: H₂O, NaCl, C₆H₆.

Ferromagnetism:-

It has attracted very strongly by a magnetic field. Besides strong attraction these subs can be permanently magnetised.

Ex: Iron, Cobalt, Nickel, Gd, Cr₂O₃.

Antiferromagnetism:-

Subs like MnO showing anti-ferr. mag. have domain structure similar to ferr. mag. Subs, but their domains are oppositely oriented and cancel out each other's mag. moment.

Ferrimagnetism:-

F. mag. is observed when the mag moments of the domains in the subs are aligned in parallel and anti-parallel direction in unequal numbers. They are weakly attracted by mag. field as compared to ferromagnetic substances Fe₃O₄ and ferrites like MgFe₂O₄ and ZnFe₂O₄. These substances also lose ferrimagnetism on heating and become paramagnetic.

