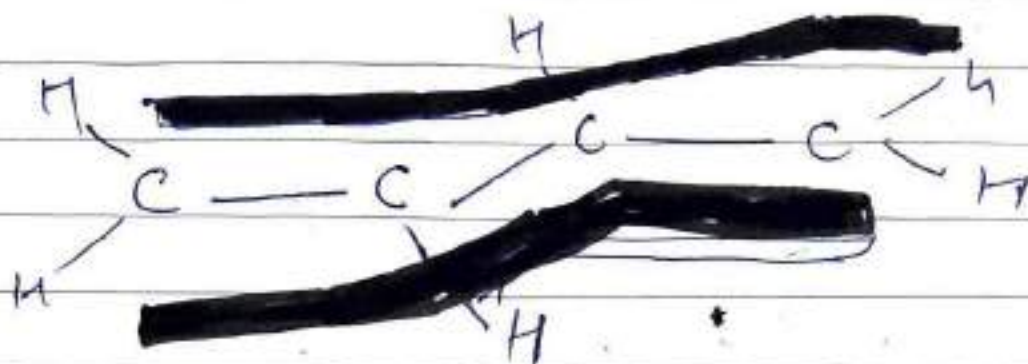in case of ψ_1 (Bonding orbital)
four π electrons to be delocalised
all over the chain $C_1 \longrightarrow C_4$

Delocalisation of π electrons.
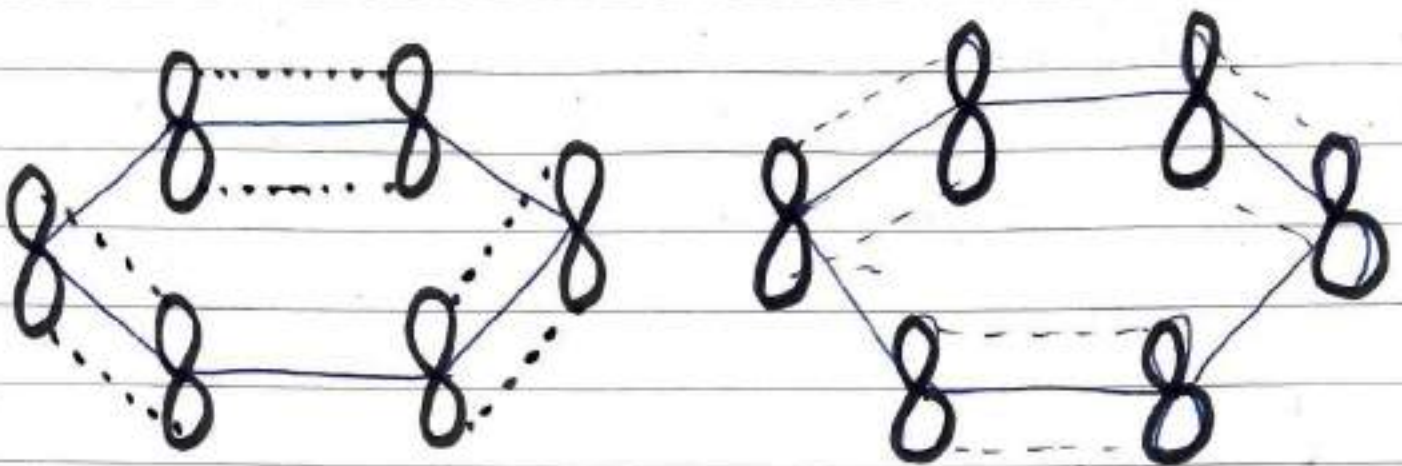
Orbital structure of Benzene

Acc. to Orbital theory, each of six e
Carbon atoms in benzene is in sp^2
hybridisation.

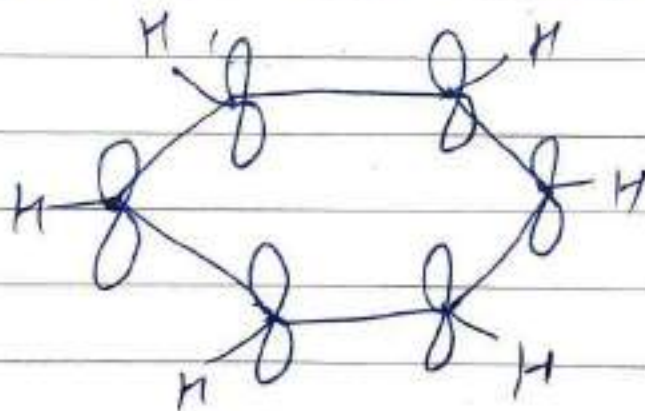→ The three hybrid of each Carbon
atom form three Sigma Bonds.
→ Unhybridised p orbital on these
three Carbon atoms for π Bond.

The Six Carbon and Six hydrogen

atoms lie in the same plane and angle between any two σ bonds 120°. Thus benzene is a planar molecule.


Possibility of overlap of unhybridised orbitals in both directions
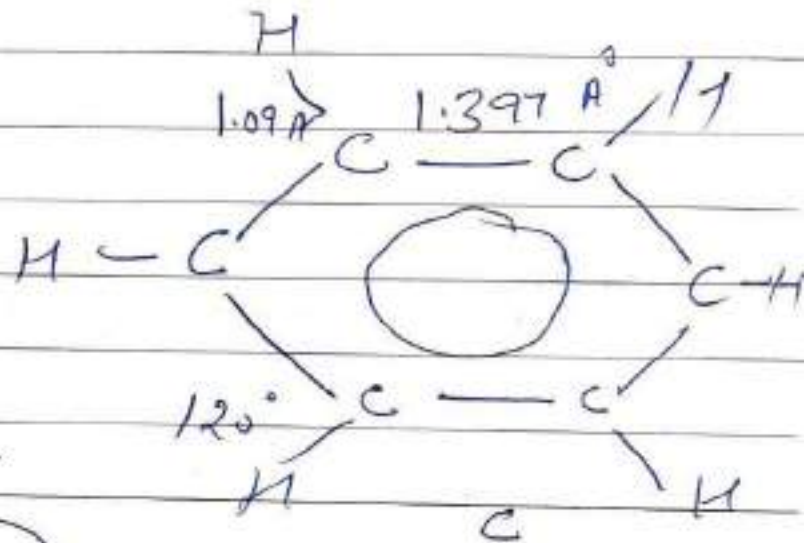

Sp² hybridised Carbon each forming three sigma bonds.

These are two Continuous ring like electron cloud, one above and other below the plane of the atoms. This process of delocalisation of π electron results in bond which are stronger than normal π bonds and hence stability of the molecule.

a

H

1.09 Å — C — 1.397 Å — C

H — C

120° — C — C

H

C

C — H

H
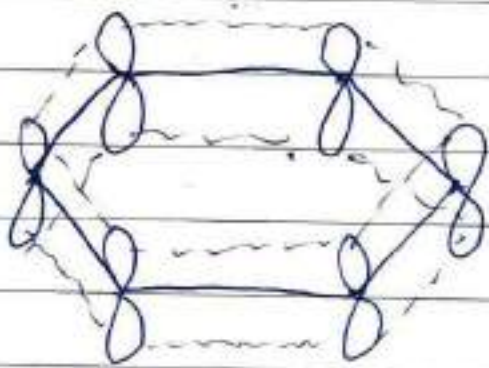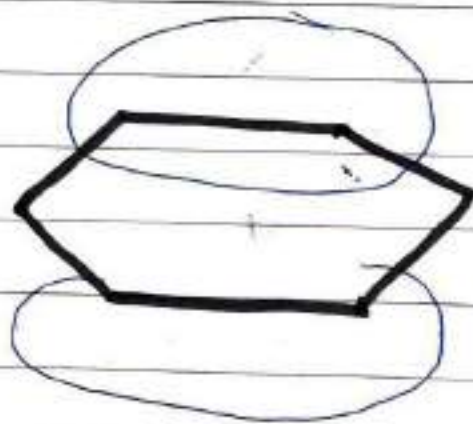
orbital picture of Benzene

Aromatic Characteristic (Aromaticity)

Benzene and all those Compounds which resemble benzene in their chemical behaviour are called aromatic Compounds.

Properties of Aromatic Compounds

① They are cyclic Compounds
② These molecules are shown to be planar by x-ray. Restricted To Addition R^ns
③ Despite Unsaturation, these go. Substitution R^n
④ They are stable. The π electrons are delocalie

Huckel Rule

Huckel formulated a simple Rule predicting wheather a Compound is aromatic or not. He derived this Rule on the basis of Quantum Mechanics. <u>Condition for a molecule to be aromatic</u>
1) Molecule or Ion must be Cyclic and must be flat or planar
2). It should have a Cyclic Cloud of π $\bar{e}$ s
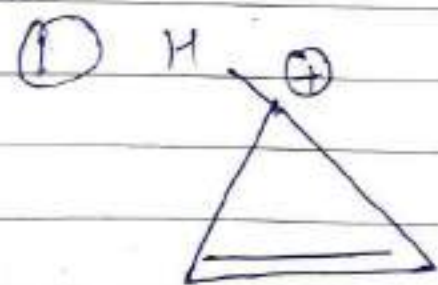3) π $\bar{e}$ cloud are delocalised over Ry

4) The total number of π electrons in the molecular species should be $4n+2$ where $n = 0, 1, 2, 3 \ldots$

It is also known as Huckel Rule or $(4n+2)$ Rule.

for $n = 0$ 2 π electrons
   $n = 1$ 6 π electrons
   $n = 2$ 10 π e^-
   $n = 3$ 14 π e^-

Applications of Huckel Rule

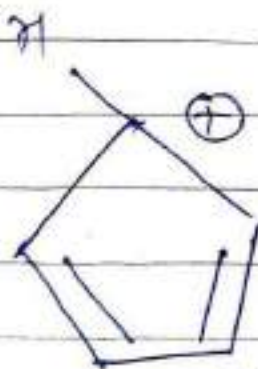① Cyclopropenyl Cation
$2\pi \bar{e}$

$4\pi e^-$ (non Aromatic)
Cyclopropenyl Anion

Monocyclic Compounds

Cyclopentadienyl Cation or anion

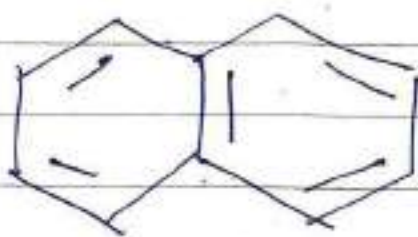4π Non aromatic

6π aromatic

2 **Poly Cyclic** → It helps in Explaining the aromaticity of Poly cyclic Compounds.

Naphthalene
$10\pi\ e^-$
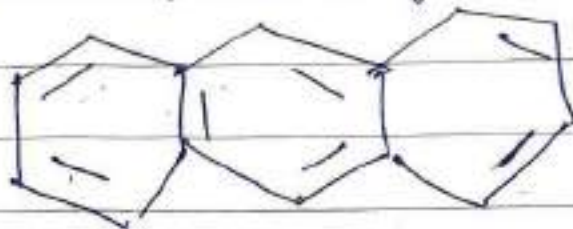
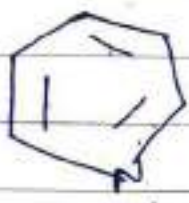Anthracene
$14\ e^-$

3. **Heterocyclic**

$6\pi\ e^-$

Organic Compounds of O, N and S.
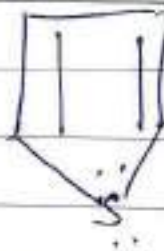
Pyridine   Furan   Thiophene   H
                                        Pyrrole

④ **Annulenes**

Completely Conjugated monocyclic polyenes Containing an even number of Carbon atoms are Called annulenes.

Their general formula is $(CH = CH)_n$
where $n = 2, 3, 4$

[4]-Annulene
Cyclobutadiene

[6]
Benzene

[8]
Cyclooctatetraene

Structures of Benzene

Dewar

1867

Claus 1867

1892

Baeyer

σ Bond
Skeleton of Benzene is

sp^2 sp^2-sp^2 C-C
$1s$
sp^2
sp^2
sp^2
sp^2
sp^2
sp^2
sp^2

Modern picture of Benzene

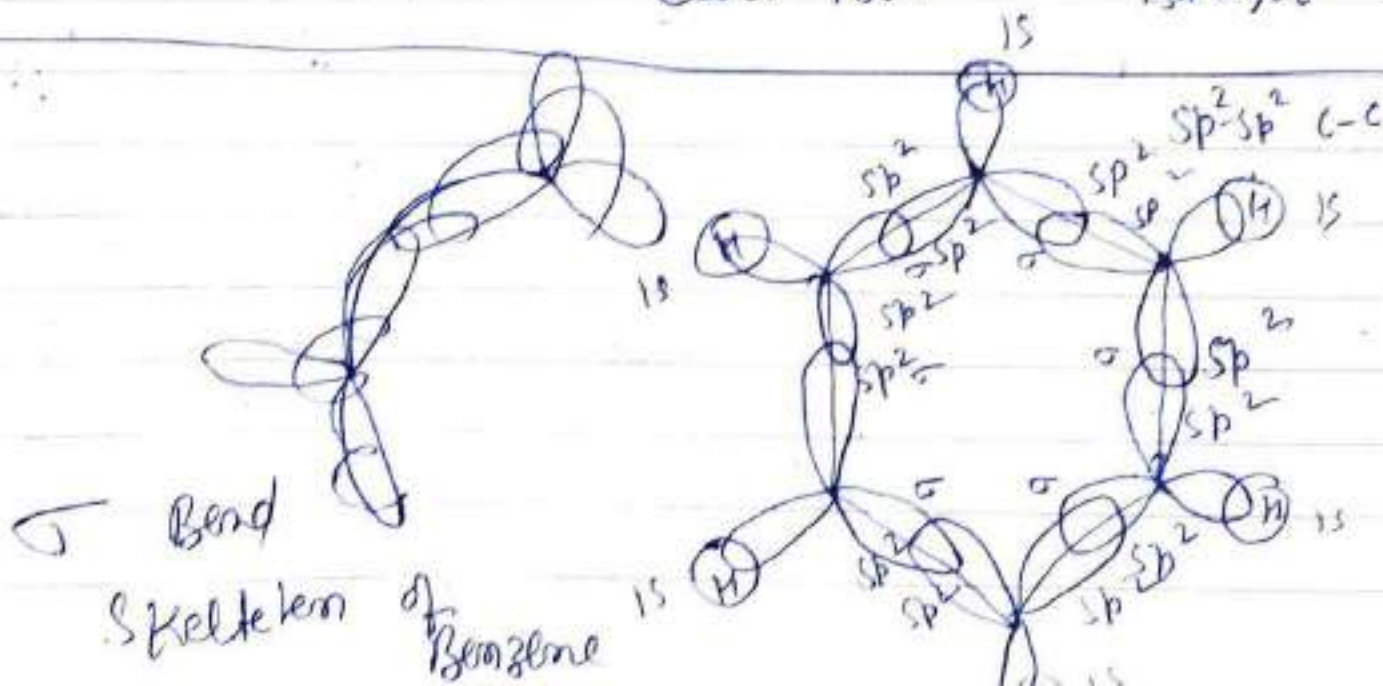Valence Bond theory have some limitations corresponding to that it could not Explain the spilling of d-orbitals and could not Explain why inner and outer orbitals Exists.

Acc to Valence Bond theory Bond b/w the metal and ligand is purely covalent.

Acc to CFT the Bond b/w metal and ligand is purely ionic

The three d orbitals

d_{xy} d_{yz} d_{zx} are identical and each consits of four lobes of high electron density in xy, yz and zx plane.

The two d orbitals

$d_{x^2-y^2}$ and d_{z^2} are identical and each Consits of four lobes of high electron density along the axes x and y

d_{z^2} have two lobes along the z axis with a ring of high electron density in xy plane.
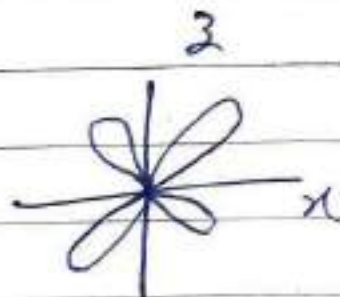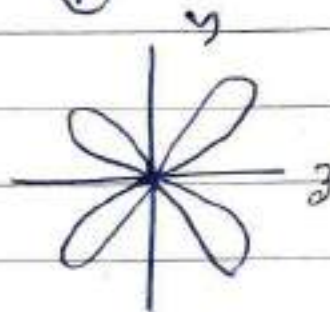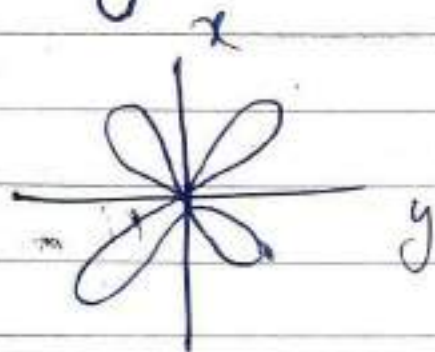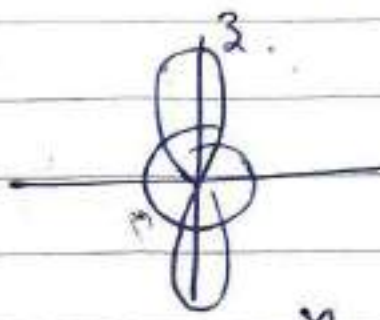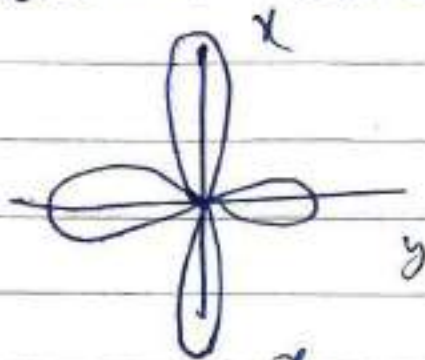
Main Points of CFT

1. Transition metal cation is surrounded by the ligands with lone pairs e^-

2. ligands are point charges, which are ionic (F^-, Cl^-, CN^-) and molecules (H_2O, NH_3, CO) with negative

each of their dipole oriented towards the metal cation

(iii) The attraction b/w metal cation and negative end of ligand is assumed to be electrostatic and purely ionic.

(iv) The valence e^- of the metal will be repelled by the -ve field of ligands

(v) The no of ligands and their arrangement around the central metal ion used have different effect on the relative energies of d-orbitals

(vi) Spectra of the metal complexes can be explained in terms of electronic Transition b/w various d orbitals

(vii) Magnetic properties depend on splitting

(VIII) It also explains why certain geometries are more favoured than others on the basis of CFT

Crystal Field Theory :→ Theory was given by Hans Bethe (1929) and John Van Vleck (1932).

Postulates of CFT :→

① CFT considers the metal - ligand bond to be ionic arising purely from electrostatic attraction b/w M-L. As these interactions are similar to Those b/w ions in a crystal that's why it has been named as <u>crystal field Theory</u>.

② CFT consider each ligand as a point of negative charge.

③ It considers the effect of ligands on The relative energies of d-orbitals of central transition — metal atom / ion.

④ The electrical field of the metal cation affects The surrounding ligands while The combined field of ligands (crystal field) will influence the electrons of central metal cation.

⑤ The Presence of ligands around central metal cation cause breaking of degeneracy of five (5) degenerate d-orbitals of metal ion.

The extent of splitting of metal d-orbitals depends upon.

(i) Number of ligands.

(ii) Arrangement of ligands around the central metal ion.

(vi) Magnetic properties of transition metal complexes depends upon splitting of d-orbitals

(7). CFT also explains why certain geometries are more favoured Than others by certain metals in terms of crystal field stabilisation energies.

(8) The colour of complexes are also explained in terms of electrostatic transition b/w various d-orbitals.

Crystal Field Theory For octahedral complexes →

In octahedral complex, The C.N. is 6. The central metal ion is at centre and ligands occupy six corners of the octahedron.

We know That all The five d-orbitals are degenerate orbitals ie all of Them have same energy but have different orientations in space

Unit - 1.

Crystal Field Theory : →

CFT was developed by Hans Bethe (1929) and John Von Vleck (1932) and gives a much satisfactory explanation for the bonding and the properties of the complexes.
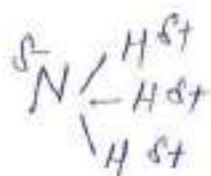
It is basically for ionic crystals hence called as crystal field theory.
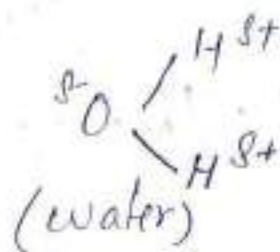
Important points of CFT : →

(1) Crystal field theory considers the metal-ligand bond is ~~reached~~ purely ionic arising purely from electrostatic interaction between the metal ion and the ligands. These interactions are similar to those between the ions in a crystal, that is why it has been named as crystal field theory (CFT). If The ligand is an anion, Then as The metal ion is cation, The forces of attraction are due to opposite charges.

If the ligand is a neutral molecule like NH_3, H_2O etc, the negative ends of their dipoles are attracted towards the central metal cation.

(II) It treats each ligand as a point of negative charge. The arrangement of the ligands around the central metal ion is such that the

(II) & repulsion b/w these negative points are minimum.

$$^{\delta-}N \Big\langle \begin{matrix} H^{\delta+} \\ \leftarrow H^{\delta+} \\ H^{\delta+} \end{matrix}$$

Ammonia (NH_3)

$$^{\delta-}O \Big\langle \begin{matrix} H^{\delta+} \\ H^{\delta+} \end{matrix}$$

(water)

(iv) The ligands surrounding the metal ion produce electrical field and this electrical field influences the energies of the orbitals of central metal ion, particularly d-orbitals.

(v) The conversion of five degenerate d-orbitals of the metal ion into different sets of orbitals having differen energies in the presence of electrical field of ligands is called crystal field splitting (CFS).
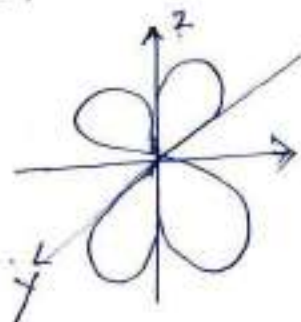
Shapes of d-orbitals :—

There are five d-orbitals. These are designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}. The shape of orbitals are. [fig; Shapes of five 3d orbitals]
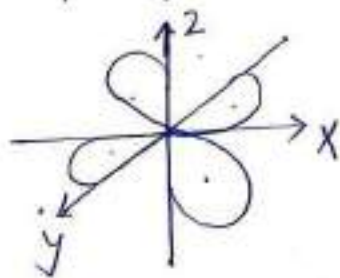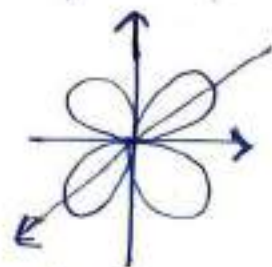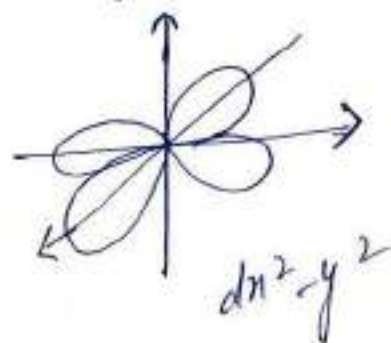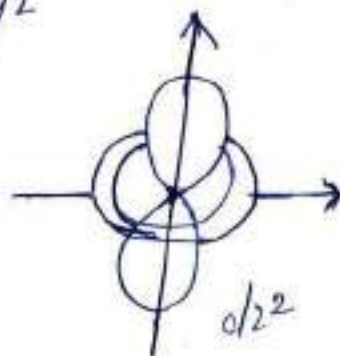

d_{xy}

d_{yz}

d_{zx}

$d_{x^2-y^2}$

d_{z^2}

Crystal field splitting in tetrahedral complexes :-)

coordination number of tetrahedral complexes is 4. tetrahedral arrangement of four ligands surrounding metal ion may be visualised by placing ligands the four of the eight corners of The cube. directions x, y and z point to the centre of The faces of the cube.
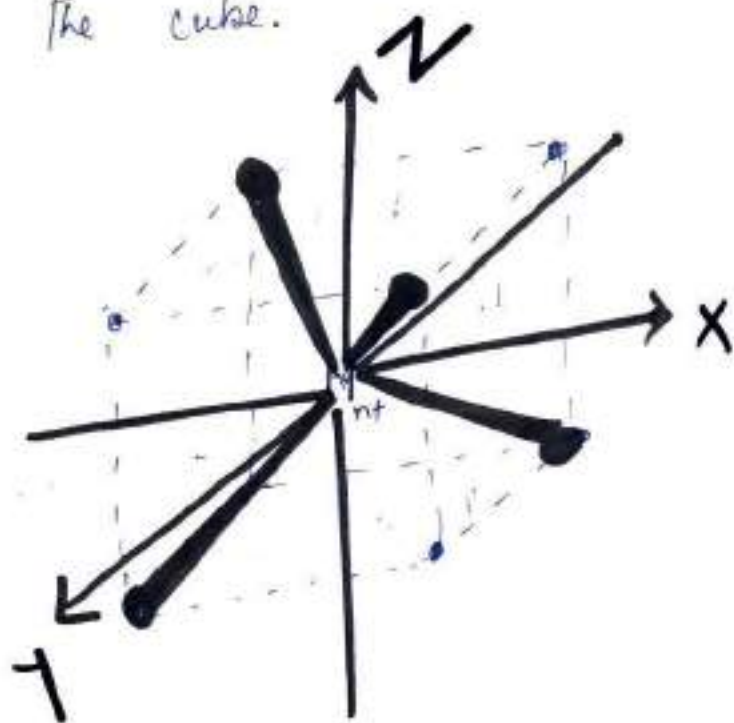

Fig 2:- Tetrahedral field of four ligands around the central metal ion.

In. tetrahedral field none of the d-orbitals point exactly towards the ligands, therefore splitting of energy will be less than that of in octahedral field.

The three d-orbitals d_{xy}, d_{yz} and d_{3n} are pointing close in direction in which the ligands are approaching while two orbitals $d_{x^2-y^2}$ and d_3^2 are lying in b/w the ligands. Therefore the energy of two orbitals will be lowered. So;- In the presence of tetrahedral field the five degenerate orbitals split up as:-

(1) $d_{x^2-y^2}$ become stable and their energies are lowered. These are designated as 'e' orbitals.

(2) The 3 orbitals d_{xy}, d_{yz} and d_{3n} become unstable and their energies are raised. These are designated as t_2 orbitals.

✱   In tetrahedral field subscript 'g' is not used. This is becoz a tetrahedral geometry has no centre of symmetry.
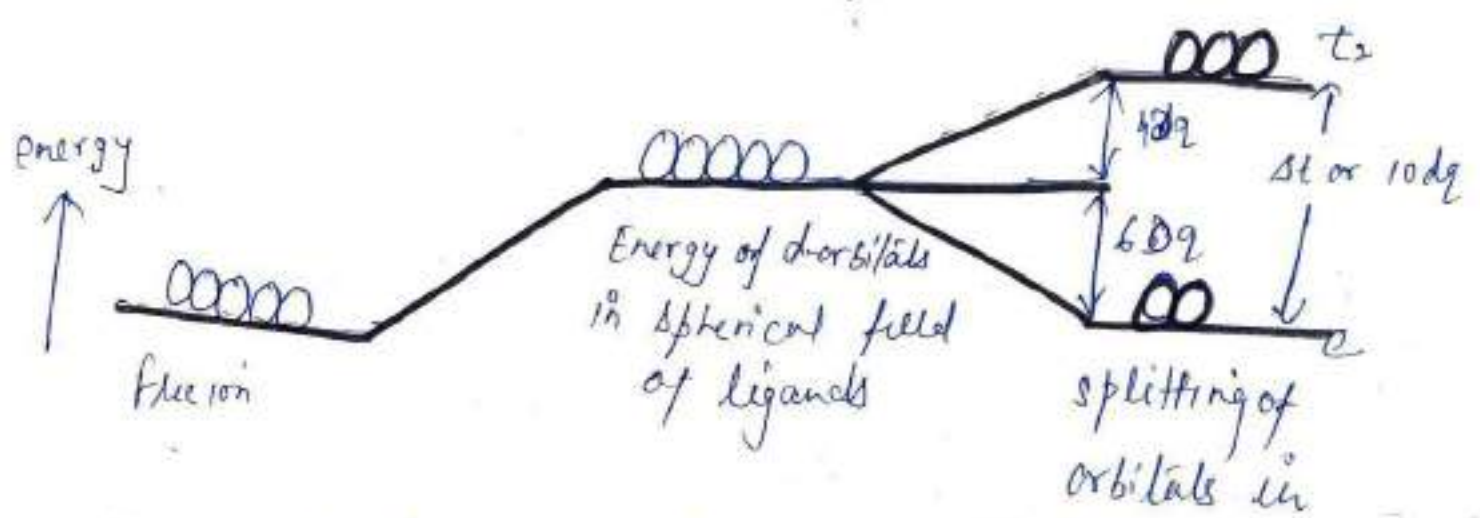

fig: crystal field splitting in tetrahedral field.

Crystal field splitting in octahedral complexes

- In an octahedral complex (C.N.=6) the metal ion is at the centre of the octahedron and the ligands are at the six corners.
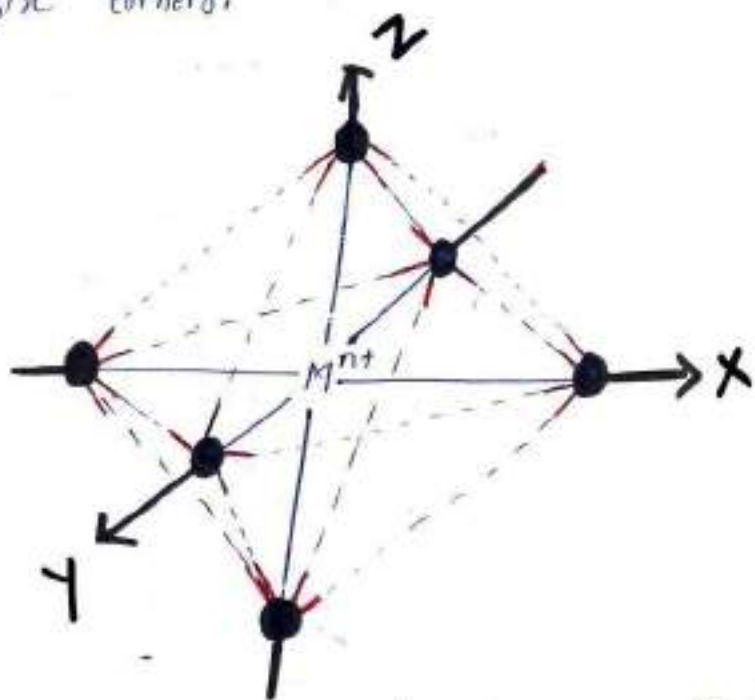

Fig:- Six ligands at the corners of an octahedran surrounding the metal ion, $\underline{M^{nt}}$.

However in the octahedral complex $\underline{MX_6}$ all the five d-orbitals will not remain of equal energy.

The Two lobes of d_{z^2} orbitals and four lobes of $d_{x^2-y^2}$ orbitals dd point directly towards the ~~axes~~ corners of The octahedron, where negative charges of ligands are concentrated.

The remaining three orbitals (d_{xy}, d_{yz}, d_{zx}) are oriented in b/w the axes.

In octahedral complexes $(\underline{d_{z^2}, d_{x^2-y^2}})$ orbitals are designated as $\underline{e_g}$ orbitals ($e-g$).

while (d_{xy}, d_{yz}, and d_{zx}) are designated as T_{2g} ~~front~~ (pronounced as t-two g) orbitals.

e_g orbitals are repelled more than the t_{2g} orbitals due to approach along the axis.

In other words the energy of d_{z^2} and $d_{x^2-y^2}$ orbitals increases much more than the energy of d_{xy}, d_{yz} and d_{zx} orbitals.

* greater the repulsion greater is increase in energy.

→ Thus in octahedral complexes, the five degener (same energy) orbitals are split upto two sets,

one set consisting of two orbitals of higher energy (e_g orbitals) and

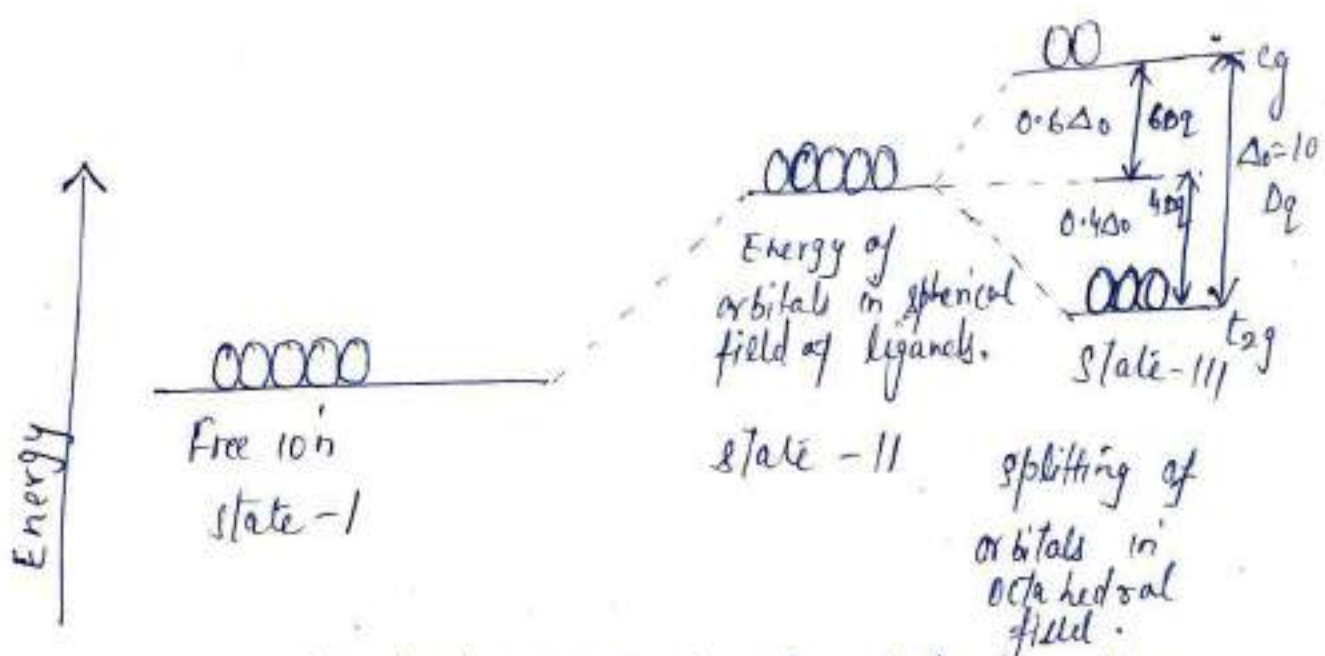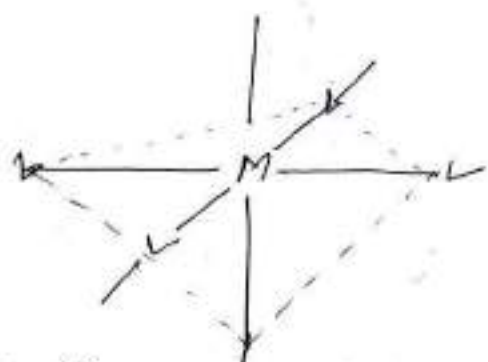other set consist of three orbitals of lower energy (t_{2g} orbitals).

Fig: Crystal field splitting in octahedral complex.

Crystal field Theory for square planar complexes.

Removal of two trans ligands from octahedron leads to the formation of square planar complex. z-axis are removed.


Magnetic properties of Transition complexes — Explanation on the basics of crystal field Theory :-

Energy level Diagram of transition metal ions :->

Ions of transition elements are formed by the loss of electrons from the atom. The configuration obtained after the loss of electrons is the electronic configuration of the ions. Whether the electron will be lost from the ns on $(n-1)$ d-orbital depends upon the stability of the electronic configuration of the atom.

e.g. consider the first transition series. As 4s orbitals are occupied first and 3d orbitals ~~are more stable~~ ~~than 3d would have the electrons of~~ later, we may except that 4s orbitals are more stable than 3d and hence the elements of first transition series would be expected to form by the loss of 3d electron

to form by the loss of $3d$ electron first. But it the $4s$ electron which loses first. This is be use after the electron has been added into the $3d$-orbital, its energy becomes lower than of $4s$ orbital and hence it becomes lower than of $4s$-orbital and hence, it becomes more stable. e.g the electronic configuration of copper (Atomic number- 29) atom is

$\underline{Cu=29}$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$
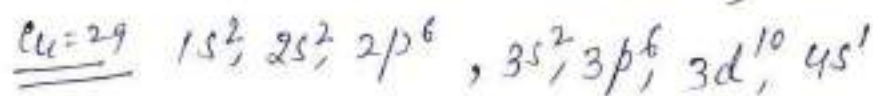
first an electron is lost form $4s$ orbital forming Cu^+ ion whose electronic configuration there fore will be- $1s^2, 2s^2, 2p^6, 3d^{10}$
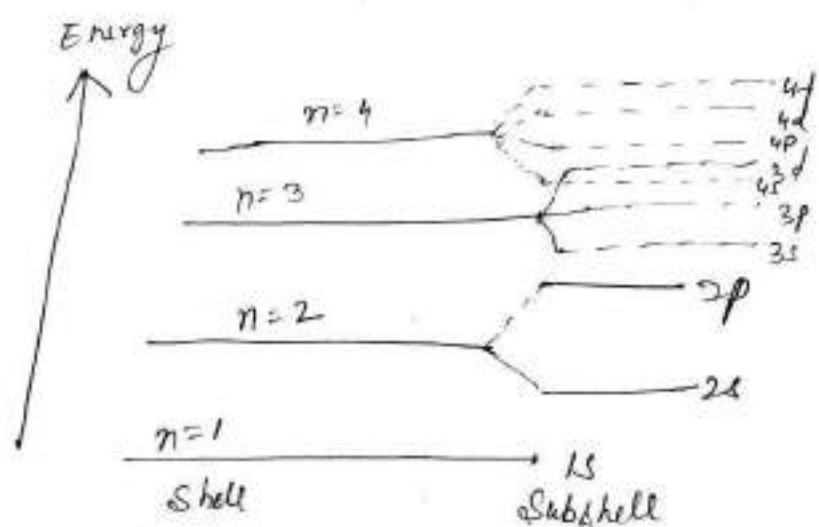

fig: Energy order of shells and subshells
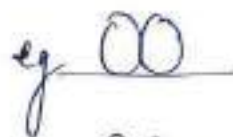
Crystal Field Stablisation Energy : →

The amount of stablisation provided by splitting of the d-orbitals into two levels is called as crystal field stablisation energy.

In octahedral field for each electron entering into t_{2g} orbital the crystal field stablisation is $-4Dq$ and for each e^- entering into e_g orbital crystal field destablisation energy is $+6Dq$.

eg

for a d^1 system (eg Ti^{3+} ion) electron will be present in any one of the three t_{2g} orbitals.

$Ti^0_{22} - 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{2\,\,2\cancel{00}}$

$Ti^{3+} - 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, \underline{3d^1}.$
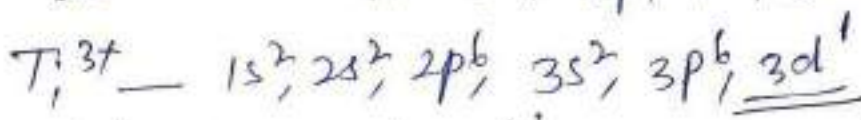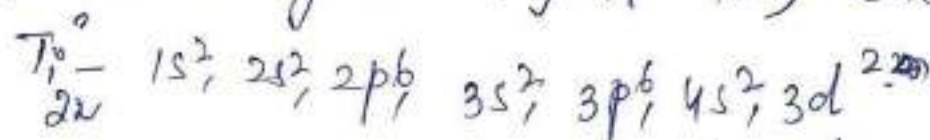
The electronic configuration may be written as t_{2g}^1.
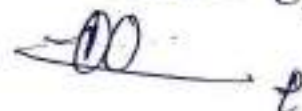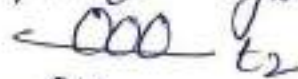
e_g ⟨ ⃝⃝ ⟩

t_{2g} ⟨ ①⃝⃝ ⟩

$CFSE = 1(-4Dq) = -4Dq.$

CFSE for tetrahedral complexes :—

In tetrahedral complexes t_2 raised by $4Dq$ whereas e orbital is lowered by $6Dq$.

eg for d^1 system

t_2 ⟨ ⃝⃝⃝ ⟩

e ⟨ ①⃝ ⟩

$CFSE = 1(-6Dq)$

$= -6Dq$

Magnetic Properties of transition complexes.
& Explanation on the basis of CFT
Magnetic Properties are of Two types.

①   Diamagnetism — The Substances which
are not attracted (repelled) by an applied
magnetic field are known as diamagnetic
substances, and The property is known as diomag-
-netism. This property is due to paired electrons.

② Paramagnetism :→ The substances which are
attracted by magnetic field are known as
paramagnetic substances. This property is known
as paramagnetism. This property is due to
the presence of unpaired electrons in their atoms
or ions due to partially filled d-orbitals.
Most of The transitions elements show paramagnetism

＊ Important :→

If we compare magnitude of crystal field splitting in octahedral and tetrahedral complexes (having same metal ion & ligands and metal ion - ligand distances) It has been observed that crystal field splitting in tetrahedral complexes is considerably less than in octahedral complexes.

$$\Delta_t = \frac{4}{9} \Delta_0$$

Reason →

① In tetrahedral complexes there are four ligands while there are six ligands in octahedral complexes. Therefore lesser Ligands produce less crystal field splitting.

② In tetrahedral field none of the orbitals is pointing directly towards the ligands and therefore splitting is less.