Limitations of Valence bond theory

(i) The Peculiar behaviour of diavalent Nickel, Palladium, Platinum and trivalent gold, i.e V.B.T. does not explain the behaviour of Complexes having d^8 Central ion. (Ni^{+2}, Pd^{+2}, ...) in forming the expected 5- Co-ordinated Complex.

(ii) It is also not clear why this this theory prefers only Square Planer Geometry of Complexes to other possible Geometries, such as tetrahedral and trigonal bipyramidal with Co-ordination No - 5.

(iii) Pauling's theory is unable to explain why Square Planar Complexes Cu^{+2} ion (d^9 system) like $[Cu(NH_3)_4]^{2+}$ are not reducing agents like inner - orbital Octahedral Complexes of Co^{+2} (d^7 System). Although in both the Cases Promotion of a non bonding d-electron to Some higher Energy level (55 kcal) is required.

(iv) Pauling's idea offered a little or no explanation to absorption Spectra of Complexes.

(v) It Can not explained Why Certain Complexes are more labile (changable) than the others.

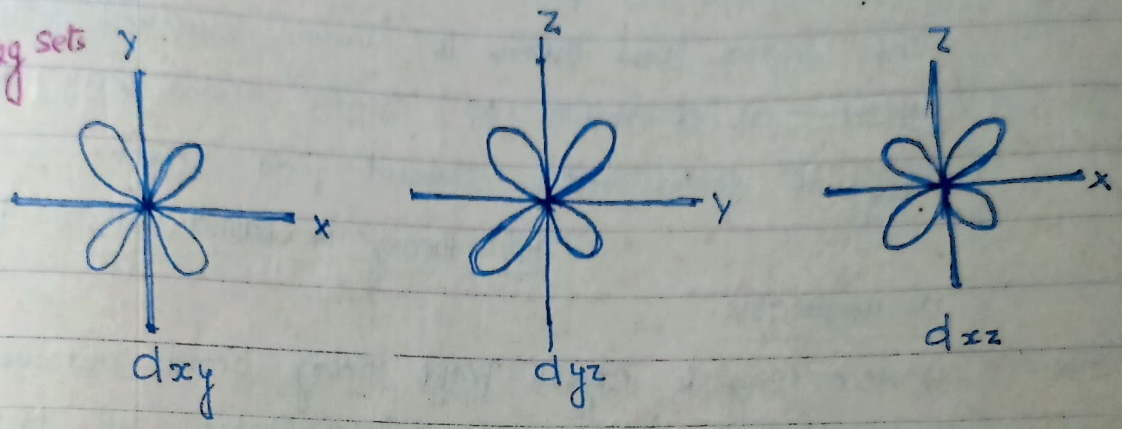
Labile Complexes are those in which one ligand Can be easily displaced by the other ligand.

(vi) It does not take into Consideration about the Splitting of d-energy levels.

Before Considering the Crystal field theory it is essential to know about the shape of the d-orbitals are five, they are shown below.

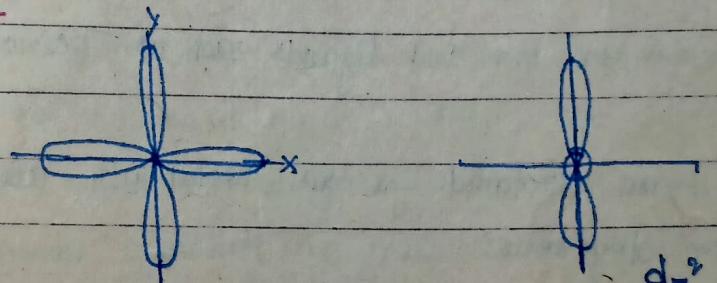
de set.

t_{2g} sets



d_{xy} d_{yz} d_{xz}

or $d\gamma$ Set / e_g sets



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

d-orbitals have been devided in two sets, These two sets are designeted by $d\epsilon$ and $d\gamma$ orbitals

The first set consist of 3 orbitals designated as d_{xy}, d_{yz} and d_{xz}.

$d\epsilon$ orbitals have maximum probability region between x,y and z axes.

The Second set, $d\gamma$ orbitals consist of two. $d_{x^2-y^2}$ and d_{z^2} orbitals., $d_{x^2-y^2}$ is oriented in xy Plane and it has maximum probability region along x and y axis. and d_{z^2} orbital is oriented along z axis and it's maximum probability region is along z axis. —

Effect on d orbital of Central metal ion by the surrounding ligands is known as C.F.T.

INTRODUCTION TO Crystal Field Theory :→

First and foremost this theory was introduced by Bethe and Van Valek and applied mainly to ionic Crystals Hence it is Called Crystal field theory. Later Orgel had great responsibility for the development of this this theory. The Crystal field theory is mainly concerned with the interaction of d-orbitals of Central metal with the surrounding ligands that produce Crystal field effect.

This theory is based upon following assumptions.

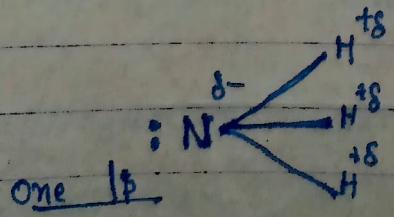
(1) According to crystal field theory bond between metal and ligand is purely electrostatic. i.e Metal - ligand bond is 100% ionic.

(2) The metal ion and ligands acts as point charge.

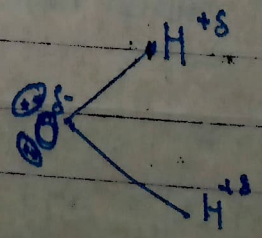
(3) In an isolated gaseous metal ion all the d-orbitals are degenerate.

(4) A Complex is considered to be a combination of Central metal ion surrounded by various ligands.

(5) In this theory - Covalent character of bond between metal and ligand is not taken into account.



One lp



Two lp.