Valence Bond Theory (VBT)

- To explain the nature of bonding in transition metal Complexes,three different theories are mostly used .

1. Valence Bond Theory (VBT)
2. Crystal Field Theory (CFT)
3. Molecular Orbital Theory (MOT)

❖ Valence Bond Theory (VBT) :

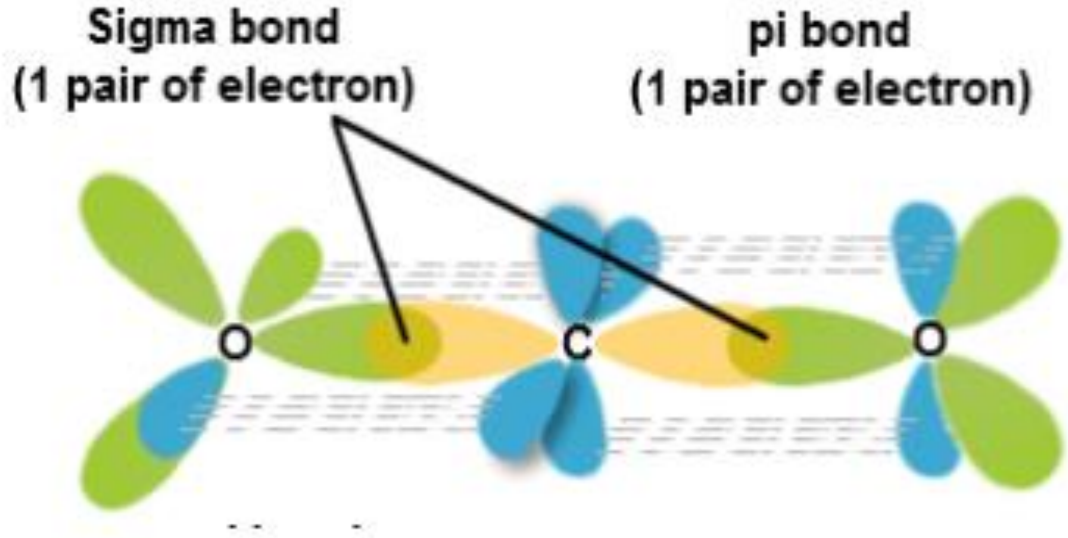
Electrons in a molecule occupy atomic orbitals rather than molecular orbitals. The atomic orbitals overlap on the bond formation and the larger the overlap the stronger the bond.

Therefore , it is a theory which describes chemical bonding. The unpaired electrons are shared and a hybrid orbital is formed in this theory.

❖ Postulates of Valence Bond Theory :

- The nature of bonding between the metals and ligands is purely covalent and arises from the orbital overlap between them.
- The central metal atom or ion makes available a no. of empty orbitals equal to its Coordination no.
- The ligands have atleast one σ-orbital containing a lone pair of electrons.

- Vacant hybrid orbitals of the metal atom or ion overlap with the filled σ-orbitals of the ligands to form ligand(L) → metal(M) σ-bond.
- The non-bonding electrons of the metal atom or ion are then arranged according to Hund’s rule in the metal orbitals which do not participate to form hybrid orbitals.
- Sigma bonds and pi bonds differ in the pattern that the atomic orbitals overlap in, i.e. pi bonds are formed from sidewise overlapping whereas the overlapping along the axis containing the nuclei of the two atoms leads to the formation of sigma bonds.



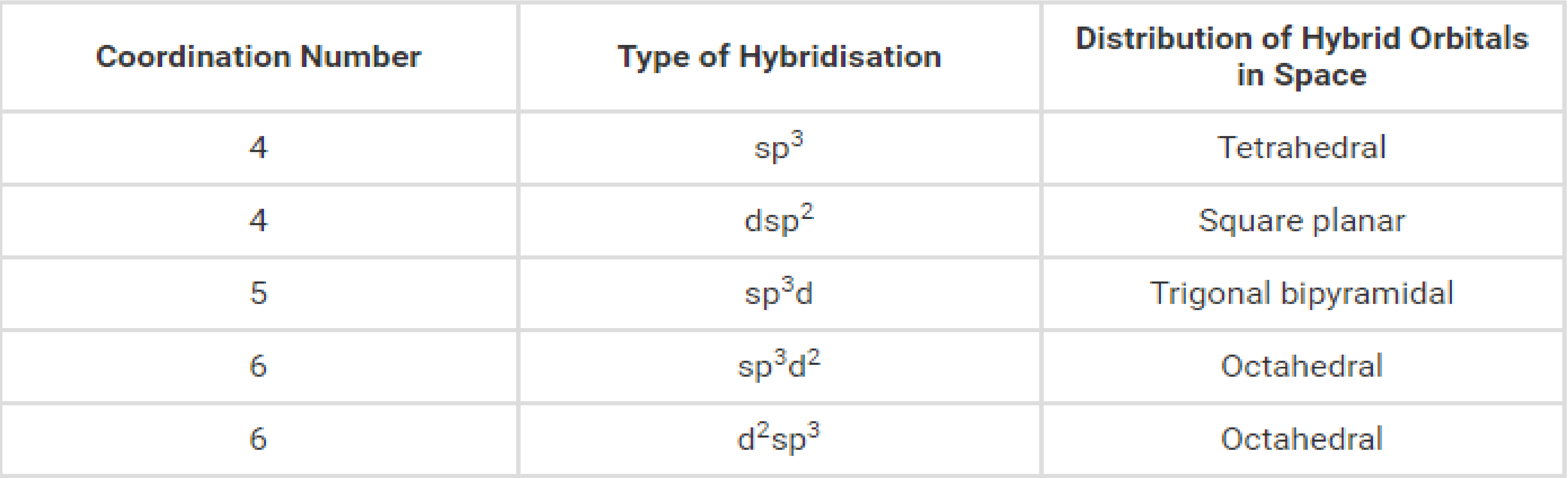
Formation of Sigma and Pi Bonds – Valence Bond Theory (VBT)

It can be noted that sigma bonds involve the head-to-head overlapping of atomic orbitals whereas pi bonds involve parallel overlapping.

Number of Orbitals and Types of Hybridization

- According to VBT theory the metal atom or ion under the influence of ligands can use its (n-1)d, ns, np, or ns, np, nd orbitals for hybridization to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on.

- These hybrid orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.



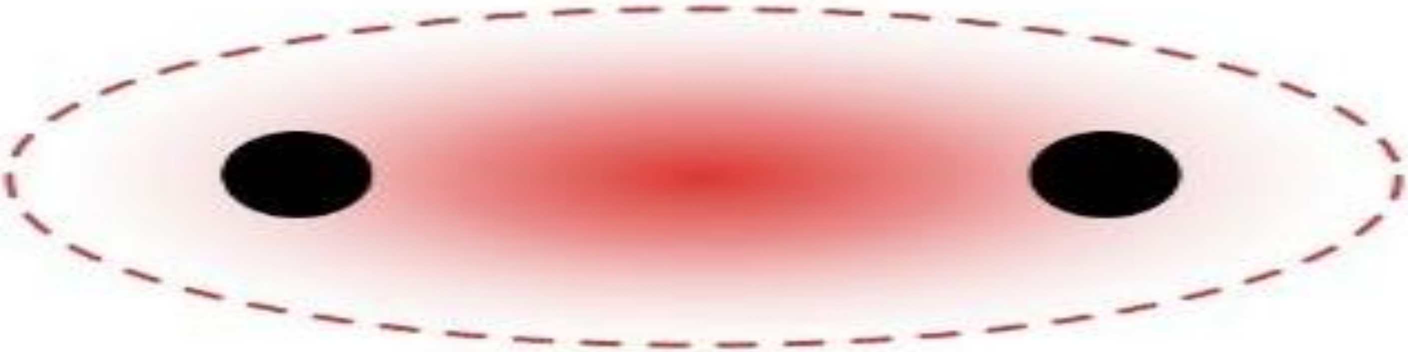
Coordination Number	Type of Hybridisation	Distribution of Hybrid Orbitals in Space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

❖ Applications of valence bond theory

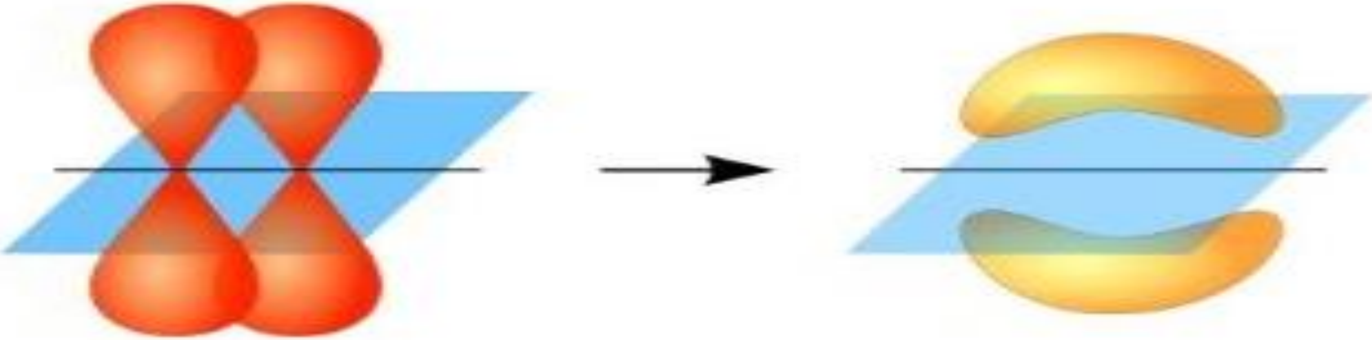
An important aspect of the Valence Bond theory is the condition of maximum overlap, which leads to the formation of the strongest possible bonds. This theory is used to explain the covalent bond formation in many molecules.

For example,

In an HF molecule the covalent bond is formed by the overlap of the 1*s* orbital of H and the 2*pz* orbital of F, each containing an unpaired electron. Mutual sharing of electrons between H and F results in a covalent bond in HF.



σ bond between two atoms: localization of electron density



Two p-orbitals forming a π-bond.

❖Limitations of the valence bond Theories

- Oh,Td and square planar complexes of d^1,d^2,d^3,d^9 ions have the same no. of unpaired electrons and hence $\mu_{exp.}$value can not predict the proper stereochemistry.
- VBT predicts only symmetrical stereo chemistry but can not explain the distorted octahedral stereochemistry of d^9 ($Cu^{2+)}$ ion.
- Ni^{2+} forms Td and Square planar complexes but Pd^{2+} and Pt^{2+} forms only square planar complex although both having same electronic configuration.

- Metal ions have been compared in the free and complex state but ligands have been ignored.

- VBT fails to explain the color and characteristics of absorption spectra of a complex.

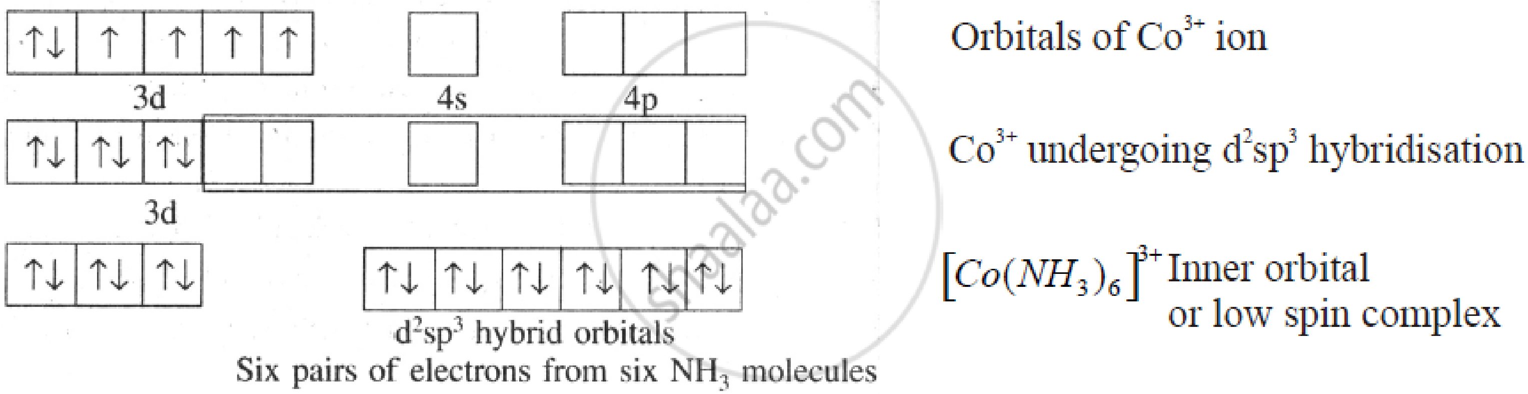
- VBT can not explain why magnetic property vary with temperature.

- VBT also fails to explains reaction rate and mechanism of reactions.

Explain the Geometry , Hybridisation,Nature of Magnetism and Magnetic moment of central metal ion of $[Co(NH_3)_6]^{3+}$

Octahedral complex, $[Co(NH_3)_6]^{3+}$. In this complex ion, the oxidation state of cobalt is +3.

It has the electronic configuration as $3d^6$. This complex involves the d^2sp^3 hybridisation.



The six pairs of electrons, one from each NH3 molecule, occupy the six hybrid orbitals. It proves that complex has octahedral geometry. An absence of unpaired electron makes this complex diamagnetic in nature.

- Explain the Geometry , Hybridization , Nature of Magnetism and Magnetic moment of central metal ion of [CoF6]3- , [Fe(CN)6]3- , [Fe(H2O)6]3+ , [MnBr4]2- , [NiCl4]2- , [PtCl4]2- , [Ni(CN)4]2- , [Ni(NH3)6]2+ , [Cu(NH3)4]2+ , [Mn(CN)6]3-