

**B.Sc. (Honours) Part-II
Paper-IIIB**

Topic: Valence Bond Theory

UG

Subject-Chemistry

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Valence bond method of explaining structures of co-ordination compounds

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Valence bond theory (VB Theory)

Valence bond theory, primarily the work of Linus Pauling regarded bonding as characterized by the overlap of atomic or hybrid orbitals of individual atoms. The postulates of valence bond theory:

- 1) The central metal atom/ion makes available a number of vacant orbitals equal to its coordination number.
- 2) These vacant orbitals form covalent bonds with the ligand orbitals.
- 3) A covalent bond is formed by the overlap of a vacant metal orbital and filled ligand orbitals. This complete overlap leads to the formation of a metal ligand, σ (sigma) bond.
- 4) A strong covalent bond is formed only when the orbitals overlap to the maximum extent. This maximum overlapping is possible only when the metal vacant orbitals undergo a process called 'hybridisation'. A hybridised orbital has a better directional characteristics than an unhybridised one.

The following table gives the coordination number, orbital hybridisation and spatial geometry of the more important geometrics

Coordination number	Types of hybridization	Geometry
2	sp	linear
4	sp ³	tetrahedral
4	dsp ²	square planar
6	d ² sp ³	octahedral
6	sp ³ d ²	octahedral

Magnetic moment

A species having at least one unpaired electron, is said to be paramagnetic.

It is attracted by an external field. The paramagnetic moment is given by the following spin-only formula.

$$\mu_s = \sqrt{n(n+2)} \text{ BM}$$

μ_s = spin-only magnetic moment n =

number of unpaired electrons

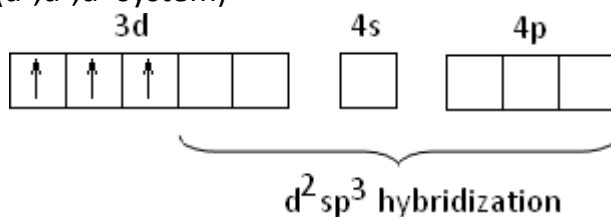
BM = Bohr magneton, the unit which expresses the magnetic moment. When the species does not contain any unpaired electron, it is diamagnetic.

Applications of valence bond theory

(i) If the ligand is very weak like F^- , H_2 , Cl^- etc. It does not force the pairing of 3d electrons and hence outer orbital octahedral complexes are formed by sp^3d^2 hybridization.

(ii) But if the ligand is strong like CN^- , $(COO)_2^{2-}$, ethylenediammine (en) etc, it forces the pairing of 3d electrons and hence inner orbital octahedral complexes are formed by d^2sp^3 hybridization

(1) Atom or ion of d-block element contain 1,2 or 3 electrons in d-orbit
(d^1, d^2, d^3 system)



Ti^{3+}, V^{3+}, Cr^{3+}

Since two 3d orbitals are available for d^2sp^3 hybridization. Hence, these systems may accept six lone pairs from six ligands and they form octahedral complexes $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$

Since due to complexation the unpaired electrons in (n-1) d-orbitals are not disturbed, the magnetic moment of free metal ions remains intact in octahedral complexes

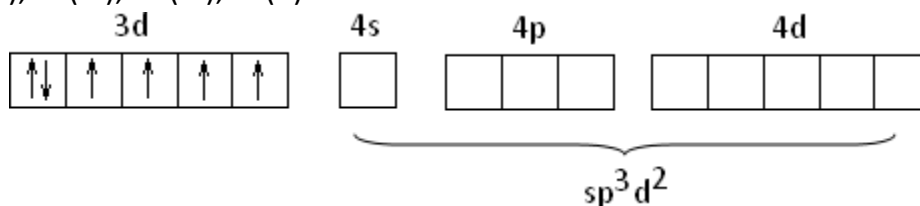
More possibility

In addition to d^2sp^3 hybridisation metal ions may undergo sp^3 or dsp^2 hybridization forming tetrahedral or square planar complexes respectively

Since in sp^3 or dsp^2 , the d-electrons are not disturbed, the magnetic moment of free metal ion remains intact in tetrahedral or square planar complex

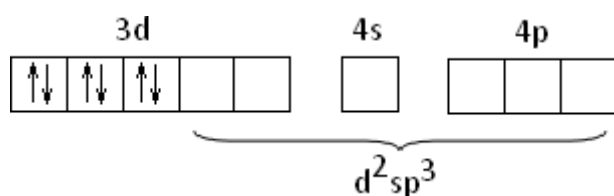
- (2) Atom or ion of d-block element contain 4,5 or 6 electrons in d-orbit (d⁴,d⁵,d⁶ system)

Mn(III), Fe(III), Co(III), Fe(II)



In above type ions, in ground state two 3-d orbitals are not vacant to participate thus 3d electrons are not disturbed and hence magnetic moment of free metal ions remains intact in outer orbital octahedral complex. Energy gap between 4s and 4d is large, the sp^3d^2 hybridisation is not perfect hybridization and hence outer orbital complexes are comparatively less stable. Moreover, 4d orbitals are more extended in space than 3d orbitals and hence sp^3d^2 hybrid orbitals are also more extended in space than d^2sp^3 hybrids. So bond length in outer orbital octahedral complexes is comparatively longer and so they are less stable. Such complex is possible if ligand is weak

Another possibility



For strong ligand like CN^- maximizes pairing of 3d electrons, two 3d orbitals may be made vacant for d^2sp^3 hybridisation forming octahedral complex. As two d-orbitals of inner shell are involved in hybridisation, complex are said to be inner orbital octahedral complex.

The energy of the orbitals involved in hybridisation is in continuation. The d^2sp^3 hybridisation is perfect and at the same time due to less extension of 3d orbitals in space, bond length is also short. So, inner orbital octahedral complexes are more stable than outer orbital octahedral complex. As the pairing of 3d electrons is forced in d^2sp^3 hybridisation in these systems, hence the magnetic moment of the free metal ion undergoes change on complexation.

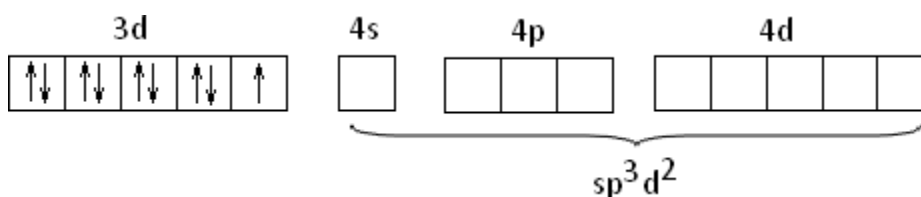
One more possibility

In addition to inner orbital octahedral and outer octahedral complexes ions may also form tetrahedral and square planar complex by sp^3 and dsp^2 hybridization

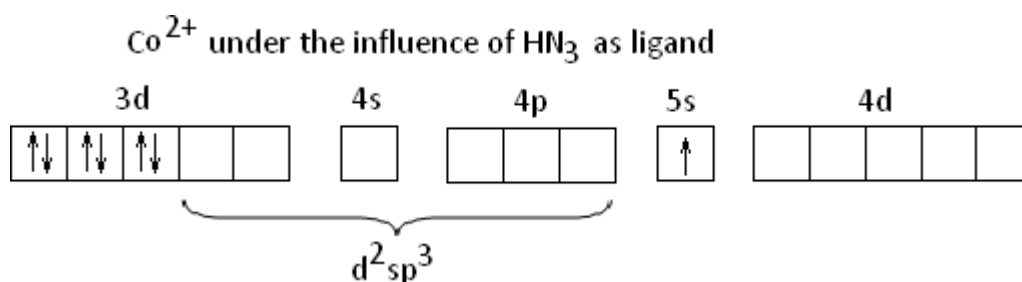
(3) Atom or ion of d-block element contain 7,8 or 9 electrons in d-orbit

(d^7, d^8, d^9 system)

Co(II), Ni(II), Cu(II)



Two vacant 3d orbitals cannot be made available for d^2sp^3 hybridization even after maximum pairing. So, there is no chance of the formation of inner orbital octahedral complex



In d^7 , with promotion of one electron to 5s or 4d, it becomes loosely bonded to the nucleus and hence, it may easily be removed and so, Co(II) will easily be oxidized to Co(III)

In d^8 , after maximum pairing of 3d electrons, one 3d orbital may be vacated for dsp^2 hybridization and hence d^7 , d^8 systems favour the formation of square planar complexes with changed magnetic nature

In d^9 , one d-orbital is not made available for dsp^2 hybridization. So there is no question of the formation of square planar complex by d^9

More possibility (weak ligand)

However they may undergo sp^3d^2 hybridization forming outer orbital octahedral complex with same magnetic properties as in free metal.

One more possibility

Also sp^3 hybridizations can easily occur favouring the formation of tetrahedral complexes with unchanged magnetic character

(4) In d^{10} Zn(II), Cu(I)

In d^{10} , 3d orbitals are completely filled up, so, it may form tetrahedral complex by sp^3 hybridization or outer orbital octahedral complexes by sp^3d^2 hybridization Magnetic properties of the free metal ion remains unchanged in tetrahedral or outer orbital octahedral complexes

Defects of Valence bond theory

While the VB theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:

- (i)** It involves a number of assumptions.
- (ii)** It does not give quantitative interpretation of magnetic data.
- (iii)** It does not explain the colour exhibited by coordination compounds.
- (iv)** It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- (v)** It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
- (vi)** It does not distinguish between weak and strong ligands.