

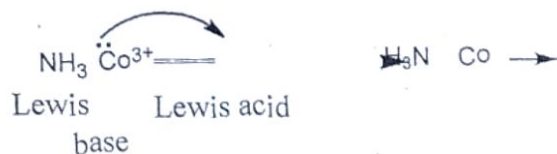
Valence Bond Theory and Crystal Field Theory

1.1 Valence bond theory

According to this theory, coordinate bond is formed between Lewis bases, which are called ligands, and the Lewis acids, which are nothing but the metal ions. Ligands are called Lewis **bases** because they **donate** lone pair of electrons and metal ions are called Lewis **acids** because they **accept** lone pair of electrons.

E.g. $[\text{Co}(\text{NH}_3)_6]^{3+}$

In this complex, the metal ion is Co^{3+} and NH_3 is the ligand.

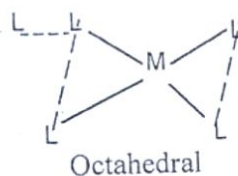
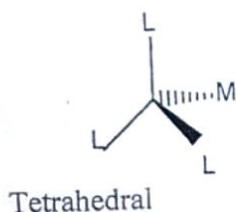


The metal s, p, d and f orbitals hybridize and the hybridized orbitals are used for bond formation. The shape of the complex formed depends up on the nature of hybridization and also the magnetic properties.

Hybridization and shape

The different types of hybridizations and the corresponding shapes are given below:

Hybridization	Shape
sp^3	Tetrahedral
dsp^2	Square planar
sp^3d^2 or d^2sp^3	octahedral



Correlation between the observed magnetic property and structure

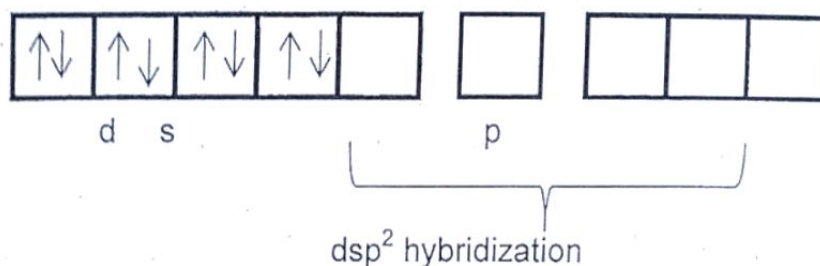
$\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})$ are usually four coordinate, square planar and diamagnetic. How to explain this with the help of valence bond theory?

If a compound is paramagnetic, it will have unpaired electrons and if the compound is diamagnetic, all the electrons will be paired.

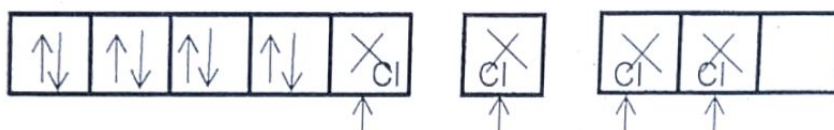
Example 1:

Let us consider the complex, $[\text{PtCl}_4]^{2-}$. This complex is square planar and diamagnetic. The oxidation state of Pt in this complex is +2. Outermost

electronic configuration of Pt atom is $5d^8 6s^2$
 Electronic configuration of Pt^{2+} ion is $5d^8$; there are five .d. orbitals and the 8 electrons are arranged as follows:



Each Cl^- will donate a pair of electrons to the vacant orbitals as shown by 'X' mark.



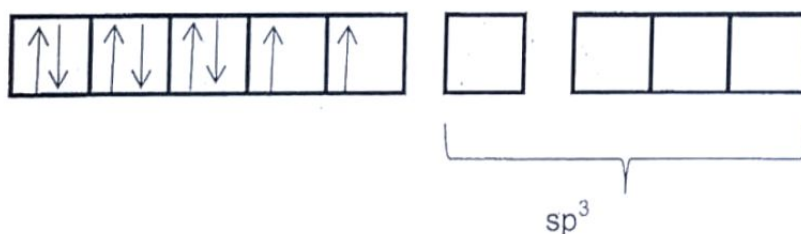
As seen above, all the electrons are paired and hence, the complex is diamagnetic.

Example 2: $[NiCl_4]^{2-}$

This complex is paramagnetic. That is, it has got unpaired electrons. Valence bond theory can explain this as follows:

Outermost electronic configuration of Ni atom is $3d^8 4s^2$

Outermost electronic configuration of Ni^{2+} is $3d^8$ and these are arranged in the five .d. orbitals as follows:



Thus there are two unpaired electrons in the .d. orbitals. Hence, the complex will be paramagnetic. The hybridization is sp^3 as shown. Therefore, the shape of the complex will be tetrahedral.

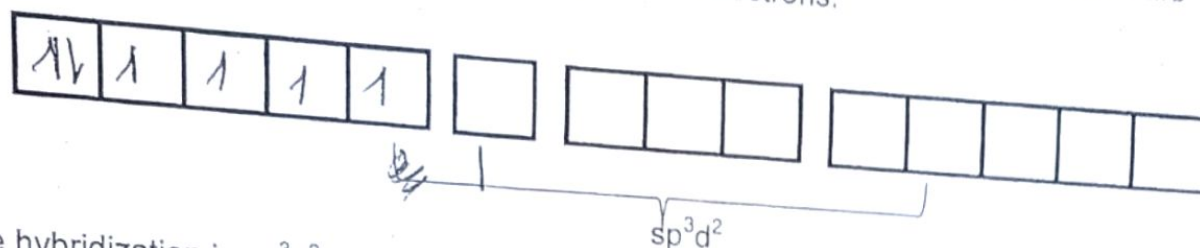
In these examples, the hybridization and shape are decided by the magnetic property of the complex. Thus, it is called **magnetic criterion of bond type**.

Example 3: $[CoF_6]^{3-}$

This complex is paramagnetic and this is explained by VBT as follows:

Outermost electronic configuration of Co is: $3d^7 4s^2$

Cobalt is in the +3 state in this complex. Therefore, the outermost electronic configuration of Co^{3+} is $3d^6$. Since the complex is paramagnetic, the electrons are arranged as follows and there are four unpaired electrons.

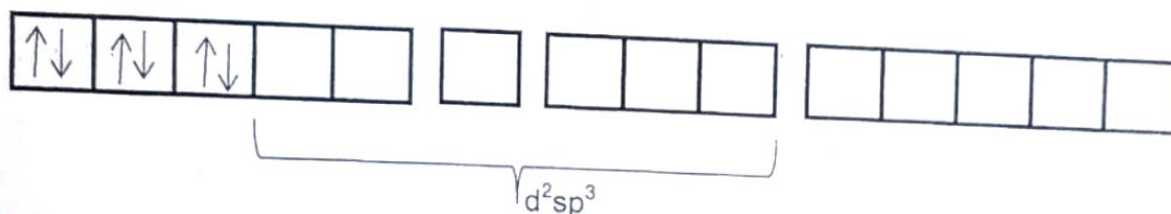


The hybridization is sp^3d^2 and the shape is octahedral.

Example 4: $[\text{Co}(\text{NH}_3)_6]^{3+}$

This complex is diamagnetic and explained by VBT as follows:
Outermost electronic configuration of Co is: $3d^7 4s^2$

Cobalt is in the +3 state in this complex. Therefore, the outermost electronic configuration of Co^{3+} is $3d^6$. Since the complex is diamagnetic, the electrons are arranged as follows:



There are no unpaired electrons and hence, the complex is diamagnetic. The hybridization is d^2sp^3 and the shape is octahedral.

2. Crystal Field Theory

Postulates

In the crystal field theory following assumptions are made-

1. Ligands are treated as point charges.
2. The ~~interaction~~ interaction between metal orbitals and ligand orbitals *is purely electrostatic*.
3. The d orbitals on the metal all have the same energy (i.e. they are degenerate) in the free atom.
4. However, when a complex is formed the ligands destroys the degeneracy of these orbitals i.e. the orbitals now have different energies.

Shapes of d-orbitals

The shapes of the five d-orbitals are given in Figure 2.2.1.

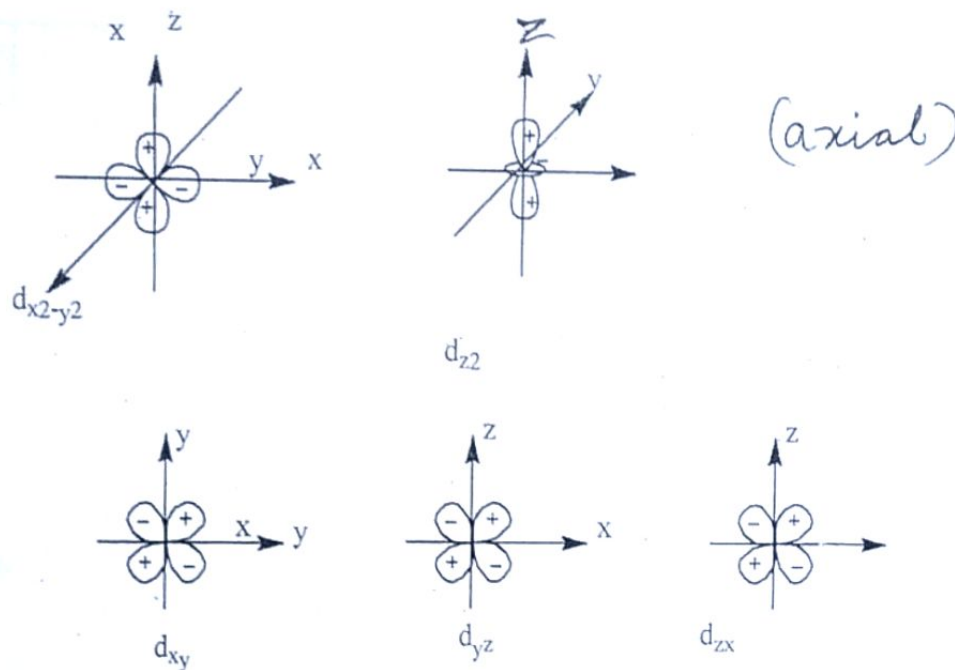
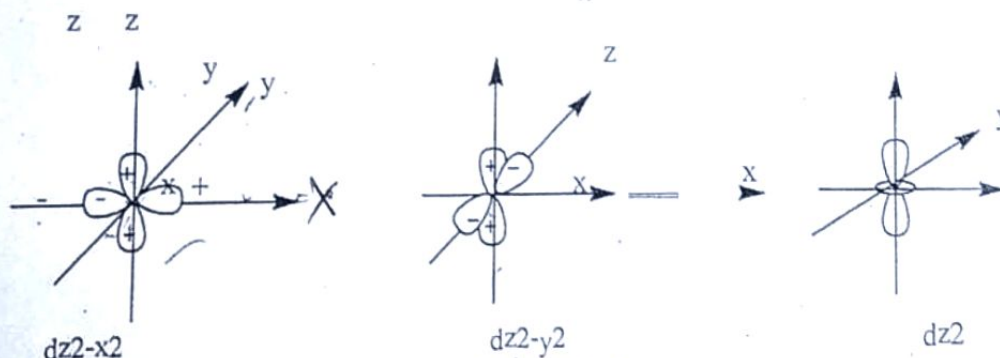


Fig 1 Shapes of d-orbitals

Shape of d_{z^2} orbital is different. Why?

Actually, d_{z^2} orbital is a linear combination of two orbitals, namely, $d_{z^2-x^2}$ and $d_{z^2-y^2}$. This is shown in Figure 2.2.1.1.



Degeneracy of d-orbitals

All the five d-orbitals are degenerate (same energy) in the isolated, gaseous metal ion. When they are surrounded by spherically symmetric field of negative charges, the orbitals are raised in energy because of the repulsion between like charges but still they are degenerate. However, in the real case, the number of ligands surrounding the metal ion may be eight or so. Now, the field is not spherical and has lower symmetry. Therefore, the five d-orbitals are no longer degenerate and are

Crystal field effects

When the metal ion is surrounded by the ligands, there is repulsion between the ligand electrons and metal d-electrons. This is called crystal field effect. This can be considered for different symmetries, viz., octahedral symmetry, tetrahedral symmetry, tetragonal symmetry and other symmetries.

Octahedral symmetry

In this case six ligands coordinate to the metal ion and form an octahedral complex. The six ligands are approaching along the coordinate axes and hence the five d-orbitals are raised in energy because of the electron-electron repulsion. However, all the d-orbitals are not raised in energy to the same extent. Those orbitals whose lobes point along the axes are raised in energy very much, while the other d-orbitals are raised in energy to a lesser extent. The reason is that the ligands considered being spheres approach along the axes. Thus, the five d-orbitals are split into two groups: the $d_{x^2-y^2}$ and d_{z^2} orbitals form one set, while the other three orbitals, d_{xy} , d_{yz} and d_{zx} form another group. The former are known as e_g (doubly degenerate) orbitals and the latter are known as t_{2g} (triply degenerate) orbitals. These are shown in Figure 2.3.1.1

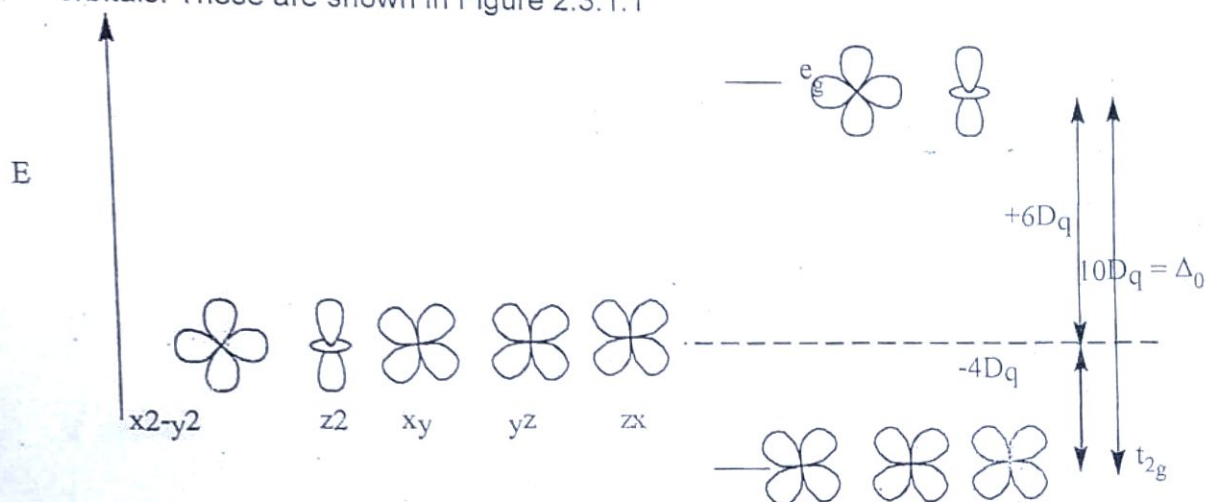
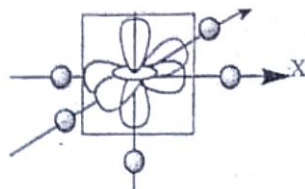


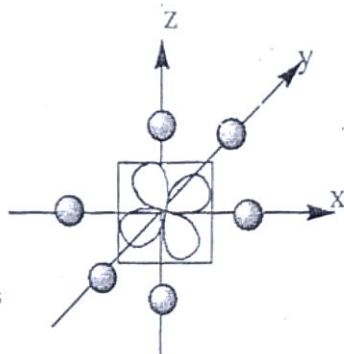
Fig 2.3.1.1 Splitting of d-orbitals

During splitting, the centre of gravity rule is obeyed. That is, 2 orbitals ($+6Dq$) + 3 orbitals ($-4Dq$) = 0. In Δ_0 , subscript 'o' stands for octahedral.

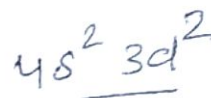
The approach of ligands with respect to $d_{x^2-y^2}$ and d_{z^2} orbitals is shown in Figure 2.3.1.2 and the approach with respect to d_{xy} orbital is shown Figure 2.3.1.3.



Ligands approaching the e_g orbitals

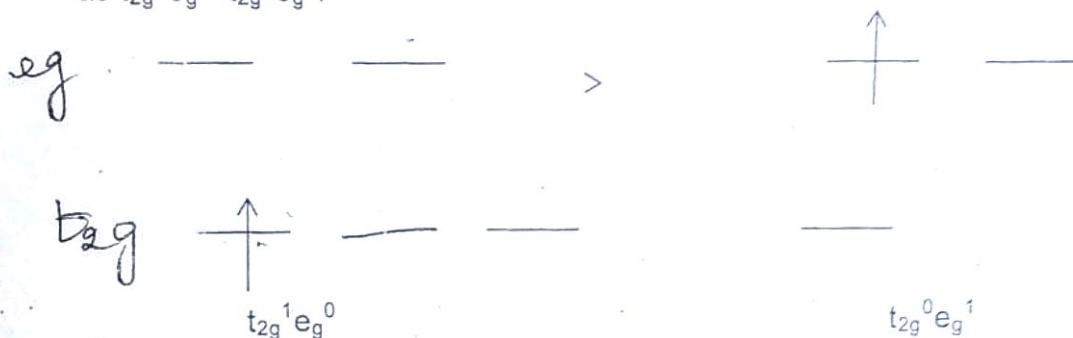


Ligands approaching the t_{2g} orbitals



Measurement of Δ_0 : $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

This aqueous solution of this complex gives a purple color. This is explained as follows. Titanium exists as Ti^{3+} in the complex and has a single d electron. This single electron in the complex occupies the lowest energy level available, namely, one of the degenerate t_{2g} orbitals. This electron absorbs energy and is excited to the e_g level. This absorbed energy appears as pink color. This transition is denoted as $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$.



Crystal field stabilization energy (CFSE)

In the above example, the single d electron in the complex is stabilized compared to the free ion or spherical field. The reason is that in the free ion or spherical field, the five d orbitals were degenerate and were having higher energy, while in the octahedral complex, the d orbitals split into two groups, viz., t_{2g} and e_g . The t_{2g} orbitals have lower energy of $-0.4 \Delta_0$ compared to the barycenter of the d-orbitals. This is called CFSE. This is schematically shown in Figure 2.3.3.1.

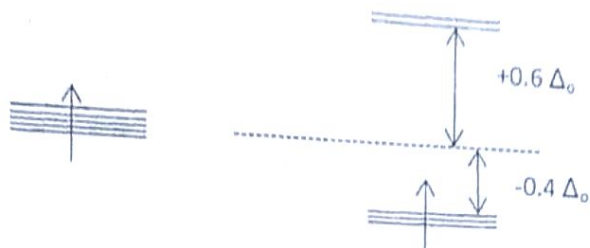
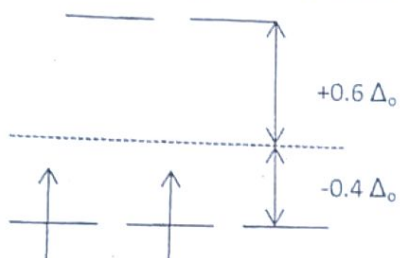


Fig 2.3.3.1 CFSE

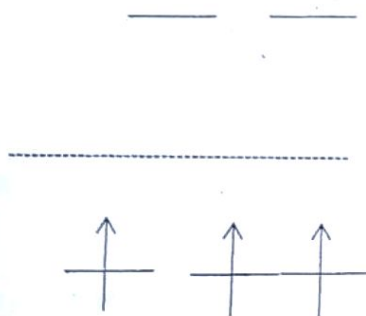
2.3.4. Splitting in d^2 and d^3 metal ions

Hund's rule is obeyed and hence the two electrons in d^2 remain unpaired in the two of the three t_{2g} orbitals. Similarly, in the d^3 case, the three electrons will occupy the three degenerate t_{2g} orbitals. Then the CFSE is calculated as follows: d^2 system:



$$\begin{aligned} \text{CFSE} &= 2(-0.4 \Delta_o) + 0(+0.6 \Delta_o) \\ &= -0.8 \Delta_o \end{aligned}$$

d^3 system:



$$\begin{aligned} \text{CFSE} &= 3(-0.4 \Delta_o) + 0(+0.6 \Delta_o) \\ &= -1.2 \Delta_o \end{aligned}$$

2.3.4.1 Strong and weak field case

d^4 system:

Here, there are two possibilities, viz., the 4th electron can go to the e_g orbital or it can pair with the electrons in the t_{2g} orbitals. It depends up on the magnitude of the splitting of the d-orbitals.

Case 1: $P < \Delta_o$

If the splitting of the d-orbitals is more, then Δ_o will be more and the e_g orbitals will have very high energy. Now, the 4th electron cannot go to the e_g orbitals but will remain paired in the t_{2g} orbitals. The pairing energy (P), that is, the energy required to overcome the repulsion between electrons during pairing, P, is less than Δ_o . ($P < \Delta_o$). This is called a **strong field case**.

Case 2: $P > \Delta_o$

Here the splitting will be less and the pairing energy will be greater than the energy of the e_g orbitals. Therefore, the electrons will go to the e_g orbitals rather than going to the t_{2g} orbitals. This is called a **weak field case**.

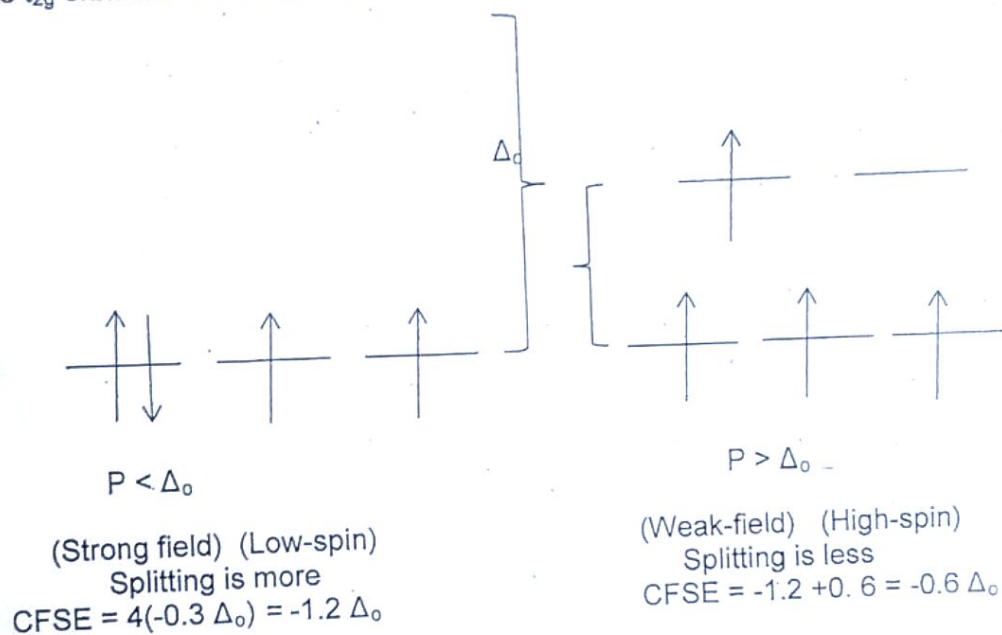


Table 2.3.4.1.1 CFSE of d^n systems

Weak field			Strong field		
Configuration	CFSE Δ_o	No of unpaired electrons	Configuration	CFSE Δ_o	No of unpaired electrons
$t_{2g}^1 e_g^0$	-0.4	1	$t_{2g}^1 e_g^0$	-0.4	1
$t_{2g}^2 e_g^0$	-0.8	2	$t_{2g}^2 e_g^0$	-0.8	2
$t_{2g}^3 e_g^0$	-1.2	3	$t_{2g}^3 e_g^0$	-1.2	3
$t_{2g}^3 e_g^1$	+0.6	4	$t_{2g}^4 e_g^0$	-1.6	2
$t_{2g}^3 e_g^2$	0	5	$t_{2g}^5 e_g^0$	-2.0	1
$t_{2g}^4 e_g^2$	-0.4	4	$t_{2g}^6 e_g^0$	-2.4	0
$t_{2g}^5 e_g^2$	-0.8	3	$t_{2g}^6 e_g^1$	-1.2	1
$t_{2g}^6 e_g^2$	-1.2	2	$t_{2g}^6 e_g^2$	-1.2	2
$t_{2g}^6 e_g^3$	-0.6	1	$t_{2g}^6 e_g^3$	-0.6	1
$t_{2g}^6 e_g^4$	0	0	$t_{2g}^6 e_g^4$	0	0

$$\Delta_o = 10Dq; -0.4\Delta_o \text{ or } -4Dq$$

Electron pairing energy (P)

Let us consider d^6 low-spin configuration, $t_{2g}^6 e_g^0$

— —

$$CFSE = 24Dq - 3P$$

$$- (6 \times 4) = 24Dq$$



Let us consider d^6 high-spin configuration, $t_{2g}^4 e_g^2$



$$CFSE = 16Dq - P$$



Composition of electron pairing energy

This is composed of two terms:

1. Inherent coulombic repulsion

This is the repulsion when two electrons occupy the same orbital. This repulsion decreases when the atomic size increases within a group when we go from top to bottom. The orbitals become bigger and diffuse so that the distance between the two electrons in the orbitals decreases and hence the repulsion decreases. Thus 5d orbitals are more diffuse than the 3d orbitals and hence electrons can be easily accommodated in the 5d orbitals. This repulsion must be overcome when two electrons are forced to occupy the same orbital.

1. Loss of exchange energy

This occurs when electrons having parallel spins are forced to have antiparallel spins. The exchange energy is proportional to the number of pairs of electrons (set of two electrons) having parallel spins. Thus the greatest loss of exchange energy occurs when the d^5 configuration (Mn^{2+} and Fe^{3+}) is forced to pair. Therefore, d^5 complexes are usually high spin complexes.