METAL LIGAND BONDING

VALENCE BOND THEORY

Valence bond theory was first applied to complexes by pauling. This theory explains satisfactorily the structure and magnetic properties of a large number of complexes. Some important features of valence bond theory are.

(1) The central metal ion must make available, a number of empty orbitals for accomodating the electrons donated by the ligands. The number of empty orbitals is equal to the co-ordination number of the metal ion for the particular complex.

(2) The atomic orbitals of central metal ion undergoes hybridisation to form new identical orbitals. These hybrid orbitals overlap with the ligand orbitals to form strong bonds.

(3) The d-orbitals involved in hybridisation may be either (n-1)d orbitals (Inner orbital complex) & outer nd orbitals (outer orbital complexes).

(4) The hybridisation of orbitals on the metal decides the geometry of the complex.

(5) Later, a π bond is formed by the donation of electrons from filled d-orbitals of the metal to the empty d & p orbitals of the ligand atom.

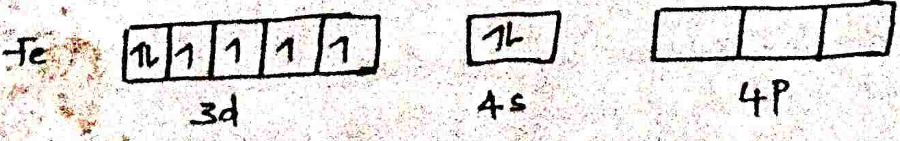
(6) If the complex contains unpaired electrons it is paramagnetic. If it does not contain unpaired electrons, it becomes diamagnetic.

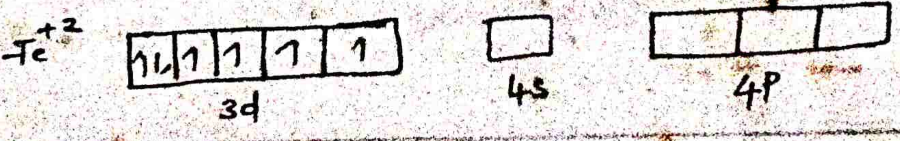
(7) under the influence of strong ligands, the electrons can be forced to pair up against the Hund's rule of maximum multiplicity

Let us consider the formation of a complex basing on Valence Bond method.

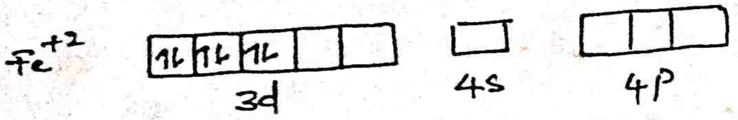
Eg: Ferrocyanide ion $\{[Fe(CN)_6]^{-4}\}$

The electronic configuration of Iron is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. In ferrocyanide ion, iron is in +2 state. The configuration of Fe^{+2} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

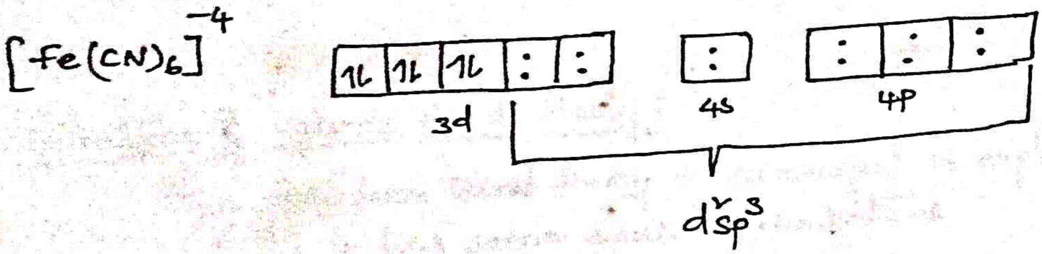




In presence of cyanide ions the electrons in the 3d-orbitals are forced to pair up against to Hunds rule. Thus after pairing the electronic configuration of Fe^{+2} becomes



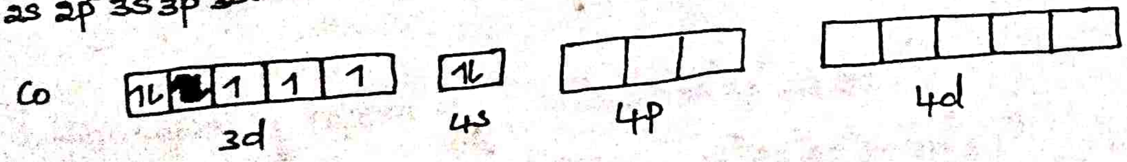
Now Fe^{+2} undergoes d^2sp^3 hybridisation to give six identical hybrid orbitals. Each of these orbitals accept an electron pair donated by cyanide ion to give the complex.

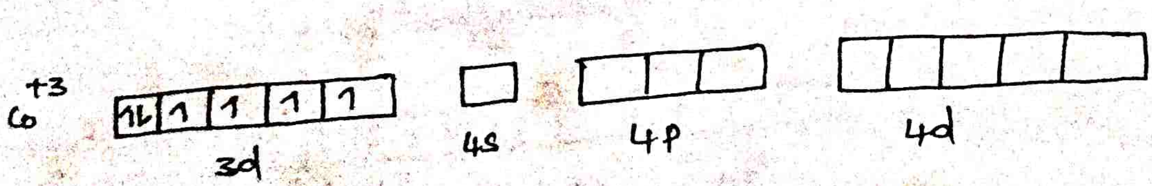


The complex is octahedral and it is diamagnetic as it has no unpaired electrons

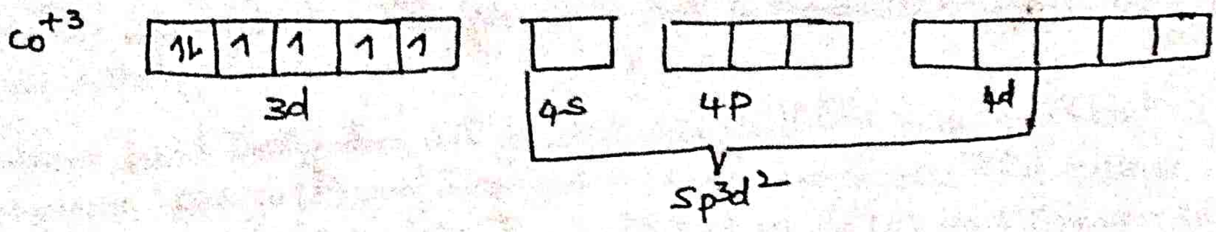
Example: $[CoF_6]^{-3}$

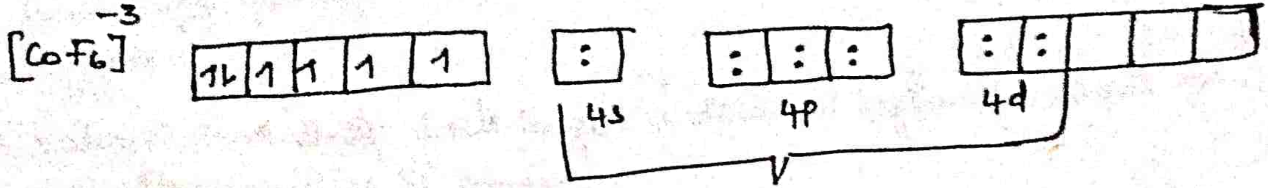
The electronic configuration of cobalt is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$. In $[CoF_6]^{-3}$ complex cobalt is in +3 oxidation state. The electronic configuration of Co^{+3} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$





Experimentally it was found that $[CoF_6]^{-3}$ is paramagnetic in nature and its magnetic moment corresponds to the presence of four unpaired electrons. Hence outer 4d orbitals are involved in hybridisation. Now Co^{+3} ion undergoes sp^3d^2 hybridisation and produces six new identical hybrid orbitals. These six sp^3d^2 hybrid orbitals accept six pairs of electrons donated by F^- ions. Hence The complex is octahedral and paramagnetic in nature.





Limitations of Valence Bond theory:

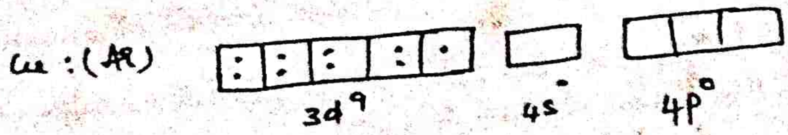
Though Valence Bond theory is successful in explaining the structure of some complexes, it has some serious limitations.

1. Valence Bond Theory cannot predict whether a tetra co-ordinated system acquires Tetrahedral or square planar geometry.

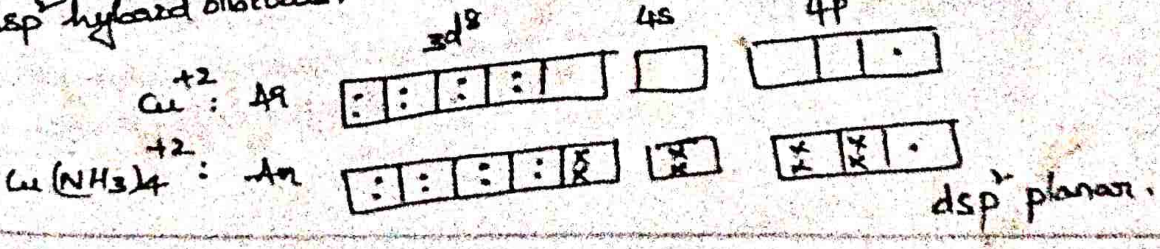
Eg: $[Cu(NH_3)_4]^{+2}$ is planar and $[Zn(NH_3)_4]^{+2}$ is tetrahedral. Valence Bond theory predicts that both these complexes should be tetrahedral.

configuration of copper is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

Cu^{+2} configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$



Since $[Cu(NH_3)_4]^{+2}$ is planar, it is assumed that one electron from the 3d orbital is promoted to the 4p orbital to vacate a d-orbital for the formation of dsp^2 hybrid orbitals.



(2) Electron spin resonance studies show that in copper(II) complexes, the electron is not in the 4p level.

(3) Valence bond Theory does not predict any distortion in symmetrical complexes. The Cu(II) and Titanium(III) complexes are distorted. Valence bond Theory failed to explain the distortions in Cu(II) and Titanium(III) complexes.

(4) Valence Bond Theory fails to give a detailed information about the magnetic properties of complexes.

(5) Valence Bond Theory does not explain the spectral properties of the complex.

Crystal Field theory:

The crystal field theory was developed by Bethe and VanVleck. This Theory considers the electrostatic interactions of the ligands with the d-orbitals of the metal ion, whereas valence bond Theory considers the bonding between the metal ion and the ligands as purely covalent. This is the basic difference between crystal field theory and valence bond theory. Important features of crystal field theory are

(1) The metal ion is considered to be situated in an electric field caused by surrounding molecules or ions i.e. ligands.

(2) Ligands are considered as point charges. If the ligands is a neutral molecule then the negative end of the dipole is oriented towards the metal ion.

(3) The attraction between the metal ion and the ligand is purely regarded as electrostatic. It means the bond is ionic.

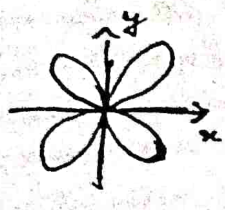
(4) The valence electrons of the metal will be repelled by the negative field of the ligands. These electrons may occupy those d-orbitals which will have their lobes away from the direction of the ligands.

(5) The number of ligands and their arrangement around the metal ion will determine the crystal field.

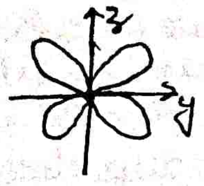
(6) The magnetic properties can be explained in terms of splitting of d-orbitals in different crystal fields.

Splitting of d-orbitals:

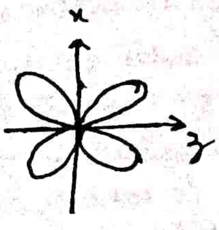
d-sublevel contains five orbitals. These orbitals can be divided into two groups depending on the nature of their orientation in space. Among the two sets, one set consists of d_{xy}, d_{yz} and d_{xz} orbitals whose lobes are oriented between the corresponding axes. The set of these orbitals is collectively known as $d\varepsilon$ orbitals (or t_{2g} orbitals)



d_{xy}

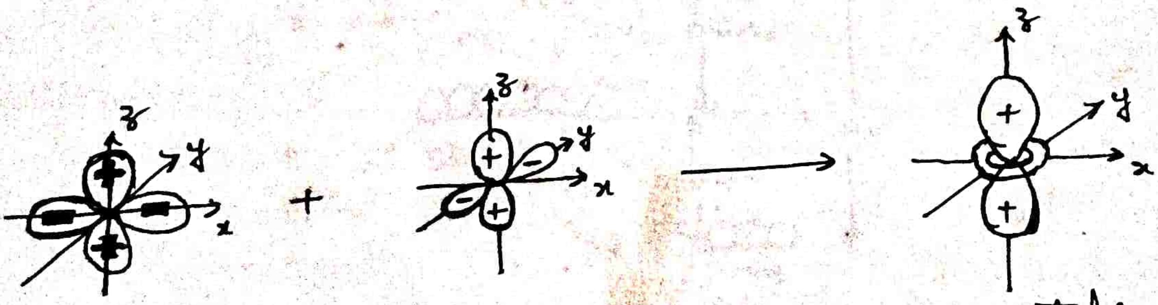


d_{yz}



d_{xz}

The other set contains two orbitals $d_{x^2-y^2}$ and d_{z^2}. The fifth d_{z^2} must be a combination of the other two orbitals $d_{y^2-z^2}$ and $d_{z^2-x^2}$. Hence d_{z^2} orbital should have average properties of these two orbitals. As both the orbitals have electron densities along z-axis, the d_{z^2} orbital will have large lobes of electron ~~de~~ density along z-axis and a ring of electron density in the xy plane



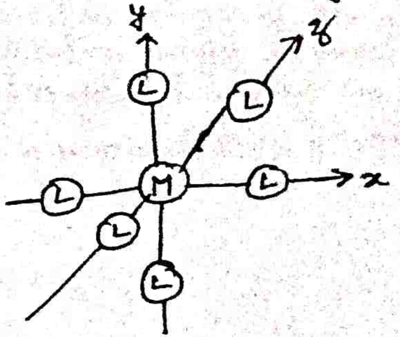
The five d-orbitals are degenerate in case of a free metal ion. However on the approach of the ligands, the d-electrons will be repelled by the lone pairs of the ligands. This repulsion will raise the energy of the d-orbitals.

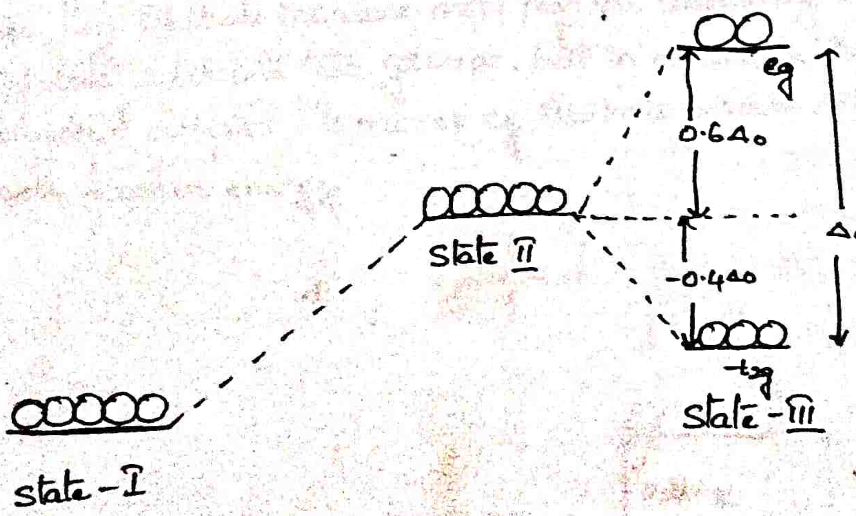
Generally, the energy of the orbitals lying in the direction of the ligands is raised to a larger extent than the orbitals lying in between the ligands. Thus under the influence of the ligands, the five degenerate d-orbitals of the metal ion will split into two groups of orbitals of different energies. This effect is known crystal field splitting or energy level splitting.

Crystal field splitting in octahedral complexes:

In an octahedral complex, the central metal ion is at the centre and the ligands occupy the six corners of octahedron.

Consider the six ligands approaching the metal ion along the axis of the co-ordinate system. In case of five d-orbitals, e_g orbitals are oriented along the axis and t_{2g} orbitals are oriented in between the axes. Hence when the ligands approach, the metal ion e_g orbitals will be repelled more than the remaining three t_{2g} orbitals. Consequently the energy of the two e_g orbitals increase much more than the energy of the t_{2g} orbitals. Thus the five d-orbitals split into two groups of different energies. The splitting of d-orbitals in an octahedral field is illustrated as shown below.



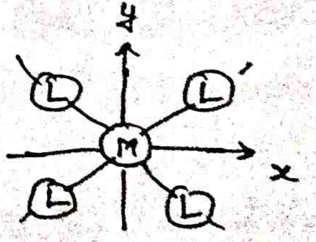


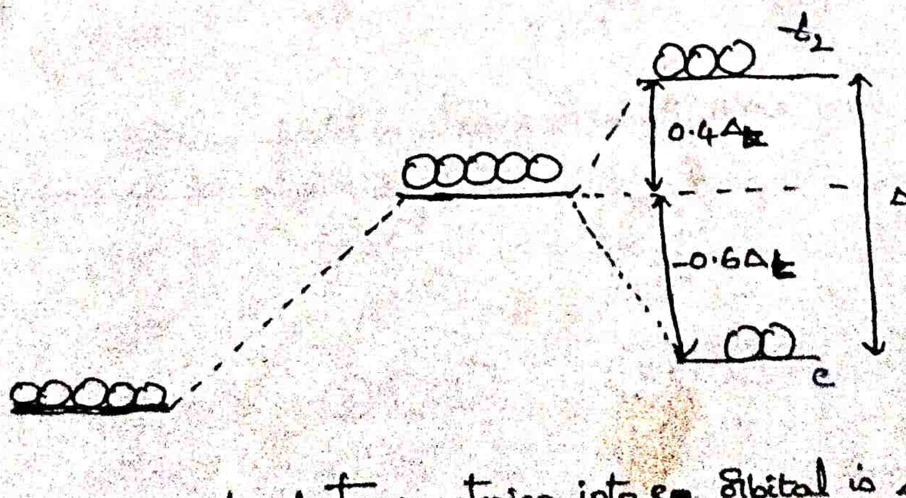
The state-I represents degeneracy of all the five d-orbitals in the isolated central ion. The state-II represents the hypothetical degeneracy of all the d-orbitals at a higher energy level. The state-III represents crystal field splitting. The energy difference between t_{2g} and e_g orbitals is commonly known as crystal field splitting and is denoted by the symbol Δ_o (The subscript 'o' represents octahedral field). It was found that the energy of the t_{2g} orbitals is $0.4\Delta_o$ less than that of the hypothetical degenerate d-orbitals. The energy of the e_g orbitals is $0.6\Delta_o$ greater than that of hypothetical degenerate state.

Generally an electron always prefer to move into an orbital of lower energy. Hence, if an octahedral complex contains one d-electron then it occupies one of the t_{2g} orbitals. This orbital has an energy of $0.4\Delta_o$ less than that of the hypothetical degenerate orbitals. Thus the complex will be $0.4\Delta_o$ more stable than predicted by the pure electrostatic theory. This energy is called crystal field stabilisation energy of the complex. for each electron entering into e_g orbital, the destabilisation energy assigned is $0.6\Delta_o$. Jorgensen (1962) developed the following equation for calculating Δ_o ie. $\Delta_o = f \times g$; f is field strength of ligand [for H_2O f is 1.00 and for Br^- it is 0.7] g is characteristic factor of metal ion.

Crystal field splitting in tetrahedral complexes:

In a tetrahedral structure the three d-orbitals of t_{2g} set are pointing close to the direction in which the ligands are approaching. While the two e_g orbitals are lying inbetween the ligands. As a result of this the energy of the three t_{2g} orbitals increase more than the remaining two e_g orbitals. Thus the five d-orbitals split into two groups, but in a reverse order when compared to octahedral complex. It means e_g orbitals possess lower energy and t_{2g} orbitals possess higher energy





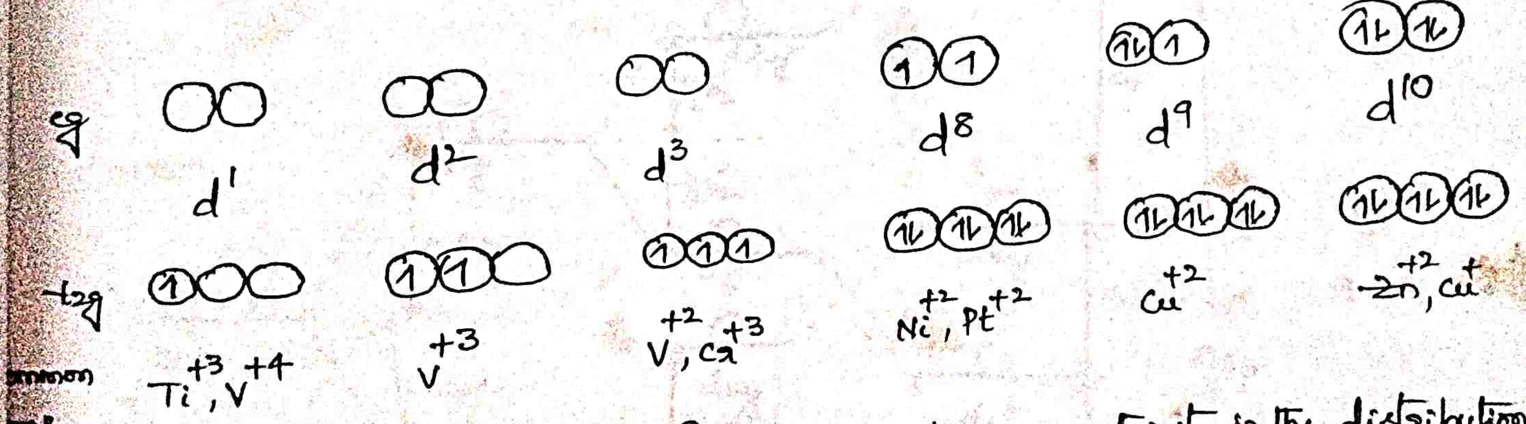
An electron entering into e_g orbital is stabilised by $0.6\Delta_t$. But the electron going into t_{2g} is destabilised by $0.4\Delta_t$. Thus the first two d-electrons will go to the two e_g orbitals.

Distribution of electrons in the d-orbitals in octahedral complexes

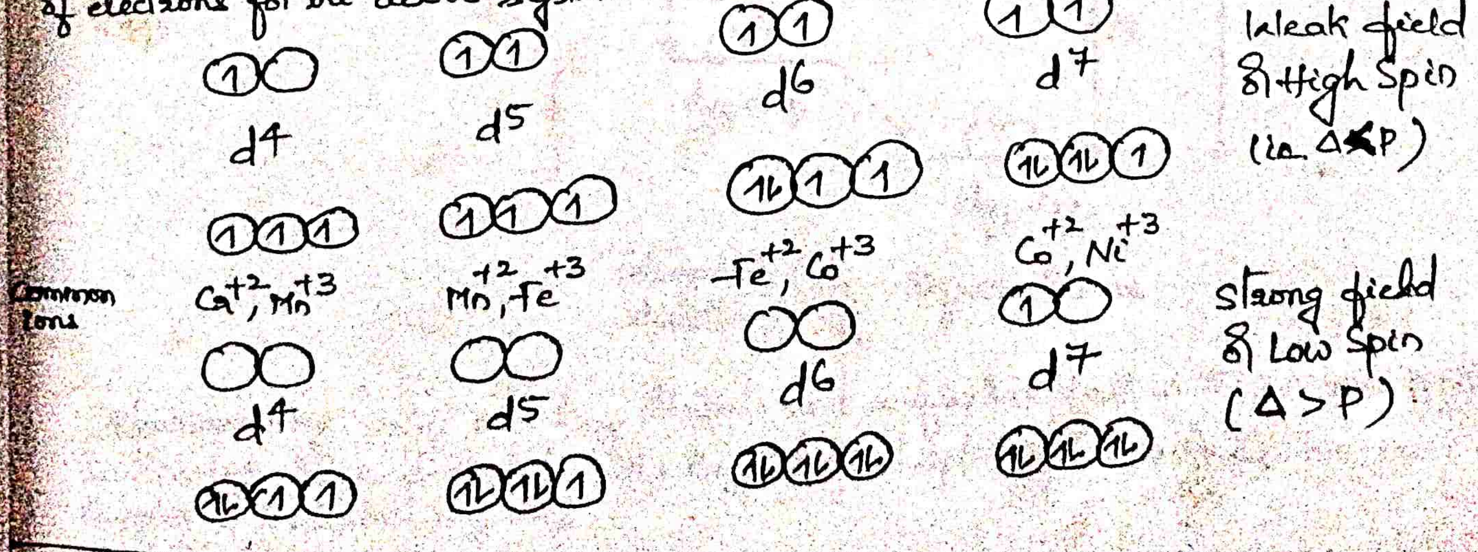
The distribution of electrons in the d-orbitals under the influence of a purely electrostatic crystal field depends upon the following factors.

1. As far as possible, the electrons occupy the lower energy orbitals.
2. The electrons which enter into different d-orbitals will have parallel spins according to Hund's rule.

For the configurations d^1, d^2, d^3, d^8, d^9 and d^{10} there is no uncertainity in the distribution of electrons, regardless of the type of the field (strong or weak field). In other cases, for d^4 – d^7 systems, there is some uncertainity in the distribution of electrons. In these systems, there are two possibilities for each system depending on the relative magnitudes of Δ and mean pairing energy, P. This leads to two cases – strong field or low spin case and weak field or high spin case. For low-spin complexes the splitting energy is greater than pairing energy (ie. Δ>P) and for high spin complexes P>Δ.



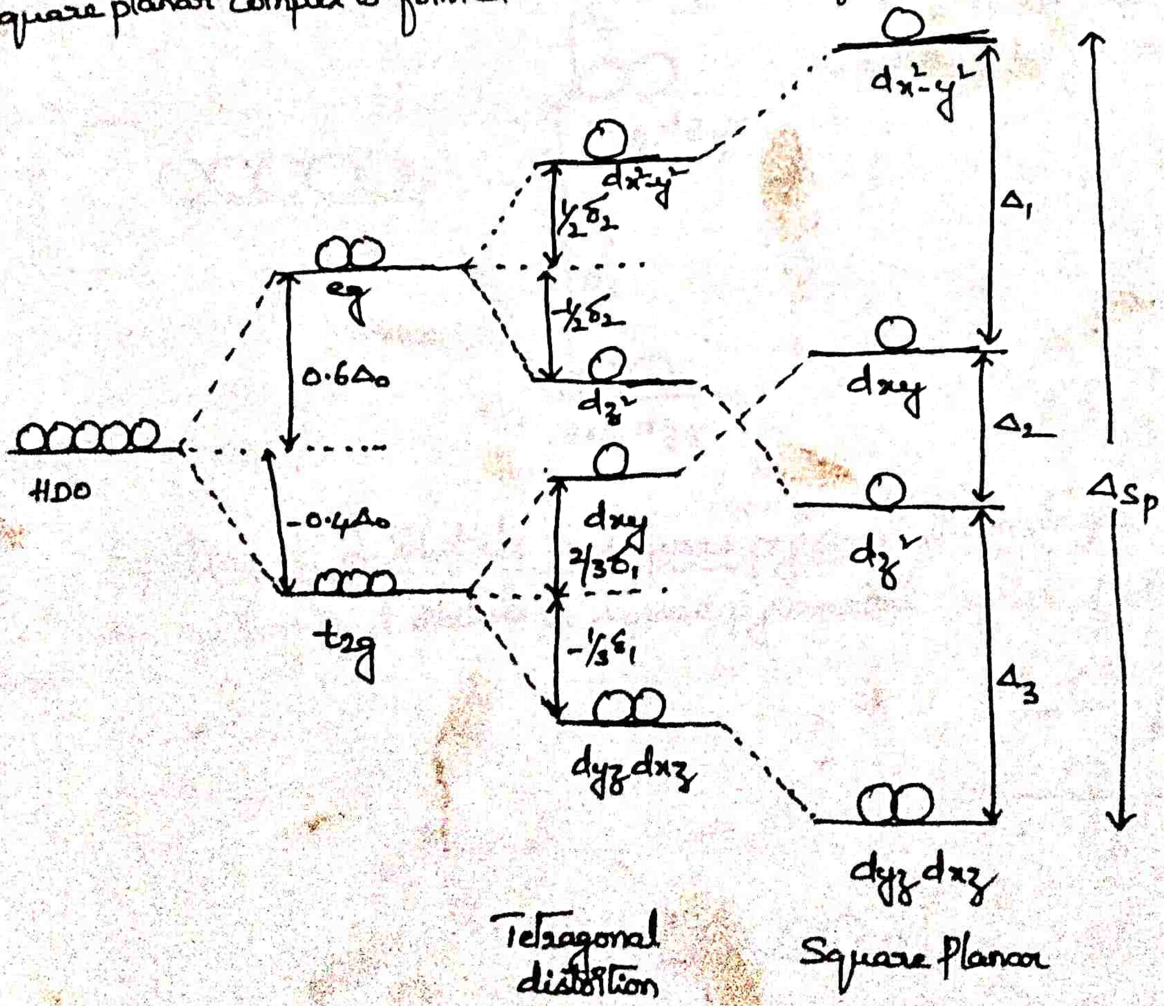
Whether a field is strong or weak there is no uncertainity in the distribution of electrons for the above systems.



Crystal field splitting in Square Planar Complex:

Crystal field theory does not consider the square planar complex as new type. Square planar complex is supposed to derived from the octahedral complex by withdrawing the two trans ligands located along z-axis. The other four ligands are placed along x and y-axis. If the ligands lying on z-axis are moved away, the remaining ligands in the xy plane tend to approach the central metal ion closely. Due to this the d-orbitals in the xy plane are repelled to a greater extent. This will increase the energy of d-orbitals in xy plane i.e. $d_{x^2-y^2}$ and d_{xy} orbitals. Simultaneously the d-orbitals lying along z-axis as well as in the xz and yz planes experience relatively smaller repulsions from the ligands. Hence the energy of d_{z^2} orbital as well as d_{zx} and d_{yz} orbitals decreases. These changes result in tetragonal structure.

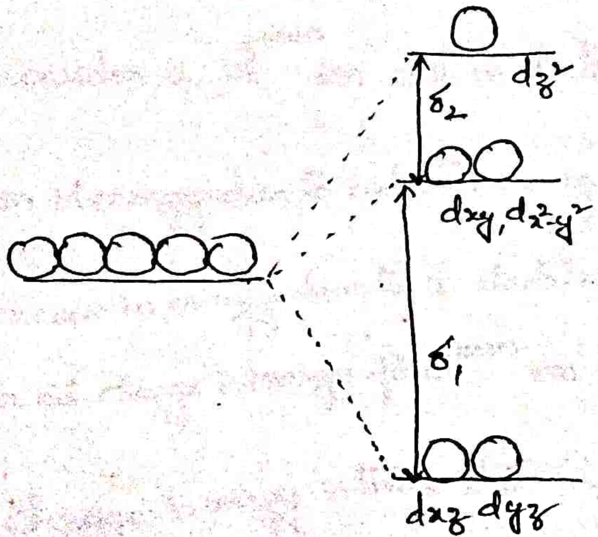
If the trans ligands lying along z-axis are removed completely, the square planar complex is formed. This will lead to further raise in the energies of



$d_{x^2-y^2}$ and d_{xy} orbitals and a further fall in the energies of the remaining three d-orbitals. The crystal field splitting in case of square planar complex is indicated by Δ_{sp}

Splitting of d-orbitals in Trigonal bipyramidal complexes:

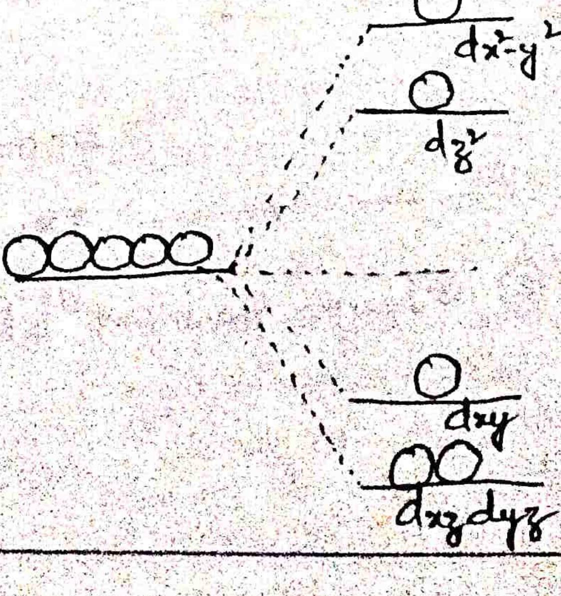
The d-orbitals are divided into three groups (1) d_{z^2} (2) d_{xy}, $d_{x^2-y^2}$ (3) d_{xz}, d_{yz}. The lobes of d_{z^2} orbitals are in the region of ligands which are approaching along z-axis. Hence an electron in this orbital should be very unstable. However the lobes of d_{xz} and d_{yz} orbitals lie between the ligands and these orbitals are relatively stable. An electron in a d_{xy} or $d_{x^2-y^2}$ orbital is remote from the axial ligands but is in proximity to the equitorial ligands. As a result an electron in one of these orbitals should be more stable than one in d_{z^2} but less stable than one in d_{xz} or d_{yz}. The splitting pattern of d-orbitals in trigonal bipyramidal crystal field is as shown below.



δ_1 is small when compared with δ_2 and δ_2 is larger comparable to Δ_o values.

Splitting of d-orbitals in square pyramidal complexes:

The splitting of d-orbitals in square pyramidal crystal field is as shown below.



Crystal field Stabilisation Energy.

In an octahedral field, under the influence of the six ligands, the d-orbitals of the central metal ion are split into two ~~sets~~ sets; t_{2g} (lower energy set) and e_g (higher energy set). The energy difference between these two sets is equal to Δ_o (or 10Dq). In the process of splitting, the energy of t_{2g} set is lowered by $\frac{2}{5}\Delta_o$ or $0.4\Delta_o$ or 4Dq while that of e_g set is raised by $\frac{3}{5}\Delta_o$ or $0.6\Delta_o$ or 6Dq relative to the energy of hypothetical degenerate d-orbitals. Thus each electron occupying t_{2g} orbital decreases the energy of d-orbitals by $-0.4\Delta_o$ or $-4Dq$ while that going into e_g orbital increases its energy by $+0.6\Delta_o$ or 6Dq. Minus and plus signs indicate respectively the decrease and increase in the energy of d-orbitals caused by their splitting under the influence of six ligands.

Consider a d^{m+n} ion with m electrons in t_{2g} and n electrons in e_g orbitals.

Gain in energy due to n electrons in e_g orbitals $= +0.6\Delta_o \times n$

Decrease in energy due to m electrons in t_{2g} orbitals $= -0.4\Delta_o \times m$

Therefore net change in energy for d^{m+n} ion $= [-0.4m + 0.6n]\Delta_o$ ①

Change in energy in terms Dq $= [-4m + 6n]Dq$ ②

This change in energy is called crystal field stabilisation energy.

If P is mean pairing energy, which is the energy required to pair two electrons against electron-electron repulsion in the same orbital and x be no of paired electrons then

CFSE for d^{m+n} ion can be given as ③

$$[-0.4m + 0.6n]\Delta_o + xP$$

Calculation of CFSE for d^3, d^4 and d^7 ions using equation ③

(i) d^3 ion: Either in strong or in weak field, the three electrons will occupy t_{2g} set resulting in a configuration $t_{2g}^3 e_g^0$

$$\therefore CFSE = [(-0.4\times3)+(0.6\times0)]\Delta_o + 0\times P$$

$$= -1.2\Delta_o$$ [for both low spin & high spin states]

(ii) d^4 ion:
Weak field: In a weak field the configuration is $t_{2g}^3 e_g^1$

$$\therefore CFSE = [(-0.4\times3)+(1\times0.6)]\Delta_o + 0\times P$$

$$= -1.2\Delta_o + 0.6\Delta_o = -0.6\Delta_o$$

Strong field: The strong field configuration is $t_{2g}^4 e_g^0$

$$\therefore CFSE = [(-0.4\times4)+(0\times0.6)]\Delta_o + 1\times \text{pairing energy}$$

$$= -1.6\Delta_o + \text{Pairing energy}.$$

(iii) d^7 ion
Weak field: In weak field the configuration is $t_{2g}^5 e_g^2$

$$\therefore CFSE = [(-0.4\times5)+(0.6\times2)]\Delta_o + 2\times \text{pairing energy}$$

$$= -0.8\Delta_o + 2P$$

Strong field: The strong field configuration is $t_{2g}^6 e_g^1$

$$\therefore CFSE = [(-0.4\times6)+(0.6\times1)]\Delta_o + 3P$$

$$= -1.8\Delta_o + 3P$$

The gain in energy achieved by the preferential filling of the lower-ly
d levels, over the energy of a completely random occupancy of all five d-levels
called the crystal field stabilisation energy.

Problem: For the $[Cr(H_2O)_6]^{+2}$ ion, the mean pairing energy, P is found to be 23,500 cm^{-1}. The magnitude of Δ_o is 13,900 cm^{-1}. calculate the CFSE for this complex ion corresponding to high spin and low spin state. Which state is more stable.

Solution: In the given complex ion chromium is in +2 oxidation state and the configuration of Cr^{+2} is d^4.

For a d^4 ion, in high spin state the configuration is $t_{2g}^3 e_g^1$

$$\therefore CFSE = [(-0.4\times3)+(1\times0.6)]\Delta_o + 0\times \text{pairing energy}$$

$$= -1.2\Delta_o + 0.6\Delta_o + 0.$$

$$= -0.6\Delta_o = -8{,}340\ cm^{-1}$$

For a d^4 ion, in low spin state the configuration is $t_{2g}^4 e_g^0$

$$\therefore CFSE = [(-0.4\times4)+(0\times0.6)]\Delta_o + 1\times \text{pairing energy}$$

$$= -1.6\Delta_o + P$$

$$= -1.6\times13{,}900 + 23{,}500$$

$$= +1{,}260\ cm^{-1}$$

$\because$ Splitting energy is less than pairing energy, high spin configuration would be stable.

Factors influencing the magnitude of Δ_o

The magnitude of Δ_o depends upon the following factors:

(1) Nature of the metal ion
(2) Nature of the ligand
(3) Geometry of the Complex.

(1) Nature of the metal ion: The influence of the nature of the metal ion on the magnitude of Δ_o can be discussed under following headings.

(a) Different charges on the cation of the same metal: The cation with a higher oxidation state has a larger value of Δ_o than that with lower oxidation state

Eg: Δ_o for $[Co(H_2O)_6]^{+2}$ is 9,300 cm^{-1}
& Δ_o for $[Co(H_2O)_6]^{+3}$ is 18,200 cm^{-1}

With increase in the oxidation state of the metal ion, the polarising power of the metal ion increases. As a result, the ligands are more effectively polarised and the ligands can approach the central metal ion much ~~closely~~ closely. The closer approach of ligands causes greater splitting.

(b) Different Charges on the cation of different metals:

Eg: Δ_o for $[V(H_2O)_6]^{+2}$ is 12,400 cm^{-1} .... $3d^3$
Δ_o for $[Cr(H_2O)_6]^{+3}$ is 17,400 cm^{-1} .... $3d^3$

In the above example two different cations having the same number of d-electrons and the same geometry but with different charges are compared. The Cr(+3) ion has greater positive charge than vanadium (+2) ion and hence exerts greater influence over the ligands than V(+2) ion. As a result of greater attraction over ligands, closer approach of the ligands towards central metal ion is possible. This closer approach brings about greater splitting.

(c) Same charges on the cation but the number of d-electrons is different:

The magnitude of Δ_o decreases with the increase in the number of d-electrons even though the two cations have same charge

Eg: Δ_o for $[Co(H_2O)_6]^{+2}$ is 9,300 cm^{-1} .... $3d^7$

Δ_o for $[Ni(H_2O)_6]^{+2}$ is 8,500 cm^{-1} .... $3d^8$

In the above example the two cations possess same charge, but the no of d-electrons are different. With increase in the number of d-electrons the closer approach of ligands is not possible and as a result the splitting energy decreases.

(d) Principal quantum number of the d-orbital: The crystal field splitting is the greatest for complexes containing 5d electrons and the least for complexes containing a metal ion with 3d electrons. Δ_o increases about 30% to 50% from $3d^n$ to $4d^n$ and by about the same amount again from $4d^n$ to $5d^n$ complexes.

Eg: Δ_o for $[Co(NH_3)_6]^{+3}$ is 23,000 cm^{-1} .... $3d^6$

Δ_o for $[Rh(NH_3)_6]^{+3}$ is 34,000 cm^{-1} .... $4d^6$

Δ_o for $[Ir(NH_3)_6]^{+3}$ is 41,000 cm^{-1} .... $5d^6$

This is due to the fact that the 5d orbitals extend farther into space and hence interact more strongly with the ligands leading to an increase in the amount of splitting.

(e) Nature of the ligands: The nature of the ligands also affects the degree of splitting of d-orbitals. The ligands having less splitting ability are called weak field ligands whereas those with greater splitting power are known as strong field ligands. The ligands are arranged in the order of their increasing splitting ability. This series is called the spectrochemical series. The splitting abilities of various ligands are determined from the spectra of their complexes.

The spectrochemical series can be given as

$I^- < Br^- < S^{-2} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < C_2O_4^{-2} < H_2O < NH_3 < en < bipy <$ phen $< -NO_2^- < CN^- < CO$

The first few ligands in the above series are known as weak field ligands. The last few ligands are called the strong field ligands. The intermediate ligands are termed as intermediate field strength ligands. This order of increasing field strength of common ligands is independent of the nature of the central metal ion and the geometry of the complex.

The position of the ligands in spectrochemical series can be explained by making use of Ligand field theory and molecular orbital theory.

3. Geometry of the complex: The degree of splitting of d-orbitals is affected by the geometry of the complex. It is known that $\Delta sp > \Delta o > \Delta t$

$$\begin{array}{ccc} \Delta sp & \Delta o & \Delta t \\ 1.3\Delta_o & \Delta o & \frac{4}{9}\Delta o \end{array}$$

JAHN TELLER EFFECT [Tetragonal Distortion of octahedral complexes]

The shape of a transition metal complex depends upon the position of the electron pairs. The electron pairs tend to be away from each other as far as possible. In addition to this tendency of electron pairs to occupy stable positions, the shapes of the metal complexes depends upon the filling up of electrons in the d-orbitals. The d-orbitals may be filled symmetrically or asymmetrically.

The d-orbitals split into two sets (t_{2g} and e_g) in an octahedral field because of the repulsions between the ligands and metal d-orbitals. If the electrons in the d-orbitals are symmetrically arranged, they will repel all six ligands equally. Thus the structure of the complex will be regular octahedron. The symmetrical arrangements of d-electrons can be given as

Electronic configuration	t_{2g}	e_g	Nature of ligand field	Examples
d^0	[ ][ ][ ]	[ ][ ]	Strong & Weak	$\overset{IV}{Ti}O_2$, $[TiF_6]^{-2}$ $[TiCl_6]^{-2}$
d^3	[↑][↑][↑]	[ ][ ]	Strong & Weak	$[Cr(oxalate)_3]^{-3}$ $[Cr(H_2O)_6]^{+3}$
d^5	[↑][↑][↑]	[↑][↑]	Weak	$[MnF_6]^{-4}$, $[FeF_6]^{-3}$
d^6	[↑↓][↑↓][↑↓]	[ ][ ]	Strong	$[Fe(CN)_6]^{-4}$, $[Co(NH_3)_6]^{+3}$
d^8	[↑↓][↑↓][↑↓]	[↑][↑]	Weak.	$[NiF_6]^{-4}$, $[Ni(H_2O)_6]^{+2}$
d^{10}	[↑↓][↑↓][↑↓]	[↑↓][↑↓]	Strong & Weak	$[Zn(NH_3)_6]^{+2}$ $[Zn(H_2O)_6]^{+2}$

All other arrangements have an asymmetrical arrangement of d-electrons. As a result of asymmetric arrangement some of the ligands will be repelled more than the others. Hence the structure of the complex would be distorted.

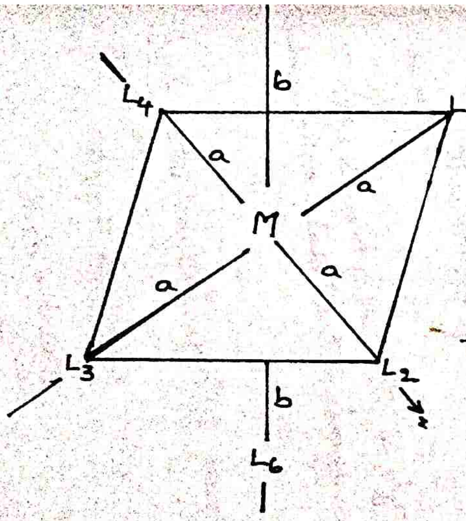
Some asymmetric electronic arrangements

Electronic configuration	t_{2g}	e_g	Nature of ligand field	Examples
d^4	↑ | ↑ | ↑	↑ |	Weak field	Cr (+II), Mn (+III)
d^7	↑↓ | ↑↓ | ↑↓	↑ |	Strong field	Co (+II), Ni (+III)
d^9	↑↓ | ↑↓ | ↑↓	↑↓ | ↑	Strong & Weak	

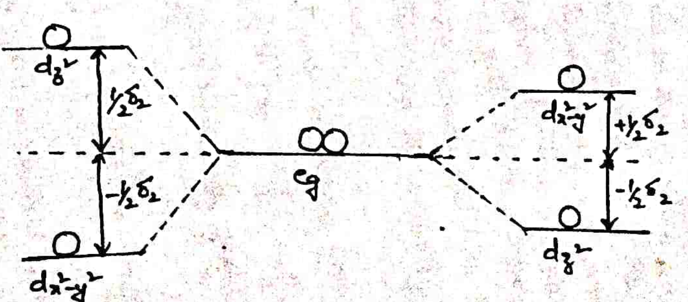
The e_g orbitals which are asymmetrically filled, are in the way of approaching ligands in an octahedral complex and they will be repelled by the ligands to a greater extent. This causes a significant distortion of the octahedral shape. The asymmetric filling of the t_{2g} orbitals has only a very small effect on the stereochemistry. The two e_g orbitals are generally degenerate. If they are asymmetrically filled then this degeneracy is destroyed.

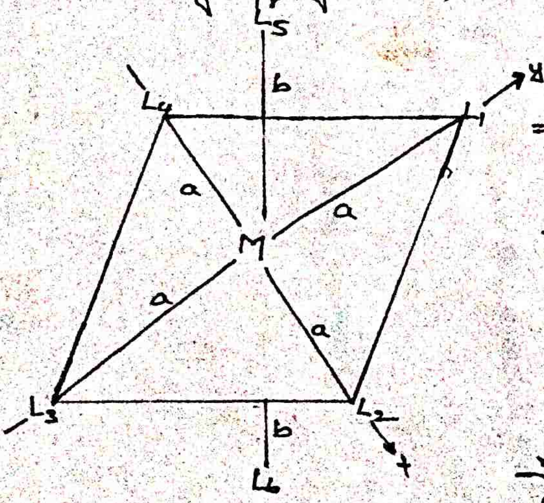
If the d_{z^2} orbital contains one more electron than the $d_{x^2-y^2}$ orbital then the ligands approaching along z-axis will encounter greater repulsions than the other four ligands. The repulsions will result in elongation of the octahedron along the z-axis. This is called tetragonal distortion. Strictly speaking it is called as tetragonal elongation.

If the extra electron is present in $d_{x^2-y^2}$ orbital then the elongation will occur along x and y axis. Thus there will be four long bonds and two short bonds. This results in compression of bonds along z-axis and is called as tetragonal compression. Tetragonal elongation is much more common than tetragonal compression.

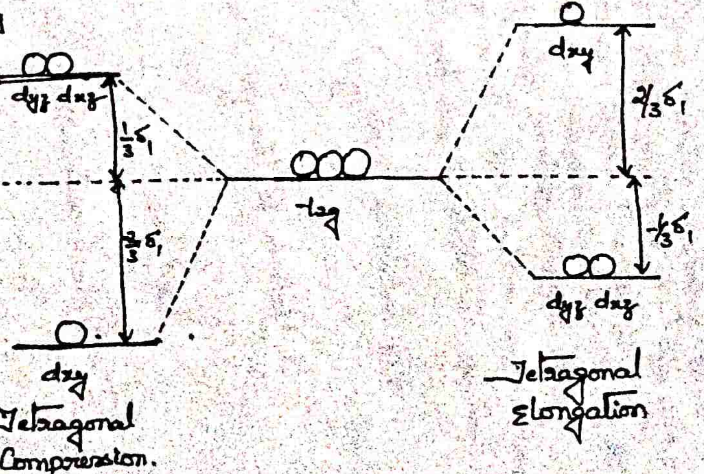


Tetragonal Elongation (a<b)





Tetragonal Compression (a>b)



Consider a metal ion with d^9 configuration (like Cu^{+2} ion). The arrangement of electrons in five d-orbitals can be written as $3d_{xy}^2\,3d_{yz}^2\,3d_{xz}^2\,(t_{2g}^6)$ and e_g^3. The arrangement of electrons in eg ~~st~~ set of d-orbitals has two possibilities. The first possibility is $d_{z^2}^2\,d_{x^2-y^2}^1$. The d_{z^2} orbital, which is filled and points towards the ligands on the z-axis, now offers greater shielding of Cu^{+2} nucleus than the half filled $d_{x^2-y^2}^1$ orbital, which points at the ligands in the xy plane. The ligands in xy plane are drawn closer to metal ion (Cu^{+2}) nucleus due to higher effective nuclear charge whereas the ligands on the z-axis move further out due to a lower effective nuclear charge. This results in four short bonds and two long bonds. This distortion is known as tetragonal elongation and the stability attained due to distortion can be calculated as follows.

The net gain in energy from split t_{2g} set of d-orbitals is zero

i.e. $4(-\frac{1}{3}\delta_1)+2(\frac{2}{3}\delta_1) = -\frac{4}{3}\delta_1+\frac{4}{3}\delta_1$

The net gain in energy from split eg set of d-orbitals

$$2(-\tfrac{1}{2}\delta_2)+1(+\tfrac{1}{2}\delta_2) = -\tfrac{2}{2}\delta_1+\tfrac{1}{2}\delta_2 = -\tfrac{1}{2}\delta_2$$

This energy gain is called Jahn-Teller stabilisation energy.

The second possibility is $d_{z^2}^1\,d_{x^2-y^2}^2$ and from this possibility also Jahn-Teller stabilisation energy can be calculated.

Note: The crystal splitting energy order of various geometries can be given as

$\Delta_{sp} > \Delta_o > \Delta_t$

$\Delta_{sp} = 1.3\Delta_o$

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

Eg: In the crystal structure of CrF_2, each Cr^{+2} is octahedrally surrounded by six fluoride ions. Among the six bonds, four Cr-F bonds have a length of 1.98 – 2.01 A° and the other two bonds have length of 2.43A°. The octahedron is said to be distorted tetragonally. The reason for the distortion can be explained as follows

The electronic configuration of Cr is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

The electronic configuration of Cr^{+2} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$

F^- being a weak ligand, the t_{2g} level contains three electrons and eg level contain one electron.

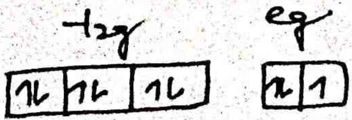
The electron in eg level may occupy either d_{z^2} or $d_{x^2-y^2}$ orbital. The $d_{x^2-y^2}$ orbital has four lobes whereas d_{z^2} orbital has two lobes pointing at the ligands. To have minimum repulsions with the ligands, the single eg electron will occupy the d_{z^2} orbital. This results in ~~plat~~ splitting of two eg orbitals and removes the degeneracy. The d_{z^2} orbital has less energy and $d_{x^2-y^2}$ orbital has higher energy.

The ligands approaching along the z-axis are subjected to greater repulsion than the four ligands along x and y axes. This causes tetragonal distortion with four short bonds and two long bonds.

Similar sort of distortion is observed in MnF_3, in which Mn is in +3 oxidation state with d^4 configuration.

Another example in which tetragonal distortion can be observed is Cu(+II)

Cu^{+2} has a d^9 configuration.



Due to asymmetric filling of eg orbitals in case of Cu^{+2} ion, a distortion is observed in the Cu(+II) complex. This sort of distortion is known as ~~known~~ Jahn Teller distortion

Jahn Teller effect can be stated as 'Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo some sort of distortion to lower its symmetry and remove the degeneracy'. In octahedral complexes distortions resulting from uneven filling of the eg orbitals are very important

Limitations of Crystal field theory:

(1) Crystal field theory does not consider the formation of π-bonding in complexes.

(2) CFT fails to explain the position of H_2O in spectrochemical series as a stronger ligand than OH^-

(3) CFT considers the bond between the metal and ligand as purely ionic. But Electron spin resonance of certain complexes proved that the M-L bond results due to overlap of the orbitals.

(4) The covalent nature of metal-ligand bond is also proved by the NMR spectra and NQR spectra.

MOLECULAR ORBITAL THEORY:

The bonding between the metal-ligand in complexes is explained basing on valence-Bond method and Crystal field theory. Similarly metal-ligand bonding in complexes can also be explained by the application of molecular orbital theory. Crystal field theory considers the bonding between the metal-ligand as purely electrostatic. But certain physical measurements like ESR, NMR and NQR suggests that there is some amount of covalent bonding in complexes. The limitations of crystal field theory are better explained by molecular orbital theory.

This theory considers the overlap of Atomic orbitals of the central metal ion and those of the ligands. The overlap of atomic orbitals of metal ion with ligand orbitals occur only when the energy and symmetry are nearly equal

In an octahedral complex, around each central metal ion or atom there will be six ligands. In an octahedral complex, fifteen atomic orbitals are available for molecular orbital construction (i.e. nine from metal ion and six from six ligands) The nine significant metal atomic orbitals are designated as $\phi_{3d_{xy}}$, $\phi_{3d_{xz}}$, $\phi_{3d_{yz}}$, $\phi_{3d_{x^2-y^2}}$, $\phi_{3d_{z^2}}$, ϕ_{4s}, ϕ_{4p_x}, ϕ_{4p_y}, ϕ_{4p_z}. Out of these nine atomic orbitals of metal ion, only six suitable atomic orbitals will overlap with group ligand σ-orbitals to form six metal-ligand σ bonds.

The nine atomic orbitals of metal ion fall into four symmetry classes. The symmetry classes are labelled ~~as~~ basing on group theoretical concept. The symmetry classes are

$4s$ — A_{1g}

$4p_x, 4p_y, 4p_z$ — T_{1u} (Three orbitals equivalent except in their spatial orientation)

$3d_{x^2-y^2}, 3d_{z^2}$ — E_g (Two orbitals equivalent except in their spatial orientation)

$3d_{xy}, 3d_{yz}, 3d_{xz}$ — T_{2g} (Three orbitals equivalent except in their spatial orientation)

Similarly, the six ligand atomic orbitals combine to form group ligand orbitals. The six ligand group orbitals are designated as Σa, $\Sigma_{x^2-y^2}$, Σ_{z^2}, Σ_x, Σ_y, Σ_z. These six ligand group orbitals are divided into three symmetry classes A_{1g}, E_g and T_{1u}. These ligand group orbitals linearly combine with metal atomic orbitals having appropriate energy and matching symmetry to form bonding and antibonding molecular orbitals

The six ligand group orbitals can be given as

$$\Sigma_a = \frac{1}{\sqrt{6}}\left(\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z}\right) \quad \text{——} \; A_{1g}$$

$$\left.\begin{aligned} \Sigma_{x^2-y^2} &= \frac{1}{2}\left(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y}\right) \\ \Sigma_{z^2} &= \frac{1}{\sqrt{12}}\left(2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y}\right) \end{aligned}\right\} \text{——} \; E_g$$

$$\left.\begin{aligned} \Sigma_x &= \frac{1}{\sqrt{2}}\left(\sigma_x - \sigma_{-x}\right) \\ \Sigma_y &= \frac{1}{\sqrt{2}}\left(\sigma_y - \sigma_{-y}\right) \\ \Sigma_z &= \frac{1}{\sqrt{2}}\left(\sigma_z - \sigma_{-z}\right) \end{aligned}\right\} \text{——} \; T_{1u}$$

As there are no appropriate energitic orbitals on the ligands the T_{2g} orbitals of metal ion remain as non bonding

Among the atomic orbitals of metal and group ligand orbitals,

(i) the 4s atomic orbital of metal and Σ_a group orbital of ligand have appropriate energy and matching symmetry and they overlap to form A_{1g} bonding MO and A_{1g}^* antibonding MO.

(ii) The $4P_x$, $4P_y$ & $4P_z$ atomic orbitals of metal overlap with T_{1u} group [i.e $\Sigma_x, \Sigma_y, \Sigma_z$] ligand orbitals to form bonding and antibonding molecular orbitals.

(iii) The $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals overlap with E_g [$\Sigma_{x^2-y^2}$ and Σ_{z^2}] orbitals to form bonding and antibonding molecular orbitals.

Fig. 6.28 shows the six metal ion σ orbitals and their matching symmetry als.

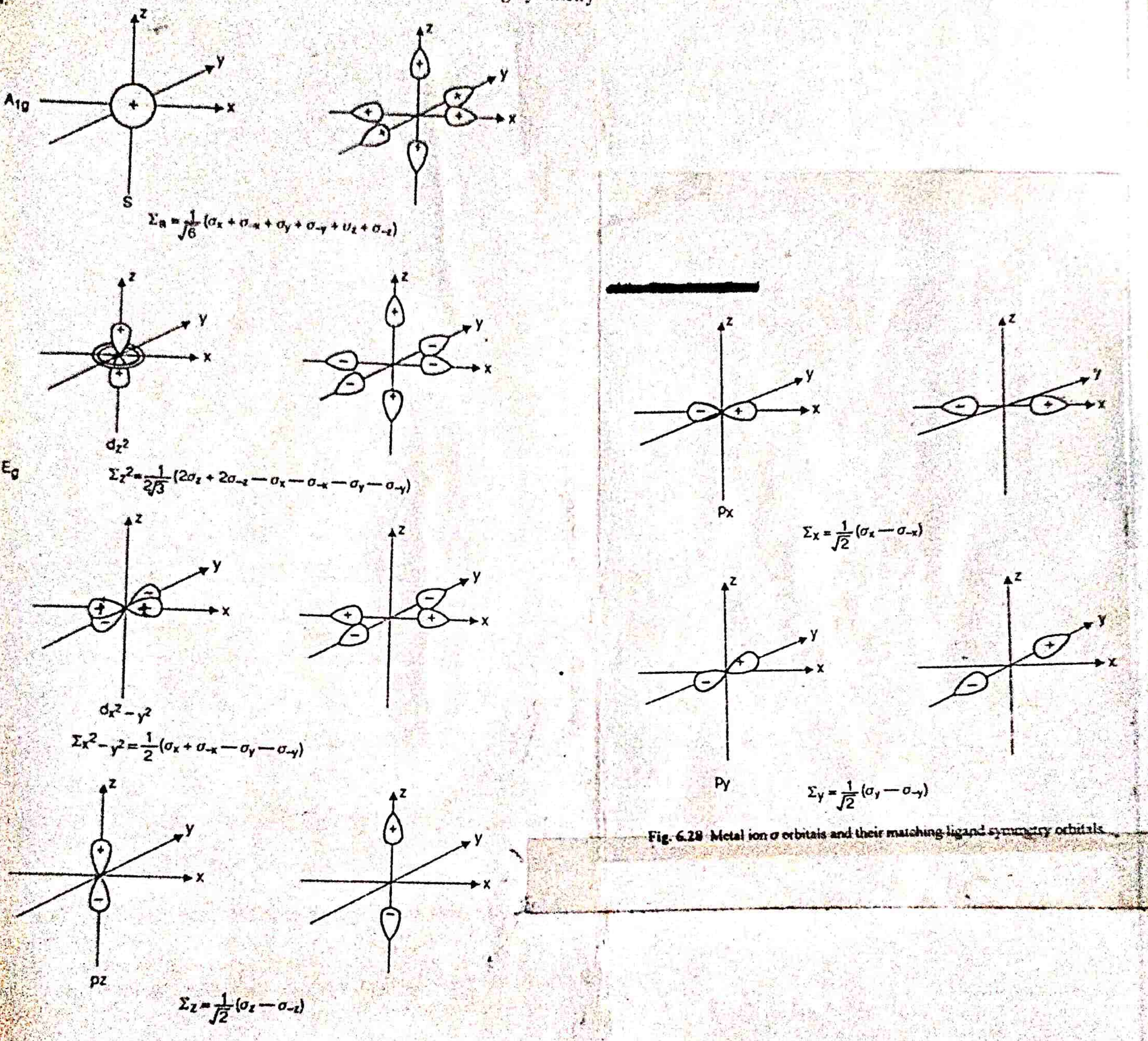


Fig. 6.28 Metal ion σ orbitals and their matching ligand symmetry orbitals.

The matched orbitals unite with maximum positive overlap than given a bonding MO and the other in which they unite with maximum negative overlap to give the corresponding anti-bonding MO. This process is illustrated for the combination of p_z and Σ_z orbitals in fig. 6.29.

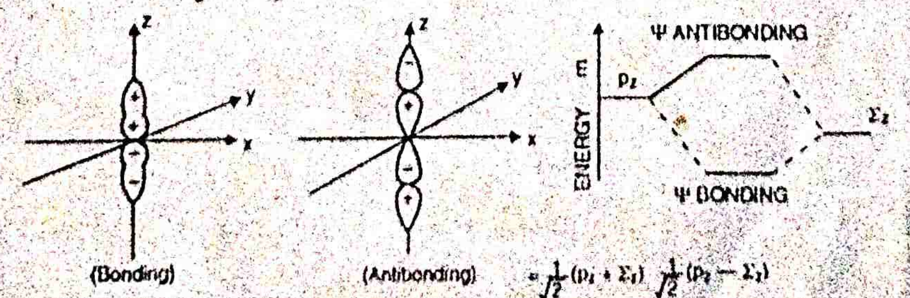
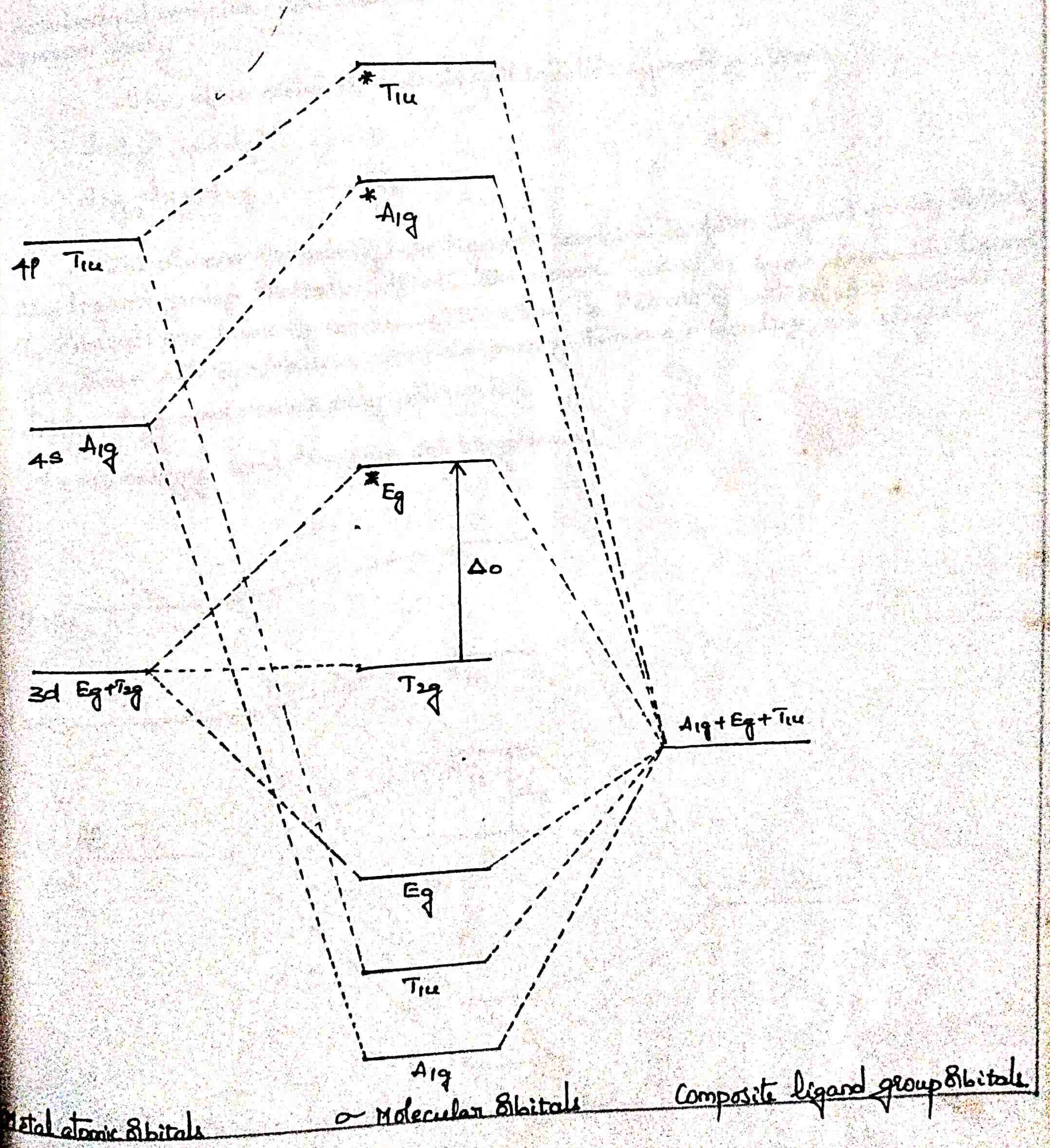


Fig. 6.29.

The mo energy level diagram for octahedral complexes can be given as

Eg: $[Co(NH_3)_6]^{+3}$ — MO configuration is $A_{1g}^{2} T_{1u}^{6} E_g^{4} T_{2g}^{6}$

$[CoF_6]^{-3}$ — MO configuration is $A_{1g}^{2} T_{1u}^{6} E_g^{4} T_{2g}^{4} E_g^{*2}$



Tetrahedral complexes:

The same procedure which is used for octahedral complexes can be applied to other geometries. As in the case of octahedral complexes, the metal ion contains the same nine valence orbitals even in a tetrahedral complex. But the symmetry of the atomic orbitals of metal in tetrahedral complex will be different from that of octahedral complex. The metal s and p orbitals have A_1 and T_2 symmetries respectively.

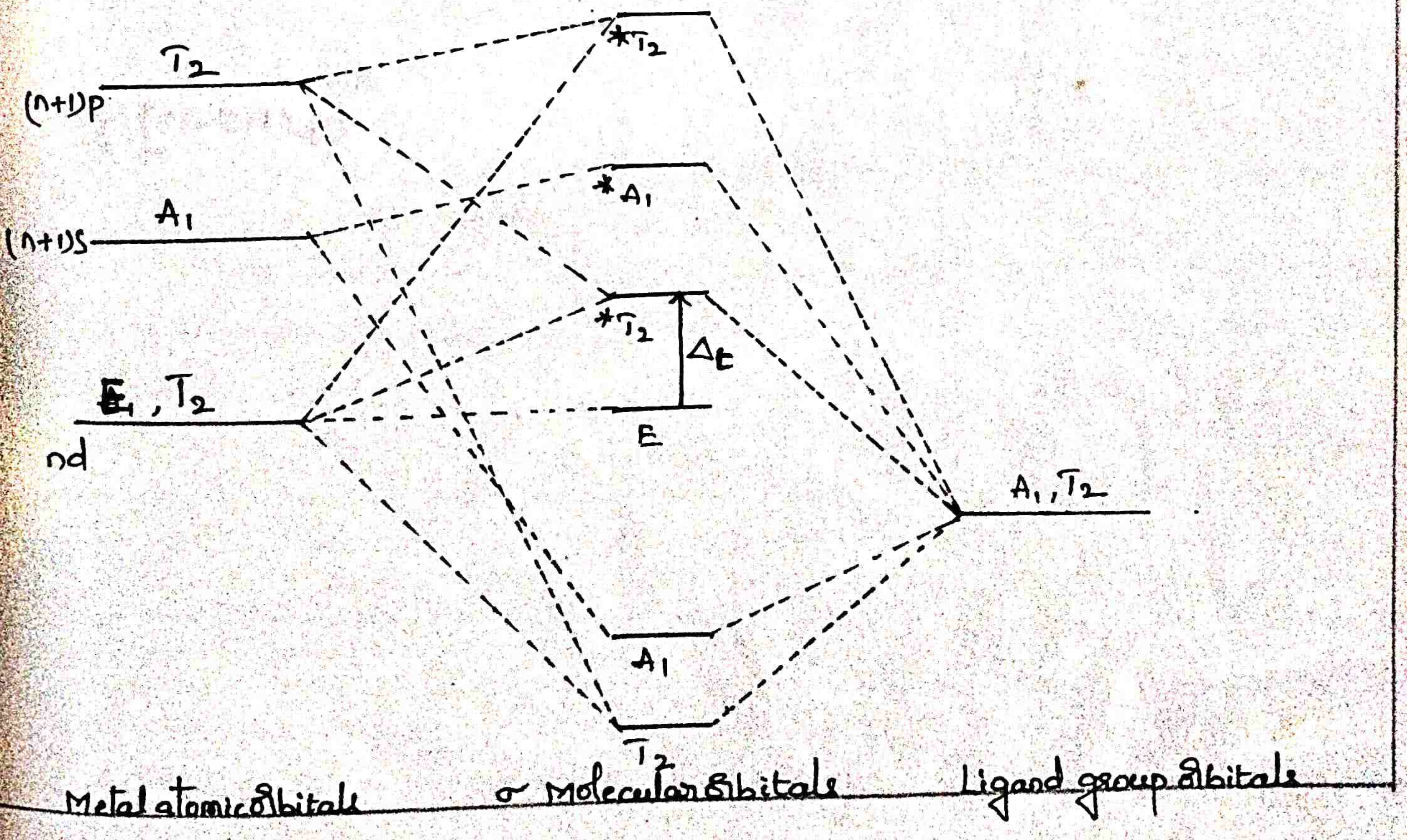
The five metal d-orbitals fall into two symmetry classes

$d_{x^2-y^2}$ and d_{z^2} — E

d_{xy}, d_{yz}, d_{xz} — T_2

The atomic orbitals of the ligands combine to form ligand group orbitals. The ligand group orbitals fall into two classes T_2 and A_1 symmetries. The ligand T_2 orbitals can linearly combine with metal T_2 orbitals of both P and d orbitals to give three sets of molecular orbitals. Among them one is bonding, one slightly antibonding and one clearly antibonding

The MO energy level diagram can be given as



Eg: $[CoCl_4]^{-2}$

In this complex Co is in +2 state [i.e. d^7 type] and there are total 15 electrons.

$[Ni(CO)_4]$ — complex ~~has~~ 18 electrons.

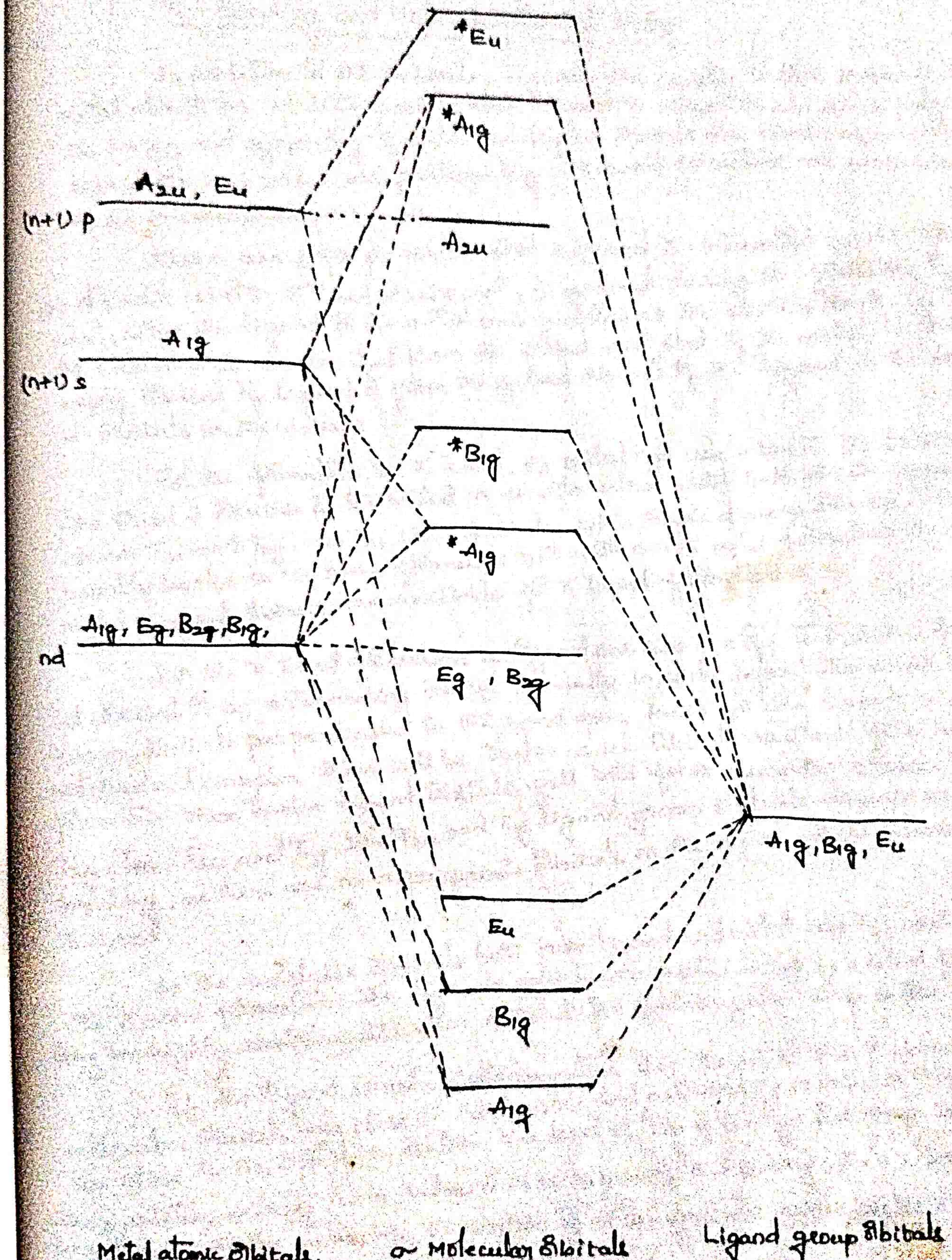
SQUARE PLANAR COMPLEXES:

In square planar complexes, the metal d-orbitals split into $A_{1g}(d_{z^2})$, $E_g(d_{xz}, d_{yz})$, $B_{2g}(d_{xy})$ and $B_{1g}(d_{x^2-y^2})$. The p orbitals also splits into $A_{2u}(p_z)$ and $E_u(p_x, p_y)$

The atomic orbitals of the ligands combine among themselves before undergoing linear combination with metal orbitals to form group ligand orbitals, these ligand group orbitals fall into A_{1g}, B_{1g}, E_u symmetry. Now the metal orbitals overlap with ligand ~~group~~ group orbitals of nearly equal energy and matching symmetry.

The MO energy level diagram can be given as

Eg: $[Ni(CN)_4]^{-2}$


*Eu
*A1g
A2u , Eu
(n+1) p
A2u
A1g
(n+1) s
*B1g
*A1g
A1g, Eg, B2g, B1g,
nd
Eg , B2g
A1g, B1g, Eu
Eu
B1g
A1g
Metal atomic orbitals.
σ Molecular orbitals
Ligand group orbitals

π- Bonding and Molecular Orbital theory:

In addition to the σ- bonds, ligands are capable to form π- bonds with a metal atom or ion. A significant metal- ligand π interaction can occur only when the energy and symmetry of metal and ligand orbitals are nearly equal. The metal ligand orbitals which are participating in π bond formation are perpendicular to the internuclear axis.

There are four possible metal- ligand π interaction (a) dπ-pπ (b) dπ-dπ (c) dπ-π* and (d) dπ-σ*. In general during the formation of π bond, either the ligand or the metal can function as the electron donor i.e. the electrons can be donated from the filled d-orbital of the metal to empty orbital of ligand or from the filled orbitals of the ligands to the empty d-orbitals on the metal.

For the formation of π-bond, the metal can use either its p or d orbitals. The P and d orbitals of the metal in an octahedral field fall into the symmetry classes T_{1u} and T_{2g}. As T_{1u} (i.e. p orbitals) set is oriented along the axis, they usually involve in σ bond formation rather than a π bond formation. So the metal T_{2g} set orbitals are available for π bond formation.

For the π bond formation, a ligand can use one of its p orbital or a d-orbital or an antibonding orbital. Usually in each ligand there will be two p-orbitals perpendicular to the bond axis. Hence for six ligands in an octahedral complex there will be twelve such orbitals available for π bond formation. These twelve ligand orbitals fall into four symmetry classes T_{2g}, T_{1u}, T_{2u} and T_{1g}. The T_{2u} and T_{1g} ligand group orbitals remain in nonbonding, as there are no appropriate orbitals on the metal for the formation of π-bond.

So the available orbitals, both from ligand and metal are T_{2g} set for the π bond formation. The ligands which are participating in π bond formation may be highly electronegative than metal or less electronegative.

Effects of π-bonding on the value of Δ_o

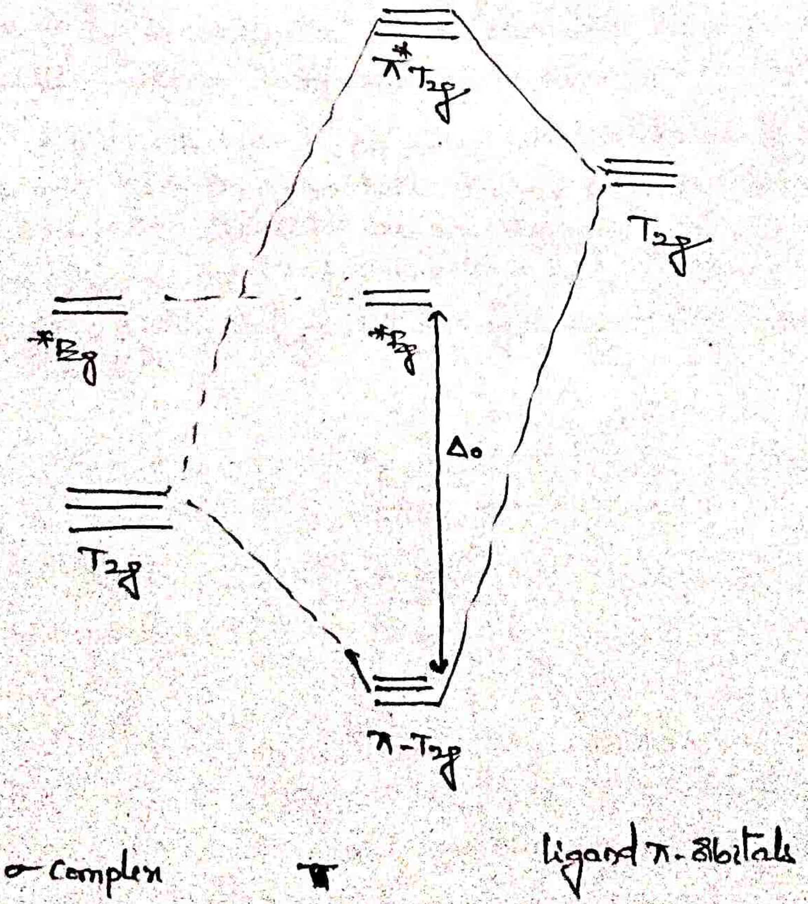
The formation of π-bonding in complexes affects the energy level of the metal T_{2g}-orbitals just as the formation of σ-bonding affects the energy of the E_g-orbitals of the central metal ion. These effects on the energy level of t_{2g} orbitals depend on two factors.

(i) Whether the ligand π-orbitals of T_{2g} symmetry are of higher or lower energy than the metal T_{2g}-orbitals and
(ii) Whether the ligand π-orbitals are filled or empty.

In π-bonding the T_{2g} set of metal will combine with ligand π-orbitals of T_{2g} symmetry to give two sets of triply degenerate Molecular orbitals i.e. T_{2g}-bonding and T_{2g}^* - Antibonding. The ~~formation~~ ~~splitting~~ formation of these bonding and antibonding molecular orbitals can take place in two ways.

(a) <u>Empty (i.e. acceptor) ligand π-orbitals of higher energy than the metal T_{2g}-orbitals.</u>

If the ligand π-orbitals are empty and of higher energy than the metal ion T_{2g} orbitals [i.e. ligand is less electronegative] then the π-bonding orbitals are close to the metal and π-antibonding T_{2g} orbitals are close to ligand group orbitals. The splitting of T_{2g} orbitals into T_{2g}-bonding and antibonding can be shown as follows.



The energy of E_g^* orbitals is unaffected by π-bonding.

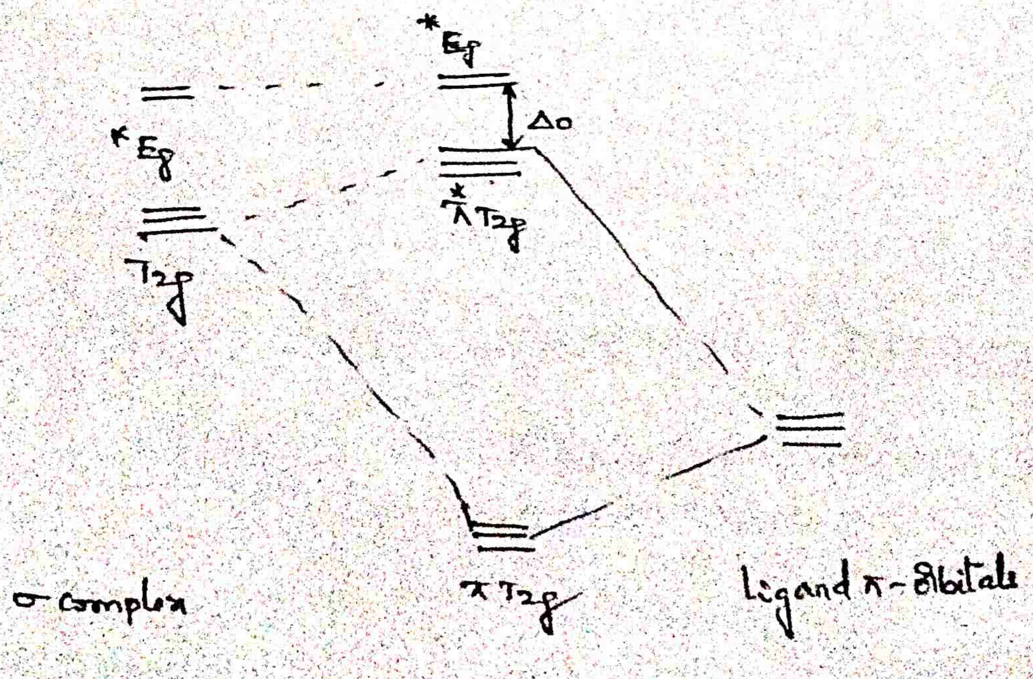
In this case the net result of π-interaction is that the metal T_{2g} orbitals are stabilised relative to the $\overset{*}{E_g}$ MO. The metal ion T_{2g} electrons will go into the T_{2g} bonding molecular orbitals of lower energy than T_{2g}^* molecular orbital and thus the value of Δ_o will be increased. In these complexes, usually the $\overset{*}{T_{2g}}$ orbitals will be empty and ligands exert a stronger field. A ligand of this type is referred to as an acceptor ligand because of the presence of empty π-orbitals in it and the π-bonding established in such a case is referred to as metal to ligand [M→L] π-bonding.

Phosphines, arsines and CO are important ~~exp~~ examples of this type of ligands.

(b) Filled (i.e. donor) ligand π-orbitals of lower energy than the metal T_{2g} orbitals:

If the ligand π-orbitals are filled and of lower energy [i.e. ligand more electronegative] than the metal T_{2g}-orbitals, the splitting of T_{2g} metal orbitals takes place as shown in the diagram. In this case the π-bonding MO's are close to the ligands and antibonding MO's are close to the metal ion or atom. The level of $\overset{*}{E_g}$ is unaffected by π-interaction. This π-interaction results in destabilisation relative to $\overset{*}{E_g}$ MO's and the value Δ_o is decreased.

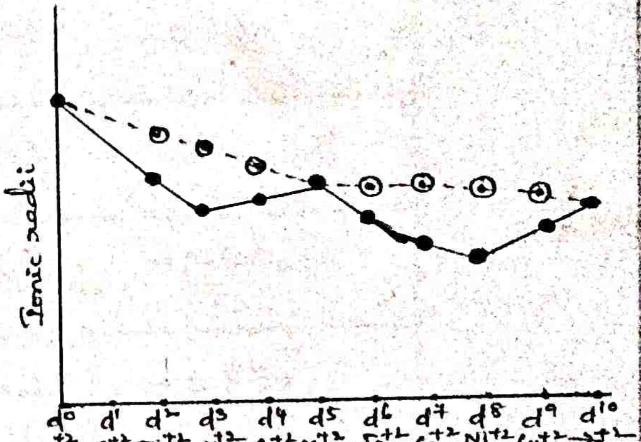
In ligands like F^-, OH^-, Cl^- etc; the 2p orbitals of ligands are filled. These electrons will fill the resultant π-T_{2g} molecular orbitals. The electrons from the 3d (t_{2g}) orbitals of the metal ion are therefore in π^* antibonding orbitals at a higher energy than they would be if π-bonding had not taken place. The ligands in this case exerts a weaker field. A ligand of this type is generally called a donor ligand because of its filled π-orbitals.



Applications of Crystal field theory:

Crystal field theory was successful in explaining the magnetic and spectral properties of complexes. In addition, Crystal field theory provided a basis for understanding and predicting a number of their structural and thermodynamic properties of complexes. Several such properties are ionic radii of transition metal ions, heats of hydration of bivalent ions of first transition series, Lattice energy, spinel and anti-spinel structures.

(i) Ionic radii of transition metal ions: The variation in ionic radii of divalent metal ions of the first transition series in their crystalline compounds can be explained using the concept of crystal field stabilisation energy. The crystalline compounds, MX_2 (metal halides), each metal ion is octahedrally surrounded by six X^- (halide) ions. The ionic radii of the transition metal ions should decrease gradually with increasing nuclear charge without making any consideration of CFSE. Thus the ionic radii for M^{+2} ions are expected to decrease smoothly from Ca^{+2} to Zn^{+2} due to the increased nuclear charge. The actual plot of these ionic radii is given in the diagram and the change in size is not regular. The decrease in size of these ions is regular in case of Ca^{+2}, Mn^{+2} & Zn^{+2} and smooth dotted line is drawn through these ions. The metal ion Ca^{+2}, Mn^{+2} and Zn^{+2} have d^0, d^5 and d^{10} configuration respectively. The CFSE for these ions is zero and they develop spherical field around the nucleus.



→ variation of ionic radii with the number of d-electrons

In Ti^{+2} ion $(t_{2g}^2 e_g^0)$, the two d electrons occupy t_{2g} orbitals of lower energy and this t_{2g} set is oriented in between the ligands. The CFSE is more for Ti^{+2} when compared with Ca^{+2} ion and the electrons are not in the direction of approaching ligands. Thus there is no shielding of the nuclear charge and the ligands are drawn ~~closed~~ closer to the nucleus. As a result, its ionic radius is less than that expected.

In V^{+2} $(t_{2g}^3 e_g^0)$, the effect of Crystal field splitting is more prominent because the t_{2g} set consists of three electrons. The increased nuclear charge has an even greater effect with V^{+2}. Hence ionic radius is less than that of Ti^{+2}.

In Cr^{+2} $(t_{2g}^3 e_g^1)$, the e_g level has one electron. The e_g orbital is oriented in the direction of the ligand. Hence it provides good shielding to the ligands. Therefore, the ligands can

Metal ion (in weak oct field)	Configuration	calculation	CFSE
Ca (II)	$4s^0 3d^0$ $[t_{2g}^0 e_g^0]$	$0(-0{\cdot}4\Delta_o)+0(0{\cdot}6\Delta_o)$	0
Sc (II)	$4s^0 3d^1$ $[t_{2g}^1 e_g^0]$	$1(-0{\cdot}4\Delta_o)+0(0{\cdot}6\Delta_o)$	$-0{\cdot}4\Delta_o$
Ti (II)	$4s^0 3d^2$ $[t_{2g}^2 e_g^0]$	$2(0{\cdot}4\Delta_o)+0(0{\cdot}6\Delta_o)$	$-0{\cdot}8\Delta_o$
V (II)	$4s^0 3d^3$ $[t_{2g}^3 e_g^0]$	$3(-0{\cdot}4\Delta_o)+0(0{\cdot}6\Delta_o)$	$-1{\cdot}2\Delta_o$
Cr (II)	$4s^0 3d^4$ $[t_{2g}^3 e_g^1]$	$3(0{\cdot}4\Delta_o)+1(0{\cdot}6\Delta_o)$	$-0{\cdot}6\Delta_o$
Mn (II)	$4s^0 3d^5$ $[t_{2g}^3 e_g^2]$	$3(-0{\cdot}4\Delta_o)+2(0{\cdot}6\Delta_o)$	0
Fe (II)	$4s^0 3d^6$ $[t_{2g}^4 e_g^2]$	$4(-0{\cdot}4\Delta_o)+2(0{\cdot}6\Delta_o)$	$-0{\cdot}4\Delta_o$
Co (II)	$4s^0 3d^7$ $[t_{2g}^5 e_g^2]$	$5(-0{\cdot}4\Delta_o)+2(0{\cdot}6\Delta_o)$	$-0{\cdot}8\Delta_o$
Ni (II)	$4s^0 3d^8$ $[t_{2g}^6 e_g^2]$	$6(-0{\cdot}4\Delta_o)+2(0{\cdot}6\Delta_o)$	$-1{\cdot}2\Delta_o$
Cu (II)	$4s^0 3d^9$ $[t_{2g}^6 e_g^3]$	$6(-0{\cdot}4\Delta_o)+3(0{\cdot}6\Delta_o)$	$-0{\cdot}6\Delta_o$
Zn (II)	$4s^0 3d^{10}$ $[t_{2g}^6 e_g^4]$	$6(-0{\cdot}4\Delta_o)+4(0{\cdot}6\Delta_o)$	0

For metals ions with d^0, d^5 and d^{10} configurations, the stabilisation energy is zero.

no longer approach so closely and hence the ionic radius increases. The ionic radius of Cr^{+2} is more than that of V^{+2} ion. But it is still smaller than the value expected and is evident from the CFSE of Cr^{+2} ion.

In case of high spin Mn^{+2} $(t_{2g}^{3}e_g^{2})$, each d orbital has one electron. This results in a spherical distribution of charge around the nucleus. Hence the octahedral radius of high spin Mn^{+2} has the value as expected basing on nuclear charge consideration alone.

Similarly, it is possible to explain the ionic radii of Fe^{+2} $[t_{2g}^{4}e_g^{2}]$, Co^{+2} $[t_{2g}^{5}e_g^{2}]$, Ni^{+2} $[t_{2g}^{6}e_g^{2}]$ and Cu^{+2} $[t_{2g}^{6}e_g^{3}]$. In Cu^{+2}, the added electron goes to the e_g set of d-orbital. Hence its ionic radius is greater than that of Ni^{+2} but smaller than that of Zn^{+2}.

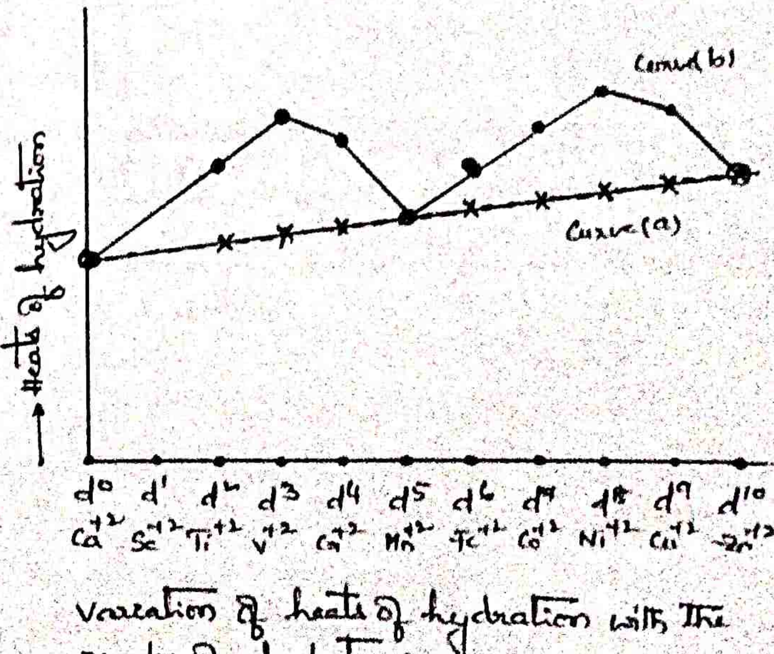
Thus the shape of the curve is explained by the crystal field splitting. If there was no crystal field splitting, then a smooth curve (dotted line from Ca^{+2} to Zn^{+2} through Mn^{+2}) would have been obtained.

(ii) Heats of hydration of bivalent ions of first transition series: Heat of hydration is the heat evolved in the process of hydration.

$$M^{+2}_{(g)} + 6H_2O(l) \longrightarrow [M(H_2O)_6]^{+2} + \text{heat of hydration.}$$

Generally six water molecules enter the co-ordination sphere to form an octahedral aqua complex. The negative sign indicates that the heat is ~~and~~ evolved in the hydration process. ($\Delta H = -ve$)

In the absence of crystal field splitting consideration, the ionic radii of divalent ions of the first rows transition ~~should~~ elements should decrease gradually from Ca^{+2} to Zn^{+2}. Hence the experimental values of heats of hydration of these ions should increase regularly from Ca^{+2} to Zn^{+2}. This is because the decrease in ionic radii values brings the ligand water molecules closer to the metal, M^{+2} ions resulting in the increased electrostatic attraction between the cation and water ligands. But this expected regular increase does not occur and is evident from curve(b) in the adjacent graph.



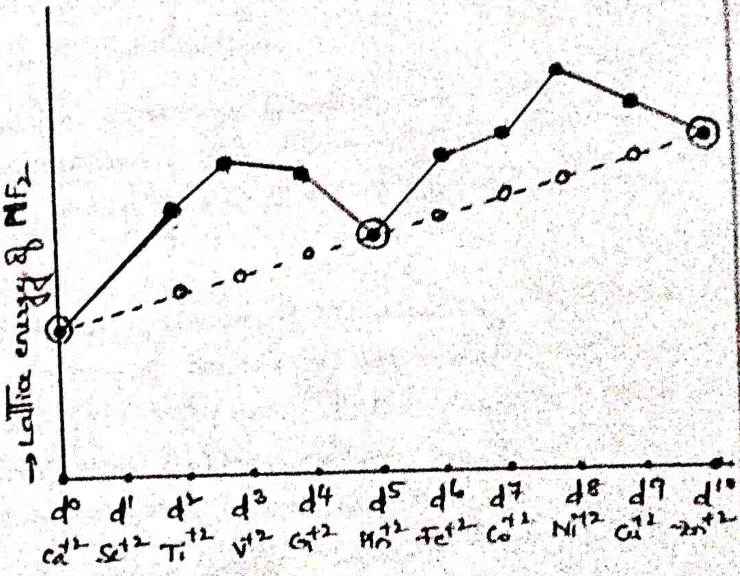
Variation of heats of hydration with the number of d-electrons.

The ions Ca^{+2}, Mn^{+2} and Zn^{+2} have zero CFSE and fall almost on the straight line in curve(a). The position of the other metal ions in curve (b) can be explained basing on CFSE.

The experimental values of hydration energy, instead of increasing regularly, shows maxima at $V^{+2}[t_{2g}^{3} e_g^{0}]$ and $Ni^{+2}[t_{2g}^{6} e_g^{1}]$ and minima at $Ca^{+2}(t_{2g}^{0} e_g^{0})$, $Mn^{+2}(t_{2g}^{3}, e_g^{2})$ and $Zn^{+2}[t_{2g}^{6} e_g^{4}]$. These maxima and minima can be explained by the concept of CFSE. All these hexahydrate ions, $[M(H_2O)_6]^{+2}$ are high-spin octahedral complexes. For high-spin complexes, CFSE is minimum (zero) d^0 $[Ca^{+2}]$, d^5 $[Mn^{+2}]$ and d^{10} $[Zn^{+2}]$ ions. Hence they show minima in the graph. CFSE will be maximum $[1.2\Delta_o]$ for d^3 (V^{+2}) and d^8 (Ni^{+2}) ions. Hence they correspond to maxima in the graph.

(iii) Lattice energy: The lattice energies of the difluorides of transition metals of the first transition series from CaF_2 to ZnF_2, are considered. In crystalline state, these fluorides possess an octahedral arrangement of F^- ions around the M^{+2} metal ions. Since the ionic radii of M^{+2} ions are expected to decrease gradually, their lattice energies should increase gradually. This is because, the lattice energy is inversely proportional to the inter-ionic distance and the radius of the anion is same in all these compounds.

The lattice energies of the fluorides of Ca^{+2}, Mn^{+2} and Zn^{+2} are as expected and almost a straight line can be drawn through the points which indicates the lattice energies of these fluorides. However, the lattice energies of all other bivalent metal fluorides were found to vary irregularly. The irregularity in their variation can be explained basing on CFSE values. The crystal field stabilisation energies are maximum for V^{+2} and Ni^{+2} ions and hence their lattice energies are maximum. The CFSE is minimum for Ca^{+2}, Mn^{+2} and Zn^{+2} ion and their lattice energies are minimum.



Variation of lattice energies with the number of d-electrons.

Evidence for Covalent Bonding in Complexes:

In Valence Bond Theory, it is assumed that the bond between Metal and ligand is a co-ordinate covalent bond and in crystal field theory it is assumed that the bond is entirely electrostatic. These two theories are very useful and successful in explaining the properties of the complexes. However, some covalent nature ~~of~~ in M-L bonds is observed. The experimental evidence for covalent bonding in complexes can be understood from the following areas (1) Optical spectra (2) magnetic susceptibilities (3) NMR spectra and (4) ESR spectra.

(1) optical Spectra:

The electronic absorption bands due to d→d transitions are forbidden ~~due~~ according to Laporte selection rule and should have zero intensity. However these transition are observed with certain intensity. The intensities of these Laporte forbidden Transitions can be accounted by two mechanisms, (1) by the mixing of the d-orbitals with other metal atom orbitals, such as s and p, in those complexes which lack a centre of symmetry, such as tetrahedral ones and/or (2) by interaction of the d orbital wave functions with ~~d~~ odd vibra-tional wave functions ('vibronic' interactions) of the complex ion.

However, the observed spectral intensities in many complex ions cannot be accounted reasonably using any ~~one~~ of these mechanisms. The observed intensities can be accounted reasonably by considering certain overlap of metal ion d-orbitals with various ligand atom orbitals.

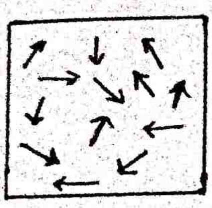
To account for various bands in the electronic spectrum, it is necessary to know about the various possible Russell-Saunders states and the energy separation between them. The energys of each state and energy separation between states depends upon interelectronic repulsion parameters. The separations between states of free metal ion and metal ion in ligand field should be unchanged. Experimentally it was observed that the separation between Russell-Saunders states is small in complexed ion than the free ion. It means that the interelectronic repulsions operative between the d-electrons are decreased in the complexed ion. This decrease of inter-electronic repulsions of d-electrons is possible only with increase in the separation between metal ion d electrons. This increase in the distance between d electrons is possible logically with increase in size of the several d-orbitals. Increase in size of d-orbital or cloud expansion is possible only when metal ion d-orbital overlap with ligand atomic orbitals. This phenomenon is Known as "Nephelauxetic effect" [from the Greek and meaning 'cloud expanding']. The overlap or combination of metal ion d-orbital with ligand atomic orbitals results in the formation of large molecular orbitals. Consequently the distance between the electrons in the d-orbitals increases and interelectronic repulsions decrease. Therefore, the interelectronic repulsions are less in complex ion [B'] when compared with free metal ion [B] i.e. $B' < B$. The interelectronic repulsion parameter [B'] for complex is less than that of a free metal ion [B].

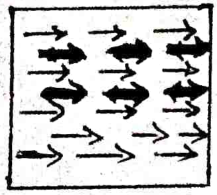
The ratio of B' to B is known as nephelauxetic ratio (β) and is usually less than one.

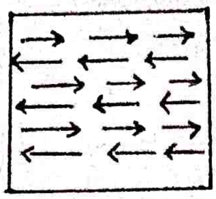
$$\Rightarrow \beta = \frac{B'}{B}$$ and β is generally less than one.

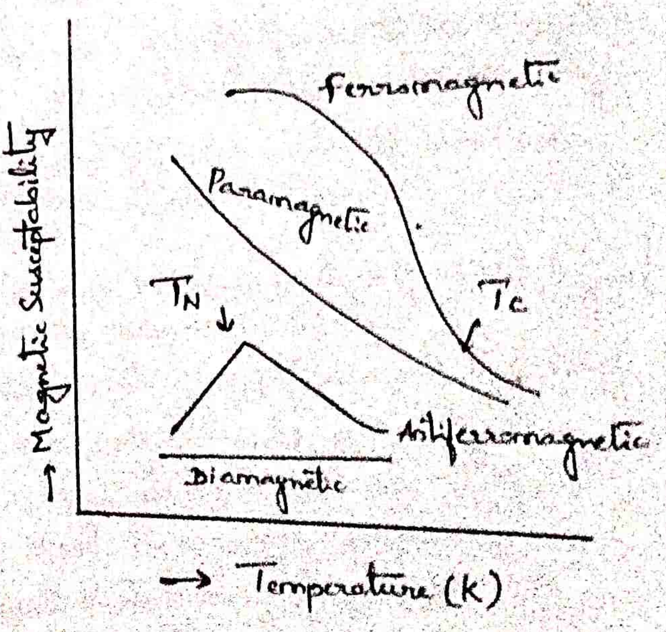
All the ligands do not have equal ability to cause equal extent of cloud expansion and depending on their ability ligands have been arranged in a series known as Nephelauxetic series. For example, the order of increasing ability to produce d cloud expansion is, in part $F^- < H_2O < NH_3 < SO_4^{2-} \sim CN^- < Br^- < I^-$. Similarly the metal ions can also be arranged in a series and ~~these~~ these series measures a tendency towards increasing covalency in the metal-ligand bond.

(2) Magnetic Susceptabilities: The existence of covalent nature in metal-ligand bond can be known from the antiferromagnetic behaviour of certain 'ionic' compounds like metal oxides VO, MnO, FeO, CoO and NiO.


Paramagnetism


~~Paramagnetism~~ ferromagnetism


Antiferromagnetism

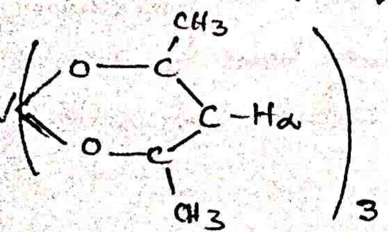


Antiferromagnetic substances follow the curie's law and Curie-weiss law at high temperature and at low temperature is particularly at low temperatures below Neel temperature, exhibit a ~~decreasing~~ increasing magnetic susceptability rather than ~~increasing~~ decreasing magnetic susceptability.

Neutron diffraction ~~stub~~ studies have demonstrated that this effect is not due to pairing of electrons within the individual ions. This decrease is due to the tendency of half of the ions to have their magnetic moments aligned antiparallel to those of the other half of the ions. This alignment can be explained as follows.

Consider the system of metal oxide in which oxide ion is present between two metal ion $M^{+2}-O^{-2}-M^{+2}$. If each metal ion possesses an unpaired electron in a d-orbital that can overlap a filled π orbital on the oxide ion, then it is possible for an electron from the oxygen to move so as to partially occupy that d-orbital. The electron transferred from oxygen must be antiparallel to that of the original d-electron and the other oxide ion π electron must have its spin parallel to that of the d electron. Now if this second electron of oxide moves partially into the d-orbital of the second metal ion, it will force the lone d electron therein to have its spin antiparallel to that of the d-electron on the first metal ion. This tendency of half of the ion to have their magnetic moments aligned antiparallel to those of the other half of the ions is possible only with overlap of metal ion orbitals with oxide π-orbitals.

(iii) NMR Spectra: NMR studies of complexes provided the evidence for the existence of covalent nature in Metal-ligand bond. For example, it is found that the resonance frequency of the ring protons, H_α, in tris (acetylacetonato) vanadium (III) is substantially shifted from its position.



The large shift must be due to the contribution of unpaired electron spin density of V(III) to the π system of the ligand. This contribution is possible only when there is substantially overlap of metal ion d-orbital with ligand atomic orbital.

(iv) ESR Spectra: Experimental evidence for the existence of covalent nature of metal-ligand bond is available from the ESR spectral studies. The ESR spectrum of $IrCl_6^{-2}$ shows a complex hyperfine structure. The hyperfine splitting arises from the interaction of the unpaired electron spin with the nuclear spin of the chlorine nucleus. This interaction is possible only when the Ir ion d orbital overlaps with the chloride ion atomic orbital. ~~such~~ Consequently this overlap results in delocalisation of ~~compaired~~ unpaired d electron of Ir ~~[illegible]~~ ~~into~~ towards chloride ion nucleus.

Similar such experimental evidences are available from NQR and Mössbauer spectroscopy.

Experimental evidence for Pi-bonding in Complexes:

The concept of π-bonding, is very important in complexes because it provides the valuable base to reasonably explain the position of ligands in Spectrochemical series. The concept of pi-bonding is also useful in understanding the ligand substitution reactions of complexes.

The carbon monoxide ligand is a weak lewis base, but forms stable complexes with various transition metal ions. The stability of metal carbonyl complexes depends on the ability of carbon ~~dioxide to~~ monoxide to accept metal electron density into its π^* orbitals. Therefore, carbon monoxide ligand is σ donor (OC → M) and a π acceptor (OC ← M). This synergistic effect increases the strength of metal-carbon bond.

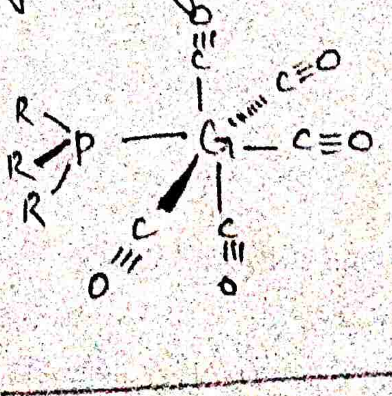
$$M + C\equiv O \longrightarrow \overset{-}{M}-C\equiv \overset{+}{O} \longleftrightarrow M=C=O. \qquad ①$$

A number of experimental evidences are available to prove the existence of π-bonding in metal carbonyls and their derivatives.

Crystallography: The M-CO bonding model described in equation ① suggests that the greater the extent of π bonding, the more the C-O bond will be lengthened and the M-C bond shortened. Thus the measure of C-O bond length of the M-C bond ~~prod~~ provides the evidence for the existence of π-bonding. The crystallographic studies are very much useful in determining the bond lengths.

The measure of metal-carbon bond lengths can be done using crystallographic method. These bonds are very sensitive to corresponding change in bond order. For example, consider methyl derivative of rhenium carbonyl complex. The experimentally determined Re-CO bond distance is 200.4 ± 0.4 pm and this is 24 pm shorter than that predicted for a σ bond only.

Similar evidence is also available from phosphine and phosphite derivatives of hexacarbonylchromium. These are obtained by replacing ~~R3P~~ CO by R_3P in $Cr(CO)_6$. The phosphine ligand is trans to one of the carbon monoxide ligand. The two trans ligands will compete for the same π orbital. Carbon monoxide is a better π acid (π acceptor) than the phosphine. As a result, the Cr-CO bond should be shorter



relative to Cr–COeq and to Cr–CO in $Cr(CO)_6$. The same is evident experimentally i.e. Cr–C bond trans to phosphorus is shorter than Cr–C bond trans to CO. When R is phenyl group Cr–C (trans to P) bond length is 184.4 pm and Cr–C (trans to CO) is 188.0 pm.

Infrared Spectroscopy: IR spectroscopy is an important experimental method for analysing metal carbonyls. In its complexes, carbon monoxide acts as a σ-donor and π-acceptor. The formation of π bond strengthens σ-bond and the formation of σ-bonds facilitates the formation π bond. This bonding mechanism is known as synergic interaction which accounts for M–C bond strength in metal carbonyl and related compounds. The carbon monoxide ligand accomodates the π-bonding electrons in its π^* MO. The presence of electrons in the π-antibonding orbitals of CO results in the reduction of C–O bond order. As a result of π bonding the bond order of Metal–carbon bond increases. The presence of multiple bonds between metal and carbon can be identified from IR stretching frequencies. This is easily achieved by studying the carbonyl stretching frequencies. An increase in the M–C bond order should cause an equal decrease in the C–O bond order and this will cause a drop in the carbonyl stretching frequency.

The CO molecule has a stretching frequency of 2155 cm^{-1}. The CO stretching frequencies of terminal CO groups in neutral metal carbonyls are found in the range 2125–1900 cm^{-1}. The same point is observed in the following three species $Ni(CO)_4$, $[Cd(CO)_4]^-$ and $[Fe(CO)_4]^{-2}$.

Species	C–O bond order	M–C bond order	Sum of bond orders	Carbonyl stretching frequency (cm^{-1})
$Ni(CO)_4$	2.64	1.33	3.97	~2060
$[Co(CO)_4]^-$	2.14	1.89	4.03	~1890
$[Fe(CO)_4]^{-2}$	1.85	2.16	4.01	~1790.

These three species are isostructural and isoelectronic. But there is a gradual increase in the excess negative charge on the metal. The excess charge will increase the extent of M–C back bonding and hence will raise the M–C bond order, consequently a corresponding decrease in C–O bond order is expected. This decrease is reflected in the decrease of carbonyl stretching frequencies. Any effect which decreases C–O bond order should necessarily increase M–C bond order because the two are roughly complementary to each other.

The carbonyl stretching frequency for $Mo(CO)_6$ is 2000 cm^{-1}. If three CO then a band occurs at ~1760 cm^{-1}. groups are replaced by dien, as in $Mo(dien)(CO)_3$ Because dien has no ~~back~~ ability to back accept. Thus if some CO groups are replaced by ligands with negligible back-accepting ability, then these CO groups remaining must accept metal π electrons to a greater extent in order to prevent unfavourable accumulation of negative charge on the metal atom. The decrease in CO stretching frequency indicates an increase in M–C bond order.

The CO stretching frequency, of a carbonyl group bridged between two ~~to~~ metal atoms is around 1850 cm^{-1} and for the carbonyl group bonded to three 3 metal atoms is even lower (1742 cm^{-1}).

<u>Photoelectron Spectroscopy</u>: photoelectron spectroscopy has been used to obtain metal-carbon stretching frequencies for Group VIB carbonyl complexes [eg $Cr(CO)_6$] The $[Cr(CO)_6]$ species on irradiation undergoes ionisation resulting in the formation of $[Cr(CO)_6]^+$. The electron lost in ionisation is from t_{2g} orbital, which of course is the orbital having appropriate symmetry to interact with the π^* orbital of carbon monoxide. the removal of this electrons should weaken the metal-carbon bond and decrease its stretching frequency. The value of M-C stretching frequency of $[Cr(CO)_6]^+$ obtained from the fine structure is 325 cm^{-1} and stretching frequency in neutral $[Cr(CO)_6]$ is observed at 379 cm^{-1}. The reduction being consistent with involvement of the t_{2g} electron in π bonding.