MOLECULAR ORBITAL THEORY

(MOT)

EXTENSION OF (CFT) TO ALLOW FOR COVALENCY

- **CFT** is based on pure electrostatic attraction and explains:
- 1-shape
- 2- spectra
- 3- colour
- 4- magnetic properties

- **Disadvantage:**
- The theory ignores covalent bonding as in:

- *compounds in the zero oxidation state have no electrostatic attraction between metal and ligand, bonding must be covalent.

- ***NMR** and **ESR** show some unpaired electron density on the ligands,suggests sharing of electrons, i,e. covalency

- *Order of ligands in spectrochemical series cannot be explained on electrostatic ground only.

CORRECTION FACTORS APPLIED TO CFT

- **Two factors were applied to allow for covalency arising from the delocalisation of
- (**d** electron) from the metal onto the ligand:

- 1- Factor **B**, (Racah parameter) is introduced for interpretation of spctra.
- If B is reduced below the value of the free metal ion, the d electrons are delocalized on the ligand.

- 2- Factor **K**, is introduced for interprtation of magnetic measurements

MOT INCORPORATES COVALENT BONDING

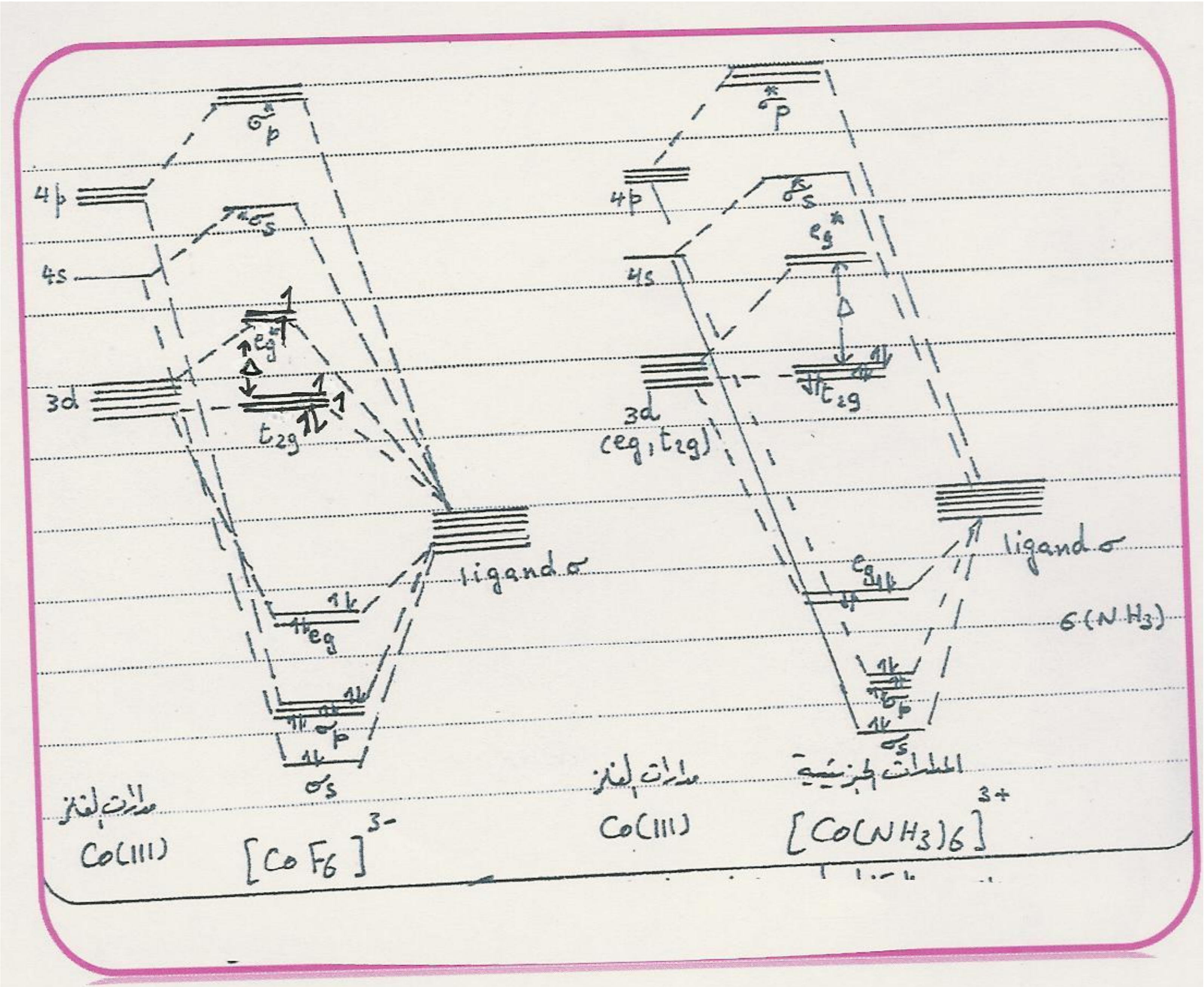
- Molecular orbital theory uses **a linear combination of orbitals** (LCAO) to represent molecular orbitals involving the whole molecule.
- **These are often divided into:**
- 1- **bonding orbitals.**

- **2- anti-bonding orbitals.**

- **3- non-bonding orbitals**

- A **molecular orbital** is merely a Schrödinger orbital that includes several, but often only two nuclei.
- If this orbital is of the type in which the electron(s) in the orbital have a higher probability of being *between* nuclei than elsewhere, the orbital will be a bonding orbital, and will tend to hold the nuclei together.

- **Example: $[Co(NH_3)_6]^{+3}$**
- Electonic configuration of **Co^{3+}** is **$[Ar]3d^6$**
- * The atomic orbitals used to make molecular orbitals are,(**two**) 3d,(**one**)4s, (**three**)4p from(cobalt) and (**six**)2p from NH_3 ligands. **Therefore:**
- ***12** atomic orbitals combine to give **12** molecular orbitals (**6** bonding molecular orbitals and **6** antibonding molecular orbitals)


4p
4s
3d
σ*p
σ*s
e_g*
Δ
t2g
ligand σ
e_g
σp
σs
مدارات الفلز
Co(III)
[CoF6]3-
4p
4s
σ*p
σ*s
e_g*
Δ
t2g
3d
(eg, t2g)
ligand σ
σ(NH3)
e_g
σp
σs
مدارات الفلز
Co(III)
المدارات الجزيئية
[Co(NH3)6]3+

- * The 12 electrons from the 6 ligands are placed
- in the 6 bonding MO.

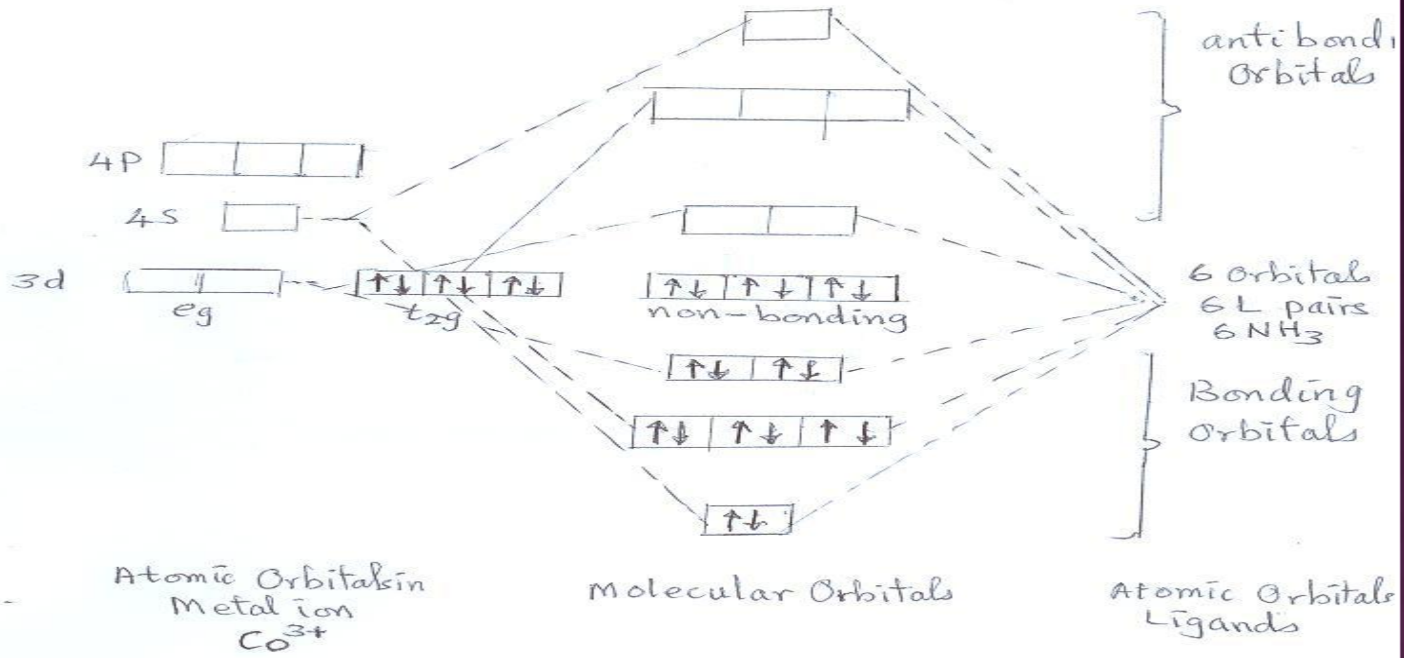
- * **CO^{3+}** has 6 electrons (3 pairs) in **t$_{2g}$** orbitals,

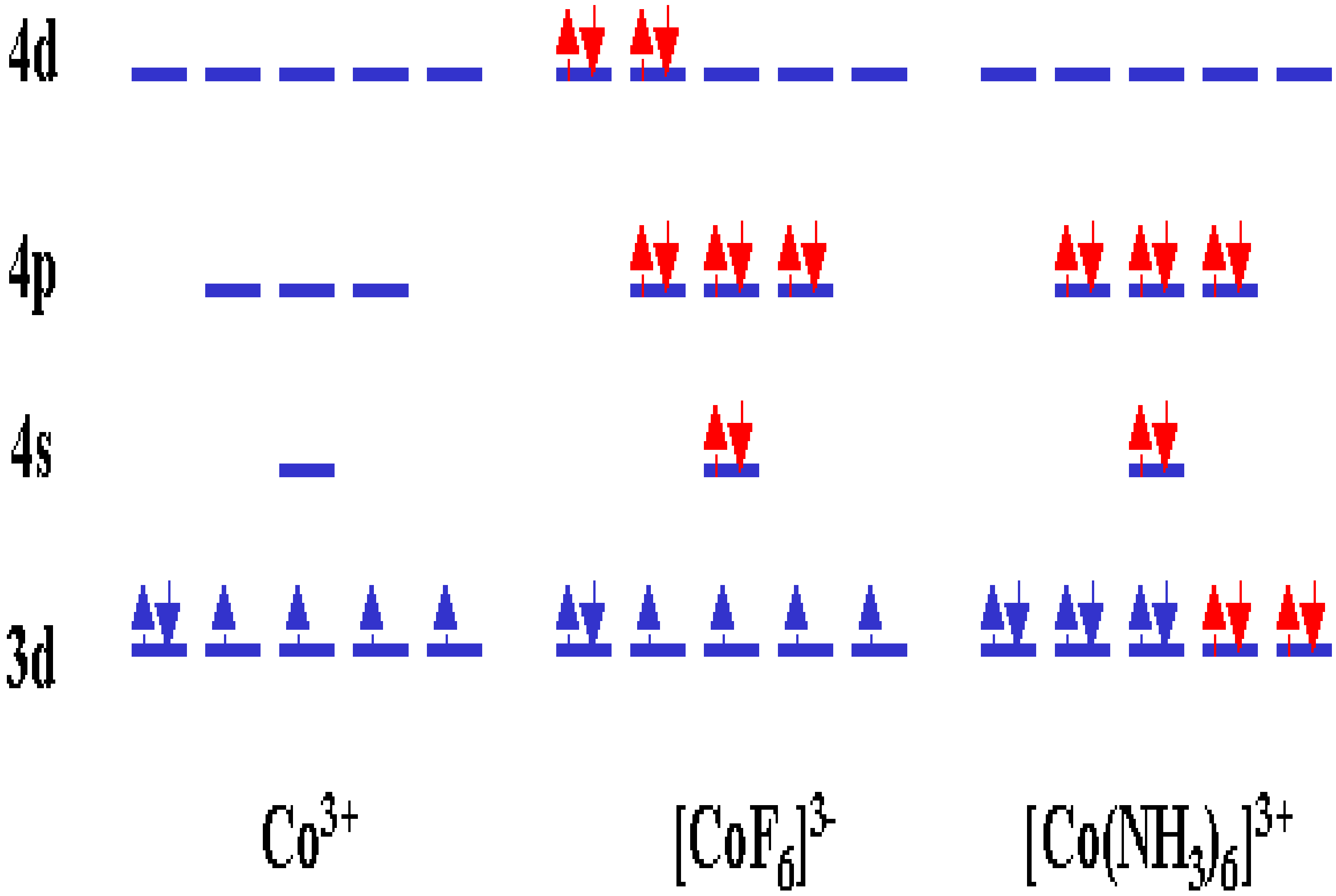
which form non-bonding MO.

*The antibonding molecular orbitals are all

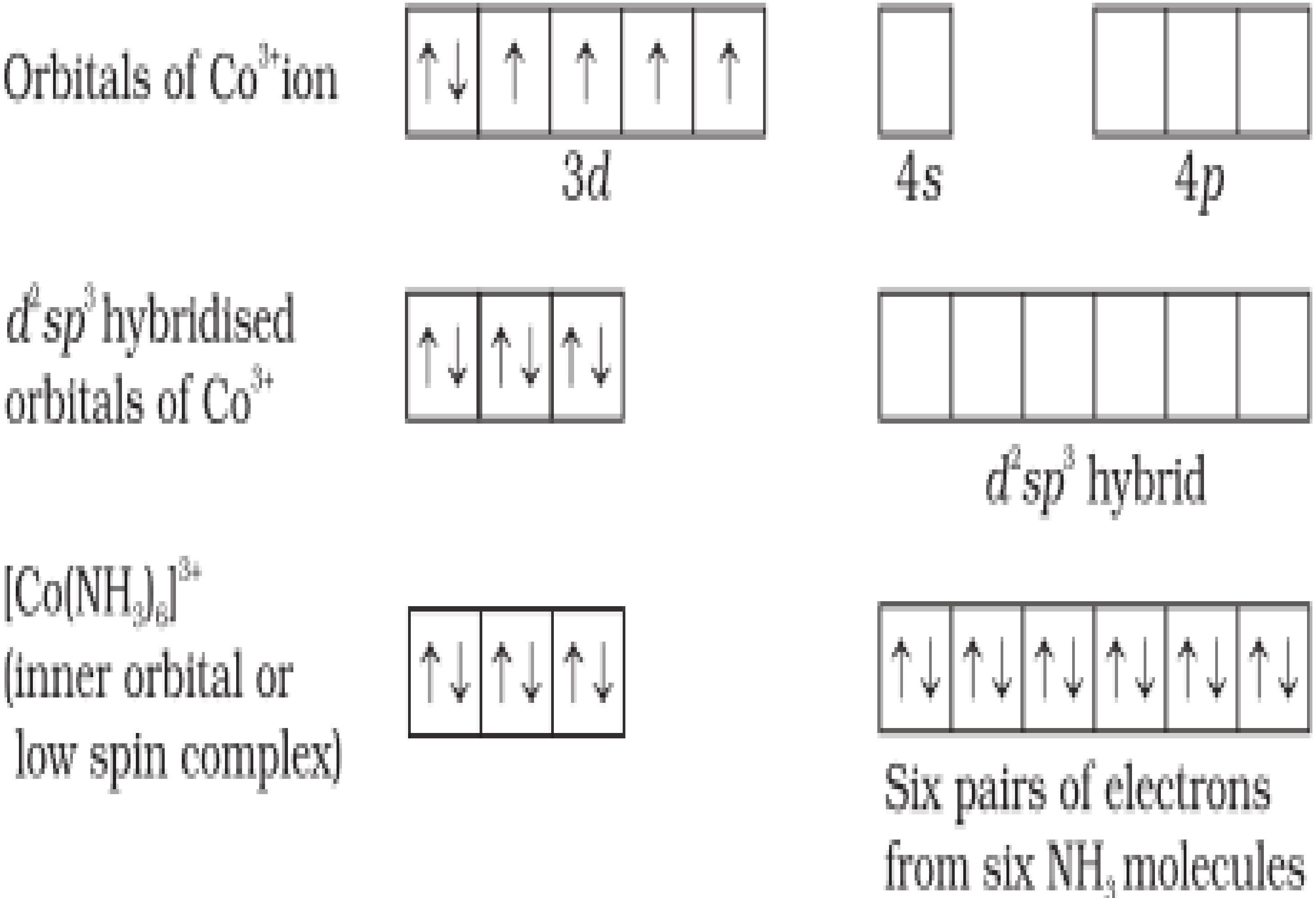
Empty.

The arrangement is shown in **Figures below:**


4P
4S
3d
eg
t2g
non-bonding
antibondi
Orbitals
6 Orbitals
6 L pairs
6 NH3
Bonding
Orbitals
Atomic Orbitals in
Metal ion
Co3+
Molecular Orbitals
Atomic Orbitals
Ligands


4d
4p
4s
3d
Co^{3+}
$[CoF_6]^{3-}$
$[Co(NH_3)_6]^{3+}$

CFT


Orbitals of Co^{3+} ion
3d
4s
4p
d^2sp^3 hybridised orbitals of Co^{3+}
d^2sp^3 hybrid
$[Co(NH_3)_6]^{3+}$ (inner orbital or low spin complex)
Six pairs of electrons from six NH_3 molecules

PREDICTION OF A COMPLEX

- 1- The complex is diamagnetic as all electrons are paired

- 2- The complex should be coloured since promotion of electrons from the non-bonding **t_{2g}** MO to the antibonding **e_g** MO is possible.

- 3- In this example,the energy jump Δ_0 is larger than the pairing energy i,e. $\Delta_0 > P$

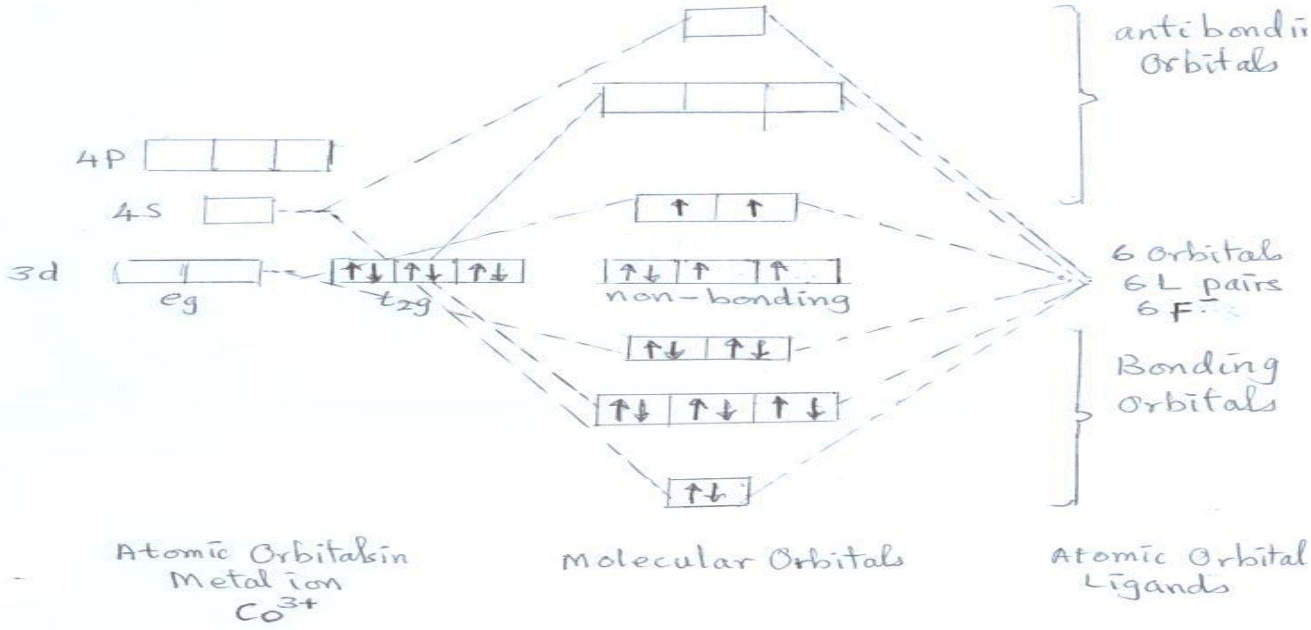
MOLECULAR ORBITALS DIAGRAM

- **Example: $[CoF_6]^{3-}$**
- A simlar molecular orbitals diagram can be drawn for this complex, but the energy of the 2p orbitals on F^- are lower than on N in NH_3.
- * This alter the spacing of the molecular orbitals energy levels.
- * In this example,the energy jump Δ_0 is smaller than the pairing energy i,e. $\Delta_0<P$

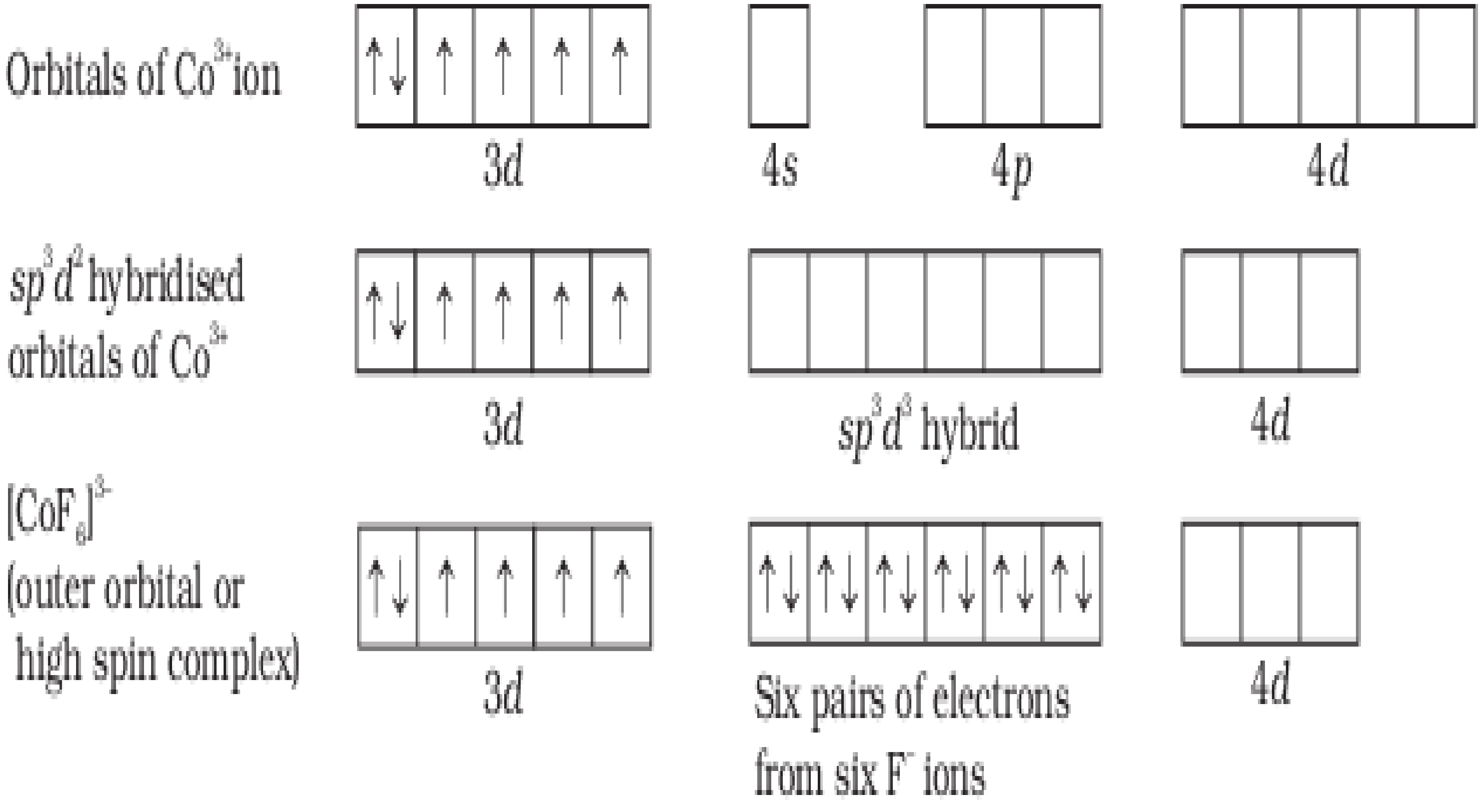
- * The non-bonding d electrons do not pair up as in the complex $[Co(NH_3)_6]^{3+}$, thus:
-
- $[CoF_6]^{3-}$ has 4 unpaired electrons and is
- a high-spin complex.

- $[Co(NH_3)_6]^{3+}$ has no unpaired electrons and
- is a low-spin complex.

- **Therefore the molecular orbital theory explains the spectra and magnetic properties of complexes


antibondi
Orbitals
4P
4S
3d
eg
t2g
non-bonding
6 orbitals
6 L pairs
6 F⁻
Bonding
orbitals
Atomic Orbitalsin
Metal ion
Co3+
Molecular Orbitals
Atomic Orbital
Ligands

CFT


Orbitals of Co3+ ion
↑↓ ↑ ↑ ↑ ↑
3d
4s
4p
4d
sp3d2 hybridised orbitals of Co3+
↑↓ ↑ ↑ ↑ ↑
3d
sp3d2 hybrid
4d
[CoF6]3- (outer orbital or high spin complex)
↑↓ ↑ ↑ ↑ ↑
3d
↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓
Six pairs of electrons from six F- ions
4d

DISADVANTAGES OF A MOT

- The **MOT** is based on wave mechanics, therefore:
- 1- Bond energies, and
- 2- Enthalpies of formation
- **CANNOT BE CALCULATED DIRECTLY**

ADVANTAGES OF MOT

- 1- Considered covalency

- 2-Considered **π bonding** in addition to σ bonding.

- **π bonding helps to explain:**
- 1- the position of some ligands in the spectrochemical series.

- 2- how metals in low oxidation state $[Ni(CO)_4]$can form complexes (cannot be explained using **CFT**)

Π BONDING HELPS TO EXPLAIN:

- 1- how metals in low oxidation state $[Ni(CO)_4]$can form complexes (cannot be explained using **CFT**)
-
- It is impossible to explain any attractive forces using the **CFT**, because of the lack of charge on the metal.

Π BONDING HELPS TO EXPLAIN:

- 2- the position of some ligands in the spectrochemical series.
- **There are two cases:**
- **a-** The ligand acts as π acceptor, accepts electrons from the metal.
- **Examples: CN^-, CO, NO^+**
- The ligand has empty **π** orbitals with the correct symmetry to overlap with the metal t_{2g} orbitals to form **π** bond, called (**back bonding**). The energy of the ligand orbitals is higer than the energy of metal orbitals, hence(**strong field ligand**)

Π BONDING HELPS TO EXPLAIN:

- **b-** The ligand acts as **π** donor, transfer charge to the metal in **π** interaction as well as **σ** interaction.
- Such a bond occurs in oxoions of metals in high oxidation state (**is short of electrons**)

- **Examples: $[MnO_4]^-$, $[CrO_4]^{2-}$**
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- The energy of the ligand orbitals is lower than the energy of metal orbitals, hence (**weak field ligand**)
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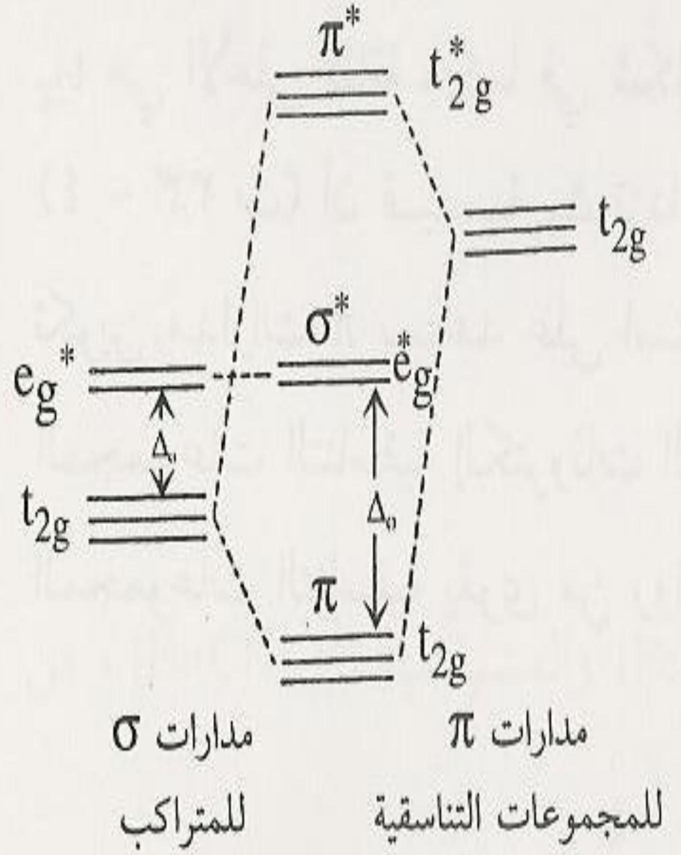
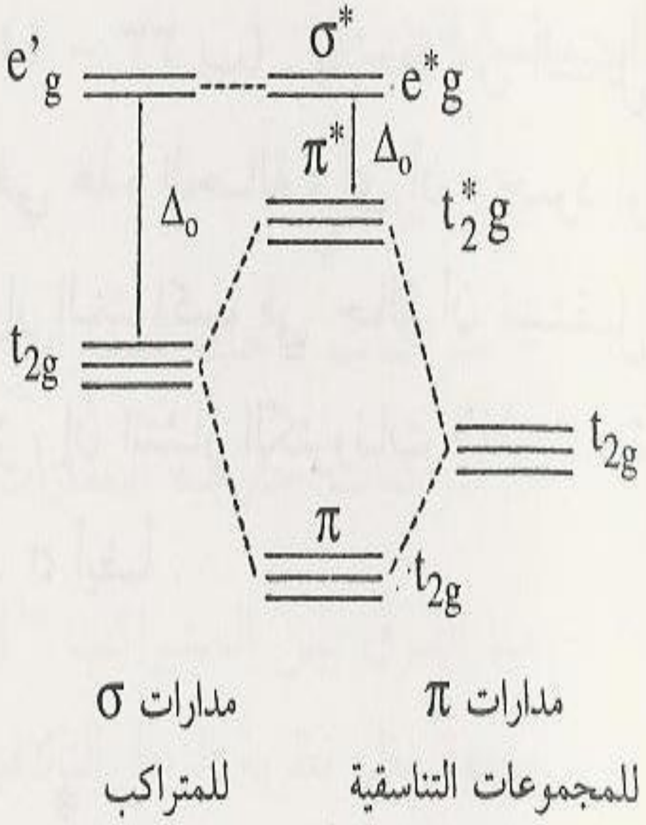

π*
t*2g
t2g
σ*
eg*
e*g
Δo
Δo
t2g
π
t2g
مدارات σ
للمتراكب
مدارات π
للمجموعات التناسقية

A


e'g
σ*
e*g
π*
Δo
Δo
t*2g
t2g
t2g
π
t2g
مدارات σ
للمتراكب
مدارات π
للمجموعات التناسقية

B