# 5. Chemical bonding theories in complex combinations

## Electronic valence theory in complex combinations

- Interpreting the chemical bond in complex combinations based on electronic valence theory, through the prism of electrovalence or covalence, means reducing this bond to either the ionic or covalent type.

- In complex combinations, as in simple combinations, purely ionic or purely covalent bonds are only borderline, purely theoretical cases. But, each bond has a certain degree of covalency and a certain degree of ionicity.

- Dealing with the relationship between the structure and properties of complex combinations can only be done by considering both types of interactions. Thus, two models were developed:
1. **The electrostatic model**, based on:
    a) pre-quantum electrostatic theory
    b) polarization theory
2. **Covalent model**

# Electronic valence theory in complex combinations

**1. Electrostatic model**

*a) Pre-quantum electrostatic theory*

- **Kossel** and **Magnum** admitted the existence of an electrostatic interaction between the central metal ion and the ligand.

- *Through the interaction of oppositely charged ions, the most stable systems that result are not those in which an ion with n positive charges coordinates n monovalent ions. It is not the neutral molecule that would be the most stable system, but the complex ions that result from this molecule.*

- Kossel gave an energetic foundation to the coordination. The following simplifying assumptions were used in his calculations:
    1. Ions are like rigid, non-deformable spheres;
    2. Only coulombic forces are exerted between ions;
    3. In the stable configuration of the system under consideration, the ions touch or are at minimum distance from each other.

# Electronic valence theory in complex combinations
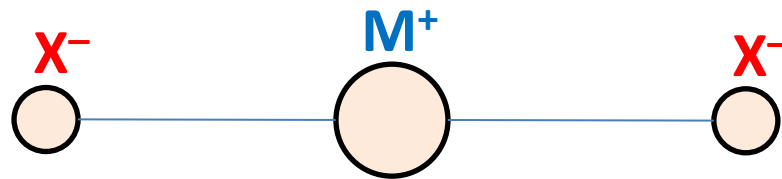
## 1. Electrostatic model
### a) Pre-quantum electrostatic theory

- For an **Mx-type** molecule, where the radii of the two ions are $r_M$ and $r_X$, respectively, the energy has the following expression:

$$E = -\frac{e^2}{d} \qquad \text{where } d = r_M + r_X$$

- For a complex ion of type **[MX$_2$]$^-$**, the potential energy has the following expression:

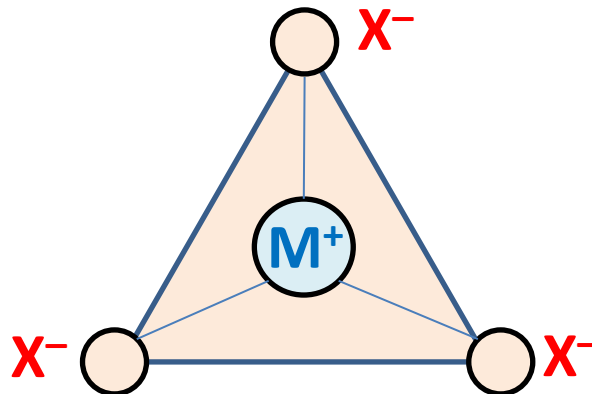$$E = -\frac{2e^2}{d} + \frac{e^2}{2d} = -1{,}5\frac{e^2}{d}$$

# Electronic valence theory in complex combinations

## 1. Electrostatic model

### a) Pre-quantum electrostatic theory

- For a complex ion of the type **[MX₃]²⁻** it is assumed, for symmetry reasons, that the negative **X-**ions arelocated at the vertices of an equilateral triangle, in the centre of which is located the metal ion **M+.** The potential energy of this system has the following expression:

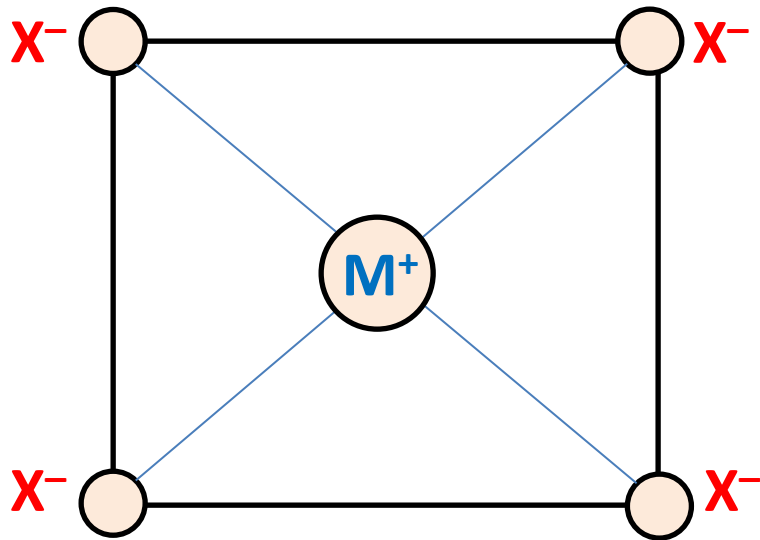$$E = -\frac{3e^2}{d} + 3 \cdot \frac{e^2}{\sqrt{3}d} = -1{,}268\frac{e^2}{d}$$

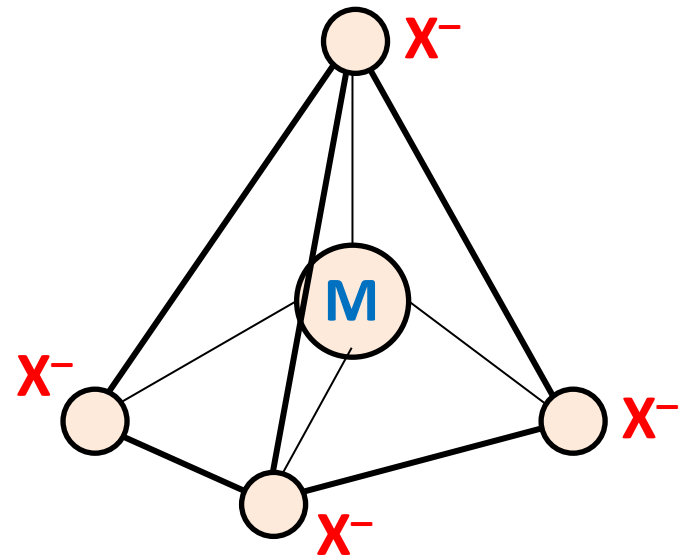# Electronic valence theory in complex combinations

## 1. Electrostatic model

### a) Pre-quantum electrostatic theory

- In the case of **[MX$_4$]$^{3-}$** complex ions, there are two possible arrangements of ligands around the central metal ion:
  - a) *arrangement in the same plane* (at the vertices of a square);
  - b) *arrangement in space* (at the vertices of a tetrahedron).

$$E = -0{,}172\frac{e^2}{d}$$

$$E = -0{,}329\frac{e^2}{d}$$

# Electronic valence theory in complex combinations

**1. Electrostatic model**
*a) Pre-quantum electrostatic theory*

- When the metal ion coordinates five or six negative ions, the potential energy has a positive value.

- Comparing the formation energies for the series of complexes shows that the most stable ions are those of the **[MX$_2$]$^-$** form, followed by the **[MX$_3$]$^-$** form. Both systems have a lower potential energy than that of the simple **MX** molecule.

- Electrostatic theory has the merit of having predicted the structure and stability of complex ions as a classical energetics problem.

- Using this theory, it has been established that *for tetracoordinate combinations the most favourable conformation is the tetrahedral one, and the octahedral conformation is preferred by hexacoordinate combinations.*

# Electronic valence theory in complex combinations

## 1. Electrostatic model

### b) Polarisation theory

- On the basis of prequantum electrostatic theory, a number of experimental facts could not be explained, such as:
  a) the preference of metal ions for certain ligands;
  b) the ability observed in metals with different electronic coatings to form complex combinations.

- *D-type* metal ions, which have $18e^-$ or incomplete shells with very good polarization properties, are characteristic complex generators.

- Metal ions of *s-* or *p-type*, which have $8e^-$ shells, have a reduced polarising action; as a result, they have a lower tendency to form complex combinations.

# Electronic valence theory in complex combinations

## 1. Electrostatic model
### b) Polarisation theory

- The attraction between the central metal ion and a molecule depends on the strength of the electric field created by the metal ion and the total momentum of that molecule.

- The total momentum of the coordinated molecule is determined by its permanent momentum P and the momentum induced p in the molecule by the field created by the metal ion: **M = P + p**

- The momentum induced in a given molecule is determined by the strength of the electrostatic field E created by the central ion and the polarizability α of the molecule: **p = α·E**. Thus, the total momentum is: **M = P + α·E**.

- **Polarisation interactions can explain the preference of metal ions with different configurations to coordinate different molecules, such as water (H2O), ammonia (NH3), etc.**

# Electronic valence theory in complex combinations

## 1. Electrostatic model
### b) Polarisation theory

- The dipole moment of water is 1.84 D and that of ammonia is 1.48 D. The deformability (polarisability) of ammonia is much higher than that of water.

- This explains why, under the conditions created by an ion with a large number of electrons in its shell, the induced momentum of ammonia is higher than that of water. As a result, the total momentum of ammonia in an electric field created by a metal ion with a large number of electrons in its shell can become larger than the total momentum of water.

- Metal ions with rare gas electron shells will preferably coordinate with water, forming stable hydrates, because under these conditions the contribution of the induced momentum to the total momentum is smaller. The other metal ions, which create strong external electric fields, will preferably coordinate ammonia.

# Electronic valence theory in complex combinations

## 2. Covalent model

- **Lewis**, in his theory of how a covalent bond is made by a pair of electrons, showed that this can also be extended to explain how complex combinations are formed.

- In contrast to the fundamental scheme of covalent bond formation, in which each atom participates with one electron in the bond, **Sidgwick** considers that *in the metal-ligand bond the electron pair is given only by the ligand.* This is therefore a ***covalent-coordinating bond***.

- In this way, the formation of complex combinations has been explained by the tendency of the central metal ion to form a stable combination through metal-ligand bonding.

- Sidgwick postulates that *the central metal atom will bind as many ligands as it needs to make a number of electrons equal to the number of electrons of the nearest rare gas*. This number represents the ***effective atomic number ($Z_{ef}$)*** of the metal atom under consideration.

# Electronic valence theory in complex combinations

## 2. Covalent model

**Examples of actual atomic number calculations:**

- $[Co(NH_3)_6]^{3+}$
  $Z_{Co} = 27$; $Z_{Co(3+)} = 27 - 3 = 24$; each donor atom - 1 pair of $e^-$
  $Z_{ef} = 24 + 6 \cdot 2 = 36 = Z_{Kr}$

- $[Fe(CN)_6]^{4-}$
  $Z_{Fe} = 26$; $Z_{Fe(2+)} = 26 - 2 = 24$; each donor atom - 1 pair of $e^-$
  $Z_{ef} = 24 + 6 \cdot 2 = 36 = Z_{Kr}$

- $[Mo(CO)_6]$
  $Z_{Mo} = 42$; each donor atom - 1 pair of $e^-$
  $Z_{ef} = 42 + 6 \cdot 2 = 54 = Z_{xe}$

The theory is, however, insufficient to explain the differences between the physical and chemical properties of these combinations, which is why it has not been widely used. It does, however, have the merit of highlighting the existence of covalent elements.

# Quantum theories of covalent-coordinate bonding

- Three main methods have been developed for the correct treatment of chemical bonding and for explaining the fundamental properties of complex combinations:
  1. **valence bond method** (VBM) - Pauling;
  2. **crystal field theory** (CFT) - Bethe & Van Vleck;
  3. **molecular orbital method** (MOM) - Mülliken.

- If CFT considers complex combinations as ionic, VBM and MOM consider them as covalent. However, the three theories are not totally opposed to each other, but complement each other.

- This allowed the development of a unified model for the treatment of binding in complex combinations, called **ligand field theory** (LFT), which resulted from combining the ideas of Bethe and Van Vleck with the ideas of Mülliken. This method seems to be the most suitable for studying complex combinations.

# Quantum theories of covalent-coordinate bonding

## *1. Valence bond method (VBM)*

- VBM is based on the idea that the metal-ligand bond in a complex combination is a two-electron bond, the number of metal-ligand bonds being equal to the coordination number of the central metal ion.

- The atomic orbitals of the metal ion participating in the formation of covalent bonds must be equivalent and differ only in their orientation in space.

- In order for these orbitals to be equivalent, Pauling assumed that *the central metal ion does not participate in bond formation with pure orbitals (s, p, d, f), but with small, hybrid orbitals,* which can be described by linear combinations of orbital wave functions corresponding to pure orbitals.

- Each hybrid orbital accepts a pair of electrons from the ligand, resulting in a σ valence bond.

# Quantum theories of covalent-coordinate bonding

## 1. Valence bond method (VBM)

- Unlike ordinary covalent σ bonds, the σ bond in complex combinations is a **donor-acceptor bond**. The ligand, which provides the bonding electrons, is the **donor** and the central metal ion is the **acceptor** (M ← L).

- Pauling's theory can explain some properties of complex combinations, such as their stability and magnetism.

- In combination with weaker or strongly electronegative donor ligands, metal-ligand bonding is achieved by electrostatic interactions. In these combinations, since there is no need to hybridise atomic orbitals, the electron distribution remains the same in the complex as in the free ion.

- Based on the idea that the focus is on hybridisation, Pauling believes that this process depends on the electronic structure, the nature of the ligands and the nature of the metal ion.

# Quantum theories of covalent-coordinate bonding

## 1. Valence bond method (VBM)

**$[Cr(H_2O)_6]^{3+}$ -** hexaaquachromium ion *(III)*

Cr (Z = 24): [Ar] $3d^5 4s^1$

$Cr^{3+}$ (Z = 21): [Ar] $3d^3$
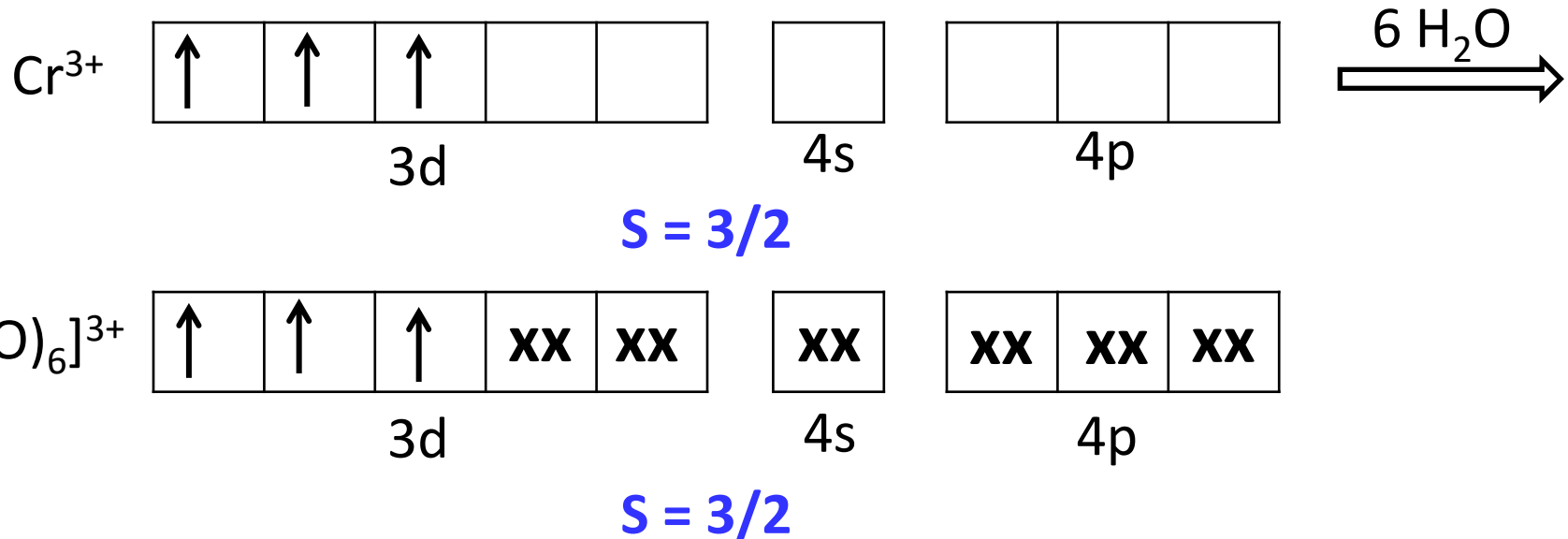


$Cr^{3+}$ 

3d        4s        4p        6 $H_2O$

**S = 3/2**

$[Cr(H_2O)_6]^{3+}$

3d        4s        4p

**S = 3/2**

*d2sp3 hybridization*

# Quantum theories of covalent-coordinate bonding

## 1. Valence bond method (VBM)

$[Fe(CN)_6]^{4-}$ - *hexacyanoferrate ion(II)*

Fe (Z = 26): [Ar] $3d^6 4s^2$

$Fe^{2+}$ (Z = 24): [Ar] $3d^6$
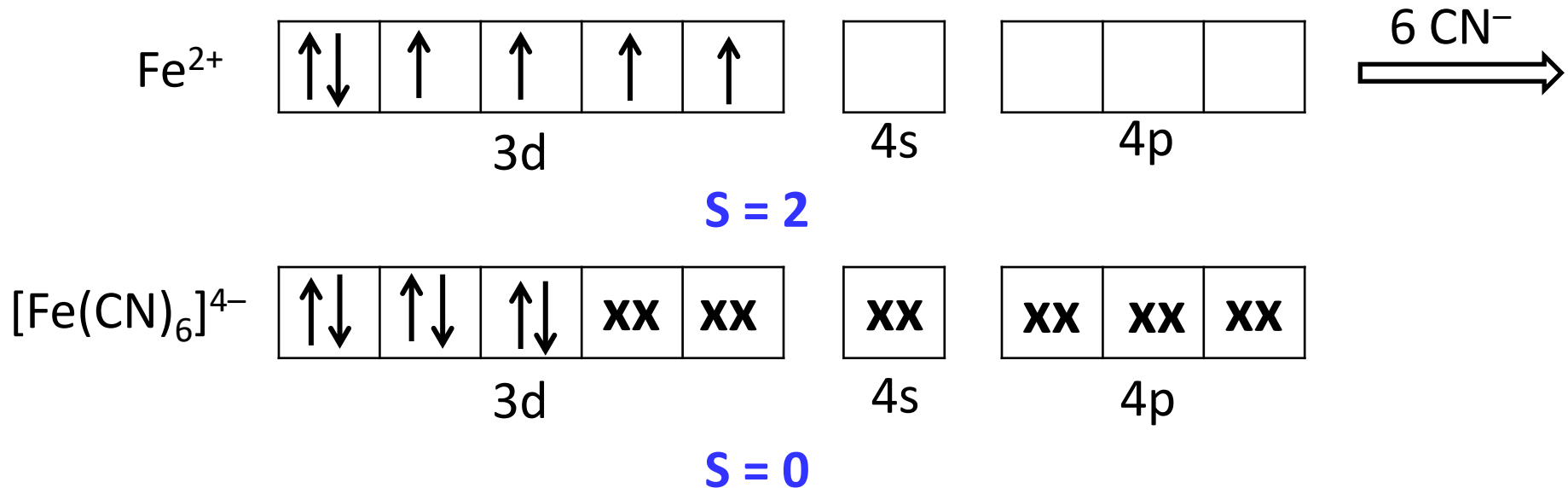


**d2sp3 hybridization**

# Quantum theories of covalent-coordinate bonding

## 1. Valence bond method (VBM)

**$[NiCl_4]^{2-}$** - *tetrachloronichelate ion(II)*

Ni (Z = 28): [Ar] $3d^8\ 4s^2$

$Ni^{2+}$ (Z = 26): [Ar] $3d^8$
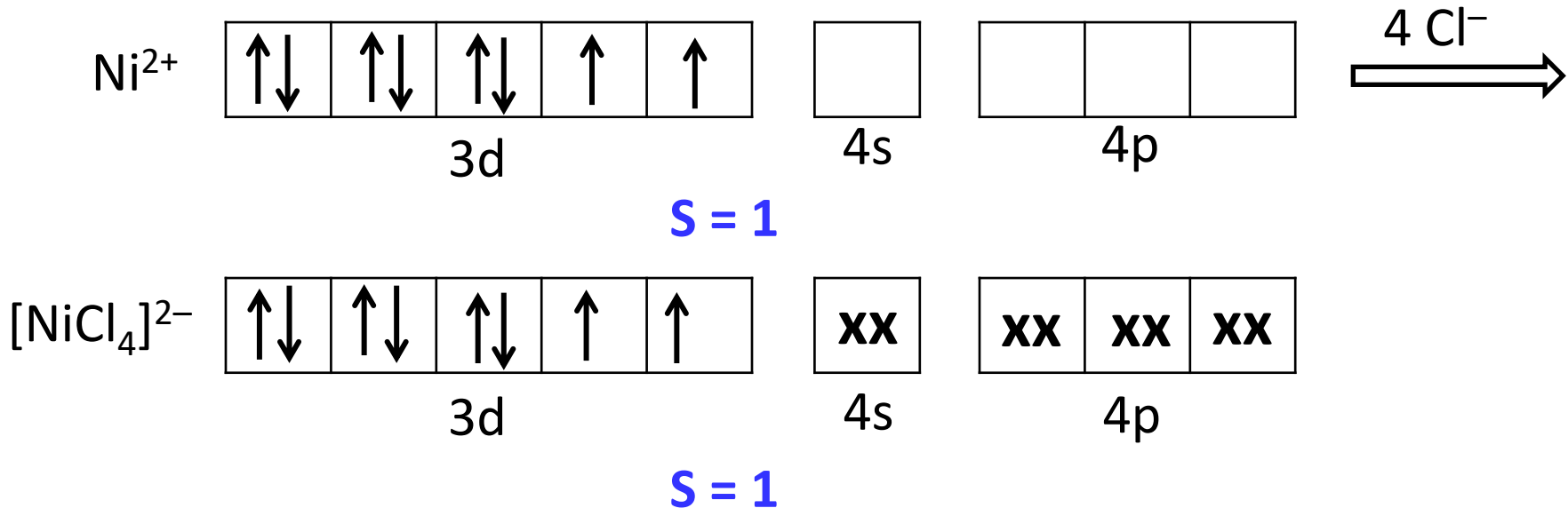


sp3 hybridization

# Quantum theories of covalent-coordinate bonding

## 1. Valence bond method (VBM)

- In the formation of the σ-bond, among the $d$ orbitals, only $d_{z^2}$ and $d_{x^2-y^2}$ participate. The $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals cannot participate in bond formation because of their orientation at 45⁰ to the metal-ligand bond. These are, however, conveniently oriented to form π bonds with the $p$ or $d$ orbitals of the ligands.

- To form π-bonds (when the ligand is the acceptor), it is necessary that the ligand has suitable orbitals in which to accept electrons from the metal ion (M → L).

- The π-bonding has the effect of strengthening the metal-ligand bond, which increases the stability of the complex combination by decreasing the negative charge accumulated on the metal ion as a result of coordination. This explains the high stability of some metal carbonyls (since the CO molecule is a weak base and has low polarisability), such as $[Ni(CO)_4]$, $[Fe(CO)_5]$, $[Mo(CO)_6]$.

# Quantum theories of covalent-coordinate bonding

## 2. Crystal Field Theory (CFT)

- CFT is an electrostatic model that shows that the *d* orbitals of the central metal ion, in a complex combination, are not degenerate but split into two or more states.

- According to CFT, all interactions between a central metal ion and its chemical vicinity are exclusively electrostatic.

- The metal ion and ligands are reduced to point charges and the covalent interaction between them is neglected.

- The role of ligands is to produce an electric field, called the **crystal field**, which destroys the spherical symmetry of the free ion.

- The nature of the *d-orbital* splitting depends on: the coordination symmetry, the number of *d-electrons* of the metal ion and the nature of the ligand.

# Quantum theories of covalent-coordinate bonding

## 2. Crystal Field Theory (CFT)

the non-participating electron pair of the ligand is modelled as a point negative charge

Ligand

repulsion
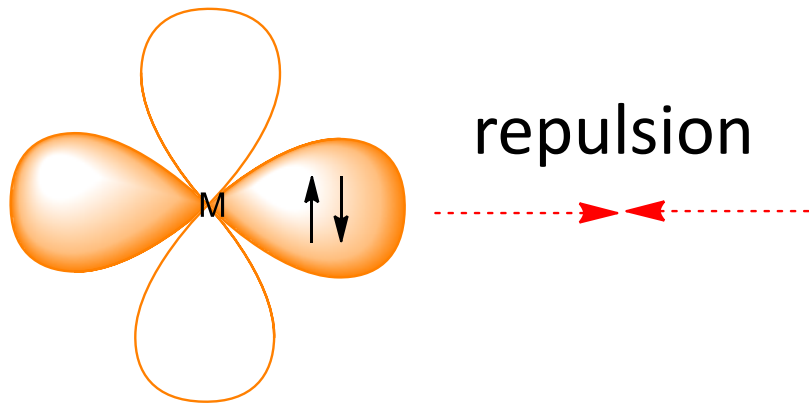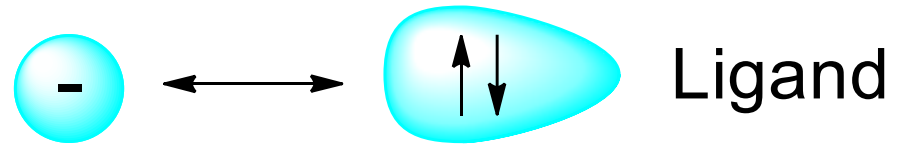
these negative point charges repel electrons from the $d$ orbitals of the central metal ion

# Quantum theories of covalent-coordinate bonding

## 2. Crystal Field Theory (CFT)

### Splitting of *d-orbitals* in octahedral field
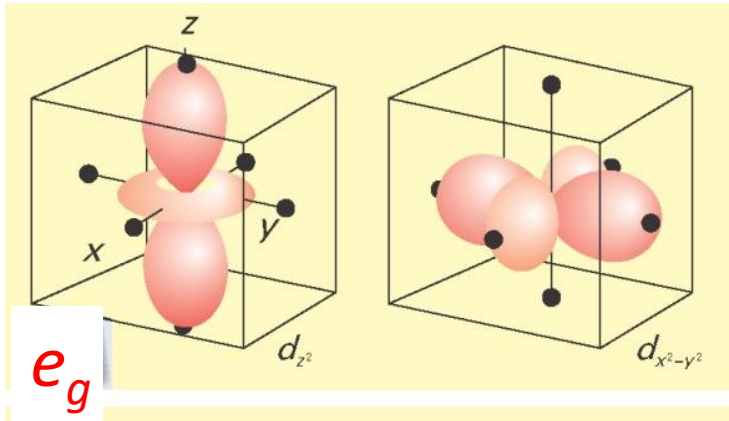


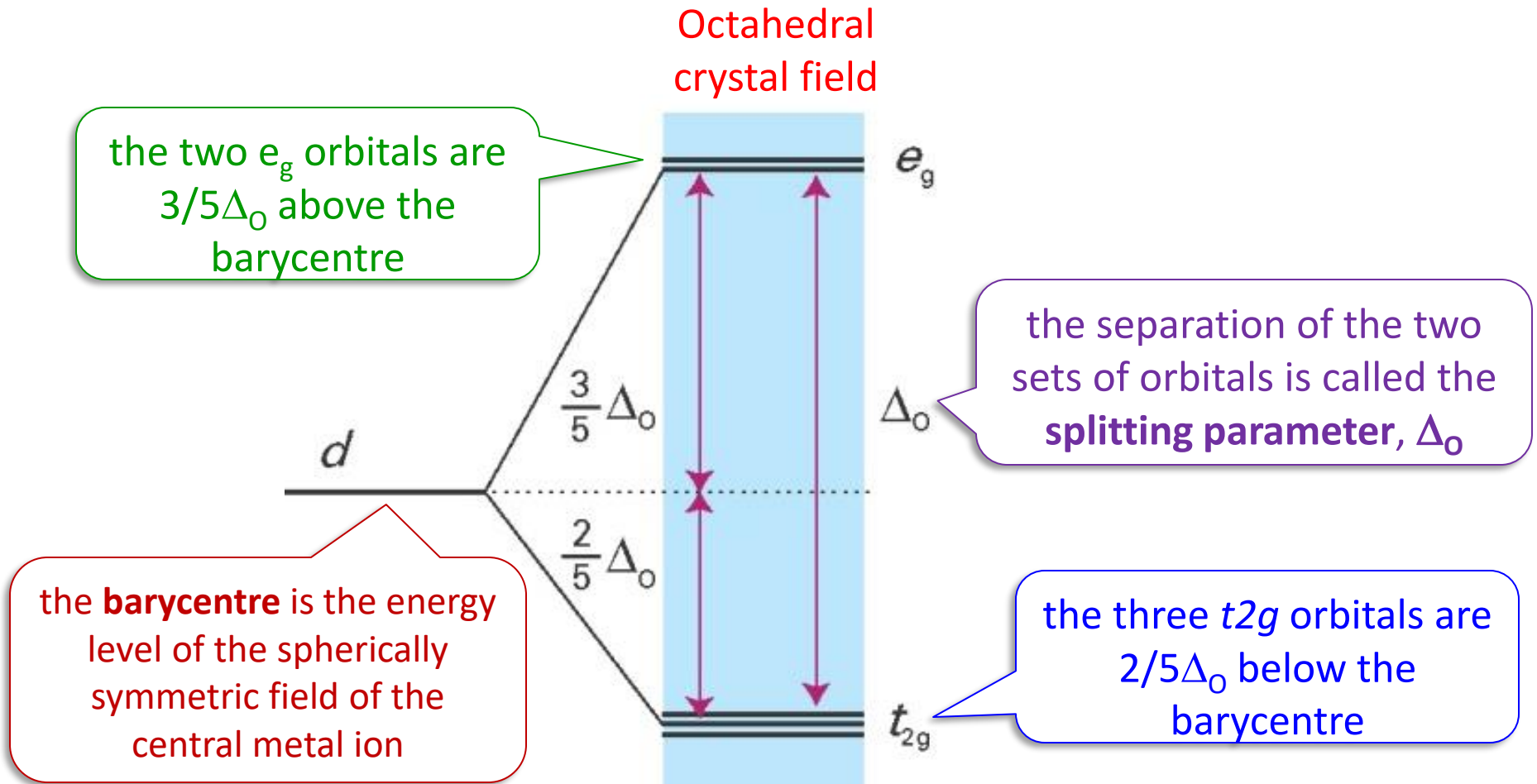the electrons in the $e_g$ orbitals are concentrated close to the ligands that are approaching
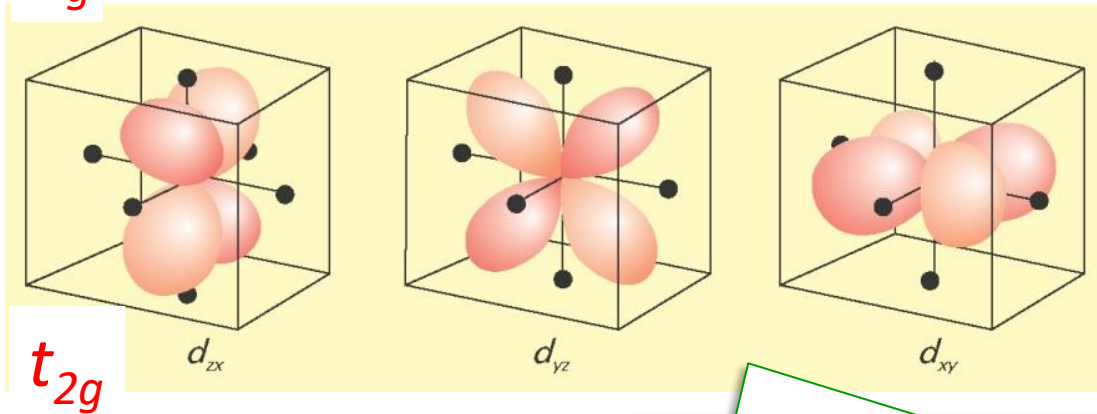
...so the electrons in $e_g$ are more strongly repelled than those in *t2g* and are at a higher energy

electrons in *t2g* orbitals are in the regions between ligands...

# Quantum theories of covalent-coordinate bonding

## *2. Crystal Field Theory (CFT)*

### Splitting of *d-orbitals* in octahedral field

Octahedral crystal field

the two $e_g$ orbitals are $3/5\Delta_O$ above the barycentre

the separation of the two sets of orbitals is called the **splitting parameter**, $\Delta_O$

$e_g$

$\frac{3}{5}\Delta_O$

$\Delta_O$

$d$

$\frac{2}{5}\Delta_O$

$t_{2g}$

the **barycentre** is the energy level of the spherically symmetric field of the central metal ion

the three *t2g* orbitals are $2/5\Delta_O$ below the barycentre

# Quantum theories of covalent-coordinate bonding

## 2. Crystal Field Theory (CFT)

### Splitting of *d-orbitals* in tetrahedral field



$t_{2g}$

$d_{zx}$    $d_{yz}$    $d_{xy}$
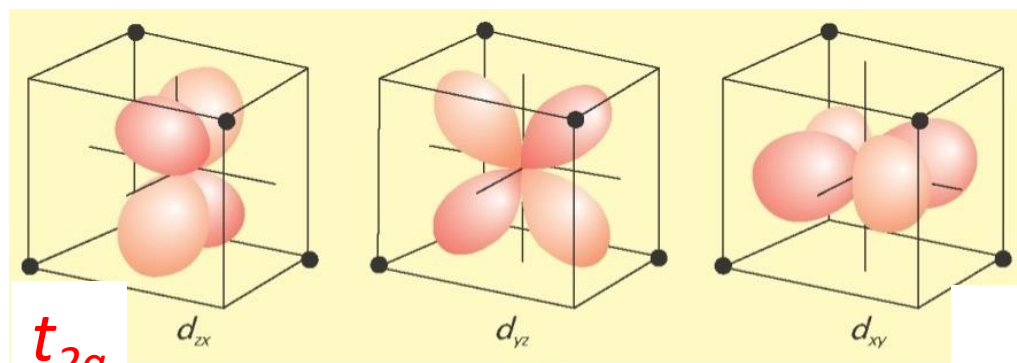
in a tetrahedral complex the *t2g* orbitals point more directly to the ligands

$e_g$

$d_{z^2}$    $d_{x^2-y^2}$
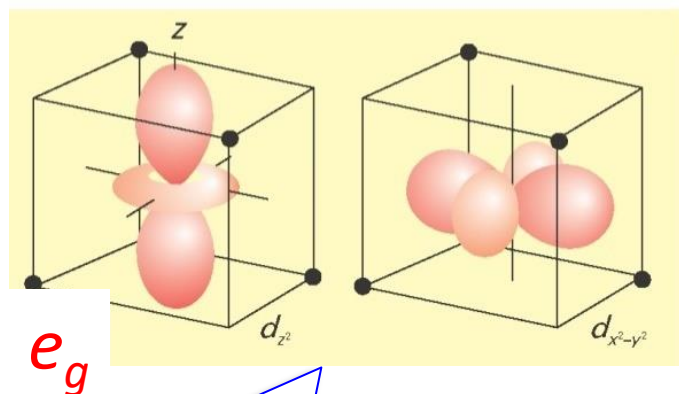
...while the $e_g$ orbitals orient themselves between the ligand positions and their negative partial charges

$d$

$\frac{2}{5}\Delta_T$

$\frac{3}{5}\Delta_T$

$t_{2g}$

$e_g$
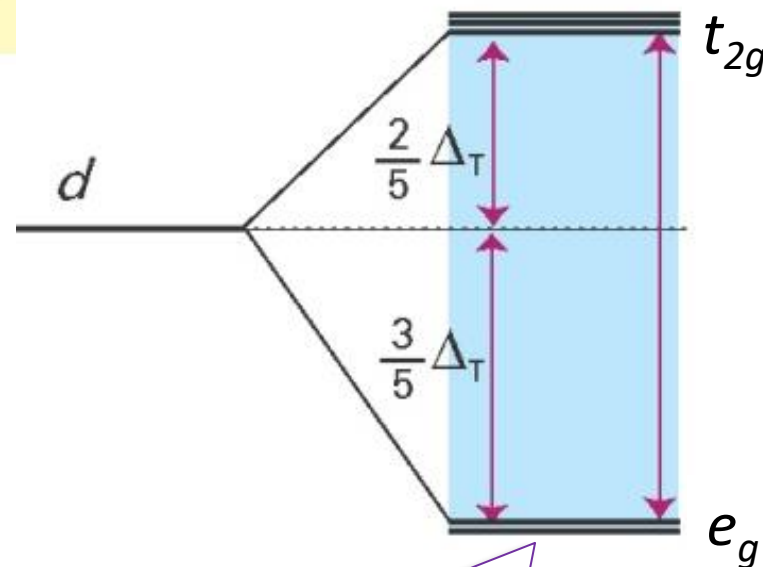
$e_g$ orbitals are energetically below $t_{2g}$ orbitals

# Quantum theories of covalent-coordinate bonding

## 2. Crystal Field Theory (CFT)

### The influence of ligands

Complexes $[Co(X)(NH_3)_5]^{n+}$ (X = I$^-$, Br$^-$, Cl$^-$, NO$_2^-$, SO$_4^{2-}$, CO$_3^{2-}$) have different colours.
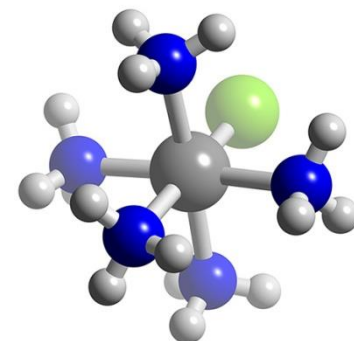
parameter $\Delta_O$ varies systematically with **ligand identity**

$[Co(X)(NH_3)_5]^{n+}$

$[Co(NO_2)(NH_3)_5](NO_3)_2$

$[CoI(NH_3)_5](NO_3)_2$

$[CoBr(NH_3)_5](NO_3)_2$

$[Co(SO_4)(NH_3)_5]NO_3$

$[CoCl(NH_3)_5](NO_3)_2$

$[Co(CO_3)(NH_3)_5]NO_3$
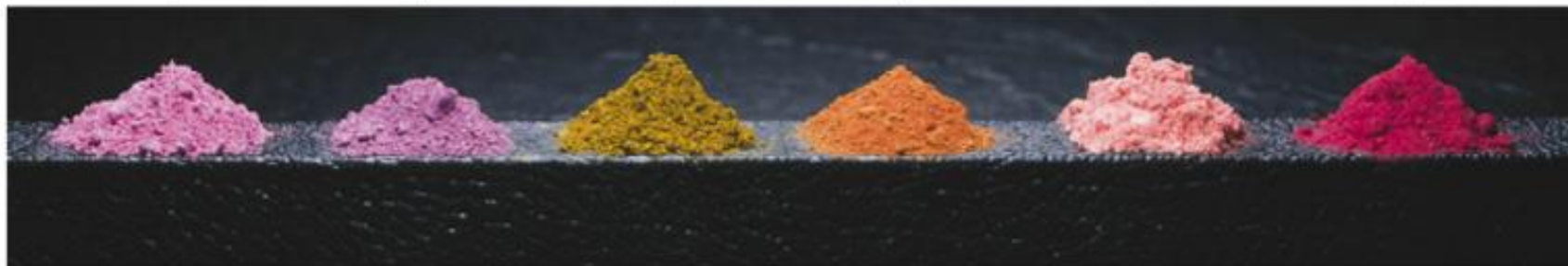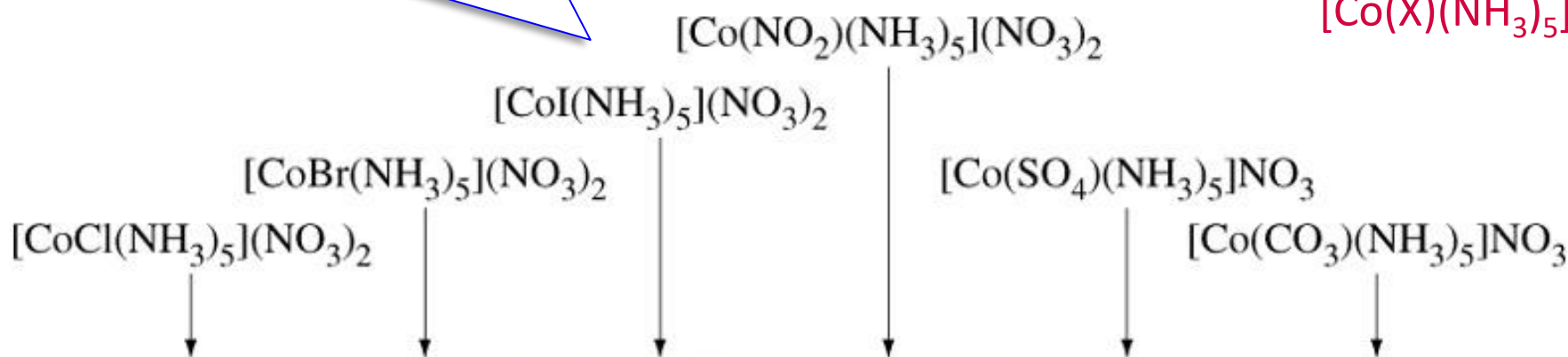
# Quantum theories of covalent-coordinate bonding

## 2. Crystal Field Theory (CFT)

### Spectrochemical series of ligands

Thus, the splitting parameter, $\Delta_O$, **increases as the ligand changes over a series of**, and this order (referred to as the "spectrochemical series") is fixed regardless of the identity of the metal ion:

$$\Delta_O \text{ (weak field)} < \Delta_O \text{ (strong field)}$$

weak-field ligand

spectrochemical series

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_2^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- <$

$CH_3CN < py < NH_3 < en < bipy < phen < NO_2^- < PPh_3 < CN^- < CO$
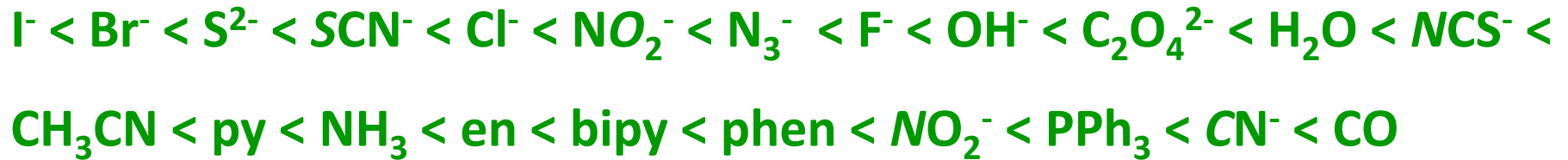
strong field ligand

weaker field          stronger field

$\Delta$ smaller          $\Delta$ larger

# Quantum theories of covalent-coordinate bonding

## 2. Crystal Field Theory (CFT)

### Ligands with strong and weak field



when $NiCl_2 \cdot 6H_2O$ is dissolved in water, the resulting solution is green

when gaseous ammonia is bubbled into solution, the colour turns blue, as **NH3** ligands **replace H2O** in the coordination sphere of the Ni2+ ion
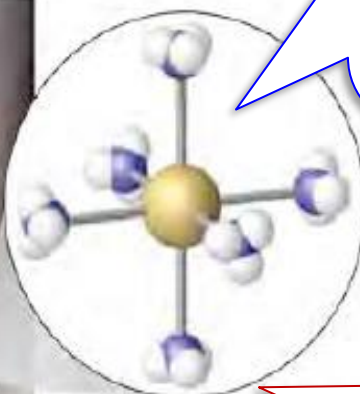
NH3 is a **stronger field ligand than H2O** in the spectrochemical series

# Quantum theories of covalent-coordinate bonding

## 2. Crystal Field Theory (CFT)

### The limits of CFT

Crystal field theory has made a great contribution to explaining properties such as spectral, magnetic and thermodynamic properties of complex combinations.

However, CFT has some limitations:

➤ It provides no explanation why some ligands are placed at a certain position in the spectrochemical series (such as CO, a neutral but very strong field ligand).

➤ Treats ligands as point charges or dipoles, thus allowing only electrostatic interactions.

➤ It does not take into account the overlap of ligand and metal orbitals (covalent interactions are not considered).

# Quantum theories of covalent-coordinate bonding

## *3. Ligand Field Theory (LFT)*

it admits that both electrostatic interaction and covalent bonding exist between the metal ion and its neighbours

is an application of molecular orbital theory that focuses on the *d* orbitals of the central metal atom

provides a more substantial framework for understanding the origins of the splitting parameter $\Delta_O$

**valence orbitals of metal and ligands** are used to form new molecular orbitals
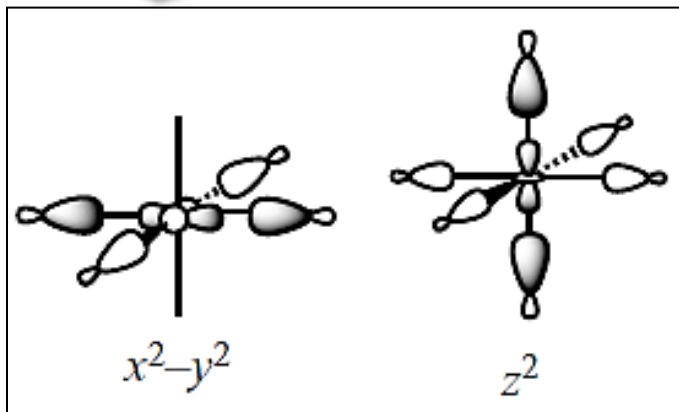
# Quantum theories of covalent-coordinate bonding

## 3. Ligand Field Theory (LFT)

**The case of octahedral complexes**
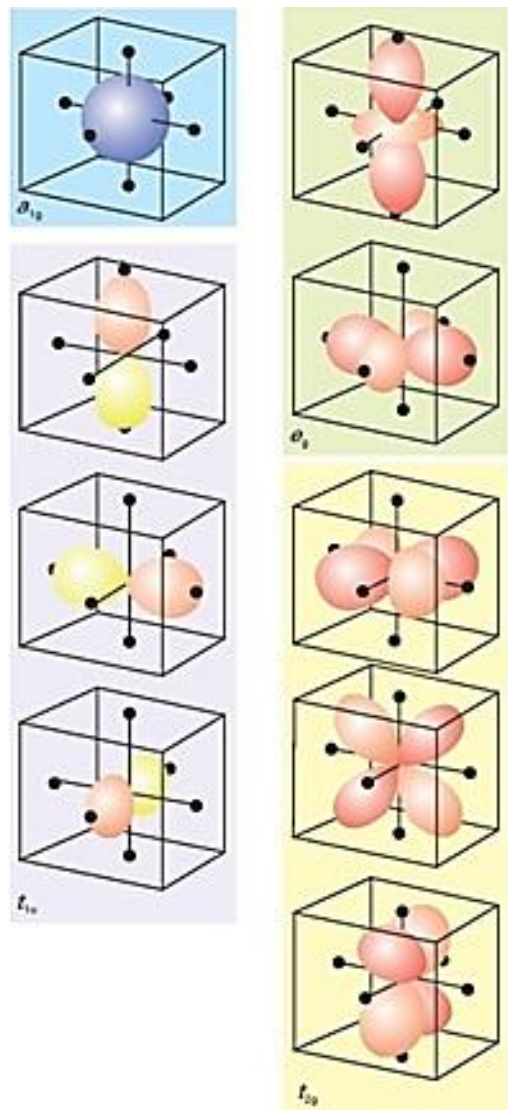


> **the valence orbitals of the metal** are divided by symmetry into four sets of orbitals

**Metal symmetry degeneration**

| | | |
|---|---|---|
| $s$ | $a_{1g}$ | 1 |
| $p_x, p_y, p_z$ | $t_{1u}$ | 3 |
| $d_{x^2-y^2}, d_{z^2}$ | $e_g$ | 2 |
| $d_{xy}, d_{xz}, d_{yz}$ | $t_{2g}$ | 3 |
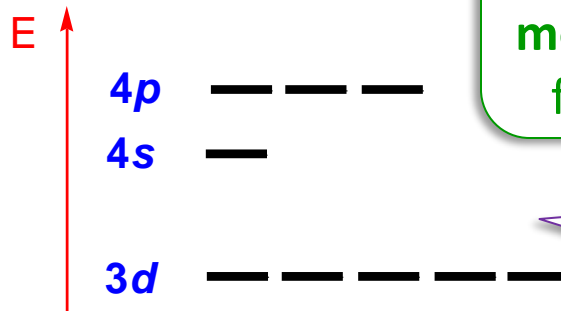
> the valence orbitals of the metal can interact with the **molecular orbitals of ligands** to form new molecular orbitals

$E$

$4p$ — — — —

$4s$ —

$3d$ — — — — —

> **valence orbitals** of $3d$ metal ions

# Quantum theories of covalent-coordinate bonding

## 3. Ligand Field Theory (LFT)

The case of octahedral complexes

Energy calculations (adjusted to agree with spectroscopic data) lead to the following energy diagram of molecular orbitals:

three $t2g$ orbitals of the triple degenerate metal remain **unbonded** and fully localized on the metal atom

the largest contribution to low energy MO comes from the atomic or molecular orbitals of the ligands and can be occupied by **12 electrons provided by the 6 ligands**

...and 6 antibonding MOs

there are six bonding MOs
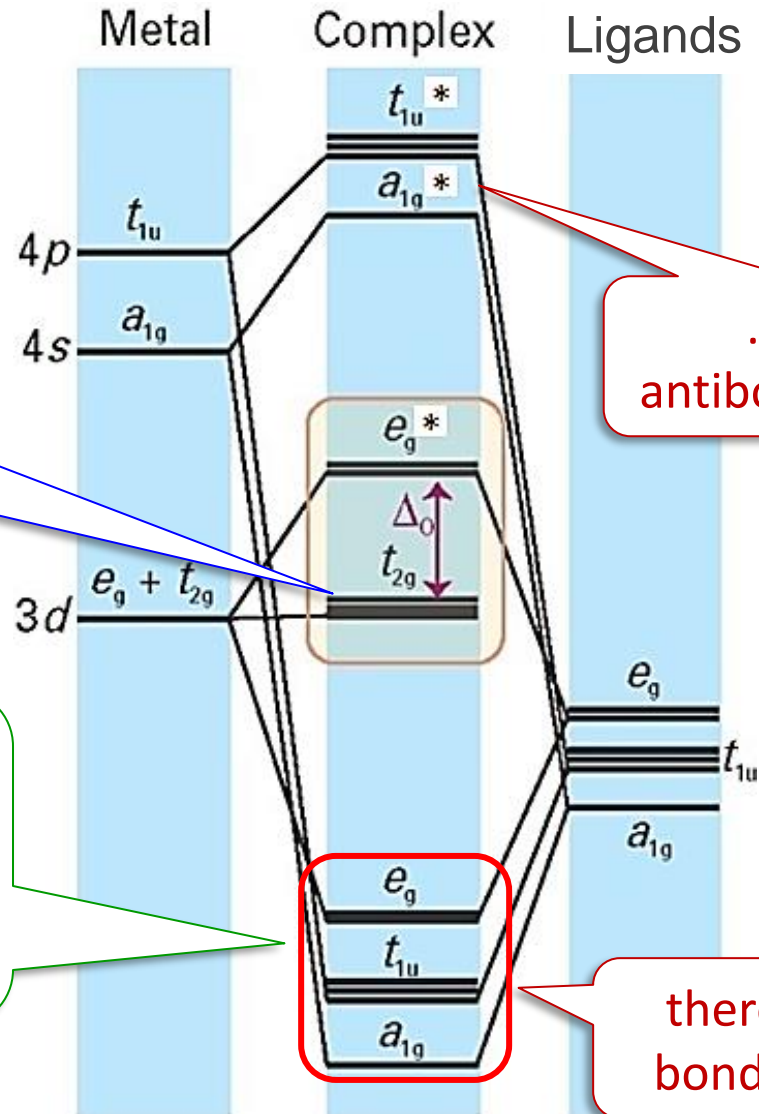
# Quantum theories of covalent-coordinate bonding
## *3. Ligand Field Theory (LFT)*

## MOLECULAR BONDING ORBITALS

$e_g$ bonding MO produced by the interaction between the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals of the metal and the ligand orbitals

$x^2-y^2$

$z^2$

$p_y$

$p_x$

$p_z$

$e_g$

$t_{1u}$

$a_{1g}$

$e_g$

$t_{1u}$

$a_{1g}$

$s$

*t1u-bonding* MO produced by the interaction between metal *p* orbitals and ligand orbitals
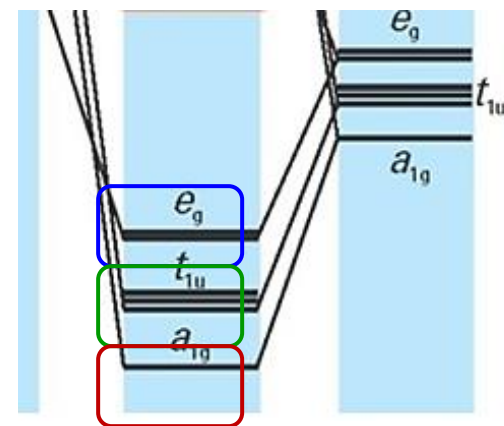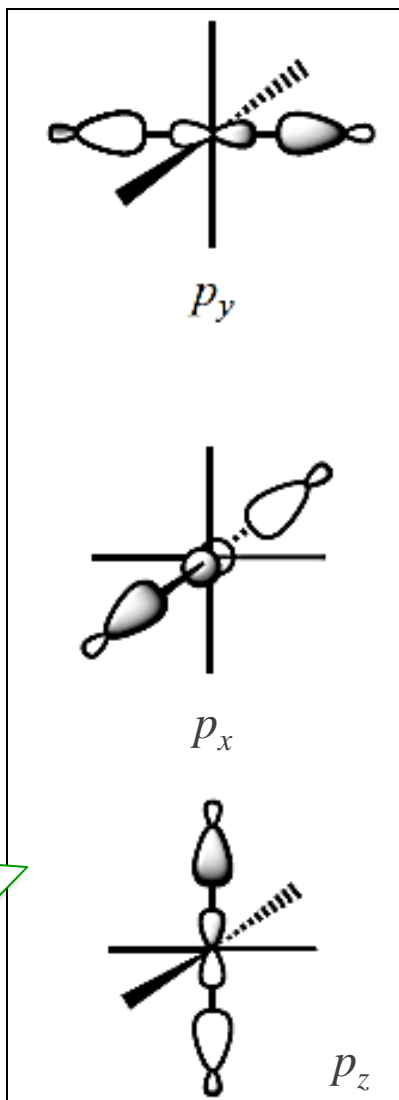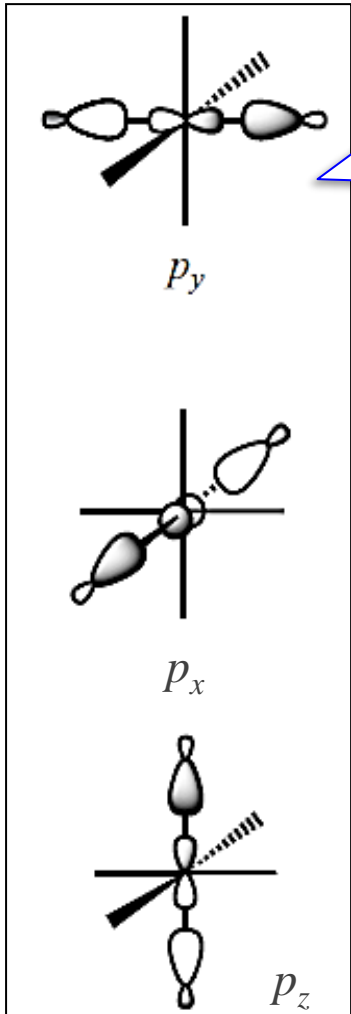
*a1g-bonding* MO produced by the interaction between metal *s* orbitals and ligand orbitals
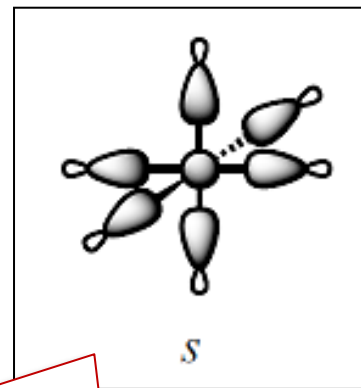
# Quantum theories of covalent-coordinate bonding
## 3. Ligand Field Theory (LFT)

### NON-BONDING MOLECULAR ORBITALS

these are the first orbitals that are occupied by the metal's electrons
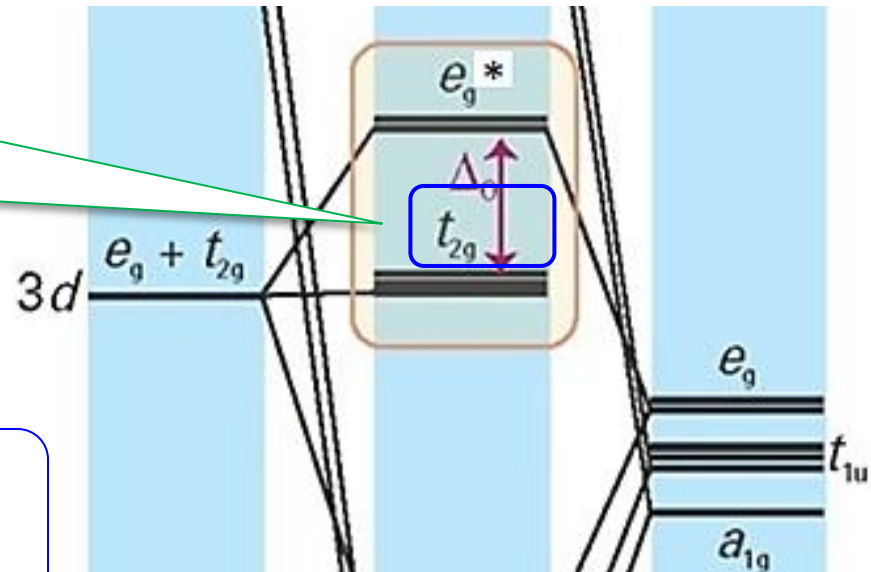
$t2g$ non-bonding orbitals ($d_{yz}$, $d_{xy}$ and $d_{xz}$ metal orbitals)
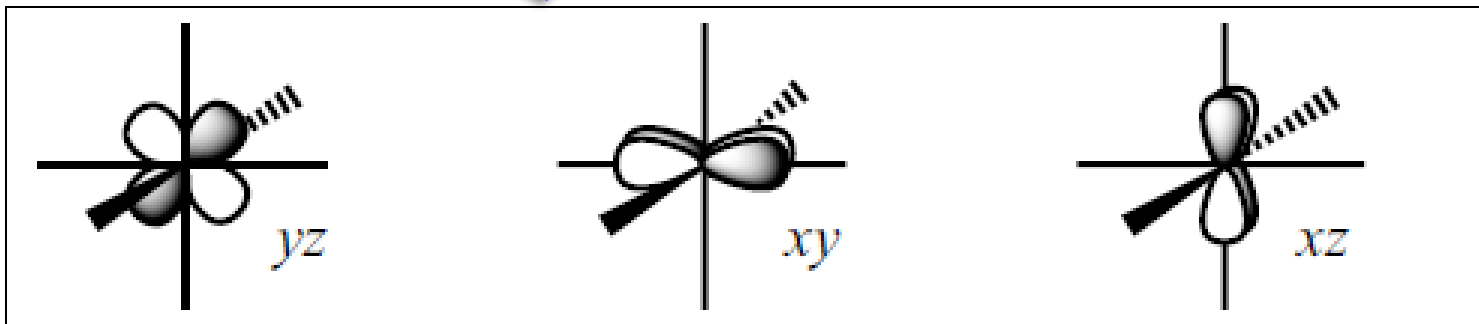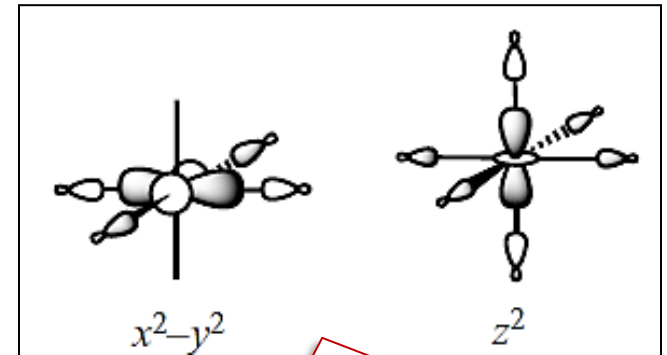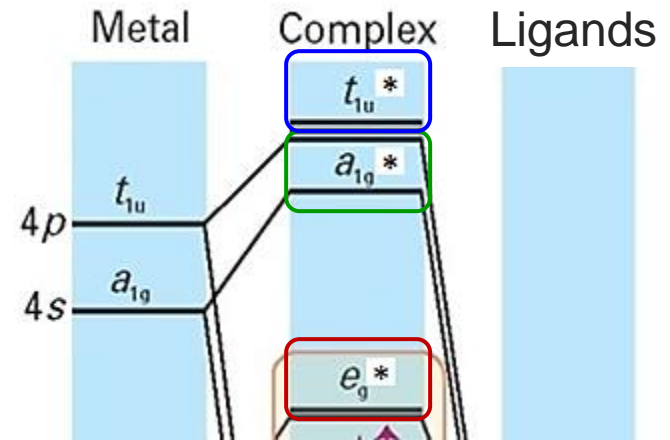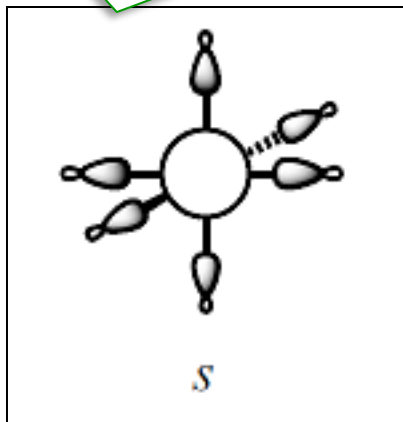
# Quantum theories of covalent-coordinate bonding
## 3. Ligand Field Theory (LFT)

## ANTIBONDING MOLECULAR ORBITALS



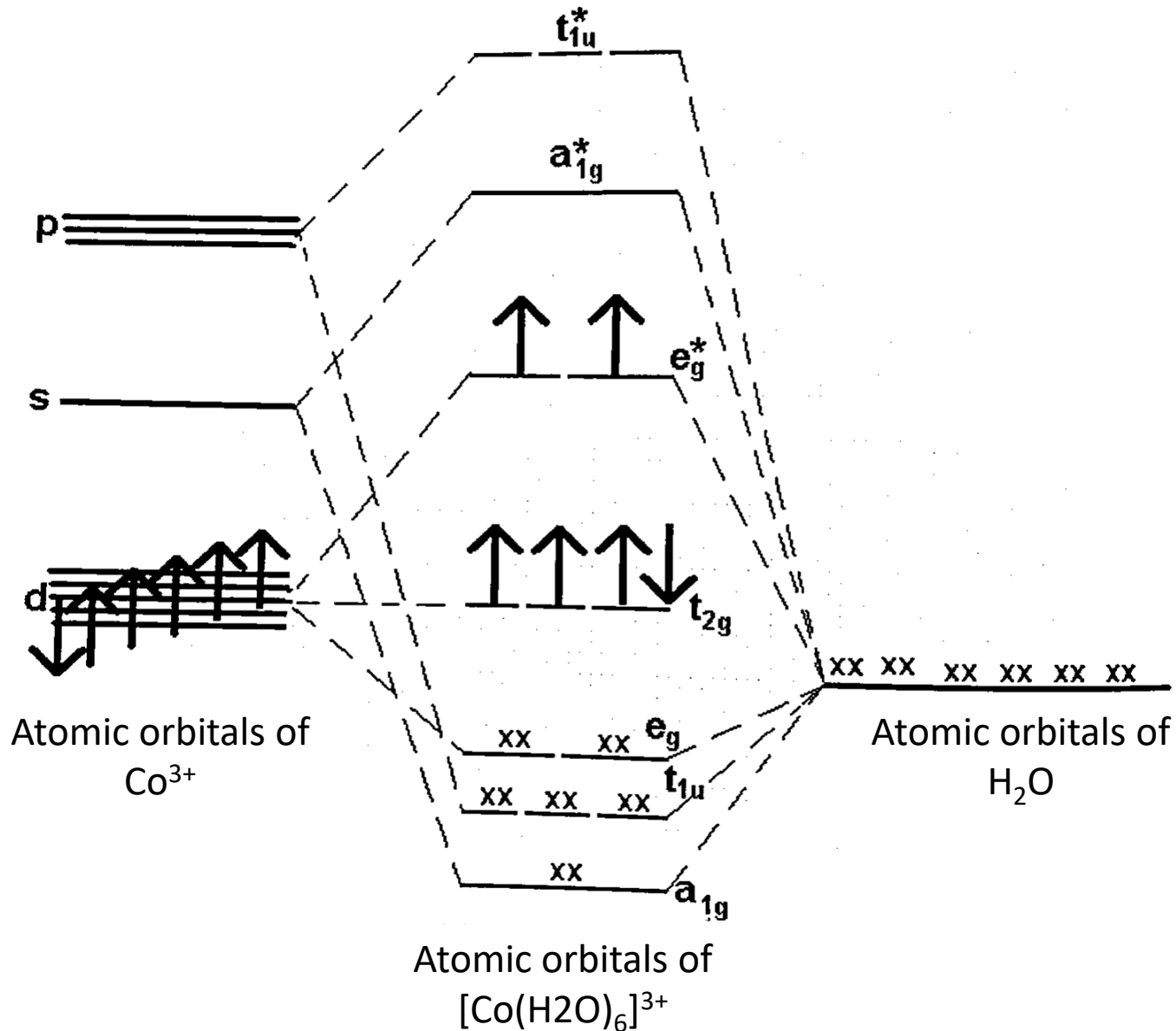$t1u*$ antibonding MO produced by interaction between metal $p$-orbitals and ligand orbitals

$a1g*$ antibonding MO produced by the interaction between the $s$ orbitals of the metal and the ligand orbitals

eg* antibonding MO produced by the interaction between the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals of the metal and the ligand orbitals

$p_y$

$p_x$

$p_z$

$s$

$x^2-y^2$

$z^2$

Metal    Complex    Ligands

$t_{1u}*$

$a_{1g}*$

$4p$    $t_{1u}$

$4s$    $a_{1g}$

$e_g*$

# Quantum theories of covalent-coordinate bonding
## 3. Ligand Field Theory (LFT)



Atomic orbitals of
Co$^{3+}$

Atomic orbitals of
[Co(H2O)$_6$]$^{3+}$
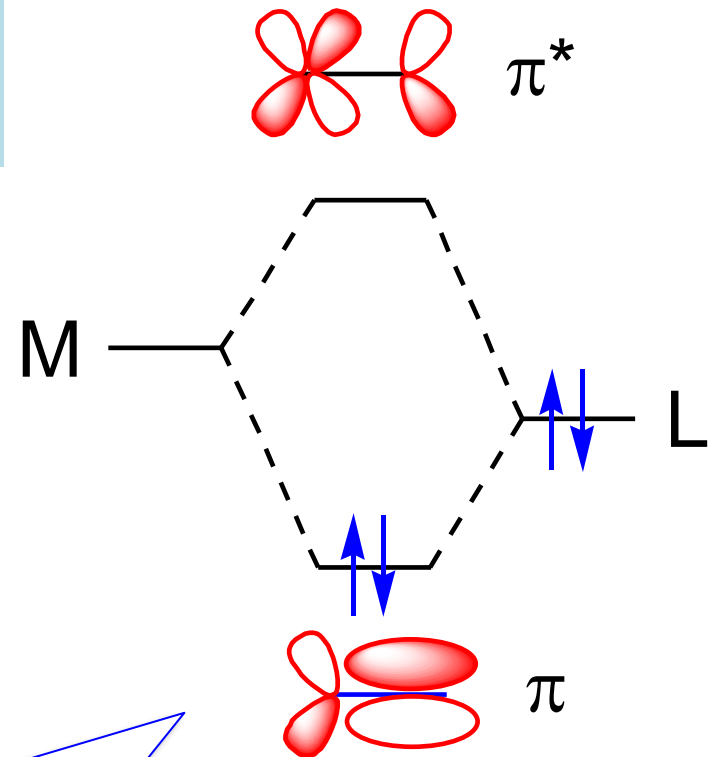
Atomic orbitals of
H$_2$O

## 3. Ligand Field Theory (LFT)

### π-DONOR LIGANDS

A π-donor ligand donates electrons to the metal centre in an interaction involving a fully occupied orbital of the ligand and a free orbital of the metal.

**Cl⁻, Br⁻, I⁻, OH⁻, H₂O**
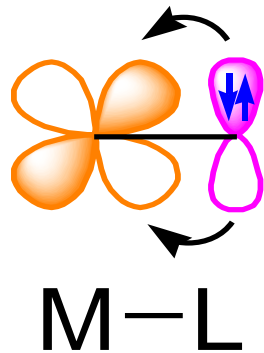


a π-donor ligand is a **Lewis alkali** with fully occupied orbitals of π symmetry around the M-L axis

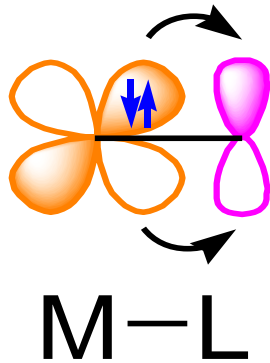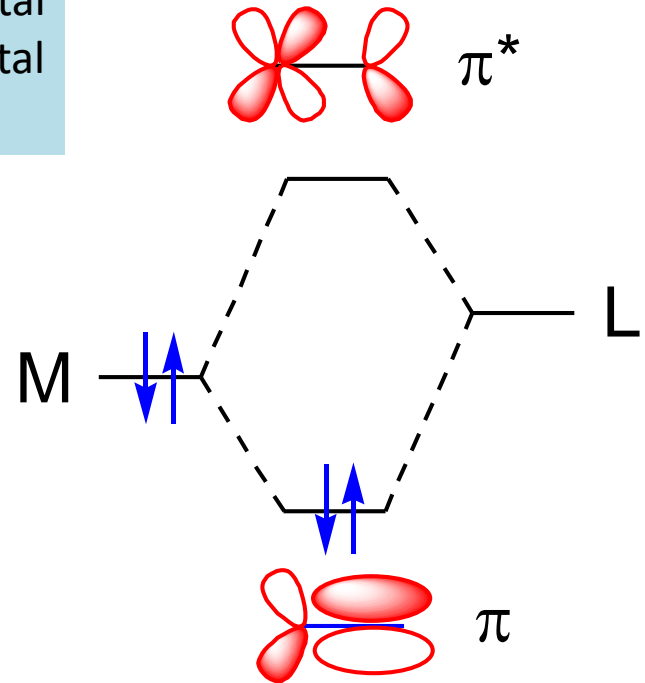interaction with metal *t2g* orbitals produces new bonding and antibonding MOs

## Π-ACCEPTOR LIGANDS

A $\pi$-acceptor ligand accepts electrons from the metal centre in an interaction involving a fully occupied orbital of the metal and a free orbital of the ligand.

## CO, CN$^-$, N$_2$, PR$_3$



M−L

a $\pi$-acceptor ligand is a **Lewis acid** with free orbitals of symmetry $\pi$ around the M-Laxis

interaction with metal *t2g* orbitals produces new bonding and antibonding MOs

# Quantum theories of covalent-coordinate bonding

## Conclusions on LFT *versus CFT*

➢ At present, ligand field theory is best suited for the study of complex combinations.

➢ In contrast to CFT, in which atoms, although undergoing some perturbations, retain their individuality even in complex combinations, in LFT they lose their individuality and in their place a new structural unit appears as a unitary whole, the complex ion.

➢ While in LFT the splitting of orbitals is largely attributed to covalent bond formation, in CFT the splitting occurs as a consequence of electrostatic repulsion exerted by the crystal field of ligands on the *d-level* electrons of the metal ion.

➢ The lower stability of $e_g$ orbitals compared to $t_{2g}$ orbitals is due, in LFT, to their antibonding character, whereas in CFT the phenomenon is attributed to an electrostatic interaction of the metal ion with the ligands.