

# Bonding in transition metal complexes

- **Crystal Field Theory (CFT)**

- Assumes electrostatic (ionic) interactions between ligands and metal ions
- Useful for understanding magnetism and electronic spectra

- **Valence Bond (VB) Theory**

- Assumes covalent M–L bonds formed by ligand electron donation to empty metal hybrid orbitals.
- Useful for rationalizing magnetic properties, but cannot account for electronic spectra.
- Offers little that cannot be covered better by other theories.

- **Molecular Orbital (MO) Theory**

- Approach using M–L general MOs
- Excellent quantitative agreement, but less useful in routine qualitative discussions

- **Ligand Field Theory (LFT)**

- Modified CFT
- Makes empirical corrections to account for effects of M–L orbital overlap, improving quantitative agreement with observed spectra

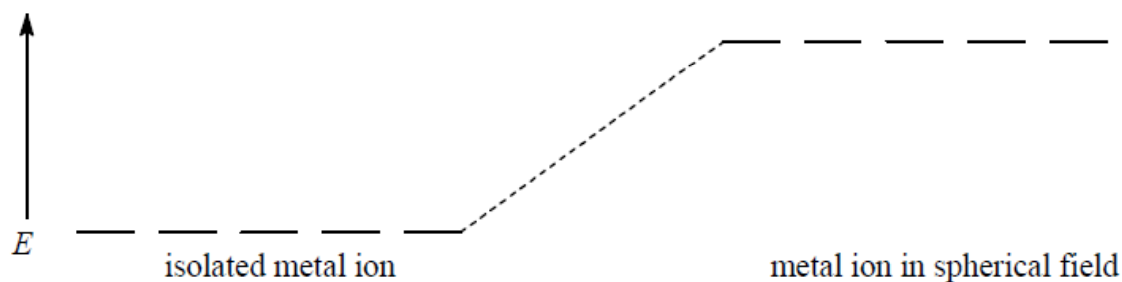
**MO used for most sophisticated and quantitative interpretations**

**LFT used for semi-quantitative interpretations**

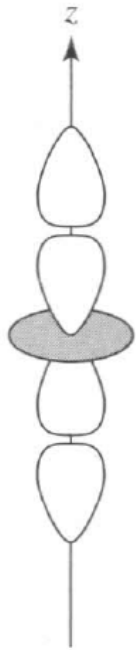
**CFT used for everyday qualitative interpretations**

# CFT energies of d orbitals in an Octahedral ( $O_h$ ) Complex

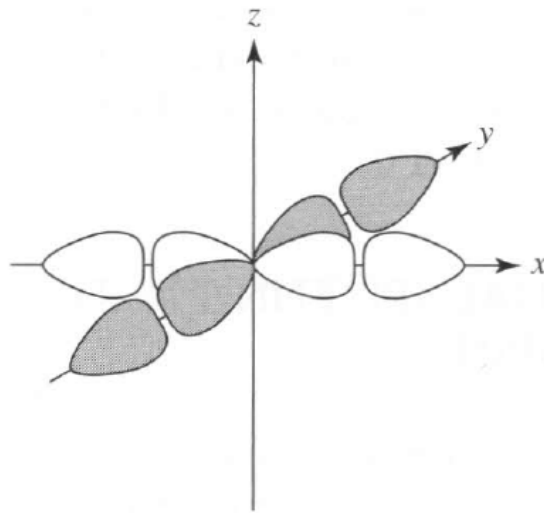
- Consider a **spherical field** equivalent to six electron pairs surrounding a central metal ion, M.
- Electron repulsions will perturb the energies of the **five degenerate d orbitals**, making them rise in energy.



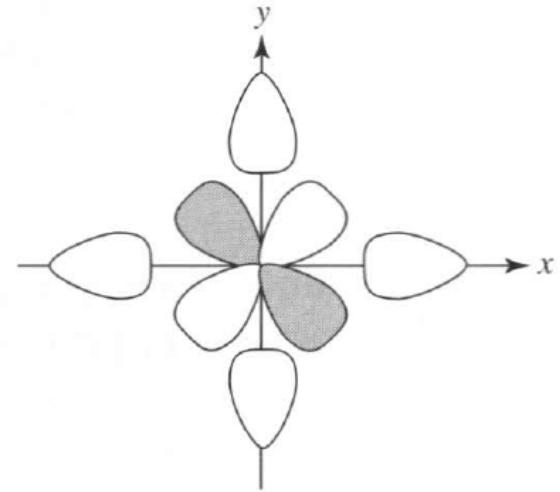
- The energies of the  $t_{2g}$  orbitals and  $e_g$  orbitals, however, depend upon their orientation to the six ligand coordination positions in an  $O_h$  ligand field.



Bonding interaction between two ligand orbitals and metal  $d_{z^2}$  orbital

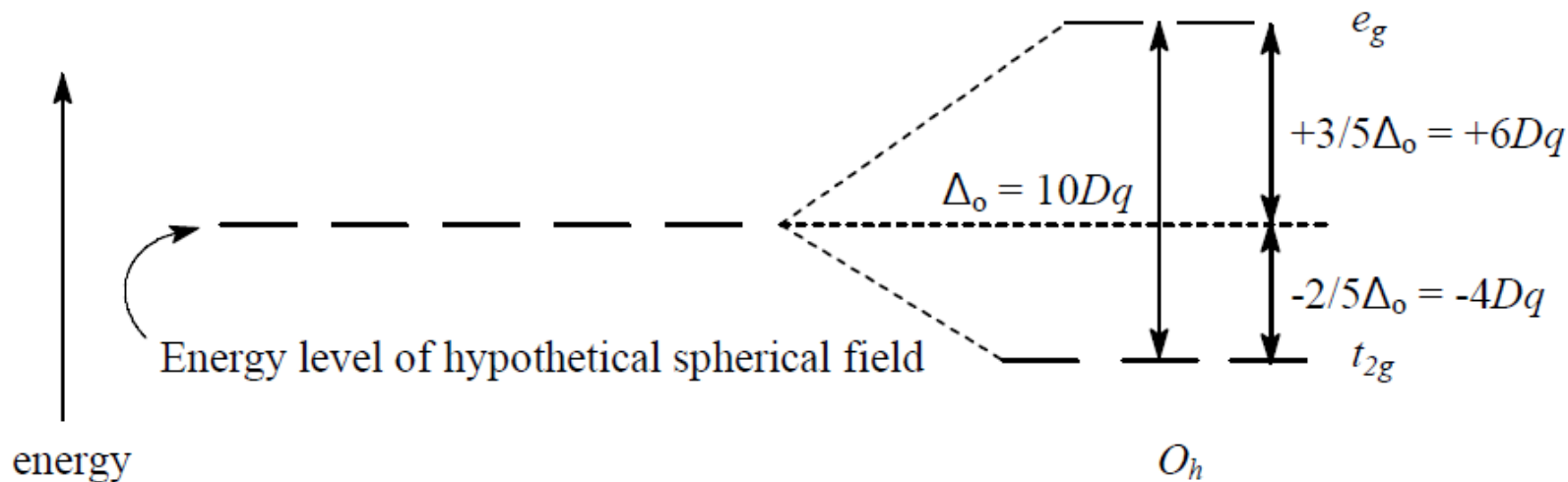


Bonding interaction between four ligand orbitals and metal  $d_{x^2-y^2}$  orbital



Nonbonding (no interaction) four ligand orbitals and metal  $d_{xy}$  orbital

- The  $e_g$  orbitals have lobes that point at the ligands and so will ascend in energy.
- The  $t_{2g}$  orbitals have lobes that lie between ligands and so will descend in energy.



**The energy gap between  $t_{2g}$  and  $e_g$  levels is designated  $\Delta_o$  (or  $10Dq$ )**

- The energy of the  $e_g$  set rises by  $+3/5 \Delta_o$  ( $+6Dq$ ) while the energy of the  $t_{2g}$  set falls by  $-2/5 \Delta_o$  ( $-4Dq$ ) resulting in no net energy change for the system.

$$\begin{aligned}
 \Delta_o E &= E(e_g) + E(t_{2g}) \\
 &= (2)(+3/5) \Delta_o + (3)(-2/5) \Delta_o \\
 &= (2)(+6Dq) + (3)(-4Dq) = 0
 \end{aligned}$$

- The magnitude of  $\Delta_o$  depends upon both the metal ion and the attaching ligands.**
- Magnitudes of  $\Delta_o$  are typically ca. 100 – 400 kJ/mol (ca. 8,375 – 33,500  $\text{cm}^{-1}$ ).

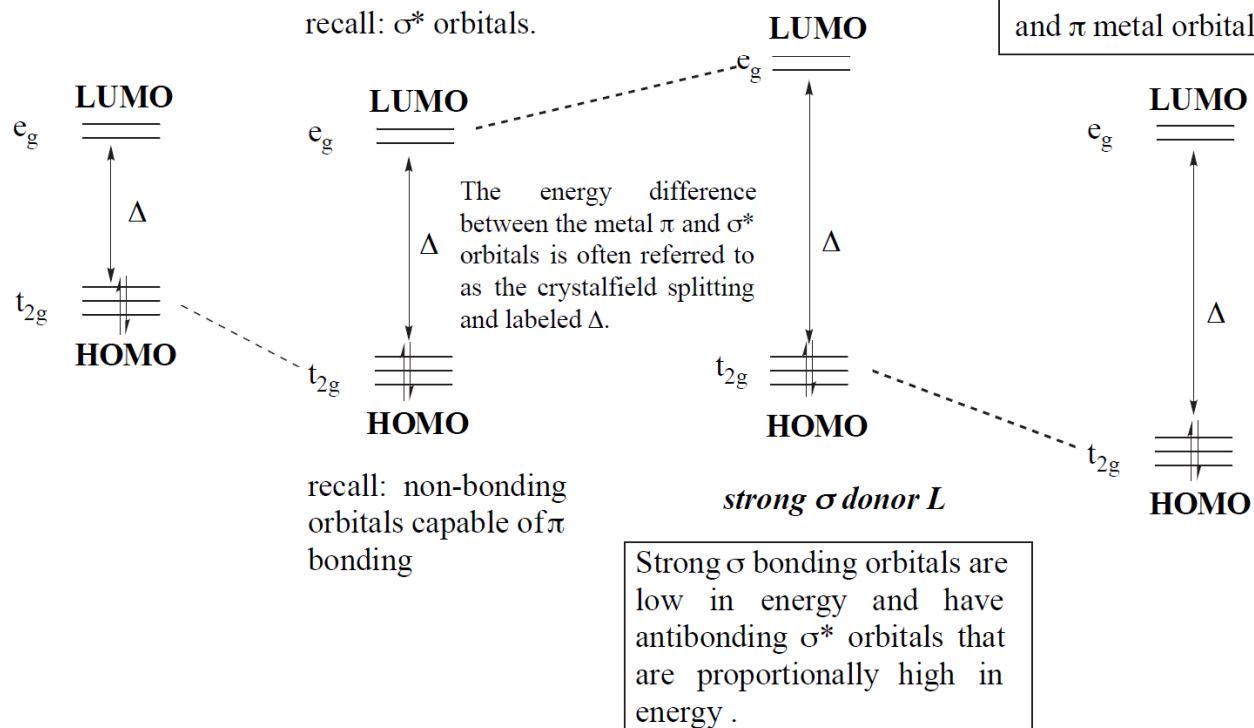
# Spectrochemical series

*strong  $\pi$  donor ligand*

Ligand to metal  $\pi$  donation increases the energy of the HOMO, making  $\Delta$  smaller.

*strong  $\pi$  acceptor L*

$\pi$ -backbonding lowers the energy of the HOMO and thus increases the energy difference  $\Delta$  between the  $\sigma^*$  and  $\pi$  metal orbitals.



**Spectrochemical series** The colors of TM complexes often arise from the absorption of visible light that corresponds to the energy gap  $\Delta$ . Electronic spectra (UV-vis) can often be used to measure  $\Delta$  directly.

$\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{N}_3^-$ ,  $\text{F}^- < \text{OH}^- < \text{O}_2^- < \text{H}_2\text{O} < \text{NCS}^- < \text{py}, \text{NH}_3 < \text{en} < \text{bpy}, \text{phen} < \text{NO}_2^- < \text{CH}_3^-$ ,  $\text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}, \text{H}^-$

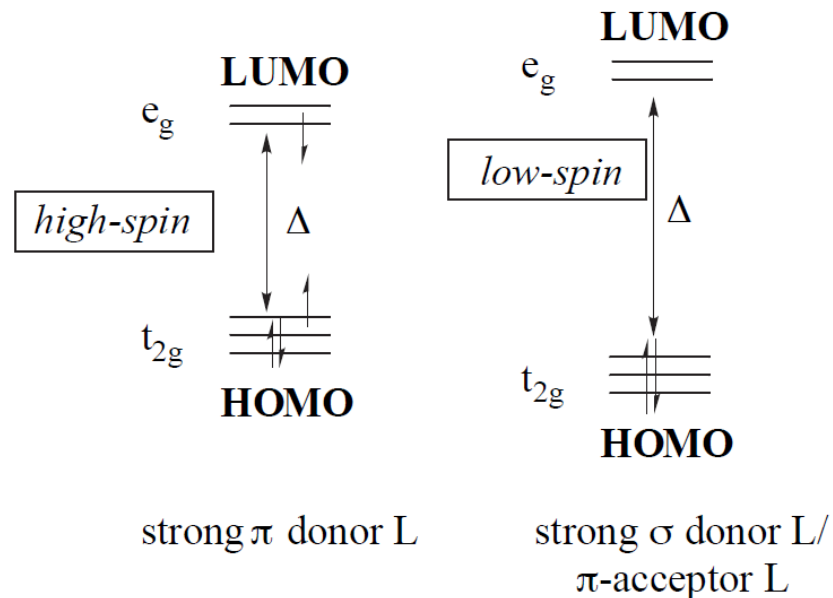
←  $\pi$ -donor low  $\Delta$  "low field ligand"  $\pi$ -acceptor/strong  $\sigma$ -donor high  $\Delta$  "high field ligand" →

- Electrons fill the d orbitals starting with the  $t_{2g}$  set in accordance with
  - The aufbau principle
  - The Pauli exclusion principle
  - Hund's rule of maximum multiplicity
- Spins of successively added electrons are parallel so long as the Pauli exclusion principle allows.
- At the point when the set of  $t_{2g}$  orbitals is half filled, an additional electron must pair if its is to occupy one of the orbitals of the degenerate set.
- But if the mean pairing energy (P) is greater than  $\Delta_o$ , a lower energy state will result by putting the electron in the higher  $e_g$  level.

$$\text{Total pairing energy } \Pi = \Pi_c + \Pi_e$$

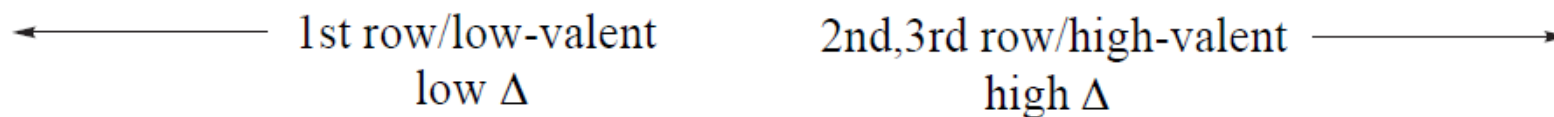
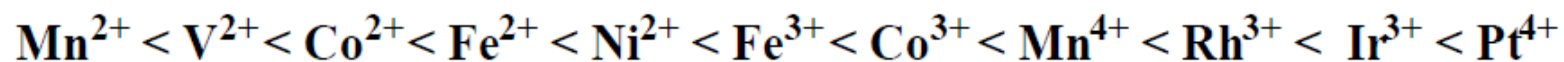
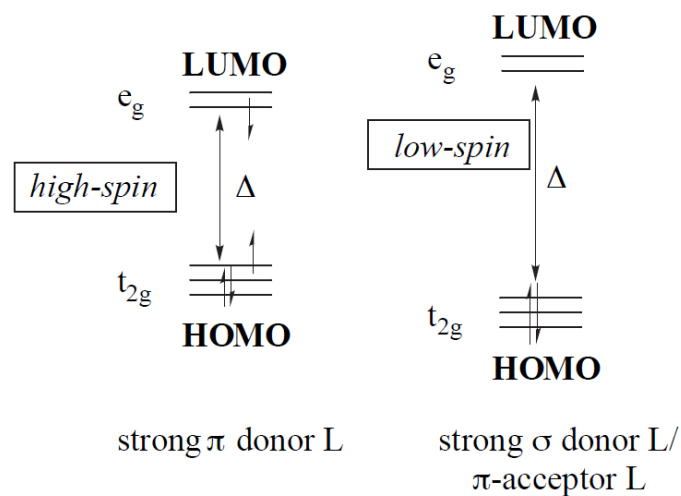
# High spin vs. low spin electron configuration

- If  $\Delta$  is low enough, electrons may rearrange to give a "high spin" configuration to reduce electron- electron repulsion that happens when they are paired up in the same orbital.
- In 1st row metals complexes, low-field ligands (strong  $\pi$  - donors) favor high spin configurations whereas high field ligands ( $\pi$ -acceptors/ strong  $\sigma$  donors) favor low spin.
- The majority of 2nd and 3rd row metal complexes are low-spin irrespective of their ligands (*greater M-L overlap; decreased  $\Pi_e$  due to larger volume of d orbitals*).





- Low-oxidation state complexes also tend to have lower  $\Delta$  than high-oxidation state complexes.
- High oxidation state  $\rightarrow$  increased  $\chi \rightarrow$  increased  $\Delta \rightarrow$  low-spin configuration



### High- and Low-Spin Configurations for $ML_6 O_h$

|          |                                   |                                     |                                    |                                     |                                     |                                     |                                     |
|----------|-----------------------------------|-------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| $e_g$    | <u>—</u><br><u>—</u>              | <u>—</u><br><u>—</u>                | <u>—</u><br><u>—</u>               | <u>—</u><br><u>1</u>                | <u>—</u><br><u>—</u>                | <u>1</u><br><u>1</u>                | <u>—</u><br><u>—</u>                |
| $t_{2g}$ | <u>—</u><br><u>—</u><br><u>1</u>  | <u>—</u><br><u>1</u><br><u>1</u>    | <u>1</u><br><u>1</u><br><u>1</u>   | <u>1</u><br><u>1</u><br><u>1</u>    | <u>1</u><br><u>1</u><br><u>1↓</u>   | <u>1</u><br><u>1</u><br><u>1</u>    | <u>1</u><br><u>1↓</u><br><u>1↓</u>  |
|          | $d^1$                             | $d^2$                               | $d^3$                              | $d^4$<br>high<br>spin               | $d^4$<br>low<br>spin                | $d^5$<br>high<br>spin               | $d^5$<br>low<br>spin                |
| $e_g$    | <u>1</u><br><u>1</u>              | <u>—</u><br><u>—</u>                | <u>1</u><br><u>1</u>               | <u>—</u><br><u>1</u>                | <u>1</u><br><u>1</u>                | <u>1</u><br><u>1↓</u>               | <u>1↓</u><br><u>1↓</u>              |
| $t_{2g}$ | <u>1</u><br><u>1</u><br><u>1↓</u> | <u>1↓</u><br><u>1↓</u><br><u>1↓</u> | <u>1</u><br><u>1↓</u><br><u>1↓</u> | <u>1↓</u><br><u>1↓</u><br><u>1↓</u> | <u>1↓</u><br><u>1↓</u><br><u>1↓</u> | <u>1↓</u><br><u>1↓</u><br><u>1↓</u> | <u>1↓</u><br><u>1↓</u><br><u>1↓</u> |
|          | $d^6$<br>high<br>spin             | $d^6$<br>low<br>spin                | $d^7$<br>high<br>spin              | $d^7$<br>low<br>spin                | $d^8$                               | $d^9$                               | $d^{10}$                            |

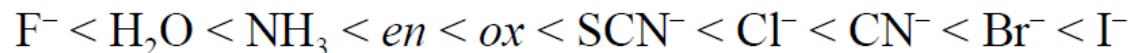
Multiplicity =  $2S + 1$

# Molecular orbital theory

- A molecular orbital (MO) is a mathematical function that describes the wave-like behavior of an electron in a molecule, i.e. a wavefunction ( $\psi$ ). This function can be used to calculate chemical and physical properties such as the probability of finding an electron in any specific region.
- MO theory is a method for determining molecular structure in which **electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule.**
- Every molecule has a set of MOs, in which it is assumed that **each MO wave function  $\psi$  may be written as a simple weighted sum of the  $n$  constituent atomic orbitals.**
- MOs are constructed in this way via a **linear combination of atomic orbitals (LCAO)** - a quantum superposition, if you like, of atomic orbitals.
- The MOs resulting from the LCAO calculation are often divided into **bonding, non-bonding and anti-bonding orbitals.**
- The shape of the MOs and their respective energies are deduced approximately from comparing both **symmetry and energy** of atomic orbitals of the individual atoms (or molecular fragments).
- This is done by using the symmetry of the molecules and orbitals involved in bonding. The first step in this process is assigning a **point group** to the molecule. Then a **reducible representation** of the bonding is determined.
- The graphs that are plotted to make this discussion clearer are called **correlation diagrams.**

# Ligand field theory

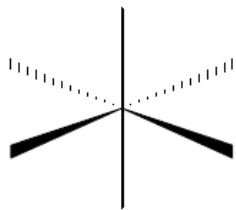
- When empirical corrections are added to CFT it is known as Ligand Field Theory (LFT).
- ***LFT represents an application of molecular orbital (MO) theory to transition metal complexes.***
- Need for corrections to CFT arise from metal-ligand orbital overlap, implying some degree of covalent M–L bonding (metal electrons delocalized onto the ligand)
- This delocalization results in lesser energy separation between the excited state energy levels (Russell-Saunders term states) in the complex than predicted for the ion in the crystal field environment.
- The disparity between free-ion and complex-ion electronic state energies is the so-called nephelauxetic effect (cloud-expanding), which depends upon both the metal ion and ligand.
- For a given metal ion, the ability of ligands to induce this cloud expanding increases according to a nephelauxetic series:



- Note that the ordering of ligands in the nephelauxetic series is not the same as the spectrochemical series.

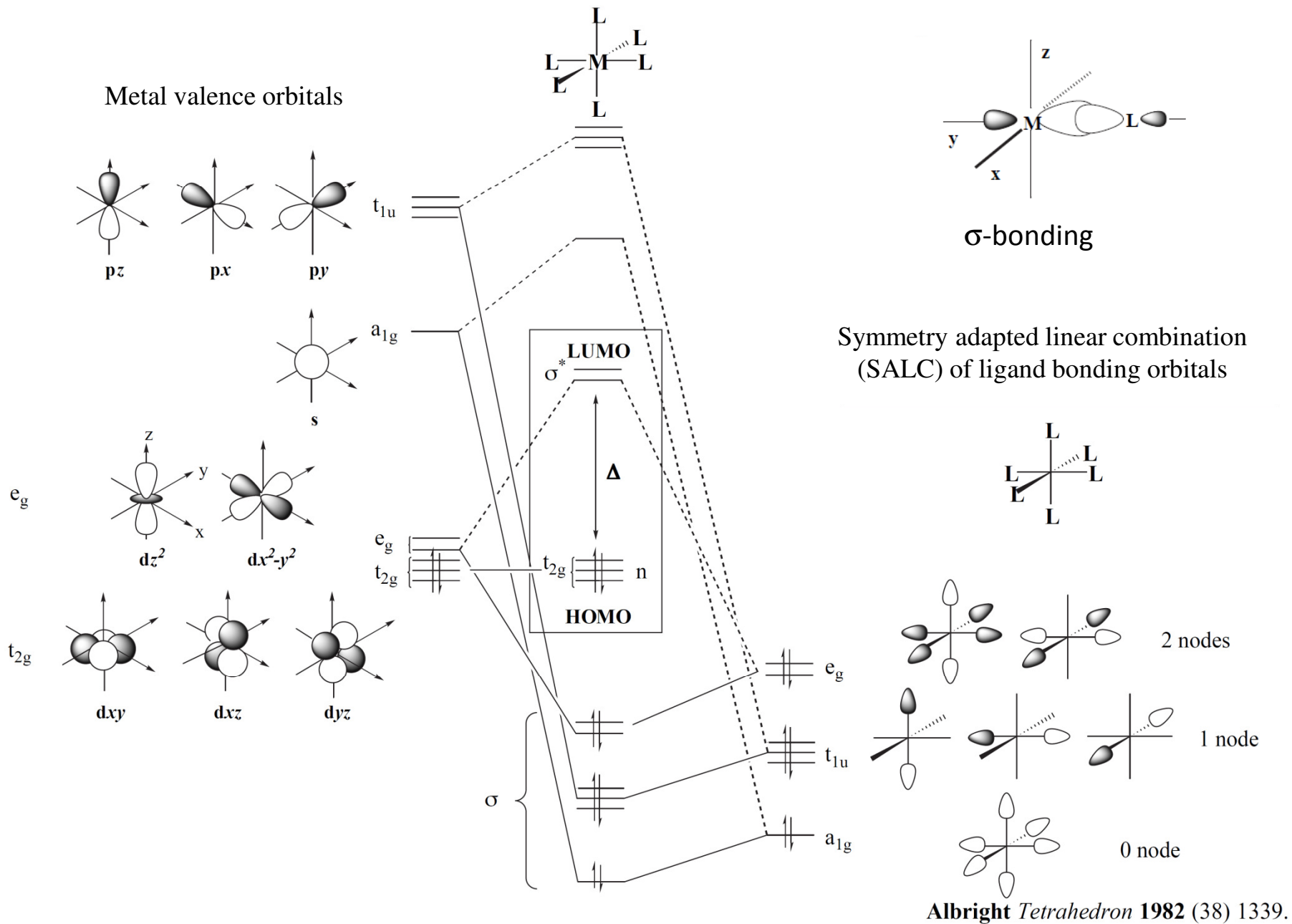
# Character table for the $O_h$ point group

| $O_h$    | $E$ | $8C_3$ | $6C_2$ | $6C_4$ | $3C_2(= C_4^2)$ | $i$ | $6S_4$ | $8S_6$ | $3\sigma_h$ | $6\sigma_d$ |                   |                                      |
|----------|-----|--------|--------|--------|-----------------|-----|--------|--------|-------------|-------------|-------------------|--------------------------------------|
| $A_{1g}$ | 1   | 1      | 1      | 1      | 1               | 1   | 1      | 1      | 1           | 1           |                   |                                      |
| $A_{2g}$ | 1   | 1      | -1     | -1     | 1               | 1   | -1     | 1      | 1           | -1          |                   |                                      |
| $E_g$    | 2   | -1     | 0      | 0      | 2               | 2   | 0      | -1     | 2           | 0           |                   | $(2z^2 - x^2 - y^2,$<br>$x^2 - y^2)$ |
| $T_{1g}$ | 3   | 0      | -1     | 1      | -1              | 3   | 1      | 0      | -1          | -1          | $(R_x, R_y, R_z)$ |                                      |
| $T_{2g}$ | 3   | 0      | 1      | -1     | -1              | 3   | -1     | 0      | -1          | 1           |                   | $(xy, xz, yz)$                       |
| $A_{1u}$ | 1   | 1      | 1      | 1      | 1               | -1  | -1     | -1     | -1          | -1          |                   |                                      |
| $A_{2u}$ | 1   | 1      | -1     | -1     | 1               | -1  | 1      | -1     | -1          | 1           |                   |                                      |
| $E_u$    | 2   | -1     | 0      | 0      | 2               | -2  | 0      | 1      | -2          | 0           |                   |                                      |
| $T_{1u}$ | 3   | 0      | -1     | 1      | -1              | -3  | -1     | 0      | 1           | 1           | $(x, y, z)$       |                                      |
| $T_{2u}$ | 3   | 0      | 1      | -1     | -1              | -3  | 1      | 0      | 1           | -1          |                   |                                      |
| $\Gamma$ | 6   | 0      | 0      | 2      | 2               | 0   | 0      | 0      | 4           | 2           |                   | $x^2 + y^2 + z^2$                    |
| $A_{1g}$ | 1   | 1      | 1      | 1      | 1               | 1   | 1      | 1      | 1           | 1           |                   |                                      |
| $T_{1u}$ | 3   | 0      | -1     | 1      | -1              | -3  | -1     | 0      | 1           | 1           | $(x, y, z)$       |                                      |
| $E_g$    | 2   | -1     | 0      | 0      | 2               | 2   | 0      | -1     | 2           | 0           |                   | $(2z^2 - x^2 - y^2,$<br>$x^2 - y^2)$ |



$$\Gamma_{\sigma} = A_{1g} + E_g + T_{1u}$$

# MO description of $\sigma$ only bonding in an $O_h$ transition metal complex



- The twelve electrons provided by the ligands alone fill the lowest three levels of MOs ( $a_{1g}$ ,  $t_{1u}$ , and  $e_g$ )
- Any electrons provided by the metal ion will result in an equivalent filling of the d orbitals ( $t_{2g}$  level and if necessary the  $e_g^*$  level)
- Electron filling above the six MOs in the lowest three levels is identical to the presumed filling of d orbitals in the CFT model.
- As with the CFT model, both high and low spin ground states are possible for  $d^4$  through  $d^7$  metal ion configurations.
- In the MO scheme  $\Delta_o$  ( $10Dq$ ) is defined as the energy separation between the  $t_{2g}$  and  $e_g^*$  levels.
- The lower  $t_{2g}$  orbitals are nonbonding and can be taken as essentially the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals of the metal ion, which is not materially different from the CFT view.
- The upper  $e_g^*$  orbitals are now seen as antibonding molecular orbitals.
- Although antibonding, the  $e_g^*$  MOs when occupied involve sharing of electron density between the metal ion and the ligands.

| Number<br>of <i>d</i><br>Electrons | Weak-Field Arrangement |    |    |                       |    | LFSE ( $\Delta_o$ ) | Coulombic<br>Energy | Exchange<br>Energy |
|------------------------------------|------------------------|----|----|-----------------------|----|---------------------|---------------------|--------------------|
|                                    | <i>t</i> <sub>2g</sub> |    |    | <i>e</i> <sub>g</sub> |    |                     |                     |                    |
| 1                                  | ↑                      |    |    |                       |    | $-\frac{2}{5}$      |                     |                    |
| 2                                  | ↑                      | ↑  |    |                       |    | $-\frac{4}{5}$      |                     | $\Pi_e$            |
| 3                                  | ↑                      | ↑  | ↑  |                       |    | $-\frac{6}{5}$      |                     | $3\Pi_e$           |
| 4                                  | ↑                      | ↑  | ↑  | ↑                     |    | $-\frac{3}{5}$      |                     | $3\Pi_e$           |
| 5                                  | ↑                      | ↑  | ↑  | ↑                     | ↑  | 0                   |                     | $4\Pi_e$           |
| 6                                  | ↑↓                     | ↑  | ↑  | ↑                     | ↑  | $-\frac{2}{5}$      | $\Pi_c$             | $4\Pi_e$           |
| 7                                  | ↑↓                     | ↑↓ | ↑  | ↑                     | ↑  | $-\frac{4}{5}$      | $2\Pi_c$            | $5\Pi_e$           |
| 8                                  | ↑↓                     | ↑↓ | ↑↓ | ↑                     | ↑  | $-\frac{6}{5}$      | $3\Pi_c$            | $7\Pi_e$           |
| 9                                  | ↑↓                     | ↑↓ | ↑↓ | ↑↓                    | ↑  | $-\frac{3}{5}$      | $4\Pi_c$            | $7\Pi_e$           |
| 10                                 | ↑↓                     | ↑↓ | ↑↓ | ↑↓                    | ↑↓ | 0                   | $5\Pi_c$            | $8\Pi_e$           |

| Number<br>of <i>d</i><br>Electrons | Strong-Field Arrangement |    |    |                       |    | LFSE ( $\Delta_o$ ) | Coulombic<br>Energy | Exchange<br>Energy | Strong Field<br>– Weak Field   |
|------------------------------------|--------------------------|----|----|-----------------------|----|---------------------|---------------------|--------------------|--------------------------------|
|                                    | <i>t</i> <sub>2g</sub>   |    |    | <i>e</i> <sub>g</sub> |    |                     |                     |                    |                                |
| 1                                  | ↑                        |    |    |                       |    | $-\frac{2}{5}$      |                     |                    | 0                              |
| 2                                  | ↑                        | ↑  |    |                       |    | $-\frac{4}{5}$      |                     | $\Pi_e$            | 0                              |
| 3                                  | ↑                        | ↑  | ↑  |                       |    | $-\frac{6}{5}$      |                     | $3\Pi_e$           | 0                              |
| 4                                  | ↑↓                       | ↑  | ↑  |                       |    | $-\frac{8}{5}$      | $\Pi_c$             | $3\Pi_e$           | $-\Delta_o + \Pi_c$            |
| 5                                  | ↑↓                       | ↑↓ | ↑  |                       |    | $-\frac{10}{5}$     | $2\Pi_c$            | $4\Pi_e$           | $-2\Delta_o + 2\Pi_c$          |
| 6                                  | ↑↓                       | ↑↓ | ↑↓ |                       |    | $-\frac{12}{5}$     | $3\Pi_c$            | $6\Pi_e$           | $-2\Delta_o + 2\Pi_c + 2\Pi_e$ |
| 7                                  | ↑↓                       | ↑↓ | ↑↓ | ↑                     |    | $-\frac{9}{5}$      | $3\Pi_c$            | $6\Pi_e$           | $-\Delta_o + \Pi_c + \Pi_e$    |
| 8                                  | ↑↓                       | ↑↓ | ↑↓ | ↑                     | ↑  | $-\frac{6}{5}$      | $3\Pi_c$            | $7\Pi_e$           | 0                              |
| 9                                  | ↑↓                       | ↑↓ | ↑↓ | ↑↓                    | ↑  | $-\frac{3}{5}$      | $4\Pi_c$            | $7\Pi_e$           | 0                              |
| 10                                 | ↑↓                       | ↑↓ | ↑↓ | ↑↓                    | ↑↓ | 0                   | $5\Pi_c$            | $8\Pi_e$           | 0                              |

NOTE: In addition to the LFSE, each pair formed has a positive Coulombic energy,  $\Pi_c$ , and each set of two electrons with the same spin has a negative exchange energy,  $\Pi_e$ . When  $\Delta_o > \Pi_c$  for  $d^4$  or  $d^5$  or when  $\Delta_o > \Pi_c + \Pi_e$  for  $d^6$  or  $d^7$ , the strong-field arrangement (low spin) is favored.

**Total pairing energy  $\Pi = \Pi_c + \Pi_e$**