

# 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

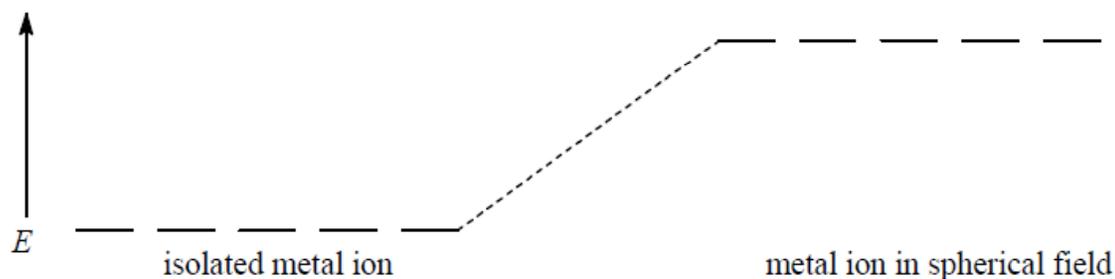
**MO used for most sophisticated and quantitative interpretations**

**LFT used for semi-quantitative interpretations**

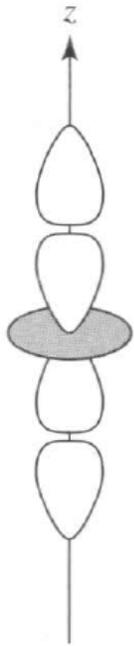
**CFT used for everyday qualitative interpretations**

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

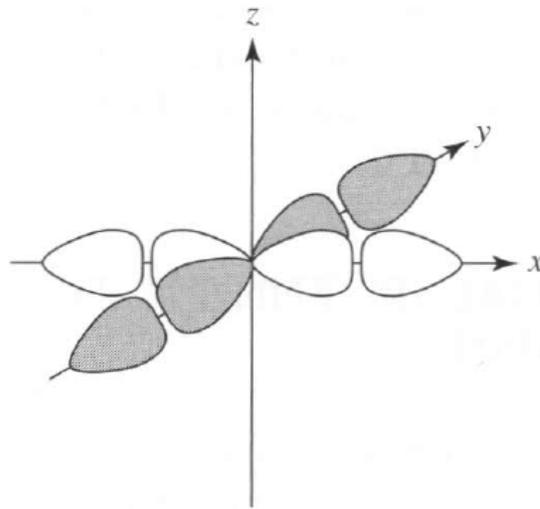
- Consider a **spherical field** equivalent to six electron pairs surrounding a central metal ion, M.
- Electron repulsions will perturb the energies of the **five degenerate d orbitals**, making them rise in energy.



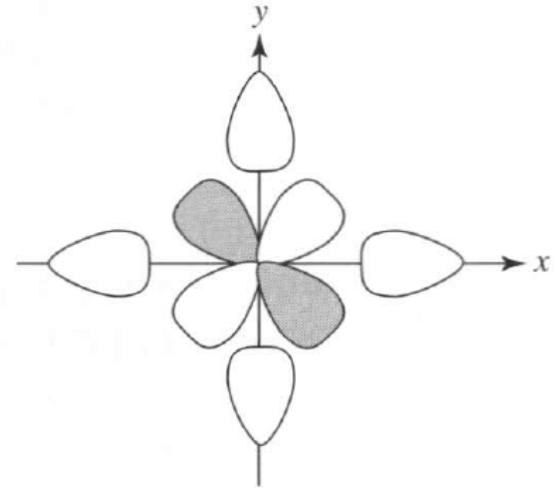
- The energies of the  $t_{2g}$  orbitals and  $e_g$  orbitals, however, depend upon their orientation to the six ligand coordination positions in an  $O_h$  ligand field.



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

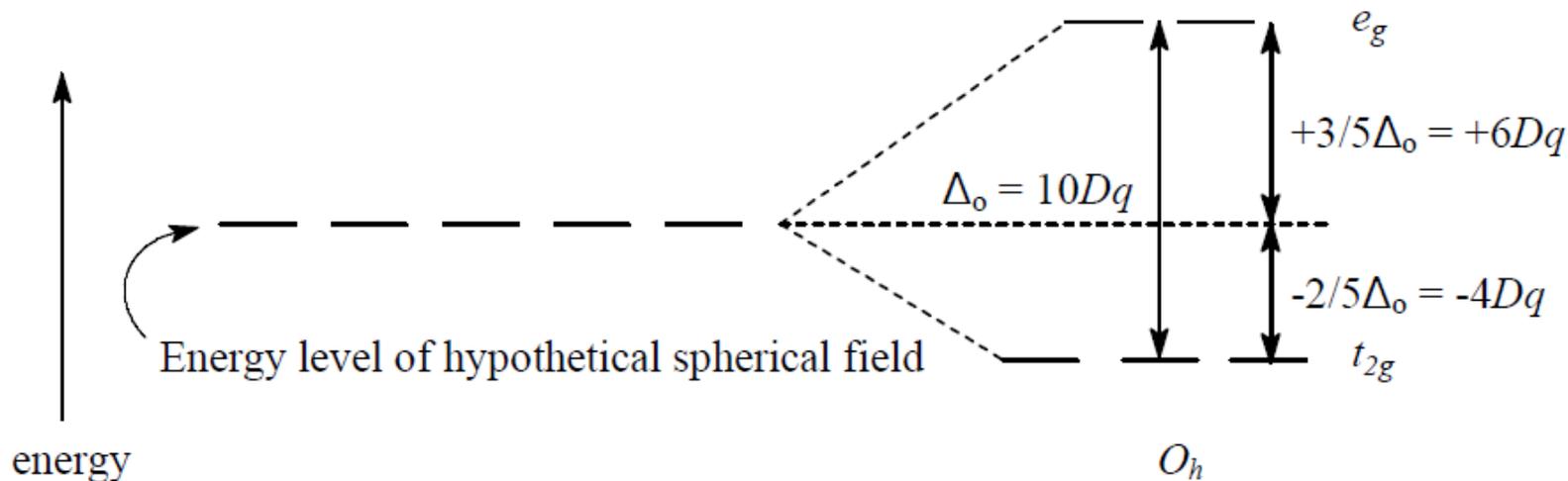


Bonding interaction between four ligand orbitals and metal  $d_{x^2-y^2}$  orbital



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  $\text{cm}^{-1}$ ).

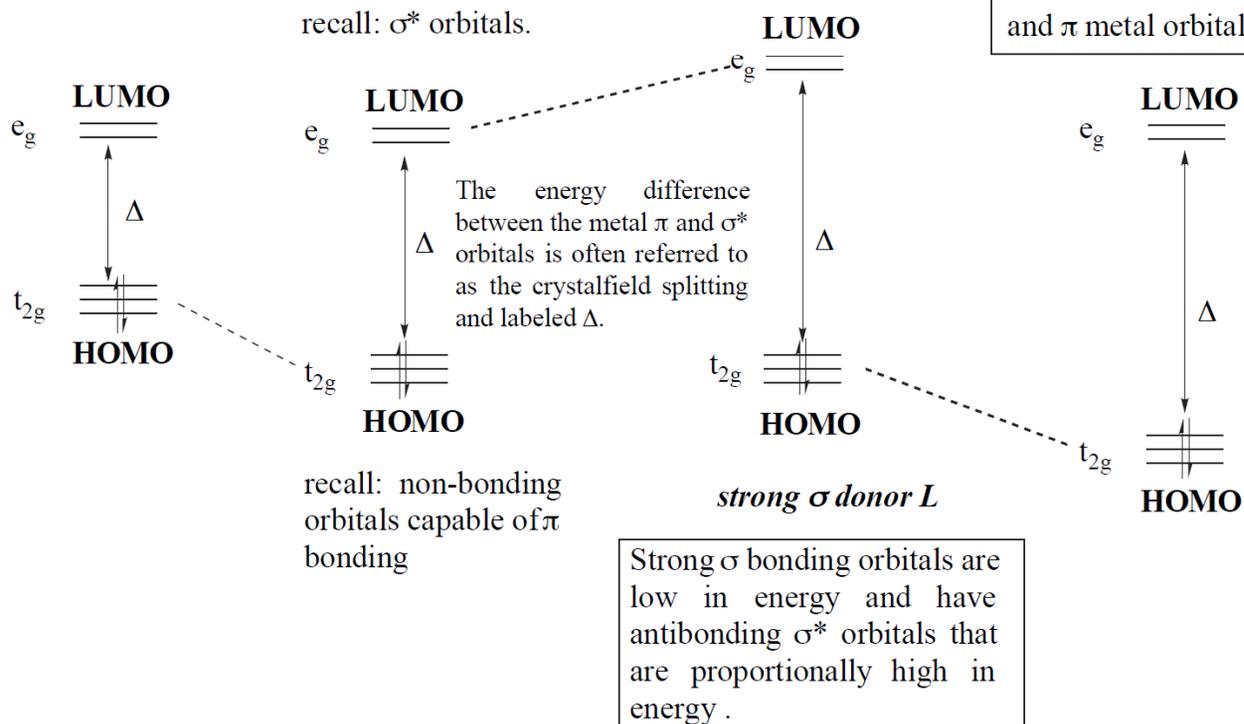
# Spectrochemical series

*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.

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

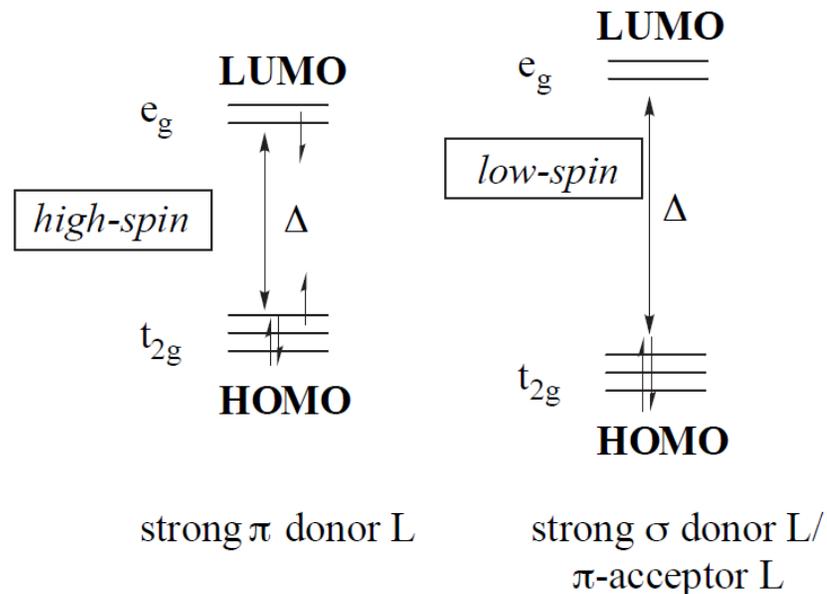
←  $\pi$ -donor low  $\Delta$  "low field ligand"  $\pi$ -acceptor/strong  $\sigma$ -donor high  $\Delta$  "high field ligand" →

- 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.

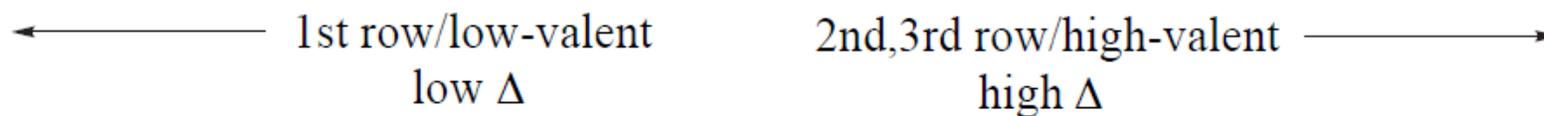
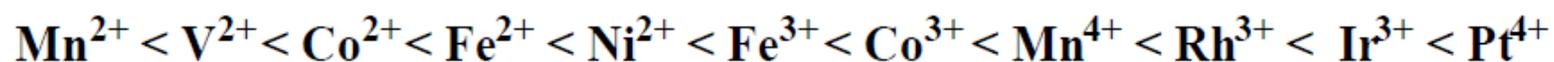
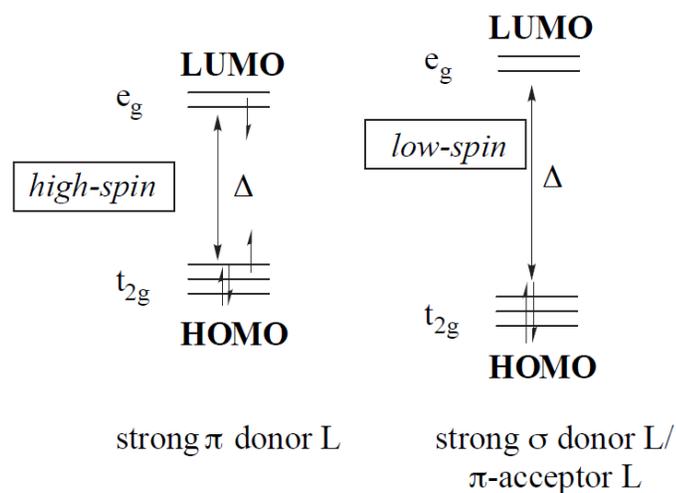
$$\text{Total pairing energy } \Pi = \Pi_c + \Pi_e$$

# 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> <u>—</u>	<u>—</u> <u>—</u>	<u>—</u> <u>—</u>	<u>—</u> <u>1</u>	<u>—</u> <u>—</u>	<u>1</u> <u>1</u>	<u>—</u> <u>—</u>
$t_{2g}$	<u>—</u> <u>—</u>	<u>—</u> <u>1</u>	<u>1</u> <u>1</u>	<u>1</u> <u>1</u>	<u>1</u> <u>1</u>	<u>1</u> <u>1</u>	<u>1</u> <u>1↓</u>
	<u>1</u> <u>—</u>	<u>1</u> <u>—</u>	<u>1</u> <u>—</u>	<u>1</u> <u>—</u>	<u>1↓</u> <u>—</u>	<u>1</u> <u>—</u>	<u>1↓</u> <u>—</u>
	$d^1$	$d^2$	$d^3$	$d^4$ high spin	$d^4$ low spin	$d^5$ high spin	$d^5$ low spin
$e_g$	<u>1</u> <u>1</u>	<u>—</u> <u>—</u>	<u>1</u> <u>1</u>	<u>—</u> <u>1</u>	<u>1</u> <u>1</u>	<u>1</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u>
$t_{2g}$	<u>1</u> <u>1</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u> <u>1↓</u>	<u>1</u> <u>1↓</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u> <u>1↓</u>
	$d^6$ high spin	$d^6$ low spin	$d^7$ high spin	$d^7$ low 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

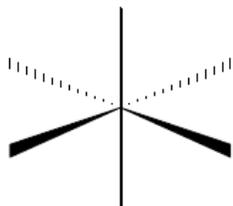
- When empirical corrections are added to CFT it is known as Ligand Field Theory (LFT).
- ***LFT represents an application of molecular orbital (MO) theory to transition metal complexes.***
- Need for corrections to CFT arise from metal-ligand orbital overlap, implying some degree of covalent M–L bonding (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.

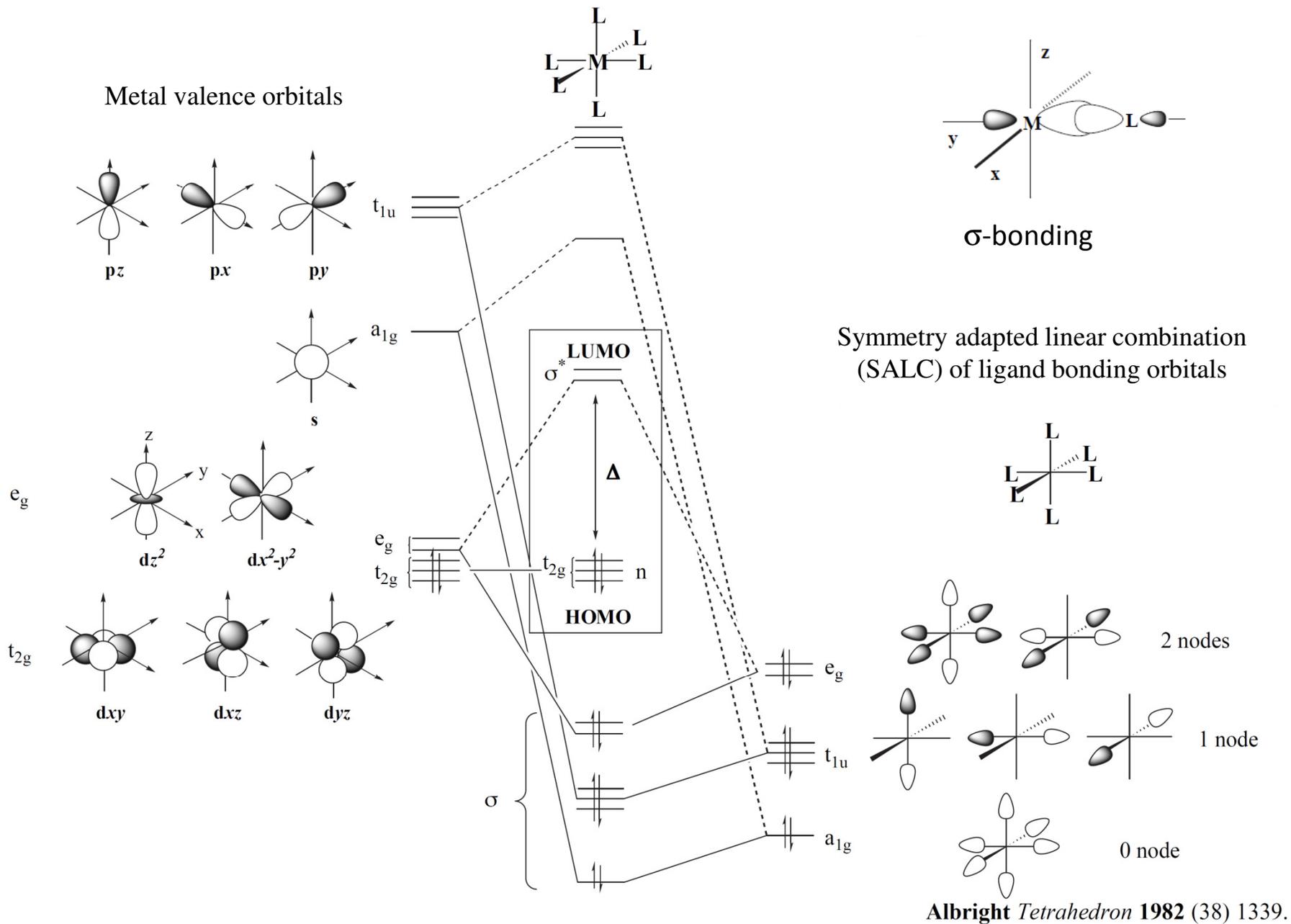
# Character table for the $O_h$ point group

$O_h$	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2(= C_4^2)$	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
$A_{1g}$	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		$(2z^2 - x^2 - y^2,$ $x^2 - y^2)$
$T_{1g}$	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		$(2z^2 - x^2 - y^2,$ $x^2 - y^2)$



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

# 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 of <i>d</i> Electrons	Weak-Field Arrangement					LFSE ( $\Delta_o$ )	Coulombic Energy	Exchange 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 of <i>d</i> Electrons	Strong-Field Arrangement					LFSE ( $\Delta_o$ )	Coulombic Energy	Exchange Energy	Strong Field – 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  $\Pi = \Pi_c + \Pi_e$**