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
CFT & $d$-subshell Splitting in an $O_h$ Field

- In the octahedral ($O_h$) environment the fivefold degeneracy among the $d$ orbitals is lifted.

- If the ligand field is of $O_h$ symmetry the $d$ subshell will separate into a set of three degenerate orbitals ($t_{2g} = d_{xy}, d_{yz}, d_{xz}$) and a set of two degenerate orbitals ($e_g = d_{x^2-y^2}, d_{z^2}$).

- Relative to the energy of the hypothetical spherical field, the $e_g$ set will rise in energy and the $t_{2g}$ set will fall in energy, creating an energy separation of $\Delta_o$ or $10 \, Dq$ between the two sets of $d$ orbitals.
• The $t_{2g}$ orbitals point between ligands.
• The $e_g$ orbitals point directly at the ligands.
• Thus, the $t_{2g}$ set is stabilized and the $e_g$ set is destabilized (relative to the energy of a hypothetical spherical electric field).
• The energy increase of the $e_g$ orbitals and the energy decrease of the $t_{2g}$ orbitals must be balanced relative to the energy of the hypothetical spherical field (aka the barycenter).

• The energy of each of the two orbitals of the $e_g$ set rises by $+3/5 \Delta_o$ ($+6Dq$) while the energy of each of the three $t_{2g}$ orbitals falls by $-2/5 \Delta_o$ ($-4Dq$).

• This results in no net energy change for the system:

$$\Delta E = E(e_g) + E(t_{2g})$$

$$= (2)(+3/5 \Delta_o) + (3)(-2/5 \Delta_o)$$

$$= (2)(+6Dq) + (3)(-4Dq) = 0$$

(The magnitude of $\Delta_o$ depends upon both the metal ion and the attaching ligands)
In an octahedral complex, electrons fill the $t_{2g}$ and $e_g$ orbitals in an aufbau manner, but for configurations $d^4 – d^7$ there are two possible filling schemes depending on the magnitude of $\Delta_0$ relative to the mean electron pairing energy, $P$.

A high-spin configuration avoids pairing by spreading the electrons across both the $t_{2g}$ and $e_g$ levels.

A low-spin configuration avoids occupying the higher energy $e_g$ level by pairing electrons in the $t_{2g}$ level.

For a given metal ion, the pairing energy is relatively constant, so the spin state depends upon the magnitude of the field strength, $\Delta_0$.

Low field strength results in a high-spin state.

High field strength results in a low-spin state.

For example, a $d^4$ configuration, the high-spin state is $t_{2g}^3e_g^1$, and the low-spin state is $t_{2g}^4e_g^0$. 

High-Spin and Low-Spin Configurations
Low field strength results in a high-spin state.

High field strength results in a low-spin state.

For a $d^4$ configuration, the high-spin state is $t_{2g}^3e_g^1$, and the low-spin state is $t_{2g}^4e_g^0$. 
MO used for most sophisticated and quantitative interpretations

LFT used for semi-quantitative interpretations

CFT used for everyday qualitative interpretations
Construction of MO diagrams for Transition Metal Complexes

\( \sigma \) bonding only scenario
General MO Approach for MX$_n$ Molecules

• To construct delocalized MOs we define a *linear combination of atomic orbitals (LCAOs)* that combine central-atom AOs with combinations of pendant ligand orbitals called SALCs:

\[
\Psi_{MO} = a \Psi \text{ (Metal AO)} \pm b \Psi \text{ (SALC } \text{nX)}
\]

*(SALC = Symmetry Adapted Linear Combination)*

• SALCs are constructed with the aid of group theory, and those SALCs that belong to a particular species of the group are matched with central-atom AOs with the same symmetry to make bonding and antibonding MOs.

\[
\Psi_{SALC} = c_1 \Psi_1 \pm c_2 \Psi_2 \pm c_3 \Psi_3 \ldots \pm c_n \Psi_n
\]
1. Use the directional properties of potentially bonding orbitals on the outer atoms (shown as vectors on a model) as a basis for a representation of the SALCs in the point group of the molecule.

point group = $O_h$
2. Generate a **reducible representation** for all possible SALCs by noting whether vectors are shifted or non-shifted by each class of operations of the group.

- Each vector shifted through space contributes 0 to the character for the class.

Each non-shifted vector contributes 1 to the character for the class.

```
point group = \( O_h \)
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<th>( O_h )</th>
<th>( E )</th>
<th>( 8C_3 )</th>
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<th>( 6C_4 )</th>
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point group = $O_h$
3. Decompose the reducible representation into its component irreducible representations to determine the symmetry species of the SALCs.

- For complex molecules with a large dimension reducible representation, identification of the component irreducible representations and their quantitative contributions can be carried out systematically using the following equation

\[ n_i = \frac{1}{h} \sum_c g_c \chi_i \chi_r \]

- The work of carrying out a **systematic reduction** is better organized by using the **tabular method**, rather than writing out the individual equations for each irreducible representation.

\[ n_i : \text{ number of times the irreducible representation } i \text{ occurs in the reducible representation} \]
\[ h : \text{ order of the group} \]
\[ c : \text{ class of operations} \]
\[ g_c : \text{ number of operations in the class} \]
\[ \chi_i : \text{ character of the irreducible representation for the operations of the class} \]
\[ \chi_r : \text{ character of the reducible representation for the operations of the class} \]
Character Table for $O_h$

point group = $O_h$

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<tr>
<th>$O_h$</th>
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</tbody>
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Transformation Properties of Central AOs

- Transformation properties for the standard AOs in any point group can be deduced from listings of vector transformations in the character table for the group.

\( s \) – transforms as the totally symmetric representation in any group.

\( p \) – transform as \( x, y, \) and \( z \), as listed in the second-to-last column of the character table.

\( d \) – transform as \( xy, xz, yz, x^2-y^2 \), and \( z^2 \) (or \( 2z^2-x^2-y^2 \))

e.g., in \( T_d \) and \( O_h \), as listed in the last column of the character table.
Mulliken Symbols
- Irreducible Representation Symbols

• In non-linear groups:

  * $A$ : non-degenerate; symmetric to $C_n$ where $\chi(C_n) = 1$.
  * $B$ : non-degenerate; anti-symmetric to $C_n$ where $\chi(C_n) = -1$.
  * $E$ : doubly-degenerate; $\chi(E) = 2$.
  * $T$ : triply-degenerate; $\chi(T) = 3$.
  * $G$ : four-fold degeneracy; $\chi(G) = 4$, observed in $I$ and $I_h$.
  * $H$ : five-fold degeneracy; $\chi(H) = 5$, observed in $I$ and $I_h$.

• In linear groups $C_{\infty v}$ and $D_{\infty h}$:

  * $\Sigma \equiv A$ : non-degenerate; symmetric to $C_\infty$; $\chi(C_\infty) = 1$.
  * $\Pi, \Delta, \Phi \equiv E$ : doubly-degenerate; $\chi(E) = 2$. 
Mulliken Symbols - Modifying Symbols

• With any degeneracy in any centrosymmetric groups:

  subscript \( g \) : \textit{gerade} ; symmetric with respect to inversion ; \( \chi_i > 0 \).

  subscript \( u \) : \textit{ungerade} ; anti-symmetric with respect to inversion ; \( \chi_i < 0 \).

• With any degeneracy in non-centrosymmetric non-linear groups:

  prime (‘) : symmetric with respect to \( \sigma_h \); \( \chi(\sigma_h) > 0 \).

  double prime (“”) : anti-symmetric with respect to \( \sigma_h \); \( \chi(\sigma_h) < 0 \).

• With non-degenerate representations in non-linear groups:

  subscript \( 1 \) : symmetric with respect to \( C_m \) (\( m < n \)) or \( \sigma_v \);
  \( \chi(C_m) > 0 \) or \( \chi(\sigma_v) > 0 \).

  subscript \( 2 \) : anti-symmetric with respect to \( C_m \) (\( m < n \)) or \( \sigma_v \);
  \( \chi(C_m) < 0 \) or \( \chi(\sigma_v) < 0 \).

• With non-degenerate representations in linear groups (\( C_{\infty v} \) and \( D_{\infty h} \)):

  subscript + : symmetric with respect to \( \infty C_2 \) or \( \infty \sigma_v \);
  \( \chi(\infty C_2) = 1 \) or \( \chi(\infty \sigma_v) = 1 \).

  subscript − : anti-symmetric with respect to \( \infty C_2 \) or \( \infty \sigma_v \);
  \( \chi(\infty C_2) = -1 \) or \( \chi(\infty \sigma_v) = -1 \).
**Systematic Reduction for $O_h$**

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### Systematic Reduction for $O_h$

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$(h = 48)$
4. The number of SALCs, including members of degenerate sets, must equal the number of ligand orbitals taken as the basis for the representation.

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

\[
d_\Gamma = 1 + 2 + 3 = 6
\]

point group = $O_h$
5. Determine the symmetries of potentially bonding central-atom AOs by inspecting unit vector and direct product transformations listed in the character table of the group.

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

point group = \(O_h\)

**Cr bonding AOs**

\(A_{1g}\) : 4s
\(T_{1u}\) : \((4p_x, 4p_y, 4p_z)\)
\(E_g\) : \((3dx^2-y^2, 3dz^2)\)

**Cr non-bonding AOs**

\(T_{2g}\) : \((3dxy, 3dxz, 3dyz)\)
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<tr>
<th>Symmetry</th>
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</tr>
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<tr>
<td>$E_g$</td>
<td>{ $dx^2-y^2$ }</td>
<td>{ }</td>
</tr>
<tr>
<td>$T_{1u}$</td>
<td>{ $p_x$, $p_y$, $p_z$ }</td>
<td>{ }</td>
</tr>
<tr>
<td>$A_{1g}$</td>
<td>$s$</td>
<td>{ }</td>
</tr>
</tbody>
</table>
6. Central-atom AOs and pendant-atom SALCs with the same symmetry species will form both bonding and antibonding LCAO-MOs.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>bonding MOs</th>
<th>anti-bonding MOs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$</td>
<td><img src="E_g_bonding.png" alt="Diagram" /></td>
<td><img src="E_g_antibonding.png" alt="Diagram" /></td>
</tr>
<tr>
<td>$T_{1u}$</td>
<td><img src="T_1u_bonding.png" alt="Diagram" /></td>
<td><img src="T_1u_antibonding.png" alt="Diagram" /></td>
</tr>
<tr>
<td>$A_{1g}$</td>
<td><img src="A_1g.png" alt="Diagram" /></td>
<td><img src="A_1g.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>
7. Central-atom AOs or pendant-atom SALCs with unique symmetry (no species match between AOs and SALCs) form nonbonding MOs.
SALCS for Common Geometries (*σ* bonding)

CN = 2

$C_{2v}$

$B_1$

$A_1$

$D_{\infty h}$

$\Sigma_u^+$

$\Sigma_g^+$
SALCS for Common Geometries ($\sigma$ bonding)

$\text{CN} = 3$

$C_{3v}$

$E$

$A_1$

$D_{3h}$

$E'$

$A_1'$
SALCS for Common Geometries (*σ bonding*)

$CN = 3$

$D_{3h}$

$E$

$A_1'$
SALCS for Common Geometries (\(\sigma\) bonding)

\(\text{CN} = 4\)

\(T_d\)

\(T_2\)

\(A_1\)
SALCS for Common Geometries ($\sigma$ bonding)

CN = 4

$D_{4h}$

$B_{1g}$

$E_u$

$A_{1g}$
SALCS for Common Geometries (σ bonding)

CN = 5

$D_{3h}$

$E$

$A_{2''}$

$A_{1'}$

$A_{1'}$
SALCS for Common Geometries \((\sigma\text{bonding})\)

CN = 6

\(O_h\)

\[E_g\]

\[T_{2g}\]

\[A_{1g}\]
Construction of MO diagrams for Transition Metal Complexes

\[ \pi \] bonding complexes
Example: Constructing a MO for Chromium Hexacarbonyl, Cr(CO)$_6$

- Each vector shifted through space contributes 0 to the character for the class.
- Each non-shifted vector contributes 1 to the character for the class.
- Each vector shifted to the negative of itself (180°) contributes -1 to the character for the class.
Example: Constructing a MO for Chromium Hexacarbonyl, Cr(CO)$_6$

point group = $O_h$

\[
\begin{array}{cccccccccc}
& O_h & E & 8C_3 & 6C_2 & 6C_4 & 3C_2 & i & 6S_4 & 8S_6 & 3\sigma_h & 6\sigma_d \\
\hline
\Gamma_\pi & & & & & & & & & & & \\
A_{1g} & & & & & & & & & & & \\
A_{2g} & & & & & & & & & & & \\
E_g & & & & & & & & & & & \\
T_{1g} & & & & & & & & & & & \\
T_{2g} & & & & & & & & & & & \\
A_{1u} & & & & & & & & & & & \\
A_{2u} & & & & & & & & & & & \\
E_u & & & & & & & & & & & \\
T_{1u} & & & & & & & & & & & \\
T_{2u} & & & & & & & & & & & \\
\hline
\Sigma & & & & & & & & & & & \\
\Sigma/h & & & & & & & & & & & \\
\hline
\end{array}
\]

$\Gamma_\pi =$

$d_\Gamma =$
Example: Constructing a MO for Chromium Hexacarbonyl, Cr(CO)$_6$

The point group is $O_h$.

<table>
<thead>
<tr>
<th>$O_h$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$6C_2$</th>
<th>$6C_4$</th>
<th>$3C_2$</th>
<th>$i$</th>
<th>$6S_4$</th>
<th>$8S_6$</th>
<th>$3\sigma_h$</th>
<th>$6\sigma_d$</th>
<th>$\Sigma$</th>
<th>$\Sigma/h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_\pi$</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$A_{1g}$</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>$E_g$</td>
<td>24</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-24</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>$T_{1g}$</td>
<td>36</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>$T_{2g}$</td>
<td>36</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>$E_u$</td>
<td>24</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-24</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>$T_{1u}$</td>
<td>36</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>12</td>
<td>0</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>$T_{2u}$</td>
<td>36</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>12</td>
<td>0</td>
<td>48</td>
<td>1</td>
</tr>
</tbody>
</table>

$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$

$d_{\Gamma} = 3 + 3 + 3 + 3 = 12$
Example: Constructing a MO for Chromium Hexacarbonyl, Cr(CO)$_6$

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

point group = $O_h$

\[ \Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u} \]

point group = $O_h$
Example: Constructing a MO for Chromium Hexacarbonyl, Cr(CO)$_6$

$\Gamma_{\sigma} = A_{1g} + E_g + T_{1u} \quad \Gamma_{\pi} = T_{1g} + T_{2g} + T_{1u} + T_{2u}$

Cr $\sigma$-bonding AOs

Cr $\pi$-bonding AOs

Cr non-bonding AOs
Example: Constructing a MO diagram for Chromium Hexacarbonyl, Cr(CO)$_6$

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

\[ \Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u} \]

**Cr \( \sigma \)-bonding AOs**

\[ A_{1g} : 4s \]
\[ T_{1u} : (4p_x, 4p_y, 4p_z) \]
\[ E_g : (3d^{\text{x}^2-\text{y}^2}, 3dz^2) \]

**Cr non-bonding AOs**

\[ T_{2g} : (3dxy, 3dxz, 3dyz) \]

**Cr \( \pi \)-bonding AOs**

\[ T_{2g} : (3dxy, 3dxz, 3dyz) \]
\[ T_{1u} : (4p_x, 4p_y, 4p_z) \]

- \( T_{2g} \) previously considered non-bonding in \( \sigma \)-bonding scheme
- \( T_{1u} \) combines with \( T_{1u} \) SALC in in \( \sigma \)-bonding scheme
- \( T_{1g}, \ T_{2u} \) \( \pi \)-SALCs are non-bonding
Symmetry

$T_{1g}$

$T_{1u}$

$T_{2g}$

$T_{2u}$

SALCs

$z$

$x$

$y$
- $T_{1u}$ AOs overlap more effectively with $T_{1u} \sigma$-SALC thus the $\pi$-bonding interaction is considered negligible or at most only weakly-bonding.
$T_{2g}$ $\pi$-MOs

$dx_y$

$dx_z$

$dy_z$

$dx_z, dy_z$ or $dx_y$
Dewar-Chatt-Duncanson model

\[ \text{Metal } d_z^2 \xrightarrow{\sigma \text{ bond}} \text{carbonyl} \]

\[ \text{Metal } d_x^2 - d_y^2 \xrightarrow{\sigma \text{ bond}} \text{carbonyl} \]

\[ \text{Metal } d_y \xrightarrow{\pi\text{-back-donation}} \text{carbonyl} \]

\[ \nu(\text{CO}) \text{ cm}^{-1} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu(\text{CO}) \text{ cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ti(CO)}_6]^2-)</td>
<td>1748</td>
</tr>
<tr>
<td>([\text{V(CO)}_6]^+)</td>
<td>1859</td>
</tr>
<tr>
<td>(\text{Cr(CO)}_6)</td>
<td>2000</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_6]^+)</td>
<td>2100</td>
</tr>
<tr>
<td>([\text{Fe(CO)}_6]^{2+})</td>
<td>2204</td>
</tr>
</tbody>
</table>
Summary of $\pi$-bonding in $O_h$ complexes

$\pi$ donor ligands result in $L \rightarrow M$ $\pi$ bonding, a smaller $\Delta_o$ favoring high spin configurations and a decreased stability.

$\pi$ acceptor ligands result in $M \rightarrow L$ $\pi$ bonding, a larger $\Delta_o$ favoring low spin configurations with an increased stability.