Example: Constructing a $\sigma$-only MO diagram for Iron Pentacarbonyl, Fe(CO)$_5$
Example: Constructing a MO for Iron Pentacarbonyl, Fe(CO)$_5$

![Diagram of Fe(CO)$_5$]

Point group = $D_{3h}$

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$\sigma_h$</th>
<th>$2S_3$</th>
<th>$3\sigma_v$</th>
<th>$\Sigma$</th>
<th>$\Sigma/h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_\sigma$</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_1'$</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>9</td>
<td>24</td>
<td>2</td>
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<tr>
<td>$A_2'$</td>
<td>5</td>
<td>4</td>
<td>-3</td>
<td>3</td>
<td>0</td>
<td>-9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E''$</td>
<td>10</td>
<td>-4</td>
<td>0</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>12</td>
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<tr>
<td>$A_1''$</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>-3</td>
<td>0</td>
<td>-9</td>
<td>0</td>
<td>0</td>
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<tr>
<td>$A_2''$</td>
<td>5</td>
<td>4</td>
<td>-3</td>
<td>-3</td>
<td>0</td>
<td>9</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>$E'''$</td>
<td>10</td>
<td>-4</td>
<td>0</td>
<td>-6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$\Gamma_\sigma = 2A_1' + E'' + A_2''$

$d_\Gamma = 2(1) + 1 + 2 = 5$
Example: Constructing a MO for Iron Pentacarbonyl, Fe(CO)$_5$

\[
\Gamma_\sigma = 2A_1' + E' + A_2''
\]

Fe bonding AOs

\[A_1' : 4s, 3dz^2\]
\[E' : (4p_x, 4p_y) (3dx^2-y^2, 3dxy)\]
\[A_2'' : (4p_z)\]

Fe non-bonding AOs

\[E'' : (3dxz, 3dyz)\]
Fe$^0$

$4p$ ($a_2''$, $e'$)

$4s$ ($a_1'$)

$3d$ ($a_1', e', e''$)

$5\text{CO}$
Construction of MO diagrams for Transition Metal Complexes

π bonding complexes
Example: Constructing a MO for Chromium Hexacarbonyl, Cr(CO)$_6$

point group = $O_h$
Example: Constructing a MO for Chromium Hexacarbonyl, Cr(CO)\textsubscript{6}

![Diagram of Chromium Hexacarbonyl]

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

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

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

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

- Cr \( \pi \)-bonding AOs
  - \( T_{2g} \) : (3\( d_{xy} \), 3\( d_{xz} \), 3\( d_{yz} \))
  - \( T_{1u} \) : (4\( p_x \), 4\( p_y \), 4\( p_z \))

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

$d_{xy}$

$d_{xz}$

$d_{yz}$

$d_{xz}, d_{yz}$ or $d_{xy}$
\[ \text{HOMO} \rightarrow \Delta_0 \rightarrow \text{LUMO} \]
Dewar-Chatt-Duncanson model

\[ \text{Metal } d_{z^2} \leftarrow \sigma \text{ bond carbonyl} \]
\[ \text{Metal } d_{x^2-y^2} \leftarrow \sigma \text{ bond carbonyl} \]
\[ \text{Metal } d_y \rightarrow \pi\text{-back-donation carbonyl} \]

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

- \([\text{Ti(CO)}_6]^{2-}\): 1748
- \([\text{V(CO)}_6]^{-}\): 1859
- \(\text{Cr(CO)}_6\): 2000
- \([\text{Mn(CO)}_6]^{+}\): 2100
- \([\text{Fe(CO)}_6]^{2+}\): 2204
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.
Example: Constructing $\pi$ MOs for Titanium Tetraisopropoxido, Ti(O\textsuperscript{i}Pr\textsubscript{4})
Example: Constructing $\pi$ MOs for Titanium Tetraisopropoxoide, Ti(O^iPr)₄

\[
\begin{bmatrix}
-1/2 & \sqrt{3}/2 \\
-\sqrt{3}/2 & -1/2
\end{bmatrix}
\begin{bmatrix}
  x \\
y
\end{bmatrix}
=
\begin{bmatrix}
x' \\
y'
\end{bmatrix}
\]

\[h = 24\]

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6S_4$</th>
<th>$6\sigma_d$</th>
<th>$\Sigma$</th>
<th>$\Sigma/h$</th>
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<td>24</td>
<td>1</td>
</tr>
</tbody>
</table>

$$\Gamma_\pi = E + T_1 + T_2$$

$$d_{\Gamma} = 2 + 3 + 3 = 8$$
Example: Constructing $\pi$ MOs for Titanium Tetraisopropoxoide, Ti(O\textsuperscript{i}Pr\textsubscript{4})

$$\Gamma_\pi = E + T_1 + T_2$$

- The O\textsuperscript{i}Pr SALCs are comprised of filled $p_x$ and $p_y$ orbitals on the O atoms.
- Ti bonding AOs
  - $E : (3dz^2, 3dx^2-y^2)$
  - $T_2 : (4p_x, 4p_y, 4p_z)$
    - $(3dxy, 3dxz, 3dyz)$
- The $T_1$ SALC is non-bonding.
- Significant overlap occurs between the $E$ SALC and the $e$ AOs on Ti ($3dz^2, 3dx^2-y^2$)
- As the $4p$ AOs on Ti ($t_2$) are primarily involved in $\sigma$-bonding we will assume that they have negligible $\pi$-interaction here.

[It is very likely that there is extensive $d$-$p$ mixing involved in this system.]