Lecture 14: Angular Overlap Method (AOM) for ML for ML\textsubscript{n} Ligand Fields

The Wolfsberg-Hemholtz approximation (Lecture 10) provided the LCAO-MO energy between metal and ligand to be,

\[ \varepsilon_\sigma = \frac{E_M^2 S_{ML}^2}{\Delta E_{ML}} \quad \varepsilon_{\sigma^*} = \frac{E_L^2 S_{ML}^2}{\Delta E_{ML}} \]

Note that \( E_M, E_L \) and \( \Delta E_{ML} \) in the above expressions are constants. Hence, the MO within the Wolfsberg-Hemholtz framework scales directly with the overlap integral, \( S_{ML} \)

\[ \varepsilon_\sigma = \frac{E_M^2 S_{ML}^2}{\Delta E_{ML}} = \beta' S_{ML}^2 \quad \varepsilon_{\sigma^*} = \frac{E_L^2 S_{ML}^2}{\Delta E_{ML}} = \beta S_{ML}^2 \]

where \( \beta \) and \( \beta' \) are constants. Thus by determining the overlap integral, \( S_{ML} \), the energies of the MOs may be ascertained relative to the metal and ligand atomic orbitals.

The **Angular Overlap Method** (AOM), provides a measure of \( S_{ML} \) and hence MO energy levels. In AOM, the overlap integral is also factored into a radial and angular product,

\[ S_{ML} = S(r) F(\theta, \phi) \]

Analyzing \( S(r) \) as a function of the M–L internuclear distance,

Under the condition of a fixed M-L distance, \( S(r) \) is invariant, and therefore the overlap integral, \( S_{ML} \), will depend only on the angular dependence, i.e., on \( F(\theta, \phi) \).
Because the $\sigma$ orbital is symmetric, the angular dependence, $F(\theta,\phi)$, of the overlap integral mirrors the angular dependence of the central orbital.

\textit{p-orbital}

...is defined angularly by a $\cos \theta$ function. Hence, the angular dependence of a $\sigma$ orbital as it angularly rotates about a p-orbital reflects the $\cos \theta$ angular dependence of the p-orbital.

\begin{align*}
\text{Similarly, the other orbitals take on the angular dependence of the central metal orbital. Hence, for a} \\
\textit{d}_{yz}-\text{orbital} \\
\textit{d}_{z^2}-\text{orbital}
\end{align*}
ML Diatomic Complexes

To begin, let’s determine the energy of the d-orbitals for a M-L diatomic defined by the following coordinate system,

There are three types of overlap interactions based on σ, π and δ ligand orbital symmetries. For a σ orbital, the interaction is defined as,

\[ E(d_{z^2}) = S_{ML}^2(\sigma) = \beta \cdot F_{\sigma}^2(\theta, \phi) = \beta \cdot 1 = e\sigma \]

The energy for maximum overlap, at \( \theta = 0 \) (see above) is set equal to 1. This energy is defined as \( e\sigma \). The metal orbital bears the antibonding interaction, hence \( d_{z^2} \) is destabilized by \( e\sigma \) (the corresponding L orbital is stabilized by \( (\beta')^2 \cdot 1 = e\delta' \)).

For orbitals of π and δ symmetry, the same holds...maximum overlap is set equal to 1, and the energies are \( e\pi \) and \( e\delta \), respectively.

\[ E(d_{yz}) = E(d_{xz}) = S_{ML}^2(\pi) = e\pi \]
\[ E(d_{xy}) = E(d_{x^2-y^2}) = S_{ML}^2(\delta) = e\delta \]
As with the $\sigma$ interaction, the $(M-L\pi)^*$ interaction for the $d$-orbitals is de-stabilizing and the metal-based orbital is destabilized by $\epsilon\pi$, whereas the $L\pi$ ligands are stabilized by $\epsilon\pi$. The same case occurs for a ligand possessing a $\delta$ orbital, with the only difference being an energy of stabilization of $\epsilon\delta$ for the $L\delta$ orbital and the energy of de-stabilization of $\epsilon\delta$ for the $\delta$ metal-based orbitals.

$S_{ML}(\delta)$ is small compared to $S_{ML}(\pi)$ or $S_{ML}(\sigma)$. Moreover, there are few ligands with $\delta$ orbital symmetry (if they exist, the $\delta$ symmetry arises from the $\pi$-systems of organic ligands). For these reasons, the $S_{ML}(\delta)$ overlap integral and associated energy is not included in most AOM treatments.

Returning to the problem at hand, the overall energy level diagrams for a $M-L$ diatomic molecule for the three ligand classes are:

**$\pi$-donor**

$\sigma$-only

**$\pi$-acceptor**

$ML_6$ Octahedral Complexes

Of course, there is more than 1 ligand in a typical coordination compound. The power of AOM is that the $\epsilon\sigma$ and $\epsilon\pi$ (and $\epsilon\delta$), energies are additive. Thus, the MO energy levels of coordination compounds are determined by simply summing $\epsilon\sigma$ and $\epsilon\pi$ for each $M(d)$-$L$ interaction.
Consider a ligand positioned arbitrarily about the metal,

![Diagram of ligand positioned around metal](image)

We can imagine placing the ligand on the metal z axis (with x and y axes of M and L also aligned) and then rotate it on the surface of a sphere (thus maintaining M-L distance) to its final coordinate position. Within the reference frame of the ligand,

![Additional diagrams of rotation and transformation](image)

related by a coordinate transformation

\[ F(\theta, \phi) \]

S\(_{ML}\) in complex \[\rightarrow\] S\(_{ML}\) (\(\sigma\) and \(\pi\)) = 1

Note, the coordinate transformation lines up the ligand of interest on the z axis so that the normalized energies, \(e_\sigma\) and \(e_\pi\) (and \(e_\delta\)) may be normalized to 1. The transformation matrix for the coordinate transformation is:

<table>
<thead>
<tr>
<th>(z^2)</th>
<th>(y_2z_2)</th>
<th>(x_2z_2)</th>
<th>(x_2y_2)</th>
<th>(x_2^2-y_2^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(z^2)</td>
<td>(\frac{1}{4}(1 + 3 \cos 2\theta))</td>
<td>0</td>
<td>(-\frac{\sqrt{3}}{2} \sin 2\theta)</td>
<td>0</td>
</tr>
<tr>
<td>(yz)</td>
<td>(\frac{\sqrt{3}}{2} \sin \phi \sin 2\theta)</td>
<td>(\cos \phi \cos \theta)</td>
<td>(\sin \phi \cos 2\theta)</td>
<td>(-\cos \phi \sin \theta)</td>
</tr>
<tr>
<td>(xz)</td>
<td>(\frac{\sqrt{3}}{2} \cos \phi \sin 2\theta)</td>
<td>(-\sin \phi \cos \theta)</td>
<td>(\cos \phi \cos 2\theta)</td>
<td>(\sin \phi \sin \theta)</td>
</tr>
<tr>
<td>(xy)</td>
<td>(\frac{\sqrt{3}}{4} \sin 2\phi (1 - \cos 2\theta))</td>
<td>(\cos 2\phi \sin \theta)</td>
<td>(\frac{1}{2} \sin 2\phi \sin 2\theta)</td>
<td>(\cos 2\phi \cos \theta)</td>
</tr>
<tr>
<td>(x^2-y^2)</td>
<td>(\frac{\sqrt{3}}{4} \cos 2\phi (1 - \cos 2\theta))</td>
<td>(-\sin 2\phi \sin \theta)</td>
<td>(\frac{1}{2} \cos 2\phi \sin 2\theta)</td>
<td>(-\sin 2\phi \cos \theta)</td>
</tr>
</tbody>
</table>
For ligands in an octahedral complex, the $\theta$ and $\phi$ for the six ligands values are,

\[
\begin{array}{c|ccccccc}
\text{Ligand} & 1 & 2 & 3 & 4 & 5 & 6 \\
\theta & 0 & 90 & 90 & 90 & 90 & 180^\circ \\
\phi & 0 & 0 & 90 & 180 & 270 & 0
\end{array}
\]

Consider the overlap of Ligand 2 in the transformed coordinate space; the contribution of the overlap of Ligand 2 with each metal orbital must be considered. This orbital interaction is given by the transformation matrix above. By substituting the $\theta = 90$ and $\phi = 0$ for Ligand 2 into the above transformation matrix, one finds,

for $d_{z^2}$ for $L_2$

\[
d_{z^2} = \frac{1}{4} (1 + 3 \cos 2\theta) d_{z^2} + 0 d_{yz} + \frac{\sqrt{3}}{2} \sin 2\theta d_{x_2 z_2} + 0 d_{x_2 y_2} + \frac{\sqrt{3}}{4} (1 - \cos 2\theta) d_{x_2^2 - y_2^2}
\]

\[
d_{z^2} = -\frac{1}{2} d_{z^2} + 0 d_{yz} + 0 d_{x_2 z_2} + 0 d_{x_2 y_2} + \frac{\sqrt{3}}{2} d_{x_2^2 - y_2^2}
\]

Thus the $d_{z^2}$ orbital in the transformed coordinate, $d_{z^2}$, has a contribution from $d_{z^2}$ and $d_{x_2^2 - y_2^2}$. Recall that energy of the orbital is defined by the square of the overlap integral. Thus the above coefficients are squared to give the energy of the $d_{z^2}$ orbital as a result of its interaction with Ligand 2 to be,

\[
E\left( d_{z^2} \right)^2 = \mathcal{S}_{\text{ML}}^2(\sigma) = \beta \cdot \mathcal{F}_{\text{L}}^2(\theta, \phi) = \frac{1}{4} d_{z^2}^2 + \frac{3}{4} d_{x_2^2 - y_2^2} = \frac{1}{4} e\sigma + \frac{3}{4} e\delta
\]

Visually, this result is logical. In the coordinate transformation, a $\sigma$ ligand residing on the z-axis (of energy $e\sigma$) is overlapping with $d_{z^2}$. This is the energy for $L_1$. The normalized energy for $L_2$ is its overlap with the coordinate transformed $d_{z^2}$:
Note, the \( d_{z^2} \) orbital is actually \( 2z^2-x^2-y^2 \), which is a linear combination of \( z^2-x^2 \) and \( z^2-y^2 \). Thus in the coordinate transformed system, \( L_2 \), as compared to \( L_1 \), is looking at the \( x^2 \) contribution of the wavefunction to \( \sigma \) bonding. Since it is \( \frac{1}{2} \) the electron density of that on the \( z \)-axis, it is \( \frac{1}{4} \) the energy (i.e., the square of the coefficient) on the \( \sigma \)-axis, hence \( \frac{1}{4} \) \( e\sigma \). The \( \delta \) component of the transformation comes from the \( 2z^2-(x^2+y^2) \) orbital functional form. Thus if \( L_2 \) has an orbital of \( \delta \) symmetry, then it will have an energy of \( \frac{3}{4} e\delta \).

The transformation properties of the other \( d \)-orbitals, as they pertain to \( L_2 \) orbital overlap, may be ascertained by completing the transformation matrix for \( \theta = 90 \) and \( \phi = 0 \),

\[
\begin{bmatrix}
\frac{1}{2} & 0 & 0 & \sqrt{3} \frac{1}{2} \\
0 & 0 & 0 & -1 \\
0 & 0 & -1 & 0 \\
0 & 1 & 0 & 0 \\
\frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2}
\end{bmatrix}
\]

The energy contribution from \( L_2 \) to the \( d \)-orbital levels as defined by AOM is,

\[
E(d_{yz}) = e\delta; \quad E(d_{xz}) = e\pi; \quad E(d_{xy}) = e\pi; \quad E(d_{x^2-y^2}) = \frac{3}{4} e\sigma + \frac{1}{4} e\delta
\]

Until this point, only the \( L_2 \) ligand has been treated. The overlap of the \( d \)-orbitals with the other five ligands also needs to be determined. The elements of the transformation matrices for these ligands are,

\[
L_1: \begin{bmatrix}
1 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1
\end{bmatrix} \quad L_3: \begin{bmatrix}
\frac{1}{2} & 0 & 0 & 0 & \sqrt{3} \frac{1}{2} \\
0 & 0 & -1 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 \\
-\frac{\sqrt{3}}{2} & 0 & 0 & -1 & 0 \\
\frac{\sqrt{3}}{2} & 0 & 0 & 0 & \frac{1}{2}
\end{bmatrix} \quad L_4: \begin{bmatrix}
\frac{1}{2} & 0 & 0 & 0 & \sqrt{3} \frac{1}{2} \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 \\
\frac{\sqrt{3}}{2} & 0 & 0 & 0 & \frac{1}{2}
\end{bmatrix}
\]

\[
L_5: \begin{bmatrix}
\frac{1}{2} & 0 & 0 & 0 & \sqrt{3} \frac{1}{2} \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & -1 & 0 & 0 & 0 \\
-\frac{\sqrt{3}}{2} & 0 & 0 & -1 & 0 \\
\frac{\sqrt{3}}{2} & 0 & 0 & 0 & \frac{1}{2}
\end{bmatrix} \quad L_6: \begin{bmatrix}
1 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1
\end{bmatrix}
\]
Squaring the coefficients for each of the ligands and then summing the total energy of each d-orbital,

<table>
<thead>
<tr>
<th></th>
<th>L1</th>
<th>L2</th>
<th>L3</th>
<th>L4</th>
<th>L5</th>
<th>L6</th>
<th>(E_{\text{TOTAL}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E(d_{z^2}))</td>
<td>(\epsilon\sigma)</td>
<td>(\frac{1}{4}e\sigma + \frac{3}{4}e\delta)</td>
<td>(\frac{1}{4}e\sigma + \frac{3}{4}e\delta)</td>
<td>(\frac{1}{4}e\sigma + \frac{3}{4}e\delta)</td>
<td>(\frac{1}{4}e\sigma + \frac{3}{4}e\delta)</td>
<td>(\epsilon\sigma)</td>
<td>(= 3\epsilon\sigma + 3e\delta)</td>
</tr>
<tr>
<td>(E(d_{yz}))</td>
<td>(\epsilon\pi)</td>
<td>(e\delta)</td>
<td>(\epsilon\pi)</td>
<td>(e\delta)</td>
<td>(\epsilon\pi)</td>
<td>(\epsilon\pi)</td>
<td>(= 4\epsilon\pi + 2e\delta)</td>
</tr>
<tr>
<td>(E(d_{xz}))</td>
<td>(\epsilon\pi)</td>
<td>(e\delta)</td>
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<td>(E(d_{x^2-y^2}))</td>
<td>(e\delta)</td>
<td>(\frac{3}{4}e\sigma + \frac{1}{4}e\delta)</td>
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<td>(e\delta)</td>
<td>(= 3\epsilon\sigma + 3e\delta)</td>
</tr>
</tbody>
</table>

As mentioned above, \(e_\delta << e_\sigma\) or \(e_\pi\)... thus \(e_\delta\) may be ignored. The \(O_h\) energy level diagram is:

\[\text{\(\pi\)-donor}\]

\[\text{\(\pi\)-acceptor}\]

\[\text{\(\sigma\)-only}\]

Note the d-orbital splitting is the same result obtained from the crystal field theory (CFT) model taught in freshman chemistry. In fact the energy parameterization scales directly between CFT and AOM

\[10\ \text{Dq} = \Delta_0 = 3\epsilon\sigma - 4\epsilon\pi\]