

MIT OpenCourseWare
<http://ocw.mit.edu>

5.04 Principles of Inorganic Chemistry II
Fall 2008

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.

Lecture 14: Angular Overlap Method (AOM) for ML for ML_n Ligand Fields

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

$$\epsilon_{\sigma} = \frac{E_M^2 S_{ML}^2}{\Delta E_{ML}} \quad \epsilon_{\sigma^*} = \frac{E_L^2 S_{ML}^2}{\Delta E_{ML}}$$

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

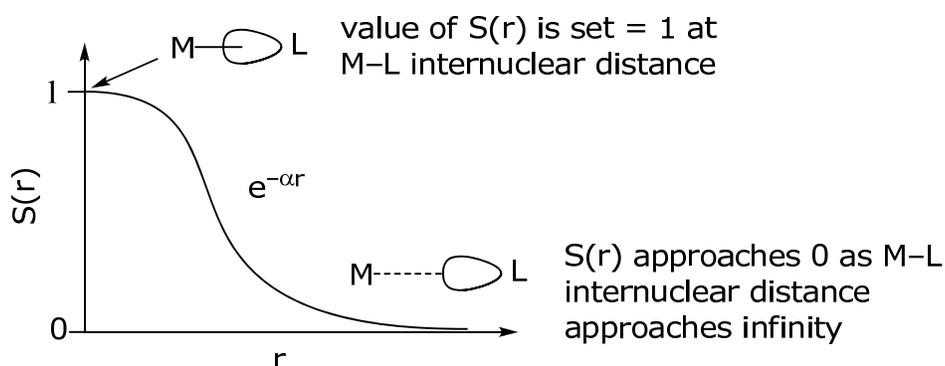
$$\epsilon_{\sigma} = \frac{E_M^2 S_{ML}^2}{\Delta E_{ML}} = \beta' S_{ML}^2 \quad \epsilon_{\sigma^*} = \frac{E_L^2 S_{ML}^2}{\Delta E_{ML}} = \beta S_{ML}^2$$

where β and β' 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,

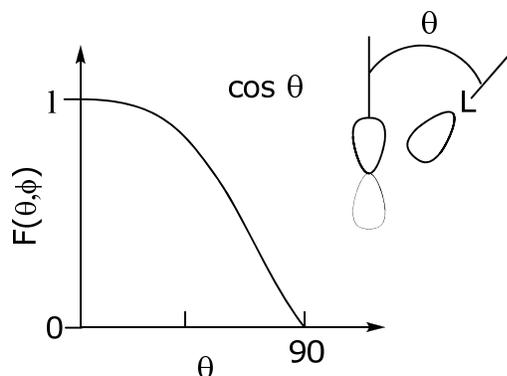


Under the condition of a fixed M-L distance, $S(r)$ is invariant, and therefore the overlap integral, S_{ML} , will depend only on the angular dependence, i.e., on $F(\theta, \phi)$.

Because the σ orbital is symmetric, the angular dependence, $F(\theta, \phi)$, of the overlap integral mirrors the angular dependence of the central orbital.

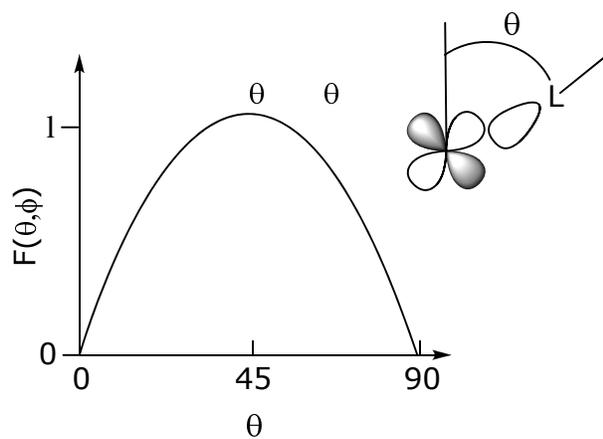
p-orbital

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

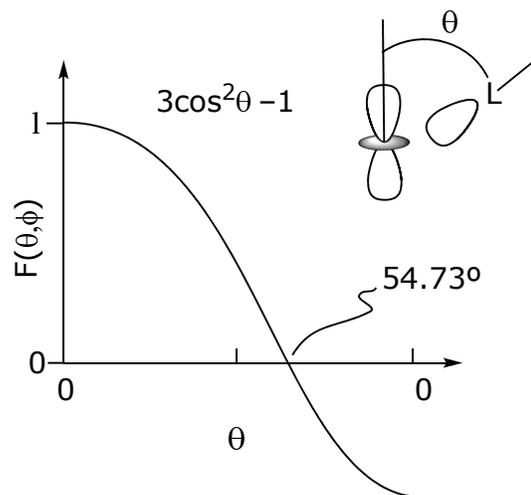


Similarly, the other orbitals take on the angular dependence of the central metal orbital. Hence, for a

d_{yz} -orbital

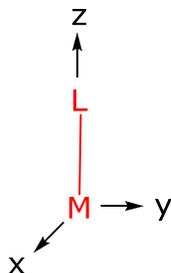


d_{z^2} -orbital

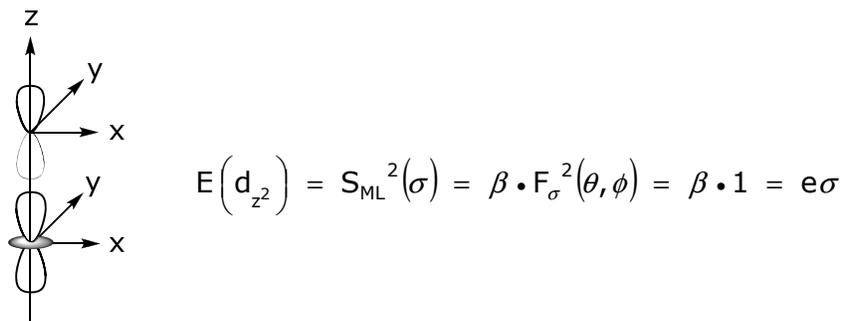


ML Diatomic Complexes

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

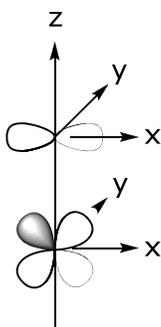


There are three types of overlap interactions based on σ , π and δ ligand orbital symmetries. For a σ orbital, the interaction is defined as,

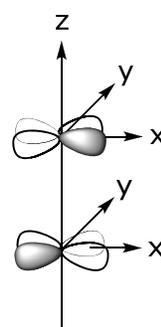


The energy for maximum overlap, at $\theta = 0$ (see above) is set equal to 1. This energy is defined as $e\sigma$. The metal orbital bears the antibonding interaction, hence d_{z^2} is destabilized by $e\sigma$ (the corresponding L orbital is stabilized by $(\beta')^2 \cdot 1 = e\sigma'$).

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.



$$E(d_{yz}) = E(d_{xz}) = S_{ML}^2(\pi) = e\pi$$

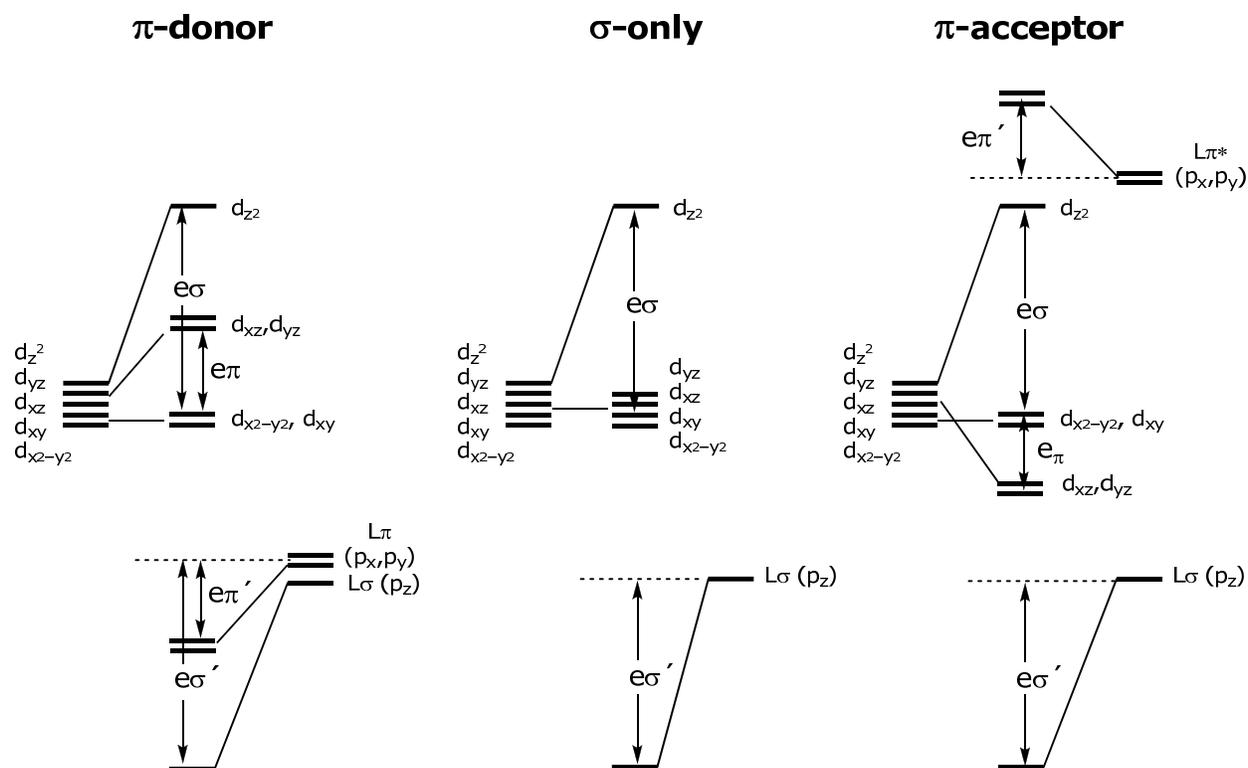


$$E(d_{xy}) = E(d_{x^2-y^2}) = S_{ML}^2(\delta) = e\delta$$

As with the σ interaction, the $(M-L\pi)^*$ interaction for the d-orbitals is de-stabilizing and the metal-based orbital is destabilized by $e\pi$, whereas the $L\pi$ ligands are stabilized by $e\pi$. The same case occurs for a ligand possessing a δ orbital, with the only difference being an energy of stabilization of $e\delta$ for the $L\delta$ orbital and the energy of de-stabilization of $e\delta$ for the δ metal-based orbitals.

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

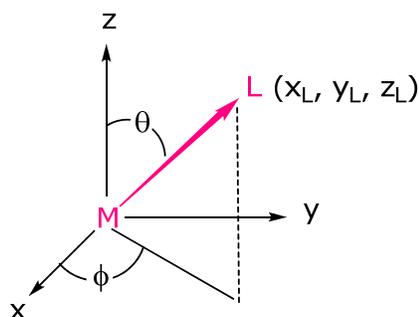
Returning to the problem at hand, the overall energy level diagrams for a M-L diatomic molecule for the three ligand classes are:



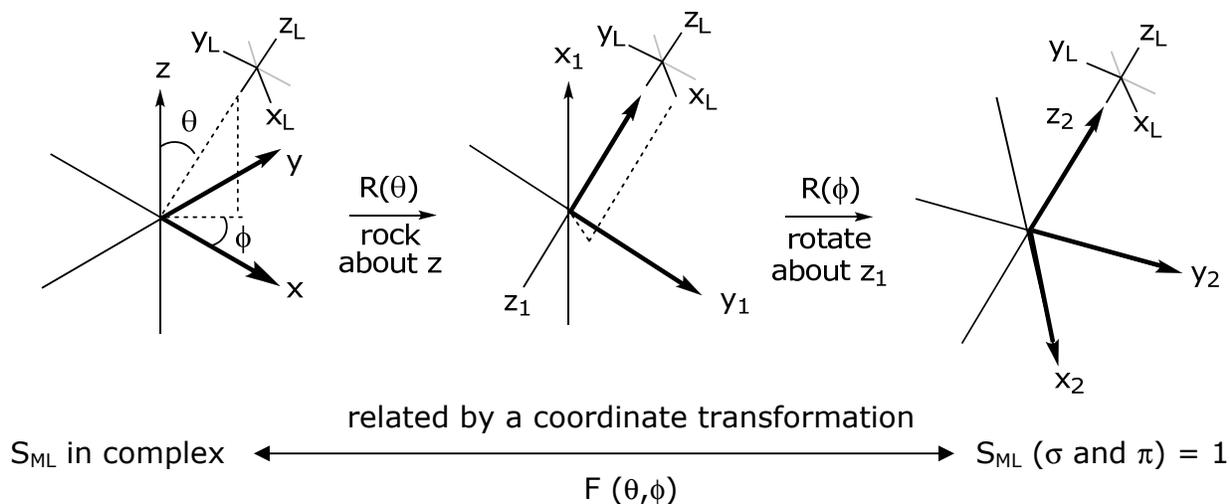
ML₆ Octahedral Complexes

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

Consider a ligand positioned arbitrarily about the metal,



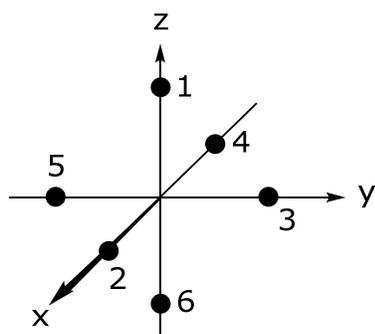
We can imagine placing the ligand on the metal z axis (with x and y axes of M and L also aligned) and then rotate it on the surface of a sphere (thus maintaining M-L distance) to its final coordinate position. Within the reference frame of the ligand,



Note, the coordinate transformation lines up the ligand of interest on the z axis so that the normalized energies, ϵ_σ and ϵ_π (and ϵ_δ) may be normalized to 1. The transformation matrix for the coordinate transformation is:

| | z_2^2 | y_2z_2 | x_2z_2 | x_2y_2 | $x_2^2 - y_2^2$ |
|-------------|--|---------------------------|--------------------------------------|---------------------------|---|
| z^2 | $\frac{1}{4}(1 + 3\cos 2\theta)$ | 0 | $-\frac{\sqrt{3}}{2}\sin 2\theta$ | 0 | $\frac{\sqrt{3}}{4}(1 - \cos 2\theta)$ |
| yz | $\frac{\sqrt{3}}{2}\sin \phi \sin 2\theta$ | $\cos \phi \cos \theta$ | $\sin \phi \cos 2\theta$ | $-\cos \phi \sin \theta$ | $-\frac{1}{2}\sin \phi \sin 2\theta$ |
| xz | $\frac{\sqrt{3}}{2}\cos \phi \sin 2\theta$ | $-\sin \phi \cos \theta$ | $\cos \phi \cos 2\theta$ | $\sin \phi \sin \theta$ | $-\frac{1}{2}\cos \phi \sin 2\theta$ |
| xy | $\frac{\sqrt{3}}{4}\sin 2\phi(1 - \cos 2\theta)$ | $\cos 2\phi \sin \theta$ | $\frac{1}{2}\sin 2\phi \sin 2\theta$ | $\cos 2\phi \cos \theta$ | $\frac{1}{4}\sin 2\phi(3 + \cos 2\theta)$ |
| $x^2 - y^2$ | $\frac{\sqrt{3}}{4}\cos 2\phi(1 - \cos 2\theta)$ | $-\sin 2\phi \sin \theta$ | $\frac{1}{2}\cos 2\phi \sin 2\theta$ | $-\sin 2\phi \cos \theta$ | $\frac{1}{4}\cos 2\phi(3 + \cos 2\theta)$ |

For ligands in an octahedral complex, the θ and ϕ for the six ligands values are,



| Ligand | 1 | 2 | 3 | 4 | 5 | 6 |
|----------|---|----|----|-----|-----|------|
| θ | 0 | 90 | 90 | 90 | 90 | 180° |
| ϕ | 0 | 0 | 90 | 180 | 270 | 0 |

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

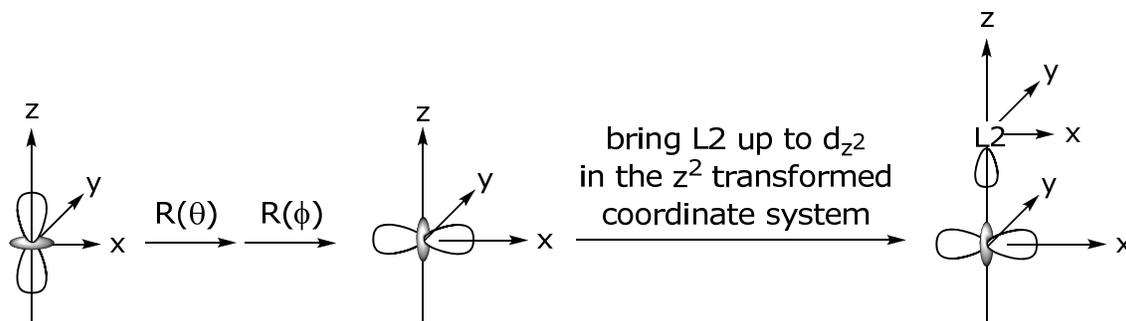
$$d_{z^2} = \frac{1}{4}(1 + 3\cos 2\theta)d_{z^2} + 0d_{y_2z_2} - \frac{\sqrt{3}}{2}\sin 2\theta d_{x_2z_2} + 0d_{x_2y_2} + \frac{\sqrt{3}}{4}(1 - \cos 2\theta)d_{x_2^2 - y_2^2}$$

$$= -\frac{1}{2}d_{z^2} + 0d_{y_2z_2} + 0d_{x_2z_2} + 0d_{x_2y_2} + \frac{\sqrt{3}}{2}d_{x_2^2 - y_2^2}$$

Thus the d_{z^2} orbital in the transformed coordinate, d_{z^2} , has a contribution from d_{z^2} and $d_{x^2 - y^2}$. 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,

$$E(d_{z^2})^{L_2} = S_{ML}^2(\sigma) = \beta \cdot F_{\sigma}^2(\theta, \phi) = \frac{1}{4}d_{z^2} + \frac{3}{4}d_{x^2 - y^2} = \frac{1}{4}e\sigma + \frac{3}{4}e\delta$$

Visually, this result is logical. In the coordinate transformation, a σ ligand residing on the z-axis (of energy $e\sigma$) is overlapping with d_{z^2} . This is the energy for L1. The normalized energy for L2 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, L2, as compared to L1, is looking at the x^2 contribution of the wavefunction to σ bonding. Since it is $1/2$ the electron density of that on the z-axis, it is $1/4$ the energy (i.e., the square of the coefficient) on the σ -axis, hence $1/4 e\sigma$. The δ component of the transformation comes from the $2z^2 - (x^2 + y^2)$ orbital functional form. Thus if L2 has an orbital of δ symmetry, then it will have an energy of $3/4 e\delta$.

The transformation properties of the other d-orbitals, as they pertain to L2 orbital overlap, may be ascertained by completing the transformation matrix for $\theta = 90$ and $\phi = 0$,

$$\begin{bmatrix} d_{z^2} \\ d_{yz} \\ d_{xz} \\ d_{xy} \\ d_{x^2-y^2} \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & 0 & 0 & 0 & \frac{1}{2} \end{bmatrix} \begin{bmatrix} d_{z^2} \\ d_{y^2z^2} \\ d_{x^2z^2} \\ d_{x^2y^2} \\ d_{x^2-y^2} \end{bmatrix}$$

The energy contribution from L2 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 L2 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,

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

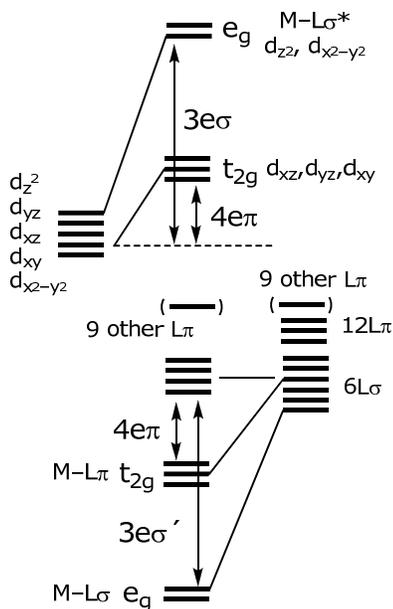
$$L_5 : \begin{bmatrix} -\frac{1}{2} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & -\frac{1}{2} \end{bmatrix} \quad L_6 : \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Squaring the coefficients for each of the ligands and then summing the total energy of each d-orbital,

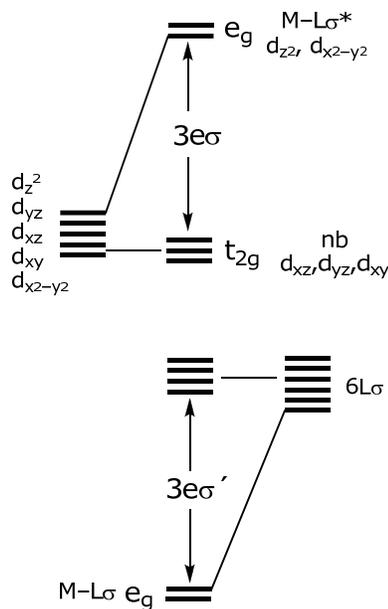
| | L1 | L2 | L3 | L4 | L5 | L6 | E _{TOTAL} |
|--|----------------|---|---|---|---|----------------|-------------------------------------|
| E(d _{z²}) | e _σ | $\frac{1}{4}e_{\sigma} + \frac{3}{4}e_{\delta}$ | $\frac{1}{4}e_{\sigma} + \frac{3}{4}e_{\delta}$ | $\frac{1}{4}e_{\sigma} + \frac{3}{4}e_{\delta}$ | $\frac{1}{4}e_{\sigma} + \frac{3}{4}e_{\delta}$ | e _σ | = 3e _σ + 3e _δ |
| E(d _{yz}) | e _π | e _δ | e _π | e _δ | e _π | e _π | = 4e _π + 2e _δ |
| E(d _{xz}) | e _π | e _π | e _δ | e _π | e _δ | e _π | = 4e _π + 2e _δ |
| E(d _{xy}) | e _δ | e _π | e _π | e _π | e _π | e _δ | = 4e _π + 2e _δ |
| E(d _{x²-y²}) | e _δ | $\frac{3}{4}e_{\sigma} + \frac{1}{4}e_{\delta}$ | $\frac{3}{4}e_{\sigma} + \frac{1}{4}e_{\delta}$ | $\frac{3}{4}e_{\sigma} + \frac{1}{4}e_{\delta}$ | $\frac{3}{4}e_{\sigma} + \frac{1}{4}e_{\delta}$ | e _δ | = 3e _σ + 3e _δ |

As mentioned above, e_δ << e_σ or e_π... thus e_δ may be ignored. The O_h energy level diagram is:

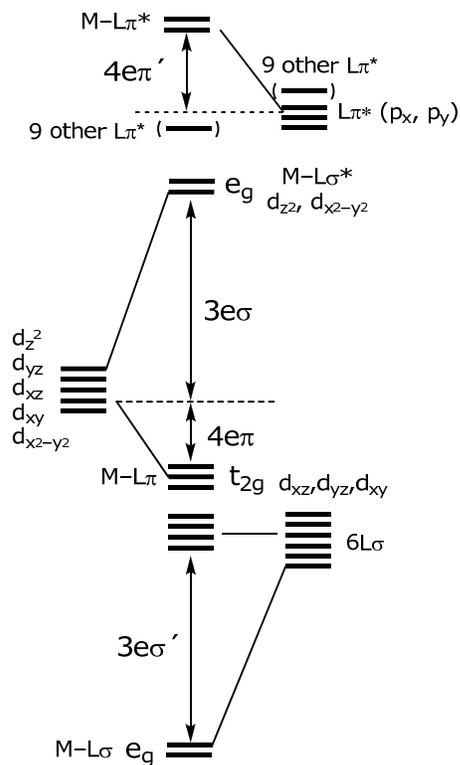
π-donor



σ-only



π-acceptor



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

$$10 Dq = \Delta_0 = 3e_{\sigma} - 4e_{\pi}$$