

1.14: Angular Overlap Method and M-L Diatomics

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

$$\varepsilon_{\sigma} = \frac{E_M^2 S_{ML}^2}{\Delta E_{ML}} \quad \varepsilon_{\sigma^*} = \frac{E_L^2 S_{ML}^2}{\Delta E_{ML}} \quad (1.14.1)$$

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}

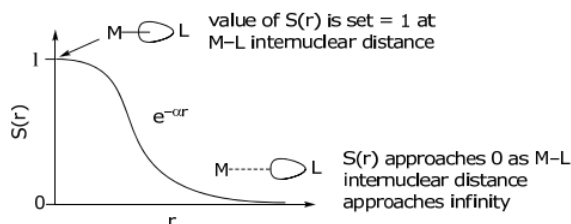
$$\varepsilon_{\sigma} = \frac{E_M^2 S_{ML}^2}{\Delta E_{ML}} = \beta' S_{ML}^2 \quad \varepsilon_{\sigma^*} = \frac{E_L^2 S_{ML}^2}{\Delta E_{ML}} = \beta S_{ML}^2 \quad (1.14.2)$$

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,

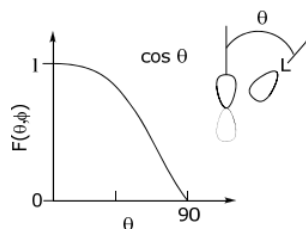


Under the condition of a fixed M-L distance, $S(r)$ is invariant, and therefore the overlap integral, S_{ML} , will depend only on the angular dependence, i.e., on $F(\theta, \phi)$.

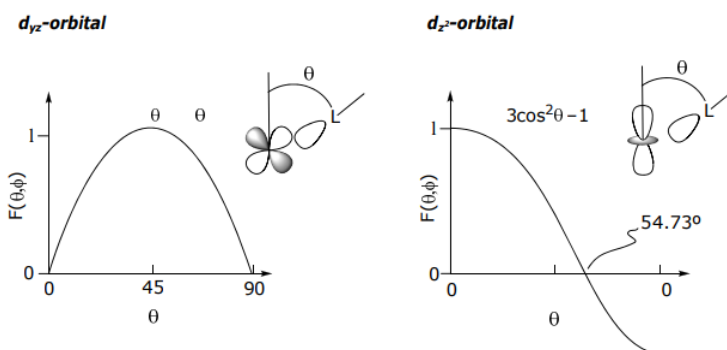
Because the σ orbital is symmetric, the angular dependence, $F(\theta, \phi)$, of the overlap integral mirrors the angular dependence of the central orbital.

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

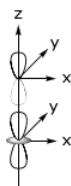


ML Diatomic Complexes

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,



$$E(d_{z^2}) = S_{ML}^2(\sigma) = \beta \cdot F_{\sigma}^2(\theta, \phi) = \beta \cdot 1 = e\sigma \quad (1.14.3)$$

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.

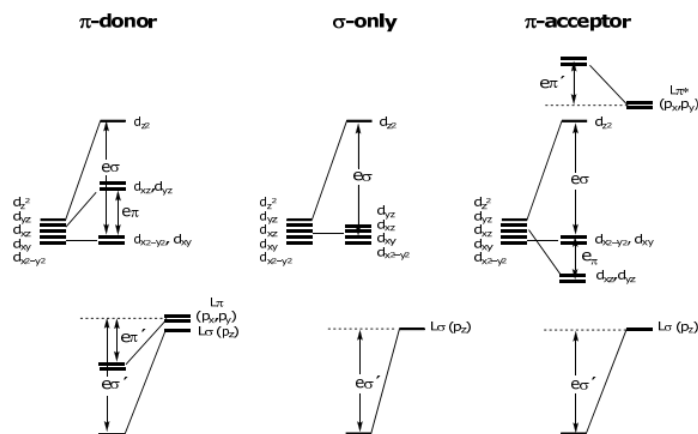


$$E(d_{yz}) = E(d_{xz}) = S_{ML}^2(\pi) = e\pi \quad E(d_{xy}) = E(d_{x^2-y^2}) = S_{ML}^2(\delta) = e\delta$$

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 π -systems of organic ligands). For these reasons, the $S_{ML}(\delta)$ overlap integral and associated energy is not included in most AOM treatments.

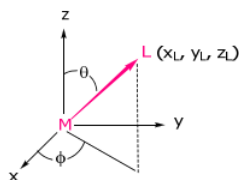
Returning to the problem at hand, the overall energy level diagrams for a M-L diatomic molecule for the three ligand classes are:



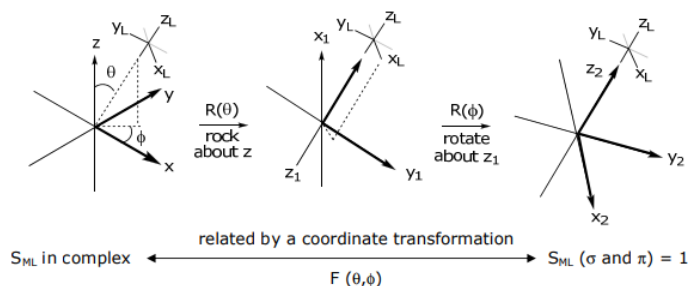
ML₆ Octahedral Complexes

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,



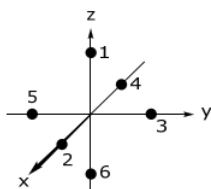
We can imagine placing the ligand on the metal z axis (with x and y axes of M and L also aligned) and then rotate it on the surface of a sphere (thus maintaining M-L distance) to its final coordinate position. Within the reference frame of the ligand,



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

	z_2^2	$y_2 z_2$	$x_2 z_2$	$x_2 y_2$	$x_2^2 - y_2^2$
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	$\frac{\sqrt{3}}{2} \sin \phi \sin 2\theta$	$\cos \phi \cos \theta$	$\sin \phi \cos \theta$	$-\cos \phi \sin \theta$	$-\frac{1}{2} \sin \phi \sin 2\theta$
xz	$\frac{\sqrt{3}}{2} \cos \phi \sin 2\theta$	$-\sin \phi \cos \theta$	$\cos \phi \cos \theta$	$\sin \phi \sin \theta$	$-\frac{1}{2} \cos \phi \sin 2\theta$
xy	$\frac{\sqrt{3}}{4} \sin 2\phi(1 - \cos 2\theta)$	$\cos 2\phi \sin \theta$	$\frac{1}{2} \sin 2\phi \sin 2\theta$	$\cos 2\phi \cos \theta$	$\frac{1}{4} \sin 2\phi(3 + \cos 2\theta)$
$x^2 - y^2$	$\frac{\sqrt{3}}{4} \cos 2\phi(1 - \cos 2\theta)$	$-\sin 2\phi \sin \theta$	$\frac{1}{2} \cos 2\phi \sin 2\theta$	$-\sin 2\phi \cos \theta$	$\frac{1}{4} \cos 2\phi(3 + \cos 2\theta)$

(1.14.4)



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

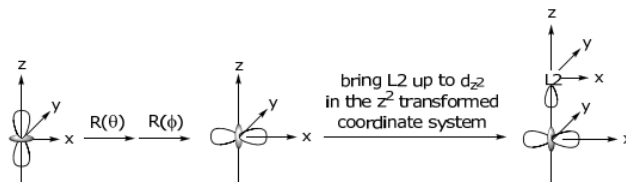
$$d_{z^2} = \frac{1}{4}(1 + 3 \cos 2\theta)d_{z^2} + 0d_{yz} - \frac{\sqrt{3}}{2}\sin 2\theta d_{xz} + 0d_{xy} + \frac{\sqrt{3}}{4}(1 - \cos 2\theta)d_{x^2-y^2}$$

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

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,

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

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 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 σ 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 σ -axis, hence $\frac{1}{4} e\sigma$. The δ component of the transformation comes from the $2z^2 - (x^2 + y^2)$ orbital functional form. Thus if L_2 has an orbital of δ 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 $\phi = 0$,

$$\begin{bmatrix} d_{z^2} \\ d_{yz} \\ d_{xz} \\ d_{xy} \\ d_{x^2-y^2} \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & 0 & 0 & 0 & \frac{1}{2} \end{bmatrix} \begin{bmatrix} d_{z^2} \\ d_{yz} \\ d_{xz} \\ d_{xy} \\ d_{x^2-y^2} \end{bmatrix} \quad (1.14.5)$$

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,

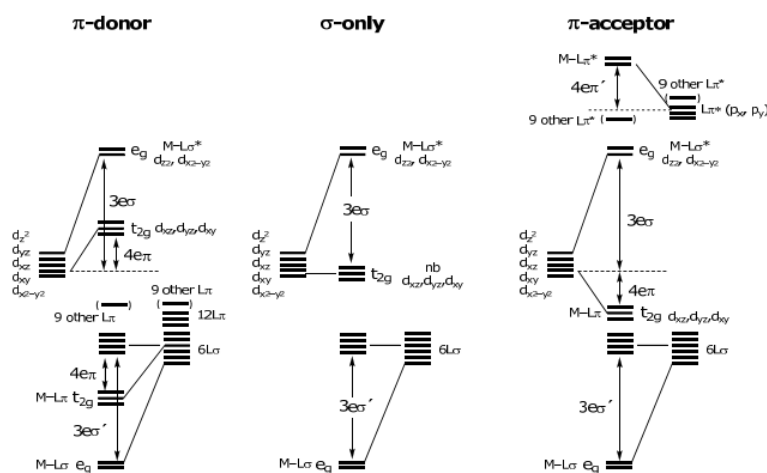
$$\begin{aligned}
 L_1 : & \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} & L_3 : & \begin{bmatrix} -\frac{1}{2} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & -\frac{1}{2} \end{bmatrix} & L_4 : & \begin{bmatrix} -\frac{1}{2} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & 0 & 0 & 0 & \frac{1}{2} \end{bmatrix} \\
 L_5 : & \begin{bmatrix} -\frac{1}{2} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & -\frac{1}{2} \end{bmatrix} & L_6 : & \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}
 \end{aligned}$$

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_{z^2})	$e\sigma$	$\frac{1}{4}e\sigma + \frac{3}{4}e\delta$	$\frac{1}{4}e\sigma + \frac{3}{4}e\delta$	$\frac{1}{4}e\sigma + \frac{3}{4}e\delta$	$\frac{1}{4}e\sigma + \frac{3}{4}e\delta$	$e\sigma$	$= 3e\sigma + 3e\delta$
E (d_{yz})	$e\pi$	$e\delta$	$e\pi$	$e\delta$	$e\pi$	$e\pi$	$= 4e\pi + 2e\delta$
E (d_{xz})	$e\pi$	$e\pi$	$e\delta$	$e\pi$	$e\delta$	$e\pi$	$= 4e\pi + 2e\delta$
E (d_{xy})	$e\delta$	$e\pi$	$e\pi$	$e\pi$	$e\pi$	$e\delta$	$= 4e\pi + 2e\delta$
E ($d_{x^2-y^2}$)	$e\delta$	$\frac{3}{4}e\sigma + \frac{1}{4}e\delta$	$\frac{3}{4}e\sigma + \frac{1}{4}e\delta$	$\frac{3}{4}e\sigma + \frac{1}{4}e\delta$	$\frac{3}{4}e\sigma + \frac{1}{4}e\delta$	$e\delta$	$= 3e\sigma + 3e\delta$

(1.14.6)

As mentioned above, $e\delta \ll e\sigma$ or $e\pi \dots$ thus $e\delta$ may be ignored. The O_h energy level diagram is:



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 parametrization scales directly between CFT and AOM

$$10 Dq = \Delta_0 = 3e\sigma - 4e\pi$$

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