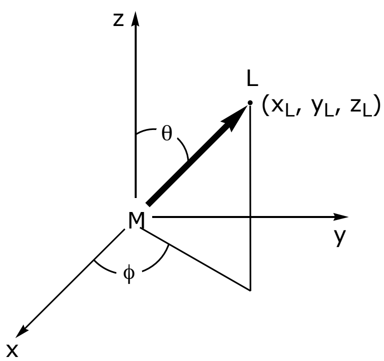
5.04, Principles of Inorganic Chemistry II

MIT Department of Chemistry

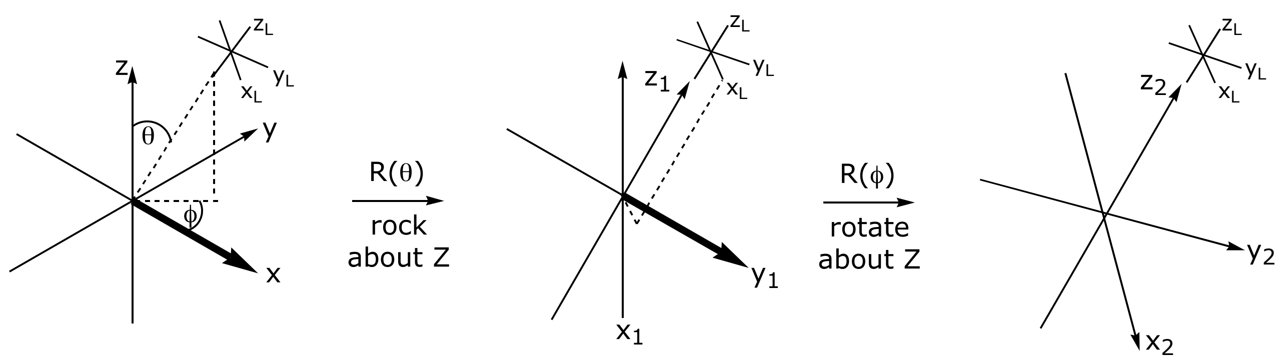
Lecture 17: AOM for ML_n Ligand Fields

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:



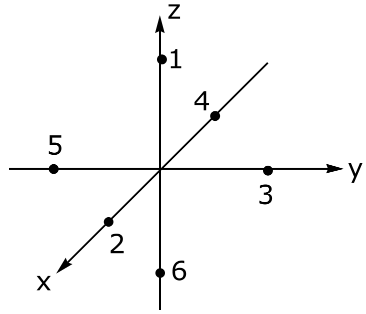
related by a coordinate transformation

S_{ML} in complex ⟵ S_{ML} (σ and π) = 1

F (θ, ϕ)

	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



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

<u>For d_{z^2} for L_2</u>

$$d_{z^2} = \frac{1}{4}\left(1+3\cos 2\theta\right)d_{z_2^2} + 0d_{y_2z_2} - \frac{\sqrt{3}}{2}\sin 2\theta d_{x_2z_2}$$

$$+ 0d_{x_2y_2} + \frac{\sqrt{3}}{4}\left(1-\cos 2\theta\right) + \frac{\sqrt{3}}{2} d_{x_2^2-y_2^2}$$

$$= -\frac{1}{2}d_{z_2^2} + 0d_{y_2z_2} + 0d_{x_2z_2} + 0d_{x_2y_2} + \frac{\sqrt{3}}{2}d_{x_2^2-y_2^2}$$

$$\begin{bmatrix} d_{z^2} \\ d_{yz} \\ d_{xz} \\ d_{xy} \\ d_{x^2-y^2} \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & 0 & 0 & 0 & \frac{1}{2} \end{bmatrix} \begin{bmatrix} d_{z_2^2} \\ d_{y_2z_2} \\ d_{x_2z_2} \\ d_{x_2y_2} \\ d_{x_2^2-y_2^2} \end{bmatrix}$$

continuing other elements of the transformation matrix may be obtained

$$Ed_{z^2} = \square\beta S_{ML}^{\ 2} = \square\frac{1}{4}d_{z_2^2} + \square\frac{3}{4}d_{x_2^2-y_2^2} = \square\frac{1}{4}\varepsilon_\sigma + \square\frac{3}{4}\varepsilon_\delta$$

Following the same procedure…. Other transformation matrices of L_i:
for other d-orbitals, E(di) is…

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

$$L_1 : \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

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

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

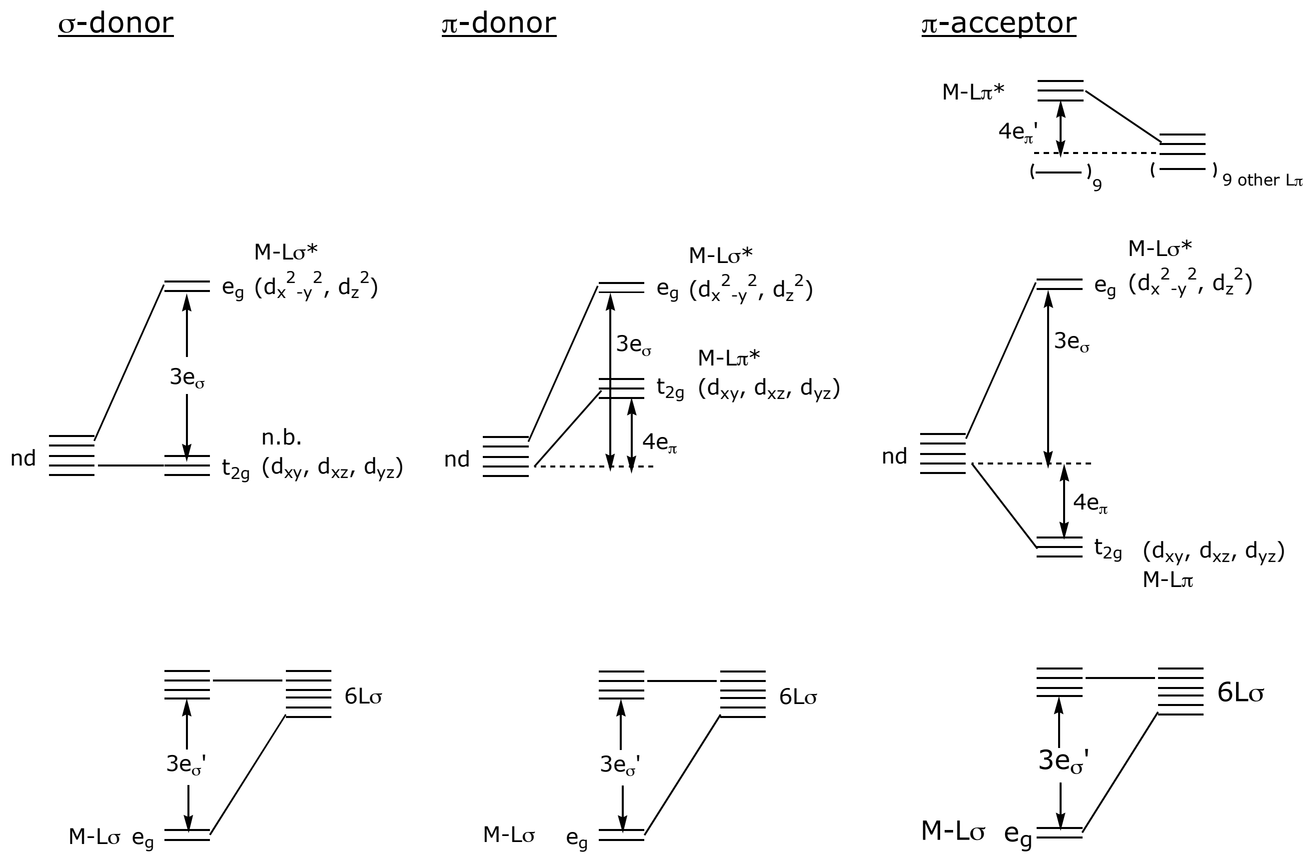
$$L_5 : \begin{bmatrix} -\frac{1}{2} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & -\frac{1}{2} \end{bmatrix}$$

$$L_6 : \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Squaring the coefficients for each of the ligands:

	L1	L2	L3	L4	L5	L6		E_{TOTAL}
$E(d_{z^2})$	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	=	$3e_\sigma + 3e_\delta$
$E(d_{yz})$	e_π	e_δ	e_π	e_δ	e_π	e_π	=	$4e_\pi + 2e_\delta$
$E(d_{xz})$	e_π	e_π	e_δ	e_π	e_δ	e_π	=	$4e_\pi + 2e_\delta$
$E(d_{xy})$	e_δ	e_π	e_π	e_π	e_π	e_δ	=	$4e_\pi + 2e_\delta$
$E(d_{x^2-y^2})$	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	=	$3e_\sigma + 3e_\delta$

As mentioned above… $e_\delta << e_\sigma$ or e_π… thus e_δ may be ignored. The O_h energy level diagram is:



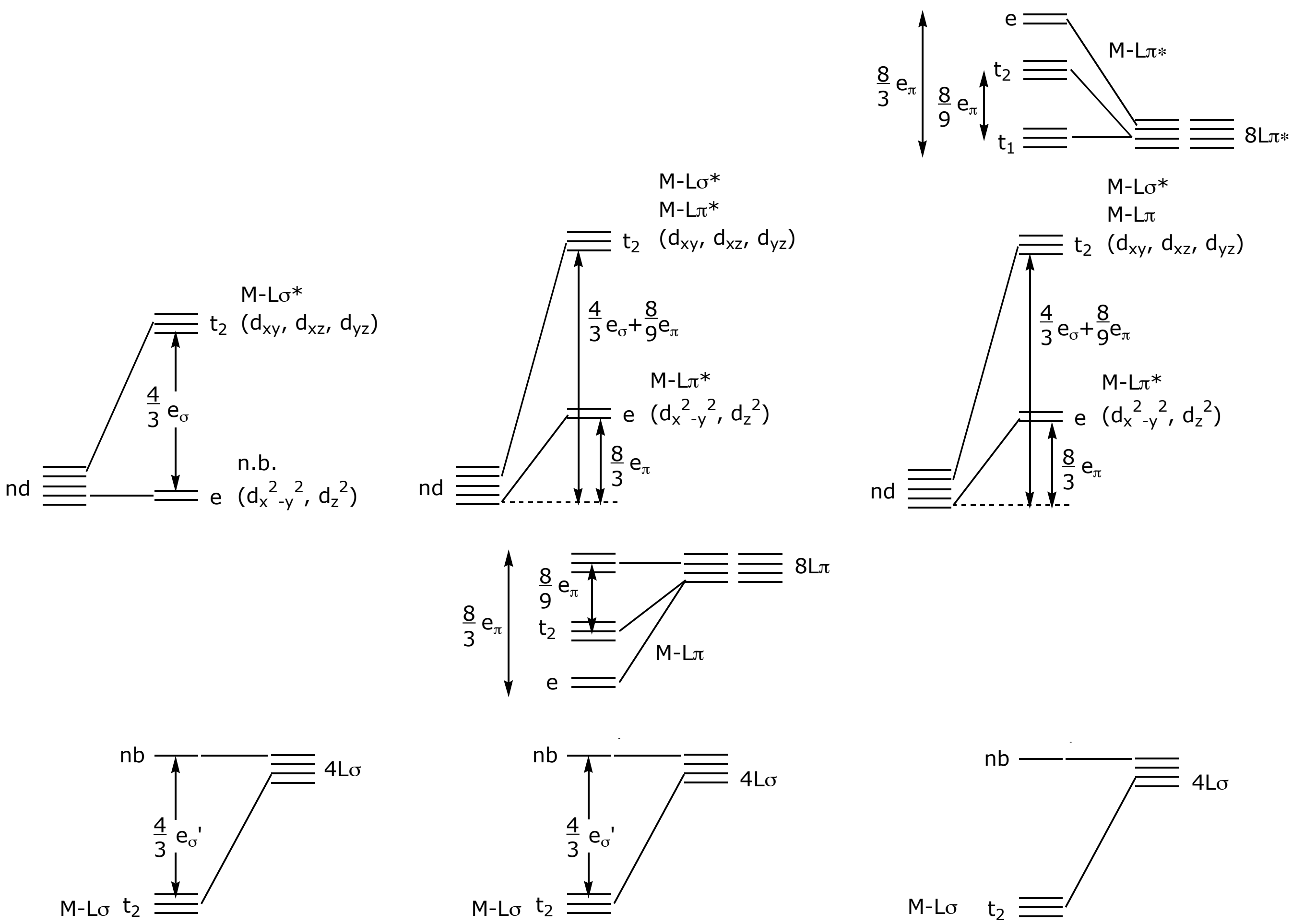
Note the d-orbital splitting is the same result obtained from the CFT model taught in Freshman chemistry. In fact the energy parameterization scales directly between CFT and AOM

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

A table of angular scaling factors for e_σ and e_π has been removed due to copyright considerations.

A list of common structures for two through six ligands has been removed due to copyright considerations.

Let's use e_σ and e_π parameters to determine the d-energy level splitting diagram for T_d complexes



Note that

$$\Delta T_d = \left(\frac{4}{3}e_\sigma + \frac{8}{9}e_\pi\right) - \frac{8}{3}e_\pi = \frac{4}{3}e_\sigma - \frac{16}{9}e_\pi = \frac{4}{9}\left(3e_\sigma - 4\pi\right) = \frac{4}{9}\Delta_0$$

↑

This is the result from CFT (inversion of e/t_2 leads to the (-) sign)

$\therefore$

$$\Delta T_d = -\frac{4}{9}\Delta_0$$