5.03, Inorganic Chemistry

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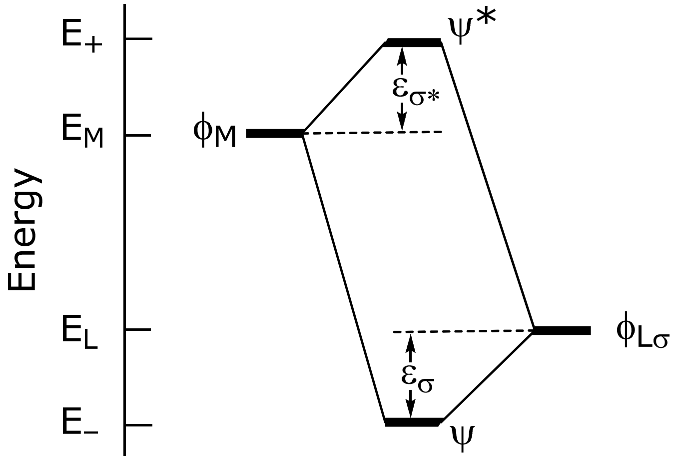
Lecture 25 Apr 11: Angular Overlap Method and Electronic Structure of Metal Complexes

The interaction energy resulting from the interaction of the metal and ligands is defined on the following energy level diagram,



where E_M is the energy of the metal orbital, E_L is the energy of the ligand orbital, $\Delta E_{ML} = E_M - E_L$, S_{ML} is the energy of overlap (i.e., the overlap integral) between the ligand and metal orbital and the interaction energies are,

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

The energies ε_σ and $\varepsilon_{\sigma*}$ are the molecular orbital (MO) energies—the energies arising from the metal and ligand orbitals. Note that E_M, E_L and ΔE_{ML} in the above expressions are constants, hence, the energy of interaction between metal and ligand scales directly with the overlap integral, S_{ML}

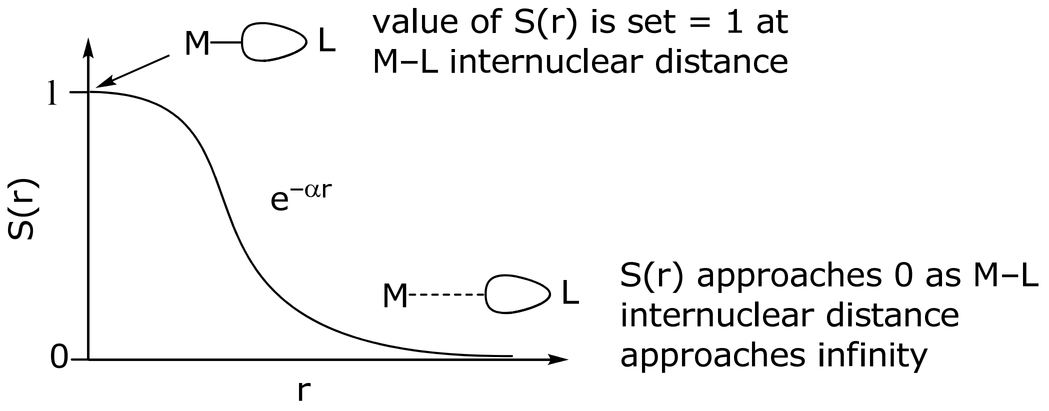
$$\varepsilon_\sigma = \frac{E_M{}^2 S_{ML}{}^2}{\Delta E_{ML}} = \beta' S_{ML}{}^2 \qquad \varepsilon_{\sigma*} = \frac{E_L{}^2 S_{ML}{}^2}{\Delta E_{ML}} = \beta\, S_{ML}{}^2$$

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,

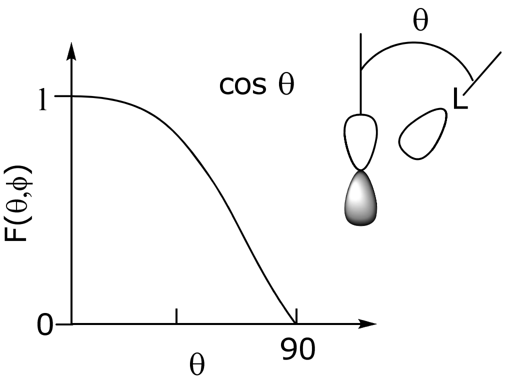


Under the condition of a fixed M–L distance, S(r) is invariant, and therefore the overlap integral, S_{ML}, will depend only on the angular dependence, i.e., on $F(\theta,\phi)$.

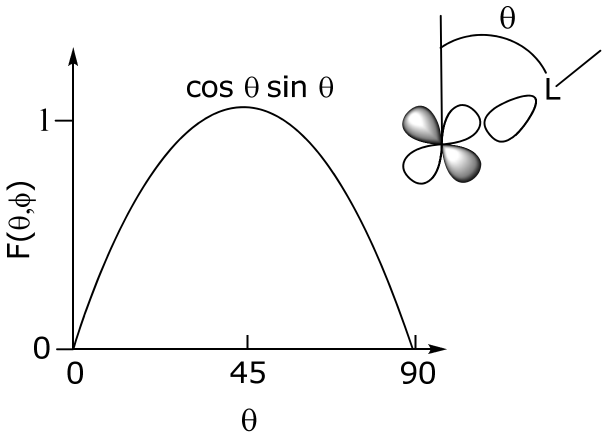
Because the σ orbital is symmetric, the angular dependence, $F(\theta,\phi)$, of the overlap integral mirrors the angular dependence of the central orbital.

p-orbital

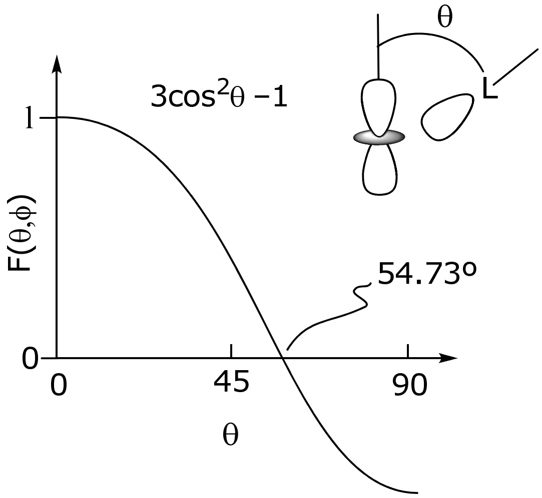
…is defined angularly by a cos θ function. Hence, the angular dependence of a σ orbital as it angularly rotates about a p-orbital reflects the cos θ angular dependence of the p-orbital.



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



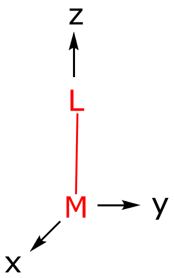
d_{yz}-orbital



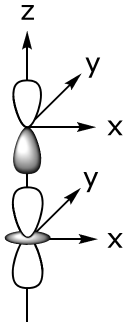
d_{z^2}-orbital

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,



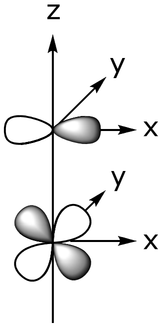
There are three types of overlap interactions based on σ, π and δ ligand orbital symmetries. For a σ orbital, the interaction is defined as,

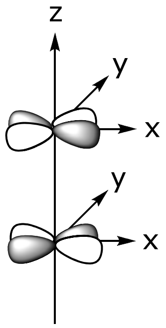


$$E\left(d_{z^2}\right) = S_{ML}^{2}(\sigma) = \beta \bullet F_{\sigma}^{2}(\theta,\phi) = \beta \bullet 1 = e\sigma$$

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 destablized by $e\sigma$ (the corresponding L orbital is stabilized by $(\beta')^2 \bullet 1 = e\sigma'$).

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.



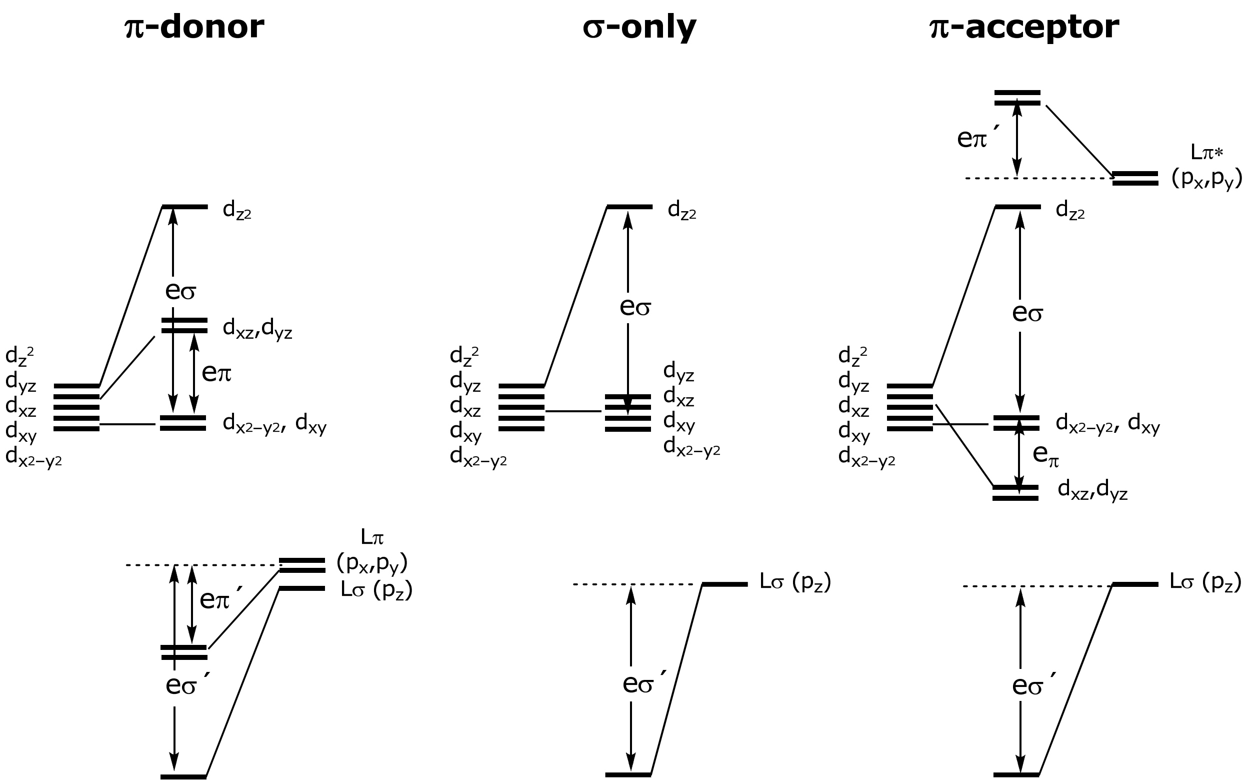


$$E\left(d_{yz}\right) = E\left(d_{xz}\right) = S_{ML}{}^2(\pi) = e\pi \qquad E\left(d_{xy}\right) = E\left(d_{x^2-y^2}\right) = S_{ML}{}^2(\delta) = e\delta$$

As with the σ interaction, the $(M–L\pi)^*$ interaction for the d-orbitals is de-stabilizing and the metal-based orbital is destablized 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.

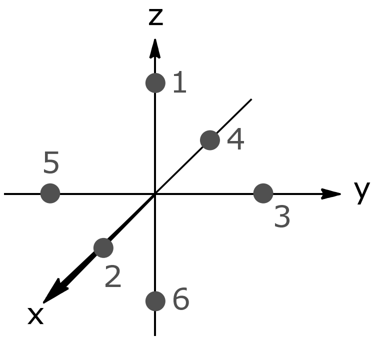
Returning to the problem at hand, the overall energy level diagrams for a M–L diatomic molecule for the three ligand classes are:



ML_6 Octahedral Complexes

Of course, there is more than one ligand in a typical coordination compound. The power of AOM is that the eσ and eπ (and eδ), energies are additive. Thus, the MO energy levels of coordination compounds are determined by simply summing eσ and eπ for each M(d)–L interaction.

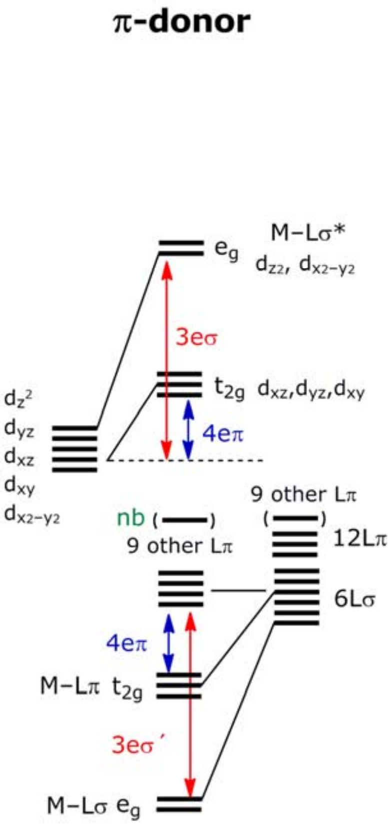
For the ligands in an octahedral complex,

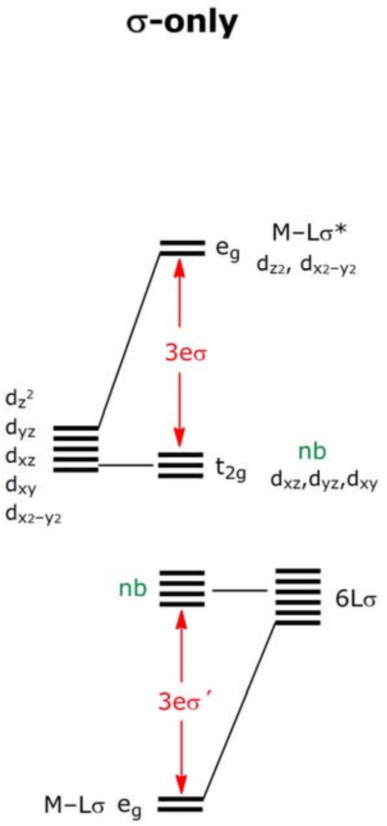


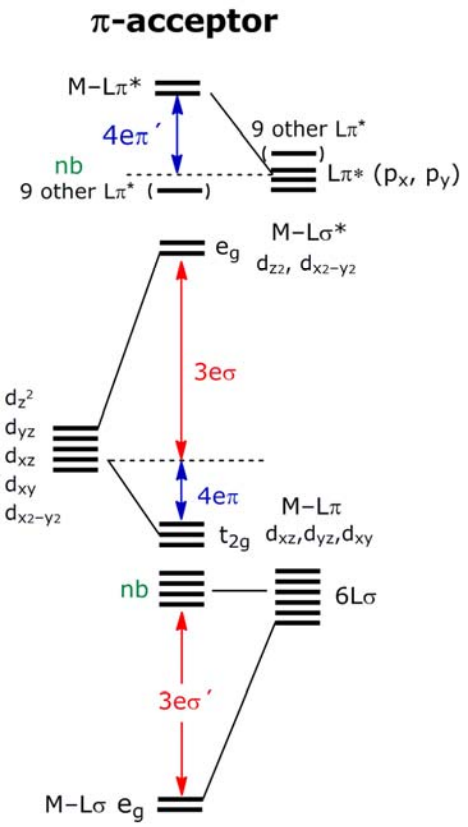
The energy for each o fthe ligands is collected in the following table. The total energy for a ligand is obtained by summing the total energy of each d-orbital,

	L1	L2	L3	L4	L5	L6	ETOTAL
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($d_{x^2-y^2}$)	$e\delta$	$\frac{3}{4}e\sigma+\frac{1}{4}e\delta$	$\frac{3}{4}e\sigma+\frac{1}{4}e\delta$	$\frac{3}{4}e\sigma+\frac{1}{4}e\delta$	$\frac{3}{4}e\sigma+\frac{1}{4}e\delta$	$e\delta$	$= 3e\sigma + 3e\delta$

Remember, $e\delta << e\sigma$ or $e\pi$… thus $e\delta$ may be ignored. The O_h energy level diagram is:



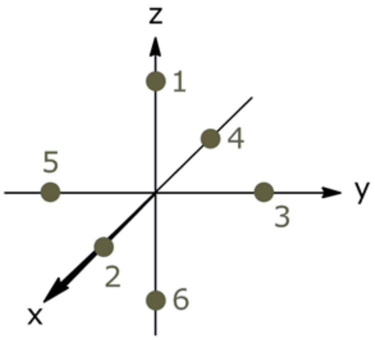


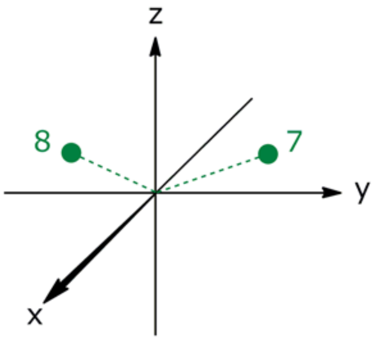


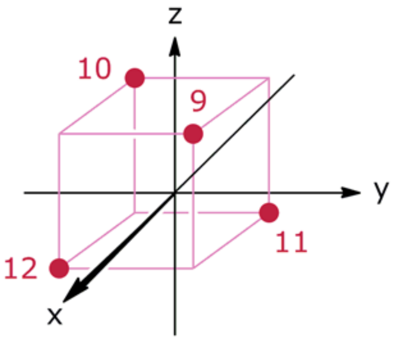
Note the d-orbital splitting is the same result obtained from the crystal field theory (CFT) model taught in freshman chemistry. In fact the energy parameterization scales directly between CFT and AOM, where Δ_o is the octahedral crystal field splitting,

$$\Delta_o = 3e\sigma - 4e\pi$$

The AOM angular scaling factors (S_{ML}^2) for ligands in the various positions shown by labels L1-L12 is summarized in the table below.







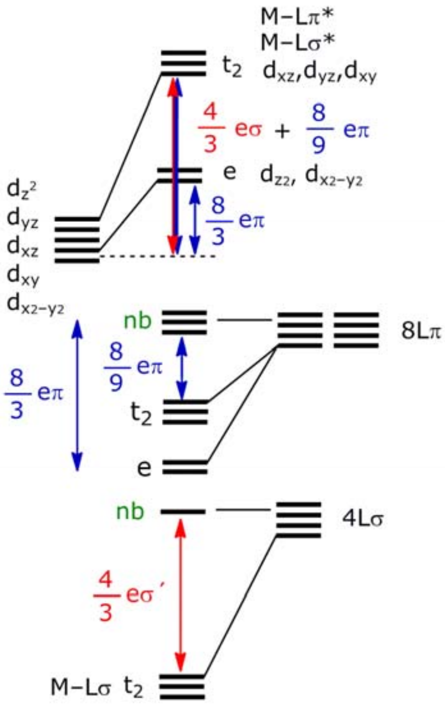
L		z^2	x^2-y^2	xz	yz	xy
1	σ	1	0	0	0	0
	π	0	0	1	1	0
2	σ	1/4	3/4	0	0	0
	π	0	0	1	0	1
3	σ	1/4	3/4	0	0	0
	π	0	0	0	1	1
4	σ	1/4	3/4	0	0	0
	π	0	0	1	0	1
5	σ	1/4	3/4	0	0	0
	π	0	0	0	1	1
6	σ	1	0	0	0	0
	π	0	0	1	1	0
7	σ	1/4	3/16	0	0	9/16
	π	0	3/4	1/4	3/4	1/4
8	σ	1/4	3/16	0	0	9/16
	π	0	3/4	1/4	3/4	1/4
9	σ	0	0	1/3	1/3	1/3
	π	2/3	2/3	2/9	2/9	2/9
10	σ	0	0	1/3	1/3	1/3
	π	2/3	2/3	2/9	2/9	2/9
11	σ	0	0	1/3	1/3	1/3
	π	2/3	2/3	2/9	2/9	2/9
12	σ	0	0	1/3	1/3	1/3
	π	2/3	2/3	2/9	2/9	2/9

You can choose any combination of ligands to construct the ligand fields of common metal complexes.

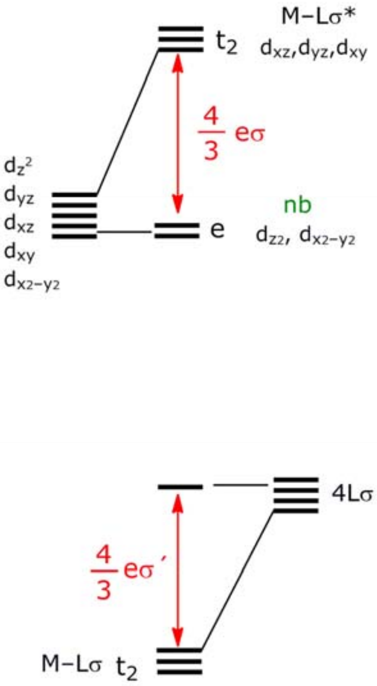
Structure	Ligands
Linear	1 and 6
Trigonal planar	2,7 and 8
Square planar	2-5
Tetrahedron	9-12
Trigonal bipyramid	1,2,7,8 and 6
Square pyramid	1-5
Octahedron	1-6

Let’s use the eσ and eπ parameters to determine the crystal field splitting energies for a tetrahedral molecule.

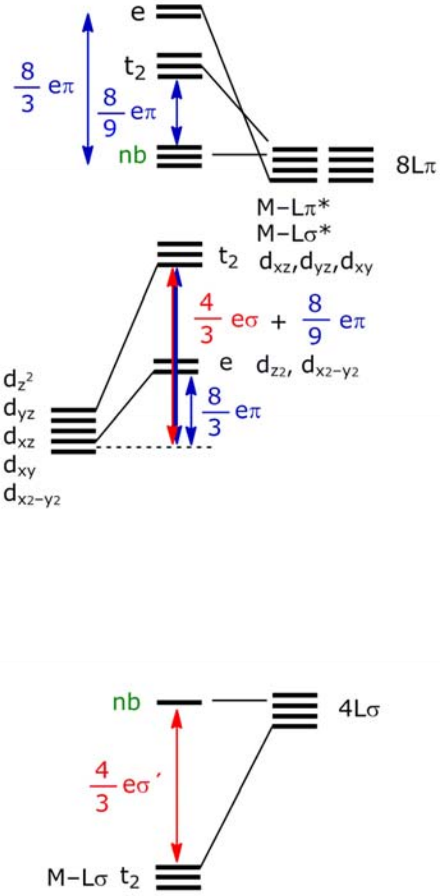
π-donor



σ-only



π-acceptor



Calculating the tetrahedral crystal field splitting,

$$\Delta_t = \left(\frac{4}{3}e\sigma + \frac{8}{9}e\pi\right) - \frac{8}{3}e\pi = \frac{4}{3}e\sigma - \frac{16}{9}e\pi$$

But realize that Δ_t is 4/9 that of Δ_o,

$$\Delta_t = \frac{4}{9}(3e\sigma - 4e\pi) = \frac{4}{9}\Delta_0$$

This is the result from 5.111 and 5.112,

$$\Delta_t = -\frac{4}{9}\Delta_0$$

i.e. that the crystal field splitting for a tetrahedral complex is (–4/9) that of an octahedral complex. Note that AOM does not give the sign…but we note that the e and t_2 levels of the tetrahedral ligand field are inverted from that of the octahedral crystal field, hence the (–) sign.