5.04 Principles of Inorganic Chemistry II
Fall 2008

Lecture 10: General Electronic Considerations of Metal-Ligand Complexes

Metal complexes are Lewis acid-base adducts formed between metal ions (the acid) and ligands (the base).
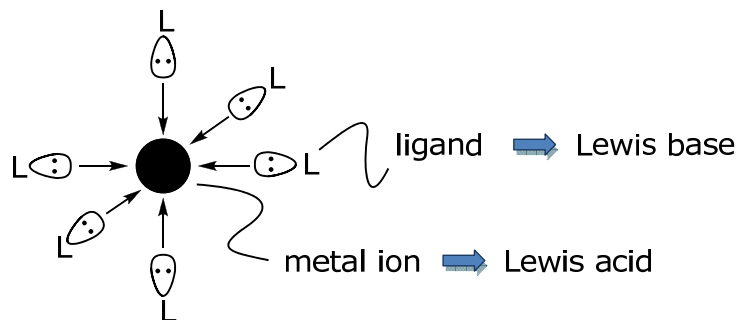
The interaction of the frontier atomic (for single atom ligands) or molecular (for many atom ligands) orbitals of the ligand and metal lead to bond formation,
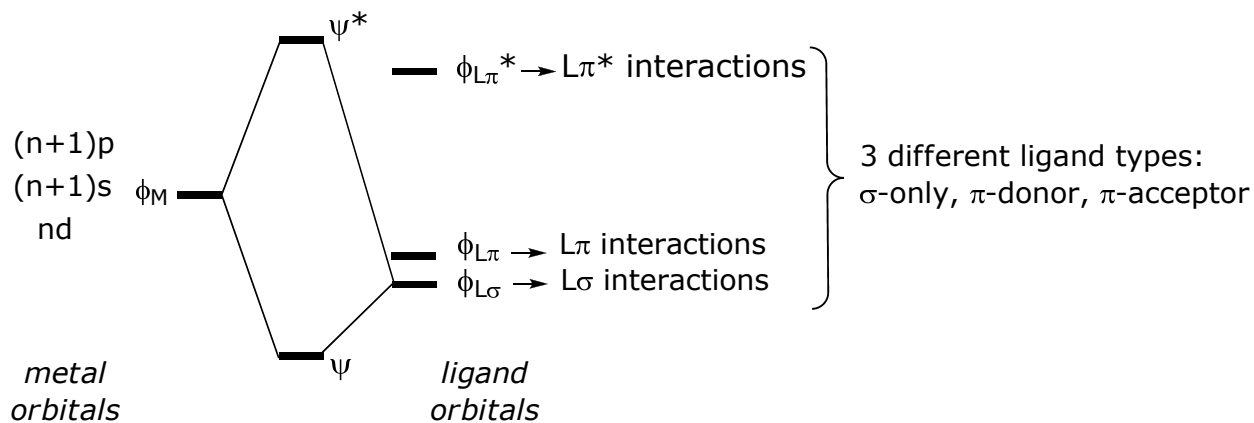
More quantitatively, the interaction energy of stabilization and destabilization, ε_σ and $\varepsilon_{\sigma*}$, respectively, is defined on the following energy level diagram,

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Prof. Daniel G. Nocera

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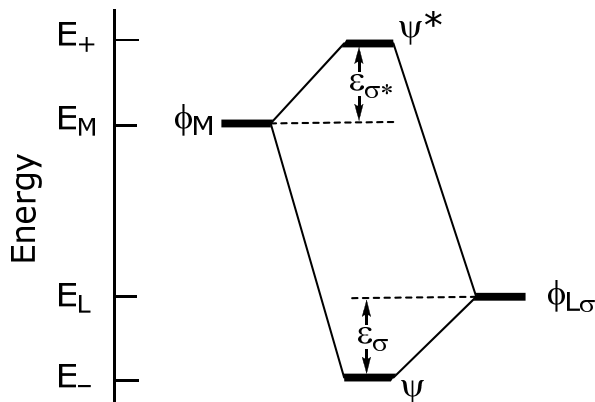
Treating this problem within the LCAO framework comprising metal and ligand orbitals yields,

$$\psi = c_M \phi_M + c_L \phi_L$$

and solving for the Hamiltonian,

$$H\psi = E\psi$$

$$\left| H - E \,\middle|\, \psi \right\rangle = \left| H - E_j \,\middle|\, c_M\phi_M + c_L\phi_L \right\rangle = 0$$

Left-multiplying by ϕ_M and ϕ_L yields the set of linear homogeneous equations,

$$c_M \left\langle \phi_M \,\middle|\, H - E \,\middle|\, \phi_M \right\rangle + c_L \left\langle \phi_M \,\middle|\, H - E \,\middle|\, \phi_L \right\rangle = 0$$

$$c_M \left\langle \phi_L \,\middle|\, H - E \,\middle|\, \phi_M \right\rangle + c_L \left\langle \phi_L \,\middle|\, H - E \,\middle|\, \phi_L \right\rangle = 0$$

which furnishes the secular determinant,

$$\begin{vmatrix} H_{MM} - E & H_{ML} - ES_{ML} \\ H_{ML} - ES_{ML} & H_{LL} - E \end{vmatrix} = \begin{vmatrix} E_M - E & H_{ML} - ES_{ML} \\ H_{ML} - ES_{ML} & E_L - E \end{vmatrix} = 0$$

Solving the above secular determinant, using the expansion $\sqrt{1+x} = 1 + \dfrac{1}{2}x - \ldots$, and realizing that $H_{MM} = E_M$ and $H_{LL} = E_L$

$$E_+ = E_M + \frac{\left(H_{ML} - E_M S_{ML}\right)^2}{\Delta E_{ML}} \qquad\qquad E_- = E_L - \frac{\left(H_{ML} - E_M S_{ML}\right)^2}{\Delta E_{ML}}$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad\qquad\qquad \downarrow \qquad\qquad \downarrow$$

$$H_{MM} \qquad \varepsilon_{\sigma *} \qquad\qquad\qquad\qquad H_{LL} \qquad \varepsilon_{\sigma}$$

The Wolfsberg-Hemholz approximation provides a value for H_{ML}, defined as

$$H_{ML} = S_{ML} (E_L + E_M)$$

Substituting H_{ML} in the above expressions for E_+ and E_- yields,

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

The derivation highlights the following general rules for the construction of MO diagrams,

(1) M—L atomic orbital mixing is proportional to the overlap of the metal and ligand orbital, i.e., S_{ML}

corollary A: only orbitals of correct symmetry can mix and $\therefore$ give a nonzero interaction energy (i.e. $S_{ML} \neq 0$)

corollary B: σ interactions typically give rise to larger interaction energies than those resulting from π interactions and π interactions are greater than δ interactions owing to more directional bonding along the series $S_{ML}(\sigma) > S_{ML}(\pi) > S_{ML}(\delta)$

(2) M–L atomic orbital mixing is inversely proportional to energy difference of mixing orbitals (i.e. ΔE_{ML}).

Another issue of interest for the construction of MOs is,

(3) The order of the E_L and E_M energy levels almost always is:

$$\sigma(L) < \pi(L) < nd < (n+1)s < (n+1)p$$

$$\vdash \quad \pi^*L \quad \longrightarrow$$
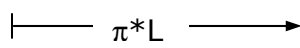
depending on the nature of the ligand

This energy ordering comes directly from Valence Orbital Ionization Energies (VOIE) of metal and main group atoms and PES spectra of molecular ligands.

VOIE's of metal atoms:

Atom	$3d^{n-1}4s \to 3d^{n-2}4s$ 3d	$3d^{n-1}4s \to 3d^{n-1}$ 4s	$3d^{n-1}4p \to 3d^{n-1}$ 4p
Sc	4.7	5.7	3.2
Ti	5.6	6.1	3.3
V	6.3	6.3	3.5
Cr	7.2	6.6	3.5
Mn	7.9	6.8	3.6
Fe	8.7	7.1	3.7
Co	9.4	7.3	3.8
Ni	10.0	7.6	3.8
Cu	10.7	7.7	4.0

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VOIE's of ligand atomic orbitals and PES spectra of selected ligands:

Atom	1s	2s	2p	3s	3p	4s	4p
H	13.6						
C		19.4	10.6				
N		25.6	13.2				
O		32.3	15.8				
F		40.2	18.6				
Si				14.9	7.7		
P				18.8	10.1		
S				20.7	11.6		
Br						24.1	12.5

PES energies of ligands are in eVs (note: a VOIE is simply the opposite of the ionization energy)
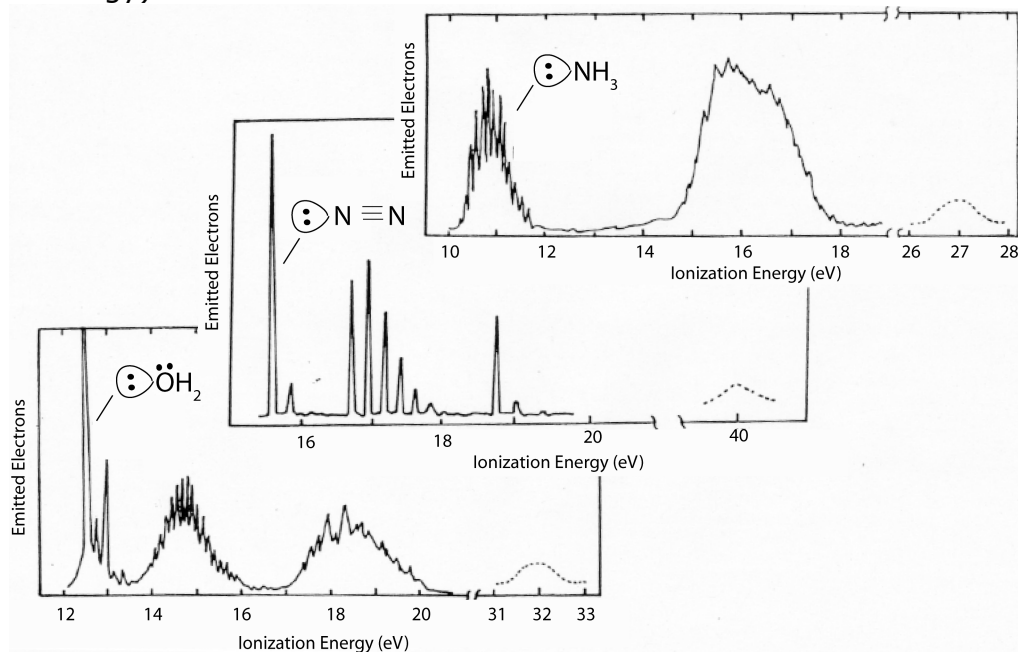
General observations:

(1)   The s orbitals are generally too low in energy to participate in bonding ($\Delta E_{ML(\sigma)}$ is very large)

(2)   Filled p orbitals are the frontier orbitals, and they have VOIEs that place them below the metal orbitals

(3)   For molecular ligands, since the frontier orbitals comprise s and p orbitals, here too filled ligand orbitals have energies that are stabilized relative to the metal orbitals