5.04 Principles of Inorganic Chemistry II
Fall 2008

Lecture 11: Frontier MO's of σ-Donor, π-Donor and π-Acceptor Ligands

Before tackling the business of the complex, the nature of the ligand frontier orbitals must be considered. There are three general classes of ligands, as defined by their frontier orbitals: σ-donor ligands, π-donor ligands and π-acceptor ligands.

σ-donor ligands

These ligands donate two e⁻s from an orbital of σ-symmetry:

$$H^- (1s^2), NH_3 (2a_1 \ell p), PR_3 (2a_1 \ell p), CH_3^- (2a_1 \ell p), OH_2 (b_1 \ell p)$$
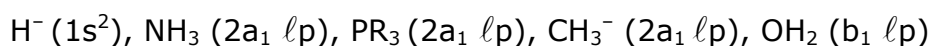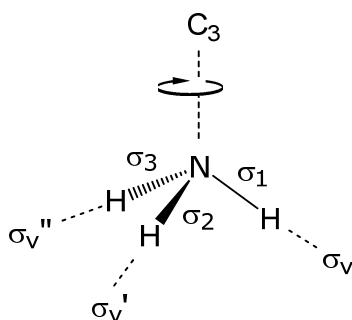
Note, some of these ligands are atomic, while others are LCAO-MOs. The frontier orbitals for bonding to the metal are thus are either atomic or molecular orbitals, depending on the nature of the ligand.

As an example of a molecular ligand, consider the ammonia ligand. Ammonia is formed from the LCAO between the valence orbitals of a central nitrogen and the three 1s orbitals of three hydrogens,

3 H(1s)   +   N (2s, 2p$_x$, 2p$_y$, 2p$_z$)   ⟹   NH$_3$
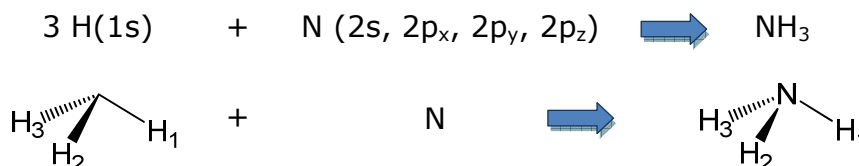
To begin this problem, the symmetry-adapted linear combinations of the three 1s orbitals must be determined. Hence, the basis will be derived from the H orbitals. Because the H(1s) orbitals can only form σ bonds, the choice of 3 σ N–H bonds is an appropriate basis set,

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The transformation properties of the σ bonds (in C_{3v} symmetry) are as follows:

$$E \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{bmatrix} \rightarrow \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{bmatrix} \qquad C_3 \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{bmatrix} \rightarrow \begin{bmatrix} \sigma_2 \\ \sigma_3 \\ \sigma_1 \end{bmatrix} \qquad \sigma_v \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{bmatrix} \rightarrow \begin{bmatrix} \sigma_1 \\ \sigma_3 \\ \sigma_2 \end{bmatrix}$$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad\qquad \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \qquad\qquad \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

$$\qquad E \qquad\qquad\qquad\qquad C_3 \qquad\qquad\qquad\qquad \sigma_v$$

These representation of this basis may be quickly ascertained by realizing that only bonds (or H(1s) orbitals) that do not move will contribute to the trace of the matrix representation,

C_{3v}	E	$2C_3$	$3\sigma_v$	
Γ_σ	3	0	1	$\rightarrow \quad a_1 + e$

Projecting out the a_1 and e SALCs of the 3H orbitals, we realize that the transformation properties of the H orbitals are preserved in the C_3 rotational subgroup,

C_{3v}	E	C_3	$C_3{}^2$	σ_v	$\sigma_v{}'$	$\sigma_v{}''$
$\sigma_1 \rightarrow$	σ_1	σ_2	σ_3	σ_1	σ_3	σ_2

this mixing is a repeat of
what is obtained under the
rotation operators

thus it is appropriate
to drop to C_3

C_3	E	C_3	$C_3{}^2$
$\sigma_1 \rightarrow$	σ_1	σ_2	σ_3

Application of the projection operator in the cyclic C_3 point group is an easy task – can simply read out the projections,

$$P^{a_1}(\sigma_1) \rightarrow 1 \cdot E\sigma_1 + 1 \cdot C_3\sigma_1 + 1 \cdot C_3{}^2\sigma_1 = \sigma_1 + \sigma_2 + \sigma_3$$

$$P^{e(1)}(\sigma_1) \rightarrow 1 \cdot E\sigma_1 + (\varepsilon^*)C_3\sigma_1 + \varepsilon\, C_3{}^2\sigma_1 = \sigma_1 + \varepsilon*\sigma_2 + \varepsilon\sigma_3$$
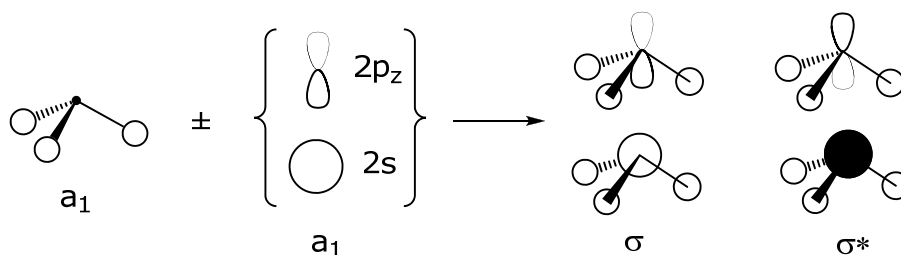
$$P^{e(2)}(\sigma_1) \rightarrow 1 \cdot E\sigma_1 + \varepsilon\, C_3\sigma_1 + (\varepsilon^*)C_3{}^2\sigma_1 = \sigma_1 + \varepsilon\sigma_2 + \varepsilon*\sigma_3$$
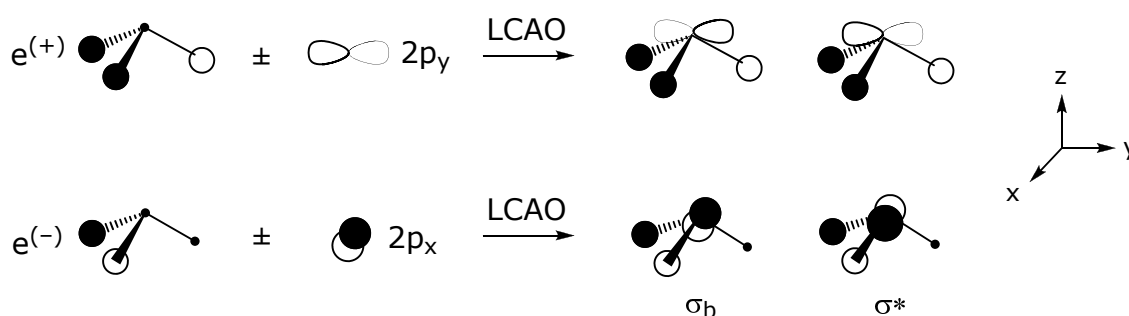
Taking appropriate linear combinations and normalizing,

$$\psi^{a_1}(L) = \frac{1}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3) \qquad \psi^{e(+)}(L) = \frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3) \qquad \psi^{e(-)}(L) = \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_3)$$
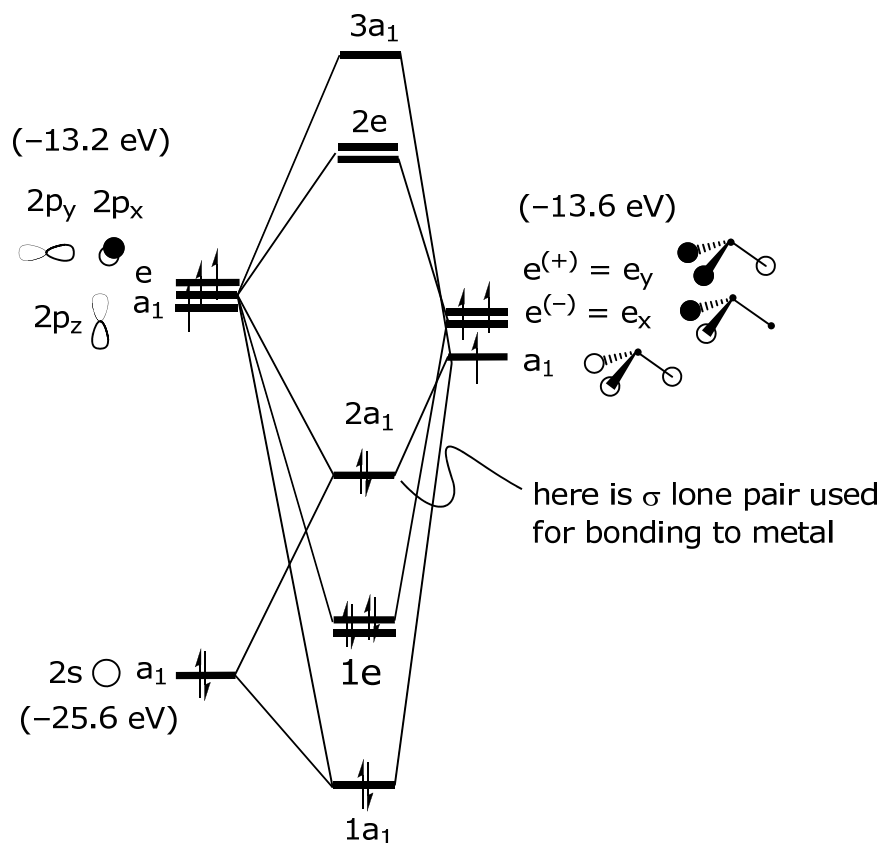

Only orbitals of the same symmetry can form a LCAO; thus the a_1 SALC of the 3H(1s) orbitals can only combine with the a1 orbitals of the central N (i.e., the 2s and $2p_z$ valence orbitals),

The $2p_y$ orbital combines with $e^{(+)}$, it is orthogonal to $e^{(-)}$, whereas the opposite is true for $2p_x$ orbital,

The MO is constructed by overlapping orbitals of the same symmetry. The greater the overlap, the greater the splitting between the orbitals. Note that the a_1 SALC participates in two types of σ interactions, one with the 2s orbital and one with the $2p_z$ orbital of nitrogen. The highest energy orbital, the ligand HOMO orbital, is used for bonding to the metal. This orbital too is composed of two types of interactions: (i) it is Lσ(a_1)–N(2s) antibonding and (ii) Lσ(a_1)–N($2p_z$) bonding in character. The energy of the atomic orbitals are shown in parenthesis.

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3a₁ — rendered as $3a_1$

$3a_1$

$2e$

(−13.2 eV)

$2p_y$ $2p_x$

e
a_1

$2p_z$

(−13.6 eV)

$e^{(+)} = e_y$
$e^{(-)} = e_x$

a_1

$2a_1$

here is σ lone pair used
for bonding to metal

$2s$ a_1

$1e$

(−25.6 eV)

$1a_1$

Simple hybridization arguments predict two different of bond energies for NH_3: (1) the lone pair and (2) the σ N–H bond. The MO diagram on the other hand predicts three different energies. The photoelectron spectrum of NH_3 exhibits three ionization energies, thus verifying the MO bonding model.

NH_3 PES Spectrum

PES Intensity

$2a_1$

$1e$

$1a_1$

10   11   12   13   14   15   16   17   18   26   27   28

Ionization Energy / eV

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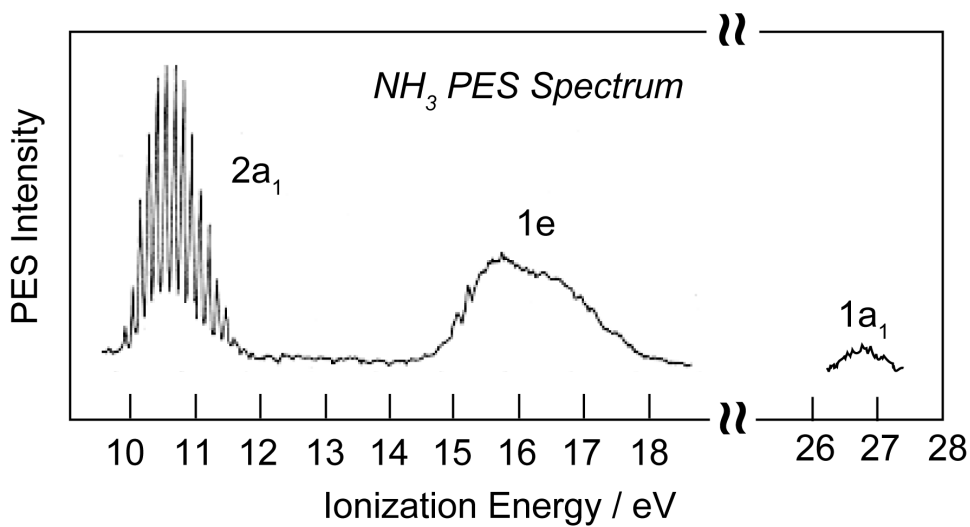
A second molecular ligand is water. The ligand has two lone pairs, but only one is used in bonding to the metal. The reason for this electronic asymmetry and why only one lone pair is only available for bonding becomes evident from the electronic structure of the water molecule.

$$\sigma_1 \quad O \quad \sigma_2 \qquad \qquad z \quad y$$
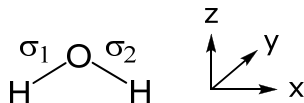
The basis set for water is the 2H(1s) orbitals and the O(2s, 2p_z, 2p_x, 2p_y) atomic orbitals. The proper symmetry adapted linear combination for the 2H(1s) orbitals may be ascertained using the above σ bonds.
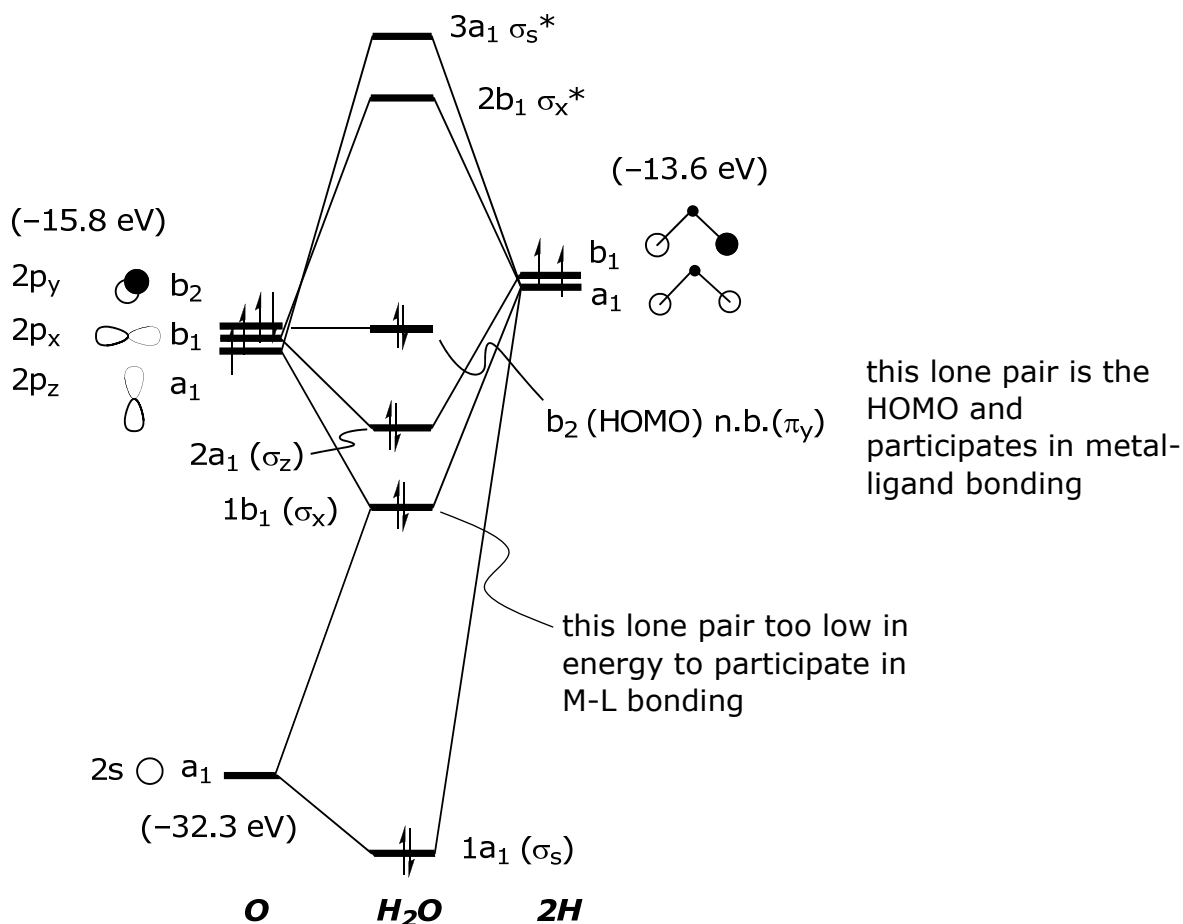
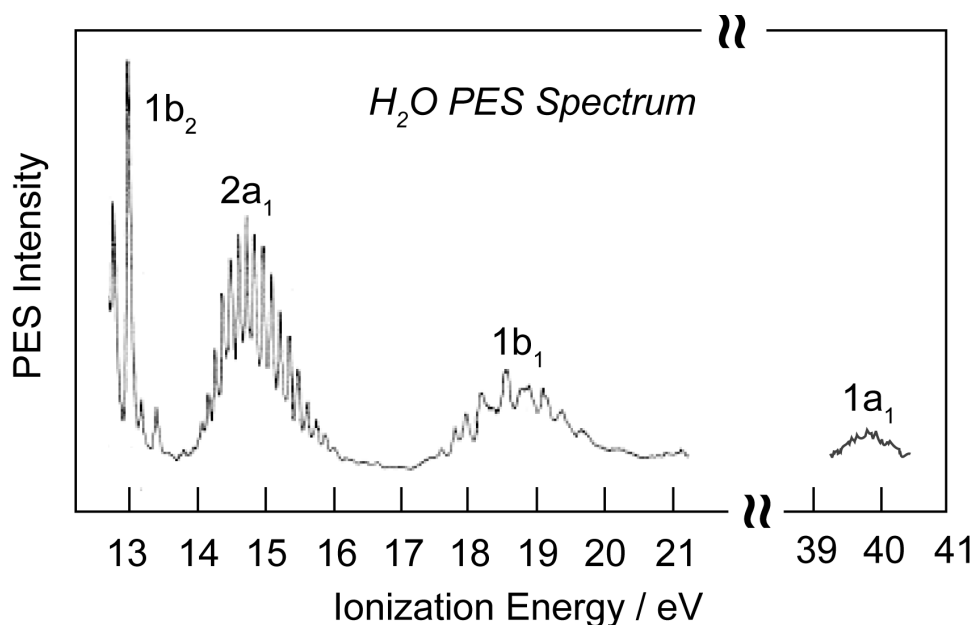| C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
Γ_σ	2	0	2	0	$\rightarrow$	$a_1 + b_1$
$\sigma_1 \rightarrow$	σ_1	σ_2	σ_1	σ_2		

Applying the projection operator,

$$P^{a_1}(\sigma_1) \;\rightarrow\; 1\cdot\overbrace{E\sigma_1}^{\sigma_1} + 1\cdot\overbrace{C_2\sigma_1}^{\sigma_2} + 1\cdot\overbrace{\sigma(xz)\cdot\sigma_1}^{\sigma_1} + 1\cdot\overbrace{\sigma(yz)\cdot\sigma_1}^{\sigma_2} \;\rightarrow\; \psi_{a_1} = \frac{1}{\sqrt{2}}\left(\sigma_1 + \sigma_2\right)$$

$$P^{b_1}(\sigma_1) \;\rightarrow\; 1\cdot E\sigma_1 + (-1)\cdot C_2\sigma_1 + 1\cdot \sigma(xz)\cdot\sigma_1 + (-1)\cdot \sigma(yz)\cdot\sigma_1 \;\rightarrow\; \psi_b = \frac{1}{\sqrt{2}}\left(\sigma_1 - \sigma_2\right)$$

The s and p_z orbitals on O have a_1 symmetry and thus will mix with the $L\sigma(a_1)$, the p_x has b_1 symmetry and will mix with $L\sigma(b_1)$ and the p_y orbital is rigorously nonbonding, i.e., does not have a symmetry counterpart of the O atom, and hence no LCAO is formed using this orbital.

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$3a_1 \sigma_s^*$

$2b_1 \sigma_x^*$

(−13.6 eV)

(−15.8 eV)

$2p_y$ b_2

$2p_x$ b_1

$2p_z$ a_1

b_1
a_1

this lone pair is the HOMO and participates in metal-ligand bonding

$2a_1 (\sigma_z)$

b_2 (HOMO) n.b.(π_y)

$1b_1 (\sigma_x)$

this lone pair too low in energy to participate in M-L bonding

2s a_1

(−32.3 eV)

$1a_1 (\sigma_s)$

O   **H₂O**   **2H**

Again, the simple hybridization picture of bonding is shown to be incorrect, and the MO bonding model is corroborated.

$1b_2$

H_2O PES Spectrum

$2a_1$

PES Intensity

$1b_1$

$1a_1$

13 14 15 16 17 18 19 20 21   39 40 41

Ionization Energy / eV

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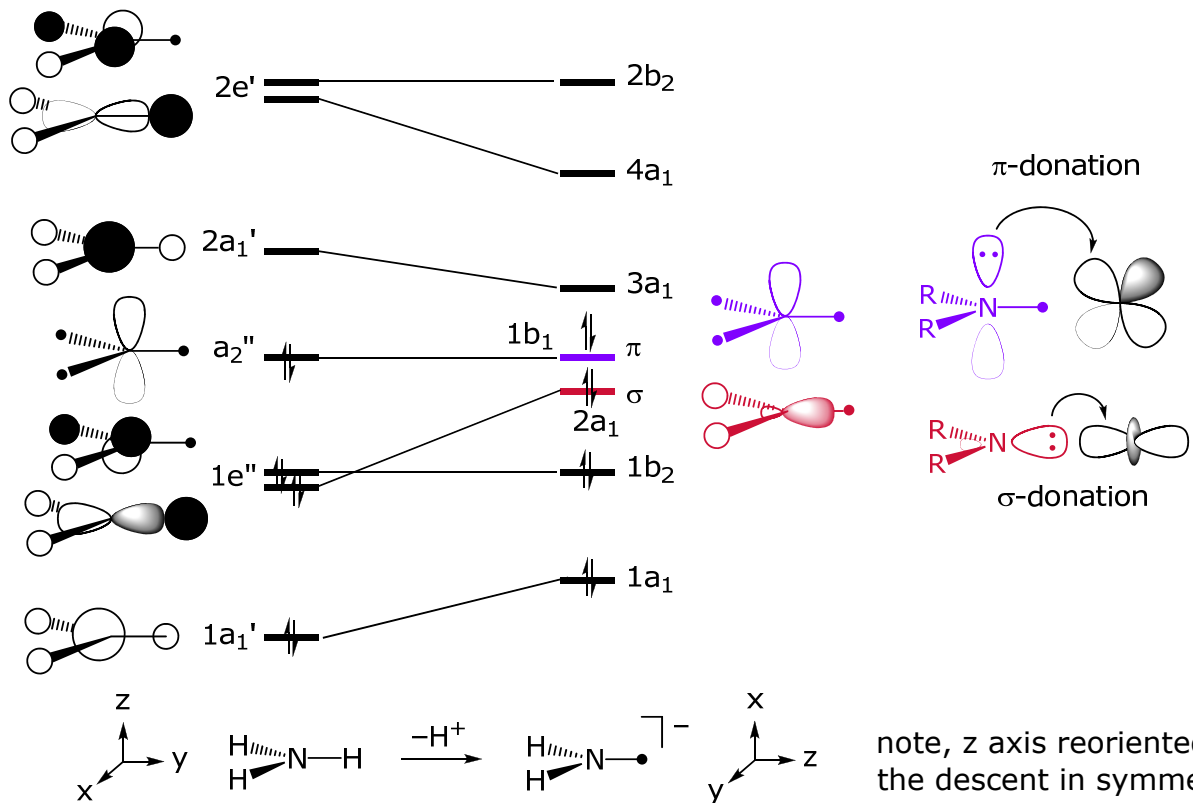Prof. Daniel G. Nocera

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π-donors

In addition to donating electron density to a metal via a σ-bond, e⁻s may be provided to the metal via a π-symmetry interaction. π-donor ligands include X^- (halide), amide (NR_2^-), sulfide (S^{2-}), oxide (O^{2-}), alkoxide (RO^-).
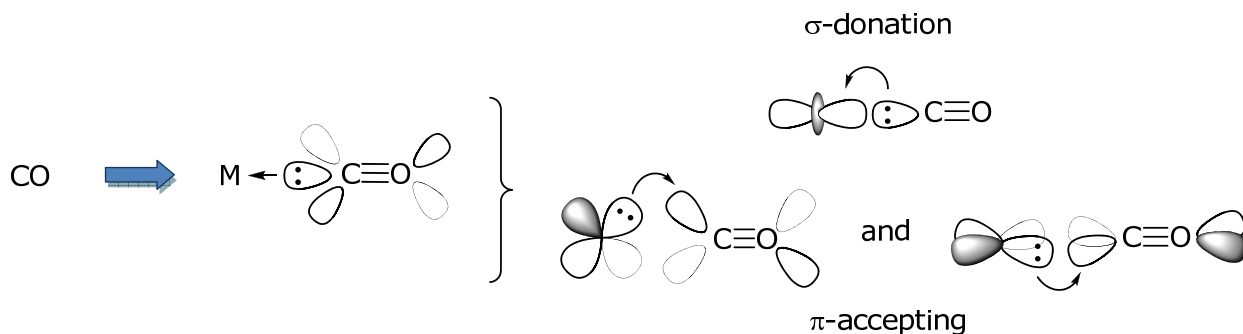

σ-donation

and

π donation

X^- (halide)

NR_2^- (amide)
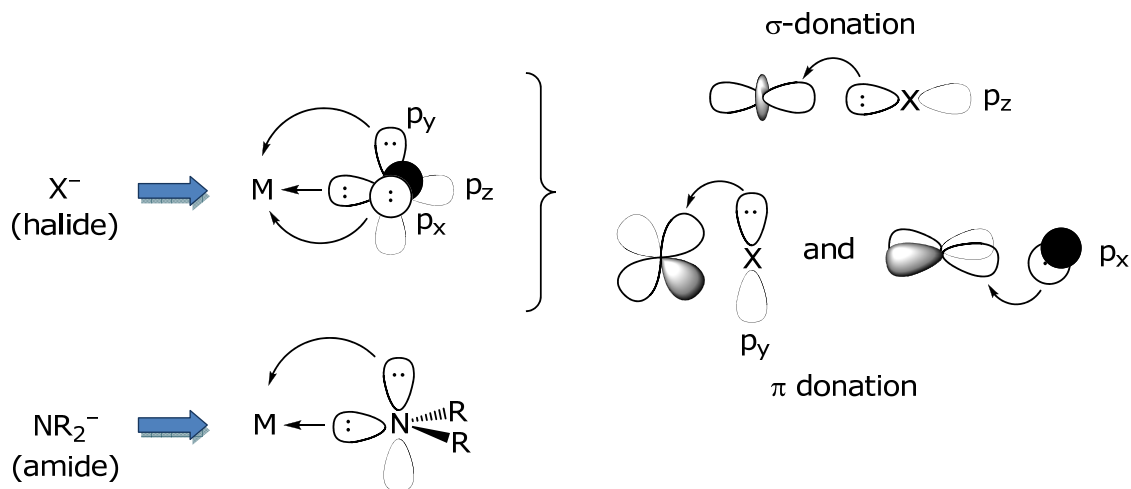
The amide MO may be constructed by beginning with the MO of "planar" NH_3, followed by its perturbation upon removal of H^+,

π-donation

σ-donation

note, z axis reoriented in the descent in symmetry

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π-acceptors

This class of ligands donate e⁻s from a σ orbital and they accept e⁻s from the metal into an empty π* orbital. CO is the archetype of this ligand class. Other π-acceptors are NO^+, CN^-, CNR. Consider the MO diagram of CO below; the HOMO is filled and of σ-symmetry, the LUMO is empty and of π* symmetry.

σ-donation

π-accepting

this orbital interaction responsible for designation of these ligands as π-**acids**

metal d orbitals situated between HOMO and LUMO

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