

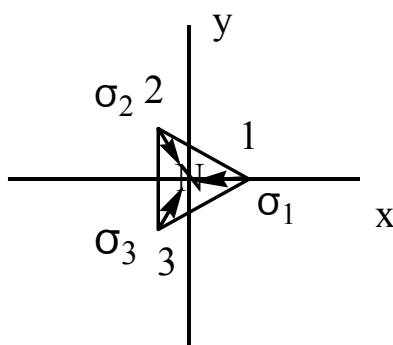
Applications: Equivalent Bond Orbitals

C734b

C734b equivalent bond orbitals

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Derive the MOs for the nitrate ion NO_3^- with D_{3h} symmetry



Let $\{\sigma_1, \sigma_2, \sigma_3\}$ denote the set of O 2p atomic orbitals pointing towards the central N-atom.

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Determine characters from those orbitals σ_i which transform into $+\sigma_i$

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
Γ_σ	3	0	1	3	0	1

Reduction yields: $\Gamma_\sigma = A_1' \oplus E'$

Next check the character table:
s-orbital **on N** transforms as A_1'
and p_x, p_y orbitals transform as E'

These are the orbitals involved in bonding.

Using: $\psi^j = N_j \sum_T \chi_j(T)^* \hat{T} \sigma_1$

$$\psi(A_1') = N(A_1') [\underbrace{\sigma_1}_E + \underbrace{(\sigma_1 + \sigma_3)}_{2C_3} + \underbrace{(\sigma_1 + \sigma_2 + \sigma_3)}_{3C_2}]$$

$$+ \underbrace{\sigma_1}_{\sigma_h} + \underbrace{(\sigma_2 + \sigma_3)}_{2S_3} + \underbrace{(\sigma_1 + \sigma_2 + \sigma_3)}_{3\sigma_v}]$$

$$= a_1' = \frac{1}{\sqrt{3}} [\sigma_1 + \sigma_2 + \sigma_3] \quad \text{in the zero-overlap approximation}$$

MO ψ_1 for NO_3^- is obtained by forming a linear combination of a_1' with AO on N of the **same symmetry** $\equiv s$

i.e. $\psi_1 = s + b_1 a_1' \quad \equiv \text{basis for } A_1'$

Note: group theory tells us which central atom orbital (s in this case) and linear combination of ligand orbitals (a_1') are involved but not the magnitude of the b_1 coefficient. That requires a Q.M. calculation.

Note: b_1 positive \rightarrow bonding
 b_1 negative \rightarrow antibonding

Next: look at E' ligand orbitals. Using projection operators and σ_1 :

$$\psi_1(E') = N_1(E') [\underset{E}{2\sigma_1} - (\underset{2C_3}{\sigma_2} + \underset{\sigma_h}{\sigma_3}) + \underset{2S_3}{2\sigma_1} - (\underset{\sigma_h}{\sigma_2} + \underset{2S_3}{\sigma_3})]$$

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$$\therefore \psi_1(E') = \frac{1}{\sqrt{6}} [2\sigma_1 - (\sigma_2 + \sigma_3)]$$

Similarly starting with σ_2 and σ_3 yields:

$$\psi_2(E') = \frac{1}{\sqrt{6}} [2\sigma_2 - (\sigma_3 + \sigma_1)]$$

$$\psi_3(E') = \frac{1}{\sqrt{6}} [2\sigma_3 - (\sigma_1 + \sigma_2)]$$

Clearly 3 basis functions are too many for a two-fold degeneracy as ψ_1 , ψ_2 and ψ_3 are not linearly independent.

Need 2 linear combinations which overlap p_x and p_y

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The first choice is easy.
Use ψ_1 as it has lots of overlap with p_x

$$\text{Why? } \psi_1(E') = \frac{1}{\sqrt{6}} [2\sigma_1 + (\sigma_2 + \sigma_3)]$$

$$\therefore \psi_2 = p_x + b_2 e_1'$$

To get the second ligand orbital take $\psi_2(E') - \psi_3(E')$ and therefore eliminate σ_1 from the combination.

This puts more overlap on p_y

$$\psi_2(E') - \psi_3(E') \propto (\sigma_2 - \sigma_3)$$

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$$\text{Normalize } \Rightarrow e_2' = \frac{1}{\sqrt{2}} (\sigma_2 - \sigma_3)$$

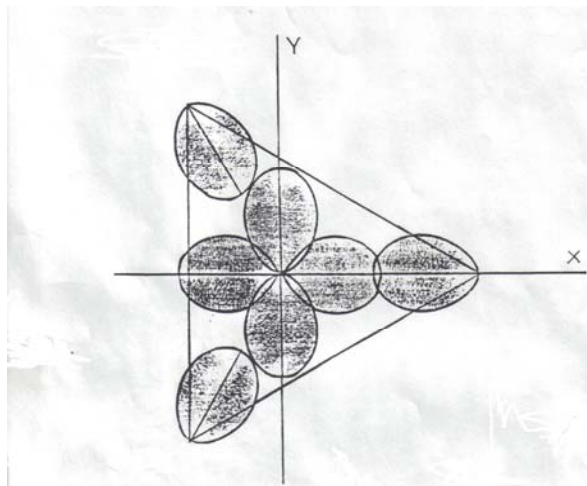
$$\therefore \psi_3 = p_y + b_3 e_2'$$

Note: the subscripts in e_1' and e_2' denote the partners in the two-fold basis.

Note: $\{\psi_1, \psi_2, \psi_3\}$ are OK symmetry-wise but they don't look like "classical" chemical bonds

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To achieve maximum overlap with ligand p-orbitals and therefore the most stability, the central atom orbitals undergo **hybridization** to make three equivalent sp² hybrids.

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To find 3 equivalent MOs \equiv bond orbitals express ψ_1, ψ_2, ψ_3 in matrix form.

$$\langle \psi_1, \psi_2, \psi_3 | = \langle s, p_x, p_y | + \langle a'_1, e'_1, e'_2 | \tilde{B}$$

where

$$\tilde{B} = \begin{pmatrix} b_1 & 0 & 0 \\ 0 & b_2 & 0 \\ 0 & 0 & b_3 \end{pmatrix}$$

Examine the ligand LCAOs more closely: $\langle a'_1, e'_1, e'_2 | = \langle \sigma_1, \sigma_2, \sigma_3 | \tilde{M}$

where

$$\tilde{M} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

Coefficients in:

↑	↑	↑
ψ_1	ψ_2	ψ_3

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$$\begin{aligned} \therefore \langle \psi_1, \psi_2, \psi_3 | &= \langle \sigma_1, \sigma_2, \sigma_3 | \tilde{M} \tilde{B} \\ &= \langle \sigma_1, \sigma_2, \sigma_3 | \tilde{B} \tilde{M} \because [\tilde{B}, \tilde{M}] = 0 \end{aligned}$$

since **B** is diagonal

$$\begin{aligned} \therefore \langle \psi'_1, \psi'_2, \psi'_3 | &= \langle \psi_1, \psi_2, \psi_3 | \tilde{M}^{-1} \\ &= \langle s, p_x, p_y | \tilde{M}^{-1} + \langle \sigma_1, \sigma_2, \sigma_3 | \tilde{B} \\ &= \langle h_1, h_2, h_3 | + \langle \sigma_1, \sigma_2, \sigma_3 | \tilde{B} \end{aligned}$$

hybrid orbitals on N

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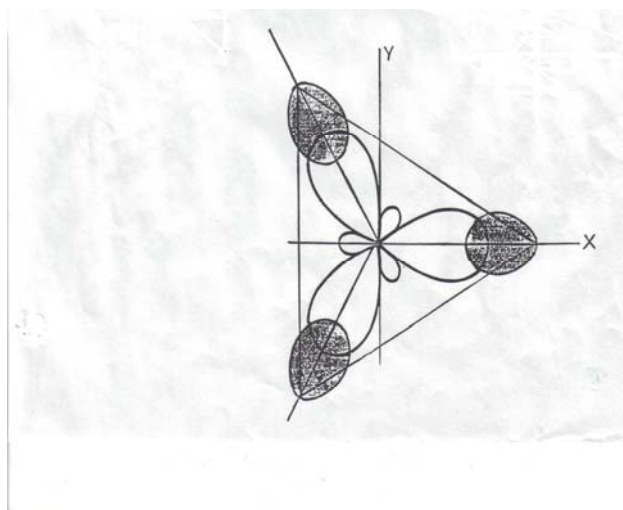
The sp^2 hybrid N orbitals are:

$$\langle h_1, h_2, h_3 | = \langle s, p_x, p_y | \tilde{M}^T \because \tilde{M}^{-1} = \tilde{M}^T$$

$$= \langle s, p_x, p_y | \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

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Approach is general (eg can be used for T_d geometry) where the ligand geometry does not corresponds to that of the p and d orbitals

Procedure is not necessary for AB_6 (O_h) or AB_4 (D_{4h}) symmetry since the ligands point at orbitals on the central atom.