

Symmetry Aspects of Qualitative MO Theory

Chemistry 673

Applications to Simple Main-Group and T.M. Molecules

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Perturbation Theory

- Begin with a system with known energies and wavefunctions, $E_1^{(0)}, E_2^{(0)}, E_3^{(0)}, \dots, \psi_1^{(0)}, \psi_2^{(0)}, \psi_3^{(0)}, \dots$ for an *unperturbed* problem with Hamiltonian $\mathcal{H}^{(0)}$.
- Introduce a “perturbation”, \mathcal{H}' , such that the new Hamiltonian for the system is $\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}'$.

$$E_i = E_i^{(0)} + E_i^{(1)} + E_i^{(2)} + \dots = E_i^{(0)} + H'_{ii} + \sum_{j \neq i} \frac{|H'_{ij}|^2}{E_i^{(0)} - E_j^{(0)}} + \dots$$

$$\psi_i = \psi_i^{(0)} + \psi_i^{(1)} + \dots = \psi_i^{(0)} + \sum_{j \neq i} \frac{H'_{ij}}{E_i^{(0)} - E_j^{(0)}} \psi_j^{(0)} + \dots$$

$$\text{where } H'_{ij} \equiv \int \psi_i^{(0)} \mathcal{H}' \psi_j^{(0)} d\tau$$

Read Handout: [subgroups&perturbation_theory.pdf](#)

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Interpretation

$$E_i^{(1)} = H'_{ii} \equiv \int \psi_i^{(0)} \mathcal{H}' \psi_i^{(0)} d\tau$$

- The *first-order* corrections to the energies, $E_i^{(1)}$, are the expectation values of the perturbed part of the Hamiltonian, \mathcal{H}' , and the *zeroth-order* wavefunctions, $\psi_i^{(0)}$, i.e., calculate what the perturbation does to the energies of the initial wavefunctions without considering changes to the

$$\psi_i^{(1)} = \sum_{j \neq i} \frac{H'_{ij}}{E_i^{(0)} - E_j^{(0)}} \psi_j^{(0)}$$

- In the each of the 1st-order corrections to the wavefunctions, $\psi_i^{(1)}$, *other* wavefunctions, $\psi_j^{(0)}$ ($j=1, 2, 3, \dots \neq i$), are *mixed* into $\psi_i^{(0)}$ to the extent that \mathcal{H}' “couples” $\psi_i^{(0)}$ and $\psi_j^{(0)}$ together.

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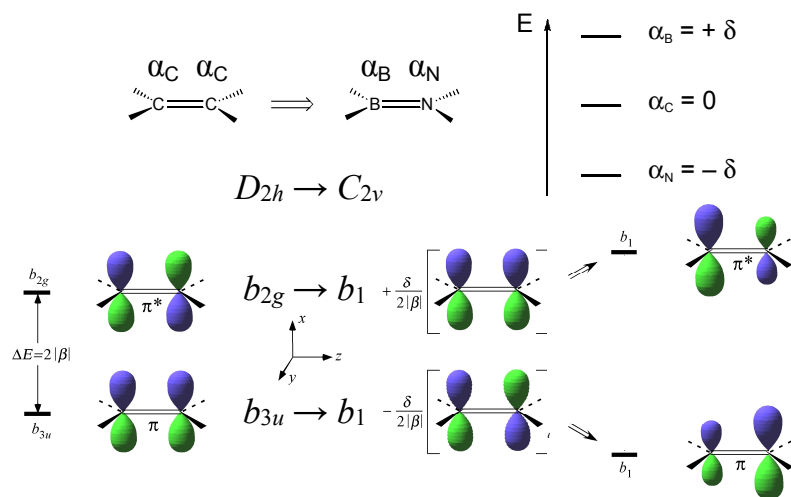
Interpretation

$$E_i^{(2)} = \sum_{j \neq i} \frac{|H'_{ij}|^2}{E_i^{(0)} - E_j^{(0)}}$$

- The *second-order* corrections to the energies, $E_i^{(2)}$, reflect the energetic corrections due to the mixing we see in the first-order wavefunctions.
- **Key symmetry implication:**
 - ★ Contributions to the 1st-order corrections to the wavefunctions, $\psi_i^{(1)}$, 2nd-order corrections to the energies, $E_i^{(2)}$, depend on the symmetry of the system *including* \mathcal{H}' . If the perturbed system *lowers* the symmetry, then \mathcal{H}' may mix $\psi_i^{(0)}$ and $\psi_j^{(0)}$ together if they belong to the same I.R. in the subgroup. If $\psi_i^{(0)}$ and $\psi_j^{(0)}$ still belong to different I.R.s in the lower symmetry subgroup, H'_{ij} will still be zero.

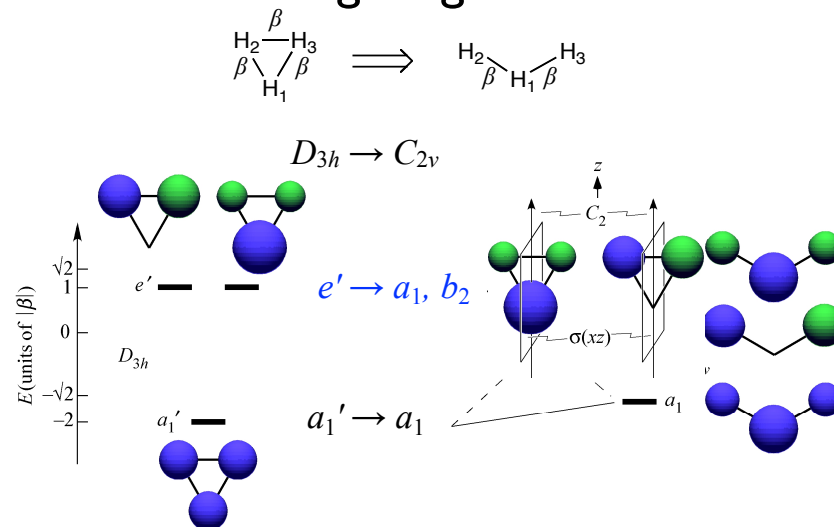
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“Electronegativity” Perturbation



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Breaking Degeneracies



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Basic Polyatomic Systems; Qualitative PMO Theory

- CH_4
 - $\text{CH}_4(T_d) \rightarrow \text{NH}_3(C_{3v}) \leftarrow \text{NH}_3$ (planar, D_{3h})
 - $\text{OH}_2(D_{\infty h}) \rightarrow \text{OH}_2(C_{2v})$
 - $\text{ML}_6(\text{O}_h, \sigma \text{ only}) \rightarrow \text{ML}_4(D_{4h})$ ($M = \text{T.M.}$)
 - $\text{ML}_6(\text{O}_h, \sigma \text{ only}) \rightarrow \text{ML}_6(\text{O}_h, \sigma + \pi)$
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T_d and T

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)
T_2	3	0	-1	-1	1	(x, y, z)

T	E	$4C_3$	$4C_3^2$	$3C_2$	
A	1	1	1	1	$x^2 + y^2 + z^2$
E	$\begin{Bmatrix} 1 & \epsilon_* & \epsilon^* & 1 \\ 1 & \epsilon^* & \epsilon & 1 \end{Bmatrix}$				$(2z^2 - x^2 - y^2, x^2 - y^2)$
T	3	0	0	-1	$(R_x, R_y, R_z); (x, y, z)$

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Angular Overlaps

Some Useful Overlap Integrals Between Central-Atom s , p , and d Orbitals and Ligand σ and π Orbitals^{a,b}

^a $\pi_{||}$ is a ligand π orbital with an axis lying in a plane containing the z -axis and the ligand; π_{\perp} is a ligand π orbital with an axis perpendicular to this plane.

^b For p_z , d_{z^2} , f_{xyz} , etc. we use z , z^2 , xyz , etc.

^c Ligand lies in the xz plane. For more general cases, a more complete table is needed.

$$\begin{aligned}
 S(s, \sigma) &= S_{\sigma} \\
 S(s, \pi) &= 0 \\
 S(z, \sigma) &= HS_{\sigma} \\
 S(z, \pi_{||}) &= IS_{\pi} \\
 S(z, \pi_{\perp}) &= 0 \\
 S(z^2, \sigma) &= \frac{1}{2}(3H^2 - 1)S_{\sigma} \\
 S(x^2 - y^2, \sigma) &= \frac{\sqrt{3}}{2}(F^2 - G^2)S_{\sigma} \\
 S(xy, \sigma) &= \sqrt{3}FGS_{\sigma} \\
 S(xz, \sigma) &= \sqrt{3}FHS_{\sigma} \\
 S(yz, \sigma) &= \sqrt{3}GHS_{\sigma} \\
 S(z^2, \pi_{||})^c &= \sqrt{3}HIS_{\pi} \\
 S(z^2, \pi_{\perp}) &= 0 \\
 S(x^2 - y^2, \pi_{||}) &= -HIS_{\pi} \\
 S(x^2 - y^2, \pi_{\perp}) &= 0 \\
 S(xy, \pi_{||}) &= 0 \\
 S(xy, \pi_{\perp}) &= IS_{\pi} \\
 S(xz, \pi_{||}) &= (I^2 - H^2)S_{\pi} \\
 S(xz, \pi_{\perp}) &= 0 \\
 S(yz, \pi_{||}) &= 0 \\
 S(yz, \pi_{\perp}) &= HS_{\pi} \\
 F &= \sin\theta\cos\phi \\
 G &= \sin\theta\sin\phi \\
 H &= \cos\theta \\
 I &= \sin\theta
 \end{aligned}$$

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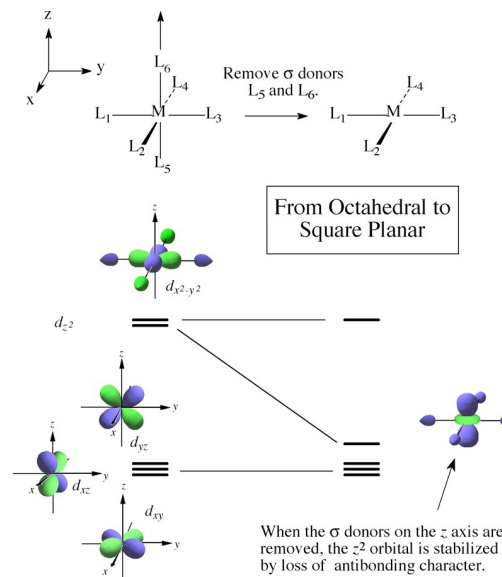
Subgroup Relationships

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O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2^2$ (C_4^2)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	$(2z^2 - x^2 - y^2, x^2 - y^2)$
E_g	2	-1	0	0	2	2	0	-1	2	0	(R_x, R_y, R_z)
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(xy, xz, yz)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	-1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	1	

C_{4v}	E	$2C_4$	C_2 (C_4^2)	$2\sigma_v$	$2\sigma_d$	
A_1	1	1	1	1	1	z
A_2	1	1	1	-1	-1	R_z
B_1	1	-1	1	1	-1	$x^2 - y^2$
B_2	1	-1	1	-1	1	xy
E	2	0	-2	0	0	(xz, yz)

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Background Topics - increasing Δ_0

- Spectrochemical Series:

$\text{NO}^+ > \text{CO} \geq \text{PF}_3 \geq \text{CN}^- > \text{NO}_2^- > \text{en} > \text{NH}_3 > \text{NCS}^- > \text{H}_2\text{O} > \text{ox} > \text{OH}^- > \text{F}^- > \text{NO}_3^- > \text{Cl}^- > \text{SCN}^- > \text{S}^{2-} > \text{Br}^- > \text{I}^-$
the series represents the confluence of several trends in electronegativity, decreasing/increasing σ -donation, and decreasing/increasing π -donation/acceptance.

- Metal trends:

$\text{Mn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{V}^{2+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{V}^{3+} < \text{Co}^{3+} < \text{Mn}^{4+} < \text{Rh}^{3+} < \text{Pd}^{4+} < \text{Ir}^{3+} < \text{Re}^{4+} < \text{Pt}^{4+}$

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Colors of Co(III) solutions



Solutions are ordered according to the ligand spectrochemical series:
(a) CN^- , (b) NO_2^- , (c) phen, (d) en, (e) NH_3 , (f) gly, (g) H_2O , (h) ox^{2-} , (i) CO_3^{2-} .

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