Symmetry Aspects of Qualitative MO Theory

Chemistry 673
Applications to Simple Main-Group and T.M. Molecules

Perturbation Theory

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

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

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

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

Read Handout: subgroups&perturbation_theory.pdf

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

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

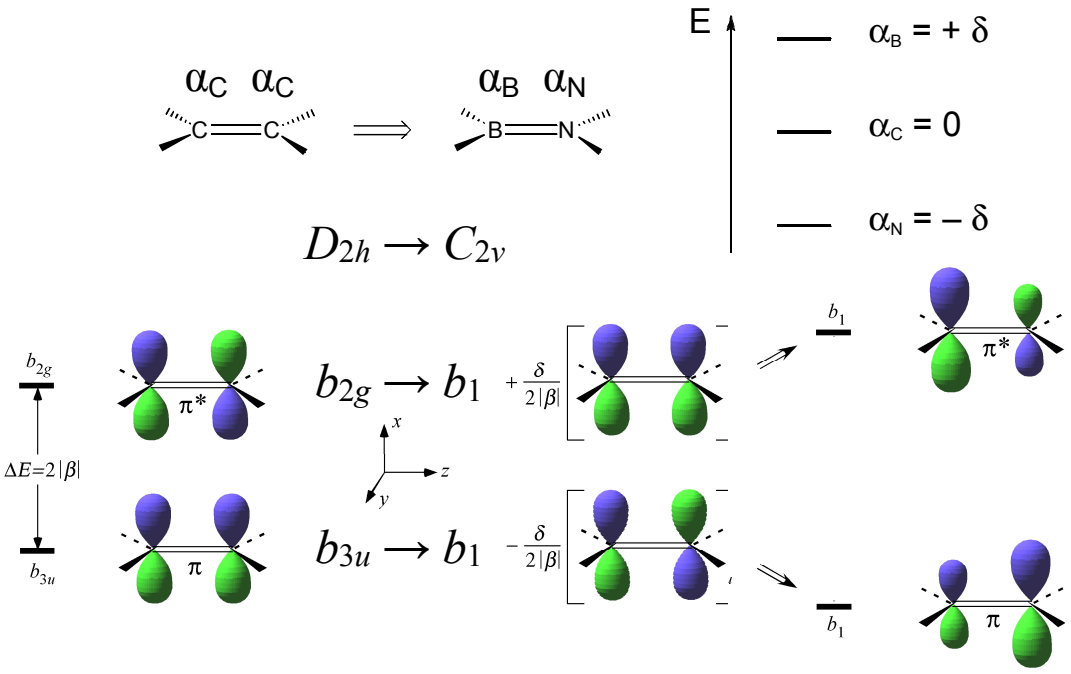
- In the each of the 1st -order corrections to the wavefunctions, $\psi_i^{(1)}$, *other* wavefunctions, $\psi_j^{(0)}$ ($j = 1, 2, 3, \ldots \neq i$), are *mixed* into $\psi_i^{(0)}$ to the extent that $\mathcal{H}'$ "couples" $\psi_i^{(0)}$ and $\psi_j^{(0)}$ together.

Interpretation

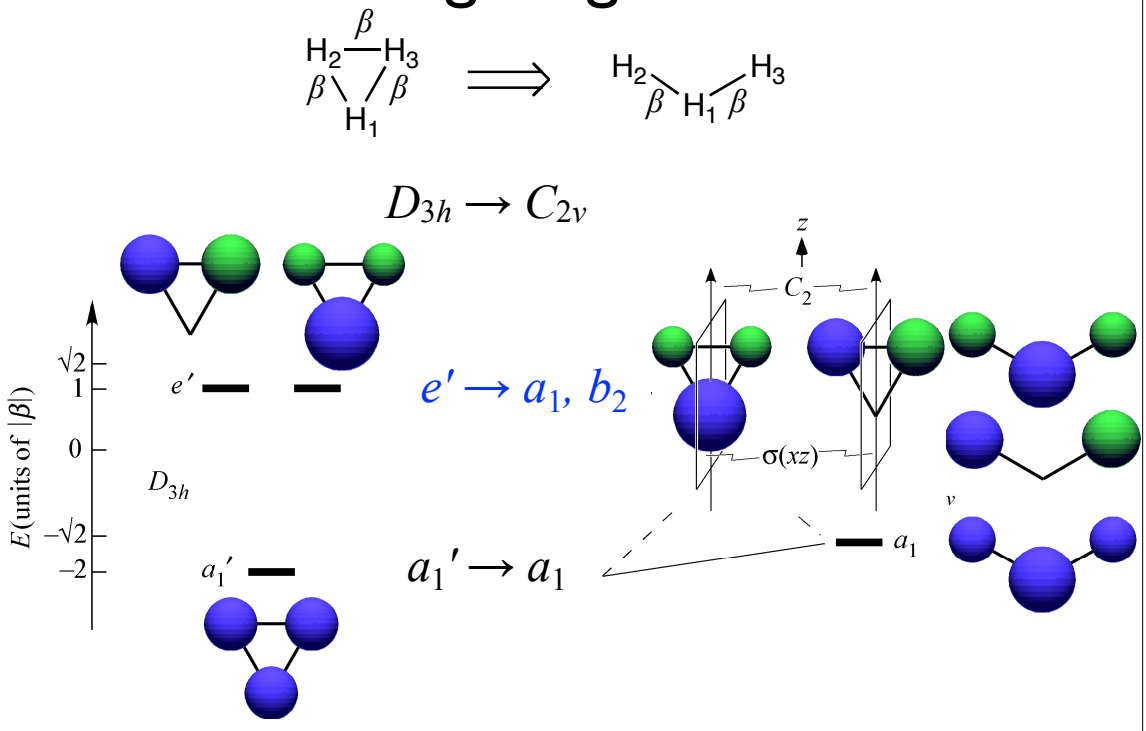
$$E_i^{(2)} = \sum_{j \neq i} \frac{\left| H'_{ij} \right|^2}{E_i^{(0)} - E_j^{(0)}}$$

- 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.

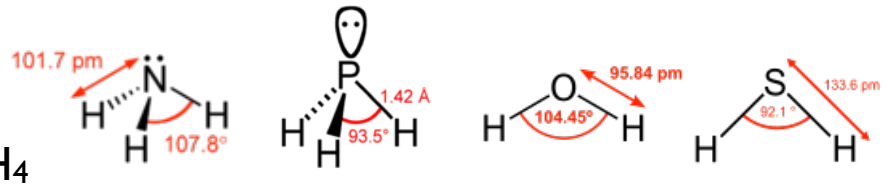
"Electronegativity" Perturbation



Breaking Degeneracies



Basic Polyatomic Systems; Qualitative PMO Theory



- CH_4
- $CH_4(T_d) \rightarrow NH_3(C_{3v}) \leftarrow NH_3$ (planar, D_{3h})
- OH_2 ($D_{\infty h}$) → $OH_2(C_{2v})$
- $ML_6(O_h, \sigma$ only) → $ML_4(D_{4h})$ (M = T. M.)
- $ML_6(O_h, \sigma$ only) → $ML_6(O_h, \sigma + \pi)$

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)	(xy, xz, yz)

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

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; $\pi_{\perp}$ 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.

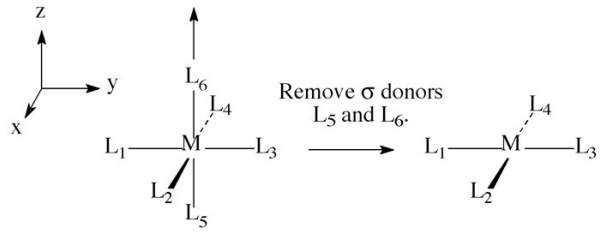
[c] Ligand lies in the *xz* plane. For more general cases, a more complete table is needed.

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

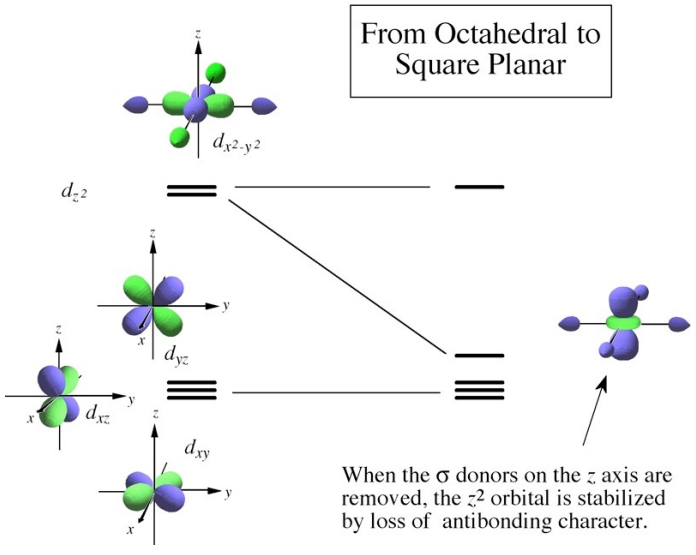
Subgroup Relationships

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ (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		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	-1		(xy, xz, yz)
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	x^2+y^2, z^2
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	(x, y) (R_x, R_y)	(xz, yz)



From Octahedral to Square Planar



When the σ donors on the z axis are removed, the z^2 orbital is stabilized by loss of antibonding character.

Background Topics - increasing Δ_o

- Spectrochemical Series:

$NO^+ > CO \geq PF_3 \geq CN^- > NO_2^- >$ *en* $> NH_3 >$ **N**$CS^- > H_2O >$ *ox* $> OH^- > F^- > NO_3^- > Cl^- >$ **S**$CN^- > S^{2-} > Br^- > I^-$

the series represents the confluence of several trends in electronegativity, decreasing/increasing σ-donation, and decreasing/increasing π-donation/acceptance.

- Metal trends:

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

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-}.