

Molecular orbital theory

CH₄ ⊕ HB

The variation method

Ground-state energy: Suppose we have a Hamiltonian H and $| \Phi_\alpha \rangle$ is a set of eigenfunctions

$$H | \Phi_\alpha \rangle = E_\alpha | \Phi_\alpha \rangle$$

with ordered energies: $E_0 \leq E_1 \leq E_2 \leq \dots$

ground-state energy; any quantum system is in $| \Phi_0 \rangle$ with the energy E_0 when all excitations are relaxed.

Variational principle: The expectation value of the Hamiltonian on a given wave function Φ is an upper bound to the exact ground-state energy

$$\langle \Phi | \Phi \rangle = 1, \quad E_0 \leq \langle \Phi | H | \Phi \rangle$$

$$\begin{aligned} \text{Proof: } \langle \Phi | H | \Phi \rangle &= \sum_{\alpha, p} \langle \Phi | \Phi_\alpha \rangle \langle \Phi_\alpha | H | \Phi_p \rangle \langle \Phi_p | \Phi \rangle \\ &= \sum_{\alpha} E_\alpha \langle \Phi | \Phi_\alpha \rangle \langle \Phi_\alpha | \Phi \rangle = \sum E_\alpha |\langle \Phi | \Phi_\alpha \rangle|^2 \end{aligned}$$

$$\begin{aligned} \langle \Phi | \Phi \rangle &= \sum \langle \Phi | \Phi_\alpha \rangle \langle \Phi_\alpha | \Phi_p \rangle \langle \Phi_p | \Phi \rangle = \\ &= \sum \langle \Phi | \Phi_\alpha \rangle \langle \Phi_\alpha | \Phi \rangle = \end{aligned}$$

$$= \sum |\langle \Phi | \Phi_\alpha \rangle|^2 = 1$$

$$\langle \Phi | H | \Phi \rangle \leq E_0 \sum_{\alpha} |\langle \Phi | \Phi_\alpha \rangle|^2 = E_0$$

Secular equation

$$F(c_1, c_2) = c_1^2 H_{AA} + c_2^2 H_{BB} + 2c_1 c_2 H_{AB} - (c_1^2 + c_2^2 + 2c_1 c_2 S_{12}) E$$

$$\frac{\delta F}{\delta c_1} = 0 \quad \frac{\delta F}{\delta c_2} = 0$$

secular equation

$$c_1(H_{AA} - E) + c_2(H_{AB} - E S_{12}) = 0 \quad \{ \quad (!)$$

$$c_1(H_{AB} - E S_{12}) + c_2(H_{BB} - E) = 0 \quad \}$$

According to linear algebra, eq (!) can be solved

only if

$$\begin{vmatrix} H_{AA} - E & H_{AB} - E S_{12} \\ H_{AB} - E S_{12} & H_{BB} - E \end{vmatrix} = 0$$

Math background: For a matrix $A = \begin{pmatrix} a_{11} & \dots & a_{1n} \\ \vdots & \ddots & \vdots \\ a_{n1} & \dots & a_{nn} \end{pmatrix}$

$|A|$ defines the determinant

$$\det(A) = |A| = \sum_j^{n!} (-)^{\text{permutation operator}} (a_{11} a_{22} \dots a_{nn})$$

The sum runs over all permutations of the matrix columns

The number of transpositions required to generate a given permutation

Variational solution of the Schrödinger equation

$$H_A = -\frac{\hbar^2}{2me} \nabla_e^2 - \frac{z_A e^2}{4\pi\epsilon_0 R_A}$$

electron on atom A

$$H_B = -\frac{\hbar^2}{2me} \nabla_e^2 - \frac{z_B e^2}{4\pi\epsilon_0 R_B}$$

electron on atom B

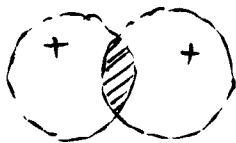
$$H_A \Phi_{1s}(A) = \varepsilon_A \Phi_{1s}(A)$$

$$H_B \Phi_{1s}(B) = \varepsilon_B \Phi_{1s}(B)$$

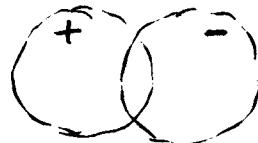
$$\Psi = c_1 \Phi_{1s}(A) + c_2 \Phi_{1s}(B)$$

$$\langle \Psi | \Psi \rangle = 1 \quad \langle c_1 \Phi_{1s}^A + c_2 \Phi_{1s}^B | c_1 \Phi_{1s}^A + c_2 \Phi_{1s}^B \rangle = 1$$

$$c_1^2 + c_2^2 + 2c_1c_2 S_{AB} = 1, \quad \overbrace{S_{AB}}^{\text{overlap integral}} = \langle \Phi_{1s}^A | \Phi_{1s}^B \rangle$$



positive overlap



negative overlap

S_{AB} measures the volume in which there is electron density from both atoms

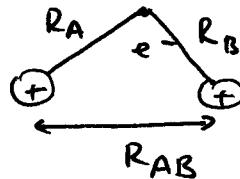
Variation method: $E = \langle \Psi | H | \Psi \rangle =$

$$\begin{aligned} &= \langle c_1 \Phi_{1s}^A + c_2 \Phi_{1s}^B | H | c_1 \Phi_{1s}^A + c_2 \Phi_{1s}^B \rangle = c_1^2 H_{AA} + c_2^2 H_{BB} + \\ &\quad \underbrace{\langle A | H | A \rangle}_{\langle A | H | B \rangle} \underbrace{\langle B | H | B \rangle}_{\langle B | H | A \rangle} \\ &+ c_1 c_2 H_{AB} + c_1 c_2 H_{BA} \end{aligned}$$

$$c_1^2 H_{AA} + c_2^2 H_{BB} + 2c_1 c_2 H_{AB} = E (c_1^2 + c_2^2 + 2c_1 c_2 S_{12})$$

Solving for electronic states

H_2^+ cation:



$$H = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_A} \nabla_A^2 - \frac{\hbar^2}{2m_B} \nabla_B^2 - \frac{z_A e^2}{4\pi\epsilon_0 R_A} - \frac{z_B e^2}{4\pi\epsilon_0 R_B} + \frac{z_A z_B}{4\pi\epsilon_0 R_{AB}}$$

kinetic energy

potential energy

$$= -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{z_A e^2}{4\pi\epsilon_0 R_A} - \frac{z_B e^2}{4\pi\epsilon_0 R_B} - \frac{\hbar^2}{2m_A} \nabla_A^2 - \frac{\hbar^2}{2m_B} \nabla_B^2 + \frac{z_A z_B}{4\pi\epsilon_0 R_{AB}}$$

electronic Hamiltonian

nuclear Hamiltonian

The Born-Oppenheimer approximation splits the total wave function into the electronic and nuclear parts

$$\Psi(r, R_A, R_B) = \overline{\psi_e(r)} \chi_n(R_A, R_B)$$

$$\left[-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{z_A e^2}{4\pi\epsilon_0 R_A} - \frac{z_B e^2}{4\pi\epsilon_0 R_B} \right] \overline{\psi_e(r)} = E_e(R_A, R_B) \overline{\psi_e(r)}$$

$$\left[-\frac{\hbar^2}{2m_A} \nabla_A^2 - \frac{\hbar^2}{2m_B} \nabla_B^2 + \frac{z_A z_B}{4\pi\epsilon_0 R_{AB}} + E_e(R_A, R_B) \right] \chi_n = \Sigma \chi_n$$

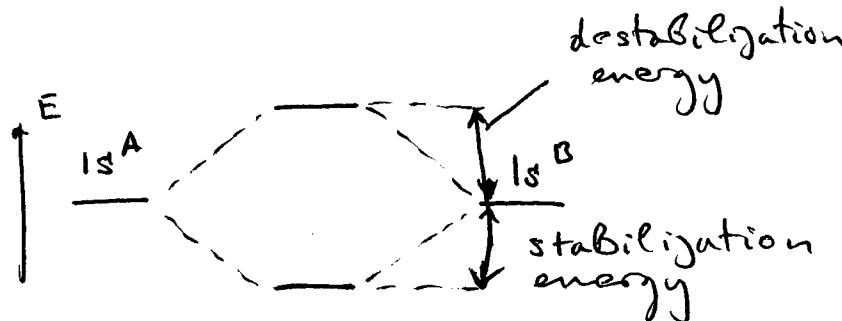
electronic terms

Secular determinant

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES_{12} \\ H_{AB} - ES_{12} & H_{BB} - E \end{vmatrix} = (H_{AA} - E)(H_{BB} - E) - (H_{AB} - ES_{12}) \times (H_{AB} - ES_{12}) = 0$$

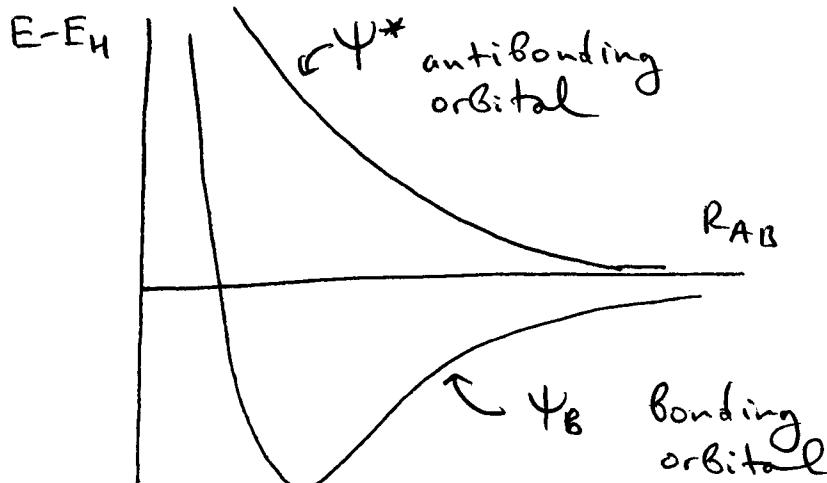
If $H_{AA} = H_{BB}$

$$E = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{12}}$$



$$\{\text{stabilization}\} = \frac{H_{AA} - H_{AB}}{1 + S_{12}} - H_{AA}$$

$$\{\text{destabilization}\} = \frac{H_{AA} + H_{AB}}{1 + S_{12}} - H_{AA}$$



$$H_{AB} = H_{AB}(R_{AB}) \rightarrow 0$$

$$R_{AB} \rightarrow \infty$$

$$S_{12} = S_{12}(R_{AB}) \rightarrow 0$$

$$R_{AB} \rightarrow \infty$$

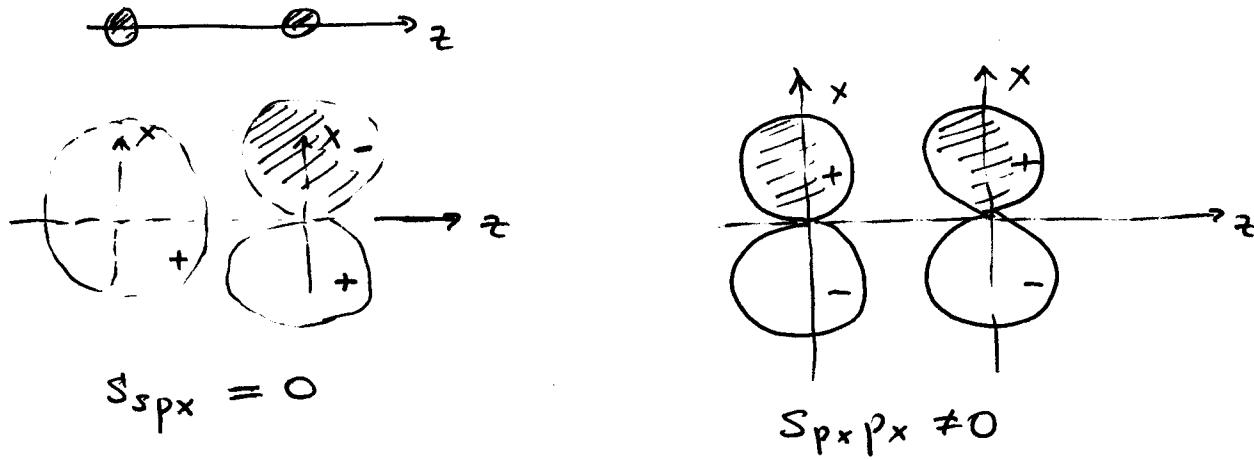
$$\Psi_B = \frac{1}{\sqrt{2+2S_{12}}} (\Phi_{1s}^A + \Phi_{1s}^B)$$

$$\Psi^* = \frac{1}{\sqrt{2+2S_{12}}} (\Phi_{1s}^A - \Phi_{1s}^B)$$

Diatomic molecules

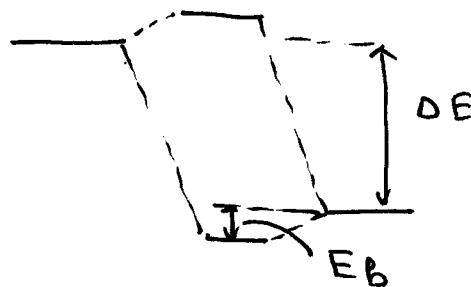
Principles of LCAO:

- ①. In order for two orbitals to form an MO, they must have the same symmetry about the internuclear axis.



If $S_{ij} = 0$, then $H_{ij} = 0$

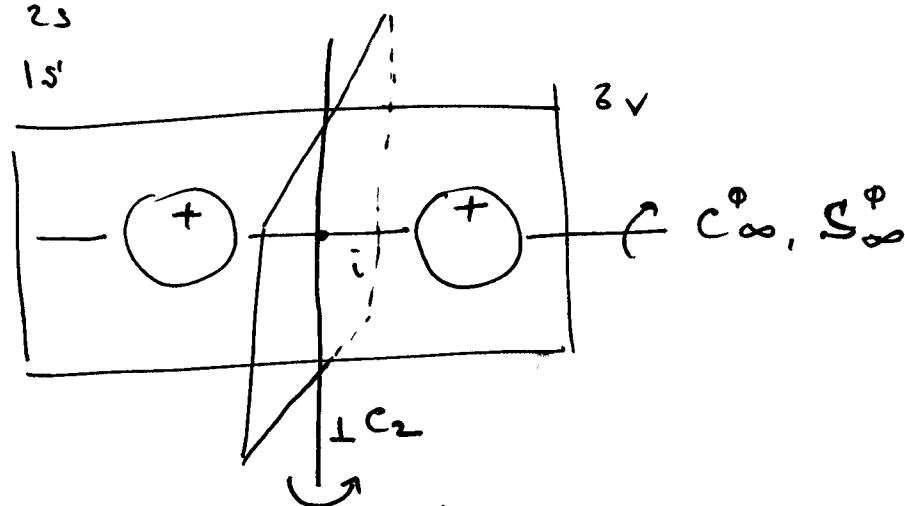
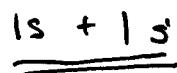
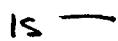
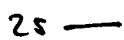
- ②. Combining orbitals of very different energies leads to only small interactions



Stabilization energy E_B decreases when ΔE increases

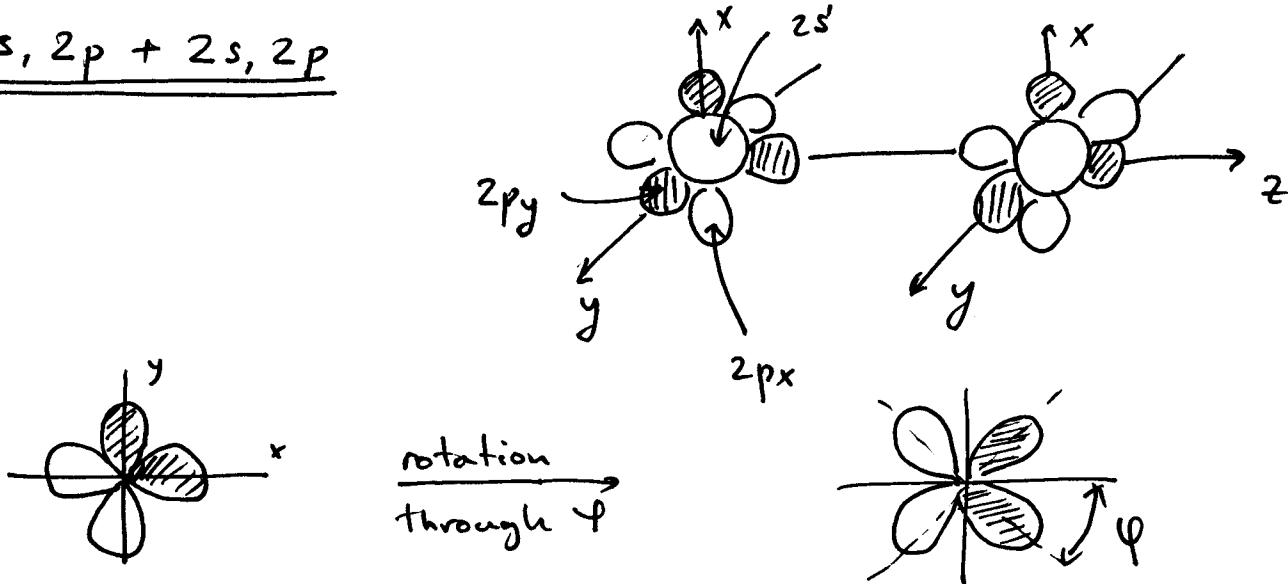
- ③ Each possible molecular orbital must form a basis for some irreducible representation of the point group of the molecule

Molecular orbitals for the second row diatomic molecules:



$D_{\infty h}$	E	$2C_{\infty}^{\phi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\phi}$	∞C_2	
$\Gamma(1s)$	2	2	2	0	0	0	$= 3g^+ + 3u^+$
Σ_g^+	1	1	1	1	1	1	$\leftarrow \psi_g$
Σ_g^+	1	1	1	-1	-1	-1	$\leftarrow \psi^*$

$2s, 2p + 2s, 2p$



$$R_\phi \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

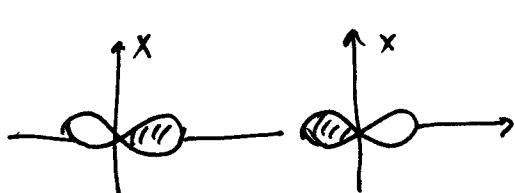
$\downarrow 2\cos\phi$

D_{00h}	E	$2C_\infty^\phi$	∞S_v	i	$2S_\infty^\phi$	∞C_2
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$P(2s, 2p)$	8	$4+4\cos\phi$	4	0	0	0
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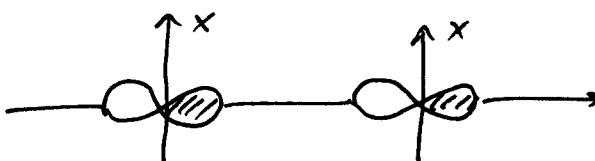
$\Gamma(2s, 2p_z)$	4	4	0	0	0	$O = 2S_g^+ + 2S_u^+$
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$P(2p_x, 2p_y)$	4	$4\cos\phi$	0	0	0	$O = \Pi_g + \Pi_u$
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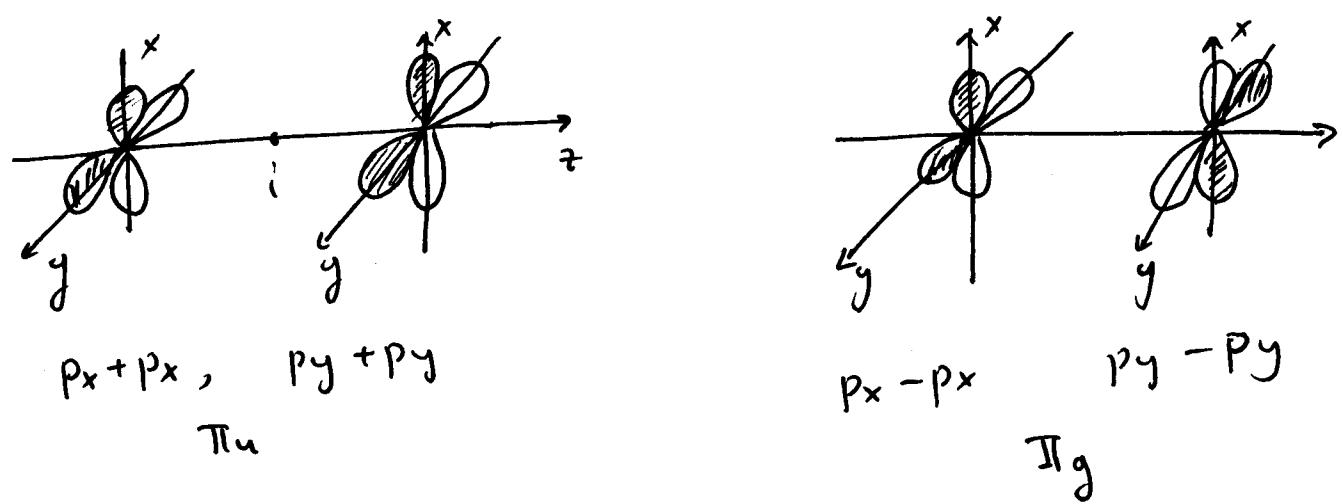
$P_z - P_z$

S_g^+

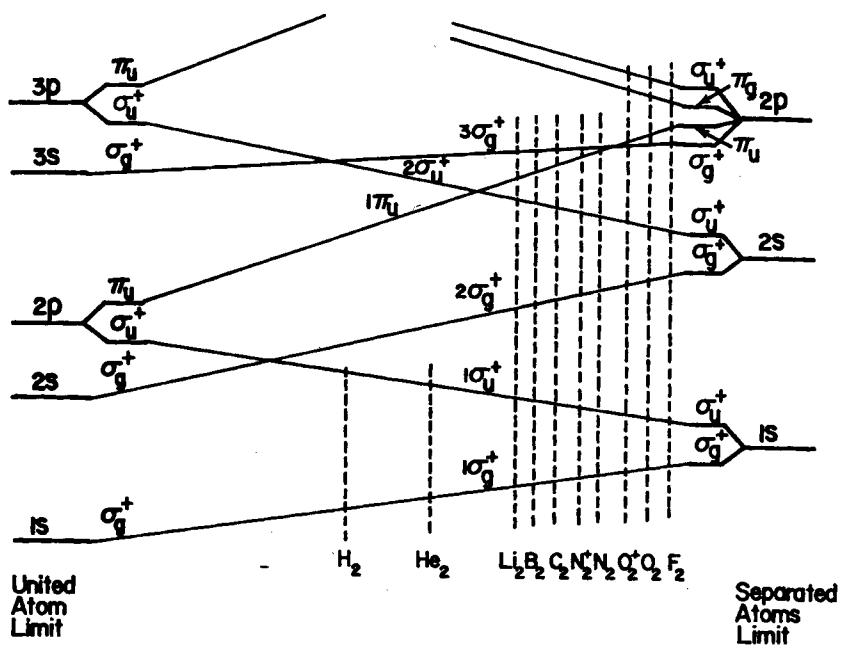
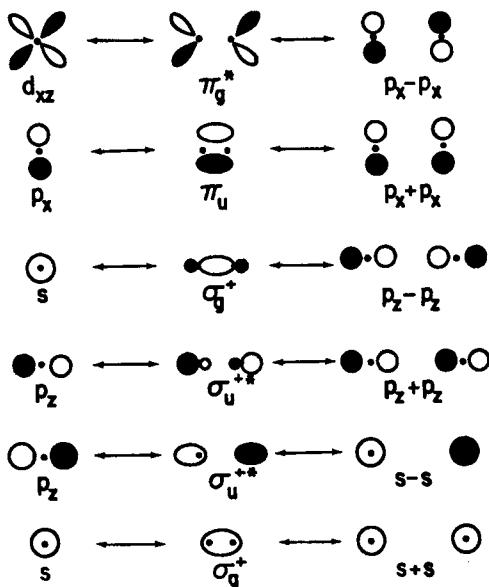


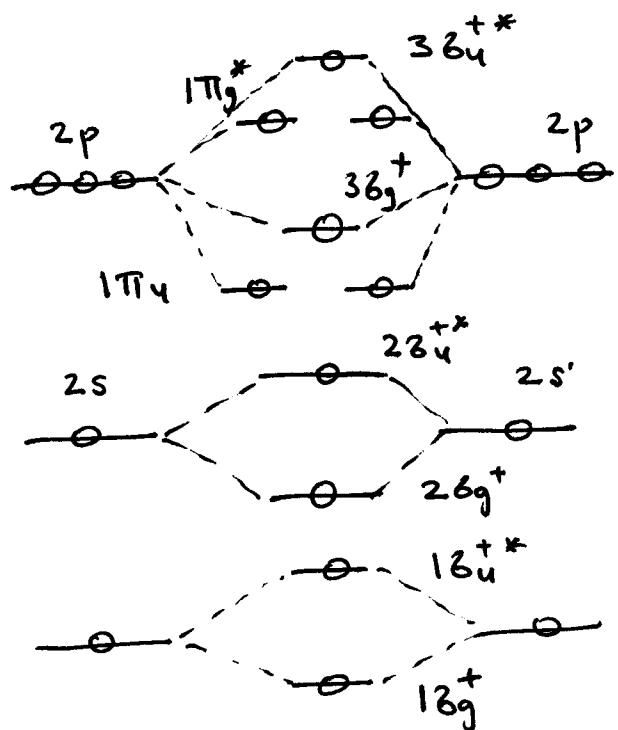
$P_z + P_z$

S_u^+



UNITED ATOM MOLECULAR ORBITAL SEPARATE ATOMS

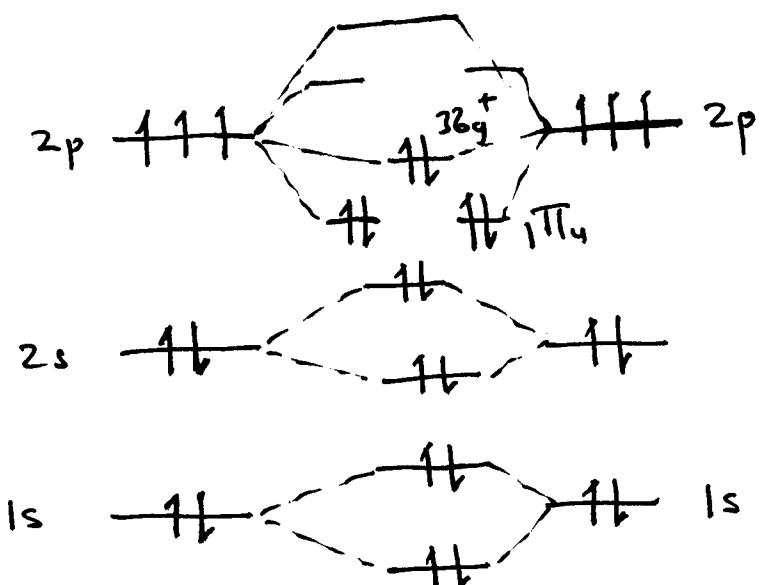




Scheme I

Li₂ - N₂

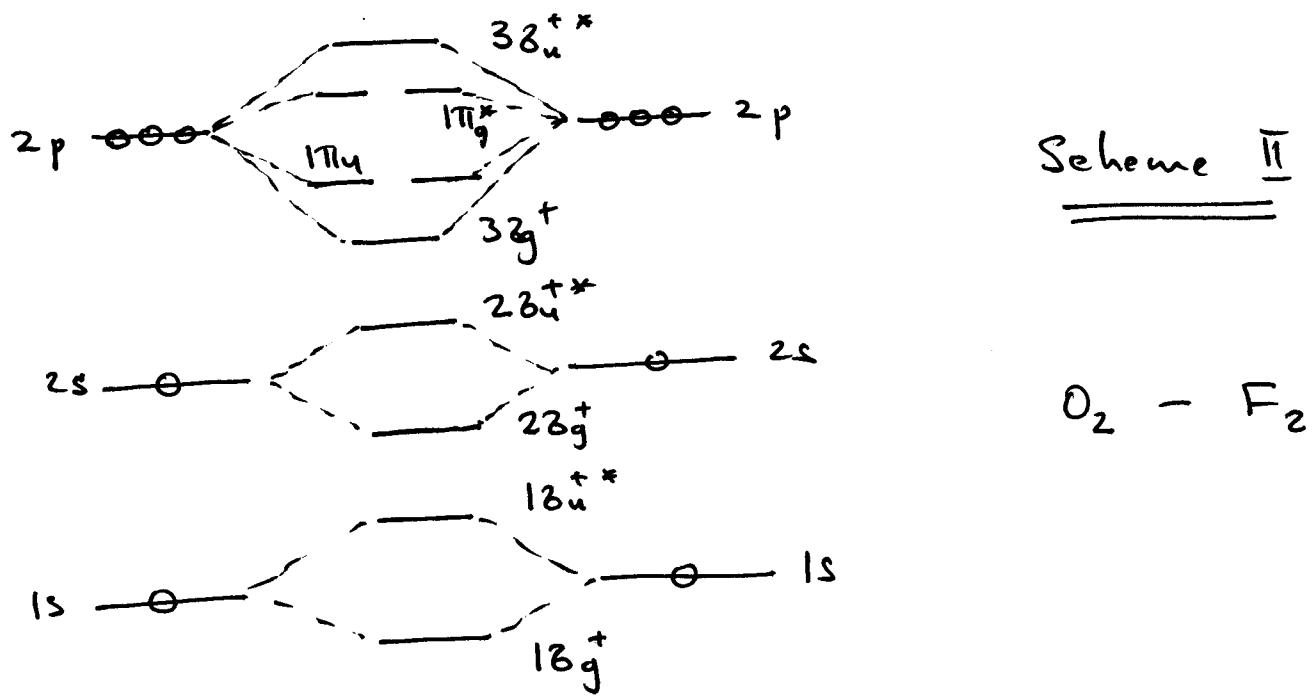
Example : N₂



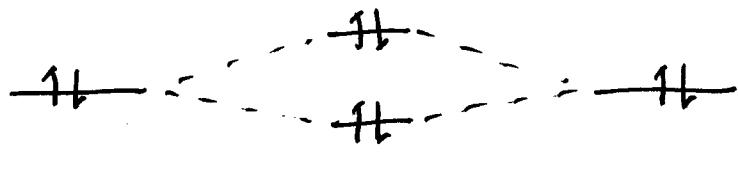
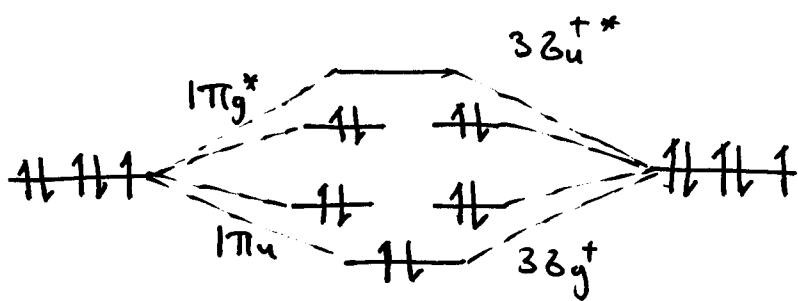
Configuration: $(1\pi_u)^4 (3s_g^+)^2$

Bond order: $6 \times \frac{1}{2} = 3$

Bond energy: 225 kcal/mol



Example : F_2



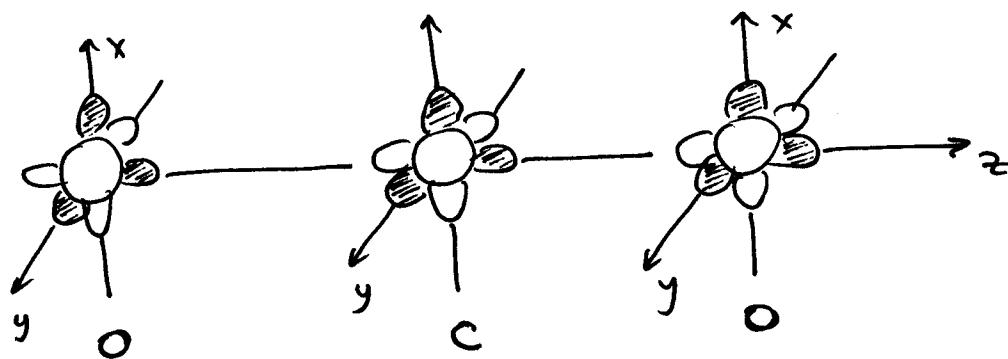
Configuration : $(3\sigma_g^+)^2 (1\pi_u)^4 (1\pi_g^*)^4$

Bond order : 1

Bond energy : 36 kcal/mol

CO_2

12 atomic orbitals, must be 12 molecular orbitals



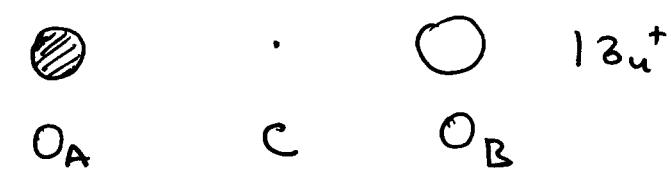
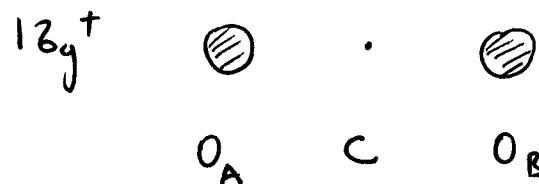
Symmetry operations generate subsets of orbitals which transform into each other:

$$\underbrace{2s}_{\text{O}}, \underbrace{2p_z}_{\text{C}}, \underbrace{\{2p_x, 2p_y\}}_{\text{O}}, \underbrace{\{2p_x, 2p_y\}}_{\text{C}}, \underbrace{2s}_{\text{C}}, \underbrace{2p_z}_{\text{C}}$$

$D_{\infty h}$	E	$2C_{\infty}^{\phi}$	∞b_v	i	$2S_{\infty}^{\phi}$	∞C_2	
$c(2s)$	1	1	1	1	1	-1	$= 3g^+$
$c(2p_z)$	1	1	1	-1	-1	-1	$= 3u^+$
$c(2p_x, 2p_y)$	2	$2\cos\phi$	0	-2	$2\cos\phi$	0	$= \pi_u$
$2o(2s)$	2	2	2	0	0	0	$= 3g^+ + 3u^+$
$2o(2p_z)$	2	2	2	0	0	0	$= \pi_u + \pi_g$
$2o(2p_x, 2p_y)$	4	$4\cos\phi$	0	0	0	0	

Σ_g^+ : C(2s), O(2s), O(2p_z)

Σ_u^+ : O(2s), C(2p_z), O(2p_z)



Π_u : O(2p_x, 2p_y), C(2p_x, 2p_y)

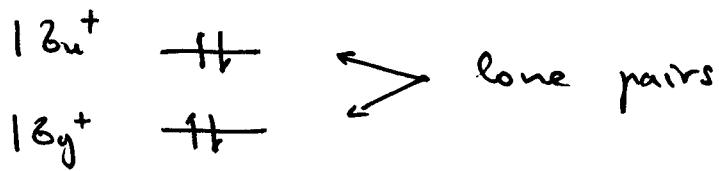
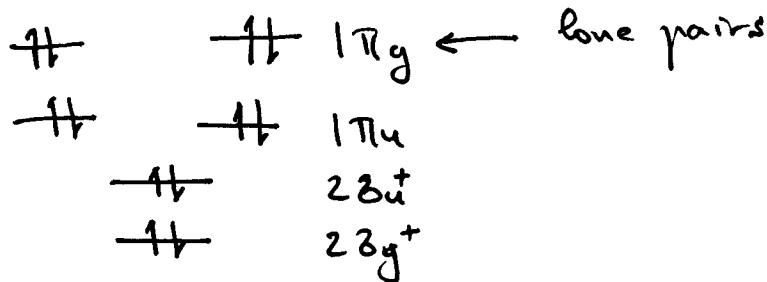
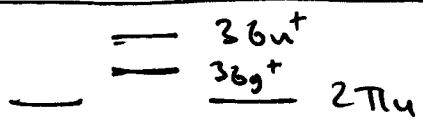


Π_g : O(2p_x, 2p_y)

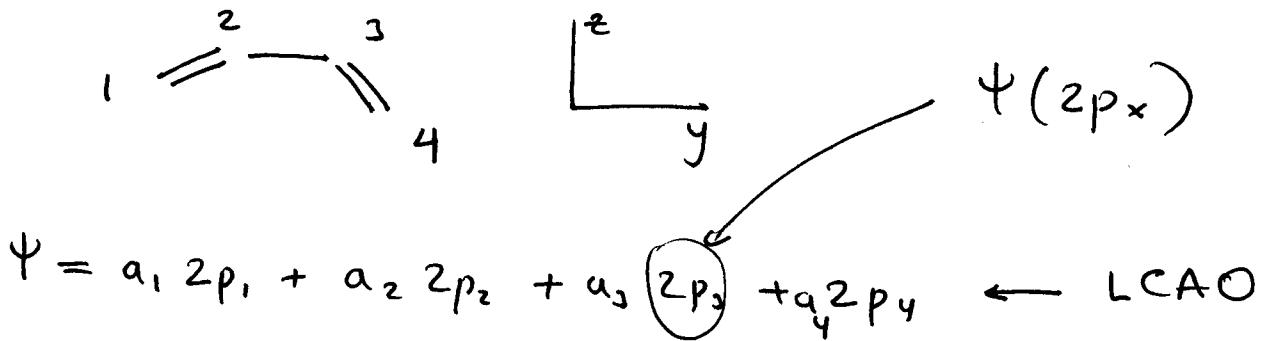


$1\Pi_g$ (nonbonding)

CO₂: Energy diagram



The Hückel method



Secular equation

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES'_{14} \\ \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots \\ H_{41} - ES_{41} & \dots & \dots & H_{44} - E \end{vmatrix} = 0$$

(1) $H_{ii} = \alpha$ for all i

(2) $S_{ij} = 0$ for all i, j

(3) $H_{ij} = \beta$ if $j = i+1, i-1$
 $= 0$ otherwise

overlap between
neighbors

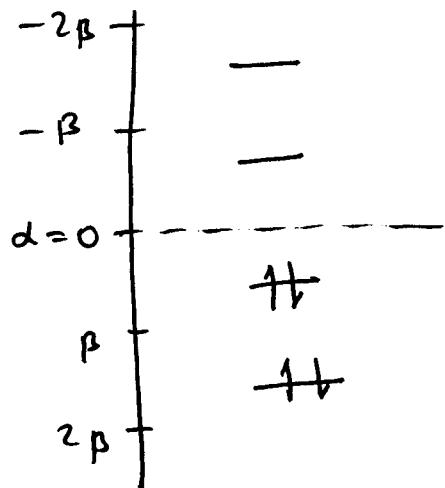
$$\beta < 0$$

For Butadiene :

$$\begin{vmatrix} \epsilon & 1 & 0 & 0 \\ 1 & \epsilon & 1 & 0 \\ 0 & 1 & \epsilon & 1 \\ 0 & 0 & 1 & \epsilon \end{vmatrix} = 0, \quad \epsilon = E/\beta$$

$$\alpha = 0$$

$$\epsilon_{1,2} = \pm 1.62 \quad \epsilon_{3,4} = \pm 0.62$$



Resonance, or delocalization, energy :

$$\beta(2 \times 0.62 + 2 \times 1.62 - 4) =$$

$$= 0.48\beta$$

Resonance energy is the energy of a conjugated system compared to the energy of double-bond components. In case of Butadiene one compares its energy to the energy of two ethylene double bonds.

Projection operators

The symmetry projector operator is defined as:

$$\hat{P}^j = \frac{\ell_j}{h} \sum_{(R)} \overbrace{\chi(R)^j}^{\text{character of } j \text{ under the}} \overbrace{R}^{\text{symmetry operation}}$$

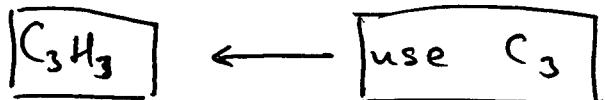
irreducible representation j
 character of j under the
 symmetry operation R
 sum over all symmetry operations

The symmetry operator acting on a given function ψ project out a component of ψ that forms a basis for the irreducible representation j .

This operator is used to generate symmetry-adapted linear combinations of atomic orbitals.

Rotational group for cyclic molecules

The rotational symmetry alone fixes the basic form of SALCs.



	C_3	E	C_3	C_3^2	
A	1	1	1	1	
E	$\begin{cases} 1 \\ 1 \end{cases}$	$\begin{cases} \varepsilon \\ \varepsilon^* \end{cases}$	$\begin{cases} \varepsilon^* \\ \varepsilon \end{cases}$	$\begin{cases} \varepsilon \\ \varepsilon \end{cases}$	$\varepsilon = e^{i\frac{\pi}{3}}$

$$\hat{P}^A \Phi_1 = \Phi_1 + \Phi_2 + \Phi_3$$

$$\begin{aligned} \hat{P}^{E(1)} \Phi_1 &= \Phi_1 + \varepsilon \Phi_2 + \varepsilon^* \Phi_3 \\ \hat{P}^{E(2)} \Phi_1 &= \Phi_1 + \varepsilon^* \Phi_2 + \varepsilon \Phi_3 \end{aligned} \quad \xrightarrow{\oplus} \quad \begin{aligned} 2\Phi_1 + (\varepsilon + \varepsilon^*)\Phi_2 + (\varepsilon^* + \varepsilon)\Phi_3 &= \\ (\varepsilon - \varepsilon^*)\Phi_2 + (\varepsilon^* - \varepsilon)\Phi_3 &= \\ = 2i \sin \frac{2\pi}{3} \Phi_2 - 2i \sin \frac{2\pi}{3} \Phi_3 \Rightarrow &= 2\Phi_1 - \Phi_2 - \Phi_3 \\ \Rightarrow \Phi_2 - \Phi_3 & \end{aligned}$$

The final set:

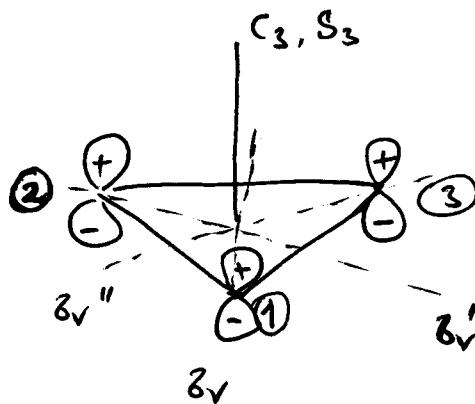
$$\Psi_A = \frac{1}{\sqrt{3}} (\Phi_1 + \Phi_2 + \Phi_3)$$

$$\Psi_E = \frac{1}{\sqrt{6}} (2\Phi_1 - \Phi_2 - \Phi_3)$$

$$\Psi_{E_2} = \frac{1}{\sqrt{2}} (\Phi_2 - \Phi_3)$$

SALCs

cyclopropenyl C_3H_3 : D_{3h}



Reducible representation:

	E	$2C_3$	$3C_2$	3σ	$2S_z$	3π
Γ :	3	0	-1	-3	0	1

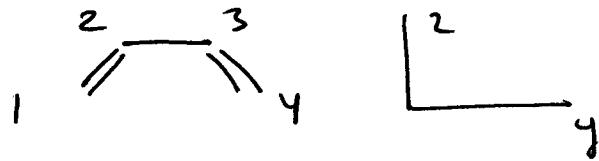
$$\Gamma = A_2'' + E''$$

$$\hat{P}^{A_2''} \varphi_i = 1 \times \varphi_1 + 1 \times \varphi_2 + (-) \times (-\varphi_3) + (-) \times (-\varphi_1) + (-) \times (-\varphi_2) + 1 \times \varphi_1 + 1 \times \varphi_3 + 1 \times \varphi_2 + 1 \times \varphi_3 + (-) \times (-\varphi_1) + (-) \times (-\varphi_2) + (-) \times (-\varphi_3) = 4(\varphi_1 + \varphi_2 + \varphi_3) \Rightarrow \frac{1}{\sqrt{3}} (\varphi_1 + \varphi_2 + \varphi_3)$$

D_{3h}	E	$2C_3$	$3C_2$	3σ	$2S_z$	3π
A_2''	1	1	-1	-1	-1	1

$$\psi_{A_2''} = \frac{1}{\sqrt{3}} (\varphi_1 + \varphi_2 + \varphi_3)$$

LCAO solution for Butadiene



C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$
ρ_π	4	0	0	-4

$$\rho_\pi = 2\alpha_2 + 2\beta_1$$

The C_{2v} symmetry operation generate two subsets that transform under C_{2v} :

$$\phi_1, \phi_4 \quad \text{and} \quad \phi_2, \phi_3$$

$$P^{A_2} \phi_1 = 2\phi_1 - 2\phi_4 \Rightarrow \frac{1}{\sqrt{2}} (\phi_1 - \phi_4)$$

$$P^{B_1} \phi_1 = 2\phi_1 + 2\phi_4 \Rightarrow \frac{1}{\sqrt{2}} (\phi_1 + \phi_4)$$

$$\psi_{A_2}^1 = \frac{1}{\sqrt{2}} (\phi_1 - \phi_4) \quad \psi_{A_2}^2 = \frac{1}{\sqrt{2}} (\phi_2 - \phi_3)$$

$$\psi_{B_1}^1 = \frac{1}{\sqrt{2}} (\phi_1 + \phi_4) \quad \psi_{B_1}^2 = \frac{1}{\sqrt{2}} (\phi_2 + \phi_3)$$

$$\langle 1_{A_2} | H | 1_{A_2} \rangle = \alpha$$

$$\langle 2_{A_2} | H | 2_{A_2} \rangle = \alpha - \beta$$

$$\langle 1_{A_2} | H | 2_{A_2} \rangle = \beta$$

$$\begin{vmatrix} -\varepsilon & 1 \\ 1 & -1-\varepsilon \end{vmatrix} = 0$$

$$\varepsilon^2 + \varepsilon - 1 = 0$$

$$\varepsilon = -\frac{1}{2} \pm \frac{\sqrt{5}}{2} = \begin{cases} -1.62 \\ +0.62 \end{cases}$$

$$\langle 1_{B_1} | H | 1_{B_1} \rangle = \alpha$$

$$\begin{vmatrix} -\varepsilon & 1 \\ 1 & +1-\varepsilon \end{vmatrix} = 0$$

$$\varepsilon^2 - \varepsilon - 1 = 0$$

$$\varepsilon = \frac{1}{2} \pm \frac{\sqrt{5}}{2} = \begin{cases} -0.62 \\ +1.62 \end{cases}$$

Molecular orbitals:

$$-\varepsilon c_1 + c_2 = 0$$

$$c_2 = \varepsilon c_1$$

$$c_1^2 + c_2^2 = 1$$

$$c_1^2 (1 + \varepsilon^2) = 1$$

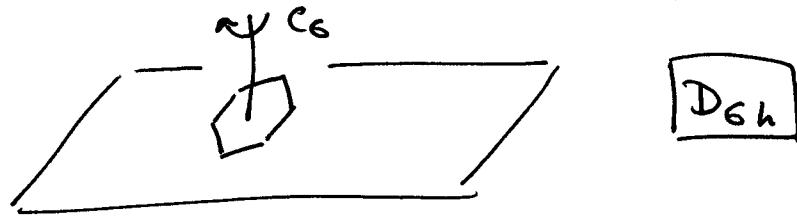
$$c_1 = \frac{1}{\sqrt{1 + \varepsilon^2}}$$

$$\Psi_1 = \frac{1}{\sqrt{1 + \varepsilon^2}} \Psi_{A_2}^1 + \frac{\varepsilon}{\sqrt{1 + \varepsilon^2}} \Psi_{A_2}^2$$

$$\Psi_2 = \frac{1}{\sqrt{1 + \varepsilon^2}} \Psi_{B_1}^1 + \frac{\varepsilon}{\sqrt{1 + \varepsilon^2}} \Psi_{B_1}^2$$

Homework. Calculate Ψ_1 and Ψ_2 for two values of ε and compare to eq 4-44 in the HB book.

LCAOs for Benzene



D_{6h}

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	S_4	$3S_V$	$3S_V'$
P_π	6	0	0	0	-2	0	0	0	0	-6	2	0

$$P_\pi = A_{2u} + B_{2g} + E_{1g} + E_{2u}$$

The essential symmetry of LCAOs is defined by the operations of the rotational subgroup C_6

C_6	E	C_6	C_3	C_2	C_3^2	C_6^5
A	1	1	1	1	1	1
B	1	-1	1	-1	1	-1
E_1	{ 1	ε	$-\varepsilon^*$	-1	$-\varepsilon$	ε^*
	{ 1	ε^*	- ε	-1	$-\varepsilon^*$	ε
E_2	{ 1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$
	{ 1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$
P_ϕ	6	0	0	0	0	0

$$P_\phi = A + B + E_1 + E_2$$

$$\begin{aligned}
 \hat{P}\Phi_1 &= \chi(E)\Phi_1 + \chi(C_6)\hat{C}_6\Phi_1 + \chi(C_6^2)\hat{C}_6^2\Phi_1 + \\
 &\quad + \chi(C_6^3)\hat{C}_6^3\Phi_1 + \chi(C_6^4)\hat{C}_6^4\Phi_1 + \chi(C_6^5)\hat{C}_6^5\Phi_1 \\
 &= \chi(E)\Phi_1 + \chi(C_6)\Phi_2 + \chi(C_6^2)\Phi_3 + \chi(C_6^3)\Phi_4 \\
 &\quad + \chi(C_6^4)\Phi_5 + \chi(C_6^5)\Phi_6
 \end{aligned}$$

$$A: \quad \Psi_1 = \Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 + \Phi_5 + \Phi_6$$

$$B: \quad \Psi_2 = \Phi_1 - \Phi_2 + \Phi_3 - \Phi_4 + \Phi_5 - \Phi_6$$

$$\begin{aligned}
 E_1: \quad \Psi_3 &= \Phi_1 + \varepsilon\Phi_2 - \varepsilon^*\Phi_3 - \Phi_4 - \varepsilon\Phi_5 + \varepsilon^*\Phi_6 \\
 \Psi_4 &= \Phi_1 + \varepsilon^*\Phi_2 - \varepsilon\Phi_3 - \Phi_4 - \varepsilon^*\Phi_5 + \varepsilon\Phi_6
 \end{aligned}$$

$$\begin{aligned}
 E_2: \quad \Psi_5 &= \Phi_1 - \varepsilon^*\Phi_2 - \varepsilon\Phi_3 + \Phi_4 - \varepsilon^*\Phi_5 - \varepsilon\Phi_6 \\
 \Psi_6 &= \Phi_1 - \varepsilon\Phi_2 - \varepsilon^*\Phi_3 + \Phi_4 - \varepsilon\Phi_5 - \varepsilon^*\Phi_6
 \end{aligned}$$

Finally:

$$\Psi(A) = \frac{1}{\sqrt{6}} (\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 + \Phi_5 + \Phi_6)$$

$$\Psi(B) = \frac{1}{\sqrt{6}} (\Phi_1 - \Phi_2 + \Phi_3 - \Phi_4 + \Phi_5 - \Phi_6)$$

$$\Psi(E_1, a) = \frac{1}{\sqrt{12}} (2\Phi_1 + \Phi_2 - \Phi_3 - 2\Phi_4 - \Phi_5 + \Phi_6)$$

$$\Psi(E_1, b) = \frac{1}{2} (\Phi_2 + \Phi_3 - \Phi_5 - \Phi_6)$$

Homework. Obtain $\Psi(E_2)$.

!

Symmetry factorizing of secular equation

Atomic orbital

$$\begin{vmatrix} H_{11}-E & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22}-E & \dots & H_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} & \dots & \dots & H_{nn}-E \end{vmatrix} = 0$$

SALCs:

dimensions of irreducible representations

$$\begin{vmatrix} \begin{matrix} l_1 \\ l_2 \end{matrix} & & & & 0 \\ 0 & \ddots & & & \\ & & \ddots & & \\ & & & \ddots & \\ & & & & 0 \end{vmatrix} = 0$$

$$\left| \begin{pmatrix} l_1 \end{pmatrix} \right| = 0 \quad \left| \begin{pmatrix} l_2 \end{pmatrix} \right| = 0 \quad \dots$$

In order for the determinant to be equal to zero each block must equal to zero.

{The n -dimensional problem is reduced a set
of low-dimension problems consistent with the
molecular symmetry.}

MO energies of Benzene

H_{AA}	0	0	0	0	0
0	H_{BB}	0	0	0	0
0	0	$\langle E_{1a} H E_{1a} \rangle$	$\langle E_{1a} H E_{1b} \rangle$	0	0
0	0	$\langle E_{1b} H E_{1a} \rangle$	$\langle E_{1b} H E_{1b} \rangle$	0	0
0	0	0	0	$\langle E_{2a} H E_{2a} \rangle$	$\langle 1 \rangle$
0	0	0	0	$\langle 1 H \rangle$	$\langle 1 H \rangle$

$$H_{AA} = \alpha + 2\beta$$

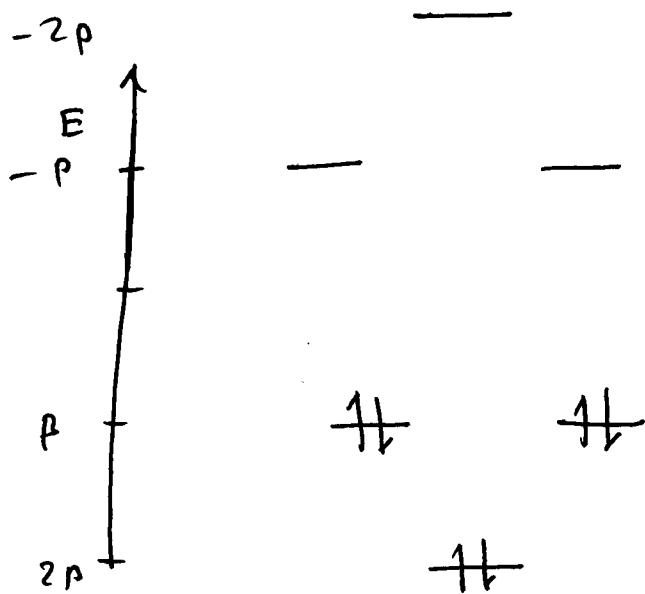
$$\langle E_{1a} | H | E_{1b} \rangle = 0$$

$$H_{BB} = \alpha - 2\beta$$

$$\langle E_{1a} | H | E_{1a} \rangle = \alpha + \beta$$

$$\langle E_{1b} | H | E_{1b} \rangle = \alpha + \beta$$

$$\langle E_{2a} | H | E_{2a} \rangle = \alpha - \beta$$



$$E_T = 2(2\beta) + 4\beta \\ = 8\beta$$

MO energies of Benzene

H_{AA}	0	0	0	0	0
0	H_{BB}	0	0	0	0
0	0	$\langle E_{1a} H E_{1a} \rangle$	$\langle E_{1a} H E_{1b} \rangle$	0	0
0	0	$\langle E_{1b} H E_{1a} \rangle$	$\langle E_{1b} H E_{1b} \rangle$	0	0
0	0	0	0	$\langle E_{2a} H E_{2a} \rangle$	$\langle 1 \rangle$
0	0	0	0	$\langle 1 H \rangle$	$\langle 1 H \rangle$

$$H_{AA} = \alpha + 2\beta$$

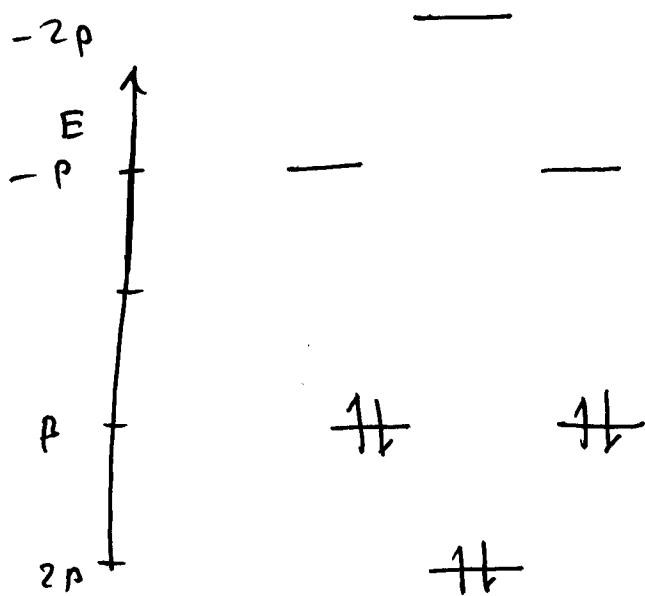
$$\langle E_{1a} | H | E_{1b} \rangle = 0$$

$$H_{BB} = \alpha - 2\beta$$

$$\langle E_{1a} | H | E_{1a} \rangle = \alpha + \beta$$

$$\langle E_{1b} | H | E_{1b} \rangle = \alpha + \beta$$

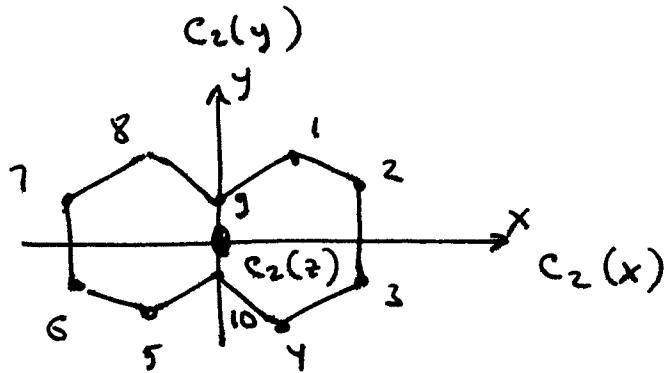
$$\langle E_{2a} | H | E_{2a} \rangle = \alpha - \beta$$



$$E_T = 2(2\beta) + 4\alpha$$

$$= 8\beta$$

Naphthalene



D_{2h} : $A_g, B_{1g}, B_{2g}, B_{3g}, A_u$

B_{1u}, B_{2u}, B_{3u}

10 p_z orbitals on 10 carbon atoms form the reducible representation Γ_{II}

E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	z_h	$z_v(xz)$	$z_v'(yz)$
P_n	10	0	-2	0	0	-10	0

$$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R) \quad h = 8$$

$$a(A_g) = \frac{1}{8} (10 - 2 + 2 - 10) = 0$$

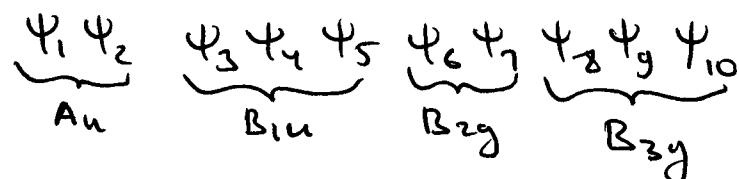
$$a(A_u) = \frac{1}{8} (10 - 2 + 10 - 2) = 2$$

$$a(B_{2g}) = \frac{1}{8} (10 + 2 + 10 + 2) = 3$$

$$a(B_{2u}) = \frac{1}{8} (10 - 2 + 10 - 2) = 2$$

$$\Gamma_{II} = 2A_u + 3B_{3g} + 3B_{1u} + 2B_{2g}$$

Secular equation:



$$\begin{vmatrix} 2 \times 2 & & & \\ & 3 \times 3 & & \\ & & 0 & \\ & & & 2 \times 2 \\ 0 & & & & 3 \times 3 \end{vmatrix} = 0$$

The symmetry operations of D_{2h} form three subsets

$$\begin{array}{l} \Phi_2 \Phi_3 \Phi_6 \Phi_7 \rightarrow \left| \begin{array}{ccccccc} E & C_2(z) & C_2(y) & C_2(x) & i & \bar{z}_{1u} & \bar{z}(xz) & \bar{z}(yz) \\ P_1 & 1 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \end{array} \right. \\ \Phi_1 \Phi_4 \Phi_5 \Phi_8 \rightarrow \left. \begin{array}{c} P_1 = A_u + B_{1u} + B_{2g} + B_{3g} \\ P_2 = A_u + B_{1u} + B_{2g} + B_{3g} \end{array} \right\} \begin{array}{l} P_{\pi} = P_1 + \\ P_2 + P_3 \end{array} \\ \Phi_9 \Phi_{10} \rightarrow P_3 = B_{1u} + B_{3g} \end{array}$$

Homework: Show that Φ_9 and Φ_{10} transform according to B_{1u} and B_{2g}

$$\begin{aligned} P_{2g} \Phi_2 &= 1 \times \Phi_2 + (-) \times \Phi_6 + (-\Phi_7) + (-1) \times (-\Phi_3) + 1 \times (-\Phi_4) \\ &\quad + (-) \times (-\Phi_2) + \Phi_3 + (-) \Phi_7 = 2\Phi_2 + 2\Phi_3 - 2\Phi_6 - 2\Phi_7 \\ &\Rightarrow \frac{1}{2} (\Phi_2 + \Phi_3 - \Phi_6 - \Phi_7) \end{aligned}$$

$$\begin{aligned} P_{2g} \Phi_1 &= \Phi_1 + (-) \times \Phi_5 + (-\Phi_8) + (-) \times (-\Phi_4) + (-\Phi_5) \\ &\quad + (-) \times (-\Phi_1) + (-\Phi_4) - \Phi_8 = 2\Phi_1 + 2\Phi_4 - 2\Phi_5 - 2\Phi_8 \\ &\Rightarrow \frac{1}{2} (\Phi_1 + \Phi_4 - \Phi_5 - \Phi_8) \end{aligned}$$

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\bar{z}(xy)$	$\bar{z}(xz)$	$\bar{z}(yz)$
B_{2g}	1	-1	1	-1	1	-1	1	-1

$$B_{2g} : \begin{aligned}\Psi_6 &= \frac{1}{2} (\Phi_2 + \Phi_3 - \Phi_6 - \Phi_7) \\ \Psi_7 &= \frac{1}{2} (\Phi_1 + \Phi_4 - \Phi_5 - \Phi_8)\end{aligned}$$

Homework. Show that the set of SALCs for Au is

$$Au: \quad \Psi_1 = \frac{1}{2} (\Phi_1 - \Phi_4 + \Phi_5 - \Phi_8)$$

$$\Psi_2 = \frac{1}{2} (\Phi_2 - \Phi_3 + \Phi_6 - \Phi_7)$$

$$B_{1u} : \quad \Psi_3 = \frac{1}{2} (\Phi_1 + \Phi_4 + \Phi_5 + \Phi_8)$$

$$\Psi_4 = \frac{1}{2} (\Phi_2 + \Phi_3 + \Phi_6 + \Phi_7)$$

$$\Psi_5 = \frac{1}{\sqrt{2}} (\Phi_9 + \Phi_{10})$$

$$B_{3g} : \quad \Psi_6 = \frac{1}{2} (\Phi_1 - \Phi_4 - \Phi_5 + \Phi_8)$$

$$\Psi_7 = \frac{1}{2} (\Phi_2 - \Phi_3 - \Phi_6 + \Phi_7)$$

$$\Psi_{10} = \frac{1}{\sqrt{2}} (\Phi_9 - \Phi_{10})$$

Secular equations:

$$Au: \quad \begin{vmatrix} \alpha - E & \beta & \\ \beta & \alpha - \beta - E & \end{vmatrix} = 0$$

$$E^2 + \varepsilon - 1 = 0 \quad (\varepsilon = E/\beta) \quad \varepsilon = -\frac{1}{2} \pm \frac{\sqrt{5}}{2}$$

$$\boxed{\varepsilon = -1.618, \quad \varepsilon = +0.618}$$

Molecular orbitals:

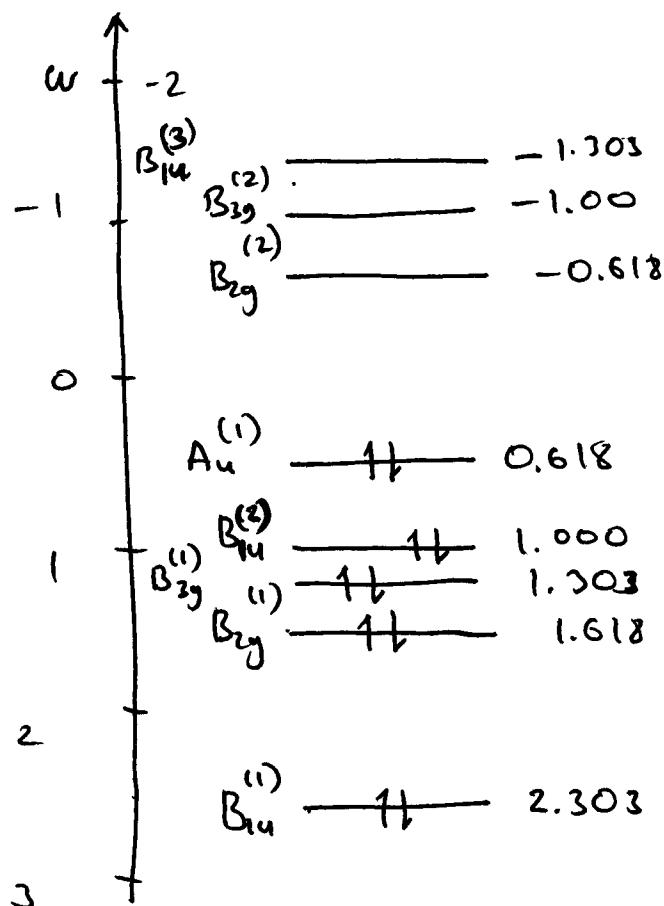
$$c_1(\alpha - E) + c_2 \beta = 0$$

$$c_1 \beta + c_2 (\alpha - \beta - E) = 0$$

$$c_1^2 + c_2^2 = 1$$

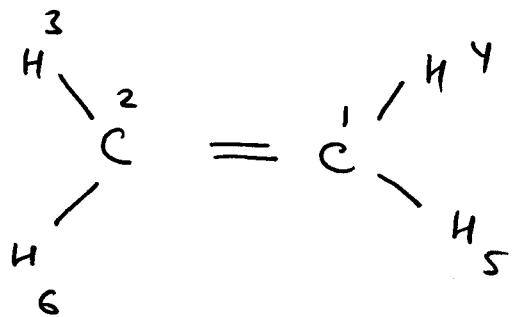
$$\epsilon = 0.618 : \Psi_{A_u}^{(1)} = 0.850 \psi_1 + 0.526 \psi_2$$

Homework: Find the energies and MOs for B_{2g} .



Ethylene

(p. 276 ⚡ HB)



D _{2h}	E	C ₂ (z)	C ₂ (y)	C ₂ (x)	i	g(x _y)	g(x _z)	g(y _z)
4H (1s)	4	0	0	0	0	4	0	$0 = a_g + b_{1g} + b_{2u}$
2C (2s)	2	0	0	2	0	2	2	$0 = a_g + b_{3u}$
2C (2p _x)	2	0	0	2	0	2	2	$0 = a_g + b_{3u}$
2C (2p _y)	2	0	0	-2	0	2	-2	$0 = b_{1g} + b_{2u}$
2C (2p _z)	2	0	0	-2	0	-2	2	$0 = b_{2g} + b_{1u}$

2p_z transform according to $b_{2g} + b_{1u} \Rightarrow$ They do not mix with any other wavefunctions

$$\hat{P}^{B_{2g}} p_z' = p_z' + (-) \times p_z^2 + 1 \times (-p_z^2) + (-) \times (-p_z') + 1 \times (-p_z^2) + (-) \times (-p_z') + 1 \times p_z' + (-) \times p_z^2 \Rightarrow$$

$$\Rightarrow \frac{1}{\sqrt{2}} (2p_z' - 2p_z^2)$$

$$\hat{P}^{B_{1u}} p_z' = \frac{1}{\sqrt{2}} (p_z' + p_z^2) \quad \leftarrow$$

Homework. Check this relation

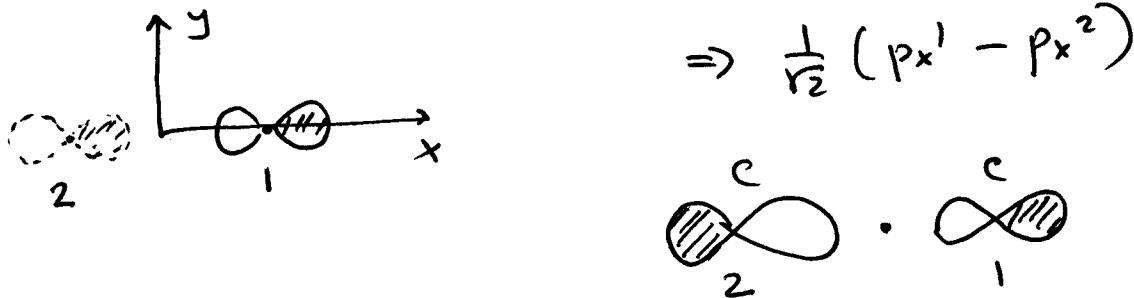
$$\Psi_{B_{2g}} = \frac{1}{\sqrt{2}} (2p_z' - 2p_z^2)$$

$$\Psi_{B_{1u}} = \frac{1}{\sqrt{2}} (2p_z' + 2p_z^2)$$

$$\hat{P}^A g |s^3 \Rightarrow \frac{1}{2} (1s^3 + 1s^4 + 1s^5 + 1s^6)$$

$$\hat{P}^A g |2s \Rightarrow \frac{1}{\sqrt{2}} (2s^1 + 2s^2)$$

$$\hat{P}^A g p_x^1 = p_x^1 - p_x^2 - p_x^2 + p_x^1 - p_x^2 + p_x^1 + p_x^1 - p_x^2 \Rightarrow$$

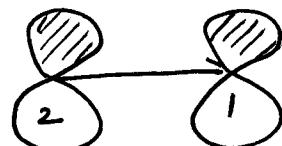


Ψ_{Ag}	$= N \left[\frac{c_1}{2} (1s^3 + 1s^4 + 1s^5 + 1s^6) + \frac{c_2}{\sqrt{2}} (2s^1 + 2s^2) + \frac{c_3}{\sqrt{2}} (p_x^1 - p_x^2) \right]$
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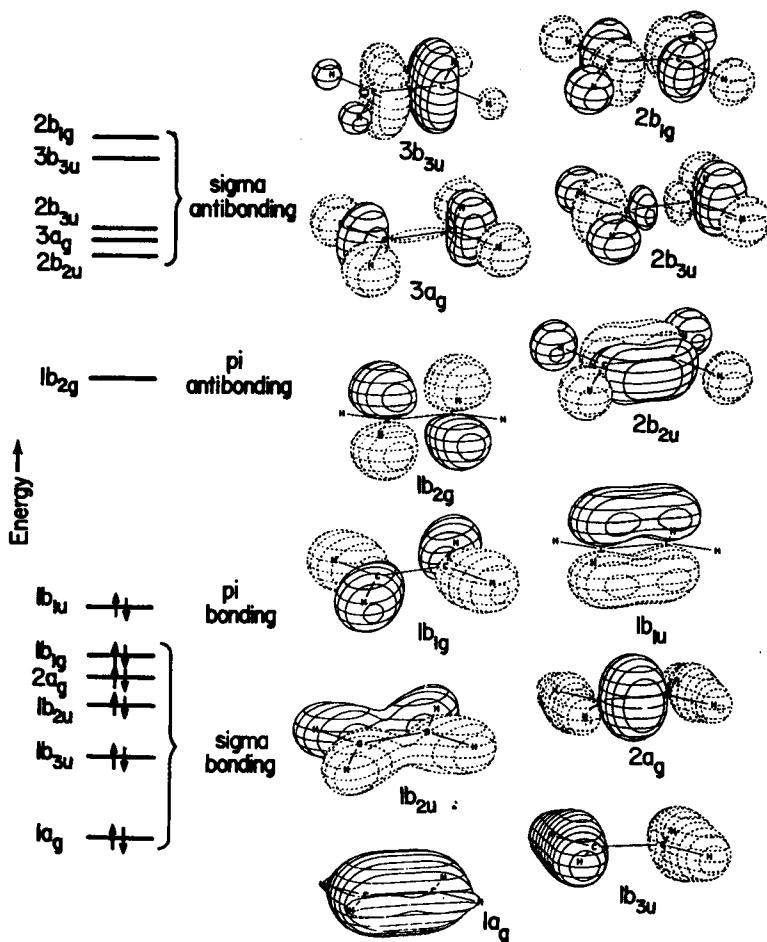
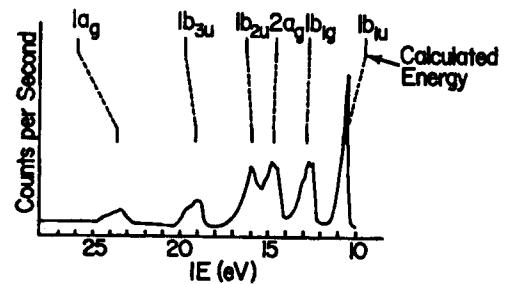
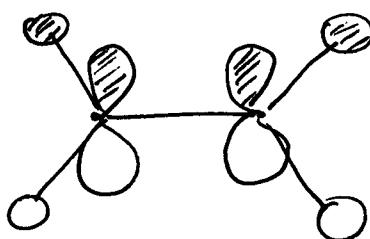
	E	$c_1(z)$	$c_2(y)$	$c_3(x)$	i	$g(xy)$	$g(xz)$	$g(yz)$
B_{2u}		1	-1	1	-1	-1	1	-1

$$\Rightarrow \frac{1}{2} (1s^3 + 1s^4 - 1s^5 - 1s^6)$$

$$\begin{aligned} \hat{P}^{B_{2u}} 2p_y^1 &= 2p_y^1 + (-) \times (-2p_y^2) + 1 \times (2p_y^2) + (-) \times (-2p_y^1) \\ &+ (-) \times (-2p_y^2) + 2p_y^1 + (-) \times (-2p_y^1) + 2p_y^2 \Rightarrow \frac{1}{\sqrt{2}} (2p_y^1 + 2p_y^2) \end{aligned}$$

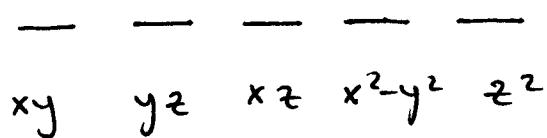


$$\Psi_{B_{2u}} = c_1 (1s^3 + 1s^4 - 1s^5 - 1s^6) + c_2 (2p_y^1 + 2p_y^2)$$

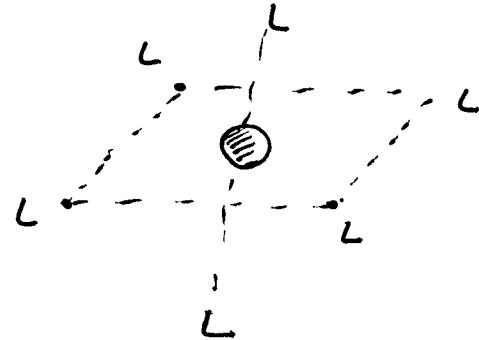


Transition metal complexes: Splitting of d-orbitals
in O_h

d-orbitals in an atom:



transition atom (ion) in
an O_h chemical environment



The general question is how the atomic states (LS atomic terms) would change (split) if an atom is placed in a chemical environment with a given symmetry.

$$\psi_d^{nul}(r, \theta, \phi) = R_{nl}(r) \Theta_{lm}(\cos\theta) e^{im\phi}$$

The new molecular orbitals can be generated from the purely rotational subgroup of O_h

	O	E	6C ₂	3C ₂	8C ₃	6C ₂	
A ₁	1	1	1	1	1	1	$x^2+y^2+z^2$
A ₂	1	-1	1	1	1	-1	
E	2	0	2	-1	0	0	(z^2, x^2-y^2)
T ₁	3	1	-1	0	-1	(x, y, z)	
T ₂	3	-1	-1	0	1		(xy, xz, yz)

If all rotations are carried out around the z-axis, the only function which is altered is $\Phi(\phi) = e^{im\phi}$.

$$\hat{R}_z(\alpha) e^{im\phi} = e^{im(\phi+\alpha)}$$

For $m = -2, -1, 0, 1, 2$:

$$\hat{R}_z(\alpha) \begin{pmatrix} e^{2i\phi} \\ e^{i\phi} \\ 1 \\ e^{-i\phi} \\ e^{-2i\phi} \end{pmatrix} = \begin{pmatrix} e^{2i(\phi+\alpha)} \\ e^{i(\phi+\alpha)} \\ 1 \\ e^{-i(\phi+\alpha)} \\ e^{-2i(\phi+\alpha)} \end{pmatrix}$$

The transformation matrix:

$$\begin{pmatrix} e^{2i\alpha} & & & \\ & e^{i\alpha} & & 0 \\ & & 1 & \\ 0 & & & e^{-i\alpha} \\ & & & e^{-2i\alpha} \end{pmatrix}$$

$$\chi(\alpha) = \frac{\sin(l + l_z)\alpha}{\sin \alpha/2} \quad (l=2)$$

$$\chi(c_2) = \frac{\sin \pi 5/2}{\sin \pi/2} = 1 \quad \leftarrow \alpha = \pi$$

$$\chi(c_3) = \frac{\sin \pi 5/3}{\sin \pi/3} = -1 \quad \leftarrow \alpha = \frac{2\pi}{3}$$

O	E	$6C_4$	$3C_2$	$8C_3$	$6C_2$	
Pd	S	-1	1	-1	1	$= E + T_2$

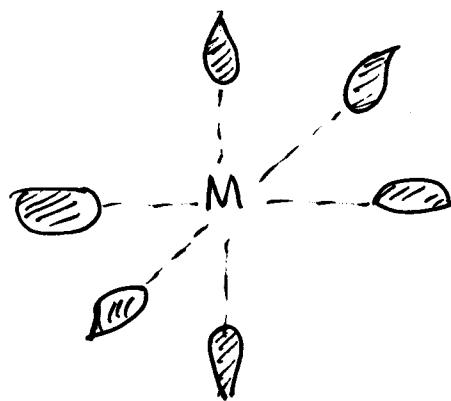
$$\text{Under } O_h : \quad P_d = E_g + T_{2g}$$

Homework : Show that the irreducible representation of p-electrons $\rightarrow T_{1u}$ in the O_h symmetry group.

The results obtained for single electrons extend to the behavior of terms arising from groups of electrons. For example, a D atomic state will split in E_g and T_{2g} in O_h . A split term has the same spin multiplicity as the parent term:

Free ion	Symmetry of the environment		
	O_h	T_d	D_{4h}
1S	$^1A_{1g}$	1A_1	$^1A_{1g}$
3P	$^2T_{1g}$	3T_1	$^3A_{2g} \ ^3E_g$
3D	$^1E_g \ ^1T_{2g}$	$^1E \ ^1T_2$	$^1A_{1g} \ ^1B_{1g} \ ^1B_{2g}$ 1E_g

Molecular orbitals for $ML(3)_6$



O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_y$	$8S_6$	$3B_1$	$6S_f$	$=$
$6L(3)$	6	0	0	2	2	0	0	0	4	2	=
$= a_{1g} + t_{1u} + e_g$											
$1M(s)$	1	1	1	1	1	1	1	1	1	1	$= a_{1g}$
$3M(p)$	3	0	-1	1	-1	-3	-1	0	1	1	$= t_{1u}$
$5M(d)$	5	-1	1	-1	1	5	-1	-1	1	1	$= t_{2g} + e_g$
$= 2t_{1u}^*$											
$= 2a_{1g}^*$											

