Polyatomic Molecules: MO's

H_2: minimal basis set: $\Psi = c_1 1s_A \pm c_2 1s_B$ (linear combination)
- $\Psi_+ \rightarrow \sigma_g 1s$
- $\Psi_- \rightarrow \sigma_u 1s$

} LCAO-MO

$\Psi = \underbrace{1s_A + 2s_A + 2p_{x,y,z,A}}_{5\text{ A.O.}} + \underbrace{1s_B + 2s_B + 2p_{x,y,z,B}}_{5\text{ A.O.}}$

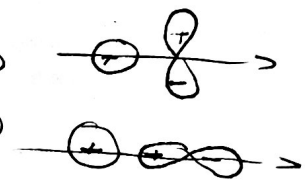
10 MO's.

(2nd row diatomic molecule Slides)

- Symmetry of A.O.'s matter

$1s + 2p_x \rightarrow 0$

$1s + 2p_z \not\rightarrow 0$

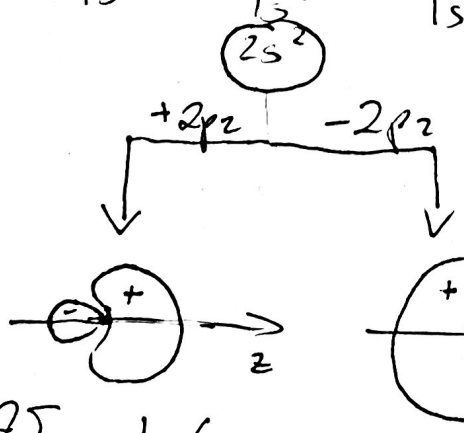


Hybridization:

↳ Defined subset of A.O.'s will create new A.O.

$BeH_2 \rightarrow$ H — Be — H (180°)

H: 1s; Be: $2s^2$, $2p_z^2$



$2p_x$ and $2p_y$ (perpendicular) are not participating.

$\Psi_{sp} = \frac{1}{\sqrt{2}}(2s_{Be} + 2p_{z,Be})$ $\quad \Psi_- = \frac{1}{\sqrt{2}}(2s_{Be} - 2p_{z,Be})$

→ Normalization:

$\int \Psi_+^* \cdot \Psi_+ \, d\tau = 1$

$N^2 \int (2s_{Be} + 2p_{z,Be})(2s_{Be} + 2p_{z,Be}) d\tau$

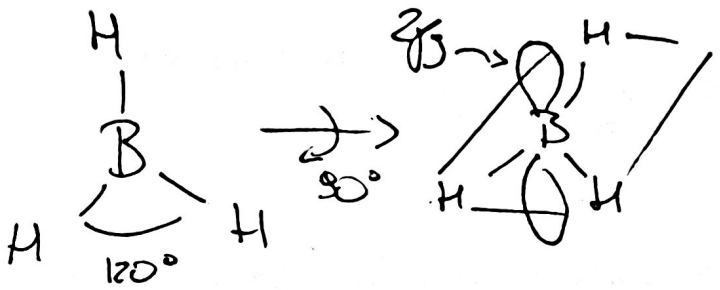
$= N^2 \left(\int 2s_{Be} \cdot 2s_{Be} \, d\tau + \int (2s_{Be} + 2p_{z,Be}) \right.$

$\left. + \int 2p_{z,Be} \cdot 2s_{Be} \, d\tau + \int 2p_{z,Be} \cdot 2s_{Be} \, d\tau \right)$

$N^2 \cdot 2 = 1$

$N = \frac{1}{\sqrt{2}}$

BH_3 molecule:



hence:

$$\psi_j = c_{j1}2s + c_{j2}2p_x + c_{j3}2p_z$$

sp^2 hybrid orbital. $\quad j = 1,2,3$

Matrix Multiplication:

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix} \begin{bmatrix} 2s \\ 2p_x \\ 2p_y \end{bmatrix}$$

Hybrid orbitals basis set

↓ Linear transformation matrix.

- 9 unknowns.
- Extra conditions

↓ A.O. basis set

We can deduce:

① $c_{11} = c_{21} = c_{31} = \frac{1}{\sqrt{3}}$

② Set H.O. along z axis: $c_{12} = \sqrt{\frac{2}{3}} \quad c_{13} = 0$ → HOs are not unique.

③ Set H.O. orthonormal: $c_{22} = c_{32} = \frac{1}{\sqrt{6}} \quad c_{23} = -c_{33} = \frac{1}{\sqrt{2}}$

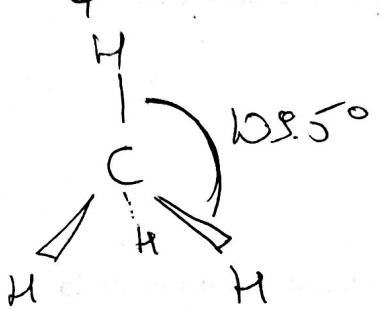
HO's are normalized

$$\sum_j^3 c_{ji}^2 = 1 \qquad j = 1,2,3$$

$$\sum_i^3 c_{ji}^2 = 1 \qquad i = 1,2,3$$

AO's has equal participation.

CH_4



$$\begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & +\frac{1}{2} \\ \frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} 2s \\ 2p_x \\ 2p_y \\ 2p_z \end{bmatrix}$$

$\Psi_1 \ldots \Psi_4$: sp^3 hybrids

Linear transformation

$2s, 2p_x, 2p_y, 2p_z$: AO.

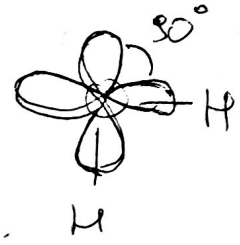
Bonding Electrons Vs Lone Pair Electrons.

VSEPR

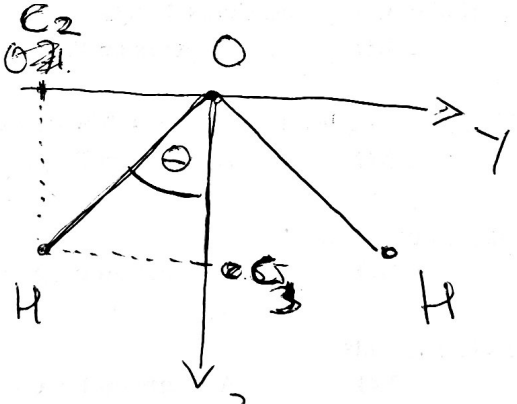
Hybrid orbitals

$$\Psi_1 = c_1 2s + c_2 2p_x + c_3 3p_z$$

A.O.



(mixing s orbital does not change)



~~$\tan\theta = \frac{0.71}{0.55} = 52.2°$~~

$$\tan\theta = \frac{c_2}{c_3}$$

if $\theta = \frac{106.5}{2} = 52.25°$ then $\frac{c_2}{c_3} = 1.29$

Exer. 10.12 and $c_1 = \pm 0.45$ ~~± 0.45~~ $\Rightarrow$ $c_2 = \pm 0.71$

$c_3 = 0.55$

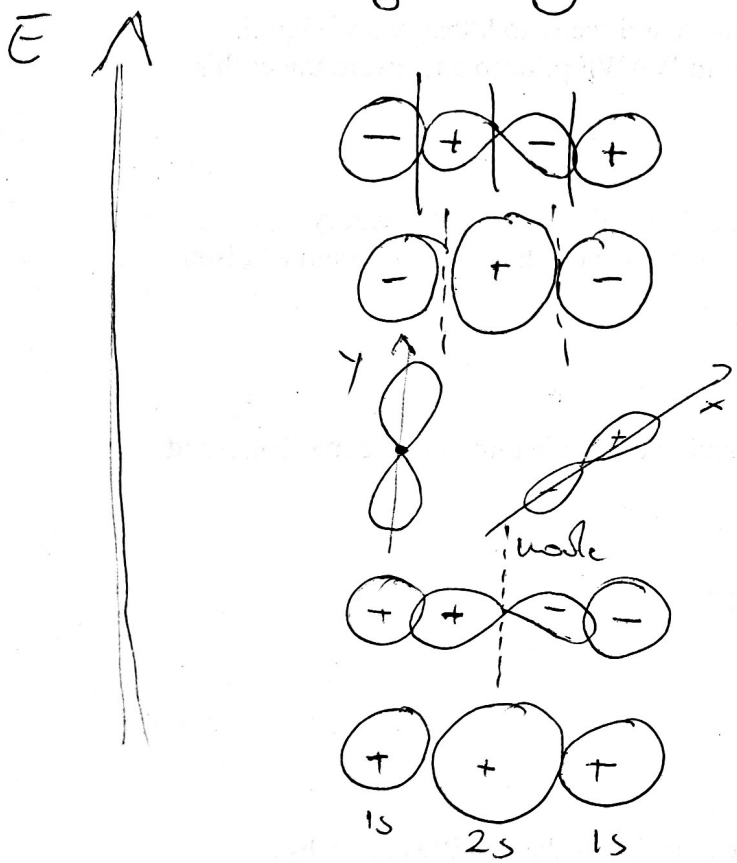
Fabd

Minimal basis set for (AH_2) molecule

$$\Psi = c_1 1s_{A_1} + c_2 1s_{B_2 B_3} + c_3 2s_A + c_4 2p_{x,A} + c_5 2p_{y,A} + c_6 2p_{z,A}$$

↓

6 MO's. Symmetry considerations for linear molecule.



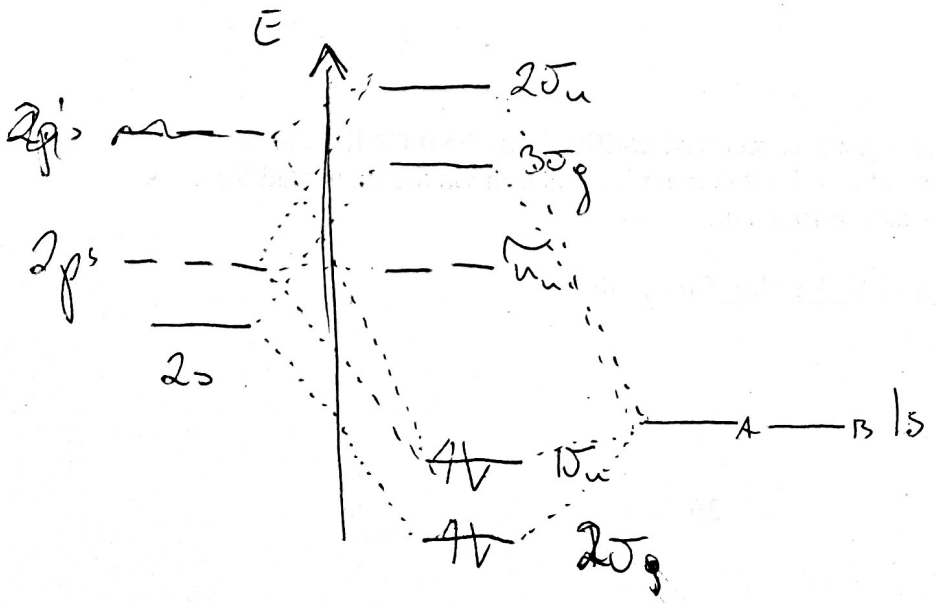
σ_u / $2p_{zA} - 2s_{uA} + 2s_{uB}$

σ_g / $2s_A - 2s_{uA} - 2s_{uB}$

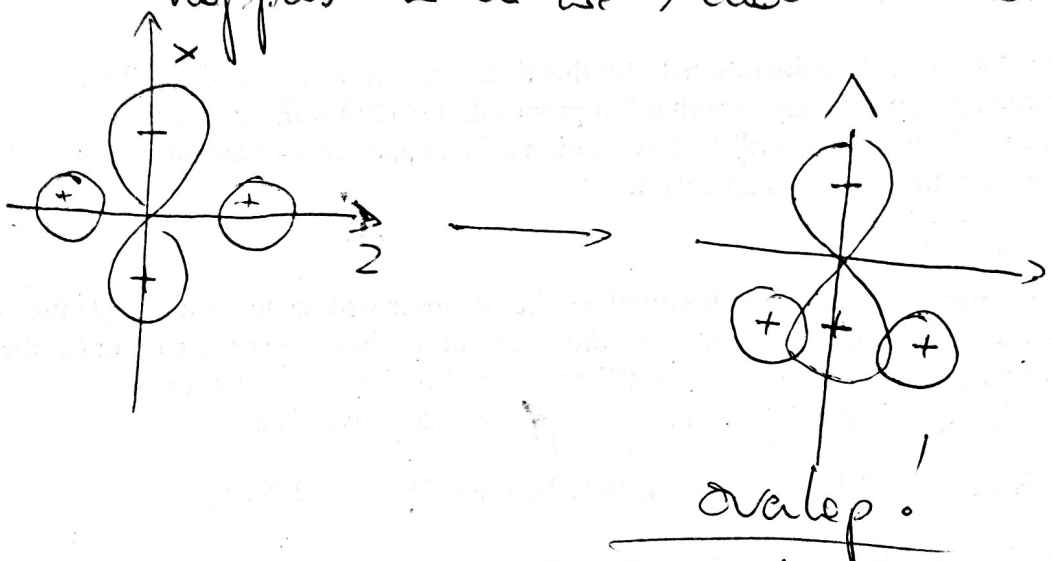
$\left[\pi_{u,y}, \pi_{u,x} \;/\; \begin{matrix} 2p_x \\ 2p_y \end{matrix}\right]$ doubly degenerate

σ_u / $2p_{zA} + 2s_{uA} - 2s_{uB}$

σ_g / $2s_A + 2s_{uA} + 2s_{uB}$



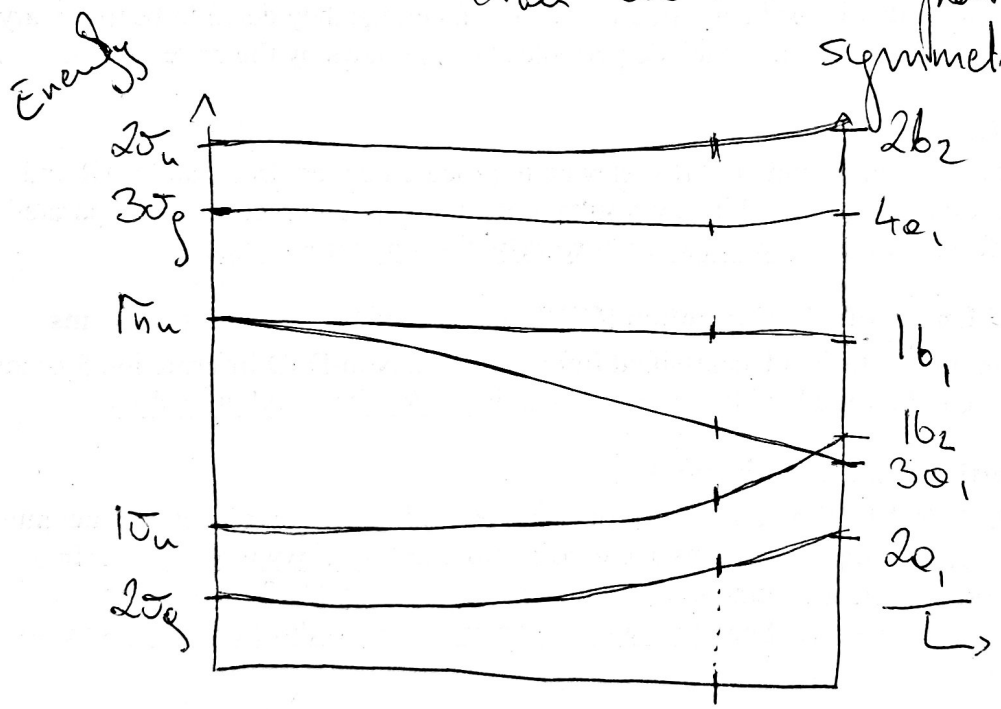
What happens when we bend the molecule?



overlap!

- the π_u orbital is stabilized.
- other does not participate due to symmetry.

10.12 / Walsh correlation.



Linear — Bond angle — H_2O 90° ↓ 104.5 ↓

BH_2 → bent.

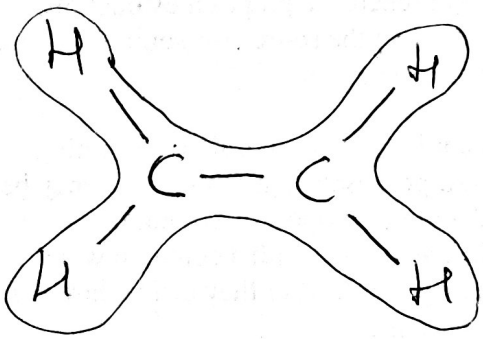
symmetry
a → sym. w.r.t. C_2
b → antisym. w.r.t. C_2
1,2 → wrt. σ

MO's: $(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$

Take a look at MO's diagrams for other molecules.

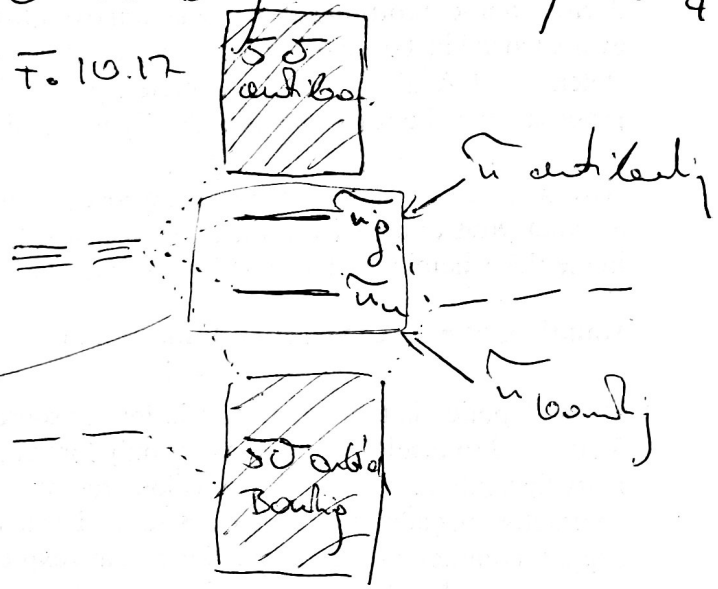
Hückel's method. (π-conjugated systems)

~~Basis~~ Assumption:



σ-bond framework of C_2H_4

T. 10.17



$$\Psi_{\pm} = c_1 p_{z,A} \pm c_2 p_{z,B}$$

Secular Determinant:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

→ Coulomb Integrals

Exchange Integrals

S → overlap Integrals

Hückel theory:

(1) $S_{ij} = \delta_{ij}$

(2) $H_{ii} = \alpha$

(3) $H_{ij} = \beta$ for (π-bonded) neighboring atoms.

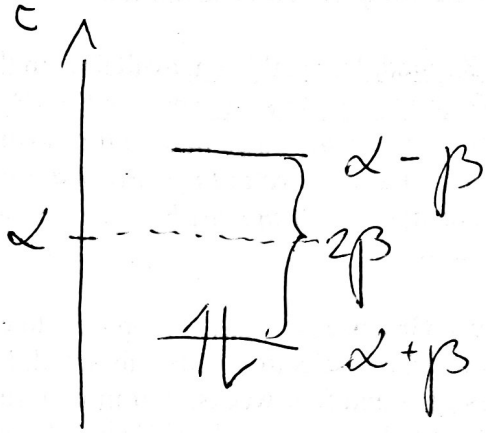
The secular Determinant becomes:

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

$$(\alpha-E)^2 - \beta^2 = 0$$

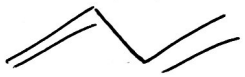
$$E_1 = \alpha + \beta$$
$$E_2 = \alpha - \beta$$

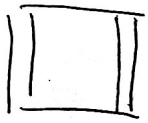
$$\psi_{\pm} = \frac{1}{\sqrt{2}}(2p_{z,A} \pm 2p_{z,B})$$



$\alpha \to 0$
$\beta \to -75\ \mathrm{kcal/Mol}$

Butadiene vs cyclobutadien.





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

$$x = \frac{\alpha - E}{\beta}$$

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

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

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$$

$$x^4 - 3x^2 + 1 = 0$$

$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

$$x = \pm 1.618 = \frac{\alpha - E}{\beta}$$

$$x = \pm 0.618$$

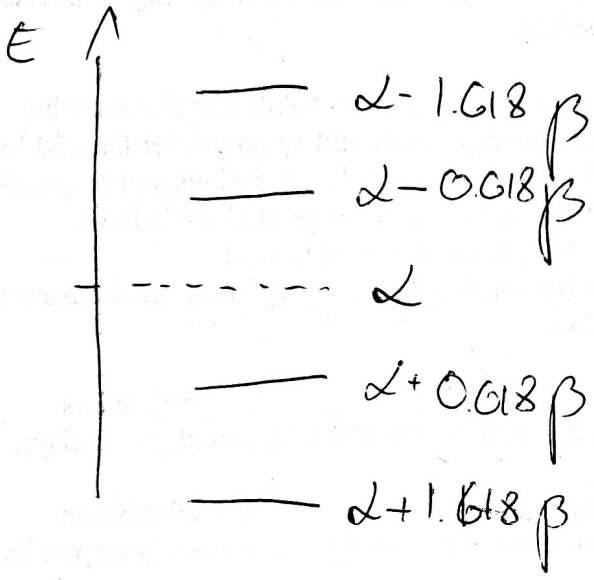
$$x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} + \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 1 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & x & 1 \\ 0 & 1 & x \\ 1 & 0 & 1 \end{vmatrix} = 0$$

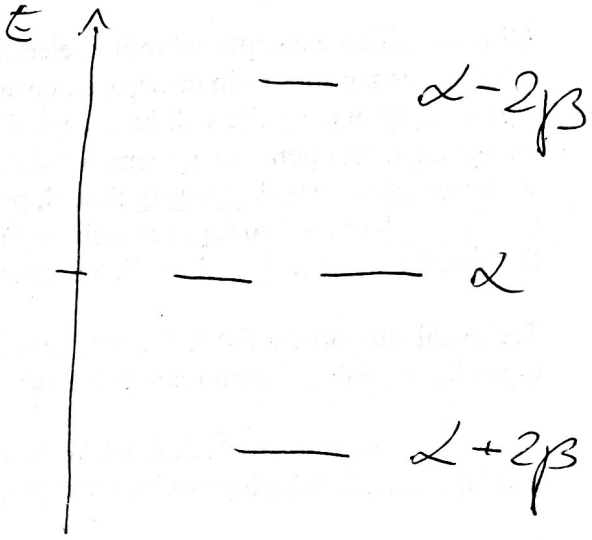
$$(x^4 - x^2 - x^2) + (x^2 - 1 + 1) - (1 - x^2 + 1) = 0$$

$$x^4 - 4x^2 = 0$$

$$x^2(x^2 - 4) = 0$$

$$x^2(x-2)(x+2) = 0$$

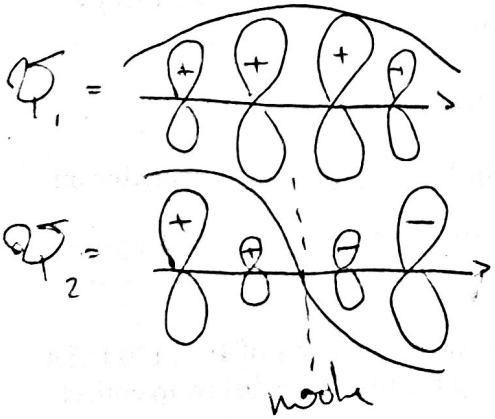




Reference: $= \rightarrow E_{=} = 2\alpha + 2\beta$

$\Delta E = E_{butadiene} - 2E_{=} = 0.427\beta$

$\Delta E = E_{cyclo} - 2E_{=} = 0\beta$



$\psi_3 \rightarrow$ 2 nodes

$\psi_4 \rightarrow$ 3 nodes

$\psi_1 =$ 0 node

$\psi_{2,3} =$ 2 nodes / degen

$\psi_4 =$ ~~4~~ nodes

Benzene -> on y va.