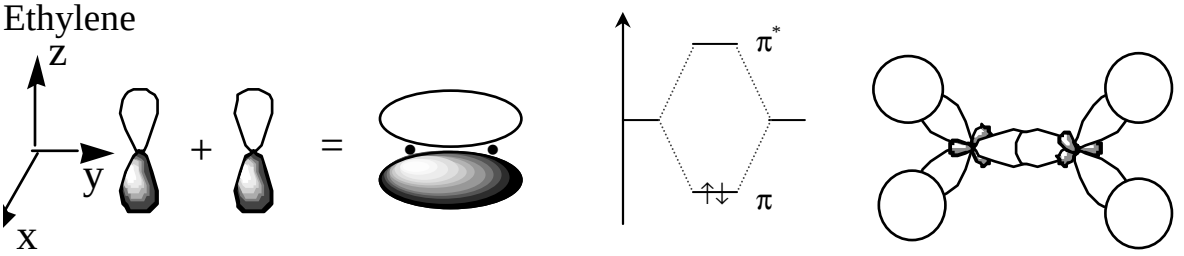
Hückel MO Theory

Ethylene



$$\Psi = c_A p_{zA} + c_B p_{zB}$$

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

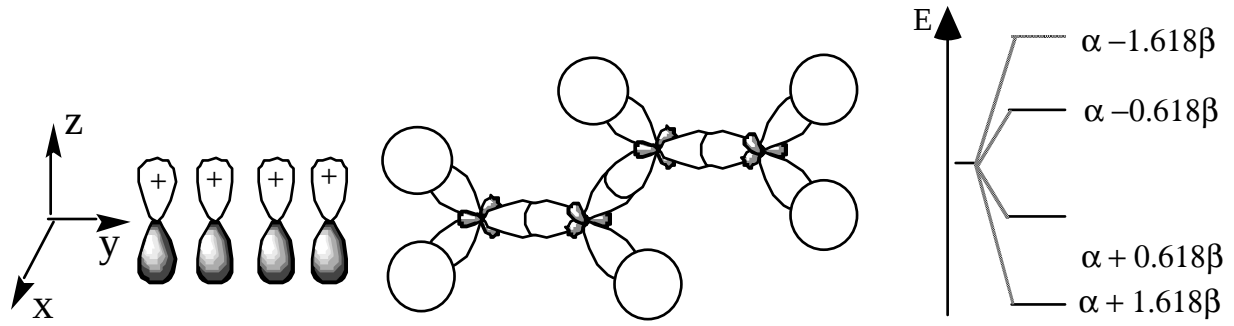
$\alpha = \int p_{zA}^{*}\, \mathcal{H}_{eff}\, p_{zA}\, d\tau$ Coulomb Integral

$\beta = \int p_{zA}^{*}\, \mathcal{H}_{eff}\, p_{zB}\, d\tau$ Resonance Integral

$S_{AB} = \int p_{zA}^{*} p_{zB}\, d\tau = 0$ Overlap Integral

$$\Psi_+ = \frac{1}{\sqrt{2}}(p_{zA} + p_{zB}) \qquad \Psi_- = \frac{1}{\sqrt{2}}(p_{zA} - p_{zB})$$

Butadiene



$$\Psi_i = c_{iA} p_{zA} + c_{iB} p_{zB} + c_{iC} p_{zC} + c_{iD} p_{zD} \qquad i = 1 \ldots 4$$

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

Approximations:

1.

2.

3.

$$x_i = \frac{(E_i - \alpha)}{\beta} \qquad E_i = \alpha + x_i \beta$$

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

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} c_{iA} \\ c_{iB} \\ c_{iC} \\ c_{iD} \end{pmatrix} = x_i \begin{pmatrix} c_{iA} \\ c_{iB} \\ c_{iC} \\ c_{iD} \end{pmatrix}$$ Eigenvector-Eigenvalue

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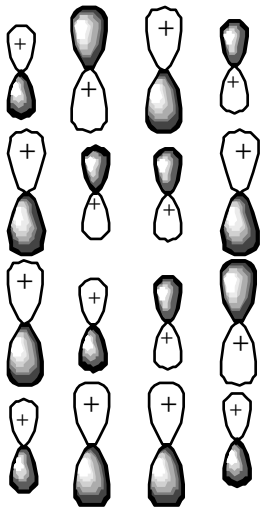
$x^4 - 3x^2 + 1 = 0$ let $y = x^2$ $y^2 - 3y + 1 = 0$

$y = \frac{3 \pm \sqrt{9-4}}{2} = 2.618, 0.382$ $x = \sqrt{y} = \pm 1.618, \pm 0.618$

$E_i = \alpha + x_i \beta = \alpha \pm 1.618 \beta$ or $\alpha \pm 0.618 \beta$

Nodes:



$\Psi_4 = 0.372p_A - 0.602p_B + 0.602p_C - 0.372p_D$

$\Psi_3 = 0.602p_A - 0.372p_B - 0.372p + 0.602p_D$

$\Psi_2 = 0.602p_A + 0.372p_B - 0.372p_C - 0.602p_D$

$\Psi_1 = 0.372p_A + 0.602p_B + 0.602p_C + 0.372p_D$

$E_{tot} = 4\alpha + 4.472\beta$

$2E_{ethylene} = 4\alpha + 4\beta$ π delocalization energy =

$P_{jk} = \sum_{i=1}^{m} n_i 2c_{ij} c_{ik} S_{jk}$ for atoms j and k and orbital i with n_i electrons

for Hückel MO's use $2S_{jk}=1$ for this purpose

$P_{AB} = \sum n_i \; c_{iA} \; c_{iB}$ look at <u>just</u> first term: i=1: $n_i=2$ and

$\Psi_1 = c_{1A} p_A + c_{1B} p_B + c_{1C} p_C + c_{1D} p_D$

$\Psi_1 = 0.372 p_A + 0.602p_B + 0.602p_C + 0.372p_D$

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ethylene: $P_{AB} = 2\frac{1 \; 1}{\sqrt{2}\sqrt{2}} = 1$

butadiene: $P_{AB} = 2(0.372)(0.602) + 2(0.602)(0.372) = 0.89$

$P_{BC} = 2(0.602)(0.602) + 2(0.372)(-0.372) = 0.45$