5. Hückel MO Theory for Conjugated Systems

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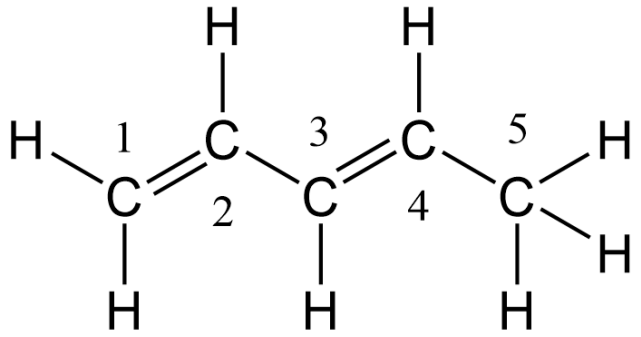
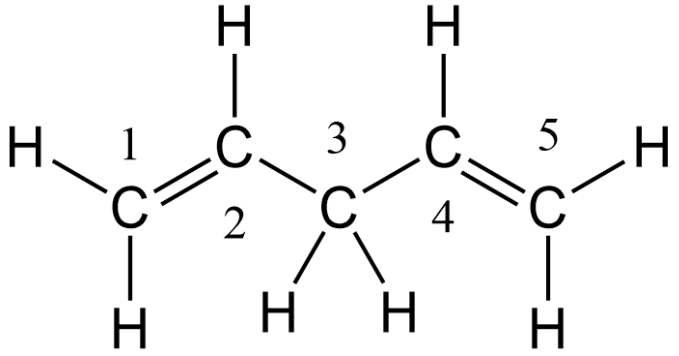
Conjugated Hydrocarbons

Conjugated hydrocarbons have alternating single and double bonds in the Lewis structure.

The network of π-bonds leads to delocalization of electrons, which gives additional stability.



1,3-pentadiene (C_5H_8)

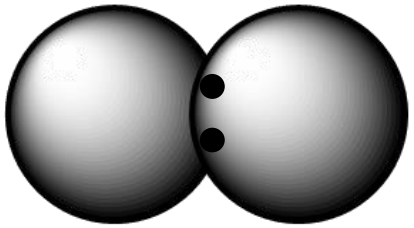


1,4-pentadiene (C_5H_8)

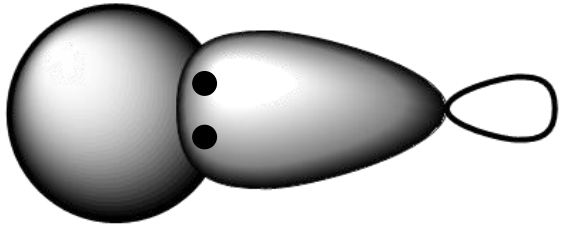
$$\Delta H^\circ_{\mathrm{f},14} - \Delta H^\circ_{\mathrm{f},13} = 31\ \mathrm{kJ\ mol^{-1}}$$

Types of Chemical Bonds in Hydrocarbons

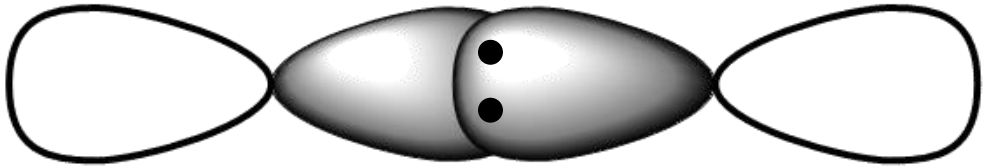
σ-bond



$\mathrm{s}-\mathrm{s}$

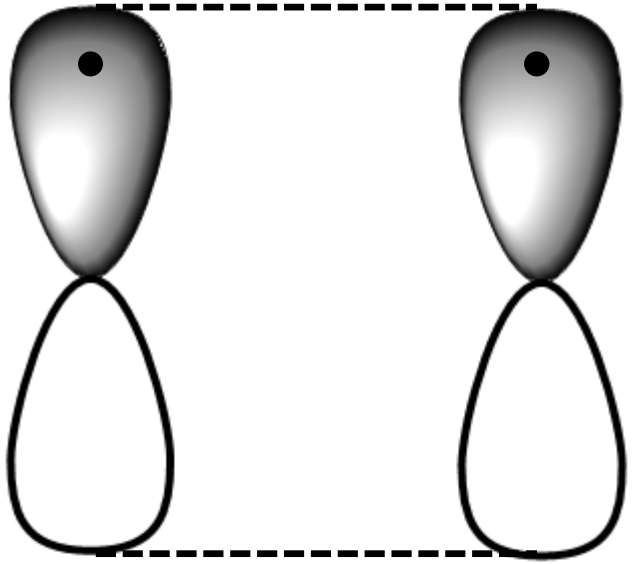


$\mathrm{s}-\mathrm{sp}^{n}$



$\mathrm{p}-\mathrm{p}$

π-bond

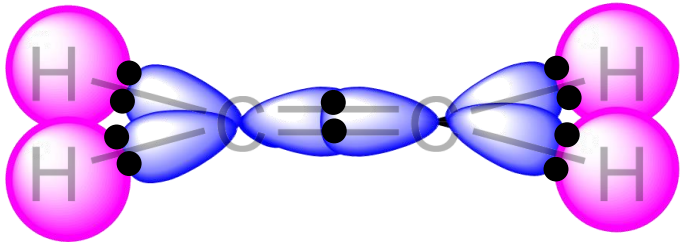


$\mathrm{p}-\mathrm{p}$

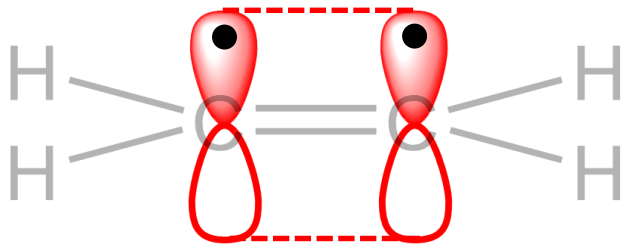
Types of Chemical Bonds in Hydrocarbons

Example: ethylene (C_2H_4)

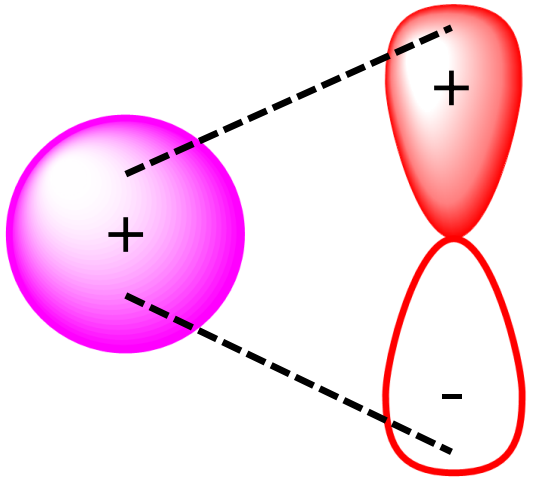
σ-bond network



π-bond network



$1s - 2p_z$: nonbonding



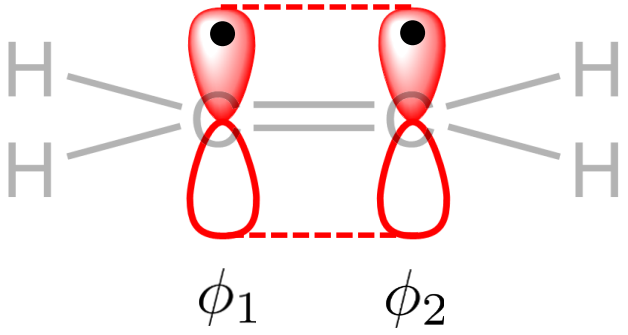
The σ-bond network ($1s$ of H atoms and sp^2 of C atoms) and π-bond network ($2p_z$ of C atoms) can be separately considered.

Hückel Molecular Orbital Theory

Assumption: the property of the planar conjugated hydrocarbons will be mostly determined by $2\mathrm{p}_z$ orbitals that forms a delocalized network.

Other orbitals are still important as they form the shape of the molecules.

Similar to what we did for H_2^+, we calculate the molecular orbitals by applying variational principle to the atomic $2\mathrm{p}_z$ orbitals.



Atomic orbitals

$$\psi_1 = c_{11}\phi_1 + c_{12}\phi_2$$

$$\psi_2 = c_{21}\phi_1 + c_{22}\phi_2$$

Molecular orbitals

Ethylene

The secular equation for ethylene is

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0,$$

where the values of the integrals are

$$S_{11} = \int |\phi_1|^2 \, d\tau = 1, \quad S_{22} = \int |\phi_2|^2 \, d\tau = 1,$$

$$S_{12} = \int \phi_1^* \phi_2 \, d\tau \sim 0, \quad S_{21} = \int \phi_2^* \phi_1 \, d\tau \sim 0,$$

$$H_{11} = \int \phi_1^* \hat{H} \phi_1 \, d\tau = \alpha, \quad H_{22} = \int \phi_2^* \hat{H} \phi_2 \, d\tau = \alpha, \quad (\alpha > 0)$$

$$H_{12} = \int \phi_1^* \hat{H} \phi_2 \, d\tau = \beta, \quad H_{21} = \int \phi_2^* \hat{H} \phi_1 \, d\tau = \beta. \quad (\beta < 0)$$

Ethylene

As a result, the secular equation becomes

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

and expanding the determinant and the solving for E gives two roots:

$$E_1 = \alpha + \beta, \quad E_2 = \alpha - \beta.$$

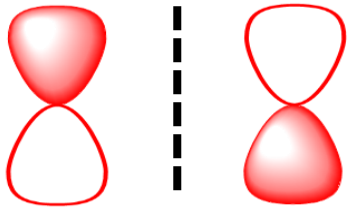
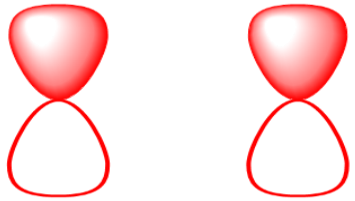
Inserting each root in the secular equation and solving the simultaneous equation

$$\begin{pmatrix} \alpha - E_n & \beta \\ \beta & \alpha - E_n \end{pmatrix} \begin{pmatrix} c_{n1} \\ c_{n2} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

yields the coefficients for molecular orbitals.

Ethylene

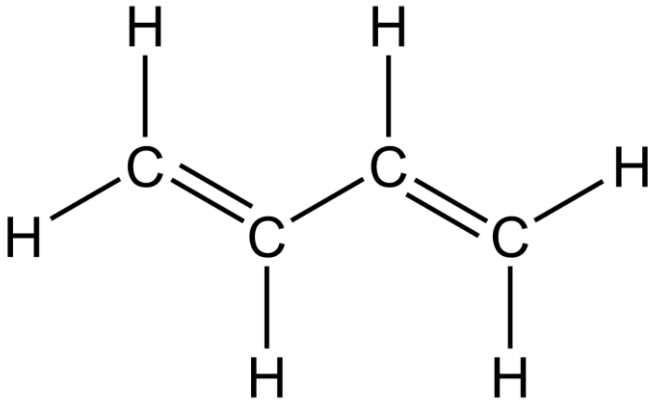
In summary, the molecular orbital diagram for ethylene is as below:

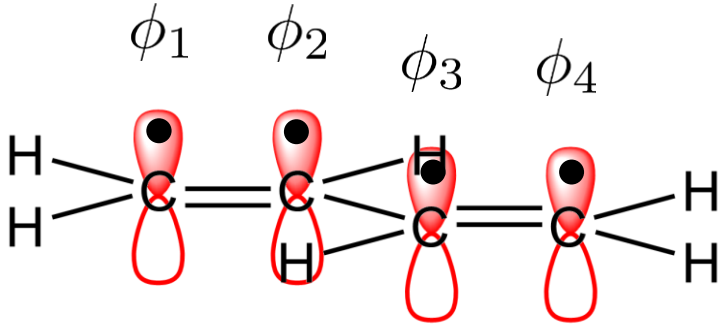
Molecular orbital		Nodes		Energy
$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$		1		$E_2 = \alpha - \beta$
$\psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$		0		$E_1 = \alpha + \beta$ $(\beta < 0)$

Energy

$$E_{\pi,\mathrm{C_2H_4}} = 2\alpha + 2\beta$$

Butadiene





We assume that the integrals in the secular equation only become significant for self- and nearest-neighbor interactions,

$$S_{mn} = \int \phi_m^* \phi_n \, d\tau = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases}$$

$$H_{mn} = \int \phi_m^* \hat{H} \phi_n \, d\tau = \begin{cases} \alpha & \text{if } m = n \\ \beta & \text{if } m \neq n, \text{ adjacent} \\ 0 & \text{if } m \neq n, \text{ non-adjacent} \end{cases}$$

Butadiene

The secular equation becomes

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} \end{vmatrix}$$

$$= \begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = \beta^4 \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0,$$

where we have defined

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

Butadiene

Expanding the matrix gives

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

which gives four roots

$$x = \pm\frac{\sqrt{5}+1}{2} \sim \pm 1.618, \quad \pm\frac{\sqrt{5}-1}{2} \sim \pm 0.618.$$

The molecular orbitals are

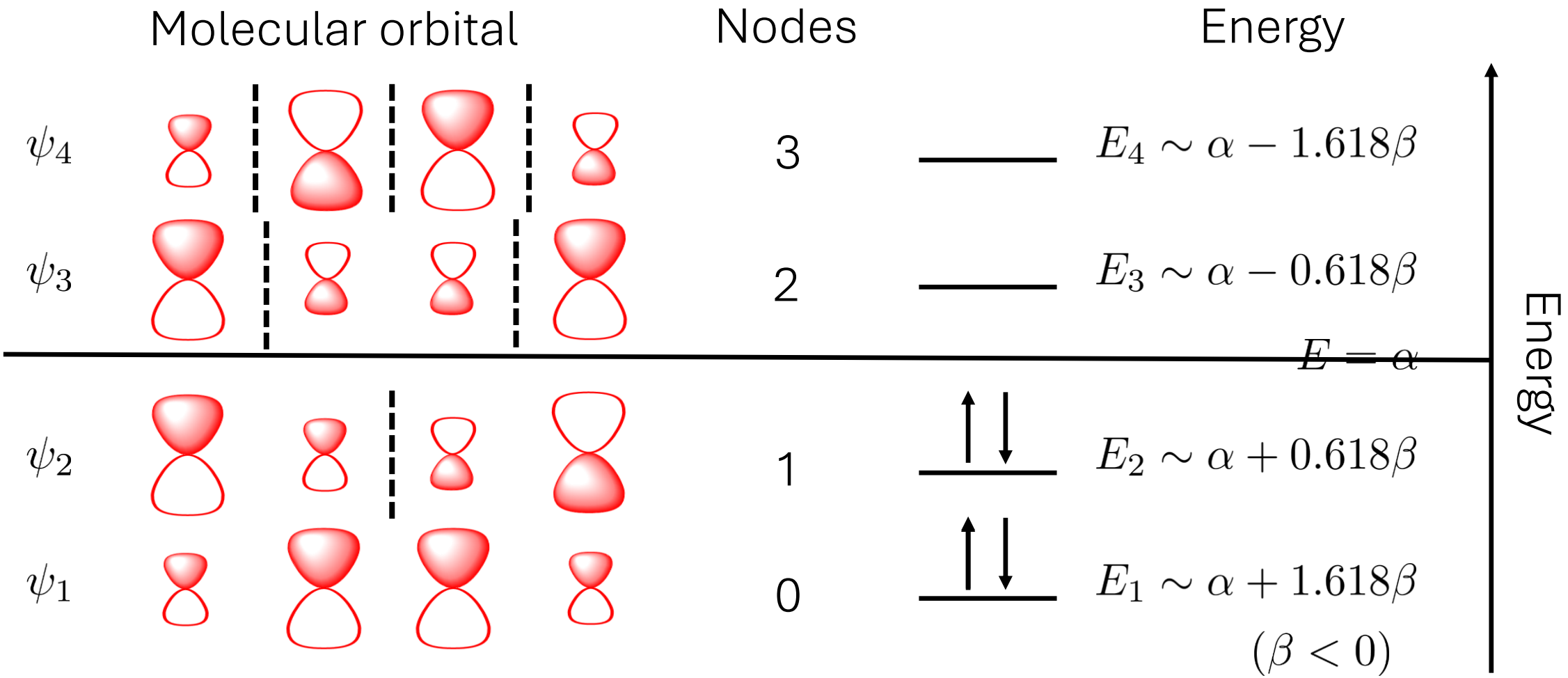
$$\psi_4 \sim 0.37\phi_1 - 0.60\phi_2 + 0.60\phi_3 - 0.37\phi_4, \qquad E_4 \sim \alpha - 1.618\beta,$$

$$\psi_3 \sim 0.60\phi_1 - 0.37\phi_2 - 0.37\phi_3 + 0.60\phi_4, \qquad E_3 \sim \alpha - 0.618\beta,$$

$$\psi_2 \sim 0.60\phi_1 + 0.37\phi_2 - 0.37\phi_3 - 0.60\phi_4, \qquad E_2 \sim \alpha + 0.618\beta,$$

$$\psi_1 \sim 0.37\phi_1 + 0.60\phi_2 + 0.60\phi_3 + 0.37\phi_4, \qquad E_1 \sim \alpha + 1.618\beta.$$

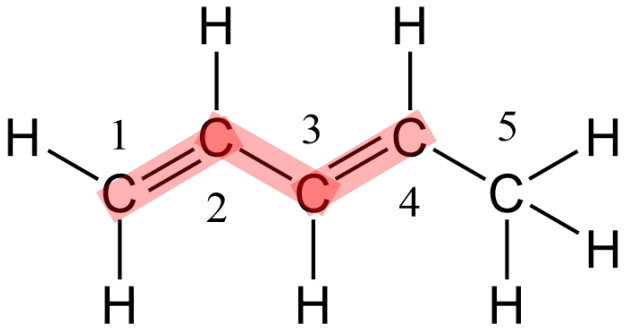
Butadiene



$$E_{\pi,\mathrm{C_4H_6}} = 4\alpha + 4.472\beta$$

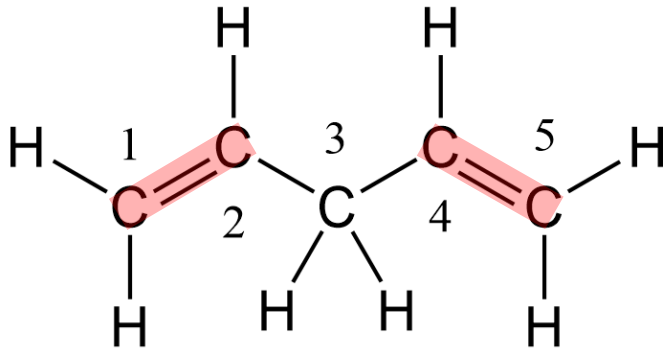
Comparison to Experimental Observation

1,3-pentadiene



$$E_{1,3} \sim E_\sigma + E_{\pi,\mathrm{C_4H_6}} = E_\sigma + 4\alpha + 4.472\beta$$

1,4-pentadiene



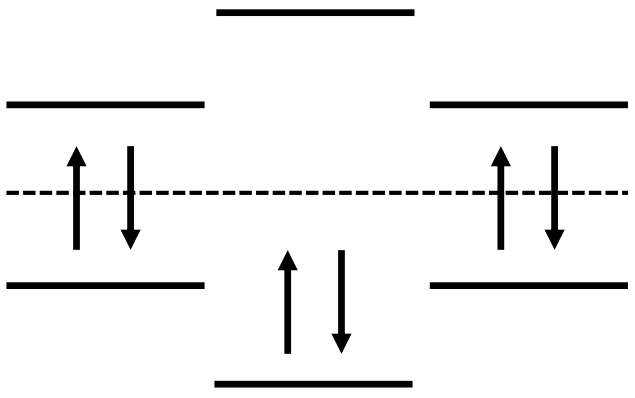
$$E_{1,4} \sim E_\sigma + 2E_{\pi,\mathrm{C_2H_4}} = E_\sigma + 2(2\alpha + 2\beta) = E_\sigma + 4\alpha + 4\beta$$

$$E_{1,3} - E_{1,4} = 0.472\beta \sim 0.472 \times (-75\ \mathrm{kJ\ mol^{-1}}) = -35\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H^\circ_{\mathrm{f},13} - \Delta H^\circ_{\mathrm{f},14} = -31\ \mathrm{kJ\ mol^{-1}}\ (\mathrm{experiment})$$

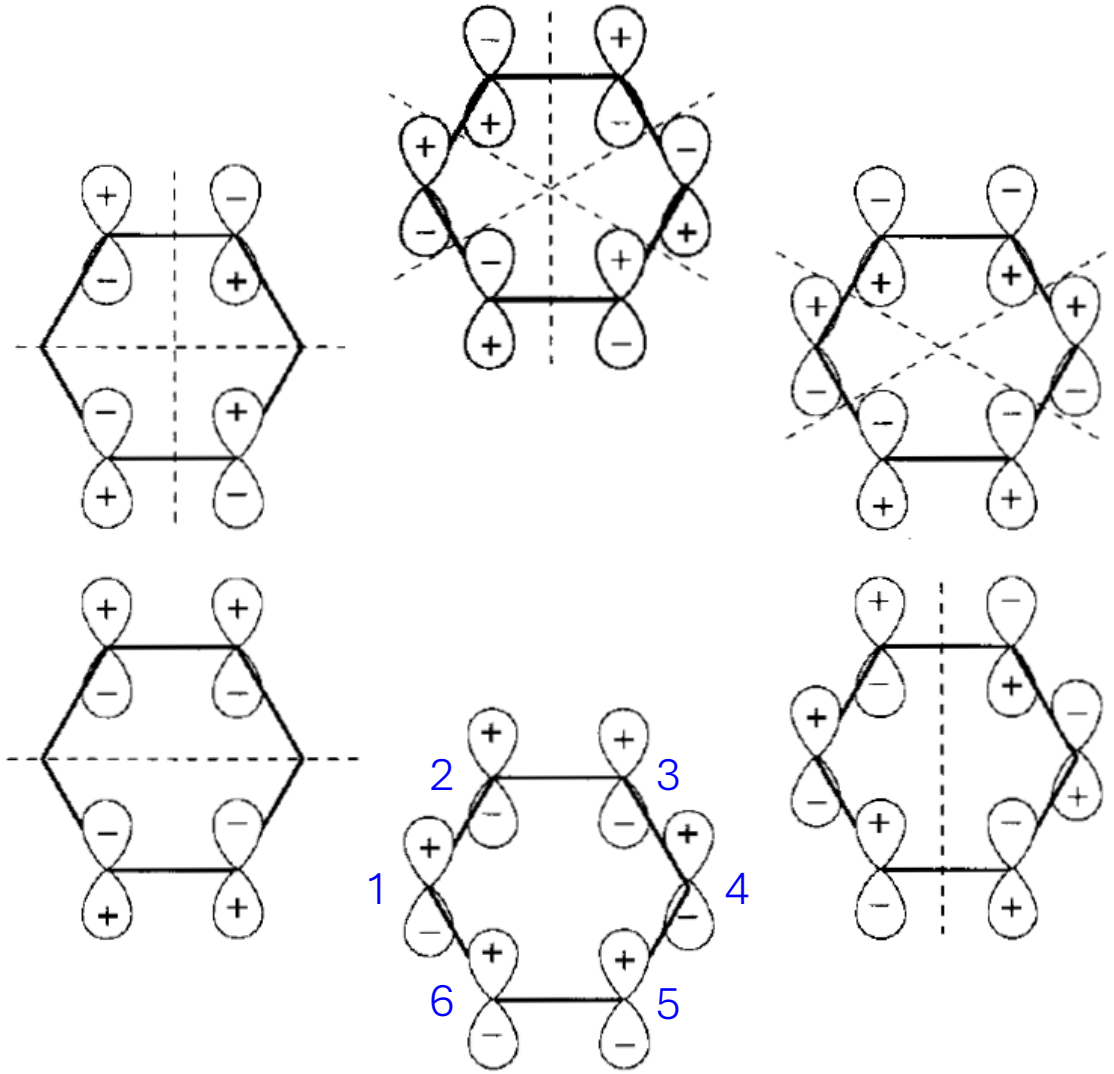
Benzene

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-E \end{vmatrix} = \beta^6 \begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0$$



Energy	Nodes
$E_6 = \alpha - 2\beta$	3
$E_4 = E_5 = \alpha - \beta$	2
$E_2 = E_3 = \alpha + \beta$	1
$E_1 = \alpha + 2\beta$	0

Benzene



$$\psi_6 = \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

$$\psi_5 = \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)$$

$$\psi_4 = \frac{1}{\sqrt{4}}(\phi_2 - \phi_3 + \phi_5 - \phi_6)$$

$$\psi_3 = \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

$$\psi_2 = \frac{1}{\sqrt{4}}(\phi_2 + \phi_3 - \phi_5 - \phi_6)$$

$$\psi_1 = \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

McQuarrie, D. A.; Simon, J. D. Physical Chemistry: a Molecular Approach, Ch. 10