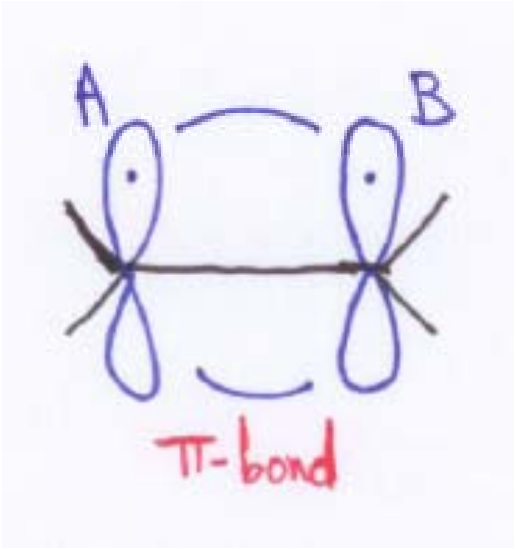
Hückel Theory of Pi-Bonding in Conjugated Hydrocarbon Molecules (Pt. 1)

Consider ethylene:



Underlying Assumptions:

1) σ –core provides fixed electrostatic potential for π electrons

2) [Usually] $$S_{ij} = \begin{cases} 0 \, , \, i \neq j \\ 1 \, , \, i = j \end{cases}$$

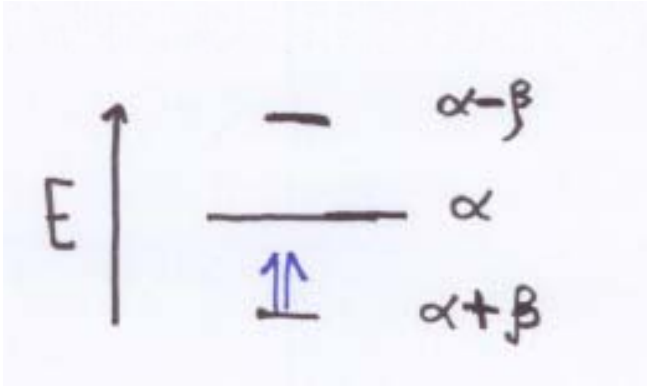
Thus, for ethylene:

$$\psi = c_1 2p_{zA} + c_2 2p_{zB} \quad \Rightarrow \quad \begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \qquad [1]$$

Parameter meaning: α=Coulomb parameter ~ -(ionization energy of isolated carbon 2pz electron)

β = Exchange parameter ~ -75 kJ/mol [empirical!]

The MO energy eigenvalues from Eq. [1] are: $E_\pi = \alpha \pm \beta$



The corresponding eigenvectors (which determine the MOs) are:

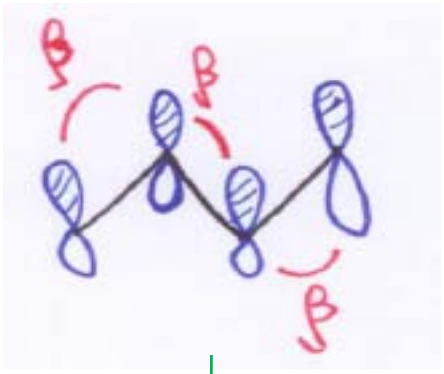
$$E_\pi = \alpha \pm \beta \quad \leftrightarrow \quad \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \frac{1}{\sqrt{2}}$$

Note: pi-bonding energy = pi-bond formation energy $\equiv E_\pi - N\alpha$

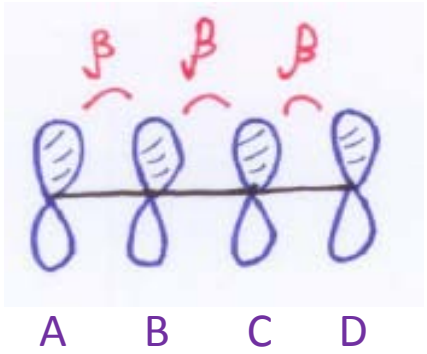
Thus, for ethylene, pi-bonding energy = 2β ≈ -150 kJ/mol

Hückel Theory of Butadiene:

$$\psi = c_A\phi_A + c_B\phi_B + c_C\phi_C + c_D\phi_D$$



idealize as



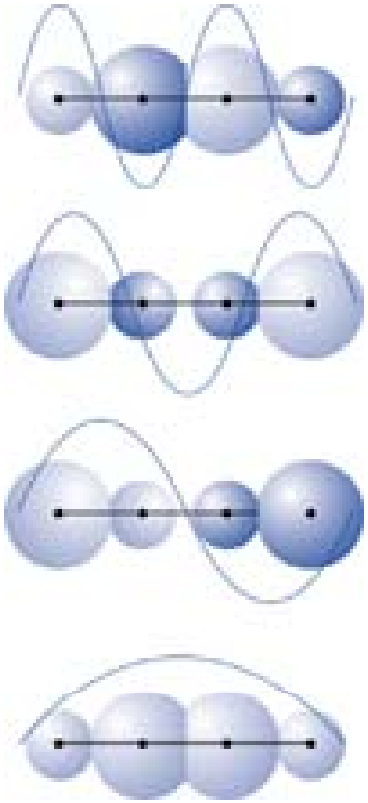
The Hückel secular determinant thus reads:

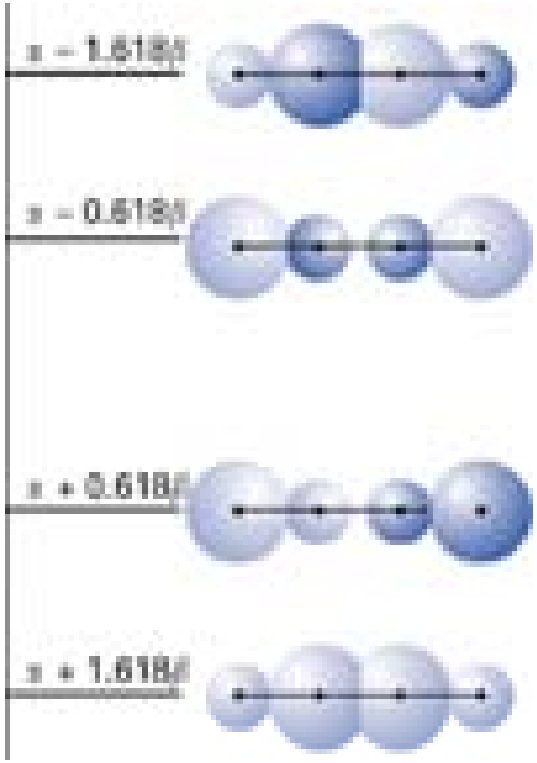
$$\begin{vmatrix} x & \beta & 0 & 0 \\ \beta & x & \beta & 0 \\ 0 & \beta & x & \beta \\ 0 & 0 & \beta & x \end{vmatrix} = 0 \quad ; \quad x \equiv \alpha - E$$

Expanding out the secular determinant implies: $x^4 - 3\beta^2 x^2 + \beta^4 = 0$

Setting $y = x^2 \quad \Rightarrow \quad x = \pm\left(\frac{3 \pm 5^{1/2}}{2}\right)^2 \beta$

The corresponding eigenfunction (MOs) look like:





Formula for the Hückel model pi-energy levels of a N-carbon linear conjugated hydrocarbon molecule:

$$E_k = \alpha + 2\beta \cos\left(\frac{k\pi}{N+1}\right) \quad ; \quad k = 1, 2, \ldots, N$$

Formula for the Hückel model pi-energy levels of a N-carbon cyclic conjugated hydrocarbon molecule:

$$E_k = \alpha + 2\beta \cos\left(\frac{2k\pi}{N}\right) \quad ; \quad k = 1, 2, \ldots, N$$

Example: benzene (N=6)