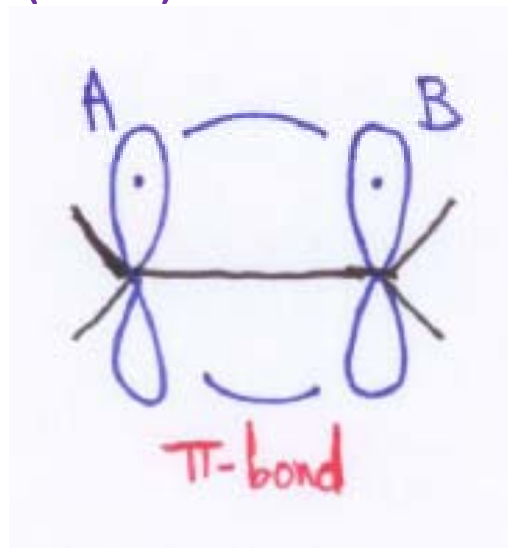


# Hückel Theory of Pi-Bonding in Conjugated Hydrocarbon Molecules (Pt. 1)

Consider ethylene:



## Underlying Assumptions:

1)  $\sigma$ -core provides fixed electrostatic potential for  $\pi$  electrons

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

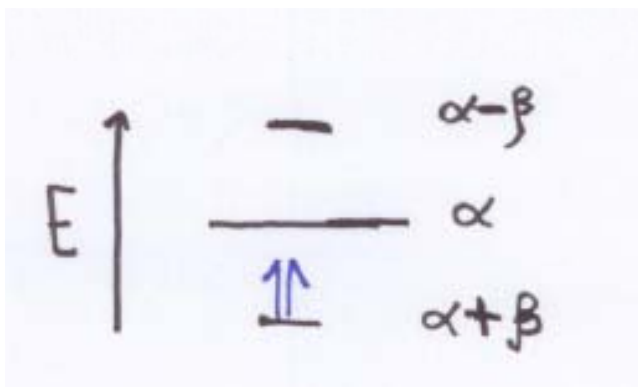
Thus, for ethylene:

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

**Parameter meaning:**  $\alpha$  = Coulomb parameter  $\sim$  -(ionization energy of isolated carbon 2pz electron)

$\beta$  = Exchange parameter  $\sim$  -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 =  $2\beta \approx -150$  kJ/mol

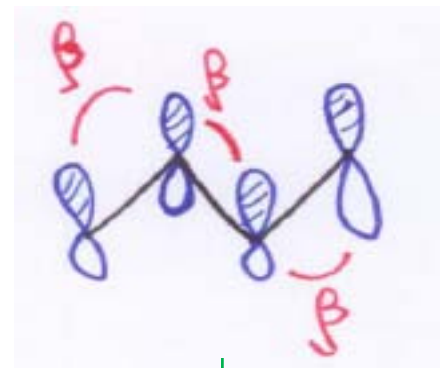
## Hückel Theory of Butadiene:

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

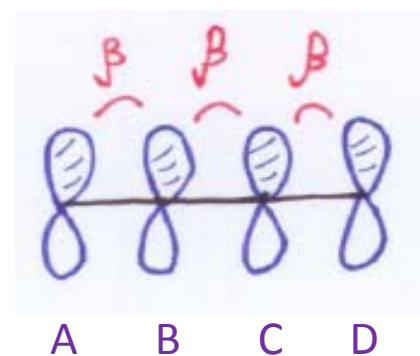
The Hückel secular determinant thus reads:

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

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

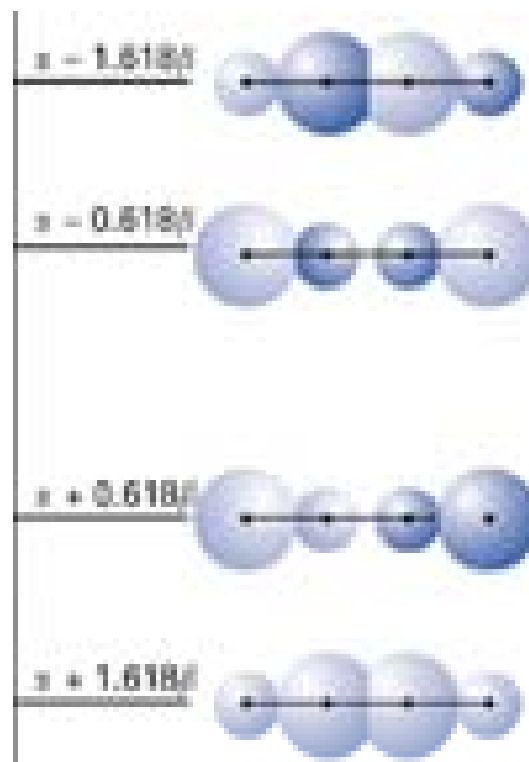
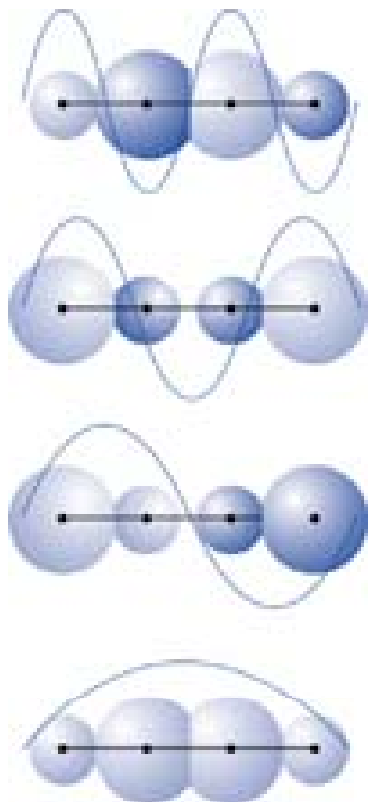


idealize as



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

The corresponding eigenfunction (MOs) look like:



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

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

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

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

Example: benzene  
(N=6)

