Lecture 10

The Hückel Model

Semiempirical Methods

It is difficult to apply ab initio methods to medium and large molecules, therefore many semiempirical methods have been developed to treat such molecules.

The earliest semiempirical methods treated only the π electrons of conjugated molecules.

1. We begins with π-electron semiempirical methods (Sections 17.1 to 17.3)
2. Then we considers general semiempirical methods (Section 17.4).
3. The molecular-mechanics method (Section 17.5) is a nonquantum-mechanical method applicable to much larger molecules than semiempirical methods.

Hückel Molecular Orbital Model

Developed by Eric Hückel in 1920's to treat π-electron systems.
Extended by Roald Hoffman in 1963 to treat σ-bonded systems.

The Hückel model has been largely superseded by more accurate MO calculations. However, it is still useful to obtain qualitative predictions of bonding and reactivity in conjugated π systems.

The earliest semiempirical methods for planar conjugated organic compounds treated the π electrons separately from the σ electrons.

1. Coulson stated that the justification for the $\sigma-\pi$ separability approximation lies in the different symmetry of the σ and π orbitals and in the greater polarizability of the π electrons, which makes them more susceptible to perturbations such as those occurring in chemical reactions.
2. In the **π-electron approximation**, the n_π -π electrons are treated separately by incorporating the effects of the electrons and the nuclei into some sort of effective π electron Hamiltonian $H\pi$

Assumptions

1. The σ and π electrons are independent of each other.

   The π electrons move in the constant electrostatic potential created by the σ electrons.

2. The carbons are sp^2 hybridized.

   The remaining p_z orbital is perpendicular to the σ molecular framework.

3. The π electron Molecular Orbitals are linear combinations of the p_z orbitals (χ_i).

$$\varphi_i = \sum_j c_{ij}\chi_j = c_{11}\chi_1 + c_{12}\chi_2 + c_{13}\chi_3 + \cdots$$

4. The total π electron Hamiltonian is a simple sum of effective one electron Hamiltonians.

$$H = \sum_i h_i = h_1 + h_2 + h_3 + \cdots$$

Linear Equations and Secular Determinant

$$\varphi_i = \sum_j c_{ij}\chi_j \quad + \quad H = \sum_i h_i$$

Variational Method

$$\sum_{j=1}^{N} c_{ij}(H_{ij} - ES_{ij}) = 0$$

One has N equations, where N is the number of carbon atoms.

$$\left| H_{ij} - ES_{ij} \right| = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{12} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{2} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

Additional Assumptions

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

5. The Orbitals are Normalized: $S_{ii} = 1$

   The overlap between orbitals is 0: $S_{ij} = 0$ ($i \neq j$)

6. The diagonal Hamiltonian elements are given by an empirical parameter, α

7. Off-diagonal Hamiltonian elements are given by an empirical parameter, β, if the carbons are adjacent

$H_{ij} = \beta$: Adjacent Carbons

$H_{ij} = 0$: Non-Adjacent Carbons

Note: $\alpha<0$ and $\beta<0$

Parameter Values

What is the value of α?

Who cares?

Since α cancels out in almost all applications, such as transition or reaction energies.

What is the value of β?

Who knows?

Estimates of the "best" value of β vary all over the place.
As noted in the text, values ranging from –30 kcal/mol to -70 kcal/mol (-130 to -290 kJ/mol) have been used.

For lack of anything better, we'll use β = -200 kJ/mol.

Application to Ethylene (C_2H_4)

Secular Determinant and Energies

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

Put in Hückel matrix elements

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

Divide all terms by β and define x by

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

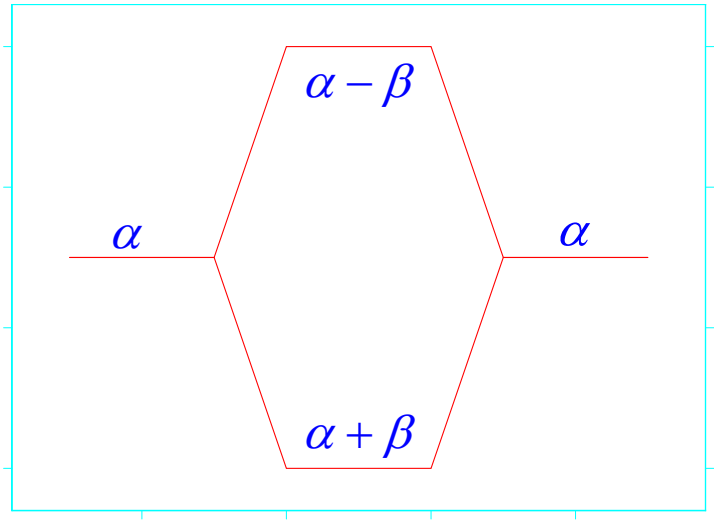
$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

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

$$x^2 - 1 = 0$$

$$x_1 = -1 = \frac{\alpha - E_1}{\beta} \qquad x_2 = +1 = \frac{\alpha - E_2}{\beta}$$

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



Molecular Orbitals

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

$$\phi = c_1\chi_1 + c_2\chi_2$$

$$(\alpha - E)c_1 + \beta c_2 = 0$$

$$\beta c_1 + (\alpha - E)c_2 = 0$$

or

$$xc_1 + c_2 = 0$$

$$c_1 + xc_2 = 0$$

$$\frac{c_2}{c_1} = -x$$

$$\phi = c_1\chi_1 + c_2\chi_2 \qquad \frac{c_2}{c_1} = -x$$

$$x_1 = -1 \qquad E_1 = \alpha + \beta \longrightarrow \frac{c_2}{c_1} = +1 \longrightarrow c_2 = c_1$$

Normalization: $1 = \langle \varphi | \varphi \rangle = \langle c_1\chi_1 + c_2\chi_2 | c_1\chi_1 + c_2\chi_2 \rangle$

$$1 = c_1^2 \langle \chi_1 | \chi_1 \rangle + c_1 c_2 \langle \chi_1 | \chi_2 \rangle + c_2 c_1 \langle \chi_2 | \chi_1 \rangle + c_2^2 \langle \chi_2 | \chi_2 \rangle$$

$$1 = c_1^2 + c_2^2$$

Note: For Hückel calculations, the normalization condition is always: $\sum_i c_i^2 = 1$

$$1 = c_1^2 + c_2^2 \qquad c_2 = c_1 \longrightarrow \boxed{\varphi_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2)}$$

$$\boxed{\varphi_1 = \frac{1}{\sqrt{2}}\left(\chi_1 + \chi_2\right)}$$

Bonding Orbital

$$x_2 = +1$$

$$E_2 = \alpha - \beta$$

$$\longrightarrow \quad \frac{c_2}{c_1} = -1 \quad \longrightarrow \quad c_2 = -c_1$$

$$1 = c_1^2 + c_2^2$$

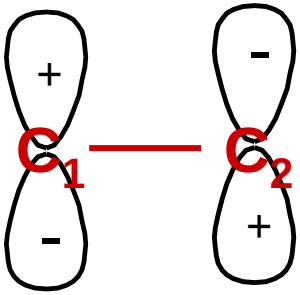
$$c_2 = -c_1$$

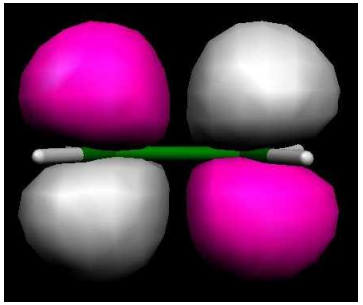
$$\longrightarrow \quad \boxed{\varphi_2 = \frac{1}{\sqrt{2}}\left(\chi_1 - \chi_2\right)}$$

Antibonding Orbital

$$E_2 = \alpha - \beta$$

$$\varphi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_2)$$

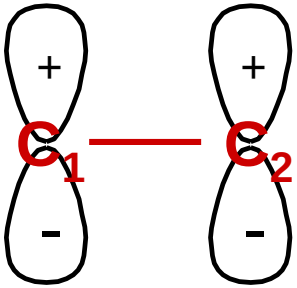


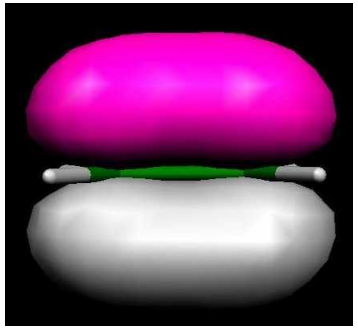


Electrons are ***not*** delocalized in ϕ_2

$$E_1 = \alpha + \beta$$

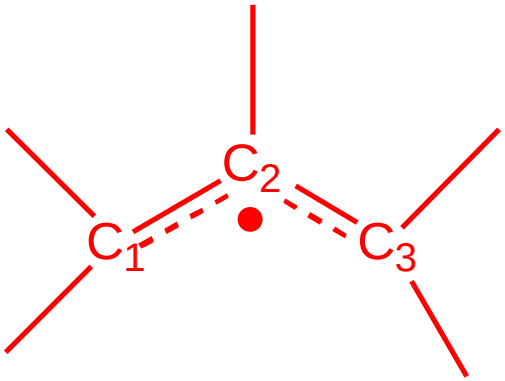
$$\varphi_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2)$$





Electrons are delocalized in ϕ_1

Application to the Allyl Radical (C_3H_5•)



The Allyl radical has 3 π electrons

Secular Determinant and Energies

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & H_{23} - ES_{23} \\ H_{13} - ES_{13} & H_{23} - ES_{23} & H_{33} - ES_{33} \end{vmatrix} = 0$$

$$\downarrow$$

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

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \xrightarrow[\text{Define } x = \frac{\alpha - E}{\beta}]{\text{Divide by } \beta} \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

$$x \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} + 0 \begin{vmatrix} 1 & x \\ 0 & 1 \end{vmatrix} = 0 \longrightarrow x\left(x^2 - 1\right) - 1\left(x - 0\right) = 0$$

$$x^3 - 2x = 0$$

on Board

$$x_1 = -\sqrt{2} = \frac{\alpha - E_1}{\beta} \qquad x_2 = 0 = \frac{\alpha - E_2}{\beta} \qquad x_3 = +\sqrt{2} = \frac{\alpha - E_3}{\beta}$$

$$E_1 = \alpha + \sqrt{2}\beta \qquad E_2 = \alpha \qquad E_3 = \alpha - \sqrt{2}\beta$$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \longrightarrow \begin{aligned} &1)\ \ xc_1 + c_2 = 0 \\ &2)\ \ c_1 + xc_2 + c_3 = 0 \\ &3)\ \ c_2 + xc_3 = 0 \end{aligned}$$

$$\begin{aligned} &From\ \ 1)\ \ c_2 = -xc_1 \\ &From\ \ 2)\ \ c_3 = -c_1 - xc_2 \\ &From\ \ 3)\ \ c_3 = -\frac{1}{x}c_2 \end{aligned}$$

$$x_1 = -\sqrt{2} \longrightarrow \begin{aligned} c_2 &= -\left(-\sqrt{2}\right)c_1 = \sqrt{2}c_1 \\ c_3 &= -\frac{1}{-\sqrt{2}}c_2 = c_1 \end{aligned}$$

$$x_2 = 0 \longrightarrow \begin{aligned} c_2 &= -(0)c_1 = 0 \\ c_3 &= -c_1 - (0)c_2 = -c_1 \end{aligned}$$

Normalization

$$c_1^2 + \left(\sqrt{2}c_1\right)^2 + c_1^2 = 1$$

$$c_1 = \frac{1}{2}$$

$$\boxed{\varphi_1 = \frac{1}{2}\left(\chi_1 + \sqrt{2}\chi_2 + \chi_3\right)}$$

Normalization

$$c_1^2 + (0)^2 + (-c_1)^2 = 1$$

$$c_1 = \frac{1}{\sqrt{2}}$$

$$\boxed{\varphi_2 = \frac{1}{\sqrt{2}}\left(\chi_1 - \chi_3\right)}$$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \longrightarrow \begin{aligned} &1)\ \ xc_1 + c_2 = 0 \\ &2)\ \ c_1 + xc_2 + c_3 = 0 \\ &3)\ \ c_2 + xc_3 = 0 \end{aligned}$$

$$From\ \ 1)\ \ c_2 = -xc_1$$

$$From\ \ 2)\ \ c_3 = -c_1 - xc_2$$

$$From\ \ 3)\ \ c_3 = -\frac{1}{x}c_2$$

$$x_3 = +\sqrt{2} \longrightarrow \begin{aligned} c_2 &= -\left(+\sqrt{2}\right)c_1 = -\sqrt{2}c_1 \\ c_3 &= -\frac{1}{+\sqrt{2}}c_2 = c_1 \end{aligned}$$

Normalization

$$c_1^2 + \left(-\sqrt{2}c_1\right)^2 + c_1^2 = 1$$

$$c_1 = \frac{1}{2}$$

$$\boxed{\varphi_3 = \frac{1}{2}\left(\chi_1 - \sqrt{2}\chi_2 + \chi_3\right)}$$

Wavefunction Check

You can always check to be sure that you've calculated the wavefunction correctly by calculating the expectation value of E and see if it matches your original calculated value.

We'll illustrate with ϕ_3.

$$E = \langle \varphi_3 | H | \varphi_3 \rangle = \left\langle \frac{1}{2}\left(\chi_1 - \sqrt{2}\chi_2 + \chi_3\right) \middle| H \middle| \frac{1}{2}\left(\chi_1 - \sqrt{2}\chi_2 + \chi_3\right) \right\rangle$$

$$= \frac{1}{4}\begin{bmatrix} \langle \chi_1 | H | \chi_1 \rangle - \sqrt{2}\langle \chi_1 | H | \chi_2 \rangle + \langle \chi_1 | H | \chi_3 \rangle \\ -\sqrt{2}\langle \chi_2 | H | \chi_1 \rangle + 2\langle \chi_2 | H | \chi_2 \rangle - \sqrt{2}\langle \chi_2 | H | \chi_3 \rangle \\ +\langle \chi_3 | H | \chi_1 \rangle - \sqrt{2}\langle \chi_3 | H | \chi_2 \rangle + \langle \chi_3 | H | \chi_3 \rangle \end{bmatrix}$$

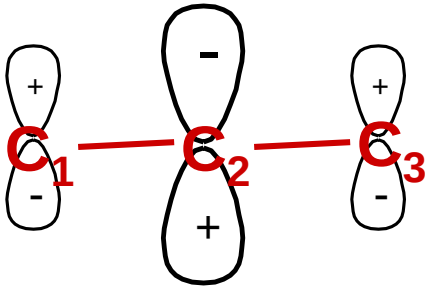
$$= \frac{1}{4}\left[\alpha - \sqrt{2}\beta + 0 - \sqrt{2}\beta + 2\alpha - \sqrt{2}\beta + 0 - \sqrt{2}\beta + \alpha\right]$$

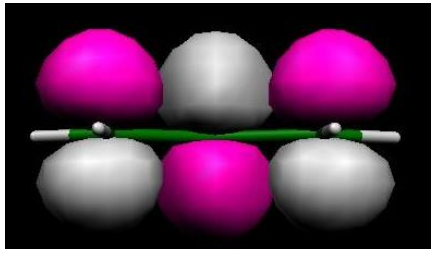
$$E = \frac{1}{4}\left[4\alpha - 4\sqrt{2}\beta\right] = \alpha - \sqrt{2}\beta$$

It checks!!

$$E_3 = \alpha - \sqrt{2}\beta$$

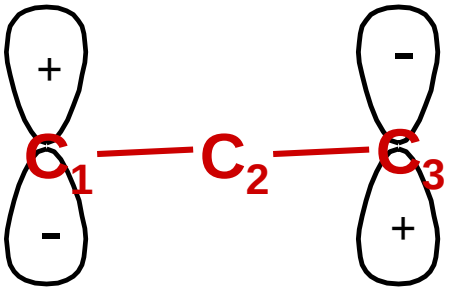
$$\varphi_3 = \frac{1}{2}\left(\chi_1 - \sqrt{2}\chi_2 + \chi_3\right)$$

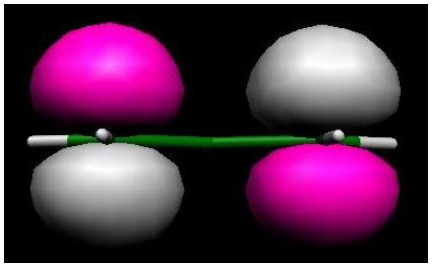




$$E_2 = \alpha$$

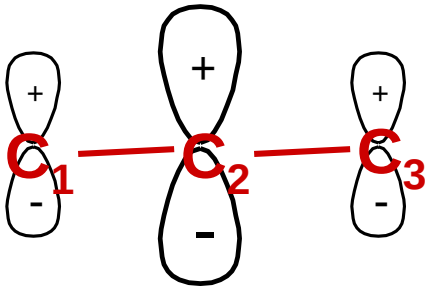
$$\varphi_2 = \frac{1}{\sqrt{2}}\left(\chi_1 - \chi_3\right)$$

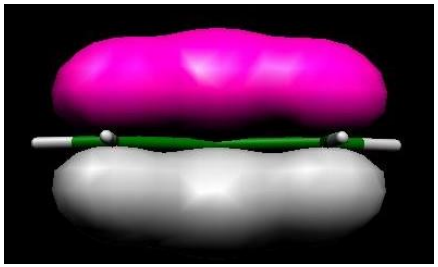




$$E_1 = \alpha + \sqrt{2}\beta$$

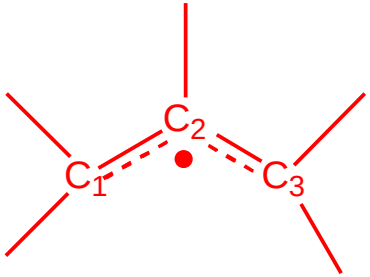
$$\varphi_1 = \frac{1}{2}\left(\chi_1 + \sqrt{2}\chi_2 + \chi_3\right)$$



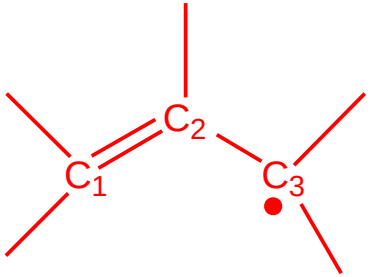


Delocalization Energy

The delocalization energy is the total π electron energy relative to the energy of the system with localized π bonds.



$$E_{Deloc} = E_{\pi} - E_{Loc}$$



$E_3 = \alpha - \sqrt{2}\beta$

$E_2 = \alpha$

$E_1 = \alpha + \sqrt{2}\beta$

$E_2 = \alpha - \beta$

$E_1 = \alpha + \beta$

$$E_{Loc} = E_{C_2H_4} + \alpha$$
$$= 2(\alpha + \beta) + \alpha$$
$$= 3\alpha + 2\beta$$

$$E_{\pi} = 2\left(\alpha + \sqrt{2}\beta\right) + \alpha = 3\alpha + 2\sqrt{2}\beta$$

$$\boxed{\begin{aligned} E_{Deloc} &= 3\alpha + 2\sqrt{2}\beta - (3\alpha + 2\beta) \\ &= 2\left(\sqrt{2} - 1\right)\beta = 0.83\beta \end{aligned}}$$

Part A: The Hückel Model and other Semiempirical Methods

- Hückel Molecular Orbital Model
- Application to Ethylene
- Application to the Allyl Radical (C_3H_5•)
- **π Electron Charge and π Bond Order**
- Application to Butadiene
- Introduction of Heteroatoms
- Semiempirical methods for sigma bonded systems

π Electron Charge and π Bond Order

π Electron Charge (aka π Charge Density)

The π electron charge on atom μ is defined by:

$$q_{\mu} \equiv \sum_{i}^{orbs} n_i c_{i\mu}^2$$

$c_{i\mu}$ is the coefficient of the i'th. MO on atom μ.

π Bond Order

The π bond order between atoms μ and ν is defined by:

$$p_{\mu\nu} \equiv \sum_{i}^{orbs} n_i c_{i\mu} c_{i\nu}$$

Application to the Allyl Radical

$$\varphi_3 = \frac{1}{2}\chi_1 - \frac{1}{\sqrt{2}}\chi_2 + \frac{1}{2}\chi_3$$

$$\varphi_2 = \frac{1}{\sqrt{2}}\chi_1 + 0\,\chi_2 - \frac{1}{\sqrt{2}}\chi_3$$

$$\varphi_1 = \frac{1}{2}\chi_1 + \frac{1}{\sqrt{2}}\chi_2 + \frac{1}{2}\chi_3$$

π Electron Charge: $q_\mu \equiv \sum_i^{orbs} n_i c_{i\mu}^2$

$$q_1 = \sum_i^{orbs} n_i c_{i1}^2 = 2\cdot\left(\frac{1}{2}\right)^2 + 1\cdot\left(\frac{1}{\sqrt{2}}\right)^2 = 1$$

$$q_2 = \sum_i^{orbs} n_i c_{i2}^2 = 2\cdot\left(\frac{1}{\sqrt{2}}\right)^2 + 1\cdot(0)^2 = 1$$

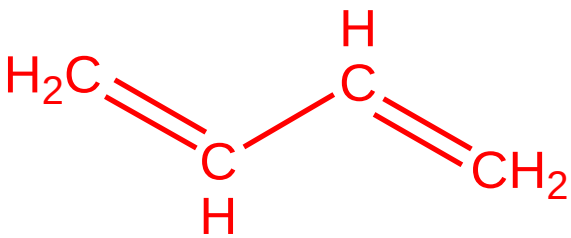
$$q_3 = \sum_i^{orbs} n_i c_{i3}^2 = 2\cdot\left(\frac{1}{2}\right)^2 + 1\cdot\left(-\frac{1}{\sqrt{2}}\right)^2 = 1$$

π Bond Order: $p_{\mu\nu} \equiv \sum_i^{orbs} n_i c_{i\mu} c_{i\nu}$

$$p_{12} = \sum_i^{orbs} n_i c_{i1} c_{i2} = 2\cdot\left(\frac{1}{2}\right)\left(\frac{1}{\sqrt{2}}\right) + 1\cdot\left(\frac{1}{\sqrt{2}}\right)(0) = \frac{1}{\sqrt{2}} = 0.71$$

$$p_{23} = \sum_i^{orbs} n_i c_{i2} c_{i3} = 2\cdot\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right) + 1\cdot(0)\left(-\frac{1}{\sqrt{2}}\right) = \frac{1}{\sqrt{2}} = 0.71$$

Application to Butadiene



1,3-Butadiene has 4 π electrons

Note: Application of the Hückel theory to Butadiene is one of your HW problems.

The solution is worked out in detail below. I will just outline the solution.

Secular Determinant and Energies

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \xrightarrow[\text{Define}]{\text{Divide by } \beta} \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

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

$$x\left[x\left(x^2-1\right)-1\left(x-0\right)\right]-1\left[1\left(x^2-1\right)-1\left(0-0\right)\right]=0$$

$$\left[x^4-x^2-x^2\right]-\left[x^2-1\right]=0$$

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

$$\Big\downarrow\ y \equiv x^2$$

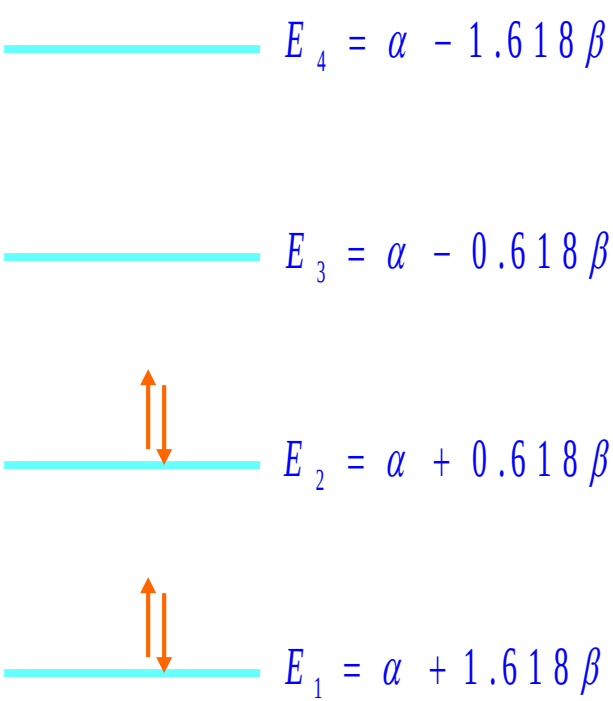
$$y^2-3y+1=0$$

$$y_a = \frac{3+\sqrt{9-4}}{2} = 2.618 = x^2 \qquad y_b = \frac{3-\sqrt{9-4}}{2} = 0.382 = x^2$$

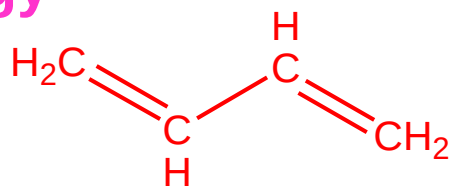
$$y_a = \frac{3+\sqrt{9-4}}{2} = 2.618 = x^2 \qquad y_b = \frac{3-\sqrt{9-4}}{2} = 0.382 = x^2$$

$$x_1 = -1.618 = \frac{\alpha - E_1}{\beta} \qquad x_2 = -0.618 = \frac{\alpha - E_2}{\beta}$$

$$x_4 = +1.618 = \frac{\alpha - E_4}{\beta} \qquad x_3 = +0.618 = \frac{\alpha - E_3}{\beta}$$



Butadiene Delocalization Energy



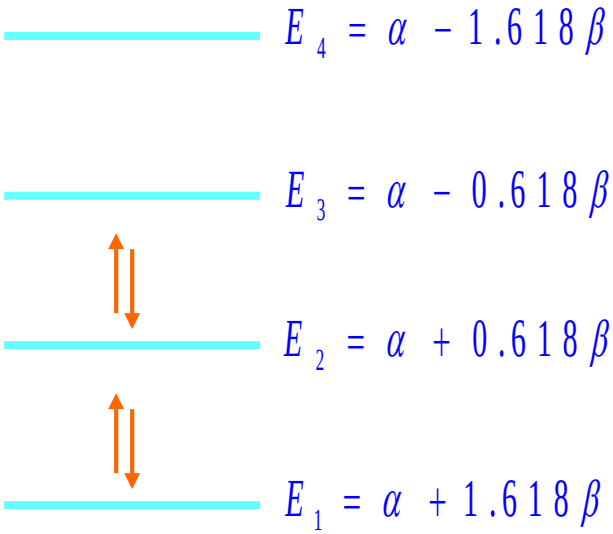
$$E_{Deloc} = E_{\pi}(C_4H_6) - 2 \cdot E_{\pi}(C_2H_4)$$

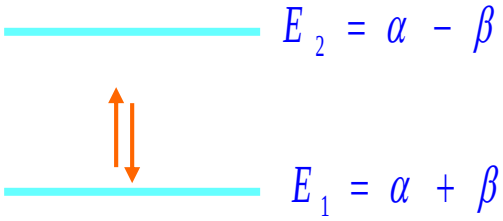
$$E_{\pi}(C_4H_6) = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$$
$$= 4\alpha + 4.472\beta$$

$$E_{\pi}(C_2H_4) = 2(2\alpha + 2\beta) = 4\alpha + 4\beta$$

$$E_{Deloc} = 4\alpha + 4.472\beta - (4\alpha + 4\beta) = 0.472\beta$$

$$E_{Deloc} \approx 0.472(-200\ kJ/mol) \approx -90\ kJ/mol$$





The additional stabilization of butadiene compared to 2 ethylenes is a result of π electron delocalization between the two double bonds.

Butadiene Wavefunctions

$$\varphi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$$

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \longrightarrow \begin{aligned} xc_1 + c_2 &= 0 \\ c_1 + xc_2 + c_3 &= 0 \\ c_2 + xc_3 + c_4 &= 0 \\ c_3 + xc_4 &= 0 \end{aligned} \xrightarrow{x_1 = -1.618} \begin{aligned} -1.618c_1 + c_2 &= 0 \\ c_1 - 1.618c_2 + c_3 &= 0 \\ c_2 - 1.618c_3 + c_4 &= 0 \\ c_3 - 1.618c_4 &= 0 \end{aligned}$$

From first equation: $c_2 = 1.618c_1$

From second equation: $c_3 = -c_1 + 1.618c_2 = -c_1 + 2.618c_1 = 1.618c_1$

From fourth equation: $c_4 = \dfrac{c_3}{1.618} = c_1$

$$\varphi = c_1\left(\chi_1 + 1.618\chi_2 + 1.618\chi_3 + \chi_4\right)$$

$$\varphi_1 = c_1\left(\chi_1 + 1.618\chi_2 + 1.618\chi_3 + \chi_4\right)$$

Normalization: $\sum_{i=1}^{4} c_i^2 = 1$ (because all overlap integrals are 0)

$$c_1^2\left[(1)^2 + (1.618)^2 + (1.618)^2 + (1)^2\right] = 1 \quad = 7.236c_1^2$$

$$c_1 = 0.372$$

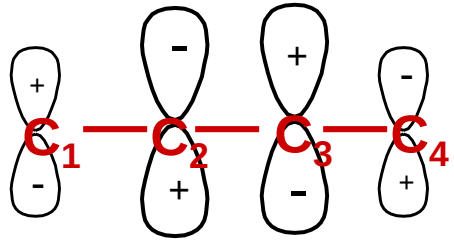
$$\varphi_1 = 0.372\left(\chi_1 + 1.618\chi_2 + 1.618\chi_3 + \chi_4\right)$$

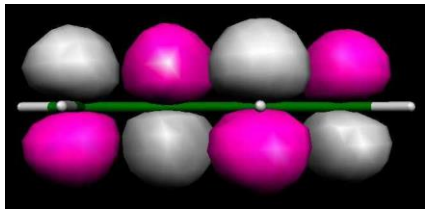
$$\boxed{\varphi_1 = 0.372\chi_1 + 0.602\chi_2 + 0.602\chi_3 + 0.372\chi_4}$$

It is straightforward to perform the same procedure to determine ϕ_2 , ϕ_3 and ϕ_4.

The results are shown on the next slide.

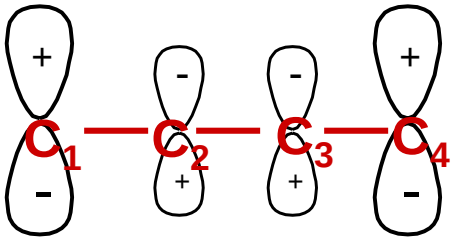
$E_4 = \alpha - 1.618\beta$

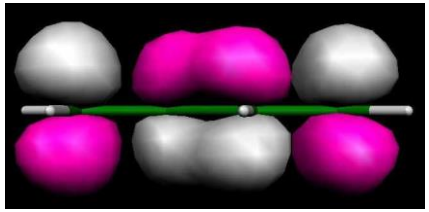




$$\varphi_4 = 0.372\chi_1 - 0.602\chi_2 + 0.602\chi_3 - 0.372\chi_4$$

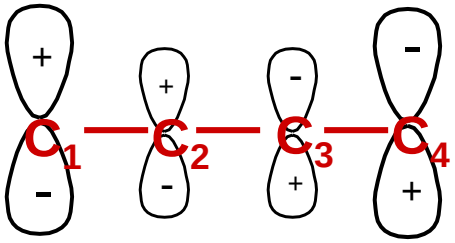
$E_3 = \alpha - 0.618\beta$

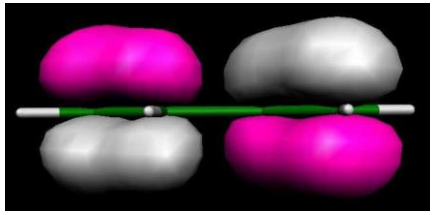




$$\varphi_3 = 0.602\chi_1 - 0.372\chi_2 - 0.372\chi_3 + 0.602\chi_4$$

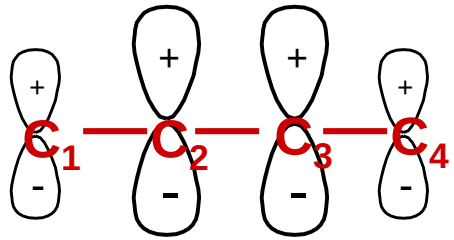
$E_2 = \alpha + 0.618\beta$

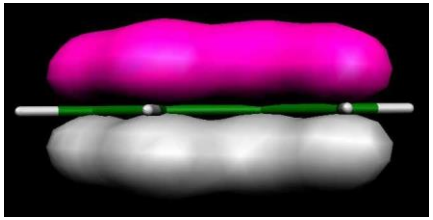




$$\varphi_2 = 0.602\chi_1 + 0.372\chi_2 - 0.372\chi_3 - 0.602\chi_4$$

$E_1 = \alpha + 1.618\beta$





$$\varphi_1 = 0.372\chi_1 + 0.602\chi_2 + 0.602\chi_3 + 0.372\chi_4$$

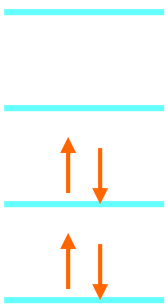
Butadiene: π Electron Charge and Bond Order

$$\varphi_4 = 0.372\chi_1 - 0.602\chi_2 + 0.602\chi_3 - 0.372\chi_4$$

$$\varphi_3 = 0.602\chi_1 - 0.372\chi_2 - 0.372\chi_3 + 0.602\chi_4$$

$$\varphi_2 = 0.602\chi_1 + 0.372\chi_2 - 0.372\chi_3 - 0.602\chi_4$$

$$\varphi_1 = 0.372\chi_1 + 0.602\chi_2 + 0.602\chi_3 + 0.372\chi_4$$



π Electron Charge: $q_\mu \equiv \sum_i^{orbs} n_i c_{i\mu}^2$

$$q_1 = 2(0.372)^2 + 2(0.602)^2 = 1.00$$

$$q_2 = 2(0.602)^2 + 2(0.372)^2 = 1.00$$

$$q_3 = 2(0.602)^2 + 2(-0.372)^2 = 1.00$$

$$q_4 = 2(0.372)^2 + 2(-0.602)^2 = 1.00$$

Actually, Butadiene (and the Allyl radical) belong to a class of hydrocarbons called "Alternant hydrocarbons", for which all $q_i = 1.0$

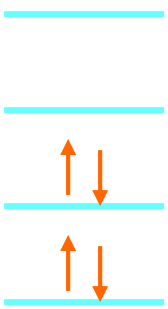
All straight-chain polyalkenes are alternant hydrocarbons.

$$\varphi_4 = 0.372\chi_1 - 0.602\chi_2 + 0.602\chi_3 - 0.372\chi_4$$

$$\varphi_3 = 0.602\chi_1 - 0.372\chi_2 - 0.372\chi_3 + 0.602\chi_4$$

$$\varphi_2 = 0.602\chi_1 + 0.372\chi_2 - 0.372\chi_3 - 0.602\chi_4$$

$$\varphi_1 = 0.372\chi_1 + 0.602\chi_2 + 0.602\chi_3 + 0.372\chi_4$$



π Bond Order: $p_{\mu\nu} \equiv \sum_i^{orbs} n_i c_{i\mu} c_{i\nu}$

$$p_{12} = 2(0.372)(0.602) + 2(0.602)(0.372) = 0.896 \approx 0.90$$

$$p_{23} = 2(0.602)(0.602) + 2(0.372)(-0.372) = 0.448 \approx 0.45$$

$$p_{34} = 2(0.602)(0.372) + 2(-0.372)(-0.602) = 0.896 \approx 0.90$$

Note: For a "full" π bond, $p_{\mu\nu} = 1$.
For a pure σ bond, $p_{\mu\nu} = 0$.

Therefore, the above bond orders reveal that the π bonds between C_1-C_2 and C_3-C_4 are not as strong as in ethylene.

$p_{23} > 0$ shows that there is significant π character in the C_2-C_3 bond.

Part A: The Hückel Model and other Semiempirical Methods

- Hückel Molecular Orbital Model
- Application to Ethylene
- Application to the Allyl Radical (C_3H_5•)
- π Electron Charge and π Bond Order
- Application to Butadiene
- **Introduction of Heteroatoms**
- Semiempirical methods for sigma bonded systems

Introduction of Heteroatoms

Introduction of a heteroatom such as N or O into a conjugated π system requires different values of α and β than those used for Carbon because the heteroatom has a different electronegativity; i.e. Eneg(C) < Eneg(N) <Eneg(O).

It is useful to put the new values of the Coulomb and Resonance Integrals, α_X and β_X (where X is the heteroatom), in terms of the original α and β.

The forms that is generally used are:

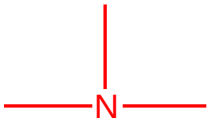
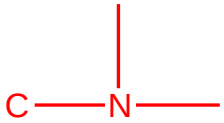
$$\alpha_X = \alpha + h_X \beta$$

and $$\beta_X = k_X \beta$$

where h_X and k_X are constants that depend upon the heteroatom.

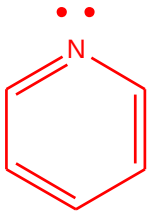
$$\alpha_X = \alpha + h_X \beta$$

$$\beta_X = k_X \beta$$

Atom	h_X	Bond	k_X
	0.5		1.0
	1.5		0.8
	2.0		0.8
	1.0		1.0
	2.0		0.4

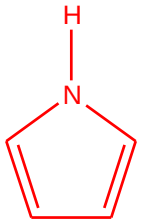
A heteroatom can donate different numbers of electrons into the π electrons depending upon its bonding.

Example: Nitrogen has 5 valence electrons



In pyridine, 4 of the 5 valence electrons are involved in (a) 2 σ bonds and (b) 2 electrons in the lone pair.

Therefore, this nitrogen will donate only 1 electron.

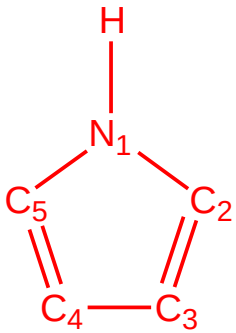


In pyrrole, 3 of the electrons will be involved in σ bonds.

This nitrogen will donate 2 electrons.

Example: π Bonding in Pyrrole

This will illustrate how a heteroatom is handled in the Hückel Molecular Orbital Model.



For pyrrole, 2 electrons are donated to the π system.

The heteroatom parameters are: $h_N = 1.5$ and $k_N = 0.8$

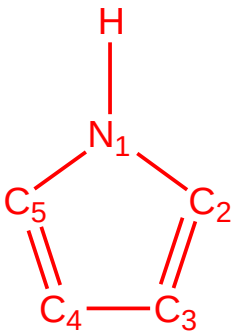
Therefore: $\alpha_N = \alpha + h_N \beta = \alpha + 1.5\beta$

$$\beta_N = k_N \beta = 0.8\beta$$

The Secular Determinant

$$\alpha_N = \alpha + 1.5\beta$$

$$\beta_N = 0.8\beta$$



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

$$\downarrow$$

$$\begin{vmatrix} \alpha + 1.5\beta - E & 0.8\beta & 0 & 0 & 0.8\beta \\ 0.8\beta & \alpha - E & \beta & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & \beta & \alpha - E & \beta \\ 0.8\beta & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \longrightarrow \begin{vmatrix} x + 1.5 & 0.8 & 0 & 0 & 0.8 \\ 0.8 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 0.8 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

$$\begin{vmatrix} x+1.5 & 0.8 & 0 & 0 & 0.8 \\ 0.8 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 0.8 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

$$\alpha_N = \alpha + 1.5\beta$$

$$\beta_N = 0.8\beta$$

This is a 5x5 Secular Determinant, which can be expanded to yield a fifth order polynomial equation, which can be solved to give:

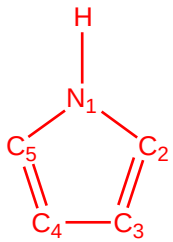
(a) five values of x.
(b) five energies.
(c) five sets of coefficients.

But, I'm just really not in the mood right now.

Howsabout I just give you the results?

No Applause, PLEASE !!!

Wavefunctions and Energies



$$\varphi_5 = \varphi_s = 0.372\chi_2 - 0.602\chi_3 + 0.602\chi_4 - 0.372\chi_5$$

$$\varphi_4 = \varphi_v = 0.374\chi_1 - 0.587\chi_2 + 0.292\chi_3 + 0.292\chi_4 - 0.587\chi_5$$

$$\varphi_3 = \varphi_r = 0.602\chi_2 + 0.372\chi_3 - 0.372\chi_4 - 0.602\chi_5$$

$$\varphi_2 = \varphi_u = 0.530\chi_1 - 0.111\chi_2 - 0.589\chi_3 - 0.589\chi_4 - 0.111\chi_5$$

$$\varphi_1 = \varphi_t = 0.725\chi_1 + 0.379\chi_2 + 0.287\chi_3 + 0.287\chi_4 + 0.379\chi_5$$

$$E_5 = E_s = \alpha - 1.618\beta$$

$$E_4 = E_v = \alpha - 1.008\beta$$

$$\uparrow\downarrow$$

$$E_3 = E_r = \alpha + 0.618\beta$$

$$\uparrow\downarrow$$

$$E_2 = E_u = \alpha + 1.189\beta$$

$$\uparrow\downarrow$$

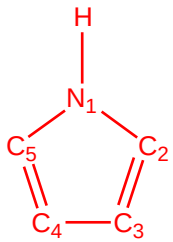
$$E_1 = E_t = \alpha + 2.320\beta$$

Note: There are 6 electrons.
Count them.

Note: Actually, I used symmetry to simplify the 5x5 determinant into a 2x2 and a 3x3 determinant

I'll show you how at the end of the chapter.

π Electron Charge



$$E_5 = E_s = \alpha - 1.618\beta$$

$$E_4 = E_v = \alpha - 1.008\beta$$

$$E_3 = E_r = \alpha + 0.618\beta$$

$$E_2 = E_u = \alpha + 1.189\beta$$

$$E_1 = E_t = \alpha + 2.320\beta$$

$$\varphi_5 = \varphi_s = 0.372\chi_2 - 0.602\chi_3 + 0.602\chi_4 - 0.372\chi_5$$

$$\varphi_4 = \varphi_v = 0.374\chi_1 - 0.587\chi_2 + 0.292\chi_3 + 0.292\chi_4 - 0.587\chi_5$$

$$\varphi_3 = \varphi_r = 0.602\chi_2 + 0.372\chi_3 - 0.372\chi_4 - 0.602\chi_5$$

$$\varphi_2 = \varphi_u = 0.530\chi_1 - 0.111\chi_2 - 0.589\chi_3 - 0.589\chi_4 - 0.111\chi_5$$

$$\varphi_1 = \varphi_t = 0.725\chi_1 + 0.379\chi_2 + 0.287\chi_3 + 0.287\chi_4 + 0.379\chi_5$$

π Electron Charge: $q_\mu \equiv \sum_i^{orbs} n_i c_{i\mu}^2$

$$q_1 = 1.61$$

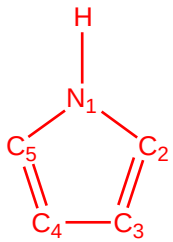
$$q_2 = 1.04$$

$$q_3 = 1.14$$

$$q_4 = 1.14$$

$$q_5 = 1.04$$

$$\sum_\mu q_\mu = 5.97 \approx 6$$



π Bond Order

$$\varphi_5 = \varphi_s = 0.372\chi_2 - 0.602\chi_3 + 0.602\chi_4 - 0.372\chi_5$$

$$\varphi_4 = \varphi_v = 0.374\chi_1 - 0.587\chi_2 + 0.292\chi_3 + 0.292\chi_4 - 0.587\chi_5$$

$$\varphi_3 = \varphi_r = 0.602\chi_2 + 0.372\chi_3 - 0.372\chi_4 - 0.602\chi_5$$

$$\varphi_2 = \varphi_u = 0.530\chi_1 - 0.111\chi_2 - 0.589\chi_3 - 0.589\chi_4 - 0.111\chi_5$$

$$\varphi_1 = \varphi_t = 0.725\chi_1 + 0.379\chi_2 + 0.287\chi_3 + 0.287\chi_4 + 0.379\chi_5$$

$$E_5 = E_s = \alpha - 1.618\beta$$

$$E_4 = E_v = \alpha - 1.008\beta$$

$$E_3 = E_r = \alpha + 0.618\beta$$

$$E_2 = E_u = \alpha + 1.189\beta$$

$$E_1 = E_t = \alpha + 2.320\beta$$

π Bond Order: $p_{\mu\nu} \equiv \sum_i^{orbs} n_i c_{i\mu} c_{i\nu}$

$$p_{12} = 0.43$$

$$p_{23} = 0.80$$

$$p_{34} = 0.58$$

$$p_{45} = 0.80$$

$$p_{15} = 0.43$$