

Oct. 26, 2009

Chem. 2430

Problem Set 1, Nov. 4, 2009, REVISED

Do the following problems from Atkins & Friedman: 8.3, 8.4, 8.7, 8.8

... plus the following two problems:

1) **Symmetry-adapted orbitals in the evaluation of the Hückel model of butadiene.** In class we discussed the Hückel model of pi-bonding in linear polyene butadiene. An underlying premise of this model is that we can represent the pi-bonding electronic orbitals of butadiene as a linear combination of 4 2pz orbitals, one located on each of the carbon atoms in the molecule. Thus, denoting the 2pz orbital located on carbon atom j as ϕ_j (taken to be unit normalized for convenience), the relevant electronic eigenfunctions are given by $\psi = \sum_{j=1}^4 c_j \phi_j$, where the c_j are superposition coefficients. They are determined via the appropriate matrix representation of the Schrödinger Eq., i.e.,

$$\mathbf{H}\vec{c} = E\vec{c}, \quad [1]$$

where the matrix element H_{ij} is given formally by $H_{jk} = \int d\vec{r} \phi_j(\vec{r}) \hat{H}_{eff} \phi_k(\vec{r})$, with \hat{H}_{eff} being the effective 1-electron Hückel Hamiltonian operator. In practice, we set $H_{jj} = \alpha$ for $j=1-4$, and $H_{jk} = \beta$ for all nearest neighbor pairs j,k (and zero for non-nearest neighbor pairs). Making the further approximation that the ϕ_j orbitals are mutually orthogonal (i.e., $\int d\vec{r} \phi_j \phi_k = 0, j \neq k$) generates the equivalent “matrix” Schrödinger Eq. noted above.

Consider the four symmetry-adapted orbitals $\chi_1 - \chi_4$ shown in Fig. 1. (Note: Orbitals χ_1, χ_2 are even under reflection through the plane which bisects the symmetry axis of the molecule, while orbitals χ_3, χ_4 are odd.)

a) Show that these orbitals form an orthonormal set, i.e., $\int d\vec{r} \chi_j^2 = 1$ and $\int d\vec{r} \chi_j \chi_k = 0; j \neq k$ for $j=1-4$.

b) Express the Hückel Hamiltonian for butadiene in this symmetry-adapted basis set. That is, let $\psi = \sum_{j=1}^4 b_j \chi_j$. Then show that Eq. 1 above is equivalent to $\tilde{\mathbf{H}}\vec{b} = E\vec{b}$, with $\tilde{H}_{jk} = \int d\vec{r} \chi_j \hat{H}_{eff} \chi_k$,

c) Show in particular that

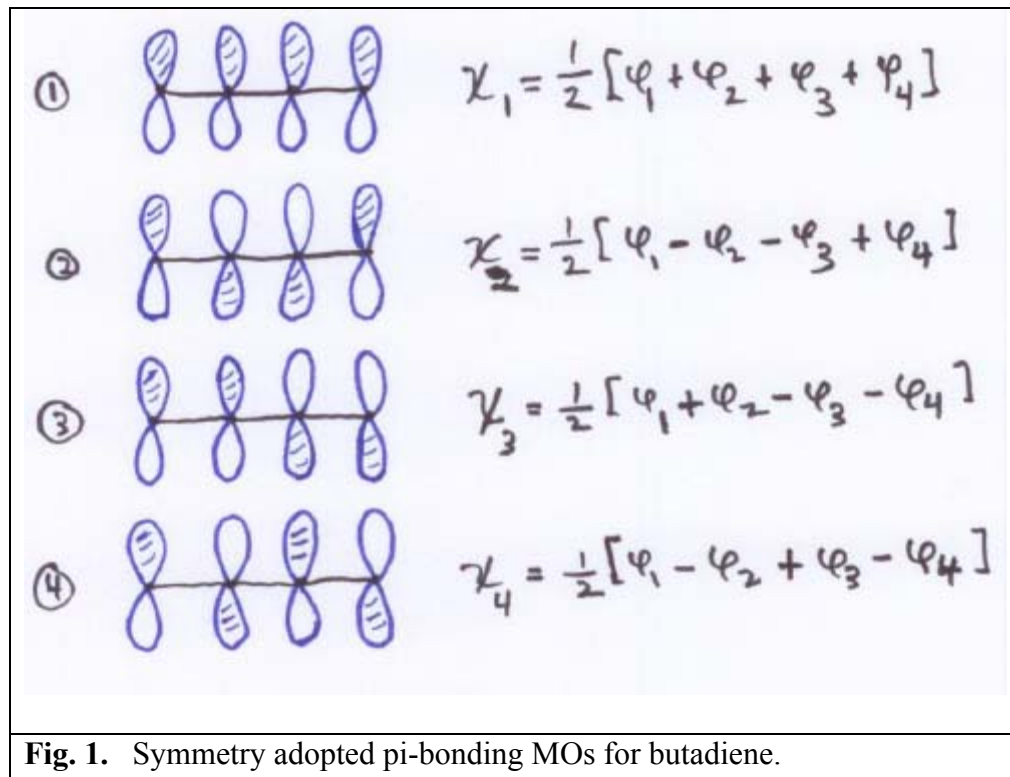
$$\tilde{H} = \begin{bmatrix} \tilde{H}_{11} & \tilde{H}_{12} & 0 & 0 \\ \tilde{H}_{21} & \tilde{H}_{22} & 0 & 0 \\ 0 & 0 & \tilde{H}_{33} & \tilde{H}_{34} \\ 0 & 0 & \tilde{H}_{43} & \tilde{H}_{44} \end{bmatrix} \quad [2]$$

where all non-zero elements are simple linear combinations of α, β . Determine these matrix elements explicitly.

d) Note that the matrix \tilde{H} is block diagonal. This implies that symmetry adapted basis functions of different symmetries *do not mix*. Thus, you can solve each of the 2x2 matrix problems contained in Eq. 2 separately. Do this! In particular:

i) Show that the 4 energy eigenvalues which emerge from this calculation are identical to those obtained in the standard treatment of butadiene within Hückel theory.

ii) Show that the corresponding 4 energy eigenfunctions (pi-bonding molecular orbitals) are identical to those obtained in the standard treatment of butadiene within Hückel theory.



2) **Alternating- β periodic conjugated pi-electron systems.** In class we discussed the Hückel theory treatment of a cyclical pi-electron system with *alternating* coupling constants β_1, β_2 . Denote the number of carbon atoms in the ring as N, and take N to be an even integer. The specific example of N=6 is illustrated in Fig. 2. Let us represent the electronic eigenfunctions of this system as $\psi = \sum_{j=1}^N c_j \phi_j$, where ϕ_j denotes the normalized 2pz orbital located on carbon atom j, and the c_j are superposition coefficients determined by solving the appropriate matrix Schrödinger Equation.

We showed in class that the eigenvector/eigenvalue equation which determines (a, b) is (see class notes for a full explanation of how these two coefficients enter into the eigenvectors of the Hückel Hamiltonian matrix):

$$\begin{bmatrix} 0 & \beta_2 e^{-2\pi i j / N} + \beta_1 e^{2\pi i j / N} \\ \beta_2 e^{2\pi i j / N} + \beta_1 e^{-2\pi i j / N} & 0 \end{bmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E' \begin{pmatrix} a \\ b \end{pmatrix}$$

where $E' = E - \alpha$. (Here α is the usual diagonal Hückel Hamiltonian matrix element, which is taken to be the same for all carbon atoms in the chain.) For a given value of j, this implies the eigenvalue pair:

$$E_j' = \pm \left[\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos(4\pi j / N) \right]^{1/2} \quad [3]$$

Since there are a total of N eigenvectors/values in all, the index j can be taken to run from $j = 1, 2, \dots, N/2$.

a) Consider the special case that $\beta_1 = \beta_2$. Take as a specific example a cyclical chain of length N=8. Calculate numerically the 8 energy eigenvalues implied by Eq. 3 above with $j = 1 - 4$, and show that the *same* 8 energies are obtained from the “standard” (single β) Hückel model energy eigenvalue formula for a cyclic pi-system, which was given in class (or can be found in the Atkins textbook).

b) In the general case $\beta_1 \neq \beta_2$, we discussed in class that for large N the allowed energy eigenvalues fall into two bands. Deduce the general location of the band edges (in terms of α, β_1, β_2), and, in particular, determine

i) the band width

ii) the band gap

predicted by this model.

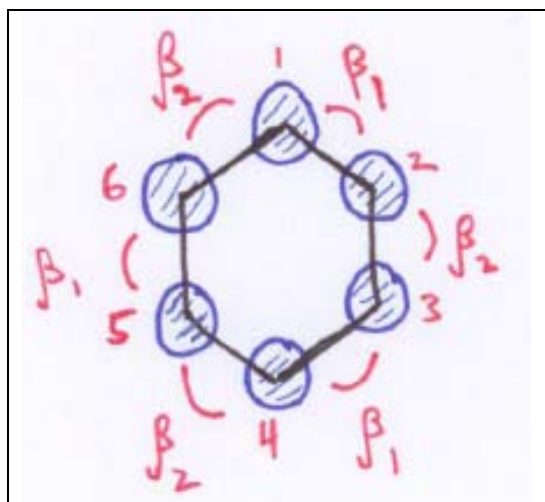


Fig. 2. Alternating coupling (β) model for a cyclic hydrocarbon with $N=6$ carbon atoms. (View is looking down from top of ring. Each orbital is of $2p_z$ type.)