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 \(\phi_j\) (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.,

\[
H \tilde{c} = E \tilde{c},
\]

where the matrix element \(H_{ij}\) is given formally by

\[
H_{jk} = \int d\bar{r} \phi_j(\bar{r}) \hat{H}_{\text{eff}} \phi_k(\bar{r}),
\]

with \(\hat{H}_{\text{eff}}\) 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 \(\phi_j\) orbitals are mutually orthogonal (i.e., \(\int d\bar{r} \phi_j \phi_k = 0, j \neq k\)) generates the equivalent “matrix” Schrödinger Eq. noted above.

Consider the four symmetry-adapted orbitals \(\chi_1-\chi_4\) shown in Fig. 1. (Note: Orbitals \(\chi_1, \chi_2\) are even under reflection through the plane which bisects the symmetry axis of the molecule, while orbitals \(\chi_3, \chi_4\) are odd.)

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

\[
\hat{H} \tilde{b} = E \tilde{b},
\]

with

\[
\hat{H}_{jk} = \int d\bar{r} \chi_j \hat{H}_{\text{eff}} \chi_k,
\]

c) Show in particular that
where all non-zero elements are simple linear combinations of $\alpha, \beta$. 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.

Fig. 1. Symmetry adopted pi-bonding MOs for butadiene.
2) **Alternating-\(\beta\) periodic conjugated pi-electron systems.** In class we discussed the Hückel theory treatment of a cyclical pi-electron system with *alternating* coupling constants \(\beta_1, \beta_2\). 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 \(\phi_j\) 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):

\[
\begin{bmatrix}
0 & \beta_2 e^{-2\pi ij/N} + \beta_1 e^{2\pi ij/N} \\
\beta_2 e^{2\pi ij/N} + \beta_1 e^{-2\pi ij/N} & 0
\end{bmatrix}
\begin{bmatrix}
a \\
b
\end{bmatrix}
= E' \begin{bmatrix}
a \\
b
\end{bmatrix}
\]

where \(E' = E - \alpha\). (Here \(\alpha\) 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:

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

[3]

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

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 \(\beta\)) 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 \(\alpha, \beta_1, \beta_2\)), and, in particular, determine

i) the band width

ii) the band gap

predicted by this model.
Fig. 2. Alternating coupling ($\beta$) model for a cyclic hydrocarbon with N=6 carbon atoms. (View is looking down from top of ring. Each orbital is of 2pz type.)