CHEMISTRY 273

PROBLEM SET #2

4. In the lecture on simplification of the Huckel hamiltonian $\underline{\underline{\mathbf{H}}}$, we wrote

$$\underline{\underline{\mathbf{H}}}' = \beta^{-1}(\underline{\underline{\mathbf{H}}} - \alpha\underline{\underline{\mathbb{1}}})$$

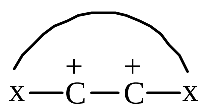
Show that $\underline{\underline{\mathbf{H}}}$ and $\underline{\underline{\mathbf{H}}}'$ have the same eigenvectors ($\underline{\underline{\mathbf{C}}} = \underline{\underline{\mathbf{C}}}'$) and that the eigenvalues are related by

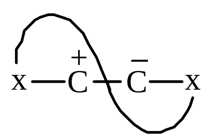
$$\underline{\underline{\mathbf{E}}} = \underline{\underline{\mathbf{E}}}'\beta + \alpha\underline{\underline{\mathbb{1}}}$$

A qualitative "feel" for the energies and wavefunctions for linear and monocyclic conjugated polyenes is of great utility in "back of the envelope chemistry." To this end, problems 5 and 6 are to be done with the help of MATLAB.

5. For the linear polyenes butadiene (C_4H_6) and hexatriene (C_6H_8)

(a) Sketch the m.o.'s à la those in ethylene:

ϕ_1: 

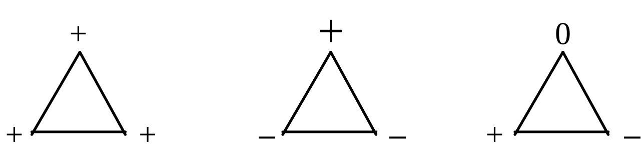
ϕ_2: 

(b) Are there any degeneracies of the energy levels in these polyenes?

(c) Compare the eigenvalues and coefficients of the a.o.'s in ϕ_i and ϕ_{N+1-i} for the *alternate* hydrocarbons. (i = 1, 2 for butadiene; i = 1, 2, 3 for hexatriene.)

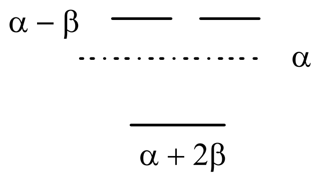
6. For the conjugated cyclic polyenes cyclobutadiene (C_4H_4) cyclopentadienyl (C_5H_5), and benzene (C_6H_6)

(a) Sketch the m.o.'s à la those in cyclopropenyl (C_3H_3):



ϕ_1 ϕ_2 ϕ_3

(b) Sketch energy level diagrams à la those for C_3H_3 below:



(c) For C_4H_4 and for C_5H_5 is there any relation between E_i and E_{N+1-i}? Is there a relationship between the coefficients for ϕ_i and ϕ_{N+1-i}?

7. The inverse square root matrix $\underline{\underline{S}}^{-1/2}$ is a very useful construct in a variety of quantum mechanical situations. This matrix is obtained by the following manipulation:

Given a unitary transformation $\underline{\underline{U}}$ which diagonalizes $\underline{\underline{S}}$ (note $\underline{\underline{S}}$ is hermitian and real)

$$\underline{\underline{\tilde{U}}}\,\underline{\underline{S}}\,\underline{\underline{U}} = \underline{\underline{D}} = \begin{pmatrix} \boldsymbol{d_1} & & \mathbf{0} & \\ & \boldsymbol{d_2} & & \mathbf{0} \\ & & \ddots & \\ \mathbf{0} & & & \boldsymbol{d_n} \end{pmatrix}$$

then $\underline{\underline{S}}^{-1/2} = \underline{\underline{U}}\,\underline{\underline{D}}^{-1/2}\underline{\underline{\tilde{U}}}$

where $\underline{\underline{D}}^{-1/2} = \begin{pmatrix} \boldsymbol{d_1^{-1/2}} & & & \\ & \boldsymbol{d_2^{-1/2}} & & \mathbf{0} \\ & & \ddots & \\ \mathbf{0} & & & \boldsymbol{d_n^{-1/2}} \end{pmatrix}$ and $d_1^{-1/2} = \sqrt{\frac{1}{d_i}}$.

It can be shown $\underline{\underline{S}}^{-1/2}$ has all the properties you would expect, for example:

$\underline{\underline{S}}^{-1/2}\underline{\underline{S}}^{-1/2} = \underline{\underline{S}}^{-1}$ and $\underline{\underline{S}}^{-1/2}\underline{\underline{S}} = \underline{\underline{S}}^{1/2}$.

(a) From the definition of $\underline{\underline{S}}^{-1/2} = \underline{\underline{U}}\,\underline{\underline{D}}^{-1/2}\underline{\underline{\tilde{U}}}$, formally proved:

$$\underline{\underline{S}}^{-1/2}\underline{\underline{S}}\,\underline{\underline{S}}^{-1/2} = \underline{\underline{\mathbb{1}}}$$

(b) Using MATLAB (or whatever) find $\underline{\underline{\mathbf{S}}}^{-1/2}$ for a "real" LCAO overlap matrix where

$S_{11} = \langle \chi_1 | \chi_1 \rangle = 1 = S_{22}$ $\quad S_{12} = \langle \chi_1 | \chi_2 \rangle = .25 = S_{21}$

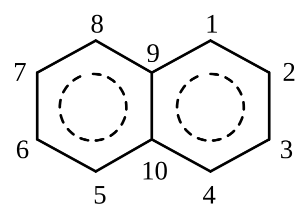
and thus

$$\underline{\underline{\boldsymbol{S}}} = \begin{pmatrix} \mathbf{1} & \mathbf{.25} \\ \mathbf{.25} & \mathbf{1} \end{pmatrix}$$

in this exercise you will need the MATLAB functions [$\underline{\underline{U}}$, $\underline{\underline{D}}$] = eig ($\underline{\underline{S}}$) for unitary transform $\underline{\underline{\mathbf{U}}}$ and eigenvalue matrix $\underline{\underline{\mathbf{D}}}$ and $\underline{\underline{U'}} \equiv \underline{\underline{\tilde{U}}}$ is the transpose of $\underline{\underline{U}}$.

problems #8 and #9 should be done with the Huckel program provided; this program will predicted bond lengths from the bond length ⇔ bond order relationship and calculate electronic populations.

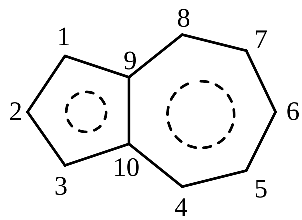
8. For naphthalene as numbered below:



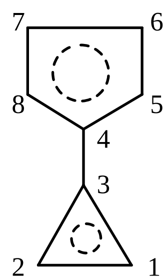
Use a Huckel calculation to predict the bond lengths and compare to these experimental values.

1-2	1.365 Å
2-3	1.404 Å
1-9	1.425 Å
9-10	1.393 Å

9. For azulene



compare the charges on atoms 1, 2 with those on 4, 5, and 6, and for



compare the charges on atoms 1, 2, 3 with those on 4, 5, 6, 7, 8.

Explain the pattern you observe in these two molecules.