Chem 1410 **Homework #5** **Jordan**

Due: Thursday, November 4, 1999

1. Consider the Hückel model for hexatriene and benzene. Using Mathcad, calculate the orbital energies.

   Compare the HOMO-LUMO gap in these two molecules. Comment on this with respect to the relative stability of hexatriene and benzene.

   The total π electron energy can be defined as $E_{tot} = \sum_{i=1}^{OCC} \varepsilon_i$, where i runs over the occupied orbitals.

   Use E_{tot} values to estimate the stabilization of benzene due to aromaticity.

Hints: Recall that you can replace a Hückel matrix with α's and β's with a matrix filled with 0's and 1's $(\alpha \rightarrow 0, \beta \rightarrow 1)$.

In Mathcad:

type m:
then at the placeholder
choose insert matrix from the top "toolbar"
enter the dimension of the matrix
enter 0's and 1's in the appropriate places
then type eigenvals(m) =
to get the eigenvalues.
multiply each eigenvalue by β and add α to get the correct Hückel eigenvalues.

Note: eigenvec(x) = will give the eigenvector associated with the eigenvalue X (you must enter the value of x).

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2. Solve for the Huckel eigenvalues of cyclobutadiene. What is the term symbol of the expected ground state? (Use the correct group theoretical label.)

3. Sketch the MO's of cyclobutadiene and label them according to the proper symmetry representations.

4. How do you expect the geometry will change in each of the following cases.
   a) allyl radical upon ionization from the HOMO.
   b) cyclopropenyl radical upon electron attachment.
   c) CO_2 upon electron attachment.
   d) acetylene upon HOMO → LUMO excitation.