Problem Set 11
(optional)

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Background:  Chapter 12, 13.2, 14.7, Handouts on variation and Hückel method (2)
Problems:  6 problems (see back for #6)

Due Date:  These problems will not be collected. You can check your results in most cases using the SHMO calculator (there is a link to the calculator from the Chem 333 home page. I will try to post answers for the others.

1. Use Mathematica to calculate HMO energies and orbital coefficients for the $\pi$ systems of the following molecules. Which orbitals are occupied and which are not?

   ![Molecules]

2. Draw cartoons of the MOs for each of the molecules in #1. Label each MO as symmetric or antisymmetric with respect to a plane of symmetry in the molecule? (Are any MOs neither symmetric nor antisymmetric?) Do the MOs become more unstable as the number of nodes increases? What are the charge distributions and bond orders in these molecules?

3. How does $E_\pi$ change when hexatriene is converted to vinylcyclobutadiene? To benzene? Obtain your answer in two ways: 1) calculate MO energies and $E_\pi$ for each molecule; 2) use first-order perturbation methods to estimate the changes in hexatriene’s MO energies, and from these, the changes in $E_\pi$.

4. ![MOs]

5. Which of these molecules contains the most (and least) stable $\pi$ system? Cyclodecapentaene? Naphthalene? Azulene? (See flip side for formulas.) You should be able to work this problem three different ways: 1) normal HMO calculations, 2) first-order perturbation methods converting the monocyclic compound into the two bicyclics, 3) Dewar’s PMO method uniting a $C_1$ and $C_0$ fragment in three different ways (note: these fragments are odd-alternant hydrocarbons). When you use Dewar’s method, make sure you figure out the orbital coefficients for the SOMOs of the two fragments.
6. Which of the molecules in this problem set are alternant hydrocarbons? Which are even-alternant? Which are odd-alternant? Do their MO energies show the expected patterns?