

ASSIGNMENT 6

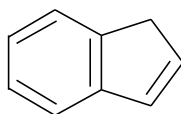
DUE: March 14, 2000

1. For Hückel theory, show that the total energy of a system can be expressed as

$$E = n \mathbf{a} + 2\mathbf{b} \sum_{\substack{\text{bonds} \\ k < l}} p_{kl}$$

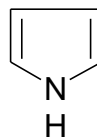
where n is the number of electrons, and p_{kl} is the total π bond order between atoms k and l . We say that $k < l$ just to make sure that each bond is counted only once.

2. Sketch the HOMO and LUMO for the indenyl anion (neutral indene is shown



here).

3. Consider the 6- π heterocyclic system, pyrrole.



One way to calculate the energy is to apply perturbation theory. Assume that for the nitrogen atom, the coulomb integral is $\mathbf{a} + \frac{3}{2}\mathbf{b}$, rather than simply \mathbf{a} . Apply first-order perturbation theory to calculate the effect of this change on the total energy.

4. With a numerical eigenvalue routine, it is also possible to solve this problem exactly. Set up the Hückel matrix for pyrrole, solve for the eigenvalues, and calculate the total energy.