

SOLUTIONS TO ASSIGNMENT 6

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.

Consider a single molecular orbital, expressed as a linear combination of carbon $2p$ orbitals.

$$\mathbf{f}_k = \sum_{i=1}^n c_{ik} p_i$$

The expectation value of the Hamiltonian over this orbital is given by

$$\begin{aligned} \langle \mathbf{f}_k | H | \mathbf{f}_k \rangle &= \left\langle \sum_i c_{ik} p_i \left| H \right| \sum_j c_{jk} p_j \right\rangle \\ &= \sum_i \sum_j c_{ik} c_{jk} \langle p_i | H | p_j \rangle \end{aligned}$$

But, $\langle p_i | H | p_i \rangle = \mathbf{a}$, and is zero if $i \neq j$, and $\langle p_i | H | p_j \rangle = \mathbf{b}$ if i and j are bonded, by definition. The total energy is just the sum of the orbital energies, weighted by the number of electrons.

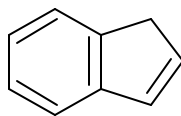
$$\begin{aligned} \text{Energy} &= \sum_k n_k \langle \mathbf{f}_k | H | \mathbf{f}_k \rangle \\ &= \sum_k n_k \sum_i \sum_j c_{ik} c_{jk} \langle p_i | H | p_j \rangle \\ &= \sum_k n_k \left(\sum_i c_{ik}^2 \langle p_i | H | p_i \rangle + \sum_{i \neq j} c_{ik} c_{jk} \langle p_i | H | p_j \rangle \right) \\ &= \sum_k n_k \left(\mathbf{a} \sum_i c_{ik}^2 + \mathbf{b} \sum_{i \neq j} c_{ik} c_{jk} \right) \end{aligned}$$

Since the wavefunction is normalized, $\sum_i c_{ik}^2 = 1$. Also, the definition of the bond order is

$$p_{ij} = \sum_k n_k c_{ik} c_{jk}$$

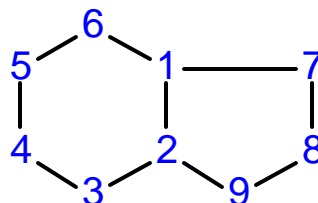
Re-arranging the sums in the expression for the energy gives the final result.

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



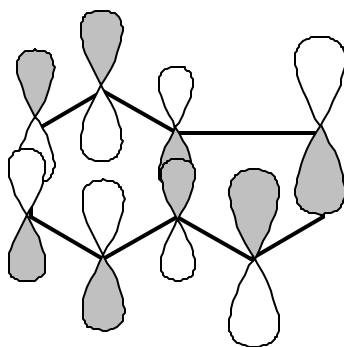
here).

We can number the molecule as follows (despite the drawing, there is a two-fold symmetry):

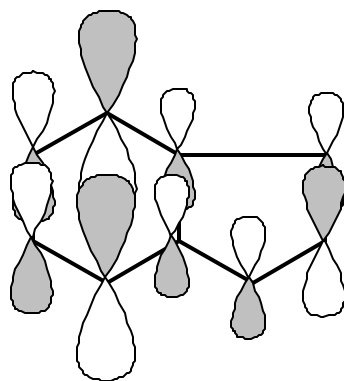


The coefficients for the HOMO and LUMO are given in the table (note that the overall sign of the wavefunction is not important. If you get coefficients which are all of the opposite sign, this is still the same wavefunction).

	Eigen	C1	C2	C3	C4	C5	C6	C7	C8	C9
HOMO	0.295	0.160	-0.160	0.336	0.259	-0.259	-0.336	0.543	0.0	-0.543
LUMO	-0.901	0.204	0.204	-0.542	0.285	0.285	-0.542	0.155	-0.343	0.155

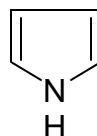


HOMO



LUMO

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.

For any wavefunction, the first-order perturbed energy is just the matrix element of the perturbation with the unperturbed wavefunction.

$$\langle \mathbf{f}_k | H' | \mathbf{f}_k \rangle = \left\langle \sum_i c_{ik} p_i \left| H' \right| \sum_j c_{jk} p_j \right\rangle$$

The perturbation in this case affects only the p orbital of the carbon that becomes nitrogen. If that is called carbon 1, then the perturbed energy is given by

$$\begin{aligned} \langle \mathbf{f}_k | H' | \mathbf{f}_k \rangle &= \left\langle \sum_i c_{ik} p_i \left| H' \right| \sum_j c_{jk} p_j \right\rangle \\ &= \langle c_{1k} p_1 | H' | c_{1k} p_1 \rangle \\ &= c_{1k}^2 \langle p_1 | H' | p_1 \rangle \\ &= c_{1k}^2 \left(\frac{3}{2} \mathbf{b} \right) \end{aligned}$$

Therefore, the total energy perturbation is just the sum of the energies of the perturbed orbitals, times the number of electrons occupying the orbital (in the same way as we calculate the total energy).

$$\begin{aligned}\text{Perturbed Energy} &= \sum_k^{\text{occupied}} n_k \langle \mathbf{f}_k | H' | \mathbf{f}_k \rangle \\ &= \left(\frac{3}{2} \mathbf{b} \right) \sum_k^{\text{occupied}} n_k c_{1k}^2\end{aligned}$$

Remember, this is the *unperturbed* wavefunction, so the coefficients are from the 6π electron carbon system, cyclopentadiene anion. The sum can be worked out directly from the coefficients, or we can recognize that this is the electron density on carbon 1, which will be 1.2 (by symmetry for the anion, or by calculation). Therefore the perturbed energy is $1.8\mathbf{b}$. The energy of cyclopentadiene anion is $2*(2+0.618+0.618) = 6.472\mathbf{b}$, so the total perturbed energy is $8.272\mathbf{b}$.

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.

The Hückel matrix for pyrrole, in the format suitable for calculation by MAPLE, is.

$$\begin{bmatrix} 3/2 & 1 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 1 & 0 \end{bmatrix}$$

The eigenvalues are $[-1.618033989, -1.196818401, .6180339900, 1.146842175, 2.549976224]$, so the total energy is $2*(2.500+1.147+0.618) = 8.630\mathbf{b}$, which is comparable to the perturbation solution, but lower (remember the variation principle).