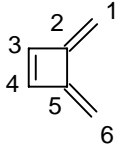
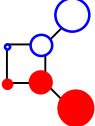


Problem Set 11

Answers to Selected Problems

Problem 1A

First, number the C in the pi system. One possible numbering scheme is shown in the table. Then construct a matrix based on this numbering scheme. Finally, obtain the eigenvalues and eigenvectors of this matrix, and convert these data into energies and orbital coefficients. Notice that *Mathematica* does not list the eigenvalues in numerical order, so you will have to sequence them yourself. On the other hand, *Mathematica* uses the same sequence for the eigenvalues and eigenvectors (and it uses your numbering scheme for the coefficients in each eigenvector).

Numbering scheme	
Matrix	$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}$
Eigenvalues & Energies	$\{2.24698, -2.24698, 0.801938, -0.801938, -0.554958, 0.554958\}$ $E_3 = \alpha + 0.55 \beta$ $E_6 = \alpha - 2.25 \beta$ $E_2 = \alpha + 0.80 \beta$ $E_5 = \alpha - 0.80 \beta$ $E_1 = \alpha + 2.25 \beta$ $E_4 = \alpha - 0.55 \beta$
Eigenvector 3 & MO 2 (these refer to the same entity; I say <u>eigenvector 3</u> in keeping with the eigenvalue list, but this eigenvalue corresponds to <u>MO 2</u>)	$\{-0.521121, -0.417907, -0.231921,$ $0.231921, 0.417907, 0.521121\}$ $\psi_2 = -.52 p_1 - .42 p_2 - .23 p_3 + .23 p_4 + .42 p_5 + .52 p_6$ 

The molecule's pi system contains 6 electrons. These electrons fill MO 1-3.

Problem 2A

Cartoons for MO 2 and 5 (eigenvectors 3 and 4) are shown below. The molecule is described by a plane of symmetry that bisects the C₂-C₅ and C₃-C₄ bonds (see problem 1A for atom numbering). This plane is a nodal surface for MO 2 and MO2 is antisymmetric with respect to this plane. The symmetry plane is not a nodal surface for MO 5 and this orbital is symmetric with respect to this plane even though it possesses two nodal surfaces.



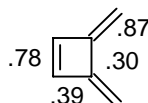
The symmetries of the MO and the # nodal surfaces are listed below. (Note: I ignore the molecular plane when I think about symmetry and count nodal surfaces of pi MOs.) Generally, the MOs become more unstable as the number of nodes increases.

MO	Symmetry wrt Plane	# nodal surfaces
6	A	3
5 (see cartoon above)	S	2
4	A	2
3	S	1
2 (see cartoon above)	A	1
1	S	0

Charge distribution: every C is neutral (this corresponds to 1.0 pi electrons on every C). A sample calculation for the pi electron density on C₁ is shown below. The calculation multiplies the occupancy of MO 1-3 (= 2) by the square of the orbital coefficient on C₁ in each orbital (it is necessary to use normalized coefficients for this calculation).

$$\text{Pi electron density on C}_1 = 2(-.232)^2 + 2(-.521)^2 + 2(.418)^2$$

Pi bond orders: the orders vary from .30 to .87 as shown on the drawing (because the molecule is symmetric, I have not shown results for all bonds). Notice that much higher bond orders (.78 and .87) are located where a double bond appears in the Lewis structure. On the other hand, the pi bond order is not zero at single bonds (.30 and .39).



A sample calculation for the C₁-C₂ pi bond order is shown below. The calculation multiplies the products of the atomic coefficients in each MO by the MO occupancy, and sums them over all occupied MOs (it is necessary to use normalized coefficients for this calculation).

$$\text{Pi bond order C}_1\text{-C}_2 = 2 \times (-.232 \times -.521) + 2 \times (-.521 \times -.418) + 2 \times (.418 \times .232)$$

Problem 3A

Method 1 – Direct calculation. A direct calculation of ΔE_π for hexatriene \rightarrow vinylcyclobutadiene requires a calculation of E_π for both molecules. This quantity is the sum of the electron energies.

SHMO (I'm lazy) gives the following energies for occupied MO:

Hexatriene occupied MO energies: $\alpha + 1.80 \beta$, $\alpha + 1.25 \beta$, $\alpha + 0.44 \beta$

$$E_\pi = 2 (\alpha + 1.80 \beta + \alpha + 1.25 \beta + \alpha + 0.44 \beta) = 6 \alpha + 7.0 \beta$$

Vinylcyclobutadiene occupied MO energies: $\alpha + 2.18 \beta$, $\alpha + 1.13 \beta$, α (2 degenerate singly occupied MO)

$$E_\pi = 2 (\alpha + 2.18 \beta + \alpha + 1.13 \beta + \alpha + \alpha) = 6 \alpha + 6.6 \beta$$

$$\Delta E_\pi = (6 \alpha + 6.6 \beta) - (6 \alpha + 7.0 \beta) = -0.4 \beta$$

Method 2 – Perturbation calculation. Hexatriene \rightarrow vinylcyclobutadiene requires an intramolecular geometry change (it also requires that I make two H disappear; since I am only interested in the pi electrons, I will invoke my magic powers: *shazam!*). An intramolecular geometry change causes first-order changes in the orbital energies: $\epsilon_i = \epsilon_i^0 + P_{ii}$. The perturbation energy is $2 \beta (c_1^0 c_4^0)$ (I only look at the coefficients on atoms that become bonded together by the geometry change.)

$$P_{11} = 2 \beta (.232 \times .521) = .24 \beta$$

$$P_{22} = 2 \beta (.418 \times -.232) = -.19 \beta$$

$$P_{33} = 2 \beta (.521 \times -.418) = -.44 \beta$$

At this point, we could combine these perturbation energies with the zero-order MO energies to get first-order MO energies. Adding these corrections to the hexatriene MO energies gives:

$$\epsilon_1 = \alpha + 1.80 \beta + .24 \beta = \alpha + 2.04 \beta \quad \text{compare to } \alpha + 2.18 \beta$$

$$\epsilon_2 = \alpha + 1.25 \beta - .19 \beta = \alpha + 1.06 \beta \quad \text{compare to } \alpha + 1.13 \beta$$

$$\epsilon_3 = \alpha + 0.44 \beta - .44 \beta = \alpha \quad \text{compare to } \alpha$$

The corrected energies are quite close to the exact answers.

ΔE_π , however, is the sum of these perturbations, so it is not necessary to calculate the corrected MO energies. In other words, $\Delta E_\pi = 2 (.24 - .19 - .44) \beta = -.78 \beta$. The exact answer is -0.4β . The perturbation calculation gives the correct direction for the change, but clearly first-order corrections alone are not quantitatively reliable.

Problem 4 does not exist

Problem 5**Method 1 – direct (S)HMO calculations. Pi energies (from SHMO)**

Cyclodecapentaene

MO energies = $\alpha + 2.00 \beta$, $\alpha + 1.62 \beta$, $\alpha + 1.62 \beta$, $\alpha + 0.62 \beta$, $\alpha + 0.62 \beta$ $E_{\pi} = 10 \alpha + 12.9 \beta$

Naphthalene

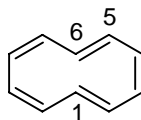
MO energies = $\alpha + 2.30 \beta$, $\alpha + 1.62 \beta$, $\alpha + 1.30 \beta$, $\alpha + 1.00 \beta$, $\alpha + 0.62 \beta$ $E_{\pi} = 10 \alpha + 13.7 \beta$

Azulene

MO energies = $\alpha + 2.31 \beta$, $\alpha + 1.65 \beta$, $\alpha + 1.36 \beta$, $\alpha + 0.89 \beta$, $\alpha + 0.48 \beta$ $E_{\pi} = 10 \alpha + 13.4 \beta$

The most stable pi system is found in naphthalene. The least stable in cyclodecapentaene.
Note: all three molecules are aromatic.

Method 2 – first-order perturbation calculation for intramolecular geometry change (convert cyclodecapentaene into other two molecules). If the orbital coefficients are the same sign, the orbital will be stabilized because $\epsilon_i = \epsilon_i^{\circ} + P_{ii}$ and the perturbation energy is $2 \beta (c_i^{\circ} c_j^{\circ})$. Based on the following drawing, I can see that joining atoms 1 and 6 produces naphthalene and joining atoms 1 and 5 produces azulene.

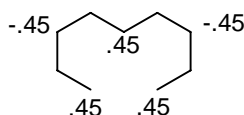


When I look at the tables of MO coefficients, I am free to choose any atom as C_1 . Once I make this choice, it fixes C_6 , but I still have two atoms to choose between for C_5 . Once I have selected all three atoms, I need to use them consistently when I refer to orbital coefficients. The following table shows my choices, but others are possible.

ϵ_i° (cyclodecapentaene)	c_1°, c_6°	P_{ii} (naphthalene)	c_1°, c_5°	P_{ii} (azulene)
0.62 β	.362, .362	.26 β	.362, -.138	-.10 β
0.62 β	-.263, -.263	.14 β	-.263, -.425	.22 β
1.62 β	-.138, .138	-.04 β	-.138, .362	-.10 β
1.62 β	-.425, .425	-.36 β	-.425, .263	-.22 β
2.00 β	-.316, -.316	.20 β	-.316, -.316	.20 β
ΔE_{π}		.40 β		0 β

The perturbation calculations predict that naphthalene's pi electrons are 0.4β more stable than cyclopentadecaene's, but the pi electrons in azulene and cyclopentadecaene have the same energy. Comparison with the exact energy changes shows that the energy differences are all *underestimated* by the perturbation calculations.

Method 3 – Dewar PMO calculation for intermolecular geometry change (convert methyl radical + nonatetraenyl radical into three other molecules). I need the NBMO coefficients for each radical. These are easily obtained using methods described elsewhere. The coefficients for nonatetraenyl radical are shown below, and the orbital coefficient for methyl radical is 1.



Uniting the two radicals changes the MO energies, but Dewar says to ignore most of the orbitals, and accept $2\Delta\epsilon_{\text{NBMO}}$ as equivalent to ΔE_{π} (the factor of 2 appears because the NBMO on the two radicals are occupied by 2 electrons). $\Delta\epsilon_{\text{NBMO}}$ is calculated by combining orbital coefficients where new bonds are created by the geometry change (rules for calculating P_{ij} have been given elsewhere). The following diagrams highlight the new bonds, and the estimated change in ΔE_{π} ($= 2\Delta\epsilon_{\text{NBMO}}$).

Cyclodecapentaene		$\Delta E_{\pi} = 2[(.45)(1)+(.45)(1)] \beta = 1.8 \beta$
Azulene		$\Delta E_{\pi} = 2[(.45)(1)+(.45)(1)] \beta = 1.8 \beta$
Naphthalene		$\Delta E_{\pi} = 2[(.45)(1)+(.45)(1)+(0.45)(1)] \beta = 2.2 \beta$

As you can see, PMO calculations are much easier to do than normal perturbation calculations, but that doesn't make them more accurate. In fact, the results in this case happen to be the same. Naphthalene's pi electrons are estimated to be 0.4β more stable than those in azulene or cyclopentadecaene.

You might have been disappointed that method 2, the first-order perturbation treatment, didn't do a better job of reproducing the exact energy differences obtained using method 1. The PMO results are no better, but they are also no worse, and I find it pleasing that such a simple method can do so well.

Problem 6

Even AHC – cyclodecapentaene and naphthalene
Odd AHC – methyl radical and nonatetraenyl radical
Non-AHC – azulene

(SH)MO energy patterns agree with the predictions of the pairing theorem:

Even AHC Both molecules – 0 NBMO, 5 BMO, 5 ABMO, **MO energies are all paired**
Odd AHC Methyl radical – 1 NBMO
Nonatetraenyl radical – 1 NBMO, 4 BMO, 4 ABMO, **BMO and ABMO energies are all paired**
Non-AHC Azulene – 0 NBMO, 5 BMO, 5 ABMO, **MO energies are not paired**