

Huckel Theory II

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In the current lesson we will expand on Huckel theory investigating the properties of molecules that are most easily determined from the molecular orbitals. These properties include: π atomic charges on atoms, π bond orders, ionization energies, electron affinities, and resonance energies. The same properties can be determined from the molecular orbitals calculated using far more sophisticated techniques than Huckel theory, but the determination is essentially the same.

Objectives: Students will be able to use Huckel calculations to

1. construct molecular orbitals as linear combinations of atomic orbitals.
2. calculate π partial atomic charges.
3. predict sites for electrophilic or nucleophilic attack from partial charges.
4. calculate π bond orders.
5. predict ionization energies and electron affinities.
6. predict resonance stabilization energies.

Knowledge Assumed:

The student should have worked through the Mathcad template: Huckel I. Some Organic Chemistry knowledge will be assumed, especially some terminology and knowledge of the "4n+2" rule.

Footnotes:

1. Lowe, John P. Quantum Chemistry, 2nd Ed., Academic Press, 1993.
2. Levine, Ira Quantum Chemistry, 5th Ed., Prentice Hall, 2000.
3. Schaad, L. J. and Hess, B. A. *J. Amer. Chem. Soc.*, **1972** 94(9) 3068-3074.

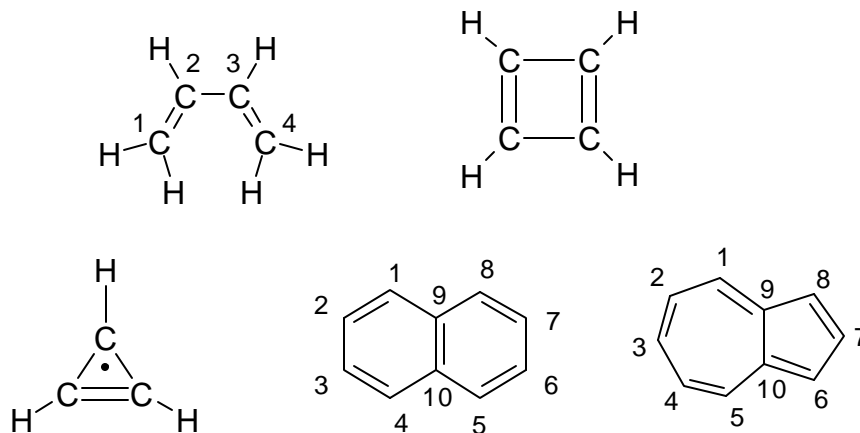
Other references relevant to the concepts presented here and to Huckel Theory in general can be found in the Huckel I lesson and **at the end of this lesson.**

Notes:

What I want you to read and study is in **maroon**, problems are in **teal** and are numbered, and equations and titles are in **black**. Please carry out your solutions to the problems in Mathcad, but organize your answers to be handed in on paper drawn neatly or with the help of a word processor (preferable) and labelled with my numbering.

Graphics in this document were generated with ISIS/Draw and Hyperchem.

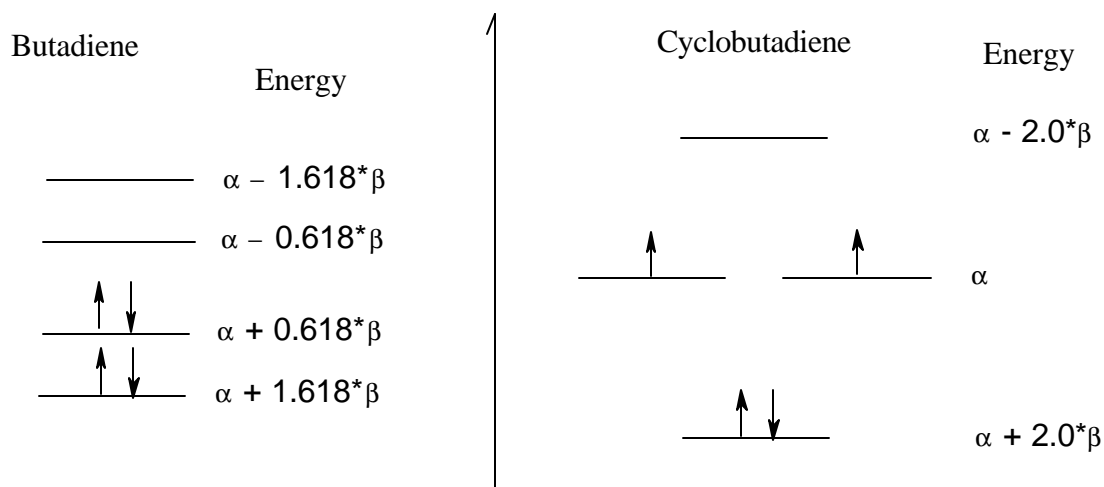
In the previous Huckel theory lesson (Huckel Theory I) we investigated the theory as we applied it to specific examples. The molecules we will investigate in this lesson are shown below (respectively): butadiene, cyclobutadiene, cyclopropenyl radical, naphthalene, and azulene.



Atom Charge Densities (ρ)

Often in organic chemistry we would like to know the "partial" charge on a carbon atom to see if it might be a good nucleophile or the site for electrophilic attack. Once the molecular orbitals have been generated this calculation is quite simple. The student must remember, however, that the π atomic charges generated here are given by π electrons only and do not say anything about charge resulting from the σ electrons. Further, the rather drastic changes assumed in Huckel theory limit the accuracy of the π atomic charges calculated. Yet, π charges do give a relative indication of the distribution of π electrons, which is important as those are the electrons most likely to be involved in chemical reactivity.

The first step in the process of determining π charge densities on carbon atoms is to generate the energy level diagram including electrons. These are shown below for two molecules treated in the Huckel I lesson, butadiene and cyclobutadiene.



Recall your results from the Huckel I lesson. The energies and molecular orbitals seem to be arbitrarily ordered. Also recall the negative sign you must include in order to get the X vector right. The eigenvalues and the coefficients are given below for butadiene.

$$\text{ORIGIN} \equiv 1$$

$$H_{\text{butadiene}} := \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad X := -\text{eigenvals}(H_{\text{butadiene}})$$

$$\text{MOs} := \text{submatrix}(\text{rsort}(\text{stack}(X^T, \text{eigenvecs}(H_{\text{butadiene}})), 1), 2, 4 + 1, 1, 4)$$

$$X := \text{sort}(X)$$

$$X = \begin{pmatrix} -1.618 \\ -0.618 \\ 0.618 \\ 1.618 \end{pmatrix} \begin{matrix} \kappa_1 \\ \kappa_2 \\ \kappa_3 \\ \kappa_4 \end{matrix}$$

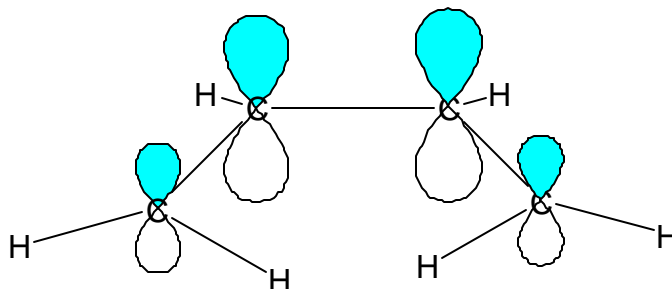
	MO1	MO2	MO3	MO4	
	0.372	0.602	0.602	-0.372	P ₁
	0.602	0.372	-0.372	0.602	P ₂
	0.602	-0.372	-0.372	-0.602	P ₃
	0.372	-0.602	0.602	0.372	P ₄

$$\text{MOs} = \begin{pmatrix} 0.372 & 0.602 & 0.602 & -0.372 \\ 0.602 & 0.372 & -0.372 & 0.602 \\ 0.602 & -0.372 & -0.372 & -0.602 \\ 0.372 & -0.602 & 0.602 & 0.372 \end{pmatrix}$$

In the above equations, note the labels that I have provided for the "X" vector and for the MOs. Note especially that the MOs are found in columns, NOT rows. The lowest energy molecular orbital is MO1 because it corresponds to the MOST NEGATIVE X value. You could also see this by noting that all of the coefficients in the first column are positive. See below:

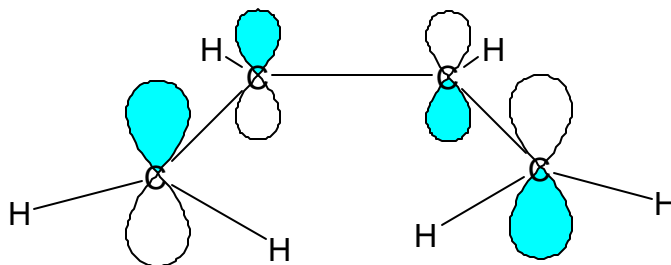
$$\text{MO1} = 0.372 \cdot P_1 + 0.602 \cdot P_2 + 0.602 \cdot P_3 + 0.372 \cdot P_4$$

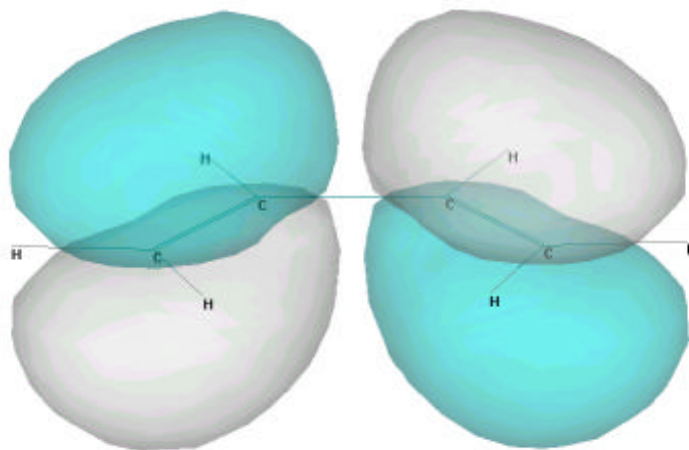
This indicates that all of the positive lobes lie above the plane formed by the carbon atoms while the negative lobes lie below that plane. The picture below shows the orientation AND relative size of the individual P orbitals. The actual overlap and delocalization are left to the student as a mental exercise.



In contrast, MO2 shows a node between carbon 2 and carbon 3, effectively disrupting the delocalization and relegating it to higher energy. The MO is represented mathematically and graphically here.

$$\text{MO2} = 0.602 \cdot P_1 + 0.372 \cdot P_2 - 0.372 \cdot P_3 - 0.602 \cdot P_4$$





This time, the overlap and delocalization of atomic orbital electron density for MO2 are depicted immediately above. Note that the END atoms possess the larger atomic orbitals as reflected in the values for the coefficients (and only hinted at in the delocalized MO2). I have depicted butadiene as a "cis" isomer, but the student must realize that the Huckel calculations DO NOT distinguish "cis" from "trans." In fact the only molecular geometry information important in Huckel theory is the connection of carbon atom to carbon atom. Also note that the numberings on MOs and Xs: 1, 2, 3, and 4 now refer to the order from lowest to highest energy, e.g. MO1 is the first MO (the first column) and the lowest energy orbital. The numbers used as subscripts for atomic orbitals, P_1 , P_2 , etc. still refer to the carbon atom numberings shown in the structure displayed earlier. Make sure you recognize MO2 as the HOMO.

1. Write the mathematical expression representing MO3 and MO4 for butadiene (as was done for MO1 and MO2). Also construct these MOs graphically by showing the orientation of atomic orbital lobes AND (qualitatively) their relative size. Don't attempt to depict delocalization of electron density. Which orbital is the LUMO?

Next we will generate the π atom charge densities from the molecular orbital coefficients. We need to define a quantity called the occupation number, n_i , which is *the average number of electrons that occupy a given orbital*. This definition has to do with the little arrows that appear in the energy level diagrams shown earlier for butadiene and cyclobutadiene. For butadiene the occupation numbers are as follows:

$$n_1=2 \quad n_2=2 \quad n_3=0 \quad n_4=0$$

The process of getting the **OCCUPATION NUMBERS** involves **first** generating the Huckel results, **then** drawing an energy level diagram **and** assigning electrons. Once assigned, it is usually a simple matter to determine the occupation numbers, and this is done by simply counting electrons. An occupation number will always lie between 0 and 2, inclusive.

The information we need to generate the π atom charge densities for each carbon atom in butadiene is summarized below.

	MO1	MO2	MO3	MO4	
$\text{MOs} =$	$\left(\begin{array}{cccc} 0.372 & 0.602 & 0.602 & -0.372 \\ 0.602 & 0.372 & -0.372 & 0.602 \\ 0.602 & -0.372 & -0.372 & -0.602 \\ 0.372 & -0.602 & 0.602 & 0.372 \end{array} \right)$				Carbon ₁
					Carbon ₂
					Carbon ₃
					Carbon ₄

$$n_1 := 2 \quad n_2 := 2 \quad n_3 := 0 \quad n_4 := 0$$

As before, I have included labels reminding the reader which orbital is which and labels indicating the carbon atom (and P orbital on each atom) to which each row of coefficients corresponds.

Only orbitals that **contain** electrons (nonzero occupation numbers) will contribute to the π charge on a given atom as reflected in the next formula.

The π charges formula appears below.

$$i := 1..4 \quad q_{\pi_i} := 1 - \left[\sum_{j=1}^4 (MO_{s_i,j})^2 \cdot n_j \right]$$

The symbol for the π atomic charges on carbon atom "i" is q_{π_i} . The symbol, $MO_{s_i,j}$, represents the number in the "ith" row and "jth" column of the MOs (coefficient) matrix. All of the i and j subscripts are active, meaning that they were created with the "[" bracket. Notice that the sum is over four terms since there are four carbon atoms contributing P orbitals to the basis set. Notice also that only the first two terms will contribute to the π charge in the case of butadiene since the occupation numbers for the last two molecular orbitals are zero. The charges are given below.

$$q_{\pi} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \begin{matrix} \text{Carbon}_1 \\ \text{Carbon}_2 \\ \text{Carbon}_3 \\ \text{Carbon}_4 \end{matrix}$$

The results here are perhaps surprising since all four atoms are predicted by Huckel theory to have the same π charge. The structure of the molecule suggests that the atoms at either end would have a different value from the atoms in the middle. At least that is my chemical intuition. It is also surprising that the charges are all zero. This means that the carbon atoms have neither lost nor gained π charge density to or from their π bonding partners. Each carbon atom contributes ONE π electron to the problem, and after the π bonding has taken place there is still an average of ONE π electron on each carbon atom in butadiene.

2. Verify the results for π atomic charges for each carbon atom in butadiene given above by EXPLICITLY expanding the summation (all 4 terms), inserting the correct values for $MO_{s_i,j}$ and n_j for each term. (Remember, for a given carbon atom the summation goes across a given row of the coefficient matrix.)

Actually the charges themselves might be used to determine the site in a molecule where electrophilic or nucleophilic substitution is most likely to occur. Recall the example from the Huckel I lesson, naphthalene. The π charges will be of no use for this molecule as all of the π charges are the same! That is why you were directed in the Huckel I lesson to investigate the HOMO and the LUMO coefficients. The rule is, **FIRST** compare the π charges, but if they are all the same, **THEN** look at the MO coefficients in the HOMO or LUMO.

3. Verify (SHOW ME) that the charges for all of the carbon atoms in naphthalene are the same. You can use the Mathcad formulas given above. The situation is similar for butadiene. Which carbon atoms in butadiene are most likely to be the sites for electrophilic and which for nucleophilic substitution?

Mastery Problem

4. For Azulene, determine the MOs and the X vector (use the ordering equations too!). Calculate the charges and decide which carbon atom is the most likely site for electrophilic and which for nucleophilic attack. Now go to the HOMO and LUMO coefficients and use the criteria described in Huckel I in order to determine the most likely carbon atom(s). Is there agreement? How should you decide if there is not?

Bond Orders (**p**)

The π bond orders require a slightly different formula for their calculation. A Bond Order tells us, relatively speaking, a bond's strength. The π bond orders are not the whole story of course, as they tell simply the π contribution to the total bond order. The equation for the π bond order appears below.

$$j := 1..4 \quad p_{\pi_{i,j}} := \sum_{k=1}^4 \text{MO}_{s_{i,k}} \cdot \text{MO}_{s_{j,k}} \cdot n_k$$

It is important to note that the π bond orders, $p_{\pi_{i,j}}$, are determined in the above formula even for atoms that are not connected together. We will focus on the π bond orders calculated for bonded atoms. It is also true that the diagonal elements:

$p_{\pi_{1,1}}$, $p_{\pi_{2,2}}$, $p_{\pi_{3,3}}$, $p_{\pi_{4,4}}$ give back the respective π charge densities. In order to get the π charges q_{π_1} , q_{π_2} , q_{π_3} , and q_{π_4} , one would have to subtract each π charge density from 1. The Bond Order matrix for butadiene is shown below with *my* labels for the original carbon atoms.

$$\begin{array}{cccc} & \text{C1} & \text{C2} & \text{C3} & \text{C4} \\ \text{C1} & & & & \\ \text{C2} & & & & \\ \text{C3} & & & & \\ \text{C4} & & & & \end{array} \quad P_{\pi} = \begin{pmatrix} 1 & 0.894 & 0 & -0.447 \\ 0.894 & 1 & 0.447 & 0 \\ 0 & 0.447 & 1 & 0.894 \\ -0.447 & 0 & 0.894 & 1 \end{pmatrix}$$

Interpretation of this matrix is straightforward. The π bond order between atom 1 and atom 2 is 0.894 whereas the π bond order between atoms 2 and 3 is 0.447. If the σ contributions to these two bonds is 1.0 (which is not a guarantee), the overall bond orders for these bonds would be 1.894 and 1.447, respectively. This indicates that the "so-called" double bonds are not exactly double bonds and the single bond is a little bit more than a single bond, a consequence of delocalization of π electron density. Still, which is the weakest bond?

Note further that the values for the 1,4 and 4,1 elements are **NEGATIVE**. No significance should be given to this value, nor to any nonzero matrix element that would indicate a bonding or antibonding interaction between non-bonded atoms.

Mastery Problem

5. Determine the occupation numbers for **cyclobutadiene**. Use the Huckel matrix given below to generate the appropriate (ordered) results. Do you need to generate the MOs in order to get the occupation numbers? Assign the occupation numbers with live subscripts, those given by the "[" bracket (so that you can use the equations above for charge densities and bond orders). Generate the π atom charge densities and π bond orders for **cyclobutadiene**.

$$H_{\text{cyclobutadiene}} := \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix}$$

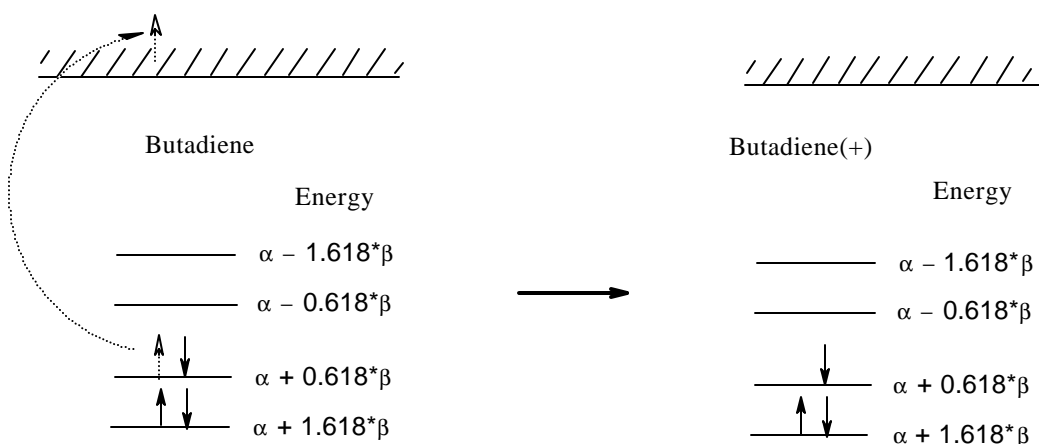
Mastery Problem

6. Generate the occupation numbers, π atom charge, and π bond orders for cyclopropenyl radical. This one is tricky because the occupation number for the HOMO is not a whole number. This is because the HOMO is doubly degenerate with only one electron to distribute between the two orbitals. The occupation number for either degenerate orbital is the AVERAGE occupation number for ONE of these degenerate orbitals.

Ionization Energies and Electron Affinities

Once we have generated the molecular orbitals, it is possible for us to begin making other predictions, in particular, the ionization energy and the electron affinity for the molecule. Once again, the results are not to be taken as precise calculations, they are simply applications intended to give the student further experience with molecular orbitals.

An example of an ionization is depicted below for butadiene. In this process an electron is removed from the molecule and a cation is formed. This sort of thing can come about in solution when driven electrochemically and readily takes place in a typical mass spectrometer. There are four electrons to choose from here. How does one decide which electron to remove? If the highest energy electron is chosen, the process is called the first ionization, and the energy necessary for the process to take place is called the first ionization energy. We can use Huckel theory to predict just how much energy it takes to remove this highest energy electron by assuming that the ionization energy is the same as the energy of the molecular orbital from which it was removed (with a sign reversal).



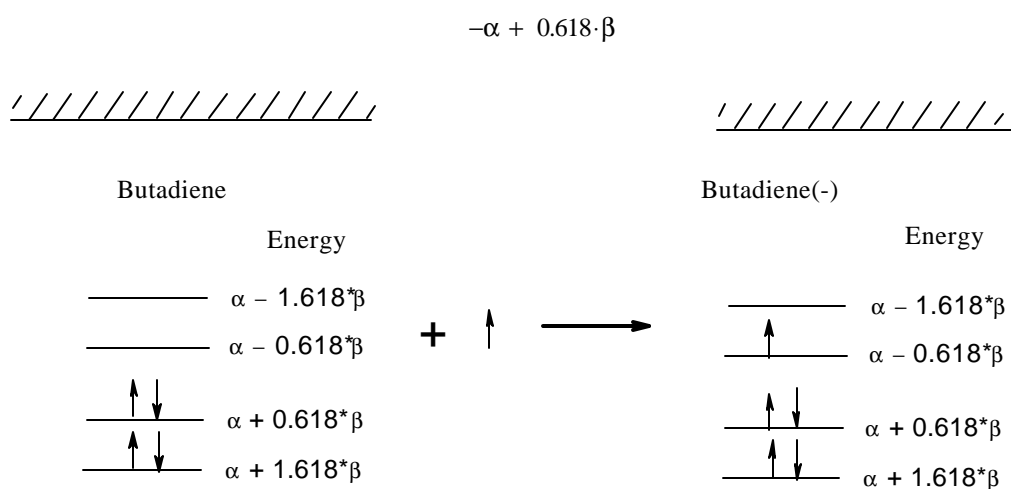
This interpretation of ionization energy in terms of the molecular orbital energy is attributed to Koopmans (1, 2). This can be justified by assuming that the energy it takes to remove an electron is the same as the energy necessary to EXCITE an electron from its molecular orbital up to the ionization continuum, the shaded region in the figure. The energy of the ionization continuum is taken to be ZERO and stands as an electrostatic reference for this problem. The energy to carry out such a process should be:

$$E_{\text{ionization}} = 0 - E_{\text{MO}} = -E_{\text{MO}}$$

Note that in this picture we can also predict the ionization energy from the next lower energy level. The first ionization energy is the energy to remove an electron from the HOMO. In the case of butadiene, the first ionization energy is predicted to be

$$-\alpha - 0.618 \cdot \beta$$

Prediction of the electron affinity can be treated in the same way. In this case, the neutral molecule absorbs an electron to form a negative ion. See below. It is assumed that the electron will be absorbed to the lowest unoccupied orbital, the LUMO, because that would be the most stable situation. In this case the process is exothermic, but since it is traditional to quote the energy RELEASED, once again the electron affinity will be given by the negative of the molecular orbital energy, and in this case it will be the energy of the LUMO.



The problem with Koopmans' theorem is that it assumes that the molecular orbitals of the cation (in the case of first ionization energy) and those of the anion (in the case of the electron affinity) are exactly the same as those of the neutral molecule. With a higher level calculation we could show that this is seldom the case although the error is often tolerable.

7. Using the values (in eV) for α and β given in the Huckel I lesson, determine the first ionization energy and electron affinity for benzene, naphthalene, allyl radical, and cyclopropenyl radical. Compare the results to the experimental values (try the NIST Webbook).

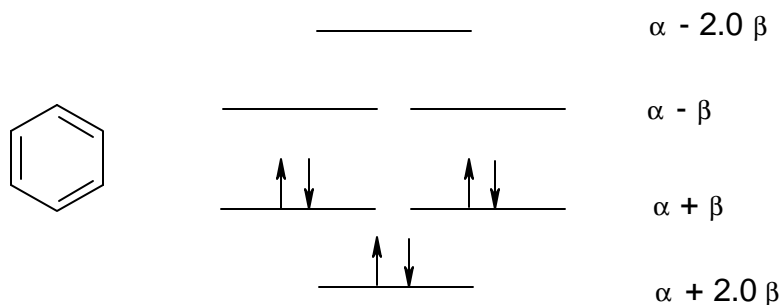
Delocalization Energy and Resonance Energy

Before we go on, let's put this notion of chemical bonding into perspective. So far we have assumed bonding to be a given, but we must ask at this point why it happens. Certainly the reason molecules form is because in so doing a more stable state of being is attained. Our understanding is that separated atoms are less stable, and therefore of **higher energy**, than the molecules formed from them. We might go further and say that it is the formation of chemical bonds that stabilizes the atoms!

It is important to remember that there is an association between higher stability and lower energy in the discussion that is to follow.

From your studies of organic chemistry you will recall that certain unsaturated planar cyclic hydrocarbons are unusually stable. We call them aromatic. The origin of this stability comes partly from the fact that the π electrons are delocalized, a property we can investigate with Huckel theory. There is, however, something more going on because there are many molecules that take advantage of π electron delocalization but are not aromatic. This extra stability comes about as a result of resonance.

The archetype for investigation of aromaticity is benzene. You generated the molecular orbitals for benzene in a **Huckel I** exercise. The molecular orbital energies and the energy level diagram for the molecular orbitals is given in the next figure.



The total π energy is simply given by the sum of the energies of the individual electrons, which in this case is $6\alpha + 8.0\beta$.* (Don't forget that since both α and β are negative numbers, $\alpha + 2.0\beta$ is indeed the lowest MO energy!) Now if we want to get a grasp on the aromatic stability of benzene caused by delocalization and resonance we need to compare benzene to something that lacks both, but is in some way still a relevant comparison. We can simply "turn off" the delocalization in benzene by taking away the connections between carbon atoms that cause delocalization, and solve the following Huckel matrix:

$$H_{\text{benzene_loc}} := \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}$$

Note that the matrix is missing connections between carbon atoms 2 and 3, 4 and 5, and 6 and 1. The molecular orbitals and X vector are given below.

$$X := -\text{eigenvals}(H_{\text{benzene_loc}})$$

$$\text{MOs} := \text{submatrix}(\text{rsort}(\text{stack}(X^T, \text{eigenvecs}(H_{\text{benzene_loc}})), 1), 2, 6 + 1, 1, 6)$$

$$X := \text{sort}(X)$$

$$X = \begin{pmatrix} -1 \\ -1 \\ -1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \quad \text{MOs} = \begin{pmatrix} 0 & 0 & 0.707 & 0 & 0 & 0.707 \\ 0 & 0 & 0.707 & 0 & 0 & -0.707 \\ -0.707 & 0 & 0 & 0 & -0.707 & 0 \\ -0.707 & 0 & 0 & 0 & 0.707 & 0 \\ 0 & -0.707 & 0 & -0.707 & 0 & 0 \\ 0 & -0.707 & 0 & 0.707 & 0 & 0 \end{pmatrix}$$

This result implies that there are now just two Huckel energies (each triply degenerate):

$$\alpha + \beta \quad \text{and} \quad \alpha - \beta$$

The total π energy of this "localized" benzene is $6 \cdot \alpha + 6 \cdot \beta$, which is different from the value for benzene by a factor of $2 \cdot \beta$. Note that because β is taken to be a negative number, the total π energy of real benzene is LOWER than the total π energy of this artificial benzene. In fact, the π energy of "localized" benzene is identical with that of three ethylene molecules. (Benzene has the same number of π electrons as three ethylene molecules.) In turning off the delocalization here we have also turned off the resonance. The factor $2 \cdot \beta$ contains both a contribution from the delocalization of electron density and from resonance. Let's see if we can calculate each contribution.

A comparison that will allow us to determine the resonance energy portion of the $2.0 \cdot \beta$ factor is the comparison between benzene and hexatriene. What we want to do is to calculate the delocalization energy of another artificial benzene that has delocalization energy but no resonance energy, "no-resonance" benzene. Hexatriene has no resonance, but is definitely a molecule in which delocalization of π electron density occurs. However, hexatriene is not a valid comparison because it lacks a "single bond" connecting the end carbons into a cycle as is the case with benzene.

Luckily, Hess and Schaad (3) developed a method for calculating the energy of delocalization "in absence of resonance" in terms of bond types. The total π energy from Huckel theory for Hexatriene is $6 \cdot \alpha + 6.988 \cdot \beta$. Hess and Schaad would add a value of $0.606 \cdot \beta$ to the hexatriene energy to correct for the lack of this "extra" single bond, and the total energy of this "no-resonance" benzene becomes: $6 \cdot \alpha + 7.594 \cdot \beta$. This gives a difference between benzene and "no-resonance" benzene of $0.406 \cdot \beta$. (found by subtracting the no-resonance value from the value for benzene found by Huckel theory: $6\alpha + 8.0\beta - (6 \cdot \alpha + 7.594 \cdot \beta)$). The fact that the difference between these two values is not zero suggests that electron delocalization is not the whole story.

The electron delocalization energy is the difference between the "no-resonance" benzene and the "localized" benzene: $6 \cdot \alpha + 7.594 \cdot \beta - (6\alpha + 6.0\beta) = 1.594 \cdot \beta$.

In order to make comparisons with other molecules it is customary to calculate the Resonance Energy Per Electron (REPE) which amounts to dividing the total resonance energy by the total number of π electrons (6 in the case of benzene). The REPE for benzene is $0.068 \cdot \beta$.

8. Calculate the delocalization energy of decapentaene. Assume there is no resonance energy in decapentaene.

9. For naphthalene, calculate the delocalization energy and the resonance energy. You will need the "no-resonance" naphthalene π energy, $10 \cdot \alpha + 13.128 \cdot \beta$, to do the calculation.

Mastery Problem

10. For azulene, determine the delocalization energy and the resonance energy. You will need the "no-resonance" azulene π energy, $10\cdot\alpha + 13.133\cdot\beta$, to do the calculation.

Compare the REPE to that of naphthalene. Calculate the π charges and bond orders for this molecule. One of the rings likes to be positive and one likes to be negative. Which is which? Draw resonance structures and argue in terms of the "4n+2" rule to justify these results. Would you expect this hydrocarbon to have much of a dipole moment? Why?

Mastery Problem

11. For cyclobutadiene determine the delocalization energy and the resonance energy. You will need to calculate the "no-resonance" cyclobutadiene π energy from the butadiene total π energy using the same correction factor used for hexatriene above ($0.606\cdot\beta$). Compare the REPE to that of benzene. Consider again the rules you learned in organic chemistry class for predicting aromaticity. Calculate the bond orders, and also compare them to those of benzene. Are the bond orders consistent? Do you expect this molecule to be stable?

A Final Word

Huckel theory is considered a highly qualitative (as opposed to quantitative) theory, yet we spend considerable energy presenting it to you. The reason for this is that many concepts can be carried over to more sophisticated Hartree-Fock and Semi-empirical theories. We can really get at the "meat" of Huckel theory, whereas the more sophisticated developments usually remain out of reach for the undergraduate student. Quantum chemistry is a challenging field to master, and it is hoped that your burden has been lightened somewhat by these two Huckel lessons.

*It is important to note that in the more sophisticated MO theory we cannot get the total electronic energy by adding up the MO energies of each electron. Such a calculation neglects the electron pairing and repulsion energies associated with the self-consistent field theory that are absent in Huckel theory. The student should remember that this determination of the total electronic energy is only correct within the assumptions of simple Huckel theory.

** This value was obtained by adding two values together to correct for the difference in atom connections between benzene and hexatriene. The first is given by Hess and Schaad for a single bond in between two double-bonded carbons and two hydrogens, $0.466 \cdot \beta$. The second is **the difference** between a double bond to which there are attached one single-bonded carbon and three hydrogens ($2.0000 \cdot \beta$) and a double bond to which are attached two singly-bonded carbons and two hydrogens ($2.0699 \cdot \beta$). This difference is $0.0699 \cdot \beta$. Since in hexatriene the **two** outer double bonds are surrounded by one single-bonded carbon and three hydrogen atoms, we need **two** of the second type of correction, so this value was added twice: $0.0699 + 0.0699 + 0.466 = 0.606$.

Additional References:

1. Roberts, John D. Notes on Molecular Orbital Calculations, W. A. Benjamin, 1961.
2. Sigalas, M. P. and Katsoulos, G. A. *J. Chem. Educ.* **1993**, 70(10), A255-A256.
3. Farrell, John J. and Haddon, Harry H. *J. Chem. Educ.* **1989**, 66(10), 839-40.