Huckel Theory I

James M. LoBue
Department of Chemistry
Georgia Southern University
jlobue@gasou.edu

In the 1930's a theory was devised by Huckel (1) to treat the π electrons of aromatic hydrocarbon systems such as benzene and naphthalene. This theory can also be applied to conjugated systems. Huckel theory can lead to some interesting, valuable predictions even though it is not a quantitative theory. The underlying premise is that the reactive properties of molecules result from the character of the highest energy electrons, which are, in the case of conjugated molecules, the π electrons.

Surprisingly, the Journal of Chemical Education has seen few papers addressing Huckel theory (2) in recent years. Usually, in order to do Huckel calculations one would either work through them with paper and pencil or use a canned computer program designed specifically for such calculations. Healy (3) provided direction in the use of Mathmatica to generate Huckel results, and many other authors in JCE over the past twenty years have described computer programs developed to carry out Huckel calculations.

It is hoped that the following offering will prove to be a new and useful tool.

Objectives: The student will be able to

1. construct a secular matrix for a conjugated system and solve it
2. interpret the results of a Huckel calculation
    a. to get an energy level diagram
    b. to fill orbitals with electrons and show HOMO and LUMO levels
    c. to generate molecular orbitals as linear combinations of atomic P orbitals
3. predict the lowest energy electronic absorption of a molecule
4. predict the most likely site for electrophilic or nucleophilic aromatic substitution.

Knowledge Assumed:

You should have seen the solution to the Schrodinger for simple systems and be aware of the postulates of quantum mechanics with an understanding of orthogonality and normalization.

A basic knowledge of molecular orbital theory would be helpful.

A passing knowledge of the linear variation method will be assumed.

You should have a reasonable knowledge of undergraduate organic chemistry.

Footnotes:

1. Huckel, Erich *Z. Physik* **1931**, 70, 204-86; Huckel, Erich Z. Physik **1931**, 72, 310-37; Huckel, Erich *Z. Physik* **1932**, 76, 628-48; Huckel, Erich Z. Physik **1933**, 83, 632-68.
2. David, Carl W. *J. Chem. Educ.* **1999**, 76(7), 999-1001; Bahnick, Donald A. *J. Chem. Educ.* **1994**, 71(2), 171-3.
3. Healy, Eamonn F. *J. Chem. Educ.* **1995**, 72(6), A120-A121.
4. Brogli, F.; Heilbronner, E. *Theor. Chim. Acta* **1972**, 26(4), 289-99.

Other References:

1. Lowe, John P. Quantum Chemistry, 2nd Ed., Academic Press, **1993**.
2. Roberts, John D. Notes on Molecular Orbital Calculations, W. A. Benjamin, **1961**.
3. Levine, Ira Quantum Chemistry, 5th Ed., Prentice Hall, **2000**.
4. Jensen, Frank Introduction to Computational Chemistry, Wiley, **1999**.

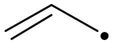
Notes to the Student:

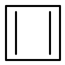
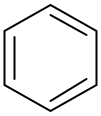
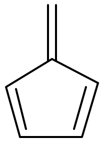
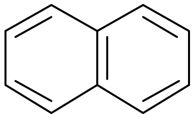
The student is to read and study what is written in **maroon.** Problems are in **teal** and are numbered, and equations and titles are in **black**. Carry out your solutions to the problems in Mathcad, but organize your answers to be handed in on paper drawn neatly or with the help of a word processor (preferable) and labeled with the problem numbering given in this document.

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

Rather than attempt a completely formal development of the theory some examples will be solved to illustrate the technique. Then, the student will be asked to solve several other examples.

The molecules whose structures appear (respectively) below will be treated by the theory. They are, in the order shown from left to right, allyl radical, butadiene, cyclobutadiene, benzene, methylene cyclopentadiene, and naphthalene.

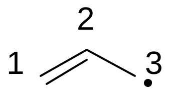


The development that follows (the **variation theorem** applied to molecular orbital theory) is mathematically involved (algebra and calculus) but not very deep conceptually. Its purpose is to justify the *purely* MATRIX development we will introduce later. Both methods give EXACTLY the same results, but with Mathcad, believe it or not, the *purely* MATRIX technique is much easier to set up and execute. The more difficult method will be presented first since the student probably DOESN'T have experience with MATRIX methods. The results for this more difficult method and for the *purely* MATRIX method are the same. If you don't see where everything is coming from at first, don't get too excited, because it is the *purely* MATRIX method we are going to emphasize. BOTH developments are methods of carrying out Huckel Theory.

Allyl Radical:

See the molecule depicted below. The formula is C_3H_5 and could be viewed as a propylene that has lost a hydrogen atom from the methyl end. The molecule is symmetrical and each carbon atom is assumed to be sp^2 hybridized. The carbon atoms must be numbered in order to keep track of them, but the numbering shown is arbitrary. All one must do is choose a numbering and then use that numbering consistently throughout subsequent calculations. The numbering establishes the connection of atoms.



The next order of business is to identify the basis set of p-type atomic orbitals. In this case there will be three: $\{P_1, P_2, P_3\}$. The subscripts refer to the numbered carbon atoms given above. These are all p-type orbitals whose lobes lie above and below the plane of the molecule, the plane defined by the carbon atoms.

In order to give you a signpost here, the ultimate objective of Huckel theory is to determine the molecular orbitals in terms of the atomic orbitals. In the case of allyl radical there will be three molecular orbitals formed. In general, there will always be as many molecular orbitals formed as there were atomic orbitals to begin with. The mathematical form of these molecular orbitals is:

$$MO_i = c_{1,i} \cdot P_1 + c_{2,i} \cdot P_2 + c_{3,i} \cdot P_3 \qquad (1)$$

The constants: $c_{1,i}, c_{2,i}$ and $c_{3,i}$ are numbers we will determine by one of the two methods outlined below. The index "i" would take on values 1, 2 and 3 for each of the **three** MOs that will result.

Now for the fun. The starting point in the application of the variation principle is to set up the expectation value for the energy, <E>, in terms of the general molecular orbital formula given in equation 1. **To make the notation easier to follow, the second index is ignored in the following development**. Remember that there will actually be **three** sets of three coefficients when the problem is completely solved.

The starting point for the allyl radical is given below.

$$\langle E \rangle = \frac{\int \overline{\psi} H \psi \, d\tau}{\int \overline{\psi} \psi \, d\tau}$$

$$\langle E \rangle = \frac{\int (c_1 \cdot P_1 + c_2 \cdot P_2 + c_3 \cdot P_3) \cdot H (c_1 \cdot P_1 + c_2 \cdot P_2 + c_3 \cdot P_3) \, d\tau}{\int (c_1 \cdot P_1 + c_2 \cdot P_2 + c_3 \cdot P_3) \cdot (c_1 \cdot P_1 + c_2 \cdot P_2 + c_3 \cdot P_3) \, d\tau}$$

H is the molecular Hamiltonian for allyl radical. This is already pretty complicated. We need to expand these products of trinomials and will do so by treating the numerator and the denominator separately.

The Numerator:

After application of the distribution principle of multiplication we get nine terms which have been separated into three integrals with three terms in each:

$$\int (c_1 \cdot c_1 \cdot P_1 \cdot HP_1 + c_1 \cdot c_2 \cdot P_2 \cdot HP_2 + c_1 \cdot c_3 \cdot P_1 \cdot HP_3)\, d\tau$$

$$+ \int (c_2 \cdot c_1 \cdot P_2 \cdot HP_1 + c_2 \cdot c_2 \cdot P_2 \cdot HP_2 + c_2 \cdot c_3 \cdot P_2 \cdot HP_3)\, d\tau$$

$$+ \int (c_3 \cdot c_1 \cdot P_3 \cdot HP_1 + c_3 \cdot c_2 \cdot P_3 \cdot HP_2 + c_3 \cdot c_3 \cdot P_3 \cdot HP_3)\, d\tau.$$

We will simplify this expression by making the following assignments:

$$\alpha = \int P_i \cdot HP_i \, d\tau$$

$$\beta = \int P_i \cdot HP_j \, d\tau$$

In the expression for β, if atom i is not connected directly to atom j, the integral will be **zero**.

These substitutions greatly compact the nine term expression, and because two of the atoms are not connected, **two** of the **nine** terms are **zero**:

$$\begin{gathered} c_1 \cdot c_1 \cdot \alpha + c_1 \cdot c_2 \cdot \beta + 0 \\ + c_2 \cdot c_1 \cdot \beta + c_2 \cdot c_2 \cdot \alpha + c_2 \cdot c_3 \cdot \beta \\ + 0 + c_3 \cdot c_2 \cdot \beta + c_3 \cdot c_3 \cdot \alpha \end{gathered}$$

The zeros have been left in intentionally for clarity.

The Denominator:

Expanding the denominator gives (nine terms again):

$$\int (c_1 \cdot c_1 \cdot P_1 \cdot P_1 + c_1 \cdot c_2 \cdot P_1 \cdot P_2 + c_1 \cdot c_3 \cdot P_1 \cdot P_3)\, d\tau$$

$$+ \int (c_2 \cdot c_1 \cdot P_2 \cdot P_1 + c_2 \cdot c_2 \cdot P_2 \cdot P_2 + c_2 \cdot c_3 \cdot P_2 \cdot P_3)\, d\tau$$

$$+ \int (c_3 \cdot c_1 \cdot P_3 \cdot P_1 + c_3 \cdot c_2 \cdot P_3 \cdot P_2 + c_3 \cdot c_3 \cdot P_3 \cdot P_3)\, d\tau$$

To simplify this expression we will assume

$$\int P_i \cdot P_j \, d\tau = \delta_{i,j}$$

The factor, $\delta_{i,j}$, is called the Kronicker delta. If $i = j$ then $\delta_{i,j}$ will be equal to 1. If $i \neq j$ then $\delta_{i,j}$ will be zero. This makes the P orbitals orthonormal.

This integral represents the OVERLAP of orbitals. If there is no overlap, the integral will be zero. However, the overlap between BONDED atoms should NOT be zero, so this integral should not be zero if atom i is connected to atom j. Surprisingly, Huckel calculations assume the overlap of bonded atoms to be ZERO, an approximation that makes the calculations simpler. In spite of this, the results are still quite useful!

1. Explain why it is a paradox to assume the above integral to be zero if $i \neq j$.

The result is that the denominator becomes

$$c_1 \cdot c_1 + c_2 \cdot c_2 + c_3 \cdot c_3.$$

Pretty simple, actually.

Thus we can write the expectation value for the energy (numerator over denominator) as

$$<E> = \frac{c_1 \cdot c_1 \cdot \alpha + 2 \cdot c_1 \cdot c_2 \cdot \beta + c_2 \cdot c_2 \cdot \alpha + 2 \cdot c_2 \cdot c_3 \cdot \beta + c_3 \cdot c_3 \cdot \alpha}{c_1 \cdot c_1 + c_2 \cdot c_2 + c_3 \cdot c_3}. \quad (2)$$

All we need to do then is to determine the "c" (coefficient) values. We will find these values by using the linear variation principle which is explained below.

The values of **a** and **b** are assumed to be constants which can be determined for a family of molecules. As a matter of fact, this has been determined for a series of conjugated, cyclic hydrocarbons by a fit of HOMO energies to ionization energies for some 33 molecules. This was done by Brogli and Heilbronner (4) in 1972. They found that **a** = -6.6 eV and **b** = -2.7 eV. The purpose presenting these values is to emphasize for the fact that these quantities are to be treated as constants, not variables.

The Linear Variation Principle

The basic concept is analogous to your typical "min-max" problem. Recall that the procedure in such a problem is to set a derivative equal to zero. In this case we seek the minimum in a function that is multidimensional rather than one that follows a simple one dimensional model like $y = f(x)$. Further, instead of dealing with variables like x and y, we will take derivatives with respect to the coefficients, c_1, c_2, and c_3 in the case of allyl radical, for instance. Yes indeed we will have to take derivatives with respect to each of these coefficients, setting each result equal to zero, symbolically.

$$\frac{\partial < E >}{\partial c_i} = 0$$

For molecules with more carbon atoms even more work would have to be done, i.e. more derivatives.

For the allyl radical let's begin by taking the derivative of equation 2 with respect to c_1.

$$\frac{\partial < E >}{\partial\ c_1} =$$

$$\frac{(2\cdot c_1\cdot\alpha + 2\cdot c_2\cdot\beta)\cdot(c_1\cdot c_1 + c_2\cdot c_2 + c_3\cdot c_3)}{(c_1\cdot c_1 + c_2\cdot c_2 + c_3\cdot c_3)^2}$$

$$- \frac{(c_1\cdot c_1\cdot\alpha + 2\cdot c_1\cdot c_2\cdot\beta + c_2\cdot c_2\cdot\alpha + 2\cdot c_2\cdot c_3\cdot\beta + c_3\cdot c_3\cdot\alpha)\cdot(2\cdot c_1)}{(c_1\cdot c_1 + c_2\cdot c_2 + c_3\cdot c_3)^2}$$

The reason this looks so nasty is that we are taking the derivative of a fraction. The procedure is (recall from Calculus I) "the derivative of the numerator times the denominator minus the numerator times the derivative of the denominator ALL over the denominator squared."

This equation can be further simplified by recognizing <E> (equation 2) in the second term, and by canceling one of the factors in the denominator in the first term. The result is

$$\frac{\partial < E >}{\partial\ c_1} = \frac{(2\cdot c_1\cdot\alpha + 2\cdot c_2\cdot\beta)}{(c_1\cdot c_1 + c_2\cdot c_2 + c_3\cdot c_3)} \quad - \quad < E > \quad \frac{2\cdot c_1}{(c_1\cdot c_1 + c_2\cdot c_2 + c_3\cdot c_3)}$$

We next set this expression equal to zero. The expression will be zero if

$$(2\cdot c_1\cdot\alpha + 2\cdot c_2\cdot\beta) \quad - < E > \quad 2\cdot c_1 = 0.$$

Of course we should then solve for c_1, but this would be a problem since we don't yet know the value for c_2. So what we have to do is go back and take the derivative of equation 2 with respect to c_2 and c_3 respectively. The result will be two more expressions that must be set equal to zero giving us three equations in the three unknowns c_1, c_2, and c_3. The three equations are given below. They have been slightly rearranged to collect like terms.

$$\begin{aligned} c_1 \cdot (\alpha - <E>) + c_2 \cdot \beta + c_3 \cdot 0 &= 0 \\ c_1 \cdot \beta + c_2 \cdot (\alpha - <E>) + c_3 \cdot \beta &= 0 \\ c_1 \cdot 0 + c_2 \cdot \beta + c_3 \cdot (\alpha - <E>) &= 0 \end{aligned} \qquad (3)$$

2. Take the derivatives with respect to c_2 and c_3 to verify these equations.

The "zero" terms have been left in the expressions to show the symmetry of the equations. Actually, there are **FOUR** unknowns here including the energy, <E>, which means we will have to bring in another equation at some point. As with any problem in which several unknowns are to be extracted from a set of equations one must always consider the possibility that there is NO solution. A test for this comes from the realm of linear algebra. A system of equations like this will have a nontrivial solution if the DETERMINANT of the MATRIX OF COEFFICIENTS gives a zero result. Now in order to understand this sentence you will have to understand what the matrix of coefficients is and, further, what a determinant is.

First, let us define what the matrix of coefficients is. From the system of equations shown above, one can see that the "coefficients" are the factors like α-<E> and β that multiply the unknowns c_1, c_2, and c_3. We will keep the equations aligned according to the "c" unknown, and then extract the coefficients to give the following matrix.

$$\text{Matcoef} := \begin{pmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{pmatrix}$$

Note that E has replaced <E> in this matrix. For the student, the entries in a given column are the coefficients of the same unknown in the original system of equations. The first column contains coefficients of c_1, the second of c_2, and the third of c_3.

Next we have to carry out the determinant operation. This linear algebraic operation is one of several common manipulations. Mathcad can do this rather trivially through the symbolics menu. The pathway is "symbolics-matrix-determinant." You must first make the cursor "surround" the matrix you are operating on. This determinant is also called the "Secular Determinant."

$$\det\left(\begin{pmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{pmatrix}\right) = 0$$

Mathcad gives a polynomial expression for the determinant in terms of the symbols, α, β, and E that can be seen below.

$$\alpha^3 - 3\cdot\alpha^2\cdot E + 3\cdot\alpha\cdot E^2 - 2\cdot\alpha\cdot\beta^2 - E^3 + 2\cdot E\cdot\beta^2$$

The secular determinant expansion must vanish for there to be a nontrivial solution to the original set of equations. Notice that if we set this expression equal to zero, the only unknown, <E>, becomes the variable in a cubic equation. That means that there will be **THREE** possible answers for the energy. This should not be surprising if you remember that THREE MOs must result from this analysis. Each of those MOs should have its own energy which as you can see is delivered by the determinant! Further examination of the determinant follows this problem.

The Mathcad operation that finds the values of <E> that make the polynomial vanish is carried out by first putting the cursor next to "E" in the above expression, and then using the symbolics menu, "Symbolics-variable-solve." The following three values for the energy result.

$$\begin{pmatrix} \alpha \\ \alpha + \sqrt{2}\cdot\beta \\ \alpha - \sqrt{2}\cdot\beta \end{pmatrix}$$

Now, the problem of finding the coefficients, c_1, c_2 and c_3 amounts to solving three equations in three unknowns, see equations (3) above. This will have to be repeated for all three energy values generated. When all is said and done, to solve the allyl radical problem will require the solution of three equations in three unknowns THREE TIMES!

For the first value of the energy, α, equations (3) become,

$$\begin{aligned} c_1\cdot(\alpha-\alpha)+c_2\cdot\beta+c_3\cdot 0 &= 0\\ c_1\cdot\beta+c_2\cdot(\alpha-\alpha)+c_3\cdot\beta &= 0\\ c_1\cdot 0+c_2\cdot\beta+c_3\cdot(\alpha-\alpha) &= 0 \end{aligned}$$

which will simplify to

$$\begin{aligned} c_2\cdot\beta &= 0\\ c_1\cdot\beta+c_3\cdot\beta &= 0\\ c_2\cdot\beta &= 0 \end{aligned}$$

This will give $c_2 = 0$ and $c_1 = -c_3$. But as yet, numerical factors for these coefficients cannot be obtained. We need another equation which we can get if we demand that the molecular orbitals be NORMALIZED.

$$MO_1 = c_1\cdot P_1 - c_1\cdot P_3 = c_1\cdot(P_1 + P_2)$$

To normalize MO_1, the following integral must be solved.

$$\int \overline{MO_1}\cdot MO_1\,d\tau = \int (c_1\cdot P_1 - c_1\cdot P_3)\cdot(c_1\cdot P_1 - c_1\cdot P_3)\,d\tau = 1$$

$$c_1\cdot c_1\cdot\int (P_1\cdot P_1 - 2\cdot P_1\cdot P_3 + P_3\cdot P_3)\,d\tau = 1$$

Recalling the expression given earlier,

$$\int P_i\cdot P_j\,d\tau = \delta_{i,j}$$

simplifies the normalization integral to,

$$c_1\cdot c_1\cdot(1 - 2\cdot 0 + 1) = c_1\cdot c_1\cdot 2 = 1$$

$$c_1 = \frac{1}{\sqrt{2}}$$

$$MO_1 = \frac{1}{\sqrt{2}} \cdot (P_1 - P_3)$$

Just one set of coefficients has been determined. The determination of the other two sets will require the substitution of the other two <E> values.

$$E = \alpha + \sqrt{2} \cdot \beta \qquad\qquad E = \alpha - \sqrt{2} \cdot \beta$$

$$\begin{aligned} c_1 \cdot (\sqrt{2} \cdot \beta) + c_2 \cdot \beta + c_3 \cdot 0 &= 0 \\ c_1 \cdot \beta + c_2 \cdot (\sqrt{2} \cdot \beta) + c_3 \cdot \beta &= 0 \\ c_1 \cdot 0 + c_2 \cdot \beta + c_3 \cdot (\sqrt{2} \cdot \beta) &= 0 \end{aligned} \qquad \begin{aligned} c_1 \cdot (-\sqrt{2} \cdot \beta) + c_2 \cdot \beta + c_3 \cdot 0 &= 0 \\ c_1 \cdot \beta + c_2 \cdot (-\sqrt{2} \cdot \beta) + c_3 \cdot \beta &= 0 \\ c_1 \cdot 0 + c_2 \cdot \beta + c_3 \cdot (-\sqrt{2} \cdot \beta) &= 0 \end{aligned}$$

Which will give,

$$MO_2 = c_1 \cdot (P_1 - \sqrt{2} \cdot P_2 + P_3) \qquad\qquad MO_3 = c_1 \cdot (P_1 + \sqrt{2} \cdot P_2 + P_3)$$

When normalized the mathematical form of the molecular orbitals is,

$$MO_2 = \frac{1}{2} \cdot (P_1 - \sqrt{2} \cdot P_2 + P_3) \qquad\qquad MO_3 = \frac{1}{2} \cdot (P_1 + \sqrt{2} \cdot P_2 + P_3)$$

So what in heaven's name is a determinant. It can be a long involved operation if the matrix is large, but Mathcad can figure it out in the wink of an eye. Just to give you an idea, though, it is easy to take the determinant of a 2X2 matrix without the help of the computer.

This is shown below. "det" means "the determinant of" in matrix-speak.

$$\det\left(\begin{pmatrix} a & b \\ c & d \end{pmatrix}\right) = a \cdot d - c \cdot b$$

The determinant of a matrix is easy to calculate if you know values for a, b, c, and d. The theorem for a 2X2 matrix is stated succinctly below.

$$\det\left(\begin{pmatrix} a & b \\ c & d \end{pmatrix}\right) = a \cdot d - c \cdot b = 0$$

So if the determinant of the above 2X2 is zero, then it must be that $a \cdot d = c \cdot b$.

3. For the following 2X2 matrices, work out the values for the determinants. Show all steps in your procedure. This is a good opportunity for you to practice the simplify function in the Symbolics menu.

$$\begin{pmatrix} 1 & 2 \\ 1.5 & 3 \end{pmatrix} \qquad \begin{pmatrix} 1 & 2 \\ 1.5 & 4 \end{pmatrix}$$

4. Given the following set of two equations in two unknowns, determine if this set of equations has a real, nontrivial (trivial means that all a's =0) solution? Explain.

$$a_1 \cdot 1 + a_2 \cdot 2 = 0$$

$$a_1 \cdot 1.5 + a_2 \cdot 3 = 0$$

In the case of the allyl problem, the determinant is a bit more complicated.

$$\det\left(\begin{pmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{pmatrix}\right)$$

It is done by reducing from one 3X3 to three 2X2s. The three 2X2s are formed by multiplying the element at the top of each column of the determinant by its MINOR. The MINOR in an NXN determinant is formed by choosing the (N-1)X(N-1) columns and rows that omit the column and row elements common to the top element. In the case of the determinant above,

$$\det\left(\begin{pmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{pmatrix}\right) = (\alpha - E) \cdot \begin{pmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{pmatrix} - \beta \cdot \begin{pmatrix} \beta & \beta \\ 0 & \alpha - E \end{pmatrix}$$

$$+ 0 \cdot \begin{pmatrix} \beta & \alpha - E \\ 0 & \beta \end{pmatrix}$$

the determinant of the matrix was made simpler because of the zeros in the original matrix.

$$\det\left(\begin{pmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{pmatrix}\right) = (\alpha - E)\cdot\left[(\alpha - E)^2 - \beta^2\right] - \beta\cdot[\beta\cdot(\alpha - E) - 0] + 0$$

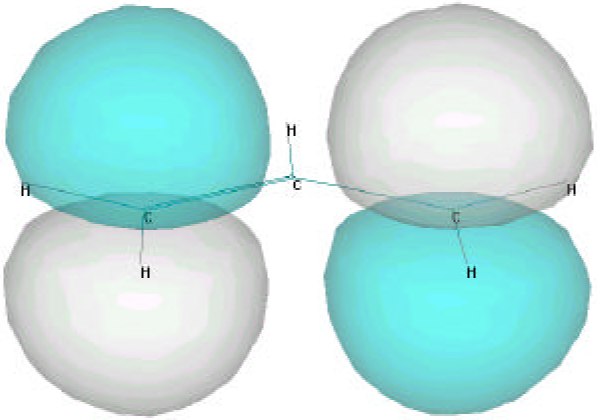
Which further simplifies to give

$$(\alpha - E)^3 - (\alpha - E)\cdot\beta^2 - \beta^2\cdot(\alpha - E) = (\alpha - E)^3 - 2\cdot\beta^2\cdot(\alpha - E) = 0$$

5. For the three energy values found earlier using Mathcad's symbolic processor, verify this equation. That is, substitute each of the energy values given to show that the expression above equals zero.

Molecular Orbital, MO_1 is shown below in the graphic that was generated using Hyperchem 5.1. Note that the orbital lobes are situated around the two end carbon atoms, but not around the middle carbon atom. This is consistent with the mathematical representation also given below in which there is no contribution from P_2. Note also that the phase of the two orbitals around the two outer carbon atoms is reversed as reflected in the minus sign shown in the mathematical representation.

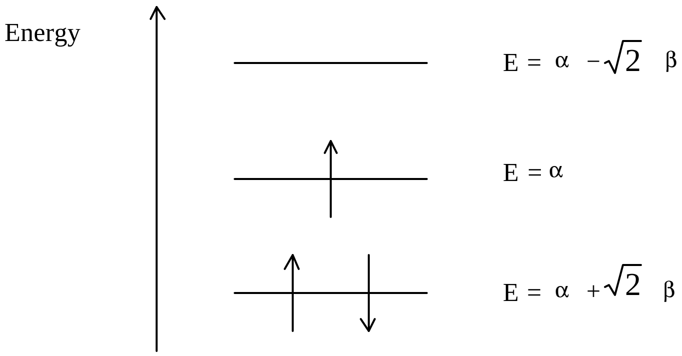
$$MO_1 = \frac{1}{\sqrt{2}}\cdot(P_1 - P_3)$$



The Huckel molecular orbital results as linear combinations of atomic, P, orbitals for the allyl radical are summarized below.

$$MO_1 = \frac{1}{\sqrt{2}} \cdot (P_1 - P_3)$$

$$MO_2 = \frac{1}{2} \cdot (P_1 - \sqrt{2} \cdot P_2 + P_3) \qquad MO_3 = \frac{1}{2} \cdot (P_1 + \sqrt{2} \cdot P_2 + P_3)$$



The energies of the molecular orbitals are displayed as an energy level diagram with electrons depicted as arrows added pairwise starting from the lowest energy level. The lowest energy is indeed the $\alpha + \sqrt{2} \cdot \beta$ value since both α and β are negative numbers. There are indeed three electrons in the π system of the allyl radical.

The energy values obtained so far refer to the energies of the molecular orbitals and NOT the total π energy of the molecule. For a highly approximate theory like Huckel Theory, one can claim that the total π energy of the molecule is the sum of the orbital energy of each electron. In the case of allyl this would give a total π energy of $3\,\alpha + 2 \cdot \sqrt{2} \cdot \beta$. For a more sophisticated molecular orbital method in which electron repulsion is taken into account, the total electronic energy cannot be assumed to be the sum of the orbital energies of the electrons. This will double-count electron repulsion energy and give an erroneous answer.

6. Show that MO_2 is normalized.

Here is a brief summary of the steps used to generate the molecular orbitals and their energies.

1. Write the molecular structure and number each conjugated carbon atom uniquely.
2. Set up the Matrix of Coefficients with α's on the diagonal of the matrix and β's off diagonal only in positions that represent carbon atoms that are bonded together.
3. Set the determinant of the Matrix of Coefficients equal to zero, and solve for all possible <E> values. There will be as many <E>'s as there are conjugated carbon atoms.
4. For each <E>, solve a system of equations to get Atomic Orbital coefficients. Use these coefficients to create the linear combination of atomic orbitals used to define the molecular orbitals. You will have to use the normalization condition to nail down the actual numerical values for the coefficients.
5. Summarize the calculation by tabulating the molecular orbitals as linear combinations of atomic orbitals along with the corresponding energy.
6. Construct an energy level diagram from the <E> values you calculated and add electrons to the diagram. You should have only as many electrons as you have carbon atoms if the molecule is neutral. If it is charged, add electron(s) for every negative charge, and remove electron(s) for every positive charge.

Huckel Theory using Mathcad's Matrix Mechanics Functions

Much of what you have learned in the lesson so far can be applied to the techniques you will learn in the remainder of the lesson. Again, you will work through an example to illustrate the techniques rather than attempting to develop a completely general formal theory. Our illustration will be butadiene.

Butadiene is a 4X4 problem.

7. Draw the structure for butadiene (using an appropriate chemical drawing program like ISIS Draw or ChemDraw and paste your structure into your file) and number your conjugated carbon atoms. Finally, give the basis set of P orbitals (labeled as you did for the atoms).

8. Construct the "Matrix of Coefficients" for butadiene as was done for the allyl radical. Pay attention to the way the atoms were connected to each other. Remember, butadiene will give you a 4X4 matrix. Remember equations (3) for allyl radical. These are repeated here for you to use as a model. Recall also the Matcoef matrix given on page 9.

$$\begin{aligned}
c_1 \cdot (\alpha - <E>) + c_2 \cdot \beta + c_3 \cdot 0 &= 0 \\
c_1 \cdot \beta + c_2 \cdot (\alpha - <E>) + c_3 \cdot \beta &= 0 \\
c_1 \cdot 0 + c_2 \cdot \beta + c_3 \cdot (\alpha - <E>) &= 0
\end{aligned} \qquad (3)$$

Here let us use a slightly different treatment of the equations in (3). The allyl equations can be simplified a bit. Dividing BOTH sides of each equation by β results in

$$c_1 \cdot \frac{(\alpha - <E>)}{\beta} + c_2 \cdot 1 + c_3 \cdot 0 = 0$$
$$c_1 \cdot 1 + c_2 \cdot \frac{(\alpha - <E>)}{\beta} + c_3 \cdot 1 = 0$$
$$c_1 \cdot 0 + c_2 \cdot 1 + c_3 \cdot \frac{(\alpha - <E>)}{\beta} = 0$$

Next, the factors on the diagonal are substituted with the following substitution,

$$X = \frac{\alpha - <\mathrm{E}>}{\beta} \qquad (4)$$

leading to the set of equations below.

$$\begin{aligned} c_1 \cdot X + c_2 \cdot 1 + c_3 \cdot 0 &= 0 \\ c_1 \cdot 1 + c_2 \cdot X + c_3 \cdot 1 &= 0 \\ c_1 \cdot 0 + c_2 \cdot 1 + c_3 \cdot X &= 0 \end{aligned} \qquad (5)$$

9. Carry out these same manipulations for butadiene producing a set of equations of four equations in 4 unknowns.

As in the previous case, the unknowns: c_1, c_2, and c_3 for the allyl radical are to be calculated. The matrix of coefficients is just a little bit different, it looks like the matrix below. This set of equations (5) could be solved by the determinant method, as we did before, giving three different values of X, which in turn could yield three values of <E> using equation (4). These values of <E> could then be substituted back into the system of equations and three different sets of coefficients generated. This is awfully tedious, so instead we will solve the Huckel problem a different way. As it turns out, the set of equations that has X's and 1's instead of α's and β's will give the same values for the coefficients with some minor adjustments. This matrix of X's and 1's is called the secular matrix.

The next step in the process is to replace the X's with zeros.

$$\begin{pmatrix} \mathrm{X} & 1 & 0 \\ 1 & \mathrm{X} & 1 \\ 0 & 1 & \mathrm{X} \end{pmatrix} \qquad \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

10. Construct the secular matrix for butadiene and then generate the matrix for the next step as shown above.

Now the powerful functions in Mathcad will be applied. Instead of taking the determinant, which you are welcome to do on your own, assign a variable name to the secular matrix for allyl radical, H_{allyl} seen below. The use of the ORIGIN function here will eliminate zero subscripts. Thus the first molecular orbital will be MO_1, and not MO_0.

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

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

The subscript ("allyl") here utilizes the "period" subscript rather than the "bracket" subscript and merely acts as a label. Make sure you understand how to get this matrix from consideration of the molecular structure.

1. Now we will let Mathcad solve for the X values. This can be done with a single step by use of the Mathcad function "eigenvals," see below. Then the energies can be determined.

$$X := -\text{eigenvals}(H_{allyl}) \qquad X = \begin{pmatrix} -1.414 \\ 0 \\ 1.414 \end{pmatrix} \qquad X = \frac{\alpha - \langle E \rangle}{\beta}$$

Note that 1.414 is the same as $\sqrt{2}$ showing that this method gives the same results as were carried out several pages earlier. See the allyl radical energy level diagram.

$$-1.414 = \frac{\alpha - E}{\beta} \qquad -1.414 \cdot \beta = \alpha - E \qquad E = \alpha + 1.414 \cdot \beta = \alpha + \sqrt{2} \cdot \beta \qquad \text{etc.}$$

For those who are detail oriented, you might have noticed the minus sign in the equation above. This results from the choice of matrix, H_{allyl}, to use with the matrix functions. Mathcad needs to work with a matrix of numbers with no variables. By this choice, the problem we are actually solving is equivalent to solving the following determinantial problem:

$$\det\left(\begin{pmatrix} 0-\lambda & 1 & 0 \\ 1 & 0-\lambda & 1 \\ 0 & 1 & 0-\lambda \end{pmatrix}\right) = 0 \qquad \text{compared to} \qquad \det\left(\begin{pmatrix} X & 1 & 0 \\ 1 & X & 1 \\ 0 & 1 & X \end{pmatrix}\right)$$

It may not be obvious to the student, but the use of the "eigenvals" function with a matrix whose diagonal elements are all zero is equivalent to the one we want to solve **except** that the signs will be reversed.

Another quirk of Mathcad's eigenvalue solver is that the list of "X" values is NOT given in order. We will deal with this quirk in the next section.

11. Generate values for X for butadiene using the "eigenvals" function. Determine the values of <E> for the molecular orbitals of butadiene using equation (4) above. Note that you get the energies without doing the determinant setting it equal to zero and then solving for <E>! You get the values of X in one step. Construct an energy level diagram like the one done earlier for allyl and put π electrons into the levels pairwise starting with the lowest energy level and stopping when you run out of electrons. Did the X values come to you in order from largest to smallest?

2. With the X values one can determine the coefficients for the MOs. Mathcad is a real work-saver here too. Instead of the tedious algebra sown for allyl, the function to use is called "eigenvecs." This lesson was originally prepared with Mathcad 7 Professional. Some earlier versions lack this function, and in that case once can use the function "eigenvec," which gives the coefficients for the molecular orbitals one at a time rather than all at once.

Continuing on with the allyl example problem, the following was constructed:

$$\mathrm{MOs} := \mathrm{eigenvecs}(H_{allyl}) \qquad \mathrm{MOs} = \begin{pmatrix} 0.5 & 0.707 & 0.5 \\ 0.707 & 0 & -0.707 \\ 0.5 & -0.707 & 0.5 \end{pmatrix} \qquad X = \begin{pmatrix} -1.414 \\ 0 \\ 1.414 \end{pmatrix}$$

The coefficients for a given MO are given by the values in a given COLUMN! Each column from left to right corresponds to each X value from top to bottom. The X vector is shown again below. (Remember that the value 0.707 is the same as $\frac{1}{\sqrt{2}}$.) The second column in MOs corresponds to the second X value, 0. In general, the X values will be presented in no particular order, as will also be true of the MOs. This is NOT the case for allyl for some reason, but will be the case for butadiene as you are about to find out. The first column will not correspond to the lowest energy molecular orbital in butadiene! This can be corrected.

12. Using the eigenvecs function, generate the butadiene molecular orbitals. Once done, construct linear combinations of the atomic P orbitals for butadiene.

Mastery Problem

13. Which LINEAR COMBINATION from problem 12 gives the lowest energy MO? What is the linear combination for the second **highest** energy MO?

It is possible to use Mathcad functions to correct this ordering problem. Here are the equations and results for allyl:

$$\mathrm{MOs} := \mathrm{submatrix}\left(\mathrm{rsort}\left(\mathrm{stack}\left(X^T, \mathrm{eigenvecs}(H_{allyl})\right), 1\right), 2, 3+1, 1, 3\right)$$

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

$$X = \begin{pmatrix} -1.414 \\ 0 \\ 1.414 \end{pmatrix} \qquad \mathrm{MOs} = \begin{pmatrix} 0.5 & 0.707 & 0.5 \\ 0.707 & 0 & -0.707 \\ 0.5 & -0.707 & 0.5 \end{pmatrix}$$

An explanation is called for here. This function takes the eigenvalues and uses them to reorder the molecular orbital coefficients. It does this by taking the NXN coefficients matrix formed with the eigenvecs function and stacks the eigen values on top of it. This can be seen below. The "X" value for a given molecular orbital lies on top of the molecular orbital.

$$\mathrm{stack}\left(X^T, \mathrm{eigenvecs}(H_{allyl})\right) = \begin{pmatrix} -1.414 & 0 & 1.414 \\ 0.5 & 0.707 & 0.5 \\ 0.707 & 0 & -0.707 \\ 0.5 & -0.707 & 0.5 \end{pmatrix}$$

Then the matrix above is sorted according to the value of X found in the top row of the matrix. This is what "rsort" does. For allyl this step is not necessary, but will be for butadiene. Finally, the molecular orbitals are separated from the X values using the "submatrix" function.

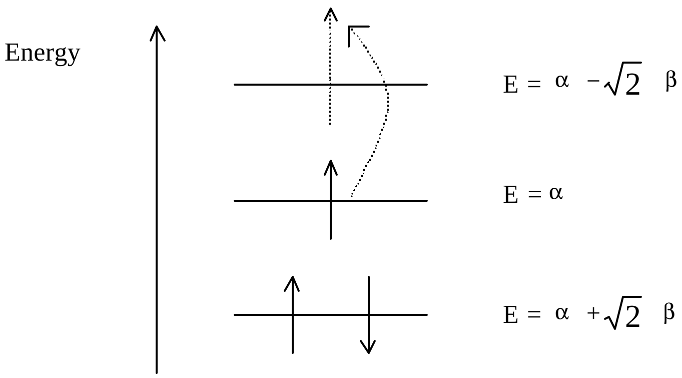
$$\mathrm{rsort}\left(\mathrm{stack}\left(X^T, \mathrm{eigenvecs}(H_{allyl})\right), 1\right) = \begin{pmatrix} -1.414 & 0 & 1.414 \\ 0.5 & 0.707 & 0.5 \\ 0.707 & 0 & -0.707 \\ 0.5 & -0.707 & 0.5 \end{pmatrix}$$

Finally, the numbers at the end of the function, 2, 3+1, 1, 3, tell the function "submatrix" to extract a new matrix from an old one by taking rows 2 through 4 from the old an converting them to the new matrix where they will become rows 1 through 3. For a molecule with n π carbon atoms, you would change the values of 3 to n.

The HOMO, the LUMO, and UV-vis Spectroscopy

Once the energies and MOs have been calculated, there are a number of predictions that can be made. In the Huckel I lesson a description of how one predicts the lowest energy UV-vis absorption wavelength will be given. You have probably already been exposed to the notion of an electronic transition. In such a process, an electron is excited from one molecular orbital to another. Usually it is the transition from the **H**ighest **O**ccupied **M**olecular **O**rbital, the HOMO, to the **L**owest **U**noccupied **M**olecular **O**rbital, the LUMO, that is most often of interest. In the case of butadiene, this process is depicted below.

Allyl Radical



As can be seen, the energy difference between the HOMO and the LUMO is:

$$\alpha - 1.414\cdot\beta - (\alpha + 1.414\cdot\beta) = -2.828\cdot\beta$$

Assuming the value of β equal to -2.7eV given earlier, the energy and the wavelength of the transition is expected to be:

$\text{eV} := 1.602\cdot 10^{-19}\cdot\text{J}$ $\quad\beta := -2.7\cdot\text{eV}$ $\quad h := 6.626\cdot 10^{-34}\cdot\text{J}\cdot\text{s}$ $\quad c := 2.998\cdot 10^{8}\cdot\frac{\text{m}}{\text{s}}$

$\text{nm} := 1\cdot 10^{-9}\cdot\text{m}$

Wavelength: $\quad\lambda := \dfrac{h\cdot c}{-2.818\cdot\beta}$ $\quad\lambda = 163\,\text{nm}$

Thus the value of allyl's lowest energy absorption is predicted to lie in the Vacuum UV, a very energetic photon would be necessary to excite this electron. Unfortunately, the correct answer is closer to 400 nm, but the fact that we can get this close is pretty amazing. Also, it is highly dependent on the method used to determine β.

Mastery Problem

14. Describe the structure and basis set, then generate the molecular orbitals (as linear combinations of atomic orbitals), <E>s, and the energy level diagram (with electrons) for the molecular orbitals of cyclobutadiene. How do your results differ from those of butadiene? Predict also the wavelength of its lowest energy electronic absorption.

Mastery Problem

15. Solve the Huckel problem for benzene. This time you don't have to generate the molecular orbitals, just the X vector and MOs matrix. Construct the energy level diagram for the molecular orbitals and insert electrons into your diagram.

Mastery Problem

16. Solve the Huckel problem for methylene cyclopentadiene (see the structure at the top of the lesson). This time you don't have to generate the molecular orbitals, just the X vector and MOs matrix. Construct the energy level diagram for the molecular orbitals and insert electrons into your diagram. Predict also the wavelength of its lowest energy absorption.

Electrophilic and Nucleophilic Substitution

The last application of Huckel Theory involves making predictions regarding some chemical reactions you encountered during your study of organic chemistry. Specifically, we will make predictions regarding electrophilic substitution and nucleophilic substitution.

An electrophile is a species in search of electron density. Huckel theory can tell us which carbon atom in a molecule has the most accessible electron density. By accessible, I mean electrons that are of HIGHEST energy, and as you know those electrons will be found within the HOMO. Now also you must know that the electrons in an orbital are spread across ALL of the atoms in the molecule in proportion to the square of the coefficients multiplying their respective atomic orbitals. Therefore, the carbon atom P orbital with the largest squared coefficient in the HOMO will be the atom most likely to undergo electrophilic aromatic substitution.

On the other hand, nucleophilic substitution involves the donation of electron density TO the molecule by a nucleophile. That election density will most likely be placed in the empty MO of lowest energy, the LUMO. The carbon atom with the largest squared coefficient in the LUMO, once again, will be the site best able to accept the donated electron density and will therefore be the site of nucleophilic substitution.

This technique is only half of the story that will be completed in the Huckel II lesson.

Mastery Problem

17. Using the structure below for naphthalene with the numbering given, generate and order the MOs matrix and the X vector. Predict the carbon atom(s) most likely to be the site for electrophilic aromatic substitution. Also predict the site(s) for nucleophilic substitution. Predict the wavelength for the lowest energy absorption in the UV-vis region of the electromagnetic spectrum.