

## Diagonalization and Hückel Molecular Orbital Theory

Solving the HMO secular equation for complex molecules can become very difficult by hand. However, we may enlist the help of the computer. The solutions to the secular equation for butadiene:

$$\begin{pmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0 \quad 1.$$

are  $E_1, E_2, \dots$ . The energies may also be obtained as the eigenvalues of the equation:

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \quad 2.$$

where we have just rearranged Equation 1 to put the energy term on the right-hand side. The mathematical procedure for solving Equation 2 is called diagonalization. There are several efficient ways to diagonalize matrices; our computer program uses Jacobi's method.

Since we don't know the values of  $\alpha$  and  $\beta$ , we must rewrite Equation 1 in a slightly different way. Dividing both sides of Eq. 1 by  $\beta$  gives:

$$\begin{pmatrix} \frac{(\alpha-E)}{\beta} & 1 & 0 & 0 \\ 1 & \frac{(\alpha-E)}{\beta} & 1 & 0 \\ 0 & 1 & \frac{(\alpha-E)}{\beta} & 1 \\ 0 & 0 & 1 & \frac{(\alpha-E)}{\beta} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0 \quad 3.$$

We now define  $x_i = \frac{(E_i - \alpha)}{\beta}$ . Substituting  $x$  into Equation 3 gives:

$$\begin{pmatrix} -x_i & 1 & 0 & 0 \\ 1 & -x_i & 1 & 0 \\ 0 & 1 & -x_i & 1 \\ 0 & 0 & 1 & -x_i \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0 \quad 4.$$

Once again, rearranging Equation 4 to put the  $x$  terms on the right-hand side gives:

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = x_i \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \quad 5.$$

where the eigenvalue is  $x_i$  and:

$$E_i = \alpha + x_i \beta \quad 6.$$

The computer program to diagonalize a matrix is available on the Web at

<http://www.colby.edu/chemistry/PCHEM/eigen.html>

All you need to do is to input the Hückel matrix with 0's on the diagonal (for carbon; see below for heteroatoms). The HMO matrix is always symmetric, so we only need to input the lower triangular part.

**Example:**

Let's use butadiene as an example:  $C_A=C_B-C_C=C_D$ . The input for butadiene is:

```

0
1      0
0      1      0
0      0      1      0

```

The output is:

```

Eigenvector 1: Eigenvalue =1.61803
0.371748
0.601501
0.601501
0.371748
-----
Eigenvector 2: Eigenvalue =0.618034
-0.601501
-0.371748
0.371748
0.601501
-----
Eigenvector 3: Eigenvalue =-0.618034
0.601501
-0.371748
-0.371748
0.601501
-----
Eigenvector 4: Eigenvalue =-1.61803
-0.371748
0.601501
-0.601501
0.371748

```

Giving the following wavefunctions and energies, from highest energy to lowest:

Eigenvector 4:  $E = \alpha - 1.6180 \beta$

$$\Psi_4 = -0.371748 p_{zA} + 0.601501 p_{zB} - 0.601501 p_{zC} + 0.371748 p_{zD}$$

Eigenvector 3:  $E = \alpha - 0.618034 \beta$

$$\Psi_3 = 0.601501 p_{zA} - 0.371748 p_{zB} - 0.371748 p_{zC} + 0.601501 p_{zD}$$

Eigenvector 2:  $E = \alpha + 0.618034 \beta$

$$\Psi_2 = -0.601501 p_{zA} - 0.371748 p_{zB} + 0.371748 p_{zC} + 0.601501 p_{zD}$$

Eigenvector 1:  $E = \alpha + 1.61803 \beta$

$$\Psi_1 = 0.371748 p_{zA} + 0.601501 p_{zB} + 0.601501 p_{zC} + 0.371748 p_{zD}$$

## Heteroatoms

Heteroatoms are introduced into the HMO matrix using two parameters,  $h$  and  $k$ . The diagonal element is the Coulomb integral, which for carbon is  $\alpha$ . The off-diagonal elements are the resonance integrals, which for directly bonded carbon atoms are  $\beta$ . The diagonal element for a heteroatom is changed to  $\alpha + h\beta$  and the off-diagonal element for directly bonded atoms is changed to  $k\beta$ . A table of  $h$  and  $k$  is given below.

| Atom | Bond Type         | $\pi$ electrons for atom | $h$ | $k$ |
|------|-------------------|--------------------------|-----|-----|
| C    | -C=C-             | 1                        | 0   | 1   |
| N    | -C=N- (pyridine)  | 1                        | 0.5 | 1.0 |
| N    | =C-N< (pyrrole)   | 2                        | 1.5 | 0.8 |
| N    | -N=N- (azo)       | 1                        | 1.0 | 1.0 |
| O    | -C=O (carbonyl)   | 1                        | 1.0 | 1.0 |
| O    | =C-O- (furan)     | 2                        | 2.0 | 0.8 |
| F    | =C-F              | 2                        | 3.0 | 0.7 |
| Cl   | =C-Cl             | 2                        | 2.0 | 0.4 |
| Br   | =C-Br             | 2                        | 1.5 | 0.3 |
| S    | =C-S- (thiophene) | 2                        | 1.5 | 0.8 |

For example, acrolein,  $C_A=C_B-C_C=O_D$ , has four total pi electrons and the input matrix is:

|   |   |   |   |  |
|---|---|---|---|--|
| 0 |   |   |   |  |
| 1 | 0 |   |   |  |
| 0 | 1 | 0 |   |  |
| 0 | 0 | 1 | 1 |  |

The lowest energy orbital is

```
Eigenvector 1: E=1.87939
0.228013
0.428525
0.57735
0.656539
-----
```

The coefficient for oxygen of 0.656539 shows that extra electron density resides on the oxygen, because of its larger electronegativity.

Another example is vinyl fluoride,  $C_A=C_B-F_C$ , with four total pi electrons and the input matrix:

|   |     |   |
|---|-----|---|
| 0 |     |   |
| 1 | 0   |   |
| 0 | 0.7 | 3 |

The two bonding MO's are:

```

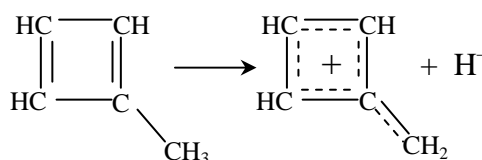
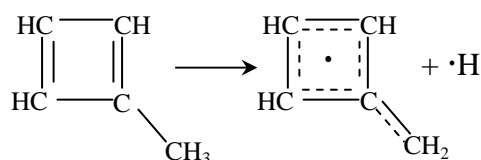
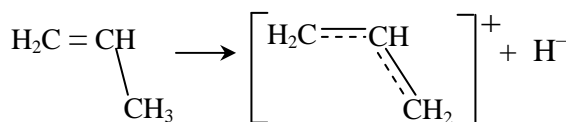
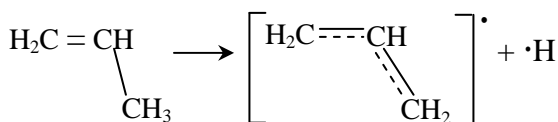
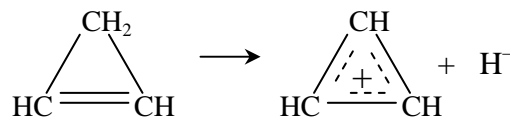
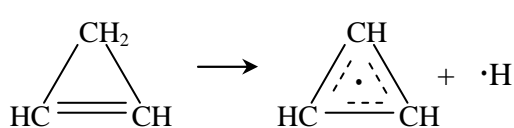
Eigenvector 1: E=3.17155
0.0748418
0.237365
0.968533
-----
Eigenvector 2: E=0.890577
0.729234
0.649439
-0.215513
-----

```

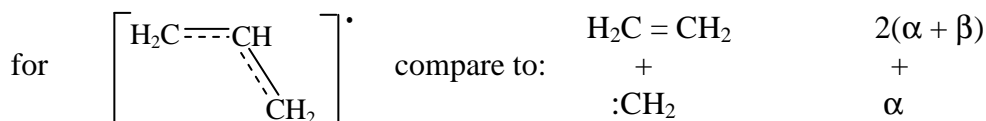
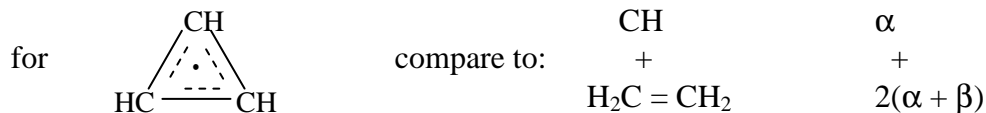
with the lowest energy orbital being primarily a lone-pair on fluorine and the next higher bonding orbital being primarily the double bond on the two carbons.

### Ions and Free Radicals

Ions and free radicals can also be studied. Example odd electron radicals are shown at left below, and even electron ions are shown at right.

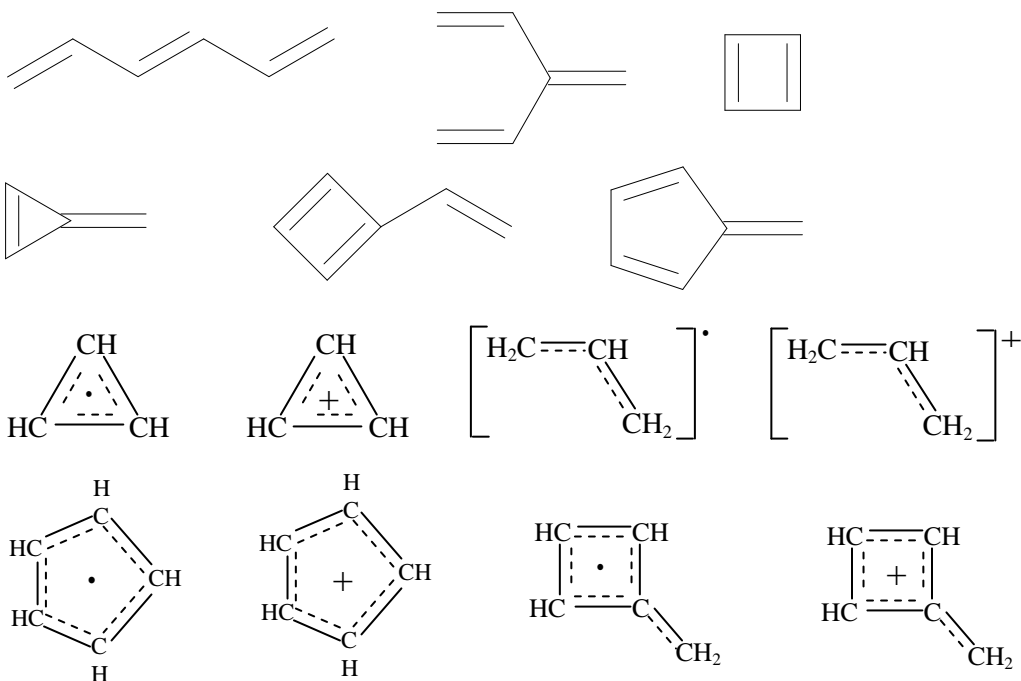


The only major difference compared to stable closed-shell systems is that the calculation of the  $\pi$ -delocalization energy of an odd-electron species includes a  $\text{CH}_2$  or  $\text{CH}$  fragment for the localized reference system. The corresponding energy of the localized fragment is just the energy of a single p-electron in an atomic  $p_z$  orbital; which is just  $\alpha$ . For example:



For the cationic even-electron species the corresponding  $\text{CH}^+$  or  $\text{CH}_2^+$  fragment does not have a  $p_z$ -electron to donate to the  $\pi$ -system. In other words, the contribution of a  $\text{CH}^+$  or  $\text{CH}_2^+$  fragment is zero. In short, the  $\alpha$  part of the difference always cancels out giving the  $\pi$ -delocalization energy as a multiple of  $\beta$ .

**Homework:** You will be assigned one of the following molecules or ions.



Please answer the nine questions that follow.

1. Number the carbon atoms in your molecule. Show the numbering. Give the corresponding Hückel determinant in terms of  $x$ 's and  $1$ 's:

2. Determine the energies and the orbital coefficients using a matrix diagonalization program. List those below or attach a printout.

3. Sketch the orbitals below with the appropriate phase for each p orbital.

4. Give the number of nodes in each wavefunction. Show the nodes in the diagrams, above. Classify each orbital as net bonding or anti-bonding.

5. Draw the energy level diagram, below, with a quantitative scale. Give the electron filling.

6. Calculate the  $\pi$ -bond order for each unique bond in the molecule.

$$P_{ij} = \sum_k n_k c_{ki} c_{kj}$$

7. Calculate the  $\pi$ -bond delocalization energy. (Remember for each isolated double bond with two electrons,  $E = 2(\alpha + \beta)$  )

8. Calculate the  $\pi$ -electron density on any two atoms of your choosing.

$$d_i = \sum_k n_k c_{ki}^2$$

9. On the energy level in part 5, indicate the lowest energy electronic transition with a vertical arrow. Label the HOMO and LUMO (or SOMO if you have a radical).