Lecture outline

Additional insight into resonance, aromaticity, and light absorption can be gained by determining the **π-MO energies**. We don't need to do a sophisticated electronic structure calculation to obtain useful information; a simple treatment of π-systems as arrays of interacting p-orbitals is sufficient for our purposes.

The method that we will be using, Hückel theory, considers only interactions between nearest-neighbor p-orbitals, and expresses the resulting π-MO energies in terms of two parameters — α, the energy of an isolated p-orbital, and **β**, the interaction energy between a pair of p-orbitals. By the conventional definition, β represents a stabilization, or energy lowering, so it is a negative number.

At the Hückel level of theory, the bonding π-MO of ethylene is at energy $E = \alpha + \beta$, and the antibonding π-MO is at energy $E = \alpha - \beta$. (Remember that β is negative.)

The most basic version of Hückel theory treats molecules like 1,3 butadiene as strings of p-orbitals that all have the *same interaction energy*, β, regardless of single vs double bonding in the Lewis structure and regardless of the distances between the orbitals. This is, of course, a horrific approximation, but it makes the calculations very simple.
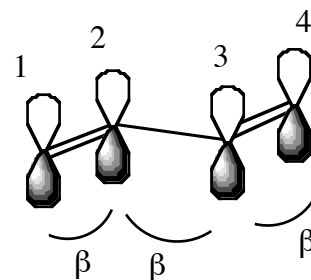
An aside for the more mathematically inclined… Hückel calculations for small molecules like butadiene can be done with paper and pencil. For *n* interacting p-orbitals, an *n* x *n* determinant is set up with each diagonal element i,i being "x", where $x = (\alpha - E)/\beta$, and each off-diagonal element i,j being 1 if atoms i and j are bonded (adjacent), and 0 if they're not.

The determinant for butadiene is:

	1	2	3	4
1	**x**	**1**	**0**	**0**
2	**1**	**x**	**1**	**0**
3	**0**	**1**	**x**	**1**
4	**0**	**0**	**1**	**x**

$= 0$

Row 1, for example, has **x** for the diagonal matrix element 1,1, a **1** for matrix element 1,2, since atoms 1 and 2 and bonded, and **0**s for elements 1,3 and 1,4, since the corresponding atoms are not bonded.

Row 2 has a **0** for the 2,4 interaction, and **1**s for the 2,1 and 2,3 interactions, since these atoms are bonded (remember, single vs double bonding in the Lewis structure is irrelevant because the Hückel simplification treats each interaction between a pair of adjacent p-orbitals as being the same.

This determinant can be reduced, via "expansion by cofactors" and then solving the resulting 3 x 3 determinants, to give the equation
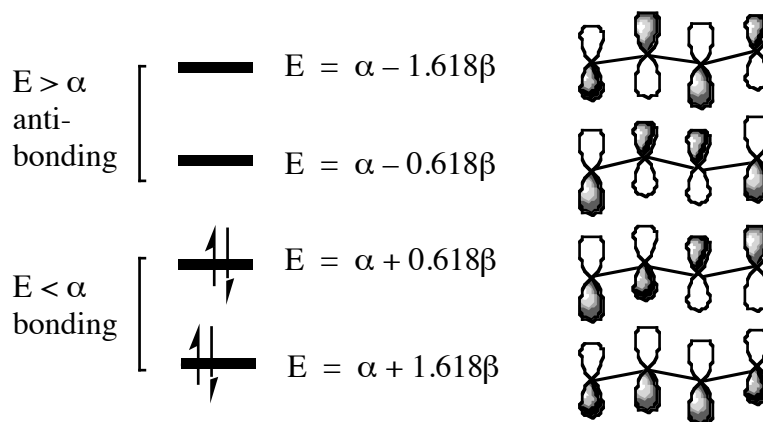
$$x^4 - 3x^2 + 1 = 0$$

Solving for x, via the quadratic formula or by completing the square, gives 4 solutions,

$$x = \pm 1.618$$
$$\text{and } x = \pm 0.618$$

Recall that "x" was defined as $x = (\alpha - E)/\beta$, so $E = \alpha - x\beta$. These four solutions give the four π-MO energies below.

The result of the calculation is the set of π-MO energies below.

The set of equations defining the individual π-MOs can also be solved to determine the relative contribution of each p-orbital to each π-MO (the "p-orbital coefficients"). This can be useful in understanding charge distributions within π-systems and reaction regiochemistry, but we don't need to be concerned with this now.

From the Hückel π-MO energies we can determine a crude resonance stabilization energy. For butadiene, we're referring to the energy lowering due to conjugation. To evaluate this we need to compare the total π-MO energy, E_π, of butadiene to that of two isolated π-bonds, i.e. ethylene.

What's the Hückel resonance energy of allyl radical? First, we need the π-MO energies. There must be a way to do these calculations — let's check the web… hey, there's a Hückel calculator developed by Arvi Rauk at the University of Calgary — **www.chem.ucalgary.ca/SHMO/** — this will be demonstrated in class.
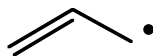
Now let's determine the aromaticity of benzene and the antiaromaticity of cyclobutadiene.