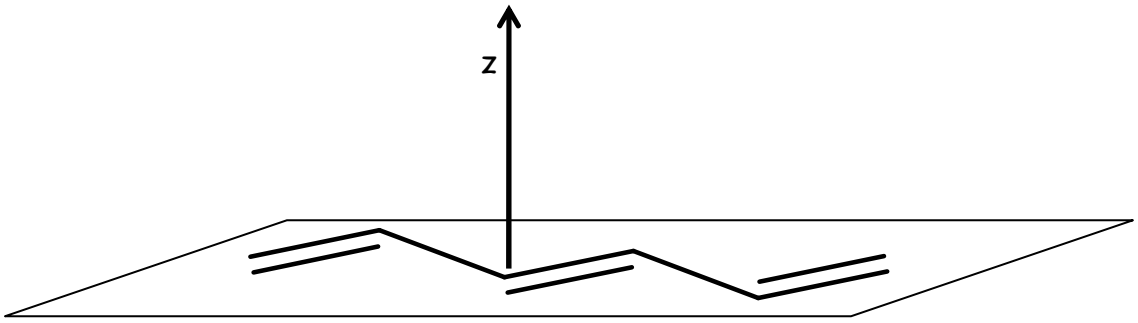
HÜCKEL MOLECULAR ORBITAL THEORY

In general, the vast majority polyatomic molecules can be thought of as consisting of a collection of two-electron bonds between pairs of atoms. So the qualitative picture of σ and π-bonding and antibonding orbitals that we developed for a diatomic like CO can be carried over give a qualitative starting point for describing the C=O bond in acetone, for example. One place where this qualitative picture is extremely useful is in dealing with conjugated systems – that is, molecules that contain a series of alternating double/single bonds in their Lewis structure like 1,3,5-hexatriene:

Now, you may have been taught in previous courses that because there are other resonance structures you can draw for this molecule, such as:

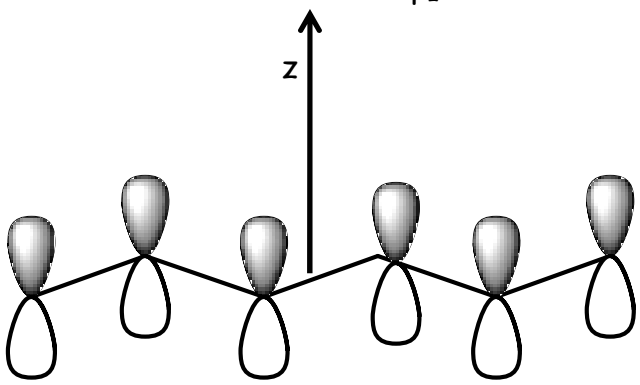
that it is better to think of the molecule as having a series of bonds of order 1 $\frac{1}{2}$ rather than 2/1/2/1/… **MO theory actually predicts this behavior, and this prediction is one of the great successes of MO theory as a descriptor of chemistry**. In this lecture, we show how even a very simple MO approximation describes conjugated systems.

Conjugated molecules of tend to be planar, so that we can place all the atoms in the x-y plane. Thus, the molecule will have reflection symmetry about the z-axis:



Now, for diatomics, we had reflection symmetry about x and y and this gave rise to π_x and π_y orbitals that were odd with respect to reflection and σ orbitals that were even. In the same way, for planar conjugated systems the orbitals will separate into σ orbitals that are even with respect to reflection

and π_z orbitals that are odd with respect to reflection about z. These π_z orbitals will be linear combinations of the p_z orbitals on each carbon atom:



In trying to understand the chemistry of these compounds, it makes sense to focus our attention on these π_z orbitals and ignore the σ orbitals. The π_z orbitals turn out to be the highest occupied orbitals, with the σ orbitals being more strongly bound. Thus, the forming and breaking of bonds – as implied by our resonance structures – will be easier if we talk about making and breaking π bonds rather than σ. Thus, at a basic level, we can ignore the existence of the σ-orbitals and deal only with the π-orbitals in a qualitative MO theory of conjugated systems. This is the basic approximation of Hückel theory, which can be outlined in the standard 5 steps of MO theory:

1) **Define a basis of atomic orbitals.** Here, since we are only interested in the π_z orbitals, we will be able to write out MOs as linear combinations of the p_z orbitals. If we assume there are N carbon atoms, each contributes a p_z orbital and we can write the μ^{th} MOs as:

$$\pi^{\mu} = \sum_{i=1}^{N} c_i^{\mu} p_z^i$$

2) **Compute the relevant matrix representations.** Hückel makes some radical approximations at this step that make the algebra much simpler without changing the qualitative answer. We have to compute two matrices, **H** and **S** which will involve integrals between p_z orbitals on different carbon atoms:

$$H_{ij} = \int p_z^i \ \hat{H} \ p_z^j d\tau \qquad\qquad S_{ij} = \int p_z^i \ p_z^j d\tau$$

The first approximation we make is that **the p_z orbitals are orthonormal**. This means that:

$$S_{ij} = \begin{cases} 1 & \text{i} = \text{j} \\ 0 & \text{i} \neq \text{j} \end{cases}$$

Equivalently, this means **S** is the identity matrix, which reduces our generalized eigenvalue problem to a normal eigenvalue problem

$$\mathbf{H}\bullet\mathbf{c}^{\alpha} = E_{\alpha}\mathbf{S}\bullet\mathbf{c}^{\mu} \quad \Rightarrow \quad \mathbf{H}\bullet\mathbf{c}^{\mu} = E_{\mu}\mathbf{c}^{\mu}$$

The second approximation we make is to assume that **any Hamiltonian integrals vanish if they involve atoms i,j that are not nearest neighbors**. This makes some sense, because when the p_z orbitals are far apart they will have very little spatial overlap, leading to an integrand that is nearly zero everywhere. We note also that the diagonal (i=j) terms must all be the same because they involve the average energy of an electron in a carbon p_z orbital:

$$H_{ii} = \int p_z^i \ \hat{H} \ p_z^i d\tau \equiv \alpha$$

Because it describes the energy of an electron on a single carbon, α is often called the on-site energy. Meanwhile, for any two nearest neighbors, the matrix element will also be assumed to be constant:

$$H_{ij} = \int p_z^i \ \hat{H} \ p_z^j d\tau \equiv \beta \qquad \text{i,j neigbors}$$

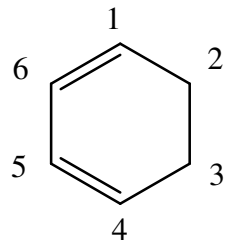
This last approximation is good as long as the C-C bond lengths in the molecule are all nearly equal. If there is significant bond length alternation (e.g. single/double/single…) then this approximation can be relaxed to allow β to depend on the C-C bond distance. As we will see, β allows us to describe the electron delocalization that comes from multiple resonance structures and hence it is often called a resonance integral. There is some debate about what the "right" values for the α, β parameters are, but one good choice is α=-11.2 eV and β=-.7 eV.

3) **Solve the generalized eigenvalue problem.** Here, we almost always need to use a computer. But because the matrices are so simple, we can usually find the eigenvalues and eigenvectors very quickly.
4) **Occupy the orbitals according to a stick diagram.** At this stage, we note that from our N p_z orbitals we will obtain N π orbitals. Further, each carbon atom has one free valence electron to contribute, for a total of N electrons that will need to be accounted for (assuming the molecule is neutral). Accounting for spin, then, there will be $N/2$ occupied molecular orbitals and $N/2$ unoccupied ones. For the ground state, we of course occupy the lowest energy orbitals.
5) **Compute the energy.** Being a very approximate form of MO theory, Hückel uses the non-interacting electron energy expression:

$$E_{tot} = \sum_{i=1}^{N} E_i$$

where E_i are the MO eigenvalues determined in the third step.

To illustrate how we apply Hückel in practice, let's work out the energy of benzene as an example.



1) Each of the MOs is a linear combination of 6 pz orbitals

$$\psi^{\mu} = \sum_{i=1}^{6} c_i^{\mu} p_z^i \qquad \rightarrow \qquad \mathbf{c}^{\mu} = \begin{pmatrix} c_1^{\mu} \\ c_2^{\mu} \\ c_3^{\mu} \\ c_4^{\mu} \\ c_5^{\mu} \\ c_6^{\mu} \end{pmatrix}$$

2) It is relatively easy to work out the Hamiltonian. It is a 6-by-6 matrix. The first rule implies that every diagonal element is α:

$$\mathbf{H} = \begin{pmatrix} \alpha & & & & & \\ & \alpha & & & & \\ & & \alpha & & & \\ & & & \alpha & & \\ & & & & \alpha & \\ & & & & & \alpha \end{pmatrix}$$

The only other non-zero terms will be between neighbors: 1-2, 2-3, 3-4, 4-5, 5-6 and 6-1. All these elements are equal to β:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & & & & \beta \\ \beta & \alpha & \beta & & & \\ & \beta & \alpha & \beta & & \\ & & \beta & \alpha & \beta & \\ & & & \beta & \alpha & \beta \\ \beta & & & & \beta & \alpha \end{pmatrix}$$

All the rest of the elements involve non-nearest neighbors and so are zero:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

3) Finding the eigenvalues of **H** is easy with a computer. We find 4 distinct energies:

$E_6 = \alpha - 2\beta$ _____

$E_4 = E_5 = \alpha - \beta$ _____ _____

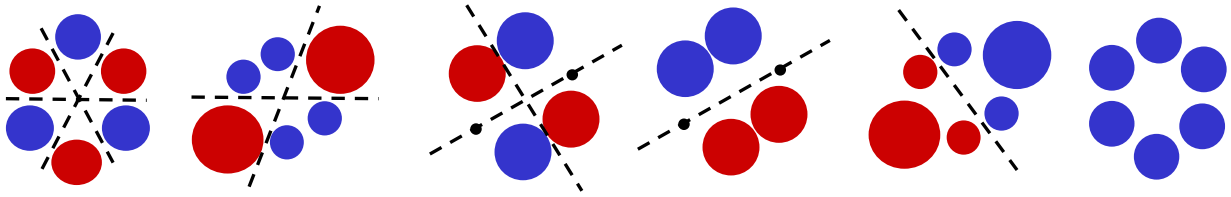
.....

$E_2 = E_3 = \alpha + \beta$ _____ _____

$E_1 = \alpha + 2\beta$ _____

The lowest and highest energies are non-degenerate. The second/third and fourth/fifth energies are degenerate with one another. With a little more work we can get the eigenvectors. They are:

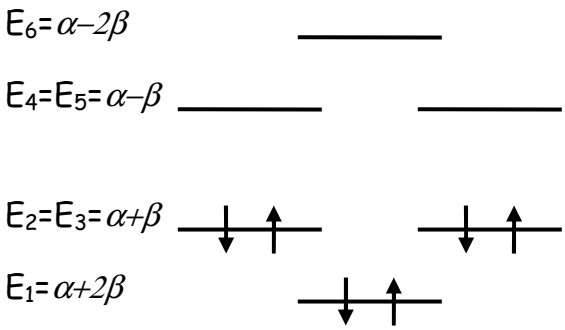
$$\mathbf{c}^6 = \frac{1}{\sqrt{6}}\begin{pmatrix} +1 \\ -1 \\ +1 \\ -1 \\ +1 \\ -1 \end{pmatrix} \quad \mathbf{c}^5 = \frac{1}{\sqrt{12}}\begin{pmatrix} +1 \\ -2 \\ +1 \\ +1 \\ -2 \\ +1 \end{pmatrix} \quad \mathbf{c}^4 = \frac{1}{\sqrt{4}}\begin{pmatrix} +1 \\ 0 \\ -1 \\ +1 \\ 0 \\ -1 \end{pmatrix} \quad \mathbf{c}^3 = \frac{1}{\sqrt{4}}\begin{pmatrix} +1 \\ 0 \\ -1 \\ -1 \\ 0 \\ +1 \end{pmatrix} \quad \mathbf{c}^2 = \frac{1}{\sqrt{12}}\begin{pmatrix} +1 \\ +2 \\ +1 \\ -1 \\ -2 \\ -1 \end{pmatrix} \quad \mathbf{c}^1 = \frac{1}{\sqrt{6}}\begin{pmatrix} +1 \\ +1 \\ +1 \\ +1 \\ +1 \\ +1 \end{pmatrix}$$



The pictures at the bottom illustrate the MOs by denting positive (negative) lobes by circles whose size corresponds to the weight of that particular p_z orbital in the MO. The resulting phase pattern is very reminiscent of a particle on a ring, where we saw that the ground state had no nodes, the first and second excited states were degenerate (sine and cosine) and had one node, the third and fourth were degenerate with two nodes. The one

difference is that, in benzene the fifth excited state is the only one with three nodes, and it is non-degenerate.

4) There are 6 π electrons in benzene, so we doubly occupy the first 3 MOs:



5) The Hückel energy of benzene is then:

$$E = 2E_1 + 2E_2 + 2E_3 = 6\alpha + 8\beta$$

Now, we get to the interesting part. What does this tell us about the bonding in benzene? Well, first we note that benzene is somewhat more stable than a typical system with three double bonds would be. If we do Hückel theory for ethylene, we find that a single ethylene double bond has an energy

$$E_{C=C} = 2\alpha + 2\beta$$

Thus, if benzene simply had three double bonds, we would expect it to have a total energy of

$$E = 3E_{C=C} = 6\alpha + 6\beta$$

which is off by 2β. We recall that β is negative, so that **the π-electrons in benzene are more stable than a collection of three double bonds**. We call this *aromatic stabilization*, and Hückel theory predicts a similar stabilization of other cyclic conjugated systems with 4N+2 electrons. This energetic stabilization explains in part why benzene is so unreactive as compared to other unsaturated hydrocarbons.

We can go one step further in our analysis and look at the bond order. In Hückel theory the bond order can be defined as:

$$O_{ij} \equiv \sum_{\mu=1}^{occ} c_i^{\mu} c_j^{\mu}$$

This definition incorporates the idea that, if molecular orbital μ has a bond between the i^{th} and j^{th} carbons, then the coefficients of the MO on those carbons should both have the same sign (e.g. we have $p_z^i + p_z^j$). If the orbital

is antibonding between i and j, the coefficients should have opposite signs(e.g. we have $p_z^i - p_z^j$). The summand above reflects this because

$$c_i^\mu c_j^\mu > 0 \qquad \text{if } c_i^\mu, c_j^\mu \text{ have same sign}$$

$$c_i^\mu c_j^\mu < 0 \qquad \text{if } c_i^\mu, c_j^\mu \text{ have opposite sign}$$

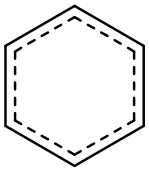
Thus the formula gives a positive contribution for bonding orbitals and a negative contribution for antibonding. The summation over the occupied orbitals just sums up the bonding or antibonding contributions from all the occupied MOs for the particular ij-pair of carbons to get the total bond order. Note that, in this summation, a doubly occupied orbital will appear twice. Applying this formula to the 1-2 bond in benzene, we find that:

$$O_{12} \equiv 2c_1^{\mu=1}c_2^{\mu=1} + 2c_1^{\mu=2}c_2^{\mu=2} + 2c_1^{\mu=3}c_2^{\mu=3}$$

$$= 2\left(\frac{+1}{\sqrt{6}}\right)\times\left(\frac{+1}{\sqrt{6}}\right) + 2\left(\frac{+1}{\sqrt{12}}\right)\times\left(\frac{+2}{\sqrt{12}}\right) + 2\left(\frac{+1}{\sqrt{4}}\right)\times\left(\frac{0}{\sqrt{4}}\right)$$

$$= 2\frac{1}{6} + 2\frac{2}{12} = \frac{2}{3}$$

Thus, the C_1 and C_2 formally appear to share 2/3 of a π-bond [Recall that we are omitting the σ-orbitals, so the total bond order would be 1 2/3 including the σ bonds]. We can repeat the same procedure for each C-C bond in benzene and we will find the same result: there are 6 equivalent π-bonds, each of order 2/3. This gives us great confidence in drawing the Lewis structure we all learned in freshman chemistry:



You might have expected this to give a bond order of 1/2 for each C-C π-bond rather than 2/3. The extra 1/6 of a bond per carbon comes directly from the aromatic stabilization: because the molecule is more stable than three isolated π-bonds by 2β, this effectively adds another π-bond to the system, which gets distributed equally among all six carbons, resulting in an increased bond order. This effect can be confirmed experimentally, as benzene has slightly shorter C-C bonds than non-aromatic conjugated systems, indicating a higher bond order between the carbons.

Just as we can use simple MO theory to describe resonance structures and aromatic stabilization, we can also use it to describe crystal field and ligand field states in transition metal compounds and the sp, sp^2 and sp^3 hybrid

orbitals that arise in directional bonding. These results not only mean MO theory is a useful tool – in practice these discoveries have led to MO theory becoming part of the way chemists **think** about molecules.