Lecture 26: Qualitative Molecular Orbital Theory: Hückel Theory

Models in Physical Chemistry

Our job is to make models that are intentionally as simple as possible. We do this to develop *intuition.* Often the models are obviously too crude to be quantitatively correct. But our goal is to find a model that is qualitatively in agreement with a large body of experimental and theoretical results. *And then we try to find examples that break the model!* This is where new insights are generated.

LCAO–MO Theory applied to H_2^+, H_2, AH, A_2, AB diatomic molecules in 5.61 has been entirely *qualitative.* We attempt to use insights about *atomic* properties as embodied in the Periodic Table to explain *molecular* properties. A key property is orbital size, based on hydrogen atom properties.

$$I_n = \frac{hc\Re}{n^{\star 2}}$$

$$r_{n^*} = a_0 n^{\star 2} = a_0 \left(\frac{hc\Re}{I_n} \right)$$

Atomic Orbital sizes, orbital energies, and non–degenerate perturbation theory generate enormous insights into the electronic properties of the valence states of diatomic molecules. From diatomic molecules we have confidence to move to larger molecules, based on the diatomic molecule–like properties of "chromophores". A chromophore is a small group of atoms in a molecule identified by LCAO-MO Theory as having a dominant role in determining a particular molecular property.

The next step is to develop a semi-quantitative model that starts with planar conjugated polyatomic molecules. This model exploits the variational method to generate molecular energy levels and wavefunctions. But the model, Hückel Theory, is based on shocking simplifications. It proves surprising predictive relationships between diverse molecular properties

and invites many ways to improve the model without doing accurate quantum mechanical calculations. This lecture is about Hückel Theory. The next two lectures show how to approach an accurate numerical Quantum Mechanical representation.

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At the end of these notes are Non-Lecture sections on Matrix Multiplication and Useful Tricks for checking a variational calculation.

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In general, the vast majority of 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 molecule like CO can be carried over given 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, such as 1,3,5–hexatriene:
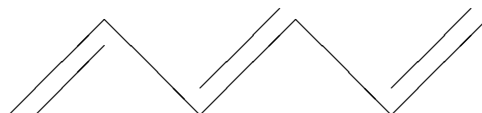

H-atoms excluded. C-atoms at ends of "bonds".

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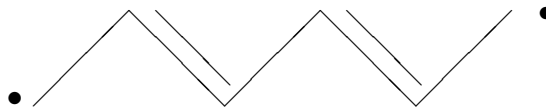

that it is better to think of the molecule as having a series of bonds of order $1\frac{1}{2}$ rather than $1/2/1/2/1/\ldots$ **MO theory actually predicts this behavior, and this prediction is one of the great successes of MO theory as a descriptor of chemistry**. In this lecture, we show how even a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

Conjugated molecules tend to be planar because the planar structure is most stable. This great simplification allows us to place all the atoms in the x–y plane. Thus, the molecule will have reflection symmetry in the xy plane:

z
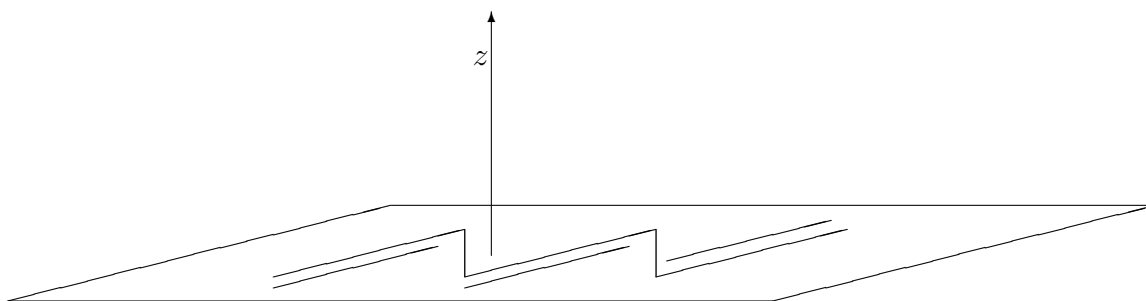
Now, for diatomic molecules, we have reflection symmetry in the xz and yz planes (z is defined as the bond axis) and this gives rise to π_x and π_y orbitals that are odd with respect to reflection in a plane that contains the bond axis and σ orbitals that are even. In that same way, for planar conjugated systems the orbitals will separate into σ orbitals that are even with respect to reflection through to xy plane and π_z orbitals that are odd with respect to reflection through the xy plane. These π_z molecular orbitals will be linear combinations of the π_z atomic orbitals on each carbon atom:

z
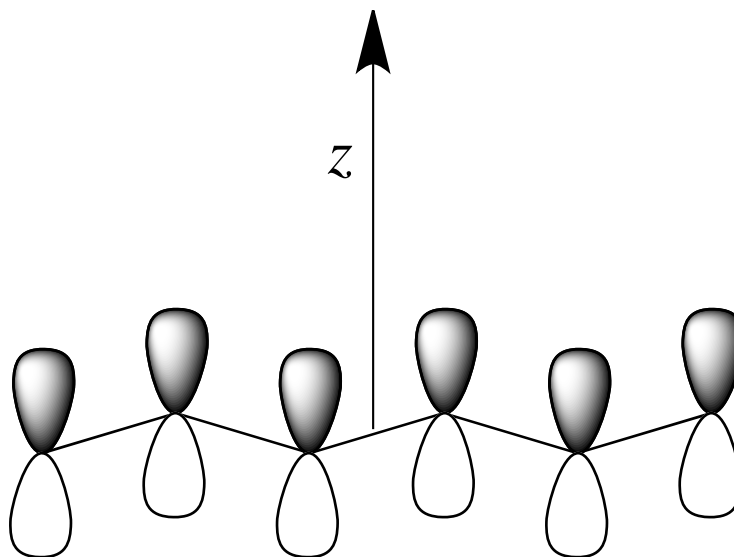
In trying to understand the chemistry of these compounds, it makes sense to focus our attention on these π_z orbitals and ignore the σ orbitals. The π_z orbitals turn out to be the highest energy occupied orbitals, with the σ orbitals being more strongly bound. Thus, the forming and breaking of bonds — as implied by our set of resonance structures — will be more easily understood if we focus on making and breaking π bonds rather than σ bonds. 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 surprising assumption is the basic approximation of Hückel theory, which can be outlined according to 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 express the π MOs as linear combinations of one p_z orbital on each carbon atom. If we assume that there are N carbon atoms, each contributes a p_z orbital, and we can write the μth MOs as:

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

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

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

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

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

Equivalently, this means **S** is the identity matrix, which reduces our generalized eigenvalue problem (see 5.61 Lecture Notes 24Supplement for an approach to the generalized eigenvalue problem) to a normal eigenvalue problem

$$\mathbf{H} \cdot \mathbf{c}^\alpha = E_\alpha \mathbf{S} \cdot \mathbf{c}^\mu \quad [\mathbf{S} \cdot \mathbf{c}^\mu = \mathbf{c}^\alpha] \quad \Rightarrow \quad \mathbf{H} \cdot \mathbf{c}^\alpha = E_\mu \mathbf{c}^\alpha.$$

The second approximation is to assume that **all Hamiltonian integrals vanish if they involve atoms i, j that are *not* nearest neighbors**. This daring simplification 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 it seems reasonable 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:

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

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

$$H_{ij} = \int p_z^i \widehat{\mathbf{H}} p_z^j d\tau \equiv \beta \qquad i, j \text{ neighbors.}$$

This last approximation is likely to be valid 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 parametrically 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 widely accepted choice is $\alpha = -11.2$ eV and $\beta = -0.7$ eV. Note both α and β are negative because they express stabilization of the orbital. [Can we ever know the sign of an off-diagonal matrix element?]

3) **Solve the generalized eigenvalue problem**. Here, we almost always need to use a computer. But because the Hückel Theory 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 that 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 theory uses the non-interacting electron energy expression (neglect of the inter–electron repulsion term, e^2/r_{ij}):

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

where E_i are the MO eigenvalues of the occupied orbitals determined in the third step.

To illustrate how we apply Hückel theory in practice, let's work out the energy of benzene as an example.
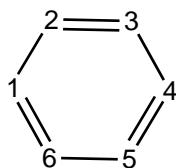
1) Each of the MOs is a linear combination of 6 p_z orbitals

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

2) It is relatively easy to work out the matrix elements of the Hamiltonian. It is a 6×6 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:
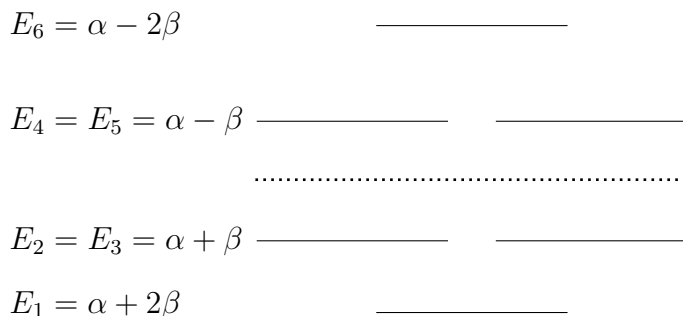
$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & & & & \beta \\ \beta & \alpha & \beta & & & \\ & \beta & \alpha & \beta & & \\ & & \beta & \alpha & \beta & \\ & & & \beta & \alpha & \beta \\ \beta & & & & \beta & \alpha \end{pmatrix}$$

Notice the β's in the 1,6 and 6,1 positions! All closed-ring structures have this often forgotten feature.

All the rest of the matrix elements involve non-nearest neighbors and thus are zero:
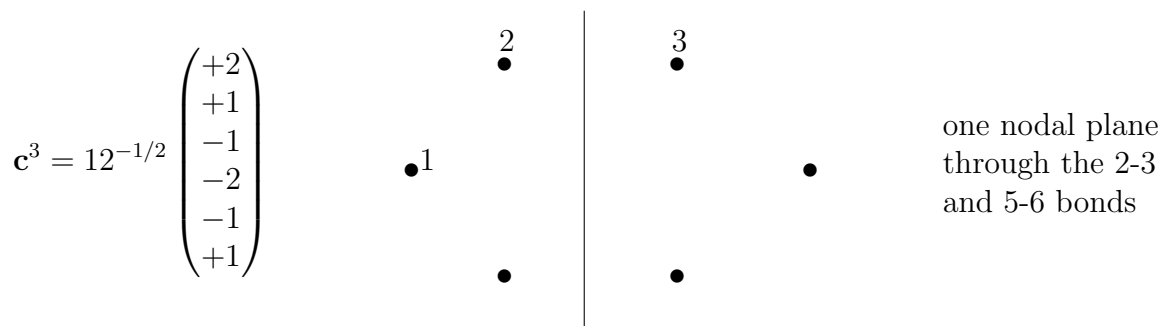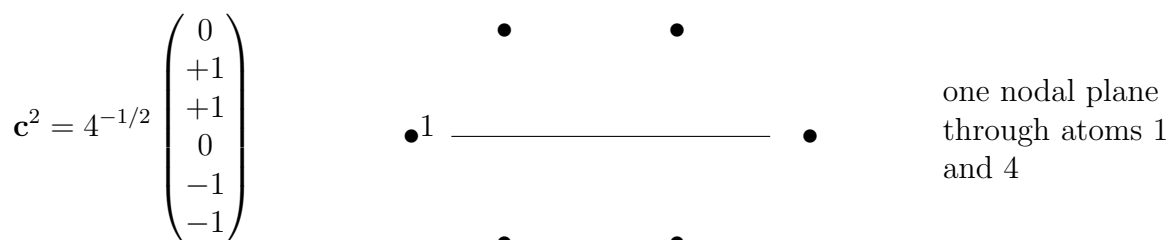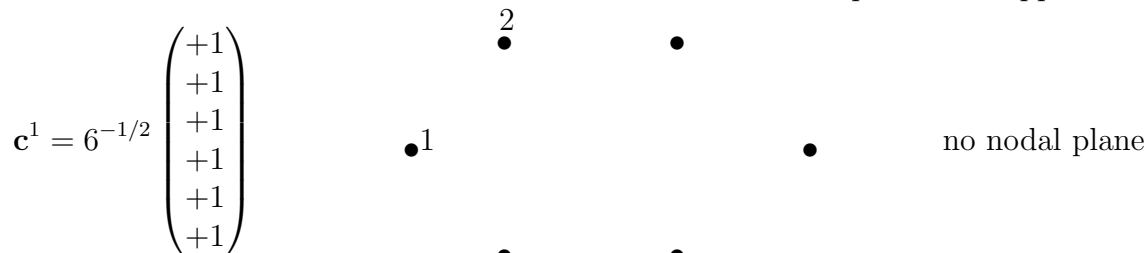
$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

3) Finding the eigenvalues of $\mathbf{H}$ is easy with a computer. We find 4 distinct energies:

$$E_6 = \alpha - 2\beta \qquad \underline{\hspace{3cm}}$$

$$E_4 = E_5 = \alpha - \beta \quad \underline{\hspace{2.5cm}} \qquad \underline{\hspace{2.5cm}}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$E_2 = E_3 = \alpha + \beta \quad \underline{\hspace{2.5cm}} \qquad \underline{\hspace{2.5cm}}$$

$$E_1 = \alpha + 2\beta \qquad\qquad \underline{\hspace{2.5cm}}$$

The lowest and highest energies are non-degenerate. The second/third and fourth/fifth energies are two-fold degenerate. With a little more work we can obtain the eigenvectors. They are:

Nodal planes go *through* atoms with 0 amplitude or *between* atoms with amplitudes of opposite signs

$$\mathbf{c}^1 = 6^{-1/2} \begin{pmatrix} +1 \\ +1 \\ +1 \\ +1 \\ +1 \\ +1 \end{pmatrix}$$

no nodal plane

$$\mathbf{c}^2 = 4^{-1/2} \begin{pmatrix} 0 \\ +1 \\ +1 \\ 0 \\ -1 \\ -1 \end{pmatrix}$$

one nodal plane through atoms 1 and 4

$$\mathbf{c}^3 = 12^{-1/2} \begin{pmatrix} +2 \\ +1 \\ -1 \\ -2 \\ -1 \\ +1 \end{pmatrix}$$

one nodal plane through the 2-3 and 5-6 bonds

$$\mathbf{c}^4 = 4^{-1/2} \begin{pmatrix} 0 \\ +1 \\ -1 \\ 0 \\ +1 \\ -1 \end{pmatrix}$$

two nodal planes through atoms 1 and 4 and bonds 2-3 and 5-6

$$\mathbf{c}^5 = 12^{-1/2} \begin{pmatrix} +2 \\ -1 \\ -1 \\ +2 \\ -1 \\ -1 \end{pmatrix}$$

two nodal planes, one through the 1-2 and 4-5 bonds, one through 3-4 and 6-1 bonds

$$\mathbf{c}^6 = 6^{-1/2} \begin{pmatrix} +1 \\ -1 \\ +1 \\ -1 \\ +1 \\ -1 \end{pmatrix}$$
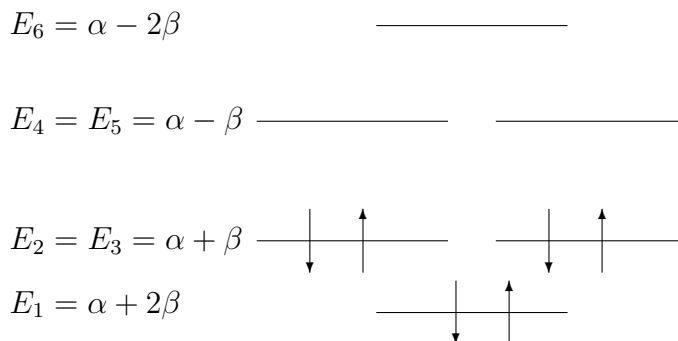
three nodal planes, each through an opposite pair of bonds.

Recall that the number of nodes⇔energy order.

We expect two-fold degeneracies for orbitals 2, 3, and 4, 5. You should verify that the six normalized MOs exactly "use up" each of the AOs.

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

$$E_6 = \alpha - 2\beta \qquad \underline{\hspace{3cm}}$$

$$E_4 = E_5 = \alpha - \beta \quad \underline{\hspace{2.5cm}} \qquad \underline{\hspace{2.5cm}}$$

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

$$E_1 = \alpha + 2\beta$$

5) The Hückel energy of benzene is then:

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

Now, we arrive at 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

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

reacall that β is negative because it represents stabilization

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

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

which is too small by 2β. We recall that β is negative, so that **the π-electrons in benzene are more stable than a collection of three isolated double bonds**. We call this "aromatic stabilization", and Hückel theory predicts a similar stabilization of other cyclic conjugated systems with $4N + 2$ electrons ($N = 1, 2, \dots$). This energetic stabilization explains in part why benzene is so unreactive 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 a molecular orbital μ includes a bond between the ith and j^{th} carbons, then the coefficients of the μth MO on those carbons must both have the same sign (e.g. we have $p_z^i + p_z^j$). If the μth orbital is antibonding between i and j, the coefficients must have opposite signs (e.g. we have $p_z^i - p_z^j$). The summand above reflects this because

$$c_i^{\mu} c_j^{\mu} > 0 \qquad \text{if } c_i^{\mu}, c_j^{\mu} \text{ have the same sign}$$
$$c_i^{\mu} c_j^{\mu} < 0 \qquad \text{if } c_i^{\mu}, c_j^{\mu} \text{ have opposite signs.}$$

Thus the formula gives a positive contribution for bonding orbitals and a negative contribution for antibonding orbitals. The summation over the occupied orbitals just sums up the bonding or antibonding contributions from all the occupied MOs for the particular i, j–pair of carbons to get the total bond order. Note that, in this summation, *each doubly occupied*

orbital will appear twice. Applying this formula to the 1-2 bond in benzene, we find that:

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

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

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

Thus, the C_1 and C_2 atoms 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 that we all learned in freshman chemistry:
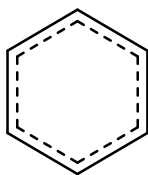
But this structure is somewhat misleading! You might have expected this structure to give a bond order of 1/2 for each C-C π-bond rather than 2/3. The extra 1/6 of a bond per carbon directly reflects the *aromatic stabilization*: because the molecule is more stable by 2β than three isolated π-bonds. 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, which indicates a higher bond order between all of the adjacent carbons.

Here, we have used the simplest possible form of MO theory to study a special class of molecules — π conjugated systems. However, we can extend this qualitative MO picture in many ways to treat a greater variety of systems:

- **Non-Nearest Neighbor (NNN) Interactions.** For benzene, adding, say, next nearest neighbor (NNN) interactions turns out to have negligible effect on the MOs. In a less highly constrained system, NNN interactions will have some effect on the MOs, but typically this effect is small. However, NNN terms do alter the energy in significant ways and thus offer additional flexibility when quantitative accuracy is desired.

- **Bond Length Alternation.** It is clear that if two bonds have different lengths, they should be associated with different values of β parameters. Shorter bonds lead to stronger orbital overlap and will generally lead to larger (more negative) values of β. We can model this by assuming that β is a function of the bond length, R. For example, we might guess something like $\beta(R) = \beta_0 e^{-\gamma R}$. The value of γ would encode the rate of decay of the atomic wavefunctions involved: more tightly held electrons would have wavefunctions that decay faster and thus have larger γ. Note that in our Hückel Theory calculation for benzene we assumed that all the β parameters for benzene are the same, which amounts to assuming that all bonds have equal (or nearly equal) length.

- **Heteroatoms and Substituents.** Even for conjugated systems, one is often interested in molecules that have *heteroatoms*, like nitrogen or oxygen, and *substituents*, like chlorine or methyl groups attached to one of the C atoms in the conjugated system. We can study these systems within the Hückel picture by using distinct values of α and β parameters for the chemically distinct atoms and bonds. The different atoms will primarily modify the α values. For examples, (i) the electronegativity of N is much larger than that of C, and (ii) an electron withdrawing substituent group will tend to make the carbon to which it is attached significantly more electrophilic (larger negative value of α) .... All of these effects are best represented by modifying α. There may also be attendant changes in β (smaller $|\beta|$ is associated with larger $|\alpha|$.) for the same reasons discussed under "bond length alternation", but these effects will be largely offset by the fact that atoms that form shorter bonds (like N) also tend to have orbitals with faster spatial decay. It is also important to note that when the site energies change, electrons will be shared unequally between the atoms, just as illustrated by LCAO-MO theory for AB polar bonding in heteronuclear diatomic molecules. In such cases, we can compute the charge on each atom using a formula similar to the bond order indicator, but involving only 1 atom:

$$q_i \equiv \sum_{\mu=1}^{occ} c_i^{\mu} c_i^{\mu}.$$

This equation gives the number of π electrons on atom i. Roughly speaking, we compute the number of electrons on the ith atom by counting up the number of "bonds" it forms with itself. For benzene you should show that $q_i = 1$ for each of the six carbon atoms in the benzene electronic ground state.

- **σ and π bonded systems.** It is straightforward, in principle, to extend the Hückel recipe to describe molecules for which both σ and π bonds are important, or where the

σ/π distinction is not clear because the molecule is not planar. One simply includes the s, p_x and p_y atomic orbitals (AOs) in addition to the p_z AOs. Equivalently, one could choose the hybrid valence bonding sp, sp^2 or sp^3 orbitals. In either case, the primary difficulty is that many more distinct orbitals would be involved, with a correspondingly large number of individually adjusted α and β parameters to be determined. Selecting parameters on this scale is something of an art and must necessarily involve a great deal of testing and empiricism. There would not be a single set of good parameters here, but generally techniques of this sort are termed "extended Hückel theory" (EHT).

- **Hückel Theory also predicts reactivity patterns**. A hetero-atom or an electron withdrawing or donating substituent gives rise to unequal bond-orders (O_{ij}) or non-zero atomic charges (q_i) and these result in activation toward reaction at predictable sites (and amounts) at various locations in the molecule. These correspond to "resonance structures" that are explicitly mixed into the electronic ground state structure by Hückel Theory.

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.

Non-Lecture

Rules for Matrix Multiplication: A_{ij} i is row, j is column

$$(\mathbf{A} \cdot \mathbf{B})_{ij} = \sum_{K=1}^{N} A_{ik} B_{kj}$$

The product of 2 square matrices of same dimension is a square matrix.

$\mathbf{c}$ is an N row by 1 column vector, $c^\dagger$ is a 1 row by N column transposed vector. $\mathbf{A}$ is an $N \times N$ square matrix.

$$\mathbf{Ac} = \begin{pmatrix} \sum_{i=1}^{N} A_{1i}c_i \\ \sum_{i=1}^{N} A_{2i}c_i \\ \ldots \\ \sum_{i=1}^{N} A_{Ni}c_i \end{pmatrix}$$

$$\mathbf{c}^{\dagger}\mathbf{A} = \left(\sum_{i=1}^{N} c_i A_{i1} \cdots \sum_{i=1}^{N} c_i A_{iN} \right)$$

$$\mathbf{c}^{\dagger}\mathbf{a} = \sum_{i=1}^{N} c_I^{\star} a_i \qquad \text{a number}$$

$$\mathbf{ac}^{\dagger} = \begin{pmatrix} a_1 c_1^{\star} \ldots a_N c_1^{\star} \\ a_1 c_2^{\star} \ldots a_N c_2^{\star} \\ \ldots \\ a_1 c_N^{\star} \ldots a_N c_N^{\star} \end{pmatrix} \qquad \text{an } N \times N \text{ square matrix}$$

Useful Tricks

When a computer solves for the eigenvalues of a matrix (e.g. $\mathbf{H}$) by "diagonalizing" it, it also provides the eigenvectors. You can check these eigenvectors for correctness and also to discover to which eigenvalue a particular eigenvector belongs. Here are some tests that the eigenvectors must pass. Suppose that the matrix is $N \times N$. This means that

(i) the eigenvectors, $\mathbf{c}^{\mu}$, are of dimension $N \times 1$ (ie. N rows and 1 column), there are N distinct eigenvectors ($\mu = 1$ to N),

(ii) each of the eigenvectors is normalized, and

(iii) orthogonal to all of the other eigenvectors, and

(iv) each basis state is exactly used up by the collection of N eigenvectors.

Let us use as an example the six eigenvectors of the Hückel Theory matrix for benzene.

(i) There are six p_z^i basis states ($i = 1$ to 6) and there are six eigenvectors.

$$\mathbf{c}^1 = 6^{-1/2} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \qquad \mathbf{c}^2 = 4^{-1/2} \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \\ -1 \\ -1 \end{pmatrix} \qquad \mathbf{c}^3 = 12^{-1/2} \begin{pmatrix} 2 \\ 1 \\ -1 \\ -2 \\ -1 \\ 1 \end{pmatrix}$$

$$\mathbf{c}^4 = 4^{-1/2} \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \\ 1 \\ -1 \end{pmatrix} \qquad \mathbf{c}^5 = 12^{-1/2} \begin{pmatrix} 2 \\ -1 \\ -1 \\ 2 \\ -1 \\ -1 \end{pmatrix} \qquad \mathbf{c}^6 = 6^{-1/2} \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \\ 1 \\ -1 \end{pmatrix}$$

(ii) These eigenvectors are normalized as shown here

$$\mathbf{c}^{1\dagger}\mathbf{c}^1 = \frac{1}{6}(1 + 1 + 1 + 1 + 1 + 1) = 1$$

$$\mathbf{c}^{2\dagger}\mathbf{c}^2 = \frac{1}{4}(0 + 1 + 1 + 0 + 1 + 1) = 1$$

$$\mathbf{c}^{3\dagger}\mathbf{c}^3 = \frac{1}{12}(4 + 1 + 1 + 4 + 1 + 1) = 1$$

$$\mathbf{c}^{4\dagger}\mathbf{c}^4 = \frac{1}{4}(0 + 1 + 1 + 0 + 1 + 1) = 1$$

$$\mathbf{c}^{5\dagger}\mathbf{c}^5 = \frac{1}{12}(4 + 1 + 1 + 4 + 1 + 1) = 1$$

$$\mathbf{c}^{6\dagger}\mathbf{c}^6 = \frac{1}{6}(1 + 1 + 1 + 1 + 1 + 1) = 1$$

(iii) These eigenvectors are mutually orthogonal, as can be shown for $6 \times 5/2 = 15$ combinations of eigenvectors, of which I will show only 6 here.

$$\mathbf{c}^{1\dagger}\mathbf{c}^2 = (6^{-1/2}) \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix} 4^{-1/2} \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \\ -1 \\ -1 \end{pmatrix} = 24^{-1/2}(0+1+1+0-1-1) = 0$$

$$\mathbf{c}^{1\dagger}\mathbf{c}^3 = (6^{-1/2})(12^{-1/2}) \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 2 \\ 1 \\ -1 \\ -2 \\ -1 \\ 1 \end{pmatrix} = 72^{-1/2}(2+1-1-2-1+1) = 0$$

$$\mathbf{c}^{1\dagger}\mathbf{c}^4 = (6^{-1/2})(4^{-1/2}) \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \\ 1 \\ -1 \end{pmatrix} = 24^{-1/2}(0+1-1+0+1-1) = 0$$

$$\mathbf{c}^{1\dagger}\mathbf{c}^5 = (6^{-1/2})(12^{-1/2}) \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 2 \\ -1 \\ -1 \\ 2 \\ -1 \\ -1 \end{pmatrix} = (72)^{-1/2}(2-1-1+-1-1) = 0$$

$$\mathbf{c}^{1\dagger}\mathbf{c}^6 = (6^{-1/2})(6^{-1/2}) \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix} 4^{-1/2} \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \\ 1 \\ -1 \end{pmatrix} = \frac{1}{6}(1-1+1-1+1-1) = 0$$

and one more for good luck!

$$\mathbf{c}^{3\dagger}\mathbf{c}^5 = (12)^{-1/2}(12^{-1/2}) \begin{pmatrix} 2 & 1 & -1 & -2 & -1 & 1 \end{pmatrix} \begin{pmatrix} 2 \\ -1 \\ -1 \\ 2 \\ -1 \\ -1 \end{pmatrix} = \frac{1}{12}(4-1+1-4+1-1) = 0.$$

(iv) Each basis state is used up among the set of eigenvectors ($\mu = 1$ to 6), e.g. for the ith basis state

$$\sum_{\mu=1}^{6} |c_i^\mu|^2 = 1$$

$i = 1$, the sum is $\dfrac{1}{6} + 0 + \dfrac{1}{3} + 0 + \dfrac{1}{3} + \dfrac{1}{6} = 1$

$i = 2$, the sum is $\dfrac{1}{6} + \dfrac{1}{4} + \dfrac{1}{12} + \dfrac{1}{4} + \dfrac{1}{12} + \dfrac{1}{6} = 1$

$i = 3$, the sum is $\dfrac{1}{6} + \dfrac{1}{4} + \dfrac{1}{12} + \dfrac{1}{4} + \dfrac{1}{12} + \dfrac{1}{6} = 1$

$i = 4$, the sum is $\dfrac{1}{6} + 0 + \dfrac{1}{3} + 0 + \dfrac{1}{3} + \dfrac{1}{6} = 1$

$i = 5$, the sum is $\dfrac{1}{6} + \dfrac{1}{4} + \dfrac{1}{12} + \dfrac{1}{4} + \dfrac{1}{12} + \dfrac{1}{6} = 1$

$i = 6$, the sum is $\dfrac{1}{6} + \dfrac{1}{4} + \dfrac{1}{12} + \dfrac{1}{4} + \dfrac{1}{12} + \dfrac{1}{6} = 1$

All OK.

(v) Correspondence between eigenvalue and eigenvector:

One expects $\mathbf{c}^{\mu\dagger}\mathbf{H}\mathbf{c}^{\mu} = E_{\mu}$.

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

$$\mathbf{H}\mathbf{c}^1 = 6^{-1/2} \begin{pmatrix} \alpha + 2\beta \\ \alpha + 2\beta \\ \alpha + 2\beta \\ \alpha + 2\beta \\ \alpha + 2\beta \\ \alpha + 2\beta \end{pmatrix} = (\alpha + 2\beta)\mathbf{c}^1$$

$$\mathbf{c}^{1\dagger}\mathbf{H}\mathbf{c}^1 = 6^{-1/2} \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix} (\alpha + 2\beta)\mathbf{c}^1$$

$$= \frac{1}{6}(\alpha + 2\beta)6 = \alpha + 2\beta \qquad \text{OK}$$

$$\mathbf{H}\mathbf{c}^2 = 4^{-1/2} \begin{pmatrix} \beta - \beta \\ \alpha + \beta \\ \beta + \alpha \\ \beta - \beta \\ -\beta - \alpha \\ -\beta - \alpha \end{pmatrix} = 4^{-1/2}(\alpha + \beta) \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \\ -1 \\ -1 \end{pmatrix} = (\alpha + \beta)\mathbf{c}^2$$

$$\mathbf{c}^{2\dagger}\mathbf{H}\mathbf{c}^2 = (\alpha + \beta) \qquad \text{OK}$$

etc.

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Fall 2017