Lecture 25, March 29, 2006

(Some material in this lecture has been adapted from Cramer, C. J. Essentials of Computational Chemistry, Wiley, Chichester: 2002; pp. 96-109.)

Recapitulation of the Variational Principle and the Secular Equation

Recall that for any system where we cannot determine exact wave functions by analytical solution of the Schrödinger equation (because the differential equation is simply too difficult to solve), we can make a guess at the wave function, which we will designate Φ, and the variational principle tells us that the expectation value of the Hamiltonian for Φ is governed by the equation

$$\frac{\int \Phi^* H \Phi d\mathbf{r}}{\int \Phi^* \Phi d\mathbf{r}} \geq E_0 \qquad (25\text{-}1)$$

where E_0 is the *correct* ground-state energy.

Not only does this lower-limit condition provide us with a convenient way of evaluating the quality of different guesses (lower is better), but it also permits us to use the tools of variational calculus to identify minimizing values for any parameters that appear in the definition of Φ.

In the LCAO (linear combination of atomic orbitals) approach, the parameters are coefficients that describe how molecular orbitals (remember, orbital is another word for a *one*-electron wave function contributing to a *many*-electron wave function) are built up as linear combinations of atomic orbitals. In particular, many-electron wave functions Φ can be written as antisymmetrized Hartree products—i.e., Slater determinants—of such one-electron orbitals ϕ, where the one-electron orbitals are defined as

$$\phi = \sum_{i=1}^{N} a_i \varphi_i \qquad (25\text{-}2)$$

where the set of N atomic-orbital basis functions φ_i is called the "basis set" and each has associated with it some coefficient a_i, where we will use the variational principle to find the optimal coefficients.

To be specific, for a given one-electron orbital we evaluate

$$E = \frac{\int \left(\sum_i a_i^* \varphi_i^* \right) H \left(\sum_j a_j \varphi_j \right) d\mathbf{r}}{\int \left(\sum_i a_i^* \varphi_i^* \right) \left(\sum_j a_j \varphi_j \right) d\mathbf{r}}$$

$$= \frac{\sum_{ij} a_i^* a_j \int \varphi_i^* H \varphi_j d\mathbf{r}}{\sum_{ij} a_i^* a_j \int \varphi_i^* \varphi_j d\mathbf{r}}$$

$$= \frac{\sum_{ij} a_i^* a_j H_{ij}}{\sum_{ij} a_i^* a_j S_{ij}}$$

(25-3)

where the shorthand notation H_{ij} and S_{ij} is used for the resonance and overlap integrals in the numerator and denominator, respectively.

If we impose the minimization condition

$$\frac{\partial E}{\partial a_k} = 0 \quad \forall\ k$$

(25-4)

we get N equations which must be satisfied in order for equation 25-4 to hold true, namely

$$\sum_{i=1}^{N} a_i \left(H_{ki} - ES_{ki} \right) = 0 \quad \forall\ k .$$

(25-5)

these equations can be solved for the variables a_i if and only if

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

(25-6)

where equation 25-6 is called the secular equation. There are N roots (i.e., N different values of E) which permit the secular equation to be true. For each such value E_j there will be a different set of coefficients, a_{ij}, which can be found by solving the set of linear equations 25-5 using that specific E_j, and those coefficients will define an optimal associated wave function ϕ_j within the given basis set.

The steps in a practical calculation are:

(1)   Select a set of N basis functions.

(2)   For that set of basis functions, determine all N^2 values of both H_{ij} and S_{ij}.

(3)   Form the secular determinant, and determine the N roots E_j of the secular equation.

(4)   For each of the N values of E_j, solve the set of linear eqs. 25-5 in order to determine the basis set coefficients a_{ij} for that MO.

Hückel Theory

To further illuminate the LCAO variational process, we will carry out the steps outlined above for a specific example. To keep things simple (and conceptual), we consider a flavor of molecular orbital theory developed in the 1930s by Erich Hückel to explain some of the unique properties of unsaturated and aromatic hydrocarbons. In order to accomplish steps (1)-(4) of the last section, Hückel theory adopts the following conventions:

(a)   The basis set is formed entirely from parallel carbon 2p orbitals, one per atom. [Hückel theory was originally designed to treat only planar hydrocarbon π systems, and thus the 2p orbitals used are those that are associated with the π system.]

(b)   The overlap matrix is *defined* to be

$$S_{ij} = \delta_{ij}$$

(25-7)

Thus, the overlap of any carbon 2p orbital with itself is unity (i.e., the p functions are normalized), and that between any two different p orbitals is zero (so we won't waste time computing overlap integrals, we'll just assume the basis functions to be orthonormal).

(c)   Matrix elements H_{ii} are set equal to the negative of the ionization potential of the methyl radical $CH_3^{\bullet}$, i.e., the orbital energy of the singly occupied 2p orbital in the prototypical system defining sp^2 carbon hybridization. This choice is consistent with our earlier discussion of the relationship between this matrix element and an ionization potential. This energy value, which is defined so as to be negative, is rarely actually written as a numerical value, but is instead represented by the symbol α. For those who *like* working with actual numbers, $\alpha = -9.9$ eV.

(d)   Matrix elements H_{ij} between nearest neighbors are also derived from experimental information. A 90° rotation about the π bond in ethylene removes all of the

bonding interaction between the two carbon 2p orbitals. That is, the (positive) cost of the following process,

$$E = E_\pi \qquad\qquad E = 2E_p$$
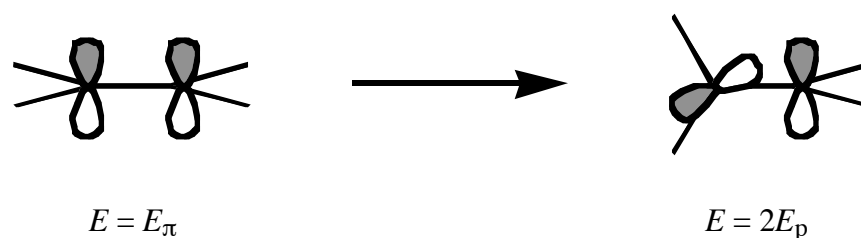
is $\Delta E = 2E_p - E_\pi$. The (negative) stabilization energy for the pi bond is distributed equally to the two p orbitals involved (i.e., divided in half) and this quantity, termed β, is used for H_{ij} between neighbors. (Note, based on our definitions so far, then, that $E_p = \alpha$ and $E_\pi = 2\alpha + 2\beta$.) Again, for those who like numbers, the π bond energy in ethylene is about 60 kcal mol^{-1}, which is 2.6 eV. Dividing that up between the two carbon atoms results in $\beta = -1.3$ eV.

(e)   Matrix elements H_{ij} between carbon 2p orbitals more distant than nearest neighbors are set equal to zero.
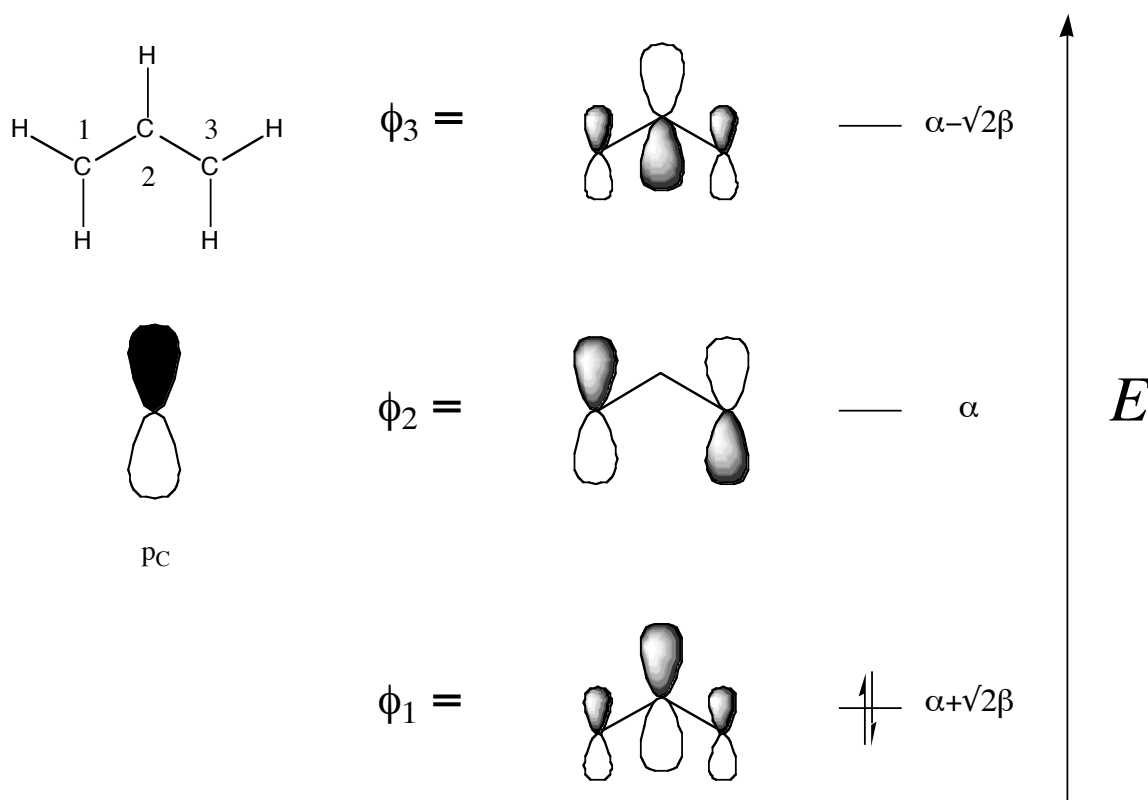
The Allyl π System

Let us now apply Hückel MO theory to the particular case of the allyl system, C_3H_3, as illustrated in the figure on the previous page. Because we have three carbon atoms, our basis set is determined from convention (a) and will consist of 3 carbon 2p orbitals, one centered on each atom. We will arbitrarily number them 1, 2, 3, from left to right for bookkeeping purposes.

The basis set size of 3 implies that we will need to solve a 3 x 3 secular equation. Hückel conventions (b)-(e) tell us the value of each element in the secular equation ($H_{11} = H_{22} = H_{33} = \alpha$, $H_{12} = H_{21} = H_{23} = H_{32} = \beta$, $H_{13} = H_{31} = 0$, $S_{11} = S_{22} = S_{33} = 1$, all other S values are 0) so that eq. 25-6 is rendered as

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{25-8}$$

The use of the Kronecker delta to define the overlap matrix ensures that E appears only in the diagonal elements of the determinant. Since this is a 3 x 3 determinant, it may be expanded using Cramer's rule as

$$(\alpha - E)^3 + (\beta^2 \bullet 0) + (0 \bullet \beta^2) - [0 \bullet (\alpha - E) \bullet 0] - \beta^2(\alpha - E) - (\alpha - E)\beta^2 = 0 \tag{25-9}$$

which is a fairly simple cubic equation in E that has three solutions, namely

$$E = \alpha + \sqrt{2}\beta, \quad \alpha, \quad \alpha - \sqrt{2}\beta \tag{25-10}$$

Since α and β are negative by definition, the *lowest* energy solution is $\alpha + \sqrt{2}\beta$. To find the MO associated with this energy, we employ it in the set of linear equations 25-5, together with the various necessary H and S values already noted above to give

$$a_1\left[\alpha - \left(\alpha + \sqrt{2}\beta\right)\bullet 1\right] + a_2\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] + a_3\left[0 - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] = 0$$

$$a_1\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] + a_2\left[\alpha - \left(\alpha + \sqrt{2}\beta\right)\bullet 1\right] + a_3\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] = 0 \tag{25-11}$$

$$a_1\left[0 - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] + a_2\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\bullet 0\right] + a_3\left[\alpha - \left(\alpha + \sqrt{2}\beta\right)\bullet 1\right] = 0$$

(the first equation comes from $k = 1$, the second from $k = 2$, and the third from $k = 3$). Some fairly trivial, if tedious, algebra reduces these equations to

$$a_2 = \sqrt{2}a_1$$
$$a_3 = a_1 \tag{25-12}$$

While there are infinitely many values of a_1, a_2, and a_3 which satisfy eq. 25-12, imposing the requirement that the wave function be normalized provides a final constraint in the form of

$$\sum_{i=1}^{3} |a_i|^2 = 1 \tag{25-13}$$

The unique values satisfying both eqs. 25-12 and 25-13 are

$$a_{11} = \frac{1}{2}, \quad a_{21} = \frac{\sqrt{2}}{2}, \quad a_{31} = \frac{1}{2} \tag{25-14}$$

where we have now emphasized that these coefficients are specific to the *lowest energy* molecular orbital by adding the second subscript "1". Since we now know both the coefficients *and* the basis functions, we may construct the lowest energy molecular orbital, i.e.,

$$\phi_1 = \frac{1}{2} p_1 + \frac{\sqrt{2}}{2} p_2 + \frac{1}{2} p_3 \tag{25-15}$$

which is illustrated in the figure above.

By choosing the higher energy roots of eq. 25-8, we may solve the sets of linear equations analogous to eq. 25-11 in order to arrive at the coefficients required to construct ϕ_2 (from $E = \alpha$) and ϕ_3 (from $E = \alpha - \sqrt{2}\beta$). Although the algebra is left as a homework problem, the results are

$$a_{12} = \frac{\sqrt{2}}{2}, \quad a_{22} = 0, \quad a_{32} = -\frac{\sqrt{2}}{2}$$

$$a_{13} = \frac{1}{2}, \quad a_{23} = -\frac{\sqrt{2}}{2}, \quad a_{33} = \frac{1}{2} \tag{25-16}$$

where these orbitals are also illustrated in the figure above. The three orbitals we have derived are the bonding, non-bonding, and antibonding molecular orbitals of the allyl system with which all organic chemists are familiar.

Importantly, Hückel theory affords us certain insights into the allyl system, one in particular being an analysis of the so-called "resonance" energy arising from electronic delocalization in the π system. By delocalization we refer to the participation of more than two atoms in a given MO. Consider for example the allyl cation, which has a total of two electrons in the π system. If we adopt a molecular aufbau principle of filling lowest energy MOs first and further make the assumption that each electron has the energy of the one-electron MO that it occupies (ϕ_1 in this case) then the total energy of the allyl cation π system is $2(\alpha + \sqrt{2}\beta)$. Consider the alternative "fully localized" structure for the

allyl system, in which there is a full (i.e., doubly-occupied) π bond between two of the carbons, and an empty, non-interacting p orbital on the remaining carbon atom (this could be achieved by rotating the cationic methylene group 90° so that the p orbital becomes orthogonal to the remaining π bond, but that could no longer be described by simple Hückel theory since the system would be non-planar—the non-interaction we are considering here is purely a thought-experiment). The π energy of such a system would simply be that of a double bond, which by our definition of terms above is $2(\alpha + \beta)$. Thus, the Hückel resonance energy, which is equal to $H_\pi - H_{localized}$, is 0.83β (remember β is negative by definition, so resonance is a favorable phenomenon). Recalling the definition of β, the resonance energy in the allyl cation is predicted to be about 40% of the rotation barrier in ethylene—roughly 25 kcal mol^{-1}.

We may perform the same analysis for the allyl radical and the allyl anion, respectively, by adding the energy of ϕ_2 to the cation with each successive addition of an electron, i.e., H_π(allyl radical) $= 2(\alpha + \sqrt{2}\beta) + \alpha$ and H_π(allyl anion) $= 2(\alpha + \sqrt{2}\beta) + 2\alpha$. In the hypothetical fully-π-localized non-interacting system, each new electron would go into the non-interacting p orbital, also contributing each time a factor of α to the energy (by definition of α). Thus, the Hückel resonance energies of the allyl radical and the allyl anion are the same as for the allyl cation, namely, 0.83β.

Unfortunately, while it is clear that the allyl cation, radical, and anion all enjoy some degree of resonance stabilization, neither experiment, in the form of measured rotational barriers, nor more complete levels of quantum theory support the notion that in all three cases the magnitude is the same. So, there is some aspect of Hückel theory that renders it incapable of accurately distinguishing between these three allyl systems. We will examine this issue shortly.

Homework

To be solved in class:

Find the shapes and energies of the 3 molecular orbitals for the cyclopropenium system. Note that this system differs from the allyl system in that it has an additional connectivity between atoms 1 and 3. How does this qualitatively change the MO picture for cyclopropenyl compared to allyl? Based on your analysis, will the cyclopropenyl anion be a singlet or a triplet? (Hint: to quickly solve the somewhat challenging cubic equation in E that comes up in the determinant, try setting $E = \alpha + c\beta$ and solve for c.)

To be turned in for possible grading Apr. 7:

Using the third (antibonding) root of the secular equation for the allyl system, verify the orbital coefficients given in eq. 25-16.