

Lecture 26, March 31, 2006

(Some material in this lecture has been adapted from Cramer, C. J. *Essentials of Computational Chemistry*, Wiley, Chichester: 2002; pp. 111-114.)

Solved Homework

In the allyl system, we had $H_{11} = H_{22} = H_{33} = \alpha$, $H_{12} = H_{21} = H_{23} = H_{32} = \beta$, $H_{13} = H_{31} = 0$, $S_{11} = S_{22} = S_{33} = 1$, and all other S values were 0. The difference in cyclopropenyl is that carbon atoms 1 and 3 are now neighbors, so that instead of $H_{13} = H_{31} = 0$, we have $H_{13} = H_{31} = \beta$. As a result, the secular equation becomes

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

which expands as

$$(\alpha - E)^3 + \beta^3 + \beta^3 - [\beta \cdot (\alpha - E) \cdot \beta] - \beta^2(\alpha - E) - (\alpha - E)\beta^2 = 0$$

or

$$(\alpha - E)^3 - 3\beta^2(\alpha - E) + 2\beta^3 = 0$$

To solve the above cubic equation in E , it is convenient to set $E = \alpha + c\beta$, in which case the equation transforms to

$$-c^3 + 3c + 2 = 0$$

The roots of this equation are -1 and 2 (it turns out that -1 is a critical point where the cubic curve just touches the x axis, so there are only two roots and it must be the case that one of these roots represents a two-fold degenerate energy level). So, the allowed energy levels are $E = \alpha + 2\beta$ (lowest energy, since α and β are negative numbers) and $\alpha - \beta$ (higher energy). If we solve for the lowest energy MO we have the linear equations

$$\begin{aligned} a_1[\alpha - (\alpha + 2\beta) \cdot 1] + a_2[\beta - (\alpha + 2\beta) \cdot 0] + a_3[\beta - (\alpha + 2\beta) \cdot 0] &= 0 \\ a_1[\beta - (\alpha + 2\beta) \cdot 0] + a_2[\alpha - (\alpha + 2\beta) \cdot 1] + a_3[\beta - (\alpha + 2\beta) \cdot 0] &= 0 \\ a_1[\beta - (\alpha + 2\beta) \cdot 0] + a_2[\beta - (\alpha + 2\beta) \cdot 0] + a_3[\alpha - (\alpha + 2\beta) \cdot 1] &= 0 \end{aligned}$$

or

$$\begin{aligned} -2a_1 + a_2 + a_3 &= 0 \\ a_1 - 2a_2 + a_3 &= 0 \\ a_1 + a_2 - 2a_3 &= 0 \end{aligned}$$

Casual inspection should indicate that this system of equations is solved by the relationship $a_1 = a_2 = a_3$, and the normalization condition can then be solved to set a specific value of $a_1 = a_2 = a_3 = 3^{-1/2}$.

So the lowest-energy MO has equal contributions from all 3 p orbitals and all 3 orbitals are in phase. This is illustrated below.

What about the next energy level, $\alpha - \beta$? That gives linear equations

$$\begin{aligned} a_1[\alpha - (\alpha - \beta) \cdot 1] + a_2[\beta - (\alpha - \beta) \cdot 0] + a_3[\beta - (\alpha - \beta) \cdot 0] &= 0 \\ a_1[\beta - (\alpha - \beta) \cdot 0] + a_2[\alpha - (\alpha - \beta) \cdot 1] + a_3[\beta - (\alpha - \beta) \cdot 0] &= 0 \\ a_1[\beta - (\alpha - \beta) \cdot 0] + a_2[\beta - (\alpha - \beta) \cdot 0] + a_3[\alpha - (\alpha - \beta) \cdot 1] &= 0 \end{aligned}$$

In this case, all 3 equations reduce to

$$a_1 + a_2 + a_3 = 0$$

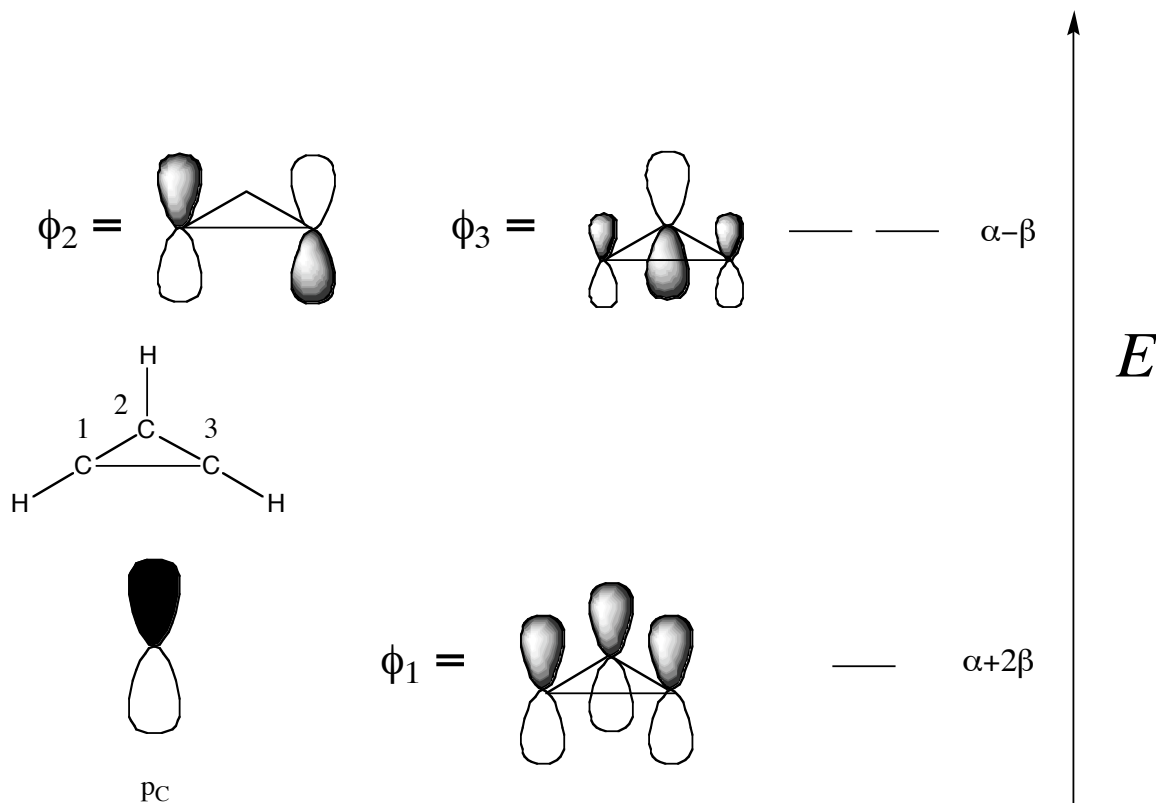
When this equation is combined with the normalization condition, there are still only two equations in 3 unknowns, so we have remaining flexibility. This implies that we have a two-fold degenerate energy. We can arbitrarily select one set of coefficients that satisfies the linear equation and normalization. Then, since we want the next orbital of that energy to be orthogonal to the first, we will have 3 equations (the linear equation, the normalization condition, and the orthogonality condition) to determine the coefficients, and we will then be done.

To make life simple, then, let's use our flexibility initially to simply eliminate one coefficient. We will set $a_2 = 0$. In that case, we have $a_1 = -a_3$, and normalization gives values of $\pm 2^{-1/2}$ for the coefficients. This orbital is also illustrated below. It has a node at carbon 2 and equal, antibonding contributions from carbons 1 and 3.

For the second orbital of energy $\alpha - \beta$, the orthogonality condition with the first is

$$\begin{aligned}
0 &= S_{23} \\
&= \left\langle \sum_{i=1}^3 a_{2i} p_i \left| \sum_{i=1}^3 a_{3i} p_i \right. \right\rangle \\
&= a_{21}a_{31} \langle p_1 | p_1 \rangle + a_{21}a_{32} \langle p_1 | p_2 \rangle + a_{21}a_{33} \langle p_1 | p_3 \rangle \\
&\quad + a_{22}a_{31} \langle p_2 | p_1 \rangle + a_{22}a_{32} \langle p_2 | p_2 \rangle + a_{22}a_{33} \langle p_2 | p_3 \rangle \\
&\quad + a_{23}a_{31} \langle p_3 | p_1 \rangle + a_{23}a_{32} \langle p_3 | p_2 \rangle + a_{23}a_{33} \langle p_3 | p_3 \rangle \\
&= a_{21}a_{31} + a_{22}a_{32} + a_{23}a_{33} \\
&= \frac{1}{\sqrt{2}} a_{31} - \frac{1}{\sqrt{2}} a_{33}
\end{aligned}$$

so we see that the orthogonality condition requires $a_1 = a_3$ for our third MO. In that case, we must have $a_2 = -2a_1$ (or 3) and normalization of the orbital provides $a_1 = a_3 = 6^{-1/2}$ and $a_2 = (2/3)^{-1/2}$. So, in this orbital, there is π bonding between the smaller p orbital contributions from carbons 1 and 3, and π antibonding between each of those p orbitals and the twice as large contribution of the p orbital from carbon 2.



So, the final two orbitals look just like those from the allyl system, but the connection between carbon atoms 1 and 3 raises the energy of the previously non-

bonding orbital (because of the new antibonding interaction) and lowers the energy of the previously only antibonding orbital (because of the new, but weak, bonding interaction). Coincidentally, the two end up degenerate.

The orbital picture permits us to make many qualitative observations that are very important to chemistry. First, it is evident that the cation (with only two electrons in the π system) will be very stable. If there were a hypothetical system having one of the p orbitals non-interacting, the total energy would simply be $2(\alpha+\beta)$ (the usual ethylene π bonding energy), but in cyclopropenium cation, the energy is $2(\alpha+2\beta)$ —an improvement of 2β . Students of organic chemistry will recall the Hückel $4n+2$ rule to note that cyclopropenium cation satisfies that rule ($n = 0$) and we call it aromatic and assign it special stability. Now, from quantum mechanics, you know why!

You can also see that the cyclopropenyl anion is likely to be a rather unhappy species. Since electrons repel one another, a simple analysis suggests that one would want to put one electron into each of the degenerate orbitals (thus keeping them further apart). In addition, since we recall from work on the He atom that a triplet is always below the open-shell singlet using the same orbitals, we would expect the cyclopropenyl anion to be a triplet (this is a reflection of the *antiaromaticity* of this 4-electron system).

So, while the cyclopropenyl cation is a well known system, and has been employed as a ligand in organometallic chemistry for years, cyclopropenyl anions have for the most part avoided any synthesis. The only instances that have permitted observation of such species have involved substituting one carbon of the cyclopropenyl system with a very strong electron-withdrawing group. This lowers the energy of the p orbital on that carbon and lifts the degeneracy of the two high energy orbitals so that the system is no longer formally antiaromatic. Such work has been done at the University of Minnesota in the labs of Professor Steven Kass using mass spectrometry to identify the cyclopropenyl anions in the gas phase.

Many-electron Wave Functions—Hartree Products

In our Hückel theory examples, we derived molecular orbitals and molecular-orbital energies using a *one-electron formalism*, and we then assumed that the energy of a many-electron system could be determined simply as the sum of the energies of the occupied one-electron orbitals (we used our prior knowledge of antisymmetry to limit ourselves to two electrons per orbital). We further assumed that the orbitals themselves are invariant to the number of electrons in the π system. One might be tempted to say that Hückel theory thus ignores electron-electron repulsion. This is a bit unfair, however. By deriving our Hamiltonian matrix elements from *experimental* quantities (ionization potentials and rotational barriers) we have implicitly accounted for electron-electron repulsion in some sort of average way, but such an approach, known as an “effective Hamiltonian” method, is necessarily rather crude. Thus, while Hückel theory continues to find use even today in qualitative studies of conjugated systems, it is rarely sufficiently accurate for quantitative assessments. To improve our models, we need to take a more sophisticated accounting of many-electron effects.

Let us examine the Schrödinger equation in the context of a one-electron Hamiltonian a bit more carefully. When the only terms in the Hamiltonian are the one-electron kinetic energy and nuclear attraction terms, the operator is “separable” and may be expressed as

$$H = \sum_{i=1}^N h_i \quad (26-1)$$

where N is the total number of electrons and h_i is the one-electron Hamiltonian defined by

$$h_i = -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^M \frac{Z_k}{r_{ik}} \quad (26-2)$$

where M is the total number of nuclei.

Eigenfunctions of the one-electron Hamiltonian defined by eq. 26-2 must satisfy the corresponding one-electron Schrödinger equation

$$h_i \psi_i = \epsilon_i \psi_i \quad (26-3)$$

Because the Hamiltonian operator defined by eq. 26-1 is separable, its many-electron eigenfunctions can be constructed as products of one-electron eigenfunctions. That is

$$\Psi_{\text{HP}} = \psi_1 \psi_2 \cdots \psi_N \quad (26-4)$$

The eigenvalue of Ψ_{HP} is readily found from proving the validity of eq. 26-4, viz.,

$$\begin{aligned} H\Psi_{\text{HP}} &= H\psi_1\psi_2\cdots\psi_N \\ &= \sum_{i=1}^N h_i\psi_1\psi_2\cdots\psi_N \\ &= (h_1\psi_1)\psi_2\cdots\psi_N + \psi_1(h_2\psi_2)\cdots\psi_N \\ &\quad + \dots + \psi_1\psi_2\cdots(h_N\psi_N) \\ &= (\epsilon_1\psi_1)\psi_2\cdots\psi_N + \psi_1(\epsilon_2\psi_2)\cdots\psi_N \\ &\quad + \dots + \psi_1\psi_2\cdots(\epsilon_N\psi_N) \\ &= \sum_{i=1}^N \epsilon_i\psi_1\psi_2\cdots\psi_N \\ &= \left(\sum_{i=1}^N \epsilon_i \right) \Psi_{\text{HP}} \end{aligned} \quad (26-5)$$

where repeated application of eq. 26-3 is used in proving that the energy eigenvalue of the many-electron wave function is simply the sum of the one-electron energy eigenvalues. A wave function of the form of eq. 26-4 is called a “Hartree product” wave function. Note that eqs. 26-1 to 26-5 provide the mathematical rigor behind the Hückel theory example presented more informally above. Note that if every ψ is normalized then Ψ_{HP} is also normalized, since $|\Psi_{\text{HP}}|^2 = |\psi_1|^2 |\psi_2|^2 \cdots |\psi_N|^2$.

As noted above, however, the Hamiltonian defined by eqs. 26-3 and 26-4 does *not* include interelectronic repulsion, computation of which is vexing because it depends not on one electron, but instead on all possible (simultaneous) pairwise interactions. We may ask, however, how useful is the Hartree product wave function in computing energies from the *correct* Hamiltonian? That is, we wish to find orbitals ψ that minimize $\langle \Psi_{\text{HP}} | H | \Psi_{\text{HP}} \rangle$. By applying variational calculus, one can show that each such orbital ψ_i is an eigenfunction of its own operator h_i defined by

$$h_i = -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^M \frac{Z_k}{r_{ik}} + V_i\{j\} \quad (26-6)$$

where the final term represents an interaction potential with all of the other electrons occupying orbitals $\{j\}$ and may be computed as

$$V_i\{j\} = \sum_{j \neq i} \int \frac{\rho_j}{r_{ij}} d\mathbf{r} \quad (26-7)$$

where ρ_j is the charge (probability) density associated with electron j . The repulsive third term on the r.h.s. of eq. 26-6 is thus exactly analogous to the attractive second term, except that nuclei are treated as point charges, while electrons, being treated as wave functions, have their charge spread out, so an integration over all space is necessary. Recall, however, that $\rho_j = |\psi_j|^2$. Since the point of undertaking the calculation is to determine the individual ψ , how can they be used in the one-electron Hamiltonians before they are known?

To finesse this problem, Hartree in 1928 proposed an iterative “self-consistent field” (SCF) method. In the first step of the SCF process, one *guesses* the wave functions ψ for all of the occupied MOs (AOs in Hartree’s case, since he was working exclusively with atoms) and uses these to construct the necessary one-electron operators h . Solution of each differential eq 26-6 (in an atom, with its spherical symmetry, this is relatively straightforward, and, as noted previously, Hartree was helped by his retired father who enjoyed the mathematical challenge afforded by such calculations) provides a *new* set of ψ , presumably different from the initial guess. So, the one-electron Hamiltonians are formed anew using these presumably more accurate ψ to determine each necessary ρ , and the process is repeated to obtain a still better set of ψ . At some point, the difference between a newly determined set and the immediately preceding set falls below some threshold criterion, and we refer to the final set of ψ as the “converged” SCF orbitals.

(An example of a threshold criterion might be that the total electronic energy change by no more than 10^{-6} a.u., and/or that the energy eigenvalue for each MO change by no more than that amount—such criteria are, of course, entirely arbitrary, and it is typically only by checking computed properties for wave functions computed with varying degrees of imposed “tightness” that one can determine an optimum balance between convergence and accuracy—the tighter the convergence, the more SCF cycles required, and the greater the cost in computational resources.)

Notice, from eq. 26-5, that the sum of the individual operators h defined by eq. 26-6 defines a separable Hamiltonian operator for which Ψ_{HP} is an eigenfunction. This separable Hamiltonian corresponds to a “non-interacting” system of electrons (in the sense that each individual electron sees simply a constant potential with which it interacts—the nomenclature can be slightly confusing since the potential *does* derive in an average way from the other electrons, but the point is that their interaction is not accounted for instantaneously). The non-interacting Hamiltonian is *not* a good approximation to the true Hamiltonian, however, because each h includes the repulsion of its associated electron with all of the other electrons, i.e., h_i includes the repulsion between electron i and electron j , but so too does h_j . Thus, if we were to sum all of the one-electron eigenvalues for the operators h_i , which according to eq. 26-5 would give us the eigenvalue for our non-interacting Hamiltonian, we would double-count the electron-electron repulsion. It is a straightforward matter to correct for this double-counting, however, and we may in principle compute $E = \langle \Psi_{\text{HP}} | H | \Psi_{\text{HP}} \rangle$ (where H is the “proper” Hamiltonian, instead of that defined by eqs. 26-1 and 26-6) not directly but rather as

$$E = \sum_i \varepsilon_i - \frac{1}{2} \sum_{i \neq j} \iint \frac{|\psi_i|^2 |\psi_j|^2}{r_{ij}} d\mathbf{r}_i d\mathbf{r}_j \quad (26-8)$$

where i and j run over all the electrons, ε_i is the energy of MO i from the solution of the one-electron Schrödinger equation using the one-electron Hamiltonian defined by eq. 26-6, and we have replaced ρ with the square of the wave function to emphasize how it is determined (again, the double integration over all space derives from the wave function character of the electron—the double integral appearing on the r.h.s. of eq. 26-8 is simply the “Coulomb integral” J_{ij}). In spite of the significant difference between the non-interacting Hamiltonian and the correct Hamiltonian, operators of the former type have important utility, and we will may have occasion to see them again later in the course.

Homework

To be solved in class:

A typical starting point for a Hartree calculation is to use a one-electron hydrogenic orbital for each electron. If one does that for He, what is V_i at the first step for a 1s

electron in He if the other electron is also in the 1s orbital? How will V_i differ in the next step? How would things be different if the other electron were in the 2s orbital?

To be turned in for possible grading Apr. 7:

What is the Hartree-product wave function for 2 non-interacting quantum mechanical harmonic oscillators (QMHOs) of reduced mass 1 a.u. in a potential having a force constant of 1 a.u., where the first QMHO is in the ground state and the second is in the first excited state? Determine the energy of the two QMHO system as an expectation value of the Hartree-product wave function. Is the correct Hamiltonian for this system separable into one-QMHO terms? If the QMHOs *were* interacting, explain how you could use perturbation theory to determine the energy of the system correct to first order (you don't have to actually do it, just explain *how* to do it).