

Chapter 7

7.1 General Principles

We begin with a brief review of MO theory as we will make use of it. As previously discussed linear combinations of atomic orbitals (LCAOs) are a useful way to treat systems within the context of group theory. With this system one can use every orbital in the molecule or just those of a particular type (e.g. just the π -system).

The LCAO Approximation

As we've seen, LCAO is just as described, the sum of the atomic orbitals in a molecule. Each molecular orbital that results is the sum of every atomic orbital in the molecule multiplied by a weighting function. In the case of a localized bond, it is likely that atomic orbitals from distal atoms will contribute negligibly, but they will still have a non-zero coefficient. Thus,

$$\psi_k = \sum_i c_{ik} \phi_i \quad 7.1-1$$

where ψ_k is some molecular orbital, c_{ik} is the weighting coefficient, and ϕ_i is one of the atomic orbitals in the molecule. Remember, there will be as many product molecular orbitals as component atomic orbitals. Each molecular orbital, ψ_k , will be comprised of every atomic orbital in the molecule, to some extent. The sum of the coefficients for each individual atomic orbital within all of the molecular orbitals will total 1. [This means that if one of the atomic orbitals in a molecule is a $2p_x$, the sum of the coefficients in front of the $2p_x$ wave function in all of the molecular orbitals will total 1. This is reasonable, because it says that the whole orbital is used with nothing left over or more than one $2p_x$ used.] This is the substance of equation 7.1-2.

As you know, $\mathcal{H}\psi = E\psi$ so, substituting into the equation above, we find that

$$\sum_i c_{ik} (\mathcal{H} - E) \phi_i = 0$$

The book does a pretty good job of explaining this and I'll leave it to you to read the rest of this subsection.

The Hückel Approximation

The problem with the LCAO is that it has too many terms to be handled easily. Literally, every MO has a term for every AO, which for even medium-small molecules can generate enormous wave function equations. To simplify, the Hückel approximation essentially discards all terms that do not arise from AOs on adjacent atoms interacting with one another.

Mathematically, it assumes that all overlap integrals ($\int \phi_i \phi_j d\tau$) equal zero, that is they are orthogonal. The Hamiltonians yield non-zero values only if the atoms are adjacent to one another.

When the Hückel approximation is applied to organic conjugated hydrocarbon systems, we find a special case. Here $\alpha = H_{ii}$ and $\beta = H_{ij}$, where α is the energy of an electron in a p - π orbital before interacting with a neighboring orbital and β is energy of interaction between the p - π orbitals on adjacent atoms. Continuing to simplify, if all were interested in relative energies, we can set α equal to zero and calculate β relative to it. In this case, energies are provided in "units" of β (as in 2β). An electron in a bond is always more stable than one in an unbonded p orbital so the absolute energy is always negative.

Bonding Character of Orbitals

For the rest of the chapter, the book employs this idea of relative energies and determines the energy of MOs *relative* to their component AOs. In this view, the weighted average energy of the AOs, its barycenter, is defined as zero. Those MOs more stable are bonding, those less stable anti-bonding. Those exactly equal are non-bonding (although in "real life" we think of orbitals very close to zero as being essentially non-bonding).

With this assumption, then the solutions to otherwise complex problems becomes much more straightforward. The book works through the naphthalene π -system and you can see that a determinant with 100 two-part terms reduces to 32 one-part terms. While not trivial, it is much more manageable.

7.2 Symmetry Factoring of Secular Equations

A big problem with the determinant on p. 140, as you've probably noticed is the off diagonal elements, particularly those way off the diagonal. These can be dealt with by employing symmetry in the form of SALCs. We know that $\int \psi_i \psi_j d\tau$ and $\int \psi_i^* \psi_j d\tau$ each equal zero unless ψ_i and ψ_j belong to the same irreducible representation (Section 5.3). This is another way of justifying zero energy values for many of the positions in the determinant, but more importantly, allows the determinant to be rearranged in such a way as to allow block factoring of matrices (see Chapter 4 notes, p. 6).

Returning to the naphthalene example, we find a D_{2h} molecule. Creating a reducible representation for the p orbitals in the π -system we find

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ	10	0	-2	0	0	-10	0	2

(To create this table, p -orbitals left along receive a "1," those flipped over a "-1," while those moving are assigned a value of "0.") Extracting this we find it to be composed of $2B_{2g} + 3B_{3g} + 2A_u + 3B_{1u}$. Now if the determinant is constructed so as to keep the orbitals within the same irreducible representation together, it block factors into 4 parts (two 2x2 & two 3x3) and all other positions become zero because their irreducible representations differ. Now, the result is not a simple reordering of the rows in the determinant on p. 140, but rather a complete reconstruction

of the determinant.

It turns out this is actually relatively simple. Rather than examine adjacent orbitals, per se, since this is employing SALC's let's use one symmetry identical set, ϕ_9 and ϕ_{10} , the bridging carbon p -orbitals. There are two linear combinations: $\phi_9 + \phi_{10}$ and $\phi_9 - \phi_{10}$, which belong to the irreducible representations B_{1u} and B_{3g} , respectively. Thus, construction of the determinant is not based on the positions of the AOs in the molecule, but rather the irreducible representations themselves. We'll return to this later.

7.3 Carbocyclic Systems

The book works through benzene employing a shortcut it presented in Chapter 6. It really isn't necessary and has the disadvantage of employing imaginary numbers that you then must be removed. Since, extracting irreducible representations from reducible representations is such an integral component of this course, it makes more sense to do it the long way, if only because of the extra practice it provides. Thus, one obtains Γ_π for benzene as presented on p. 143, that reduces to A_{2u} , B_{2g} , E_{1g} , and E_{2u} .

Now employ the projection operators for each of these irreducible representations. For A_{2u} , one obtains

$$A_{2u}: 4\phi_1 + 4\phi_2 + 4\phi_3 + 4\phi_4 + 4\phi_5 + 4\phi_6 \quad \propto \quad \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$B_{2g}: 2\phi_1 - 2\phi_2 + 2\phi_3 - 2\phi_4 + 2\phi_5 - 2\phi_6 \quad \propto \quad \frac{1}{\sqrt{6}} (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

$$E_{1g}: 4\phi_1 + 2\phi_2 - 2\phi_3 - 4\phi_4 - 2\phi_5 + 2\phi_6 \quad \propto \quad \frac{1}{\sqrt{12}} (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

The other function $\frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6)$ is generated as described on p. 6 of the Chapter 6

notes. (Note: If you set this up wrong, you get the correct answer by adding the functions instead of subtracting them. The other result is the original function generated by the projection operators.)

E_{2u} : Do this one on your own.

At this point, one can construct the pictures shown on p. 147 and order them in terms of energy. Here we find the A_{2u} representation is lowest in energy, E_{1g} next, E_{2u} , finally B_{2g} highest. The ordering can be accomplished by simply counting the nodal planes. We know that bonds result in a release in energy and the presence of nodes disrupts bonding. We also know that all 6 p -orbitals are identical and so are the interactions between them. Thus, we can simply count the nodal planes and assume that energy increases with their increasing number.

Now, we can calculate the energies of each. For that we must create the determinant for benzene, recalling that $\alpha = H_{ii}$ and $\beta = H_{ij}$ where $\beta = 0$ for $i \neq j \pm 1$.

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

If you've forgotten, the formula/methodology for solving a determinant may be found at:

<http://en.wikipedia.org/wiki/Determinant>. More simply, it can be done as follows. Each p -

orbital in the ring interacts with 2 adjacent p -orbitals identically. In this case, if the interaction is constructive (bonding) one stabilizes the system by 1β , if the interaction is destructive

(antibonding) it destabilizes the system by 1β . Thus, in the A_{1u} MO, we find that each p -orbital

has an energy of $\alpha + 2\beta$, so the average of all six orbitals is the same. The E_{1g} case is, perhaps,

more useful to illustrate the point.

$$2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6$$
$$E = 2(\alpha + \beta + \beta) + (\alpha + \beta - \beta) + (\alpha + \beta - \beta) + 2(\alpha + \beta + \beta) + (\alpha + \beta - \beta) + (\alpha + \beta - \beta)$$
$$= 8\alpha + 8\beta$$

This then reduces to $\alpha + \beta$. You should try this for the E_{2u} and B_{2g} representations.

Delocalization Energy and The $4n+2$ Rule

Both of these sections seem reasonably self-explanatory and are left to you to read.

7.4 More General Cases of LCAO-MO π Bonding