The Simple Hückel Method and its Applications Lecture 3

Learning Outcomes:

1. Application of HMO theory to understand terms like charge and mobile bond orders, delocalization energies, calculations for excited states, frontier orbitals, calculation of spin densities, anion and cation radicals.

2. Applications of these concepts to the allyl system and butadiene and their ion radicals.

3. Some useful concepts

Once we have learnt how to obtain the orbital energies and coefficients, let us now see how what further properties may be obtained.

3.1 π electron charge densities and π electron bond orders

Once the eigenvectors have been found, they can be used to calculate some physically meaningful properties. The square of a coefficient on an atomic orbital can be taken as the fraction of an electron found near that atom by each electron in the atomic orbital. Thus, the π-electron charge density (a misnomer), q_r at atom r is given by

$$q_r = \sum_i n_i c_{ir}^2$$

where n_i is the number of electrons in the i^{th} molecular orbital and c_{ir} is the coefficient of atom r in the i^{th} molecular orbital.

The π-electron charge on atom r is taken as the number of electrons that an atom contributes to the π system minus the charge density, q_r. For example, if a carbon atom contributes one electron to the π system and has a π-electron charge density of 1.023, then the charge on the carbon atom ($Q_r = 1 - q_r$) is -0.023.

For ethylene, the π electron charge density on carbon atom 1 in the ground state is thus calculated as

$$q_1 = 2 \cdot \left(\frac{1}{\sqrt{2}} \right)^2 = 1$$

Similarly, q_2 is also unity, and there is no net charge on any of the carbon atoms in ethylene. As expected, electrons are not transferred from on carbon atom to the other.

Bonding takes place when there is significant sharing of electron density *between* two atoms. For an occupied orbital, the electron sharing is large when the wave function is large between the adjacent atoms. Thus, the bond order between adjacent atoms is considered to be large when the coefficients on the adjacent atoms are large and have the same sign, For adjacent atoms *r* and *s*, the bond order is given by

$$p_{rs} = \sum_i n_i c_{ir} c_{is}$$

where c_{ir} and c_{is} are the coefficients of atom *r* and *s*, respectively, in the i^{th} molecular orbital, and the sum is taken over all orbitals. For the case of ethylene, there is only one bond and we find that

$$p_{12} = 2 \cdot \left(\frac{1}{\sqrt{2}} \right) \cdot \left(\frac{1}{\sqrt{2}} \right) = 1,$$

which indicates that there is one π bond between the carbon atoms.

These results make good chemical sense: the π-electron atomic charges on the two carbons should be the same due to symmetry, and as there are two π electrons only, we would expect a unit charge on each carbon atom. A π-electron bond order of 1 is also entirely reasonable - if we add to this the σ-electron bond order of 1, we get a total bond order of 2, which is consistent with the structural formula of ethylene.

3.2 Delocalization Energies

The total π-electron energy of butadiene is

$$E_\pi = \sum_{i=1}^{N} n_i \varepsilon_i = 2\varepsilon_1 + 2\varepsilon_2 = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) = 4\alpha + 4.472\beta$$

If we had just a pair of two non-interacting carbon-carbon double bonds (*e.g.* two isolated ethene molecules), their energy would be twice the energy of one ethylene molecule, *i.e.*

$$E_\pi(\text{butadiene}) - 2E_\pi(\text{ethylene}) = \underbrace{0.472\beta}_{\substack{\text{delocalization energy}\\ \text{of butadiene}}}$$

This result provides a convincing theoretical explanation for the well-known differences between the heats of hydrogenation (ΔH^0_{298}) of molecules containing isolated and conjugated double bonds:

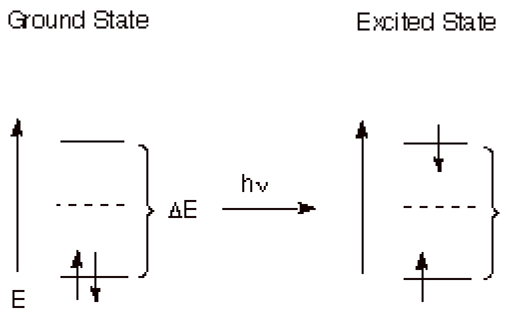
- Standard heat of hydrogenation for 1-butene ($H_2C{=}CH{-}CH_2{-}CH_3$): -126.8 kJ/mol
- For a pair of isolated butene double bonds: -253.6 kJ/mol
- For *trans*-1,3-butadiene: -238.9 kJ/mol

The difference of -238.9-(-253.6) = 14.7 kJ/mol must follow from the greater stability of conjugated double bonds as predicted by HMO theory.

3.3 Excited States

In ethene, only the bonding MO is occupied, but the anti-bonding MO is vacant. It contributes nothing to the energy of the system. It is sometimes described as a virtual MO. The question sometimes arises of what use is the concept of an antibonding MO or of any virtual orbital. Essentially it is that the presence of this MO reminds us of the ability of the molecule to accept an electron into this orbital in the context of a reaction. There are two principal ways in which the anti-bonding MO ceases to be a virtual orbital and becomes a real, occupied MO.

When a molecule absorbs radiation which satisfies the Einstein equation $\Delta E = h\nu$, it promotes an electron from the bonding MO to the anti-bonding MO. This excited state of the original molecule is highly energetic and capable of undergoing potentially useful chemistry (photochemistry) which the more stable ground state is incapable of.



3.4 Frontier Orbitals

The highest energy occupied MO is designated the HOMO, and the lowest energy vacant (unoccupied) MO is termed the LUMO. In a radical species, the orbital which contains the odd electron is termed the SOMO (singly occupied MO).

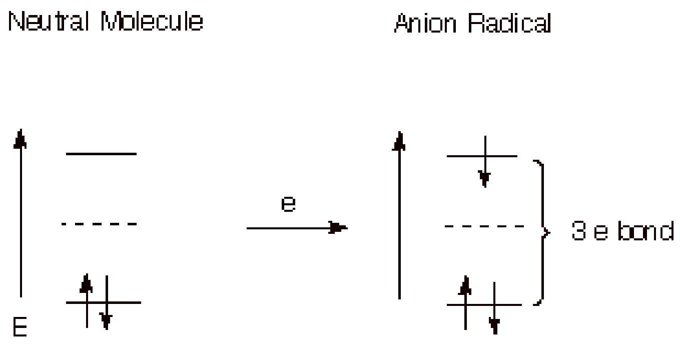
3.5 Spin Densities or Odd Electron Densities

Since the SOMO of a radical (or ion radical) species exclusively controls the distribution of the spin (the odd electron), the spin density or odd electron density (or radical character) can be calculated just from the SOMO coefficients. Square the coefficient of a given atom in the SOMO to obtain the spin density (ρ_r).

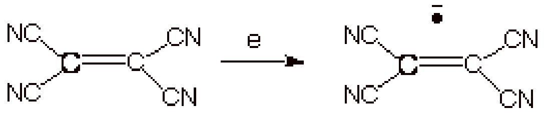
$$\rho_r = c_{r,\mathrm{SOMO}}{}^2$$

3.6 Anion Radicals

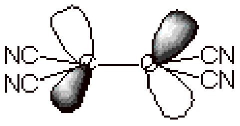
In the context of purely thermal chemistry, as opposed to photochemistry, electrons may be transferred from an electron rich species (called a single electron donor) to a neutral molecule to form a negatively charged species which also has an unpaired electron in the antibonding MO. These species are called anion radicals. Again, they have an electron in a relatively high energy antibonding orbital, so they are much more reactive, in general than the original neutral molecule. They, in fact, are excellent representatives of species having a *three electron bond.* Since the electron in the anti-bonding orbital diminishes the π bonding present in the molecule, the species is highly reactive. Electron donors suitable for transferring electrons to antibonding MOs of neutral molecules include alkali metals, negative electrodes, and some electron rich organic molecules.



The energy required to introduce an electron into the antibonding MO of a neutral molecule in solution is called the *reduction potential*. The higher the energy of the anti-bonding MO into which the electron must be introduced, the more negative the potential needed for the electron transfer. Reduction potentials as typically measured are relative, not absolute, and are typically referred to the saturated calomel electrode (SCE). In general, two structural factors are especially important in lowering the energy of the appropriate anti-bonding MO and thus the reduction potential of a substrate molecule (*i.e.,* making it easier to reduce). First, the more extended the conjugated system, the lower the energy of the anti-bonding MO and the more easily reducible the substrate. Second, π bonds which have strongly electron-withdrawing groups attached, which can stabilize the negative charge of the anion radical, also have lower energy anti-bonding MOs. One of the more easily reducible organic substrates is tetracyanoethylene. The anion radical of this substrate is so stable that its salts can be isolated. A detailed single crystal neutron diffraction study of one such salt reveals the distribution of the odd electron and thus the shape of the antibonding MO. Interestingly, the AOs on the central carbons are bent back, away from one another, in order to minimize overlap, which is negative, antibonding overlap. The knowledge of the shapes of anti-bonding MOs comes in handy in several connections which we will be considering further on. Incidentally, the MO which has the single electron is often referred to as the SOMO (singly occupied MO). This orbital is especially important because it determines where the odd electron is and also, largely, the negative charge.



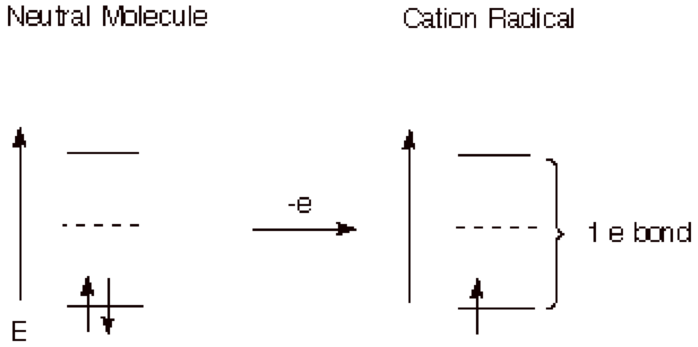
shape of ABMO

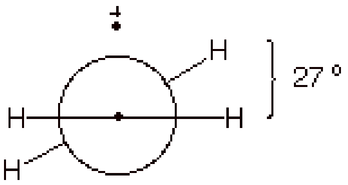


The SOMO has also applications in ESR spectra, some of which we shall take up in a future section.

3.7 Cation Radicals and One Electron Bonds

Cation radicals are reactive organic species which can be formed by removing an electron from an occupied MO of a neutral molecule. The π bond in such a system is an excellent example of a one electron bond. Nevertheless, these species are highly reactive, since they do not have the typical strong two electron bond. The weakening of the π bond in the ethene cation radical is reflected in the structure of this species which, unlike ethene, is twisted by *ca.* 27^o out of planarity.



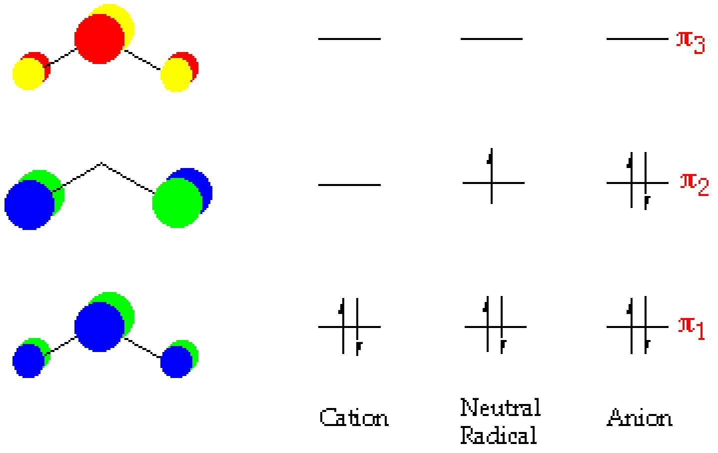


4. Applications to some systems

4.1 Allylic conjugation

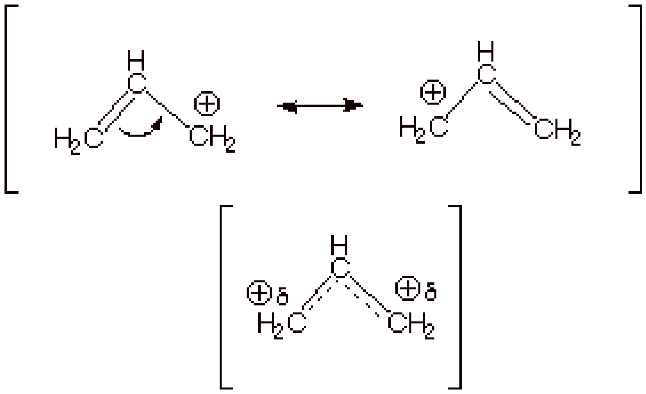
4.1.1. MOs of the Allyl System (Radical, Cation, and Anion)

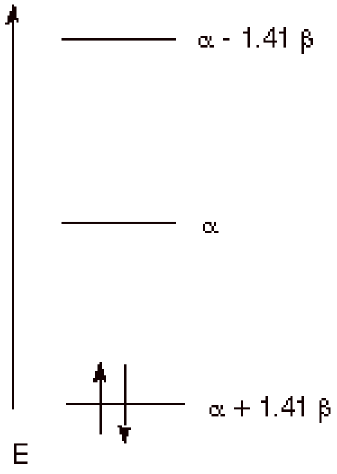
The energy diagram for the neutral, cationic and anionic allyl species is shown below:



4.1.2 The π Bonding Energy and Delocalization Energy of the Allyl Carbocation

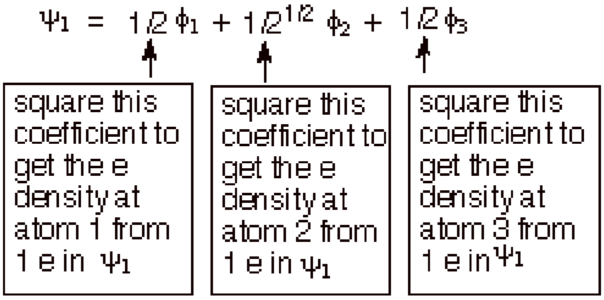
The allyl carbocation has two π electrons, as may be seen by examining a canonical structure of the ion. The double bond of the latter contributes two π electrons, while the carbocation center has a vacant 2*p* AO and does not contribute any electron. The energy level diagram is therefore as shown below. Note that the total π electron energy is more negative (more bonding) than the two electrons of the ethene π bond by 0.82 *β*. This is the delocalization energy, i.e., the additional stabilization of these two electrons derived from their delocalization over three atoms, instead of just two. Formally, the key to the lowering of the energy is the lower energy of the BMO in the allyl system than in the ethene system.





$E(\pi) = 2(\alpha + 1.41\ \beta) = 2\alpha + 2.82\ \beta$

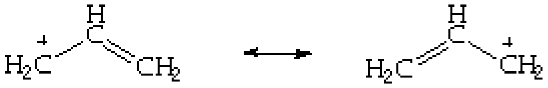
We might also note that since the BMO is heavily concentrated on the central carbon atom, most of the electron density of the allyl cation is located at C2. Therefore, the positive charge is at C1 and C3 as typical resonance structures of the allyl cation indicate. If one calculates the electron densities, it is found that, in precise agreement with the resonance theory, there is exactly zero positive charge on the central carbon and exactly one-half unit of positive charge on each of the terminal atoms. As shown in the diagram below, the contribution to the electron density at a specific atom from a single electron in the BMO is given by the square of the coefficient of that atom in the BMO. For atoms 1 and 3, that is 1/4; for atom 2 it is 1/2.



Since there are two electrons in this MO, we must double this, giving 1/2 for C1 and C3 and 1.0 for C2. To be neutral, each carbon should have exactly 1.0 2*p* electron, so the net charge at C2 is zero, and at C1 and C3 it is +1/2.

Exercise 1. As an exercise, calculate the charge densities at C1, C2, and C3 in the allyl cation, radical, and anion. The radical, as we will see, has 3 electrons, and the anion has 4. As a further exercise, see if you can calculate the spin distribution in the radical, assuming that **all** of the electron spin comes from the singly occupied MO (the SOMO). Then compare these results with the results of applying simple resonance theory to the cation, radical, and anion.

The MOs for the allyl cation are sketched below. It is represented in resonance theory as two canonical forms:



Resonance structures for the allyl cation

5. Butadiene

5.1. Energy Levels and Delocalization Energy of 1,3-Butadiene

The simplest conjugated diene, 1,3-butadiene, has a conjugated system in which the π electrons are delocalized over four carbon atoms. The energy levels are shown in Figure 2. Since there are four basis set AOs, there are four MOs, two of them are bonding and two are anti-bonding. Note the symmetrical disposition of the MOs about the nonbonding level.

5.2. Electron Densities and Charge Densities in Butadiene.

Exercise 2. Calculate the q_r's and Q_r's for neutral butadiene. By symmetry, of course, the results for C1 and C4 are identical, as are those for C2 and C3. Are the results physically reasonable?

We had noted that the energy levels and wave functions of butadiene are paired. The same is true for ethylene and allyl radical. The π-electron density on each carbon atom is also unity, so that the net charge on each carbon atom is zero. This is not special to these three systems, but is true for all alternant systems and is called the pairing theorem. All acyclic conjugated systems are alternant.

5.3 π-Bond Order in Butadiene

According to the formula for calculating the bond order

$$p_{rs} = \sum_i n_i c_{ir} c_{is}$$

Using the wave functions given in class, the bond order between atoms 1 and 2 is calculated as

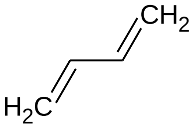
$p_{12} = 2\times0.37\times0.60 + 2\times0.60\times0.37 = 0.888$

By symmetry, $p_{34} = p_{12}$.

In contrast,

$p_{23} = 2\times0.60\times0.60+2\times0.37\times(-0.37) = 0.446$

Thus, the central bond is weaker than the terminal bonds. This is consistent with the common representation of 1,3-butadiene.



5.4. Ion Radicals of Butadiene.

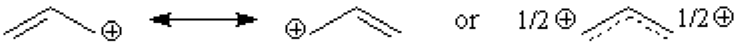
The cation radical of butadiene is formed when one electron is removed from neutral butadiene.

Exercise 3. Construct the energy level diagram of butadiene cation radical. Assuming that all of the charge and spin arise from the singly occupied MO (SOMO; a good approximation), calculate the charge (Q_r) and spin (ρ_r) at each carbon atom (again, you may use symmetry considerations, i.e., C1 = C4 and C2 = C3)). Do the same for the butadiene anion radical, which has one additional electron (five) compared to neutral butadiene. Compare the charge and spin densities in the anion and cation radicals. If the anion radical were to be protonated, where would it be likely to react? Write an equation for this reaction. Similarly, if the cation radical were to react with a nucleophile such as hydroxide ion, where would it react? Draw the equation for this reaction also.

Sample Problem 1

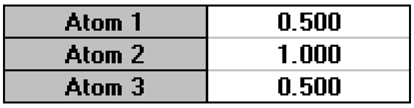
Compare the valence bond model and the Hückel molecular orbital model for the allyl cation.

For the valence bond model we would draw two resonance structures and describe the allyl cation as a hybrid of the two:



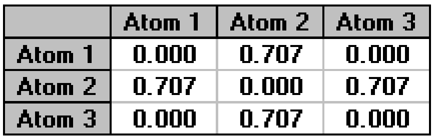
This model shows that there should be a 1/2 positive charge on each terminal carbon, no charge on the middle carbon, and 1/2 of a π bond between each pair of carbons.

Having constructed the Hückel matrix and carried out the calculation, we find that the HMO model gives the following results for the electron densities:



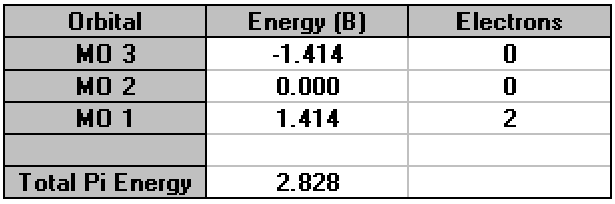
Atom 1	0.500
Atom 2	1.000
Atom 3	0.500

Since a neutral carbon with a *p* orbital on it would have one electron in the *p* orbital, this result is the same as we get from the valence bond model: 0.5 positive charge on each end carbon (they are short by 0.5 electron!), and no charge on the middle carbon. The result of the bond order calculation is:



	Atom 1	Atom 2	Atom 3
Atom 1	0.000	0.707	0.000
Atom 2	0.707	0.000	0.707
Atom 3	0.000	0.707	0.000

Notice that the HMO model predicts a 0.707 π bond order between atoms 1 and 2 and between atoms 2 and 3. This is different from the 0.5 π bond order predicted from the valence bond model. Together they add up to 1.414 total π bond order, or 0.414 *excess* π bond order. This excess bond order is a reflection of the stability gained by *delocalizing* the electrons. This same stabilization is reflected in the energy of the π system:



Orbital	Energy (B)	Electrons
MO 3	-1.414	0
MO 2	0.000	0
MO 1	1.414	2
Total Pi Energy	2.828	

The total π energy is 2.828 β. Recall that for a single isolated π bond (allyl cation has just one), the energy is 2β. Thus the Hückel delocalization energy is (2.828β - 2β) or 0.828β. Again, this is a measure of the energy gained by delocalizing the electrons. It is not something we can predict quantitatively from the valence bond model.