The MOs of a Homonuclear Diatomic Molecule

Calculations

Consider a homonuclear diatomic molecule $A_2$, whose two atoms $A$ are identical. For the sake of simplicity, we will assume that each atom uses one (and only one) valence AO to form the bond. These interacting AOs, which we will call $\phi_1$ and $\phi_2$, are chosen so as to be mathematically real. The following procedure is used to calculate the resulting MOs:

1. The two nuclei are held at a certain fixed distance from each other (i.e. we apply the Born–Oppenheimer approximation).
2. The time-independent Schrödinger Equation (2.4) is written for the molecule, multiplied on the left-hand side by $\Psi$, and integrated over all space [Equation (2.5)]:
   \[ H\Psi = E\Psi \]  
   \[ \langle \Psi|H|\Psi \rangle = E\langle \Psi|\Psi \rangle \]
3. Each MO is expressed as a linear combination of atomic orbitals (LCAOs):
   \[ \Psi = c_1\phi_1 + c_2\phi_2 \]  
   In Equation (2.6), we know $\phi_1$ and $\phi_2$. Calculating an MO $\Psi_i$ therefore involves evaluating its associated energy $E_i$ and the coefficients $c_{i1}$ and $c_{i2}$ of its LCAO expansion. Incorporating Equation (2.6) in Equation (2.5) gives
   \[ \langle c_1\phi_1 + c_2\phi_2|H|c_1\phi_1 + c_2\phi_2 \rangle = E\langle c_1\phi_1 + c_2\phi_2|c_1\phi_1 + c_2\phi_2 \rangle \]

   The linearity of integrals (p. 7), allows the left-hand side of Equation (2.7) to be expressed as
   \[ \langle c_1\phi_1 + c_2\phi_2|H|c_1\phi_1 + c_2\phi_2 \rangle = \langle c_1\phi_1|H|c_1\phi_1 \rangle + \langle c_1\phi_1|H|c_2\phi_2 \rangle + \ldots \]
   \[ = c_1^2\langle \phi_1|H|\phi_1 \rangle + c_2^2\langle \phi_2|H|\phi_2 \rangle + \ldots \]

   To express this more simply, let us set
   \[ \langle \phi_1|H|\phi_1 \rangle = \alpha_i \]
   \[ \langle \phi_1|H|\phi_2 \rangle = \beta_{ij} \]
   \[ \langle \phi_2|\phi_1 \rangle = S_{ij} \]

   where $\alpha_i$ is termed the Coulomb integral, $\beta_{ij}$ the resonance integral and $S_{ij}$ the overlap integral. We are using normalized AOs, so $S_{ii} = 1$. Furthermore, the two atoms are identical, so
   \[ \alpha_1 = \alpha_2 \quad \text{and} \quad \beta_{12} = \beta_{21} \]

---

3In physical terms, $\beta_{12} = \beta_{21}$, simply means that the force binding atom 1 to atom 2 is the same as the force binding 2 to 1.
Thus, Equation (2.7) can be written as
\[(c_1^2 + c_2^2)\alpha + 2c_1c_2\beta - E(c_1^2 + c_2^2 + 2c_1c_2S) = 0\] (2.8)
where \(\alpha, \beta\) and \(S\) are parameters and \(c_1, c_2\) and \(E\) are unknowns.

4. Let us now choose \(c_1\) and \(c_2\) so as to minimize \(E\) (variational method). To do this, we differentiate Equation (2.8), and set the partial derivatives to zero:
\[
\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0
\]
thus obtaining the secular equations:
\[
(\alpha - E)c_1 + (\beta - ES)c_2 = 0 \tag{2.9}
\]
\[
(\beta - ES)c_1 + (\alpha - E)c_2 = 0
\]
These equations are homogeneous in \(c_i\). They have a nontrivial solution if the secular determinant (i.e. the determinant of the coefficients of the secular equations) can be set to zero:
\[
\begin{vmatrix}
\alpha - E & \beta - ES \\
\beta - ES & \alpha - E
\end{vmatrix}
= (\alpha - E)^2 - (\beta - ES)^2 = 0 \tag{2.10}
\]
The solutions to Equation (2.10) are
\[
E_1 = \frac{\alpha + \beta}{1+S} \quad \text{and} \quad E_2 = \frac{\alpha - \beta}{1-S} \tag{2.11}
\]
\(E_1\) and \(E_2\) are the only energies which an electron belonging to the diatomic molecule \(A_2\) can have. Each energy level \(E_i\) is associated with a molecular orbital \(\Psi_i\) whose coefficients may be obtained by setting \(E = E_i\) in Equation (2.9) and solving these equations, taking into account the normalization condition:
\[
\left\langle \Psi_i \right| \left. \Psi_i \right\rangle = c_{i1}^2 + c_{i2}^2 + 2c_1c_2S = 1 \tag{2.12}
\]
The solutions are
\[
\Psi_1 = \frac{1}{\sqrt{2(1+S)}}(\varphi_1 + \varphi_2) \quad \text{and} \quad \Psi_2 = \frac{1}{\sqrt{2(1+S)}}(\varphi_1 - \varphi_2) \tag{2.13}
\]
Figure 2.2 gives a pictorial representation of Equation (2.11) and (2.13).

\[\text{Figure 2.2} \quad \text{The MOs of the homonuclear diatomic} \ A_2. \ \varphi_1 \ \text{and} \ \varphi_2 \ \text{are arbitrarily drawn as s orbitals. Note that the destabilization of} \ \Psi_2 \ \text{is greater than the stabilization of} \ \Psi_1.\]
An in-phase overlap is bonding and lowers the MO energy, whereas an out-of-phase overlap is antibonding and raises the MO energy.

The Parameters

The Coulomb Integral $\alpha$

To a first approximation, the Coulomb integral $\alpha_A$ gives the energy of an electron occupying the orbital $\phi_A$ in the isolated atom $A$. Therefore, its absolute value represents the energy required to remove an electron from $\phi_A$ and place it at an infinite distance from the nucleus where, by convention, its energy is zero. Consequently, $\alpha_A$ is always negative and its absolute value increases with the electronegativity of $A$.

The Resonance Integral $\beta$

The absolute value of the resonance integral gives a measure of the $A_1A_2$ bond strength. It increases with increasing overlap. We will see that $S_{12}$ measures the volume common to $\phi_1$ and $\phi_2$, which encloses the electrons shared by $A_1$ and $A_2$. Large values of $S_{12}$ thus imply strong bonding between $A_1$ and $A_2$. When $S_{12}$ is zero, $\beta_{12}$ is also zero. It follows that two orthogonal orbitals cannot interact with each other. Conversely, the more two orbitals overlap, the more they interact. Stereoelectronic control results from this principle of maximum overlap: the best trajectory is that corresponding to the best overlap between the reagent and the substrate. The principle of maximum overlap is often expressed in terms of the Mulliken approximation:

$$\beta_{12} = kS_{12}$$ (2.14)

where the proportionality constant $k$ is negative. Basis AOs are generally chosen with the same sign, so the overlap integrals are positive and the resonance integrals negative.

The Overlap Integral

Consider two overlapping orbitals $\phi_i$ and $\phi_j$. They define four regions in space:

- Region 1 lies outside $\phi_i$ and $\phi_j$, where both orbitals have small values. The product $\phi_i \phi_j$ is negligible.
- Region 2 (enclosed by $\phi_i$ but outside $\phi_j$) and region 3 (enclosed by $\phi_j$ but outside $\phi_i$) also have negligible values for $\phi_i \phi_j$: one component is appreciable, but the other is very small.
- Region 4, where both $\phi_i$ and $\phi_j$ are finite. The value of $S_{ij}$ comes almost exclusively from this region where the two orbitals overlap (hence the term `overlap integral').

$^{6}$ $\beta_{12}$ is sometimes said to represent the coupling of $\phi_1$ with $\phi_2$. This originates in the mathematical analogy between the interaction of two AOs and the coupling of two pendulums. The term resonance integral has similar roots (Coulson C. A., Valence, Oxford University Press, Oxford, 2nd edn, p. 79).
Mulliken Analysis

The MOs in the diatomic molecules discussed above have only two coefficients, so their chemical interpretation poses few problems. The situation becomes slightly more complicated when the molecule is polyatomic or when each atom uses more than one AO. Overlap population and net atomic charges can then be used to give a rough idea of the electronic distribution in the molecule.

Overlap Population

Consider an electron occupying $\Psi_1$. Its probability density can best be visualized as a cloud carrying an overall charge of one electron. To obtain the shape of this cloud, we calculate the square of $\Psi_1$:

$$\langle \Psi_1 | \Psi_1 \rangle = c_{11}^2 \langle \phi_1 | \phi_1 \rangle + 2c_{11}c_{12}S_{12} + c_{12}^2 \langle \phi_2 | \phi_2 \rangle = 1$$

Equation (2.15) may be interpreted in the following way. Two portions of the cloud having charges of $c_{11}^2$ and $c_{12}^2$ are essentially localized within the orbitals $\phi_1$ and $\phi_2$ and 'belong' to $\Lambda_1$ and $\Lambda_2$, respectively. The remainder has a charge of $2c_{11}c_{12}S$ and is concentrated within the zone where the two orbitals overlap. Hence this last portion is termed the overlap population of $\Lambda_1\Lambda_2$. It is positive when the AOs overlap in phase (as in $\Psi_1$) and negative when they are out of phase (as in $\Psi_2$). The overlap population gives the fraction of the electron cloud shared by $\Lambda_1$ and $\Lambda_2$. A positive overlap population strengthens a bond, whereas a negative one weakens it. We can therefore take $2c_{11}c_{12}S$ as a rough measure of the $\Lambda_1\Lambda_2$ bond strength.

Net Atomic Charges

It is often useful to assign a net charge to an atom. This allows the nuclei and electron cloud to be replaced by an ensemble of point charges, from which the dipole moment of the molecule can be easily calculated. It also allows the reactive sites to be identified: positively charged atoms will be preferentially attacked by nucleophiles, whereas negatively charged atoms will be favored sites for electrophiles.

The net charge on an atom is given by the algebraic sum of its nuclear charge $q_n$ and its electronic charge $q_e$. The latter is usually evaluated using the Mulliken partition scheme, which provides a simple way of dividing the electron cloud among the atoms of the molecule. Consider an electron occupying the molecular orbital $\Psi_1$ of the diatomic $\Lambda_1\Lambda_2$. The contribution of this electron to the electronic charge of $\Lambda_i$ is then $c_{1i}^2$ plus half of the overlap population. In the general case:

$$q_e(\Lambda) = \sum_{i,j} n_i c_{i\Lambda} c_{j\Lambda} S_{ij}$$

---

1In a polyelectronic molecule, it is necessary to sum over all electrons and calculate the total overlap population to obtain a measure of the bond strength.

2This rule is not inviolable. See pp. 87, 96 and 175.
where $S_{ij}$ is the overlap integral of $\phi_i$ and $\phi_j$, $n_i$ is the number of electrons which occupy $\Psi_i$ and $c_{iA}$ and $c_{iB}$ are the coefficients of $\phi_i$ and $\phi_j$ in the same MO. The summation takes in all of the MOs $\Psi_i$ and all of the atoms $j$ in the molecule.

**MOs of a Heteronuclear Diatomic Molecule**

**Calculations**

A heteronuclear diatomic molecule is comprised of two different atoms A and B. For simplicity, we will again assume that only one AO on each atom is used to form the bond between A and B. The two relevant AOs are then $\phi_A$ of energy $\alpha_A$ and $\phi_B$ of energy $\alpha_B$. The calculation is completely analogous to the case of the homonuclear diatomic given above. For a heteronuclear diatomic molecule AB, Equation (2.10) — where the secular determinant is set to zero — becomes

$$\begin{bmatrix} \alpha_A - E & \alpha_B - E \\ \alpha_B - E & \beta - ES \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = 0$$

Equation (2.17) is a second-order equation in $E$ which can be solved exactly. However, the analogs of expressions Equation (2.11) and (2.13) are rather unwieldy. For qualitative applications, they can be approximated as follows:

$$E_1 \approx \alpha_A + \frac{(\beta - \alpha_A S)^2}{\alpha_A - \alpha_B} \quad E_2 \approx \alpha_B + \frac{(\beta - \alpha_B S)^2}{\alpha_B - \alpha_A}$$

$$\Psi_1 \approx N_1 \left( \phi_A + \frac{\beta - \alpha_A S}{\alpha_A - \alpha_B} \phi_B \right) \quad \Psi_2 \approx N_2 \left( \phi_B + \frac{\beta - \alpha_B S}{\alpha_B - \alpha_A} \phi_A \right)$$

where $N_1$ and $N_2$ are normalization coefficients. Equations (2.18) assume that $E_1$ and $E_2$ are not very different from $\alpha_A$ and $\alpha_B$, respectively. Using this approximation, it is possible to rewrite Equation (2.17) in the form

$$\alpha_A - E_1 = \frac{(\beta - E_1 S)^2}{\alpha_B - E_1} \approx \frac{(\beta - \alpha_A S)^2}{\alpha_B - \alpha_A}$$

which is equivalent to Equations (2.18). Equations (2.18) and (2.19) are shown pictorially in Figure 2.3.

**Figure 2.3** MOs of a heteronuclear diatomic molecule. $\phi_A$ and $\phi_B$ are arbitrarily shown as s orbitals.
Huckel Molecular Orbital theory (HMO theory).

An approximate theory that gives us a very quick picture of the MO energy diagram and MO’s of molecules without doing a lot of work.

Structure and bonding in highly conjugated systems nicely treated by HMO. Look at examples:

Ethene – look at the $\pi$ bond in this simple molecule first.

Each carbon has a $2p_z$ orbital perpendicular to plane of molecule. Use LCAO-MO to get two MO’s, which gives rise to 2x2 secular determinant:

$$\begin{vmatrix}
\alpha_A - E_{\text{trial}} & \beta - E_{\text{trial}} S \\
\beta - E_{\text{trial}} S & \alpha_B - E_{\text{trial}}
\end{vmatrix} = 0$$

HMO approx:

Set all overlap integrals $S = 0$

Recognize the $\alpha$ integrals are equal

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

This gives quadratic $(\alpha - E)^2 - \beta^2 = 0$

Roots $E = \alpha + \beta, \alpha - \beta$

Total $\pi$ bond energy $= 2 (\alpha + \beta )$

Stabilization due to bond formation $= 2\beta$

$\beta$ is intrinsically negative and $\sim -2.4$ eV for C-C bond ($\sim -230$ kJ/mol)
Butadiene.

\[
\begin{array}{c}
\text{C} = \text{C} \\
\text{C} = \text{C} \\
\end{array}
\]

Treat sigma bonding framework using VB theory as follows:

Still have an unused p orbital available on each C, perpendicular to plane of molecule.

Edge on view:

These extensively overlap to form a delocalized \( \pi \) system.

Treat \( \pi \) system by HMO as follow:

a. basis set is composed of four 2pz orbitals (perpendicular to plane).

   Therefore will get 4 x 4 matrix or secular determinant

b. HMO approx:

   1) Set all overlap integrals \( S = 0 \)
2) Set all resonance integrals between non-neighbors = 0
\[ \beta_{13}, \beta_{14}, \beta_{24} \text{ etc.} = 0 \]

3) Set all other resonance integrals (\(\beta\)) equal to one another.

Resulting Sec detm

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

Generates a quartic polynomial in E which has four roots.

Therefore

4 \pi-orbital MO
4 energies (roots of secular determinant)

They are: \[ E = \alpha \pm 1.62 \beta, \alpha \pm 0.62 \beta \]

Energy diagram:
Spectroscopic transition HOMO → LUMO (called frontier orbitals)

HOMO = highest occupied molecular orbital (here MO $2\pi$)

LUMO = lowest unoccupied molecular orbital (here MO $3\pi$)

$\Delta E_{trans} = LUMO - HOMO = (\alpha - 0.62 \beta) - (\alpha + 0.62 \beta) = -1.24\beta$

Compare wave functions with particle in box:

Delocalized system have extra stability (=deloc energy DE)

Calculate it:

$DE = \text{Energy of } \text{c=c-c=c} - \text{Energy of } \text{c=c-c=c}$

Allow electrons To delocalize

2 separate $\pi$ bonds like in ethene

$= [2(\alpha + 1.62 \beta) + 2(\alpha + 0.62 \beta)] - 2(2\alpha + 2\beta)$

$= 4\alpha + 4.48\beta - (4\alpha + 4\beta)$

$= 0.48\beta \sim -110 \text{ kJ/mol of stabilization}$
Benzene – cyclic delocalized system.

6x6 secular determinant =

\[
\begin{array}{cccccc}
\alpha - E & \beta & 0 & 0 & 0 & \beta \\
\beta & \alpha - E & \beta & 0 & 0 & 0 \\
0 & \beta & \alpha - E & \beta & 0 & 0 \\
0 & 0 & \beta & \alpha - E & \beta & 0 \\
\beta & 0 & 0 & 0 & \beta & \alpha - E
\end{array}
\]

= 0

due to cyclic connection

=Energy eigenvalues are E = \( \alpha + 2\beta \), \( \alpha + \beta \), \( \alpha + \beta \)

Calculate delocalization energy DE:

Total pi electron energy = \( 2(\alpha + 2\beta) + 4(\alpha + \beta) \) = \( 6\alpha + 8\beta \)

Energy of three C=C in ethane = \( 2\alpha + 2\beta \)

DE = difference = \( 2\beta = -460 \) kJ/mol
Introduction to Frontier Molecular Orbital Theory

- General Reviews
  Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*
  Kirby, A. J. *Stereoelectronic Effects.*

Universal Effects Governing all Chemical Reactions

- Steric Effects
  Nonbonding interactions (van der Waals repulsion) between substituents within a molecule or between reacting molecules

- Nondirectional Electronic Effects (Inductive Effects):
  rate decreases as R becomes more electronegative

- General Reaction Types
  Radical Reactions (~10%): \( A\cdot + B\cdot \rightarrow A-B \)
  Polar Reactions (~90%): \( A(\cdot) + B(+ \rightarrow A-B \)
  FMO concepts extend the donor-acceptor paradigm to non-obvious families of reactions

- Consider stabilization energy (\( \Delta E \)) when bringing atoms A & B together:

\[
\Delta E = -\frac{Q_A Q_B}{\epsilon R} + \sum_{m,n} \frac{(c_m^A c_n^B)^2}{(E_m^A - E_n^B)}
\]

- Stereoelectronic Effects
  Geometrical constraints placed upon ground and transition states by orbital overlap considerations.

  Fukui Postulate for reactions:
  During the course of chemical reactions, the interaction of the highest filled (HOMO) and lowest unfilled (antibonding) molecular orbital (LUMO) in reacting species is very important to the stabilization of the transition structure.
The H$_2$ Molecule (again!!)

Let's combine two hydrogen atoms to form the hydrogen molecule. Mathematically, linear combinations of the 2 atomic 1s states create two new orbitals, one is bonding, and one antibonding:

- **Rule one**: A linear combination of n atomic states will create n MOs.

Let's now add the two electrons to the new MO, one from each H atom:

- **Rule Two**: $(C_1)^2 + (C_2)^2 = 1$

The squares of the C-values are a measure of the electron population in neighborhood of atoms in question

- **Rule Three**: bonding$(C_1)^2$ + antibonding$(C^*_1)^2$ = 1

In LCAO method, both wave functions must each contribute one net orbital

Consider the pi-bond of a C=O function: In the ground state pi-C–O is polarized toward oxygen. Note (Rule 2) that the antibonding MO is polarized in the opposite direction.
Bonding Generalizations

- Bond strengths (Bond dissociation energies) are composed of a covalent contribution ($\delta E_{\text{covalent}}$) and an ionic contribution ($\delta E_{\text{ionic}}$).

\[ \text{Bond Energy (BDE)} = \delta E_{\text{covalent}} + \delta E_{\text{ionic}} \]

When one compares bond strengths between C–C and C–X, where X is some other element such as O, N, F, Si, or S, keep in mind that covalent and ionic contributions vary independently. Hence, the mapping of trends is not a trivial exercise.

The following generalizations on covalent bonding are useful.

- Overlap between orbitals of comparable energy is more effective than overlap between orbitals of differing energy.

For example, consider elements in Group IV, Carbon and Silicon. We know that C-C bonds are considerably stronger by Ca. 20 kcal mol\(^{-1}\) than C-Si bonds.

For $\pi$ Bonds:

This is a simple notion with very important consequences. It surfaces in the delocalized bonding which occurs in the competing anti (favored) and syn (disfavored) E2 elimination reactions. Review this situation.

- Orbital orientation strongly affects the strength of the resulting bond.

For $\sigma$ Bonds:

- An anti orientation of filled and unfilled orbitals leads to better overlap.

This is a corollary to the preceding generalization.

There are two common situations.

Case-1: Anti Nonbonding electron pair & C–X bond

Case-2: Two anti sigma bonds

- Weak bonds will have corresponding low-lying antibonds.

Formation of a weak bond will lead to a corresponding low-lying antibonding orbital. Such structures are reactive as both nucleophiles & electrophiles.
Donor-Acceptor Properties of Bonding and Antibonding States

Donor Acceptor Properties of C-C & C-O Bonds

Consider the energy level diagrams for both bonding & antibonding orbitals for C-C and C-O bonds.

- The greater electronegativity of oxygen lowers both the bonding & antibonding C-O states. Hence:
  - $\sigma$ C-C is a better donor orbital than $\sigma$ C-O
  - $\sigma^*$ C-O is a better acceptor orbital than $\sigma^*$ C-C

Donor Acceptor Properties of C$_{sp3}$-C$_{sp2}$ & C$_{sp3}$-C$_{sp2}$ Bonds

- The greater electronegativity of C$_{sp2}$ lowers both the bonding & antibonding C-C states. Hence:
  - $\sigma$ C$_{sp3}$-$\sigma$ C$_{sp3}$ is a better donor orbital than $\sigma$ C$_{sp3}$-$\sigma$ C$_{sp2}$
  - $\sigma^*$ C$_{sp3}$-$\sigma$ C$_{sp2}$ is a better acceptor orbital than $\sigma^*$ C$_{sp3}$-$\sigma$ C$_{sp3}$

Hierarchy of Donor & Acceptor States

Following trends are made on the basis of comparing the bonding and antibonding states for the molecule CH$_3$-X where X = C, N, O, F, & H.

- $\sigma$-bonding States: (C–X)
  - CH$_3$-CH$_3$, CH$_3$-H, CH$_3$-NH$_2$, CH$_3$-OH, CH$_3$-F
  - decreasing $\sigma$-donor capacity
  - poorest donor

- $\sigma$-anti-bonding States: (C–X)
  - CH$_3$-H, CH$_3$-CH$_3$, CH$_3$-NH$_2$, CH$_3$-OH, CH$_3$-F
  - Increasing $\sigma^*$-acceptor capacity
  - best acceptor

The following are trends for the energy levels of nonbonding states of several common molecules. Trend was established by photoelectron spectroscopy.

Nonbonding States

- H$_3$P, H$_2$S, H$_3$N, H$_2$O, HCl
  - decreasing donor capacity
  - poorest donor
Electrons in 2s states "see" a greater effective nuclear charge than electrons in 2p states.

This becomes apparent when the radial probability functions for s and p-states are examined: The radial probability functions for the hydrogen atom s & p states are shown below.

Electrons in s-states "see" a higher nuclear charge. This is even more obvious in an electron density map (see http://www.shef.ac.uk/chemistry/orbitron/). The s-orbitals have maximal electron density at the nucleus, and the p-orbitals have none.

This correctly implies that the stability of nonbonding electron pairs is directly proportional to the % of s-character in the doubly occupied orbital.

The above trend indicates that the greater the % of s-character at a given atom, the greater the electronegativity of that atom.

There is a linear relationship between %s character & Pauling electronegativity.

There is a direct relationship between %s character & hydrocarbon acidity.
Hyperconjugation: Carbocation Stabilization

- The interaction of a vicinal bonding orbital with a p-orbital is referred to as hyperconjugation.

This is a traditional vehicle for using valence bond to denote charge delocalization.

The graphic illustrates the fact that the C-R bonding electrons can "delocalize" to stabilize the electron deficient carbocationic center.

Note that the general rules of drawing resonance structures still hold: the positions of all atoms must not be changed.

Stereoelectronic Requirement for Hyperconjugation: coplanar orientation between interacting orbitals

The Molecular Orbital Description

- $\sigma^* C-R$
- $\sigma C-R$

Take a linear combination of $\sigma C-R$ and Csp$_2$ p-orbital:

The new occupied bonding orbital is lower in energy. When you stabilize the electrons in a system you stabilize the system itself.

Physical Evidence for Hyperconjugation

- Bonds participating in the hyperconjugative interaction, e.g. C–R, will be lengthened while the C(+)–C bond will be shortened.

First X-ray Structure of an Aliphatic Carbocation

The Adamantane Reference (MM2)


More substituted carbocations have more adjacent C-R bonds to act as donors to the empty p orbital

Hence, more substituted carbocations are more stable.
"Negative" Hyperconjugation/Anomeric Effect

- Delocalization of nonbonding electron pairs into vicinal antibonding orbitals is also possible.

This delocalization is referred to as "negative" hyperconjugation.

Since nonbonding electrons prefer hybrid orbitals rather than p orbitals, this orbital can adopt either a syn or anti relationship to the vicinal C–R bond.

The Molecular Orbital Description

- Overlap between two orbitals is better in the anti orientation as stated in "Bonding Generalizations" handout.

The Expected Structural Perturbations

<table>
<thead>
<tr>
<th>Change in Structure</th>
<th>Spectroscopic Probe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shorter C–X bond</td>
<td>X-ray crystallography</td>
</tr>
<tr>
<td>Longer C–R bond</td>
<td>X-ray crystallography</td>
</tr>
<tr>
<td>Stronger C–X bond</td>
<td>Infrared Spectroscopy</td>
</tr>
<tr>
<td>Weaker C–R bond</td>
<td>Infrared Spectroscopy</td>
</tr>
<tr>
<td>Greater e-density at R</td>
<td>NMR Spectroscopy</td>
</tr>
<tr>
<td>Less e-density at X</td>
<td>NMR Spectroscopy</td>
</tr>
</tbody>
</table>
We now conclude that this is another example of negative hyperconjugation.

The Anomeric Effect and Related Issues

Infrared evidence for lone pair delocalization into vicinal antibonding orbitals.

The N–H stretching frequency of cis-methyl diazene is 200 cm⁻¹ lower than the trans isomer.

\[ \nu \text{N–H} = 2188 \text{ cm}^{-1} \]

\[ \nu \text{N–H} = 2317 \text{ cm}^{-1} \]

The low-frequency shift of the cis isomer is a result of N–H bond weakening due to the anti lone pair on the adjacent (vicinal) nitrogen which is interacting with the N–H antibonding orbital. Note that the orbital overlap is not nearly as good from the trans isomer.

N. C. Craig & co-workers JACS 1979, 101, 2480.

Aldehyde C–H Infrared Stretching Frequencies

The IR C–H stretching frequency for aldehydes is lower than the closely related olefin C–H stretching frequency. For years this observation has gone unexplained.

\[ \nu \text{C–H} = 2730 \text{ cm}^{-1} \]

\[ \nu \text{C–H} = 3050 \text{ cm}^{-1} \]

We now conclude that this is another example of negative hyperconjugation.

The Anomeric Effect

It is not unexpected that the methoxyl substituent on a cyclohexane ring prefers to adopt the equatorial conformation.

\[ \Delta G^\circ = +0.8 \text{ kcal/mol} \]

What is unexpected is that the closely related 2-methoxytetrahydropyran prefers the axial conformation:

\[ \Delta G^\circ = -0.6 \text{ kcal/mol} \]

That effect which provides the stabilization of the axial OR conformer which overrides the inherent steric bias of the substituent is referred to as the anomeric effect.

Principal HOMO-LUMO interaction from each conformation is illustrated below:

Since the antibonding C–O orbital is a better acceptor orbital than the antibonding C–H bond, the axial OMe conformer is better stabilized by this interaction which is worth ca 1.2 kcal/mol.

Other electronegative substituents such as Cl, SR etc. also participate in anomeric stabilization.

This conformer preferred by 1.8 kcal/mol

Why is axial C–Cl bond longer?
$\text{CH}_2=\text{CH}_2$

$\Delta E$

$+1.5 \text{ eV}$

$-10.52 \text{ eV}$
### HOMO and LUMO Energies and Orbital Coefficients of Common Alkenes

![](image.png)

<table>
<thead>
<tr>
<th>Alkene</th>
<th>HOMO (eV)</th>
<th>(c_1)</th>
<th>(c_2)</th>
<th>LUMO (eV)</th>
<th>(c_3)</th>
<th>(c_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_2\text{=CH}_2)^a</td>
<td>-10.52</td>
<td>0.71</td>
<td>0.71</td>
<td>+1.5</td>
<td>0.71</td>
<td>-0.71</td>
</tr>
<tr>
<td>(\text{CH}_2\text{=CHCl})^a</td>
<td>-10.15</td>
<td>0.44</td>
<td>0.30</td>
<td>+0.5</td>
<td>0.67</td>
<td>-0.54</td>
</tr>
<tr>
<td>(\text{CH}_2\text{=CHMe})^a</td>
<td>-9.88</td>
<td>0.67</td>
<td>0.56</td>
<td>+1.8(^{a,b})</td>
<td>0.67</td>
<td>-0.65</td>
</tr>
<tr>
<td>(\text{MeCH=CHMe}) &amp;</td>
<td>-9.13(^c) &amp; &amp; &amp;+2.22(^d) &amp; &amp;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{EtCH=CH}_2) &amp;</td>
<td>-9.63(^e) &amp; &amp; &amp;+2.01(^e) &amp; &amp;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| \(\begin{array}{c}
\text{c_1} \\
\text{c_2} \\
\text{c_3} \\
\text{c_4}
\end{array}\) | -8.94\(^{f,g}\) & & &+2.1\(^g\) & & |
| \(\text{CH}_2\text{=CHOMe}\)^a | -9.05,-8.93\(^c\) | 0.61    | 0.39    | +2.0      | 0.66    | -0.72 |
| \(\text{CH}_2\text{=CHSMe}\)^a | -8.45     | 0.34    | 0.17    | +1.0      | 0.63    | -0.48 |
| \(\text{CH}_2\text{=CHNMe}_2\)^a | -9.0      | 0.50    | 0.20    | +2.5      | 0.62    | -0.69 |
| \(\text{CH}_2\text{=CHCO}_2\text{Me}\) | -10.72    | 0.43    | 0.33    | 0         | 0.69    | -0.47 |
| \(\text{CH}_2\text{=CHCN}\) | -10.92    | 0.60    | 0.49    | 0         | 0.66    | -0.54 |
| \(\text{CH}_2\text{=CHNO}_2\)^a | -11.4     | 0.62    | 0.60    | +0.7      | 0.54    | -0.32 |
| \(\text{CH}_2\text{=CHPh}\) | -8.48     | 0.49    | 0.32    | +0.8      | 0.48    | -0.33 |
| \(\text{CH}_2\text{=CHCHO}\)^b | -10.89\(^b\) | 0.58\(^a\) | 0.48\(^a\) | +0.60\(^b\) | 0.404\(^b\) | -0.581\(^b\) |
| \(\text{CH}_2\text{=CHCHO/BF}_3\)^b | -12.49    | & & &+0.43 | 0.253    | -0.529 |
| \(\text{CH}_2\text{=CHCO}_2\text{H}\)^b | -10.93    | & & &+2.91 | 0.461    | -0.631 |
| \(\begin{array}{c}
\text{O} \\
\text{O}
\end{array}\) | -10.29\(^h\) & & &-1.91\(^i\) & & |
Influence of a conjugating substituent on alkene HOMO and LUMO energies.
HOMO

LUMO

+ 1.0 eV

+ 9.03 eV

- 0.42
- 0.42
+ 0.56
+ 0.56

- 0.41
- 0.41
+ 0.41
+ 0.41

+ 0.57
+ 0.57
- 0.57
- 0.57
Relative HOMO and LUMO energies of electron-rich and electron-poor dienes.
<table>
<thead>
<tr>
<th>Diene</th>
<th>HOMO$^a$</th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>LUMO</th>
<th>$c_3$</th>
<th>$c_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-9.07; -8.85$^b$</td>
<td>0.57</td>
<td>-0.57</td>
<td>+1.0; 3.38$^b$</td>
<td>0.56</td>
<td>0.56</td>
</tr>
<tr>
<td>Me</td>
<td>-9.78$^a$; -8.54</td>
<td>0.314</td>
<td>0.315</td>
<td>+3.51</td>
<td>0.629$^c$</td>
<td>0.617$^c$</td>
</tr>
<tr>
<td>Me</td>
<td>-9.04$^a$; -8.72</td>
<td>0.340</td>
<td>0.296</td>
<td>+3.38</td>
<td>0.56$^d$</td>
<td>0.55$^d$</td>
</tr>
<tr>
<td>Me</td>
<td>-8.76$^a$</td>
<td></td>
<td></td>
<td></td>
<td>2.18$^e$</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>-8.39$^a$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>-8.16$^a$</td>
<td>0.408$^f$</td>
<td>0.416$^f$</td>
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</tr>
<tr>
<td>Ph</td>
<td>-8.77$^a$</td>
<td>0.572$^g$</td>
<td>0.335$^g$</td>
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</tr>
<tr>
<td>MeO</td>
<td>-8.21$^{a,b}$; -8.24$^b$</td>
<td>0.235$^b$</td>
<td>0.313$^b$</td>
<td>+3.77$^b$</td>
<td>0.644$^c$</td>
<td>0.609$^c$</td>
</tr>
<tr>
<td>OMe</td>
<td>-8.62$^a$</td>
<td>0.352$^b$</td>
<td>0.103$^b$</td>
<td>+3.60$^b$</td>
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</tr>
<tr>
<td>SMe</td>
<td>-7.94</td>
<td>0.240</td>
<td>0.256</td>
<td>+3.25</td>
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</tr>
<tr>
<td>SMe</td>
<td>-8.37</td>
<td>0.399</td>
<td>0.201</td>
<td>+3.25</td>
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</table>
HOMO_{butadiene}–LUMO_{ethene} interactions that control the Diels–Alder cyclization.
HOMO$_\text{diene}$–LUMO$_\text{alkene}$ interactions of butadiene and representative alkenes
Regioselectivity of 1-Alkyl-1,3-butadienes with Electron Deficient Alkenes

\[
\text{R} + \text{Z} \rightarrow \text{65} + \text{66}
\]

<table>
<thead>
<tr>
<th>R</th>
<th>Z</th>
<th>65/66</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>CHO</td>
<td>8:1</td>
</tr>
<tr>
<td>Me</td>
<td>C≡N</td>
<td>10:1</td>
</tr>
<tr>
<td>Me</td>
<td>CO₂Me</td>
<td>6.8:1</td>
</tr>
<tr>
<td>i-Pr</td>
<td>CO₂Me</td>
<td>5:1</td>
</tr>
<tr>
<td>n-Bu</td>
<td>CO₂Me</td>
<td>5.1:1</td>
</tr>
<tr>
<td>t-Bu</td>
<td>CO₂Me</td>
<td>4.1:1</td>
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</tbody>
</table>