

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 φ_1 and φ_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 Ψ , and integrated over all space [Equation (2.5)]:

$$\mathbf{H}\Psi = E\Psi \quad (2.4)$$

$$\langle \Psi | \mathbf{H} | \Psi \rangle = E \langle \Psi | \Psi \rangle \quad (2.5)$$

3. Each MO is expressed as a linear combination of atomic orbitals (LCAOs):

$$\Psi = c_1\varphi_1 + c_2\varphi_2 \quad (2.6)$$

In Equation (2.6), we know φ_1 and φ_2 . Calculating an MO Ψ_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

$$\langle c_1\varphi_1 + c_2\varphi_2 | \mathbf{H} | c_1\varphi_1 + c_2\varphi_2 \rangle = E \langle c_1\varphi_1 + c_2\varphi_2 | c_1\varphi_1 + c_2\varphi_2 \rangle \quad (2.7)$$

The linearity of integrals (p. 7), allows the left-hand side of Equation (2.7) to be expressed as

$$\begin{aligned} \langle c_1\varphi_1 + c_2\varphi_2 | \mathbf{H} | c_1\varphi_1 + c_2\varphi_2 \rangle &= \langle c_1\varphi_1 | \mathbf{H} | c_1\varphi_1 \rangle + \langle c_1\varphi_1 | \mathbf{H} | c_2\varphi_2 \rangle + \dots \\ &= c_1^2 \langle \varphi_1 | \mathbf{H} | \varphi_1 \rangle + c_2^2 \langle \varphi_2 | \mathbf{H} | \varphi_2 \rangle + \dots \end{aligned}$$

To express this more simply, let us set

$$\langle \varphi_i | \mathbf{H} | \varphi_i \rangle = \alpha_i$$

$$\langle \varphi_i | \mathbf{H} | \varphi_j \rangle = \beta_{ij}$$

$$\langle \varphi_i | \varphi_j \rangle = S_{ij}$$

where α_i is termed the *Coulomb integral*, β_{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,³ 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

$$(c_1^2 + c_2^2)\alpha + 2c_1c_2\beta - E(c_1^2 + c_2^2 + 2c_1c_2S) = 0 \quad (2.8)$$

where α , β 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*:

$$\begin{aligned} (\alpha - E)c_1 + (\beta - ES)c_2 &= 0 \\ (\beta - ES)c_1 + (\alpha - E)c_2 &= 0 \end{aligned} \quad (2.9)$$

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:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0 \quad (2.10)$$

The solutions to Equation (2.10) are

$$E_1 = \frac{\alpha + \beta}{1 + S} \quad \text{and} \quad E_2 = \frac{\alpha - \beta}{1 - S} \quad (2.11)$$

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 Ψ_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:

$$\langle \Psi_i | \Psi_i \rangle = c_{i1}^2 + c_{i2}^2 + 2c_{i1}c_{i2}S = 1 \quad (2.12)$$

The solutions are

$$\Psi_1 = \frac{1}{\sqrt{2(1+S)}}(\varphi_1 + \varphi_2) \quad \text{and} \quad \Psi_2 = \frac{1}{\sqrt{2(1-S)}}(\varphi_1 - \varphi_2) \quad (2.13)$$

Figure 2.2 gives a pictorial representation of Equation (2.11) and (2.13).

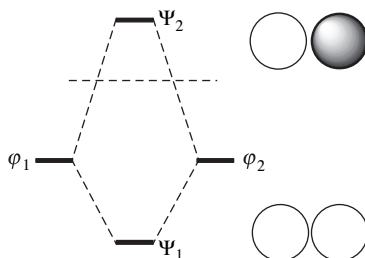


Figure 2.2 The MOs of the homonuclear diatomic A_2 . φ_1 and φ_2 are arbitrarily drawn as s orbitals. Note that the destabilization of Ψ_2 is greater than the stabilization of Ψ_1 .

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 α

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

The Resonance Integral β

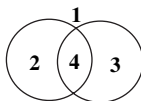
The absolute value of the resonance integral gives a measure of the A_1A_2 *bond strength*.⁶ It increases with increasing overlap. We will see that S_{12} measures the volume common to φ_1 and φ_2 , which encloses the electrons shared by A_1 and A_2 . Large values of S_{12} thus imply strong bonding between A_1 and A_2 . When S_{12} is zero, β_{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*:

$$\beta_{12} \approx kS_{12} \quad (2.14)$$

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 φ_i and φ_j . They define four regions in space:



- Region **1** lies outside φ_i and φ_j , where both orbitals have small values. The product $\varphi_i \varphi_j$ is negligible.
- Region **2** (enclosed by φ_i but outside φ_j) and region **3** (enclosed by φ_j but outside φ_i) also have negligible values for $\varphi_i \varphi_j$: one component is appreciable, but the other is very small.
- Region **4**, where both φ_i and φ_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 β_{12} is sometimes said to represent the coupling of φ_i with φ_j . 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 Ψ_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 Ψ_1 :

$$\langle \Psi_1 | \Psi_1 \rangle = c_{11}^2 \langle \phi_1 | \phi_1 \rangle + 2c_{11}c_{12}S_{12} + c_{12}^2 \langle \phi_2 | \phi_2 \rangle = 1 \quad (2.15)$$

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 ϕ_1 and ϕ_2 and 'belong' to A_1 and A_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 A_1A_2 . It is positive when the AOs overlap in phase (as in Ψ_1) and negative when they are out of phase (as in Ψ_2). The overlap population gives the fraction of the electron cloud shared by A_1 and A_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 measure⁷ of the A_1A_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.⁸

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 Ψ_1 of the diatomic A_1A_2 . The contribution of this electron to the electronic charge of A_1 is then c_{11}^2 plus half of the overlap population. In the general case:

$$q_e(A) = \sum_{i,j} n_i c_{iA} c_{jA} S_{ij} \quad (2.16)$$

⁷In 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.

⁸This rule is not inviolable. See pp. 87, 96 and 175.

where S_{Aj} is the overlap integral of φ_A and φ_j , n_i is the number of electrons which occupy Ψ_i and c_{iA} and c_{ij} are the coefficients of φ_A and φ_j in the same MO. The summation takes in all of the MOs Ψ_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 φ_A , of energy α_A and φ_B of energy α_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

$$(\alpha_A - E)(\alpha_B - E) - (\beta - ES)^2 = 0 \quad (2.17)$$

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:

$$E_1 \approx \alpha_A + \frac{(\beta - \alpha_A S)^2}{\alpha_A - \alpha_B} \quad E_2 \approx \alpha_B + \frac{(\beta - \alpha_B S)^2}{\alpha_B - \alpha_A} \quad (2.18)$$

$$\Psi_1 \approx N_1 \left(\varphi_A + \frac{\beta - \alpha_A S}{\alpha_A - \alpha_B} \varphi_B \right) \quad \Psi_2 \approx N_2 \left(\varphi_B + \frac{\beta - \alpha_B S}{\alpha_B - \alpha_A} \varphi_A \right) \quad (2.19)$$

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

$$\alpha_A - E_1 = \frac{(\beta - E_1 S)^2}{\alpha_B - E_1} \approx \frac{(\beta - \alpha_A S)^2}{\alpha_B - \alpha_A} \quad (2.20)$$

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

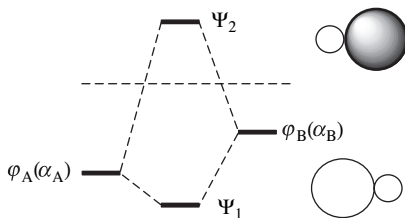


Figure 2.3 MOs of a heteronuclear diatomic molecule. φ_A and φ_B are arbitrarily shown as s orbitals.

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 π 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 2×2 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:

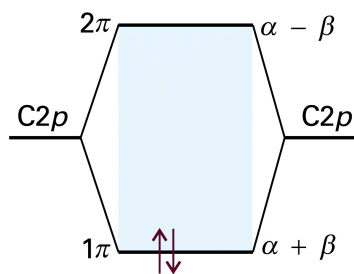
Set all overlap integrals $S = 0$

Recognize the α integrals are equal

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

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

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

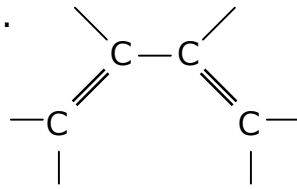


Total π bond energy = $2(\alpha + \beta)$

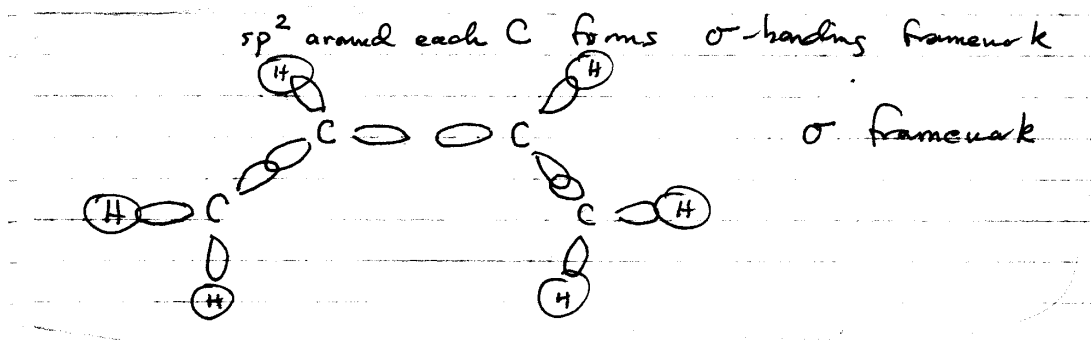
Stabilization due to bond formation = 2β

β is intrinsically negative and ~ -2.4 eV for C-C bond (~ -230 kJ/mol)

Butadiene.

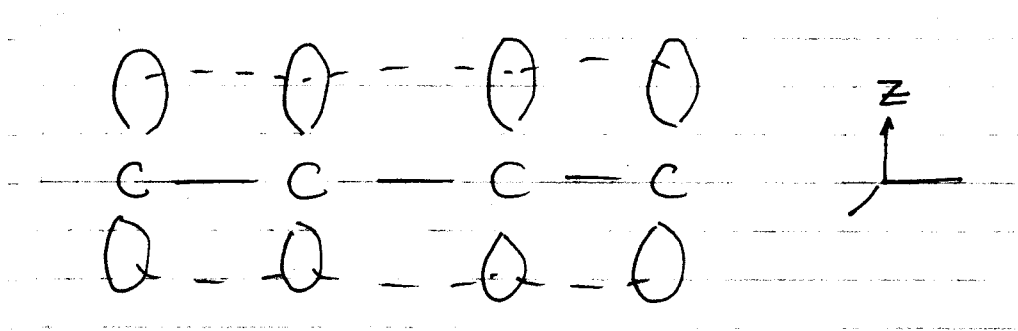


Treat sigma bonding framework using VB theory as follows:



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 π system.

Treat π system by HMO as follow:

- basis set is composed of four $2p_z$ orbitals (perpendicular to plane).

Therefore will get 4 x 4 matrix or secular determinant

- HMO approx:

- 1) Set all overlap integrals $S = 0$

2) Set all resonance integrals between non-neighbors = 0
 $\beta_{13}, \beta_{14}, \beta_{24}$ etc. = 0

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

Resulting Sec detm

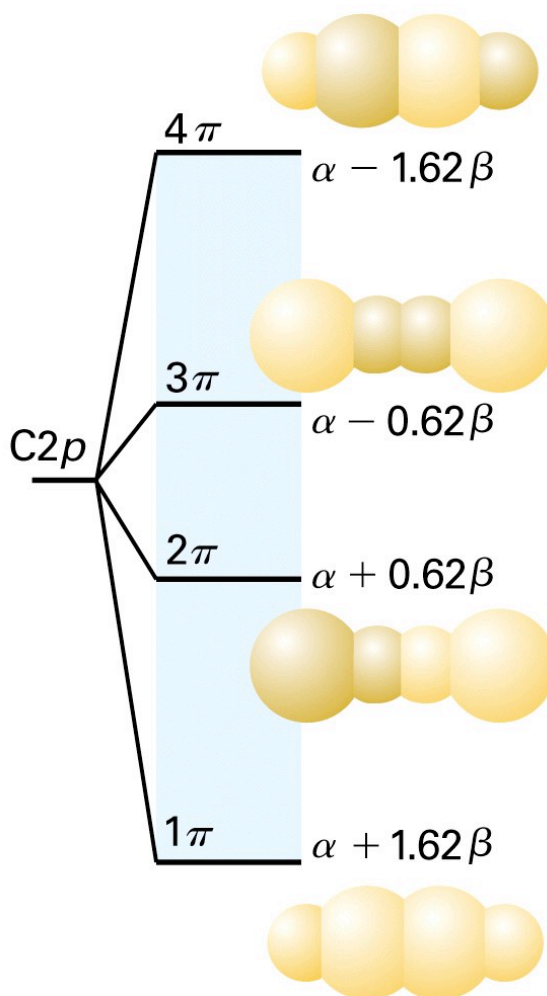
$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

Generates a quartic polynomial in E which has four roots.

Therefore 4 π -orbital MO
 4 energies (roots of secular determinant)

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

Energy diagram:



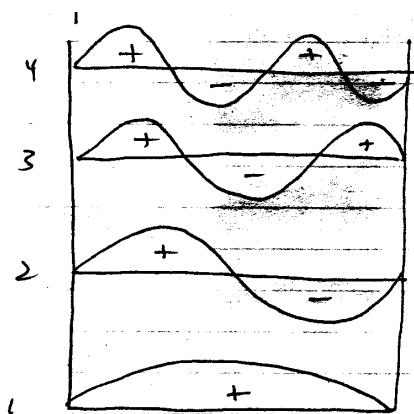
Spectroscopic transition HOMO → LUMO (called frontier orbitals)

HOMO = highest occupied molecular orbital (here MO 2π)

LUMO = lowest unoccupied molecular orbital (here MO 3π)

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

Compare wave functions with particle in box:



Delocalized system have extra stability (=deloc energy DE)

Calculate it:

$$\text{DE} = \text{Energy of } \text{C}=\text{C}-\text{C}=\text{C} \quad - \quad \text{Energy of } \text{C}=\text{C}-\text{C}=\text{C}$$

↑
↑

Allow electrons
To delocalize
2 separate
 π bonds
like in ethene

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

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

$$= 0.48\beta \sim -110 \text{ kJ/mol of stabilization}$$

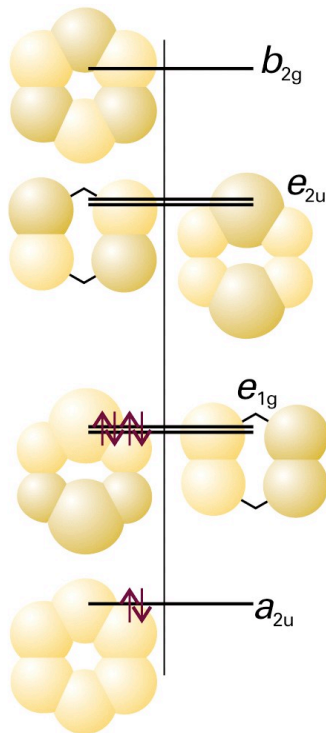
Benzene – cyclic delocalized system.

6x6 secular determinant =

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

↑
due to cyclic connection

=Energy eigenvalues are $E = \alpha \pm 2\beta, \alpha \pm \beta, \alpha \pm \beta$



Calculate delocalization energy DE:

$$\text{Total pi electron energy} = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

$$\text{Energy of three C=C in ethane} = 2\alpha + 2\beta$$

$$\text{DE} = \text{difference} = 2\beta = -460 \text{ kJ/mol}$$

Introduction to Frontier Molecular Orbital Theory

General Reviews

Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*

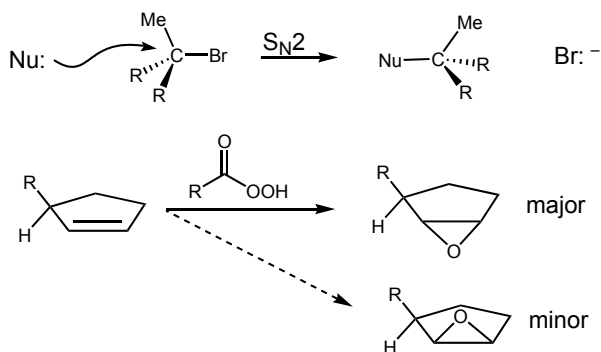
Fukui, *Acc. Chem. Res.* **1971**, *4*, 57.

Kirby, A. J. *Stereoelectronic Effects*.

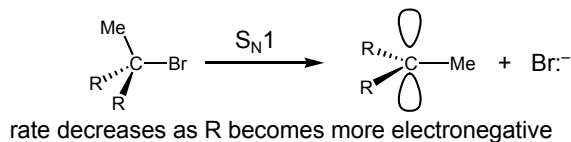
Universal Effects Governing all Chemical Reactions

Steric Effects

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



Nondirectional Electronic Effects (Inductive Effects):



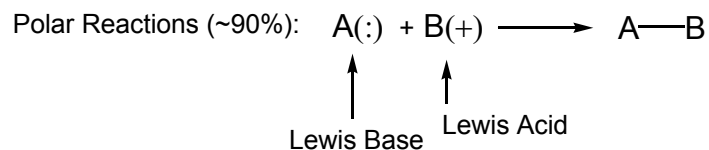
Stereoelectronic Effects

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.

General Reaction Types



FMO concepts extend the donor-acceptor paradigm to non-obvious families of reactions

Consider stabilization energy (ΔE) when bringing atoms A & B together:

$$\Delta E = - \underbrace{\frac{Q_A Q_B}{\epsilon R}}_{\text{Coulomb Term}} + \underbrace{\frac{2 \sum_m \sum_n (c_m^A c_n^B \beta)^2}{(E_m - E_n)}}_{\text{Orbital Term}}$$

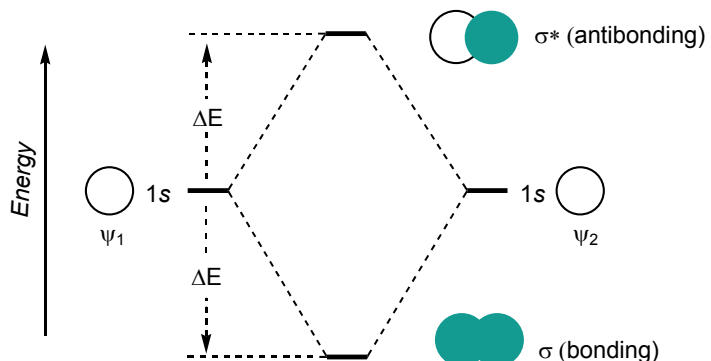
Q: Charge density
 ϵ : Dielectric constant
 R: distance of A to B
 c: coefficient of MO m of species A, or MO n of species B
 β : Overlap Integral
 E: Energy of MO

The H₂ Molecular Orbitals

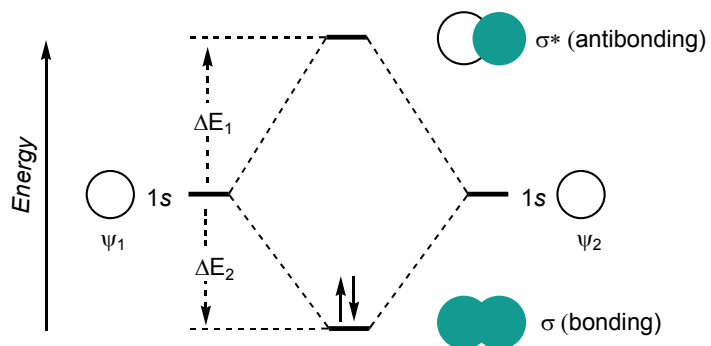
The H₂ Molecule (again!!)

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:



Note that ΔE_1 is greater than ΔE_2 . Why?

Linear Combination of Atomic Orbitals (LCAO): Orbital Coefficients

Each MO is constructed by taking a linear combination of the individual atomic orbitals (AO):

$$\text{Bonding MO} \quad \sigma = C_1\psi_1 + C_2\psi_2$$

$$\text{Antibonding MO} \quad \sigma^* = C_1^*\psi_1 - C_2^*\psi_2$$

The coefficients, C_1 and C_2 , represent the contribution of each AO.

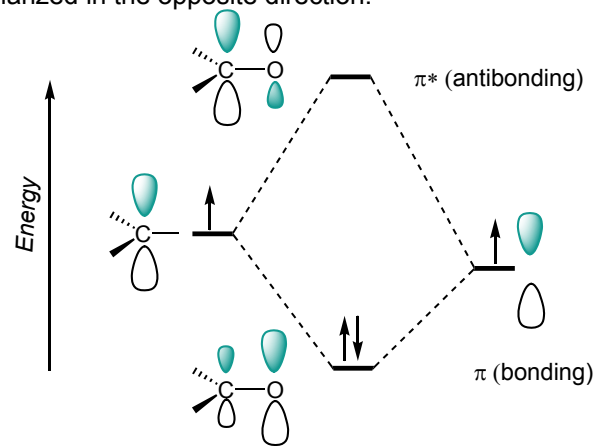
- **Rule Two:** $(C_1)^2 + (C_2)^2 = 1$

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 (δE_{cov}) and an ionic contribution (δE_{ionic}).**

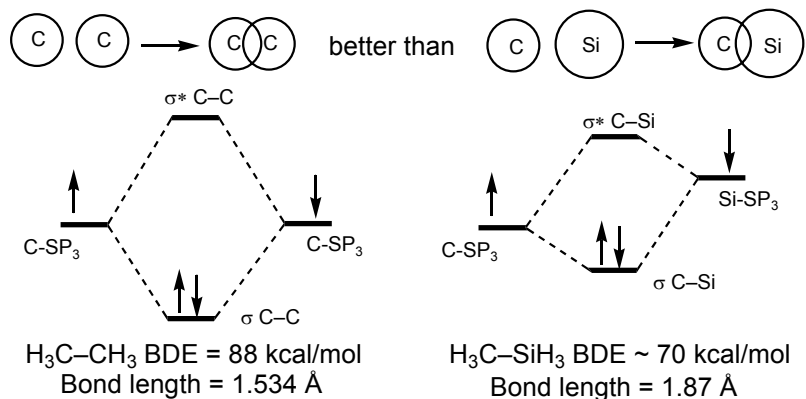
$$\text{Bond Energy (BDE)} = \delta E_{covalent} + \delta E_{ionic}$$

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.



This trend is even more dramatic with pi-bonds:

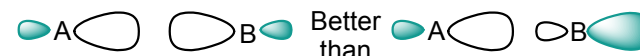
$$\pi \text{ C-C} = 65 \text{ kcal/mol} \quad \pi \text{ C-Si} = 36 \text{ kcal/mol} \quad \pi \text{ Si-Si} = 23 \text{ kcal/mol}$$

- **Weak bonds will have corresponding low-lying antibonds.**

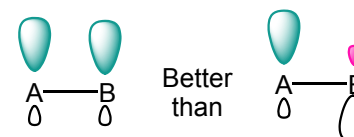
Formation of a weak bond will lead to a corresponding low-lying antibonding orbital. Such structures are reactive as both nucleophiles & electrophiles

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

For σ Bonds:



For π Bonds:



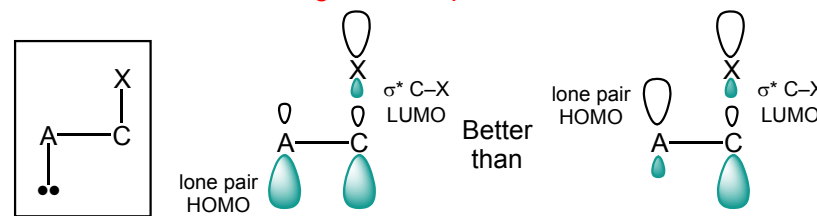
This is a simple notion with very important consequences. It surfaces in the delocalized bonding which occurs in the competing anti (favored) syn (disfavored) E2 elimination reactions. Review this situation.

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

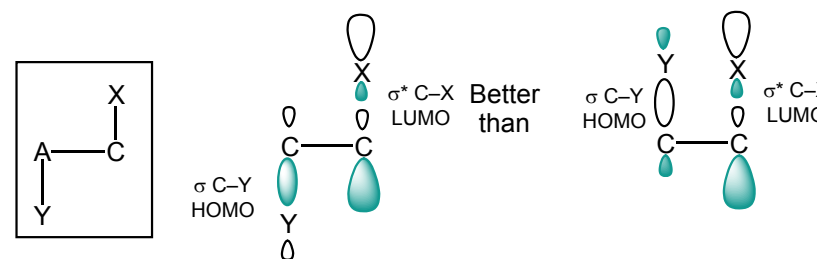
This is a corollary to the preceding generalization.

There are two common situations.

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



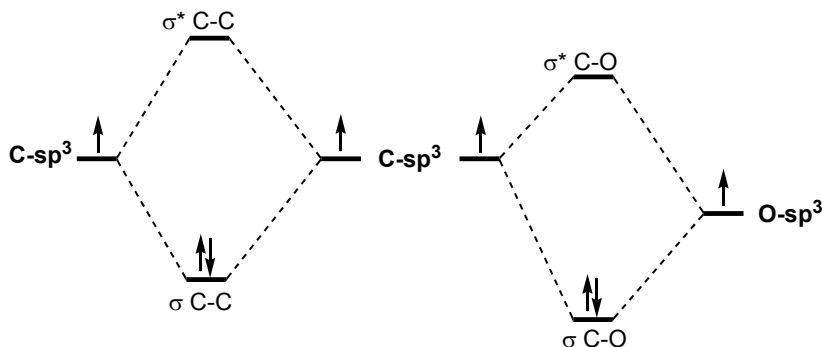
Case-2: Two anti sigma bonds



Donor-Acceptor Properties of Bonding and Antibonding States

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

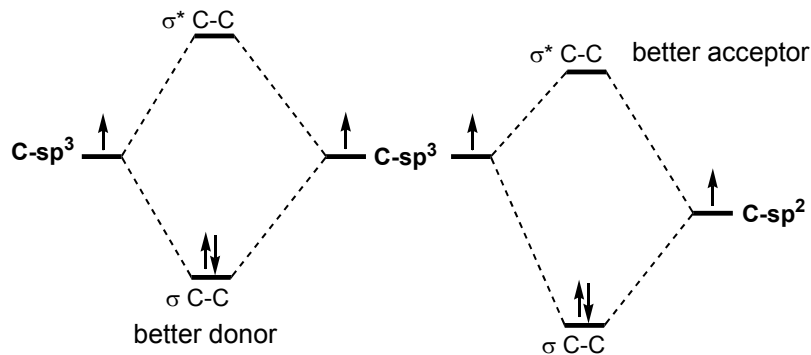
Consider the energy level diagrams for both bonding & antibonding orbitals for C-C and C-O bonds.



■ The greater electronegativity of oxygen lowers both the bonding & antibonding C-O states. Hence:

- σ C-C is a better donor orbital than σ C-O
- σ^* C-O is a better acceptor orbital than σ^* C-C

Donor Acceptor Properties of C_{sp^3} - C_{sp^3} & C_{sp^3} - C_{sp^2} Bonds

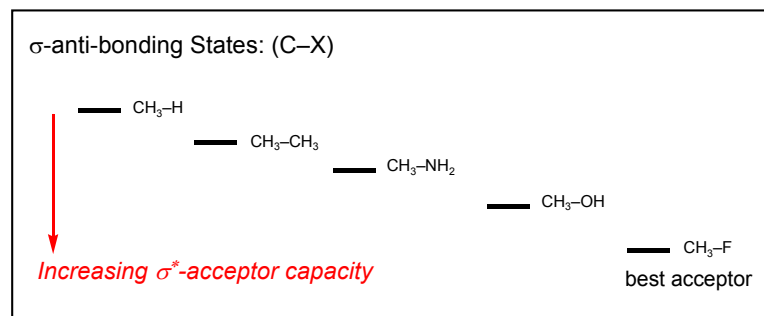
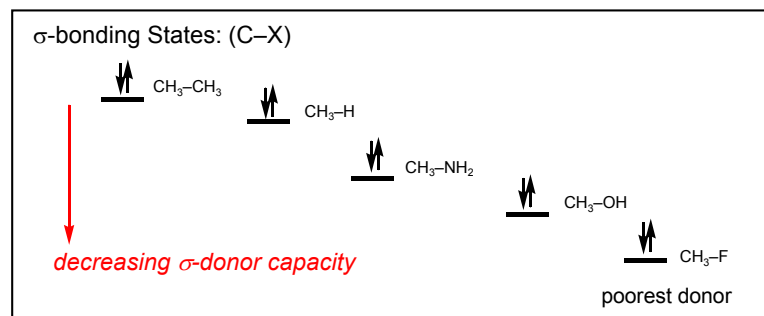


■ The greater electronegativity of C_{sp^2} lowers both the bonding & antibonding C-C states. Hence:

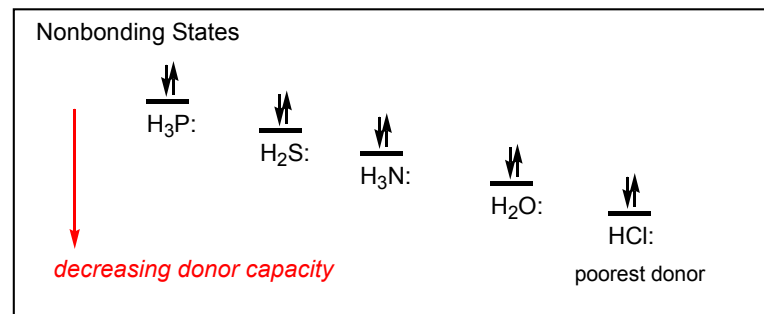
- σ C_{sp^3} - C_{sp^3} is a better donor orbital than σ C_{sp^3} - C_{sp^2}
- σ^* C_{sp^3} - C_{sp^2} is a better acceptor orbital than σ^* C_{sp^3} - C_{sp^3}

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 $X = C, N, O, F, \text{ \& H}$.



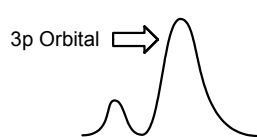
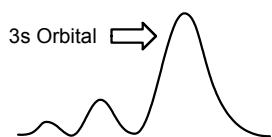
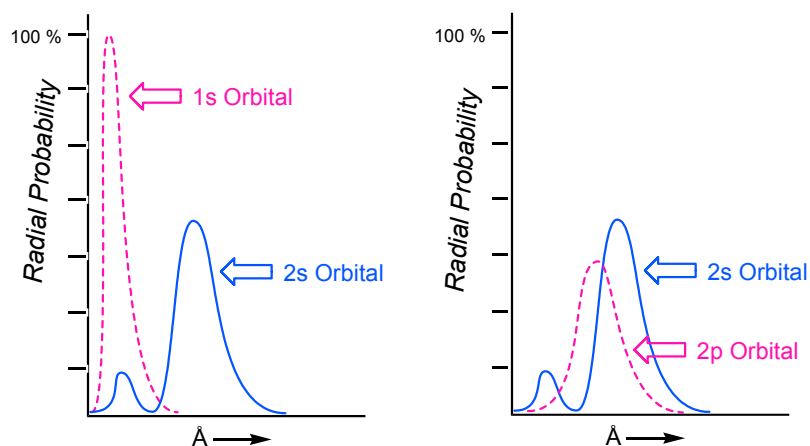
The following are trends for the energy levels of *nonbonding states* of several common molecules. Trend was established by photoelectron spectroscopy.



Hybridization vs Electronegativity

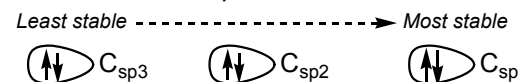
Electrons in 2s states "see" a greater effective nuclear charge than electrons in 2p states.

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.

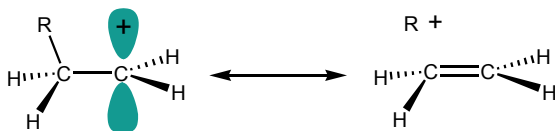
There is a linear relationship between %s character & Pauling electronegativity

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.

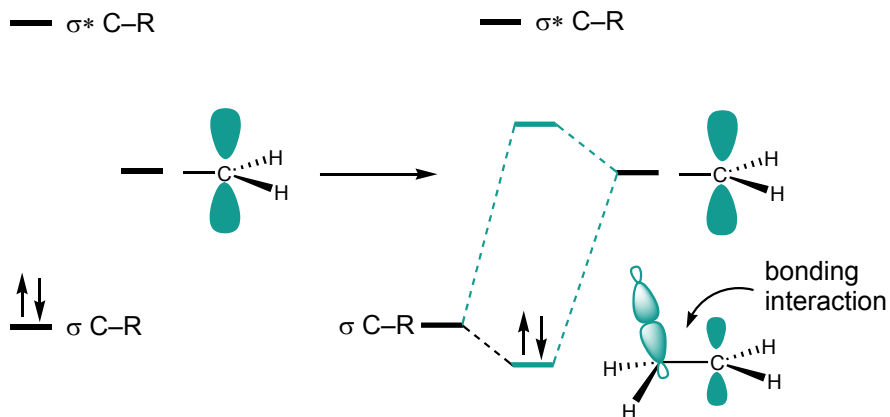


The graphic illustrates the fact that the C-R bonding electrons can "delocalize" to stabilize the electron deficient carbocationic center.

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



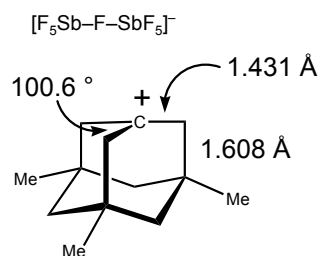
- Take a linear combination of σ C-R and Csp_2 p-orbital:

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

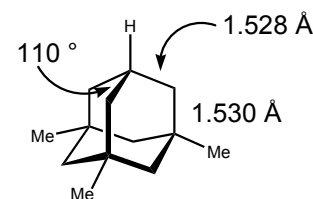
Physical Evidence for Hyperconjugation

- 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



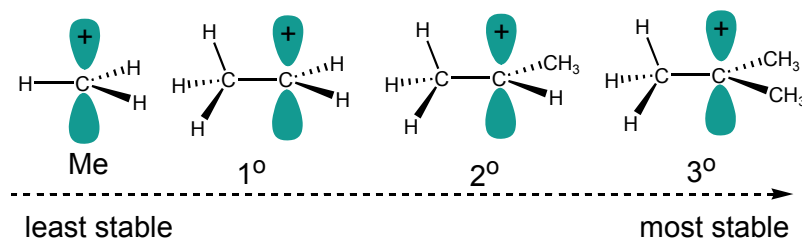
The Adamantane Reference (MM2)



T. Laube, *Angew. Chem. Int. Ed.* **1986**, 25, 349

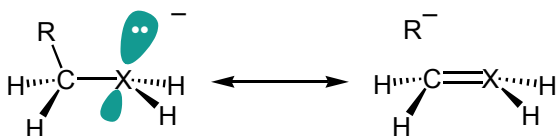
More substituted carbocations have more adjacent C-R bonds to act as donors to the empty p orbital

Hence, more substituted carbocations are more stable.



"Negative" Hyperconjugation/Anomeric Effect

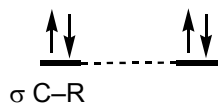
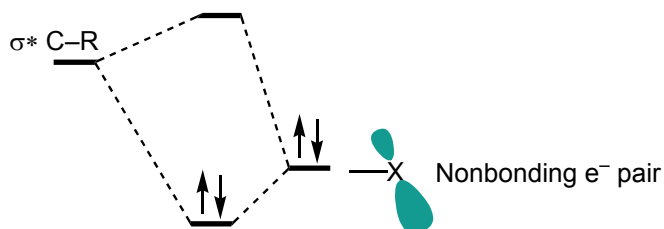
- Delocalization of nonbonding electron pairs into vicinal antibonding orbitals is also possible



This delocalization is referred to as "negative" hyperconjugation

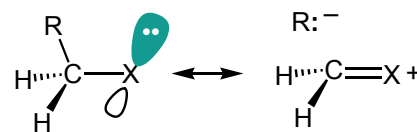
Since nonbonding electrons prefer hybrid orbitals rather than p orbitals, this orbital can adopt either a syn or anti relationship to the vicinal C-R bond.

The Molecular Orbital Description

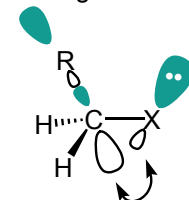


As the antibonding C-R orbital decreases in energy, the magnitude of this interaction will increase

Syn Orientation

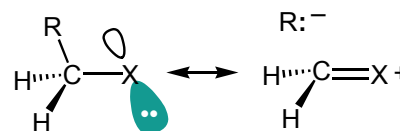


antibonding σ^* C-R

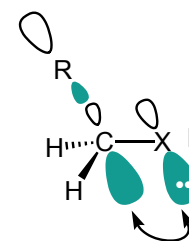


filled hybrid orbital

Anti Orientation



antibonding σ^* C-R



filled hybrid orbital

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

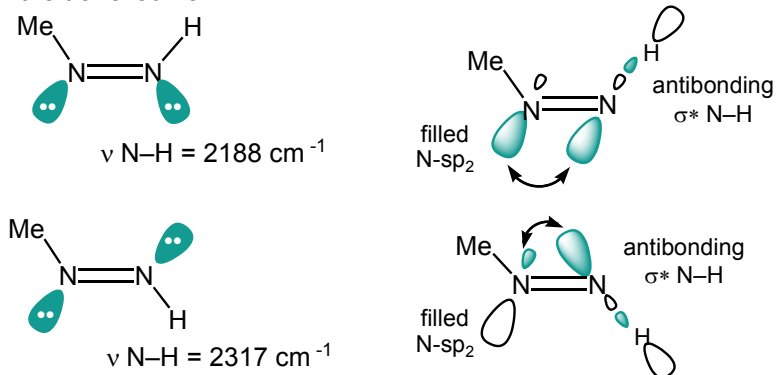
The Expected Structural Perturbations

Change in Structure	Spectroscopic Probe
■ Shorter C-X bond	X-ray crystallography
■ Longer C-R bond	X-ray crystallography
■ Stronger C-X bond	Infrared Spectroscopy
■ Weaker C-R bond	Infrared Spectroscopy
■ Greater e-density at R	NMR Spectroscopy
■ Less e-density at X	NMR Spectroscopy

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.

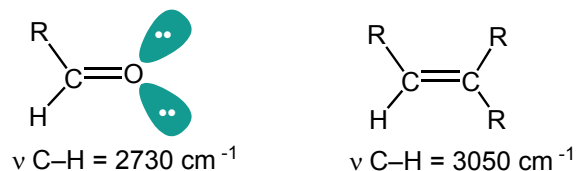


■ The low-frequency shift of the *cis* isomer is a result of N–H bond weakening due to the anti lone pair on the adjacent (vicinal) nitrogen which is interacting with the N–H antibonding orbital. Note that the orbital overlap is not nearly as good from the *trans* isomer.

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

Aldehyde C–H Infrared Stretching Frequencies

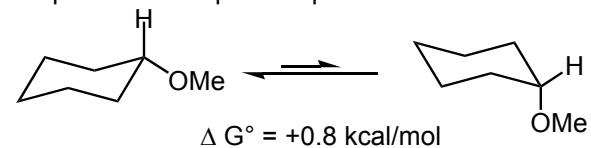
The IR C–H stretching frequency for aldehydes is lower than the closely related olefin C–H stretching frequency. For years this observation has gone unexplained.



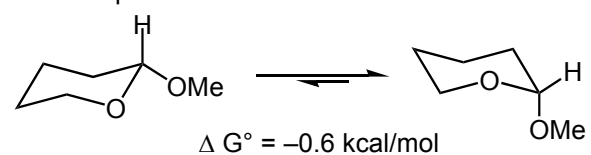
■ We now conclude that this is another example of negative hyperconjugation.

The Anomeric Effect

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

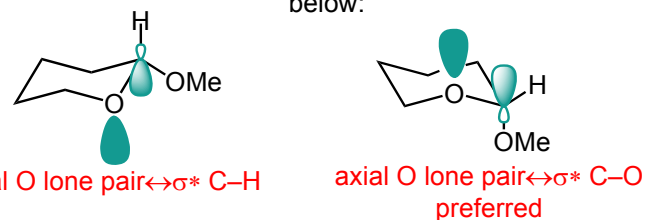


What is unexpected is that the closely related 2-methoxytetrahydropyran prefers the axial conformation:



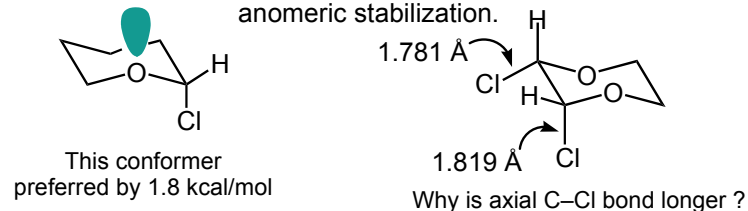
■ That effect which provides the stabilization of the axial OR conformer which overrides the inherent steric bias of the substituent is referred to as the anomeric effect.

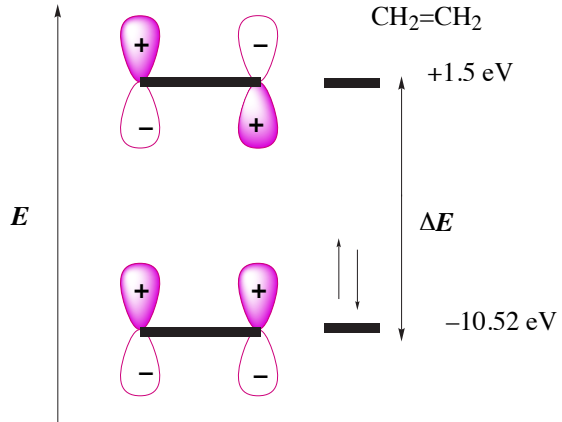
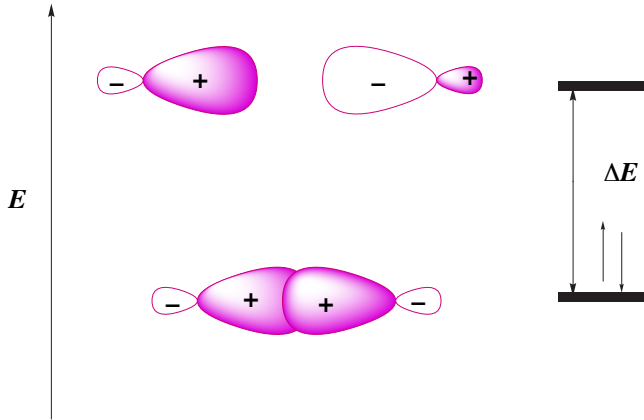
Principal HOMO-LUMO interaction from each conformation is illustrated below:

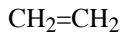


■ Since the antibonding C–O orbital is a better acceptor orbital than the antibonding C–H bond, the axial OMe conformer is better stabilized by this interaction which is worth ca 1.2 kcal/mol.

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







+0.69

-0.47

+0.71

-0.71

+0.66

-0.72

+1.5 eV

+2.0 eV

0 eV

-10.52 eV

-9.05 eV

-10.72 eV

+0.43

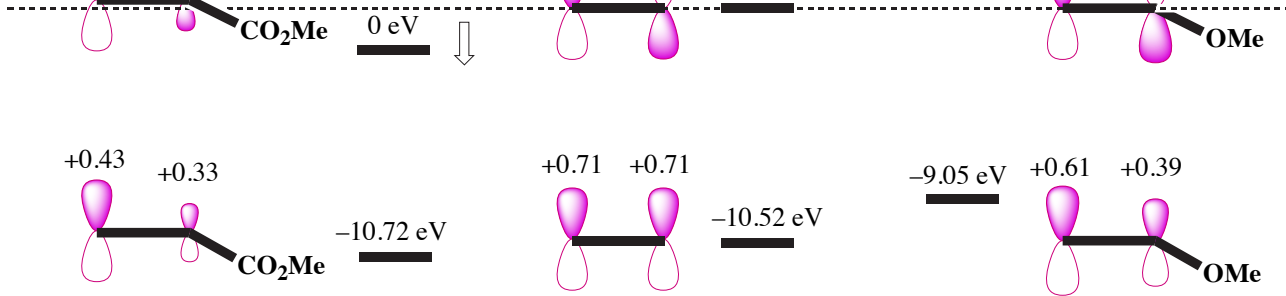
+0.33

+0.71

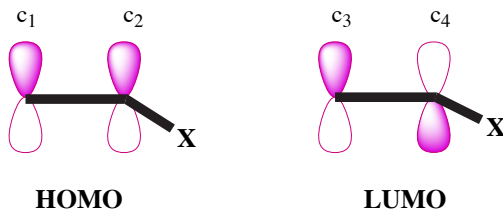
+0.71



+0.61

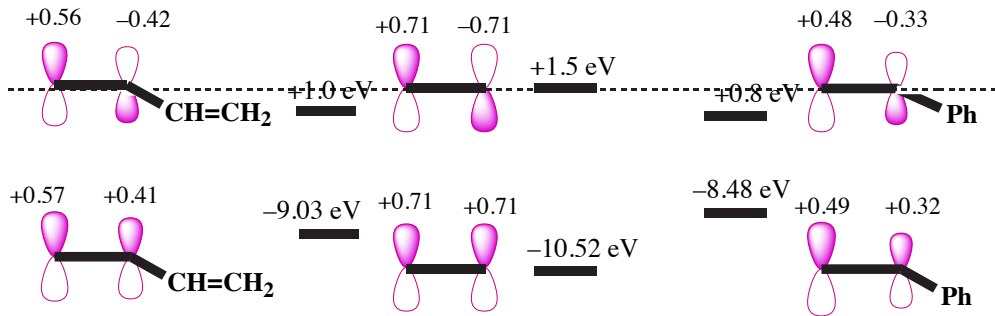
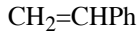
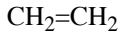
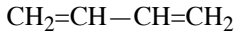
+0.39

 CO_2Me OMe CO_2Me OMe 

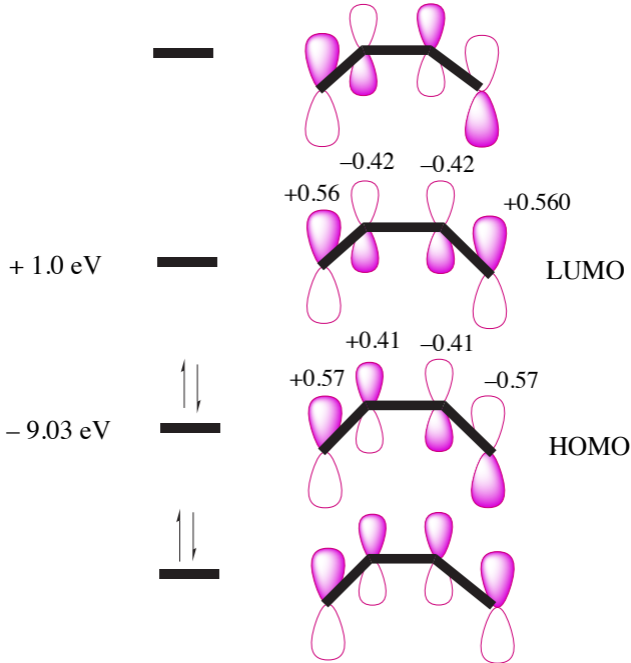
HOMO and LUMO Energies and Orbital Coefficients of Common Alkenes

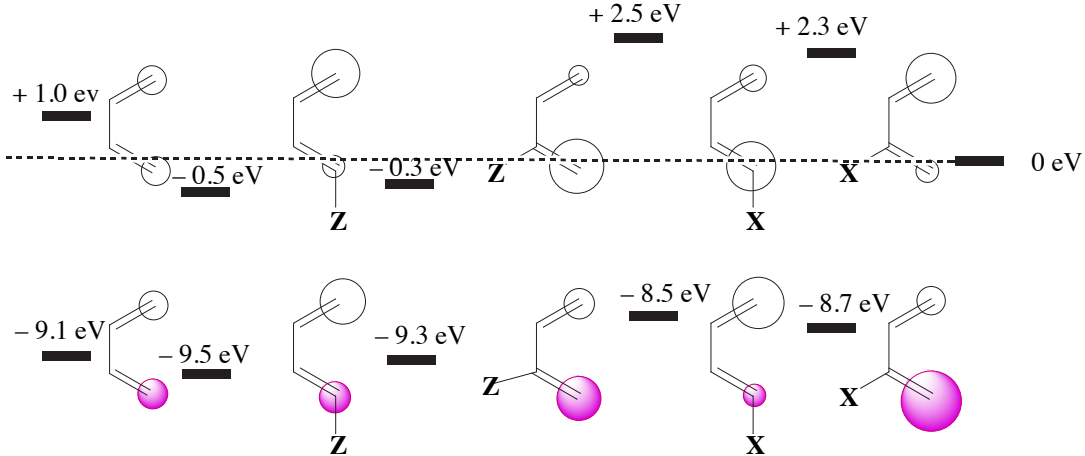


Alkene	HOMO (eV)	c_1	c_2	LUMO (eV)	c_3	c_4
CH ₂ =CH ₂ ^a	-10.52	0.71	0.71	+1.5	0.71	-0.71
CH ₂ =CHCl ^a	-10.15	0.44	0.30	+0.5	0.67	-0.54
CH ₂ =CHMe ^a	-9.88	0.67	0.56	+1.8 ^{a,b}	0.67	-0.65
MeCH=CHMe	-9.13 ^c			+2.22 ^d		
EtCH=CH ₂	-9.63 ^e			+2.01 ^e		
	-8.94 ^{f,g}			+2.1 ^g		
CH ₂ =CHOMe ^a	-9.05;-8.93 ^c	0.61	0.39	+2.0	0.66	-0.72
CH ₂ =CHSMe ^a	-8.45	0.34	0.17	+1.0	0.63	-0.48
CH ₂ =CHNMe ₂ ^a	-9.0	0.50	0.20	+2.5	0.62	-0.69
CH ₂ =CHCO ₂ Me	-10.72	0.43	0.33	0	0.69	-0.47
CH ₂ =CHCN	-10.92	0.60	0.49	0	0.66	-0.54
CH ₂ =CHNO ₂ ^a	-11.4	0.62	0.60	+0.7	0.54	-0.32
CH ₂ =CHPh	-8.48	0.49	0.32	+0.8	0.48	-0.33
CH ₂ =CHCHO	-10.89 ^b	0.58 ^a	0.48 ^a	+0.60 ^b	0.404 ^b	-0.581 ^b
CH ₂ =CHCHO/BF ₃ ^b	-12.49			+0.43	0.253	-0.529
CH ₂ =CHCO ₂ H ^b	-10.93			+2.91	0.461	-0.631
	-10.29 ^h			-1.91 ⁱ		



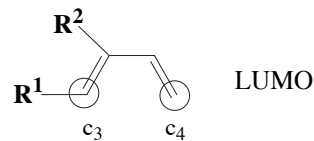
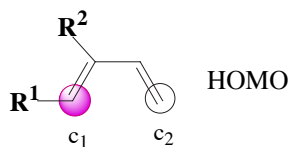
Influence of a conjugating substituent on alkene HOMO and LUMO energies.


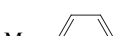
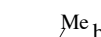

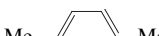


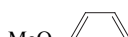

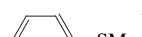
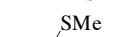


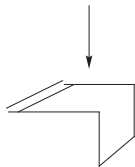
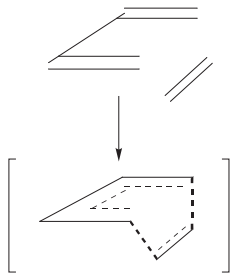
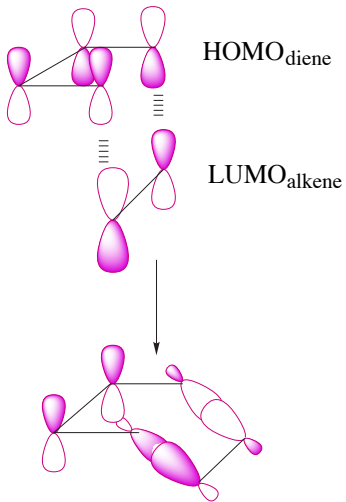


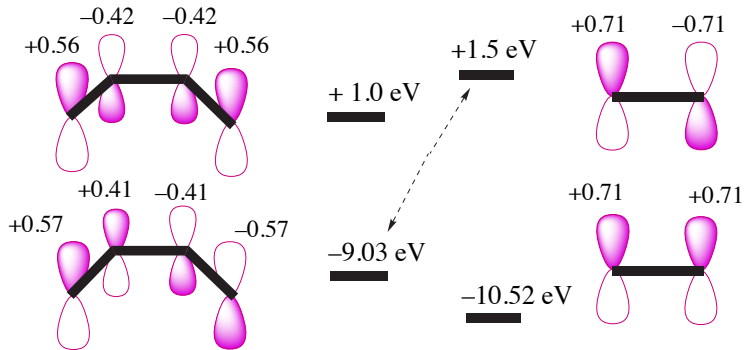
Relative HOMO and LUMO energies of electron-rich and -poor dienes.

HOMO, LUMO Energies and Orbital Coefficients for Substituted Dienes

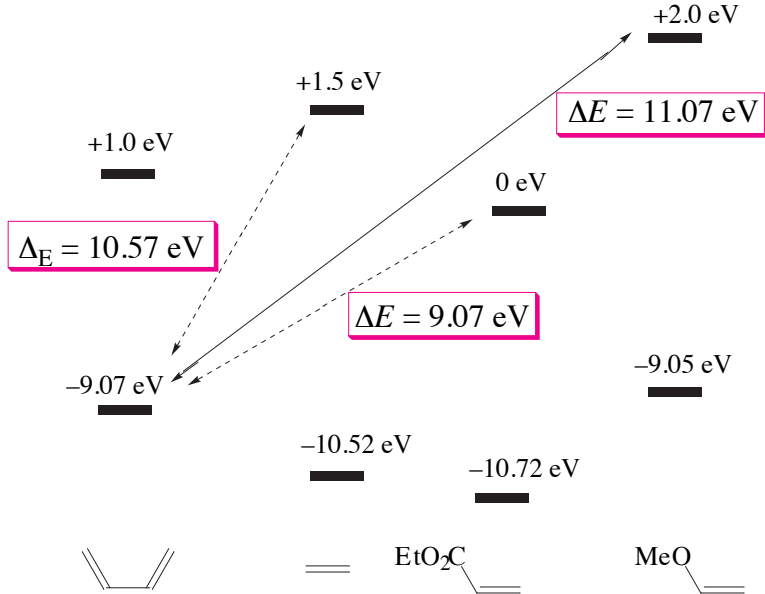


<u>Diene</u>	<u>HOMO</u> ^a	<u>c</u> ₁	<u>c</u> ₂	<u>LUMO</u>	<u>c</u> ₃	<u>c</u> ₄
 a	-9.07;-8.85 ^b	0.57	-0.57	+1.0;3.38 ^b	0.56	0.56
 b	-9.78 ^a ;-8.54	0.314	0.315	+3.51	0.629 ^c	0.617 ^c
 b	-9.04 ^a ;-8.72	0.340	0.296	+3.38	0.56 ^d	0.55 ^d
 b	-8.76 ^a			2.18 ^e		
 b	-8.39 ^a					
 b	-8.16 ^a	0.408 ^f	0.416 ^f			
 b	-8.77 ^a	0.572 ^g	0.335 ^g			
 b	-8.21 ^a ;-8.24 ^b	0.235 ^b	0.313 ^b	+3.77 ^b	0.644 ^c	0.609 ^c
 b	-8.62 ^a	0.352 ^b	0.103 ^b	+3.60 ^b		
 b	-7.94	0.240	0.256	+3.25		
 b	-8.37	0.399	0.201	+3.25		



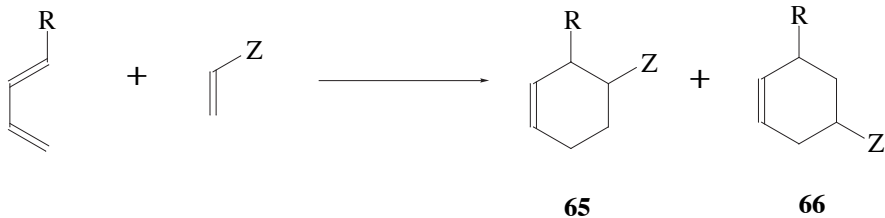


HOMO_{butadiene}-LUMO_{ethene} interactions that control the Diels-Alder cyclization.

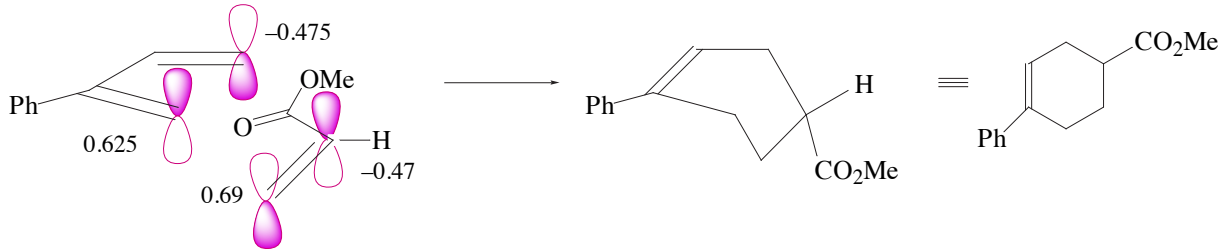


HOMO_{diene}-LUMO_{alkene} interactions of butadiene and representative alkenes

Regioselectivity of 1-Alkyl-1,3-butadienes with Electron Deficient Alkenes



R	Z	<u>65/66</u>
Me	CHO	8:1
Me	C≡N	10:1
Me	CO ₂ Me	6.8:1
<i>i</i> -Pr	CO ₂ Me	5:1
<i>n</i> -Bu	CO ₂ Me	5.1:1
<i>t</i> -Bu	CO ₂ Me	4.1:1



Ph

0.625

-0.475

OMe

O

H

-0.47

0.69

Ph

H

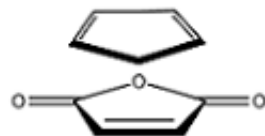
CO₂Me

≡

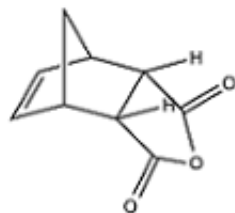
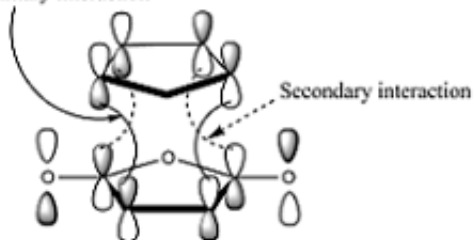
Ph

CO₂Me

Endo



Primary interaction

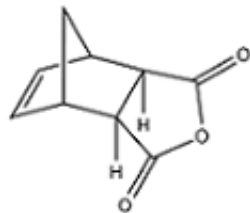
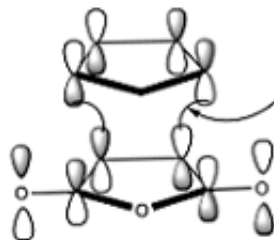


Favored

Exo



Only primary interaction



Not favored