

Molecular Orbital Theory

Hückel molecular orbital theory as originally developed only worked for conjugated, all carbon compounds

The range of compounds that could be studied would expand if heteroatoms could be considered

Empirically this was done by comparing energy values for heteroaromatic compounds

Need to adjust the coulomb and resonance integral values

Remember that the coulomb integral for an electron on a carbon was defined as α (regardless of what else was attached to the carbon)

The resonance integral for two bonded carbons in conjugation was defined as β (if the two carbons were not bonded the resonance integral was set at 0)

For heteroatoms these values were adjusted by adding an amount of β value:

$$\begin{aligned}\alpha' &= \alpha + h\beta \\ \beta' &= k\beta\end{aligned}$$

Molecular Orbital Theory

The h and k correction values are different depending upon what heteroatom is in conjugation

Heteroatom	h
N•	0.5
N:	1.5
N+	2.0
O•	1.0
O:	2.0
O+	2.5
F:	3.0
Cl:	2.0
Br:	1.5

Heteroatom Bond	k
C-N•	1.0
C-N:	0.8
C=O•	1.0
C-O:	0.8
C-F:	0.7
C-Cl:	0.4
C-Br:	0.3
C-C	0.9
C=C	1.1

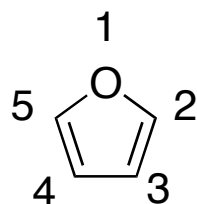
*Need to pay attention to how many electrons are located on heteroatom (N• vs. N:)

*Consistent with this analysis C-C single bonds are different than C=C double
(only bonds in resonance have k = 1)

Molecular Orbital Theory

Using these corrections values a variety of conjugated compounds that contain heteroatoms can have their Hückel molecular orbital energies and coefficients determined

Consider furan:



$$\begin{vmatrix} x + 2.0 & 0.8 & 0 & 0 & 0.8 \\ 0.8 & x & 1.1 & 0 & 0 \\ 0 & 1.1 & x & 0.9 & 0 \\ 0 & 0 & 0.9 & x & 1.1 \\ 0.8 & 0 & 0 & 1.1 & x \end{vmatrix} = 0$$

By solving this determinant thus the Hückel values for furan can be determined

While solving determinants might be difficult by hand,
there are many computer programs that can handle this task trivially

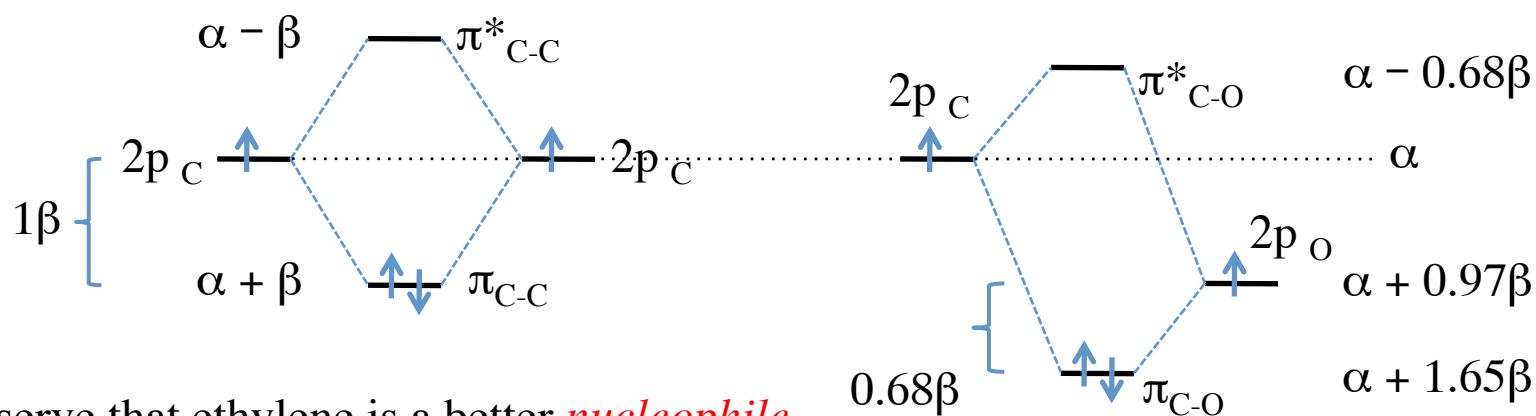
A convenient online tool can be found on the webpage of Arvi Rauk, University of Calgary
<http://www.ucalgary.ca/rauk/shmo>

*Remember to use the correct values for the heteroatoms chosen (the empirical corrections are different depending on system [Rauk uses 2.09 for O: for example])

Molecular Orbital Theory

Can compare how the quantitative values obtained with a very simple Hückel molecular orbital calculation relate to the qualitative predictions made earlier

Consider the reactivity of ethylene versus formaldehyde, we stated how the more electronegative oxygen atom would have a lower energy atomic orbital resulting in less mixing with the carbon 2p orbital



Also observe that ethylene is a better *nucleophile* and formaldehyde is a better *electrophile*

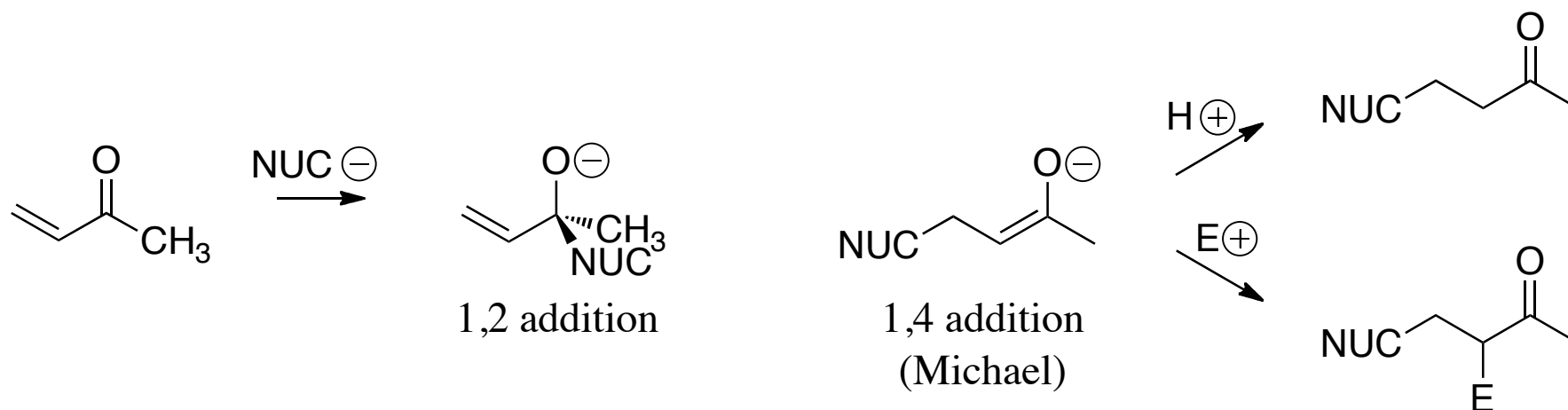
With Hückel we can determine the energy levels of these atomic and molecular orbitals ($2p_C$ by definition is at α level, $2p_O$ is at $\alpha + 0.97\beta$)

The MO energy levels can be determined

Find that atomic orbitals closer in energy have more mixing like predicted

Molecular Orbital Theory

What does Hückel molecular orbital theory predict about reactions with Michael acceptors?



When reacting with a nucleophile, the nucleophile can react in two different ways:

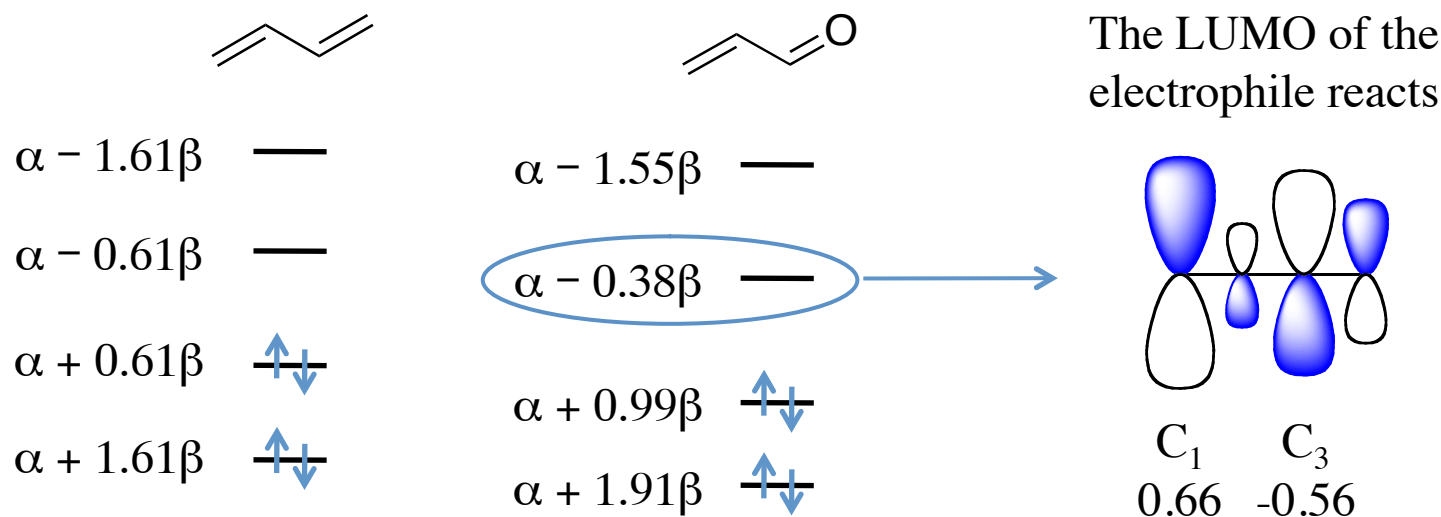
- 1) React directly on the carbonyl carbon (called a 1,2 addition)
- 2) React instead at the β -position (called a 1,4 addition)

In a 1,4 addition, initially an enolate is formed which can be neutralized in work-up to reobtain the carbonyl

Or the enolate can be reacted with a different electrophile in a second step to create a product that has substitution at both the α and β positions

Molecular Orbital Theory

Hückel MO can calculate the orbitals for a Michael acceptor



Coefficient in LUMO is largest on C_1 and C_3

The energy levels for an all carbon analog have already been determined for butadiene

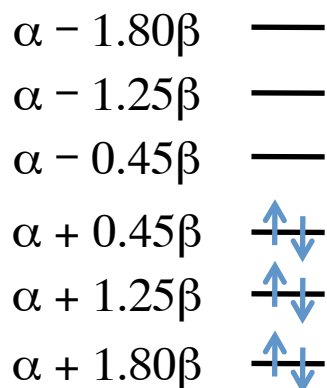
The Michael acceptor should be a better electrophile than butadiene, but where does reaction occur?

The energy levels for an α,β unsaturated Michael acceptor can be determined by using the appropriate correction factors for oxygen

As expected, the electronegative oxygen atom lowers the energy level of each MO relative to butadiene (although each MO is lowered by different amounts)

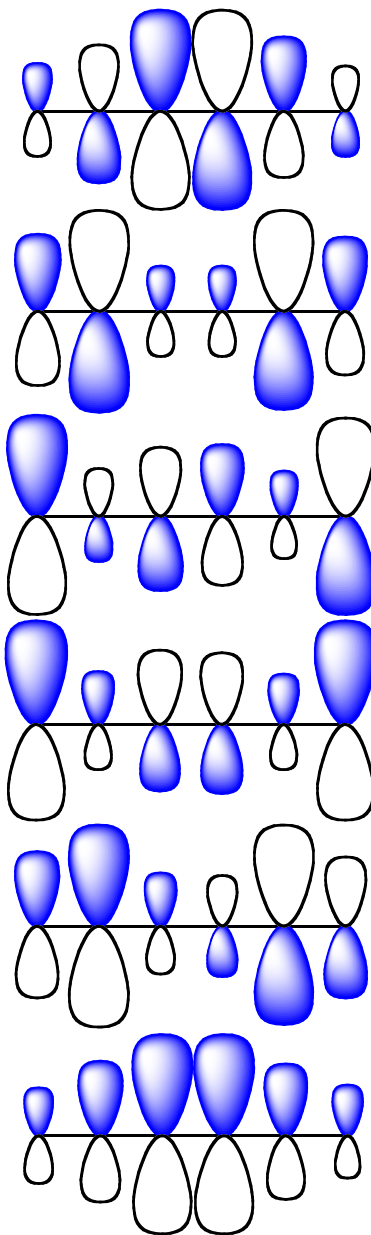
In addition to the energy level for the various MOs in a system, the *symmetry* and *size* of the coefficient on each atom is important

Consider the conjugated hexatriene (the energy levels were determined using the Frost mnemonic)



The lowest energy MO has 0 nodes

The size of the coefficient on each atom, however, is not identical

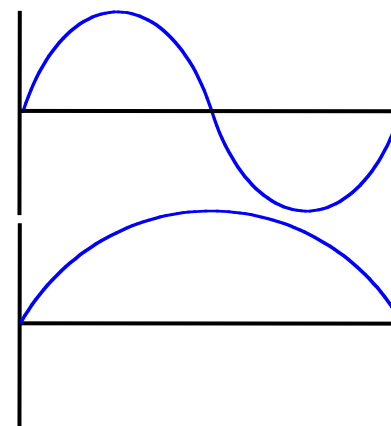


Wave equation can be modeled as the first harmonic of a particle in a box

The wave has higher amplitude toward the middle of the box and lowest at the sides of the box

The second orbital has 1 node located at middle of the box

Each successive orbital has 1 more node symmetrically placed



Molecular Orbital Theory

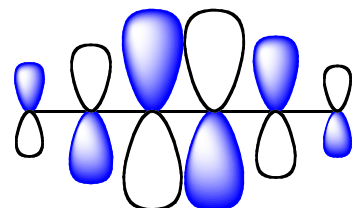
The symmetry of the orbitals also changes in addition to the size of the coefficients

Consider the relationship of the carbons on the periphery of hexatriene (C_1 and C_6)

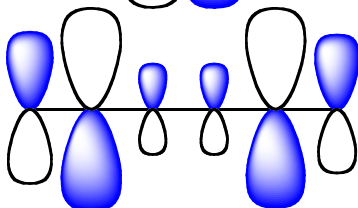
If the sign of the coefficients is the same, then the MO is considered symmetric (S) while if the signs are different the MO is considered antisymmetric (A)

The symmetry of the orbitals alternates going from lowest energy to highest energy

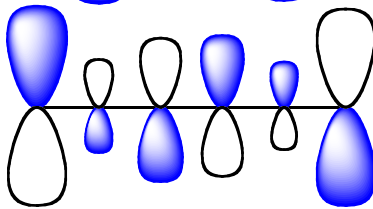
The lowest energy orbital must be S because there are 0 nodes



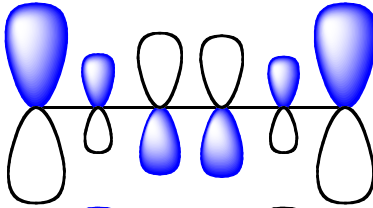
A



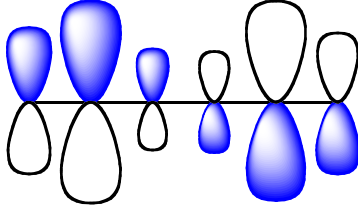
S



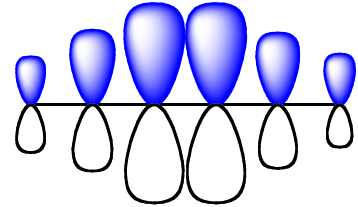
A



S



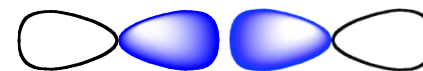
A



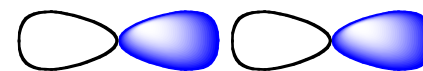
S

The symmetry of the orbitals affects whether reactions occur when forming new bonds

Only orbitals of the same symmetry can react (bonds do not form at nodal points, which would be the result when different symmetries interact)



σ bond

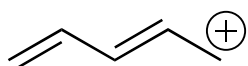


σ^* bond

Molecular Orbital Theory

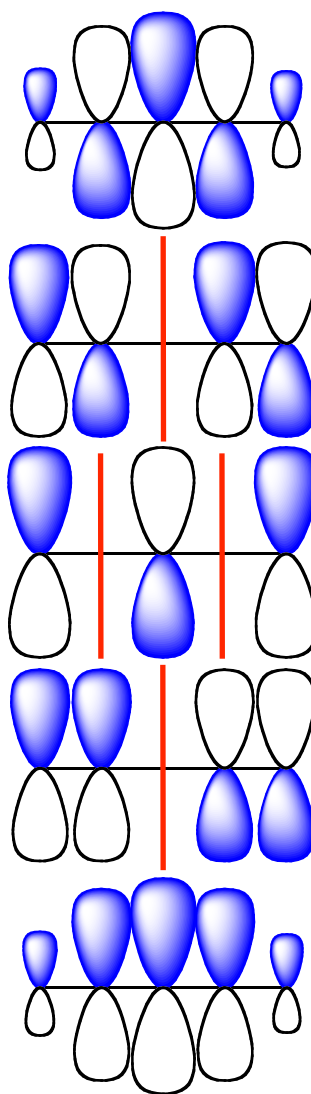
The symmetry is different with linear chains with odd number of carbons

Consider a pentadienyl cation



With 5-atoms, the lowest energy MO still has 0 nodes and thus must be symmetric (although again the size of the coefficients is different)

With each successive orbital, the symmetry will change



S Due to the odd number of atoms, however, the nodes can occur at the atom site

A In the second lowest MO for example, the central atom (C_3) must have the first harmonic place a node in the center of the box, thus being placed at the central atom

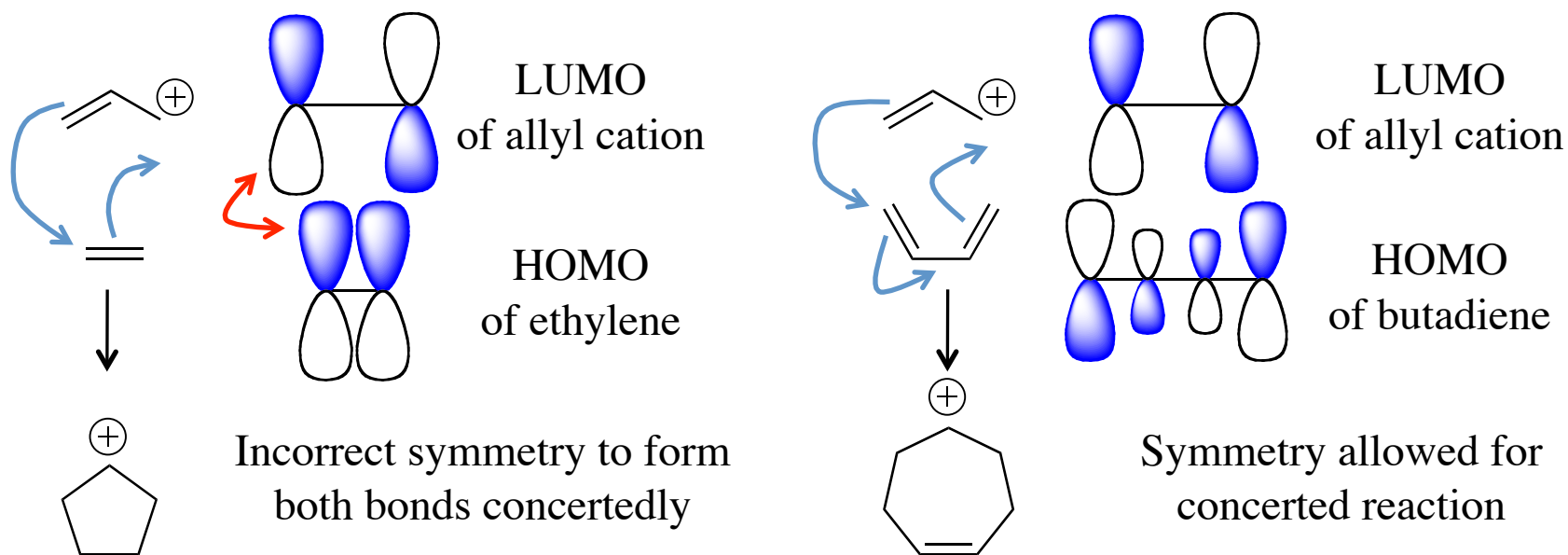
A Nodes also occur at atom sites in other MOs

S

Molecular Orbital Theory

Symmetry considerations of linear conjugated systems
aid in the consideration of concerted reactions

Consider the concerted reaction of allyl cation with either ethylene or butadiene



Using Valence Bond Theory, the reaction should occur with either ethylene or butadiene

Using Molecular Orbital Theory, however, first need to consider the *symmetry* of the interacting orbitals

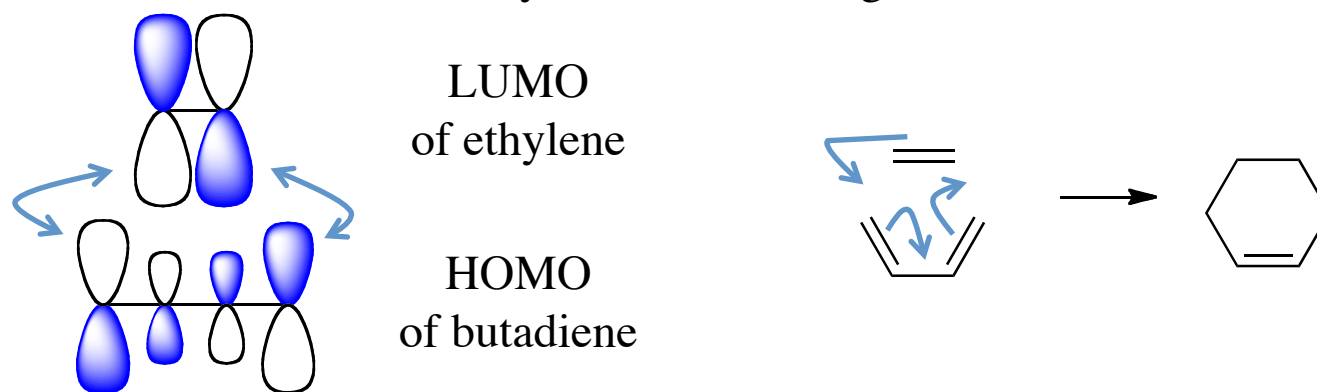
Experimentally it is observed that butadiene does react with allyl cation, but ethylene does not
(Valence Bond Theory cannot make this prediction)

Molecular Orbital Theory

In a concerted reaction therefore each bond that is formed must be symmetry allowed for reaction to occur

Consider another common concerted reaction called a Diels-Alder reaction, a substituted butadiene reacts with a substituted ethylene

Typically the butadiene component reacts through the HOMO and the ethylene reacts through the LUMO



Reaction is symmetry allowed

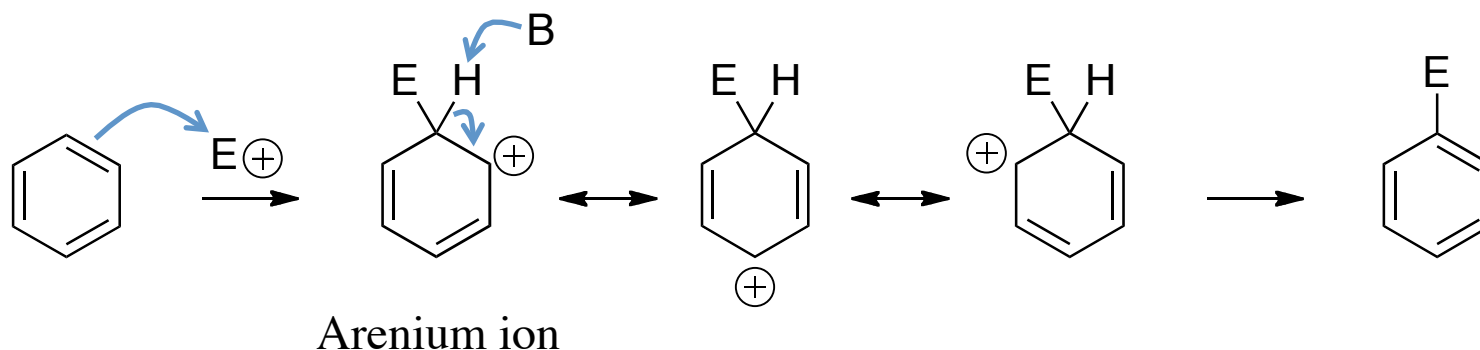
To increase the rate of a Diels-Alder reaction, the energy difference between the HOMO of butadiene and the LUMO of ethylene needs to be lowered

Electron donating substituents *raise* the energy of a MO
and electron withdrawing substituents *lower* the energy of a MO,
therefore want donating substituents on butadiene and withdrawing substituents on ethylene

Molecular Orbital Theory

Consider regiochemistry for reactions of conjugated compounds

Conjugated aromatic compounds react through an electrophilic aromatic substitution



The aromatic ring reacts as the nucleophile (therefore reacts through its HOMO)
and the electrophile reacts through its LUMO

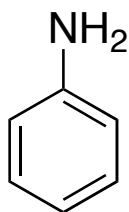
If we can determine the energy levels of the aromatic compound
(and the coefficients which indicate where the electron density is located)
the regiochemistry with substituted aromatic compounds can be predicted

There are two approaches for any compound:

- 1) Consider all molecular orbitals (generally gives better results)
- 2) Consider only the frontier molecular orbitals (easier to calculate but less certainty)

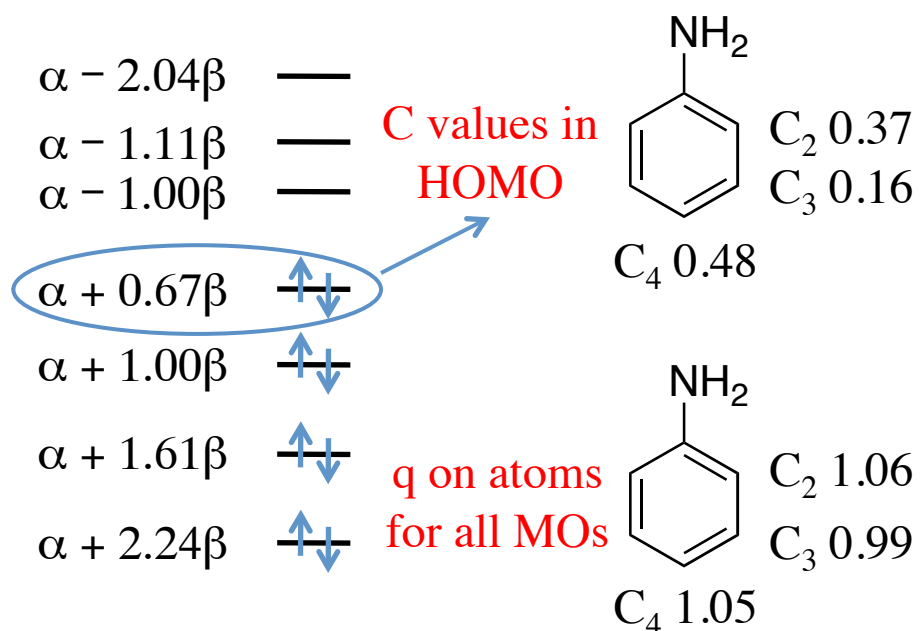
Molecular Orbital Theory

Consider substituted benzene derivatives

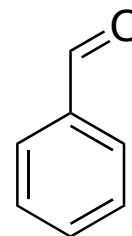


Aniline

(7 p orbitals, 8 electrons in conjugation)

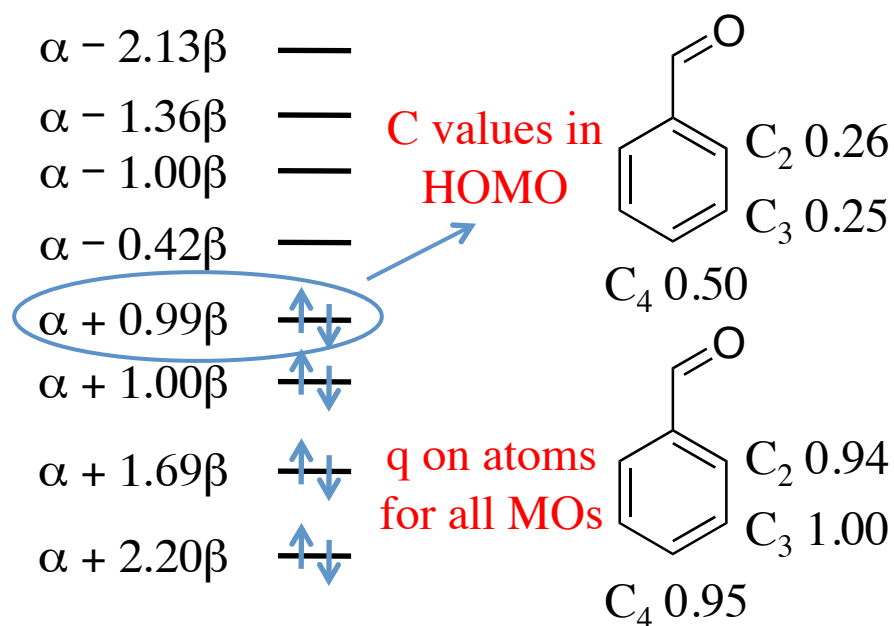


Both the FMO and charge on atoms with all MOs favor ortho/para substitution



Benzaldehyde

(8 p orbitals, 8 electrons in conjugation)



All MOs correctly predicts substitution at meta position, but FMO does not ¹³²

Oxidation-Reduction

Many conjugated compounds can be oxidized or reduced in solution using standard electrochemical techniques

Oxidation: removing an electron

Electron must be removed from the highest occupied molecular orbital

Molecules with HOMOs closer to α (nonbonding level) have smaller oxidation potentials

Reduction: adding an electron

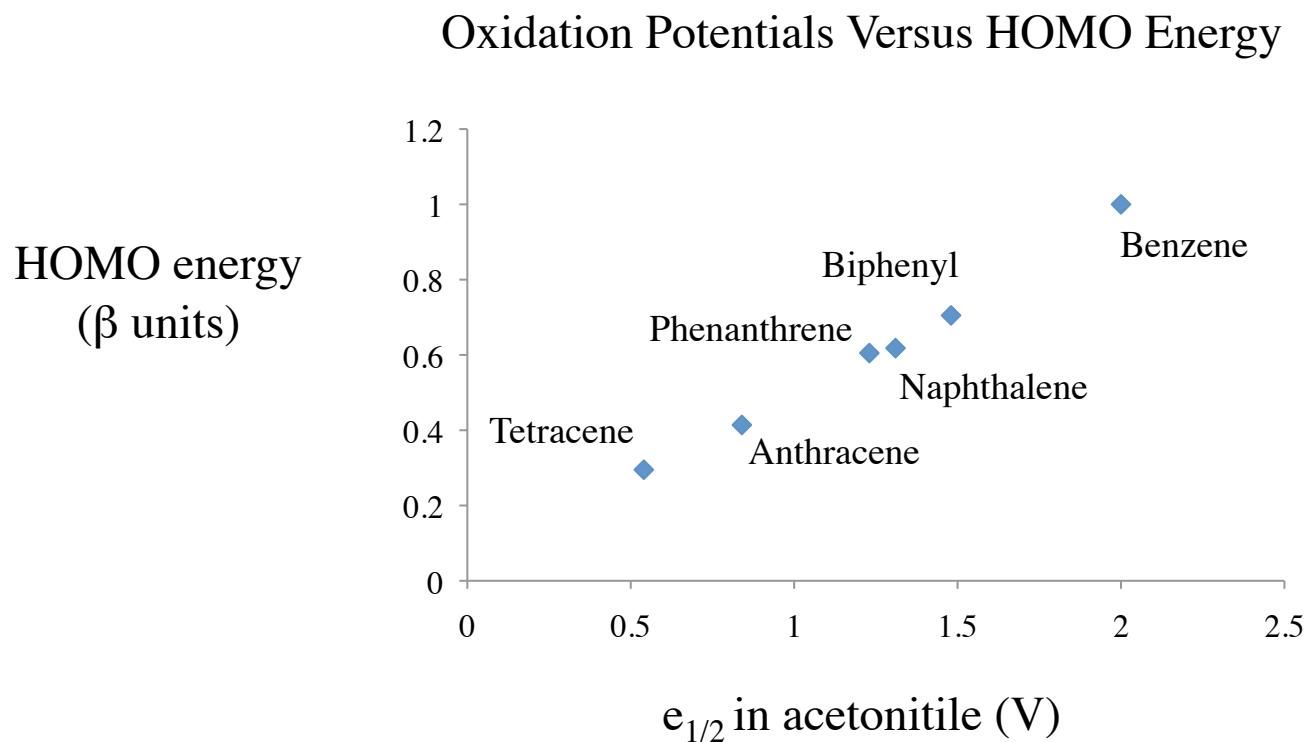
Electron must go into orbital that is not filled and is lowest in energy

Molecules with LUMOs closer to α have lower reduction potentials

While Hückel molecular orbital theory (or any other MO theory) does well to predict oxidation or reduction potentials, theory cannot account for other effects such as solvation effects on potential or π electron repulsion caused by adding or removing an electron

Oxidation-Reduction

Considering the limitations in solvation effects and electron-electron repulsion, the correlation of potentials with Hückel values is strong



A similar correlation exists for reduction potential versus LUMO energy values

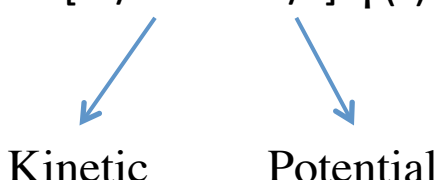
Molecular Orbital Theory

In general, Molecular Orbital Theory treats electrons as belonging to the entire molecule and located in regions of space where the electrons reside on time average (in contrast to Valence Bond Theory which treats electrons as held between specific atom pairs)

In theory, all properties of a molecule could be determined exactly if an exact solution of a molecular orbital theory was obtainable (therefore would not need to synthesize compounds, merely have the computer “*synthesize*” them)

Problem is that the Schrödinger equation is not solvable except for one electron systems

In a one electron system:

$$[-1/2 \nabla^2 - Z/r] \psi(r) = E \psi(r)$$


Kinetic Potential

Z = nuclear charge,
 r = distance

This equation is solvable
(it is how the shapes of s and p orbitals are obtained – from one electron solutions)

Molecular Orbital Theory

When there is more than 1 electron (as in almost all compounds except hydrogen atom)
there are additional terms in the Schrödinger equation

This leads to the more recognizable form of the Schrödinger equation:

$$\hat{H}\psi = E\psi$$

Where the Hamiltonian can be expressed as:

$$\hat{H} = \overset{\text{electrons}}{-\frac{1}{2} \sum \nabla_i^2} \quad \overset{\text{nuclei}}{-\frac{1}{2} \sum \frac{1}{M_A} \nabla_A^2} \quad \overset{\text{electron/nuclei}}{-\sum \sum \frac{Z_A}{r_{iA}}} \quad \overset{\text{electrons}}{+\sum \sum \frac{1}{r_{ij}}} \quad \overset{\text{nuclei}}{+\sum \sum \frac{(Z_A Z_B)}{R_{AB}}}$$

This equation is not solvable, too many variables,
therefore exact solutions have not been obtained

A first approximation is the so-called Born-Oppenheimer approximation
(nuclei do not move)

This approximation simplifies the Hamiltonian by removing the nuclei only terms

$$\hat{H}_{\text{el}} = \overset{\text{electrons}}{-\frac{1}{2} \sum \nabla_i^2} \quad \overset{\text{electron/nuclei}}{-\sum \sum \frac{Z_A}{r_{iA}}} \quad \overset{\text{electrons}}{+\sum \sum \frac{1}{r_{ij}}} \quad \text{(called the electron Hamiltonian)}$$

Molecular Orbital Theory

The Born-Oppenheimer approximation still leads to an unsolvable Hamiltonian

*Biggest problem is the electron-electron interactions

All molecular orbital theories try to overcome this limitation
by using different approximations

Hartree-Fock approximation

-Electrons move independently of each other
(obviously false, as electrons are charged species and thus the energy of one electron
is dependent on the location of the other electrons)

To correct for this electron-electron interaction, different MO theories
have an electron move *within an average field* of all other electrons (Z_{eff})
(Self-Consistent-Field SCF)

Molecular Orbital Theory

Linear Combination of Atomic Orbitals (LCAO)

$$\psi = \sum C_{\mu i} \Phi_{\mu}$$

Molecular orbitals can be described as a combination of simple atomic orbitals



(1 electron case is solvable)

Correlated Models

*Biggest problem has to do with how electrons interact with each other

-Hartree-Fock treats them as independent
(to correct use a Z_{eff} term)

Different models treat this correlation in different ways

Molecular Orbital Theory

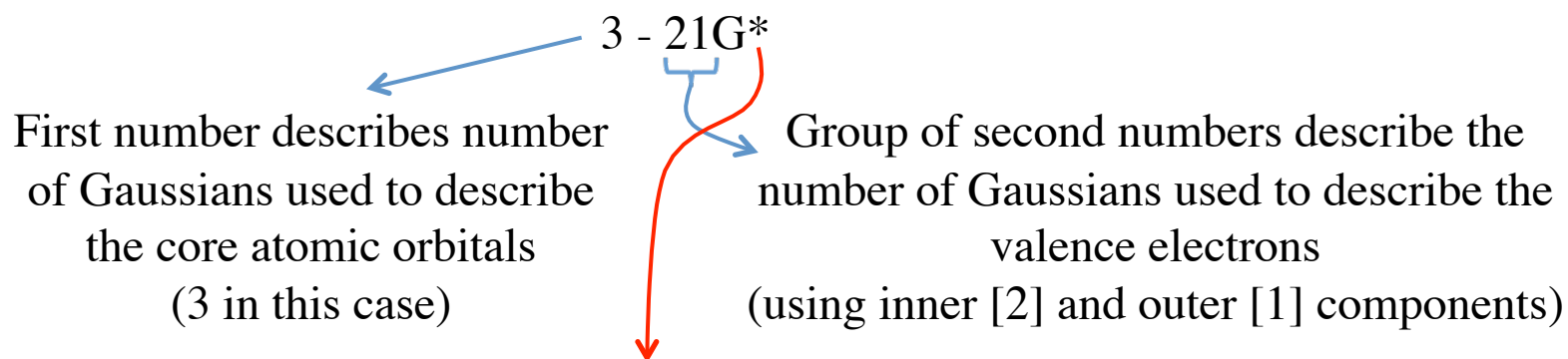
Density Functional Models (DFT theory)

The electron correlation can be estimated by only knowing the electron density
(not exact individual electron positions)

Basis Sets

Regardless of what approach one uses to minimize the error caused by electron-electron repulsion and their effect on solving the Schrödinger equation, the type of basis set used indicates what is being used to describe the molecular orbitals

Typically use Gaussian type functions to describe the orbitals



*indicates inclusion of “d” type function
(allow electron placement away from nuclei – important for 3rd row atoms)