Molecular Orbital Theory

While FMO theory allows prediction of reactions (by thermodynamics, regio or stereochemistry), all predictions seen so far have been *qualitative*

We have predicted that HOMO or LUMO levels raise or lower due to degree of mixing of orbitals and the charge, or electronegativity, of orbitals that are being mixed

Ideally we would like a *quantitative* method to predict reactions

In theory this is possible if we can solve the Schrödinger equation
$$\hat{H}\Psi = E\Psi$$

Ψ = electronic wave function
(Ψ^2 describes where electrons are located)

$\hat{H}$ = Hamiltonian operator

E = energy value

The Schödinger equation thus means the energy levels for a molecule are quantized

Molecular Orbital Theory

To solve the Schrödinger equation, first use the Born-Oppenheimer approximation which states that we can fix the location of the nuclei and consider only motion of the electrons

(if everything is moving like in reality, then there are far too many unknowns for the number of equations, impossible to solve)

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

Multiple each side by Ψ and then integrate over all space

$$\int \Psi \hat{H} \Psi \, d\tau = \int \Psi E \Psi \, d\tau$$

Since E is only a number, it can be brought out of the integral and solve for E

$$E = \frac{\int \Psi \hat{H} \Psi \, d\tau}{\int \Psi \Psi \, d\tau}$$

If consider a diatomic molecule with LCAO, $\Psi_{MOL} = c_1\phi_1 + c_2\phi_2$

$$E = \frac{\int (c_1\phi_1 + c_2\phi_2)\hat{H}(c_1\phi_1 + c_2\phi_2) \, d\tau}{\int (c_1\phi_1 + c_2\phi_2)^2 \, d\tau}$$

Molecular Orbital Theory

If we rewrite equation after multiplying with the operator term:

$$E = \frac{\int (c_1\phi_1\hat{H}c_1\phi_1 + c_1\phi_1\hat{H}c_2\phi_2 + c_2\phi_2\hat{H}c_1\phi_1 + c_2\phi_2\hat{H}c_2\phi_2)\, d\tau}{\int (c_1^2\phi_1^2 + 2c_1\phi_1c_2\phi_2 + c_2^2\phi_2^2)\, d\tau}$$

Some common terms:

1) $\int \phi_a\phi_b\, d\tau = S_{ab}$

Overlap Integral
(related to overlap of atomic orbitals)

2) $\int \phi_a\hat{H}\phi_a\, d\tau = H_{aa}$

Coulomb Integral
(related to binding energy of electron in an orbital)

3) $\int \phi_a\hat{H}\phi_b\, d\tau = H_{ab}$

Resonance Integral
(related to energy of an electron in the field of 2 or more nuclei)

Molecular Orbital Theory

Substitute these common terms into energy solutions

$$E = \frac{c_1{}^2 H_{11} + 2c_1 c_2 H_{12} + c_2{}^2 H_{22}}{c_1{}^2 S_{11} + 2c_1 c_2 S_{12} + c_2{}^2 S_{22}}$$

This equation will thus hold valid for each valid solution,
the different solutions for E correspond to the different MO energy levels

To obtain the solutions, need to undertake a partial derivative
with respect to each coefficient to minimize the energy with respect to the coefficient

$$\delta E / \delta C_1 = 0 \qquad\qquad \delta E / \delta C_2 = 0$$

For the partial derivative with respect to C1:

$$E(2C_1 S_{11} + 2C_2 S_{12}) = 2C_1 H_{11} + 2C_2 H_{12}$$

$$C_1(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) = 0$$

For the partial derivative with respect to C2:

$$C_1(H_{12} - ES_{12}) + C_2(H_{22} - ES_{22}) = 0$$

Molecular Orbital Theory

The solutions of the partial derivatives were written by grouping the terms for each coefficient to write the equation in a *secular equation* form

$$C_1(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) = 0$$

$$C_1(H_{12} - ES_{12}) + C_2(H_{22} - ES_{22}) = 0$$

Secular Equations

This allows the equations to be written in a *secular determinant*

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

Secular Determinant

Diagonal elements: Coulomb integrals
(terms dealing with each nuclei)

Off-Diagonal elements: Resonance integrals
(terms dealing with different nuclei)

Remember that this secular determinant was formed considering the mixing of two atomic orbitals, therefore obtain a 2 x 2 determinant

Molecular Orbital Theory

Have already used some assumptions to get to the secular determinant:

1) Assumed a form for the atomic orbitals (ϕ)

2) Assumed a linear combination of atomic orbitals (LCAO)

3) Assumed a form for the Hamiltonian ($\hat{H}$) (variation principle)

Cannot solve the secular determinant with these assumptions alone!

Biggest problem is dealing with how an electron is affected
by being in the presence of other electrons (electron-electron repulsion)

The qualitative orbital pictures we have already used
(atomic s or p orbitals) assume 1 electron systems,
the shape of orbitals cannot be solved once electrons are correlated

Molecular Orbital Theory

In order to solve the secular determinant, more assumptions need to be applied

Different molecular orbital theories are simply using different types
of assumptions to solve the secular determinant

A very simple type of assumptions is to use Hückel MO theory

1) Factor out the σ framework
*applies only to conjugated π system
(therefore will look at systems by combining p orbitals on adjacent carbons)

2) $H_{aa} = \alpha$
(assume H_{aa} does not vary with substituents on carbon)

3) $H_{ab} = \beta$　　　　　　α and β are
(when a and b are adjacent atoms)　　negative numbers

4) $H_{ab} = 0$
(for nonadjacent atoms)

5) $S_{aa} = 1$

6) $S_{ab} = 0$
(overlap integral can be neglected for adjacent atoms, worst assumption)

Hückel Molecular Orbital Theory

Apply the Hückel assumptions to the secular determinant

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

Divide all terms by β and let $(\alpha - E)/\beta = x$

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

$$x^2 - 1 = 0$$

$$x^2 = 1$$

$$x = \pm 1$$

When $x = +1$

$(\alpha - E)/\beta = +1$

$E = \alpha - \beta$

With a 2 x 2 determinant, will have two energy solutions

When $x = -1$

$(\alpha - E)/\beta = -1$

$E = \alpha + \beta$

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Hückel Molecular Orbital Theory

Remember that this was a Hückel calculation for two p orbitals in conjugation
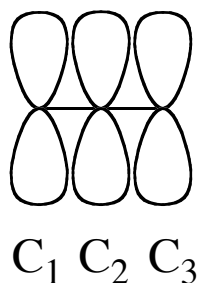(therefore these energy solutions are for ethylene)

$E = \alpha - \beta$

α

α

$E = \alpha + \beta$
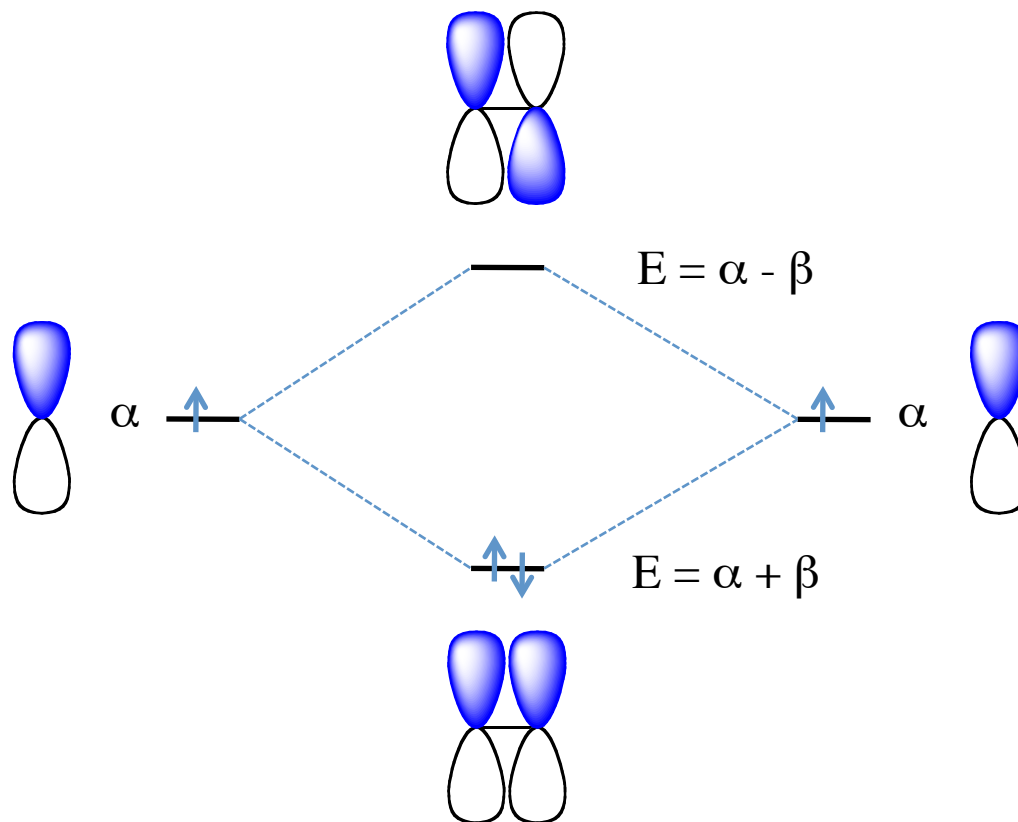
$E_\pi = 2\alpha + 2\beta$

Hückel Molecular Orbital Theory

Determining Hückel MO energy levels is rather straightforward if the structure is known

Consider an allyl system with three contiguous p orbitals

$C_1 \; C_2 \; C_3$

	C_1	C_2	C_3			
Atom 1	$\alpha - E$	β	0	x	1	0
Atom 2	β	$\alpha - E$	β = 0 =	1	x	1
Atom 3	0	β	$\alpha - E$	0	1	x

This entry will represent the energy terms for the C_1 coefficient on atom 1

The determinant can thus be simplified further by
dividing each term by β and setting $x = (\alpha-E)/\beta$

Hückel Molecular Orbital Theory

Linear algebra techniques can be used to reduce a 3 x 3 determinant in order to solve

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - 1\begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} + 0\begin{vmatrix} 1 & x \\ 0 & 1 \end{vmatrix} = 0$$

The 2 x 2 determinants can then be multiplied out to obtain the solutions for x

$$x(x^2-1) \quad - 1(x-0) \quad + 0 \quad = 0$$

$$x^3 - 2x = 0$$

$$x = 0, \sqrt{2}, -\sqrt{2}$$

*always obtain the same number of solutions as orbitals that were combined
(a 3 x 3 determinant thus has 3 solutions for x)

Hückel Molecular Orbital Theory

Things that can be determined from the Hückel molecular orbitals:

1) Energy level of molecular orbitals

By solving the secular determinant,
the solutions are the energy levels for the molecular orbitals

$$x = (\alpha - E)/\beta$$

When x = 0 $\quad\quad\quad\quad$ E = α $\quad\quad\quad\quad$ Because α is the energy
of an isolated p orbital,
this corresponds to the *nonbonded* level

When x = +$\sqrt{2}$ $\quad\quad\quad\quad$ E = α - $\sqrt{2}\beta$ $\quad\quad\quad\quad$ Because β is
a negative number,
this corresponds to an *antibonding* level

When x = -$\sqrt{2}$ $\quad\quad\quad\quad$ E = α + $\sqrt{2}\beta$

This will be the lowest energy MO,
and corresponds to a *bonding* MO

Hückel Molecular Orbital Theory

Things that can be determined from the Hückel molecular orbitals:

2) Can use energy levels to determine stabilization energy

*Need to compare E_π for allyl versus a reference compound

To quantitate stabilization caused by conjugation of the three contiguous p orbitals, the allyl can be compared to ethylene and an isolated p orbital that is not conjugated

E_π(allyl cation) $= 2\alpha + 2\sqrt{2}\beta$ $\qquad\qquad$ E_π(ethylene + p) $= 2\alpha + 2\beta$

Difference $= (2\alpha + 2\sqrt{2}\beta) - (2\alpha + 2\beta) = 0.828\beta$

E_π(allyl radical) $= 3\alpha + 2\sqrt{2}\beta$ $\qquad\qquad$ E_π(ethylene + p) $= 3\alpha + 2\beta$

Difference $= (3\alpha + 2\sqrt{2}\beta) - (3\alpha + 2\beta) = 0.828\beta$

Since the extra electron is at the nonbonding level between the cation, radical and anion, they are all calculated to have the same stabilization energy

Experimentally it is known that the cation is more stable due to less electron-electron repulsion

Hückel Molecular Orbital Theory

Things that can be determined from the Hückel molecular orbitals:

3) Determine orbital coefficients

With each energy solution for the secular determinant, the coefficients can be determined (the coefficients are unique for each MO, different MOs can have different coefficient values)

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

$$C_1 x + C_2 = 0$$

$$C_1 + C_2 x + C_3 = 0$$

$$C_2 + C_3 x = 0$$

Appears to be three equations and three unknowns ($C_1 + C_2 + C_3$), but always have another equation for each MO where the $\Sigma C^2 = 1$

When x = 0

$$C_2 = 0$$

$$C_1 + C_3 = 0$$

Since $\Sigma C^2 = 1$, therefore $C_1 = 1/\sqrt{2}$ and $C_3 = -1/\sqrt{2}$

Hückel Molecular Orbital Theory

When x = $-\sqrt{2}$

$$-\sqrt{2}C_1 + C_2 = 0$$

$$C_1 - \sqrt{2}C_2 + C_3 = 0$$

$$C_2 - \sqrt{2}C_3 = 0$$

$$C_1{}^2 + C_2{}^2 + C_3{}^2 = 1$$

$$C_1 = \tfrac{1}{2}, C_2 = 1/\sqrt{2}, C_3 = \tfrac{1}{2}$$
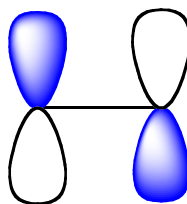
When x = $+\sqrt{2}$

$$C_1 = \tfrac{1}{2}, C_2 = -1/\sqrt{2}, C_3 = \tfrac{1}{2}$$
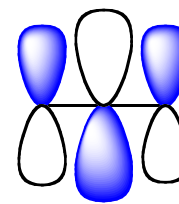
$E = \alpha + \sqrt{2}\beta$ $E = \alpha$ $E = \alpha - \sqrt{2}\beta$
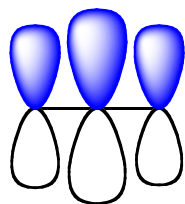
Zero nodes,   1 node at C_2,   2 nodes,
C_2 coefficient largest $C_2 = C_3$ coefficient C_2 coefficient largest

Hückel Molecular Orbital Theory

Things that can be determined from the Hückel molecular orbitals:

4) Determine charge on a given carbon

Remember that the square of the coefficient value is related
to the probability of finding electron density

q_i = (electrons in orbital 1)$(C_{i1})^2$ + (electrons in orbital 2)$(C_{i2})^2$ + (for each filled orbital)

Consider the allyl anion
(has four electrons total in conjugated system)

$$q_1 = (2)(1/2)^2 + (2)(1/\sqrt{2})^2$$

$$q_1 = 1.5 \; \pi \text{ electrons}$$

$$q_2 = 1 \; \pi \text{ electron}$$

$$q_3 = 1.5 \; \pi \text{ electrons}$$

The allyl anion thus has more charge on atoms C_1 and C_3 (equal amount of charge) than on C_2

Hückel Molecular Orbital Theory

Things that can be determined from the Hückel molecular orbitals:

5) Determine π bond order

The coefficients can also describe how much bond order is between various atoms

$$P_{ij} = \Sigma N_r C_{ri} C_{rj}$$

π bond order between atoms i and j
N = # of electrons in orbital
r = each successive orbital

Allyl system:

Ψ_1: C_1 ½, C_2 $1/\sqrt{2}$, C_3 ½
Ψ_2: C_1 $1/\sqrt{2}$, C_2 0, C_3 $-1/\sqrt{2}$
Ψ_3: C_1 ½, C_2, $-1/\sqrt{2}$, C_3 ½

Consider allyl radical:

$P_{1\text{-}2} = 2(1/2)(1/\sqrt{2}) + 1(1/\sqrt{2})(0) = 1/\sqrt{2}$

$P_{2\text{-}3} = 2(1/\sqrt{2})(1/2) + 1(0)(-1/\sqrt{2}) = 1/\sqrt{2}$

π bond order identical for $P_{1\text{-}2}$ and $P_{2\text{-}3}$

Hückel Molecular Orbital Theory

Any conjugated system can thus have the molecular orbital energy levels determined using Hückel MO theory

In addition to the energy level solutions, once the secular determinant is solved the electron location ($\sim C^2$) can be determined in each orbital and thus the overall charge and bond order can also be determined

As the molecule becomes more complicated, however, solutions of the secular determinant are more difficult

Consider styrene:
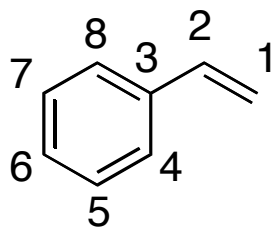
Label each carbon to make writing the determinant easier

The determinant will thus be 8 x 8

A carbon with itself will be x, a carbon bonded to an adjacent carbon is 1, and everything else is 0

$$
\begin{vmatrix}
x & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & x & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & x & 1 & 0 & 0 & 0 & 1 \\
0 & 0 & 1 & x & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & x & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & x & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & x & 1 \\
0 & 0 & 1 & 0 & 0 & 0 & 1 & x
\end{vmatrix} = 0
$$

Now just solve the determinant! 113

Hückel Molecular Orbital Theory

Fortunately there have been a couple of simplifications developed to solve certain types of conjugated systems more easily

With linear conjugated systems can use a Frost mnemonic

Consider butadiene which is only 1 atom longer than the allyl system solved earlier, this compound would require solving a 4 x 4 determinant
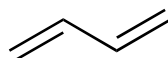
With the Frost mnemonic, consider a half circle with a radius of 2β, the center point at α, and the long axis pointing towards the bottom

*Place N+1 equidistant wedges in half circle
(N is # of carbon atoms in linear conjugated system)

*Wherever the lines of each wedge hit the half circle, this corresponds to the energy level of that molecular orbital
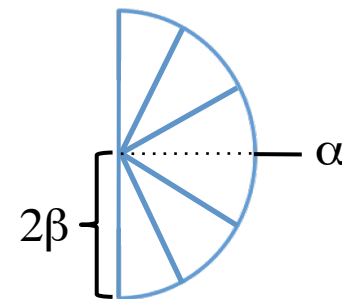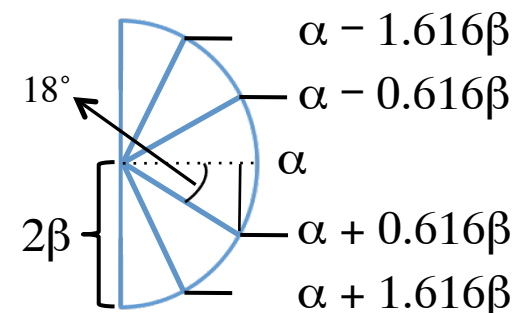
Butadiene would thus have 5 wedges

Hückel Molecular Orbital Theory

*Place N+1 equidistant wedges in half circle
(N is # of carbon atoms in linear conjugated system)

*Wherever the lines of each wedge hit the half circle, this
corresponds to the energy level of that molecular orbital

$\alpha - 1.616\beta$

$\alpha - 0.616\beta$

α

$\alpha + 0.616\beta$

$\alpha + 1.616\beta$

$18°$

2β

Butadiene would thus have 5 wedges

The energy levels of the molecular orbitals can be determined with simple trigonometry

Since all 5 wedges are equidistant, each wedge must form an angle of 36° (180°/5 = 36°)

The first wedge is thus 18° below the middle line, and the second is 54° below (18° + 36°)

$$\sin 18° = z/2\beta$$
$$z = \pm 0.616\beta$$

$$\sin 54° = z/2\beta$$
$$z = \pm 1.616\beta$$

The antibonding orbitals are symmetrically placed above α,
thus all four energy levels are determined

Hückel Molecular Orbital Theory

Another simplification is for flat, fully conjugated carbon ring systems
(called Frost circle)

Consider a full circle with radius of 2β and the center at the α level

Use a polygon with equal bond lengths corresponding to the number of atoms in the ring

Place polygon in ring with one point directly at the bottom

Wherever the points of the polygon hit the ring corresponds to an energy level
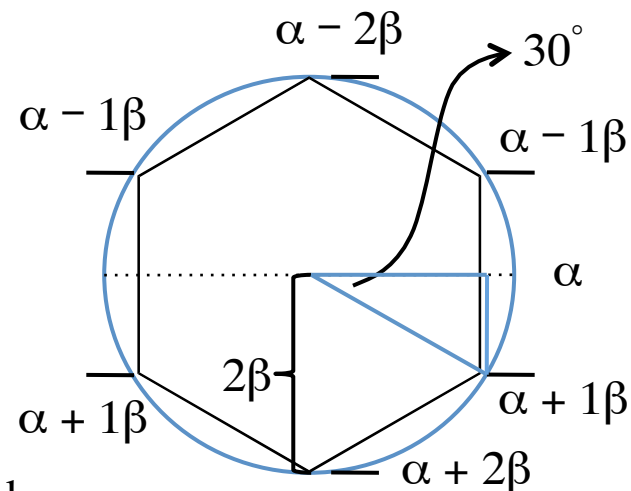
Consider benzene

The lowest energy molecular orbital is thus $\alpha + 2\beta$

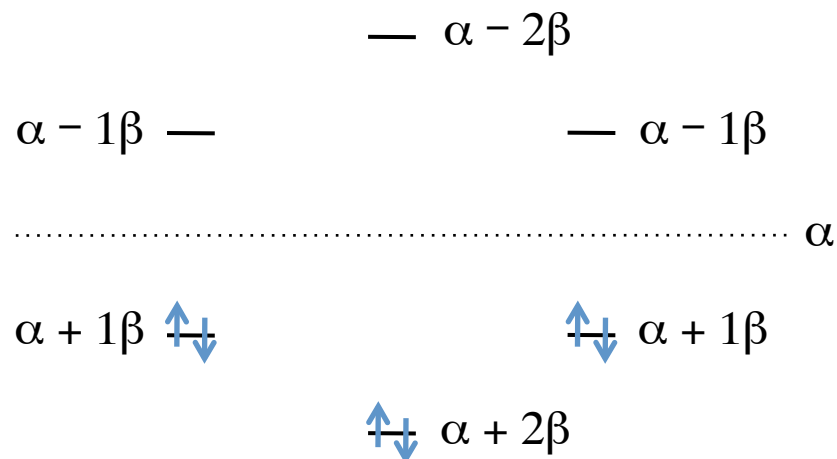Use trigonometry to find the energy level of other orbitals

$$\sin 30° = z/2\beta$$

$$z = 1\beta$$

All the molecular orbitals of benzene can thus be determined

$\alpha - 2\beta$
$30°$
$\alpha - 1\beta$
$\alpha - 1\beta$
α
2β
$\alpha + 1\beta$
$\alpha + 1\beta$
$\alpha + 2\beta$

Hückel Molecular Orbital Theory

By determining the molecule orbital energy levels for benzene, the E_π can be determined

—— $\alpha - 2\beta$

$\alpha - 1\beta$ ——   —— $\alpha - 1\beta$

·· α

$\alpha + 1\beta$ ⇅   ⇅ $\alpha + 1\beta$

⇅ $\alpha + 2\beta$

There are 6 π electrons in benzene

*all electrons are in a bonding MO

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

What is the delocalization energy for benzene? How much is aromatic stabilization?

As with all relative questions, need to ask "compared to what compound?"

Could compare to three isolated double bonds that do not resonate
(therefore 3 ethylene units)

Each ethylene $= 2\alpha + 2\beta$, therefore 3 ethylene units corresponds to $6\alpha + 6\beta$
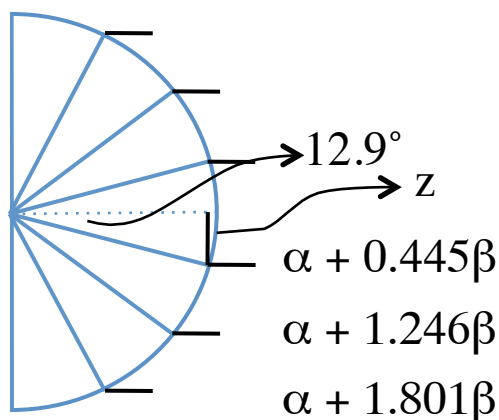
In this comparison, benzene is more stable by 2β units

Hückel Molecular Orbital Theory

What is the delocalization energy resulting from a ring in benzene?

Would need to compare to compound with same number of p orbitals,
but a linear compound and not a ring (therefore hexatriene)

Can use the Frost mnemonic to determine the energy levels for hexatriene

$12.9°$

z

$\alpha + 0.445\beta$

$\alpha + 1.246\beta$

$\alpha + 1.801\beta$

Need 7 equidistant wedges for hexatriene

$$180°/7 = 25.7°$$

$$\sin 12.9° = z/2\beta, z = 0.445\beta$$

Energy level of remaining orbitals
can be determined in similar manner
(and the antibonding will be symmetric
with bonding orbitals, therefore merely α - #β)

$$E_\pi(\text{hexatriene}) = 2(\alpha + 1.801\beta) + 2(\alpha + 1.246\beta) + 2(\alpha + 0.445\beta) = 6\alpha + 7\beta$$

Therefore the stabilization caused by the ring delocalization in benzene
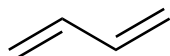is calculated to be 1β unit by Hückel molecular orbital theory

Hückel Molecular Orbital Theory

Qualitatively, one could argue that "resonance" stabilization is partly
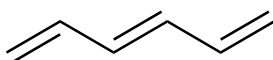a result of reduction of electron-electron repulsion

$H_2C=CH_2$
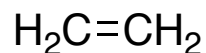
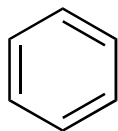Ethylene, 2 electrons in 1 bond

$$E_\pi = 2\alpha + 2\beta$$

Butadiene, 4 electrons in 3 bonds

$$E_\pi = 4\alpha + 4.472\beta$$

Hexatriene, 6 electrons in 5 bonds

$$E_\pi = 6\alpha + 7\beta$$

Benzene, 6 electrons in 6 bonds

$$E_\pi = 6\alpha + 8\beta$$

*The symmetry of the orbital placement is also key, as we will see when considering why
some cyclic compounds are "antiaromatic"