

CHAPTER 10
SEMIEMPIRICAL METHODS AND APPLICATIONS OF SYMMETRY
OUTLINE

Homework Questions Attached

PART A: The Hückel Model and other Semiempirical Methods

SECT	TOPIC
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- | | |
|----|--|
| 1. | Hückel Molecular Orbital Model |
| 2. | Application to Ethylene |
| 3. | Application to the Allyl Radical ($\text{C}_3\text{H}_5\bullet$) |
| 4. | π Electron Charge and π Bond Order |
| 5. | Application to Butadiene |
| 6. | Introduction to Heteroatoms |
| 7. | Semiempirical Methods for Sigma Bonded Systems |

PART B: Applications of Symmetry

SECT	TOPIC
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|----|---|
| 1. | UV/Visible Absorption Selection Rules |
| 2. | Application to Butadiene |
| 3. | Application to Carbene |
| 4. | Use of Symmetry in Simplifying MO Calculations |
| 5. | Construction of SALCs: Application to the Allyl Radical |
| 6. | Solution to the Allyl Radical Using SALCs |
| 7. | Application to π -Bonding in Pyrrole |

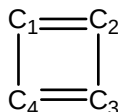
Chapter 10 Homework

PART A: The Hückel Model and other Semiempirical Methods

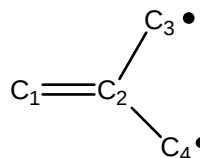
1. Write the Secular determinant for the following molecules in terms of
(i) α , β and E , (ii) $x = (\alpha - E)/\beta$

In molecules with heteroatoms, check PP slides for appropriate heteroatom parameters

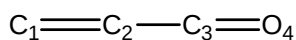
- (a) Square cyclobutadiene



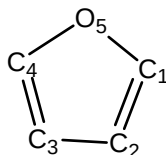
- (b) Trimethylenemethane
This is a diradical species.
I've drawn one of 3 resonance forms



- (c) Acrolein

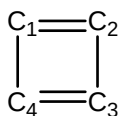


- (d) Furan



2. How many electrons does the oxygen atom in (a) Acrolein, (b) Furan, contribute to the pi electron system.

3. Let's consider Cyclobutadiene:



In the solution to Prob. 1 (a), we showed that the secular determinant is:

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

With a bit of algebra, it can be shown that the above determinant expands to give:
 $x^4 - 4x^2 = 0$

- (a) Solve this equation to obtain the 4 energy levels.

Note: Two of the four energies are degenerate.

(b) It can be shown (with a bit more algebra) that the **non-normalized** molecular orbitals of cyclobutadiene are:

$$\phi_1 = c_1(\chi_1 + \chi_2 + \chi_3 + \chi_4)$$

$$\phi_2 = c_1(\chi_1 - \chi_3)$$

$$\phi_3 = c_2(\chi_2 - \chi_4)$$

$$\phi_4 = c_1(\chi_1 - \chi_2 + \chi_3 - \chi_4)$$

Determine the **normalized** molecular orbitals.

(c) Calculate the total π energy and the Delocalization energy.

(d) Calculate the π electron charge for each atom.

(e) Calculate the π bond order for each bond.

4. Consider 1,3-butadiene: $C_1=C_2-C_3=C_4$

Note: The solution to this problem is given in the Chap. 12 PowerPoint presentation.

(a) Write the Secular Determinant.

(b) Solve the Secular Determinant to obtain the 4 energy levels.

(c) Determine the normalized coefficients of the molecular orbitals corresponding to each energy.

(d) Calculate the total π energy and the Delocalization energy.

(e) Calculate the π electron charge for each atom.

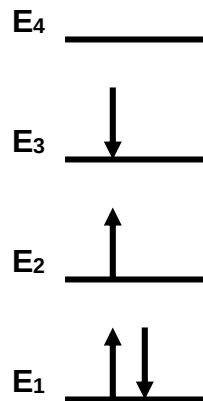
(f) Calculate the π bond order for each bond.

5. Consider butadiene in the lowest excited state (figure to right).

Note: The energies and orbitals are the same as in the ground state.

(a) Calculate the π electron charge on each atom.

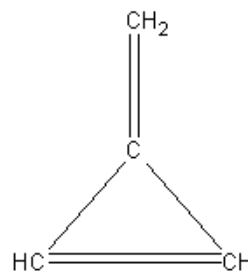
(b) Calculate the π bond order for each bond.



PART B: Applications of Symmetry

6. Methylenecyclopropene belongs to the C_{2v} point group.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

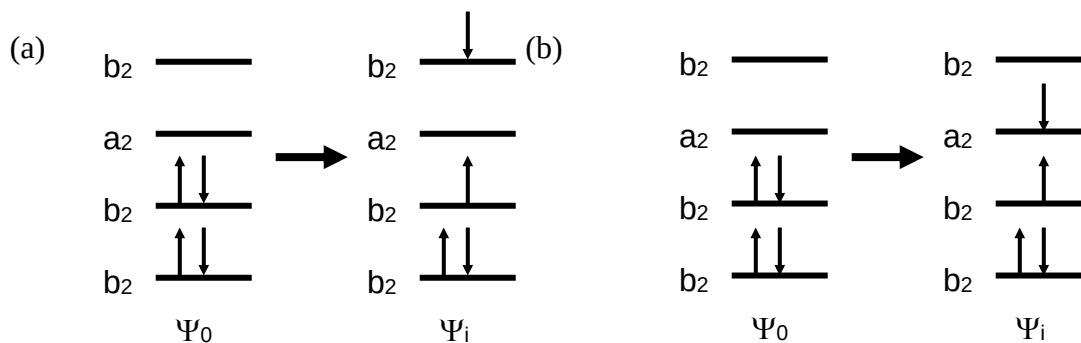


Shown below are two electronic transitions.

The letter to the left of each orbital is its representation.

For each transition, give:

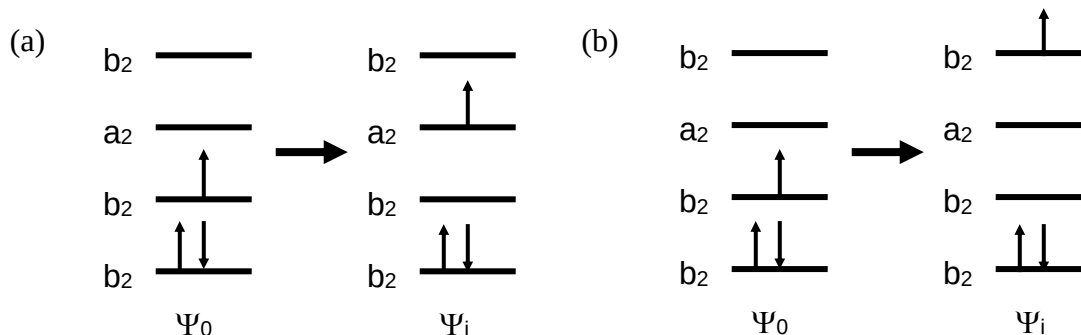
- the representations of the ground state, Ψ_0 , and the excited state, Ψ_i .
- whether or not the transition is allowed.
- if it is allowed, is the transition polarized parallel to or perpendicular to the principal axis.



7. Now consider two transitions of the Methylenecyclopropene cation.

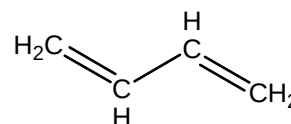
For each transition, give:

- the representations of the ground state, Ψ_0 , and the excited state, Ψ_i .
- whether or not the transition is allowed.
- if it is allowed, is the transition polarized parallel to or perpendicular to the principal axis.



8. Consider trans-1,3-butadiene, which has C_{2h} symmetry. In class (and in the PP presentation), we solved the 4x4 Secular Determinant to determine the Hückel Energies and Molecular Orbitals.

C_{2h}	E	C_2	i	σ_h	
A_g	1	1	1	1	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	xz, yz
A_u	1	1	-1	-1	z
B_u	1	-1	-1	1	x, y



- It can be shown that the p_z orbitals, χ_1 , χ_2 , χ_3 and χ_4 can be combined to give 4 SALCs, two belonging to the B_g and two to the A_u representation. Use projection operators to determine the 4 SALCs for butadiene. Normalize the SALCs.
- Determine the 2x2 Secular Determinants corresponding to the B_g and A_u representations.
- Solve the 2x2 Secular Determinants to determine the energies and wavefunctions belonging to the B_g and A_u representations.

Chapter 10

Semiempirical Methods and Applications of Symmetry

Part A: The Hückel Model and other Semiempirical Methods

Part B: Applications of Symmetry

Slide 1

Part A: The Hückel Model and other Semiempirical Methods

- **Hückel Molecular Orbital Model**
- Application to Ethylene
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Slide 2

Hückel Molecular Orbital Model

Developed by Eric Hückel in 1920's to treat π -electron systems.
Extended by Roald Hoffman in 1963 to treat σ -bonded systems.

The Hückel model has been largely superseded by more accurate MO calculations. However, it is still useful to obtain qualitative predictions of bonding and reactivity in conjugated π systems.

The model is also very useful in learning how to perform the Secular Determinant and Molecular Orbital calculations of the type used in Hartree-Fock theory, but at a much simpler level.

Slide 3

Assumptions

1. The σ and π electrons are independent of each other.
The π electrons move in the constant electrostatic potential created by the σ electrons.
2. The carbons are sp^2 hybridized.
The remaining p_z orbital is perpendicular to the σ molecular framework.
3. The π electron Molecular Orbitals are linear combinations of the p_z orbitals (χ_i).

$$\varphi_i = \sum_j c_{ij} \chi_j = c_{i1} \chi_1 + c_{i2} \chi_2 + c_{i3} \chi_3 + \dots$$

4. The total π electron Hamiltonian is a simple sum of effective one electron Hamiltonians.

$$H = \sum_i h_i = h_1 + h_2 + h_3 + \dots$$

Slide 4

Linear Equations and Secular Determinant

$$\varphi_i = \sum_j c_{ij} \chi_j \quad + \quad H = \sum_i h_i$$

Variational Method

$$\sum_{j=1}^N c_{ij} (H_{ij} - ES_{ij}) = 0$$

One has N equations, where N is the number of carbon atoms.

$$|H_{ij} - ES_{ij}| = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

Slide 5

Additional Assumptions

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

5. The Orbitals are Normalized: $S_{ii} = 1$
The overlap between orbitals is 0: $S_{ij} = 0$ ($i \neq j$)
6. The diagonal Hamiltonian elements are given by an empirical parameter, α
7. Off-diagonal Hamiltonian elements are given by an empirical parameter, β , if the carbons are adjacent

$H_{ij} = \beta$: Adjacent Carbons

$H_{ij} = 0$: Non-Adjacent Carbons

Note: $\alpha < 0$ and $\beta < 0$

Slide 6

Parameter Values

What is the value of α ?

Who cares?

α cancels out in almost all applications, such as transition or reaction energies.

What is the value of β ?

Who knows?

Estimates of the “best” value of β vary all over the place.

As noted in the text, values ranging from -30 kcal/mol to -70 kcal/mol (-130 to -290 kJ/mol) have been used.

For lack of anything better, we'll use $\beta = -200$ kJ/mol.

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Application to Ethylene (C₂H₄)

Secular Determinant and Energies

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

Put in Hückel matrix elements

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

Divide all terms by β and define x by $x = \frac{\alpha - E}{\beta}$

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

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

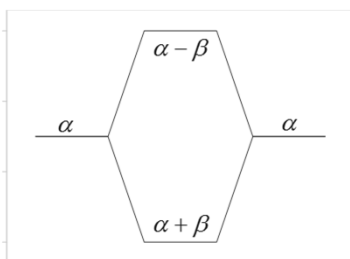
$$x^2 - 1 = 0$$

$$x_1 = -1 = \frac{\alpha - E_1}{\beta}$$

$$E_1 = \alpha + \beta$$

$$x_2 = +1 = \frac{\alpha - E_2}{\beta}$$

$$E_2 = \alpha - \beta$$



Slide 10

Molecular Orbitals

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

$$\downarrow \phi = c_1 \chi_1 + c_2 \chi_2$$

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

$$\downarrow \text{or}$$

$$\begin{aligned} x c_1 + c_2 &= 0 \\ c_1 + x c_2 &= 0 \end{aligned}$$

$$\downarrow$$

$$\frac{c_2}{c_1} = -x$$

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$$\begin{aligned} \phi &= c_1 \chi_1 + c_2 \chi_2 & \frac{c_2}{c_1} &= -x \\ x_1 &= -1 & \frac{c_2}{c_1} &= +1 & \longrightarrow & c_2 = c_1 \\ E_1 &= \alpha + \beta \end{aligned}$$

Normalization: $1 = \langle \phi | \phi \rangle = \langle c_1 \chi_1 + c_2 \chi_2 | c_1 \chi_1 + c_2 \chi_2 \rangle$

$$1 = c_1^2 \langle \chi_1 | \chi_1 \rangle + c_1 c_2 \langle \chi_1 | \chi_2 \rangle + c_2 c_1 \langle \chi_2 | \chi_1 \rangle + c_2^2 \langle \chi_2 | \chi_2 \rangle$$

$$1 = c_1^2 + c_2^2$$

Note: For Hückel calculations, the normalization

condition is always: $\sum_i c_i^2 = 1$

$$\begin{aligned} 1 &= c_1^2 + c_2^2 \\ c_2 &= c_1 \end{aligned} \longrightarrow \boxed{\phi_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2)}$$

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$$\phi_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2)$$

Bonding Orbital

$$\begin{array}{l} x_2 = +1 \\ E_2 = \alpha - \beta \end{array} \longrightarrow \frac{c_2}{c_1} = -1 \longrightarrow c_2 = -c_1$$

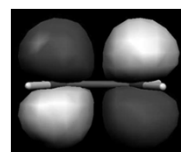
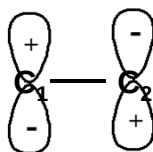
$$\begin{array}{l} 1 = c_1^2 + c_2^2 \\ c_2 = -c_1 \end{array}$$

$$\phi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_2)$$

Antibonding Orbital

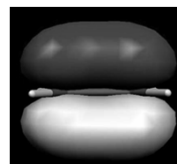
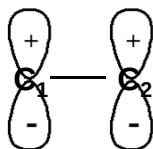
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$$E_2 = \alpha - \beta \quad \frac{1}{\sqrt{2}}(\chi_1 - \chi_2)$$



Electrons are **not** delocalized in ϕ_2

$$E_1 = \alpha + \beta \quad \uparrow \downarrow \quad \frac{1}{\sqrt{2}}(\chi_1 + \chi_2)$$



Electrons are delocalized in ϕ_1

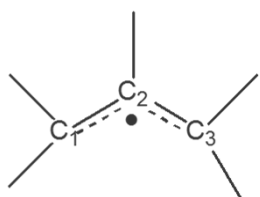
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Application to the Allyl Radical ($\text{C}_3\text{H}_5\cdot$)



The Allyl radical has 3 π electrons

Secular Determinant and Energies

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & H_{23} - ES_{23} \\ H_{13} - ES_{13} & H_{23} - ES_{23} & H_{33} - ES_{33} \end{vmatrix} = 0$$



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

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$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad \xrightarrow[\text{Define } x = \frac{\alpha - E}{\beta}]{\text{Divide by } \beta} \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

$$x \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} + 0 \begin{vmatrix} 1 & x \\ 0 & 1 \end{vmatrix} = 0 \longrightarrow x(x^2 - 1) - 1(x - 0) = 0$$

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

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on
Board

$$x_1 = -\sqrt{2} = \frac{\alpha - E_1}{\beta}$$

$$\downarrow$$

$$E_1 = \alpha + \sqrt{2}\beta$$

$$x_2 = 0 = \frac{\alpha - E_2}{\beta}$$

$$\downarrow$$

$$E_2 = \alpha$$

$$x_3 = +\sqrt{2} = \frac{\alpha - E_3}{\beta}$$

$$\downarrow$$

$$E_3 = \alpha - \sqrt{2}\beta$$

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$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \longrightarrow \begin{array}{l} 1) \quad xc_1 + c_2 = 0 \\ 2) \quad c_1 + xc_2 + c_3 = 0 \\ 3) \quad c_2 + xc_3 = 0 \end{array}$$

From 1) $c_2 = -xc_1$

From 2) $c_3 = -c_1 - xc_2$

From 3) $c_3 = -\frac{1}{x}c_2$

$$x_1 = -\sqrt{2} \longrightarrow \begin{array}{l} c_2 = -(-\sqrt{2})c_1 = \sqrt{2}c_1 \\ c_3 = -\frac{1}{-\sqrt{2}}c_2 = c_1 \end{array}$$

$$x_2 = 0 \longrightarrow \begin{array}{l} c_2 = -(0)c_1 = 0 \\ c_3 = -c_1 - (0)c_2 = -c_1 \end{array}$$

Normalization

$$c_1^2 + (\sqrt{2}c_1)^2 + c_1^2 = 1 \quad 4c_1^2$$

$$c_1 = \frac{1}{2}$$

$$\boxed{\varphi_1 = \frac{1}{2}(\chi_1 + \sqrt{2}\chi_2 + \chi_3)}$$

Normalization

$$c_1^2 + (0)^2 + (-c_1)^2 = 1 \quad 2c_1^2$$

$$c_1 = \frac{1}{\sqrt{2}}$$

$$\boxed{\varphi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3)}$$

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$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \longrightarrow \begin{array}{l} 1) \quad xc_1 + c_2 = 0 \\ 2) \quad c_1 + xc_2 + c_3 = 0 \\ 3) \quad c_2 + xc_3 = 0 \end{array}$$

From 1) $c_2 = -xc_1$
From 2) $c_3 = -c_1 - xc_2$
From 3) $c_3 = -\frac{1}{x}c_2$

$$x_3 = +\sqrt{2} \longrightarrow \begin{array}{l} c_2 = -\left(+\sqrt{2}\right)c_1 = -\sqrt{2}c_1 \\ c_3 = -\frac{1}{+\sqrt{2}}c_2 = c_1 \end{array}$$

Normalization

$$c_1^2 + \left(-\sqrt{2}c_1\right)^2 + c_1^2 = 1 \quad \text{Note: } 1 \neq c_1^2$$

$$c_1 = \frac{1}{2}$$

$$\phi_3 = \frac{1}{2}(\chi_1 - \sqrt{2}\chi_2 + \chi_3)$$

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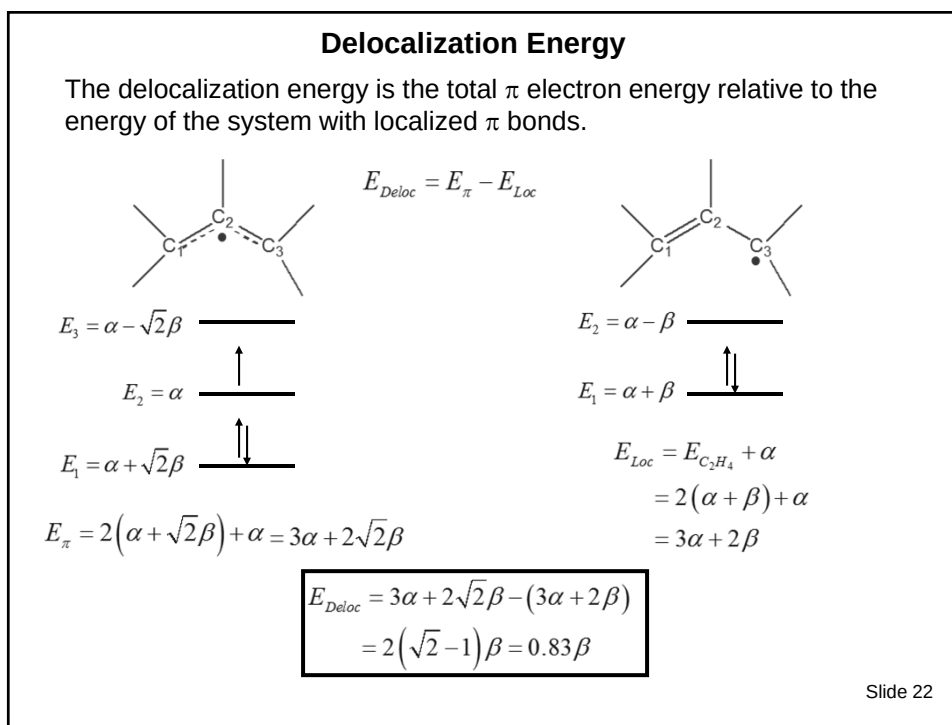
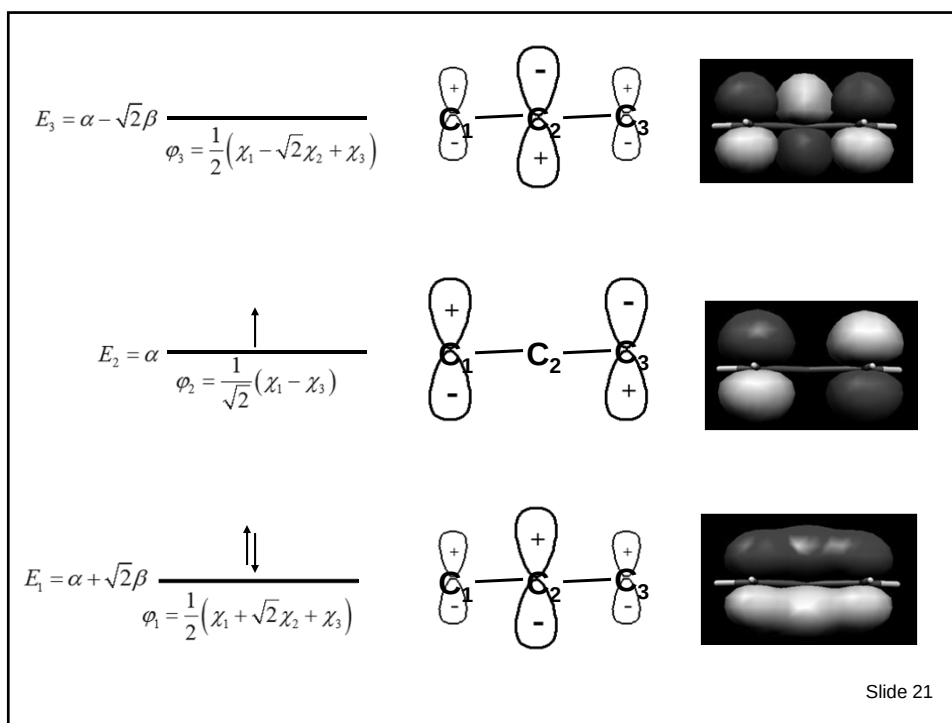
Wavefunction Check

You can always check to be sure that you've calculated the wavefunction correctly by calculating the expectation value of E and see if it matches your original calculated value.

We'll illustrate with ϕ_3 .

$$\begin{aligned} E &= \langle \phi_3 | H | \phi_3 \rangle = \left\langle \frac{1}{2}(\chi_1 - \sqrt{2}\chi_2 + \chi_3) \middle| H \middle| \frac{1}{2}(\chi_1 - \sqrt{2}\chi_2 + \chi_3) \right\rangle \\ &= \frac{1}{4} \left[\begin{array}{l} \langle \chi_1 | H | \chi_1 \rangle - \sqrt{2} \langle \chi_1 | H | \chi_2 \rangle + \langle \chi_1 | H | \chi_3 \rangle \\ - \sqrt{2} \langle \chi_2 | H | \chi_1 \rangle + 2 \langle \chi_2 | H | \chi_2 \rangle - \sqrt{2} \langle \chi_2 | H | \chi_3 \rangle \\ + \langle \chi_3 | H | \chi_1 \rangle - \sqrt{2} \langle \chi_3 | H | \chi_2 \rangle + \langle \chi_3 | H | \chi_3 \rangle \end{array} \right] \\ &= \frac{1}{4} [\alpha - \sqrt{2}\beta + 0 - \sqrt{2}\beta + 2\alpha - \sqrt{2}\beta + 0 - \sqrt{2}\beta + \alpha] \\ E &= \frac{1}{4} [4\alpha - 4\sqrt{2}\beta] = \alpha - \sqrt{2}\beta \quad \text{It checks!!} \end{aligned}$$

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π Electron Charge and π Bond Order

π Electron Charge (aka π Charge Density)

The π electron charge on atom μ is defined by:

$$q_{\mu} \equiv \sum_i^{\text{orbs}} n_i c_{i\mu}^2$$

$c_{i\mu}$ is the coefficient of the i 'th. MO on atom μ .

π Bond Order

The π bond order between atoms μ and ν is defined by:

$$p_{\mu\nu} \equiv \sum_i^{\text{orbs}} n_i c_{i\mu} c_{i\nu}$$

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Application to the Allyl Radical

$$\begin{array}{c}
 \overline{\varphi_3 = \frac{1}{2}\chi_1 - \frac{1}{\sqrt{2}}\chi_2 + \frac{1}{2}\chi_3} \\
 \uparrow \\
 \overline{\varphi_2 = \frac{1}{\sqrt{2}}\chi_1 + 0\chi_2 - \frac{1}{\sqrt{2}}\chi_3} \\
 \updownarrow \\
 \overline{\varphi_1 = \frac{1}{2}\chi_1 + \frac{1}{\sqrt{2}}\chi_2 + \frac{1}{2}\chi_3}
 \end{array}$$

π Electron Charge: $q_\mu \equiv \sum_i^{orbs} n_i c_{i\mu}^2$

$$q_1 = \sum_i^{orbs} n_i c_{i1}^2 = 2 \cdot \left(\frac{1}{2}\right)^2 + 1 \cdot \left(\frac{1}{\sqrt{2}}\right)^2 = 1$$

$$q_2 = \sum_i^{orbs} n_i c_{i2}^2 = 2 \cdot \left(\frac{1}{\sqrt{2}}\right)^2 + 1 \cdot (0)^2 = 1$$

$$q_3 = \sum_i^{orbs} n_i c_{i3}^2 = 2 \cdot \left(\frac{1}{2}\right)^2 + 1 \cdot \left(-\frac{1}{\sqrt{2}}\right)^2 = 1$$

π Bond Order: $p_{\mu\nu} \equiv \sum_i^{orbs} n_i c_{i\mu} c_{i\nu}$

$$p_{12} = \sum_i^{orbs} n_i c_{i1} c_{i2} = 2 \cdot \left(\frac{1}{2}\right) \left(\frac{1}{\sqrt{2}}\right) + 1 \cdot \left(\frac{1}{\sqrt{2}}\right) (0) = \frac{1}{\sqrt{2}} = 0.71$$

$$p_{23} = \sum_i^{orbs} n_i c_{i2} c_{i3} = 2 \cdot \left(\frac{1}{\sqrt{2}}\right) \left(\frac{1}{2}\right) + 1 \cdot (0) \left(-\frac{1}{\sqrt{2}}\right) = \frac{1}{\sqrt{2}} = 0.71$$

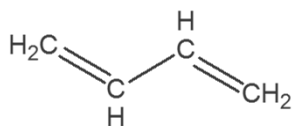
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Part A: The Hückel Model and other Semiempirical Methods

- Hückel Molecular Orbital Model
- Application to Ethylene
- Application to the Allyl Radical ($C_3H_5\bullet$)
- π Electron Charge and π Bond Order
- **Application to Butadiene**
- Introduction of Heteroatoms
- Semiempirical methods for sigma bonded systems

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Application to Butadiene



1,3-Butadiene has 4 π electrons

Note: Application of the Hückel theory to Butadiene is one of your HW problems.

The solution is worked out in detail below. I will just outline the solution.

Secular Determinant and Energies

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad \xrightarrow[\text{Define}]{\text{Divide by } \beta} \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

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

$$x[x(x^2 - 1) - 1(x - 0)] - 1[1(x^2 - 1) - 1(0 - 0)] = 0$$

$$[x^4 - x^2 - x^2] - [x^2 - 1] = 0$$

$$x^4 - 3x^2 + 1 = 0$$

$$\downarrow y \equiv x^2$$

$$y^2 - 3y + 1 = 0$$

$$y_a = \frac{3 + \sqrt{9 - 4}}{2} = 2.618 = x^2$$

$$y_b = \frac{3 - \sqrt{9 - 4}}{2} = 0.382 = x^2$$

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$$y_a = \frac{3 + \sqrt{9 - 4}}{2} = 2.618 = x^2$$

$$x_1 = -1.618 = \frac{\alpha - E_1}{\beta}$$

$$x_4 = +1.618 = \frac{\alpha - E_4}{\beta}$$

$$y_b = \frac{3 - \sqrt{9 - 4}}{2} = 0.382 = x^2$$

$$x_2 = -0.618 = \frac{\alpha - E_2}{\beta}$$

$$x_3 = +0.618 = \frac{\alpha - E_3}{\beta}$$

$$E_4 = \alpha - 1.618\beta$$

$$E_3 = \alpha - 0.618\beta$$

$$E_2 = \alpha + 0.618\beta$$

$$E_1 = \alpha + 1.618\beta$$

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Butadiene Delocalization Energy

$$E_{Deloc} = E_{\pi}(C_4H_6) - 2 \cdot E_{\pi}(C_2H_4)$$

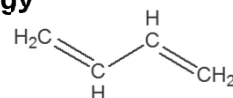
$$E_{\pi}(C_4H_6) = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) \\ = 4\alpha + 4.472\beta$$

$$E_{\pi}(C_2H_4) = 2(2\alpha + 2\beta) = 4\alpha + 4\beta$$

$$E_{Deloc} = 4\alpha + 4.472\beta - (4\alpha + 4\beta) = 0.472\beta$$

$$E_{Deloc} \approx 0.472(-200 \text{ kJ/mol}) \approx -90 \text{ kJ/mol}$$

The additional stabilization of butadiene compared to 2 ethylenes is a result of π electron delocalization between the two double bonds.



$$E_4 = \alpha - 1.618\beta$$

$$E_3 = \alpha - 0.618\beta$$

$$E_2 = \alpha + 0.618\beta$$

$$E_1 = \alpha + 1.618\beta$$



$$E_2 = \alpha - \beta$$

$$E_1 = \alpha + \beta$$

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Butadiene Wavefunctions

$$\varphi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$$

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \longrightarrow \begin{array}{l} xc_1 + c_2 = 0 \\ c_1 + xc_2 + c_3 = 0 \\ c_2 + xc_3 + c_4 = 0 \\ c_3 + xc_4 = 0 \end{array} \xrightarrow{x_1 = -1.618} \begin{array}{l} -1.618c_1 + c_2 = 0 \\ c_1 - 1.618c_2 + c_3 = 0 \\ c_2 - 1.618c_3 + c_4 = 0 \\ c_3 - 1.618c_4 = 0 \end{array}$$

From first equation: $c_2 = 1.618c_1$

From second equation: $c_3 = -c_1 + 1.618c_2 = -c_1 + 2.618c_1 = 1.618c_1$

From fourth equation: $c_4 = \frac{c_3}{1.618} = c_1$

$$\varphi = c_1(\chi_1 + 1.618\chi_2 + 1.618\chi_3 + \chi_4)$$

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$$\varphi_1 = c_1(\chi_1 + 1.618\chi_2 + 1.618\chi_3 + \chi_4)$$

Normalization: $\sum_{i=1}^4 c_i^2 = 1$ (because all overlap integrals are 0)

$$c_1^2[(1)^2 + (1.618)^2 + (1.618)^2 + (1)^2] = 1 = 7.236 c_1^2$$

$$c_1 = 0.372$$

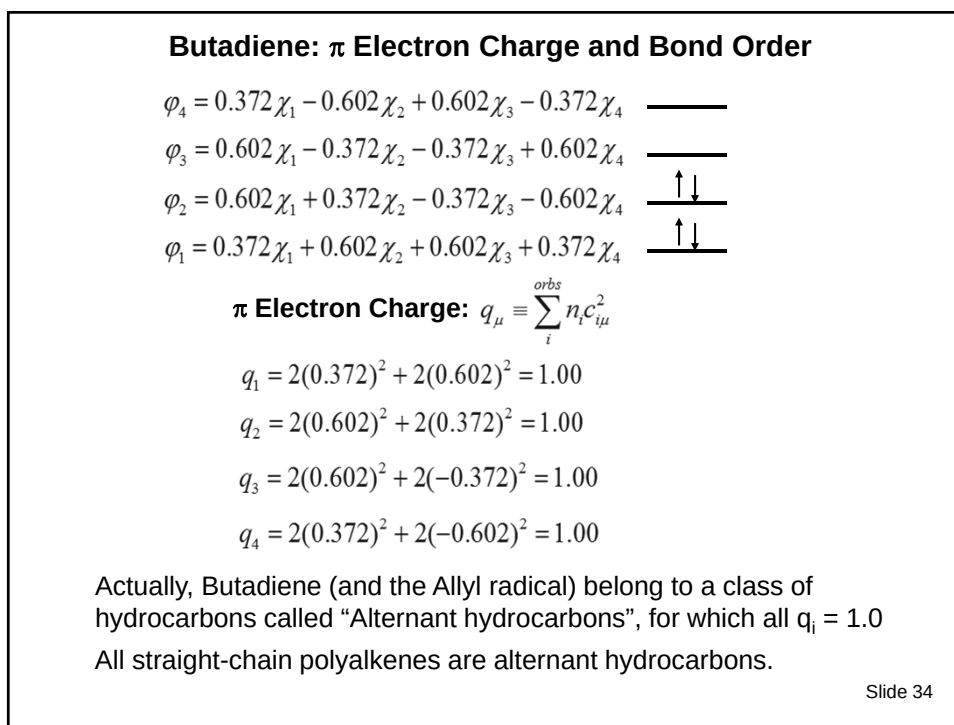
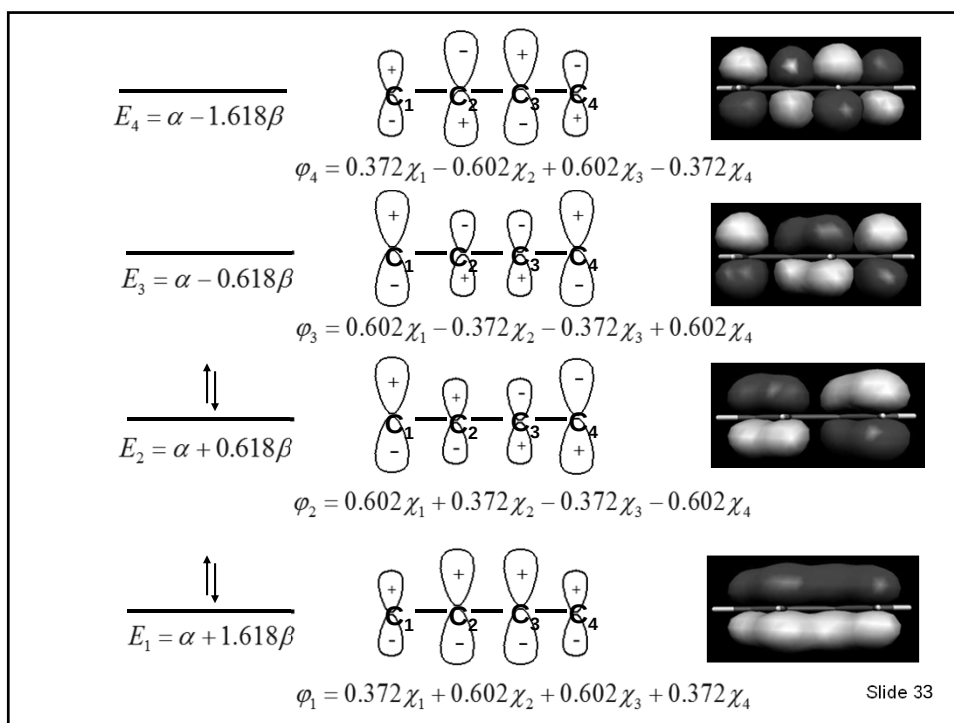
$$\varphi_1 = 0.372(\chi_1 + 1.618\chi_2 + 1.618\chi_3 + \chi_4)$$

$$\varphi_1 = 0.372\chi_1 + 0.602\chi_2 + 0.602\chi_3 + 0.372\chi_4$$

It is straightforward to perform the same procedure to determine ϕ_2 , ϕ_3 and ϕ_4 .

The results are shown on the next slide.

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$$\begin{aligned}
 \varphi_4 &= 0.372\chi_1 - 0.602\chi_2 + 0.602\chi_3 - 0.372\chi_4 & \text{---} \\
 \varphi_3 &= 0.602\chi_1 - 0.372\chi_2 - 0.372\chi_3 + 0.602\chi_4 & \text{---} \\
 \varphi_2 &= 0.602\chi_1 + 0.372\chi_2 - 0.372\chi_3 - 0.602\chi_4 & \uparrow\downarrow \\
 \varphi_1 &= 0.372\chi_1 + 0.602\chi_2 + 0.602\chi_3 + 0.372\chi_4 & \uparrow\downarrow
 \end{aligned}$$

$$\text{\textbf{\textit{\pi} Bond Order:}} \quad p_{\mu\nu} \equiv \sum_i^{\text{orbs}} n_i c_{i\mu} c_{i\nu}$$

$$p_{12} = 2(0.372)(0.602) + 2(0.602)(0.372) = 0.896 \approx 0.90$$

$$p_{23} = 2(0.602)(0.602) + 2(0.372)(-0.372) = 0.448 \approx 0.45$$

$$p_{34} = 2(0.602)(0.372) + 2(-0.372)(-0.602) = 0.896 \approx 0.90$$

Note: For a “full” π bond, $p_{\mu\nu} = 1$.
For a pure σ bond, $p_{\mu\nu} = 0$.

Therefore, the above bond orders reveal that the π bonds between C_1 - C_2 and C_3 - C_4 are not as strong as in ethylene.

$p_{23} > 0$ shows that there is significant π character in the C_2 - C_3 bond.

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Part A: The Hückel Model and other Semiempirical Methods

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- Semiempirical methods for sigma bonded systems

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Introduction of Heteroatoms

Introduction of a heteroatom such as N or O into a conjugated π system requires different values of α and β than those used for Carbon because the heteroatom has a different electronegativity; i.e. $\text{Ene}(\text{C}) < \text{Ene}(\text{N}) < \text{Ene}(\text{O})$.

It is useful to put the new values of the Coulomb and Resonance Integrals, α_X and β_X (where X is the heteroatom), in terms of the original α and β .

The forms that is generally used are:

$$\alpha_X = \alpha + h_X \beta$$

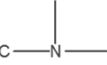
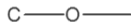
$$\text{and } \beta_X = k_X \beta$$

where h_X and k_X are constants that depend upon the heteroatom.

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$$\alpha_X = \alpha + h_X \beta$$

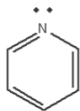
$$\beta_X = k_X \beta$$

Atom	h_X	Bond	k_X
	0.5		1.0
	1.5		0.8
	2.0		0.8
	1.0		1.0
	2.0		0.4

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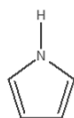
A heteroatom can donate different numbers of electrons into the π electrons depending upon its bonding.

Example: Nitrogen has 5 valence electrons



In pyridine, 4 of the 5 valence electrons are involved in
(a) 2 σ bonds and (b) 2 electrons in the lone pair.

Therefore, this nitrogen will donate only 1 electron.



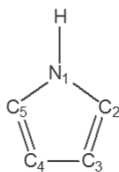
In pyrrole, 3 of the electrons will be involved in σ bonds.

This nitrogen will donate 2 electrons.

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Example: π Bonding in Pyrrole

This will illustrate how a heteroatom is handled in the Hückel Molecular Orbital Model.



For pyrrole, 2 electrons are donated to the π system.

The heteroatom parameters are: $h_N = 1.5$ and $k_N = 0.8$

Therefore: $\alpha_N = \alpha + h_N \beta = \alpha + 1.5\beta$

$$\beta_N = k_N \beta = 0.8\beta$$

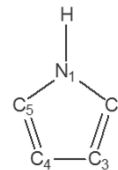
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The Secular Determinant

$$\alpha_N = \alpha + 1.5\beta$$

$$\beta_N = 0.8\beta$$

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



$$\begin{vmatrix} \alpha + 1.5\beta - E & 0.8\beta & 0 & 0 & 0.8\beta \\ 0.8\beta & \alpha - E & \beta & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & \beta & \alpha - E & \beta \\ 0.8\beta & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \longrightarrow \begin{vmatrix} x + 1.5 & 0.8 & 0 & 0 & 0.8 \\ 0.8 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 0.8 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

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$$\begin{vmatrix} x + 1.5 & 0.8 & 0 & 0 & 0.8 \\ 0.8 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 0.8 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

$$\alpha_N = \alpha + 1.5\beta$$

$$\beta_N = 0.8\beta$$

This is a 5x5 Secular Determinant, which can be expanded to yield a fifth order polynomial equation, which can be solved to give:

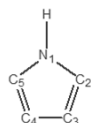
- (a) five values of x.
- (b) five energies.
- (c) five sets of coefficients.

But, I'm just really not in the mood right now.

Howsabout I just give you the results?

No Applause, PLEASE !!!

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Wavefunctions and Energies

$$E_5 = E_s = \alpha - 1.618\beta$$

$$E_4 = E_v = \alpha - 1.008\beta$$



$$E_3 = E_r = \alpha + 0.618\beta$$



$$E_2 = E_u = \alpha + 1.189\beta$$



$$E_1 = E_t = \alpha + 2.320\beta$$

$$\phi_s = \phi_s = 0.372\chi_2 - 0.602\chi_3 + 0.602\chi_4 - 0.372\chi_5$$

$$\phi_4 = \phi_v = 0.374\chi_1 - 0.587\chi_2 + 0.292\chi_3 + 0.292\chi_4 - 0.587\chi_5$$

$$\phi_3 = \phi_r = 0.602\chi_2 + 0.372\chi_3 - 0.372\chi_4 - 0.602\chi_5$$

$$\phi_2 = \phi_u = 0.530\chi_1 - 0.111\chi_2 - 0.589\chi_3 - 0.589\chi_4 - 0.111\chi_5$$

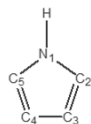
$$\phi_1 = \phi_t = 0.725\chi_1 + 0.379\chi_2 + 0.287\chi_3 + 0.287\chi_4 + 0.379\chi_5$$

Note: There are 6 electrons.
Count them.

Note: Actually, I used symmetry to simplify the 5x5 determinant into a 2x2 and a 3x3 determinant

I'll show you how at the end of the chapter.

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$$E_5 = E_s = \alpha - 1.618\beta$$

$$E_4 = E_v = \alpha - 1.008\beta$$



$$E_3 = E_r = \alpha + 0.618\beta$$



$$E_2 = E_u = \alpha + 1.189\beta$$



$$E_1 = E_t = \alpha + 2.320\beta$$

π Electron Charge

$$\phi_s = \phi_s = 0.372\chi_2 - 0.602\chi_3 + 0.602\chi_4 - 0.372\chi_5$$

$$\phi_4 = \phi_v = 0.374\chi_1 - 0.587\chi_2 + 0.292\chi_3 + 0.292\chi_4 - 0.587\chi_5$$

$$\phi_3 = \phi_r = 0.602\chi_2 + 0.372\chi_3 - 0.372\chi_4 - 0.602\chi_5$$

$$\phi_2 = \phi_u = 0.530\chi_1 - 0.111\chi_2 - 0.589\chi_3 - 0.589\chi_4 - 0.111\chi_5$$

$$\phi_1 = \phi_t = 0.725\chi_1 + 0.379\chi_2 + 0.287\chi_3 + 0.287\chi_4 + 0.379\chi_5$$

$$\pi \text{ Electron Charge: } q_\mu \equiv \sum_i^{\text{orbs}} n_i c_{i\mu}^2$$

$$q_1 = 1.61$$

$$q_2 = 1.04$$

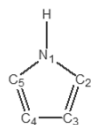
$$q_3 = 1.14$$

$$q_4 = 1.14$$

$$q_5 = 1.04$$

$$\sum_\mu q_\mu = 5.97 \approx 6$$

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$$E_5 = E_s = \alpha - 1.618\beta$$

$$E_4 = E_v = \alpha - 1.008\beta$$



$$E_3 = E_r = \alpha + 0.618\beta$$



$$E_2 = E_u = \alpha + 1.189\beta$$



$$E_1 = E_t = \alpha + 2.320\beta$$

π Bond Order

$$\varphi_5 = \varphi_s = 0.372\chi_2 - 0.602\chi_3 + 0.602\chi_4 - 0.372\chi_5$$

$$\varphi_4 = \varphi_v = 0.374\chi_1 - 0.587\chi_2 + 0.292\chi_3 + 0.292\chi_4 - 0.587\chi_5$$

$$\varphi_3 = \varphi_r = 0.602\chi_2 + 0.372\chi_3 - 0.372\chi_4 - 0.602\chi_5$$

$$\varphi_2 = \varphi_u = 0.530\chi_1 - 0.111\chi_2 - 0.589\chi_3 - 0.589\chi_4 - 0.111\chi_5$$

$$\varphi_1 = \varphi_t = 0.725\chi_1 + 0.379\chi_2 + 0.287\chi_3 + 0.287\chi_4 + 0.379\chi_5$$

$$\pi \text{ Bond Order: } p_{\mu\nu} \equiv \sum_i^{orbs} n_i c_{i\mu} c_{i\nu}$$

$$p_{12} = 0.43$$

$$p_{23} = 0.80$$

$$p_{34} = 0.58$$

$$p_{45} = 0.80$$

$$p_{15} = 0.43$$

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Part A: The Hückel Model and other Semiempirical Methods

- Hückel Molecular Orbital Model
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- **Semiempirical methods for sigma bonded systems**

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Semiempirical Methods for Sigma Bonded Systems

The Hückel model was developed to treat only π bond systems.

A number of methods have been developed to treat systems with σ bonded molecules as well as molecules with both σ and π bonds.

Three of the most popular are:

- (1) Pariser-Pople-Parr (PPP) Model
- (2) The Extended Hückel model
- (3) MNDO methods

We will discuss each method qualitatively.

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Pariser-Pople-Parr (PPP) Model

The Hückel Model neglects repulsion between electron.
The PPP Model introduces interelectron repulsion into the effective Hamiltonian:

$$H_{\text{PPP}} = H_{\text{Hückel}} + H_{\text{Repulsion}}$$

The inclusion of $H_{\text{Repulsion}}$ introduces Coulomb Integrals into the expression for the Energy.

However, these integrals are not calculated.

They are represented by empirical parameters.

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The Extended Hückel Model

As the title suggests, this is an extension of the Hückel Model to treat σ bonded molecules, developed by Roald Hoffmann (in 1963).

The concept is the same in that one assumes that:

1. The Molecular Orbitals are linear combinations of atomic orbitals (χ_i).

$$\varphi_i = \sum_j c_{ij} \chi_j = c_{i1} \chi_1 + c_{i2} \chi_2 + c_{i3} \chi_3 + \dots$$

2. The total Hamiltonian is a simple sum of effective one electron Hamiltonians.

$$H = \sum_i h_i = h_1 + h_2 + h_3 + \dots$$

3. If one applies the variational principle, then a Secular Determinant is obtained.

$$\left| H_{ij} - ES_{ij} \right| = 0$$

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$$\left| H_{ij} - ES_{ij} \right| = 0$$

3. The orbitals for Core shell electrons are ignored. Valence shell atomic orbitals are given by STOs; e.g. 2s, 2p_x, 2p_y, 2p_z
4. The parameters in the Secular Determinant are determined as follows:
 - Overlap integrals, S_{ij} are calculated directly (unlike the Hückel model where they are assumed to be zero)
 - Coulomb Integrals, H_{ii} , are set equal to the negative of the valence shell ionization energies.
 - Resonance Integrals, H_{ij} , are calculate with the Wolfsberg-Helmholtz formula

$$H_{ab} \approx K \left[\frac{H_{aa} + H_{bb}}{2} \right] S_{ab} \quad K \approx 1.75$$

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MNDO Methods

An *ab initio* Hartree-Fock calculation on a molecule requires the calculation of $\sim b^4/8$ integrals.

If one uses a high level basis set on a medium size molecule (10-20 atoms), a typical number of basis functions might be $b=400$, resulting in $\sim 3 \times 10^9$ integrals.

A very great percentage of the time required for a Hartree-Fock calculation is in the evaluation of these integrals.

There have been a number of semiempirical methods developed which approximate these integrals. The most popular of these methods is the MNDO (Modified Neglect of Differential Overlap) series of methods developed by M. J. S. Dewar.

I'll comment briefly on them.

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Assumptions:

- Core (inner shell) electrons are not treated explicitly. An empirical core-core repulsion term is introduced.
- A minimal basis set with single ns , np_x , np_y , np_z atomic orbitals is used to represent valence shell electrons.
- Overlap integrals are neglected.
- The one-center and two-center integrals are either ignored or approximated by empirical parameters.

The empirical parameters are obtained by finding the values that give the best agreement with experimental data; i.e. Heats of Formation, Ionization Energies, Dipole Moments, etc.

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The three different MNDO methods are:

MNDO: The original of the methods. In general, this is not as accurate as later methods.

AM1: This stands for Austin Model 1
Dewar had moved to UT-Austin and wanted to give credit to his new university.
This method improves upon the parameterization of the integrals.

PM3: This stands for Parametric Method 3
This improves the parameterization method still further.

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Because the integrals are determined empirically, and are not calculated, MNDO methods are thousands of times as fast as *ab initio* calculations.

The results are generally not as accurate as *ab initio* calculations, but the MNDO methods are good for:

- (a) Semi-quantitative results.
- (b) Calculations on very large molecules, where *ab initio* calculations are not feasible.

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Chapter 10

Semiempirical Methods and Applications of Symmetry

Part B: Applications of Symmetry

Slide 1

Part B: Applications of Symmetry

- **UV/Visible Absorption Selection Rules**
- Application to Butadiene
- Application to Carbene
- Use of Symmetry in Simplifying MO Calculations
- Construction of SALCs: Application to the Allyl Radical
- Solution to the Allyl Radical using SALCs
- Application to π -Bonding in Pyrrole

Slide 2

Spectroscopic Selection Rules

When light (of frequency ω) is shined on a sample, the light's electric vector interacts with the molecule's dipole moment, which adds a perturbation to the molecular Hamiltonian.

$$H = H^{(0)} + H^{(1)} = H^{(0)} - \vec{\mu} \cdot \vec{E} = H^{(0)} - \mu E \cos(\omega t)$$

The perturbation “mixes” the ground state wavefunction (Ψ_0) with various excited states (Ψ_i). A simpler way to say this is that the light causes transitions between the ground state and the excited states.

Consider a transition between the ground state (Ψ_0) and the i 'th. excited state (Ψ_i).

Time dependent perturbation theory can be used to show that the intensity of the absorption is proportional to the square of the “transition moment”, M_{0i} .

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$$Intensity = C \cdot [M_{0i}]^2$$

The transition moment is: $M_{0i} = \langle \Psi_i | \hat{\mu} | \Psi_0 \rangle = \int \Psi_i^* \hat{\mu} \Psi_0 d\tau$

$\hat{\mu}$ is the dipole moment operator: $\hat{\mu} = e\vec{r}_i = e(x\vec{i} + y\vec{j} + z\vec{k})$

$$M_{0i} = \langle \Psi_i | \hat{\mu} | \Psi_0 \rangle = e \langle \Psi_i | x\vec{i} + y\vec{j} + z\vec{k} | \Psi_0 \rangle$$

$$M_{0i} = e \langle \Psi_i | x | \Psi_0 \rangle \vec{i} + e \langle \Psi_i | y | \Psi_0 \rangle \vec{j} + e \langle \Psi_i | z | \Psi_0 \rangle \vec{k}$$

$$M_{0i} = M_{0i}^x \vec{i} + M_{0i}^y \vec{j} + M_{0i}^z \vec{k}$$

$$M_{0i}^x = e \langle \Psi_i | x | \Psi_0 \rangle$$

$$M_{0i}^y = e \langle \Psi_i | y | \Psi_0 \rangle$$

$$M_{0i}^z = e \langle \Psi_i | z | \Psi_0 \rangle$$

Thus, the transition moment has x, y and z components.

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Selection Rules for UV/Vis Absorption Spectra

Let's use Group Theory to predict whether specific electronic transitions in some molecules can be excited by the absorption of UV radiation.

We want to determine whether the components of the transition moment are nonzero.

$$M_{0i}^x = e \langle \Psi_i | x | \Psi_0 \rangle$$

$$M_{0i}^y = e \langle \Psi_i | y | \Psi_0 \rangle$$

$$M_{0i}^z = e \langle \Psi_i | z | \Psi_0 \rangle$$

A question which must be resolved is how to determine the representation of the overall electronic wavefunction (both Ψ_0 and Ψ_i) from the representations of the individual MOs.

However, first let's take a short detour to briefly discuss "spin-forbidden" transitions.

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Spin Forbidden Transitions

When considering electronic transitions (i.e. UV and Vis. Spectroscopy), the total wavefunction is actually the product of a spatial function and a spin wavefunction.

$$\Psi_0^{tot}(\vec{r}, S_0) = \Psi_0(\vec{r}) \cdot \Psi_0^{Spin}(S_0) \quad \Psi_i^{tot}(\vec{r}, S_i) = \Psi_i(\vec{r}) \cdot \Psi_i^{Spin}(S_i)$$

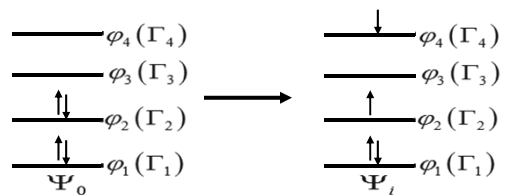
$$M_{0i} = \langle \Psi_i^{tot} | \hat{\mu} | \Psi_0^{tot} \rangle = \langle \Psi_i \cdot \Psi_i^{Spin}(S_i) | \hat{\mu} | \Psi_0 \cdot \Psi_0^{Spin}(S_0) \rangle$$

$$M_{0i} = \langle \Psi_i | \hat{\mu} | \Psi_0 \rangle \langle \Psi_i^{Spin}(S_i) | \Psi_0^{Spin}(S_0) \rangle$$

It can be shown that spin wavefunctions corresponding to different values of S are orthogonal: $\langle \Psi_i^{Spin}(S_i) | \Psi_0^{Spin}(S_0) \rangle = \delta_{S_i, S_0}$

Therefore, the transition moment is zero unless the total spin quantum number is conserved; e.g. Singlet $\rightarrow$ Triplet transitions are forbidden.

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Note that I left the spins paired in the excited state (i.e. this is the singlet form of the excited state).

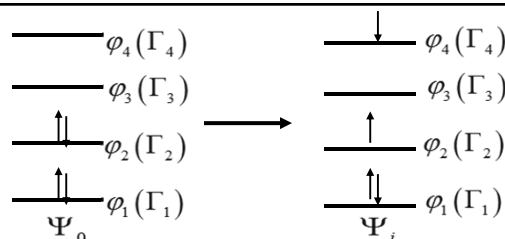
That's because, as we just saw, absorptions involving a change in spin multiplicity are "spin forbidden".

How do we get the representations, $\Gamma(\Psi_0)$ and $\Gamma(\Psi_i)$, from the individual Γ_i 's of the MOs?

It's easy!! The representation of the total wavefunction is the direct product of the representations of all MOs with 1 or 2 electrons (we count the representation twice when the orbital has 2 electrons)

$$\Gamma(\Psi_0) = \Gamma_1 \times \Gamma_1 \times \Gamma_2 \times \Gamma_2 \quad \Gamma(\Psi_i) = \Gamma_1 \times \Gamma_1 \times \Gamma_2 \times \Gamma_4$$

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$$\Gamma(\Psi_0) = \Gamma_1 \times \Gamma_1 \times \Gamma_2 \times \Gamma_2 \quad \Gamma(\Psi_i) = \Gamma_1 \times \Gamma_1 \times \Gamma_2 \times \Gamma_4$$

$$\Gamma(\Psi_0) = A_1 \text{ (or } A_g, \dots) \quad \Gamma(\Psi_i) = \Gamma_2 \times \Gamma_4$$

If the ground state contains only doubly occupied orbitals, then it belongs to the totally symmetric representation.

All doubly occupied orbitals can be ignored when determining the representation of an excited electronic state.

Note: It is conventional to use small letters (e.g. a_{1g}) to characterize the representation of individual MOs and large capital letters (e.g. A_{1g}) to characterize the representation of the total wavefunction.

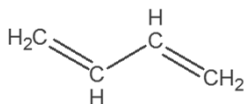
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Part B: Applications of Symmetry

- UV/Visible Absorption Selection Rules
- **Application to Butadiene**
- Application to Carbene
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Application to Butadiene

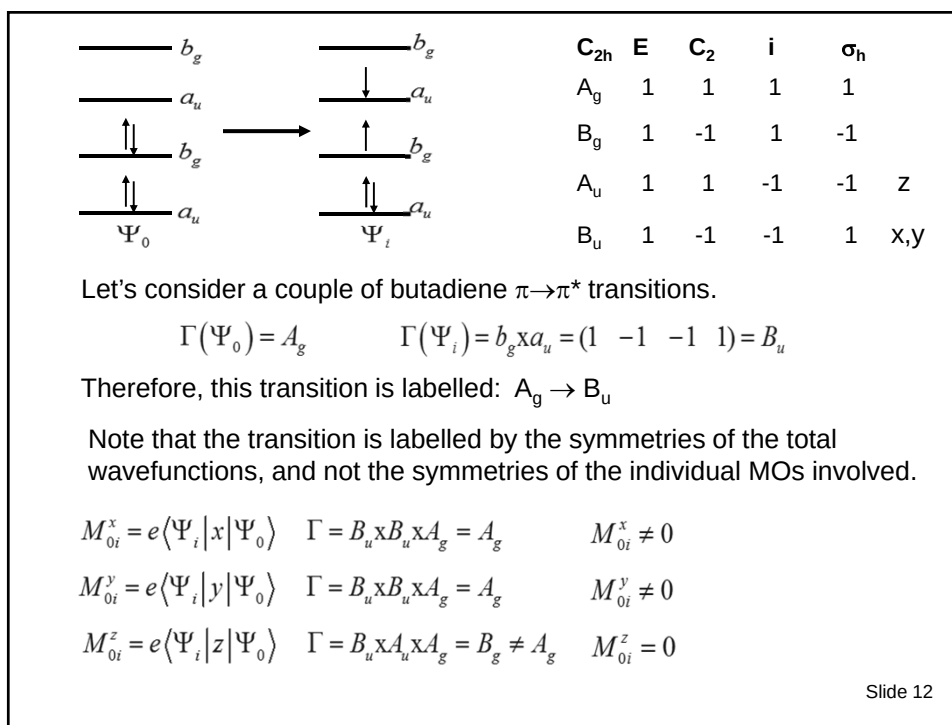
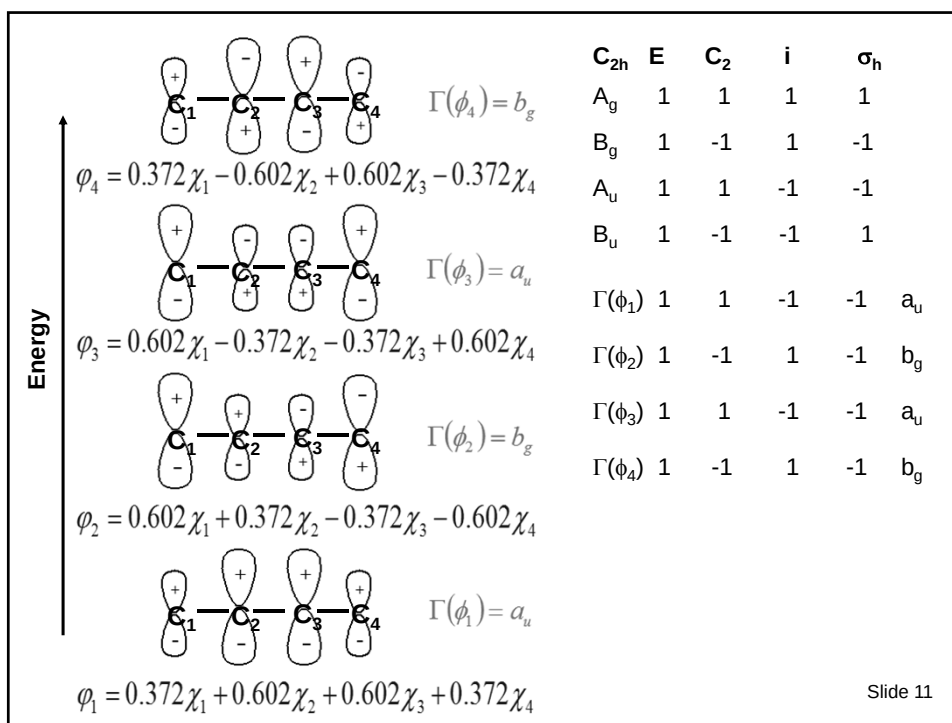


C_{2h}	E	C_2	i	σ_h
A_g	1	1	1	1
B_g	1	-1	1	-1
A_u	1	1	-1	-1
B_u	1	-1	-1	1

Trans 1,3-butadiene belongs to the C_{2h} point group.

The four Hückel orbitals were developed in earlier in this chapter.

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Polarization of Electronic Transitions

$\text{--- } b_g$	$\text{--- } b_g$	C_{2h}	E	C_2	i	σ_h
$\text{--- } a_u$	$\downarrow$	A_g	1	1	1	1
$\uparrow\downarrow$	$\uparrow$	B_g	1	-1	1	-1
$\text{--- } b_g$	$\text{--- } b_g$	A_u	1	1	-1	-1
$\uparrow\downarrow$	$\uparrow\downarrow$	B_u	1	-1	-1	1
Ψ_0	Ψ_i					z
						x,y

$$M_{0i}^x \neq 0 \quad \text{Note that } M_{0i}^z = 0.$$

$$M_{0i}^y \neq 0 \quad \text{Consider a single crystal of butadiene}$$

$$M_{0i}^z = 0 \quad \text{(not likely for this molecule)}$$

If incoming light is polarized along the z-axis (C_2), it will **not** be absorbed.

Therefore, the polarization of this transition is Perpendicular

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$\text{--- } b_g$	$\text{--- } b_g$	C_{2h}	E	C_2	i	σ_h
$\text{--- } a_u$	$\downarrow$	A_g	1	1	1	1
$\uparrow\downarrow$	$\uparrow$	B_g	1	-1	1	-1
$\text{--- } b_g$	$\text{--- } b_g$	A_u	1	1	-1	-1
$\uparrow\downarrow$	$\uparrow\downarrow$	B_u	1	-1	-1	1
Ψ_0	Ψ_i					z
						x,y

Let's consider a second butadiene $\pi \rightarrow \pi^*$ transition.

$$\Gamma(\Psi_0) = A_g \quad \Gamma(\Psi_i) = b_g \times b_g = (1 \ 1 \ 1 \ 1) = A_g$$

Therefore, this transition is labelled: $A_g \rightarrow A_g$

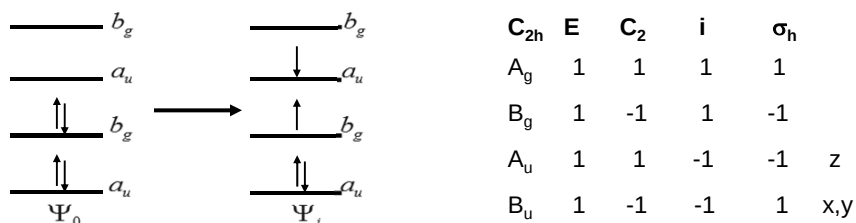
$$M_{0i}^x = e \langle \Psi_i | x | \Psi_0 \rangle \quad \Gamma = A_g \times B_u \times A_g = B_u \neq A_g \quad M_{0i}^x = 0$$

$$M_{0i}^y = e \langle \Psi_i | y | \Psi_0 \rangle \quad \Gamma = A_g \times B_u \times A_g = B_u \neq A_g \quad M_{0i}^y = 0$$

$$M_{0i}^z = e \langle \Psi_i | z | \Psi_0 \rangle \quad \Gamma = A_g \times A_u \times A_g = A_u \neq A_g \quad M_{0i}^z = 0$$

Therefore, this is **not** an allowed transition.

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$$\Gamma(\Psi_0) = A_g \quad \Gamma(\Psi_i) = b_g \times a_u = B_u$$

Back to: $A_g \rightarrow B_u$

You may have learned a shortcut in another course.

Shortcut: If the representation of the excited state is the same as x , y , or z , the transition is allowed.

Corky: Shortcuts are Nice!!!

Mookie: That's right, Corkster, except when they don't work.

Like on tests!!!

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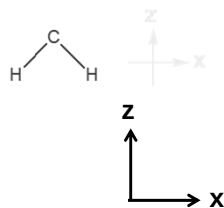
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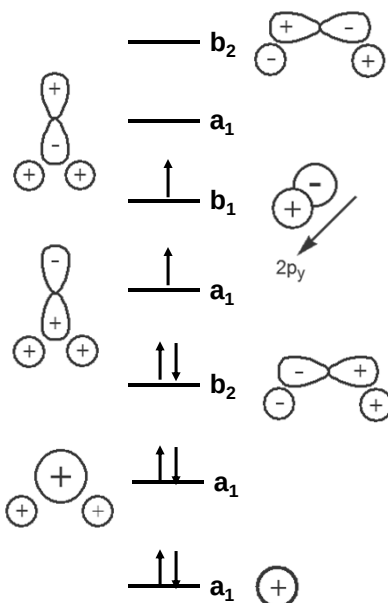
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Carbene UV Selection Rules

Carbene: 8 electrons
C_{2v} symmetry
Triplet GS



We will consider only transitions arising from the a₁ and b₁ frontier orbitals.



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		C _{2v}	E	C ₂	σ _v (xz)	σ _{v'} (yz)
Ψ_0	a_1	A ₁	1	1	1	1
	b ₁	A ₂	1	1	-1	-1
	a ₁	B ₁	1	-1	1	-1
	b ₂	B ₂	1	-1	-1	1

$$\Gamma(\Psi_0) = a_1 \times b_1 = B_1 \quad \Gamma(\Psi_i) = a_1 \times a_1 = A_1$$

Therefore, the overall transition is: B₁ → A₁

$$M_{0i}^x = e \langle \Psi_i | x | \Psi_0 \rangle \quad \Gamma = A_1 \times B_1 \times B_1 = A_1 \quad M_{0i}^x \neq 0$$

$$M_{0i}^y = e \langle \Psi_i | y | \Psi_0 \rangle \quad \Gamma = A_1 \times B_2 \times B_1 = A_2 \quad M_{0i}^y = 0$$

$$M_{0i}^z = e \langle \Psi_i | z | \Psi_0 \rangle \quad \Gamma = A_1 \times A_1 \times B_1 = B_1 \quad M_{0i}^z = 0$$

This transition is **allowed** and is polarized **perpendicular** to the principal axis.

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$\begin{array}{c} \text{--- } b_2 \\ \text{--- } a_1 \\ \uparrow \\ \text{--- } b_1 \\ \uparrow \\ \text{--- } a_1 \\ \Psi_0 \end{array}$	$\longrightarrow$	$\begin{array}{c} \text{--- } b_2 \\ \uparrow \\ \text{--- } a_1 \\ \text{--- } b_1 \\ \uparrow \\ \text{--- } a_1 \\ \Psi_i \end{array}$	C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
			A_1	1	1	1	1	z
			A_2	1	1	-1	-1	
			B_1	1	-1	1	-1	x
			B_2	1	-1	-1	1	y

$$\Gamma(\Psi_0) = a_1 \times b_1 = B_1 \quad \Gamma(\Psi_i) = a_1 \times a_1 = A_1$$

Therefore, this transition is labelled: $B_1 \rightarrow A_1$

This transition is allowed and is polarized perpendicular to the principal axis.

Corky: Right!! And the shortcut also predicts that the transition is allowed because the excited state representation (A_1) is the same as "z"

Mookie: But the shortcut predicts the wrong polarization.

Corky: Well, half right ain't bad!!

Mookie: Oy Vey!!

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$\begin{array}{c} \text{--- } b_2 \\ \text{--- } a_1 \\ \uparrow \\ \text{--- } b_1 \\ \uparrow \\ \text{--- } a_1 \\ \Psi_0 \end{array}$	$\longrightarrow$	$\begin{array}{c} \uparrow \\ \text{--- } b_2 \\ \text{--- } a_1 \\ \uparrow \\ \text{--- } b_1 \\ \text{--- } a_1 \\ \Psi_i \end{array}$	C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
			A_1	1	1	1	1	z
			A_2	1	1	-1	-1	
			B_1	1	-1	1	-1	x
			B_2	1	-1	-1	1	y

$$\Gamma(\Psi_0) = a_1 \times b_1 = B_1 \quad \Gamma(\Psi_i) = b_1 \times b_2 = A_2 \quad \text{Overall Transition: } B_1 \rightarrow A_2$$

Mookie: Okay, Corky, go ahead and use the shortcut.

Corky: Well, the excited state belongs to A_2 . Since none of x, y, or z is A_2 , the transition is forbidden. Piece of Cake!!

Mookie: If you don't mind, I'll work it the long way just to make sure.

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Ψ_0 → Ψ_i

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

$\Gamma(\Psi_0) = a_1 \times b_1 = B_1$ $\Gamma(\Psi_i) = b_1 \times b_2 = A_2$ Overall Transition: $B_1 \rightarrow A_2$

$M_{0i}^x = e \langle \Psi_i | x | \Psi_0 \rangle$ $\Gamma = A_2 \times B_1 \times B_1 = A_2$ $M_{0i}^x \neq 0$
 $M_{0i}^y = e \langle \Psi_i | y | \Psi_0 \rangle$ $\Gamma = A_2 \times B_2 \times B_1 = A_1$ $M_{0i}^y \neq 0$
 $M_{0i}^z = e \langle \Psi_i | z | \Psi_0 \rangle$ $\Gamma = A_2 \times A_1 \times B_1 = B_2$ $M_{0i}^z \neq 0$

The shortcut predicts that this is a forbidden transition.
 Actually it is allowed and is polarized perpendicular to the principal axis.

Mookie: So, Corky. What do you think of your shortcut now??
 Corky: Huh? Waddya Say?
 I didn't hear a thing you said. I was watching "Survivor".

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Use of Symmetry in MO Calculations

The molecular orbitals of a molecule must belong to (i.e. transform as) one of the irreducible representations of the point group to which the molecule belongs.

If instead of using the original atomic orbitals, If you perform a calculation with Symmetry Adapted Linear Combinations (SALCs) which belong to representations of the molecule's point group, the calculation is simplified.

Consider, for example, using SALCs, S_i , of the original atomic orbitals:

$$S_1 = \sum a_j \chi_j \quad [A_1]$$

$$S_2 = \sum b_j \chi_j \quad [A_1]$$

$$S_3 = \sum c_j \chi_j \quad [B_1]$$

$$S_4 = \sum d_j \chi_j \quad [B_1]$$

The A_1 and B_1 in brackets are the representations to which each S_i belongs.

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It can be shown from Group Theory that if one forms the Secular Determinant by using matrix elements of the S_i rather than χ_i , then the Determinant is "Block Diagonalized"

Let's say that ψ_i belongs to Γ_i and ψ_j belongs to Γ_j . Remember that the Hamiltonian belongs to A_1 (A_{1g} etc) Then the Hamiltonian matrix element is :

$$\int S_i H S_j d\tau = \int S_i(\Gamma_i) H(A_1) S_j(\Gamma_j) d\tau$$

This integral is non-zero only if the Direct Product is:

$$\Gamma_i \times \Gamma_j = A_1$$

As we learned in Chapter 5, this is true only if $\Gamma_i = \Gamma_j$;
i.e. if the two SALCs, S_i and S_j belong to the same representation.

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Let's say that a system has four SALCs, with two belonging to the A_1 and two to the B_1 representation. Then the 4x4 Secular Determinant will be "Block Diagonalized", as follows:

$$\begin{array}{c}
 \chi_1 \\
 \chi_2 \\
 \chi_3 \\
 \chi_4
 \end{array}
 \begin{vmatrix}
 H_{11}-E & H_{12} & 0 & 0 \\
 H_{12} & H_{22}-E & 0 & 0 \\
 0 & 0 & H_{33}-E & H_{34} \\
 0 & 0 & H_{34} & H_{44}-E
 \end{vmatrix} = 0
 \quad
 \begin{array}{l}
 S_1 = \sum a_j \chi_j [A_1] \\
 S_2 = \sum b_j \chi_j [A_1] \\
 S_3 = \sum c_j \chi_j [B_1] \\
 S_4 = \sum d_j \chi_j [B_1]
 \end{array}$$

It can be further shown that if a Secular Determinant is block diagonalized, then one break the determinant down into smaller determinants.

$$\begin{vmatrix}
 H_{11}-E & H_{12} \\
 H_{12} & H_{22}-E
 \end{vmatrix} = 0
 \quad \text{and} \quad
 \begin{vmatrix}
 H_{33}-E & H_{34} \\
 H_{34} & H_{44}-E
 \end{vmatrix} = 0$$

Thus, a 4x4 Secular Determinant, which requires solution of a 4th. order polynomial, has been simplified into two 2x2 Secular Determinants, which can be solved more easily.

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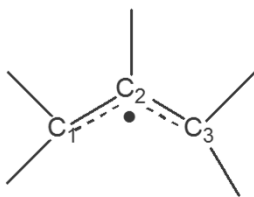
Construction of SALCs

As discussed above, if Symmetry Adapted Linear Combinations (SALCs) of atomic orbitals are used instead of the orbitals themselves, then there is a significant simplification of the Secular Determinant.

In this section, we are going to learn:

- How to determine the number of SALC's of each of the irreducible representations of the point group that can be formed from an equivalent set of atomic orbitals.
- How to generate the SALCs

We will demonstrate these methods on the Allyl Radical, which has C_{2v} symmetry.



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One can calculate the number of each type of irreducible representation (e.g. $A_1, A_2, \dots$) are contained in a reducible representation formed from a set of equivalent Atomic Orbitals.

The required formula (derived from the Great Orthogonality Theorem) is:

$$n_j = \frac{1}{h} \sum_R Tr_j(R) \cdot Tr_{Red}(R)$$

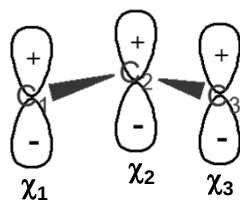
In this formula:

- R refers to one of the symmetry operations of the group.
- h is the order of the group (the number of symm. operations).
- $Tr_{red}(R)$ is the Trace (or Character) corresponding to operation R in the reduced representation.
- $Tr_j(R)$ is the Trace (or Character) corresponding to operation R in the j'th. irreducible representation.
- n_j is the number of times that the j'th. irreducible representation appears in the reducible representation

Note: The text uses the more common symbol, χ , to represent the character (or trace). However, we're already using χ to represent atomic orbitals.

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SALCs of the Allyl Radical



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

The 3 atomic p_z orbitals will form the basis for the reducible representation.

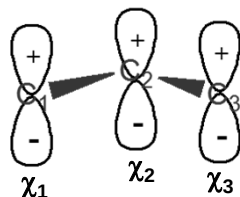
To form the reducible representation, Γ_{Red} , one performs each symmetry operation.

If the orbital is unchanged, it contributes +1 to $\text{Tr}(R)$

If the orbital changes sign, it contributes -1 to $\text{Tr}(R)$

If the orbital moves to a new atom, it contributes 0 to $\text{Tr}(R)$

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C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

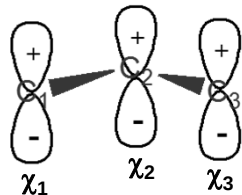
When E is applied, all 3 orbitals are unchanged: $\Gamma_{\text{Red}}(E) = +3$

When C_2 is applied, 1 and 3 exchange, 2 changes sign: $\Gamma_{\text{Red}}(C_2) = -1$

When σ_v is applied, all 3 change sign: $\Gamma_{\text{Red}}(\sigma_v) = -3$

When σ_v' is applied, 1 and 3 exchange, 2 is unchanged: $\Gamma_{\text{Red}}(\sigma_v') = +1$

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$$n_j = \frac{1}{h} \sum_R Tr_j(R) \cdot Tr_{Red}(R)$$

h=4

	C_{2V}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
A_1	1	1	1	1	1
A_2	1	1	-1	-1	-1
B_1	1	-1	1	-1	-1
B_2	1	-1	-1	1	1
Γ_{Red}	+3	-1	-3	+1	

Generate the number of times each representation appears in Γ_{Red}

$$n_{A_1} = \frac{1}{4} [1 \cdot 3 + 1 \cdot (-1) + 1 \cdot (-3) + 1 \cdot (1)] = 0$$

$$n_{A_2} = \frac{1}{4} [1 \cdot 3 + 1 \cdot (-1) + (-1) \cdot (-3) + (-1) \cdot (1)] = 1$$

$$n_{B_1} = \frac{1}{4} [1 \cdot 3 + (-1) \cdot (-1) + 1 \cdot (-3) + (-1) \cdot 1] = 0$$

$$n_{B_2} = \frac{1}{4} [1 \cdot 3 + (-1) \cdot (-1) + (-1) \cdot (-3) + (1) \cdot 1] = 2$$

$$\Gamma_{Red} = 1A_2 + 2B_2$$

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Construction of the SALCs

One uses a projection operator:

$$S(j) = N \sum_R Tr_j(R) \cdot R(\chi_i)$$

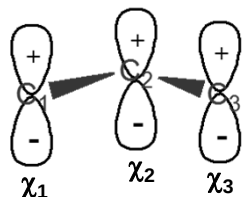
	C_{2V}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
A_1	1	1	1	1	1
A_2	1	1	-1	-1	-1
B_1	1	-1	1	-1	-1
B_2	1	-1	-1	1	1
Γ_{Red}	+3	-1	-3	+1	

$R(\chi_i)$ represents the result of operating on a (arbitrary) atomic orbital.

$Tr_j(R)$ is the trace of the j'th irreducible representation for operation R

N is the normalization constant

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$$S(j) = N \sum_R Tr_j(R) \cdot R(\chi_i)$$

A₂ SALC

C _{2v}	E	C ₂	σ _v (xz)	σ _v '(yz)
A ₁	1	1	1	1
A ₂	1	1	-1	-1
B ₁	1	-1	1	-1
B ₂	1	-1	-1	1
Γ _{Red}	+3	-1	-3	+1

$$\Gamma_{\text{Red}} = 1A_2 + 2B_2$$

We'll use χ_1 to generate the SALC

$$S_1(A_2) = N[1 \cdot E(\chi_1) + 1 \cdot C_2(\chi_1) + (-1) \cdot \sigma_v(\chi_1) + (-1) \cdot \sigma_v'(\chi_1)]$$

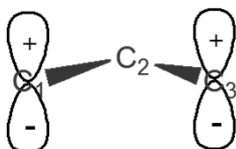
$$S_1(A_2) = N[1 \cdot \chi_1 + 1 \cdot (-\chi_3) + (-1) \cdot (-\chi_1) + (-1) \cdot \chi_3]$$

$$S_1(A_2) = N(2\chi_1 - 2\chi_3) = N(\chi_1 - \chi_3)$$

Normalized:

$$S_1(A_2) = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3)$$

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Let's demonstrate that S_1 belongs to the A₂ representation.

$$E(S_1) = E\left(\frac{1}{\sqrt{2}}(\chi_1 - \chi_3)\right) = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) = +S_1$$

$$C_2(S_1) = C_2\left(\frac{1}{\sqrt{2}}(\chi_1 - \chi_3)\right) = \frac{1}{\sqrt{2}}(-\chi_3 + \chi_1) = +S_1$$

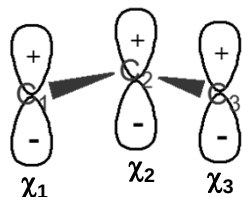
$$\sigma_v(S_1) = \sigma_v\left(\frac{1}{\sqrt{2}}(\chi_1 - \chi_3)\right) = \frac{1}{\sqrt{2}}(-\chi_1 - (-\chi_3)) = -S_1$$

$$\sigma_v'(S_1) = \sigma_v'\left(\frac{1}{\sqrt{2}}(\chi_1 - \chi_3)\right) = \frac{1}{\sqrt{2}}(\chi_3 - \chi_1) = -S_1$$

The signs on the transformed values of S_1 match those of the A₂ representation.

C _{2v}	E	C ₂	σ _v (xz)	σ _v '(yz)
A ₁	1	1	1	1
A ₂	1	1	-1	-1
B ₁	1	-1	1	-1
B ₂	1	-1	-1	1
Γ _{Red}	+3	-1	-3	+1

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$$S(j) = N \sum_R Tr_j(R) \cdot R(\chi_i)$$

B₂ SALCs

C _{2v}	E	C ₂	σ _v (xz)	σ _v '(yz)
A ₁	1	1	1	1
A ₂	1	1	-1	-1
B ₁	1	-1	1	-1
B ₂	1	-1	-1	1
Γ _{Red}	+3	-1	-3	+1

$$\Gamma_{\text{Red}} = 1A_2 + 2B_2$$

We'll use χ_1 to generate the first SALC

$$S_2(B_2) = N[1 \cdot E(\chi_1) + (-1) \cdot C_2(\chi_1) + (-1) \cdot \sigma_v(\chi_1) + 1 \cdot \sigma_v'(\chi_1)]$$

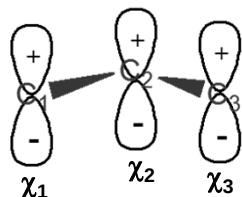
$$S_2(B_2) = N[1 \cdot \chi_1 + (-1) \cdot (-\chi_3) + (-1) \cdot (-\chi_1) + 1 \cdot \chi_3]$$

$$S_2(B_2) = N(2\chi_1 + 2\chi_3) = N(\chi_1 + \chi_3)$$

Normalized:

$$S_2(B_2) = \frac{1}{\sqrt{2}}(\chi_1 + \chi_3)$$

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$$S(j) = N \sum_R Tr_j(R) \cdot R(\chi_i)$$

B₂ SALCs

C _{2v}	E	C ₂	σ _v (xz)	σ _v '(yz)
A ₁	1	1	1	1
A ₂	1	1	-1	-1
B ₁	1	-1	1	-1
B ₂	1	-1	-1	1
Γ _{Red}	+3	-1	-3	+1

$$\Gamma_{\text{Red}} = 1A_2 + 2B_2$$

We'll use χ_2 to generate the second SALC

$$S_3(B_2) = N[1 \cdot E(\chi_2) + (-1) \cdot C_2(\chi_2) + (-1) \cdot \sigma_v(\chi_2) + 1 \cdot \sigma_v'(\chi_2)]$$

$$S_3(B_2) = N[1 \cdot \chi_2 + (-1) \cdot (-\chi_2) + (-1) \cdot (-\chi_2) + 1 \cdot \chi_2]$$

$$S_3(B_2) = 4N\chi_2$$

Normalized:

$$S_3(B_2) = \chi_2$$

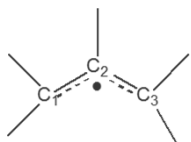
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Part B: Applications of Symmetry

- UV/Visible Absorption Selection Rules
- Application to Butadiene
- Application to Carbene
- Use of Symmetry in Simplifying MO Calculations
- Construction of SALCs: Application to the Allyl Radical
- **Solution to the Allyl Radical using SALCs**
- Application to π -Bonding in Pyrrole

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Solution for the Allyl Radical Using SALCs



Allyl belongs to the C_{2v} point group.
The plane of the molecule is the x-y plane.

The SALCs are: $S_1(A_2) = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3)$

$$S_2(B_2) = \frac{1}{\sqrt{2}}(\chi_1 + \chi_3)$$

$$S_3(B_2) = \chi_2$$

In this section, we will use the above SALCs to derive the energy levels and molecular orbitals in the Allyl radical.

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The Allyl Secular Determinant using Symmetry

$$\begin{array}{ccc}
 & S_1 & S_2 & S_3 \\
 \begin{array}{c} S_1 \\ S_2 \\ S_3 \end{array} & \begin{vmatrix} H_{11}-E & H_{12} & H_{13} \\ H_{12} & H_{22}-E & H_{23} \\ H_{13} & H_{23} & H_{33}-E \end{vmatrix} & = 0
 \end{array}
 \quad
 \begin{array}{l}
 S_1 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \quad [A_2] \\
 S_2 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_3) \quad [B_2] \\
 S_3 = \chi_2 \quad [B_2]
 \end{array}$$

Matrix Elements

$$\begin{aligned}
 H_{11} &= \langle S_1 | H | S_1 \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \left| H \right| \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \right\rangle \\
 H_{11} &= \frac{1}{2}(\langle \chi_1 | H | \chi_1 \rangle - \langle \chi_1 | H | \chi_3 \rangle - \langle \chi_3 | H | \chi_1 \rangle + \langle \chi_3 | H | \chi_3 \rangle) \\
 \boxed{H_{11} = \frac{1}{2}(\alpha - 0 - 0 + \alpha) = \alpha}
 \end{aligned}$$

$$\begin{aligned}
 H_{22} &= \langle S_2 | H | S_2 \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_1 + \chi_3) \left| H \right| \frac{1}{\sqrt{2}}(\chi_1 + \chi_3) \right\rangle \\
 H_{22} &= \frac{1}{2}(\langle \chi_1 | H | \chi_1 \rangle + \langle \chi_1 | H | \chi_3 \rangle + \langle \chi_3 | H | \chi_1 \rangle + \langle \chi_3 | H | \chi_3 \rangle) \\
 \boxed{H_{22} = \frac{1}{2}(\alpha + 0 + 0 + \alpha) = \alpha}
 \end{aligned}$$

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Matrix Elements (Cont'd.)

$$\begin{array}{ccc}
 & S_1 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \quad [A_2] \\
 & S_2 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_3) \quad [B_2] \\
 & S_3 = \chi_2 \quad [B_2]
 \end{array}$$

$$\boxed{H_{33} = \langle S_3 | H | S_3 \rangle = \langle \chi_2 | H | \chi_2 \rangle = \alpha}$$

$$\begin{aligned}
 H_{12} &= \langle S_1 | H | S_2 \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \left| H \right| \frac{1}{\sqrt{2}}(\chi_1 + \chi_3) \right\rangle \\
 H_{12} &= \frac{1}{2}(\langle \chi_1 | H | \chi_1 \rangle + \langle \chi_1 | H | \chi_3 \rangle - \langle \chi_3 | H | \chi_1 \rangle - \langle \chi_3 | H | \chi_3 \rangle) \\
 \boxed{H_{12} = \frac{1}{2}(\alpha + 0 - 0 - \alpha) = 0}
 \end{aligned}$$

$$\begin{aligned}
 H_{13} &= \langle S_1 | H | S_3 \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \left| H \right| \chi_2 \right\rangle \\
 H_{13} &= \frac{1}{\sqrt{2}}(\langle \chi_1 | H | \chi_2 \rangle - \langle \chi_3 | H | \chi_2 \rangle) \\
 \boxed{H_{13} = \frac{1}{\sqrt{2}}(\beta - \beta) = 0}
 \end{aligned}$$

$$\begin{aligned}
 H_{23} &= \langle S_2 | H | S_3 \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_1 + \chi_3) \left| H \right| \chi_2 \right\rangle \\
 H_{23} &= \frac{1}{\sqrt{2}}(\langle \chi_1 | H | \chi_2 \rangle + \langle \chi_3 | H | \chi_2 \rangle) \\
 \boxed{H_{23} = \frac{1}{\sqrt{2}}(\beta + \beta) = \frac{2}{\sqrt{2}}\beta = \sqrt{2}\beta}
 \end{aligned}$$

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$$\begin{aligned}
 S_1 &= \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \quad [A_2] \\
 S_2 &= \frac{1}{\sqrt{2}}(\chi_1 + \chi_3) \quad [B_2] \\
 S_3 &= \chi_2 \quad [B_2]
 \end{aligned}$$

$$\begin{vmatrix} S_1 & S_2 & S_3 \\ H_{11} - E & H_{12} & H_{13} \\ S_2 & H_{22} - E & H_{23} \\ S_3 & H_{13} & H_{33} - E \end{vmatrix} = 0$$

$$\begin{vmatrix} \alpha - E & 0 & 0 \\ 0 & \alpha - E & \sqrt{2}\beta \\ 0 & \sqrt{2}\beta & \alpha - E \end{vmatrix} = 0$$

A₂ "block"

B₂ block

Divide by β

Define $x = \frac{\alpha - E}{\beta}$

$$\begin{vmatrix} x & 0 & 0 \\ 0 & x & \sqrt{2} \\ 0 & \sqrt{2} & x \end{vmatrix} = 0$$

A₂ "block"

B₂ block

A₂ "Block"

$$x = 0 = \frac{\alpha - E}{\beta} \longrightarrow E_a = \alpha \quad [= E_2]$$

$$\varphi_a = S_1 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \quad [= \varphi_2]$$

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$$\begin{vmatrix} x & 0 & 0 \\ 0 & x & \sqrt{2} \\ 0 & \sqrt{2} & x \end{vmatrix} = 0$$

A₂ "block"

B₂ block

B₂ Block

$$\begin{vmatrix} x & \sqrt{2} \\ \sqrt{2} & x \end{vmatrix} = 0 \longrightarrow x^2 - 2 = 0 \longrightarrow \begin{matrix} x_b = -\sqrt{2} \\ x_c = +\sqrt{2} \end{matrix}$$

$x_b = -\sqrt{2} = \frac{\alpha - E_b}{\beta} \longrightarrow E_b = \alpha + \sqrt{2}\beta \quad [= E_1]$

$x_c = +\sqrt{2} = \frac{\alpha - E_c}{\beta} \longrightarrow E_c = \alpha - \sqrt{2}\beta \quad [= E_3]$

B₂ Wavefunctions

$$\begin{aligned}
 \varphi_b &= \varphi_1 = c_b [S_2 + S_3] \\
 \varphi_b &= \varphi_1 = c_b \left[\frac{1}{\sqrt{2}}(\chi_1 + \chi_3) + \chi_2 \right] \\
 \varphi_b &= \varphi_1 = c' [\chi_1 + \sqrt{2}\chi_2 + \chi_3] \\
 \varphi_b &= \varphi_1 = \frac{1}{2} [\chi_1 + \sqrt{2}\chi_2 + \chi_3]
 \end{aligned}$$

Similarly

$$\begin{aligned}
 \varphi_c &= \varphi_3 = c_c [S_2 - S_3] \\
 \varphi_c &= \varphi_3 = c_b \left[\frac{1}{\sqrt{2}}(\chi_1 + \chi_3) - \chi_2 \right] \\
 \varphi_c &= \varphi_3 = c' [\chi_1 - \sqrt{2}\chi_2 + \chi_3] \\
 \varphi_c &= \varphi_3 = \frac{1}{2} [\chi_1 - \sqrt{2}\chi_2 + \chi_3]
 \end{aligned}$$

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Allyl with Symmetry: Summary

$$S_1 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \quad [A_2]$$

$$S_2 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_3) \quad [B_2]$$

$$S_3 = \chi_2 \quad [B_2]$$

$$\begin{array}{ccc|c} \text{"block"} & & & \\ \hline x & 0 & 0 & \\ \hline 0 & x & \sqrt{2} & \\ \hline 0 & \sqrt{2} & x & \\ \hline \end{array} = 0$$

B_2
block

A_2 Block

$$x = 0 = \frac{\alpha - E}{\beta}$$

$$E_a = \alpha \quad [=E_2]$$

$$\varphi_a = S_1 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \quad [= \varphi_2]$$

B_2 Block

$$\begin{vmatrix} x & \sqrt{2} \\ \sqrt{2} & x \end{vmatrix} = 0 \rightarrow \begin{array}{l} x_b = -\sqrt{2} \\ x_c = +\sqrt{2} \end{array}$$

$$x_b = -\sqrt{2} = \frac{\alpha - E_b}{\beta}$$

$$E_b = \alpha + \sqrt{2}\beta \quad [=E_1]$$

$$\varphi_b = \varphi_1 = \frac{1}{2}[\chi_1 + \sqrt{2}\chi_2 + \chi_3]$$

$$x_c = -\sqrt{2} = \frac{\alpha - E_c}{\beta}$$

$$E_c = \alpha - \sqrt{2}\beta \quad [=E_3]$$

$$\varphi_c = \varphi_3 = \frac{1}{2}[\chi_1 - \sqrt{2}\chi_2 + \chi_3]$$

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Part B: Applications of Symmetry

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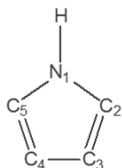
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Example: π Bonding in Pyrrole

This will illustrate how a heteroatom is handled as well as provide another example of the use of symmetry.

The calculations are worked out in detail in the slides below.

I'll just outline the procedure (relatively quickly), but the slides will provide you with another worked out example.



For pyrrole, 2 electrons are donated to the π system.

The heteroatom parameters are: $h_N = 1.5$ and $k_N = 0.8$

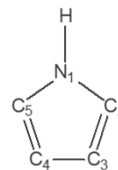
Therefore: $\alpha_N = \alpha + h_N \beta = \alpha + 1.5\beta$

$$\beta_N = k_N \beta = 0.8\beta$$

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A partial Character Table for the C_{2v} point group is:

	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
A_2	1	1	-1	-1
B_2	1	-1	-1	1



The 5 SALCs belong to the A_2 and B_2 representations.

$$S_a = \frac{1}{\sqrt{2}}(\chi_2 - \chi_5) \quad [A_2]$$

$$S_c = \frac{1}{\sqrt{2}}(\chi_2 + \chi_5) \quad [B_2]$$

$$S_b = \frac{1}{\sqrt{2}}(\chi_3 - \chi_4) \quad [A_2]$$

$$S_d = \frac{1}{\sqrt{2}}(\chi_3 + \chi_4) \quad [B_2]$$

$$S_e = \chi_1 \quad [B_2]$$

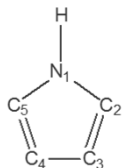
We'll demonstrate (on the board) that S_a belongs to the A_2 and S_c to the B_2 representation.

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A₂ Block

$$\alpha_N = \alpha + 1.5\beta$$

$$\beta_N = 0.8\beta$$



$$S_a = \frac{1}{\sqrt{2}}(\chi_2 - \chi_5) \quad [A_2]$$

$$S_b = \frac{1}{\sqrt{2}}(\chi_3 - \chi_4) \quad [A_2]$$

$$\begin{vmatrix} H_{aa} - E & H_{ab} \\ H_{ab} & H_{bb} - E \end{vmatrix} = 0$$

$$H_{aa} = \langle S_a | H | S_a \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_2 - \chi_5) \left| H \right| \frac{1}{\sqrt{2}}(\chi_2 - \chi_5) \right\rangle$$

$$H_{aa} = \frac{1}{2} [\langle \chi_2 | H | \chi_2 \rangle - \langle \chi_2 | H | \chi_5 \rangle - \langle \chi_5 | H | \chi_2 \rangle + \langle \chi_5 | H | \chi_5 \rangle]$$

$$H_{aa} = \frac{1}{2} [\alpha - 0 - 0 + \alpha] = \alpha$$

$$H_{bb} = \langle S_b | H | S_b \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_3 - \chi_4) \left| H \right| \frac{1}{\sqrt{2}}(\chi_3 - \chi_4) \right\rangle$$

$$H_{bb} = \frac{1}{2} [\langle \chi_3 | H | \chi_3 \rangle - \langle \chi_3 | H | \chi_4 \rangle - \langle \chi_4 | H | \chi_3 \rangle + \langle \chi_4 | H | \chi_4 \rangle]$$

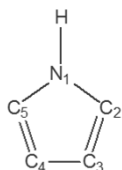
$$H_{bb} = \frac{1}{2} [\alpha - \beta - \beta + \alpha] = \alpha - \beta$$

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A₂ Block

$$\alpha_N = \alpha + 1.5\beta$$

$$\beta_N = 0.8\beta$$



$$S_a = \frac{1}{\sqrt{2}}(\chi_2 - \chi_5) \quad [A_2]$$

$$S_b = \frac{1}{\sqrt{2}}(\chi_3 - \chi_4) \quad [A_2]$$

$$\begin{vmatrix} H_{aa} - E & H_{ab} \\ H_{ab} & H_{bb} - E \end{vmatrix} = 0$$

$$H_{ab} = \langle S_a | H | S_b \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_2 - \chi_5) \left| H \right| \frac{1}{\sqrt{2}}(\chi_3 - \chi_4) \right\rangle$$

$$H_{ab} = \frac{1}{2} [\langle \chi_2 | H | \chi_3 \rangle - \langle \chi_2 | H | \chi_4 \rangle - \langle \chi_5 | H | \chi_3 \rangle + \langle \chi_5 | H | \chi_4 \rangle]$$

$$H_{ab} = \frac{1}{2} [\beta - 0 - 0 + \beta] = \beta$$

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A₂ Block

$$H_{aa} = \alpha$$

$$H_{bb} = \alpha - \beta$$

$$H_{ab} = \beta$$

$$\begin{vmatrix} H_{aa} - E & H_{ab} \\ H_{ab} & H_{bb} - E \end{vmatrix} = 0 \longrightarrow \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - \beta - E \end{vmatrix} = 0$$

$$\begin{vmatrix} x & 1 \\ 1 & x-1 \end{vmatrix} = 0 \quad \text{where} \quad x = \frac{\alpha - E}{\beta}$$

$$x^2 - x - 1 = 0 \longrightarrow x = \frac{1 \pm \sqrt{(-1)^2 - 4(1)(-1)}}{2} = \frac{1 \pm \sqrt{5}}{2} = \frac{1 \pm 2.236}{2}$$

I will name the energies $E_r, E_s, \dots$ so that I can renumber them according to order of increasing energy at the end of the problem.

$$x_r = \frac{1 - 2.236}{2} = -0.618 = \frac{\alpha - E_r}{\beta} \quad x_s = \frac{1 + 2.236}{2} = +1.618 = \frac{\alpha - E_s}{\beta}$$

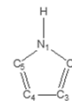
$$E_r = \alpha + 0.618\beta$$

$$E_s = \alpha - 1.618\beta$$

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A₂ Block

Wavefunctions



$$S_a = \frac{1}{\sqrt{2}}(\chi_2 - \chi_3) \quad [A_2]$$

$$S_b = \frac{1}{\sqrt{2}}(\chi_3 - \chi_4) \quad [A_2]$$

$$\varphi = c_a S_a + c_b S_b + \begin{vmatrix} x & 1 \\ 1 & x-1 \end{vmatrix} = 0 \longrightarrow \begin{matrix} xc_a + c_b = 0 \\ c_a + (x-1)c_b = 0 \end{matrix} \longrightarrow \begin{matrix} c_b = -xc_a \\ c_b = -\frac{c_a}{x-1} \end{matrix}$$

$$x_r = -0.618 \longrightarrow c_b = +0.618c_a \longrightarrow \varphi_r = c_a (S_a + 0.618S_b)$$

$$\varphi_r = c_a \left(\frac{1}{\sqrt{2}}[\chi_2 - \chi_3] + 0.618 \frac{1}{\sqrt{2}}[\chi_3 - \chi_4] \right) = c_a (0.707\chi_2 + 0.437\chi_3 - 0.437\chi_4 - 0.707\chi_5)$$

$$\text{Normalization: } c_a = \frac{1}{\sqrt{(0.707)^2 + (0.437)^2 + (-0.437)^2 + (-0.707)^2}} = 0.851$$

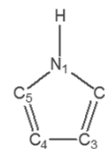
$$\varphi_r = 0.602\chi_2 + 0.372\chi_3 - 0.372\chi_4 - 0.602\chi_5$$

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$$S_a = \frac{1}{\sqrt{2}}(\chi_2 - \chi_5) \quad [A_2]$$

$$S_b = \frac{1}{\sqrt{2}}(\chi_3 - \chi_4) \quad [A_2]$$

A₂ Block



$$x_s = +1.618$$

$$E_r = \alpha - 1.618\beta$$

Analogously



$$\varphi_s = 0.372\chi_2 - 0.602\chi_3 + 0.602\chi_4 - 0.372\chi_5$$

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B₂ Block

$$\alpha_N = \alpha + 1.5\beta$$

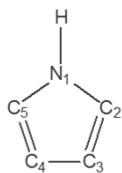
$$\beta_N = 0.8\beta$$

$$S_c = \frac{1}{\sqrt{2}}(\chi_2 + \chi_5) \quad [B_2]$$

$$S_d = \frac{1}{\sqrt{2}}(\chi_3 + \chi_4) \quad [B_2]$$

$$S_e = \chi_1 \quad [B_2]$$

$$\begin{vmatrix} H_{cc} - E & H_{cd} & H_{ce} \\ H_{cd} & H_{dd} - E & H_{de} \\ H_{ce} & H_{de} & H_{ee} - E \end{vmatrix} = 0$$



$$H_{cc} = \langle S_c | H | S_c \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_2 + \chi_5) \left| H \right| \frac{1}{\sqrt{2}}(\chi_2 + \chi_5) \right\rangle$$

$$H_{cc} = \frac{1}{2} [\langle \chi_2 | H | \chi_2 \rangle + \langle \chi_2 | H | \chi_5 \rangle + \langle \chi_5 | H | \chi_2 \rangle + \langle \chi_5 | H | \chi_5 \rangle]$$

$$H_{cc} = \frac{1}{2} [\alpha + 0 + 0 + \alpha] = \alpha$$

$$H_{dd} = \langle S_d | H | S_d \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_3 + \chi_4) \left| H \right| \frac{1}{\sqrt{2}}(\chi_3 + \chi_4) \right\rangle$$

$$H_{dd} = \frac{1}{2} [\langle \chi_3 | H | \chi_3 \rangle + \langle \chi_3 | H | \chi_4 \rangle + \langle \chi_4 | H | \chi_3 \rangle + \langle \chi_4 | H | \chi_4 \rangle]$$

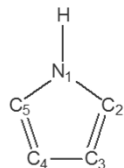
$$H_{dd} = \frac{1}{2} [\alpha + \beta + \beta + \alpha] = \alpha + \beta$$

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B₂ Block

$$\alpha_N = \alpha + 1.5\beta$$

$$\beta_N = 0.8\beta$$



$$S_c = \frac{1}{\sqrt{2}}(\chi_2 + \chi_5) \quad [B_2]$$

$$S_d = \frac{1}{\sqrt{2}}(\chi_3 + \chi_4) \quad [B_2]$$

$$S_e = \chi_1 \quad [B_2]$$

$$\begin{vmatrix} H_{cc} - E & H_{cd} & H_{ce} \\ H_{cd} & H_{dd} - E & H_{de} \\ H_{ce} & H_{de} & H_{ee} - E \end{vmatrix} = 0$$

$$H_{ee} = \langle S_e | H | S_e \rangle = \langle \chi_1 | H | \chi_1 \rangle$$

$$H_{ee} = \alpha_N = \alpha + 1.5\beta$$

$$H_{cd} = \langle S_c | H | S_d \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_2 + \chi_5) \left| H \right| \frac{1}{\sqrt{2}}(\chi_3 + \chi_4) \right\rangle$$

$$H_{cd} = \frac{1}{2} [\langle \chi_2 | H | \chi_3 \rangle + \langle \chi_2 | H | \chi_4 \rangle + \langle \chi_5 | H | \chi_3 \rangle + \langle \chi_5 | H | \chi_4 \rangle]$$

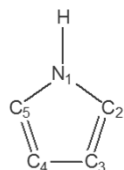
$$H_{cd} = \frac{1}{2} [\beta + 0 + 0 + \beta] = \beta$$

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B₂ Block

$$\alpha_N = \alpha + 1.5\beta$$

$$\beta_N = 0.8\beta$$



$$S_c = \frac{1}{\sqrt{2}}(\chi_2 + \chi_5) \quad [B_2]$$

$$S_d = \frac{1}{\sqrt{2}}(\chi_3 + \chi_4) \quad [B_2]$$

$$S_e = \chi_1 \quad [B_2]$$

$$\begin{vmatrix} H_{cc} - E & H_{cd} & H_{ce} \\ H_{cd} & H_{dd} - E & H_{de} \\ H_{ce} & H_{de} & H_{ee} - E \end{vmatrix} = 0$$

$$H_{ce} = \langle S_c | H | S_e \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_2 + \chi_5) \left| H \right| \chi_1 \right\rangle = \frac{1}{\sqrt{2}} (\langle \chi_2 | H | \chi_1 \rangle + \langle \chi_5 | H | \chi_1 \rangle)$$

$$H_{ce} = \frac{1}{\sqrt{2}} (\beta_N + \beta_N) = \sqrt{2}\beta_N = \sqrt{2} \cdot 0.8\beta = 1.131\beta$$

$$H_{de} = \langle S_d | H | S_e \rangle = \left\langle \frac{1}{\sqrt{2}}(\chi_3 + \chi_4) \left| H \right| \chi_1 \right\rangle = \frac{1}{\sqrt{2}} (\langle \chi_3 | H | \chi_1 \rangle + \langle \chi_4 | H | \chi_1 \rangle) = 0$$

$$H_{de} = \frac{1}{\sqrt{2}} (0 + 0) = 0$$

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$$\begin{aligned}
 H_{cc} &= \alpha \\
 H_{dd} &= \alpha + \beta \\
 H_{ee} &= \alpha + 1.5\beta \\
 H_{cd} &= \beta \\
 H_{ce} &= 1.131\beta \\
 H_{de} &= 0
 \end{aligned}$$

$$\begin{vmatrix} H_{cc} - E & H_{cd} & H_{ce} \\ H_{cd} & H_{dd} - E & H_{de} \\ H_{ce} & H_{de} & H_{ee} - E \end{vmatrix} = 0 \longrightarrow \begin{vmatrix} \alpha - E & \beta & 1.131\beta \\ \beta & \alpha + \beta - E & 0 \\ 1.131\beta & 0 & \alpha + 1.5\beta - E \end{vmatrix} = 0$$

$$\begin{vmatrix} x & 1 & 1.131 \\ 1 & x+1 & 0 \\ 1.131 & 0 & x+1.5 \end{vmatrix} = 0 \quad \text{where} \quad x = \frac{\alpha - E}{\beta}$$

$$x \begin{vmatrix} x+1 & 0 \\ 0 & x+1.5 \end{vmatrix} - 1 \begin{vmatrix} 1 & 0 \\ 1.131 & x+1.5 \end{vmatrix} + 1.131 \begin{vmatrix} 1 & x+1 \\ 1.131 & 0 \end{vmatrix} = 0$$

$$x[(x+1)(x+1.5) - 0] - 1[x+1.5 - 0] + 1.131[0 - 1.131(x+1)] = 0$$

↓ Reduces to

$$x^3 + 2.5x^2 - 0.779x - 2.779 = 0$$

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B₂ Block

$$x^3 + 2.5x^2 - 0.779x - 2.779 = 0$$

This cubic equation can be solved numerically to yield the roots,
 $x = -2.320, -1.189, +1.008$

Remember that we're initially naming our roots (and wavefunctions) r, s (A_2) and t, u, v (B_2). We'll put them in numerical order according to increasing energy at the end.

$$x_t = -2.320 = \frac{\alpha - E_t}{\beta} \quad x_u = -1.189 = \frac{\alpha - E_u}{\beta} \quad x_v = +1.008 = \frac{\alpha - E_v}{\beta}$$

$E_t = \alpha + 2.320\beta$

$E_u = \alpha + 1.189\beta$

$E_v = \alpha - 1.008\beta$

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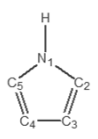
$$S_c = \frac{1}{\sqrt{2}}(\chi_2 + \chi_5) \quad [B_2]$$

$$S_d = \frac{1}{\sqrt{2}}(\chi_3 + \chi_4) \quad [B_2]$$

$$S_e = \chi_1 \quad [B_2]$$

B₂ Block

Wavefunctions



$$\varphi = c_c S_c + c_d S_d + c_e S_e + \begin{vmatrix} x & 1 & 1.131 \\ 1 & x+1 & 0 \\ 1.131 & 0 & x+1.5 \end{vmatrix} = 0 \longrightarrow \begin{aligned} xc_c + c_d + 1.131c_e &= 0 \\ c_c + (x+1)c_d &= 0 \\ 1.131c_c + (x+1.5)c_e &= 0 \end{aligned}$$

$$c_d = -\frac{c_c}{x+1} \quad \text{From Second Eqn.}$$

$$c_e = -\frac{1.131c_c}{x+1.5} \quad \text{From Third Eqn.}$$

$$x_t = -2.320$$

$$E_t = \alpha + 2.320\beta$$

$$c_d = -\frac{c_c}{-2.320+1} = +0.758c_c$$

$$c_e = -\frac{1.131c_c}{-2.320+1.5} = 1.379c_c$$

$$\varphi_t = c_c (S_c + 0.758S_d + 1.379S_e)$$

$$\varphi_t = c_c \left(\frac{1}{\sqrt{2}}[\chi_2 + \chi_5] + 0.758 \frac{1}{\sqrt{2}}[\chi_3 + \chi_4] + 1.379\chi_1 \right)$$

$$\varphi_t = c_c (1.379\chi_1 + 0.707\chi_2 + 0.536\chi_3 + 0.536\chi_4 + 0.707\chi_5)$$

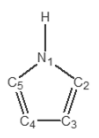
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$$S_c = \frac{1}{\sqrt{2}}(\chi_2 + \chi_5) \quad [B_2]$$

$$S_d = \frac{1}{\sqrt{2}}(\chi_3 + \chi_4) \quad [B_2]$$

$$S_e = \chi_1 \quad [B_2]$$

B₂ Block



$$\varphi_t = c_c (1.379\chi_1 + 0.707\chi_2 + 0.536\chi_3 + 0.536\chi_4 + 0.707\chi_5)$$

Normalization: $c_c = \frac{1}{\sqrt{(1.379)^2 + (0.707)^2 + (0.536)^2 + (0.536)^2 + (0.707)^2}} = 0.536$

$$\varphi_t = 0.725\chi_1 + 0.379\chi_2 + 0.287\chi_3 + 0.287\chi_4 + 0.379\chi_5$$

$$x_u = -1.189$$

$$E_u = \alpha + 1.189\beta$$

$$x_v = +1.008$$

$$E_v = \alpha - 1.008\beta$$

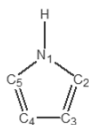
Analogously ↓

$$\varphi_u = 0.530\chi_1 - 0.111\chi_2 - 0.589\chi_3 - 0.589\chi_4 - 0.111\chi_5$$

Analogously ↓

$$\varphi_v = 0.374\chi_1 - 0.587\chi_2 + 0.292\chi_3 + 0.292\chi_4 - 0.587\chi_5$$

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Wavefunctions and Energies

$$\overline{E_5 = E_s = \alpha - 1.618\beta} \quad \varphi_s = \varphi_s = 0.372\chi_2 - 0.602\chi_3 + 0.602\chi_4 - 0.372\chi_5$$

$$\overline{E_4 = E_v = \alpha - 1.008\beta} \quad \varphi_4 = \varphi_v = 0.374\chi_1 - 0.587\chi_2 + 0.292\chi_3 + 0.292\chi_4 - 0.587\chi_5$$

$$\begin{array}{c} \uparrow \downarrow \\ \overline{E_3 = E_r = \alpha + 0.618\beta} \end{array} \quad \varphi_3 = \varphi_r = 0.602\chi_2 + 0.372\chi_3 - 0.372\chi_4 - 0.602\chi_5$$

$$\begin{array}{c} \uparrow \downarrow \\ \overline{E_2 = E_u = \alpha + 1.189\beta} \end{array} \quad \varphi_2 = \varphi_u = 0.530\chi_1 - 0.111\chi_2 - 0.589\chi_3 - 0.589\chi_4 - 0.111\chi_5$$

$$\begin{array}{c} \uparrow \downarrow \\ \overline{E_1 = E_t = \alpha + 2.320\beta} \end{array} \quad \varphi_1 = \varphi_t = 0.725\chi_1 + 0.379\chi_2 + 0.287\chi_3 + 0.287\chi_4 + 0.379\chi_5$$

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