CHAPTER 10
SEMIEMPIRICAL METHODS AND APPLICATIONS OF SYMMETRY
OUTLINE

Homework Questions Attached

PART A: The Hückel Model and other Semiempirical Methods

<table>
<thead>
<tr>
<th>SECT</th>
<th>TOPIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Hückel Molecular Orbital Model</td>
</tr>
<tr>
<td>2.</td>
<td>Application to Ethylene</td>
</tr>
<tr>
<td>3.</td>
<td>Application to the Allyl Radical (C₃H₅•)</td>
</tr>
<tr>
<td>4.</td>
<td>π Electron Charge and π Bond Order</td>
</tr>
<tr>
<td>5.</td>
<td>Application to Butadiene</td>
</tr>
<tr>
<td>6.</td>
<td>Introduction to Heteroatoms</td>
</tr>
<tr>
<td>7.</td>
<td>Semiempirical Methods for Sigma Bonded Systems</td>
</tr>
</tbody>
</table>

PART B: Applications of Symmetry

<table>
<thead>
<tr>
<th>SECT</th>
<th>TOPIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>UV/Visible Absorption Selection Rules</td>
</tr>
<tr>
<td>2.</td>
<td>Application to Butadiene</td>
</tr>
<tr>
<td>3.</td>
<td>Application to Carbene</td>
</tr>
<tr>
<td>4.</td>
<td>Use of Symmetry in Simplifying MO Calculations</td>
</tr>
<tr>
<td>5.</td>
<td>Construction of SALCs: Application to the Allyl Radical</td>
</tr>
<tr>
<td>6.</td>
<td>Solution to the Allyl Radical Using SALCs</td>
</tr>
<tr>
<td>7.</td>
<td>Application to π-Bonding in Pyrrole</td>
</tr>
</tbody>
</table>
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) \( \alpha, \beta \) and \( E \), (ii) \( x = (\alpha - E)/\beta \)

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

   (a) Square cyclobutadiene

   \[
   \begin{array}{c}
   \text{C}_1 \\
   \text{C}_2 \\
   \text{C}_3 \\
   \text{C}_4 \\
   \end{array}
   \]

   (b) Trimethylenemethane

   This is a diradical species.

   I’ve drawn one of 3 resonance forms

   \[
   \begin{array}{c}
   \text{C}_1 \\
   \text{C}_2 \\
   \text{C}_4 \\
   \text{C}_3 \cdot \\
   \end{array}
   \]

   (c) Acrolein

   \[
   \begin{array}{c}
   \text{C}_1 \\
   \text{C}_2 \\
   \text{C}_3 \\
   \text{O}_4 \\
   \end{array}
   \]

   (d) Furan

   \[
   \begin{array}{c}
   \text{C}_1 \\
   \text{O}_5 \\
   \text{C}_3 \\
   \text{C}_2 \\
   \text{C}_4 \\
   \end{array}
   \]

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.

   \textbf{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:

\[
\begin{align*}
\phi_1 &= c_1 (\chi_1 + \chi_2 + \chi_3 + \chi_4) \\
\phi_2 &= c_1 (\chi_1 - \chi_3) \\
\phi_3 &= c_2 (\chi_2 - \chi_4) \\
\phi_4 &= c_1 (\chi_1 - \chi_2 + \chi_3 - \chi_4)
\end{align*}
\]

Determine the normalized molecular orbitals.

(c) Calculate the total \(\pi\) energy and the Delocalization energy.

(d) Calculate the \(\pi\) electron charge for each atom.

(e) Calculate the \(\pi\) bond order for each bond.

4. Consider 1,3-butadiene: \[\overset{C_1}{\underset{C_2}{-}} \overset{C_3}{\underset{C_4}{-}}\]

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 \(\pi\) energy and the Delocalization energy.

(e) Calculate the \(\pi\) electron charge for each atom.

(f) Calculate the \(\pi\) 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 \(\pi\) electron charge on each atom.

(b) Calculate the \(\pi\) bond order for each bond.
PART B: Applications of Symmetry

6. Methylene cyclopropene belongs to the $C_{2v}$ point group.

\[
\begin{array}{cccccc}
C_{2v} & E & C_2 & \sigma_{xz} & \sigma'_{yz} \\
A_1 & 1 & 1 & 1 & 1 & z, x^2, y^2, z^2 \\
A_2 & 1 & 1 & -1 & -1 & R_z, xy \\
B_1 & 1 & -1 & 1 & -1 & x, R_y, xz \\
B_2 & 1 & -1 & -1 & 1 & y, R_x, yz \\
\end{array}
\]

Shown below are two electronic transitions. The letter to the left of each orbital is its representation.

For each transition, give:

(i) the representations of the ground state, $\Psi_0$, and the excited state, $\Psi_1$.

(ii) whether or not the transition is allowed.

(iii) if it is allowed, is the transition polarized parallel to or perpendicular to the principal axis.

(a) \[ \begin{array}{c}
\begin{array}{c}
\psi_0 \\
a_2 & b_2 \\
b_2 & b_2 \\
b_2 & b_2 \\
\end{array}
\end{array} \rightarrow \begin{array}{c}
\begin{array}{c}
\psi_1 \\
a_2 & a_2 \\
b_2 & b_2 \\
b_2 & b_2 \\
\end{array}
\end{array} \]

(b) \[ \begin{array}{c}
\begin{array}{c}
\psi_0 \\
\psi_1 \\
\psi_0 \\
\psi_1 \\
\end{array}
\end{array} \]
7. Now consider two transitions of the Methylene cyclopropene cation. For each transition, give:
(i) the representations of the ground state, \( \Psi_0 \), and the excited state, \( \Psi_1 \).
(ii) whether or not the transition is allowed.
(iii) if it is allowed, is the transition polarized parallel to or perpendicular to the principal axis.

(a) ![Diagram of transition a]
(b) ![Diagram of transition b]

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.

\[
\begin{array}{cccc}
\text{C}_{2h} & \text{E} & \text{C}_2 & \text{i} \\
\text{Ag} & 1 & 1 & 1 \\
\text{Bg} & 1 & -1 & 1 \\
\text{Au} & 1 & 1 & -1 \\
\text{Bu} & 1 & -1 & -1 \\
\end{array}
\]

(a) ![Diagram of butadiene]

It can be shown that that the p\(_z\) orbitals, \( \chi_1, \chi_2, \chi_3 \) and \( \chi_4 \) 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.

(b) Determine the 2x2 Secular Determinants corresponding to the B\(_g\) and A\(_u\) representations.

(c) Solve the 2x2 Secular Determinants to determine the energies and wavefunctions belonging to the B\(_g\) and A\(_u\) representations.
Chapter 10
Semiepirical Methods and Applications of Symmetry

Part A: The Hückel Model and other Semiempirical Methods

Part B: Applications of Symmetry

Part A: The Hückel Model and other Semiempirical Methods

• Hückel Molecular Orbital Model
• Application to Ethylene
• Application to the Allyl Radical (C₃H₅•)
• π Electron Charge and π Bond Order
• Application to Butadiene
• Introduction of Heteroatoms
• Semiempirical methods for sigma bonded systems
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.

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 sp² 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).
   \[ ϕ_i = ∑_j c_j χ_j = c_{i1} χ_1 + c_{i2} χ_2 + c_{i3} χ_3 + \cdots \]

4. The total π electron Hamiltonian is a simple sum of effective one electron Hamiltonians.
   \[ H = ∑_i h_i = h_1 + h_2 + h_3 + \cdots \]
Linear Equations and Secular Determinant

\[ \varphi_i = \sum_j c_j \chi_j + H = \sum_i h_i \]

Variational Method

\[ \sum_{j=1}^{N} c_j (H_{ij} - ES_{ij}) = 0 \]

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

\[ |H_{ij} - ES_{ij}| = 0 \]

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

Additional Assumptions

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, \( \alpha \)

7. Off-diagonal Hamiltonian elements are given by an empirical parameter, \( \beta \), if the carbons are adjacent

\[ H_{ij} = \beta: \text{Adjacent Carbons} \]
\[ H_{ij} = 0: \text{Non-Adjacent Carbons} \]

Note: \( \alpha < 0 \) and \( \beta < 0 \)
Parameter Values

What is the value of $\alpha$?

Who cares?
$\alpha$ cancels out in almost all applications, such as transition or reaction energies.

What is the value of $\beta$?

Who knows?
Estimates of the “best” value of $\beta$ 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.

Part A: The Hückel Model and other Semiempirical Methods

• Hückel Molecular Orbital Model

• Application to Ethylene

• Application to the Allyl Radical ($C_3H_5^*$)

• $\pi$ Electron Charge and $\pi$ Bond Order

• Application to Butadiene

• Introduction of Heteroatoms

• Semiempirical methods for sigma bonded systems
Application to Ethylene (C\textsubscript{2}H\textsubscript{4})

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 \( \beta \) and define \( x \) by

\[
x = \frac{\alpha - E}{\beta}
\]

\[
\begin{vmatrix}
x \\
1
\end{vmatrix}
\begin{vmatrix}
1 \\
x
\end{vmatrix} = 0
\]

\[
x^2 - 1 = 0
\]

\[
x_1 = -1 = \frac{\alpha - E_1}{\beta}
\]

\[
x_2 = 1 = \frac{\alpha - E_2}{\beta}
\]

\[
E_1 = \alpha + \beta
\]

\[
E_2 = \alpha - \beta
\]
Molecular Orbitals

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

\[\phi = c_1 \chi_1 + c_2 \chi_2\]

\[(\alpha - E)c_1 + \beta c_2 = 0\]

\[\beta c_1 + (\alpha - E)c_2 = 0\]

or

\[x_1 c_1 + c_2 = 0\]

\[c_1 x_2 = 0\]

\[\frac{c_2}{c_1} = -x\]

\[\phi = c_1 \chi_1 + c_2 \chi_2\]

\[\frac{c_2}{c_1} = -x\]

\[E_i = \alpha + \beta\]

\[
\begin{align*}
\chi_1 &= -1 \\
E_i &= \alpha + \beta
\end{align*}
\]

Normalization:

\[1 = \langle \phi | \phi \rangle = \langle c_1 \chi_1 + c_2 \chi_2 | c_1 \chi_1 + c_2 \chi_2 \rangle\]

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

\[1 = c_1^2 + c_2^2\]

Note: For Hückel calculations, the normalization condition is always:

\[\sum_i c_i^2 = 1\]

\[1 = c_1^2 + c_2^2\]

\[c_2 = c_1\]

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

Bonding Orbital

$x_2 = +1$

$E_2 = \alpha - \beta$

$\frac{c_2}{c_1} = -1 \quad c_2 = -c_1$

$1 = c_1^2 + c_2^2$

$c_2 = -c_1$

Antibonding Orbital

Slide 13

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

$E_2 = \alpha - \beta$

Electrons are \textit{not} delocalized in $\phi_2$

$E_1 = \alpha + \beta$

Electrons are delocalized in $\phi_1$

Slide 14
Part A: The Hückel Model and other Semiempirical Methods

- Hückel Molecular Orbital Model
- Application to Ethylene
- Application to the Allyl Radical (C$_3$H$_5$•)
  - $\pi$ Electron Charge and $\pi$ Bond Order
- Application to Butadiene
- Introduction of Heteroatoms
- Semiempirical methods for sigma bonded systems

Application to the Allyl Radical (C$_3$H$_5$•)

The Allyl radical has 3 $\pi$ electrons

Secular Determinant and Energies

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

\[
\begin{vmatrix}
\alpha - E & \beta & 0 \\
\beta & \alpha - E & \beta \\
0 & \beta & \alpha - E
\end{vmatrix} = 0
\]
\[
\begin{vmatrix}
\alpha - E & \beta & 0 \\
\beta & \alpha - E & \beta \\
0 & \beta & \alpha - E
\end{vmatrix} = 0
\]
Define
\[x = \frac{\alpha - E}{\beta}\]
\[x^3 - 2x = 0\]
\[x_1 = \sqrt{2} \frac{\alpha - E}{\beta}\]
\[x_2 = 0 \frac{\alpha - E}{\beta}\]
\[x_3 = -\sqrt{2} \frac{\alpha - E}{\beta}\]
\[E_1 = \alpha + \sqrt{2} \beta\]
\[E_2 = \alpha\]
\[E_3 = \alpha - \sqrt{2} \beta\]

\[
\begin{vmatrix}
x & 1 & 0 \\
1 & x & 1 \\
0 & 1 & x
\end{vmatrix} = 0
\]
1) \(xc_1 + c_2 = 0\)
2) \(c_1 + xc_2 + c_3 = 0\)
3) \(c_2 + xc_3 = 0\)
\[c_2 = -\sqrt{2} c_1\]
\[c_3 = -\frac{1}{\sqrt{2}} c_2 = c_1\]
\[E_1 = \frac{1}{2}\]
\[\varphi_1 = \frac{1}{2} \left( x_1 + \sqrt{2} x_2 + x_3 \right)\]

\[
\begin{vmatrix}
x & 1 & 0 \\
1 & x & 1 \\
0 & 1 & x
\end{vmatrix} = 0
\]
1) \(xc_1 + c_2 = 0\)
2) \(c_1 + xc_2 + c_3 = 0\)
3) \(c_2 + xc_3 = 0\)
\[c_2 = 0 c_1 = 0\]
\[c_3 = -c_1(0)c_2 = -c_1\]
\[c_1 = \frac{1}{\sqrt{2}}\]
\[\varphi_2 = \frac{1}{\sqrt{2}} (x_1 - x_3)\]
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 $\phi_3$.

\[
E = \langle \phi_3 | H | \phi_3 \rangle = \frac{1}{4} \left( x_1 - \sqrt{2} x_2 + x_3 \right) \begin{pmatrix} x_1 - \sqrt{2} x_2 + x_3 \end{pmatrix}
\]

\[
= \frac{1}{4} \left[ x_1^2 - 2 x_1 x_2 + x_1 x_3 - \sqrt{2} x_1 x_2 + x_2^2 - \sqrt{2} x_2 x_3 + x_3^2 \right]
\]

\[
E = \frac{1}{4} \left[ -\sqrt{2} \beta + 0 - \sqrt{2} \beta + 2 \alpha - \sqrt{2} \beta + 0 - \sqrt{2} \beta + \alpha \right]
\]

\[
E = -\sqrt{2} \beta + \alpha + \alpha - \sqrt{2} \beta = \alpha - \sqrt{2} \beta \quad \text{It checks!!}
\]
Delocalization Energy

The delocalization energy is the total $\pi$ electron energy relative to the energy of the system with localized $\pi$ bonds.

\[
E_{\text{Deloc}} = E_\pi - E_{\text{Loc}}
\]

\[
E_1 = \alpha - \sqrt{2}\beta
\]

\[
E_2 = \alpha + \sqrt{2}\beta
\]

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

\[
E_{\text{Loc}} = E_{c\mu_s} + \alpha
\]

\[
E_{\text{Deloc}} = 3\alpha + 2\sqrt{2}\beta - (3\alpha + 2\beta)
\]

\[
= 2(\sqrt{2} - 1)\beta = 0.83\beta
\]
Part A: The Hückel Model and other Semiempirical Methods

- Hückel Molecular Orbital Model
- Application to Ethylene
- Application to the Allyl Radical (C₃H₅⁺)
- $\pi$ Electron Charge and $\pi$ Bond Order
- Application to Butadiene
- Introduction of Heteroatoms
- Semiempirical methods for sigma bonded systems

$\pi$ Electron Charge and $\pi$ Bond Order

$\pi$ Electron Charge (aka $\pi$ Charge Density)

The $\pi$ electron charge on atom $\mu$ is defined by:

$$q_\mu = \sum_{\text{orb}} n_i c_{i\mu}^2$$

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

$\pi$ Bond Order

The $\pi$ bond order between atoms $\mu$ and $\nu$ is defined by:

$$P_{\mu\nu} = \sum_{\text{orb}} n_i c_{i\mu} c_{i\nu}$$
Application to the Allyl Radical

**π Electron Charge:** $q_\pi = \sum_{i} \alpha_i^2 \xi_i$

- $q_1 = \sum_{i} \alpha_i^2 = 2 \cdot \left(\frac{1}{2}\right)^2 + 1 \cdot \left(\frac{1}{\sqrt{2}}\right)^2 = 1$
- $q_2 = \sum_{i} \alpha_i^2 = 2 \cdot \left(\frac{1}{\sqrt{2}}\right)^2 + 1 \cdot (0)^2 = 1$
- $q_3 = \sum_{i} \alpha_i^2 = 2 \cdot \left(\frac{1}{2}\right)^2 + 1 \cdot \left(-\frac{1}{\sqrt{2}}\right)^2 = 1$

**π Bond Order:** $P_{\pi \nu} = \sum_{i} \alpha_i^2 \xi_i^2$

- $P_{12} = \sum_{i} \alpha_i^2 \xi_i^2 = 2 \cdot \left(\frac{1}{2}\right) \cdot \left(\frac{1}{\sqrt{2}}\right) + 1 \cdot \left(\frac{1}{\sqrt{2}}\right) (0) = \frac{1}{\sqrt{2}} = 0.71$
- $P_{23} = \sum_{i} \alpha_i^2 \xi_i^2 = 2 \cdot \left(\frac{1}{\sqrt{2}}\right) \cdot \left(\frac{1}{2}\right) + 1 \cdot (0) \left(-\frac{1}{\sqrt{2}}\right) = \frac{1}{\sqrt{2}} = 0.71$

Part A: The Hückel Model and Other Semiempirical Methods

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

1,3-Butadiene has 4 \( \pi \) 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

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

Divide by \( \beta \)

Define

\[
\begin{vmatrix}
x & 1 & 0 & 0 \\
1 & x & 1 & 0 \\
0 & 1 & x & 1 \\
0 & 0 & 1 & x \\
\end{vmatrix} = 0
\]

\[
x \left[ x(x^2 - 1) - 1(x - 0) \right] - 1 \left[ (x^2 - 1) - 1(0 - 0) \right] = 0
\]

\[
\left[ x^4 - x^2 - x^2 \right] - \left[ x^2 - 1 \right] = 0
\]

\[
x^4 - 3x^2 + 1 = 0
\]

\[
y = x^2
\]

\[
y^2 - 3y + 1 = 0
\]

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

\[
y_b = \frac{3 - \sqrt{9 - 4}}{2} = 0.382 = x^2
\]
The additional stabilization of butadiene compared to 2 ethylenes is a result of \( \pi \) electron delocalization between the two double bonds.
Butadiene Wavefunctions

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

From first equation:
\[ c_2 = 1.618 c_1 \]

From second equation:
\[ c_3 = -c_1 + 1.618 c_2 = -c_1 + 2.618 c_1 = 1.618 c_1 \]

From fourth equation:
\[ c_4 = \frac{c_1}{1.618} = c_1 \]

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

Normalization:
\[ \sum_{i=1}^{4} \varphi_i^2 = 1 \quad \text{(because all overlap integrals are 0)} \]

\[ c_1^2 \left[ (0)^2 + (1.618)^2 + (1.618)^2 + (1)^2 \right] = 1 \quad c_1 = 0.372 \]

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

\[ \varphi_1 = 0.372 \chi_1 + 0.602 \chi_2 + 0.602 \chi_3 + 0.372 \chi_4 \]

It is straightforward to perform the same procedure to determine \( \phi_2 \), \( \phi_3 \) and \( \phi_4 \).

The results are shown on the next slide.
Butadiene: $\pi$ Electron Charge and Bond Order

$$\varphi_4 = 0.372X_1 - 0.602X_2 + 0.602X_3 - 0.372X_4$$

$$\varphi_3 = 0.602X_1 - 0.372X_2 - 0.372X_3 + 0.602X_4$$

$$\varphi_2 = 0.602X_1 + 0.372X_2 - 0.372X_3 - 0.602X_4$$

$$\varphi_1 = 0.372X_1 + 0.602X_2 + 0.602X_3 + 0.372X_4$$

$\pi$ Electron Charge: $q_\mu = \sum \eta_i c_{\mu i}^2$

- $q_1 = 2(0.372)^2 + 2(0.602)^2 = 1.00$
- $q_2 = 2(0.602)^2 + 2(-0.372)^2 = 1.00$
- $q_3 = 2(0.602)^2 + 2(-0.372)^2 = 1.00$
- $q_4 = 2(0.372)^2 + 2(-0.602)^2 = 1.00$

Actually, Butadiene (and the Allyl radical) belong to a class of hydrocarbons called "Alternant hydrocarbons", for which all $q_\mu = 1.0$.

All straight-chain polyalkenes are alternant hydrocarbons.
\[ \varphi_4 = 0.372 \chi_1 - 0.602 \chi_2 + 0.602 \chi_3 - 0.372 \chi_4 \]
\[ \varphi_3 = 0.602 \chi_1 - 0.372 \chi_2 - 0.372 \chi_3 + 0.602 \chi_4 \]
\[ \varphi_2 = 0.602 \chi_1 + 0.372 \chi_2 - 0.372 \chi_3 - 0.602 \chi_4 \]
\[ \varphi_1 = 0.372 \chi_1 + 0.602 \chi_2 + 0.602 \chi_3 + 0.372 \chi_4 \]

\[ \pi \text{ Bond Order: } p_{\mu\nu} = \sum \psi_{\mu} \psi_{\nu} \]
\[ p_{12} = 2(0.372)(0.602) + 2(0.602)(0.372) = 0.896 \approx 0.90 \]
\[ p_{23} = 2(0.602)(0.602) + 2(0.372)(-0.372) = 0.448 \approx 0.45 \]
\[ p_{34} = 2(0.602)(0.372) + 2(-0.372)(-0.602) = 0.896 \approx 0.90 \]

\textbf{Note:} For a “full” \( \pi \) bond, \( p_{\mu\nu} = 1 \).
For a pure \( \sigma \) bond, \( p_{\mu\nu} = 0 \).

Therefore, the above bond orders reveal that the \( \pi \) 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 \( \pi \) character in the \( C_2-C_3 \) bond.

\textbf{Part A: The Hückel Model and other Semiempirical Methods}

• Hückel Molecular Orbital Model
• Application to Ethylene
• Application to the Allyl Radical (\( C_3H_5^* \))
• \( \pi \) Electron Charge and \( \pi \) Bond Order
• Application to Butadiene
• \textbf{Introduction of Heteroatoms}
• Semiempirical methods for sigma bonded systems
Introduction of Heteroatoms

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

It is useful to put the new values of the Coulomb and Resonance Integrals, \( \alpha_X \) and \( \beta_X \) (where \( X \) is the heteroatom), in terms of the original \( \alpha \) and \( \beta \).

The forms that is generally used are:

\[
\alpha_X = \alpha + h_X \beta \\
\beta_X = k_X \beta
\]

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

<table>
<thead>
<tr>
<th>Atom</th>
<th>( h_X )</th>
<th>Bond</th>
<th>( k_X )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.5</td>
<td>C----N----</td>
<td>1.0</td>
</tr>
<tr>
<td>N</td>
<td>1.5</td>
<td>C----N----</td>
<td>0.8</td>
</tr>
<tr>
<td>O</td>
<td>2.0</td>
<td>C----O----</td>
<td>0.8</td>
</tr>
<tr>
<td>O</td>
<td>1.0</td>
<td>C----O----</td>
<td>1.0</td>
</tr>
<tr>
<td>Cl</td>
<td>2.0</td>
<td>C----Cl----</td>
<td>0.4</td>
</tr>
</tbody>
</table>
A heteroatom can donate different numbers of electrons into the \( \pi \) electrons depending upon its bonding.

Example: Nitrogen has 5 valence electrons

In pyridine, 4 of the 5 valence electrons are involved in (a) 2 \( \sigma \) 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 \( \sigma \) bonds. This nitrogen will donate 2 electrons.

**Example: \( \pi \) 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 \( \pi \) system.

The heteroatom parameters are: \( h_N = 1.5 \) and \( k_N = 0.8 \)

Therefore: \[
\begin{align*}
\alpha_N &= \alpha + h_N \beta = \alpha + 1.5 \beta \\
\beta_N &= k_N \beta = 0.8 \beta
\end{align*}
\]
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 !!!
Wavefunctions and Energies

\[ \phi_1 = \phi_7 = 0.372 X_1 - 0.602 X_5 + 0.602 X_4 - 0.372 X_3 \]
\[ \phi_2 = \phi_8 = 0.374 X_1 - 0.587 X_5 + 0.292 X_4 - 0.587 X_3 \]
\[ \phi_3 = \phi_9 = 0.602 X_1 + 0.372 X_5 - 0.372 X_4 - 0.602 X_3 \]
\[ \phi_4 = \phi_{10} = 0.530 X_1 - 0.111 X_5 - 0.589 X_4 - 0.111 X_3 \]
\[ \phi_5 = \phi_{11} = 0.725 X_1 + 0.379 X_5 + 0.287 X_4 + 0.379 X_3 \]

\[ E_1 = E_2 = \alpha - 1.618 \beta \]
\[ E_4 = E_5 = \alpha - 1.008 \beta \]
\[ E_3 = E_6 = \alpha + 0.618 \beta \]
\[ E_2 = E_7 = \alpha + 1.189 \beta \]
\[ E_1 = E_8 = \alpha + 2.320 \beta \]

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.

Slide 43

\[ \pi \text{ Electron Charge} \]

\[ \phi_1 = \phi_7 = 0.372 X_1 - 0.602 X_5 + 0.602 X_4 - 0.372 X_3 \]
\[ \phi_2 = \phi_8 = 0.374 X_1 - 0.587 X_5 + 0.292 X_4 - 0.587 X_3 \]
\[ \phi_3 = \phi_9 = 0.602 X_1 + 0.372 X_5 - 0.372 X_4 - 0.602 X_3 \]
\[ \phi_4 = \phi_{10} = 0.530 X_1 - 0.111 X_5 - 0.589 X_4 - 0.111 X_3 \]
\[ \phi_5 = \phi_{11} = 0.725 X_1 + 0.379 X_5 + 0.287 X_4 + 0.379 X_3 \]

\[ \pi \text{ Electron Charge: } q_\mu \equiv \sum \frac{\alpha n C_{i\mu}^2}{n} \]
\[ q_1 = 1.61 \]
\[ q_2 = 1.04 \]
\[ q_3 = 1.14 \]
\[ q_4 = 1.14 \]
\[ q_5 = 1.04 \]
\[ \sum q_\mu = 5.97 \approx 6 \]

Slide 44
Part A: The Hückel Model and other Semiempirical Methods

- Hückel Molecular Orbital Model
- Application to Ethylene
- Application to the Allyl Radical (C₃H₅•)
- \( \pi \) Electron Charge and \( \pi \) Bond Order
- Application to Butadiene
- Introduction of Heteroatoms
- Semiempirical methods for sigma bonded systems

\[ \pi \text{ Bond Order} \]
\[ \phi_s = \phi_i = 0.372 \chi_1 - 0.602 \chi_3 + 0.602 \chi_4 - 0.372 \chi_5 \]
\[ \phi_s = \phi_i = 0.374 \chi_1 - 0.587 \chi_3 + 0.292 \chi_4 + 0.292 \chi_5 - 0.587 \chi_4 
\]
\[ \phi_s = \phi_i = 0.602 \chi_1 + 0.372 \chi_3 - 0.372 \chi_4 - 0.602 \chi_5 \]
\[ \phi_s = \phi_i = 0.530 \chi_1 - 0.111 \chi_2 - 0.589 \chi_3 - 0.589 \chi_4 - 0.111 \chi_5 \]
\[ \phi_s = \phi_i = 0.725 \chi_1 + 0.379 \chi_3 + 0.287 \chi_4 + 0.287 \chi_5 + 0.379 \chi_4 \]

\[ \pi \text{ Bond Order: } P_{\mu \nu} = \sum_{\alpha \beta} n_{c_{\mu \alpha} c_{\nu \beta}} \]
\[ P_{12} = 0.43 \]
\[ P_{23} = 0.80 \]
\[ P_{34} = 0.58 \]
\[ P_{45} = 0.80 \]
\[ P_{55} = 0.43 \]
Semiempirical Methods for Sigma Bonded Systems

The Hückel model was developed to treat only \( \pi \) bond systems.

A number of methods have been developed to treat systems with \( \sigma \) bonded molecules as well as molecules with both \( \sigma \) and \( \pi \) 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.

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.
The Extended Hückel Model

As the title suggests, this is an extension of the Hückel Model to treat \( \sigma \) 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 \((\chi_i)\).
   \[
   \varphi_i = \sum_j c_{ij} \chi_j = c_{11} \chi_1 + c_{12} \chi_2 + c_{13} \chi_3 + \cdots
   \]

2. The total Hamiltonian is a simple sum of effective one electron Hamiltonians.
   \[
   H = \sum_i h_i = h_1 + h_2 + h_3 + \cdots
   \]

3. If one applies the variational principle, then a Secular Determinant is obtained.
   \[
   |H_{\vec{y}} - E S_{\vec{y}}| = 0
   \]

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

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.
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.

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.
Chapter 10

Semiempirical Methods and Applications of Symmetry

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 \( \pi \)-Bonding in Pyrrole
Spectroscopic Selection Rules

When light (of frequency $\omega$) 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.

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

The perturbation “mixes” the ground state wavefunction ($\Psi_0$) with various excited states ($\Psi_i$). 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 ($\Psi_0$) and the i’th excited state ($\Psi_i$).

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

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

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: $\hat{\mu} = ei\vec{n} = e(\hat{x} \hat{i} + \hat{y} \hat{j} + \hat{z} \hat{k})$

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

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

\[ M_{0i} = M_{0i}^x \hat{i} + M_{0i}^y \hat{j} + M_{0i}^z \hat{k} \]

\[ M_{0i}^x = e\langle \Psi_i | x | \Psi_0 \rangle \]
\[ M_{0i}^y = e\langle \Psi_i | y | \Psi_0 \rangle \]
\[ M_{0i}^z = e\langle \Psi_i | z | \Psi_0 \rangle \]

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

\[ M_{ij}^x = e\langle \Psi_i | x | \Psi_0 \rangle \]
\[ M_{ij}^y = e\langle \Psi_i | y | \Psi_0 \rangle \]
\[ M_{ij}^z = e\langle \Psi_i | z | \Psi_0 \rangle \]

A question which must be resolved is how to determine the representation of the overall electronic wavefunction (both \( \Psi_0 \) and \( \Psi_i \)) from the representations of the individual MOs.

However, first let’s take a short detour to briefly discuss “spin-forbidden” transitions.

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.

\[ \Psi_i^{\text{tot}}(\vec{r}, S) = \Psi_i(\vec{r}) \cdot \Psi_i^{\text{spin}}(S) \]
\[ \Psi_0^{\text{tot}}(\vec{r}, S) = \Psi_0(\vec{r}) \cdot \Psi_0^{\text{spin}}(S) \]

\[ M_{0i} = \langle \Psi_0 \big| \hat{\mu} \big| \Psi_i^{\text{tot}} \rangle = \langle \Psi_0 \big| \Psi_i^{\text{spin}}(S) \big| \hat{\mu} \big| \Psi_0^{\text{spin}}(S_0) \rangle \]
\[ M_{0i} = \langle \Psi_i \big| \hat{\mu} \big| \Psi_0^{\text{tot}} \rangle = \langle \Psi_i^{\text{spin}}(S) \big| \Psi_0^{\text{spin}}(S_0) \rangle \]

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

Therefore, the transition moment is zero unless the total spin quantum number is conserved; e.g. Singlet \( \rightarrow \) Triplet transitions are forbidden.
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)
\[ \Gamma(\Psi_0) = \Gamma_1 x \Gamma_1 x \Gamma_2 x \Gamma_4 \]
\[ \Gamma(\Psi_i) = \Gamma_1 x \Gamma_1 x \Gamma_2 x \Gamma_4 \]

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 \( \Gamma_i \)'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)

\[ \Gamma(\Psi_0) = \Gamma_1 x \Gamma_1 x \Gamma_2 x \Gamma_4 \]
\[ \Gamma(\Psi_i) = \Gamma_1 x \Gamma_1 x \Gamma_2 x \Gamma_4 \]
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 $\pi$-Bonding in Pyrrole

---

**Application to Butadiene**

<table>
<thead>
<tr>
<th>$C_{2h}$</th>
<th>E</th>
<th>C₂</th>
<th>i</th>
<th>$\sigma_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_g$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

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

The four Hückel orbitals were developed in earlier in this chapter.
Let's consider a couple of butadiene $\pi\rightarrow\pi^*$ transitions.

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

Note that the transition is labelled by the symmetries of the total wavefunctions, and not the symmetries of the individual MOs involved.
Polarization of Electronic Transitions

\[ b_z \quad \alpha_u \quad \uparrow b_z \quad \alpha_u \quad \Psi_0 \quad \Psi'_0 \quad \Downarrow \quad \Downarrow
\]

\[ C_{2h} \quad E \quad C_2 \quad i \quad \sigma_h \]

\begin{align*}
A_g & : 1 & 1 & 1 & 1 \\
B_g & : 1 & -1 & 1 & -1 \\
A_u & : 1 & 1 & -1 & -1 & z \\
B_u & : 1 & -1 & -1 & 1 & x,y
\end{align*}

Note that \( M_{0i}^z = 0 \).

Consider a single crystal of butadiene (not likely for this molecule)

If incoming light is polarized along the z-axis (C\(_2\)), it will \textbf{not} be absorbed.

Therefore, the polarization of this transition is Perpendicular

---

Let’s consider a second butadiene \( \pi \rightarrow \pi^* \) transition.

\[ \Gamma (\Psi_0) = A_g \]

\[ \Gamma (\Psi') = b_z x b_z^* = (1 \ 1 \ 1 \ 1) = A_g \]

Therefore, this transition is labelled: \( A_g \rightarrow A_g \)

\[ M_{0i}^x = e \langle \Psi' | x | \Psi_0 \rangle \quad \Gamma = A_g x B_g x A_g = B_g \neq A_g \quad M_{0i}^x = 0 \]

\[ M_{0i}^y = e \langle \Psi' | y | \Psi_0 \rangle \quad \Gamma = A_g x B_g x A_g = B_g \neq A_g \quad M_{0i}^y = 0 \]

\[ M_{0i}^z = e \langle \Psi' | z | \Psi_0 \rangle \quad \Gamma = A_g x A_g x A_g = A_g \neq A_g \quad M_{0i}^z = 0 \]

Therefore, this is \textbf{not} an allowed transition.
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!!!

---

**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 $\pi$-Bonding in Pyrrole
Carbene UV Selection Rules

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

We will consider only transitions arising from the \( a_1 \) and \( b_1 \) frontier orbitals.

Thereupon, the overall transition is: \( B_1 \rightarrow A_1 \)

\[
\begin{align*}
\Gamma (\Psi_0) &= a_1b_1 = B_1 \\
\Gamma (\Psi_1) &= a_1a_1 = A_1
\end{align*}
\]

\[
\begin{array}{ccc}
C_{2v} & E & C_2 \quad \sigma_v(xz) \quad \sigma_v(yz) \\
A_1 & 1 & 1 & 1 & 1 & z \\
A_2 & 1 & 1 & -1 & -1 \\
B_1 & 1 & -1 & 1 & -1 & x \\
B_2 & 1 & -1 & -1 & 1 & y
\end{array}
\]

\[
\begin{align*}
M_{0i}^{z} &= e \langle \Psi_1 | x \Psi_0 \rangle \quad \Gamma = A_1 \times B_1 \times B_1 = A_1 \quad M_{0i}^{z} \neq 0 \\
M_{0i}^{y} &= e \langle \Psi_1 | y \Psi_0 \rangle \quad \Gamma = A_1 \times B_1 \times B_1 = A_2 \quad M_{0i}^{y} = 0 \\
M_{0i}^{x} &= e \langle \Psi_1 | z \Psi_0 \rangle \quad \Gamma = A_1 \times A_1 \times B_1 = B_1 \quad M_{0i}^{x} = 0
\end{align*}
\]

This transition is allowed and is polarized \textbf{perpendicular} to the principal axis.
**Slide 19**

\[
\begin{array}{ccc}
\begin{array}{c}
\text{b}_2 \\
\text{a}_1 \\
\text{b}_1 \\
\Psi_0
\end{array} & \rightarrow & \begin{array}{c}
\text{b}_2 \\
\text{a}_1 \\
\text{b}_1 \\
\Psi_i
\end{array} \\
\hline
\text{C}_2\text{v} & \text{E} & \text{C}_2 & \sigma_v(xz) & \sigma_v(yz) \\
\hline
\text{A}_1 & 1 & 1 & 1 & 1 & \text{Z} \\
\text{A}_2 & 1 & 1 & -1 & -1 \\
\text{B}_1 & 1 & -1 & 1 & -1 & \text{x} \\
\text{B}_2 & 1 & -1 & -1 & 1 & \text{y}
\end{array}
\]

Therefore, this transition is labelled: \( \text{B}_1 \rightarrow \text{A}_1 \)

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 (\( \text{A}_1 \)) is the same as “z”

Mookie: But the shortcut predicts the wrong polarization.

Corky: Well, half right ain’t bad!!

Mookie: Oy Vey!!

**Slide 20**

\[
\begin{array}{ccc}
\begin{array}{c}
\text{b}_2 \\
\text{a}_1 \\
\text{b}_1 \\
\Psi_0
\end{array} & \rightarrow & \begin{array}{c}
\text{b}_2 \\
\text{a}_1 \\
\text{b}_1 \\
\Psi_i
\end{array} \\
\hline
\text{C}_2\text{v} & \text{E} & \text{C}_2 & \sigma_v(xz) & \sigma_v(yz) \\
\hline
\text{A}_1 & 1 & 1 & 1 & 1 & \text{Z} \\
\text{A}_2 & 1 & 1 & -1 & -1 \\
\text{B}_1 & 1 & -1 & 1 & -1 & \text{x} \\
\text{B}_2 & 1 & -1 & -1 & 1 & \text{y}
\end{array}
\]

\( \Gamma (\Psi_0) = a_1 b_1 = B_1 \) \hspace{1cm} \( \Gamma (\Psi_i) = a_1 c_1 = A_1 \)

Corky: Well, the excited state belongs to \( \text{A}_2 \). Since none of \( x \), \( y \), or \( z \) is \( \text{A}_2 \), the transition is forbidden. Piece of Cake!!

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

Corky: Well, the excited state belongs to \( \text{A}_2 \). Since none of \( x \), \( y \), or \( z \) is \( \text{A}_2 \), the transition is forbidden. Piece of Cake!!

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

$$
S_i = \sum a_i \chi_i \quad \text{[A$_1$]}
$$

$$
S_2 = \sum b_i \chi_i \quad \text{[A$_2$]}
$$

$$
S_3 = \sum c_i \chi_i \quad \text{[B$_1$]}
$$

$$
S_4 = \sum d_i \chi_i \quad \text{[B$_2$]}
$$

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

It can be shown from Group Theory that if one forms the Secular Determinant by using matrix elements of the $S_i$ rather than $\chi_i$, then the Determinant is “Block Diagonalized”

Let’s say that $\psi_i$ belongs to $\Gamma_i$, and $\psi_j$ belongs to $\Gamma_j$. Remember that the Hamiltonian belongs to $A_1$ ($A_{1g}$ etc)

Then the Hamiltonian matrix element is:

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

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

$$
\Gamma_i \chi A_1 \chi \Gamma_j = A_1
$$

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.
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:

$$\begin{vmatrix}
H_{11} - E & H_{12} & 0 & 0 \\
H_{12} & H_{22} - E & 0 & 0 \\
0 & 0 & H_{33} - E & H_{34} \\
0 & 0 & H_{43} & H_{44} - E
\end{vmatrix} = 0$$

$$S_1 = \sum a_i \chi_i \ [A_1]$$
$$S_2 = \sum b_j \chi_j \ [A_1]$$
$$S_3 = \sum c_k \chi_k \ [B_1]$$
$$S_4 = \sum d_l \chi_l \ [B_1]$$

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

$$\begin{vmatrix}
H_{11} - E & H_{12} \\
H_{12} & H_{22} - E
\end{vmatrix} = 0 \quad \text{and} \quad \begin{vmatrix}
H_{33} - E & H_{34} \\
H_{43} & H_{44} - E
\end{vmatrix} = 0$$

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.

---

**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 $\pi$-Bonding in Pyrrole
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:

(a) 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.

(b) How to generate the SALCs

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

One can calculate the number of each type of irreducible representation (e.g. $A_1$, $A_2$, ...) 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:

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

Note: The text uses the more common symbol, $\chi$, to represent the character (or trace). However, we’re already using $\chi$ to represent atomic orbitals.
SALCs of the Allyl Radical

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

To form the reducible representation, $\Gamma_{\text{Red}}$, 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 $\text{Tr}(R)$

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 $\sigma_v$ is applied, all 3 change sign: $\Gamma_{\text{Red}}(\sigma_v) = -3$
When $\sigma_v'$ is applied, 1 and 3 exchange, 2 is unchanged: $\Gamma_{\text{Red}}(\sigma_v') = +1$
Generate the number of times each representation appears in $\Gamma_{\text{Red}}$:

\[
n_j = \frac{1}{h} \sum_{R} \text{Tr}_j(R) \cdot \text{Tr}_{\text{Red}}(R)
\]

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

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

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

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

**Construction of the SALCs**

One uses a projection operator:

\[
S(j) = N \sum_{R} \text{Tr}_j(R) \cdot R(\chi_i)
\]

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

$\text{Tr}_j(R)$ is the trace of the $j$'th irreducible representation for operation $R$

$N$ is the normalization constant
We’ll use $\chi_1$ to generate the SALC

$$S(J) = N \sum_{\chi} \text{Tr}_J(R) \cdot R(\chi)$$

### A$_2$ SALC

Normalized:

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

Let’s demonstrate that $S_1$ belongs to the A$_2$ representation.

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

The signs on the transformed values of $S_1$ match those of the A$_2$ representation.
We'll use $\chi_1$ to generate the first SALC

$$\begin{align*}
S_1(B_2) &= N\left[1 \cdot E(\chi_1) + (-1) \cdot C_2(\chi_1) + (-1) \cdot \sigma_v(\chi_1) + 1 \cdot \sigma_v'(\chi_1)\right] \\
S_2(B_2) &= N\left[1 \cdot \chi_1 + (-1) \cdot (-\chi_1) + (-1) \cdot (-\chi_1) + 1 \cdot \chi_3\right] \\
S_3(B_2) &= N(2\chi_1 + 2\chi_3) = N(\chi_1 + \chi_3)
\end{align*}$$

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

B₂ SALCs

We'll use $\chi_2$ to generate the second SALC

$$\begin{align*}
S_1(B_2) &= N\left[1 \cdot E(\chi_2) + (-1) \cdot C_2(\chi_2) + (-1) \cdot \sigma_v(\chi_2) + 1 \cdot \sigma_v'(\chi_2)\right] \\
S_2(B_2) &= N\left[1 \cdot \chi_2 + (-1) \cdot (-\chi_2) + (-1) \cdot (-\chi_2) + 1 \cdot \chi_3\right] \\
S_3(B_2) &= 4N\chi_2
\end{align*}$$

Normalized: $S_3(B_2) = \chi_2$
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 \( \pi \)-Bonding in Pyrrole

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:

\[
S_x(A_1) = \frac{1}{\sqrt{2}} (\chi_1 - \chi_2)
\]
\[
S_z(B_2) = \frac{1}{\sqrt{2}} (\chi_1 + \chi_2)
\]
\[
S_y(B_1) = \chi_2
\]

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

<table>
<thead>
<tr>
<th>$S_1$</th>
<th>$S_2$</th>
<th>$S_3$</th>
<th>$S_1 = \frac{1}{\sqrt{2}}(x_1 - x_3)$ [A$_i$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>$H_{12} - E$</td>
<td>$H_{13}$</td>
<td>$H_{12} = \frac{1}{\sqrt{2}}(x_1 - x_3)$ [A$_i$]</td>
</tr>
<tr>
<td>$S_2$</td>
<td>$H_{12}$</td>
<td>$H_{12} - E$</td>
<td>$H_{22} = \frac{1}{\sqrt{2}}(x_1 + x_3)$ [B$_i$]</td>
</tr>
<tr>
<td>$S_3$</td>
<td>$H_{13}$</td>
<td>$H_{13}$</td>
<td>$H_{33} = x_2$ [B$_i$]</td>
</tr>
</tbody>
</table>

Matrix Elements

\[
H_{11} = \langle S_1 | H | S_1 \rangle = \left( \frac{1}{\sqrt{2}}(x_1 - x_3) \right) \left( \frac{1}{\sqrt{2}}(x_1 - x_3) \right)
\]
\[
H_{12} = \frac{1}{2}((x_1 | H | x_1) - (x_1 | H | x_1) - (x_1 | H | x_1) + (x_1 | H | x_1))
\]
\[
H_{13} = \frac{1}{2}(\alpha - 0 - 0 + \alpha) = \alpha
\]
\[
H_{22} = \langle S_2 | H | S_2 \rangle = \left( \frac{1}{\sqrt{2}}(x_1 + x_3) \right) \left( \frac{1}{\sqrt{2}}(x_1 + x_3) \right)
\]
\[
H_{22} = \frac{1}{2}((x_1 | H | x_1) + (x_1 | H | x_1) + (x_1 | H | x_1) + (x_1 | H | x_1))
\]
\[
H_{22} = \frac{1}{2}(\alpha + 0 + 0 + \alpha) = \alpha
\]

Matrix Elements (Cont’d.)

\[
H_{21} = \langle S_1 | H | S_2 \rangle = \langle x_1 | H | x_3 \rangle = \alpha
\]
\[
H_{12} = \langle S_1 | H | S_2 \rangle = \left( \frac{1}{\sqrt{2}}(x_1 - x_3) \right) \left( \frac{1}{\sqrt{2}}(x_1 + x_3) \right)
\]
\[
H_{13} = \frac{1}{2}((x_1 | H | x_1) + (x_1 | H | x_1) - (x_1 | H | x_1) - (x_1 | H | x_1))
\]
\[
H_{12} = \frac{1}{2}(\alpha + 0 - 0 - \alpha) = 0
\]
\[
H_{11} = \langle S_1 | H | S_1 \rangle = \langle x_1 | H | x_3 \rangle
\]
\[
H_{12} = \frac{1}{\sqrt{2}}((x_1 | H | x_3) - (x_1 | H | x_3))
\]
\[
H_{12} = \frac{1}{\sqrt{2}}(\beta - \beta) = 0
\]
\[
H_{21} = \langle S_1 | H | S_2 \rangle = \left( \frac{1}{\sqrt{2}}(x_1 + x_3) \right) \left( \frac{1}{\sqrt{2}}(x_1 + x_3) \right)
\]
\[
H_{22} = \frac{1}{2}((x_1 | H | x_3) + (x_1 | H | x_3))
\]
\[
H_{22} = \frac{1}{2}(\beta + \beta) = \frac{2}{\sqrt{2}} \beta = \sqrt{2} \beta
\]
\[ S_1 = \frac{1}{\sqrt{2}} (x_1 - x_2) \quad [A_2] \]
\[ S_2 = \frac{1}{\sqrt{2}} (x_1 + x_2) \quad [B_2] \]
\[ S_3 = x_2 \quad [B_2] \]

\[
\begin{bmatrix}
  0 & 0 & 0 \\
  \alpha - E & \sqrt{2} \beta & \alpha - E \\
  0 & \frac{\sqrt{2} \beta}{\beta} & \alpha - E \\
\end{bmatrix}
\]

\[ \text{Block} \]

Divide by \( \beta \)

\[
\begin{bmatrix}
  0 & 0 & 0 \\
  x & \sqrt{2} & 0 \\
  0 & \frac{\sqrt{2}}{x} & 0 \\
\end{bmatrix}
\]

\[ \text{Block} \]

\[ x = 0 \quad \Rightarrow \quad E_s = \alpha \quad [E_2] \]
\[ \varphi_s = S_1 = \frac{1}{\sqrt{2}} (x_1 - x_2) \quad [\varphi_2] \]

**A_2 “Block”**

\[ S_1 = \frac{1}{\sqrt{2}} (x_1 - x_2) \quad [A_2] \]
\[ S_2 = \frac{1}{\sqrt{2}} (x_1 + x_2) \quad [B_2] \]
\[ S_3 = x_2 \quad [B_2] \]

\[ \varphi = c_2 S_2 + c_3 S_3 \]
\[ x_2 c_2 + \sqrt{2} c_3 = 0 \]
\[ -\sqrt{2} c_2 + \sqrt{2} c_3 = 0 \]

**B_2 Block**

\[ \begin{bmatrix} x & \sqrt{2} \\ \sqrt{2} & x \end{bmatrix} = 0 \quad \Rightarrow \quad x^2 - 2 = 0 \quad \Rightarrow \quad x_s = -\sqrt{2} \quad x_+ = +\sqrt{2} \]
\[ x_+ = \frac{\alpha - E_+}{\beta} \quad \Rightarrow \quad E_s = \alpha + \sqrt{2} \beta \quad [E_+] \]
\[ x_+ = \frac{\alpha - E_+}{\beta} \quad \Rightarrow \quad E_s = \alpha - \sqrt{2} \beta \quad [E_-] \]

**B_2 Wavefunctions**

\[ \varphi_2 = \varphi_1 = c_2 [S_2 + S_3] \]
\[ \varphi_3 = \varphi_1 = c_3 \left[ \frac{1}{\sqrt{2}} (x_1 + x_2) \right] \]
\[ \varphi_3 = \varphi_2 = c_3 \left[ \frac{1}{\sqrt{2}} (x_1 + x_2) + x_2 \right] \]
\[ \varphi_3 = \varphi_2 = c_3 \left[ x_1 + \sqrt{2} x_2 + x_3 \right] \]
\[ \varphi_3 = \varphi_2 = \frac{1}{2} \left[ x_1 + \sqrt{2} x_2 + x_3 \right] \]

Similarly

\[ \varphi_2 = \varphi_3 = c_1 \left[ S_2 - S_3 \right] \]
\[ \varphi_2 = \varphi_3 = c_2 \left[ x_1 + \sqrt{2} x_2 + x_3 \right] \]
\[ \varphi_2 = \varphi_3 = c_3 \left[ x_1 - \sqrt{2} x_2 + x_3 \right] \]

\[ \varphi_2 = \varphi_3 = \frac{1}{2} \left[ x_1 - \sqrt{2} x_2 + x_3 \right] \]
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 \(\pi\)-Bonding in Pyrrole
Example: $\pi$ 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 $\pi$ system.

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

Therefore:
\[
\alpha_N = \alpha + h_N \beta = \alpha + 1.5 \beta \\
\beta_N = k_N \beta = 0.8 \beta
\]

Student:

\[
\begin{array}{c|ccccc}
\text{E} & \text{A}_2 & \text{B}_2 & \sigma_v(xz) & \sigma_v'(yz) \\
\hline
\text{C}_2 & 1 & 1 & -1 & -1 \\
\sigma_v(xz) & 1 & -1 & -1 & 1
\end{array}
\]

The 5 SALCs belong to the $A_2$ and $B_2$ representations.

\[
S_a = \frac{1}{\sqrt{2}} (x_2 - x_3) \ \ [A_2] \\
S_b = \frac{1}{\sqrt{2}} (x_2 + x_3) \ \ [B_2] \\
S_c = \frac{1}{\sqrt{2}} (x_1 - x_4) \ \ [A_2] \\
S_d = \frac{1}{\sqrt{2}} (x_1 + x_4) \ \ [B_2] \\
S_e = x_1 \ \ [B_2]
\]

We’ll demonstrate (on the board) that $S_a$ belongs to the $A_2$ and $S_c$ to the $B_2$ representation.
**A2 Block**

\[ \alpha_N = \alpha + 1.5 \beta \]
\[ \beta_N = 0.8 \beta \]

\[ S_a = \frac{1}{\sqrt{2}} (x_2 - x_5) \quad [A_2] \]
\[ S_b = \frac{1}{\sqrt{2}} (x_1 - x_4) \quad [A_2] \]

\[ H_{aa} = \langle S_a | H | S_a \rangle = \left( \frac{1}{\sqrt{2}} (x_2 - x_5) \right) H \left( \frac{1}{\sqrt{2}} (x_2 - x_5) \right) \]

\[ H_{ab} = \frac{1}{2} \left[ \langle x_2 | H | x_2 \rangle - \langle x_5 | H | x_5 \rangle - \langle x_3 | H | x_5 \rangle + \langle x_5 | H | x_3 \rangle \right] \]

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

\[ H_{ba} = \frac{1}{2} [\langle x_5 | H | x_2 \rangle - \langle x_3 | H | x_5 \rangle - \langle x_5 | H | x_3 \rangle + \langle x_3 | H | x_5 \rangle] \]

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

---

**A2 Block**

\[ \alpha_N = \alpha + 1.5 \beta \]
\[ \beta_N = 0.8 \beta \]

\[ S_a = \frac{1}{\sqrt{2}} (x_2 - x_5) \quad [A_2] \]
\[ S_b = \frac{1}{\sqrt{2}} (x_1 - x_4) \quad [A_2] \]

\[ H_{aa} = \langle S_a | H | S_a \rangle = \left( \frac{1}{\sqrt{2}} (x_2 - x_5) \right) H \left( \frac{1}{\sqrt{2}} (x_2 - x_5) \right) \]

\[ H_{ab} = \frac{1}{2} \left[ \langle x_2 | H | x_2 \rangle - \langle x_5 | H | x_5 \rangle - \langle x_3 | H | x_5 \rangle + \langle x_5 | H | x_3 \rangle \right] \]

\[ H_{ba} = \frac{1}{2} [\beta - 0 - 0 + \beta] = \beta \]
**A₂ Block**

\[
H_{aa} = \alpha \quad H_{bb} = \alpha - \beta \quad H_{ab} = \beta
\]

Find the values of \(\alpha\) and \(\beta\) using the determinants:

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

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

where

\[
x = \frac{\alpha - E}{\beta}
\]

\[
x^2 - x - 1 = 0 \quad \Rightarrow \quad x = \frac{1 \pm \sqrt{(-1)^2 - 4(1)(-1)}}{2} = \frac{1 \pm \sqrt{5}}{2} = \frac{1 \pm 2.236}{2}
\]

I will name the energies \(E_n, E_{n+1}, \ldots\), so that I can renumber them according to order of increasing energy at the end of the problem.

\[
x_1 = \frac{1 - 2.236}{2} = -0.618 = \frac{\alpha - E_1}{\beta}
\]

\[
x_2 = \frac{1 + 2.236}{2} = +1.618 = \frac{\alpha - E_2}{\beta}
\]

\[
E_1 = \alpha + 0.618 \beta
\]

\[
E_2 = \alpha - 1.618 \beta
\]

---

**A₂ Block**

\[
S_a = \frac{1}{\sqrt{2}} (\chi_2 - \chi_3) \quad [A_1]
\]

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

Wavefunctions

\[
\psi = c_a S_a + c_b S_b
\]

\[
\begin{vmatrix}
1 & 1 \\
1 & x - 1
\end{vmatrix} = 0
\]

\[
c_a + c_b = 0
\]

\[
c_b + (x-1)c_a = 0
\]

\[
c_a = -x c_a
\]

\[
c_b = -c_b
\]

\[
x_1 = -0.618
\]

\[
E_a = \alpha + 0.618 \beta
\]

\[
\varphi_a = c_a \left( \frac{1}{\sqrt{2}} (\chi_2 - \chi_3) + 0.618 \frac{1}{\sqrt{2}} (\chi_3 - \chi_4) \right) = c_a \left( 0.707 \chi_1 + 0.437 \chi_2 - 0.437 \chi_3 - 0.707 \chi_4 \right)
\]

Normalization:

\[
c_a = \frac{1}{\sqrt{(0.707)^2 + (0.437)^2 + (-0.437)^2 + (-0.707)^2}} = 0.851
\]

\[
\varphi_a = 0.602 \chi_2 + 0.372 \chi_3 - 0.372 \chi_4 - 0.602 \chi_1
\]

---

Slide 49

Slide 50
A₂ Block

\[ S = \frac{1}{\sqrt{2}} (x_d - x_i) \quad [A₁] \]

\[ S = \frac{1}{\sqrt{2}} (x_i - x_d) \quad [A₂] \]

\[ x_i = +1.618 \]

\[ E = \alpha - 1.618\beta \]

Analogously

\[ \varphi = 0.372x_2 - 0.602x_3 + 0.602x_4 - 0.372x_5 \]

---

B₂ Block

\[ \alpha_s = \alpha + 1.5\beta \quad \beta_N = 0.8\beta \]

\[ S = \frac{1}{\sqrt{2}} (x_i + x_d) \quad [B₁] \]

\[ S = \frac{1}{\sqrt{2}} (x_i + x_d) \quad [B₂] \]

\[ S = x_i \quad [B₃] \]

\[ H_{\alpha s} = \langle S | H | S \rangle = \frac{1}{\sqrt{2}} (x_i + x_d) \quad H \quad \frac{1}{\sqrt{2}} (x_i + x_d) \]

\[ H = \frac{1}{2} \left[ \langle x_i | H | x_i \rangle + \langle x_i | H | x_d \rangle + \langle x_d | H | x_i \rangle + \langle x_d | H | x_d \rangle \right] \]

\[ H_{\alpha s} = \frac{1}{2} \left[ \alpha + 0 + 0 + \alpha \right] = \alpha \]

\[ H_{\beta N} = \langle S | H | S \rangle = \frac{1}{\sqrt{2}} (x_i + x_i) \quad H \quad \frac{1}{\sqrt{2}} (x_i + x_i) \]

\[ H_{\beta N} = \frac{1}{2} \left[ \langle x_i | H | x_i \rangle + \langle x_i | H | x_i \rangle + \langle x_i | H | x_i \rangle + \langle x_i | H | x_i \rangle \right] \]

\[ H_{\beta N} = \frac{1}{2} \left[ \alpha + \beta + \beta + \alpha \right] = \alpha + \beta \]
\[ \alpha_N = \alpha + 1.5 \beta \]
\[ \beta_N = 0.8 \beta \]
\[ S_z = \frac{1}{\sqrt{2}} (x_3 + x_4) \quad [B_1] \]
\[ S_x = \frac{1}{\sqrt{2}} (x_3 + x_4) \quad [B_2] \]
\[ S_y = x_1 \quad [B_3] \]

\[ H_{\alpha} = \langle S_z \mid H \rangle S_z = \langle x_3 + x_4 \mid H \rangle \]
\[ H_{\alpha} = \langle S_x \mid H \rangle S_x = \langle x_3 + x_4 \mid H \rangle \]
\[ H_{\alpha} = \langle S_y \mid H \rangle S_y = \langle x_1 \mid H \rangle \]

\[ H_{\alpha} = \frac{1}{\sqrt{2}} (\beta + 0 + \beta) = \beta \]

---

\[ \alpha_N = \alpha + 1.5 \beta \]
\[ \beta_N = 0.8 \beta \]
\[ S_z = \frac{1}{\sqrt{2}} (x_3 + x_4) \quad [B_1] \]
\[ S_x = \frac{1}{\sqrt{2}} (x_3 + x_4) \quad [B_2] \]
\[ S_y = x_1 \quad [B_3] \]

\[ H_{\alpha} = \langle S_z \mid H \rangle S_z = \langle x_3 + x_4 \mid H \rangle \]
\[ H_{\alpha} = \langle S_x \mid H \rangle S_x = \langle x_3 + x_4 \mid H \rangle \]
\[ H_{\alpha} = \langle S_y \mid H \rangle S_y = \langle x_1 \mid H \rangle \]

\[ H_{\alpha} = \frac{1}{\sqrt{2}} (\beta \beta) = \sqrt{2} \beta = \sqrt{2} \cdot 0.8 \beta = 1.131 \beta \]

\[ H_{\alpha} = \frac{1}{\sqrt{2}} (0 + 0) = 0 \]
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.

- \( x_1 = -2.320 = \frac{\alpha - E_1}{\beta} \)
- \( x_2 = -1.189 = \frac{\alpha - E_2}{\beta} \)
- \( x_3 = +1.008 = \frac{\alpha - E_3}{\beta} \)

\[ E_1 = \alpha + 2.320 \beta \quad E_2 = \alpha + 1.189 \beta \quad E_3 = \alpha - 1.008 \beta \]
\[ S_e = \frac{1}{\sqrt{2}} (x_2 + x_5) \quad [B_2] \]
\[ S_d = \frac{1}{\sqrt{2}} (x_3 + x_4) \quad [B_2] \]
\[ S_s = x_1 \quad [B_2] \]
\[ \varphi = c_e S_e + c_d S_d + c_s S_s \]

**Wavefunctions**

\[ \begin{array}{ccc}
  x & 1 & 1.131 \\
  1 & x+1 & 0 \\
  1.131 & 0 & x+1.5
\end{array} \]

\[ \Rightarrow \begin{array}{c}
  xc_e + c_d + 1.131c_s = 0 \\
  c_e + (x+1)c_d = 0 \\
  1.131c_e + (x+1.5)c_s = 0
\end{array} \]

From Second Eqn.
\[ c_e = -\frac{c_s}{x+1} \quad c_d = -\frac{c_s}{-2.320+1} = +0.758c_e \]
\[ c_s = -\frac{1.131c_e}{x+1.5} = 1.379c_e \]

From Third Eqn.
\[ E_s = \alpha + 2.320\beta \quad E_d = \alpha - 1.131\beta \]
\[ E_s = \alpha - 1.131\beta \]

\[ \varphi_e = c_e \left( S_e + 0.758S_d + 1.379S_s \right) \]
\[ \varphi_d = c_e \left( \frac{1}{\sqrt{2}} (x_2 + x_5) + 0.758 \frac{1}{\sqrt{2}} (x_3 + x_4) + 1.379 x_1 \right) \]
\[ \varphi_s = c_e \left( 1.379 x_1 + 0.707 x_2 + 0.536 x_3 + 0.536 x_4 + 0.707 x_5 \right) \]

---

\[ S_e = \frac{1}{\sqrt{2}} (x_1 + x_5) \quad [B_2] \]
\[ S_d = \frac{1}{\sqrt{2}} (x_3 + x_4) \quad [B_2] \]
\[ S_s = x_1 \quad [B_2] \]
\[ \varphi = c_e (1.379x_1 + 0.707x_2 + 0.536x_3 + 0.536x_4 + 0.707x_5) \]

**Normalization:**
\[ c_e = \frac{1}{\sqrt{(1.379)^2 + (0.707)^2 + (0.536)^2 + (0.536)^2 + (0.707)^2}} = 0.536 \]

\[ \varphi_e = 0.725x_1 + 0.379x_2 + 0.287x_3 + 0.287x_4 + 0.379x_5 \]

\[ x_e = -1.189 \quad x_e = +1.008 \]
\[ E_e = \alpha + 1.189\beta \quad E_s = \alpha - 1.008\beta \]

Analogously
\[ \varphi_e = 0.530x_1 - 0.111x_2 - 0.589x_3 - 0.589x_4 - 0.111x_5 \]
\[ \varphi_s = 0.374x_1 - 0.587x_2 + 0.292x_3 + 0.292x_4 - 0.587x_5 \]
Wavefunctions and Energies

\[ E_4 = E_2 = \alpha - 1.618 \beta \]
\[ \phi_4 = \phi_2 = 0.372 \chi_2 - 0.602 \chi_3 + 0.602 \chi_4 - 0.372 \chi_5 \]

\[ E_3 = E_1 = \alpha - 1.008 \beta \]
\[ \phi_3 = \phi_1 = 0.374 \chi_1 - 0.587 \chi_2 + 0.292 \chi_3 + 0.292 \chi_4 - 0.587 \chi_5 \]

\[ E_2 = E_0 = \alpha + 0.618 \beta \]
\[ \phi_2 = \phi_0 = 0.602 \chi_2 + 0.372 \chi_3 - 0.372 \chi_4 - 0.602 \chi_5 \]

\[ E_1 = E_{-1} = \alpha + 1.189 \beta \]
\[ \phi_1 = \phi_{-1} = 0.530 \chi_1 - 0.111 \chi_2 - 0.589 \chi_3 - 0.589 \chi_4 - 0.111 \chi_5 \]

\[ E_0 = E_{-2} = \alpha + 2.320 \beta \]
\[ \phi_0 = \phi_{-2} = 0.725 \chi_1 + 0.379 \chi_2 + 0.287 \chi_3 + 0.287 \chi_4 + 0.379 \chi_5 \]