

**Class Worksheet 5**

**The Hückel theory**

Hückel theory considers the \( \pi \) electron systems of conjugated and aromatic hydrocarbons. It adopts the following conventions:

1. The basis set is formed entirely from parallel carbon 2p orbitals, one per atom. The wavefunction (or, to be more precise, each MO), takes the form:
   \[
   \Psi = c_1 p_1 + c_2 p_2 + \ldots + c_n p_n
   \]

2. The overlap matrix is defined by \( S_{ij} = \delta_{ij} \). Thus, the overlap of any carbon 2p orbital with itself is unity (i.e., the p functions are normalized), and that between any two p orbitals is zero.

3. Matrix elements \( H_{ii} \) are set equal to an empirical value, denoted \( \alpha \). In practice, \( \alpha \) is determined as the negative of the ionization potential of the methyl radical, i.e., the orbital energy of the singly occupied 2p orbital in the prototypical system defining sp\(^2\) carbon hybridization.

4. Matrix elements \( H_{ij} \) between the nearest neighbor \( s \) are also derived from experimental (empirical) information and denoted \( \beta \).

5. Matrix elements \( H_{ij} \) between carbon 2p orbitals more distant than nearest neighbors are set equal to zero.

Therefore, for a linear conjugated molecule with \( N \) carbon atoms, the Hamiltonian matrix looks like this:

\[
\hat{H} = \begin{pmatrix}
\alpha & \beta & 0 & 0 & \ldots & 0 \\
\beta & \alpha & \beta & 0 & \ldots & 0 \\
0 & \beta & \alpha & \beta & \ldots & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & \ldots & 0 & \beta & \alpha
\end{pmatrix}
\]

while for a cyclic one:

\[
\hat{H} = \begin{pmatrix}
\alpha & \beta & 0 & 0 & \ldots & \beta \\
\beta & \alpha & \beta & 0 & \ldots & 0 \\
0 & \beta & \alpha & \beta & \ldots & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
\beta & 0 & \ldots & 0 & \beta & \alpha
\end{pmatrix}
\]

The overlap matrix \( S \) is a unit matrix. The equations of the Hückel theory therefore reduce to a simple eigenvalue problem \( \hat{H}\mathbf{c} = E\mathbf{c} \).

1. Use Hückel theory to solve the electronic problem for the allyl system \( \text{C}_3\text{H}_5^+ \).
a) Calculate the eigenvalues and sketch the energy diagram and the molecular orbitals.
b) Write a Slater determinant for the electronic ground state of allyl cation.

c) Compare HOMO and LUMO molecular orbitals from your Hückel theory results to the HF/STO-3G calculations (don’t forget to optimize the molecule before computing the orbitals). Report the number of nodes and energies for the HOMO, LUMO and LUMO+1.

<table>
<thead>
<tr>
<th></th>
<th>Hückel</th>
<th>HF/STO-3G</th>
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</thead>
<tbody>
<tr>
<td>MO</td>
<td># nodes</td>
<td># nodes</td>
</tr>
<tr>
<td>HOMO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LUMO</td>
<td></td>
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<tr>
<td>LUMO + 1</td>
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</tbody>
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2. Write Slater determinants for the ground state electronic configurations of:
   a) He (1s^2)

   b) Be (1s^2 2s^2)