7: Hückel theory for polyatomic molecules

Introduction

Approximate treatment of $\pi$ electron systems in organic molecules:

Approximations

1. $\pi$ and $\sigma$ frameworks completely separated

2. Trial wavefunctions can be used of the form: $\Psi = \sum_i c_i p_i^\pi$

3. $H_{ii} = \langle p_i | \hat{H} | p_i \rangle = \alpha$ same for all atoms

4. $H_{ij} = \langle p_i | \hat{H} | p_j \rangle = \beta$ $i$ bonded to $j$

   $= 0$ otherwise.

   Note that $\beta$ is negative.

5. $S_{ij} = \langle p_i | p_j \rangle = \delta_{ij}$,

   where $\delta_{ij} = 1$ when $i = j$ and $\delta_{ij} = 0$ when $i \neq j$. 
Optimize orbital coefficients as before using the variation principle.

Know already that this leads to secular equations

\[
\begin{pmatrix}
\alpha - E & \beta \\
\beta & \alpha - E
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2
\end{pmatrix}
= 0.
\]

So the energies are the solutions of the secular determinant

\[
\left| \begin{array}{cc}
\alpha - E & \beta \\
\beta & \alpha - E
\end{array} \right| = 0.
\]

Wavefunctions obtained by substituting the energies \(E_\pm\) back into secular equation:

\[
\Psi_\pm = \frac{1}{\sqrt{2}} (p_1 \pm p_2)
\]

Thus, with respect to two non-bonded \(p^\pi\) electrons, ethene has a \(\pi\) stabilization energy of \(2\beta\) (i.e., \(\beta\) for each electron).

See Sheet 2, question 1 for a problem involving the allyl radical.
Butadiene

There is nothing in Hückel theory that distinguishes \textit{cis}— from \textit{trans}—, or indeed linear, butadiene.

As before, the trial wavefunction,
\[
\Psi = c_1 p_1 + c_2 p_2 + c_3 p_3 + c_4 p_4,
\]
is optimized using the variation principle. The secular equation can be written down directly

\[
\begin{pmatrix}
\alpha - E & \beta & 0 & 0 \\
\beta & \alpha - E & \beta & 0 \\
0 & \beta & \alpha - E & \beta \\
0 & 0 & \beta & \alpha - E
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2 \\
c_3 \\
c_4
\end{pmatrix} = 0.
\]

Multiplying out this leads to a quartic equation. Although this can be solved, here we will use of symmetry to simplify the algebra.
Butadiene has a two-fold symmetry axis. Form symmetry adapted linear combinations (SALCs) of atomic orbitals

\[ \chi_1 = \frac{1}{\sqrt{2}}(p_1 + p_4) \]
\[ \chi_2 = \frac{1}{\sqrt{2}}(p_2 + p_3) \]
\[ \chi_3 = \frac{1}{\sqrt{2}}(p_2 - p_3) \]
\[ \chi_4 = \frac{1}{\sqrt{2}}(p_1 - p_4) \]

\( \chi_1 \) and \( \chi_2 \) are symmetric (A), and \( \chi_3 \) and \( \chi_4 \) are antisymmetric (B) with respect to the \( C_2 \) operation.

Let

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

\( H_{ij} \) and \( S_{ij} \) vanish if \( i \) and \( j \) are of different symmetry:

\[
\begin{pmatrix}
\alpha - E & \beta & 0 & 0 \\
\beta & \alpha + \beta - E & 0 & 0 \\
0 & 0 & \alpha - \beta - E & \beta \\
0 & 0 & \beta & \alpha - E \\
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2 \\
c_3 \\
c_4 \\
\end{pmatrix}
= 0.
\]

Matrix becomes block diagonal.
Look at some of the **matrix elements**

\[
H_{11} = \langle \chi_1 | \hat{H} | \chi_1 \rangle = \langle \frac{1}{\sqrt{2}} (p_1 + p_4) | \hat{H} | \frac{1}{\sqrt{2}} (p_1 + p_4) \rangle \\
= \frac{1}{2} \left\{ \langle p_1 | \hat{H} | p_1 \rangle + \langle p_4 | \hat{H} | p_4 \rangle + \langle p_1 | \hat{H} | p_4 \rangle + \langle p_4 | \hat{H} | p_1 \rangle \right\} \\
= \alpha
\]

\[
H_{14} = \langle \chi_1 | \hat{H} | \chi_4 \rangle = \langle \frac{1}{\sqrt{2}} (p_1 + p_4) | \hat{H} | \frac{1}{\sqrt{2}} (p_1 - p_4) \rangle \\
= \frac{1}{2} \left\{ \langle p_1 | \hat{H} | p_1 \rangle - \langle p_4 | \hat{H} | p_4 \rangle - \langle p_1 | \hat{H} | p_4 \rangle + \langle p_4 | \hat{H} | p_1 \rangle \right\} \\
= 0
\]

\[
H_{33} = \langle \chi_3 | \hat{H} | \chi_3 \rangle = \langle \frac{1}{\sqrt{2}} (p_2 - p_3) | \hat{H} | \frac{1}{\sqrt{2}} (p_2 - p_3) \rangle \\
= \frac{1}{2} \left\{ \langle p_2 | \hat{H} | p_2 \rangle + \langle p_3 | \hat{H} | p_3 \rangle - \langle p_2 | \hat{H} | p_3 \rangle - \langle p_3 | \hat{H} | p_2 \rangle \right\} \\
= \alpha - \beta
\]

Note that, as before, the overlap integrals in the SALC basis are

\[
S_{ij} = \delta_{ij}
\]
Now solve the upper $2 \times 2$ determinant.

$$ (\alpha - E)(\alpha + \beta - E) - \beta^2 = 0 $$

$$ E_{\pm} = \alpha \pm \frac{1 \pm \sqrt{5}}{2} \beta $$

$$ E_1 = \alpha + 1.62\beta \quad E_3 = \alpha - 0.62\beta $$

To get molecular orbital corresponding to $E_1$ substitute $E_1$ into secular equations

$$ -1.62\beta c_1 + \beta c_2 = 0 $$

$$ c_1 = \frac{c_2}{1.62} $$
But wavefunction needs to be normalized

\[ \psi_1 = N \left[ \frac{1}{\sqrt{2}} (p_1 + p_4) + 1.62 \frac{1}{\sqrt{2}} (p_2 + p_3) \right] \]

\[ \langle \psi_1 | \psi_1 \rangle = N^2 \left[ \frac{1}{2} + \frac{1}{2} + \frac{1.62^2}{2} + \frac{1.62^2}{2} \right] = 1 \]

So

\[ \psi_1 = 0.37p_1 + 0.60p_2 + 0.60p_3 + 0.37p_4 \]

Similarly, find MO \( \psi_3 \) associated with energy level \( E_3 \)

\[ \psi_3 = 0.60p_1 - 0.37p_2 - 0.37p_3 + 0.60p_4 \]
From the lower $2 \times 2$ determinant one obtains

\[ E_2 = \alpha + 0.62\beta \quad E_4 = \alpha - 1.62\beta \]

with the normalized wavefunctions

\[ \Psi_2 = 0.60p_1 + 0.37p_2 - 0.37p_3 - 0.60p_4 \]

and

\[ \Psi_4 = 0.37p_1 - 0.60p_2 + 0.60p_3 - 0.37p_4 \]
Charge density on atoms

Once the wavefunctions of the MOs are known the charge densities on each atom, $q_i$, can be obtained from

$$q_i = \sum_k n_k (c_i^k)^2,$$

where the sum over $k$ is over all occupied molecular orbitals, and $n_k$ is the occupation number of MO $k$ (either 0, 1 or 2 for non-degenerate orbitals).

$(c_i^k)^2$ is the square of the coefficient in the $k$th orbital on the $i$th atom.

For butadiene, this reads (for atoms 1 and 2)

$$q_1 = 0.37^2 \times 2 + 0.60^2 \times 2 = 1$$
$$q_2 = 0.60^2 \times 2 + 0.37^2 \times 2 = 1$$

and similarly for atoms 3 and 4.

That the charge densities on all the atoms are equal is a general property of the ground states of **alternant hydrocarbons**.

These also have a **pairing of the MO energies** $E = \alpha \pm x\beta$.

See MKT for more details.
Resonance stabilization energy

In Hückel theory the resonance stabilization energy provides an indication of the increased molecular stability that arises from $\pi$ bonding.

For the ground electronic state of butadiene the total electronic energy is

$$E_{\text{tot}} = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = 4\alpha + 4.48\beta$$

Thus the resonance stabilization energy is

$$\Delta E = E_{\text{tot}} - 4\alpha = 4.48\beta$$

This stabilization can be compared with that of $4\beta$ that would be generated from two isolated $\pi$ bonds (i.e. in two isolated ethene molecules).

$$\Delta E_{\text{deloc}} = \Delta E - 4\beta = 0.48\beta.$$ 

This energy provides a measure of the delocalization energy, the extra stabilization that arises from delocalization of the electrons over the $\pi$ system.
**Bond order**

Provides an indication of the strength of the $\pi$ bond between adjacent atoms $i$ and $j$

$$\rho_{ij} = \sum_k n_k c_i^k c_j^k.$$  

The sum is over MO's $k$, with $n_k$ the occupation number of those orbitals. For butadiene

$$\rho_{12} = 2 (0.37 \times 0.60) + 2 (0.60 \times 0.37) = 0.89$$

$$\rho_{23} = 2 (0.60 \times 0.60) + 2 (0.37 \times -0.37) = 0.45$$

Suggests a partial $\pi$ bond between the central atoms, so the terminal bonds might be shorter than the central bond.

**Bond lengths in excited states**

Similar treatment for excited electronic state.

$$\rho_{12} = 2 (0.37 \times 0.60) + (0.60 \times 0.37) + (0.60 \times -0.37) = 0.45$$

$$\rho_{23} = 2 (0.60 \times 0.60) + (0.37 \times -0.37) + (-0.37 \times -0.37) = 0.72$$

Outer bonds expand, inner bond contracts on excitation to the excited electronic state.

(See Spectroscopy lectures, and the Franck-Condon principle - vibrational excitation accompanies electronic transition.)
ESR spectrum of the radical cation

The strength of the hyperfine coupling to the protons is proportional to the unpaired electron density on the adjacent carbon atom.

For the butadiene cation, \([C_4H_6]^+\),

\[
a_1 = a(c_1^2)^2 = a \times 0.60^2 = 0.36a
\]

\[
a_2 = a(c_2^2)^2 = a \times 0.37^2 = 0.14a
\]

where \(a\) is a universal constant. The following spectrum is therefore predicted:
Susceptibility to electrophilic attack

Rate of reaction is proportional to the barrier height. Estimate relative barriers for different pathways.

\[ \Delta E = \Delta E_\sigma + \Delta E_\pi \]

Suppose that \( \Delta E_\sigma \) is insensitive to position of attack.

\[ \Delta E_\pi = \pi^\text{\#} - E^{\text{butadiene}}_\pi = \text{change in resonance stabilization} \]

\[ E^{\text{butadiene}}_\pi = 4\alpha + 4.48\beta \]

**Attack at central carbon**

\[ E^{\#}_\pi(1) \simeq 2\alpha + 2\beta \quad \# \text{ a bit like ethene} \]

\[ \Delta E_\pi(1) = -2\alpha - 2.48\beta \]

**Attack at terminal carbon**

\[ E^{\#}_\pi(2) \simeq 2\alpha + 2\sqrt{2}\beta \quad \# \text{ a bit like allyl cation} \]

\[ \Delta E_\pi(2) = -2\alpha - 1.65\beta \]

**Attack at terminal atom preferred.**

Many approximate methods for calculating the *localization energy* have been devised (e.g., frontier orbitals) - see recommended texts.
8: Applications of Hückel Theory

Aromaticity

π MOs of a cyclic polyene ($N$ carbon atoms)

The secular equation for a cyclic polyene is given by:

\[
\begin{pmatrix}
\alpha - E & \beta & 0 & 0 & 0 & \beta \\
\beta & \alpha - E & \beta & 0 & 0 & 0 \\
0 & \beta & \alpha - E & \beta & 0 & 0 \\
0 & 0 & \beta & \alpha - E & \beta & 0 \\
0 & 0 & 0 & \beta & \alpha - E & \beta \\
\beta & 0 & 0 & 0 & \beta & \alpha - E \\
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2 \\
c_3 \\
c_4 \\
c_5 \\
c_6 \\
\end{pmatrix}
= 0
\]

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

A general row of the secular equations gives

\[
c_{n-1} + xc_n + c_{n+1} = 0
\]

For even membered rings ($N = 2l$ where $l$ is an integer)

\[
c_{2l+n} = c_n
\]
Hence try:

\[ c_n^k = e^{i \frac{k \pi (n-1)}{2l}} \]  \( \text{coefficient on } n^{th} \text{ atom for } k^{th} \text{ MO} \)

where

\[ k = 0, \pm 1, \pm 2, \ldots, +l \]

Substitute \( c_n^k \) back into equation for coefficients

\[ e^{i \frac{k \pi (n-1)}{2l}} + xe^{i \frac{k \pi n}{2l}} + e^{i \frac{k \pi (n+1)}{2l}} = 0 \]

or

\[ \left( e^{-i \frac{k \pi}{l} + x + e^{i \frac{k \pi}{l}}} \right) e^{i \frac{k \pi n}{l}} = 0 \]

or

\[ x = -2 \cos \frac{k \pi}{l} \]

Therefore

\[ E_k = \alpha + 2\beta \cos \frac{k \pi}{l} \quad k = 0, \pm 1, \pm 2 \ldots, +l \]
Hence, the resulting energy levels can be displayed diagrammatically

\[ E_k = \alpha + 2\beta \cos \frac{k\pi}{l} \equiv \alpha + 2\beta \cos \theta \quad k = 0, \pm 1, \pm 2, \ldots, +l, \]

where \( \theta = \frac{k\pi}{l} \) correspond to the angles subtended by the vertices of a regular polyhedron.

\[ E = 4\alpha + 4\beta \equiv \] two ethenes. No extra resonance stabilization due to delocalization. Note unpaired electrons and degenerate ground state.

\[ E = 6\alpha + 8\beta, \] i.e. \( 2\beta \) lower than three ethenes - extra resonance stabilization due to delocalization.

\[ E = 8\alpha + 4(1+\sqrt{2})\beta, \] i.e. \( 4(\sqrt{2}-1)\beta \) lower than four ethenes - extra resonance stabilization but with unpaired electrons and degenerate ground state.
For odd membered rings \((N = 2l + 1)\)

\[ c_{2l+1+n} = c_n \]

Hence

\[ c_n^k = e^{ik2\pi n/(2l+1)} \quad k = 0, \pm 1, \pm 2, \cdots, \pm l \]

Therefore

\[ E_k = \alpha + 2\beta \cos \frac{2\pi k}{2l+1} \quad k = 0, \pm 1, \pm 2 \cdots, \pm l \]

Origin of the \(4n + 2\) \(\pi\)-electron rule for stability of aromatic molecules.
Perturbation theory and steric interactions

Find approximately the properties of a system from those of a system with a slightly different (simpler) Hamiltonian.

**General result** - just quote

“First order energy”

\[ \Delta E_k = \langle \Psi_k | \Delta \hat{H} | \Psi_k \rangle \]

- \( \Delta E_k \) — change in energy of the \( k^{th} \) orbital on perturbation
- \( \Psi_k \) — orbital \( k \) of the original (unperturbed) problem
- \( \Delta \hat{H} \) — difference between the original Hamiltonian and the full one (i.e. the perturbation)
Example 1

Find the $\pi$ MO energies of $\text{H}_2\text{H}_2\text{O}$ having solved the butadiene problem.

The only major difference is in the energy of the oxygen atom $p_\pi$ orbital with respect to that of carbon, i.e.

$$\langle p_4 | \hat{H} | p_4 \rangle = \alpha_O < \alpha_C$$

However, we can estimate the energy lowering ($\sim 0.6\beta$) and can write

$$\alpha_O = \alpha_C + 0.6\beta$$

Now use butadiene MOs in

$$\Delta E_k = \langle \Psi_k | \Delta \hat{H} | \Psi_k \rangle$$

$$= \left\langle \sum_i c_i^k p_i | \Delta \hat{H} | \sum_j c_j^k p_j \right\rangle$$

$$= \sum_{i,j} c_i^k c_j^k \langle p_i | \Delta \hat{H} | p_j \rangle$$

(1)
But the only matrix element which is affected is $\langle p_4 | \hat{H} | p_4 \rangle$ such that

$$\Delta E_k = (c_k^4)^2 \langle p_4 | \Delta \hat{H} | p_4 \rangle = (c_k^4)^2 0.6\beta.$$ 

All other terms in Eqn. (1) are zero.
**Example 2**

In butadiene the \( \pi \) bond order between the central (2-3) atoms is less than the terminal (1-2, 3-4) bonds.

Matrix element \( H_{23} \) is less negative than \( H_{12} \) and \( H_{34} \). Let

\[
H_{12} = H_{34} = \beta \quad H_{23} = \beta + \delta,
\]

where \( \beta \) is negative (as usual), but \( \delta \) is positive.

Find shift in the MO energies due to this effect. Perturbation to Hamiltonian only involves \( \langle p_2 | \hat{H} | p_3 \rangle \), therefore

\[
\Delta E_k = (c_2^k c_3^k + c_3^k c_2^k) \langle p_2 | \Delta \hat{H} | p_3 \rangle = 2c_2^k c_3^k \delta.
\]

Tending to the energy level pattern for two ethenes.
Non-crossing rule

Consider mixing of two orbitals $\phi_1$ and $\phi_2$

$$\Psi = c_1\phi_1 + c_2\phi_2.$$ 

The orbitals $\phi_i$ could be the MOs that we have just been considering for butadiene.

We know that the energies of the mixed orbitals will be the solutions of the secular equations (see Problem sheet 1)

$$E_\pm = \frac{1}{2} \left\{ (H_{AA} + H_{BB}) \pm \sqrt{(H_{AA} - H_{BB}) + 4H_{AB}^2} \right\}.$$ 

So $E_+ = E_- \text{ only if } H_{AB} = 0.$

In general, $H_{AB} = 0$ only if the states have different symmetry (otherwise in region of crossing there will always be some small term in the Hamiltonian which mixes the two orbitals).

![Diagram showing the non-crossing rule with states of the same symmetry not crossing](attachment:image.png)

**States of the same symmetry cannot cross.**
Correlation diagrams

Non-crossing rule is helpful in determining reaction pathways based on orbital symmetry arguments.

Consider the ring opening of cyclobutene.

Two categories of ring-opening.
The ground electronic state of cyclobutene ($\sigma^2\pi^2$) smoothly correlates with the ground state ($\psi_1^2\psi_2^2$) of butadiene in the **conrotatory** mode, giving $A$ for thermal reaction.

From the first excited electronic state ($\sigma^2\pi\pi^*$) of cyclobutene there is a smooth correlation with the excited state ($\psi_1^2\psi_2\psi_3$) of butadiene in the **disrotatory** mode, giving $A$ for photon-initiated reaction.

This is the basis of Woodward-Hoffmann rules.