Huckel Molecular Orbital Theory for Buckminsterfullerene

1. Number the carbons after inspection of the molecular structure and fill in data needed below.

Natoms := 60  
\( \text{The number of carbon atoms and } \pi\text{-electrons.} \)

Nocc := 30  
\( \text{The number of occupied molecular orbitals.} \)

2. Create a 60 x 60 null matrix.

\[
H_{n,n} := \begin{cases} 
1 & \text{if } (j = i + 1) \text{ or } (j = i - 1) \\
0 & \text{otherwise} 
\end{cases} 
\]

3. Form the Huckel matrix from the null matrix using the results of part 1.

\[
\begin{align*}
H_{1,5} := 1 & \quad H_{1,9} := 1 \\
H_{5,1} := 1 & \quad H_{9,1} := 1
\end{align*}
\]

\[
\begin{align*}
H_{2,12} := 1 & \quad H_{3,15} := 1 \\
H_{4,18} := 1 & \quad H_{6,20} := 1 \\
H_{7,22} := 1 & \quad H_{1,1} := \text{if} \{(j = i + 1) \text{ or } (j = i - 1), 1, 0\}
\end{align*}
\]
4. Calculate the eigenvalues and eigenvectors. It is not feasible to look at the eigenvectors as a group because that would require displaying a 60 x 60 matrix. The eigenvalues will be displayed later.

\[
E := \text{eigvals}(H) \quad C := \text{submatrix}(\text{rsort}(\text{stack}(E^T, \text{eigenvecs}(H)), 1), 2, \text{Natoms} + 1, 1, \text{Natoms})
\]

5. Use the eigenvectors to calculate selected \(\pi\)-electron densities and \(\pi\)-bond orders. If \(r = s\) you are calculating the \(\pi\)-electron density on carbon \(r\). If \(r\) is not equal to \(s\) you are calculating the \(r\)-\(s\) \(\pi\)-bond order. Several examples are given below. These calculations can be used to show that all the carbons have the same \(\pi\)-electron density and that there are only two physically meaningful \(\pi\)-bond orders.

\[
r := 1 \quad s := 1 \quad 2 \sum_{i=1}^{\text{Noec}} \left[ \left( C^{(i)}_r \right) \left( C^{(i)}_s \right) \right] = 1.144 \quad \pi\text{-electron density on carbon 1}
\]

\[
r := 1 \quad s := 2 \quad 2 \sum_{i=1}^{\text{Noec}} \left[ \left( C^{(i)}_r \right) \left( C^{(i)}_s \right) \right] = 0.456 \quad \pi\text{-bond order between carbons 1 and 2}
\]

\[
r := 1 \quad s := 5 \quad 2 \sum_{i=1}^{\text{Noec}} \left[ \left( C^{(i)}_r \right) \left( C^{(i)}_s \right) \right] = 0.547 \quad \pi\text{-bond order between carbons 1 and 5}
\]

\[
r := 1 \quad s := 9 \quad 2 \sum_{i=1}^{\text{Noec}} \left[ \left( C^{(i)}_r \right) \left( C^{(i)}_s \right) \right] = 0.691 \quad \pi\text{-bond order between carbons 1 and 9}
\]

Note that these result are consistent with the familiar valence bond structures for \(C_{60}\) which show that each carbon has two single bonds and one double bond.

6. Display the energy eigenvalues: \(E := \text{sort}(E)\)

\[
\begin{pmatrix}
-3 \\
-2.757 \\
-2.757 \\
-2.757 \\
-2.757 \\
-2.303 \\
-2.303 \\
-2.303 \\
-2.303 \\
-2.303 \\
\end{pmatrix}
\begin{pmatrix}
-1.562 \\
-1 \\
-1 \\
-1 \\
-1 \\
-1 \\
-1 \\
-1 \\
-1 \\
\end{pmatrix}
\begin{pmatrix}
0.139 \\
0.139 \\
0.382 \\
0.382 \\
0.382 \\
1.303 \\
1.303 \\
1.303 \\
1.303 \\
\end{pmatrix}
\begin{pmatrix}
1.618 \\
1.618 \\
1.618 \\
1.618 \\
2 \\
2 \\
2 \\
2 \\
2 \\
\end{pmatrix}
\]

\(i := 1..15 \quad E_i = 
\begin{pmatrix}
-2.303 \\
-2.303 \\
-1.82 \\
-1.82 \\
-1.82 \\
-1.562 \\
-1.562 \\
-1.562 \\
\end{pmatrix}
\)

\(i := 16..30 \quad E_i = 
\begin{pmatrix}
-1 \\
-1 \\
-0.618 \\
-0.618 \\
-0.618 \\
\end{pmatrix}
\)

\(i := 31..45 \quad E_i = 
\begin{pmatrix}
1.303 \\
1.303 \\
1.303 \\
1.438 \\
1.438 \\
\end{pmatrix}
\)

\(i := 46..60 \quad E_i = 
\begin{pmatrix}
2 \\
2 \\
2 \\
2 \\
\end{pmatrix}
\)

\(i := 61..75 \quad E_i = 
\begin{pmatrix}
1.618 \\
1.618 \\
2.562 \\
2.562 \\
2.618 \\
2.618 \\
2.618 \\
\end{pmatrix}
\)
The energy eigenvalues can also be displayed graphically as follows:

Attention should be drawn to the nine-fold degenerate state at $E = -1$. $C_{60}$ belongs to the icosahedral point group and the largest degeneracy permitted is 5-fold. Thus, this state is an example of the accidental degeneracy of a 5-fold degenerate state and a 4-fold degenerate state.

7. It is easy to show that this manifold of energy states is in agreement with the basic facts about $C_{60}$. For example, it is diamagnetic and a non-conductor. Placing the 60 $\pi$-electrons is the lowest available energy states completely fills all the bonding molecular orbitals. The HOMO has an energy of $-0.618 \beta$ and contains ten paired electrons giving a diamagnetic and non-conducting electronic structure. The LUMO is three-fold degenerate and not far away in energy. This is consistent with the fact that $C_{60}$ has a high electron affinity and forms ionic compounds with alkali metals such as potassium. For example, $K_3C_{60}$ (three unpaired electrons in the LUMO) is a conductor and becomes a superconductor at low temperatures, while $K_6C_{60}$ (six paired electrons in the LUMO) is a non-conductor.

The Hückel calculation can be extended with a simple example of modeling. Since the results of the following calculation require the assignment of a value for $\beta$, the results should not be taken too seriously. The HOMO-LUMO gap is $0.757 \beta$. Giving $|\beta|$ a typical value 2.5 eV enables one to calculate the wavelength of light required to promote an electron from the HOMO to the LUMO.

$$\lambda = \frac{\hbar c}{h c} = 655 \text{ nm}$$

This result is just barely within the visible region and not in particularly good agreement with a known visible transition around 400 nm. However, it should be noted that the HOMO-LUMO transition is formally forbidden. The HOMO-LUMO+1 is allowed and the energy gap is $|\beta|$ which would give an optical transition at 496 nm, in better agreement with the experimental value. There are a number of very weak features in the visible spectrum between 440 and 670 nm any of which may be attributable to the forbidden HOMO-LUMO transition. However, it is also true that small amounts of other fullerenes may be contributing to this part of the visible spectrum.
8. Calculate the $\pi$-electron stabilization energy per carbon atom. This is calculated by summing the energies of the occupied orbitals and multiplying by two. Subtract from this the $\pi$-electron binding energy of the equivalent number of ethylene molecules and divide by the number of carbon atoms, which is the same as the number of $\pi$-electrons.

$$\Delta E_\pi := \frac{\sum_{i=1}^{N_{occ}} |E_i| - N_{atoms}}{N_{atoms}}$$

$\Delta E_\pi = 0.553$

Recall that the $\pi$-electron stabilization energy per carbon atom for benzene is 0.333.