3.29: A Numerical Huckel MO Calculation on C60
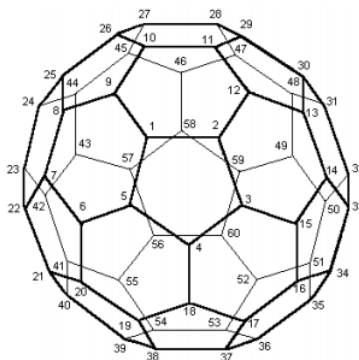
1. Number the carbons after inspection of the molecular structure and fill in data needed below.

$$\text{Natoms} = 60 \quad \text{the number of carbon atoms and } \pi - \text{electrons}$$
$$\text{Nocc} = 30 \quad \text{the number of occupied molecular occupied}$$

2. Create a 60 x 60 null matrix.

$$i = 1 .. \text{Natoms} \quad j = 1 .. \text{Natoms} \quad H_{i, j} = 0$$

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

$$k = 1 .. \text{Natoms - 1} \quad H_{k, k+1} = 1$$

$$
\begin{array}{lllllll}
H_{1, 5} = 1 & H_{1, 9} = 1 & H_{2, 12} = 1 & H_{3, 15} = 1 & H_{4, 18} = 1 & H_{6, 20} = 1 & H_{7, 22} = 1 \\
H_{8, 25} = 1 & H_{10, 26} = 1 & H_{11, 29} = 1 & H_{13, 30} = 1 & H_{14, 33} = 1 & H_{16, 34} = 1 & H_{17, 37} = 1 \\
H_{19, 38} = 1 & H_{21, 40} = 1 & H_{23, 42} = 1 & H_{24, 44} = 1 & H_{27, 45} = 1 & H_{28, 47} = 1 & H_{31, 48} = 1 \\
H_{32, 50} = 1 & H_{35, 51} = 1 & H_{36, 53} = 1 & H_{39, 54} = 1 & H_{41, 55} = 1 & H_{43, 57} = 1 & H_{46, 58} = 1 \\
H_{49, 59} = 1 & H_{52, 60} = 1 & H_{56, 60} = 1 & H_{j, i} = H_{i, j} & H = -H &
\end{array}
$$

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.

$$\text{E} = \text{eigenvals(H)} \quad \text{C} = \text{submatrix}\left(\text{rsort}\left(\text{stack}\left(\text{E}^{T}, \text{eigenvecs(H)}\right), 1\right), 2\text{Natoms} +1, 1, \text{Natoms}\right)$$

5. Use the eigenvectors to calculate selected π-electron densities and π-bond orders. If r = s you are calculating the π-electron density on carbon r. If r is not equal to s you are calculating the r-s π-bond order. Several examples are given below. These calculations can be used to show that all the carbons have the same π-electron density and that there are only two physically meaningful π-bond orders.
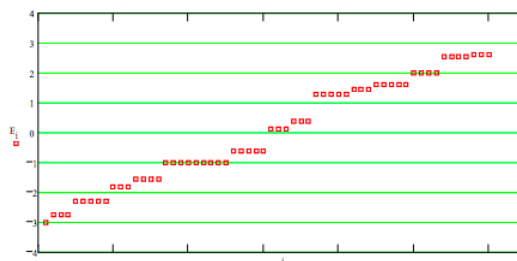
$$
\begin{array}{llll}
r = 1 & s = 1 & 2\sum_{i=1}^{\text{Nocc}} \left(C^{<i>}\right)_r, \left(C^{<i>}\right)_s = 1 & \pi - \text{electron density on carbon 1} \\
r = 1 & s = 2 & 2\sum_{i=1}^{\text{Nocc}} \left(C^{<i>}\right)_r, \left(C^{<i>}\right)_s = 0.476 & \pi - \text{bond order between carbons 1 and 2} \\
r = 1 & s = 5 & 2\sum_{i=1}^{\text{Nocc}} \left(C^{<i>}\right)_r, \left(C^{<i>}\right)_s = 0.476 & \pi - \text{bond order between carbons 1 and 5} \\
r = 1 & s = 9 & 2\sum_{i=1}^{\text{Nocc}} \left(C^{<i>}\right)_r, \left(C^{<i>}\right)_s = 0.601 & \pi - \text{bond order between carbons 1 and 9}
\end{array}
$$

Note that the π-bond order is higher for bonds that fuse two hexagons compared to bonds that fuse a hexagon and a pentagon.

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

$i = 1..15$	E_i	$i = 16..30$	E_i	$i = 31..45$	E_i	$i = 46..60$	E_i
	-3		-1.562		0.139		1.618
	-2.757		-1		0.139		1.618
	-2.757		-1		0.139		1.618
	-2.757		-1		0.382		1.618
	-2.303		-1		0.382		2
	-2.303		-1		0.382		2
	-2.303		-1		1.303		2
	-2.303		-1		1.303		2
	-2.303		-1		1.303		2.562
	-1.82		-1		1.303		2.562
	-1.82		-0.618		1.303		2.562
	-1.82		-0.618		1.438		2.562
	-1.562		-0.618		1.438		2.618
	-1.562		-0.618		1.438		2.618
	-1.562		-0.618		1.618		2.618

The energy eigenvalues can also be displayed graphically as follows: $i = 1..60$

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 π-electrons is the lowest available energy states completely fills all the bonding molecular orbitals. The HOMO has an energy of -.618 |β| 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 Huckel calculation can be extended with a simple example of modeling. Since the results of the following calculation require the assignment of a value for β, the results should not be taken too seriously. The HOMO-LUMO gap is .757 |β|. Giving |β| 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.

$$eV = 1.6021777(10)^{-19} \text{joule} \quad h = 6.62608(10)^{-34} \text{joule sec} \quad c = 2.99792458(10)^8 \tfrac{m}{sec}$$

$$\beta = 2.5 eV \qquad nm = 10^{-9} m \qquad \lambda = 1nm$$

$$\text{Given} \qquad \tfrac{hc}{\lambda} = .757|\beta| \qquad \text{Find}(\lambda) = 655nm$$

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 |β| 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 transtion. However, it is also true that small amounts of other fullerenes may be contributing to this part

of the visible spectrum.

8. Calculate the π-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 π-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 π-electrons.

$$\Delta E_\pi = \frac{2\sum_{i-1}^{\text{Nocc}}|E_i| - \text{Natoms}}{\text{Natoms}} \qquad \Delta E_\pi = 0.553$$

Recall that the π-electron stabilization energy per carbon atom for benzene is 0.333.

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