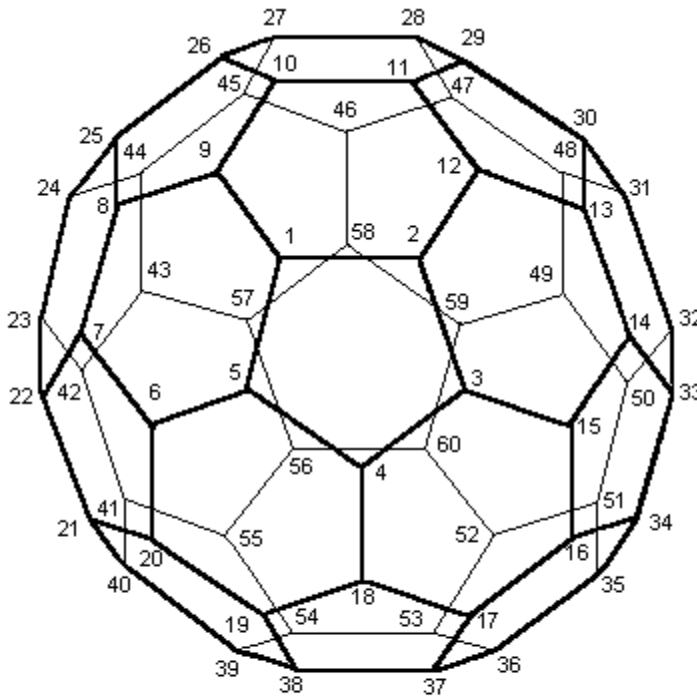


Huckel Molecular Orbital Theory for Buckminsterfullerene

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



Natoms := 60 The number of carbon atoms and π -electrons.

Nocc := 30 The number of occupied molecular orbitals.

2. Create a 60 x 60 null matrix.

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

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

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

$H_{1,5} := 1$ $H_{1,9} := 1$ $H_{2,12} := 1$ $H_{3,15} := 1$ $H_{4,18} := 1$ $H_{6,20} := 1$ $H_{7,22} := 1$

$H_{8,25} := 1$ $H_{10,26} := 1$ $H_{11,29} := 1$ $H_{13,30} := 1$ $H_{14,33} := 1$ $H_{16,34} := 1$ $H_{17,37} := 1$

$H_{19,38} := 1$ $H_{21,40} := 1$ $H_{23,42} := 1$ $H_{24,44} := 1$ $H_{27,45} := 1$ $H_{28,47} := 1$ $H_{31,48} := 1$

$H_{32,50} := 1$ $H_{35,51} := 1$ $H_{36,53} := 1$ $H_{39,54} := 1$ $H_{41,55} := 1$ $H_{43,57} := 1$ $H_{46,58} := 1$

$H_{49,59} := 1$ $H_{52,60} := 1$ $H_{56,60} := 1$ $H_{j,i} := H_{i,j}$ $H := -H$

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.

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

5. Use the eigenvectors to calculate selected 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.

$$r := 1 \quad s := 1 \quad 2 \cdot \sum_{i=1}^{\text{Nocc}} (C^{<i>})_r \cdot (C^{<i>})_s = 1 \quad \pi\text{-electron density on carbon 1}$$

$$r := 1 \quad s := 2 \quad 2 \cdot \sum_{i=1}^{\text{Nocc}} (C^{<i>})_r \cdot (C^{<i>})_s = 0.476 \quad \pi\text{-bond order between carbons 1 and 2}$$

$$r := 1 \quad s := 5 \quad 2 \cdot \sum_{i=1}^{\text{Nocc}} (C^{<i>})_r \cdot (C^{<i>})_s = 0.476 \quad \pi\text{-bond order between carbons 1 and 5}$$

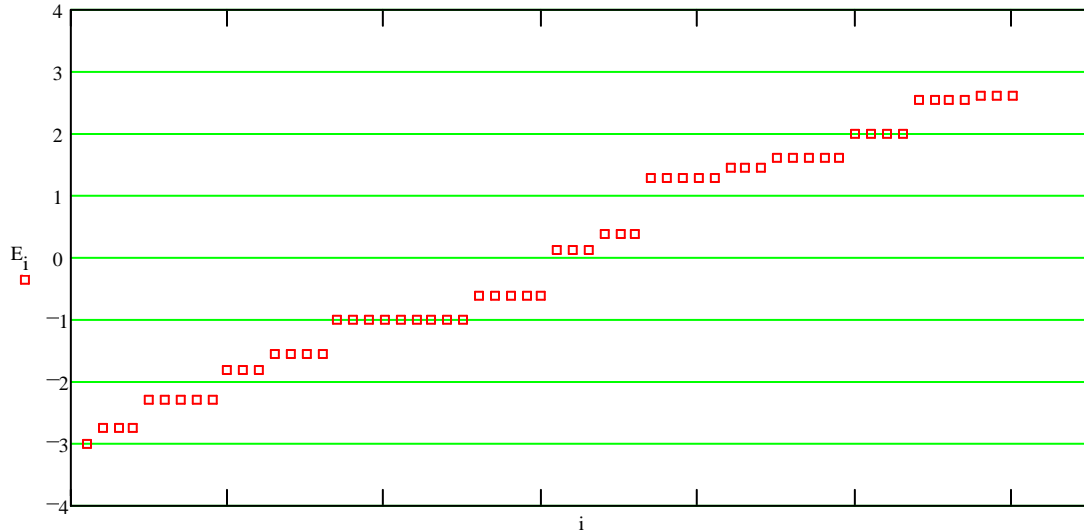
$$r := 1 \quad s := 9 \quad 2 \cdot \sum_{i=1}^{\text{Nocc}} (C^{<i>})_r \cdot (C^{<i>})_s = 0.601 \quad \pi\text{-bond order between carbons 1 and 9}$$

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

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

$i := 1..15$	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 in 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 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 $0.757 |\beta|$. 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.

$$eV := 1.6021777 \cdot 10^{-19} \cdot \text{joule} \quad h := 6.62608 \cdot 10^{-34} \cdot \text{joule} \cdot \text{sec} \quad c := 2.99792458 \cdot 10^8 \cdot \frac{\text{m}}{\text{sec}}$$

$$\beta := -2.5 \cdot \text{eV} \quad \text{nm} := 10^{-9} \cdot \text{m} \quad \lambda := 1 \cdot \text{nm}$$

$$\text{Given} \quad \frac{h \cdot c}{\lambda} = 0.757 \cdot |\beta| \quad \text{Find}(\lambda) = 655 \cdot \text{nm}$$

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 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.

$$\Delta E_{\pi} := \frac{2 \cdot \sum_{i=1}^{N_{\text{occ}}} |E_i| - N_{\text{atoms}}}{N_{\text{atoms}}} \quad \Delta E_{\pi} = 0.553$$

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