Electronic structure of the fullerene

i) The fullerene molecule

The fullerene is an approximate spherical molecule with 60 Carbon atoms. There are 12 pentagons (polygon with 5 bonds) and 20 hexagons (polygon with 6 bonds) such that each pentagon is surrounded by 5 hexagons and each hexagon is surrounded by 3 pentagons and 3 hexagons. (Fig. 1)

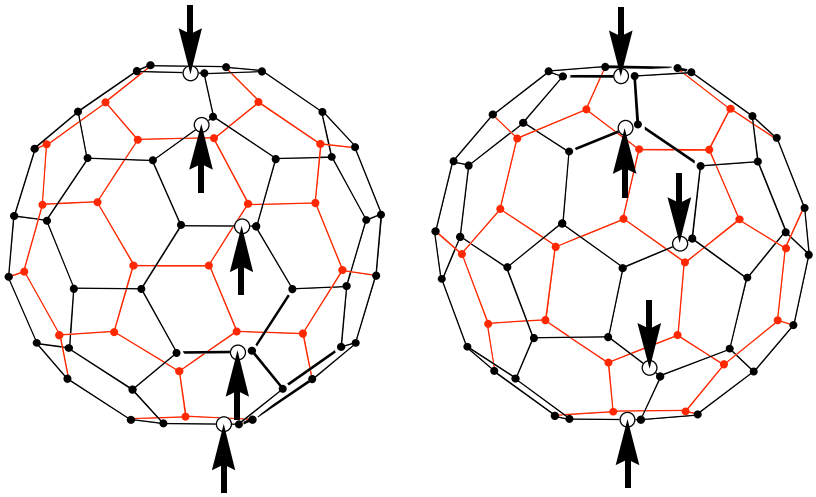


Figure 1. C60 (black in front, red in back). Carbon atoms at every point with bonds in between. The same molecule rotated such that pentagons on top and at bottom (displaying D5d-symmetry, left) and hexagons on top and at bottom (displaying D3d-symmetry, right). Mesh cut open at five positions (circles with arrows) like to a sphere cut by a half-meridian.

In order to have an easy understanding of the network of bonds in the fullerene it is cut at at five positions (analogous to a sphere cut by a meridian, Fig. 1) and displayed flat (changed bond lengths, now represented by thickness of lines: single bond, thin line, double bond thick line, Fig. 2).

To evaluate the electronic wavefunctions and their energy spectrum of the fullerene we use the step-potential model (where each bond is approximated by a one-dimensional potential step) and include branching conditions at every Carbon atom. The potential troughs at the Carbon atoms are not considered.

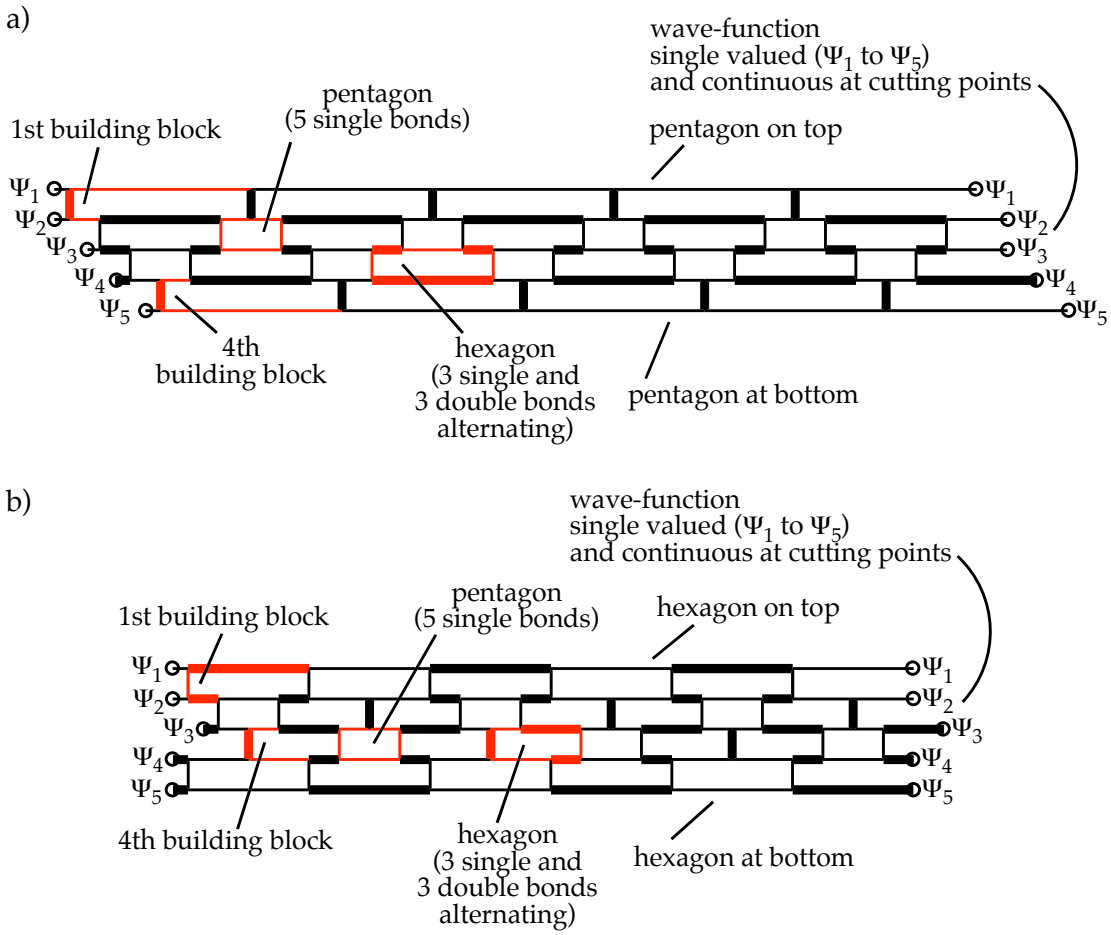


Figure 2. Schematic representation of the fullerene molecule to show the network of bonds. The approximate spherical molecule is cut at five positions and displayed flat. Bond lengths represented by thickness of lines: single bond (thin line), double bond (thick line). Representation of same molecule slightly rotated such that a) pentagons on top and at bottom (displaying D5d-symmetry) and b) hexagons on top and at bottom (displaying D3d-symmetry). The building block (joining two bonds with one linking bond by two branchings) is the smallest unit to assemble the network of bonds in the fullerene (five lines with regular linkages). By inspection one can observe two patterns of building blocks for the network (with short notation building block joining Ψ_1 & Ψ_2 = a, Ψ_2 & Ψ_3 = b, Ψ_3 & Ψ_4 = c, Ψ_4 & Ψ_5 = d and proceeding from right, first building block, to left, 30th building block):

bcdcba bcdcba bcdcba bcdcba bcdcba (case 2a)

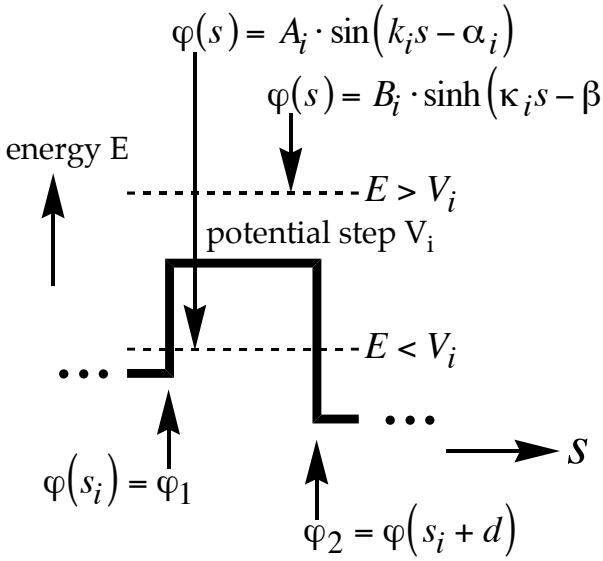
cbcdabcbad cbcdabcbad cbcdabcbad (case 2b)

ii) The step potential model.

The general solution (Figure 3) of the one-dimensional Schrödinger equation with the potential $V(s)$ composed of step potentials V_i

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{ds^2}+V_i\right)\cdot\varphi(s)=E\cdot\varphi(s) \qquad (1)$$

is a wavefunction $\varphi(s)$ of energy E > V_i (case of free electron) and E < V_i (case of tunneling electron). The values of the wavefunction and its derivative at the left border of step i, $\varphi_1=\varphi(s_i)$ and $\varphi_1'=\frac{d\varphi}{ds}(s_i)$, and at the right border of step i, $\varphi_2=\varphi(s_i+d)$ and $\varphi_2'=\frac{d\varphi}{ds}(s_i+d)$, are connected by (using the addition theorems for sin, cos, sinh and cosh)



amplitude A_i and B_i

phase α_i and β_i

wavevector

$$k_i=\sqrt{\frac{2m_e}{\hbar^2}(E-V_i)}$$

$$\kappa_i=\sqrt{\frac{2m_e}{\hbar^2}(V_i-E)}$$

average bond length d

mass of electron m_e

Figure 3. Solving the Schrödinger equation (1) by the transfer matrix method derived in equations (2) to (6). Singled out step potential V_i. Case E > V_i (free electron) and case E < V_i (tunneling electron). Wavefunction at the left border (s_i) and right border (s_i+d) of step i.

$$\begin{aligned}\varphi_2 &= \varphi\left(s_i + d\right) = A_i \cdot \sin\left(k_i\left(s_i + d\right) - \alpha_i\right)\\ &= \varphi_1 \cdot \cos\left(k_i d\right) + \varphi_1' \cdot \sin\left(k_i d\right) / k_i\\ \varphi_2' &= \varphi'\left(s_i + d\right) = A_i \cdot k_i \cos\left(k_i\left(s_i + d\right) - \alpha_i\right)\\ &= \varphi_1' \cdot \cos\left(k_i d\right) - \varphi_1 \cdot k_i \sin\left(k_i d\right)\end{aligned} \qquad E > V_i \qquad (2)$$

$$\begin{aligned}\varphi_2 &= \varphi\left(s_i + d\right) = A_i \cdot \sinh\left(\kappa_i\left(s_i + d\right) - \alpha_i\right)\\ &= \varphi_1 \cdot \cosh\left(\kappa_i d\right) + \varphi_1' \cdot \sinh\left(\kappa_i d\right) / \kappa_i\\ \varphi_2' &= \varphi'\left(s_i + d\right) = A_i \cdot \kappa_i \cosh\left(\kappa_i\left(s_i + d\right) - \alpha_i\right)\\ &= \varphi_1' \cdot \cosh\left(\kappa_i d\right) + \varphi_1 \cdot \kappa_i \sinh\left(\kappa_i d\right)\end{aligned} \qquad E < V_i \qquad (3)$$

The linear equations (2) and (3) are written in short notation

$$\begin{pmatrix}\varphi_2\\ \varphi_2'\end{pmatrix} = \begin{pmatrix}a & b\\ c & a\end{pmatrix} \cdot \begin{pmatrix}\varphi_1\\ \varphi_1'\end{pmatrix} \qquad (4)$$

with the 2×2-matrix (called transfer matrix M_T over the potential step) which gives the value φ_2 of the wavefunction and its derivativ φ_2' knowing the value φ_1 of the wavefunction and its derivativ φ_1' .

$$M_T = \begin{pmatrix}a & b\\ c & a\end{pmatrix} = \begin{pmatrix}\cos\left(k_i d\right) & \sin\left(k_i d\right)/k_i\\ -k_i \sin\left(k_i d\right) & \cos\left(k_i d\right)\end{pmatrix} \qquad E > V_i \qquad (5)$$

$$M_T = \begin{pmatrix}a & b\\ c & a\end{pmatrix} = \begin{pmatrix}\cosh\left(\kappa_i d\right) & \sinh\left(\kappa_i d\right)/\kappa_i\\ \kappa_i \sinh\left(\kappa_i d\right) & \cosh\left(\kappa_i d\right)\end{pmatrix} \qquad E < V_i \qquad (6)$$

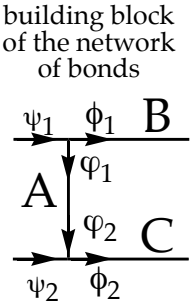
iii) Solving the Schrödinger equation for the fullerene molecule.

The transfer matrix $\mathbf{M_q}(E)$ over the q-th building block ABC (joining transfer over three bonds with two branching conditions) is given by the 4×4-matrix

$$\mathbf{M_q}(\varepsilon) = \begin{pmatrix} \mathbf{a_B} & \mathbf{b_B} & 0 & 0 \\ \mathbf{c_B} & \mathbf{d_B} & 0 & 0 \\ 0 & 0 & \mathbf{a_C} & \mathbf{b_C} \\ 0 & 0 & \mathbf{c_C} & \mathbf{d_C} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{1} & \mathbf{0} & 0 & 0 \\ \mathbf{-a_A} & \mathbf{1} & \mathbf{-b_A} & 0 \\ 0 & 0 & \mathbf{1} & \mathbf{0} \\ \mathbf{c_A} & 0 & \mathbf{d_A} & \mathbf{1} \end{pmatrix} \tag{7}$$

The left matrix of product (7) is simply the transfer matrix simultaneously over both bonds B and C. The right matrix of product (7) is the transfer matrix over the bond A including the branching to bonds B and C (Figure 4, note that arrows fix the signs)

$$\begin{aligned} &\psi_1 = \varphi_1 = \phi_1 \\ &\psi_1' - \varphi_1' - \phi_1' = 0 \end{aligned} \quad \text{and} \quad \begin{aligned} &\psi_2 = \varphi_2 = \phi_2 \\ &\psi_2' + \varphi_2' - \phi_2' = 0 \end{aligned} \tag{8}$$



$$\begin{pmatrix} \psi_1 \\ \psi' \\ \psi_2 \\ \psi_2' \end{pmatrix} = \mathbf{M_q}(E) \begin{pmatrix} \psi_1 \\ \psi' \\ \psi_2 \\ \psi_2' \end{pmatrix}$$

Figure 4. The building block ABC and its branching (total of 30 building blocks ABC that make up the fullerene molecule, see Figure 2).

For this transfere over bond A including the branching conditions the derivatives φ_1' and φ_2' of the wavefunction are needed knowing the values φ_1 and φ_2 of the wavefunction. Therefore the transfer matrix M_T (with $b \neq 0$) is transformed

$$\begin{pmatrix} \varphi_1' \\ \varphi_2' \end{pmatrix} = \begin{pmatrix} a_A & b_A \\ c_A & d_A \end{pmatrix} \cdot \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix} = \begin{pmatrix} -\frac{a}{b} & \frac{1}{b} \\ -\frac{1}{b} & \frac{a}{b} \end{pmatrix} \cdot \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix} \tag{9}$$

The solutions (with energy values E_n) of an electron in the network of bonds of the fullerene are wavefunctions which are single valued (values $\Psi_{p,left} = \Psi_{p,right}$) and continuous (derivatives $\Psi'_{p,left} = \Psi'_{p,right}$) at the 5 cutting points p = 1 to p = 5 (Figure 2), thus we have

$$\psi_{left}(E_n) = \begin{pmatrix} \psi_1 \\ \psi'_1 \\ \psi_2 \\ \psi'_2 \\ \psi_3 \\ \psi'_3 \\ \psi_4 \\ \psi'_4 \\ \psi_5 \\ \psi'_5 \end{pmatrix} = \psi_{right}(E_n) = \mathbf{M}_{10\times 10}(E_n) \cdot \psi_{left}(E_n) \quad , \qquad (10)$$

where the matrix $\mathbf{M}_{10\times 10}(E)$ is the transfer matrix over the network of bonds:

$$\mathbf{M}_{10\times 10}(E) = \begin{pmatrix} \mathbf{E}_{2\times 2} & 0 & 0 \\ 0 & \mathbf{M}_{30}(E) & 0 \\ 0 & 0 & \mathbf{E}_{4\times 4} \end{pmatrix} \cdot \ldots \cdot \begin{pmatrix} \mathbf{E}_{6\times 6} & 0 \\ 0 & \mathbf{M}_4(E) \end{pmatrix} \cdot$$

$$\begin{pmatrix} \mathbf{E}_{4\times 4} & 0 & 0 \\ 0 & \mathbf{M}_3(E) & 0 \\ 0 & 0 & \mathbf{E}_{2\times 2} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{E}_{2\times 2} & 0 & 0 \\ 0 & \mathbf{M}_2(E) & 0 \\ 0 & 0 & \mathbf{E}_{4\times 4} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{M}_1(E) & 0 \\ 0 & \mathbf{E}_{6\times 6} \end{pmatrix} \qquad (11)$$

The product (11) is a product of 30 10×10-matrices where the 4×4-matrix $\mathbf{M_q}(E)$ of product (7) is particularly embodied in the q-th 10×10-matrix (by use of the $j \times j$-identity matrix $\mathrm{E}_{j\times j}$): it represents the q-th building block ABC which is displaced along the network in a particular pattern. The particular pattern of displacement applied in the product (11) corresponds to the case of Figure 2a. Equation (10) can be written as $\mathbf{M}_{10\times 10}(E_n) = \mathbf{E}_{10\times 10}$ and is best solved by the method of Singular values (see Mathematica).