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Energy gap between highest occupied molecular orbital and lowest unoccupied molecular orbital in multiwalled fullerenes

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We report on the electronic structure of the C_{60}-C_{240} multiwalled fullerene (onion) near the Fermi level. The analytical expressions for the hybridizations of the π orbitals on the fullerene shells were derived. The difference between the Fermi levels of individual fullerenes is obtained. The highest occupied molecular orbital–lowest unoccupied molecular orbital energy gap for the C_{60}-C_{240} carbon fullerene onion is calculated. The charge transfer from the outer shell to the inner shell in the base state of the onion is determined. Splitting and the shift of the energy levels of the onion as a result of intershell interaction are predicted.

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I. INTRODUCTION

Recently, the problem of low-energy electronic states in spheroidal fullerenes as well as the influence of a weak uniform external magnetic field pointed in the z and x directions has been considered [1–3]. The main findings were the discovery of the fine structure with a specific shift of the electronic levels upward due to spheroidal deformation and the Zeeman splitting of electronic levels due to a weak uniform magnetic field. In addition, it was shown that the external magnetic field modified the density of electronic states and did not change the number of zero modes. It was found that modification of the electronic spectrum of the spheroidal fullerenes in the case of the x-directed magnetic field differs markedly from the case of the z-directed magnetic field [2,3]. This gives an additional possibility for experimental study of the electronic structure of deformed fullerene molecules.

The field-theory model where the specific structure of carbon lattice, geometry, and the topological defects (pentagons) were taken into account was explored in [2,3]. As the result of this approach, it was found in [2] that the zero-energy states corresponding to the highest occupied molecular orbital (HOMO) and the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) energy gap were approximately 1.1 eV for the YO-C_{240} fullerene which was in good agreement with data predicted in [4] (YO denotes the Yoshida-Osawa structure). The next step is to concentrate on the electronic properties of the multiwalled carbon structures (onions). Some attempts to describe the electronic structure of multiwalled fullerenes were presented in [5–7]. However, the prediction of the HOMO-LUMO gap of the fullerene onions is missing in the referred publications. This information, in our understanding, could be important and valuable especially for experimentalists. Accordingly, we were aimed to find a different theoretical approach for calculation of the gap.

We used the idea presented in [8,9] where the curvature effects in carbon nanotubes were studied as a function of chirality. The result is that π orbitals are found to be significantly rehybridized in all nanostructures, so that they are never situated normally to the fullerene surface (in our case) but are tilted by the hybridization angle. The tilting of the π orbitals should be observable by atomic resolution scanning tunneling microscopy measurement. We derived the exact analytical expression for the hybridizations of the π orbitals on the fullerene shells and then used the expressions for computations of the HOMO-LUMO gap for the fullerene carbon onion.

At very large fullerenes with several hundred atoms a transition from single-shell fullerenes to nested multishell structures was determined in [10]. Accordingly, multishell fullerenes are locally similar to graphite where similar intershell interactions γ_1 as in the bilayer graphite between shells can be used. Similar intershell interactions as in graphite could also be used for the fullerene onion because the spacing between shells in the onion is almost the same as the interlayer spacing in graphite ~3.4 Å [11]. Moreover, the π states near the HOMO-LUMO gap and more strongly bound σ states have also a similar character as the corresponding states in graphite [12].

In the presented paper we focus on C_{60}-C_{240} fullerene onion. The paper is organized as follows. The influence of the curvature on the hybridization of fullerene π orbitals is computed in Sec. II. The model is explained in Sec. III. The calculated HOMO-LUMO gap and energy splitting are discussed in Sec. IV. We close the paper with several remarks in Sec. V.

II. TREATMENT OF HYBRIDIZATION OF FULLERENE π ORBITALS

We consider the case of the C_n-C_m fullerene onion, where n,m are numbers of atoms on the inner and outer shell, respectively, e.g., $n,m=60,240,540\ldots$ and $m>n$. The hybridization of the orbitals of the inner and outer shell is different in these fullerene onions. Because of the curvature the coordinates of $\vec{\tau}_i$ in space are (Fig. 1)

$$\vec{\tau}_1 = d(\cos\theta;0;-\sin\theta),$$

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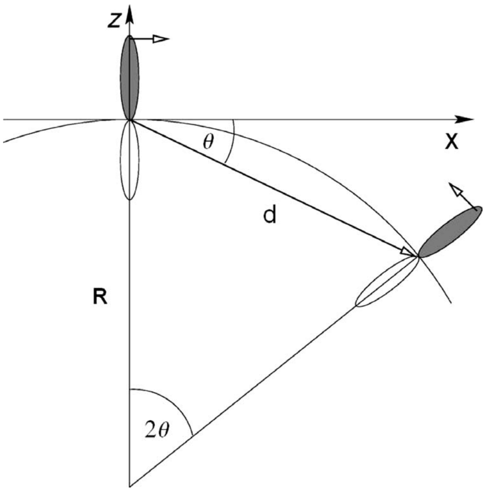

FIG. 1. Schematic cross section of a bond in a fullerene with radius R. The angle between the bond $\vec{\tau}_1$ and x axis is θ.

$$\vec{\tau}_2 = d(e_x;-e_y;e_z), \quad \vec{\tau}_3 = d(e_x;e_y;e_z), \tag{1}$$

where $\sin\theta = d/2R$. We assume that the angle between the bonds $\vec{\tau}_1, \vec{\tau}_2$ and also $\vec{\tau}_1, \vec{\tau}_3$ is 120° [9]. It means that we have equations for unknown e_x, e_y, e_z,

$$\cos(2\pi/3) = (\vec{\tau}_1 \cdot \vec{\tau}_2)/|\vec{\tau}_1||\vec{\tau}_2|, \tag{2}$$

$$\cos(2\pi/3) = (\vec{\tau}_1 \cdot \vec{\tau}_3)/|\vec{\tau}_1||\vec{\tau}_3|, \tag{3}$$

with the condition

$$e_x^2 + e_y^2 + e_z^2 = 1. \tag{4}$$

From the equations above we get

$$e_x = -(d/2R)\tan\theta - 1/(2\cos\theta),$$

$$e_y = \sqrt{\left[1 - \frac{1}{4(1-d^2/4R^2)} - 2\left(\frac{d}{2R}\right)^2 \frac{1}{(1-d^2/4R^2)}\right]},$$

$$e_z = -d/2R, \tag{5}$$

where R is the radius of the fullerene molecules and d is the nearest-neighbor length.

The radii of the inner and outer shell are different thus we need to calculate the values for the outer fullerene shell $\epsilon = \langle\pi|H|\pi\rangle$ and $\tilde{\epsilon}$ for the inner one. First, one needs to construct three hybrids along the three directions of the bonds. These directions are

$$\vec{e}_1 = (\cos\theta;0;-\sin\theta),$$

$$\vec{e}_2 = (e_x;-e_y;e_z), \quad \vec{e}_3 = (e_x;e_y;e_z). \tag{6}$$

The requirement of orthonormality for the hybrid wave functions determines uniquely the fourth hybrid denoted by $|\pi\rangle$ which corresponds to the p_z orbital in graphite. The hybridization of the σ bonds, therefore, changes from the uncurved expression to $|\sigma_1\rangle = s_1|s\rangle + \sqrt{1-s_1^2}(\cos\theta|p_x\rangle - \sin\theta|p_z\rangle)$, $|\sigma_2\rangle = s_2|s\rangle + \sqrt{1-s_2^2}(e_x|p_x\rangle - e_y|p_y\rangle + e_z|p_z\rangle)$, $|\sigma_3\rangle = s_3|s\rangle + \sqrt{1-s_3^2}(e_x|p_x\rangle + e_y|p_y\rangle + e_z|p_z\rangle)$. The mixing parameters s_i, D_j can be determined by the orthonormality conditions $\langle\sigma_i|\sigma_j\rangle = \delta_{ij}$, $\langle\pi|\sigma_i\rangle = 0$, and $\langle\pi|\pi\rangle = 1$.

We got the analytical expressions for the hybridizations of the π orbital on the fullerene shell in the following form:

$$|\pi\rangle = D_1|s\rangle + D_2|p_x\rangle + D_4|p_z\rangle, \tag{7}$$

and for the Fermi level on the fullerene shell

$$\epsilon = \langle\pi|H|\pi\rangle = D_1^2\langle s|H|s\rangle + D_2^2\langle p_x|H|p_x\rangle + D_4^2\langle p_z|H|p_z\rangle, \tag{8}$$

where

$$D_1 = \frac{d}{2R}\frac{\sqrt{1-A^2}\sqrt{1-B^2}(\sqrt{1-d^2/4R^2}-e_x)}{\sqrt{1-A^2}\sqrt{1-d^2/4R^2}B - A\sqrt{1-B^2}e_x}D_4 = \alpha D_4, \tag{9}$$

$$D_2 = \frac{d}{2R}\frac{\sqrt{1-A^2}B - \sqrt{1-B^2}A}{\sqrt{1-A^2}\sqrt{1-d^2/4R^2}B - A\sqrt{1-B^2}e_x}D_4 = \beta D_4, \tag{10}$$

$$D_4 = 1/\sqrt{1+\alpha^2+\beta^2}, \tag{11}$$

and

$$A = \sqrt{\frac{(e_x\sqrt{1-d^2/4R^2} + d^2/4R^2)^2}{2e_ye_y - 1 + (e_x\sqrt{1-d^2/4R^2} + d^2/4R^2)^2}}, \tag{12}$$

$$B = \sqrt{1 - 1/2e_ye_y}. \tag{13}$$

Now we can use the above expressions for computation of the HOMO-LUMO gap for, e.g., C_{60}-C_{240} fullerene onion. We obtained the numerical values for the π orbital in the case of the inner C_{60} fullerene molecule

$$|\pi\rangle \approx 0.289|s\rangle - 0.068|p_x\rangle + 0.955|p_z\rangle, \tag{14}$$

where it was assumed that $R = 3.5$ Å [11]. For the outer C_{240} fullerene molecules we have

$$|\pi\rangle \approx 0.144|s\rangle - 0.007|p_x\rangle + 0.990|p_z\rangle, \tag{15}$$

where it was assumed that $R = 7.1$ Å [11]. The value $d = 1.44$ Å [11] as the nearest-neighbor length or average bond length on the fullerene shell was used in our calculations.

Hence, in the case of the C_{60} molecules we have

$$\tilde{\epsilon} = \langle\pi|H|\pi\rangle = 0.083\langle s|H|s\rangle + 0.005\langle p_x|H|p_x\rangle + 0.911\langle p_z|H|p_z\rangle, \tag{16}$$

and for the C_{240} fullerene we have

$$\epsilon = 0.021\langle s|H|s\rangle + 0.980\langle p_z|H|p_z\rangle, \tag{17}$$

In the expressions above we used [13]

$$\langle s|H|s\rangle \approx -12 \text{ eV}, \tag{18}$$

$$\langle p_x|H|p_x\rangle = \langle p_y|H|p_y\rangle = \langle p_z|H|p_z\rangle \approx -4 \text{ eV}, \tag{19}$$

thus the energy difference is

$$\epsilon - \tilde{\epsilon} \approx 1.024 \text{ eV}. \tag{20}$$

III. C_{60}-C_{240} HOMO, LUMO ENERGIES

To describe the electronic structure of the C_{60}-C_{240} onion, we begin with the tight-binding Hamiltonian

$$\hat{H} = \sum_{i} \hat{\varepsilon} c_i^\dagger c_i + \sum_{\langle ij\rangle} \tilde{\gamma}_0 (c_i^\dagger c_j + \text{H.c.}) + \sum_{i} \varepsilon d_i^\dagger d_i + \sum_{\langle ij\rangle} \gamma_0 (d_i^\dagger d_j + \text{H.c.}) + \sum_{k,l} V_{kl} (d_k^\dagger c_l + \text{H.c.}), \tag{21}$$

where $\tilde{\gamma}_0(\gamma_0)$ is a hopping integral on the $C_{60}(C_{240})$ molecule and $c_i^\dagger$ $(d_i^\dagger)$ creates electrons on the ith atomic orbital of the inner (outer) shell; V_{kl} describe the interaction between shells. We take into account a different curvature of the C_{60} and C_{240} molecules. The following formula for dependence of the hopping integral on curvature was used [14]:

$$\gamma_0(R) = \gamma_0(\infty)\left[1 - \tfrac{1}{2}(d/R)^2\right]. \tag{22}$$

Considering the value of $\tilde{\gamma}_0$ at 2.5 eV [4,15] for the hopping integral of the C_{60} fullerene Eq. (22) resulted in $\gamma_0 = 2.675$ eV for hopping integral of the C_{240} fullerene.

The electronic wave function has the form [15]

$$|\psi_m\rangle = |\psi_m^{\text{in}}\rangle + |\psi_m^{\text{out}}\rangle, \tag{23}$$

where

$$|\psi_m^{\text{in}}\rangle = \frac{1}{\sqrt{5}} \sum_{n=1}^{5} \exp\left(i\frac{2\pi}{5}mn\right)(|n,\text{inner}\rangle), \tag{24}$$

and $|n,\text{inner}\rangle$ describes an electronic state which is the linear combination

$$|n,\text{inner}\rangle = \frac{1}{\sqrt{12}} \sum_{i=1}^{12} a_i c_i^\dagger |\text{vacuum}\rangle. \tag{25}$$

Here the sum is over 12 atomic orbitals localized at site i of the nth slice of the icosahedron of the inner shell and similarly for the outer shell

$$|\psi_m^{\text{out}}\rangle = \frac{1}{\sqrt{5}} \sum_{n=1}^{5} \exp\left(i\frac{2\pi}{5}mn\right)(|n,\text{outer}\rangle), \tag{26}$$

where

$$|n,\text{outer}\rangle = \frac{1}{\sqrt{48}} \sum_{i=1}^{48} b_i d_i^\dagger |\text{vacuum}\rangle. \tag{27}$$

The possible values of m are $m = 0, \pm 1, \pm 2$. Now we use the values of the highest occupied molecular orbital HOMO(H) and the lowest unoccupied molecular orbital LUMO(L) for C_{60} and C_{240}, as computed in [4]. We have HOMO(C_{60})$=-1.545$ eV, LUMO(C_{60})$=0.346$ eV, it means that

$$\langle \psi_{m,H}^{\text{in}} | \hat{H} | \psi_{m,H}^{\text{in}} \rangle = -1.545, \tag{28}$$

and

$$\langle \psi_{m,L}^{\text{in}} | \hat{H} | \psi_{m,L}^{\text{in}} \rangle = 0.346. \tag{29}$$

The values HOMO, LUMO of the C_{240} isolated fullerene were corrected within our model. Formula (22) was used in order to consider the influence of the rehybridization on the hopping integral γ_0 of fullerenes with different radius. The HOMO(C_{240}) equals -1.168 eV, LUMO(C_{240}) is 0.160 eV for isolated fullerenes. The HOMO states of both fullerenes are fivefold degenerate. The LUMO states are threefold degenerate. The quantum numbers of HOMO states are $m = 0, \pm 1, \pm 2$ and the quantum numbers of LUMO states are $m = 0, \pm 1$ [15].

In the C_{60}-C_{240} onion we must add the value 1.024 eV to the C_{240} fullerene energies. The values HOMO(C_{240}) equal -0.144 eV and LUMO(C_{240}) equal 1.184 eV were obtained when the interaction between shells was not taken into account. This leads to

$$\langle \psi_{m,H}^{\text{out}} | \hat{H} | \psi_{m,H}^{\text{out}} \rangle = -0.144, \tag{30}$$

and

$$\langle \psi_{m,L}^{\text{out}} | \hat{H} | \psi_{m,L}^{\text{out}} \rangle = 1.184. \tag{31}$$

Thus we finally obtained the gap between HOMO(C_{240}) and LUMO(C_{60}) which is about 0.490 eV in the C_{60}-C_{240} onion. The interaction between shells shall be included into our model. If the position of the shells in the onion does not change the symmetry of individual shells, the interaction between shells mixes only the states with the same symmetry. We suppose that the states which are mainly affected by this interaction are the HOMO(C_{240}) and LUMO(C_{60}) states because they are the closest to each other. The HOMO state of the outer shell with quantum numbers $m = \pm 2$ will not be affected by interaction between shells. The states which are affected are HOMO states of the outer shell and LUMO states of the inner shell with quantum numbers $m = 0, \pm 1$. However, there is a mixing only between states with the same quantum number m. We assume that all 12 atoms of nth slice of the inner shell have approximatively the same interaction with nth slice of the outer shell

$$\langle \text{vacuum} | a_i c_i \hat{V} \sum_{j=1}^{48} b_j d_j^\dagger | \text{vacuum} \rangle = \gamma_1, i = 1, 2, \ldots, 12, \tag{32}$$

where

$$\hat{V} = V_{k,l}(d_k^\dagger c_l + \text{H.c.}) \tag{33}$$

is the interaction Hamiltonian. So we approximatively have

$$\langle \psi_{m,L}^{\text{in}} | \hat{V} | \psi_{m,H}^{\text{out}} \rangle = \frac{1}{\sqrt{12}} \sum_{i=1}^{12} \langle \text{vacuum} | a_{i,L} c_i \hat{V} \frac{1}{\sqrt{48}} \sum_{j=1}^{48} b_{j,H} d_j^\dagger | \text{vacuum} \rangle = \gamma_1/2. \tag{34}$$

We look for the solution in the form [16]

TABLE I. The values of HOMO, LUMO, and HOMO-LUMO energy gaps for isolated fullerenes and fullerene onion; d (Å), nearest neighbor length; R (Å), radius of fullerene; γ_1, intershell interaction; HOMO, LUMO and HOMO-LUMO gaps are calculated in electron volts.

	d (Å)	R (Å)	HOMO	LUMO	HOMO-LUMO	HOMO-LUMO C_{60}-C_{240} ($\gamma_1=0$)	HOMO-LUMO C_{60}-C_{240} ($\gamma_1=0.35$)
C_{60}	1.44	3.5	−1.545	0.346	1.891	0.490	0.505
C_{240}	1.44	7.1	−1.168	0.160	1.328		

$$\Psi_m = c_1\psi^{\text{out}}_{m,H} + c_2\psi^{\text{in}}_{m,L}, \tag{35}$$

where $\psi^{\text{out}}_{m,H}$ is a HOMO state of the C_{240} fullerene and $\psi^{\text{in}}_{m,L}$ is a LUMO state of the C_{60} fullerene. We are mainly interested in HOMO, LUMO states of the C_{60}-C_{240} fullerene onion. We have secular equations

$$\epsilon_H c_1 + \frac{1}{2}\gamma_1 c_2 = Ec_1, \tag{36}$$

$$\frac{1}{2}\gamma_1 c_1 + \epsilon_L c_2 = Ec_2, \tag{37}$$

where

$$\langle\psi^{\text{out}}_{m,H}|H|\psi^{\text{out}}_{m,H}\rangle = \epsilon_H = -0.144 \ \text{eV}, \tag{38}$$

$$\langle\psi^{\text{in}}_{m,L}|H|\psi^{\text{in}}_{m,L}\rangle = \epsilon_L = 0.346 \ \text{eV}, \tag{39}$$

$$\langle\psi^{\text{out}}_{m,H}|H|\psi^{\text{in}}_{m,L}\rangle = \frac{\gamma_1}{2}. \tag{40}$$

The solutions can be expressed in the form

$$\Psi_{m,1} = 0.945\psi^{\text{out}}_{m,H} - 0.327\psi^{\text{in}}_{m,L}, \tag{41}$$

with energy $E_1=-0.159$ eV and

$$\Psi_{m,2} = 0.996\psi^{\text{in}}_{m,L} + 0.085\psi^{\text{out}}_{m,H}, \tag{42}$$

with energy $E_2=0.361$ eV. The HOMO state of the outer shell with quantum numbers $m=\pm 2$ remains also the HOMO state of the C_{60}-C_{240} fullerene onion. The LUMO state of the onion is threefold degenerate and is a mixing of HOMO C_{240} and LUMO C_{60} states ($\Psi_{m,2}$ state). This mixed state has energy 0.361 eV. The value of the HOMO-LUMO gap for the C_{60}-C_{240} fullerene onion is 0.505 eV when the interaction between shells is taken into account. The interaction energy of $\gamma_1=0.35$ eV close to the value presented in [17,18] was used in our calculations. The values of the HOMO, LUMO and HOMO-LUMO gaps are summarized in Table I.

IV. DISCUSSION

We assume that all the atoms of the inner shell have a similar interaction with atoms on the outer shell. Although this is a rough approximation it gives good results in the case of double wall carbon nanotubes [19]. The rehybridization of the π orbital method was used in order to compute the influence of a curvature of the fullerene shell on the matrix elements. The influence of the rehybridization on the hopping integral γ_0 was taken into account according to relation (22). We obtained the 1.024 eV difference between the "Fermi levels" of individual fullerenes in the C_{60}-C_{240} onion. Therefore, we got a gap between HOMO(C_{240}) and LUMO(C_{60}) which is about 0.490 eV when the interaction between shells is not taken into account. When the interaction between the inner and outer shell is taken into account, the HOMO state is doublefold degenerate (it is HOMO state of the outer shell with quantum number $m=\pm 2$). The LUMO state of this onion is a superposition of the HOMO state of the C_{240} fullerene and the LUMO state of the C_{60} fullerene with quantum numbers $m=0,\pm 1$($\Psi_{m,2}$ states). The result is about 0.505 eV HOMO-LUMO gap in the C_{60}-C_{240} fullerene onion. There is a charge transfer from the outer shell to the inner shell in the base state of the onion. $\Psi_{m,1}$ are bonding states of fullerene onion with energy −0.159 eV. In these states electrons are delocalized with probability 0.89 at the outer shell and 0.11 at the inner shell. These electrons are localized at the outer shell when interaction between shells is not taken into account. We can see that in the first excitation state the electron is localized mainly in the inner shell and the hole is localized in the outer shell. If the mutual positions of the shells in this double wall system do not preserve the symmetry of the individual fullerenes, the lifting of degeneracy can be different. Generally m will not be a good quantum number; consequently HOMO and LUMO states of double wall system will be a mixture of the HOMO states of C_{240} with $m=0,\pm 1,\pm 2$ and LUMO states of C_{60} with $m=0,\pm 1$. In this case the HOMO and LUMO levels of C_{60}-C_{240} onion will have one single degenerate state.

V. CONCLUSION

We found a HOMO-LUMO gap reduction in C_{60}-C_{240} system in comparison with individual fullerenes. The HOMO level is doubly degenerate and LUMO level is threefold degenerate in this double wall spherical system. There is a delocalization of electrons between the outer and inner shells. The probability to find electrons on the inner shell is larger than the probability to find electrons on the outer shell. The approach described in the paper can also be used for calculations of HOMO-LUMO gaps of the other fullerene onions and moreover for the multiwalled fullerenes. The parameters required for computations of the HOMO-LUMO gaps using our exact analytical expressions, Eqs. (7)–(13), are the following: the radius, the nearest-neighbor length of the isolated fullerenes, and the intershell interaction. This information about fullerenes can be found in several articles, e.g., [4,11,20]. The experimental determination of the HOMO-LUMO gap for the C_{60}-C_{240} fullerene onion we consider is an important forthcoming step for verification of our prediction.

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