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How the spheroidal deformation changes the spectra of fullerenes

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Abstract. The spheroidal geometry of a slightly elliptically deformed sphere was used as a possible approach to fullerenes. We are interested in the elliptically deformed fullerenes like big C_{240} molecule. The low-lying electronic levels are described by the Dirac equation in (2+1) dimensions. We show how a small deformation of spherical geometry evokes a shift of the electronic spectra compared to the sphere. The effect of a weak uniform magnetic field on the electronic structure of slightly deformed fullerene molecules was also studied. We found that behavior of the electronic spectra if the magnetic field is pointed in the x direction differs markedly from the case of the magnetic field pointed in the z direction, where z is chosen to be the symmetry axis of the fullerene. We briefly report also the C_{60}-C_{240} fullerene onion.

1. Introduction

Recently, we have considered the problem of the low energy electronic states in spheroidal fullerenes [1] as well as the influence of a weak uniform external magnetic field pointed in the z and x directions [2, 3]. The main findings were a discovery of fine structure with a specific shift of the electronic levels upwards 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 modifies the density of electronic states and does not change the number of zero modes. We found that modification of the electronic spectrum of the spheroidal fullerenes in the case of x-directed magnetic field differs markedly from the case of the z-directed magnetic field. This gives an additional possibility for experimental study of the electronic structure of deformed fullerene molecules.

We have explored in the Ref. [2, 3] the field-theory model where the specific structure of carbon lattice, geometry, and the topological defects (pentagons) were taken into account. Following the Euler's theorem one has to insert twelve pentagons into hexagonal network in order to form the fullerenes. In the framework of continuum description in our model we extend the Dirac operator by introducing the Dirac monopole field inside the spheroid to simulate the elastic vortices due to twelve pentagonal defects. Our studies covered slightly elliptically deformed molecules in a weak uniform external magnetic field pointed in the x,z directions.

As the result of this approach we found that the zero-energy states correspond to the HOMO (highest occupied molecular orbital) and the HOMO-LUMO energy gap is approximately 1.1 eV for YO-C_{240} fullerene which was in good agreement with some another prediction [4]. We extend our previous model of fullerenes to the fullerene onion. We used the idea published in [5]

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 normaly to the fullerenes surface, but are titled by the hybridization angle. We computed HOMO-LUMO gap for concretely C_{60}-C_{240} carbon onion.

2. Formulation of the model and the results

Geometry, topological defects and the peculiarity of graphene lattice have a pronounced effect on the electronic structure of fullerene molecules. Spheroidal fullerenes can be considered as the initially flat hexagonal network which has been wrapped into closed monosurface by using of twelve disclinations [6]. We start from the tight-binding model of graphite layer with a trial wave function taken in the form

$$\chi(\vec{r}) = \psi_A(\vec{r})\chi_A(\vec{K},\vec{r}) + \psi_B(\vec{r})\chi_B(\vec{K},\vec{r}). \tag{1}$$

As is seen, the trial function is described by smoothly varying envelope functions $\psi_{A,B}(\vec{r})$ multiplying by Bloch functions $\chi_{A,B}(\vec{K},\vec{r})$. Within the $\vec{k}\vec{p}$ approximation one obtains the equations algebraically identical to the two-dimensional Dirac equation, where the two-component wave function ψ represents graphite sublattices A and B. Following the approach developed in [7, 8] let us write down the Dirac operator for free massless fermions on the Riemannian spheroid S^2. The Dirac equation on a surface Σ in the presence of the abelian magnetic monopole field W_μ and the external magnetic field A_μ is written as [9]

$$i\gamma^\alpha e_\alpha^{\ \mu}[\nabla_\mu - iW_\mu - iA_\mu]\psi = E\psi, \tag{2}$$

where e_α^μ is the zweibein, $g_{\mu\nu} = e_\mu^\alpha e_\nu^\beta \delta_{\alpha\beta}$ is the metric, the orthonormal frame indices $\alpha,\beta = \{1,2\}$, the coordinate indices $\mu,\nu = \{1,2\}$, and $\nabla_\mu = \partial_\mu + \Omega_\mu$ with

$$\Omega_\mu = \frac{1}{8}\omega_\mu^{\ \alpha\ \beta}[\gamma_\alpha,\gamma_\beta], \tag{3}$$

being the spin connection term in the spinor representation (see [10, 11] for details). The energy in (2) is measured from the Fermi level.

This model allows us to study the structure of electronic levels near the Fermi energy. It is convenient to consider this problem by using of the Cartesian coordinates x, y, z in the form

$$x = a\ \sin\theta\cos\phi; \quad y = a\ \sin\theta\sin\phi; \quad z = c\ \cos\theta. \tag{4}$$

The Riemannian connection reads

$$\omega_{\phi 2}^1 = -\omega_{\phi 1}^2 = \frac{a\cos\theta}{\sqrt{a^2\cos^2\theta + c^2\sin^2\theta}}\ ; \quad \omega_{\theta 2}^1 = \omega_{\theta 1}^2 = 0. \tag{5}$$

Within the framework of the perturbation scheme the spin connection coefficients are written as

$$\omega_{\phi 2}^1 = -\omega_{\phi 1}^2 \approx \cos\theta(1 - \delta\sin^2\theta), \tag{6}$$

where $c = a + \delta a$ and terms to first order in δ are taken into account. In spheroidal coordinates, the only nonzero component of W_μ in region R_N is found to be (see Ref. [1])

$$W_\phi \approx g\cos\theta(1 + \delta\sin^2\theta) + G(1 - \cos\theta) - \delta G\sin^2\theta\cos\theta. \tag{7}$$

Firstly we assume that the external magnetic field B is chosen to be pointed in the x direction, so that $\vec{A} = B\,(0,-z,y)\,/2$. One obtains

$$A_\phi = -\frac{1}{2}Bac\sin\theta\cos\theta\cos\phi, \tag{8}$$

$$A_\theta = -\frac{1}{2}Bac\sin\phi. \tag{9}$$

The Dirac matrices can be chosen to be the Pauli matrices, $\gamma_1 = -\sigma_2, \gamma_2 = -\sigma_1$. By using the substitution

$$\begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = \sum_j \frac{e^{i(j+G)\phi}}{\sqrt{2\pi}} \begin{pmatrix} u_j(r) \\ v_j(r) \end{pmatrix}, j = 0, \pm1, \pm2, \ldots \tag{10}$$

where j is the angular momentum, we obtain the Dirac equation for functions u_j and v_j in the form

$$\left(-i\sigma_1\frac{1}{a}(\partial_\theta + \frac{\cot\theta}{2} + i\frac{1}{2}Ba^2\sin\phi) + \frac{\sigma_2}{a\sin\theta}\left(j - m\cos\theta + \frac{1}{2}Ba^2\sin\theta\cos\theta\cos\phi\right) + \delta\hat{\mathcal{D}}_1\right)\times$$
$$\times \begin{pmatrix} u_j(\theta) \\ v_j(\theta) \end{pmatrix} = E\begin{pmatrix} u_j(\theta) \\ v_j(\theta) \end{pmatrix}, \tag{11}$$

where $m = g - G$ and

$$\hat{\mathcal{D}}_1 = -\frac{\gamma_1}{a}\sin\theta\,(j - 2m\cos\theta) - \gamma_1\frac{Ba}{2}\sin^2\theta\cos\theta\cos\phi. \tag{12}$$

The square of the nonperturbative part of the Dirac operator takes the form

$$\begin{aligned}\hat{\mathcal{D}}_0^2 &= -\frac{1}{a^2}\left(\partial_\theta^2 + \frac{\cos\theta}{\sin\theta}\partial_\theta - \frac{1}{4} - \frac{1}{4\sin^2\theta}\right) + \frac{(j - m\cos\theta)^2}{a^2\sin^2\theta} \\ &+\sigma_3\frac{m - j\cos\theta}{a^2\sin^2\theta} + BV(\theta,\phi).\end{aligned} \tag{13}$$

From the equations above we finally find the low energy electronic spectrum of spheroidal fullerenes in the form

$$E_{jn} = E^0_{jn} + E^{\delta B_x}. \tag{14}$$

Next we have assumed that the external magnetic field is pointed in the z direction so that $\vec{A} = B\,(y, -x, 0)\,/2$. The only nonzero part of the external magnetic field reads

$$A_\phi = -\frac{1}{2}Ba^2\sin^2\theta. \tag{15}$$

After the calculations describe in Ref. [2] we obtain the Dirac equation for functions u_j and v_j in the form

$$\left(-i\sigma_1\frac{1}{a}(\partial_\theta + \frac{\cot\theta}{2}) + \frac{\sigma_2}{a\sin\theta}\left(j - m\cos\theta - \frac{1}{2}Ba^2\sin^2\theta\right) + \delta\hat{\mathcal{D}}_1\right)\times$$
$$\times \begin{pmatrix} u_j(\theta) \\ v_j(\theta) \end{pmatrix} = E\begin{pmatrix} u_j(\theta) \\ v_j(\theta) \end{pmatrix}, \tag{16}$$

where the spheroidal perturbation part is

$$\hat{\mathcal{D}}_1 = -\frac{\gamma_1}{a}\sin\theta\,(j - 2m\cos\theta) - \gamma_1\frac{Ba}{2}\sin^3\theta. \tag{17}$$

Since we consider the case of a weak magnetic field the terms with B^2 and δB can be neglected in calculations. Finally, in the linear in δ approximation, the low energy electronic spectrum of spheroidal fullerenes takes the form

$$E_{jn} = E^0_{jn} + E^\delta_{jn} + E^{\delta B_z}_{jn}, \tag{18}$$

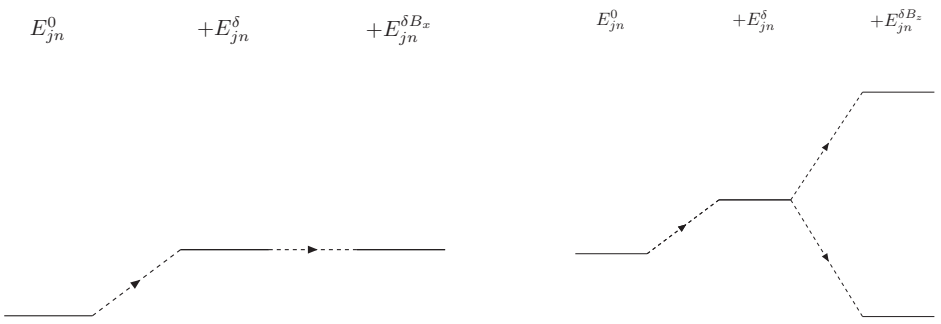

Figure 1. The schematic picture of the first electronic level E_{jn} of spheroidal fullerenes in a weak uniform magnetic field pointed in the x (left) and z (right) directions.

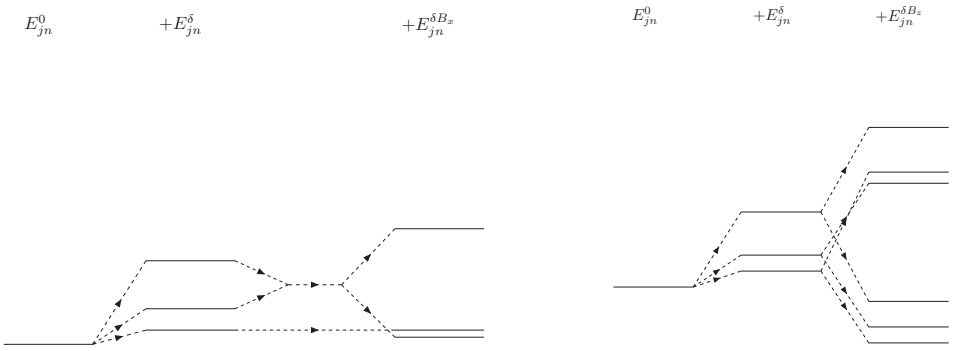

Figure 2. The schematic picture of the second electronic level E_{jn} of spheroidal fullerenes in a weak uniform magnetic field pointed in the x (left) and z (right) directions.

where

$$E^0_{jn} = (n + |j| + 1/2)^2 - m^2, \tag{19}$$

describes the spectrum for spherical fullerene.

Tables with the numerical values of the electronic spectra influenced by a weak uniform external magnetic field pointed in the z and x directions and all analytical expressions above are presented in [2, 3]. The experimental data for our calculations of YO-C_{240} fullerene was found in [12, 13]. As is seen in Figs.1,2, there is a marked difference between the behavior of the first and second energy levels in magnetic field. Indeed, in both cases the energy levels become shifted due to a spheroidal deformation. However, the uniform magnetic field does not influence the first energy level. The splitting takes place only for the second level. This is clearly illustrated in Fig.1 and Fig.2, which schematically show the structure of the first and second levels in the uniform magnetic field pointed in x direction. The case of the z-directed magnetic field is also shown for comparison. We can conclude that there is a possibility to change the structure of electronic levels in spheroidal fullerenes by altering the direction of the magnetic field. It would be interesting to test this prediction in experiment.

3. $C_{60} - C_{240}$ fullerene onion

Now we consider the case of $C_{60} - C_{240}$ fulleren onion. In this fullerene onion the hybridization of the orbitals of the inner and outer shell is different. Due to the curvature the coordinates of $\overrightarrow{\tau_i}$ in space are

$$\overrightarrow{\tau_1} = d(\cos\theta; 0; -\sin\theta), \tag{20}$$

$$\overrightarrow{\tau_2} = d(e_x; -e_y; e_z), \tag{21}$$

$$\overrightarrow{\tau_3} = d(e_x; e_y; e_z). \tag{22}$$

Where $\sin\theta = d/2R$ and

$$e_x = -\frac{d}{2R}\tan\theta - \frac{1}{2\cos\theta}, \tag{23}$$

$$e_y = \left(1 - \frac{1}{4(1-\frac{d^2}{4R^2})} - 2\left(\frac{d}{2R}\right)^2 \frac{1}{(1-\frac{d^2}{4R^2})}\right), \tag{24}$$

$$e_z = -\frac{d}{2R}, \tag{25}$$

R is the radius of the fullerene molecules and d is the nearest neighbor length. It was assumed that the angle between the bonds $\overrightarrow{\tau_1}, \overrightarrow{\tau_2}$ and also $\overrightarrow{\tau_1}, \overrightarrow{\tau_3}$ is 120^o [14]. We get the numerical values for the π orbital in the case of C_{60} fullerene molecule

$$|\pi\rangle \approx\ 0.289|s\rangle - 0.068\ |p_x\rangle + 0.955|p_z\rangle. \tag{26}$$

It was assumed that $R = 3.5$Å. For C_{240} fullerene molecules we have

$$|\pi\rangle \approx\ 0.144|s\rangle - 0.007\ |p_x\rangle + 0.990|p_z\rangle. \tag{27}$$

It was assumed that $R = 7.1$Å. Hence, in the case of C_{60} molecule, one has

$$\tilde{\epsilon} = 0.083\langle s|H|s\rangle + 0.005\langle p_x|H|p_x\rangle + 0.911\langle p_z|H|p_z\rangle, \tag{28}$$

and for C_{240}

$$\epsilon = 0.021\langle s|H|s\rangle + 0.980\langle p_z|H|p_z\rangle. \tag{29}$$

Finally, we obtain

$$\epsilon - \tilde{\epsilon} \approx 1.024\ eV. \tag{30}$$

Now we use the values of highest occupied molecular orbital (HOMO) computed in [4] and the lowest unoccupied molecular orbital (LUMO) energy levels for C_{60} and C_{240} fullerenes. We have HOMO(C_{60})=$-1.545eV$, LUMO(C_{60})=$0.346eV$, and HOMO(C_{240})=$-1.092eV$, LUMO(C_{240})=$0.149eV$ for isolated fullerenes. In the $C_{60} - C_{240}$ onion we must add the value $1.024eV$ to the C_{240} fullerene energies. So we get approximately the following values in a slightly interacting onion for the C_{240} fullerene. HOMO(C_{240})=$-0.068eV$, LUMO(C_{240})=$1.173eV$. So we get a gap between HOMO(C_{240}) and LUMO(C_{60}) which is about $0.414eV$. If the interaction between the shells is not very strong, the value of the gap could not be strongly influenced. 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.

4. Conclusion

We have studied the influence of the uniform magnetic field on the energy levels of spheroidal fullerenes. The case of the x-directed magnetic field was considered and compared with the case of the z-th direction. The z axis is defined as the rotational axis of the spheroid with maximal symmetry. The most important finding is that the splitting of the electronic levels depends on the direction of the magnetic field. We found that the structure of the electronic levels is crucially depend on the direction of the external magnetic field which could be also checked in experiment. To compute the influence of a curvature of the surface on the matrix elements of the secular equation, we used two methods. The rehybridization of the π orbital method was used for the computation of diagonal matrix elements. To compute the nondiagonal matrix element, we used

the curvature tensor. In the case of small interaction between shells in $C_{60} - C_{240}$ fullerene onion we get the difference 1.024 eV between the "Fermi levels" of individual fullerenes. Therefore we get a gap between HOMO(C_{240}) and LUMO(C_{60}) which is about $0.414eV$. As in [4] we used for both C_{60} and C_{240} the value 2.5 eV for transfer integrals in both the shells. There ought to be also made a correction to different curvatures of these fullerenes. Howewer, we think that this correction does not change significantly the HOMO-LUMO gap. It would be interesting to test this predictions of the HOMO-LUMO gap for the $C_{60} - C_{240}$ fullerene onion in experiment.

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References

[1] M. Pudlak, R. Pincak and V.A. Osipov 2006 Phys. Rev. B **74** 235435
[2] M. Pudlak, R. Pincak and V.A. Osipov 2007 Phys. Rev. A **75** 025201
[3] M. Pudlak, R. Pincak and V.A. Osipov 2007 Phys. Rev. A **75** 065201
[4] Y.L.Lin, F.Nori 1994 Phys.Rev. B **49** 5020
[5] A.Kleiner, S.Eggert 2001 Phys.Rev. B **64** 113402
[6] H. Kroto 1997 Rev.Mod.Phys. **69** 703
[7] J. Gonzales, F. Guinea and M.A.H. Vozmediano 1993 Nucl.Phys.B **406** 771
[8] D.V. Kolesnikov and V.A. Osipov 2006 Eur.Phys.Journ. B **49** 465
[9] N.D. Birrell and P.C.W. Davies, *Quantum Fields in Curved Space*, (Cambridge 1982)
[10] M. Nakahara, *Geometry, Topology and Physics*, (Institute of Physics Publishing Bristol 1998)
[11] M.Göckeler and T.Schücker, *Differential geometry, gauge theories, and gravity* (Cambridge University Press 1989)
[12] M. Yoshida and E. Osawa 1993 Fullerene Sci. Tech. **1** 55
[13] J. P. Lu and W. Yang 1994 Phys. Rev. B **49** 11421
[14] R.A.Jishi, M.S.Dresselhaus 1992 Phys.Rev. B **45** 11305