Depolarisation of spherical–membrane quantum well: Gap renormalisation for closed–shell fullerenes

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(December 31, 1999)

An anomalous large level shift is newly found to correct the one–electron spectrum of a closed–shell carbon nanocluster, for example, the spectrum which was described within the model of a thin quantum well rolled into a sphere. As a result of the interaction with zero–point oscillations of the confined modes of the electric field, the one–electron energy levels heighten. The depolarization depends on the electron momentum, why it does not shift the rotational spectrum as a whole. Surprisingly the shift in a spherical closed–shell cluster of an arbitrary size is described by an universal law. The non-equidistant shift of the levels results in an increase of an one-electron gap by 1.4 times.

I. INTRODUCTION

One–electron approximation (owing to its cheapness) is often used for carbon nanoclusters though at an expense of uncontrolled incorrectness. It is worth to be aware when the simple approach fails because a true many–body calculation seems to be too complicated to apply it for any new cluster appearing in the large fullerene family. While a complete account for Coulomb interaction has to include all renormalization effects, a summing of some of diagrams can lead to the depolarization lost. A model estimation will be performed below which captures some physics, usually covered only by the sophisticated many–body theory. We stress that our term is a counterpart of the standard vertex renormalization (*i.e.*, electron–hole attraction), as increasing the one–electron gap.

In the paper we go to reveal the depolarization correction which follows from an interaction of an electron with an electromagnetic field created by all other valence electrons of the closed–shell cluster. Therefore, the electron interaction is treated selfconsistently within the approach. This continues our consideration of C_{60} in frame of a simple quantum mechanical model, namely, the model of the spherical–membrane quantum well (SMQW) [1], which has fruitful analogies with a standard quantum well model in the theory of low–dimensional structures.

The group of full rotations, SO(3), was shown to be useful in the fullerene physics to label the one–electron states [1–3], to simplify a theory of an electron–electron interaction on the sphere [4] and surface plasmons [5], as well as to facilitate a computation of a high–harmonic generation spectrum in the fullerene [6]. An essential simplification is achieved (also in the depolarization calculation) using the spherical symmetry because of the angular momentum subspaces [7] can be separated readily in many cases. For a linear dipole response, the SO(3) symmetry cancels a lot of matrix elements and allows one to get analytically the solution for the selfconsistent RPA response function of C_{60} [1,3,8,9]. A peak of a collective excitation shows up in this spectrum, resulting from fast coherent oscillations of a total electron density of valence states.

This surface density oscillation can be thought as a confined electrical field mode or the surface plasmon (which was studied before [1,3,5,10]). A zero–point oscillation of an electromagnetic vacuum is well known to manifest itself as a Casimir force between close surfaces of a polarizable substance, as a van–der–Waals interaction, as a standard Lamb shift in a hydrogen–like atom. We will consider in the paper the shift of electron levels in the field fluctuations of the confined modes (connected with the nanocluster), which effect is much stronger than of the zero–point oscillations of the free electromagnetic field.

Below we will show that, within the spherical–symmetry of SMQW model, the one–electron level shift due to the interaction with the zero–point oscillations of the electric field of the local collective mode (or the depolarization) results in a strong renormalization of a gap of the closed–shell fullerene. The relative gap increment is independent of the cluster size.

II. PERTURBATION THEORY FOR ENERGY LEVEL SHIFT

We put forward a semiclassical theory of an energy level shift (LS) for an arbitrary shell object in Ref. [11], keeping the simplicity of the one–electron calculation and outlining the depolarization. The method follows the book [12].

For completeness we give here the bases of the computation. The frequency of the (zero–point) oscillations of the external field is much higher than the inverse period of the electron orbit. Therefore, the adiabatic approximation has to be used. It means that the fast (field) variables can be integrated out in a motion equation for the (slow) electron. A simple model for the depolarization states that the LS results from short fast deflections of the electron from its original orbit in the random high–frequency field of the electromagnetic wave. The energy correction is given by the second order perturbation theory (see the diagram in Fig.1) and reads as:

$$\overline{\Delta H} = \langle H(r+\delta) - H(r) \rangle = \left\langle \nabla H \cdot \vec{\delta} + \frac{1}{2}\nabla^2 H \; \vec{\delta}\cdot\vec{\delta} + \dots \right\rangle = \frac{1}{4}\nabla^2 H \; \overline{\delta^2} + o(\overline{\delta^2}) \tag{1}$$

where $H(r)$ is the unperturbed (one–electron) Hamiltonian and $H(r+\delta)$ is the Hamiltonian with account for the electron deflection δ. The energy difference is expanded in series on δ, then averaged over the fluctuations and a first nonzero contribution is taken. The small parameter of the perturbation theory will be proved in the end of the section. It is the ratio of the deflection to a characteristic length of the potential which estimates Laplasian, $\overline{\delta^2}\nabla^2 \sim \overline{\delta^2}/R_C^2 \ll 1$. We stress that the spherical symmetry allows us to limit the calculation to the subspace of the fixed angular momentum as well as to get the eigen modes of the confined field. The angular momentum plays the role of the simple momentum for a space invariant system. It conserves for definite types of diagrams (for example, the bubble diagrams). That means that the spherical plasmon modes do not mix.

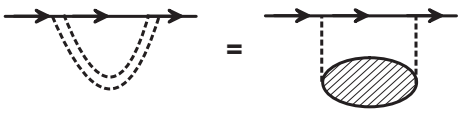

FIG. 1. The diagram representing the depolarization level shift of the SMQW electron. Within our approximation the shift results from the electric field of the surface plasmon mode which is depicted as the shaded mass operator in the right. Due to the imposed spherical symmetry the angular momentum conserves for the two–leg diagram.

The expression for the mean square of the deflection, $\overline{\delta^2}$, caused by the zero–point fluctuation of the confined electromagnetic modes, was deduced in Ref. [11]. A contribution from the free electromagnetic field, which will not be considered below, was also calculated and shown to be miserable comparing with the confined field. We will not repeat the derivation completely but refer to the expression (5) of that article, which gives the deflection from the spherical modes, $|L\rangle$, as follows:

$$\overline{\delta^2} = \sum_{L=1}^{L_c} (2L+1)\overline{\delta_L^2} \simeq \frac{\pi 2^{3/2}}{3}\left(\frac{R}{N a_B}\right)^{3/2} a_B^2 \; \left(L_{\rm c} + \frac{1}{2}\right)^{3/2}, \tag{2}$$

where R is a nanocluster radius, $a_B = \hbar^2/me^2$ is the Bohr radius (atomic length unit), $L_{\rm c}$ is the maximum allowed angular momentum of the plasmon state. A number of atoms of the cluster, N, reads as follows:

$$N = \frac{4\pi R^2}{3\sqrt{3}\, b^2/4}, \tag{3}$$

where $b \sim 1.4$ Å is the carbon–carbon distance in the graphite–like lattice of the nanocluster. Using this definition we are able to evaluate the mean square deflection. For the infinitely large cluster ($R, N \to \infty$) the (infinitely large) angular momentum can be related to the (finite) 2D wave–number of the surface excitation via: $\hat{L} \simeq \hat{k}R$. The maximum wave–number $k_{\max} \sim \pi/\sqrt{3}b$ lies on the "Brilluene zone" [13] boundary. Substituting the corresponding angular momentum value $L_{\rm c} + 1/2 \sim \pi R/(b\sqrt{3})$ and the number of atoms into the expression (2) we get the semiclassical value of the electron deflection. In the units of the atomic length it reads as:

$$\frac{\overline{\delta^2}}{a_B^2} = \frac{3^{5/4}}{2^{9/2}\sqrt{\pi}}\left(\frac{b}{a_B}\right)^{3/2}\left(\frac{b}{R}\right)^{3/2}\left(L_{\rm c}+\frac{1}{2}\right)^{3/2} = \frac{3^{1/2}\pi}{2^{9/2}}\left(\frac{b}{a_B}\right)^{3/2} \simeq 1.03. \tag{4}$$

Though the estimation is semiquantitative, the deflection seems to be of the order of the atomic unit, which proves the expansion (1). It follows from Eq.(4) that the perturbation theory works as long as the potential changes on the scale larger than the atomic one.

The first result of the model is that the mean square deflection of the electron in the SMQW does not depend on the radius, neither on the number of atoms. It is ocularly because of the density of the valence electrons is constant (precisely, it grows slightly with N reflecting the fact that the hexagonal carbon lattice of the spherical cluster includes 12 pentagons those lessen the density, which becomes insignificant for the large enough cluster). The independence of the deflection on the number of atoms follows from the extreme quantization both of the electron and the field mode.

III. LEVEL ORDERING IN SMQW AND ANGULAR MOMENTUM DEPENDENT SHIFT

Suppose that the one–electron model works for some cluster C_N. To make a numerical estimation we will think about C_{60}, which spectrum was well studied experimentally. The result does not depend essentially on the one–electron model chosen, therefore, in order to present a manifestation of the depolarization, the simplest SMQW model will be used for the bare level ordering. Then the one–electron Hamiltonian reads as [1]:

$$H_o = E_n + \frac{\hbar^2}{2mR^2}\hat{L}^2, \tag{5}$$

where E_n is the energy of a lowest level of $n-$th radial series; an orbital quantization energy $\hbar\omega_o \equiv \hbar^2/mR^2$ defines the SO(3) level spacing between states $|n, LM\rangle$ which are the eigenstates of the angular momentum operator and are $2L+1$ degenerated. We will refer below to the single series with $n=1$ corresponding to π electron system of the nanocluster, therefore the radial index will be omitted. It will be convenient to substitute the classical value $L+1/2$ for the angular momentum operator eigenvalues [7], which is correct for the large enough momentum.

Let us rewrite the orbital energy of the $L-$th electron state in the following form:

$$E_L^{(o)} = \frac{\hbar\omega_o}{2}\left(L+\frac{1}{2}\right)^2 \simeq \frac{8\pi}{3\sqrt{3}}\left(\frac{a_B}{b}\right)^2 \frac{\left(L+\frac{1}{2}\right)^2}{N} E_B = E_{\max}^{(o)}\frac{\left(L+\frac{1}{2}\right)^2}{N}, \tag{6}$$

where $E_B = e^2/a_B$ is the atomic energy unit. The meaning of the energy $E_{\max}^{(o)} = E_B(a_B/b)^2 8\pi/3\sqrt{3} \simeq 16.8$ eV will become clear in the end of the section. The expression (6) is derived using the surface carbon density appearing in the denominator of Eq.(3).

The electrons move within a very thin spherical shell layer (spherical membrane) which is approximated by a delta–function $\delta(r-R)$. Hence, we use 2D–Laplasian operator in Eq.(1), which is nothing more than its angular part in the radial co–ordinate system $\hat{L}^2/R^2$. Evidently, one has $\langle\nabla^2 H_o\rangle \sim \frac{\hbar^2}{2mR^2}\frac{1}{R^2}\left(L+\frac{1}{2}\right)^4$. Finally, Eq.(1) yields the SMQW level shift as follows:

$$\delta E_L = \frac{\pi^3\sqrt{2}}{9\sqrt{3}}\left(\frac{a_B}{b}\right)^{5/2}\frac{\left(L+\frac{1}{2}\right)^4}{N^2}E_B, \tag{7}$$

here the last fraction is dimensionless. As it will be shown, it is actually independent of the nanocluster size for some characteristic L, *e.g.* for L_F — Fermi momentum dividing the empty levels from the occupied ones.

The second result of the model is that the universal law for the level shift is independent on the specific nanocluster (excluding the trivial dependence in N which also drops as will be explained in the end of the section). The depolarisation heightens the one–electron energy as:

$$E_L = E_L^{(o)}\left(1+\kappa\frac{\hat{L}^2}{N}\right), \tag{8}$$

where $\kappa \sim 0.36$ is the numerical coefficient depending only on the carbon atom density: $\kappa = \sqrt{a_B/b}\,\pi^2/(2^{2.5}3)$. In the contraction limit $L \to kR$, the rest term goes to the squared wave–number $\hat{L}^2/N \to (kb)^2$ with the accuracy of some factor. The lowest level does not shift because of the zero value of the angular momentum (in contrast to the standard Lamb shift which originates from the interaction with the charge of the hydrogen–like nuclei core. This charge is concentrated in the co–ordinate origin, therefore, the maximum Lamb shift is for the lowest, s, state). Note that the $L=0$ term is absent in Eq.(2) owing to no monopole plasmon exists.

Let us evaluate the maximum depolarization LS. It occurs for the maximum angular momentum $L_{\max}+1/2$ which is derived from the sum of the electron states. Because the total number of (double degenerate due to the spin) $\pi-$states equals the number of carbon atoms, $N = \sum_{L=0}^{L_{\max}}(2L+1) = (L_{\max}+1)^2$, we substitute for $L_{\max}+1/2 \sim \sqrt{N}$. Now the meaning of the energy $E_{\max}^{(o)}$, entered Eq.(6), is clear. It is the upper limit for the bare energy (see spectra in Fig.2). From Eq.(8) the maximum depolarization LS reads as:

$$\frac{\delta E_L}{E_L^{(o)}} \le \frac{\pi^2}{12\sqrt{2}}\sqrt{\frac{a_B}{b}}\frac{(L_{\max}+1/2)^2}{N} = \kappa \simeq 0.36. \tag{9}$$

As we claimed before, the LS for the fixed (upper) level does not depend neither on the state label L nor on the cluster size N. Let us now reflect on the size scaling of the shift of the state $|L\rangle$. The only state with L increasing as $\sqrt{N}$ has a physical sense because of such momentum, scaling with the cluster size, remains in the same point of the "Brilluene zone". The LS of this fixed state constitutes the fixed percentage (of the bare energy) which is equal for any cluster size. The depolarisation for the different L varies from 0 for the lowest state of a closed–shell cluster, to κ for the upper one. The universality for our scaling law means that for an arbitrary cluster size and an arbitrary state momentum the relative LS falls into the same straight line as shown in Fig.2. Clearly, Eq.(9) proves that the perturbation theory is applicable as its correction is still less than unity for the highest possible level which has the maximum shift.

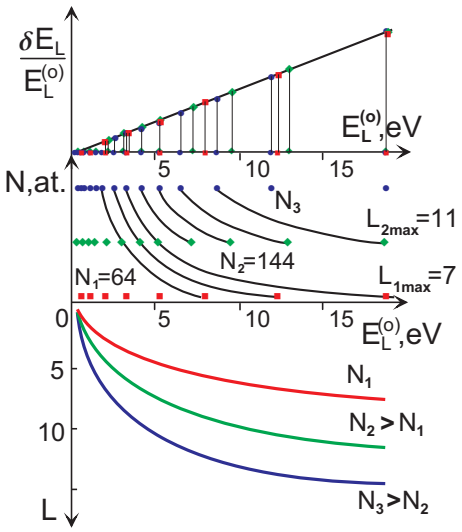

FIG. 2. The universal law for the depolarization level shift. Bottom: The bare SMQW electron energy levels for 3 different cluster sizes: $N_1 = 64, N_2 = 144, N_3 = 196$. The number of atoms is chosen to form the closed shells. Note that the upper energy $E^{(o)}_{\max}$ is the same for all clusters. Middle: Fan–like diagram for the energy levels of the fixed state $|L\rangle$, depending on N. Top: The level shift depends on the cluster size and L but all data falls into the same straight line.

IV. GAP INCREASE WITHIN SMQW–DEPOLARIZATION MODEL

Within the closed–shell model the optical gap occurs between the levels $|L_F\rangle$ and $|L_F + 1\rangle$ (see Fig.3) with the value:

$$E^{(o)}_g = \frac{\hbar\omega_o}{2}\left[(L_F+1)(L_F+2) - L_F(L_F+1)\right] = \hbar\omega_o(L_F+1). \tag{10}$$

The gap value does depend on the cluster size, decreasing to the zero as N going to infinity in order to approach the gapless graphite. For the buckminsterfullerene C_{60} ($R \sim 3.6$ Å) the orbital energy quantum is $\hbar\omega_o \sim 0.3$ eV, and the Fermi momentum is about $4-5$ (the uncertainty is due to the exact number of π electrons is more than 50 for $L_F = 4$ and less than 72 for $L_F = 5$). Then the estimation for the one–electron gap, $1.5 - 1.8$ eV, is in a reasonable agreement with the experimental value about 1.8 eV. We note that the cluster radius has to be a fitting parameter due to the 2D approximation lying in the base of the SMQW model.

The gap should increase owing to the zero–point oscillations. It is because of the higher level shifts faster. The energy difference between L_F and $L_F + 1$ levels reads as:

$$E_g = \hbar\omega_o(L_F+1)\left(1 + 2\frac{(L_F+1)^2}{N}\kappa\right), \tag{11}$$

where the parameter $\kappa \simeq 0.36$ is the same as before. Within the closed–shell approximation, similarly to what done to get Eq.(9), the Fermi momentum follows from the condition: $N = 2\sum_{L=0}^{L_F}(2L+1) = 2(L_F+1)^2$, because of the number of the occupied states is one half of the total number of states. Thus Eq.(11) becomes extremely simple and contains no fitting parameters. The gap correction is universal for any closed–shell spherical cluster and amounts about 40 % to the bare value:

$$E_g = E_g^{(o)}(1+\kappa) \simeq 1.36 E_g^{(o)}. \tag{12}$$

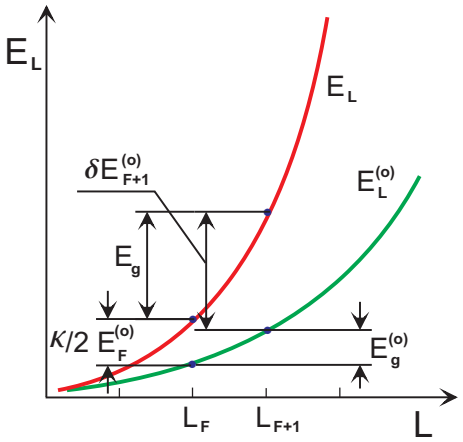

FIG. 3. The gap renormalisation due to the depolarisation level shift. The bare and shifted energy are shown depending on the state angular momentum, which dependence is given schematically. The states below L_F are occupied. The states above are free according to the closed–shell model.

V. CONCLUSIONS

In the paper we deduced the semiclassical theory of the *depolarization* level shift (LS) in the electronic spherical–shell system for the fullerene nanoclusters. The LS materializes by the adiabatic interaction of the charge carrier with the local field of the fast zero–point oscillations of the plasmon modes *confined* to the cluster spherical surface. The analytical expression was derived for the depolarization LS. It is shown that the perturbation theory is applicable even for the highest (unoccupied) electron level which has the largest shift. The LS depends on the cluster size as well as on the angular momentum of the one–electron state. As a function of the bare one–electron energy all levels shifts, even for different clusters, collapse onto a straight line (Fig.2). Though, for the scaling, solely the fixed state with L^2/N =const (for example, the state at the Fermi level) has a physical sense. The relative energy correction of this fixed state is the same for a cluster of any size. The more the number of atoms, the higher the Fermi momentum, while the ratio L_F^2/N, contained in the expression for the depolarization, remains a constant number about 1/2. Therefore, the Fermi level correction is independent of the size. This universal law for the LS which is non–equal for the states above and below the Fermi level (see Fig.3) gives a universal rise to the one–electron gap. As the result the renormalized gap in any closed–shell spherical cluster is wider by 1.36 times.

Acknowledgments. This work was partially supported by RFBR grants no. 96-15-96348 and 99-02-18170.

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