The anomalous level shift due to local electric modes of the confined systems *

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(June 5, 1999)

The shift of the electron energy level due to the coupling with the surface electromagnetic mode of the cluster is studied. The energy shift is shown to depend on the cluster size and to be much larger than the standard Lamb shift due to the delocalized electromagnetic modes. The angular momentum theory is developed for the calculation of the high-frequency response of the cluster and applied, within the spherical approach, for the computation of the energy shift in the fullerene as an example.

The zero fluctuation of the electromagnetic vacuum are well known to manifest itself as the Casimir force between close surfaces of polarizable substance, as the Van-der-Waals interaction, as the origin of the radiative lifetime and the shift of the energy levels of the charge carrier in the system placed in some cavity. The paper considers the shift of the electron levels in the field of the zero-fluctuations of the modes connected with the cluster, the cavity or the quantum box.

The most simple manifestation of the influence of the zero-fluctuation modes is the energy level shift (Lamb shift) which is the difference between the electron levels of the different symmetry those are to interact with the electromagnetic field in different degree. We raise an issue of the value of the level shift (LS) in a confined system (0D object). Its distinguishing feature is the confinement of the electromagnetic field in the volume of the charge carrier motion.

FIG. 1. The diagram related to the level shift considered in the paper. The main contribution comes from the plasmon mode which is depicted as the shaded mass operator in the right.

Let us consider LS of the charge carrier semiclassically following the book [1]. The

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frequency of oscillations of the external field (of zero fluctuations) is much higher than the inverse period of the electron orbit. Therefore, the adiabatic approximation will be used. The estimated value of LS results from the short fast deflections of the electron from its original orbit in the high-frequency field of the electromagnetic wave of the zero-fluctuation. The shift is given by the second order (see diagram in Fig.1) perturbation theory as

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

(1)

where \(H(r)\) is the unperturbed Hamiltonian and \(H(r + \delta)\) is the Hamiltonian with account for the electron deflection.

The classical charge deflects from its path, acted upon by the force \(e\vec{E}\). Let us express all fluctuation fields \(\vec{E}\) in terms of the eigen modes related to the specific system (cluster or quantum box). Within the linear response theory (see Appendix A), the electron deflection reads as:

$$\delta^2 = 2 \sum_{\alpha} \delta^2_{\alpha} = 2 \frac{e^2}{m^2} \sum_{\alpha} E^2_{\alpha} \left( \frac{1}{2\omega_\alpha (\omega_\alpha + \omega_0)} \right)^2$$

(2)

here \(e\) and \(m\) are the electron charge and mass, \(\omega_0\) is the atomic frequency. The multiplier 2 accounts for two polarisations of the light. It is easy to check that the higher the frequency of the mode, the larger the partial shift due to this mode. Hence, the local modes of the maximal frequency, those are plasmons, are of the most importance in expression (2).

The amplitude of the electric field \(E_{\alpha}\) of the fixed mode with the quantum numbers \(\alpha\) is related to its zero-oscillation frequency \(E^2_{\alpha} \propto \hbar \omega_\alpha\). For example, for surface plasmons of the fullerene cluster it was calculated in [2]: \(E^2_{L} = \hbar \omega_L \pi (L + 1/2)/R^3\).

The LS due to the electromagnetic modes of a free space (3D vacuum) follows from Eq.(2) when one substitutes the wave vector \(k\) instead of \(\alpha\). We change the sum into the integral. This results (in 3D-space) in well-known formula:

$$\overline{\delta^2} = \frac{e^2 \hbar}{2\pi m^2 c^3} \ln \frac{\omega_{\text{max}}}{\omega_{\text{min}}} = \frac{a^3}{2\pi} a_B^2 \ln \frac{\omega_{\text{max}}}{\omega_{\text{min}}}$$

(3)

where the wave vector of the electron, which is non-relativistic one, limits the integration region from above: \(\omega_{\text{max}} \sim mc^2/\hbar\), while atomic frequency gives the lower limit: \(\omega_{\text{min}} \sim \omega_0\). The mean deflection is less than the Bohr radius \(a_B \approx 0.53 \, \text{Å}\) in \(a^3\) times, where \(a \approx 1/137\) is the fine constant. As a result the LS is quite small and does not affect the spectrum essentially.
This is not true if one considers the local modes related to some system. Let us calculate the surface modes of the metallic sphere of the radius \( R \). It was shown that the plasmon modes in clusters and other nanoscale 0D-quantum confined systems (with imposed central symmetry) can be reproduced with the high accuracy by the classic hydrodynamics of the charged liquid on the surface of the spherical box. Therefore, the solution for the modes of the metal sphere gives the plasmon frequencies. The equation system to solve is in Appendix B. The frequency of the mode is proportional to the multipole index of the mode \( L \)

\[
\omega_L = \sqrt{\frac{L(L+1)}{2L+1} \frac{N e^2}{m R^3}}
\]

and in contraction limit the dependence is a square root: \( \omega_L \propto \sqrt{(L+1/2)/R} \). Here \( N \) is the number of valence electrons.

The local modes donate to the LS and the term in the mean squared deflection, additional to Eq.(3), reads as

\[
\overline{\delta^2} = \frac{\pi e^2 \hbar}{m^2} \sqrt{2} \left( \frac{m R}{N e^2} \right)^{3/2} \sum_{L=1}^{L_{\text{max}}} \sqrt{L + \frac{1}{2}}
\]

\[
\times \frac{\pi 2^{3/2}}{3} \left( \frac{R}{Na_B} \right)^{3/2} a_B^2 \left( L_{\text{max}} + \frac{1}{2} \right)^{3/2}
\]

where \( L_{\text{max}} \) is the maximal allowed multipole index defined by the box radius.

This results in the anomalous large LS comparing with the LS related to the delocalized photon modes. The ratio of these shifts, as illustrated by the example of \( \text{C}_60 \), can amount about 1000. Evidently, the ratio the larger, the less the radius of the system. At the cluster size 100 times larger than \( \text{C}_60 \) (~3.6 Å), the shift related to the confined modes becomes of the same order than the standard LS.

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

APPENDIX A: ON THE LINEAR RESPONSE OF THE ELECTRON

The electron trembling in the high-frequency field \( \mathcal{E}_L \) of the plasma oscillator \( |\alpha\rangle \) can be treated semiclassically and its deflection \( \delta \) is described by Newton law:
\[ m \ddot{\delta} + m \omega_0^2 \delta = -e \mathcal{E}, \]  

(A1)

here \( e \) is the electron charge and \( m \) is the electron mass which is supposed to be isotropic within the cluster.

For the Fourier component of the external field which is proportional to \( e^{-i \omega t} \) we get the polarizability of the carrier in the form

\[
\frac{\varepsilon^2}{m(\omega^2 - \omega_0^2)} \rightarrow \frac{\varepsilon^2}{2m \omega (\omega + \omega_0)}.
\]

Here we use the fact that the frequency dependence can be decomposed into two terms

\[
\frac{1}{\omega^2 - \omega_0^2} = \frac{1}{2 \omega} \left( \frac{1}{\omega + \omega_0} + \frac{1}{\omega - \omega_0} \right)
\]

where the last term corresponds to the absorption of the photon and should be omitted for the zero fluctuation field.

The total deflection is given by the sum of this expression over all \( \alpha \) (the integral over \( k \) for 3D photons).

**APPENDIX B: ON THE SPHERICAL SURFACE PLASMONS**

One of the examples of 0D system, which plasmon can be described within the classical approach, is the fullerene, the sixty-carbon-atom ball of the high symmetry. The \( C_{60} \) electron structure symmetry reflects (i) the local triangular symmetry of graphite-like lattice distorted by (ii) the global homology of the curved closed surface. The first was shown to be of small importance for the plasmon. The global symmetry — \( \text{SO}(3) \) spherical topology of the fullerene — is quantitatively captured within the quantum mechanical model of Spherical Shell Quantum Well [3]. Then the classical hydrodynamics of the charged liquid on the surface of the sphere describes the response of 240 valence electrons of the cluster.

The equation system to solve reads as follows:

\[
\begin{align*}
\partial_t j &= -\frac{ne^2}{m} \nabla \varphi, \\
\partial_t \sigma + \nabla j &= 0,
\end{align*}
\]

(B1)

where \( n = 240/4\pi R^2 \) is the valence electron density for \( C_{60} \), \( \varphi \) is the acting electrical potential, \( \sigma \) is the surface density fluctuation defining the lateral current density, \( j \), on the surface of
the sphere of radius $R$. $\nabla$ is the 2D nabla operator along the surface. The solution is given in complete spherical harmonics $P^{\ell}(r)Y_{\ell M}^M(\Omega)$. The use of Gauss–Ostrogradskii theorem $(2\ell + 1)\varphi_{\ell M}/R = 4\pi\sigma_{\ell M}$ allows one to relate the potential and the density fluctuation.

The plasmon energy corresponds to so-called bubble diagram in the secondary quantization formalism. Let us consider the space integrals in this matrix element (Fig.2). The typical integral in the vertex of the diagram is $\langle LM|\lambda\mu|AM\rangle$. Any spherical diagram with two legs can be rewritten [4] into the closed diagram, which depicts the $3j$ (or $6j$ and higher symmetry) symbol, bearing no dependence on co-ordinates, and into the straight line, which denotes the angular momentum delta-function, representing the angular momentum conservation through the process. The same argument works for the level shift considered above. That is why the angular momentum subspaces are treated separately in this paper.

![Diagram](Fig.2)

FIG. 2. The angular momentum diagram [4] shows that the matrix element is equivalent to the product of the $3j$–symbol and the delta–function of the incoming and outgoing angular moments.

The solution of Eq. (B1) is the surface mode of the spherical symmetry with the frequency:

$$\omega^2 = \frac{ne^2}{m} \frac{4\pi R}{2L + 1} \frac{L(L + 1)}{R^2} \rightarrow \frac{2\pi ne^2 L + 1/2}{m} \frac{L}{R},$$

which goes to the 2D–plasmon frequency when $L = kR \rightarrow \infty$ (the contraction limit).
