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Renormalization of electron energy in 0D systems due to depolarization shift

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Abstract. A giant level shift, resulting from the interaction of an electron in a spherical quantum dot with zero-point oscillations of confined modes of the electric field, is divulged. This electron potential energy renormalization depends on the dot radius which has to show up in experiment. The size scaling of the depolarization effect is computed semiclassically. A change of the optical properties of the matrix surrounding the dot also provides a method with which to study the shift experimentally.

1. Introduction

A complete quantum dot (QD) theory, taking into account all the sophisticated physics of this object, is still a challenge for a theorist. The main reason is that the scale of the calculation is much larger than an atomic one (this complicates *ab initio* techniques). At the same time, the number of particles is too small to use solid state approximations to their full extent. For example, a one-electron picture of a quantum confinement potential, arising from the conduction band discontinuity on the QD boundary, does not always yield accurate electron levels.

In this paper we put forward a model to inspect the electrodynamical correction to the one-electron potential energy in a spherical QD. It was shown [1] that a similar correction turns out to be significant for a 'natural quantum dot' C_{60}. A *depolarization* level shift due to the interaction with an electromagnetic field is not negligible, as it might be thought, when taking into account *localized* electromagnetic modes. We present the scaling analysis of some different mechanisms for the level shift (LS) and propose a possible experimental manifestation of the depolarization effect.

In order to appraise the LS a simple *spherical* QD model in the frame of an *effective mass* approximation was applied. How is our result sensitive to the model used? The size scaling of the depolarization shift is preserved, being mainly dependent on a corresponding density of states of the field, while the prefactor might be smaller within other approaches, though it is not easy to evaluate explicitly. Of course, the actual shape of the QD will also change the prefactor, though in experiments with a QD array the shape factor is averaged.

For the sake of theoretical clarity the simplest Hamiltonian was taken for the one-electron spectrum calculation. The group of full rotations, $SO(3)$, was chosen to label bare electron states. It is possible to perform an analytic quantum mechanical calculation of the RPA response within the spherical model [2]. The massive peak of a collective excitation is known to show up in the spectrum, resulting from fast coherent oscillation of the total electron density of valence states. Thus, within our model the electron–electron interaction is dealt with self-consistently. Of course, the number of valence electrons involved in the collective motion must not be small. This is believed to be fulfilled for a typical QD possessing some hundreds of atoms or even more.

A surface charge density oscillation can be thought of as a confined electric field mode or a multipole surface plasmon. We will reflect on the shift of the electron level in the field of zero-point oscillations of the modes connected with the QD, of which the depolarization effect is a billion times stronger than that of free-field zero-point oscillations, so the name 'giant LS' is used.

The classical description of the electromagnetic surface modes, via the dielectric functions of the matrix and QD materials, gives the true plasmon state frequencies [3] and will be used below. Once more, the final result does not depend too greatly on the computational approach. Instead of giving a rigorous solution, our model sketches out the (many-body) depolarization semiclassically, avoiding much routine computational intricacy.

The paper proceeds as follows: a brief model description is given after the introduction. Then, the model will be applied to a 3D plasmon, which will demonstrate our calculation technique. However, the LSs from free modes are too small to have experimental importance. Section 4 deals with the confined modes, which result in a much larger depolarization shift. The numerical estimations and the scaling properties of the LS will be given with respect to a possible experiment. A brief summary will follow.

2. Semiclassical theory for energy level shift

We have considered semiclassically the LS for an arbitrary shell object in [4]. The method follows the one proposed

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by Migdal [5] to calculate the Lamb shift for a hydrogen-like atom. The frequency of the zero-point oscillations of the external field is much higher than the inverse period of the electron orbit $\omega_p \gg 1/\tau$. Therefore, the adiabatic approximation has to be used and one divides the fast (field) and slow (electron) variables. An electron is subjected to short fast deflections from its original orbit in the high-frequency field of the electromagnetic wave of the zero-point oscillation. Then the potential energy shift is given by second-order perturbation theory as

$$\delta E = \langle H(r+\delta) - H(r)\rangle = \langle \nabla H \cdot \vec{\delta} + \tfrac{1}{2}\nabla^2 H \vec{\delta}\cdot\vec{\delta} + \cdots\rangle, \quad (1)$$

where $H(r)$ is the unperturbed Hamiltonian and $H(r+\delta)$ is the Hamiltonian accounting for the random electron deflection δ. The angle brackets represent the quantum mechanical average over the fast variables of the field (or, equally, over the random electron deflections). The perturbed Hamiltonian is expanded in series on δ (that implies δ to be much smaller than the classical electron orbit radius) and a first nonzero contribution is taken.

The simplest QD Hamiltonian is considered to have only the rotational correction which is given by

$$\delta H = \frac{\hat{L}^2}{2mR^2}\left(-2\frac{\delta}{R} + 3\frac{\delta^2}{R^2} + \cdots\right), \quad (2)$$

where R relates to the spherical QD radius; m is the electron mass, which is supposed to be constant within the dot; $\hat{L}$ is the angular momentum operator. On averaging, the first-order term disappears. So far the LS decreases with the QD size and the dependence includes an R^{-4} factor, besides some power hidden in the mean square deflection $\overline{\delta^2}$.

We will show that the dependence of $\overline{\delta^2}$ on R is different for different electric modes (confined and free field). The giant deflection is representative for the giant LS and, therefore, the function $\overline{\delta^2}(R)$ will be studied specifically. In addition to the potential energy correction described in this paper, a kinetic energy term shifts levels. This LS could be even larger† but, for the specific QD problem, it raises the spectrum as a whole, in contrast to (2), which increases the level distance and, therefore, changes optical transition frequencies.

3. Bulk plasmon contribution to LS

First we consider bulk 3D-plasmon modes that could shift the electron level. Nearly self-evidently the bulk plasmon shift is negligible, even though it explains our method in the cleanest manner. The mean square deflection, caused by the 3D mode (which is not confined at all), decreases with the QD size too rapidly. The small factor, contained in the 3D LS, arises essentially from the expression for $\overline{\delta^2}$, which scales as $1/N$, where N is the number of atoms in the QD. This will be explained below.

Within the semiclassical approach, the deflection of the electron can be computed with the use of Newton's law: $m\partial_t^2\delta = e\mathcal{E}$, where e is the electron charge, $\mathcal{E}$ is the field strength due to the zero-point oscillation of some mode and m is the electron effective mass. The square of the deflection is the sum over plasmon states:

$$\overline{\delta^2} = \frac{e^2}{(2m)^2}\int \mathrm{d}^D k \frac{\overline{\mathcal{E}_k^2}}{\omega_k^4}. \quad (3)$$

The dimension of the field, D, is equal to three. The mean square of the electric field strength, in turn, can be rewritten as the zero-point oscillation frequency $\overline{\mathcal{E}_k^2} = 2\pi\hbar\omega_k$ through the quantized field normalization.

Note that the 3D plasmon frequency $\omega_p = \sqrt{4\pi e^2 n_{3D}/m}$ does not depend on the quantum number $\boldsymbol{k}$, hence, the mean square deflection contains the total number of states affecting the QD electron level according to equation (3), where the upper integration limit is $k_{max} \sim 1/R$. In the 3D case it gives rise to the factor $R^{-3} \sim N^{-1}$ proposed at the beginning of the section.

This result will change for other confined electric modes because of their different densities of states. This produces the different N-scaling factor for the LSs from these modes.

The prefactor of the deflection, for any mode considered here, depends equally on the square root of the density of electrons, which is conveniently converted to r_s, a characteristic length, via the following definition: $2\pi r_s^3 n_{3D}/3 = 1$. Then, for 3D plasmon the deflection reads as

$$\overline{\delta^2} = a_B^2 \frac{\sqrt{6}}{6^4\pi}\left(\frac{r_s}{a_B}\right)^{3/2}\left(\frac{r_s}{R}\right)^3 \propto N^{-1}, \quad (4)$$

where the atomic length unit, $a_B = \hbar^2/me^2 \simeq 0.53$ Å, or the Bohr radius, gives the scale of the deflection (note that this definition does not include any permittivity, unlike an exciton Bohr radius in semiconductors). Equation (4) proves our supposition that the Hamiltonian variation scale is larger than $\delta < a_B$.

The depolarization (the ratio of the level shift, δE, to the bare energy, $E^{(0)}$) due to the 3D modes is given by:

$$\Delta_{3D} = \frac{\delta E}{E^{(0)}} = \frac{1}{72\sqrt{6}\pi}\sqrt{\frac{a_B}{r_s}}\left(\frac{r_s}{R}\right)^5 \propto N^{-5/3}. \quad (5)$$

The crude estimation of the prefactor (with $r_s \sim 2$ Å that is close to typical electron densities [7]) shows that even for the small QD with $N = 100$ the shift is 10^{-6} of the bare energy and will not be resolved because of a number of other additional factors affecting the level position. Naturally, the depolarization increases with the (polarizable) valence electron density. The LS disappears in a pure classical limit $\hbar \to 0$.

To give a complete picture we note that the standard LS due to the zero-point oscillations of the free electromagnetic vacuum modes can be written as

$$\Delta_{vac} = \frac{6\alpha^3}{\pi}\left(\frac{a_B}{r_s}\right)^2\left[\ln\frac{r_s}{\alpha a_B} + \ln\frac{R}{r_s}\right]\left(\frac{r_s}{R}\right)^2 \propto N^{-2/3}, \quad (6)$$

† The ratio ⟨kinetic energy correction⟩/⟨potential energy correction⟩ = ⟨k.e.⟩/⟨p.e.⟩ $\sim m\,\omega^2 / \nabla^2 V$ can be large at large plasmon frequency. Within a semiclassical theory both terms were applied for the Lamb shift problem in an atom [6]. As discussed in the text, in our QD depolarization problem, the k.e. yields an uniform shift while the p.e. contribution displaces different electron levels to different extents. It follows from the expression for these two terms that the p.e. contains the bare Hamiltonian while the k.e. does not.

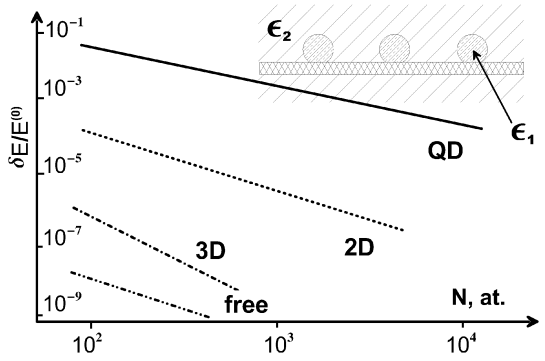

Figure 1. The level shift of QD electron, calculated for four different depolarization mechanisms. The giant shift, which results from the zero-point oscillations of the electric field of the QD surface mode, is shown as a full line. The 2D plasmon, the matrix bulk plasmon mode and the free-field shifts are shown as broken lines. The slopes and the prefactors of these depolarization shifts are derived analytically and explained in the text. Inset: the scheme of the QD structure modelled. Spherical QDs with dielectric function ϵ_1 are embedded in a medium with dielectric function ϵ_2.

where $\alpha \simeq 1/137$ is the fine-structure constant, and the logarithmic dependence of the last term in square brackets on N does not add any extra to the result and has to be ignored. Though the LS exponent, $\partial \log \Delta_{\rm vac}/\partial \log N$, is smaller than in equation (5) the prefactor is tiny ($\sim 10^{-7}$) because of α^3.

4. Depolarization: confined modes

Let us consider the specific behaviour of the LS materialized by the zero-point oscillations of the confined plasmon modes. The depolarization in a carbon shell cluster was shown [3] to be independent of the cluster size. The mean square deflection also scales as a zero power of size $\overline{\delta^2} \propto N^0$. While it is interesting in itself, the carbon cluster matter will not be considered in this paper. However, there are confined modes in our QD problem that enhance the electrodynamical correction to the electron potential energy.

With the decrease of the dimension of the field $D = 3, 2, 0$ the plasmon density of states increases. Hence, the interaction of the electron with the plasmon field increases, as will be evident from the size scaling of $\overline{\delta^2}$.

Two possible candidates for confined plasmon modes in the QD system, that have different densities of states, are the 2D plasmon and 0D spherical mode. The former mode can arise because of some interface presumably grown within the structure (see the inset in figure 1). It might be a conducting wetting layer, if it is thick enough to confine the electromagnetic field. The 2D plasmon naturally originates at the interface between a semiconductor structure and a metal [8]. At the boundary of two dielectrics a surface plasmon is known to propagate [9]. Its contribution will be discussed elsewhere as being smaller than 2D-plasmon LS by a factor of at least 10^{-2} owing to the fast space field decay.

The 0D mode is the inherent property of the spherical inclusion of foreign material in any matrix. The calculation of the mode frequency is slightly cumbersome (see [3] for details). This surface QD mode has the quantum numbers L, M, the angular momentum and its projection on an axis, instead of the 2D wavevector, $\boldsymbol{k}$, for the standard 2D plasmon.

4.1. 2D plasmon

The frequency of the 2D plasmon is well known [10] to depend on its 2D wavevector as: $\omega_k = \sqrt{2\pi e^2 n_{\rm 2D} k/m}$. We will rewrite the 2D electron density, as before, in terms of the characteristic length $\pi r_s^2 n_{\rm 2D}/2 = 1$, and perform the integration over the plasmon states. Then the mean square deflection can be expressed as

$$\overline{\delta^2} = a_B^2 \frac{1}{32} \left(\frac{r_s}{a_B}\right)^{3/2} \left(\frac{r_s}{R}\right)^{3/2} \propto N^{-1/2}. \qquad (7)$$

The scaling in N has a lower exponent, that reflects the different density of the confined field (plasmon) states. Substituting $\overline{\delta^2}$ into the Hamiltonian given by equation (2), one obtains the depolarization as follows:

$$\Delta_{\rm 2D} = \frac{3}{32} \sqrt{\frac{a_B}{r_s}} \left(\frac{r_s}{R}\right)^{7/2} \propto N^{-7/6}. \qquad (8)$$

The shift depends on the inverse size almost linearly. However, the prefactor dominates at some moderate size of QD and lessens the LS to 10^{-3} for $N = 100$. The depolarization is still too small to expect experimental consequences. To be precise, the result also depends on w, the distance between the 2D electrons and the QD. It is simply included in the consideration by multiplying equation (8) by a factor $\sqrt{\pi}{\rm Erf}(\sqrt{w/R})/(2\sqrt{w/R})$ (where the error function is that according to [11]), and the depolarization declines fourfold at $w/R \sim 10$.

4.2. QD confined plasmon: mode of cavity

The $\overline{\delta^2}$ considered above is less for larger QD size; which is not the case for the giant deflection due to the completely localized modes [1]. The localized modes are the surface plasmons of the spherical inclusion (with a dielectric function ϵ_1) in the matrix (with a different dielectric function ϵ_2). The frequency of the mode, ω_L, that we consider, is nearly the frequency of the bulk plasmon in the matrix, ω_{p2}, with a weak dependence on the mode angular momentum [3]. The electric field of the zero-point oscillation is given by the formula $\mathcal{E}_L^2 = \pi(L + 1/2)\hbar\omega_L/R^3$. The summation over all states below some critical value $L_{\rm c}$ gives the mean square deflection:

$$\overline{\delta^2} = a_B^2 \frac{\pi}{9\sqrt{6}} \left(\frac{r_s}{a_B}\right)^{3/2} \left(\frac{r_s}{R}\right)^{3} \left(L_{\rm c} + \frac{1}{2}\right)^3, \qquad (9)$$

where it is natural to limit the summation above the excitation, of which the wavelength is about d, the bulk lattice constant†. We found that $\overline{\delta^2}$ does not depend on the QD size:

$$\overline{\delta^2} = a_B^2 \frac{\pi^4}{9\sqrt{6}} \left(\frac{r_s}{a_B}\right)^{3/2} \left(\frac{r_s}{d}\right)^{3} \propto N^0. \qquad (10)$$

† For an infinitely large sphere, the contraction limit is fulfilled: $R, N, L \to \infty$, but $R/L = {\rm const}$, then the (infinitely large) angular momentum can be related to the (finite) 2D wavevector via $L \simeq kR$. Substituting the maximum wavenumber $k_{\rm max} \sim \pi/d$ into this expression we obtain the maximum angular momentum as $L_{\rm c} + 1/2 \sim \pi R/d$, where d is the lattice constant. Then the critical angular momentum divided by the radius becomes some constant $(L_{\rm c} + \frac{1}{2})/R \sim \pi/d$.

Hence, the level shift depends on the size as R^{-2} (which comes from equation (2)):

$$\Delta = \frac{\pi^4}{3\sqrt{6}}\sqrt{\frac{a_B}{r_s}}\left(\frac{r_s}{d}\right)^3\left(\frac{r_s}{R}\right)^2 \propto N^{-2/3}. \qquad (11)$$

Our estimation shows that the 0D level correction, becoming of the order of 50%, will play the important role for a QD of 100 atoms and smaller. We collected all studied contributions to the depolarization LS and plot them on a log–log scale versus the QD size in figure 1.

The depolarization due to the localized surface QD modes is large enough to propose an experiment supporting our model. It is easy to see that $\overline{\delta^2} \sim \omega_L^{-3}$, whence the LS depends on the mode frequency as well. Therefore, changing the optical properties of the matrix surrounding the QD, one shifts the levels. If the bare energy level, $E^{(0)}$, lies deep in the potential well, its position is nearly independent of the well depth, which changes along with the matrix parameters. The deep bare level energy depends only† on the well width $\sim R$ [12]. Hence, in principle, keeping the same QD size and covering it with different materials, one will solely derive the depolarization LS, since it is distinguishable from the standard space quantization LS. At present, a technological realization of a QD system is restricted by another important factor, a strain due to the lattice mismatch, which contributes to the electron energy to a large extent but is beyond the scope of this paper as it has a different origin.

5. Summary

The effect of the zero-point oscillations of the free and confined electromagnetic field on the level of the confined electron in the spherical QD is reviewed. The depolarization due to an interaction with the zero-point oscillations of the field (produced by all other valence electrons) shifts up the bare one-electron state and increases the interlevel distance that seems to be a counterpart to the vertex correction (electron–hole interaction, for example) which lowers the transition frequency. This indicates that the studied depolarization effect should be taken into account for a many-body computation of a QD spectrum.

To the best of our knowledge, the scaling dependence of the depolarization level shift for the QD is calculated for the first time. The size dependence of the LS is different for the four cases considered in this paper. This scaling reflects that the different densities of states work in different mechanisms of the depolarization due to the different 3D, 2D and 0D modes of the electric field involved. Our model allows a theorist to skip a tedious quantum electrodynamical calculation but obtain the analytical self-consistent estimation for the (many-body) level shift in a nanoscale system with strong quantization. The result is not just of theoretical importance.

Although the depolarization decreases with the QD size in general, the localized surface electromagnetic mode (which is specific to the QD as a void in the matrix material) results in the giant level shift which could possibly be resolved experimentally for the QD made from some hundred atoms. Another method to detect the effect could be the measurement of a deep-level position in similar QDs buried by substances with distinct optical characteristics (density of valence electrons) but similar lattice parameters to avoid extra strain. Then the localized plasmon frequency changes along with the prefactor of the depolarization shift, which could be observed by optical spectroscopy of the QD system.

A recent paper [13] presents for the first time the direct experimental data for the bandgap dependence on the size of small carbon clusters measured by scanning tunnelling spectroscopy. The clusters were deposited on a substrate and gave an example of a QD system with a minimum stress (free boundary); therefore, only two contributions (space quantization and depolarization) are to be considered. The observed cusp on the curve $E_g(R)$ can be easily explained within our model as the disappearance of the depolarization correction. It has to happen at a cluster size of about 10 Å, which is consistent with experiment. Further work on this is now in progress.

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† The energy level comparison for spherical QDs of infinite and finite depth shows that the lowest radial series, which is dealt with here, depends only slightly on the potential depth, that is, the classical orbit radius is nearly the same ($\sim R$) for any reasonably deep QD which contains more than a single level.