# Reduced Polarizability and Local-Field Effect in Self-Assembled Ensemble of Nanoparticles

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This article is focused on the studying of the local-field effect in a nanoparticle's ensemble. We proposed a simple model of an open spherical semiconductor nanoparticle in exciton regime, which boundary is approximated by delta-potential. This approach allows us to examine the homogeneous and core-shell nanoparticles taking into account the influence of the environment. Using the reduced polarizability of a nanoparticle we developed the self-consisting method of calculation of the dielectric constant for the NP's ensemble in a polymer matrix and analyzed the influence of the local-field effect on the optical response.

**Keywords:** Ensemble of nanoparticle, Polarizability, Dielectric constant, Local-field effect.

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## 1. INTRODUCTION

In recent time the focus has moved from the synthesis of a homogenous nanoparticles (NPs) to the area preparation of complex systems based on the core-shell structures of the complex compositions [1, 2] and the molecular complexness (block-copolymers, dendrimers, etc.) [3, 4]. Such systems can be used in sensor units [5], biology and medicine [6-8]. Also, the systems of several NPs (or quantum dots) are applying for constructing of the qubits [9] and the new functional elements [10] designed to solving the problems of modern microelectronic. The preparation of the NP's ensemble with the exactly optical response has made it possible to manufacture artificial metamaterials [11].

For the development of these researches together with the experiment it is necessary to develop the usable theoretical investigations. In the way of constructing the theoretical model of NP it is necessary to consider the interaction of a quantum system with the environment. As the result it leads to a nonuniform broadening of the energy levels of the electron states related with a finite lifetime.

As well known, the external electric fields leads to a uniform broadening. Moreover, the local-field effect appears as a result of the dipole-dipole interaction between the NPs. The local-fields effect in the atomic systems and in the immersion medium with high refractive index has been investigated in detail (see, e.g., the review [12]). Let us note also that such an effect in an ensemble of NPs has been studied within the framework of the Maxwell-Garnett formalism [13]. In recent time the local-field in the presence of the metallic nanoparticles are study intensively. With such systems is related the Raman scattering affiliations [14] and the fluorescence resonant energy transfer [15]. However, these approaches operate with the macroscopic dielectric constant of NPs which is not correct for the semiconductor NP less than 5 nm.

In view of this reasons we present a model of an open spherical nanoparticle, which allows us to calculate the quasi-stationary spectrum of NP in the exciton regime (the broadening in this case is associated with

the probability of the electron tunneling to the environment). The tunneling probability determines by the properties of the NP's surface (shell). Based on the polarizability features we propose a method of self-consistent calculation of the dielectric constant for NP's ensemble embedded in a polymer matrix taking into account the local-field effect.

## 2. MODEL

### 2.1 Energy Structure of an Open Nanoparticle

Now we examine the problem of the boundary in an open spherical NP. Such a system is the core of direct-gap semiconductor without (or with) a shell buried in a polymer matrix (see Fig. 1a). The shell can be composed of a semiconductor, ligand, etc.
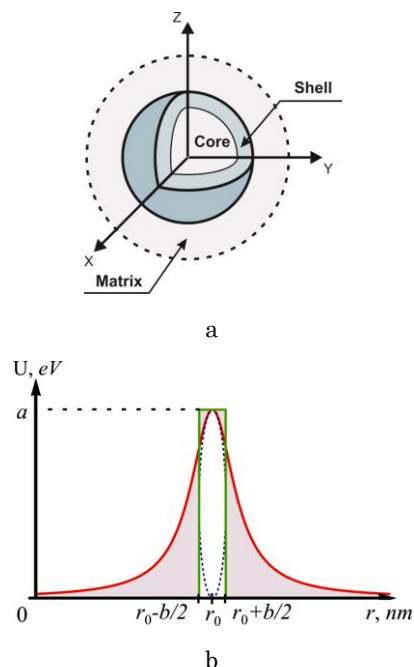


a



b

**Fig. 1** – Schematic representation of a nanoparticle (a), the boundary energy barrier (b): versiera (red line), plotted on the basis of an inscribed ellipse (dashed line)

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Usually, the boundary (or shell) is approximated by a rectangular barrier [16], but it is not correct for the thin layer (~ 1 monolayer). Therefore, we propose potential in the form of versiera (Fig. 1b)

$$U_{An}(r) = \frac{a \cdot b^2}{(r - r_0)^2 + b^2},\qquad(2.1)$$

where $a$ and $b$ are the height and width of potential barrier, respectively. It can be shown that in the limiting case $b \to 0$ the versiera function tends to Dirac delta-function:

$$U(r) = \Theta \cdot \delta(r - r_0).\qquad(2.2)$$

Here, $\Theta \sim a \cdot b / \pi$ is the coefficient penetrability of delta-potential. First, this approach reduces the number of equations, which are necessary to describe the core-shell NP, and, secondly, the parameter $\Theta$ can serve as the phenomenological parameter, in the case when the properties of interface are not exactly known.

The standard boundary conditions at $r = 0$ and asymptotic behavior of the Bessel and Neumann functions lead to following expression for radial part of the wave function in spherical coordinates:

$$R_{kl}(r) = \begin{cases} C_1 j_l(k_1 r), & r < 0, \\ C_2 h_l^{(1)}(k_2 r), & r \ge 0. \end{cases}\qquad(2.3)$$

The continuity conditions of the wave functions, the discontinuity of the first derivatives at the NP's boundary and the normalization condition give the transcendental equation:

$$\frac{m_2}{m_1} \frac{j_{l+1}(k_1 r_0)}{j_l(k_1 r_0)} - \frac{k_1}{k_2} \frac{h_{l+1}^{(1)}(k_2 r_0)}{h_l^{(1)}(k_2 r_0)} - \frac{2 m_2 \Theta}{k_1 \hbar^2} +$$
$$+ \frac{l}{k_1 r_0}\left(1 - \frac{m_2}{m_1}\right) = 0.\qquad(2.4)$$

Here, $l$ is orbital quantum number, $m_1$ and $m_2$ are the effective masses of the electron (or hole) in the NP and in the environment. Solution of equation (2.4) describes the quasi-stationary electron (hole) states.

Coulomb interaction between the electron and hole can be calculated as the matrix element

$$V_c = \left\langle \psi_{nl}^{nl}(\vec{r}_e, \vec{r}_h) \left| \frac{e^2}{\varepsilon |\vec{r}_e - \vec{r}_h|} \right| \psi_{n'l'}^{n'l'}(\vec{r}_e, \vec{r}_h) \right\rangle,\qquad(2.5)$$

where $\varepsilon$ is the material's dielectric constant, $\psi_{nl}(\vec{r}_e, \vec{r}_h)$ is the two-particle wave function. As a result, the energy spectrum of exciton with the band gap for bulk materials $E_g$ has the form:

$$E^{ex} = \tilde{E}_{nl}^e + \tilde{E}_{n'l'}^h - V_c + E_g.\qquad(2.6)$$

## 2.2 Polarizability

Using the results presented above the optical response of the structure under consideration can be investigated. Early, in the case of the dipole transition in direct-gap semiconductor the static polarizability of the quantum dot's ground state have been calculated by means of the Lorentz formula

$$\alpha_L(\omega) = \frac{e}{\mu}\sum_n \frac{F_{n'n}}{\omega_{n'n}^2 - \omega^2 + i\gamma_{n'}\omega}.\qquad(2.7)$$

Here, $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass of exciton, $\omega_{n'n} = \omega_{n'} - \omega$ and $F_{n'n}$ is the oscillator strength determined by the dipole matrix element:

$$F_{n'n} = \frac{2\mu\omega_{n'n}}{\hbar}\left|\langle n'|\vec{r}_e - \vec{r}_h|n\rangle\right|^2.\qquad(2.8)$$

We have demonstrated that the static polarizability of the quantum dot depends on the radius as $\alpha_L(\omega) \sim r_0^4$ [17]. This feature was observed in the experimental studies [18, 19] and it is a consequence of the quantum size effects.

However, (2.7) does not include a uniform broadening of the energy level in the external electric field. Therefore, we use the expression for the dynamical polarizability of the two-level quantum system in the rotating-wave approximation. It may be written through the transition oscillator strength

$$\alpha(\omega) = \frac{e^2 F_{12}}{2\mu\omega_{12}} \frac{\omega_{12} - \omega + i\gamma_2}{(\omega_{12} - \omega)^2 + \gamma_2^2 + \omega_R^2/4},\qquad(2.9)$$

where $\omega_R = |\mathbf{d}_{12}|E_0/\hbar$ is the Rabi frequency, $F_{12}$ is the transition oscillator strength, $\gamma_2 = (\gamma + \Gamma)/2$ represents the broadening of the excited stationary state associated with the spontaneous emission and the probability of an electron tunneling from the NP to the environment. Rabi frequency determines the uniform broadening of the quasy-stationary state and plays significant role in the polarizability at $\omega_R \ge \gamma/\hbar$.

For comparison we have plotted the dynamic polarizability values in two approaches (2.7) and (2.9) as shown in Fig. 2. Calculations were performed for the colloidal CdS NP in a gelatin with following physical parameters: a band gap of the bulk material $E_g(\text{CdS}) = 2.42$ eV, the effective masses are $m_e/m_0 = 0.2$, $m_h/m_0 = 0.7$, $m_e(gel)/m_0 = 1$ ($m_0$ is a mass of the free electron) [20].

## 2.3 Dielectric Constant

The values of the NP's polarizability allow us to describe the optical response of the heterogeneous medium such as the NP's ensemble embedded in a polymer matrix. As mentioned above, it is necessary to take into account the local-field effect.

As it known, the correction of the local field for a homogeneous isotropic medium is $4\pi\vec{P}/3$, where $\vec{P}$ is the macroscopic polarization of the medium [21]. Accordingly, we obtain

$$\vec{E}_{loc} = \vec{E} + 4\pi/3\vec{P}\qquad(2.10)$$

This expression is the starting point for constructing the theoretical models of the dielectric constant of a heterogeneous medium. For example, using the expressions $\vec{P} = \chi\vec{E}_{loc}$ and $\varepsilon = 1 + 4\pi\chi$ ($\chi$ – susceptibility of the system) the Clausius-Mosotti formula describing the dielectric constant of atomic particles compared to vacuum can be obtained in the following form:
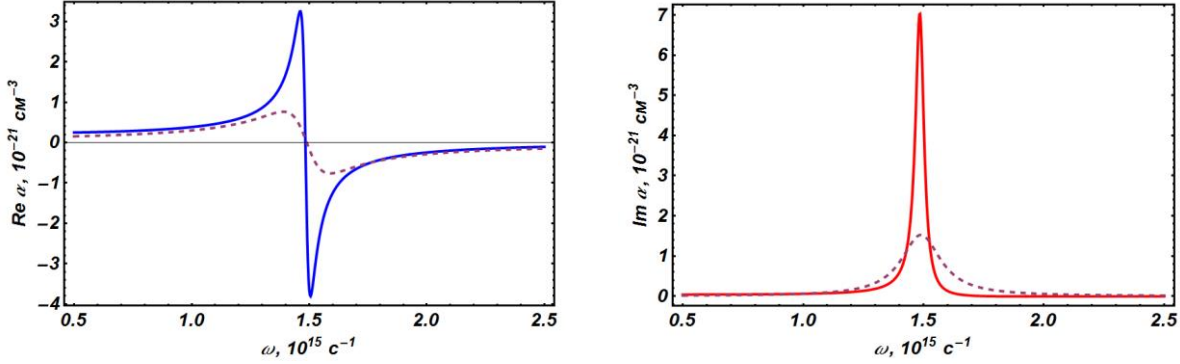
**Fig. 2** – Real (left) and imaginary (right) parts of the dynamic polarizability versus frequency of the external electric field in the Lorentz formalism (solid line) and the probability amplitude method (dashed line) for NP $d_0 = 2.6$ nm

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\alpha \qquad (2.11)$$

where $N$ and $\alpha$ are the concentration and polarizability of a particle, respectively.

In contrast to the atomic gas, the problem of NPs in a polymer matrix consists in the fact that particles are suspended not in a vacuum but in a dielectric. This problem can be reduced to an equivalent vacuum condition by introducing a relative dielectric constant $\varepsilon' = \varepsilon/\varepsilon_m$ ($\varepsilon_m$ – dielectric constant of the matrix), which shows how the dielectric constant of the dispersed phase $\varepsilon' = \varepsilon_1 + i\varepsilon_2$ reduces the external electric field insight a heterogeneous medium in vacuum, in assumption that the dielectric constant of a medium is $\varepsilon'$.

Usually, for such a system the Maxwell-Garnett formalism is used:

$$\frac{\varepsilon' - \varepsilon_m}{\varepsilon' + 2\varepsilon_m} = \sum_i \vartheta_i \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} . \qquad (2.12)$$

Here $\varepsilon_i$ is the dielectric constant of a dispersed component, $\vartheta_i$ is the volume fraction of $i$-th phase. The expiration (2.12) is usual assumption of the effective medium theory [13]. Note that this expression leads from the Mie's formula for the polarizability of spherical metal particles with radius $r_0$:

$$\alpha_{Mie} = r_0 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} . \qquad (2.13)$$

This formula describes the non-interacting randomly arranged particles with the uniform polarization. As we can see, (2.13) does not include the influence of quantum size effect on the polarizability. To resolve this problem, we have used the Clausius-Mosotti formula for ensemble of NPs in a dielectric matrix:

$$\frac{\varepsilon' - \varepsilon_m}{\varepsilon' + 2\varepsilon_m} = \frac{4\pi}{3} \sum_i N_i \alpha_i . \qquad (2.14)$$

After reducing of (2.14) we get the expression for calculation of the dielectric constant in the system "ensemble of NPs/polymer matrix" taking into account the size distribution $f(r)$:

$$\varepsilon(\omega) = \varepsilon_m \frac{1 + 2\vartheta \sum_i f(r_i)\bar{\alpha}_i(\omega, r)}{1 - \vartheta \sum_i f(r_i)\bar{\alpha}_i(\omega, r)} \qquad (2.15)$$

where $\bar{\alpha}(\omega, r) = \alpha(\omega, r)/r_0^3$ is the reduced polarizability and $\vartheta = V \cdot N$ is the volume fraction. Let us note that the condition of applicability of the dipole-dipole approximation for the system under consideration is $\vartheta \leq 0.4$.

The relation (2.15) is the final step in iterative procedure of the self-consistent calculation of the dielectric constant for the heterogeneous medium in the frame of described method, which is refinement of the effective media method (Fig. 3). The initial step of iteration is the bulk dielectric constant $\varepsilon_b(\text{CdS}) = 5.5$. The iterative procedure is terminated when the variation of the dielectric constant remained to $10^{-5}$.
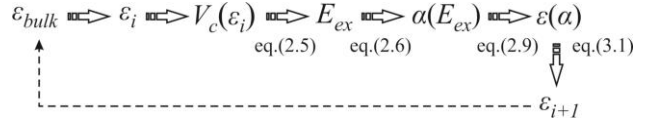


**Fig. 3** – Flow diagram of the self-consistent calculation of the dielectric constant

The numerical comparison (2.15) with

$$\varepsilon_0(\omega) = \varepsilon_m + 3\vartheta \sum_i f(r_i)\bar{\alpha}_i(\omega, r) , \qquad (2.16)$$

gives the local-field effect correction to the dielectric constant. In similar manner, we compared our result with the Maxwell-Garnett formalism in the form:

$$\varepsilon_{MG}(\omega) = \varepsilon_m \frac{\varepsilon_b(1 + 2\vartheta') + 2\varepsilon_m(1 - \vartheta')}{\varepsilon_b(1 - \vartheta') + \varepsilon_m(2 + \vartheta')} . \qquad (2.17)$$

Here, $\vartheta' = N \cdot \Sigma f(r_i)V(r_i)$ is the volume fraction with the concentration $N$ and the size dispersion of the individual NPs. We have used the Lifshitz-Slezov (LS) distribution [22] and the experimental distribution obtained from the TEM images of the NP's ensemble [23]. In the cases of the gelatin matrix the static dielectric constant is $\varepsilon_m = 2.2$.

## 3. RESULTS AND DISCUSSION

The obtained dielectric constants are shown in fig. 4. Our numerical analysis shows the "small" difference between (2.15), (2.16) and (2.17) at low NP's volume fraction (less than 0.01). But, as soon the volume fraction grows the local-field effect leads to correction for the transition energy 1s-1s by 0.080 eV for $\vartheta = 0.1$ and 0.150 eV for $\vartheta = 0.2$.

In the case of the experimental NP's size distribution the self-consistent method and the Maxwell-Garnett approach give the close values of the dielectric constant, namely, the difference is about 2-15 % versus the volume fraction (Fig. 4a). However, for the LS distribution the difference consists about 30 % (Fig. 4b). Such a difference is due to the fact that in contrast to the experimental distribution the LS distribution supposes the existence of NPs with small sizes (see inset in Fig. 4a). Note that (2.17) formula leads to higher values of the dielectric constant because the quantum size effect has not taken into account.

In order to verify our model of open NP we have calculated the transition energy 1s-1s. The numerical data are presented in Fig. 5a. Also, in Fig. 5a we have shown the experimental data and the results of the semi-

empirical models for colloidal CdS NPs in a water [24]. As can be seen from figure, a comparison of the numerical and experimental findings shows a good agreement for NPs with sizes more than 2 nm. For the smaller particles (less than 2 nm) we have the overestimated values of the transfer energy due to the non-applicability of the effective mass method for the calculation of the energy spectrum of these systems. Thus, the presented model gives the true results for the ensemble of NPs with an average diameter more than 1.8 nm.

The linear absorption spectra in the wavelength range corresponding to the interband transition 1s-1s [25] was calculated in order to demonstrate the role of the local-field effect in an optical response of a NP's ensemble. In comparison, we have selected three cases of the dielectric constant: the value of the bulk material $\varepsilon_b$, the Maxwell-Garnett approach $\varepsilon_{MG}$ and the self-consistent method $\varepsilon$. Fig. 5b also shows the experimental dependence of the absorption spectrum CdS NPs in a gelatin matrix [23]. Note that the broadening caused by fluctuations of the NP's sizes and the distance between them has taken into account phenomenologically.
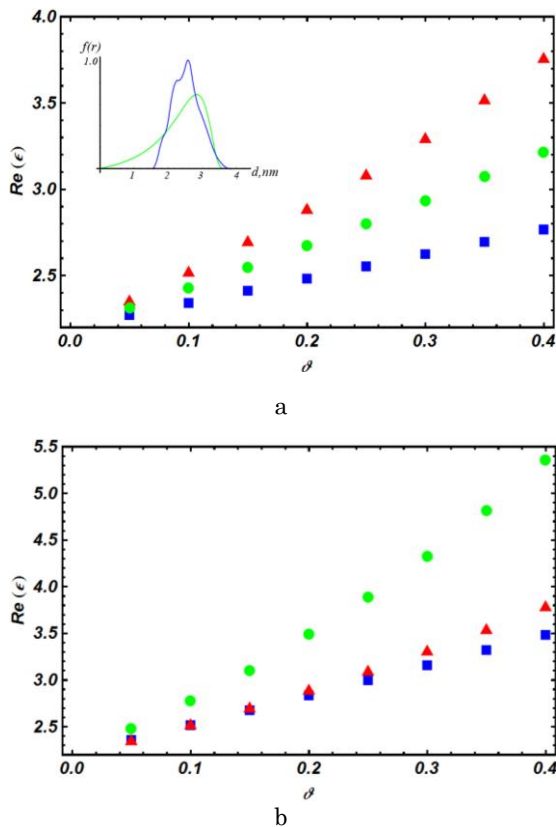


a



b

**Fig. 4** – Static dielectric constants of CdS NP's ensemble versus volume fraction of the dispersed phase within framework: the self-consisting method excluding (square) / including (triangle) the local field effect and the Maxwell Garnett formalism (dot): with the experimental size distribution (a), LS size distribution (b). The inset (a) shows the experimental (blue line) and the LS (green line) size distributions
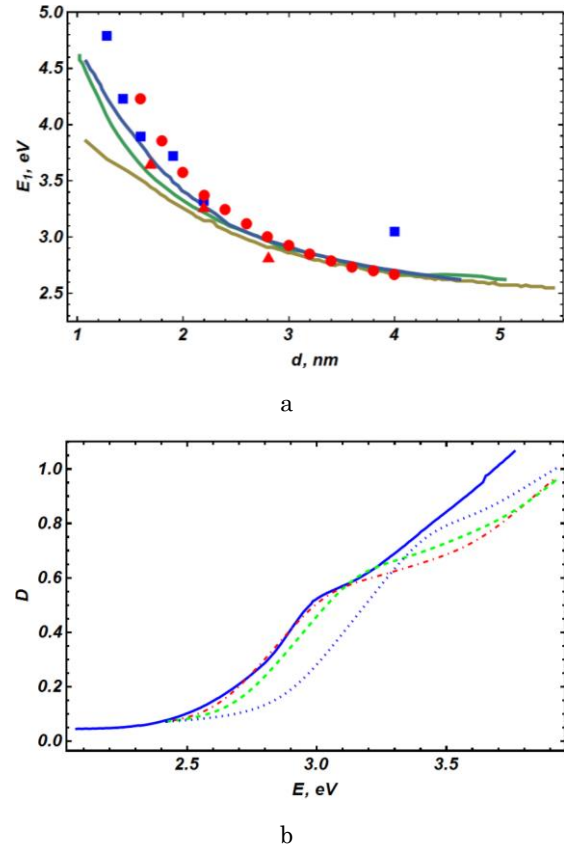


a



b

**Fig. 5** – The energy of optical transition 1s-1s $E_1$ versus CdS NP's diameter $d$ in a water (a), linear absorption for experimental size distribution of CdS NPs with a mean radius 1.30 nm (b): experimental absorption (solid line), $\varepsilon_b = 5.5$ (dotted line), $\varepsilon_{MG} = 3.1$ (dashed line) and $\varepsilon = 2.6$ (dash-dotted line)

## 4. CONCLUSIONS

In this paper we have proposed a simple model of an open spherical semiconductor nanoparticle in exciton regime. The delta-potential at the boundary of a nanoparticle allows us to introduce the environment effects.

Based on the quasi-stationary spectrum we have calculated the polarizability taking into account such factors as the spontaneous decay, the probability of electron tunneling to environment and the uniform broadening in the presence of an electric field. Using the Clausius-Mosotti formula and the reduced polarizability we have presented the self-consistent method for calculation of the dielectric constant of the NP's ensemble embedded in a polymer matrix.

On the example of CdS NP's ensemble embedded in a gelatinous matrix the significant difference between the dielectric constant for nanoparticles and the bulk semiconductor material is demonstrated.

It is also shown that the correction of the local-field effect of the energy of first excited state has a value about ~ 0.1 eV. This statement is confirmed by agreement of our results with the experimental data and, the result of other numerical models. Thus, the developed approach, is a refinement of the effective media method and in contrast to Maxwell-Garnett approach can be applied for the ensembles of semiconductor NPs with an average size more than 2 nm.

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