Permittivity of Thin Quantum Dot Film with Local Field Effects

M. N. Anokhin, **A. A. Tishchenko**, **and M. N. Strikhanov**
National Research Nuclear University "MEPhI", Moscow, Russia

Abstract— It is known that electronic properties of a quantum dot (QD) depend on its size and shape. Spectrum of emission light of a QD is changed by tuning their core diameter. For example, the cadmium selenite (CdSe) QDs emit blue light when the diameter of the core is 2 nm and emit red light when it is 7 nm [1]. Because of it QDs have a good potential for using in different light emitting devices including organic light emitting diodes (OLEDs). For example, QDs gives a good opportunity for design white OLEDs etc..

1. INTRODUCTION

QD films have a lot of applications in optoelectronic devices because of their unique properties of QD. Such as size- and shape-tunable optical and electronic properties (e.g., the band gap in a QD proportional to its size). QDs are bright and photostable and can show a very high photoluminescence quantum efficiency (around 90%) [2, 3]. So QD films are very perspective for using in different kinds of electronic and optoelectronic device applications [4]. For example, light emitting diodes (QD-LEDs), field-effect transistors (FETs) and photodetectors.

2. DIELECTRIC PROPERTIES OF THIN QUANTUM DOT FILM

Let us consider a thin film of the amorphous substance $2b$ wide. It is composed of N uniformly located spherically symmetric QDs. Let all the QDs be anisotropic and have polarizability $\alpha_{ij}(\omega)$:

$$\alpha_{ij}(\omega) = \alpha_{\perp}(\omega)(\delta_{ij} - e_i e_j) + \alpha_{\parallel}(\omega) e_i e_j. \tag{1}$$

We work in the dipole approximation as a QD diameter is considerably smaller than the wave-length of light:

$$\mathbf{j}^{mic}(\mathbf{r}, \omega) = (-i\omega) \sum_b \mathbf{d}(\mathbf{R}_b, \omega)\, \delta(\mathbf{r} - \mathbf{R}_b), \tag{2}$$

where $\mathbf{d}(\mathbf{R}_b, \omega)$ is the moment dipolaire of the b-th molecule, $b = \overline{1, N}$, N is the total number of molecules of the substance.

Let put in vacuum a source creating the field $\mathbf{E}_0$. Linearity of Maxwell's equations allows us to obtain the Fourier transform of the solution of Maxwell's equations in a medium as sum of an external field (which has not yet interacted with any of the molecules) and a sum of all the secondary fields created by all the molecules [5]:

$$E_i^{mic}(\mathbf{r}, \omega) = E_i^0(\mathbf{r}, \omega) + \frac{1}{2\pi^2} \int d^3 l S_{ij}(\mathbf{l}, \omega)\, \alpha_{jk}(\omega) \sum_b E_k^{mic}(\mathbf{R}_b, \omega) \exp\{-i\mathbf{l}(\mathbf{R}_b - \mathbf{r})\}, \tag{3}$$

where

$$S_{ij}(\mathbf{l}, \omega) = \frac{(\omega/c)^2 \delta_{ij} - l_i l_j}{l^2 - (\omega/c)^2 - i0}. \tag{4}$$

Averaging (3) over the location of other QDs we find the local field E_i^{loc}:

$$\begin{aligned} E_i^{loc}(\mathbf{R}_a, \omega) = E_i^0(\mathbf{R}_a, \omega) + \frac{1}{2\pi^2} \int d^3 l S_{ij}(\mathbf{l}, \omega)\, \alpha_{jk}(\omega) \\ \int d^3 R_{ba} N w(\mathbf{R}_{ba})\, E_k^{loc}(\mathbf{R}_a + \mathbf{R}_{ba}, \omega) \exp\{-i\mathbf{l}\mathbf{R}_{ba}\}, \end{aligned} \tag{5}$$

where $w(\mathbf{R}_{ba})$ is the probability density of finding the b-th molecule at the distance $\mathbf{R}_{ba} = \mathbf{R}_b - \mathbf{R}_a (k = \overline{1, N-1})$:

$$w(\mathbf{R}) = \frac{1}{V}[1 - f(\mathbf{R})], \tag{6}$$

where $f(\mathbf{R})$ is the radial distribution function, that in fact describes the structure of film.

Averaging over the coordinates of all the QDs of the substance we obtain the macroscopic field:

$$E_i(\mathbf{R},\omega) = E_i^0(\mathbf{R},\omega) + \frac{1}{2\pi^2}\int d^3R' S_{ij}\left(-\mathbf{R}',\omega\right) P_j\left(\mathbf{R}+\mathbf{R}',\omega\right), \tag{7}$$

where

$$S_{ij}\left(-\mathbf{R}',\omega\right) = \int d^3q S_{ij}(\mathbf{l},\omega)\exp\left\{-i\mathbf{l}\mathbf{R}'\right\}, \tag{8}$$

$$P_j(\mathbf{R},\omega) = n\alpha_{jk}(\omega) E_k^{loc}(\mathbf{R},\omega), \tag{9}$$

where n is the number density:

$$n = \frac{N}{V} \tag{10}$$

Now we can obtain a relation between the macroscopic field $\mathbf{E}$ and the local field $\mathbf{E}^{loc}$:

$$E_i(\mathbf{R},\omega) = E_i^0(\mathbf{R},\omega) + \frac{1}{2\pi^2}\int d^3R' S_{ij}\left(-\mathbf{R}',\omega\right) P_j\left(\mathbf{R}+\mathbf{R}',\omega\right). \tag{11}$$

We write this equation in the coordinates ($\mathbf{q}$, z, ω):

$$\begin{aligned} E_i(\mathbf{q},z,\omega) &= E_i^{loc}(\mathbf{q},z,\omega) \\ &+4\pi n\int\frac{d^2R'}{(2\pi)^3}\int\limits_{-b-Z}^{b-Z} dZ'\exp\left\{i\mathbf{q}\mathbf{R}'\right\} f\left(\mathbf{R}'\right) S_{ij}\left(-\mathbf{R}',\omega\right)\alpha_{jk}(\omega) E_k^{loc}(\mathbf{q},z,\omega). \end{aligned} \tag{12}$$

Equation which connects the Fourier transforms of the local and macroscopic fields [6]:

$$t_{ik}(\mathbf{q},\omega) E_k^{loc}(\mathbf{q},\omega) = E_i(\mathbf{q},\omega), \tag{13}$$

where

$$t_{ik}(\mathbf{q},\omega) = \delta_{ik} + 4\pi n\int\frac{d^2R'}{(2\pi)^3}\int\limits_{-b-Z}^{b-Z} dZ'\exp\left\{i\mathbf{q}\mathbf{R}'\right\} f\left(\mathbf{R}'\right) S_{ij}\left(-\mathbf{R}',\omega\right)\alpha_{jk}(\omega). \tag{14}$$

Taking into account that:

$$4\pi P_i(\mathbf{q},z,\omega) = \left[\varepsilon_{ij}(\mathbf{q},z,\omega) - \delta_{ij}\right] E_j(\mathbf{q},z,\omega). \tag{15}$$

And using Eq. (9) and Eq. (13) we obtain the dielectric permittivity:

$$\varepsilon_{ik}(\mathbf{q},z,\omega) = \delta_{ik} + 4\pi n\alpha_{ij}(\omega) t_{jk}^{-1}(\mathbf{q},z,\omega). \tag{16}$$

In the long-wave approximation:

$$n^{-1/3} \ll q^{-1} \ll c/\omega. \tag{17}$$

$$\varepsilon_{ik}(z,\omega) = \varepsilon_\perp(z,\omega)\left(\delta_{ik} - e_ie_k\right) + \varepsilon_\parallel(z,\omega) e_ie_k, \tag{18}$$

where

$$\begin{aligned} \varepsilon_\perp(z,\omega) &= \frac{1+4\pi n\alpha_\perp(\omega)(2/3-c(z))}{1-4\pi n\alpha_\perp(\omega)(1/3+c(z))} \\ \varepsilon_\parallel(z,\omega) &= \frac{1+4\pi n\alpha_\parallel(\omega)(2/3-c(z))}{1-4\pi n\alpha_\parallel(\omega)(1/3+c(z))}, \end{aligned} \tag{19}$$

$$c(z) = \int d^3l\int\limits_{Z-b}^{Z+b}\frac{dZ'}{2\pi}\exp\left\{il_zZ'\right\} f\left(\mathbf{l}_\perp,-Z'\right). \tag{20}$$

The radial distribution function $f(\mathbf{R})$ is defined as:

$$f\left(\mathbf{R}\right) = n\left(\mathbf{R}\right)/n, \tag{21}$$

where $n(\mathbf{R})$ is the local number density, that determines number of QDs $dN(\mathbf{R})$ in the differential of volume dV on the distance $\mathbf{R}$ from the fixed QD:

$$n\left(\mathbf{R}\right) = \frac{dN\left(\mathbf{R}\right)}{dV} \tag{22}$$

Function $f(\mathbf{R})$ can be found experimentally. For example, using x-ray diffraction [7].

3. DISCUSSION

In this work we study a natural variation of dielectric properties of a very thin film consisting of QDs, with thickness in some QD diameters. For such thin film usually used macroelectrodinamical approach does not work, which needs improving of existing techniques. We manage to obtain the generalized Clausius-Mossotti relation for dielectric permittivity of thin film from the first principles with help of the local field theory [5–7]. The distinctive feature of the local field theory is that it permits to take into account interaction between the QDs, and to express the results through the properties of single QD and radial function of distribution, characterizing their mutual disposition. In article [5] such method was developed for an amorphous substance occupying a half-space. Here we develop this technique for the case of very thin layer using dipole approximation assuming that a QD diameter is considerably smaller than the wave-length of light. We obtain the conditions when resonance lines for system of interacting QDs are shifted in comparison with the resonance lines of a single QD, which is defined by local field effects.

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