OPTICAL ABSORPTION OF SEMICONDUCTOR NANOCRYSTALS IN STRONG ELECTRIC FIELDS

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Abstract

Here we present a simple analytical model describing electroabsorption of semiconductor nanocuboids in a wide range of electric field strengths. Using the developed model, we study all the basic electroabsorption effects, including the Stark effect, the Franz-Keldysh effect, and the field-induced broadening of the spectral lines in the nanocrystals spectra. Results of our study can prompt the development of new nanocrystal-based lasers, energy harvesting devices, and electrooptical sensing methods for measuring strong near-fields of plasmonic nanostructures.

Keywords: Electroabsorption, Stark effect, Franz-Keldysh effect

1. INTRODUCTION

Electric field based control over the absorption properties of semiconductor nanocrystals is attractive for applications due to its dynamic nature and the fact that it does not require altering the structure and changing the positions of the nanocrystals [1, 2]. The scope of electric field applications in the nanocrystal-based devices is narrowed by the lack of a simple physical model that can be used to predict the absorption of nanocrystals in the presence of electric fields stronger than 100 kV/cm.

In this Paper, we develop such a model for cubical nanocrystals and use it to study electroabsorption in the electric fields of various intensities. We predict that in the strong fields, the absorption spectra of nanocrystals become inverted - the initially allowed transitions vanish from the spectra, while the forbidden transitions appear as the pronounced absorption peaks. We also show that nanocrystals absorption spectra are significantly broadened in the moderate electric fields due to the overlapping of the transitions of the both types. Our predictions can be applied in the devices that depend on the absorption of nanocrystals, which includes solar panels and lasers [3, 4].

2. SEMICONDUCTOR NANOCUBOID

2.1. Wave functions and energy spectrum

In this Paper, we study nanocrystals in the shape of rectangular cuboids - nanocuboids - positioned in the homogeneous static electric field **F**. We assume that a nanocuboid with dimensions $L_x \times L_y \times L_z$ has an impenetrable surface so that the motion of the charge carriers inside it obey Schrödinger equation

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2 - V(\mathbf{r})\right)\Psi_{\mathbf{n}} = E_{\mathbf{n}}\Psi_{\mathbf{n}}, \quad (1)$$

where m^* is the effective mass of an electron or a hole, $V(\mathbf{r})$ is the potential created by the electric field inside the nanocrystal, and $\mathbf{n} = (n_x, n_y, n_z)$ is the set of quantum number describing spatial confinement of charge carriers. Without loss of generality we assume that the electric field inside the nanocrystal is simply external

electric field **F** reduced by the factor of the nanocrystal's static electric permittivity ε, so that the potential energy is given by

$$V(\mathbf{r}) = -\frac{q}{\varepsilon}(\mathbf{r},\mathbf{F}). \tag{2}$$

With that assumption, we can factorize the wave function into the one-dimensional functions as $\Psi_{\mathbf{n}}(\mathbf{r}) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$, represent the confinement energy in the form $E_{\mathbf{n}} = E_{n_x} + E_{n_y} + E_{n_z}$, and obtain three simple equations instead of Eq. (1):

$$\left(-\frac{\hbar^2}{2m^*}\frac{\mathrm{d}^2}{\mathrm{d}v^2} - \frac{qvF_v}{\varepsilon}\right)\psi_{n_v} = E_{n_v}\psi_{n_v}, \tag{3}$$

where $v = x, y, z.$ In order to solve this equation, we use a substitute

$$\sigma(v) = -\left(\frac{2m^* qF_v}{\hbar^2\varepsilon}\right)^{1/3}\left(v + \frac{E_{n_v}\varepsilon}{qF}\right), \tag{4}$$

which gives us Airy equation

$$\frac{\mathrm{d}^2\psi_{n_v}}{\mathrm{d}\sigma^2} - \sigma\psi_{n_v} = 0. \tag{5}$$

Its solution is well known and given by

$$\psi_{n_v}(\sigma) = A_{n_v}\mathrm{Ai}(\sigma) + B_{n_v}\mathrm{Bi}(\sigma). \tag{6}$$

The unknown coefficients are related to each other through the boundary conditions - as the wave functions must vanish on the nanocrystal surface, $\psi_{n_v}\left[\sigma(l_v/2)\right] = \psi_{n_v}\left[\sigma(-l_v/2)\right] = 0,$ and

$$B_{n_v} = -A_{n_v}\mathrm{Ai}\left[\sigma(l_v/2)\right]/\mathrm{Bi}\left[\sigma(l_v/2)\right]. \tag{7}$$

Using the normalization condition, we get

$$A_{n_v} = \left(\int\left\{\mathrm{Ai}\left[\sigma(v)\right] - \mathrm{Bi}\left[\sigma(v)\right]\mathrm{Ai}\left[\sigma(l_v/2)\right]/\mathrm{Bi}\left[\sigma(l_v/2)\right]\right\}^2 \mathrm{d}v\right)^{-1/2}. \tag{8}$$

Finally, energy spectrum can be derived from the equation

$$\mathrm{Ai}\left[\sigma(l_v/2)\right]/\mathrm{Bi}\left[\sigma(l_v/2)\right] = \mathrm{Ai}\left[\sigma(-l_v/2)\right]/\mathrm{Bi}\left[\sigma(-l_v/2)\right], \tag{9}$$

whose solution gives one-dimensional energies E_{n_v}. The resonant energy of an arbitrary interband transition is given by

$$E_{\mathbf{nm}} = E_{\mathbf{n}} + E_{\mathbf{m}} + E_g, \tag{10}$$

with E_g being the bandgap energy.

2.2. Electroabsorption spectra

Excitation of the nanocrystal with the light of frequency ω and intensity I results in the electron-hole generation rate

$$W(\omega,\mathbf{F}) = \frac{4\pi e^2 E_p I}{m_0 c\omega^2} \sum_{\mathbf{m}} \sum_{\mathbf{n}} \left| J_{\mathbf{nm}}(\mathbf{F}) \right|^2 \Gamma_{\mathbf{nm}}(\omega). \tag{11}$$

Here m_0 is the free electron mass, E_p is the Kane energy (it is about 20 eV in the typical semiconductors), and the overlap integral is given by $J_{\mathbf{nm}}(\mathbf{F}) = J_{n_x m_x}(F_x) J_{n_y m_y}(F_y) J_{n_z m_z}(F_z)$, where

$$J_{n_x m_x} = \int \psi_{n_x} \psi_{m_x} \mathrm{d}v \tag{12}$$

is the one-dimensional overlap integral of charge carriers' wave function. The interband transition lineshape is approximated by the Lorenzian:

$$\Gamma_{\mathbf{nm}}(\omega) = \frac{1}{\pi} \frac{\gamma}{(\omega - \omega_{\mathbf{nm}})^2 + \gamma^2}, \tag{13}$$

where 2γ is the linewidth and $\hbar\omega_{\mathbf{nm}} = E_{\mathbf{nm}}$. The absorption spectrum described by Eq. (10) depends on both the direction and strength of the electric field. If the nanocrystals in the ensemble are oriented chaotically, then this spectrum should be averaged over all the possible directions of **F**, i.e.

$$K(\omega,\mathbf{F}) = \frac{1}{4\pi} \int W(\omega,\mathbf{F}) \, \mathrm{d}\varphi \, \mathrm{d}\vartheta, \tag{14}$$

where $\mathbf{F} = (F\cos\varphi\sin\theta, F\sin\varphi\sin\theta, F\cos\theta)$, $F = |\mathbf{F}|$.

3. RESULTS AND DISCUSSION

Now we can analyze all the major electroabsorption features using the developed model. The dominant physical process that determines electroabsorption in semiconductor nanocrystals is the spatial separation of the charge carriers inside the nanocrystals. The static electric field entrains positively charged holes and negatively charged electrons in the opposite directions, which affects the way the charge carries interact with each other. In particular, it changes the value of the overlap integral of their wave functions, thus reducing or increasing the absorption rate upon the given transition in the spectrum, as is described by Eq. (11). This is known as the *quantum-confined Franz-Keldysh effect* [5, 6].

It is illustrative to consider a one-dimensional nanostructure first, e.g. quantum well, as all the three dimensional equation are derived from the one-dimensional ones. In **Figure 1** we demonstrate the spatial separation of the electrons and holes in CdSe quantum well of the width L = 20 nm. It is clearly seen that in the weak fields the charge carriers (both in their ground states with n = 1) are located near the nanostructure center, and the overlap integral J is maximal. When the strength of electric field is increased, the carriers are moved to the sides of the well, so that the overlapping decreases to zero.

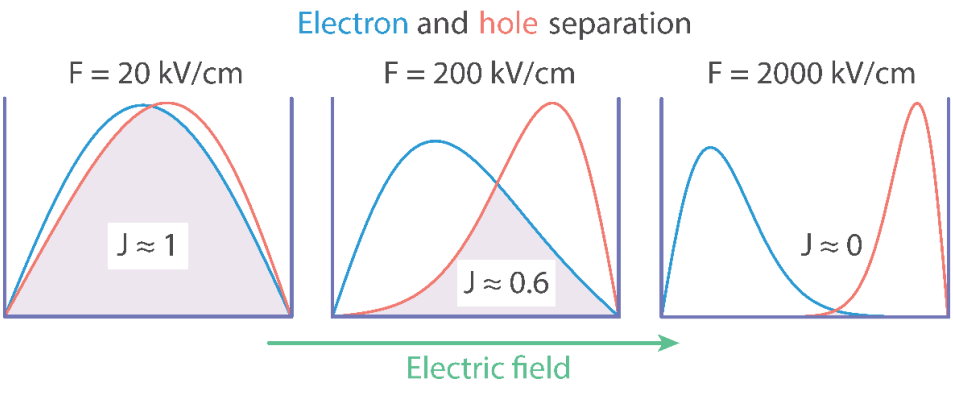

Figure 1 Wave functions of the electron and hole in their ground states, confined in the infinite potential well of the size L = 20 nm. The well is assumed to be made from CdSe. Here, J is the one-dimensional overlap integral of the electron's and hole's wave functions

As the result of the charge carrier separation, the probabilities of the dipole-allowed interband transitions between the states with the same quantum numbers are reducing with the field strength. On the contrary, the overlapping of the states with different quantum numbers, which is zero in the absence of external fields, becomes positive when the electric field is applied to the nanostructure, and the probabilities of the *dipole-forbidden* transitions are increased.

As is seen from **Figure 2a,** the overlap integrals and therefore probabilities of one-dimensional dipole-allowed transition 1→1, 2→2, and 3→3 are monotonously decreasing with the field strength up to 300 kV / cm. If the field is strengthened further, the probability of the fundamental transition is approaching zero, while probabilities of the secondary transitions starts growing again. It should be noted that in the typical electroabsorption nanocrystal-based devices, electric fields are much weaker than 300 kV / cm, and it can be assumed that the probabilities of all the dipole-allowed transitions are reducing with the field strength.

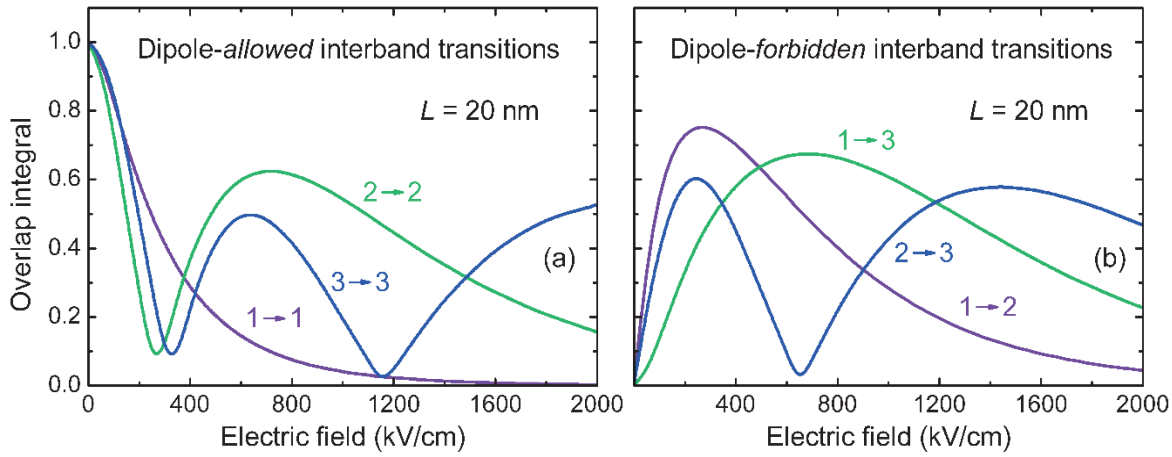

Figure 2 One-dimensional overlap integrals of (a) dipole-allowed interband transitions 1→1, 2→2, and 3→3, and (b) dipole-forbidden interband transitions 1→2, 1→3, and 2→3 in the CdSe quantum well of the size L = 20 nm

The overlap integrals of forbidden transitions 1→2, 1→3, and 2→3, shown in **Figure 2b**, are all zero when the electric field is absent and monotonously grows with the field strength up to 200 kV / cm. Further, the probabilities of the transitions occurring from the ground state, 1→2 and 1→3, are approaching zero, while the probability of transition 2→3 is varying with the field strength. So, in the strong electric field the *inversion of selection rules* is observed, as the dipole-allowed transitions become forbidden, while the initially forbidden transitions become allowed.

Figures 3a-3d show the electroabsorption spectra of 20 × 20 × 20 nm^3 CdSe quantum dots for the different field strengths, containing only the spectral lines of allowed transition 111→111 and forbidden transition 111→112. In accordance with the above discussion, the absorption peak of the forbidden transition is absent in the weak fields and appears in the spectrum when the field becomes stronger, while the fundamental absorption peak vanishes. At that, both peaks are red-shifted due to the reduction of the confinement energies induced by the field strength, which is called *quantum-confined Stark effect* [7, 8] and described by Eqs. (9) and (10).

In the moderate electric fields (F ~ 100 - 200 kV / cm), the two absorption peaks are of the similar intensity and overlap with each other, and the total spectrum is significantly broadened. This *field-induced broadening* of electroabsorption spectra [9, 10] can be used to increase the absorption range of the nanocrystals.

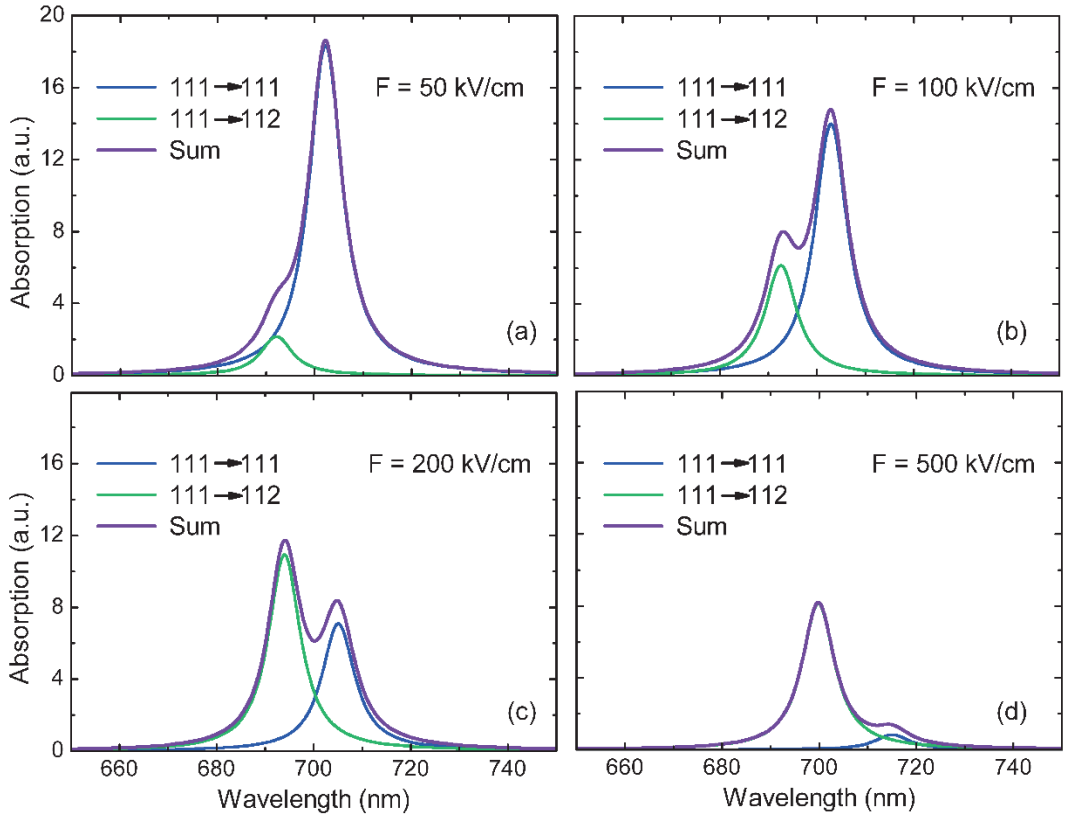

Figure 3 Electroabsorption spectra of cubical 20 × 20 × 20 nm^3 CdSe quantum dots in the electric field of the strength (a) 50 kV / cm, (b) 100 kV / cm, (c) 200 kV / cm, and (d) 500 kV / cm. The blue line shows the fundamental absorption peak, the green line corresponds to the first dipole-forbidden transition, and the purple line shows the total absorption spectrum in all the panels.

4. CONCLUSION

In this Paper, we developed an analytical model, which allows to calculate electroabsorption in semiconductor nanocuboids - cubical nanocrystals. Using the developed model, we explained the main electroabsorption effects and predicted that in the strong electric fields, the selection rules of the interband absorption become inverted, which totally changes the absorption spectrum. The application of the moderate-strength electric field can be used to broaden the spectrum and thus increase the range of absorption. These features of electroabsorption can find its application in the nanocrystal-based solar panels, lasers, and electrooptical sensors.

ACKNOWLEDGEMENTS

This work was funded by Grant 14.B25.31.0002 and Government Assignment No.3.17.2014/K of the Ministry of Education and Science of the Russian Federation.

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