Optical Line Width in Quantum Dot or Nanotransistor

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The width of the spectral line of the optical transitions in quantum dots is studied theoretically on the basis of the electron coupling to the longitudinal optical phonons in polar semiconductors. With using the self-consistent Born approximation to the electronic self-energy, we are able to reproduce one of the main experimental results obtained on CdSe and CuBr quantum dots, namely the linear dependence of the width of the optical line on the inverse of the quantum dot diameter. In addition to it, the theory allows to expect certain resonance features on the linear dependence of line width. Extensions of the present line-width theory may appear suitable in order to reach a better agreement in describing adequately the behavior of the line width in CdSe and InAs quantum dots. [DOI: 10.1380/ejssnt.2010.136]

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I. INTRODUCTION

Such nanoobjects like individual quantum dots (QDs) are similar to single atoms or molecules. Despite the relative simplicity of such systems their behavior has not yet been satisfactorily understood. Because of the complete confinement of the charge carriers in all three dimensions, the energy spectrum of the stationary states of the charge carriers is discrete. In some cases we like to reduce approximately the electronic system of a quantum dot to a two energy level system with two non-degenerate electronic states. Such a simple model system, with the inclusion of the electron-phonon interaction in the quantum dot, is not regarded to be understood enough (see [1]).

The electron-phonon coupling the electronic system of quantum dots leads to a quick relaxation of its electronic energy. Because of this interaction the spectral lines of the optical transitions appear to show a finite width, and in certain cases the spectral line profiles display a special shape of the homogeneous spectral density [2]. The present understanding of the processes in the individual quantum dots is currently conducted along several directions. For example, the speed of the electronic energy relaxation has been interpreted with the help of at least two mechanisms, one of them is considering purely electron-electron interaction, while the other one is using only the electron-phonon interaction [3-5]. The question of the optical line shape of the optical transitions in the individual quantum dot electronic system has so far been discussed perhaps only with help of the electron-phonon interaction [2].

We discuss theoretically the full width at the half maximum (FWHM) of the optical transitions main peak (e.g. optical emission) in the individual quantum dots electronic subsystem, confining the electronic interaction to the coupling with the longitudinal optical phonons in polar semiconductors. The theoretical conclusions are then compared to available experiments.

II. OUTLINE OF THE METHOD

Studying the optical emission we deal with an annihilation of an electron occupying the conduction band states with a hole particle in the valence band states. In an analogy with what we did earlier [4], we assume the hole particle as heavy. In this case the spectrum of the holes in the valence band states would be dense on the energy scale. The holes would relax very quickly to their lowest energy state by the available first order processes of the perturbation calculation. From this reason, we can regard the holes sitting in their ground state only as a static potential contributing to the electronic potential well. The holes thus have their electronic spectral density equal to simply a delta function of the energy variable.

The electronic spectral density of the electron-hole excitation then reduces to just the electronic spectral density of the electron in the conduction band states. Therefore, reducing the hole particle to just a static potential influencing the electronic motion, we reduce the question of the optical line shape properties of the optical transitions of the electron-hole excitation to a much simpler problem of the electronic spectral density in the conduction band states of the quantum dot [2].

In the presently used model the quantum dot will be assumed to have a cubic shape with infinitely deep electronic potential. We shall assume that an electron in a quantum dot has only two bound states in the quantum dot. We confine ourselves to the lowest energy states in the cubic dot. Namely, we take into account only the electronic ground state (n = 0) and a single one of the triply degenerate excited states (n = 1). The electronic spin will be neglected. We shall confine the total number...
The electron are assumed to interact with phonons in the quantum dot. This interaction will be assumed to be the well known Froehlich’s coupling, which can be supposed to be the strongest mechanism of the electron-phonon scattering in the polar semiconductors. In the non-equilibrium Green’s functions approach, the electron-phonon interaction will be considered in the self-consistent Born approximation (SCBA) to the electronic self-energy, in calculating the electronic spectral density and the electron relaxation kinetics [4]. Let us also remark that we neglect the so called ‘overheating’ effect referring the reader to the references cited in [6]. The electronic spectral density in a quantum dot was considered theoretically in an earlier reference [3]. The electronic spectral density is given by the self-consistent equation for the electronic self-energy [4]:

\[
M_n^R(E) = \sum_{m=0}^{1} \alpha_{nm} [(1-N_m + \nu_{LO})G_m^R(E-E_{LO})
\quad + (N_m + \nu_{LO})G_m^R(E + E_{LO})].
\] (1)

Here in the self-consistent equation, \(M_n^R(E)\) is the retarded electronic self-energy for the \(n\)-th electronic state, dependent on the energy variable \(E\). \(G_m^R\) is the retarded electronic Green’s function depending on the retarded self-energy, \(E_{LO}\) is the optical phonon energy. The electron-phonon interaction constant, together with the form-factors due to the shape of the quantum dots, are hidden in the constants \(\alpha_{nm}\) [4]. The phonon distribution \(\nu_{LO}\) is given by the Bose-Einstein distribution function of the optical phonons at the temperature of the atomic lattice of the quantum dot. The electronic distribution \(N_m\) is the electronic occupation of the energy level \(m\). In contrast to the phonon distribution, which is kept constant here, the electronic distribution is understood in the present calculation to be given by the stationary electronic distribution, namely by such an electronic distribution for which the time derivative of the electronic distribution function is zero:

\[
\frac{dN_1}{dt} = 0.
\] (2)

This condition means that the relaxation and the up-conversion of the electronic distribution achieves after a short time period a steady state electronic distribution. The earlier numerical calculations show that the process of achieving the steady state electronic distribution lasts much shorter time than is the typical time of the luminescence optical transition in a quantum dot. The reader is refered to the paper [4] for details about the up-conversion effect of the electronic relaxation under the self-consistent Born approximation. The spectral density of the optical transition is thus identified here with the electronic spectral density corresponding to the lowest energy state \(n = 0\) and the electronic distribution is the steady-state distribution with respect to the relaxation and up-conversion mechanism.

We determine the electronic spectral density of the \(n = 0\) state. It is calculated numerically, solving the equation (1) for the electronic self-energy, at a given lattice temperature and in the dependence on the latteral size \(d\) of the dot. As the first step, the steady state distribution of the electronic charge between the two states \(n = 0, 1\) is found at the given lattice temperature. Then, as the second step, the electronic spectral density of the \(n = 0\) state is evaluated at this distribution, with the help of the equation (1). The line-width is then graphically determined for the main peak of the \(n = 0\) spectral density. This procedure is relatively straightforward in the case of the InAs material. In this case the phonon satellites of the zero-phonon peak are rather weak and do not tend to coalesce with the zero-phonon peak. The CdSe material differs from the InAs material by a stronger polaron coupling constants. It appears that the above outlined procedure of obtaining the FWHM of the zero-phonon line cannot be always easily used. This difficulty is met especially at a certain range of the CdSe quantum dot diameter. We shall return this question later in this text.

III. NUMERICAL RESULTS FOR INAS AND CDSE QUANTUM DOTS

The attention is paid to the zero-phonon feature of the electronic spectral density of the lower-energy state \(n = 0\). The material parameters of InAs and CdSe bulk materials are used in the numerical calculations. The lattice temperature is set to 10 K. The plot of FWHM against \(1/d\) in InAs quantum dot is shown in Fig. 1. The open circles mark the computed points. FWHM of the zero-phonon peak of the electronic spectral density is determined for the stationary distribution of the electron occupation among the two energy levels. This electronic distribution is calculated from a condition, see eq.(2), that the electronic transition rate between the two energy levels, due to the electron-phonon interaction, is zero [3].

The experimental characteristics of the optical spectra [7,8] can be compared with the theory. We see first of all an interesting agreement of the theory with the experiments on CdSe and CuBr. Namely, in Fig. 1 we see that the calculated FWHM dependance on \(1/d\) in InAs
quantum dots is nearly linear. Denoting the quantity FWHM as $W$, the dependence of $W$ on the lateral size of the dot $d$ is approximately given by the simple function $W(d) = \lambda/d$, where $\lambda$ is a constant. The papers [7,8] show the dependence of FWHM on $1/d$ in CdSe nanocrystals, while the paper [8] gives the dependence of $W(d) = \lambda/d$ also for the CuBr nanocrystals. Unfortunately, besides CdSe and CuBr, we have not been able to find a similar experimentally detected approximate linear dependence of FWHM on $1/d$ in other materials, including InAs.

The theoretically determined dependence of the FWHM on $1/d$ has an important feature, which is the presence of certain modulations of the linear dependence in the form of small dips in the overall linear dependence. These modulations come out rather weak in the case of the InAs quantum dot calculation. The observed small dips appear in InAs quantum dot at such values of the lateral size $d$ of the assumed cubic quantum dot at which the electronic energy level separation $\Delta E$ equals to an integer $m$ multiple of the longitudinal optical phonon energy $E_{LO}$, namely, $\Delta E = mE_{LO}$. In Fig. 1 we display the points of the detailed calculation of the dependence. We pay a detailed attention to the vicinity of the resonances corresponding to the integers $m = 1$ and $m = 2$. The resonance features, to which we have paid our attention, are calculated in detail in the region of about $(1/d) \in (0.02, 0.07)$.

The calculated resonances corresponding to the integer larger than $m = 4$ are expected to be weak. The resonances in the InAs cubic quantum dot, corresponding to $m = 1, 2$ and 3 are, respectively, at the inverse lateral size equal to 0.0279, 0.039 and 0.0483, expressed in the units of $1/nm$. We do not pay a further attention in the present work to the individual resonance features in the Fig. 1, postponing a detailed consideration of the shape of the resonance features to another work. An experimental verification of the presence of the resonance features in the functional dependence of the FWHM on the inverse lateral size of the dot would help to further estimate the role of the electron-LO-phonon interaction in QDs.

The overall magnitude of the FWHM comes out from the theory smaller than it is reported in the experimental paper [9]. The discrepancy between the size of the FWHM in theory and experiment may indicate a need to consider an extension of the presently used model with only two nondegenerate bound states model of the InAs quantum dot. An improvement of the present model could be done by extending the model to include more states and by considering further details of the conduction band of InAs [10].

The samples with the nanoparticles of the materials CdSe and CuBr are perhaps the only two cases so far for which there is the experimentally determined dependence available of the FWHM dependence on the inverse lateral size in quantum dots. In these two cases the experimentally found dependence of FWHM gives us clearly a straight line without resonances [7,8]. The dependence $W(d) = \lambda/d$ obtained by the theoretical calculation shows a rather strong modulation of the expected straight line $W(d) = \lambda/d$ in CdSe (Fig. 2). The presence of the strong resonance modulation of the function can be ascribed to a much stronger electron-phonon coupling in CdSe than it is in InAs. The polaron constant in CdSe is 0.460, while in InAs it amounts only to 0.052. Because the resonance peaks are expected to be caused by the electron-phonon interaction, the resonance features might be more significant in the materials with the stronger coupling. The presence of the resonance features in the theoretical result in Fig. 2, is in a contrast with the absence of the resonance features in the experimental data measured on CdSe and CuBr [7,8]. The resonance dips corresponding to our simple model of the cubic quantum dot should occur for $m = 1, 2, 3, 4$ and 5, respectively, at $1/d$ equal to 0.0558, 0.0775, 0.095, 0.11 and at 0.1227 nm$^{-1}$. Obviously, the calculated pattern of the resonance modulation in CdSe dots is missing an order observed in the case of InAs dots.

In addition to this, the magnitude itself of the FWHM parameter, at a given value of the lateral size, comes out larger in the theory than in experiment on CdSe dots [7,8]. Interestingly, the experimental measurement [11] gives the line-width rather close to the present theoretical results. We see that the optical line width is the physical property of the semiconductor quantum dots, which is rather sensitive to the degree of approximation of the electronic self-energy in these structures. An extension of the self-consistent Born approximation need be considered.

Quite recently, FWHM dependence on the lateral quantum dot size has been measured in the ref. [12] in a range of the quantum dot diameters close to about 6 nm. For this range of the quantum dot sizes the authors obtained the values of the FWHM about 115 meV, which appears to be much larger that it is measured in the other experiments [7,8]. The data given in the reference [12] do not allow us so far to see whether the approximate dependence $W(d) = \lambda/d$ is supported by the measured data. More measurements of the linewidths of the optical features is needed.

The numerically determined data in Fig. 2 could not be extended to $1/d$ larger than 0.14 of $1/nm$, because we meet there a difficulty when calculating the quantum dot optical spectra. The difficulty was in the effect of the coalescence of the phonon satellites with the zero-phonon line of the phonon multiplet corresponding to the lower energy state $n = 0$. The onset of a coalescence in the experimentally observed spectra has not yet been mentioned in the available experimental sources.

As we have seen, the theoretical determination of the width of the spectral line depends on the degree of the
upconversion of the electronic occupation to the excited states. In the luminescence experiment, in which the luminescence time is long enough (nanoseconds) for the electron to fulfill the upconversion process, the line width might come rather long. In the accumulated photon echo used in the experiments [7,8] the upconversion process may be performed only to a small degree, which depends on the time interval between the excitation pulse and the pulse in which the signal is detected. From this reason we think that the overall width of the line, computed here with the upconversion completed, might be overestimated to a degree, which requires a more detailed information on the time scales in the experiment on accumulated photon echo.

Another case, in which the line width can play a role, is the open system of a quantum dot with contacts, or a nanotransistor [13]. When the current-voltage characteristics through the nanotransistor is to be determined theoretically, the electronic spectral line shape may depend on the time which the electron spends within the nanotransistor’s quantum dot. In this way the electronic spectral line shape can be verified through the transport measurement. In the calculation of the of the current-voltage characteristics the electronic distribution function, or the electronic upconversion, would enter the calculation even through the determination of the electronic spectral densities of the electronic states.

IV. SUMMARY

The property of the linear shape of the FWHM dependence on the inverse of the lateral size, \( W(d) = \lambda/d \), is explained by the electron-phonon mechanism which uses the idea of the multiple scattering of the electron on the optical phonons. The line width dependence on the lateral size of the quantum dot thus underlines the significance of the multiple scattering of the charge carriers in the dot and emphasizes the non-adiabatic mechanism of the interaction between the electrons and the lattice vibrations. Let us emphasize that the theory of the present numerical calculations uses the treatment of the electron-phonon coupling which goes beyond any finite order perturbation approach. The theoretical procedure of the estimation of the line width utilizes the process of the electronic upconversion for the finding of the electronic distribution in the quantum dot two-level model system. The linear type of the dependence, \( W(d) = \lambda/d \), is explained in the intermediate-to-strong electron-phonon coupling materials CdSe and CuBr. So far the present state of experimental results does not allow to verify the same dependence in the weak coupling material of InAs.

The features of the resonance modulating the linear dependence of the line width, on the inverse lateral size, seem to have a regular structure in InAs dots. Therefore, the simple resonance pattern might perhaps be found first of all in another weak coupling semiconductors quantum dots.

Acknowledgments

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