Coherent multiphonon energy relaxation in a quantum dot

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Abstract. A new defect-assisted mechanism of multiphonon intraband carrier relaxation in semiconductor quantum dots, where the carrier is found in a coherent superposition of the initial, final, and defect states, is proposed. It is shown that this mechanism is capable of explaining the observed trends in temperature dependences of the intraband relaxation rates for PbSe and CdSe colloidal nanocrystal quantum dots.

1. Introduction

Recent experimental studies of PbSe nanocrystals (NCs) have revealed an unexpectedly fast intraband relaxation in semiconductor quantum dots (QDs) with energy separation between adjacent electron (or hole) levels exceeding by far the optical phonon energies [1, 2]. A pronounced temperature dependence of the observed relaxation rates [2] suggests that underlying mechanism should involve multiphonon transitions while Auger-like relaxation processes [3] are ruled out due to a nearly symmetric energy spectra in the conduction and valence bands of PbSe.

The multiphonon transitions between otherwise orthogonal quantized electronic states in a QD may occur due to nonadiabaticity of the electron-phonon system [4, 5, 6, 7]. A model study performed in conjunction with the experiments on PbSe NCs revealed that, in order for this mechanism to be responsible for the experimentally observed temperature dependence of the relaxation rate, the electron-phonon coupling should be stronger than one would expect [7]. However, the study of detailed models of electron-phonon interaction in quantum dots (upon which the judgement about the coupling strength is based) has always been a weak point in approaches to energy relaxation [8] and Raman [9] processes. In case of PbSe NCs the situation is further obscured by the fact that the widely accepted model of their electronic structure [10] which would be natural to pick for an estimate of electron-phonon coupling strength fails to describe absorption spectra of PbSe NCs [1] and is therefore not quite reliable. Thus, instead of seeking to either confirm or rule out this mechanism we will concentrate on examining other possibilities for the fast energy relaxation.

As it has been proposed for epitaxially grown QDs [11], such possibilities can be provided by a localized state of an impurity or defect close to the QD surface. In case of the experiment of Ref. [1] such states can correspond to deep impurities in the silica host surrounding PbSe NCs occurring in an appreciable proximity to the NC surface. Otherwise they can be due
to surface states. An electron trapped to the impurity is strongly localized which assures its strong coupling to local lattice vibrations. One can then consider a relaxation process involving the interior QD levels as the initial (2) and final (0) states, and the state at the impurity as an intermediate (1) state as shown in Fig. 1. Although processes of this type have been theoretically investigated [8, 11, 12], all these studies considered the relaxation as a two step process, so the relaxation time \( \tau \equiv \tau_{2 \rightarrow 0} = \tau_{2 \rightarrow 1} + \tau_{1 \rightarrow 0} \). But if \( \tau_{1 \rightarrow 0} \) is shorter than the phonon lifetime in state 1 then the transition 2 \( \rightarrow \) 0 must be treated as a coherent quantum mechanical process. Such process represents a new mechanism of phonon-assisted carrier relaxation in QDs and its studying is the scope of the present work. Similar processes have been considered for capture or generation of electron-hole pairs by impurities in bulk semiconductors [13, 14].

Another system where the proposed mechanism can play the key role is provided by CdSe colloidal nanocrystals. In the recent experiments on such quantum dots the fast intraband relaxation of electrons has been observed in the absence of the holes [15]. The electrons were injected into the quantum dots instead of being optically generated, and the pump-probe measurements were subsequently carried out [15]. These experiments showed that intraband relaxation times vary significantly with surface modification suggesting involvement of a surface state such as the empty \( s^{−} \) state of the surface Cd\(^{2+} \) atoms [15]. A faster relaxation rate was observed for lower temperatures [15] though more thorough studies of the temperature dependences of the relaxation rate in CdSe colloidal nanocrystals are desirable.

2. The transition rate
We consider the relaxation process in the framework of an approach based on calculation of overlap integrals between eigenfunctions belonging to shifted parabolic potentials (see e.g. [12]). These potentials for our system are schematically depicted in Fig. 1b. For the quantum dot states the potentials are given by [6]

\[
V_0(q) = \frac{M \omega_0^2 q^2}{2} + \varepsilon_0, \quad V_2(q) = \frac{M \omega_0^2 q^2}{2} + \varepsilon_2.
\]

Here \( \omega_0 \) is the frequency of the local vibrational mode, \( q \) is the corresponding configurational coordinate, and \( M \) is the mass of the impurity’s ion. The adiabatic potential for the intermediate state is given by [6]

\[
V_1(q) = \frac{M \omega_0^2 (q + q_0)^2}{2} + \tilde{\varepsilon}_1,
\]

where \( q_0 = \sqrt{2S/(M\omega)} \) and \( \tilde{\varepsilon}_1 = \varepsilon_1 - S \omega_0 \).

Let us introduce the eigenfunctions \( \psi_n^{(2)}(q) \), \( \psi_n^{(1)}(q) \), and \( \psi_n^{(0)}(q) \) in the adiabatic potentials \( V_2(q) \), \( V_1(q) \), and \( V_0(q) \), respectively. These are eigenfunctions of the harmonic oscillator satisfying the following relation \( \psi_n^{(2)}(q) = \psi_n^{(1)}(q - q_0) = \psi_n^{(0)}(q) \). Then the transition rate \( W_{2 \rightarrow 0} \) is given by the Fermi golden rule (\( \hbar = 1 \))

\[
W_{2 \rightarrow 0} = \frac{2\pi Z}{\omega_0} \langle |M_{2 \rightarrow 0}|^2 \rangle,
\]

where

\[
\langle |M_{2 \rightarrow 0}|^2 \rangle = (1 - e^{-\beta \omega_0}) \sum_{m=0}^{\infty} e^{-\beta m \omega_0} |M_m|^2,
\]

\[
M_m = \sum_{n=0}^{\infty} \frac{\langle \psi_m^{(2)} | \psi_n^{(1)} \rangle \langle \psi_n^{(1)} | \psi_{m+n}^{(2)} \rangle}{(m - n) \omega_0 + \varepsilon_2 - \varepsilon_1 + S \omega_0 + i\gamma n},
\]
and \( \beta \) is inverse temperature. The energy \( \delta \)-function in Eq. (3) has been integrated out yielding the phonon density of states \( \omega^{-1} \) while the value of \( \omega_0 \) is adjusted to make the number \( p = (\varepsilon_2 - \varepsilon_0)/\omega_0 \) integer. We also took into account that the width of the intermediate state is given by the number of phonons in that state \( n \) times the phonon decay rate \( \gamma \), as is shown in [16], see also [17].

The relaxation is most efficient when the energy of the intermediate state is in resonance with that of the initial and final states. We will assume that the resonance condition is always fulfilled and, therefore,

\[
\varepsilon_2 - \varepsilon_1 + S\omega_0 = l\omega_0, \quad l \in \mathbb{N}.
\]

In this case the term with \( n = l + m \) becomes dominant in Eq. (5), and we obtain

\[
M_m \approx \frac{-i}{\gamma(l + m)} \langle \psi_1^{(2)} | \psi_{l+m}^{(1)} \rangle \langle \psi_{l+m}^{(1)} | \psi_2^{(2)} \rangle.
\]

3. Results and discussion
At zero temperature, only the contribution with \( m = 0 \) survives in Eq. (4), the relaxation rate depends only on the value of the matrix element \( |M_0| \). For the fixed energy difference \( \varepsilon_2 - \varepsilon_1 + S\omega_0 \equiv \omega_0 \), i.e. the vertical shift between the parabolas (2) and (1) on Fig. 1b, \( |M_0|^2 \) reaches an optimum for a certain value of the Huang-Rhys factor \( S \). This can be understood using quasiclassical language. According to the quasiclassical theory, the overlap integral of eigenfunctions belonging to different adiabatic potentials is maximum at those energy values.

Figure 1. (a) Temperature dependences of the relaxation time calculated for different values of the impurity level position \( l = 1, 2, 3, 5, 7 \). (b) Energy diagram representing adiabatic potentials for the quantum dot states (0 and 2) and the impurity level (1), given by Eqs. (1)-(2). Calculated for \( Z = (2.5)^4 \) meV, \( \gamma = 0.2 \) ps\(^{-1} \), \( S = 5.7 \), \( p = 13 \), and \( \varepsilon_2 - \tilde{\varepsilon}_1 = \omega_0 \).
where the adiabatic curves intersect [6]. The optimal value of the Huang-Rhys factor, which is $S \approx 5.7$ for $p = 13$ and $l = 1$, corresponds to the situation where both intersection points are close to the energy level with $m = 0$, see Fig. 1b. For the same reasons the matrix element $|M_1|$ is also large, exact calculation shows that $|M_1/M_0| \approx 2$ for $l = 1$.

As temperature is increased, thermal activation leads to increasing importance of the terms in the r.h.s. of Eq. (4) with $m > 0$. In the meantime, relative contribution of the term with $m = 0$ to the transition rate decreases due to the factor of $1 - \exp(-\beta\omega_0)$ in Eq. (4). Therefore, the character of the temperature dependence of the relaxation rate is determined by the ratio of $|M_0|$ and $|M_1|$. Since $|M_1|$ exceeds $|M_0|$ the relaxation time decreases with temperature for $l = 1$, as shown in Fig. 1a (solid curve). For $l > 1$ intersection points would be closer to the level with $m = 0$ than to the level with $m = 1$ resulting in $|M_0| > |M_1|$. This will lead to increasing temperature dependence of the relaxation time, see Fig. 1a.

Therefore, the present mechanism can reproduce both increasing and decreasing temperature dependences of the relaxation time. Those are two types of temperature dependences observed experimentally [2, 15]. Note that when temperature sweeps from zero to 300 K, relaxation time in Fig. 1a changes within one order of magnitude which is consistent with experimental observations [2, 15].

4. Conclusions
We have proposed a new defect-assisted mechanism of multiphonon intraband carrier relaxation in semiconductor QDs, where the carrier is found in a coherent superposition of the initial, final, and defect states. The proposed mechanism is capable of reproducing both decreasing, as it was observed for PbSe NCs [2], and increasing, as it was reported for CdSe QDs [15], temperature dependences of the relaxation time. For reasonable values of parameters, the change in the relaxation time with temperature rise from cryogenic to room temperatures was found within one order of magnitude, in agreement with experimental observations [2, 15].

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