Multiexciton Absorption and Multiple Exciton Generation in CdSe Quantum Dots

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Efficient multiple-exciton generation (MEG) in semiconductor quantum dots has been recently reported. The MEG efficiency has so far been evaluated assuming that the change (bleaching) of the absorption spectrum due to MEG is linearly proportional to the number of excitons N_X. Here, we critically examine this assumption using atomistic pseudopotential calculations for colloidal CdSe nanocrystals. We find that the bleaching of the first absorption peak depends nonlinearly on N_X, due to carrier-carrier interactions. This nonlinearity mandates an upper bound of 1.5 to the value of the normalized bleaching that can be attributed to MEG, significantly smaller than the limit of 2.0 predicted by the linear scaling assumption. Thus, measured values of the normalized bleaching in excess of 1.5 cannot be due entirely to MEG, but must originate in part from other mechanisms.

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In conventional photovoltaic devices, each absorbed photon from the solar spectrum generates typically one electron-hole pair, which can then be collected to produce electricity [1]. One of the most effective ways to increase the efficiency of solar cells would be to increase the average number of electron-hole pairs per absorbed photon. In bulk semiconductors, this is possible via a mechanism known as impact ionization, in which the excess photon energy $\Delta E = \hbar\omega - E_g$ (where ω is the photon frequency and E_g is the semiconductor band gap) is converted into up to $\Delta E/E_g$ additional electron-hole pairs, instead of being lost to heat. However, in bulk semiconductors, the impact ionization process is efficient only at very high photon energies [2,3], so it does not contribute significantly to the efficiency of existing photovoltaic devices. Recently, there have been several reports of efficient multiple-exciton generation (MEG) in semiconductor quantum dots [4–13]. For example, Schaller *et al.* [8] reported photon-to-exciton conversion efficiencies as high as 700% in PbSe colloidal nanocrystals (NCs). These results have generated widespread interest, both from a fundamental point of view [14] and because of their implications for solar-energy conversion [15]. Assuming that the photo-generated carriers can be extracted from the NCs before they recombine, MEG has the potential to increase the efficiency of solar cells by as much as 50% [16].

Although several mechanisms have been proposed in the literature to explain the origin of MEG in semiconductor NCs [6,17–19], the validity of the methods used for quantifying its efficiency has not been carefully examined. The efficiency of MEG in NCs has often been inferred from the modulation of the absorption spectrum at the fundamental band gap ($1S$ absorption peak), as measured by transient pump-probe spectroscopy [4–9]. In those experiments, the change of the $1S$ absorption peak, $\Delta\alpha_{1S}(\hbar\omega, t)$, was measured as a function of the pump excitation energy $\hbar\omega$ and the probe delay time t. To determine the exciton population, $\Delta\alpha_{1S}$ was assumed to be linearly proportional to the average number of "spectator" electron-hole pairs N_X that occupy the $1S$ exciton level (with $N_X \leq g_{1S}$, the degeneracy of the $1S$ level):

$$\Delta\alpha_{1S} \propto N_X. \tag{1}$$

In well-passivated colloidal NCs, multi excitons decay nonradiatively by Auger recombination, with characteristic time $\tau_A \sim 100$ ps [20,21], whereas single excitons decay radiatively, with characteristic time $\tau_R \sim 10$ ns. Thus, at time $t = t_\infty$ after photo-excitation (with $\tau_A \ll t_\infty \ll \tau_R$), only one exciton remains in each photo-excited dot. Under the assumption of Eq. (1), it follows that

$$\frac{\Delta\alpha_{1S}(t)}{\Delta\alpha_{1S}(t_\infty)} = N_X(t). \tag{2}$$

Equation (2) allows one to obtain the time evolution of the exciton population, $N_X(t)$, directly from the measured value of the ratio $\Delta\alpha_{1S}(t)/\Delta\alpha_{1S}(t_\infty)$. Since MEG is believed to occur on a very fast time scale (200 fs or less) compared to Auger recombination [4], the value of N_X immediately after photo-excitation provides a direct measure of the number of electron-hole pairs generated by MEG. Equation (2) has been widely used in the literature [4–9] to derive the efficiency of the MEG process as a function of the excitation energy.

While Eqs. (1) and (2) take into account "Pauli-blocking" effects, which describe the reduced availability of final states in optical transitions due to state filling, they neglect carrier-carrier interactions, which are known to shift the energy of the optical transitions and to change their oscillator strength [22,23]. In this work, we critically examine the effects of carrier-carrier interactions on the interpretation of modulation spectroscopy data. Using an atomistic pseudopotential approach, we calculate the dependence of the absorption spectrum of CdSe NCs on the number of spectator electron-hole pairs. Electron-electron, hole-hole, and electron-hole interactions are taken into account in a many-body, configuration-interaction treatment of multiexciton states. We find the following:

(i) $\Delta\alpha_{1S}/\alpha_{1S}$ depends nonlinearly on the exciton population N_X, which suggests that Eq. (1), and consequently Eq. (2), are incorrect. Indeed, the $1S$ absorption peak is already ~80% bleached when a single exciton is present in the dot, whereas the linear assumption of Eq. (1) would predict a 50% bleaching. (ii) As a consequence of this nonlinear dependence, MEG efficiencies obtained from Eq. (2) are significantly underestimated, assuming that the bleaching of the $1S$ absorption peak is solely due to MEG. We also find that (iii) the maximum value of the ratio $\Delta\alpha_{1S}(t)/\Delta\alpha_{1S}(t_\infty)$ that can be attributed to MEG is ~1.3 at low temperature (~ 1.5 at room temperature). Measured values of $\Delta\alpha_{1S}(t)/\Delta\alpha_{1S}(t_\infty)$ in excess of 1.5 cannot be due entirely to MEG, but must originate in part from other bleaching mechanisms.

The calculations were performed using the atomistic many-body pseudopotential method described in Ref. [24]. In this approach, the potential experienced by the electrons in the NC is given by the superposition of screened atomic pseudopotentials, which are fitted to reproduce transition energies, effective masses, deformation potentials, and first-principles wave functions of bulk CdSe [25]. We consider here nearly spherical CdSe NCs having the wurtzite lattice structure. The Cd and Se atoms at the surface of the NC are passivated by ligandlike potentials (centered along the direction of the surface dangling bonds), which act to remove surface-state levels from the band gap. The single-particle energies and wave functions are obtained by solving the Schrödinger equation in a plane-wave basis set, and are then used as input for a many-body configuration-interaction (CI) calculation of the excited states. The excited-state wave functions are expanded as linear combinations of Slater determinant (configurations) obtained by promoting one or more electrons from the valence band to the conduction band. Coulomb and exchange interactions between carriers (holes and electrons) are screened by a distance-dependent and size-dependent dielectric function [24]. The diagonalization of the CI Hamiltonian yields the excited-state energies $\{E_n(N_X)\}$ and wave functions $\{\Psi_n(N_X)\}$ as a function of the number of spectator excitons N_X. The CI basis set used in this work consists of all the configurations constructed from the 32 highest-energy valence states (24 in the case of the triexciton) and the 8 lowest-energy conduction states. The changes in the absorption spectrum due to the presence of spectator excitons are converged to within ~1% with respect to the CI basis set. For example, we find that the low-temperature bleaching of the first absorption peak of a $R = 1.9$ nm CdSe NC in the presence of one exciton (see below) is 75.1% when we use a CI basis set constructed from the four highest-energy valence states and the two lowest-energy conduction states ($n_V = 4$, $n_C = 2$), 76.7% for $n_V = 8$, $n_C = 8$, and 77.0% in the full CI calculation.

Figure 1 shows the calculated low-temperature absorption spectrum of three CdSe NCs, both in the absence ($N_X = 0$) and in the presence ($N_X = 1$ and $N_X = 2$) of

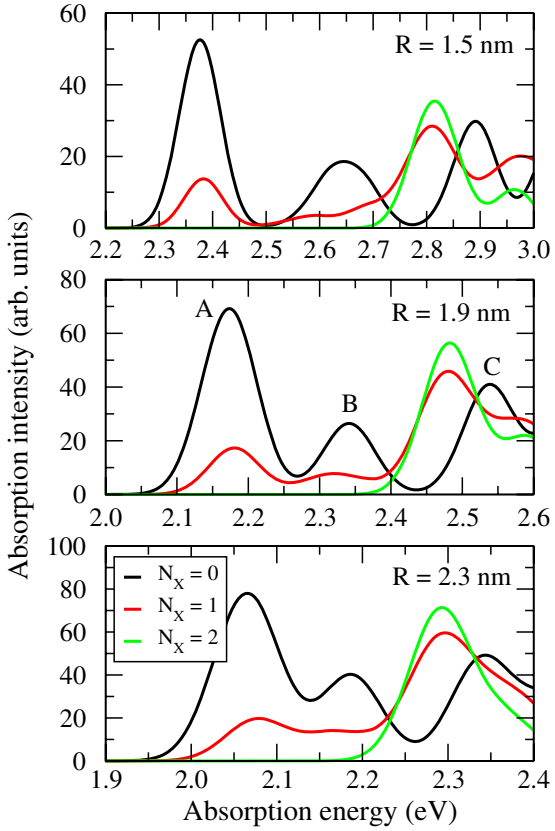

FIG. 1 (color online). Calculated absorption spectra of three CdSe NCs of radius $R = 1.5$, 1.9, and 2.3 nm, for different numbers of spectator excitons: $N_X = 0$, $N_X = 1$, and $N_X = 2$. The optical transitions are broadened by a 50 meV Gaussian convolution function. This broadening is comparable with the experimental inhomogeneous broadening due to size-distribution effects. The three main absorption features are denoted as A, B, and C (middle panel).

spectator excitons. The excitons are assumed to have fully thermalized before absorption occurs. Figure 2 shows a schematic diagram of the optical transitions that contribute to the absorption spectrum of Fig. 1. The linear absorption spectrum ($N_X = 0$) shows three main features, denoted A, B, and C in Fig. 1. Peak A ($1S$ exciton) originates from transitions between the two highest-energy S-like hole levels (S_{h1} and S_{h2} in Fig. 2(a)) and the lowest-energy S-like electron level (S_e). Peak B corresponds to transitions from the next S-like hole level [$2S_h$ in Fig. 2(a)] to the lowest-energy electron level (S_e). Peak C originates from transitions between P-like hole states [P_h in Fig. 2(a)] and P-like electron states (P_e). A detailed discussion of the linear absorption spectrum of CdSe NCs was presented in Ref. [26].

When one or more excitons are loaded into a NC, the energies and intensities of the optical transitions change. We see from Fig. 1 that for $N_X = 1$, the intensity of peaks A and B is significantly attenuated, compared to the case where no spectator excitons are present. For $N_X = 2$, peaks A and B are completely bleached, due to Pauli blocking of

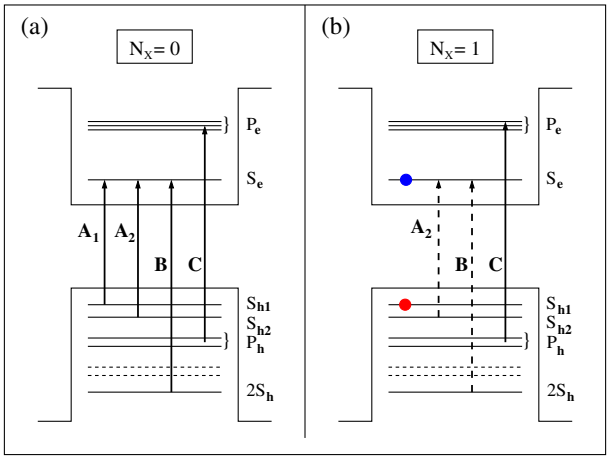

FIG. 2 (color online). Schematic diagram of the interband transitions contributing to the low-energy absorption spectrum of CdSe NCs for (a) $N_X = 0$ and (b) $N_X = 1$. The electron and hole single-particle energy levels are indicated by horizontal lines. Interband absorption transitions are denoted by vertical arrows. Note that in (b), transition A_1 is forbidden, while transitions A_2 and B are attenuated (dashed vertical arrows).

interband transitions that have the lowest-energy electron level (S_e) as their final state [Fig. 2(b)]. Peak C shifts to lower energy (by 50–100 meV, depending on the NC size), but is not bleached by the presence of up to two excitons, because the P_h and P_e levels are unoccupied.

Having established the dependence of the absorption spectrum on N_X, we examine now the consequences of our results for evaluating the MEG efficiency. The effects of spectator excitons on the $1S$ absorption peak are shown in more detail in Fig. 3(a) in the case of a CdSe NC of radius $R = 1.9$ nm. In CdSe NCs with the wurtzite lattice structure, the valence-band levels S_{h1} and S_{h2} are split by crystal-field effects [24,27]. As a result, peak A splits into two subpeaks, denoted A_1 and A_2 in Fig. 3(a) [corresponding to the $S_{h1} \rightarrow S_e$ and $S_{h2} \rightarrow S_e$ transitions in Fig. 2(a)]. When one exciton is present in the NC ($N_X = 1$), peak A_1 is completely bleached (at low temperature), while peak A_2 is strongly attenuated, and is shifted to lower energy. This is a consequence of carrier-carrier Coulomb and exchange interactions. The lowest-energy single-exciton level in CdSe NCs—originating mostly from the (S_{h1}, S_e) configuration—is fourfold degenerate in the absence of electron-hole coupling. This degeneracy is lifted by electron-hole exchange interactions [24,27]. The lowest-energy exciton state is doubly degenerate and has total angular momentum $F = 2$. When an additional electron-hole pair is created by optical absorption, the result is a biexciton. The lowest-energy biexciton state—originating primarily from the (S_{h1}^2, S_e^2) configuration—is a singlet state and has total angular momentum $F = 0$. Thus, the transition $(S_{h1}, S_e) \rightarrow (S_{h1}^2, S_e^2)$ is optically forbidden, which explains why peak A_1 is suppressed in the presence of a spectator exciton [Fig. 3(a)]. The A_2 transition is strongly attenuated when $N_X = 1$ [Fig. 3(a)] because the S_e electron level is partially

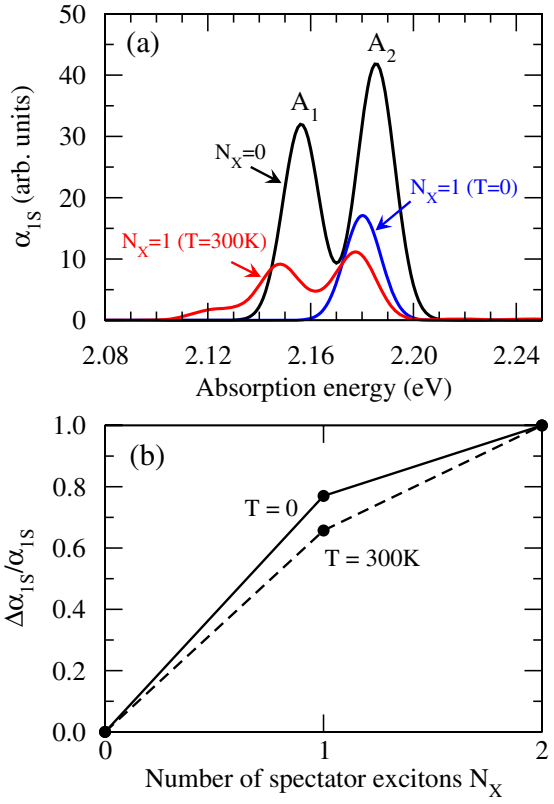

FIG. 3 (color online). Part (a) shows the first absorption peak of an $R = 1.9$ nm CdSe NC, calculated with ($N_X = 1$) and without ($N_X = 0$) a spectator exciton. A 10 meV Gaussian broadening factor was used. Part (b) shows the ratio $\Delta\alpha_{1S}(N_X)/\alpha_{1S}(0)$, calculated for the same NC, as a function of N_X.

occupied. Furthermore, the A_2 transition shifts to lower energy, due to carrier-carrier Coulomb interactions. Note that at room temperature, peak A_1 is partially restored, and there is a buildup of oscillator strength at lower energies [Fig. 3(a)], due to thermal redistribution of the single-exciton occupation factors.

Figure 3(b) shows the dependence of the ratio $\rho(N_X) = \Delta\alpha_{1S}(N_X)/\alpha_{1S}(0)$ on N_X. The ratio $\rho(N_X)$ was calculated by integrating the area of the $1S$ peak ($A_1 + A_2$) in Fig. 3(a), to account for the low experimental energy resolution due to inhomogeneous broadening. Note that $\rho(N_X)$ does not depend on the broadening factor used in the calculations. In previous studies of MEG efficiency, the ratio $\Delta\alpha_{1S}(N_X)/\alpha_{1S}(0)$ was assumed to depend linearly on N_X [see Eq. (1)]. We find instead that $\Delta\alpha_{1S}(N_X)/\alpha_{1S}(0)$ depends nonlinearly on N_X. Indeed, for $N_X = 1$, we obtain $\rho = 0.77$ at $T = 0$, and $\rho = 0.66$ at $T = 300$ K [Fig. 3(b)], versus $\rho = 0.5$ expected from the linear scaling assumption. In general, nonlinear effects are expected to become increasingly significant as N_X approaches the degeneracy number g_{1S}. Interestingly, Schaller *et al.* [4] found that in PbSe NCs, where $g_{1S} = 8$ [18], $\rho(N_X)$ depends nonlinearly on N_X for $N_X > 3$. However, they as-

TABLE I. Calculated ratio $R_{1S}^{\max} = \Delta\alpha_{1S}(2)/\Delta\alpha_{1S}(1)$ at $T \approx 0$ and $T = 300$ K for three CdSe NCs of different size.

Radius (nm)	$R_{1S}^{\max}$ ($T \approx 0$)	$R_{1S}^{\max}$ ($T = 300$ K)
1.5	1.32	1.49
1.9	1.30	1.52
2.3	1.29	1.55

sumed a linear dependence (up to $N_X = 7$) to estimate the number of electron-hole pairs produced by MEG [8].

Since the efficiency of MEG in NCs is often derived from Eq. (2), it is interesting to consider the ratio $R_{1S}^{\max} = \Delta\alpha_{1S}(2)/\Delta\alpha_{1S}(1)$. The maximum number of excitons that can be loaded into the $1S$ exciton level of a CdSe NC is 2, so $R_{1S}^{\max}$ represents the maximum value that the ratio $\Delta\alpha_{1S}(t)/\Delta\alpha_{1S}(t_\infty)$ can have due to MEG. The calculated values of $R_{1S}^{\max}$ are summarized in Table I. We find that $R_{1S}^{\max} \sim 1.3$ at low temperature (~ 1.5 at room temperature), for all of the NC sizes considered here. This result suggests that any measured value of $\Delta\alpha_{1S}(t)/\Delta\alpha_{1S}(t_\infty)$ in excess of 1.5 cannot be attributed entirely to MEG, but must have a different physical origin.

Schaller *et al.* [6,7] reported values of $\Delta\alpha_{1S}(t)/\Delta\alpha_{1S}(t_\infty)$ as large as 1.65 in CdSe NCs of radius $R = 3.2$ nm ($E_g = 2.0$ eV) for excitation energy $\hbar\omega = 3.1E_g$. One possibility is that this value is consistent with our calculated value of $R_{1S}^{\max}$ within the experimental and theoretical error bars, and that the MEG efficiency at $\hbar\omega = 3.1E_g$ is $\geq 200\%$ [28], significantly larger than the value of 165% [6,7] obtained from the linear approximation of Eq. (2). It is also possible, however, that other mechanisms may contribute to the large experimental value of $\Delta\alpha_{1S}(t \sim 0)/\Delta\alpha_{1S}(t_\infty)$ at high excitation energy ($\hbar\omega = 3.1E_g = 6.2$ eV). These mechanisms could be analogous to surface effects affecting the modulation spectroscopy of bulk semiconductors [29]. For instance, a change of surface state occupation, due to excitation of the passivation agents or to transfer of carriers to localized surface states, can induce short-lived changes in the dielectric function, and thus in the absorption spectrum [29].

In addition to transient absorption spectroscopy, time-resolved photoluminescence (PL) has recently been used to evaluate the efficiency of MEG in CdSe NCs, with conflicting results [9,30]. Schaller *et al.* [9] reported agreement between the MEG efficiency evaluated using PL and transient absorption. The PL signal was assumed to depend linearly on the number of excitons. Nair *et al.* [30] reported instead no appreciable MEG in CdSe NCs for excitation energies up to $3.1E_g$. These very different results appear to be related to different sample preparations [13].

In conclusion, we have shown that the bleaching of the absorption spectrum of semiconductor NCs depends nonlinearly on the number of excitons present in the NCs. As a result, current estimates of MEG efficiency in NCs should be revised upwards, if the bleaching is entirely due to MEG. This nonlinearity also mandates an upper bound to the value of the bleaching ratio $\Delta\alpha_{1S}(t)/\Delta\alpha_{1S}(t_\infty)$ that can be attributed to MEG. Experimental observations of bleaching ratios in excess of this maximum value indicate that other mechanisms, besides MEG, are at least partially responsible for the modulation of the absorption spectrum.

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