Efficiency of the coherent biexciton admixture mechanism for multiple exciton generation in InAs nanocrystals

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Abstract
We study the coherent mixing between two-particle (single exciton) and four-particle (biexciton) states of a semiconductor nanocrystal resulting from the Coulomb coupling between states with different numbers of electron-hole pairs. Using a simple model of the nanocrystal wave functions and an envelope function approach, we estimate the efficiency of the multiple exciton generation (MEG) process resulting from such coherent admixture mechanism, including all the relevant states in a very broad energy interval. We show that in a typical ensemble of nanocrystals with an average radius of 3nm, the onset of the MEG process appears about 1 eV above the lower edge of the biexciton density of states. This is due to the angular momentum conservation that imposes selection rules and limits the available MEG pathways, thus taking over the role of momentum conservation that hinders this process in bulk. The efficiency of the MEG process reaches 50% for photon energies around 5 eV. The MEG onset shifts to lower energies and therefore the efficiency increases in a certain energy range as the radius grows. The energy dependence of the MEG efficiency differs considerably between ensembles with small and large inhomogeneity of nanocrystal sizes.

Keywords: semiconductor nanostructures, impact ionization, optical absorption

(Some figures may appear in colour only in the online journal)

1. Introduction

Confining the carriers to a nanometer-scale volume of a semiconductor nanostructure not only leads to qualitative modification of the energy spectrum but also changes the relative role of various kinetic processes that take place in these systems. In particular, it has been proposed [1] that an enhancement of impact ionization processes in nanostructures due to relaxed momentum conservation can be exploited to increase the efficiency of solar cells by enabling multiple exciton generation (MEG) upon absorption of a single high-energy photon. A prerequisite for such a process is the spectral overlap between the confined single-exciton (X) and biexciton (BX) states, which means that the confinement depth must be at least comparable to the band gap. This requirement is satisfied in nanocrystals (NCs) of narrow band semiconductors, hence these systems are the focus of the investigation into nanoscale impact ionization. In spite of the initial controversy concerning the actual efficiency of the MEG process in NCs [2–7], which arises from the experimental difficulty of extracting the real MEG yields [8–10], direct measurements of the photocurrent from nanocrystal-based structures [11, 12] confirm the initial expectation that efficiency enhancement due to the MEG process is feasible. Among many material systems used in the studies of MEG in NCs, InAs shows the favorable features of an energy gap tuneable across the relevant range of the solar spectrum and a particularly small electron-to-hole mass ratio, which makes the impact ionization process energetically possible at the lower edge of the biexciton spectrum [4].

In the single-particle picture, only the transitions leading to the creation of a single electron-hole pair (exciton) are optically active. Therefore, the MEG process requires Coulomb interactions that couple configurations with different...
numbers of excitons. Such inter-band Coulomb couplings are indeed present in semiconductor NCs and can be theoretically computed by various methods [13–24]. In their presence, there are various scenarios that can lead to the MEG effect. For instance, one can think of a sequential process in which the initially created high-energy exciton subsequently decays into the biexciton states that form a quasi-continuum with very high density of states (DOS) at sufficiently high energies. The rates for such a process have been calculated using atomistic methods [13, 14, 16]. On the other hand, biexciton states can be created coherently due to the Coulomb-induced mixing between the X and BX states [25, 26]. In this picture, an admixture of BX states to X states increases the average number of excitons in the resulting few-particle eigenstate, while the admixture of certain X states to BX states can make the latter optically active. As a result, the NC state emerging from a single photon absorption can involve more than one electron-hole pair on average.

In this paper, we estimate the efficiency of MEG resulting from the admixture mechanism in an InAs. We use the method for calculating the Coulomb couplings between X and BX states based on the envelope function \((k \cdot p)\) approach developed in our previous paper [25], which is a low-cost approximate method that allows us to build statistics over many X and BX states in a broad energy window and for a distribution of nanocrystal sizes. The predicted efficiencies are in the range of several up to 50% for photon energies below 5 eV, which is roughly consistent with experimental findings for different material systems [9, 27].

The paper is organized as follows. In section 2, we present the model and the method used to estimate the efficiencies. The results are discussed in section 3. Section 4 concludes the paper.

2. Model and method

We use the simple model of a spherical nanocrystal as in [25]. The carrier states are modeled by single-band wave functions with envelopes corresponding to a simple spherical potential well with infinite barriers, with a constant hole effective mass and a self-consistent, energy-dependent electron mass [25, 28]. Thus, each single particle state is characterized by the band and the three quantum numbers \((n, l, m)\) for the envelope wave function. Two kinds of few-particle configurations are relevant here: The first group are optically active (bright) states with one electron-hole (e-h) pair, referred to as single exciton (X) states. In our model, for such states to be bright (in the sense of a dipole-allowed transition), the quantum numbers \(n, l, m\) of the electron and the hole must be the same, while the values of \(m\) must be opposite. In addition, the band angular momentum (‘spin’) projection of the hole must be specified to fully characterize the state. Only the states with holes from the \(j = 3/2\) valence band can be bright. The second group are states with two e-h pairs, referred to as biexciton (BX) states. These are labeled by the full set of quantum numbers for the two electron and two hole states, as well as the spin (singlet-triplet) configuration of the two electrons and the subband (‘spin’) configuration of the two holes.

Only the diagonal (first order) Coulomb correction to the energies of X and BX states as well as the electron and hole exchange energies for the BX states are taken into account. This is done on the usual mesoscopic level of envelope functions. In addition, the intraband Coulomb coupling (i.e., coupling between configurations with a different number of e-h pairs), which is relevant for the effect to be discussed here, is included. On the mesoscopic level, these Coulomb terms vanish in the single band approximation due to orthogonality of Bloch functions [25, 26], hence they are taken on the microscopic level involving the Bloch functions, in the first order of the expansion in terms of \(a/R\), where \(a\) is the lattice constant and \(R\) is the nanocrystal radius (see [25, 26] for details). All the Coulomb couplings taken into account include both the direct interaction term as well as interaction mediated by surface polarization which is due to the dielectric discontinuity on the nanocrystal border. Here we only include couplings corresponding to the creation of an e-h pair with electron intraband relaxation, with the other hole being a ‘spectator’. The values of all the parameters, corresponding to an InAs nanocrystal, are as in [25]. We choose to model NCs with radii about 3 nm, which lies in the range of sizes documented in the literature [4, 9].

An inhomogeneous ensemble of nanocrystals is modeled by assuming a Gaussian distribution of nanocrystal radii \(f(R)\), with the average \(R_0\) and standard deviation \(\sigma_R\). In practice, the size dependence of the Coulomb couplings is given by a simple \(1/R\) or \(1/R^2\) scaling [25], while the energies have been computed for 7 values of \(R\) in the range \((2.7, 3.3)\) meV and approximated by a quadratic fit, which yields a good quantitative approximation in the required range of nanocrystal radii.

The BX admixture to an X state \(|X_0\rangle\) in a nanocrystal of a given radius is obtained (as in [25]) by diagonalizing the Hamiltonian including only the X state in question and the BX states \(|BX_i\rangle\) directly and sufficiently strongly coupled to \(|X_0\rangle\). The criterium for the selection of these ‘sufficiently strongly coupled’ BX states out of the infinite number of such states is as follows: If \(h_{ji}\) is the magnitude of the coupling matrix element between the two states and \(\Delta E_{ji}\) is the energy separation between them, then a given state BX is included if the ratio \(q_{ji} = |h_{ji}/\Delta E_{ji}|\) is larger than 0.01. Note that \(q_{ji}^2\) is the perturbative measure of the admixture of a given state BX to X. After diagonalization of the Hamiltonian constructed in this way, we select the eigenstate \(|\Psi_{X0}^{(i)}\rangle\) with the highest X contribution as the new nominally single-exciton state and its BX admixture is determined as

\[
x_{BX/X}^{(i)} = \sum_j \left(\langle BX|\Psi_{0}^{(i)}\rangle\right)^2 = 1 - \left|\langle X|\Psi_{0}^{(i)}\rangle\right|^2.
\]

In the calculation of the MEG efficiency as a function of the photon energy, we need the relative absorption by a given state and the resulting number of e-h pairs. For a nominally single-exciton state, the former is proportional to the brightness \(S_j = (1-x_{BX/X})S_0\) of this state, where the nominal
brightness $s_j = 1$ for a heavy-hole exciton and $s_j = 1/3$ for a light-hole exciton. The contribution of this state to the overall absorption of an inhomogeneous ensemble is $f(R)S_j$. On the other hand, its relative contribution to the e-h pair production is $f(R)S_j (1 + x_{\text{BX/X}})$. The bright X admixture to BX states is determined in a similar way. We diagonalize the Hamiltonian containing only the BX state in question (denoted $|\text{BX}_j\rangle$) and all the bright X states $|X_i\rangle$ directly and sufficiently strongly coupled to the BX state (those for which $q \geq 0.01$). We identify the eigenstate $|\Phi^j\rangle$ which has the biggest BX component and treat it as the new, corrected BX state. The single-exciton admixture to this state is equal to

$$x_{X/\text{BX}}^{(j)} = 1 - \left| \langle \text{BX}_{j} | \Phi^{(j)} \rangle \right|^2.$$  

The brightness of the BX states is $S_{j} = \sum x_{X/\text{BX}}^{(j)} s_{j}$, where $x_{j}$ and $s_{j}$ are the admixtures of various X states and their nominal brightness, respectively (in the vast majority of cases, there is only one sufficiently strongly coupled X state). The relative contribution to the absorption is $f(R)S_{j}$ and the relative contribution to the e-h pair production is $f(R)S_{j}(1 + x_{X/\text{BX}})$.  

In practice, since the largest Coulomb couplings found for our model of the nanocrystal with a 3 nm radius are around 40 meV, we include admixed states with energies up to 10 eV (in the whole relevant range of radii) in order to provide quantitatively correct results in the 5 eV energy range of interest.  

We then simulate an inhomogeneous nanocrystal ensemble by sampling the radius distribution at 0.003 nm intervals and compute the dependence of the MEG efficiency on energy as a histogram with the energy axis divided into finite bins of $\delta E = 20$ meV width. In the energy bin $j$ with a central energy $\varepsilon_j$, the total absorption rate is calculated (up to a constant factor) as

$$\alpha_j = \sum_{nj} f(R_{n}) S_{j}(R_{n}) \Theta(\delta E/2 - |\varepsilon_j - E_{j}(R_{n})|),$$  

where $n$ numbers the nanocrystals in the simulated ensemble, $j$ runs through all the X and BX states, $\Theta$ is the Heavyside step function, and we have explicitly written the $R$-dependence of the energy and brightness of the state $j$. The e-h pair production rate is

$$\beta_j = \sum_{nj} f(R_{n}) S_{j}(R_{n}) \left(1 + x_{\text{BX/X}}^{(j)}\right) \Theta(\delta E/2 - |\varepsilon_j - E_{j}(R_{n})|),$$

$$+ \sum_{nj} f(R_{n}) S_{j}(R_{n}) (2 - x_{\text{X/BOX}}^{(j)}) \Theta(\delta E/2 - |\varepsilon_j - E_{j}(R_{n})|),$$  

Where the first sum runs through the X states and the second one through the BX states. The MEG efficiency is then

$$F(\varepsilon_j) = \frac{\beta_j}{\alpha_j} - 1,$$

that is, $F = 1$ corresponds to 100% biexciton generation.

3. Results  

We begin the discussion of the results with an overview of the typical values of X and BX admixtures to the BX and X states, respectively, as well as their dependence on the nanocrystal radius.  

In figure 1(a), (b) we show the BX admixture to a few selected low-energy states (the exact information on the energies is contained in the appendix) as a function of the radius $R$. The value of this admixture remains very low even for states up to 1 eV above the lowest BX state, which is due to selection rules that exclude coupling between excited bright X states and the lowest BX states [25]. The admixture to X states with $\pm 1/2$ hole spin projection is typically slightly higher than to those with $\pm 3/2$ hole spin.

Figure 1(c), (d) presents the BX admixture for selected states with higher energies. In general, much higher values are obtained in this case. The $R$ dependence clearly has a resonant character and peaks for some nanocrystal radii, when the coupled X and BX states cross. As shown in figure 1(c), (d), there is only very weak dependence on the value of the quantum number $m$ and on the hole spin projection in the X state.

Figure 2 shows the admixture of X states to BX states. In most cases, this value does not exceed 0.01, irrespective of the energy of a given BX state (see appendix for detailed information on the states selected for this figure) hence these states remain nearly completely dark. However, as illustrated by the case (3) in figure 2, resonant enhancement of the admixture may happen in the case of a resonance between the chosen BX state and one of the X states. Then, in a relatively narrow peak, the admixture reaches 0.5. In spite of the large

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**Figure 1.** Admixture of BX states to bright X states as a function of the nanocrystal radius. The states are labeled by their quantum numbers $n$, $l$, $m$. Solid (dashed) lines correspond to excitons with the hole spin projections of $\pm 3/2$ and $\pm 1/2$, respectively. In (a,b) selected low-energy states are shown. In (c,d) we show some states of higher energy.
number of states sufficiently strongly coupled to one of the bright states with energy below 5 eV (about 7500 BX states for \( R = 3 \) nm in our model), there are only several tens of such resonances in this energy window.

Finally, figure 3 shows the dependence of the MEG efficiency on the photon energy. In a nearly homogeneous ensemble of nanocrystals (figure 3(a)), the efficiency reaches 1 in certain energy intervals. Comparison with the absorption spectrum shows that this happens only for energies where absorption is nearly absent. Clearly, the reason for such an efficient biexciton generation is the discrete nature of the single exciton DOS; in a weakly inhomogeneous ensemble there are extended energy intervals where no bright single exciton states are present so that all the absorption originates from the quasi-continuous background of nearly purely biexcitonic states.

This picture is different in an ensemble of nanocrystals with a broader size distribution (figure 3(b)). Now both the absorption and the MEG efficiency become quasi-smooth functions of the photon energy and both grow nearly monotonically. The onset of the MEG (the MEG threshold) is clearly marked at 3.5 eV, which should be contrasted with the nominal onset of the BX DOS at \( \sim 2.5 \) eV for \( R = 3 \) nm. This shift of the MEG onset to energies considerably higher than the lower edge of the BX spectrum is due to the selection rules imposed by angular momentum conservation [25], which exclude the Coulomb coupling to the lowest BX states. This shows that the momentum conservation, that was supposed to restrict the impact ionization in bulk materials and was expected to be overcome in NCs, reappears in the form of angular momentum conservation and again adversely affects the impact ionization process. This contradicts the original expectations based solely on energy conservation and predicting MEG onset at the BX DOS edge for systems with a small electron-to-hole mass ratio [4].

The evolution of the energy dependence of the MEG efficiency with increasing inhomogeneity is shown in more detail in figure 3(c). Here one can see that already at \( \sigma = 0.04 \) nm the overlap of the inhomogeneously broadened absorption peak is sufficient to suppress the large values of the efficiency, leaving only a few marked maxima. These MEG efficiency peaks are then washed out as the inhomogeneity grows further.

In figure 3(d) we show the MEG efficiency for three ensembles with different average nanocrystal radii. The two features that can be noticed are a shift of the MEG threshold towards lower energies and larger overall values of the MEG efficiency for larger nanocrystals. The former follows rather trivially from the increasing confinement volume that shifts the onset of the BX DOS down, bringing also the coupled BX states to lower energies. This is consistent with the experimental evidence and theoretical calculations (although for a different material) [29] which show the MEG onset in bulk shifted towards lower energies as compared to NCs. The latter is a consequence of the down-shifted threshold in the MEG onset area around 4 eV photon energy. For larger energies, it may be a coincidence resulting from the shifts in the maxima and minima of the efficiency. With our method, we are not able to study larger NCs due to the growing numerical cost. In particular, we cannot reach the transition between the confined and bulk regimes, where the momentum conservation should emerge (this is also precluded by our choice of boundary conditions, appropriate for spherically symmetric systems, but not for bulk). An interesting point is, nevertheless, that the density of confined BX states scales as \( R^2 \), while the Coulomb couplings responsible for the X-BX mixing decrease as \( 1/R^2 \); hence the two effects tend to cancel and the position of the MEG onset may indeed be the dominating factor.

4. Conclusions

We have estimated the quantum efficiency of the multiple exciton generation via coherent, Coulomb-induced mixing of bright exciton and biexciton states. Although the mixing is, in general, rather weak due to small values of the Coulomb coupling elements (not exceeding a few tens of meV), it can
become much stronger near the crossing point between the X and BX energies at particular values of the nanocrystal radius. The relatively low computational cost of the envelope function method used in our calculations has allowed us to include all the relevant states in a 10 eV energy window.

An interesting property that emerges from our calculations is the high MEG yield in the energy intervals where the single exciton DOS vanishes in a weakly inhomogeneous ensemble. Although this result has been obtained in our simple model of nanocrystal wave functions, it essentially follows from the discrete nature of single-exciton spectrum for moderate energies and the much more dense, quasi-continuous spectrum of biexciton states. Therefore, it should be a general feature of highly homogeneous nanocrystal ensembles. Whether this can be exploited in applications depends on the technological feasibility of building a structure in which the very weak absorption of biexciton states is accumulated to yield a considerable overall carrier injection.

In contrast, for less homogeneous nanocrystal ensembles, both the absorption and MEG efficiency are smooth functions of the photon energy, with a threshold at about 3.5 eV for nanocrystals with 3 nm radius, which is 1 eV above the formal onset of the biexciton DOS. This shift, which contradicts the general expectation for a system with a very small electron-to-hole mass ratio, results from the angular momentum selection rules for impact ionization in a spherical NC. The threshold shifts to lower energies for larger nanocrystals. The efficiencies of the MEG process reach 50% for the photon energies about 5 eV and average radius of 3.0 nm and increase for larger nanocrystals, mostly due to the downshift of the lower edge of the BX DOS which shifts also the MEG threshold.

While we have chosen the InAs material system for our study, the quantitative features of our results follow to a large extent from the discrete spectrum of confined carriers and from the existence of angular momentum selection rules. Hence, they should hold generally. We would expect that for materials with a band structure like InAs (hence the same selection rules) also quantitative results will be similar up to some energy shifts and some modification of the particular values. The latter, however, cannot be easily predicted in detail for a different material, since the interplay of the Coulomb coupling strength and density of X and BX states is hard to capture in terms of a simple dependence on dielectric constants and carrier masses even for a simple model of carrier states.

Appendix A. Information on the states used in the figures

In this appendix we present the detailed information about the states shown in figure 1 and figure 2.

Table A1. Energies of single exciton states for three values of the nanocrystal radius.

| state | energy (eV) |
|-------|-------------|
| n l R | 2.4 nm | 3.0 nm | 3.6 nm |
| 1 0 | 1.59 | 1.30 | 1.11 |
| 1 1 | 2.34 | 1.86 | 1.57 |
| 1 2 | 3.11 | 2.45 | 2.03 |
| 1 3 | 3.92 | 3.05 | 2.51 |
| 1 4 | 4.77 | 3.67 | 3.00 |
| 1 5 | 5.66 | 4.32 | 3.52 |
| 2 0 | 3.41 | 2.67 | 2.21 |
| 2 1 | 4.39 | 3.39 | 2.78 |
| 2 2 | 5.41 | 4.14 | 3.37 |
| 2 3 | 6.47 | 4.91 | 3.97 |
| 3 0 | 5.66 | 4.31 | 3.50 |

Table A2. Quantum numbers, spin configurations, and energies of biexciton states used in figure 2. Labels (1)–(5) refer to that figure.

| state | energy (eV) |
|-------|-------------|
| e e h h ΣΣ | 2.4 nm | 3.0 nm | 3.6 nm |
| (1) 100 100 211 200 S T(3/2)5 | 4.66 | 3.56 | 2.92 |
| (2) 111 100 210 110 T d S(1/2)5 | 4.87 | 3.87 | 3.13 |
| (3) 100 100 151 141 S S(1/2)4 | 5.78 | 4.31 | 3.47 |
| (4) 210 100 211 110 S T(3/2)5 | 6.21 | 4.84 | 4.01 |
| (5) 121 100 230 122 T0 S | 6.55 | 4.96 | 4.02 |

bright states are those with identical quantum numbers n, l for the electron and the hole (shown in the leftmost columns). Shifts induced by mixing with different BX states lead to differences between the energies of X states with different values of m as well as between states with different projections of the hole spin. However, these differences are very small, within 10 meV, hence we show only the energies of the state with 3/2 hole spin projection and m = 0.

Table A2 shows the full data on the states presented in figure 2. Here the first four columns contain the quantum numbers nlm for the two electrons and the two holes (negative values of m are denoted by a bar over the number) and the next two columns show the spin configurations: For the electron, this is just singlet (S) or one of the three triplet states (T(3/2)k) with the total spin projection 0 or ±1. For two-hole states with both holes with ±3/2 or with both holes with ±1/2 spin projection, the basis configurations are also singlet or triplet, with the additional upper index (3/2) or (1/2), respectively. In addition, configurations in which one hole has a 1/2 spin projection and the other one has 3/2 spin projection appear in our calculations. For these, we introduce the symmetrized and antisymmetrized spin states, denoted S(1/2)↑↓, A(1/2)↑↓, etc, where thin and thick arrows correspond to hole states with the angular momentum projection 1/2 and 3/2, respectively. The final three columns show the energies of the state for three radii of a nanocrystal, as in the previous table.
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