Multiple excitons and the electron–phonon bottleneck in semiconductor quantum dots: An \textit{ab initio} perspective

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Abstract

The article presents the current perspective on the nature of photoexcited states in semiconductor quantum dots (QDs). The focus is on multiple excitons and photo-induced electron–phonon dynamics in PbSe and CdSe QDs, and the advocated view is rooted in the results of \textit{ab initio} studies in both energy and time domains. As a new type of material, semiconductor QDs represent the borderline between chemistry and physics, exhibiting both molecular and bulk-like properties. Similar to atoms and molecules, the electronic spectra of QD show discrete bands. Just as bulk semiconductors, QDs comprise multiple copies of the elementary unit cell, and are characterized by valence and conduction bands. The electron–phonon coupling in QDs is weaker than in molecules, but stronger than in bulk semiconductors. Unlike either material, the QD properties can be tuned continuously by changing QD size and shape. The molecular and bulk points of view often lead to contradicting conclusions. For example, the molecular view suggests that the excitations in QDs should exhibit strong electron-correlation (excitonic) effects, and that the electron–phonon relaxation should be slow due to the discrete nature of the optical bands and the mismatch of the electronic energy gaps with vibrational frequencies. In contrast, a finite-size limit of bulk properties indicates that the kinetic energy of quantum confinement should be significantly greater than excitonic effects and that the electron–phonon relaxation inside the quasi-continuous bands should be efficient. Such qualitative differences have generated heated discussions in the literature. The great potential of QDs for a variety of applications, including photovoltaics, spintronics, lasers, light-emitting diodes, and field-effect transistors makes it crucial to settle the debates. By synthesizing different viewpoints and presenting a unified atomistic picture of the excited state processes, our \textit{ab initio} analysis clarifies the controversies regarding the phonon bottleneck and the generation of multiple excitons in semiconductor QDs. Both the electron–hole and charge-phonon interactions are strong and, therefore, optical excitations can directly generate multiple excitons, while the electron–phonon relaxation exhibits no bottlenecks, except at low excitation energies and in very small QDs.

1. Introduction

Inorganic semiconductor crystals reduced to a nanometer size represent a novel material with a variety of unique optical, electrical and mechanical properties that can be controlled not only by the type of material, but also by the size, shape and topology of the nanocrystal [1]. Many of the new or enhanced physical processes taking place in the nanocrystals are brought about by the quantum-mechanical confinement of the electronic and vibrational wave-functions to (quasi-)zero dimensions, motivating the name – quantum dots (QDs). Examples of interesting and significant physics include carrier multiplication [2–6], Coulomb [7] and spin [8] blockades, high fluorescence yields [9] and optical gains [10], the Kondo effect [11], electron [12] and nuclear [13] spin switching, etc. QDs show great promises in such areas as photovoltaics [2–6,14], spintronics [15,16], and quantum computing [17]. QDs have been used to make lasers [18], field-effect transistors [19], light-emitting diodes [20], quantum emitter antennas [21], fluorescent biological imaging probes [22] and thermopower devices [23].

The QD response to the external perturbations that are used to activate and utilize the QD properties depends on the details of the excitation, charge, spin and phonon dynamics, which are intimately intertwined and cover a range of timescales and mechanisms. In particular, the phonon-mediated relaxation of electronic excitations in semiconductor QDs is ubiquitous and plays a crucial role in a variety of applications. For example, the efficiencies of QD lasers [18] and photovoltaic devices [2–6,14], depend on the electron–phonon relaxation rates. QD applications in quantum information processing [15] are limited by the phonon-induced dephasing of electron [24] and spin [16,25] states. The electron–phonon interactions define the linewidths in the QD optical spectra [9,24]. Inelastic electron–phonon scattering affects electron
unnelling through QDs and is responsible for the transport blockade and energy loss [7]. The electron–phonon dynamics remains the focus of many experimental [2–7,14–18,26–30] and theoretical [3,7,24,30–40] studies. While a variety of time-resolved experimental techniques are extensively used to probe the intricate dynamical features [2–6,9,14–18,26–30], most of the theoretical approaches focus on the QD structure and spectra [3,7,30–36,40] and relatively few efforts are devoted to the direct time-domain modeling [24,37–39] of the experimental data.

Generation of multiple excitons (MEs) upon absorption of only a single photon, a process that is also known as carrier multiplication, is one of the most remarkable features of semiconductor QDs [2–6,14]. In bulk semiconductors, the probability of this process is low due to the strict selection rules operational in a periodic system and weak electron–hole Coulomb interaction. A molecule is usually too small to support a ME in an interesting energy range and would be chemically unstable if such a state were created. MEs could be extremely valuable for solar energy harvesting. In a typical photovoltaic material, the higher energy excitations created by photons at the blue end of the solar spectrum rapidly relax to the lowest excited state at the red end of the spectrum by coupling to phonons. Significant amounts of solar energy are thus lost to heat, limiting the maximum thermodynamic efficiency of a solar cell to 32% [14]. If the energy lost to heat could instead be used to generate multiple charge carriers, the efficiency could be greatly increased. MEs were discovered in lead salts [2,3,5], followed by observation in other materials, including CdSe [4] and even Si [6], which is the most widely used solar cell material. The search for MEs was initially motivated by the phonon bottleneck hypothesis [14], arguing that in QDs of decreasing size, the electron–phonon relaxation should dramatically slow down due to a mismatch between the vibrational quanta and electronic energy gaps. A slower relaxation would allow for other processes to occur, and for the creation of MEs in particular. Surprisingly, the phonon bottleneck was not observed [27–29] in the QDs that exhibit MEs. This apparent paradox between the existence of MEs and the absence of the phonon bottleneck can be rationalized by the results of the recent energy and time domain ab initio studies of the electronic excitations and electron–phonon dynamics in PbSe and CdSe QDs [24,37–40].

This Article is constructed in the following order. After a review of the key processes that occur in semiconductor QDs upon photon absorption, the electron–phonon relaxation and the phonon bottleneck hypothesis are analyzed in detail. Then, the photoexcited states of semiconductor QDs are closely examined, and the proposed mechanisms for the generation of MEs are discussed. The nature of the photoexcited electronic state and its coupling to phonons are considered simultaneously. The paper concludes with a summary and outlook for future research directions.

2. Photoinduced electronic processes in semiconductor quantum dots

Electronic photoexcitation of a semiconductor QD gives rise to complicated dynamics which involve both electronic and vibrational degrees of freedom. The key processes of interest to the current discussion are presented schematically in Fig. 1 using the single-particle electron–hole representation. Initially in the ground electronic state, the QD absorbs a high-energy photon, which creates an electron–hole pair. This high-energy exciton relaxes to a low-energy exciton by electron–phonon coupling and releases the extra electronic energy into heat. The relaxation in PbSe and CdSe QDs occurs on pico- and subpicosecond timescales [27–29]. The lowest energy exciton lives for a long time, ca. nanoseconds, since the nonradiative relaxation to the ground state is prevented by a substantial mismatch between the fundamental electronic energy gap and the phonon frequencies. The ground state is recovered by fluorescence. The emitted photon energy is significantly lower than the energy of the absorbed photon.

Alternatively, the absorbed photon can generate a bie exciton, i.e. a doubly excited state involving two electron–hole pairs. Bieexcitons can be created either directly from the ground state or by populating the high-energy exciton first. Both scenarios require strong electron–hole Coulomb interaction, i.e. strong electron–correlation in the quantum-chemistry language. Electron–correlation complicates the single-particle representation. Additionally, a photon can excite a superposition of the high-energy exciton and bie exciton. In all cases, the bie exciton is created as coherent quantum state, which has to dissociate into two uncorrelated low-energy excitons that fluoresce sequentially, as observed in the experiments [2–6]. The dissociation of the coherent bie exciton can occur by dephasing via coupling to phonons. The specific details of the QD electronic structure and the excitonic nature of the photoexcited states depend strongly on the type of the semiconductor and differ significantly for PbSe and CdSe QDs.

In addition to the processes depicted in Fig. 1, one can observe Auger phenomena, in which electrons and holes exchange the excitation energy. The Auger channels can speed up the electron–phonon relaxation in such materials as CdSe, in which the valence band (VB) manifold of states is denser than the conduction band (CB) manifold and, as a result, holes relax faster than electrons [26]. Surface defects due to unsaturated dangling bonds and missing atoms, as well as electronic states localized on the ligands used to passivate the surface, can promote charge transfer from the QD core to the surface, e.g. hole trapping. This process can be responsible for the QD fluorescence blinking [41], since a charge separated state does not emit light.
3. Electron–phonon relaxation and the phonon bottleneck

The first prediction of the slowed electron–phonon relaxation in quantized structures, known as the phonon bottleneck, was made by Nozik and co-workers [42]. It was assumed that the electron and hole cooling requires multiphonon processes when the quantized electronic levels are separated by more than a phonon energy $h\nu$. The multiphonon cooling time was estimated as $\tau_c \sim \omega^{-1} \exp(\Delta E/kT)$, where $\omega$ is the phonon frequency and $\Delta E$ is the energy separation between the quantized levels. More complete models for the slowed electron–phonon relaxation in semiconductor QDs have subsequently been proposed [43,44].

3.1. The controversial experimental results

Extensive experimental investigations of the relaxation dynamics of the photogenerated charge carriers in QDs have produced controversial results. Many reports both support [45–53] and contradict [27–29,54–59] the existence of a phonon bottleneck. A number of groups have investigated QDs created with III–V semiconductor materials, such as GaAs, InAs and InP, and reported slowed charge-carrier cooling due to the QD quantization effects [45–48]. Relaxation of both hot electrons [45–47] and holes [48] was considerably slowed down relative to the bulk materials. The studies of QDs of the II–VI type, CdSe in particular, found two relaxation time scales, whose relative weights depended upon the molecules capping the QDs [29,49–53]. A phonon bottleneck was observed similar to the III–V QDs. In addition, a new, faster relaxation component was found and attributed to the Auger mechanism for electron relaxation, whereby the excess electron energy is transferred to a hole, which then relaxes rapidly through its dense spectrum of states. If the hole is removed and trapped by the molecules capping the QD surface, the Auger mechanism for the hot electron relaxation is inhibited, and the overall relaxation time increases. In contradiction, many investigations exist in the literature wherein a phonon bottleneck was not observed. These results were reported for both III–V QDs [54,55] and II–VI QDs [56,57]. In some cases [58,59] hot-electron relaxation was found to be slowed, but not sufficiently to enable the authors to conclude that this was evidence for a phonon bottleneck.

Recent studies of lead salt [27,28] and CdSe [29] QDs showed ultrafast electron relaxation on picosecond timescales. Not only was the phonon bottleneck not observed, but also the relaxation rate grew with decreasing dot size. Having rather unique electronic properties [60], including the nearly symmetric VB and CB as well as weak surface effects, lead salt QDs, such as PbS and PbSe, exclude the relaxation channels associated with the Auger-type electron–hole energy transfer and the hole trapping at the surface seen, for instance, with CdSe [26]. Therefore, lead salts are perfectly suited for studies of the electron–phonon relaxation. The effective masses of electrons and holes in lead salts are not only similar, they are also small, promising strong quantum confinement effects [60] and inducing quantization of bulk electronic bands. The bulk PbSe exciton localization length equals 46 nm, and PbSe crystals with diameters smaller than this number are in the quantum confinement regime. In these experiments, it is customary to study dots a few nanometers in size.

3.2. Time-domain ab initio results for PbSe quantum dots

In order to model the electron–phonon relaxation in PbSe QDs, we performed [38] time-domain ab initio simulations, which combined time-domain density functional theory with non-adiabatic molecular dynamics. The details of this state-of-the-art technique can be found in Refs. [61–63]. The study showed that the phonon bottleneck exists only at low energies and in very small QDs. As expected based on the similarity between the VB and CB, the relaxation was nearly symmetric with respect to the band-gap. The absence of the phonon bottleneck at the higher energies was explained by the high densities of electron and hole states. While not all states were optically active due to strong optical selection rules, most of them facilitated the phonon-induced relaxation. Phonons of proper symmetry could be found to couple essentially every pair of electronic states.

Fig. 2 shows a 32 atom PbSe nanocrystal 1 nm in diameter. This small QD preserves the PbSe bulk topology, however, notable structural relaxation is observed compared to the ideal periodic bulk structure. The electron densities of the four vacant orbitals closest to the edge of the CB are also shown in Fig. 2. The density envelopes exhibit roughly S- and P-symmetries, which are significantly modified by the local atomic structure. This agrees with the effective mass theory [32,33], which represents the electron and hole wavefunctions as products of Bloch functions that vary on the atomic level and S-, P-, D-, etc. envelope functions that encompass the whole QD and are eigenstates of particle in a spherical well. The S- and P-symmetries of the corresponding hole states at the edge of the VB are less pronounced.

The evolution of the density of states (DOS) of the 32 atom PbSe QD is presented in Fig. 3a over a 3.5 ps time interval. The z-axis gives the state density as a function of energy and time. The shape of the calculated DOS follows the experimental data [27,28]. The three main peaks on each side of the gap can be attributed to the expected $S_x (S_h), P_x (P_h),$ and $D_z (D_h)$ levels of electrons (holes). The separation of the S-state from the main manifold is more pronounced with the electrons than the holes, the latter having a slightly higher DOS. The difference in the electron and hole DOS for PbSe QDs is not nearly as dramatic as, for instance, for CdSe QDs [26,30], as illustrated below. The arrows in Fig. 3a show the energies of the electron and hole excitations, which match three times the QD energy gap in correspondence with experiment [2]. The similarity in the electron and hole state structure results in the selection rules that favor symmetric photoexcitations across the gap [60].

The electron–phonon relaxation dynamics that follow the initial photoexcitation indicated by the arrows in Fig. 3a are shown in Fig. 3b. The figure presents a three-dimensional plot of the product of DOS and the state occupations as a function of energy and time. The carriers visit multiple states during the relaxation, but none of the intermediate states play any special role. Comparison of the DOS in Fig. 3a with the population dynamics in Fig. 3b, shows for both electrons and holes that the initial photoexcitation peaks vanish and reappear at the gap states. The holes decay slightly faster than the electrons due to the higher DOS.
than the electrons, due to their higher DOS. The relaxation is complete within a picosecond. However, while the holes decay all the way to the band-gap state, the electronic population at 1 ps is localized primarily within the P-state manifold. The relaxation to the lowest energy S-state occurs significantly slower. This final stage of the electron relaxation could be interpreted as the phonon bottleneck. However, most of the photoexcitation energy is lost very rapidly, showing no evidence of the bottleneck, in agreement with the experiments [27,28].

Analysis of the phonon modes that induce the relaxation of the charge carriers to the edges of their bands shows that spheroidal acoustic phonons [60] with frequencies around 100 cm\(^{-1}\) and below dominate both electron and hole dynamics. The longitudinal optical modes with frequencies around 200 cm\(^{-1}\) and above are also important, but to a lesser extent. The electron–phonon coupling involving the acoustic modes is strong, because these modes modulate the QD size and shape, changing the electronic energies and wavefunctions. The changes in the electronic properties induced by the optical modes, which involve local atomic displacements, tend to average out. The majority of the electronic transitions result in exchange of energy that exceeds the energy of a single phonon, indicating that the charge-phonon relaxation in the PbSe QDs can occur via the multi-phonon mechanism [27,28].

The more recent simulations of the electron–phonon relaxation in larger PbSe QDs and CdSe QDs [64] produce results that are qualitatively similar to the data discussed above.

3.3. Atomistic vs. effective mass descriptions

How can one explain the absence of the phonon bottleneck in the relaxation of the high-energy excitations in the PbSe QDs? It can be easily rationalized by considering the QD optical spectra, as described at the atomistic level. Fig. 4 presents the optical absorption spectra of the 32 and 136 atom PbSe QDs with 1 and 1.5 nm diameters, respectively. The vertical lines show the energies and oscillator strengths of individual electron–hole excitations, while the thick continuous lines show the spectra.

![Fig. 4. Electronic absorption spectra of the Pb16Se16 and Pb68Se68 QDs. The three lowest energy bands can be characterized as S–S, S–P and P–P transitions based on the electron and hole wave-function symmetries. The atomistic calculations show that each band arises due to multiple excitations of varying intensity, as indicated by the heights of the vertical lines. Only in very small QDs and at low energies are the excited states separated by large gaps. At high energies relevant for the generation of MEs, the gaps between the states are small, rationalizing the absence of the phonon bottleneck.](image-url)
accounting for finite widths of the individual excitations. The spectra exhibit distinct bands, which are observed experimentally [27,28,60] and are predicted by the effective mass theory [3,32,33]. The strongest peaks correspond to symmetric transitions between S–S, P–P, etc. states of holes and electrons as expected based on the optical selection rules. The slight asymmetry in the electron and hole DOS, Fig. 3a, is sufficient to allow asymmetric transitions, e.g. S–P [65].

The fact that each optical band is composed of many individual excitations constitutes the key insight provided by the atomistic description [38] and rationalizes the absence of the phonon bottleneck. The spacing between the excited state energies is very small, except for the first few excitations. While the optical absorption spectrum indeed shows discrete bands that can be attributed to S–S, P–P, etc. transitions between the hole and electron states, as described in the effective mass theory [3,32,33], each band is composed of multiple excitations between pairs of hole and electron states. There is no contradiction between the effective mass and \textit{ab initio} results. The optical selection rules, which are clearly defined in the effective mass approach, are also seen in the \textit{ab initio} calculation, in which most of the states are weakly optically active. In contrast to the optical selection rules, which are determined by the \( x, y \) and \( z \) components of light-polarization, the electron–phonon coupling selection rules are much more relaxed. Multiple phonons of various symmetries couple most of the electronic states, facilitating the non-radiative relaxation. While not all electronic states are equally optically active, the majority of them take part in the relaxation.

The deviations from the idealized \( S, P, \) etc. state description occur, since QDs are not perfect spheres. The underlying crystal structure, geometry relaxation, surface effects and thermal atomic fluctuations all together are responsible for lifting the ideal state degeneracy. Consider the following order of magnitude estimate. The Pb and Se atoms contain 14 and 6 valence electrons, respectively, averaging 10 per atom. A typical PbSe QD contains on the order of 1000 atoms and, therefore, 10000 valence electrons. Assuming that the valence and conduction bands are 10 eV wide in energy, an average spacing between the states is on the order of 0.001 eV. To produce energy gaps of 0.1 eV seen in the optical spectra, the states must be 100-fold degenerate on the average. These are single-particle electron and hole states. The number of two-particle electron–hole excitations is \((10000)^2 = 10^9\). The degeneracy of the two-particle excitations must be enormous in order to create large energy gaps. Thermal atomic motion with energy of \( k_B T = 0.025 \) eV at room temperature alone will lift the degeneracy.

Even though the electron–phonon relaxation in QDs occurs on a picosecond timescale, as measured experimentally [27–29] and calculated by the time-domain \textit{ab initio} approach [38], and no bottleneck is observed, the relaxation is nevertheless slower than the generation of MEs, with the measured upper bound of 250 fs [3,4]. In order to understand the mechanisms for creating MEs in the semiconductor QDs, we first discuss the nature of the optically excited state in PbSe and CdSe QDs in more detail, using a sophisticated quantum-chemical approach describing the electron-correlation (excitonic) effects with a high level of accuracy [40,66].

4. The nature of the electronically excited states in semiconductor quantum dots

Characterizing the excited states in the semiconductor QDs as single or MEs requires a proper single-particle description and a rigorous account of the electron–hole Coulomb interaction. The non-interacting single-particle picture is provided by the Hartree–Fock approximation, which excludes electron-correlation effects altogether. The electron–hole interaction is treated by the symmetry adapted cluster (SAC) theory with configuration interaction (CI) [66]. SAC-CI starts with the Hartree–Fock description and explicitly includes the electron-correlation (excitonic) effects through the cluster expansion of the ground state wave function. High-order excitation operators are applied to the correlated ground state. The method goes beyond single excitations, up to six-tuples, thereby allowing us to qualify the excited states as single or MEs [40].

First, consider small PbSe and CdSe clusters, which do preserve the bulk topologies and which can be treated at the SAC-CI level. The SAC-CI spectra for the PbSe\(_4\) and CdSe\(_4\) QDs are shown in Fig. 5. Because of the lower symmetry, CdSe\(_4\) shows a more complex spectrum with a greater number of allowed transitions. The spectrum agrees with the experimental data [67]. The SAC-CI approach provides detailed information on the nature of the photo-excited states, characterizing the excitation as one-electron, two-electron, etc. Fig. 6 shows the fraction of multi-electron excitations as a function of excitation energy. At low energies, the excited states of both PbSe and CdSe are single excitons. A sharp qualitative transformation in the nature of the electronic excitations is seen in both materials at an energy 2.5–3 times the first excitation energy. Above this threshold, the excited states become predominantly

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**Fig. 5.** Electronic spectra of the PbSe\(_4\) and CdSe\(_4\) QD clusters calculated at a high \textit{ab initio} level, fully including the Coulomb electron–hole interaction. The data for CdSe\(_4\) are in agreement with the available experimental measurements [67]. Both spectra show appreciable intensity at energies above 8 eV, corresponding to double excitons (see Fig. 6). MEs become optically allowed due to strong interaction between electrons and holes in the quantum confinement regime. The result indicates that MEs can be created directly upon absorption of a single photon.

**Fig. 6.** The contribution of double excitons to the excited electronic states of the PbSe\(_4\) and CdSe\(_4\) QD clusters. Double excitons appear sharply at energies about 3-times the lowest excitation energy. Above the threshold, practically all PbSe states are MEs, while CdSe shows single excitons, MEs and their superpositions. The fact that most PbSe states above the threshold are MEs rationalizes why ME were first observed in this specific material [2,3]. In general, the high-energy excited states should exhibit mixed character, as represented by CdSe. Thus, all three mechanisms proposed for the generation of MEs, including the impact ionization [14,36], dephasing [3] and direct [4,40] process, should function in parallel in the majority of semiconductor QDs.
MEs. This key result indicates that ME states can be excited directly. The direct photogeneration of MEs rationalizes why MEs can be observed nearly instantaneously [3,4] and why the electron–phonon relaxation bottleneck [14,27–29] is not required in order to create MEs. Examination of the ME contributions to the high-energy excitations shows an important difference between the PbSe and CdSe QDs. Almost all highly excited states of PbSe are MEs. That is why MEs were first discovered in this type of QD [2]. In contrast, CdSe exhibits a mixture of single excitons, MEs and superpositions of single and MEs.

The origin of the sharp transition from single to MEs seen in Fig. 6 with both PbSe and CdSe QDs, as well as the qualitative difference between the two materials, can be understood by considering the non-interacting particle DOS provided by the Hartree–Fock approximation. Fig. 7 shows the single-particle DOS for the 8, 136 and 360 atom PbSe QDs, and the 12, 66 and 222 atom CdSe QDs. The band structure of the PbSe QDs is significantly more symmetric than that of the CdSe QDs. This approximate mirror symmetry between the CB and VB of PbSe QDs is significantly more symmetric than that of the CdSe QDs. This approximate mirror symmetry between the CB and VB of PbSe QDs is predicted by the effective mass band theory, which assigns similar masses to electrons and holes in lead salts [3]. In contrast, CdSe QDs have strongly asymmetric bands, with the holes about six times heavier than electrons.

Inspection of the DOS shown in Fig. 7 leads to the following important observations. First, the single-particle energy gaps are significantly greater, by a factor of 3, than the excitation energies computed by SAC-CI (Fig. 5) indicating that the electron-correlation effects are very important in small QDs [31,68]. Second, the small QDs provide a good representation of the DOS of the large QDs, so that the conclusions derived above for the small dots based on the SAC-CI calculations should also hold for the large dots. Third, the PbSe DOS contains secondary gaps for both electrons and holes, denoted by $E_{\text{CAP}}$ in Fig. 7. No such gaps exist in the CdSe DOS.

Why are the high-energy states for PbSe dominated by MEs, while CdSe exhibits a mixture of single and multiple excitons at high energies, as shown in Fig. 6? With a continuum of electron and hole states, higher energy single excitons should occur at the same energies as MEs. This indeed happens in CdSe. In PbSe, however, double excitons start and single excitons stop precisely in the energy gap seen in both the VB and CB, labeled by $E_{\text{CAP}}$ in Fig. 7. At higher excitation energies, which are well beyond the considered energy window, single excitations into the available states beyond $E_{\text{CAP}}$ become possible. At these higher energies, the single and MEs will presumably be excited in PbSe in tandem, as found for CdSe. In general, based on the high symmetry of the PbSe band structure shown in Fig. 7, one can expect that the superpositions of single and MEs in which the fraction of multiple excitations in Fig. 6 is between 0 and 1, will occur less frequently in PbSe than in CdSe.

### 5. Proposed mechanisms for the generation of multiple excitons

The ab initio analysis of the electronically excited states in the semiconductor QDs allows us to assess critically the proposed alternative mechanisms for ME generation [3,4,14,36]. Different proposals echo the rapidly changing views on MEs and the phonon bottleneck, and reflect the variety in the electronic structure of the materials exhibiting MEs. The ab initio electronic structure calculations [40] discussed above show three types of photoexcited states in the semiconductor QDs, suggesting that three different mechanisms can be responsible for the ultrafast generation of MEs, a distinct mechanism for each type of the photoexcited state.

#### 5.1. The impact ionization process

As in bulk materials, MEs in QDs can be created by an incoherent Coulomb scattering mechanism, in which a high-energy carrier relaxes to its ground state and excites valence electrons across the band-gap, producing additional electron–hole pairs. The effect is known as impact ionization (II) [14,36], which is the inverse of the Auger recombination, and is seen in other quantum confinement materials, such as carbon nanotubes [69]. Recent atomistic pseudopotential calculations [36] were used to argue that the conventional II mechanism can explain both the low-energy thresholds and the ultrafast ME generation rates.

The efficiency of II in semiconductor QDs depends on the following factors: First, the densities of single and ME states show very different energy dependence. By pure combinatorics, the number of two-particles excitations at high energies is significantly larger than the number of single-particle excitations. The ME DOS increases significantly faster with energy than does the single exciton DOS. The lowest excitations, up to energies of twice the band-gap, are single excitons. The DOS of the smaller QDs provides a good approximation for the DOS of the larger QDs, suggesting that the high level ab initio results obtained with the small clusters, Fig. 6, are indeed representative for these materials. The DOS of PbSe is quite unique [60], while the CdSe DOS represents a general case expected for the majority of semiconductor QDs.

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**Fig. 7.** The electron and hole DOS for the PbSe and CdSe QDs of varying size. The DOS were computed in the single-particle Hartree–Fock representation excluding the Coulomb electron–hole interaction. The single-particle band-gaps are much larger than the first excitation energies, Fig. 5, emphasizing the importance of the electron–hole interaction. The single-particle energy gaps $E_{\text{CAP}}$, appearing in the valence and conduction bands of PbSe are responsible for the nearly perfect switch from single to double excitons in Fig. 6. There are no such gaps in the DOS of CdSe, which shows single excitons at all energies and MEs at high energies. The DOS of the smaller QDs exhibits a mixture of single excitons, MEs and superpositions of single and MEs. The origin of the sharp transition from single to MEs seen in Fig. 6 with both PbSe and CdSe QDs, as well as the qualitative difference between the two materials, can be understood by considering the non-interacting particle DOS provided by the Hartree–Fock approximation. Fig. 7 shows the single-particle DOS for the 8, 136 and 360 atom PbSe QDs, and the 12, 66 and 222 atom CdSe QDs. The band structure of the PbSe QDs is significantly more symmetric than that of the CdSe QDs. This approximate mirror symmetry between the CB and VB of PbSe QDs is predicted by the effective mass band theory, which assigns similar masses to electrons and holes in lead salts [3]. In contrast, CdSe QDs have strongly asymmetric bands, with the holes about six times heavier than electrons.

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**Fig. 6.** The DOS of PbSe and CdSe QDs.

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**Fig. 5.** Proposed mechanisms for the generation of multiple excitons.

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**Fig. 4.** MEs in PbSe QDs.

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**Fig. 3.** CdSe QDs.
Second, the II efficiency depends on the coupling between single and MEs. Even though the ME DOS dominates the single exciton DOS at high energies, many matrix elements coupling the single and ME states vanish by the selection rules enforced by the two-particle Coulomb interaction. The calculation [36] shows that to the first order, a large fraction (over 98%) of the coupling matrix elements vanish and that it is important to take into account the existence of the higher order many-body interactions.

The analysis of the rates of II, which creates MEs from single excitons, and the Auger recombination of ME into single excitons performed in Ref. [36] indicates that the former overtakes the later by two orders of magnitude already at an energy equal three times the band-gap. Quite remarkably, the Auger recombination rate is approximately independent of the excitation energy due to compensation between the linear growth of the single exciton DOS and the increasing fraction of vanishing transition matrix elements. At the same time, the II rate grows rapidly with energy.

The II mechanism provides an incoherent rate process and assumes that the electronic dephasing of the initial state occurs on a very fast time scale. This assumption is supported by the ab initio calculations [24,39], with results in Table 1 discussed below. The II process explains how the high-energy excitations generating singly excited states (see CdSe in Fig. 6) can produce MEs on the ultrafast timescale.

5.2. The dephasing mechanism

Ellingson et al. [3] proposed that a photon of energy greater than twice the fundamental band-gap creates a coherent superposition of degenerate single and MEs. In this scenario, the efficiency of ME generation relies on the difference in the rates of phonon-induced dephasing for single and MEs. The mechanism is supported by the ab initio calculations [40] discussed above (see Fig. 6) as well as by the dephasing rates [24,39] shown in Table 1. A superposition of singly and multiply excited states is indeed one of the possible photoexcitation types. Dephasing involving MEs proceeds faster than dephasing involving single excitons. The dephasing mechanism also accounts for the damped coherent oscillation seen in the experimental signal [3].

In the dephasing mechanism, the photoexcited superposition of single and ME states dephases by coupling to phonons. Immediately following the photoexcitation, the electronic population oscillates between the two types of states coupled by the Coulomb interaction. Then, the electronic energy decays into the phonon energy. Assuming that MEs couple to phonons more strongly than do single excitons, the energy decay is faster when the electronic population localizes in the ME state. Thus, the final surviving electronic state is a ME [3].

One can easily argue that MEs should couple to phonons more strongly than do single excitons. The change in the electron density and, therefore, the distortion in the atomic lattice induced by two excited particles, should be more significant than those induced by one excited particle. This key assumption is supported by the data shown in Table 1.

5.3. The direct mechanism

Shaller et al. [4] proposed that a single absorbed photon generates a bi-exciton instantaneously by a second order perturbative process involving bi-exciton coupling to virtual single exciton states. This is indeed what happens in the ab initio calculations [40]. Photoexcitation of multi-electron states is forbidden in the independent-particle description. However, the Coulomb interaction between independent electrons and holes couples singly and multiply excited states, generating a non-vanishing oscillator strength for the direct multi-electron excitations, Figs. 5 and 6. The calculations show that the direct photogeneration of MEs is particularly efficient in PbSe, rationalizing why MEs were first discovered in this material [2].

The doubly excited states generated by absorbing a single photon must dissociate into two low-energy singly excited states, in order for the two single excitons to emit independently of each other. This dissociation process has not been investigated yet by an atomistic calculation. However, one can assume, similarly to the dephasing processes encountered in the II and dephasing mechanisms, that a coherent doubly excited state loses coherence and becomes an incoherent sum of singly excited states via phonon-induced dephasing.

6. Relationship between electron–phonon dynamics and generation of multiple excitons

Electron–phonon coupling is responsible for two distinct processes occurring within the electronic subsystem, namely, relaxation and pure-dephasing. Often, the two processes are combined under the common name of dephasing. However, one must distinguish between them when considering the effect of the electron–phonon coupling on ME generation.

According to the common spectroscopic notation [70], the inverse dephasing time $T_2$, which determines the homogeneous optical line-width $\Gamma$, is given by the sum of the inverse relaxation $T_1$ and pure-dephasing $T_2$ times

$$\frac{1}{\Gamma} = \frac{1}{T_2} + \frac{1}{2T_1}.$$ 

The process of pure-dephasing is often called decoherence [71], since it results in a loss of phase information in a coherent quantum superposition of states without loss of energy. The electron–phonon relaxation times $T_1$ have been discussed in the phonon-bottleneck section, while the pure-dephasing times $T_2$ between the pairs of the states shown in Fig. 1 are presented in Table 1, Ref. [39] (also see Ref. [24]).

The electron–phonon relaxation time $T_1$ determines the existence of the phonon-bottleneck, which requires $T_1$ to be large at least for some pairs of electronically excited states. As indicated by the time-domain atomistic ab initio calculations [38] (Fig. 3b) $T_1$ is short for most transitions, except for those between the lowest energy electron S and P-state manifolds in the small PbSe QD. The rapid dephasing assumed in the incoherent II process [36] refers to the pure-dephasing (decoherence) time $T_2$. The data of Table 1 show that pure-dephasing of superpositions of electronic states in the semiconductor quantum dots takes 10–20 fs. This is an order of magnitude faster than the measured ME generation time [3], in agreement with the II description.

The dephasing mechanism [3] for the generation of MEs assumes that superpositions of single and MEs decay via MEs. In this case, the term ‘dephasing’ refers to the overall $T_2$. The data of

### Table 1

<table>
<thead>
<tr>
<th>Quantum dot</th>
<th>State pair</th>
<th>Pure-dephasing time $T_2$, fs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$<em>{33}$Se$</em>{33}$</td>
<td>Low-exciton/ground</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>High-exciton/low-exciton</td>
<td>18</td>
</tr>
<tr>
<td>Pb$<em>{68}$Se$</em>{68}$</td>
<td>Low-exciton/ground</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>High-exciton/biexciton</td>
<td>9</td>
</tr>
<tr>
<td>Pb$<em>{68}$Se$</em>{68}$</td>
<td>Low-exciton/ground</td>
<td>11</td>
</tr>
</tbody>
</table>


7

One can easily argue that MEs should couple to phonons more strongly than do single excitons. The change in the electron density and, therefore, the distortion in the atomic lattice induced by two excited particles, should be more significant than those induced by one excited particle. This key assumption is supported by the data shown in Table 1.
Table 1 indicates that pure-dephasing $T_2$ of superpositions of states involving MEs is indeed faster than that involving only single excitons. Whether or not the relaxation time $T_2$ for MEs is shorter than for single excitons remains to be tested by an ab initio time-domain simulation. The pure-dephasing time shown in Table 1 for the superposition between the high-exciton and biexciton indicates that such superpositions decohere very rapidly by coupling to phonons, therefore, showing that the dephasing mechanism can produce MEs on an ultrafast time-scale.

The dissociation of the ME states into independent low-energy singly-excited states that emit photons sequentially can occur by a pure-dephasing (decoherence) process. The dissociation is required as the final step before the photon emission in all three ME generation mechanisms. The loss of coherence between a correlated ME state and two independent single-exciton state has not yet been investigated by an ab initio approach.

The above discussion shows not only that the electron–phonon coupling governs the relaxation rate and the existence of the phonon bottleneck, but also that it is essential in all three proposed mechanisms for the generation of MEs. The electron–phonon interaction guarantees that high energy single excitons can decay into MEs by an incoherent II rate process. It ensures that the superpositions of single and ME states lose energy through the ME channel. Finally, it can explain how coherent MEs created according to all three mechanisms, and the direct photoexcitation in particular, dissociate into uncorrelated single excitons.

7. Conclusions and outlook

The ab initio atomistic description of the electronically excited states and electron–phonon dynamics in the semiconductor QDs in both energy and time domains provides unique and fundamental insights into the QD properties. The time-domain modeling [38] of the phonon-induced electronic relaxation performed with the novel approach [61] combining time-domain density functional theory and non-adiabatic molecular dynamics unifies the two, seemingly contradicting, experimental observations. In spite of the large line spacing in the CdSe and PbSe QD optical spectra, the phonon bottleneck to the electron–phonon relaxation does not exist. The simulation shows that the fast relaxation and the absence of the bottleneck are due to the high density of electron and hole states. Except for the lowest excitation energies and smallest QDs, the spacing between the state energies matches the phonon frequencies. The QD spectra are composed of multiple individual excitations that combine into distinct bands according to the optical selection rules. The selection rules are much more stringent for optical than for electron–phonon transitions. Even though relatively few excitations are strongly optically active, most of the excited states are available during the relaxation.

The sophisticated SAC-CI electronic structure calculations clarify the nature of the photoexcited states in the semiconductor QDs by explicitly including the high-order electron–hole interactions [40]. MEs are found in the QD spectra above an energy threshold. PbSe in particular exhibits a unique electronic structure, creating energy windows in which MEs completely dominate single excitons. The calculations rationalize why MEs were first discovered in the PbSe QDs, while in CdSe the other mechanisms should also play key roles.

The electron–phonon interaction not only is responsible for the electronic energy relaxation which competes with the productive ME generation, but also causes dephasing and loss of coherence between the electronic states. The pure-dephasing processes are involved in all three proposed ME creation scenarios. The ab initio simulations [24,39] show that the phonon-induced dephasing of the electronic transitions occurs rapidly in the semiconductor QDs, supporting the ultrafast generation of MEs by the incoherent II mechanism. MEs dephase faster than single excitons, supporting the dephasing mechanism. The phonon-induced dephasing is likely to be the process which is responsible for the dissociation of MEs into independent single excitons.

A number of open questions remain in the investigations of the mechanisms and rates of the ME generation and the electron–phonon relaxation dynamics. Apart from the experimental controversies regarding the existence of MEs [72] and the phonon bottleneck [27,29,38], several theoretical issues need to be solved. The mechanism of the dissociation of MEs into uncorrelated single excitons is not yet established, even though we argue here that the process can occur by the phonon-induced dephasing. This step is essential to complete the ME generation picture.

Recently, MEs were discovered in Si [6]. This discovery could lead to a major breakthrough in the solar cell industry, which is almost entirely Si-based, provided that MEs can dissociate into free charge carriers and that the free charge carriers can be extracted from Si QDs. In contrast to PbSe and CdSe, Si is an indirect band-gap semiconductor. Whether or not the mechanisms of ME generation and electron–phonon relaxation remain the same in this alternative type of semiconductor is not yet clear. Recent experiments show that small Si QDs with quantum confinement energies greater than 1 eV behave similarly to the direct gap QDs [73]. In this respect, Ge provides additional advantages, since the confinement-induced transformation to the pseudo-direct gap regime is less demanding in Ge than in Si [74].

A possible reason why some experimental groups find no evidence of exciton multiplication [72], while other groups do observe MEs [2–6] may be related to the surface conditions of the nanocrystals, including surface passivation by ligands or a shell of another semiconductor. Surface states can speed up electron–phonon relaxation, open up the Auger relaxation channels and provide charge traps. The role of the excited surface states has not yet been addressed in ab initio studies.

Assemblies of QDs with other materials, such as molecular chromophores [37], organic or inorganic semiconductors, and so on, present a new set of theoretical questions regarding the interface. This article focuses on the nature and dynamics of the electronic excitations in the semiconductor QDs. Similar issues can be found with the spin states [15,16], as well in the metallic QD clusters [75]. The unique opportunities provided by the ab initio descriptions in time and energy domains motivate one to extend the current efforts to other related materials and problems.

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References


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