Pseudopotential theory of Auger processes in CdSe quantum dots

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Auger rates are calculated for CdSe colloidal quantum dots using atomistic pseudopotential wavefunctions. We predict the dependence of Auger electron cooling on size and on correlation effects (included via configuration interaction). Auger multi-exciton recombination rates are predicted for bi-excitons as well as for tri-excitons. The results agree with recent measurements and shed light on the significance of the dot surface on Auger multi-exciton decay.

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Auger effects are expected to play a central role in carrier relaxation in nanostructures [1]-[10]. Two types of Auger effects, ilustrated in Fig. 1, are prominent:

(i) *Electron cooling (Figs. 1a,b*: In the 3D bulk, or a 2D quantum well, the relaxation of an excited electron to its ground state usually occurs by phonon emission. The discrete nature of the electronic states of 0D dots is expected [2] to prevent phonon-assisted electron relaxation (phonon bottleneck). Multi-phonon (combined LO $\pm$ LA) effects [3], or polaronic effects [4, 5], may allow electronic relaxation to occur within a limited energy range around the phonon energy $\hbar\omega_0$. However, this may not be sufficient to remove the phonon bottleneck in small, strongly confined quantum dots. On the other hand, electron relaxation rates in CdSe quantum dots were observed to be fast ($\tau \sim 0.3$ ps in 2.3 nm radius nanocrystals [6], $\tau = 0.9 - 1.2$ ps for samples of size 4.3 nm [7]). It was proposed [8] that in a photoexcited quantum dot the "hot" electron can transfer its energy to the hole via an Auger process involving electron-hole scattering (Fig. 1a,b).

(ii) *Auger multi-exciton recombination* (Fig. 1c,d): A ground-state biexciton can decay into an excited-state monoexciton. Due to a large number of final monoexciton excited states, the efficiency of this process competes with radiative recombination (i.e. $\tau_{e-h}^{2\to1} < \tau_{rad}$), and effectively quenches the PL intensity [9]. These events can lead to photoionization (when one of the final electron or hole states is unbound), which was invoked to explain PL intermittency effects [10]. The inverse Auger process (creation of two e-h pairs from a single excited exciton) has been advocated [11] as a mechanism of enhancing solar cell efficiency. A similar Auger process involves the decay of a ground state tri-exciton into an excited bi-exciton; this $3 \to 2$ Auger decay (Fig. 1d) can be even faster than the $2 \to 1$ decay (Fig. 1c). Yet another type of Auger process involves the decay of a ground state trion into a hot electron (τ_e in Fig. 1e) or a hot hole (τ_h in Fig. 1f).

All Auger effects illustrated in Fig. 1 are at the heart of quantum dot carrier dynamics, and produce phenomena distinct from bulk physics. Recently, femtosecond carrier dynamics studies (see [1, 6, 9] and references therein) have been performed on colloidal quantum dots. These experiments have revealed various carrier relaxation times, which have been attributed to different Auger relaxation processes. Since, however, the interpretation of the results in terms of specific decay mechanisms is uncertain, there is a need for accurate theoretical calculations for specific Auger decay processes. Auger effects in quantum dots have been previously modeled using $\mathbf{k}\cdot\mathbf{p}$ [8, 13] and tight-binding [14] Hamiltonians. However, the conventional $\mathbf{k}\cdot\mathbf{p}$ description for the highly excited states involved in Auger transitions might not be sufficiently accurate [15]. Furthermore, the choice of the boundary conditions for the $\mathbf{k}\cdot\mathbf{p}$ wavefunctions near the surface could be problematic [16], and as we will see later, such region plays a critical role in some of the Auger processes. There are also problems due to the lack of atomistic description of the wavefunctions for multi-exciton Auger effects which involve exchange- and Coulomb-like integrals. The same problems exist in the tight-binding method which lack explicit basis functions [14]. Thus, there is a need for realistic and quantitatively reliable methods to calculate the Auger effects in quantum dots.

We have applied our pseudopotential many-body approach [17] to calculate different Auger processes in CdSe quantum dots. We will show that such calculations produce quantitative agreement with experiments, reveal the dependence of cooling rates on excitation energy, predict the ratios between $\tau_{e-h}^{3\to2}$ and $\tau_{e-h}^{2\to1}$, the hidden relations between $\tau_{e-h}^{2\to1}$ and τ_e and τ_h, and the role of the dot surface in Auger multi-exciton recombination.

Method of calculation: although there is no momentum