Excitonic Effects in Phonon-Mediated Relaxation in Semiconductor Nanocrystals

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The Bethe-Salpeter equation (BSE) can be used to calculate singlet exciton energies. Theoretically predicted observables, such as band gap, that are calculated using these excitonic energies have been shown to better match experimental observations than predicted results based on independent orbital approximation (IOA) energies for electrons and holes [1]. One can hypothesize that adequately accounting for bound exciton states could also better replicate time dependent observables, such as nonradiative and radiative lifetimes in photo-excited semiconductor nanomaterials.

In our study, we use a basis of orbitals from density functional theory (DFT) simulation as a foundation to solve the BSE for bound singlet excitons. We then use the excitonic wavefunctions from BSE results to construct a linear transformation matrix that transforms IOA-based phonon-mediated relaxation calculations, or nonadiabatic couplings (NACs), into an excitonic basis. These NACs are then used to construct parameters for the equations of motion of the dissipative reduced density matrix in the excitonic basis. A set of relaxation rates for such equations is known as the Redfield tensor, which can be used to calculate dynamic observables such as nonradiative decay lifetimes [2], photoluminescence (PL) emission spectra, and photoluminescent quantum yield (PLQY).

We compute the IOA and excitonic picture nonradiative relaxation rates and PL spectrum for a family of atomistic models of semiconductor quantum dots (QDs), including Si, PbSe, and CdSe, in the regime of quantum confinement. We also compare IOA predicted, excitonic predicted, and experimental PLQY. For a model of a ~1 nm diameter Si QD, the nonradiative relaxation rates show that hot excitons relax sooner in the excitonic picture than in the IOA picture. A smaller band gap and different available relaxation pathways in the excitonic picture seem to be the main contributors to this observed effect. For certain initial excitations, the simulated PL emission spectrum in the excitonic picture for the same model has an intensity that is 5 orders of magnitude greater than in the IOA picture. The presence of a bright exciton in the lowest excitation in the Si QD makes a strong argument in support of the excitonic approach in the treatment of time-resolved processes.

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