II.K.9 Excited States in Semiconductor Quantum Dots

Oleg Prezhdo, Heather Jaeger
Department of Chemistry, University of Rochester
120 Trustee Rd.
Rochester, NY 14627
(585) 275-4231; (585) 276-0205
E-mail: oleg.prezhdo@rochester.edu

Abstract

The current perspective on the nature of photoexcited states in semiconductor quantum dots (QDs) is presented. 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 and also exhibit conduction and valence bands as in bulk semiconductors. 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 critical to settle the debates. By synthesizing different viewpoints and presenting a unified \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.

Technical Barriers

While solar-to-electric energy conversion is an established technology, current solar cells are either too expensive or too inefficient for widespread application. Many alternative designs of photovoltaic (PV) systems have been proposed, yet the precise relationships between structure and spectral properties as well as the specific mechanisms of the energy transduction are still being unraveled. Our theoretical studies will address the fundamental aspects of solar energy transfer resulting in a predictive framework for the design of efficient, cost-saving PV devices for the production of hydrogen.

Progress Report

The time-domain modeling [1] of the phonon-induced electronic relaxation performed with the novel approach [2] 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.

Sophisticated \textit{ab initio} electronic structure calculations clarify the nature of the photoexcited states in the semiconductor QDs by explicitly including the high-order electron–hole interactions. Multi-excitons (ME) 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. Electronic structure calculations have also led to much progress on achieving a thorough understanding of the excitation properties of these materials when they are altered with charging, doping, or dangling bonds. The calculations show that the defects introduce new intra-band transitions, blue-shift the optical absorption spectra and increase the threshold for ME generation. Generally, doping and charging have similar effects on the excited state properties, while dangling bonds cause less severe changes.

The excited state properties determined in the ab initio calculations indicate that three mechanisms of the ME generation can take place in the semiconductor QDs. These include the incoherent II process, [3,4] the dephasing mechanism, [5] and the direct excitation mechanism. [6] Which mechanism is more important depends on the material under study. The direct mechanism should be particularly efficient in PbSe QDs, while in CdSe the other mechanisms will also play key roles.

Future Directions

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 [8] and the phonon bottleneck, [9, 10, 11] 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 completing the ME generation picture.

Recently, MEs were discovered in Si. [13] 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 bandgap 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. [14] In this respect, Ge provides additional advantages, since the confinement-induced transformation to the pseudodirect gap regime is less demanding in Ge than Si. [15]

Assemblies of QDs with other materials, such as molecular chromophores, [16] organic or inorganic semiconductors, and so on, present a new set of theoretical questions regarding the interface. 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.

References

Publication list (including patents) acknowledging the DOE grant or contract