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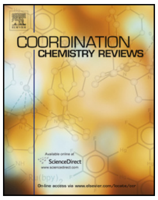

Review

Time-domain *ab initio* modeling of excitation dynamics in quantum dots

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ABSTRACT

The review discusses the results of *ab initio* time-dependent density functional theory and non-adiabatic molecular dynamics simulations of photoinduced dynamics of charges, excitons, plasmons, and phonons in semiconductor and metallic quantum dots (QDs). The simulations create an explicit time-domain representation of the excited-state processes, including elastic and inelastic electron–phonon scattering,

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multiple exciton generation, fission, and recombination. These nonequilibrium phenomena control the optical and electronic properties of QDs. Our approach can account for QD size and shape, as well as chemical details of QD structure, such as dopants, defects, core/shell regions, surface ligands, and unsaturated bonds. Each of these variations significantly alters the properties of photoexcited QDs. The insights reported in this review provide a comprehensive understanding of the excited-state dynamics in QDs and suggest new ways of controlling the photo-induced processes. The design principles that follow, guide development of photovoltaic cells, electronic and spintronic devices, biological labels, and other systems rooted in the unique physical and chemical properties of nanoscale materials.

1. Introduction

Quantum dots (QDs) are nanoscale clusters of bulk material whose electronic excitations are confined in all three spatial dimensions. Every material has its own exciton Bohr radius, which is the physical size of an excitation in the bulk of that particular material. When the dimensions of a nanocrystal reach this characteristic length, it starts to exhibit the effects of quantum confinement much like a particle in a box. This allows for the properties of the QD to be tuned continuously by changing the cluster's size and shape. Once the system reaches the subnanometer scale, it begins to behave like a molecule; its structure varies from bulk and its properties change discontinuously with cluster size.

The unique physical and chemical properties [1–4] of semiconducting and metallic nanocrystals form the basis for a variety of applications, ranging from optical sensors [5,6] and probes [7,8], to photovoltaic [9,10], optical [11], electronic [12], optoelectronic [13], and spintronic [14] devices, and to light-emitting [15] and imaging [16] technologies. The excited state dynamics in semiconducting [17] and metallic [18] QDs are very intricate [19]. For instance, high absorption cross sections, decreased electron–phonon relaxation rates [20,21], and generation of multiple electron–hole pairs [22–24] make QDs outstanding photovoltaic materials since all these features provide opportunities to utilize photon energy in excess of the band-gap [20,25]. Electron–hole and charge–phonon interactions have both fundamental and practical importance, since both interactions contribute to the overall efficiency of a photovoltaic device. Phonon-induced dephasing of spin and electron states influences charge and energy transfer processes. Inelastic scattering is responsible for energy loss during charge tunneling though QDs.

Relaxation and pure-dephasing are two related but distinct phenomena that result from electron–phonon interactions. Relaxation is an inelastic process that leads toward energy losses. Electron–phonon pure-dephasing is an elastic process, and therefore conserves electronic energy. Pure-dephasing determines the homogenous linewidths in optical spectra. It transforms a coherent superposition of states into uncorrelated state ensembles. When considering MEG, electron–phonon relaxation competes with and inhibits it. At the same time, destruction of superpositions of SEs and MEs occur due to elastic electron–phonon scattering. Phonon-induced pure-dephasing of coherent superpositions of single and ME states destroys the quantum mechanical entanglement between the states and is an essential component of excited state dynamics in QDs.

Nanocrystals are sufficiently large objects that can support multiple excitations. Therefore, Auger-type processes, which create and annihilate charges and excitons, play a particularly important role. For instance, multiple exciton generation (MEG), also known as carrier multiplication (CM), is the process in which a single high-energy photon is absorbed and creates two or more electron–hole pairs [23,26–28], This phenomenon provides potential for increasing photovoltaic device efficiencies [24]. MEG happens in bulk, but is typically more efficient in QDs [24,29]. This is because in bulk materials crystal momentum, a pseudo-momentum associated with electrons in a lattice, needs to be conserved. This requirement enforces strict selection rules and causes the energy needed to form a biexciton to be more than simply two times the band-gap. A lack of translational symmetry in QDs voids the need to conserve crystal momentum [30]. In addition, Coulomb interaction between electrons and holes is enhanced due to the closer proximity of charge carriers inside a nanocrystal [31].

The current review presents a cutting edge *ab initio* description of the time-dependent dynamics of photoexcited states in semiconductor and metallic QDs. The *ab initio* methods are used to study excited state composition, evolution and relaxation. The time-dependent atomistic nature of the methods provides powerful tools for studying the role of surface ligands, dopants, defects, unsaturated bonds, size, shape and other realistic aspects of QDs. The described simulations provide a comprehensive perspective on the elastic and inelastic scattering dynamics of photoexcited charge carriers in nanoscale materials, directly mimicking numerous time-resolved experiments, and offering insights into the fundamental mechanisms underlying QD applications in optics, photovoltaics, electronics and related fields.

2. Theoretical approaches

We use a wide array of *ab initio* methods to study the photoexcited dynamics of QDs. The simulations described in this review treat many-body interactions in the electronic degrees of freedom for either fixed nuclear coordinates, or nuclei evolving classically or semiclassically. We refer readers interested in a detailed description of the methods and their numerical implementation to Prezhdo et al. [32] and Akimov et al. [33]. Symmetry adapted cluster (SAC) theory with configuration interactions (CI) is used to study the nature of photoexcited states and to describe photoinduced MEG for fixed nuclei. Exciton dynamics, including impact ionization (II) and electron–phonon relaxation, are modeled using time-dependent density functional theory (TDDFT). Here, excitons are coupled to phonon motions with nonadiabatic molecular dynamics (NAMD) methods. The optical response formalism is used to obtain information on electron–phonon dephasing, which has an influence in the exciton formation as well as relaxation.

2.1. Hartree–Fock method provides a mean-field picture

Even the smallest QDs consist of hundreds of atoms leading to systems with tens of thousands of electrons. For example, a $Pb_{68}Se_{68}$ QD with diameter of only 2 nm already has 8000 electrons. Solving for the exact many-body wavefunction for this system would be impossible. Fortunately, physically motivated approximations have been shown to bring tractability to the many-body problem. One of the simplest and earliest methods developed is the Hartree–Fock (HF) approach. The HF theory was introduced to solve the electronic Schrödinger equation for a given set of nuclear coordinates. The basic assumption behind the HF method is that the many-electron wavefunction can be written as a properly symmetrized product of one-electron orbitals. An individual electron in the system feels an electrostatic field from the central