The International Society for Optical Engineering

SPIE Newsroom

10.1117/2.1200608.0384

Modeling photoexcited carrier interactions in semiconductor nanostructures

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A new computational approach can fully account for the effects of quantum and dielectric confinement.

The ability to control the composition of semiconductor heterostructures would allow us to engineer materials with the electronic and optical properties we want. Possible applications include tunable lasers,[1] photovoltaic panels,[2,3] and biological labels.[4] Though well developed for semiconductor quantum wells and superlattices, this approach is only now starting to be used in the field of semiconductor nanocrystals, also known as semiconductor quantum dots. Typical heterostructures synthesized as quantum dots are colloidal core-shell nanomaterials (e.g., CdTe/CdSe, InAs/InP, CdS/ZnSe, InP/$ZnCdSe_2$).[5] In contrast to homogeneous quantum dots, these nanostructures are driven by an interface between two semiconductor materials, which produces a number of interesting and technologically useful physical properties.

Resonant interaction of laser pulses with these semiconductor nanostructures leads to the generation of interacting electron-hole pairs known as excitons. The dynamics of the excitons stem from two major effects: quantum and dielectric confinement. Quantum confinement arises from the scattering of the photoexcited carriers at the potential energy walls produced by the surface of the nanocrystals, and results in the formation of discrete carriers, quantum states whose energies can be tuned by varying the nanocrystals' size. The latter effect originates from the Coulomb interaction of the photoexcited carriers with their electrostatic images produced by the polarized nanocrystal surface. This polarization significantly contributes to the net Coulomb interactions between them.

The interface between the semiconductor core and shell materials creates a step potential for electrons and holes, and therefore contributes to the quantum confinement. There are two typical topologies for the conduction- and valence-band confinement-potential alignments: type I and type II nanostructures (see Figure 1). In type I nanostructures, the extrema of the conduction and valence bands *both* lie either in the core or in the shell, and the localization of the carriers in the narrow band-gap region can be achieved. From a practical point of view, localization of the carriers within the core material can reduce their interaction with the surface traps, thus enhancing the emission efficiency crucial for photo-emitting and laser applications. In contrast, in type II nanostructures—where the conduction and the valence bands extrema lie in *different* regions of the nanostructure—spatial separation of electrons and holes can be achieved. As a result, the non-radiative electron-hole recombination process can be suppressed, increasing exciton lifetime.

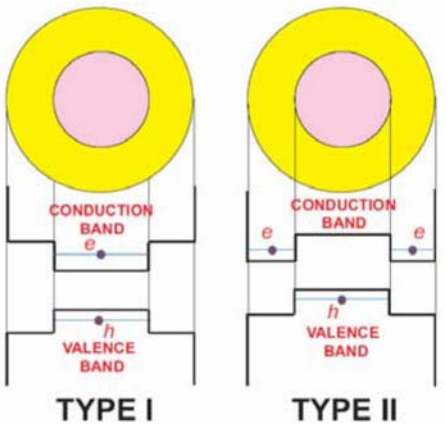

Figure 1. *Cross section of core-shell nanostructures and typical type I and II profiles of the valance- and conduction-band confinement potentials.*

The difference between the dielectric constants of the core and shell materials also leads to an interface polarization that contributes to carrier confinement. In addition to the electrostatic interactions with the image charges created by the surface polar-

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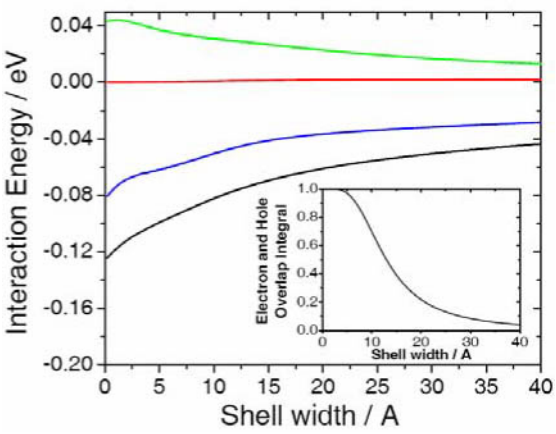

Figure 2. *Shown are components of the total (blue line) electron-hole (in 1S quantum state) Coulomb interaction energy for type II CdTe/CdSe nanostructure with the core radius of 20 A. Black - direct Coulomb coupling; red - electron (hole) interacting with hole (electron) image; green - electron and hole self-interactions with images. The inset: the integral of the overlapping electron and hole wavefunctions.*

ization, the images produced by the core-shell interface polarization must be taken into account. Thus, properly chosen core and shell materials can significantly reduce or enhance the Coulomb interactions between the carriers.

To provide guidelines for the experimental study and design of the core-shell heterostructures with desirable electronic and optical properties, we developed a reliable tool for computing the carrier interaction energies that incorporates the effects of the quantum and dielectric confinements.

Because quantum confinement dominates carrier kinetic energies in small (1–5nm) colloidal nanocrystals, we first solved the Schrödinger equations for the non-interacting carriers, and then accounted for Coulomb interactions using perturbation theory. To provide an adequate description of the Coulomb interaction, we solved the Poisson equation by matching the boundary conditions at the core-shell and shell-environment interfaces, and obtained an exact expression that was used in the simulations. The expression has three different components reflecting the effect of dielectric confinement: direct Coulomb interaction between the photoexcited carriers; the interaction of each carrier with the electrostatic images of the other carriers; and self-interaction of the charges with their own images (the dielectric solvation energy).

Figure 2 shows an example of the interplay between these three components. The main contribution to the total Coulomb interaction (blue line) in CdTe/CdSe nanostructures comes from the direct Coulomb (black line) and charge-image self-interaction terms (green line). The net energy slowly reduces with the growing size of the shell as the carriers localize in different parts of the nanostructure.

In conclusion, we have developed a reliable computational approach for the study of electrostatic interactions in core-shell semiconductor heterostructures. In our calculations, we have fully accounted for the effects of both quantum and dielectric confinement. The technique has been validated against experimental data, and will be used to guide the efficient design of functional core-shell nanomaterials.

This work was carried out under the auspices of the National Nuclear Security Administration of the US Department of Energy at Los Alamos National Laboratory. The research at LANL is supported by Center for Integrated Nanotechnology and the Center for Nonlinear Studies. This support is gratefully acknowledged.

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