

# Pseudopotential Theory of Electronic Excitations in Semiconductor Nanostructures

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## ABSTRACT

The calculation of the optical and electronic properties of semiconductor nanostructures is still based for the most part on highly approximated, continuum-like models such as the effective-mass approximation, which do not take into account the atomistic structure of the quantum dots. We present here an *atomistic* pseudopotential approach to the calculation of excited states in semiconductor nanostructures. This approach involves two steps: (i) The single-particle Schrödinger equation for the nanostructure is solved using  $O(N)$  methods. (ii) The electronic excited states (such as excitons, multi-excitons, etc.) are then calculated by solving the many-particle Schrödinger equation in a basis set of Slater determinants (configuration interaction expansion). Applications of this method to predict the optical emission spectra of neutral and charged excitons, bi-excitons and tri-excitons in CdSe colloidal quantum dots are discussed.

**Keywords:** quantum dots, excitons, pseudopotentials.

## 1 INTRODUCTION

Semiconductor nanostructures are the building blocks of a new generation of electronic and optical devices that can lead to applications in fields as diverse as quantum computing [1], biological labeling [2], and solar energy conversion [3]. These nanostructures can now be synthesized with a high degree of control over their size and shape distribution, and can often be arranged into highly ordered, three-dimensional superstructures. One of the most promising approaches to nanostructure fabrication is by colloidal-chemistry synthesis. This approach yields well defined nanocrystals that are typically a few nanometers in size, and contain from a few hundred to several thousand atoms.

As these chemically-synthesized nanocrystals are only a few atomic layers across, it is important to consider the atomistic character of the wave functions when calculating their optical and electronic properties. Yet, electronic-structure calculations for colloidal nanocrystals are often performed using continuum methods based on the effective-mass approximation, which misses the atomistic structure of the nanocrystal. Here we present an atomistic, pseudopotential approach to the calculation of electronic excitations of semiconductor nanostructures. The many-

particle excited-state wave functions of the nanostructure are expanded as linear combinations of Slater determinants obtained from atomistic single-particle wave functions. We illustrate this approach with calculations of the optical emission spectra of neutral and charged excitons and multiexcitons in CdSe colloidal nanocrystals.

## 2 METHOD

Our approach to the calculation of electronic excitations in semiconductor nanostructures has two steps, as described in the following. (i) First, we solve the single-particle Schrödinger equation

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + \hat{V}_{NL} + \hat{V}_{SO} \right] \psi_i(\mathbf{r}, \sigma) = \varepsilon_i \psi_i(\mathbf{r}, \sigma), \quad (1)$$

where  $V(\mathbf{r}) = \sum_{\mathbf{R}} v(\mathbf{r} - \mathbf{R})$  is the local pseudopotential, given by the superposition of screened atomic potentials  $v(\mathbf{r} - \mathbf{R})$  centered at the atomic positions  $\{\mathbf{R}\}$ .  $\hat{V}_{NL}$  is the non-local pseudopotential operator, and  $\hat{V}_{SO}$  is the spin-orbit operator. The screened atomic potentials  $v(\mathbf{r})$ , as well as  $\hat{V}_{NL}$  and  $\hat{V}_{SO}$ , are fitted to experimental bulk transition energies, effective masses, and deformation potentials, and to ab-initio calculated bulk wave functions [4]. Equation (1) is solved by expanding the wave functions  $\psi_i(\mathbf{r}, \sigma)$  in a plane-wave basis set, and using the folded-spectrum method [5] to calculate the band-edge single-particle energies and wave functions. The computational cost of the folded-spectrum method scales only linearly with the size of the nanostructure. This approach fully includes inter-valley coupling and intra-band coupling, which are brought about in nanostructures by the lack of translational symmetry. (ii) In the next step, we construct the many-particle configuration-interaction (CI) Hamiltonian, which describes the interactions between carriers:

$$\begin{aligned} \hat{H}_{CI} = & \sum_{i \in C} \varepsilon_i c_i^* c_i - \sum_{j \in V} \varepsilon_j d_j^* d_j \\ & + \frac{1}{2} \sum_{ijkl \in C} J_{ijkl}^{CC} c_i^* c_j^* c_l c_k + \frac{1}{2} \sum_{ijkl \in V} J_{ijkl}^{VV} d_i^* d_j^* d_l d_k \\ & - \sum_{ik \in V, j \in C} (J_{ijkl}^{VC} - K_{ijkl}^{VC}) c_i^* d_j^* c_l d_k. \end{aligned} \quad (2)$$

Here  $c_i^*(c_i)$  is the creation (annihilation) operator for an electron in the conduction-band state  $i$ ,  $d_i^*(d_i)$  is the creation (annihilation) operator for a hole in the valence-band state  $i$ , and V,C denote the valence-band and conduction-band manifolds, respectively. The single-particle energies  $\varepsilon_i$  are taken from the solution of Eq. (1). The Coulomb and exchange integrals of Eq. (2) are screened by the static dielectric function  $\varepsilon(\mathbf{r}, \mathbf{r}')$  of the nanostructure:

$$J_{ijkl} = \sum_{\sigma\sigma'} \int \int \psi_i^*(\mathbf{r}, \sigma) \psi_j^*(\mathbf{r}', \sigma') \frac{e^2}{\varepsilon(\mathbf{r}, \mathbf{r}') |\mathbf{r} - \mathbf{r}'|} \times \psi_k(\mathbf{r}, \sigma) \psi_l(\mathbf{r}', \sigma') d\mathbf{r} d\mathbf{r}' \quad (3)$$

We use a phenomenological model for the dielectric constant  $\varepsilon(\mathbf{r}, \mathbf{r}')$ , as described in Ref. [6]. The sums in Eq. (2) are restricted to the single-particle states included in an “active space”, consisting of the first several conduction states above the conduction-band minimum and the first several valence states below the valence-band maximum. The Coulomb and exchange integrals of Eq. (3) are computed via Fourier Transform solution of the associated Poisson equations [6]. The CI Hamiltonian of Eq. (2) is then diagonalized in the basis set of Slater determinants obtained by exciting one or more electrons from the valence states to the conduction states in the active space. The diagonalization of the CI Hamiltonian is performed using a conjugate-gradients algorithm that yields the low-energy many-particle eigenvalues  $\{E_\alpha\}$  and wave functions  $\{\Psi_\alpha\}$  of the nanostructure. Finally, the emission spectrum is calculated using the Fermi golden rule:

$$I(\omega) \propto \frac{2\pi}{\hbar} \sum_i n_i(T) \sum_f \left| \langle \Psi_i | \hat{r} | \Psi_f \rangle \right|^2 \delta(E_f - E_i - \hbar\omega), \quad (4)$$

where the sums run over the many-particle initial states  $\{\Psi_i\}$  and the final states  $\{\Psi_f\}$ ,  $\hat{r}$  is the dipole operator, and  $n_i(T)$  is the temperature-dependent occupation factor of the initial state  $\Psi_i$ .

### 3 RESULTS

In semiconductor nanocrystals multiple electrons and holes - created via optical excitation, doping, etc. - can coexist in a very small volume, which is often smaller than the bulk exciton Bohr radius. As a result, inter-particle interactions, described by the Coulomb integrals of Eq. (3), are strongly enhanced compared to the corresponding bulk materials. This in turn affects the spectroscopic properties of the nanoparticles. Recently, time-resolved photoluminescence spectroscopy [7-10] has been used to detect short-lived optical emission from highly excited semiconductor nanocrystals. The appearance of additional emission bands - both to the red and to the blue of the neutral exciton peak - as the excitation intensity was

increased, was attributed to radiative recombination of charged excitons and multiexcitons. However, the physical origin of these additional emission bands has remained elusive. In particular, high-energy emission bands to the blue of the single-exciton emission line have been attributed to either charged biexcitons [7] or neutral triexcitons [8,9].

To address these unresolved issues, we have calculated the emission spectra of neutral excitons (one hole + one electron, or 1h+1e), charged excitons (2h+1e or 1h+2e), multiexcitons (2h+2e, 3h+3e, etc.) and charged multiexcitons (e.g. 3h+2e or 2h+3e), using the atomistic pseudopotential approach described above [11]. We have considered nearly-spherical CdSe nanocrystals ranging in radius from 1.9 to 2.3 nm. The nanocrystals have the wurtzite lattice structure of bulk CdSe. The surface dangling bonds are passivated using ligand-like potentials to remove surface states from the band gap.

Figure 1 shows the emission spectra of the neutral exciton X and of the charged biexcitons  $XX^+$  (3h+2e) and  $XX^-$  (2h+3e) of a CdSe nanocrystal of radius  $R=1.9$  nm.

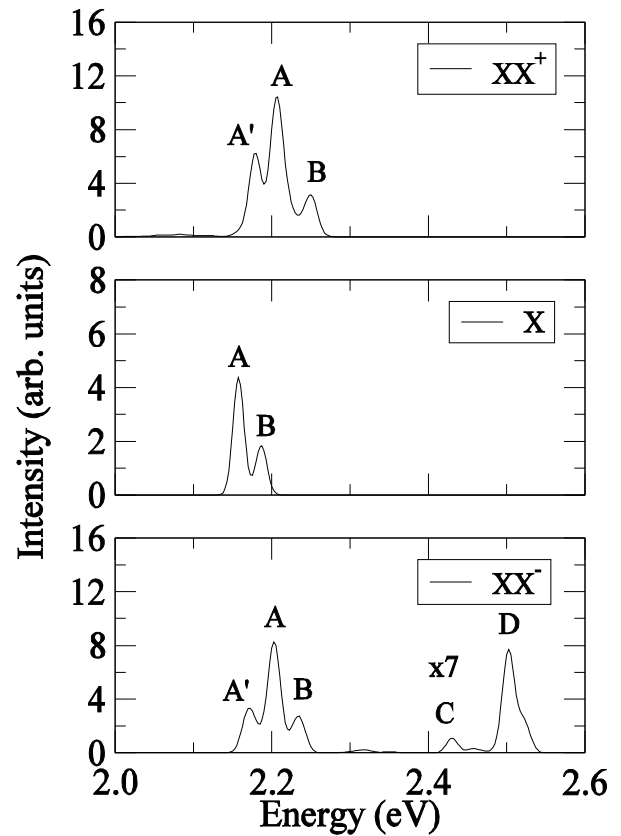


Fig. 1. Calculated room-temperature optical emission spectra of the positively charged biexciton ( $XX^+$ ), the neutral exciton (X), and the negatively charged biexciton ( $XX^-$ ) of a spherical CdSe nanocrystal of radius  $R=1.9$  nm. The emission peaks are labeled according to their different spectroscopic origin (see text).

Peak A in Fig. 1 originates from the radiative recombination of an electron in the S-like level  $e_1$  (lowest-energy conduction-band level) with a hole in the S-like level  $h_1$  (highest-energy valence-band level). Peak B originates from the recombination of an electron in  $e_1$  with a hole in  $h_2$ . The  $h_1$  and  $h_2$  energy levels are separated by the crystal field splitting due to the hexagonal wurtzite lattice structure of CdSe ( $\sim 25$  meV in bulk CdSe). The  $h_2$  level is thermally occupied by holes at room temperature. The peaks labeled A' in Fig. 1 originate from transitions from the ground state of the charged biexcitons  $XX^+$  and  $XX^-$  to excited states of the charged excitons  $X^+$  and  $X^-$ , respectively. In the case of the negatively charged biexciton  $XX^-$ , we observe additional, weak emission peaks at higher energy (denoted C and D in Fig. 1), which originate from thermal occupation of higher-energy  $XX^-$  initial states and from correlation-induced configuration mixing in the  $XX^-$  ground state. As we can see from Fig. 1, peaks A and B shift to higher energy when additional electrons and/or holes are present in the nanocrystals. For example, peak A shifts to the blue by  $\sim 70$  meV in the case of  $XX^+$ , compared to peak A of the single exciton X. This blueshift is due to strong inter-particle interactions in the  $XX^+$  ground state.

Figure 2 shows the room-temperature tri-exciton (XXX) and single-exciton (X) emission spectra of a  $R=2.3$  nm CdSe nanocrystal. The presence of spectator electrons and holes in the tri-exciton leads to the following effects. (i) The main emission peak (labeled A in Fig. 2) shifts slightly to the red. This peak originates from the radiative recombination of an electron in the S-like conduction level  $e_1$  with a hole in the S-like valence levels  $h_1$  or  $h_2$  (similarly to peak A in Fig. 1). (ii) Peak B in Fig. 2 originates from the radiative recombination of a P-like electron with a P-like hole, and is characteristic of tri-exciton emission. We find that, because of strong S-S inter-particle interactions, P-like single-particle hole levels are occupied in the tri-exciton ground state, even though the two highest-energy valence-band levels (which can accommodate up to four holes) are both S-like.

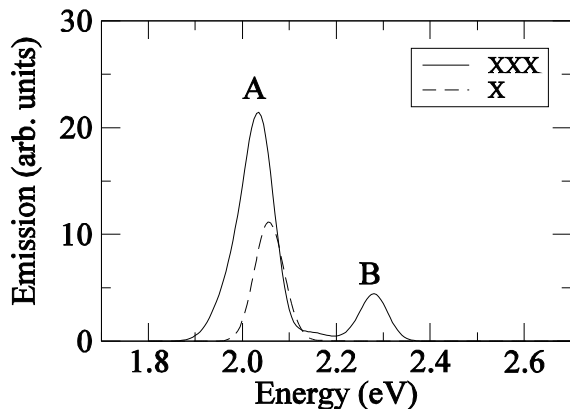


Fig. 2. Calculated room-temperature tri-exciton emission spectrum of a CdSe nanocrystal of radius  $R=2.3$  nm (solid line). Also shown is the room-temperature single-exciton emission peak (dashed line).

The position of the calculated emission peaks and the splitting between peak A and peak B are in excellent agreement with recent experimental measurements of tri-exciton emission spectra in CdSe colloidal nanocrystals [8,9].

## CONCLUSIONS

In conclusion, we have presented an atomistic pseudopotential approach to calculate electronic excitations of semiconductor nanostructures. This method has two steps: (i) The single-particle pseudopotential Schrödinger equation for the nanostructure is solved in a plane-wave basis set. (ii) The electronic excited states (such as excitons, multi-excitons, etc.) are then calculated by solving the many-particle Schrödinger equation in a basis set of Slater determinants (configuration interaction expansion). We have illustrated this approach with calculations of the optical emission spectra of neutral excitons, charged excitons, and multiexcitons in CdSe colloidal nanocrystals.

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