Optical transitions in charged CdSe quantum dots

Alberto Franceschetti and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

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depends on the relative spin orientation of the spectator particles and the photoexcited electron and hole. Therefore, in the presence of spectator electrons or holes the excitonic transitions can split into spin-multiplet lines. (iii) The excitation energies ΔE

$_{h,e}$ can depend on whether the spectator particles are delocalized over the quantum dot or localized at the surface of the dot. (iv) By occupying previously empty conduction levels, the spectator particles can block optical transitions that would be otherwise allowed in a neutral dot (Pauli blocking). These physical effects and the practical ability to inject carriers in colloidal and self-assembled quantum dots[1,2] open the way to novel engineering of the optical

spectator electrons or holes can alter the optical transitions in quantum dots, leading to Coulomb shifts, exchange splittings, and Pauli blocking.

The single-particle energies ε_i and wave functions $\psi_i(\mathbf{r},\sigma)$ of the quantum dot are obtained by solving the pseudopotential Schrödinger equation (atomic units are used in the following)

$$[-\nabla^2/2+V_{ps}(\mathbf{r})+\hat{V}_{nl}]\psi_i(\mathbf{r},\sigma)=\varepsilon_i\psi_i(\mathbf{r},\sigma), \qquad (3)$$

where $V_{ps}(\mathbf{r})$ is the total pseudopotential of the quantum dot and $\hat{V}_{nl}$ is a short-range operator that accounts for the nonlocal part of the potential as well as spin-orbit coupling. The total pseudopotential $V_{ps}(\mathbf{r})$ is calculated from the superposition of screened atomic pseudopotentials, which are fitted[11] to reproduce the measured bulk transition energies, deformation potentials, and effective masses, as well as the bulk single-particle wave functions calculated using density-functional theory in the local-density approximation.

The excited states of the quantum dot are expanded in terms of Slater determinants obtained by creating holes in the valence band and adding electrons to the conduction band. Since correlation effects due to charging are small[12] on the scale of the Coulomb and exchange energies of Eqs. (1) and (2), we retain in the many-body expansion only Slater determinants having the same single-particle energy. This allows us to accurately treat the electron-electron, electron-hole, and hole-hole Coulomb and exchange interactions. In this approximation we neglect (i) the response of the single-particle wave functions to the electrostatic field set up by the net charge (i.e., self-consistent effects), and (ii) the coupling between orbital configurations with different energies (i.e., configuration-interaction effects). These assumptions are sufficiently accurate in three-dimensional quantum structures in the strong-confinement regime.[12–15] In Ref. 13 we compared the electron-hole Coulomb energies of neutral ($Q=0$) quantum dots calculated using unperturbed single-particle wave functions with the results of a self-consistent Hartree calculation. We found that the Coulomb energies change by less than 5% when self-consistent effects are taken into account. In Ref. 14 we showed that the main effect of the configuration interaction on the excitonic energy levels of quantum dots is a nearly uniform down shift of 2–5 meV.

The many-body Hamiltonian is then diagonalized in the basis of the Slater determinants. The Coulomb and exchange matrix elements are calculated using the atomistic wave

next two levels (h_3 and h_4) have a p-like envelope function. We find that this sequence of energy levels is typical of a wide range of nanocrystal sizes.

Figure 1 shows the calculated absorption spectrum (color lines) and the lowest emission energies (black vertical lines) as a function of the net charge Q present in the quantum dot. We assume that the system relaxes to the electronic ground state before an electron-hole pair recombines (in emission) or is created (in absorption). We can identify three groups of peaks (denoted A, B, and C in Fig. 1) in the absorption spectrum. Group A originates from the $h_1 \rightarrow e_1$ transition (A_1) and the $h_2 \rightarrow e_1$ transition (A_2). The splitting between the A_1 and A_2 peaks corresponds to the crystal-field splitting (finite in wurtzite-structure quantum dots) between the single-particle levels h_1 and h_2 (see Table I). Peaks B_1 and B_2 originate from the $h_9 \rightarrow e_1$ and the $h_{23} \rightarrow e_1$ transitions, respectively. The hole states h_9 and h_{23} have a small s-like component, so they are optically coupled to the s-like electron state e_1. Group C originates from the $(h_3,h_4) \rightarrow (e_2,e_3,e_4)$ transitions, and shows a fine structure consisting of multiple optically allowed lines. This structure arises from the fact that the h_3 and h_4 hole states (as well as the e_2, e_3, and e_4 electron states) are nondegenerate (see Table I). Further splitting is induced by electron-hole, electron-electron, and hole-hole exchange interactions between the optically excited electron-hole pair and the spectator particles, as shown by Eqs. (1) and (2). In the following we discuss the main features of the absorption and emission spectra in the presence of spectator charges.

Pauli blocking of the $h_n \rightarrow e_1$ transitions. Figure 1 shows that the low-energy absorption peaks A_1, A_2, B_1, and B_2 disappear when two or more electrons are loaded in the dot (Q