Exciton dissociation and interdot transport in CdSe quantum-dot molecules

Alberto Franceschetti and Alex Zunger*

$$u_e^B = \frac{1}{\sqrt{2}} \left({}_e^L + {}_e^R \right); \quad u_e^A = \frac{1}{\sqrt{2}} \left({}_e^L - {}_e^R \right), \qquad 5)$$

where the superscript L and R denote the left-hand-side and right-hand-side dot, respectively. The electron and hole bonding and antibonding wave functions are delocalized over the two quantum dots. When the electron-hole interaction is taken into account, one would expect that in the ground state the electron and the hole would be localized in the same quantum dot, as shown in the upper part of Fig. 1. However, mean-field approaches that estimate the electron-hole interaction using the unperturbed wave functions of Eqs. 4), 5) are unable to break the symmetry of the electron-hole pair, and lead to an unphysical solution where the electron and separately the hole) resides on the two dots with equal probability. This is true even for self-consistent mean-field techniques such as conventional Hartree-Fock or LDA approaches) that calculate iteratively the potential experienced by the electron due to the electrostatic field generated by the hole. We conclude that mean-field approaches, which have been used successfully to calculate the electron-hole interaction in strongly-confined quantum dots, fail to describe the electron-hole localization in quantum dot arrays, and are unable to predict, even qualitatively, the exciton dissociation energy.

In this paper we show that the exciton dissociation energy ΔE

culation based on single-particle wave functions calculated via our pseudopotential approach for a dot molecule.

We consider here spherical CdSe quantum dots having the wurtzite lattice structure. The diameter of the dots is D

that $J_{h,e}^{\text{pol}}$ decreases rapidly as ϵ_{out} increases. As a result, the total $\Delta E(L)$ decreases.

In order to test the accuracy of the CI expansion, we have calculated the dissociation energy using a larger CI basis set, consisting of 64 electron-hole pairs (256 including spin). This basis set is constructed from s and p valence and conduction states. We find that for $L = 43$ Å and $\epsilon_{\text{out}} = 6.1$ the exciton dissociation energy changes from 164 meV to 166 meV when the larger basis set is used. This suggests that in the dot molecule, as in the single dot, configuration mixing has a small effect on the electron-hole interaction, because of the large separation between the single-particle energy levels.

We next test a simplified model for $\Delta E(L)$. The dissociation energy $\Delta E(L)$ can be estimated by subtracting the electrostatic attraction between the two charged dots from the dissociation energy at infinite distance $\Delta E(\infty)$:

$$\Delta E(L) = \Delta E(\infty) - \frac{e^2}{\epsilon_{\text{out}} L}. \qquad (13)$$

This simple expression makes two fundamental assumptions: i) that the interaction between the charged dots can be approximated by the interaction between two pointlike charges at distance L and ii) that the electronic coupling between the single-particle wave functions is negligible. We see from Fig. 3 (solid lines) that this approximation works remarkably well, even at small dot-dot separations, suggesting that the assumptions i) and ii) are adequate for CdSe nanocrystals.

In summary, we have shown that a pseudopotential calculation for a dot molecule, coupled with a basic CI calculation of the exciton energy levels, provides directly the exciton dissociation energy $\Delta E(L, \epsilon_{\text{out}})$, including the effects of wave function overlap, bonding-antibonding splitting, screened Coulomb attraction between the electron and the hole in different dots, and polarization effects. We find that ΔE decreases as L decreases and as ϵ_{out} increases.

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*Email address: azunger@nrel.gov

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