Exciton dissociation and interdot transport in CdSe quantum-dot molecules

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One of the most important parameters that determine the transport properties of a quantum dot array is the exciton dissociation energy, i.e., the energy ΔE required to dissociate an exciton into an electron and a hole localized in different dots. We show that a pseudopotential calculation for a dot molecule, coupled with a basic configuration interaction calculation of the exciton energy levels, provides directly the exciton dissociation energy, including the effects of wave function overlap, screened Coulomb attraction between the electron and the hole in different dots, and polarization effects. We find that ΔE decreases as the interdot distance decreases and as the dielectric constant of the medium increases.

The success of electronic devices based on semiconductor quantum dots hinges on the ability to efficiently inject charge or spin into dots, and to transport carriers between dots. For example, in quantum dot photovoltaic devices bound electron-hole pairs (excitons) generated by light absorption must be dissociated and the resulting carriers collected by electrodes.[1,2] Many quantum dot devices are based on arrays of dots, where transport occurs via hopping of electrons and/or holes from one dot to the next dot.[2] The most important parameters that control transport in a quantum dot array are (i) the potential barrier between the dots, which is small in semiconductor-embedded dot arrays [such as InAs dots embedded in GaAs (Ref. 3)], and large in colloidal dot arrays (such as CdSe dots surrounded by organic ligands[4]) and (ii) the energy ΔE required to dissociate an electron-hole pair localized in a quantum dot and place the electron in one dot and the hole in another dot, shown schematically in Fig. 1.

For two identical quantum dots at large distance from each other ($L \rightarrow \infty$), the exciton dissociation energy is

$$\Delta E(\infty) = (E_{1,0} + E_{0,1}) - (E_{1,1} + E_{0,0}), \quad (1)$$

where $E_{M,N}$ denotes the ground-state total energy of a quantum dot with M holes in the valence band and N electrons in the conduction band. Rearranging the terms in Eq. (1), it is easy to see that

$$\Delta E(\infty) = (E_{1,0} + E_{0,1} - 2E_{0,0}) - (E_{1,1} - E_{0,0}) \equiv \varepsilon_{\text{gap}}^{\text{qp}} - \varepsilon_{\text{gap}}^{\text{opt}}, \quad (2)$$

where the quasiparticle gap $\varepsilon_{\text{gap}}^{\text{qp}}$ is the energy of a noninteracting electron-hole pair (first bracket), and the optical gap $\varepsilon_{\text{gap}}^{\text{opt}}$ is the energy of an interacting electron-hole pair (second bracket). Thus, $\Delta E(\infty)$ is simply the electron-hole interaction energy in one dot: $\Delta E(\infty) = J_{h,e}$. The total electron-hole energy $J_{h,e}$ can be separated into two contributions:

$$J_{h,e}(\epsilon_{\text{in}}, \epsilon_{\text{out}}) = J_{h,e}^{\text{dir}}(\epsilon_{\text{in}}) + J_{h,e}^{\text{pol}}(\epsilon_{\text{in}}, \epsilon_{\text{out}}), \quad (3)$$

where $J_{h,e}^{\text{dir}}(\epsilon_{\text{in}})$ is the *direct* Coulomb attraction between the orbital densities $|\psi_e(\mathbf{r})|^2$ and $|\psi_h(\mathbf{r})|^2$, mediated by the dielectric constant ϵ_{in} inside the quantum dot, while $J_{h,e}^{\text{pol}}(\epsilon_{\text{in}}, \epsilon_{\text{out}})$ is the *polarization* contribution arising from

the interaction of the electron with the image charge of the hole.[5] Thus, $\Delta E(\infty)$ depends on both ϵ_{in} and ϵ_{out}.

For two quantum dots at *finite* distance L, the exciton dissociation energy $\Delta E(L)$ is modified by (i) the attractive Coulomb interaction between the charged dots (i.e., the dot with a hole and the dot with an additional electron) and (ii) the quantum-mechanical coupling between single-particle wave functions, which becomes important when the interdot distance L is small or when the potential barrier between the dots is small. In this paper we discuss how to calculate $\Delta E(L)$. We first show that a simple mean-field approach is inappropriate.

When the electron (e) and hole (h) orbitals of two quantum dots spatially overlap, the interaction between them gives rise to bonding (B) and antibonding (A) states

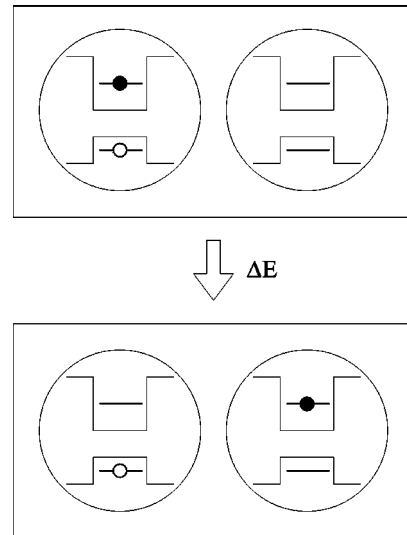$$u_h^B = \frac{1}{\sqrt{2}}(\psi_h^L + \psi_h^R); \quad u_h^A = \frac{1}{\sqrt{2}}(\psi_h^L - \psi_h^R) \quad (4)$$

FIG. 1. The exciton dissociation energy ΔE is the energy required to dissociate an electron-hole pair localized in one dot and place the electron and the hole in different dots.

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

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 can be properly calculated by expanding the exciton wave functions in terms of Slater determinants constructed from the electron and hole bonding and antibonding states. We calculate ΔE for CdSe colloidal nanocrystals as a function of (i) the interdot distance L and (ii) the dielectric constant ϵ_{out} of the material surrounding the dots. We find that the dissociation energy *decreases* when L is *reduced* or when ϵ_{out} *increases*. For example, for 34.1-Å-diameter CdSe nanocrystals surrounded by organic molecules we find that ΔE can be reduced down to less then 150 meV.

The single-particle energies ε_i and wave functions ψ_i are calculated using an atomistic pseudopotential approach. The total pseudopotential of the system (dot + surrounding material) is obtained from the superposition of screened atomic pseudopotentials

$$V_{ps}(\mathbf{r}) = \sum_i v_\alpha(\mathbf{r} - \mathbf{R}_{i,\alpha}), \quad (6)$$

where $v_\alpha(\mathbf{r} - \mathbf{R}_{i,\alpha})$ is the atomic pseudopotential for an atom of type α located at the position $\mathbf{R}_{i,\alpha}$. The atomic pseudopotentials v_α are fitted 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.[6] The single-particle Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ps}(\mathbf{r}) + \hat{V}_{nl} \right] \psi_i(\mathbf{r}, \sigma) = \varepsilon_i \psi_i(\mathbf{r}, \sigma), \quad (7)$$

is then solved for the states close in energy to the band edges (here $\hat{V}_{nl}$ is a short-range operator that accounts for the nonlocal part of the potential as well as spin-orbit coupling).

In the configuration interaction (CI) approach, the many-body exciton wave functions $|\Psi^{(\alpha)}\rangle$ are expanded as a linear combination of Slater determinants obtained by exciting one electron from the valence band to the conduction band[7]

$$|\Psi^{(\alpha)}\rangle = \sum_{h,e} A_{h,e}^{(\alpha)} d_h^\dagger c_e^\dagger |\Psi_0\rangle = \sum_{h,e} A_{h,e}^{(\alpha)} |\Psi_{h,e}\rangle, \quad (8)$$

where $|\Psi_0\rangle$ is the ground state of the quantum dot, $d_h^\dagger$ creates a hole in the valence-band state h, and $c_e^\dagger$ creates an electron in the conduction-band state e. The CI Hamiltonan matrix elements are then

$$\langle \Psi_{h,e} | \hat{H} | \Psi_{h',e'} \rangle = (\varepsilon_e - \varepsilon_h + \Sigma_e^{\text{pol}} + \Sigma_h^{\text{pol}}) \delta_{h,h'} \delta_{e,e'} - J_{he,h'e'}$$
$$+ K_{he,h'e'}. \quad (9)$$

Here Σ_e^{pol} and Σ_h^{pol} are the electron and hole polarization self-energies, respectively. They are due to the interaction of the electron (or the hole) with the surface polarization charge generated by the dielectric mismatch between the dot and the surrounding material.[8] The electron-hole Coulomb energies $J_{he,h'e'}$ are calculated as

$$J_{he,h'e'} = e \sum_\sigma \int \psi_{h'}^*(\mathbf{r}, \sigma) \psi_h(\mathbf{r}, \sigma) \Phi_{e,e'}(\mathbf{r}) d\mathbf{r}. \quad (10)$$

Here $\Phi_{e,e'}(\mathbf{r})$ is the electrostatic potential generated by the "charge distribution" $e \sum_\sigma \psi_c^*(\mathbf{r}, \sigma) \psi_{c'}(\mathbf{r}, \sigma)$, and satisfies the Poisson equation in a dielectrically inhomogeneous medium:

$$\nabla \cdot \boldsymbol{\epsilon}(\mathbf{r}) \nabla \Phi_{e,e'}(\mathbf{r}) = -4\pi e \sum_\sigma \psi_e^*(\mathbf{r}, \sigma) \psi_{e'}(\mathbf{r}, \sigma). \quad (11)$$

The Poisson equation is solved on a real-space grid by discretizing the Laplacian operator. Equation (11) reduces to a linear system, which is solved iteratively using a conjugate-gradients algorithm.[8] The electron-hole *exchange* energies $K_{he,h'e'}$ are small (only a few meV for the quantum dots considered here) and will be neglected in the following.

As discussed above, mean-field approaches retaining only a single configuration in the expansion of Eq. (8) are inadequate to calculate the exciton dissociation energy. The simplest CI basis set for an electron-hole pair in a double dot system consists of Slater determinants obtained by promoting an electron form either the bonding or antibonding valence states [Eq. (4)] to the bonding or antibonding conduction states [Eq. (5)]. Thus, the basic CI basis set includes four Slater determinants, each of them being fourfold degenerate because of the spin degrees of freedom. The diagonalization of the CI Hamiltonian [Eq. (9)] in this basis set yields four exciton states. The two (nearly degenerate) low-energy solutions correspond to the electron and the hole being localized in the same dot, whereas the two (also nearly degenerate) higher-energy solutions correspond to the electron and hole localized in different dots. Thus, the exciton dissociation energy $\Delta E(L)$, including the effects of bonding-antibonding splitting, polarization effects, and electron-hole Coulomb interaction can be obtained from a simple CI cal-
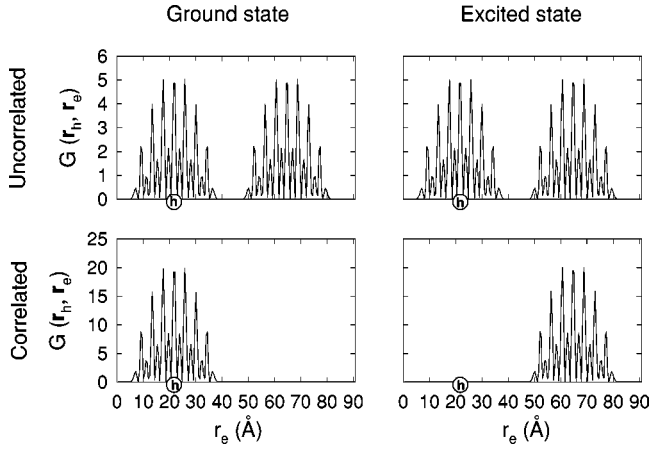
FIG. 2. Electron-hole correlation function $G(\mathbf{r}_h, \mathbf{r}_e)$ of a CdSe-dot molecule ($L = 43$ Å). The hole is kept fixed at the position indicated by the circle, while the electron is moved along the line connecting the centers of the two quantum dots. In the uncorrelated (mean-field) solution the electron is delocalized over the two quantum dots, regardless of the position of the hole. In the correlated (CI) ground-state solution the electron and the hole are localized in the same dot, while in the excited-state solution they are localized in different dots.

FIG. 3. The dissociation energy ΔE is shown as a function of the interdot distance L (center-to-center distance) for a few values of the dielectric constant ϵ_{out}. The circles are the results of a full pseudopotential calculation. The solid lines correspond to the model of Eq. (13). The panel on the left-hand side shows the dissociation energies $\Delta E(\infty)$ (in meV) at infinite interdot separation.

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 $D = 34.1$ Å, and the surface dangling bonds are passivated using ligandike potentials. Using the pseudopotential approach described in Ref. 4, we estimate the macroscopic dielectric constant of these CdSe dots (for exciton screening) to be 6.1. For the calculation of the exciton dissociation energies, we construct a large supercell containing two identical quantum dots separated by a distance L (center-to-center distance). The dots are aligned in the plane perpendicular to the wurtzite c axis. The single-particle wave functions of the double-dot system show the characteristic bonding-antibonding splitting of a molecular system, and are equally distributed between the two dots (this is true regardless of the interdot distance L).

To see how the introduction of ''left-right correlation'' via CI leads to broken-symmetry solutions, we show in Fig. 2 the electron-hole correlation function

$$G^{(\alpha)}(\mathbf{r}_h, \mathbf{r}_e)$$

$$= \sum_{\sigma_h, \sigma_e} \langle \Psi^{(\alpha)} | \hat{\psi}^{\dagger}(\mathbf{r}_h \sigma_h, \mathbf{r}_e \sigma_e) \hat{\psi}(\mathbf{r}_h \sigma_h, \mathbf{r}_e \sigma_e) | \Psi^{(\alpha)} \rangle$$

$$(12)$$

for a fixed value of $\mathbf{r}_h$ and varying $\mathbf{r}_e$. We see that in the uncorrelated solution the electron wave function is equally distributed between the two quantum dots. When ''left-right correlation'' is introduced, in the ground-state solution the electron ''gravitates'' around the hole, while in the excited-state solution the electron is repelled by the hole. The energy difference between these two solutions is the exciton disso-
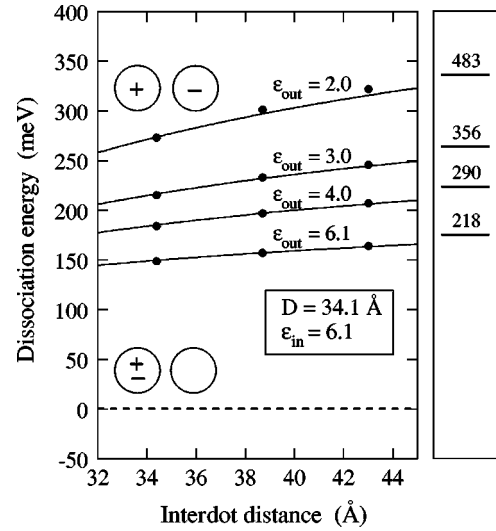
ciation energy ΔE. We have calculated $\Delta E(L, \epsilon_{out})$ as a function of the inter-dot distance L and of the dielectric constant ϵ_{out} of the material surrounding the two dots. Figure 3 shows $\Delta E(L)$ for a few values of ϵ_{out}, while Fig. 4 shows ΔE as a function of ϵ_{out} for a few values of the interdot separation L. We see that the dissociation energy decreases monotonically as the distance between the dot decreases. This is due to the increased electrostatic attraction between the two charged dots when the interdot distance decreases. Also, the dissociation energy *decreases* when the dielectric constant increases. This appears at first counterintuitive, since when the dielectric constant increases the interaction between the two charged dots decreases due to the larger screening, so $\Delta E(L)$ should increase. However, $\Delta E(\infty)$ of Eq. (2) also depends on ϵ_{out}: it becomes less positive as ϵ_{out} increases. In fact, pseudopotential calculations[8] have shown
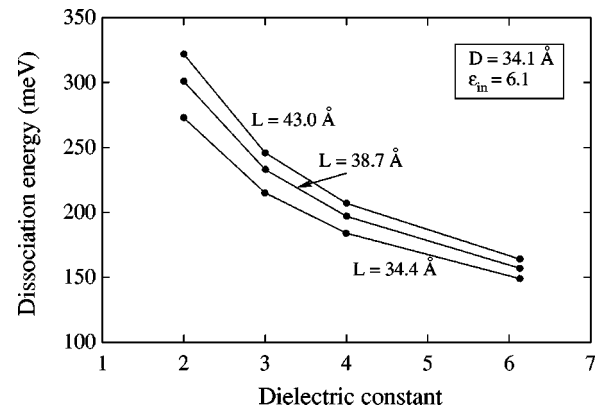

FIG. 4. The dissociation energy ΔE is shown as a function of the dielectric constant ϵ_{out}, for a few values of the interdot distance L. The solid lines are guides for the eye.

that $J_{h,e}^{pol}$ 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 $\epsilon_{out} = 6.1$ 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 $\Delta E(\infty)$:

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

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 $\Delta E(L, \epsilon_{out})$, 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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