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Stark effect in semiconductor nanocrystals: tight-binding approach

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Abstract

The influence of an external uniform electric field on the electron energy structure and charge densities of semiconductor nanocrystals is investigated. We study both uniform and multilayer nanocrystals as well as artificial molecules, i.e. systems built of two coupled quantum dots. We work in the framework of an empirical tight-binding theory, that allows the study of effects not accessible within the effective mass approach. The electric field can destroy the delocalized character of bonding-like and antibonding-like states of artificial molecules but can also lead to the formation of other field-tunable states.

Keywords: Quantum dots; Artificial molecules; Stark effect

The effects of an electric field on the electronic and optical properties of semiconductor quantum dots have been intensively investigated for the last few years [1–6]. This is because the external field can be used to control electron transfer between the coupled nanocrystals in quantum dot-based single electron devices and to control elementary qubit operations in such systems [3,7,8]. The electric field also makes possible the mapping of the electronic wavefunctions of quantum dots in scanning-tunneling-microscopy experiments [9].

In the majority of theoretical works devoted to the study of Stark effects in quantum dots the effective mass approximation or **kp** theory (both based on the continuum medium approximation) were used. These approaches account only for the global effects of the electric field in quantum dots, but miss the microscopic effects that occur on an atomic scale.

In this work we perform a preliminary study of the electric field effects in quantum dots using an atomistic approach, i.e., an empirical tight-binding theory (TB). In this approach the one-particle wavefunction $\Psi(\mathbf{r}) = \sum_J \sum_\alpha c_{\alpha,J}\phi_\alpha(\mathbf{r}-\mathbf{R_J})$, is represented in an orthogonal basis set of atomic orbitals $\phi_\alpha(\mathbf{r}-\mathbf{R_J})$, where α denotes an orbital of a given symmetry, centered at the atomic site $\mathbf{R_J}$ [10]. In our model, each atom is described by five orbitals (s, p_x, p_y, p_z, and s^*). The interaction in the Hamiltonian is restricted to on-site and nearest neighbors only; the Hamiltonian matrix elements $t_{\alpha'\alpha}R'_J R_J = \langle \phi_{\alpha'}(\mathbf{r}-\mathbf{R'_J})|H|\phi_\alpha(\mathbf{r}-\mathbf{R_J})\rangle$

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are treated as empirical parameters obtained by fitting the bulk-band structure to experimentally known band gaps and effective masses. The surface dangling bonds are passivated by shifting their energies high above the conduction band edges. The one particle quantum dot states are found by diagonalizing the TB Hamiltonian matrix.

A static external electric field is described by adding $e\vec{F}\vec{r}$, where F is the electric field, to the one particle Hamiltonian.[1] This is accomplished by including dipole matrix elements between atomic orbitals on the same and neighboring atoms, in the TB Hamiltonian matrix. The small off-site dipole matrix elements are neglected. The on-site dipole moments are

$$\langle \alpha J|\mathbf{r}|\beta J\rangle = \delta_{\alpha\beta}\mathbf{R_J} + \langle \alpha J|\mathbf{r} - \mathbf{R_J}|\beta J\rangle. \quad (1)$$

The first term in Eq. (1) represents the global effect. The dipole matrix elements between different orbitals on the same site (the second term in Eq. (1)) are taken from Ref. [11].

We consider uniform, CdS, and two-layer, ZnS/CdS, spherical nanocrystals, that are now almost routinely synthesized by wet chemistry methods [12]. We study also artificial molecules, i.e., double-dots built of two coupled nanocrystals touching each other (having a single common surface atom and several bonds created between the nanocrystals).

In Fig. 1, several lowest electron energy levels (s- and p-type in the conduction band region) of a uniform CdS nanocrystal of radius $R = 2.33$ nm are shown versus the electric field. For $F = 0$ the wavefunction corresponding to the ground state has a global s-symmetry (the charge density is spherically symmetric, see Fig. 3 and Ref. [13]). The first excited level is triply degenerate and the corresponding wavefunctions have p-type global symmetry (see Fig. 3) and are unpolarized. For $F > 0$ the ground state energy decreases quadratically, in agreement with second-order perturbation theory. The excited levels split. The highest level from the first excited p-type triplet is polarized along the field axis and is less affected by the field. This is because it is more difficult to move and squeeze in a quantum dot the charge density that contains a nodal plane perpendicular to the field axis. The degeneracy of two another p-type energy levels (the ones having nodal planes parallel to $\vec{F}$) is also lifted. A closer inspection of their global densities reveals that they are polarized along the projections of the bonds on the plane perpendicular to the field. This is a purely atomistic effect (caused by the second term in Eq. (1)), not present when the calculations are performed in the effective mass approach [1].

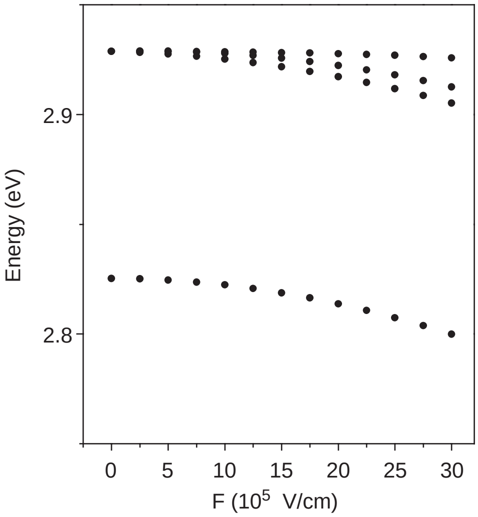

Fig. 1. Electron energy levels of a single CdS nanocrystal vs. electric field. The energy of the ground state has been shifted up by 0.1 eV.

Let us now consider an artificial molecule built of two CdS nanocrystals of radii 2.91 and 1.86 nm, just touching each other (their centers are 4.66 nm apart). Several lowest electron energy levels versus an electric field applied along the artificial molecule axis are shown in Fig. 2. As shown in Ref. [13], for $F = 0$ the lowest state has s-type symmetry and is entirely localized in the bigger dot, while the next almost degenerate quartet (a–d in Fig. 2) is formed from the s-type state of the smaller dot and three degenerate p-type states from the larger dot. The lowest level in this quartet has bonding-like character, while

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[1] The electric field inside a spherical nanocrystal is homogeneous, $F_{ins} = 3F/(2+\varepsilon)$, where ε is the relative dielectric constant. We assume the same for double dots. In the STM experiments [9,1] F is up to 3×10^6 V/cm.

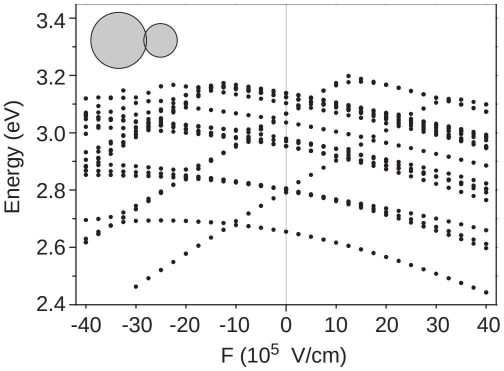

Fig. 2. Electron energy levels of a double CdS nanocrystal (inset) vs. electric field applied along the axis of the quantum dot molecule.

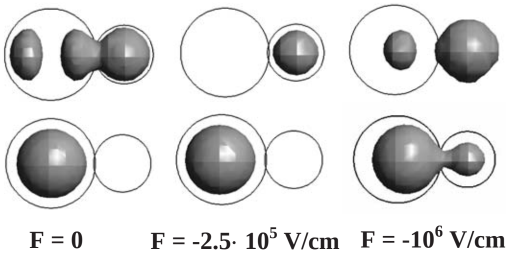

Fig. 3. Double CdS quantum dot. Charge densities of the two lowest energy levels for several field values.

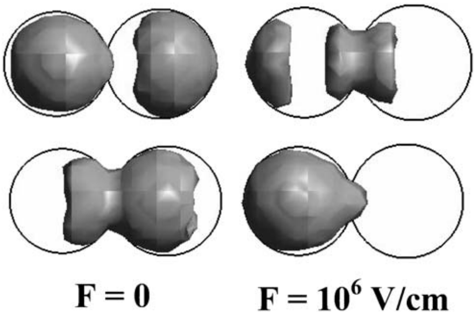

Fig. 4. Double ZnS/CdS nanocrystal. Charge densities of the two lowest energy levels for $F = 0$ and 10^6 V/cm.

the uppermost one is antibonding-like. Both have delocalized character.

For $F > 0$ the energy levels split, but since the double dot system is not symmetric, they behave differently for different signs of the field. A strong splitting of the bonding- and antibonding-like states is observed for even moderate fields. For a field of 2.5×10^5 V/cm (0.25 V applied bias) these states completely lose their delocalized character: the lowest one transforms into the s-type state, localized in the larger dot, while the upper one becomes an s-type state located in the smaller dot. For stronger fields, the formation of another delocalized, i.e., field tunable state occurs ($F = -10^6$ V/cm in Fig. 2). The evolution of the charge densities of the states corresponding to the two lowest energy levels is shown in Fig. 3.

Let us finally consider a double quantum dot built of two ZnS/CdS nanocrystals almost equal in size (ZnS core radius 1.75 nm, CdS shell thickness 0.58 nm). Since the energy gap of the bulk ZnS is wider than the gap of CdS, the ZnS core acts as a barrier and the CdS surface clad plays the role of a thin external well: the lowest states have densities localized mainly in the CdS clad. The coupling in such nanocrystals is then stronger than in the case of uniform dots. Electron and hole energy levels and charge densities of such an artificial molecule have been studied in Ref. [13]. The lowest state is a bonding combination of the s-type states of individual ZnS/CdS nanocrystals and has its density localized mainly in the region where the CdS surface shells of both nanocrystals overlap. The first excited state is an antibonding combination of such states. In Fig. 4 the charge densities of these states are shown for two different field values, $F = 0$ and 10^6 V/cm. For $F \neq 0$ the density of the ground state is shifted to one of the dots and gets the character of the s-state. However, the density of the second state looks, for $F = 10^6$ V/cm, like a combination of the p-type state localized in one dot, combined symmetrically with an s-type state of another dot. This can be easily understood, since for the case of touched but not-interacting dots, their energy levels are shifted for $F = 10^6$ V/cm in such a way, that the perturbed s-type level of one nanocrystal has an energy close to that of the perturbed p-type level of another nanocrystal.

In summary, we have studied the influence of an external electric field on the electron energy levels and charge densities of spherical CdS nanocrystals and artificial molecules formed by two interacting

CdS or ZnS/CdS quantum dots. All the calculations have been performed in the tight-binding approximation. We have found that even in spherical nanocrystals the degeneracy of the p-type levels is totally lifted. This effect is missed in the approaches based upon the continuum medium approximation. We have shown also, that the electric field can destroy the delocalized character of some double-dot states, leading simultaneously to the formation of other field-tunable states for such field values, for which split levels of different symmetries cross.

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