QUANTUM DOT MOLECULES AND CHAINS

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Abstract A review of results from theoretical investigations of several systems composed of two or more coupled quantum dots (known as *artificial molecules* or *quantum dot solids*) is presented. All the calculations are performed within an empirical tight-binding theory. It is shown that coupling between nanocrystals can split and reorder energy levels and change state symmetries. The results help to understand and explain differences observed in optical spectra of arrays of quantum dots in comparison to the spectra obtained for non-interacting nanocrystals. We show also how an external electric field influences the properties of coupled quantum dots.

1. Introduction

By analogy to diatomic molecules and crystalline solids, *artificial* and *quantum dot solids* can be built from coupled semiconductor nanocrystals. Coupled dots created by etching techniques or electrical confinement from quantum-well systems were studied first due to their possible applications as single-electron resonant tunneling devices [1, 2, 3, 4, 5, 6, 7, 8]. Systems of vertically stacked self-assembled quantum dots are intensively investigated now to determine how the coupling between nanocrystals in a dense array of such dots influences properties and performance of quantum dot lasers [9, 10, 11, 12]. Linear chains of electrically confined quantum dots have been proposed recently for a realization of multi-qubit gates [13].

The densest ensembles of quantum dots are obtained for chemically synthesized nanocrystals [14, 15, 16, 17, 18]. Kagan et al [14] first found luminescence from close-packed CdSe nanocrystals totally different than

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the luminescence of non-interacting dots in a dilute solution. Several another experiments [16, 17] have shown that optical properties of dense arrays of chemically synthesized nanocrystals are significantly different from properties of individual dots.

We present here a review of the results of our investigations on the formation of delocalized states in coupled quantum dots and linear chains of nanocrystals. We work within the empirical tight-binding theory which, as a microscopic approach, is well suited for precise investigation of the coupling on the atomic scale. The presented results help to explain why the optical properties of coupled nanocrystals are so different form the properties of individual quantum dots. We present also some preliminary results showing how an external electric field influences delocalized states in coupled systems.

2. Theory

In the empirical tight-binding approach (TB) the one-particle wavefunction is represented in an orthogonal basis set of atomic orbitals $\phi_\alpha(\mathbf{r}-\mathbf{R_J})$ [19],

$$\Psi(\mathbf{r}) = \sum_{\mathrm{J}} \sum_{\alpha} \mathrm{c}_{\alpha,\mathrm{J}} \phi_\alpha(\mathbf{r}-\mathbf{R_J}), \tag{1}$$

where α denotes an orbital of a given symmetry and $\mathbf{R_J}$ is an atomic site. In our model, each atom is described by 5 orbitals (s, p_x, p_y, p_z, and s^*). We assume that atoms occupy the sites of a zinc-blend structure. Only atoms embedded in a volume of a given system are taken into account. The interaction in the Hamiltonian is restricted to on-site and nearest neighbors only. The Hamiltonian matrix elements

$$t_{\alpha'\alpha R'_J R_J} = \langle \phi_{\alpha'}(\mathbf{r}-\mathbf{R'_J})|H|\phi_\alpha(\mathbf{r}-\mathbf{R_J})\rangle \tag{2}$$

are treated as empirical parameters obtained by fitting bulk-band structure to experimentally known band gaps and effective masses. There are 13 different TB parameters for each material. 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 with the use of an iterative eigenvalue solver.

To study linear infinite chains of nanocrystals we first define the supercell of a given chain. The TB wavefunction components corresponding to atomic sites at opposite supercell boundaries differ in phase by e^{iqD}, where D is the chain period. Therefore, the TB elements for $\mathbf{R_J}$ and $\mathbf{R'_J}$ at adjacent supercells are $t_{\alpha'\alpha R'_J R_J} = e^{iqD} t_{\alpha'\alpha R'_J R_J+D}$. 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. This is accomplished by including dipole matrix elements between atomic orbitals on the same and neighboring atoms, in the TB Hamiltonian matrix. The off-site dipole matrix elements are naturally much smaller than the on-site ones and are neglected. The on-site dipole moments are

$$\langle \alpha J | \mathbf{r} | \beta J \rangle = \delta_{\alpha\beta} \mathbf{R_J} + \langle \alpha J | \mathbf{r} - \mathbf{R_J} | \beta J \rangle. \tag{3}$$

The dipole matrix elements between different orbitals on the same site (the second term in Eq. 3) are taken from [21].

3. Artificial Molecule of Two CdS Nanocrystals

We first consider a quantum dot molecule built of two spherical CdS nanocrystals of radii 2.9 nm and 1.9 nm, respectively. The sizes of the nanocrystals are similar to CdSe nanocrystals studied in [14] (3.1 nm and 1.9 nm), for which very different luminescence was observed depending on whether the sample was liquid mixture of such dots or a close-packed quantum dot solid. The lowest conduction band energy level (Ls) of the larger nanocrystal has energy 2.6548 eV above the valence band-edge of the bulk CdS [20]. The TB wavefunction of this state reveals a global s-type symmetry. The first excited state energy level (Lp), with energy 2.8010 eV, is triply degenerate: the corresponding wavefunctions have global p-type symmetry. The lowest conduction band energy level (Ss) of the smaller dot is also of s-type and has energy 2.7981 eV, i.e. close to the first excited level of the larger nanocrystal.

When the two nanocrystals are close but not directly connected, the energy spectrum of such a system is a simple sum of the spectra of individual nanocrystals. This is because the surrounding medium is not represented in the TB wavefunction, and no interaction is mediated between the quantum dots. The case of nanocrystals that just touch each other, is modeled by putting the dot centers at distance D that is only 0.1 nm smaller than the sum of the dots radii. In such a case the nanocrystals have only one common atom and 16 new chemical bonds created between the nearest atoms[1]. Although the spherical symmetry is broken, the lowest electron state is still localized entirely in the larger nanocrystal and has s-type symmetry. However, the degeneracy of the p-type excited state (Lp) is lifted and four new states of quantum dot molecule are formed from three (Lp) states of the larger dot and the (Ss) state of the smaller nanocrystal. Their energies are: 2.7913, 2.8009, 2.8010, 2.8059 eV (see Fig. 2). Figure 1 shows charge density isosurfaces of these states. The lowest state of the quartet has clearly bonding-like character, while the highest one is antibonding-like. The two almost degenerate levels (the second and the third) have p-type symmetry in the

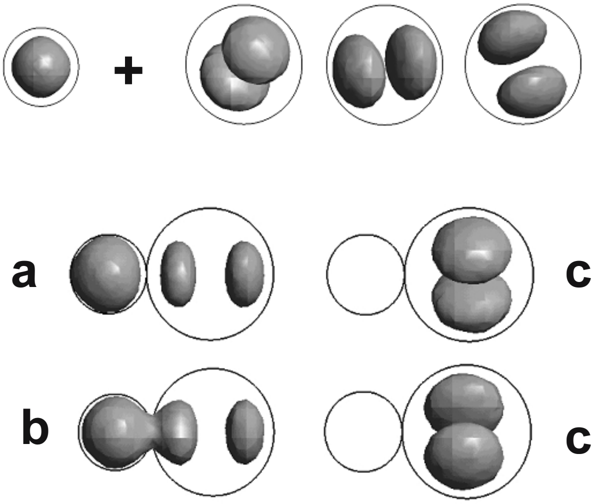

Figure 1. Quantum dot molecule built of two CdS spherical nanocrystals of radii 1.9 and 2.9 nm; dot centers separation distance $D = 4.7$ nm. Density isosurfaces (50%) of the four states (bottom) of double dot created by s-type state of smaller dot and three p-type states of larger nanocrystal (top). (b) bonding-like state, (a) antibonding-like state, (c) p-like states.

plane perpendicular to the artificial molecule axis and are entirely localized in the larger dot. The appearance of delocalized states in systems of nanocrystals that merely touch each other explains how the excitation transfer can occur in close-packed solids of chemically synthesized nanocrystals [14].

When the two nanocrystals are closer connected the energy of the ground state decreases only slightly, the energies of the quasi-degenerate doublet do not change, while the bonding- and antibonding-like states dramatically change their energies. This is shown in Fig. 2. For $D =$ 3.6 nm, the level splitting of the *artificial molecule* is about 50 meV.

How an external electric field influences the energy spectra and charge densities of coupled dots is important because electric field can be used to control electron transfer between coupled dots and thus to control elementary qubit operations in such systems [22, 23, 24]. On the other hand, experimental mapping of the electron wavefunctions in quantum dots has been shown possible by using scanning tunneling microscopy (STM) [25]. In such experiments, quantum dot systems are also subjected to strong electric fields. Here, we study Stark effects in the above-mentioned double CdS quantum dot. We assume that a homogeneous external electric field, F is applied in the direction of the axis of the *artificial molecule*. The problem of finding the field inside a nanocrystal

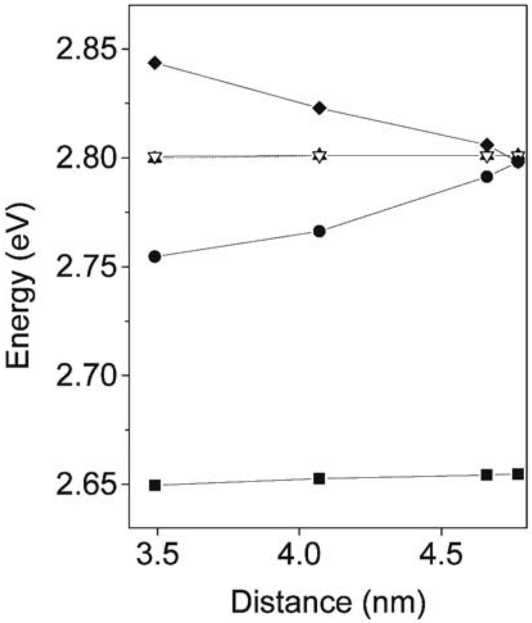

Figure 2. Four lowest electron energy levels of a double CdS quantum dot (radii 1.9 and 2.9 nm) *versus* distance between dot centers. The rightmost values correspond to the case when dots have only a single common atom.

is not trivial. The field can be found analytically for a limited number of cases, such as the spherical isotropic dielectric dot[26]. As for the spherical nanocrystal, we assume that the electric field inside a double dot is homogeneous. In addition, we assume that the same relation between internal and external fields, $F_{\text{ins}} = 3F/(2+\epsilon)$ where ϵ is the relative dielectric constant, holds for double and single dots. In the STM experiment [27] a bias up to 3 V was applied between the tip and the substrate. Assuming the tip-substrate distance ~ 10 nm, we study fields up to 3×10^6 V/cm.

Several lowest electron energy levels of the double CdS quantum dot versus electric field are shown in Fig. 3. Since the double dot system is not symmetric, the energy levels split and 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 loose their delocalized character (point marked as z in Fig. 3): the lowest one transforms into the s-type state, localized almost entirely in the larger dot, while the upper one becomes an s-type state located in the smaller dot. The localization occurs because the energy splitting of this bonding-like state is only

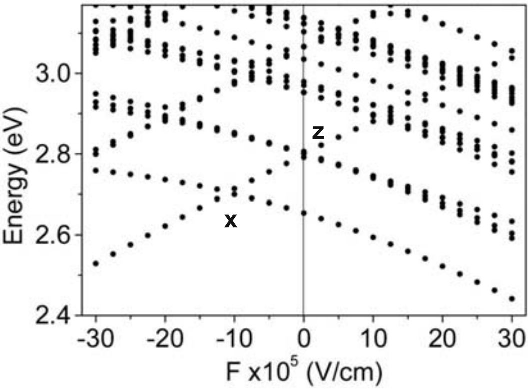

Figure 3. Electron energy levels of a double CdS nanocrystal *versus* electric field applied along the axis of the quantum dot molecule.

about 7 meV (see Fig. 2), while the energy shift by such a field is about 70 meV. Figures 3 and 4 show also that stronger field can lead to formation of another field tunable state (point marked as x in Fig. 3): for $F = -10 \times 10^5$ V/cm a delocalized state built of s-type states of both nanocrystals is created.

4. Linear Chain of ZnS/CdS Nanocrystals

In this section we study the formation of bands for infinite linear chains of two-layer nanocrystals. We study nanocrystals built of an internal ZnS core of radius 5 nm and an external CdS clad of thickness 1 nm. Such nanocrystals, called also *quantum dot-quantum wells* are synthesized by the wet-chemistry methods [28, 29]. Since the energy

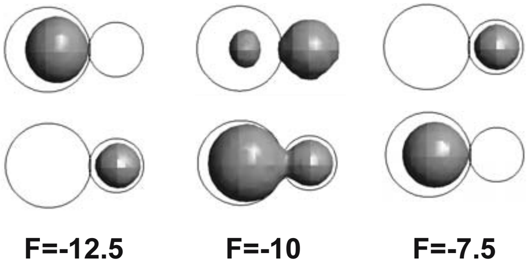

Figure 4. Quantum dot molecule built of two CdS spherical nanocrystals of radii 1.9 and 2.9 nm; dot centers separation distance $D = 4.7$ nm. Density isosurfaces of two lowest electron electron states *versus* electric field F (corresponds to point marked as x in Fig. 3).

gap of the bulk ZnS is 3.7 eV and the gap of CdS is 2.5 eV, the ZnS core act as a barrier and the CdS clad plays a role of a thin spherical external well. The lowest electron and hole states have densities localized mainly in the CdS shell, i.e. pushed away from the dot center. The coupling in such nanocrystals is then stronger than in the case of uniform dots.

In Fig. 5 the minibands, originating from several lowest electron energy levels of individual ZnS/CdS nanocrystals, are shown for three different values of the superlattice period $D = 12$ nm, 11 nm and 10 nm (note that $D = 12$ nm corresponds to a chain formed by the nanocrystals that just touch each other). For $D = 12$ nm the minibands are very narrow; their energies are almost the same as the energy levels of individual dots. When D decreases, excited state minibands become wider. However, the most striking effect is that the ground miniband detaches down from the spectrum and becomes extremely narrow. This can be understood by looking at the charge density of the ground state for a system built of two such nanocrystals. This is shown in Fig. 6. When the distance between dot centers equals $2R$, where R is the dot radius, the ground state is an extended state, delocalized in all nanocrystals. When the distance between dot centers decreases, the ground state (and thus all states in the ground miniband) becomes more localized in the region where the dots overlap because the CdS well in this region be-

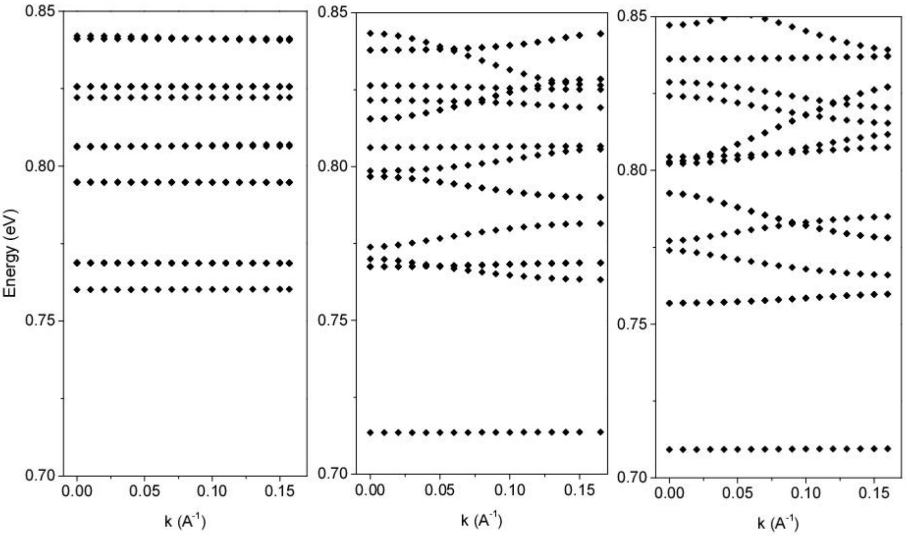

Figure 5. Minibands $E(k)$ for a linear chain of ZnS/CdS nanocrystals; ZnS core radius 5 nm, total dot radius 6 nm. Superlattice period (from left to right): 12 nm, 11 nm and 10 nm.

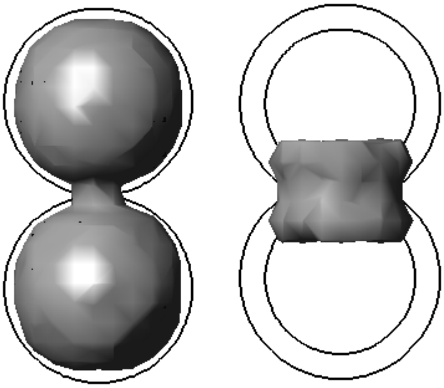

Figure 6. Density isosurfaces of the lowest electron state for a ZnS/CdS quantum dot molecule (as in Fig. 5). Top: nanocrystals just touch each other, bottom: nanocrystals overlap on in the range of CdS clad thickness.

comes wider in the (x, y) plane and the energy of this state decreases. When the overlap d reaches the thickness of the CdS clad (i.e. 1 nm), the ground state is no longer an extended state, it becomes highly localized in the overlap region; the miniband converts into strongly degenerate energy level [30].

The hole states behave in an analogous way. As a result the effective gap decreases significantly and the absorption edge is strongly redshifted [20], in agreement with experimental observations [16, 17].

5. Two Vertically Stacked Self-Organized InAs/GaAs Quantum Dots

For the chemically synthesized nanocrystals studied in the previous sections, the coupling and interaction between quantum dots could be described in the TB method only when the nanocrystals at least touched each other. However, this is not a significant limitation to modeling the coupling between nanocrystals made by wet synthesis. These nanocrystals are usually surrounded by a large-gap dielectric medium and the interaction of separated dots is negligibly weak in such a medium. In contrast, the coupling between self-organized quantum dots is through the surrounding barrier material. In this case the coupling between spatially separated dots can be described within the TB approach because the coupling is mediated by the barrier atoms.

We have studied two vertically stacked lens-shape InAs quantum dots of base size 6 nm and height 1.2 nm on a 2 monolayer (ML) thick wetting layers (WL), embedded in a large box of GaAs [31]. In such quantum dots the strain effects can be significant and can influence coupling effects between the dots [32]. Here we neglect the strain effects [2], since we want to show how the coupling between two vertically stacked quantum dots influences their energy spectra.

For very large separation between the dots, the energy spectrum of the double system is the same as the spectrum of an individual dot, with all the energy levels doubly degenerate. When the separation distance decreases, the degeneracy is lifted and splitting caused by the coupling between dots appears. This coupling is strong enough that even for distance $d_c = 18$ ML separating the dot centers, the splitting of the electron energy levels is about 10 meV. When $d_c = 8$ ML (i.e. there are still 6 ML of GaAs separating the two InAs wetting layers) the splitting of the electron energy levels reaches ~ 200 meV. As a consequence, the split ground energy level starts to cross with the excited level, which also splits, and the symmetry of the consecutive states changes. This is shown in Fig. 7, where isosurfaces of densities of the two lowest electron states are shown for $d_c = 10$ and 6 ML. The hole levels start to cross for larger d_c because the hole energy spectrum is denser. Isosurfaces of densities of the four lowest hole states for $d_c = 12$ and 6 ML are shown in Fig. 8. Note that for $d_c = 6$ ML the top of the lower dot touches the bottom of the upper wetting layer, while for $d_c = 12$ ML the distance between these two points is only 1.8 nm. However, the consecutive hole states have completely different symmetries and polarizations for these two separation distances. The figure shows also that when the self-organized quantum dots are close enough in a vertical stack, well delocalized states are formed. Since changes of symmetries of the electron

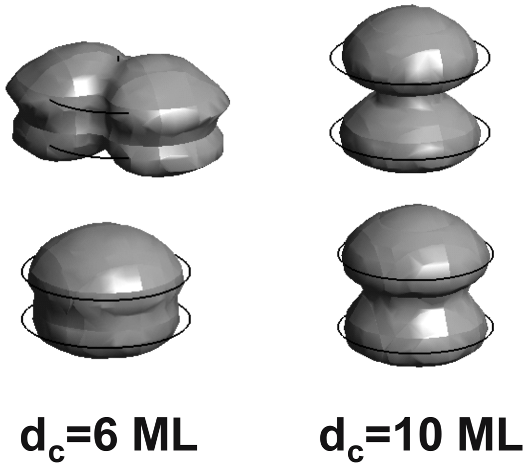

Figure 7. Density isosurfaces (50%) of the ground (bottom) and first excited (top) electron states for two vertically stacked self-organized quantum dots *versus* distance d_c between dot centers.

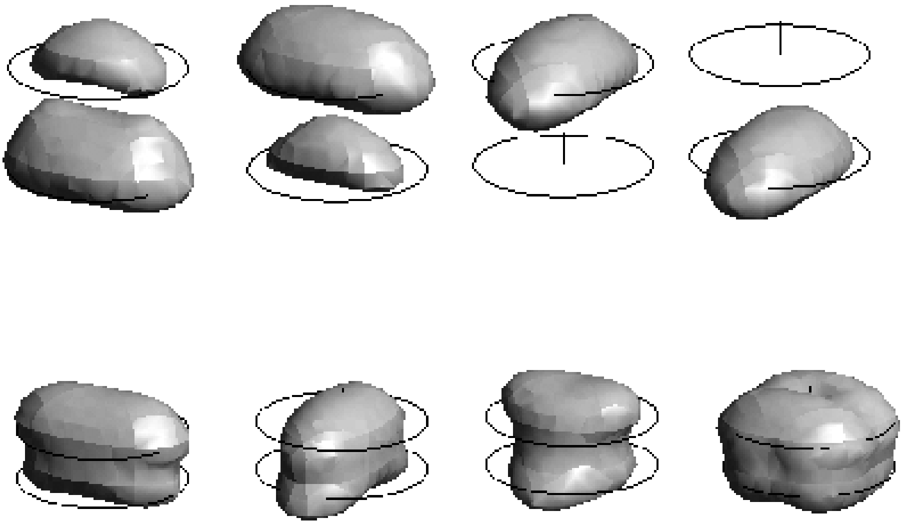

Figure 8. Density isosurfaces (50%) of several lowest hole states (from left to right) for two vertically stacked self-organized lens-type quantum dots for two distances between dot centers: 12 ML (top) and 6 ML (bottom). Circles and vertical bars mark lens base position and height, respectively.

and hole states occur for different d_c, the optical properties of quantum dot lasers can strongly depend on the separation distance between the layers of self-organized quantum dots.

6. Conclusions

The results of theoretical investigations of several systems composed of two or more coupled quantum dots have been reviewed. We have investigated both chemically synthesized nanocrystals and self-organized quantum dots. By studying charge densities of the states of coupled nanocrystals we have shown the formation of delocalized states in such systems. Our results provide an understanding of differences observed between optical spectra of close-packed nanocrystals and spectra of non-interacting quantum dots. For vertically stacked self-organized quantum dots, the order of energy levels and symmetry of the states depends strongly on the distance between the neighboring dots. A weak electric field can destroy delocalization of states in quantum dot molecules and solids.

Notes

1. The total number of atoms in a double quantum dot is 5333.
2. they can be investigated using the *valence force field method* [33].

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