Artificial Molecules

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ABSTRACT: Double semiconductor nanocrystals, called *artificial molecules* by analogy to *artificial atoms* (quantum dots), are investigated. Empirical tight-binding and $\mathbf{k} \cdot \mathbf{p}$ theories are used to obtain electronic structure, charge density distributions, and optical absorption spectra for single and double nanocrystals. We show how the bonding and antibonding *molecular orbitals* are formed from the wavefunctions of individual nanocrystals when the nanocrystals are joined together to form an artificial molecule. Formation of quantum dot lattices and interpretation of experimental data for close-packed solids of nanocrystals are discussed. © 2002 Wiley Periodicals, Inc. Int J Quantum Chem 90: 1075–1082, 2002

Key words: artificial atoms; artificial molecules; molecular orbitals; optoelectronics; quantum dots

Introduction

The physics of semiconductor quantum dots (QDs) is one of the most rapidly developing fields of contemporary condensed-matter science. Quantum dots exhibit discrete, size-dependent electronic and optical properties that make QDs particularly attractive for potential applications in novel optoelectronics devices. Due to the discrete nature of their energy levels, QDs are also called *artificial atoms* [1].

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The smallest QDs are nanocrystals that are synthesized in colloidal solutions [2, 3]. They are most frequently spherical or tetrahedral [4, 5] and can be built of several concentric layers (shells) of different semiconductors with the shell thickness down to a single monolayer. Formation of close-packed QD solids or systems built of several coupled nanocrystals has also been achieved [4, 6]. Absorption and luminescence spectra of QD solids are significantly different from the spectra obtained for *noninteracting* nanocrystals [7, 8]. This has been interpreted recently in terms of the evolution from localized to delocalized electronic states in close-packed QD ensembles [8].

The first step toward understanding the physics of QD solids is to study systems built of two coupled nanocrystals. In this article we investigate sev-

eral such systems. We show how the electronic structure of two nanocrystals changes when they are joined together to form an artificial molecule. We show that the electronic structure of two coupled nanocrystals is qualitatively similar to the structure of a diatomic molecule. The formation of bondinglike and antibondinglike *artificial molecular* orbitals is also shown. The changes in optical properties of such systems are discussed. All the results are obtained within the empirical tight-binding theory [9]. For comparison, some calculations are performed also in the effective mass approximation [10].

Theory

To calculate one-electron states in nanoparticle systems, we use the empirical tight-binding (ETB) method [9, 11]. We assume that atoms occupy the sites of a regular fcc lattice with a two-atom basis. Only the atoms embedded in a volume of a given shape are taken into account, for example, inside a sphere or tetrahedron for single nanocrystals or inside two slightly overlapping spheres for double dots. Each atom is described by its outer valence *s* orbital, the three outer *p* orbitals and an extra *s** orbital to include the effect of higher lying states. The ETB is thus equivalent to the linear combination of atomic orbitals (LCAO) method, in which the effective Hamiltonian matrix elements are treated as empirical parameters. The LCAO molecular orbital wavefunction is

$$\Psi(\mathbf{r}) = \sum_n \sum_i c_{ni}\phi_i(\mathbf{r}-\mathbf{R_n}) \qquad (1)$$

when n is the atomic site index and i is the orbital index. We include on-site and nearest-neighbor coupling between orbitals. No spin-orbit effects are included in the calculations reported here, so all results presented here are independent of spin. We exclude the effects of surface states by passivating the surface dangling bonds. The passivation is modeled by shifting the energy of the dangling bonds above the conduction band so that they do not modify states near the band gap. There are 13 empirical parameters that are adjusted to reproduce known band gaps and effective masses of the bulk structures.

The discrete electron energy levels close to the valence band (VB) and conduction band (CB) edges are found by diagonalizing the Hamiltonian with an iterative solver. Spectra (transition rates) are calculated by evaluating the dipole matrix elements using conduction and valence eigenstates [Eq. (1)] found in ETB calculations. The atomic dipole matrix elements [12] are used as the on-site dipole matrix elements. The dipole matrix elements between bonding orbitals on nearest-neighbor sites are chosen by reasonable guesses. To study the symmetry of the states, we calculate the charge density distribution accumulated in a layer (a lattice constant thick) parallel to the equatorial plane of the investigated nanocrystals and projected onto this plane.

For some cases we perform also calculations within the envelope function approximation and effective mass approach [10]. The one-band equations are used to calculate the CB states, whereas the two-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian is used to study VB energy levels [13]. In the case of double quantum dots (DQDs), the spherical symmetry is broken and the calculations are performed in cylindrical coordinates using the finite differences method on a two-dimensional grid.

TABLE I

The lowest conduction band energy levels (in eV) of the single CdS nanocrystals and the hetero-dot.[a]

CdS 2.91 nm NC1	Double dot DQD	CdS 1.86 nm NC2
2.6548 (1)	2.6543 (1)	
2.8010 (3)	2.7913 (1)	2.7981 (1)
	2.8009 (1)	
	2.8010 (1)	
	2.8059 (1)	
2.9528 (3)	2.9526 (1)	
	2.9527 (1)	
	2.9528 (1)	
2.9793 (2)	2.9702 (1)	
	2.9793 (1)	
3.0387 (1)	3.0351 (1)	3.0660 (3)

[a] The degeneracy of each level is shown in parentheses.

Results

HETERO-DOT ARTIFICIAL MOLECULE

We study first a DQD built of two different spherical CdS nanocrystals, NC1 and NC2, of radii 2.91 nm and 1.86 nm, respectively. The centers of the nanocrystals are separated by 4.65 nm along the

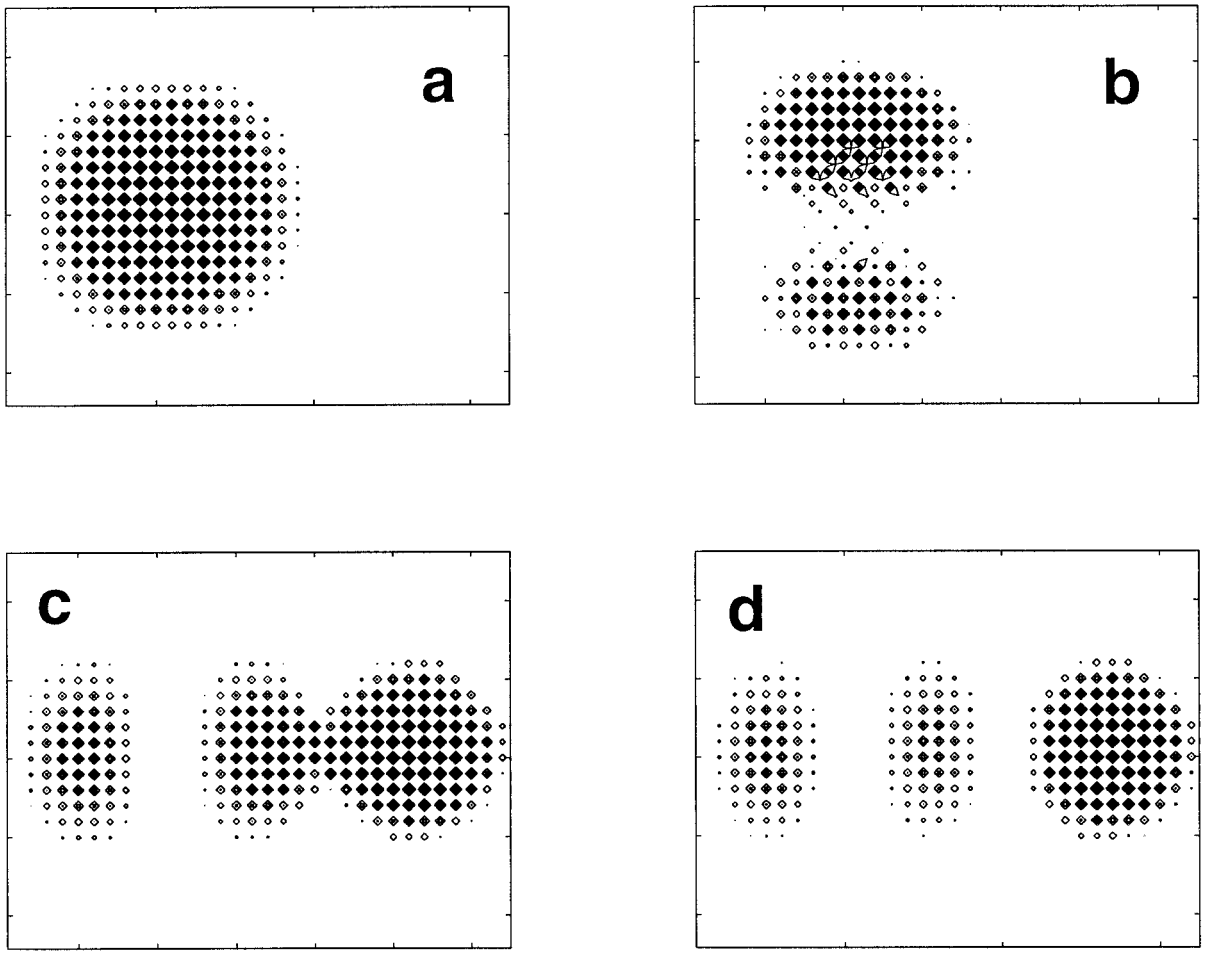

FIGURE 1. XY-in-plane densities of four CB states of the hetro-dot CdS artificial molecule. NC1 is situated in the left half of the plots. (a) The lowest *s*-state (2.6543 eV) localized in NC1; (b) one of the two *p*-type states polarized perpendicular to the DQD axis; (c) the bonding orbital; (d) the antibonding orbital.

x-axis defined by the eight-element cubic unit cell. Both dots are centered at a Cd atom. The system contains 5333 atoms, but only one is common to both nanocrystals that are joned by just 16 bonds of the total number of 1088 surface atoms. If the centers of dots are separated by more than 4.8 nm, then the dots do not have a single common atom and the energy spectrum is the trivial sum of the energy spectra of the two individual dots.

In Table I the lowest CB energy levels of the single nanocrystals and the double dot are shown. The smaller nanocrystal (NC2) has, of course, a larger effective gap and larger separation between the energy levels. The energies of these levels are close to the energies of some of the levels of the bigger nanocrystal (NC1). The spectrum of the double dot is at least as dense as the spectrum of NC1, but because the spherical symmetry is broken, the degeneracy is removed. The charge densities of those energy levels of the double nanocrystal that do not have corresponding levels in NC2 are localized exclusively in NC1 (see Fig. 1a).

The lowest states of NC1 and NC2 have *s* symmetry (in terms of the envelope function). The energy of the lowest *s*-type state of NC2 coincides with the first excited state of NC1, which has *p* symmetry. As for a diatomic molecule, four *molecular orbitals* are formed from these four single-nanocrystal states (one *s* state of NC2 and three *p* states of NC1). Two of them are polarized perpendicular to the double-dot axis. They are of *p*-type and are localized in NC1 (see Fig. 1b). The other ones are polarized along the DQD axis and have their densities distributed in the entire double dot. The one with the lowest energy, 2.7913 eV (in the triplet), has a character of a sum of p_x orbital of NC1 and *s* orbital of NC2 and a nature of *bonding orbital.*

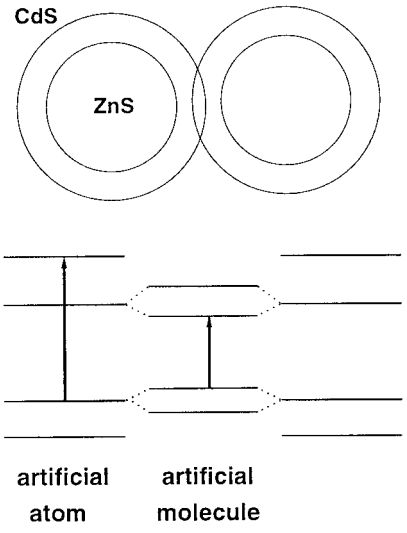

FIGURE 2. The investigated homo-dot artificial molecule. The two lowest CB and VB levels of the single dot (left and right) and double dot (middle) are schematically shown. The lowest optically active transitions are indicated by arrows.

The other one with the highest energy in the triplet, 2.8059 eV, is an antibonding orbital (p_x (NC1) − s(NC2)). Their charge densities in the XY plane are shown in Figure 1.

Similar formation of molecular-type orbitals occurs for higher CB states and for VB states. It is confirmed that the effect is still present even if both nanocrystals are surrounded by thin (<0.3 nm) wide-gap semiconductor layers.

The p-type states of individual nanocrystals (the VB states closest to the gap or the first excited states in the CB) are, essentially, unpolarized. Even in the case when such states do not form molecular-type orbitals in the double dot, they are strongly affected by the presence of a neighboring nanocrystal. The p states become polarized. One of them gets the character of a p_x state (polarized along the DQD axis) and the other two are combinations of p_y and p_z states.

The formation of delocalized molecular-type states in the system of two neighboring nanocrystals joined merely by a few atoms is consistent with the observed changes in the absorption and luminescence spectra of close-packed QD solids [8] when compared with the spectra of samples containing noninteracting nanocrystals.

HOMO-DOT ARTIFICIAL MOLECULE

The formation of molecular orbitals is even more pronounced if the artificial molecule is formed from two nearly identical QDs. In this case, the states of one dot will be nearly resonant with states of the same symmetry in the other dot, and strong coupling is possible.

In this section we consider a QD molecule built from two nearly identical multishell QD, as shown schematically in Figure 2. Each dot is composed of a ZnS core and a CdS clad of thickness 0.58 nm (two monolayers). CdS has the lower-bulk band gap and acts as a well in these core/clad dots. The core radii of the two nanocrystals, denoted AQD1 and AQD2, are 1.86 nm and 1.75 nm, respectively. The dot centers are separated by 4.66 nm in X direction. This configuration allows the two nanocrystals to be centered at Cd atoms and to overlap by 0.12 nm (one common atom and only 16 joining bonds of the total number of 1024 surface atoms). The entire systems contains 4621 atoms.

In Table II the energies of the lowest CB and highest VB levels of the individual nanocrystals and double dot are shown.

The lowest CB state of each nanocrystal has s symmetry. Their energies differ by only 16 meV. Their charge densities are spherically symmetric and localized mainly in the lower band-gap CdS clad (see Fig. 3a). After joining these two nanocrystals to build a double dot, two delocalized molecular-type states are formed: a bonding orbital $s + s$ with energy 3.0915 eV and an antibonding orbital with energy 3.1191 eV. The energy difference in-

TABLE II

The lowest CB and the highest VB energy levels (eV) of two single ZnS/CdS nanocrystals and the double dot.[a]

AQD1	Double dot	AQD2
Conduction band		
3.1074 (1)	3.0915 (1)	3.1233 (1)
	3.1191 (1)	
	3.1581 (1)	
3.1784 (3)	3.1784 (1)	
	3.1787 (1)	
	3.2021 (1)	
	3.2025 (1)	3.2027 (3)
	3.2043 (1)	
Valence band		
	−0.1979 (1)	
	−0.2189 (1)	
	−0.2268 (1)	
−0.2327 (3)	−0.2323 (1)	
	−0.2334 (1)	
	−0.2477 (1)	−0.2494 (3)

[a] The degeneracy of each level is shown in parentheses.

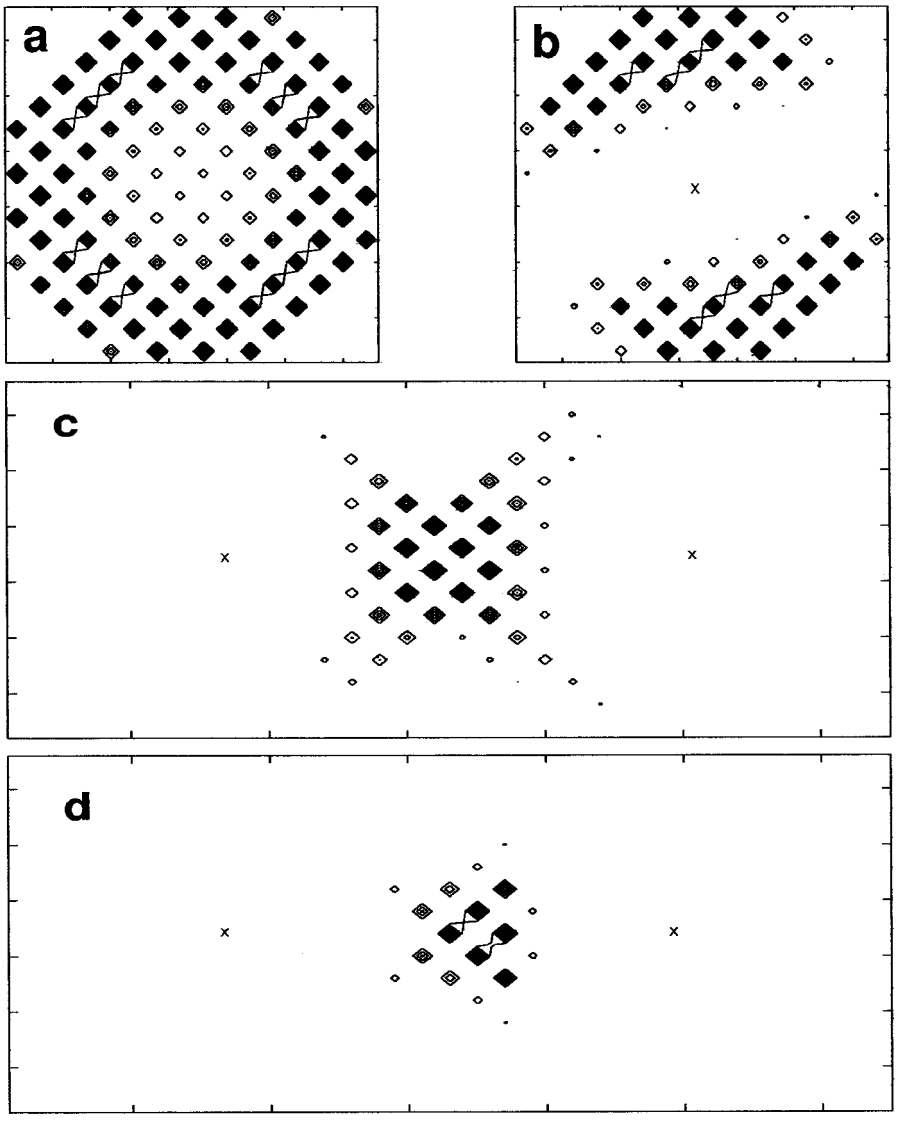

FIGURE 3. XY-in-plane densities of single and double ZnS/CdS nanocrystals. (a) The *s* CB state of the single nanocrystal; (b) one of the three VB *p* states; (c) the lowest CB bonding state of the double dot; (d) the highest VB bonding state of the double dot.

creases to 28 meV from the interdot coupling. The density of the bonding state is almost exclusively localized in the region where the two nanocrystals overlap. This is shown in Figure 3c.

The level splitting is even more pronounced for VB states. Here, a bonding state of the artificial molecule is built from a combination of the p_x states localized at each nanocrystal. The energy difference between the lowest bonding and the highest antibonding DQD states that originate from the *p* states of individual nanocrystals increases to 50 meV (from 17 meV for noninteracting dots). The density of the VB bonding state is again strongly localized in the region where the two dots overlap.

In calculations of the energy structure of semiconductor QDs the $\mathbf{k} \cdot \mathbf{p}$ method and the envelope function approximation (EFA) have been most widely used so far in the literature. It is worthwhile to ascertain whether the formation of molecular-type orbitals in double dot systems, predicted by atomistic tight-binding theory, results also from the effective mass approach.

Thus, for comparison with the predictions of ETB theory, the calculations for a double homo-dot

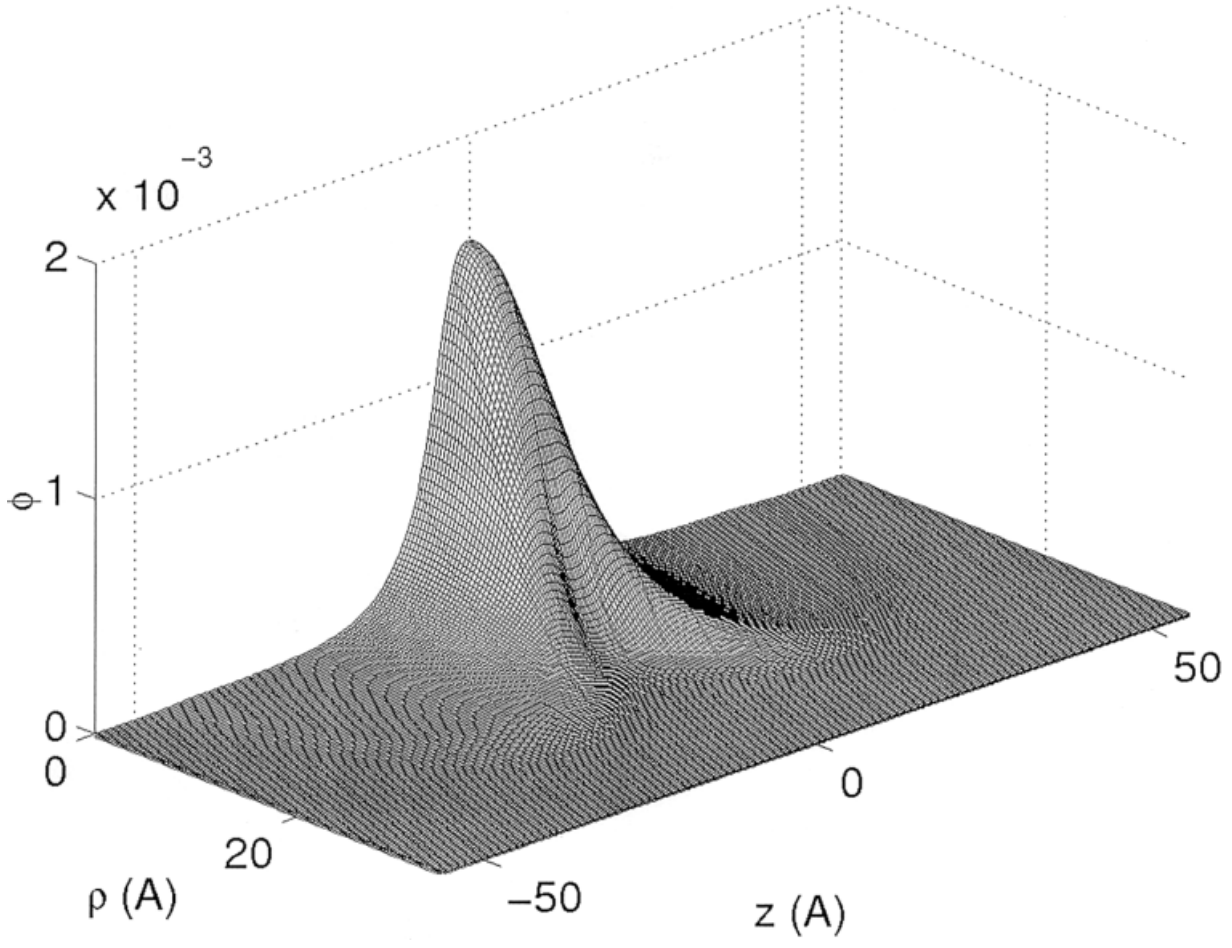

FIGURE 4. Square of the envelope function of the lowest CB level of homo-dot artificial molecule calculated in cylindrical coordinates (ρ, z in Å) within the $\mathbf{k} \cdot \mathbf{p}$ EFA approach. The origin of coordinates is taken in the middle of the distance between the centers of nanocrystals. (This figure corresponds to Fig. 3c).

artificial molecule were been performed using the $\mathbf{k} \cdot \mathbf{p}$ method and the EFA. Two identical spherical ZnS/CdS nanocrystals (almost the same in size as the ones used in ETB calculations) were considered. The offset of the CB between ZnS and CdS was taken as 0.8 eV and for the VB as 0.4 eV. The same electron effective mass $m^* = 0.2$ and Luttinger hole parameters $\gamma = 1.303$ and $\gamma_1 = 3.89$ (corresponding to ZnS medium [14, 15] with $m_{hh} = 0.78$ and $m_{lh} = 0.15$) were used for both materials for simplicity. For the hole states the two-band Hamiltonian was used [13]. The calculations were performed using finite-differences method on two-dimension grid in cylindrical coordinates. The lowest electron state and the highest hole state wavefunctions of the double dot are presented in Figures 4 and 5, respectively. One can again see a strong localization and bonding character of these states.

The changes in the charge distributions of the states in two ZnS/CdS nanocrystals that arise when the dots are joined together to form an artificial molecule influence significantly optical properties of these systems. For single ZnS/CdS nanocrystals, the lowest optically active transition occurs between the first-excited electron state, a p-type state, and the lowest hole state, also a p-type state. The effective optical gap is 3.4 eV. When the two nanocrystals form the double dot, the degeneracy is removed and the electron-hole energy levels separation decreases. Additionally, the lowest electron state loses its s character and the lowest hole state loses its p characters: now they are localized in the same spatial region and have non-negligible dipole matrix element. The lowest optically active transition occurs now at 3.28 eV. The absorption spectra for both cases are shown in Figure 6.

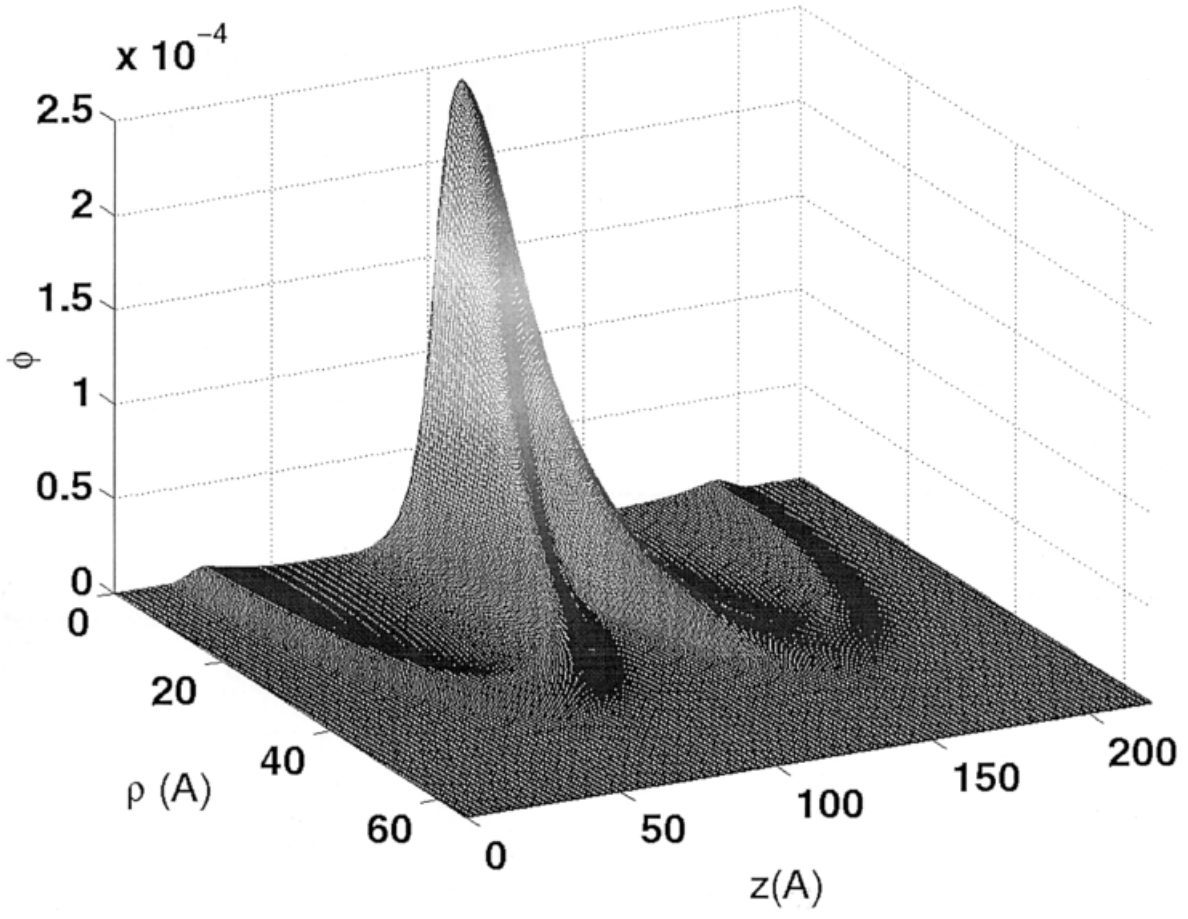

FIGURE 5. The same as in Figure 4, but for the hole state. This corresponds to Figure 3d. The origin of *z*-axis is set out of the double dot.

TETRAHEDRAL NANOCRYSTALS

The chemically synthesized nanocrystals are not always spherically symmetric. Frequently, they have tetrahedral shape [5, 16]. Recently, tetrahedral CdS clusters and micro-sized crystals composed of such clusters were investigated [16]. It was observed that the effective gap in crystals built of tetrahedral nanoclusters joined by vertex atoms can be redshifted by more than 100 meV in comparison with the gap of noninteracting nanocrystals.

To see how the electronic structure of tetrahedral nanocrystal might be perturbed by the presence of a neighboring tetrahedron that contacts it through a single vertex, we consider a single tetrahedral nanocrystal and remove a single atom from one of the vertices. The *p*-type orbitals of a single ideal tetrahedron are unpolarized, and the corresponding energy level is triply degenerate. Breaking the symmetry lifts partially the degeneracy. The resulting energy levels differ by less than 0.2 meV. One of them remains doubly degenerate and the corresponding orbitals remain unpolarized. The nondegenerate orbital is now strongly polarized along the axis pointing the broken vertex. This is shown in Figure 7. This strong polarization, which occurs when even one atom of the tetrahedron is changed, suggests that strong molecular-type bonding between the neighboring CdS clusters should occur and could reduce the forbidden energy gap.

Conclusions

Two systems of DQDs, one built of two CdS nanocrystals of different size and the other composed of two nearly identical ZnS/CdS QDs, have been investigated by the empirical tight-binding method. Double-dot systems built by coupling two nanocrystals, each one containing several thousand atoms and joined by just several bonds, exhibits

energy spectra and optical properties very different from the individual nanocrystals.

We have shown that when two spherical nanocrystals form a double dot, new states having charge densities distributed in the entire double dot can appear. These new states appear mainly when the energy levels of individual nanocrystals are close. As for diatomic molecules, some of these states have bonding character and other states have antibonding character. This suggests that the formation of delocalized states in systems containing close-packed nanocrystals is possible and that extended states contribute to the absorption and luminescence spectra observed in such systems.

Calculations for artificial molecules were performed using the $\mathbf{k} \cdot \mathbf{p}$ method and the EFA. It has been shown that both theories, the ETB and the $\mathbf{k} \cdot \mathbf{p}$, predict the formation of molecular-type orbitals in double-dot systems.

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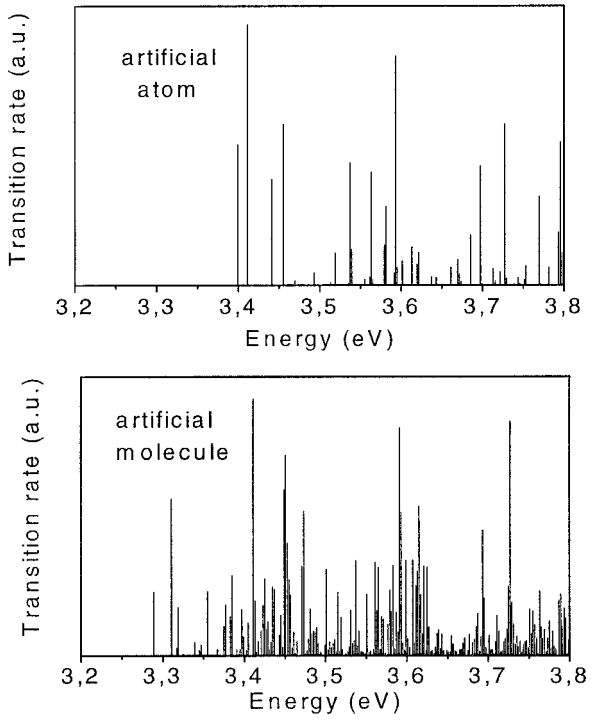

FIGURE 6. Absorption spectrum of an artificial atom (single ZnS/CdS nanocrystal) and an artificial molecule (double dot).

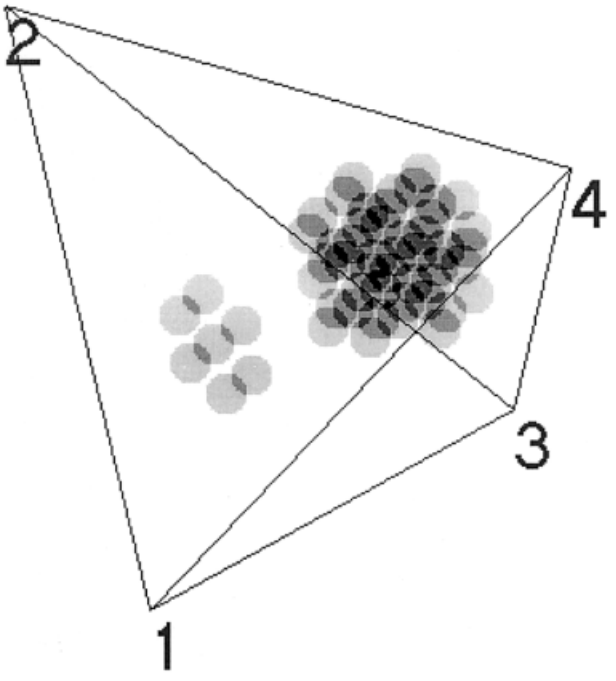

FIGURE 7. Charge density of the nondegenerate *p*-type orbital for the tetrahedral CdS cluster with a single atom removed from the fourth vertex.

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