PHYSICAL REVIEW B **72**, 195316 (2005)

Collective excitations in charged nanocrystals and in close-packed arrays of charged nanocrystals

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(Received 17 September 2005; published 9 November 2005)

We present self-consistent tight binding calculations of the dielectric response of charged semiconductor nanocrystals. We predict collective effects such as the oscillation in opposite phase of the additional electron and of the plasma of valence electrons near the resonance. In arrays of charged nanocrystals, the coupling between infrared light and collective excitations is shown to be strong, the real part of the dielectric constant becoming negative in some part of the spectrum. Transverse and longitudinal excitation modes obeying the Lyddane-Sachs-Teller equation are predicted.

DOI: 10.1103/PhysRevB.72.195316 PACS number(s): 73.21.La, 78.67.Hc, 73.22.Lp, 71.15.−m

I. INTRODUCTION

One fascinating challenge for material research is to design artificial materials with new properties using microstructures and nanostructures of metals or semiconductors as building blocks. For example, composite materials based on small metallic structures are actively studied for plasmon excitations.[1] In this paper, we consider collective excitations in semiconductor nanostructures, in particular in close-packed arrays of semiconductor nanocrystals which are very promising systems both for their optical[2,3] and transport properties that can be nicely controlled by doping.[4,5] Our objective is to study the specific properties which arise from the charging of nanocrystals and from the proximity of the quantum dots in the arrays. We present calculations of the frequency dependent dielectric constant of these systems using a self-consistent quantum-mechanical and atomistic approach, allowing one to go well beyond previous studies which mainly dealt with single-particle spectra of individual nanocrystals.[6] In nanocrystals charged with one—or two—electron(s) and irradiated by an electromagnetic field with a frequency close to an excitation energy, we show that the plasma made by all the valence electrons oscillates in opposite phase with respect to the extra electron. In arrays of charged nanocrystals, we predict collective effects induced by the long-range interaction between these oscillations which strongly couple to infrared photons.

II. DESCRIPTION OF THE SYSTEM

We consider three-dimensional arrays of semiconductor nanocrystals. Each nanocrystal is characterized by discrete electronic states and, in the case of direct gap semiconductors,[5–7] the lowest unoccupied states are typical of an artificial atom, the ground state having a S-like envelope function and the first excited state a threefold P-like orbital degeneracy. When each nanocrystal is charged by $n=1$ or 2 electrons filling the S level, the lowest dipole-allowed optical excitations arise from the $S\rightarrow P$ transitions[7,8] at the energy ω_{sp}. Obviously, this is an independent-particle picture beyond which one needs to go, in particular in the case of a close-packed array of nanocrystals where long-range Coulomb interactions are likely to play an active role.[9–11] In each nanocrystal, the dipole corresponding to the $S\rightarrow P$ transition dynamically responds to the sum of three electric fields: the external one, the field induced by the dipoles in the other nanocrystals, and the field created by the response of the valence electrons. Furthermore, these dynamical processes occur in a complex way due to the inhomogeneity of the system leading to so-called local field effects.[6] It is usually believed that the role of the valence electrons is just to screen the external electric field, and thus their effect on the optical response of neutral nanocrystals is usually modeled by a simple local field factor. We will see that the situation is more complicated in the case of charged nanocrystals.

III. ANALYTICAL MODEL OF THE DIELECTRIC RESPONSE

A. Case of a single nanocrystal

In order to describe the dielectric response of these systems, let us first discuss a simple analytical model. The neutral nanocrystal is described by an homogeneous sphere of radius R and of dielectric constant ϵ_b independent of the frequency. The polarizability of the sphere is thus $\alpha_b=R^3(\epsilon_b-1)/(\epsilon_b+2)$. When the nanocrystal is charged by $n\leqslant 2$ electrons, the bare dynamical $S\rightarrow P$ polarizability is given[12] by $\alpha_e(\omega)=2n\omega_{\mathrm{sp}}|\langle x\rangle|^2/(\omega_{\mathrm{sp}}^2-\omega^2)$, where $\langle x\rangle=\langle S|x|P_x\rangle$ is the dipole matrix element. A small imaginary part can be added to the energy $\omega\rightarrow\omega+i\eta$ to avoid divergencies and to describe the broadening of the transition line shape. The total polarizability α_{tot} of the charged nanocrystal is not however the sum of α_b and α_e due to the Coulomb interaction between polarization charges that brings self-consistency into the problem. For the sake of simplicity, we make the crude approximation that the polarization due to

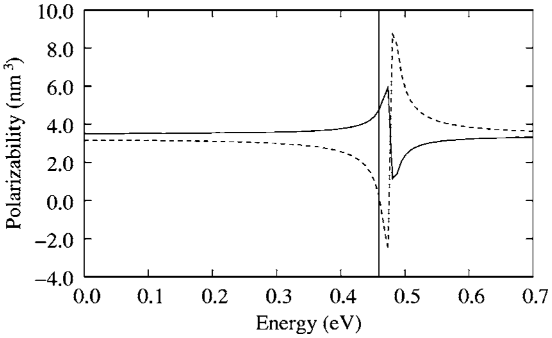

FIG. 1. Polarizability (real part) of a nanocrystal (R=1.69 nm) charged with one electron calculated from Eq. (2) using $\omega_{\mathrm{sp}}=0.46$ eV (vertical line), ϵ_b=8.12, and η=5 meV. Continuous line: total polarizability of the sphere $[\alpha_{\mathrm{tot}}(\omega)]$. Dashed line: response of the valence electrons $[\alpha_{\mathrm{val}}(\omega)]$.

the extra electron is uniform in the sphere and is given by $\alpha_e \mathbf{E}_{\mathrm{in}}/\Omega$ where $\mathbf{E}_{\mathrm{in}}$ is the self-consistent field inside the nanocrystal and Ω is the volume of the sphere. Thus the total polarization inside the nanocrystal is given by

$$\mathbf{P}=\frac{1}{4\pi}\left[(\epsilon_b-1)+\frac{3\alpha_e}{R^3}\right]\mathbf{E}_{\mathrm{in}}, \tag{1}$$

where the first term in parenthesis describes the polarization due to the valence electrons. The field inside the nanocrystal is moreover given by $\mathbf{E}_{\mathrm{in}}=\mathbf{E}_{\mathrm{ext}}-4\pi\mathbf{P}/3$ where $\mathbf{E}_{\mathrm{ext}}$ is the external field and the second term is the depolarization field in the sphere.[12] Combining these equations and $\Omega\mathbf{P}=\alpha_{\mathrm{tot}}\mathbf{E}_{\mathrm{ext}}$, we obtain

$$\alpha_{\mathrm{tot}}(\omega)=\alpha_b\left[\frac{\omega_{\mathrm{sp}}^2+\omega_{\mathrm{sp}}\omega_0/(\epsilon_b-1)-\omega^2}{\omega_{\mathrm{sp}}^2+\omega_{\mathrm{sp}}\omega_0/(\epsilon_b+2)-\omega^2}\right], \tag{2}$$

where $\omega_0=6n|\langle x\rangle|^2/R^3$ can be easily calculated using the effective mass expressions for the S and P states[6] ($|\langle x\rangle|\approx 0.27R$). Using typical parameters (e.g., an InAs nanocrystal of radius R=1.69 nm[13]), Fig. 1 shows that $\alpha_{\mathrm{tot}}(\omega)$ presents a resonance above ω_{sp} as expected from Eq. (2). But the most interesting message of this simple model is given by plotting the contribution α_{val} of the polarizability coming from the valence electrons. From Eq. (1), we have $\alpha_{\mathrm{val}}=(\epsilon_b-1)/(\epsilon_b-1+3\alpha_e/R^3)\alpha_{\mathrm{tot}}$ leading to

$$\alpha_{\mathrm{val}}(\omega)=\alpha_b\left[\frac{\omega_{\mathrm{sp}}^2-\omega^2}{\omega_{\mathrm{sp}}^2+\omega_{\mathrm{sp}}\omega_0/(\epsilon_b+2)-\omega^2}\right]. \tag{3}$$

We see by comparing this expression with Eq. (2) that in some range of energy near the resonance the numerator becomes negative while the denominator remains positive, and thus $\alpha_{\mathrm{val}}(\omega)$ is negative as shown in Fig. 1 where the transition has been slightly broadened. In this energy range, the plasma of valence electrons and the extra electron oscillate, but in opposite phase. This unexpected phenomenon is the result of two effects: the polarizability of the additional electron is large because the oscillator strength is concentrated into a single line ($S\rightarrow P$),[7] and there is a strong Coulomb repulsion between the electron and the plasma.

B. Case of an array of nanocrystals

If we now consider an array of nanocrystals on a simple cubic lattice of parameter a, its macroscopic dielectric constant $\epsilon_M(\omega)$ can be calculated using the Clausius-Mossotti relation[12] if we treat each nanocrystal as an artificial atom of polarizability α_{tot}:

$$\frac{\epsilon_M(\omega)-1}{\epsilon_M(\omega)+2}=\frac{4\pi\alpha_{\mathrm{tot}}(\omega)}{3a^3}. \tag{4}$$

We then obtain an expression of the form $\epsilon_M(\omega)=\epsilon_M(\infty)\times(\omega^2-\omega_L^2)/(\omega^2-\omega_T^2)$ with

$$\omega_L^2=\omega_{\mathrm{sp}}^2+\frac{1+\frac{8\pi}{3}\left(\frac{R}{a}\right)^3}{1+\frac{8\pi}{3}\left(\frac{R}{a}\right)^3\left(\frac{\epsilon_b-1}{\epsilon_b+2}\right)}\frac{\omega_0^2}{(\epsilon_b+2)},$$

$$\omega_T^2=\omega_{\mathrm{sp}}^2+\frac{1-\frac{4\pi}{3}\left(\frac{R}{a}\right)^3}{1-\frac{4\pi}{3}\left(\frac{R}{a}\right)^3\left(\frac{\epsilon_b-1}{\epsilon_b+2}\right)}\frac{\omega_0^2}{(\epsilon_b+2)}. \tag{5}$$

This expression means that there are two excitation modes in the system, a transverse one at frequency ω_T (twofold degenerate, optically active) and a longitudinal one (plasmon) at frequency ω_L such that $\omega_L>\omega_T>\omega_{\mathrm{sp}}$.

IV. RPA TIGHT BINDING CALCULATIONS OF THE DIELECTRIC RESPONSE

A. Case of a single nanocrystal

If this analytical model is useful to catch the physics of the system, it cannot be of quantitative value because of the approximations made: the polarization inside the dot is not uniform, the Clausius-Mossotti relation is only valid for very dilute systems, and therefore local field effects are not properly described. In addition, it is well known that the effective dielectric constant of small nanocrystals is size dependent.[6,13,14] Thus calculations based on a microscopic description are required. Tight binding (TB) methods are a very good starting point to address this problem by providing accurate single-particle states and energies in a wide range of nanocrystal sizes (see the Appendix). Dielectric properties can then be computed using, e.g., the random-phase approximation (RPA) for the electron-electron interactions,[14] a self-consistent time-dependent Hartree method.[15] We thus calculate the RPA response function $\chi(\omega)$ which connects the first-order density fluctuation $\delta\rho(\omega)$ to the external potential $V_{\mathrm{ext}}(\omega)$, such that formally $\delta\rho(\omega)=\chi(\omega)V_{\mathrm{ext}}(\omega)$.[16] To proceed, we first compute the independent particle response function $\chi_0(\omega)$ (the non self-consistent one)[15,17] taking into account the occupancy of the S level by the extra electron(s). We then introduce self-consistency at the Hartree level, which leads to the integral equation

$$\chi(\omega)=\chi_0(\omega)+\chi_0(\omega)v\chi(\omega), \tag{6}$$

where v is the electron-electron interaction. In tight binding, the electron density and potential are averaged on each atom,

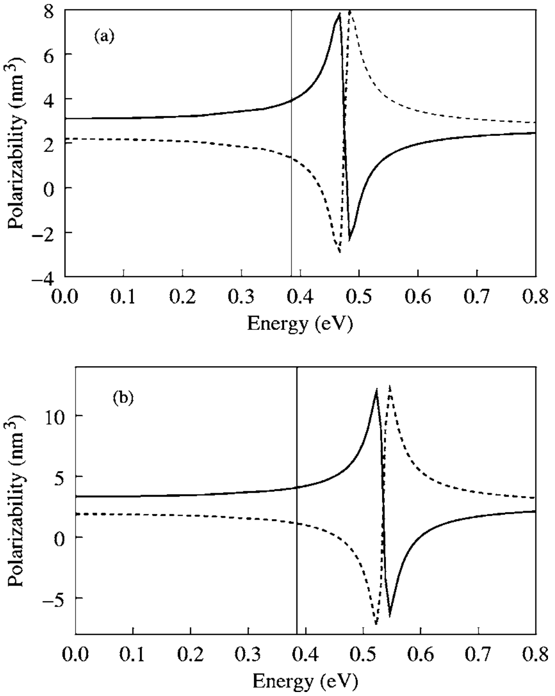

FIG. 2. Polarizability (real part) of a CdSe nanocrystal (R $=1.69$ nm) charged with one electron calculated in RPA (η $=10$ meV). Continuous line: total polarizability of the sphere. Dashed line: response of the valence electrons only. The vertical line indicates the single-particle transition (ω=0.38 eV). (a) Nanocrystals charged with n=1 electron; (b) n=2.

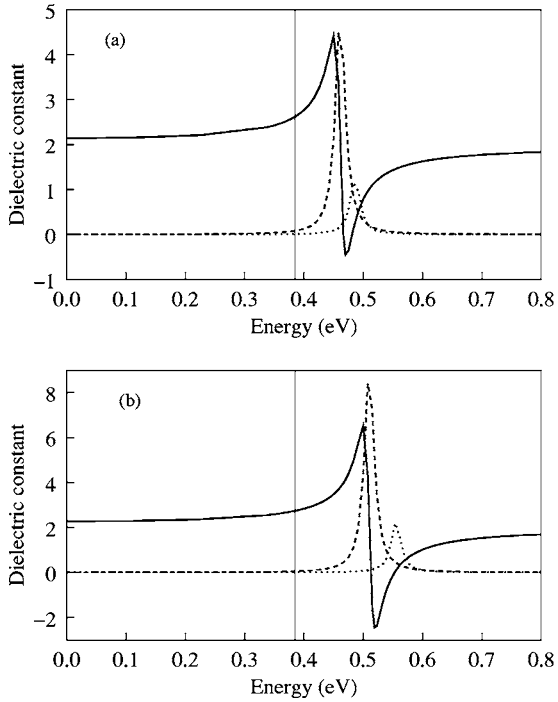

FIG. 3. Dielectric constant ϵ_M [Re(ϵ_M): straight line, Im(ϵ_M): dashed line, $-$Im($1/\epsilon_M$): dotted line] of a cubic array of CdSe nanocrystals (R=1.69 nm, a=3.66 nm, η=10 meV). (a) Nanocrystals charged with n=1 electron; (b) n=2. The vertical line indicates the single-particle transition (ω=0.38 eV).

and thus all quantities in Eq. (6) are described by matrices whose size is given by the number of atoms in the system (see Refs. 6, 14, and 18 for further details). For example, the potential energy of an electron on an atom i_0 induced by an electron on an atom j_0 is simply given by $v_{i_0,j_0}=e^2/|\mathbf{R}_{i_0,j_0}|$ where $\mathbf{R}_{i_0,j_0}$ is the vector joining the two atoms.

The TB RPA polarizability of a CdSe nanocrystal containing 715 CdSe atoms is shown in Fig. 2, as well as the component coming from valence electrons. A broadening factor η of 10 meV was used.[19] The full calculation basically confirms the simple model, i.e., a blue shift of the transition with respect to the single-particle energy, and opposite polarizations of the valence electrons and of the additional electron near the resonance. Similar results are obtained for InAs nanocrystals.

B. Case of an array of nanocrystals

To apply the TB RPA to arrays of nanocrystals, we use the fact that the independent particle response function χ_0 is the same as for the single nanocrystal since the dots are supposed to be chemically uncoupled. Thus we just have to replace v in Eq. (6) by v^{ar}, the Coulomb potential due to the induced charges in all the nanocrystals. But a numerical problem arises because in a homogeneous electric field the induced charges are the same on all the atoms which are equivalent by translation. Thus, $v^{\mathrm{ar}}_{i_0,j_0}$ is given by $\Sigma_j e^2/|\mathbf{R}_{i_0,j_0 j}|$ where $j_0 j$ denotes the atom j_0 in the nanocrystal j, and it is easy to check that this sum over all the nanocrystals of the system is divergent. Of course, this divergence should cancel out in the final result due to the fact that the sum of the induced charges in each nanocrystal is exactly zero (i.e., there are only dipolar or multipolar interactions between nanocrystals). In order to solve this problem, we follow a usual approach: we consider an external electric field oscillating in space and characterized by a wave vector $\mathbf{q}$, we calculate all the quantities as a function of $\mathbf{q}$, then let $\mathbf{q}\rightarrow 0$. The matrix elements of $v^{\mathrm{ar}}(\mathbf{q})$ take the form $v^{\mathrm{ar}}_{i_0,j_0}(\mathbf{q})$ $=\Sigma_j e^2 \exp(i\mathbf{q}\cdot\mathbf{R}_{j_0 j})/|\mathbf{R}_{i_0,j_0 j}|$ which are convergent when $\mathbf{q}\neq 0$. The sums are calculated following Ewald's method.[20] We then compute the dielectric matrix of the system $\epsilon(\mathbf{q})$ $=I-v^{\mathrm{ar}}(\mathbf{q})\chi_0$ and the macroscopic dielectric constant $\epsilon_M(\omega)$ from $\epsilon^{-1}(\mathbf{q})$ for $\mathbf{q}\rightarrow 0$, as required to take into account the local field effects.[6,21] Details on the method are given in Ref. [18].

Figure 3 presents the macroscopic dielectric constant $\epsilon_M(\omega)$ of a periodic array of CdSe nanocrystals, each containing 715 CdSe atoms. Quite similar results are obtained for InAs nanocrystals (Fig. 4). The charging with one electron has a profound impact on Re(ϵ_M) which, near the resonance, strongly differs from its value at ω=0. It proves that the optical properties of arrays of semiconductor nanocrystals cannot be obtained from usual perturbation theory (Fermi golden rule) in which the refractive index of the system is supposed to be constant (this conclusion also holds for single quantum dots). Figure 3 also shows that the peak in Im(ϵ_M), at the transverse frequency ω_T, shifts to higher energy when the nanocrystals are charged with two electrons.

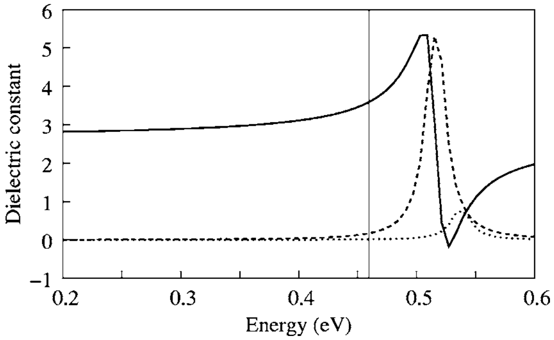

FIG. 4. Dielectric constant ϵ_M [Re(ϵ_M): straight line, Im(ϵ_M): dashed line, $-$Im($1/\epsilon_M$): dotted line] of a cubic array of InAs nanocrystals ($R=1.69$ nm, $a=3.65$ nm, $\eta=10$ meV) charged with two electrons ($n=2$). The vertical line indicates the single-particle transition ($\omega=0.46$ eV).

There is also an energy region where Re(ϵ_M) becomes negative which means that electromagnetic waves cannot propagate and are reflected at the surface of the system.[12] Longitudinal modes also show up, in agreement with the simple model. They arise when Re(ϵ_M)=0, giving rise to an important peak in the energy loss function $-$Im($1/\epsilon_M$). The occurrence of a region with Re(ϵ_M)<0 obviously depends on the value taken for the broadening of the transition line, here fixed at $\eta=10$ meV. As shown by the analytical model, it is also interesting to note that the dielectric constant around the resonance fulfills the Lyddane-Sachs-Teller relation $\omega_L^2/\omega_T^2 = \epsilon_M(0)/\epsilon_M(\infty)$ which was established for the phonon-photon coupling in ionic materials. Here the photon is strongly coupled with the collective modes induced by the charges in the nanocrystals, these latter playing here the role of the ions.

The results of Figs. 3 and 4 have been obtained for a supercell lattice corresponding to a gap of 2.7 Å between each nanocrystal to simulate close-packed arrays in which the artificial atoms are linked by Van der Waals bonds. Performing the same calculations with a gap of 3.7 Å between the nanocrystals gives results almost identical (thus they are not shown) simply due to the fact that it leads to a change in the lattice parameter of only 3%. Obviously, if the distance between artificial atoms becomes of the order of the diameter, one should see a strong decrease of the collective effects (in the limit of a small density of nanocrystals, the dielectric constant and its dependence on the lattice parameter is well given by the Clausius-Mossotti relation).

V. COMPARISON WITH EXPERIMENTS

Let us discuss now the experimental situation. To our knowledge, there is no measured dielectric constant of charged nanocrystal arrays in the literature. We hope that this work will stimulate research efforts to test our predictions, for example by measuring the reflectivity of a nanocrystal array as a function of the photon energy in the vicinity of the intraband transition (in the best case, a total reflection could be obtained). Another complementary approach would be to measure the energy-loss spectrum of fast electrons to look at the plasmon modes.

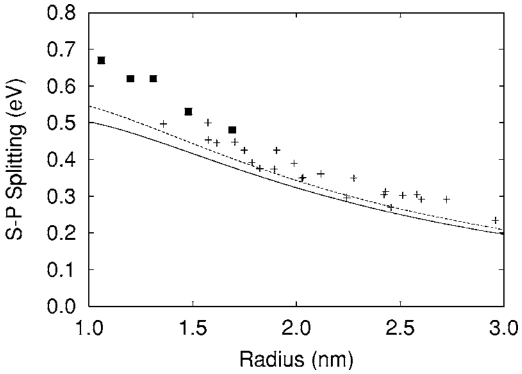

FIG. 5. $S\rightarrow P$ transition energy in CdSe nanocrystals as function of size. Experiments (Ref. 22): +. Theory: single-particle energy ω_{sp} (line), same but including the self-energy correction $\Sigma_p - \Sigma_s$ (dashed line), RPA peak energy (■).

Since experimental data on nanocrystal arrays are not available, let us consider results obtained on ensembles of isolated particles. Figure 5 reproduces the $S\rightarrow P$ transition energy of CdSe nanocrystals measured as a function of the radius by the group of Guyot-Sionnest.[22] These data are obtained by infrared absorption on nanocrystals dispersed in solution, either on photoexcited nanocrystals or on n-type nanocrystals,[8] the two approaches giving close results. We compare these values with the TB single-particle transition energy ω_{sp} and the energy of the peak in Im(α_{tot}) (Fig. 5). Even if the RPA figures cannot be calculated in the whole experimental range, the agreement between theory and experiment is fairly good.

VI. BEYOND RPA

Even if the agreement between theory and experiments in Fig. 5 is already within the expected accuracy of tight binding calculations, it is interesting to discuss some limitations of the RPA. In principle, the best approach to treat the problem would be to perform a GW calculation starting from the configuration of a nanocrystal charged with one electron, and then to solve the Bethe-Salpeter equation to derive the optical spectrum. From this, we deduce that RPA calculations miss two effects.[17] First, the RPA does not include self-energy effects which account for the interaction between the P electron or S "hole" with the polarization charges they induce at the surface of the nanocrystal.[23,24] Second, the RPA misses exchange-correlation effects in the response function, and notably the attraction between the P electron and S hole in the $S\rightarrow P$ transition. However, these "excitonic" and self-energy effects will largely cancel each other, because the $S\rightarrow P$ transition does not change the charge state of the nanocrystal.[23,24] Therefore it should not affect the conclusions drawn in this paper concerning the importance of collective effects.

A calculation based on a GW plus Bethe-Salpeter approach is obviously very heavy, even in tight binding,[23,24] and thus it is well beyond the scope of the present paper. Another possible but less justified approach to treat the problem could be to calculate the $S\rightarrow P$ transition energy as the

TABLE I. Tight binding parameters for wurtzite CdSe (orthogonal sp^3 model, two-center integrals up to second-nearest-neighbor interactions), for Cd—H and Se—H (two-center integrals restricted to nearest-neighbor interactions) using notations of Slater and Koster (Ref. 26). Neighbors are indicated as 1=1st, 2=2nd. Δ is the spin-orbit coupling (Ref. 27). Lattice parameters: a =4.299 Å and c=7.01 Å.

Tight binding parameters for CdSe (eV)					
E_s^{Cd}	1.70734	E_p^{Cd}	5.39164	E_s^{Se}	−11.39201
E_p^{Se}	0.90756	Δ_{Cd}	0.22700	Δ_{Se}	0.48000
$V_{ss}(1)$	−1.15622	$V_{s\sigma}(1)$	2.36338	$V_{\sigma s}(1)$	−1.62238
$V_{\sigma\sigma}(1)$	3.25867	$V_{\pi\pi}(1)$	−0.39548	$V_{ss}^{\text{Cd}}(2)$	−0.12948
$V_{s\sigma}^{\text{Cd}}(2)$	−0.05565	$V_{\sigma\sigma}^{\text{Cd}}(2)$	0.42834	$V_{\pi\pi}^{\text{Cd}}(2)$	−0.25463
$V_{ss}^{\text{Se}}(2)$	0.02024	$V_{s\sigma}^{\text{Se}}(2)$	0.10783	$V_{\sigma\sigma}^{\text{Se}}(2)$	0.21199
$V_{\pi\pi}^{\text{Se}}(2)$	0.02379				
Tight binding parameters for Cd−H and Se−H (eV)					
E_{H}	0.00000	V_{ss}	−3.50000	$V_{s\sigma}$	4.50000

difference between two quasiparticle energies corresponding to the injection of an extra electron in the S and P states, respectively. This could be obtained once again using a GW calculation but now starting from the configuration of a neutral nanocrystal. Then the $S\rightarrow P$ transition energy would be approximately given by $\omega_{\text{sp}}+\Sigma_p-\Sigma_s$ where Σ_s (Σ_p) is the self-energy correction to the S (P) level. We have shown in Refs. 6 and 23 that this self-energy correction is well approximated by $\langle\psi|V_{\text{ind}}|\psi\rangle/2$ where V_{ind} is the potential for the interaction between the electron in the state ψ with the polarization charges that it induces at the surface of the nanocrystal, the factor 2 coming from the adiabatic building-up of the potential. We calculate the self-energy corrections using for ψ the effective mass wave functions and for V_{ind} its expression in classical electrostatics describing the nanocrystal as a dielectric sphere (see Ref. 23). This leads to a $S\rightarrow P$ transition energy blue-shifted with respect to the single-particle energy ω_{sp} but still below the RPA value (Fig. 5), confirming the conclusion drawn in the previous paragraph.

TABLE II. Tight binding (TB) values of the direct gap energy and of the effective masses in the conduction band (CB) and valence band (VB) of bulk CdSe compared to experimental (Ref. 28) or semi-empirical pseudopotential values of Ref. 29. A and B denote the two highest valence bands; ∥ and ⊥ stand for parallel and perpendicular to the c axis, respectively.

	Bandgap (eV)				
	Experimental	TB			
E_g	1.850	1.805			
CB effective mass (in units of the free electron mass)					
	Experimental	TB			
m_e^*	0.130	0.128			
VB effective masses (in units of the free electron mass)					
	Pseudopotential	TB		Pseudopotential	TB
$m_A^{\perp}$	0.290	0.226	$m_B^{\perp}$	0.440	0.406
$m_A^{\parallel}$	1.830	1.580	$m_B^{\parallel}$		0.159

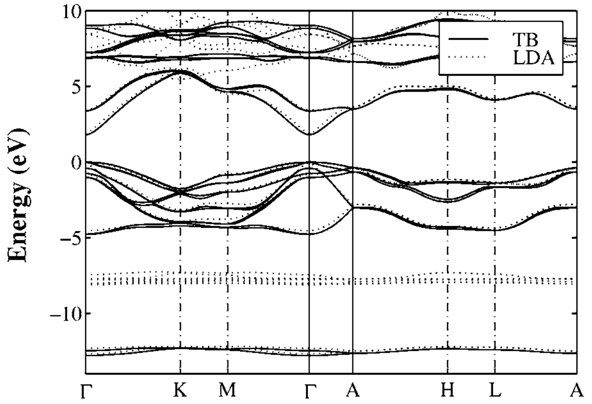

FIG. 6. Band structure of bulk CdSe calculated in tight binding (continuous lines) compared to the one calculated in local density approximation (LDA) (dashed line) including a rigid shift of the conduction band to fit the experimental band gap. The LDA bands at about −8 eV are d bands which obviously cannot be reproduced in the sp^3 TB model.

Finally, it is particularly important to note that, despite its short-range (i.e., intradot) errors, the RPA is expected to account quite well for long-range Coulomb correlations, hence for interactions between neighboring nanocrystals.[25] It thus catches the relevant physics in nanocrystal arrays.

VII. CONCLUSION

In conclusion, calculations in TB RPA prove that the charging of a nanocrystal strongly modifies its dielectric response due to collective electronic effects. In arrays of nanocrystals, we show that it is possible to engineer the dielectric constant by controlling the doping or by filling the lowest unoccupied level using pump excitation. It would be also interesting to play on the nature and on the spatial ordering of the quantum dots.

ACKNOWLEDGMENTS

This work is supported in part by the European Community's Human Potential Programme under Contract No. HPRN-CT-2002-00320, NANOSPECTRA. We thank Professor Guyot-Sionnest for providing experimental data of Ref. 22 prior publication and for helpful discussions.

APPENDIX: TIGHT BINDING CALCULATIONS

The single-particle energy levels and wave functions of nanocrystals are calculated with an orthogonal sp^3 tight binding model including up to second nearest neighbor interactions. The tight binding parameters (Table I) are fitted to the bulk CdSe band structure (Fig. 6) and to the experimental effective masses when they are known with sufficient accuracy (in the conduction band) and otherwise to effective masses obtained by pseudopotential calculations[29] (Table II). The reference band structure was calculated using the *ab* *initio* pseudopotential code ABINIT (Refs. 30 and 31) in the local density approximation and was corrected to the band-gap problem. The surface dangling bonds of nanocrystals are saturated by pseudohydrogen atoms.

The confinement energy, i.e., the shift with respect to the band edge, for the S and P states in the conduction band is well fitted by the analytical expression $K/(d^2+ad+b)$ where d is the diameter. With the energy given in electron-volt and d in nanometer, we have $K=12.060$, $a=2.499$, $b=4.016$ for the S state and $K=22.894$, $a=1.786$, $b=8.452$ for the P state. Similar expression holds for the highest occupied state in the valence band with $K=-4.430$, $a=2.816$, $b=-0.601$.

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