Single-electron charging in quantum dots with large dielectric mismatch

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Semiconductor quantum dots characterized by a strong dielectric mismatch with their environment are studied theoretically through direct diagonalization of the many-body Hamiltonian. The enhancement of the electron-electron Coulomb interaction, arising from polarization effects, is found to induce a strong increase in addition energies with increasing dielectric mismatch. For large dielectric mismatch, the excited many-body states can undergo reconstructions as the dot is filled with carriers even in the absence of external magnetic fields.

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I. INTRODUCTION

Semiconductor quantum dots (QD's) are structures where carrier confinement at the nanometer scale is achieved in all spatial directions; the energy spectrum is therefore discrete, as in natural atoms, and the Coulomb interaction among electrons is enhanced owing to the large spatial overlap of their wave functions. In recent years, a large experimental and theoretical effort has lead to the demonstration of QD devices where the strong Coulomb interaction is exploited to allow control of charge injection at the single-electron level:[1–3] Single-electron transistors (SET's) are a fascinating manifestation of many-body physics at work. A reason for the importance of SET's is in the extremely low power required for their operation (of the order of nanowatts). This opens the way to their possible integration in bioenvironments, which is generally incompatible with the large power dissipation of current microelectronic transistors (at least six orders of magnitude larger).

A specific characteristic of organic environments is their huge dielectric mismatch with typical inorganic-semiconductor QD structures. Quantum dots with a large dielectric mismatch to the surrounding medium have been prepared and studied by different techniques in recent years. They comprise QD's embedded in glasses[4] and organic materials, including those fabricated by colloidal techniques[5–8] or inserted in biological environments.[9] In most of these systems, photons have been the primary probe for investigating or modifying the electronic properties of the dots. More recently, it was shown that spherical nanocrystals in low-dielectric-constant matrices can be built into a single-electron device, and that capacitance or tunneling spectroscopies can be used to obtain their addition spectra.[6–8,10] The effects of the large dielectric mismatch have been, however, overlooked in the interpretation of single-electron charging phenomena in these dots.

In this article we present a theoretical calculation of these effects, based on the direct solution of the exact few-particle Hamiltonian for the dots. For large electron numbers, where the dimension of the Hilbert space becomes excidingly big, we also make use of a Hubbard-like approximation to the full Hamiltonian.[11] We show that the enhancement of the electron-electron Coulomb interaction, arising from the buildup of large polarization charges at the interfaces, produces new features in the addition spectra, namely: (i) a strong increase in the absolute values of addition energies, and (ii) the possible occurrence of ''reconstructions'' of the electronic configurations as the dot is filled with electrons. The operation of single-electron devices in organic environments is therefore expected to involve phenomena that modify the relevant energy scale and charge distribution with respect to conventional QD devices embedded in inorganic semiconductor matrices. These phenomena may be relevant for applications of SET's as sensors of dielectric properties at the nanoscale.

II. THEORETICAL APPROACH

The key quantities that are used to characterize these systems experimentally are the addition energies $E_{add}(N)$ (the variation of the energy required to add an electron to a QD containing N electrons, analogous to the differences between electron affinities in natural atoms). These are defined as differences between the QD chemical potentials, μ, as one electron is added to the dot: $E_{add}(N)=\mu(N+1)-\mu(N)$. In turn, the chemical potential of the QD with N electrons is $\mu(N)=E_0(N)-E_0(N-1)$, where $E_0(N)$ are the ground-state energies in the dot.

To calculate $E_0(N)$ we need to know the ground-state configuration of the many-electron system. The full many-body Hamiltonian is

$$\hat{H}=\sum_{a\sigma}\epsilon_a\hat{c}^{\dagger}_{a\sigma}\hat{c}_{a\sigma}+\frac{1}{2}\sum_{abcd\sigma\sigma'}V_{abcd}\hat{c}^{\dagger}_{a\sigma},\hat{c}^{\dagger}_{b\sigma'}\hat{c}_{c\sigma'}\hat{c}_{d\sigma}, \tag{1}$$

where $\hat{c}^{\dagger}_{a\sigma}$ ($\hat{c}_{a\sigma}$) is the fermionic creation (destruction) operator in the eigenstate $|a\sigma\rangle$ of the single-particle Hamiltonian (a stands for the set of orbital quantum numbers, σ for spin); ϵ_a are the single-particle energies; V_{abcd} are the interaction integrals

$$V_{abcd}=\int\int\phi^*_a(\mathbf{r})\phi^*_b(\mathbf{r}')V(\mathbf{r},\mathbf{r}')\phi_c(\mathbf{r}')\phi_d(\mathbf{r})d\mathbf{r}\,d\mathbf{r}' \tag{2}$$

where $\phi_a(\mathbf{r})$ are the single-particle envelope functions.[12]

The effect of spatial modulation of the dielectric constant ε enters in the determination of the Coulomb integrals. The interaction $V(\mathbf{r},\mathbf{r}')$ between two charges, sitting at positions $\mathbf{r}$ and $\mathbf{r}'$, is the solution of Poisson equation $\nabla_{\mathbf{r}}\cdot\varepsilon(\mathbf{r})\nabla_{\mathbf{r}}V(\mathbf{r},\mathbf{r}')=-e^2\delta(\mathbf{r}-\mathbf{r}')$. When the dielectric constant is spatially homogeneous, i.e., $\varepsilon(\mathbf{r})=\varepsilon_0$, then $V(\mathbf{r},\mathbf{r}')=e^2/[4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|]$. The space dependence of $\varepsilon(\mathbf{r})$ modifies $V(\mathbf{r},\mathbf{r}')$, hence modifying the Coulomb matrix elements (2).[13] Note that the renormalization of the interaction gives also rise to a self-energy term. This term is known to be small (see Ref. 13) and is therefore neglected in this paper. For low-symmetry structures, the Poisson equation must be solved numerically,[13] while for spherical QD's an analytic expression of the potential can be obtained:[15]

$$V(\mathbf{r}_i,\mathbf{r}_j)=\frac{e^2}{\varepsilon_1}\frac{1}{|r_i-r_j|}+\frac{e^2}{\varepsilon_1 R_\varepsilon}\sum_{k=0}^{\infty}\frac{(k+1)(\varepsilon-1)}{(k\varepsilon+k+1)}\left(\frac{r_i r_j}{R_\varepsilon^2}\right)^k P_k(\cos\Theta_{ij}), \tag{3}$$

where $\varepsilon=\varepsilon_1/\varepsilon_2$, and $\varepsilon_1(\varepsilon_2)$ is the dielectric constant of the inner (outer) material. R_ε is the radius of the sphere of dielectric mismatch, which can be larger than the radius of confinement R_d, as, e.g., in core-shell QD's (see inset of Fig. 3). Note that the same effective potential enters the determination of the optical spectra of QD's, producing a strong increase in the exciton binding energies.[13,15] Once the V_{abcd} are obtained from Eqs. (2) and (3), we calculate $\hat{H}$ [Eq. (1)] and diagonalize it in the space generated by the set of Slater determinants (SD's) $|\Phi\rangle=c^\dagger_{a_1\sigma_1}c^\dagger_{a_2\sigma_2}\cdots c^\dagger_{a_N\sigma_N}|0\rangle$.[11]

Because of the spherical symmetry $\hat{H}$ commutes with total orbital and spin angular momenta $\hat{\mathbf{L}},\hat{\mathbf{S}}$ (in our model we neglect spin-orbit coupling) and with their projections $\hat{L}_z,\hat{S}_z$. This can be exploited to put $\hat{H}$ in block-diagonal form, thus reducing the dimension of the matrices to be diagonalized.[14] This reduction, however, cannot compensate for the exponential growth of the dimensionality of the space generated by the set of SD's, when we increase N or the number of single-particle shells. Hence for larger N the matrices to be diagonalized become too big and it is necessary to adopt some kind of approximation in the computation of correlated states.

With this purpose we introduce a Hubbard-like approximation,[11] whereby only the ''semidiagonal'' elements of the Hamiltonian are retained, i.e., those containing the Coulomb integrals $U_{ab}=V_{abba}$ (direct terms) and $J_{ab}=V_{abab}$ (exchange terms). For our single-site problem, the latter Hamiltonian is diagonal in the basis of the SD's with eigenvalues

$$E_\Phi=\langle\Phi|\hat{H}|\Phi\rangle=\sum_{a\sigma}\varepsilon_a n_{a\sigma}+\frac{1}{2}\sum_{ab\sigma}U_{ab}n_{a-\sigma}n_{b\sigma}+\frac{1}{2}\sum_{ab\sigma}(U_{ab}-J_{ab})n_{a\sigma}n_{b\sigma}, \tag{4}$$

where $n_{a\sigma}=\langle\Phi|\hat{c}^\dagger_{a\sigma}\hat{c}_{a\sigma}|\Phi\rangle$ is the occupation number of the state $|a\sigma\rangle$. The solution is therefore much simpler than the diagonalization of the exact Hamiltonian. The accuracy of this approximation—which was shown to be excellent in the case of conventional III-V dots[11]—depends critically on the ratio between the Coulomb and kinetic terms in the Hamiltonian, which is strongly modified by dielectric confinement. Its validity for the ground state of the QD's studied here is confirmed a posteriori by comparison with the exact results available for small N.

III. RESULTS

In the following we will consider prototype spherical CdSe and InAs QD's similar to those investigated in Refs. 7, 8, and 10, with $\varepsilon_1>\varepsilon_2$. The embedding medium is assumed to be homogeneous, with varying values of ε_2; the dielectric constant inside the CdSe dot is $\varepsilon_1=10$, and inside the InAs QD is $\varepsilon_1=10.9$. Given the large band offsets (the embedding medium is insulating), for simplicity the confining potential can be assumed to be an infinite well of radius R_d. As the

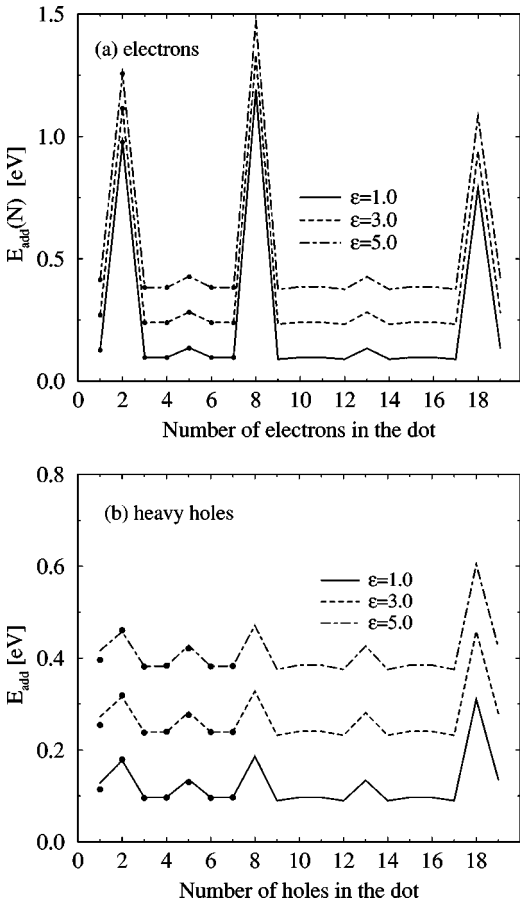

FIG. 1. Calculated addition energies (a) for electrons and (b) for heavy holes as a function of the number N of particles in the dot (addition spectrum). Results are shown for a CdSe QD (dielectric constant $\varepsilon_1=10$, $R_d=R_\varepsilon=2$ nm). Each curve corresponds to a different value of $\varepsilon=\varepsilon_1/\varepsilon_2$. Full circles represent results obtained by diagonalizing the exact Hamiltonian, while lines connect results obtained within the Hubbard approximation.

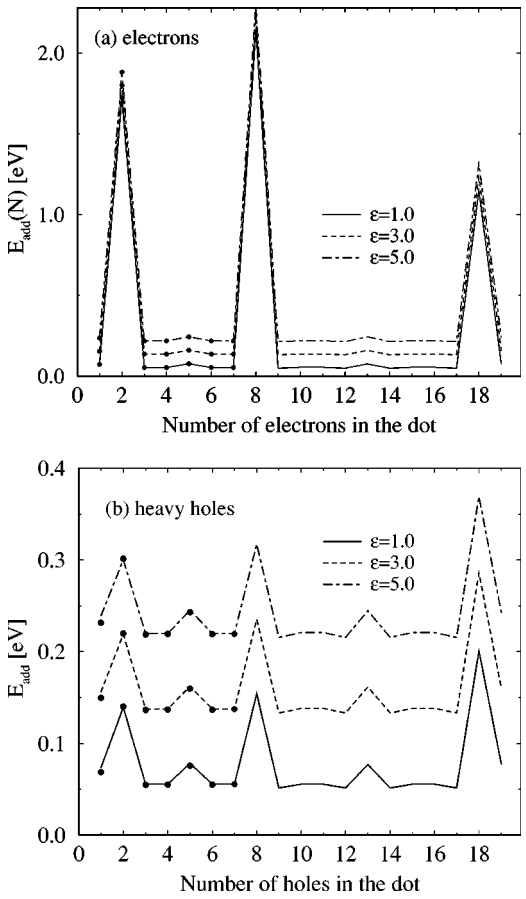

FIG. 2. Calculated addition energies (a) for electrons and (b) for heavy holes as a function of the number N of particles in the dot (addition spectrum). Results are shown for an InAs QD (dielectric constant $\varepsilon_1=10.9$, $R_d=R_\varepsilon=3.2$ nm). Each curve corresponds to a different value of $\varepsilon=\varepsilon_1/\varepsilon_2$. Full circles represent results obtained by diagonalizing the exact Hamiltonian, while lines connect results obtained within the Hubbard approximation.

QD shape is spherical, Coulomb integrals are calculated from Eq. (3).

A. Ground state and addition energies

Results for electron and heavy-hole addition spectra are shown in Fig. 1, for a CdSe QD with $R_\varepsilon=R_d=2$ nm and in Fig. 2 for an InAs QD, with $R_\varepsilon=R_d=3.2$ nm. Solid lines are for a nanostructure with no dielectric mismatch ($\varepsilon_1=\varepsilon_2$). The peaks at $N=2$, $N=8$, and $N=18$ correspond to the addition of one electron (or hole) to a QD with a closed *s*, *p*, and *d* shell, respectively; the weaker peaks at $N=5$ and $N=13$ correspond to the addition of one electron to a QD with a half-filled outer shell where all spins are parallel (according to Hund's rule). When $\varepsilon_1>\varepsilon_2$ the spectra are shifted upward, since a larger energy is needed to add new electrons to the QD due to the enhanced Coulomb repulsion. Note that in this system the shift is almost rigid, and no significant anomalies in the ordering of ground-state energies and shell filling are observed. This is due to the linear dependence on ε of the $k=0$ term which is dominant in the power series in Eq. (3), combined with the fact that the electron configurations entering the many-body ground state turn out to be unchanged even with strong dielectric mismatch. We point out that this feature can be assessed only through diagonalization of the exact many-body Hamiltonian.[16]

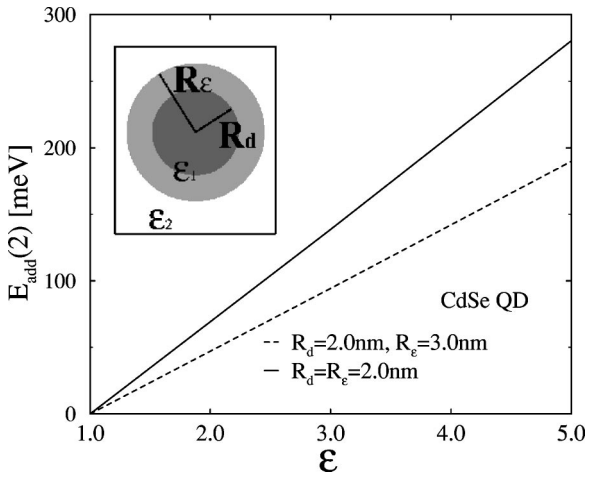

FIG. 3. Dependence of the electron addition energy on the dielectric mismatch $\varepsilon=\varepsilon_1/\varepsilon_2$ for a CdSe QD. Solid line: the dielectric mismatch occurs at the QD interface $R_\varepsilon=R_d=2$ nm (see inset); dashed line: the dielectric mismatch occurs at a remote interface (core-shell QD) $R_\varepsilon=3$ nm, $R_d=2$ nm. The energies are referred to $E_{add}(2)$ calculated for $\varepsilon=1$. The linear dependence of the addition energy is almost identical for all values of N.

It is worth stressing that the energy scale of addition energies of both electrons and holes is strongly affected by ε_2; this is shown for electron and hole addition in Figs. 1 and 2. Dielectric mismatch must be taken into account for any meaningful comparison with experiments; if it is neglected, the observation of such large addition energies (strong Coulomb interaction) might be incorrectly attributed to an unphysical (too strong) confinement.[17] Conversely, these results suggest that the dependence of addition energies on ε_2 could be exploited to discriminate environments with different dielectric properties. Figure 3 indeed shows that such dependence is practically linear and steep; this is true even when the dielectric mismatch is spatially separated from the confining interface,[13] as, e.g., for core-shell dots,[6] because of the long-range field generated by polarization charges.

Experimental data are so far available only for QD's in a specific environment. Our results are in good agreement with the electron addition energies measured as a function of the dot size, particularly for InAs dots[7] whose size and structure (spherical shape) are best characterized. In Fig. 4 we compare results of our computations for $E_{add}(1)$ (addition of the second electron) with experimental findings reported in Ref. 7, for different values of the radius $R_d=R_\varepsilon$. The agreement is good and the expected behavior $(1/R_d)$-like (dashed line in figure) is reproduced. We have obtained the best accordance with experimental data with $\varepsilon\simeq1.9$, i.e., $\varepsilon_2\simeq5.7$. This is in agreement with the value $\varepsilon_2\simeq6$, obtained in a similar way in Ref. 18. Also the experimental finding that the values of $E_{add}(N)$ corresponding to the addition of p electrons are all very similar is reproduced, even if in experimental data half-shell peaks do not appear, may be due to lack of resolution.

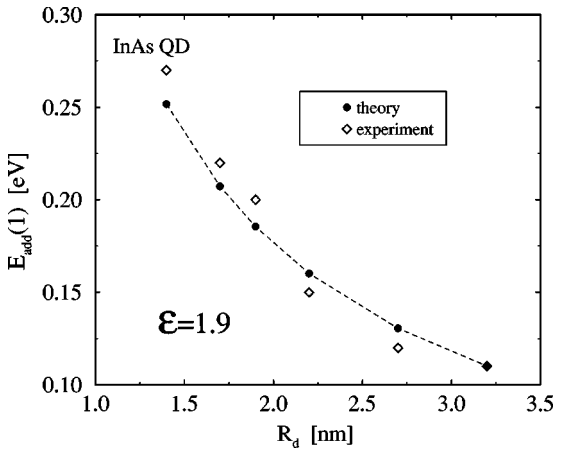

FIG. 4. Comparison of theoretical (our results) and experimental (data from Ref. 7) values of $E_{add}(1)$ (addition of the second electron), for an InAs QD with $\varepsilon=1.9$, for different values of $R_d=R_\varepsilon$.

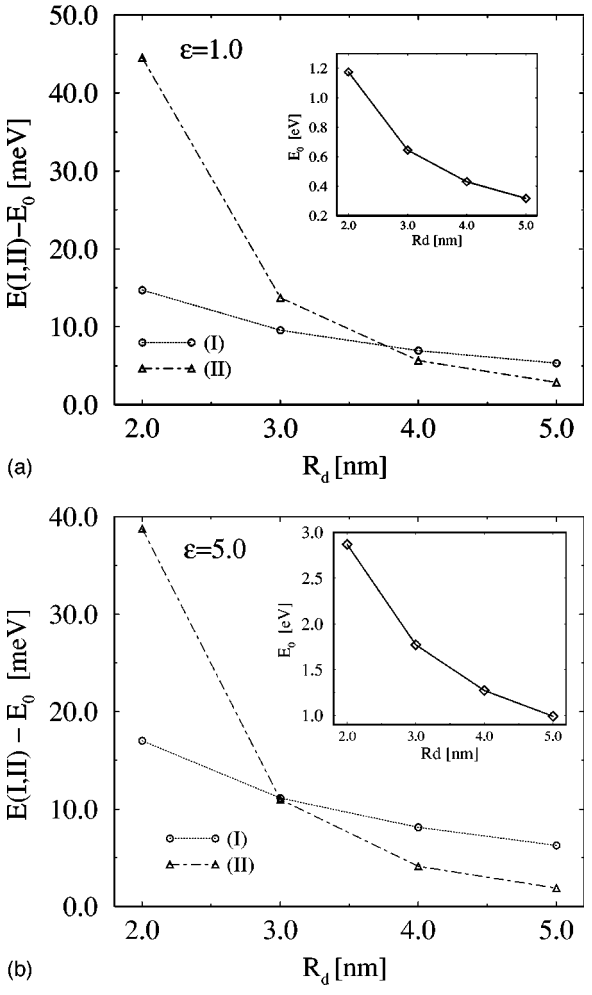

FIG. 5. Dependence on R_d of the eigenenergies of the levels (I) and (II) with respect to the ground-state energy E_0, for $N=4$ heavy holes in a CdSe QD, with (a) no dielectric mismatch: $\varepsilon=1$; (b) strong dielectric mismatch: $\varepsilon=5$. In the inset it is reported the dependence of E_0 on R_d.

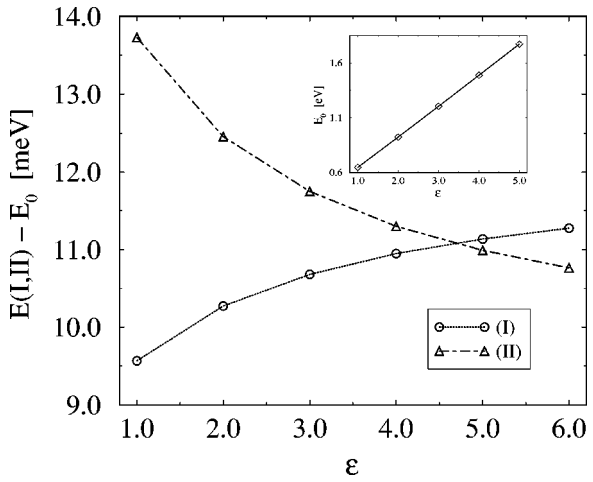

FIG. 6. Dependence on ε of the eigenenergies of the levels (I) and (II), with respect to the ground-state energy E_0, for $N=4$ heavy holes in a CdSe QD of radius $R_d=3$ nm. In the inset it is reported the dependence of E_0 on ε.

Full-shell peaks are overestimated in our computation with respect to experimental findings, expecially for the lower values of R_d. This can be attributed to our simplified single-particle model yelding too great confinement energies.[18,19]

B. Excited states

The interplay between the single-particle energies and the interaction terms determines the overall structure of the energy spectrum of the QD. By means of exact diagonalizations we have studied the first lower excited levels as a func-

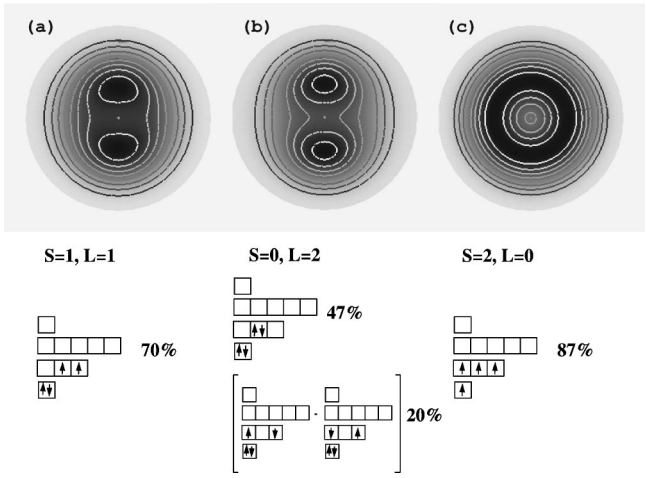

FIG. 7. Total charge density distribution in a vertical plane passing for the z axis, for $N=4$ heavy holes in a CdSe QD ($R_\varepsilon=R_d=3$ nm; $\varepsilon_1=10$; $\varepsilon_2=2$). The three lowest eigenstates of the exact Hamiltonian are shown: (a) is one of the many-body states of lowest energy, with total spin and angular momentum $S=1$, $L=1$; (b) and (c) correspond to the excited states I ($S=0$, $L=2$) and II ($S=2$, $L=0$), respectively. Below the contour plots, the dominant (SD) terms contributing to the many-body states are indicated schematically with their weight. The sequence of the degenerate single-particle levels in each SD corresponds to the $1s$, $1p$, $1d$, $2s$ states of the QD.

tion of ε and R_d. Figure 5 shows that, for a fixed number of particles (CdSe QD with $N=4$ holes in this case), as the dot size is increased the second excited state (II) decreases in energy until it becomes lower than the first (I).[20] This ''reconstruction'' may also occur in the absence of a strong mismatch, but its quantitative prediction for a given dot is strongly ε-dependent, as is apparent by comparing Figs. 5 and 6. To illustrate the nature of this effect, in Fig. 7 we show the total hole charge distribution associated with the many-body ground and excited states, as well as their main Slater-determinant components. In terms of single-particle configurations, it appears that with increasing Coulomb interaction it becomes more favorable for one of the holes to leave the lowest single-particle shell ($n=1,\ l=0$; see caption of Fig. 7) in order to reduce the repulsion with the second hole in the same shell, thus being promoted to a higher single-particle level ($n=1,\ l=1$). As a result, the symmetry and spatial extension of the total charge density distribution is strongly rearranged.

This excited-level reconstruction emerges only when interaction energies are much stronger than single-particle energies. We do not find any reconstruction for electrons in CdSe QD's and for electrons and holes in InAs QD's, because they have smaller effective masses and hence greater single-particle energies.

We point out that this type of effects depends critically on the structure of the many-body states and is not accurately described by Hubbard-like approaches;[16] since excited states of QD's are now directly accessible experimentally[21] this must be kept in mind when comparing theory and experiment.

No inversion in energy ordering involving the many-body ground state is found for the dots examined here. However, our exact diagonalization calculations show that the energy differences between ground and excited many-body states can be very small, particularly for larger dots (Fig. 5) and large N. Reconstructions involving the ground state, thus changing completely the structure of the addition spectra, are therefore possible and will depend on the detailed dot geometry.

IV. CONCLUSION

In summary, we have shown that addition spectra are strongly affected by the enhancement of the Coulomb interaction that arises when a quantum dot is embedded in a medium of lower dielectric constant: addition energies are increased, and also the nature and energy ordering of many-body states may be modified with respect to the case of good dielectric matching. These phenomena must be taken into account for a correct quantitative interpretation of experiments and may be relevant for applications of single electron transistors as sensors of dielectric properties at the nanoscale. Good accordance has been found with recent experiments on InAs QD's.

ACKNOWLEDGMENTS

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[1] R. C. Ashoori, Nature (London) **379**, 413 (1996).

[2] L. P. Kouwenhoven, C. M. Marcus, P. L. McEuen, S. Tarucha, R. M. Westervelt, and N. S. Wingreen, in *Mesoscopic Electron Transport*, edited by L. Sohn, L. P. Kouwenhoven, and G. Shon (Kluwer, Dordrecht, 1997).

[3] L. Jacak, P. Hawrylak, and A. Wójs, *Quantum Dots* (Springer, Berlin, 1998).

[4] U. Woggon, *Optical Properties of Semiconductor Quantum Dots* (Springer, Berlin, 1996).

[5] C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993).

[6] A. P. Alivisatos, Science **271**, 933 (1996); MRS Bull. **23**, 18 (1998).

[7] U. Banin, YunWei Cao, D. Katz, and O. Millo, Nature (London) **400**, 542 (1999).

[8] B. Alperson, I. Rubinstein, G. Hodes, D. Porath, and O. Millo, Appl. Phys. Lett. **75**, 1751 (1999).

[9] See, e.g., M. Bruchez, Jr., M. Moronne, P. Gin, S. Weiss, and A. P. Alivisatos, Science **281**, 2013 (1998); W. C. Chan and S. Nie, *ibid.* **281**, 2016 (1998).

[10] D. L. Klein, R. Roth, A. K. Kim, A. P. Alivisatos, and P. McEuen, Nature (London) **389**, 6991 (1997).

[11] M. Rontani, F. Rossi, F. Manghi, and E. Molinari, Appl. Phys. Lett. **72**, 957 (1998); Phys. Rev. B **59**, 10 165 (1999).

[12] We neglect band mixing and nonparabolicity, and we assume effective masses of $0.11m_e$ and $1.0m_e$ for electrons and heavy holes in CdSe, respectively, and $0.023m_e$ and $0.41m_e$ for electrons and heavy holes in InAs. With these simplifying approximations we expect that only the lowest single-particle states will be reproduced accurately (Ref. 19). The physics of many-body interactions is however not expected to depend on these assumptions.

[13] G. Goldoni, F. Rossi, and E. Molinari, Phys. Rev. Lett. **80**, 4995 (1998).

[14] With Slater determinants it is straightforward to put $\hat{H}$ in block diagonal form with respect to the operators $\hat{L}_z$ and $\hat{S}_z$, but it is complex and inconvenient to find the block diagonal form with respect to the whole set $(|\hat{\mathbf{L}}|,|\hat{\mathbf{S}}|,\hat{L}_z,\hat{S}_z)$. In this work we limit ourselves to the first few operators.

[15] L. E. Brus, J. Chem. Phys. **80**, 4403 (1994).

[16] Our results show that the occurrence of reconstructions can often be assessed only on the basis of full many-body calculations. In practice, we have found that single-Slater determinant calculations predict some ground-state reconstructions that are not reproduced by exact diagnoalization.

[17] A preliminary discussion of this point is given by G. Goldoni, F. Rossi, A. Orlandi, M. Rontani, F. Manghi, and E. Molinari, Physica E **6**, 482 (2000).

[18] A. Franceschetti, A. Williamson, and A. Zunger, cond-mat/9908417 (unpublished).

[19] A. I. Ekimov, F. Hache, M. C. Schanne-Klein, D. Ricard, A. V. Rodina, I. A. Kurdryavtsev, T. V. Yazeva, A. V. Rodina, and A. L. Efros, J. Opt. Soc. Am. B **10**, 101 (1993).

[20] This effect is the result of a delicate balance between single particle energies and Coulomb integrals: it occurs in this regime of dot size and occupation only for hole states due to the lower single-particle level spacing.

[21] L. P. Kouwenhoven, T. H. Oosterkamp, M. W. S. Danoesastro, M. Eto, D. G. Austing, T. Honda, and S. Tarucha, Science **278**, 1788 (1997); D. R. Stewart, D. Sprinzak, C. M. Marcus, C. I. Duruz, and J. S. Harris, Jr., *ibid.* **278**, 1784 (1997).