From independent particles to Wigner localization in quantum dots: The effect of the dielectric environment

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The influence of image charges on the electron correlation in two-electron spherical quantum dots is investigated. The image charges induced by the dielectric mismatch between the quantum dot and the surrounding medium can induce a transition from volume to surface states, the latter being localized mainly in the self-polarization potential well. Coulomb interaction and correlation effects in these surface states depend strongly upon the ratio of dielectric constants: If $\varepsilon_{dot}<\varepsilon_{out}$ the bare electron-electron Coulomb interaction can be screened by the polarizatization terms, then, the kinetic energy dominates, the correlation energy becomes negligible and the electrons behave almost as independent particles. However, if $\varepsilon_{dot}>\varepsilon_{out}$ a strongly enhanced angular correlation can lead to the formation of a Wigner-type molecule even in the high electronic density and small dot-size regimes.

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Quantum dots are nanosize clusters of semiconductor material embedded in another semiconducting medium, in a glass dielectric matrix, aqueous solution or simply in air or a vacuum. In the continuous medium models, like, e.g., effective mass approximation, differences of the dielectric constants between quantum dot and surrounding medium lead to the appearance of surface image charges of any excess electrons (or holes) in the quantum dot. These charges yield self-polarization of carriers and polarization of the Coulomb interaction between them. As the result, the excess particles in quantum dots undergo the so-called dielectric confinement, which in extreme cases of large dielectric mismatch, can compete with the quantum size effect, strongly influencing the electronic and optical properties of quantum dots.

The influence of dielectric mismatch on the energy structure and optical properties of semiconductor nanocrystals have been studied for more that two decades,[1] beginning with the pioneering work by Brus.[2] The main numerical difficulty appears in the calculation of the self-energy. This is because the self-polarization potential is nonintegrable across the interface of the dielectric mismatch. The source of this divergence is the steplike dielectric constant profile at the quantum dot boundary. Several approximate solutions of this problem, as for example application of an infinite barrier at the dot boundary[2] or the regularization method,[3] were addressed in the literature. An alternative solution has been proposed[4,5] in which the steplike dielectric function is replaced by a continuous variation of dielectric constant within a thin layer (of the order of a lattice constant) located at the interface. The advantage of this model is that, contrary to the regularization method, it scales correctly with the size. A convenient rewriting of the resulting self-polarization potential, which eludes the low convergence and numerical inaccuracy coming from computational cutoff errors,[6,7] has been successfully applied by us in the study of the influence of image charges on the donor impurity states in quantum dots.[6–8]

Two examples of the shape of the self-polarization potential are shown in Fig. 1. The potentials presented therein are calculated for two distinct cases studied later in this paper, namely (A) $\varepsilon_{dot}=4$, $\varepsilon_{out}=80$ and (B) $\varepsilon_{dot}=4$, $\varepsilon_{out}=1$. Either case represents a nanocrystal with a rather small dielectric constant (e.g., SiO_2) embedded in higher or lower permittivity media. In the first case the self-polarization potential has a weak repulsive character outside the quantum dot and forms a narrow, deep attractive well within the quantum dot, close to the interface. In the second case the weak repulsive potential arises inside the quantum dot, and the narrow, deep well also appears close to the surface, but now it is located in the surrounding medium (usually a barrier-acting medium). Depending upon the relative weight of spatial and dielectric confinements, a transition from volume to surface states induced by image charges may occur.[9] In this paper we show that, although in both cases the electrons can be equally trapped in this narrow surface potential well leading to surfacelike states, the Coulomb interaction and the correlation effects are completely different in each case. It should be mentioned that the influence of dielectric mismatch on many-electron states and addition energy spectra in spherical quantum dots has been studied by several authors.[9–11] However, the majority of works were devoted to investigating only the case of $\varepsilon_{dot}>\varepsilon_{out}$ and, to our knowledge, a detailed investigation of the role of the self-energy and polarization effects on the electronic interaction and the correlation effects of spherical nanocrystals with a large dielectric mismatch has not been performed to date.

We investigate the role of image charges on the correlation effects in a system of two electrons in a spherical quantum dot in two distinct regimes, i.e., $\varepsilon_{dot}<\varepsilon_{out}$ and $\varepsilon_{dot}>\varepsilon_{out}$. In particular, when $\varepsilon_{dot}\ll\varepsilon_{out}$ [case (A) in Fig. 1] both electrons are trapped in the thin surface self-polarization potential. This is mainly due to the self-energy-induced localization of the monoelectronic ground ($n=1$, $\ell=0$) and sev-

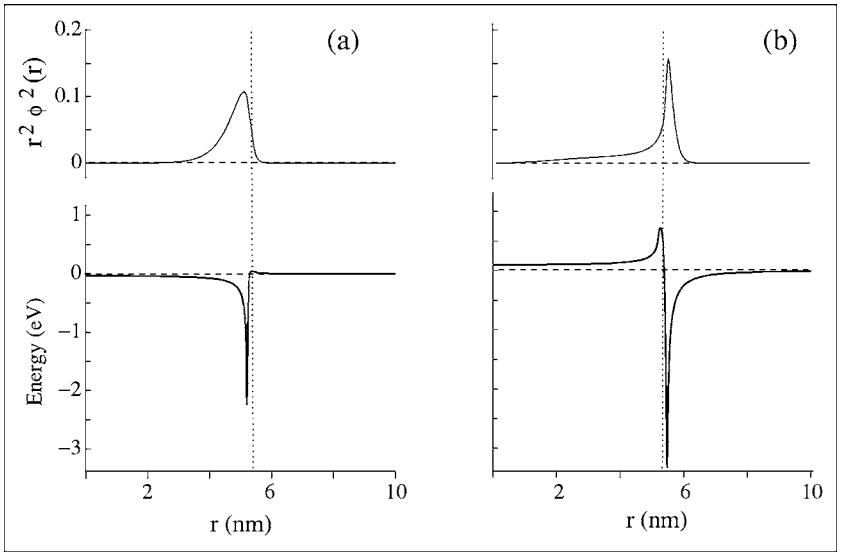

FIG. 1. Self-polarization potential (lower panel) for a $R=53.5$ Å, $\varepsilon_{dot}=4$ quantum dot surrounded by (a) an $\varepsilon_{out}=80$ dielectric medium [case (A) in the text] and (b) an $\varepsilon_{out}=1$ dielectric medium [case (B) in the text]. The corresponding radial density of the one-electron ϕ_{1s} state for $m^*_{dot}=0.5$, $m^*_{out}=1$, $V_0=0.9$ eV is shown in the upper panel for each case. The vertical dotted line indicates the quantum dot edge.

eral energetically low-lying excited states ($n=1$, $\ell \neq 0$) in the deep, attractive well. We show that in these cases the bare Coulomb repulsion is almost totally screened by the polarization effects. As a consequence, the kinetic energy dominates, the correlation effects becomes negligible and both electrons behave almost as independent particles. In the second case, $\varepsilon_{dot} > \varepsilon_{out}$ [case (B) in Fig. 1], both electrons can equally be trapped in a surface self-polarization potential. However, now the Coulomb repulsion is not screened but enhanced. We show that in this case, the strong angular correlation between the electrons in the thin spherical self-energy well can lead to the formation of a Wigner-type molecule. The formation of Wigner molecules in two- and three-dimensional quantum dots in the absence of an external magnetic field has been related up until now with the low electron density and large quantum dot sizes.[12–18] Here we demonstrate that it can be achieved in small quantum dots by the presence of image charges regardless of the electron density. In short, we show that by changing the dielectric constant of the environment, the behavior of the electrons in a quantum dot can be tuned between two limiting cases, that is, from almost independent particles to a Wigner-type localization. Since nowadays there is a widespread interest in developing the so-called *high-k* and *low-k* materials, this result may be of practical interest in developing nanoscopic devices which could operate in the dielectric confinement regime.

Our model consists of a spherical nanocrystal of radius $R=53.5$ Å and a dielectric constant $\varepsilon_{dot}=4$. The nanocrystal is surrounded by a medium with a dielectric constant ε_{out}. We work within the effective mass approximation and we consider only the conduction band states. The values of the effective mass inside and outside the nanocrystal are taken as $m^*_{dot}=0.5$ and $m^*_{out}=1$, respectively, and a potential barrier $V_0=0.9$ eV at the dot boundary is assumed.[20] Since we focus mainly on the influence of different dielectric environments on two-electron states of such systems, we do not consider any particular quantum dot material (although these parameters are close to those of SiO_2).

To account for two-electron states we first solve the one-particle effective-mass Schrödinger equation including the self-energy potential. The radial parts of the exact single-particle eigenfunctions $\phi_{n\ell m}(\vec{r})$ are determined numerically on the grid extending far beyond the dot radius, R. Products of the basis functions $\phi_{n\ell m}$ are then used to construct configuration-interaction (CI) expansions $\Psi_{LS}=\Sigma_j \Phi_j$ of the symmetry- and spin-adapted two-electron configurations, where L and S are the total angular and total spin quantum numbers, respectively. The two-electron Hamiltonian containing Coulomb interaction and polarization terms[5] is then diagonalized in the CI basis set. As a result, we get two-particle wave functions $\Psi_{LS}(\vec{r}_1,\vec{r}_2)$ and energies $E(^{2S+1}L)$. We use as many single-particle basis functions $\phi_{n\ell m}$ and as long a CI expansion as are needed to achieve convergence and the required accuracy.

From the wave function, we can define the radial pair density $P(r_1,r_2)$,

$$P(r_1,r_2) = 2\int |\Psi(\vec{r}_1,\vec{r}_2)|^2 r_1^2 r_2^2 \sin\theta_1 \sin\theta_2 d\phi_1 d\phi_2 d\theta_1 d\theta_2, \tag{1}$$

to study radial correlations, and the angular correlation density $Z(\theta)$,

$$Z(\theta) = N_Z |\Psi((r_{max},0,0),(r_{max},\theta,0))|^2, \tag{2}$$

[with r_{max} corresponding to the coordinates $r_1=r_2$ of the $P(r_1,r_2)$ maximum and N_Z represents the appropriate normalization factor], in order to study angular correlations.

Let us consider first the case of the nanocrystal surrounded by a medium of $\varepsilon_{out}=80$ [case (A)], i.e., a quantum dot embedded in a high permittivity environment. The self-energy potential compared to the barrier height is shown in Fig. 1(a). The figure also shows the radial density of the one-electron ϕ_{1s} state. The radial pair density, $P(r_1,r_2)$, of the two-electron ground state is displayed in Fig. 2(a). Both single and two-electron functions are strongly confined in a thin self-energy well at the quantum dot surface. For the sake of comparison, the radial pair density of the ground state of

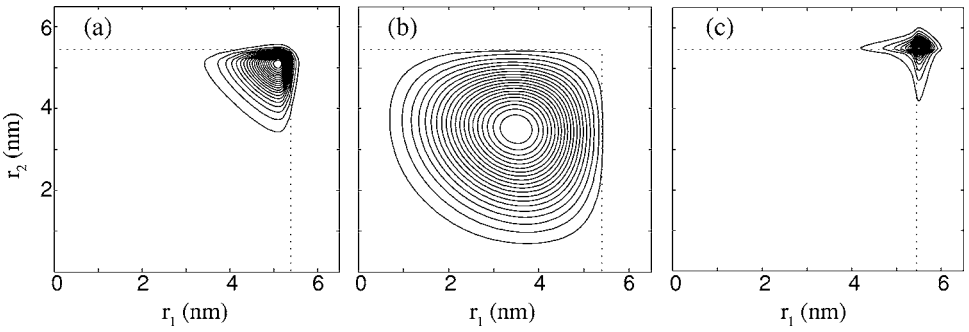

FIG. 2. Radial pair density $P(r_1,r_2)$ of the two-electron ground state for a $R=53.5$ Å, $\varepsilon_{dot}=4$, $m^*_{dot}=0.5$, $m^*_{out}=1$, $V_0=0.9$ eV quantum dot for three different surrounding dielectric constants, (a) $\varepsilon_{out}=80$, (b) $\varepsilon_{out}=4$ (unpolarized dot), and (c) $\varepsilon_{out}=1$. Dotted lines indicate the quantum dot edge.

the same nanocrystal, but surrounded by an environment with neither self-energy nor polarization effects ($\varepsilon_{out}=\varepsilon_{dot}=4$), is shown in Fig. 2(b). To account for the Coulomb interaction and the electron correlation effects, one should compare the ground state (^1S_g) energy with the energy $E(1s^2)$ of the ground configuration of two independent, that is to say noninteracting, particles in the same quantum dot (see Table I). The result thus obtained, $\Delta E=E(^1S_g)-E(1s^2)=0.005$ eV, compared to $\Delta E=0.083$ eV that corresponds to the *unpolarized* quantum dot ($\varepsilon_{out}=4$), is apparently surprising. Since, in the case of a nanocrystal embedded in high permittivity media, the attractive self-energy potential well appears on the quantum dot side of the interface and the one-particle wave functions have negligible tails in the surrounding spatial barrier-acting medium (where $\varepsilon\neq\varepsilon_{dot}$), it is possible to estimate bare Coulomb interaction and polarization effects separately. To this end, we calculate the energy of the ground state, $E_{BC}(^1S_g)$, of the two particles *only* interacting via the bare Coulomb term (with $\varepsilon=\varepsilon_{dot}=4$). The energy difference $E_{BC}(^1S_g)-E(1s^2)$ amounts to 0.049 eV. We then conclude that the bare Coulomb interaction is far from being negligible, but it is almost totally screened by the positive (stabilizing) polarization charges. As a result, the electrons in such a system can be viewed as almost independent particles with negligible correlation effects.[21] This can also be seen by analyzing the coefficients in the CI expansion (Table I): the largest coefficient corresponds to the $1s^2$ configuration and amounts to 0.956. The next important configuration is $1p^2$ with a coefficient of 0.287, all other configurations being almost negligible.

TABLE I. Ground state total energy E_{TOT}, the same energy excluding polarization terms in the electron-electron interaction potential E_{BC}, and $1s^2$ configuration total energy E_{1s^2} (eV) of an $\varepsilon_{dot}=4$, $R=53.5$ Å, spherical nanocrystal embedded in three different dielectric media (ε_{out}). The conduction band edge is taken as the origin of energy. The relevant coefficients of the corresponding CI expansions are also included.

	ε_{out}		
	80	4	1
E_{TOT}	−0.287	0.128	0.447
E_{BC}	−0.243	0.128	0.395
E_{1s^2}	−0.292	0.045	0.236
$c_0(1s^2)$	0.956	0.856	0.637
$c_1(1p^2)$	0.287	0.445	0.672
$c_2(1d^2)$			0.281
$c_3(1s2s)$		0.261	0.228

Let us now consider case (B) of $\varepsilon_{out}=1$, i.e., the same quantum dot embedded in a low permittivity medium like air or a vacuum. The radial density of the one-electron ϕ_{1s} state and the radial pair density of the ground two-electron state are presented in Figs. 1(b) and 2(c), respectively. As in the previous case, both single-particle and two-electron functions are also now strongly confined in a thin self-energy well at the quantum dot surface.[22] However, in the present case, the total Coulomb interaction is quite large.[23] It amounts to $\Delta E=0.211$ eV.

The estimation of the polarization effects alone is not as straightforward in this case as in the previous one, because, as can be seen in Fig. 1(b), the low-lying one-electron wave functions are, to a relevant extent, localized in the barrier region where $\varepsilon_{out}\neq\varepsilon_{dot}$. One can, however, calculate $E_{BC}(^1S_g)$ using ε_{out} in the bare Coulomb term. The energy difference $E_{BC}(^1S_g)-E(1s^2)=0.159$ eV allows us to make an estimation of 0.052 eV for the extra unstabilization due to the surface-induced charges. To the contrary of what happen in case (A), in case (B) the image charges are negative and they enhance, instead of screening, the bare Coulomb interaction, and the correlation effects are now far from being negligible. The relevant CI coefficients obtained are displayed in Table I. We can see that the most important contribution comes from the $1p^2$ configuration. Next to it, the $1s^2$ configuration arises with a similar weight, the remaining contributions being far smaller. Since both the $1s$ and $1p$ one-electron functions are mainly localized in the thin surface self-energy well, the $1s^2$ and $1p^2$ configurations must undergo a strong angular correlation. We can see this by looking at the angular correlation density $Z(\theta)$ displayed in Fig. 3, which shows a comparison of $Z(\theta)$ corresponding to the two cases investigated in this paper and, additionally, the unpolarized quantum dot (i.e., $\varepsilon_{dot}=\varepsilon_{out}=4$). In Fig. 3 we can see a progressive angular localization of the electronic density. In case (A) $Z(\theta)$ is large in the whole θ domain, which reflects the independent dynamics of both electrons. The case of the unpolarized quantum dot represents the transition to case (B), where the probability of low or intermediate values of θ is very small, which can be viewed as a Wigner-type localization in the high electron density regime. It should be pointed out that the electron density localization is extremely strong in these cases since a high self-energy-induced radial localization also occurs [see Figs. 2(a) and 2(c)]. It should

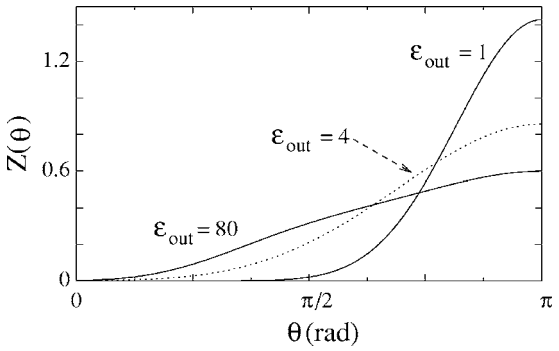

FIG. 3. Angular correlation density $Z(\theta)$ corresponding to the same cases as in Fig. 2.

also be stressed that the angular localization is certainly a correlation effect [it becomes important only in case (B) of high correlation], but the radial localization is mainly a monoelectronic effect coming from the strong localization in the self-polarization well of the energetically low-lying single-particle eigenfunctions [radial localization is important in both cases (A) and (B), regardless of low/high correlation].

In summary, we have investigated the role of image charges on the correlation effects in a system of two electrons in a spherical quantum dot embedded in high ($\varepsilon_{\text{out}}=80$) and low ($\varepsilon_{\text{out}}=1$) permittivity media. Our findings show that a transition from almost independent particles to Wigner-type localization of the conduction band electrons may be attained by tuning an appropriate dielectric response of the surrounding medium.

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[20] It should be pointed out that dielectric and spatial confinements are highly nonadditive (Ref. 6). In particular, a large V_0 would prevent the self-polarization potential to confine the electronic density at the QD border in case (B).
[21] We do not use the quantum-chemical definition of the correlation energy and the correlation effects. In this paper correlation is understood as the contribution of excited configurations to the exact wave function in comparison to the ground configuration ($1s^2$).
[22] Despite this strong confinement, the system is, formally, in the weak confinement regime because the QD radius is larger than the effective Bohr radius a_B^*. An increasing of a_B^*, and therefore a formal transition to the strong confinement regime, while ε_{dot} remained constant, can be achieved by means of a severe decreasing of the effective mass. This would yield a severe increasing of the kinetic energy so that the image charges would eventually be unable to recover the Wigner molecule limit.
[23] The enhancement of Coulomb interactions in systems embedded in low permittivity media is a well-known phenomenon (Refs. 1, 2, and 19). However, in our case, the enhancement is extremely high due to the fact that the electron density is strongly confined in a thin shell, just beyond the QD border, where the dielectric constant is unity.