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Shape effects on the one- and two-electron ground state in ellipsoidal quantum dots

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The ground state of two conduction-band electrons confined in ellipsoidally shaped quantum dots has been calculated within the effective-mass approximation, using both a perturbative scheme and a variational approach. The problem is studied using prolate spheroidal coordinates, which allows us to exactly solve the single-particle problem and therefore to make a suitable ansatz for the two-electron variational wave function. The different contributions arising from the Coulomb repulsion and dielectric effects are calculated and discussed. The dot anisotropy is shown to strongly influence the electron-electron correlation.

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I. INTRODUCTION

The progress in manipulating very small structures (usually referred to as nanostructures) has given the possibility of realizing low-dimensional systems[1–5] and opened new perspectives in device fabrication such as single-electron transistors,[6] memory devices, and lasers.[7] From the technological point of view the study of very small structures has allowed the improvement of device performances (lower heat dissipation, faster response, etc.). On the other hand, the wide interest in studying, both theoretically and experimentally, nanostructures is given from the fact that on reducing the structure dimensions the confinement of holes and electrons shows surprising features which can be understood only in the framework of quantum mechanics. As the particle de Broglie wavelength becomes comparable with the structure dimensions, quantum effects become relevant, giving rise to a discrete spectrum of energy levels like for atoms. This has gained for quantum dots the name of artificial atoms.[1,8–10]

The improvement of both experimental methods of confining electrons and investigation techniques such as capacitance spectroscopy has allowed the study of single-electron features of quantum dots.[11–19] In particular addition spectra (that is, the energy required to add one electron to an N-electron system) have been widely measured and studied. Many theoretical investigations have also been done, in which the quantum dot is simulated with a confinement potential for electrons and holes, assumed to be in the form of a spherical potential well,[20,21] isotropic[22–28] or anisotropic[29] harmonic potential (parabolic confinement), on-site repulsive potential,[30] infinite barrier at the dot boundary,[31] and Gaussian potential.[32] There have been many numerical approaches for studying few- and many-electron properties of these potentials (such as variational calculations, Hartree and Hartree-Fock methods, power series expansions, WKB approach, and several diagonalization techniques). Most of these models use the effective-mass approximation for electrons and holes. However, pseudopotential calculations[33] have shown the need of an atomistic description of small nanocrystals, which is the best way of taking into account interband coupling and the wave function decay outside the dot, both consequences of quantum confinement. Nevertheless, it is important to stress that the effective-mass approximation begins failing as very small dimensions are reached as shown, for example, in Refs. 34 and 35 and that it has been widely used to explain many properties of quantum dot spectra. Moreover, the main problems with the effective-mass approximation arise for exciton spectra,[36] because they involve hole states. In our case we want only to investigate large-dot conduction-band electron states, for which we believe that the simpler effective-mass approximation should reproduce realistic results.

It is worth pointing out two other important aspects about the progress in quantum dots fabrication. First, shape control of semiconductor colloidal nanocrystals has been demonstrated to be possible. Rod-, arrow-, teardrop-, and tetrapod-shaped CdSe nanocrystals have been fabricated,[37,38] using suitable chemical reagents in the so-called *bottom-up* approach and *oriented attachment*. Rodlike quantum dot geometry has been varied from a nearly spherical one to a highly anisotropic one. These very recent developments open the possibility to investigate experimentally the relation between quantum confinement and the actual dot shape and anisotropy. Second, doping of colloidal quantum dots has been realized,[39] using an electron transfer technique commonly employed for organic polymers. In this way conduction-band electron properties (such as infrared spectra) can be investigated.

The theoretical aspects of single- and many-particle properties of anisotropic quantum dots have been studied for circular, elliptic, and triangular vertical quantum dots,[40] ellipsoidally deformed vertical quantum dots,[41] quantum confinement within an ellipsoidally deformed harmonic potential,[29] and ellipsoidal quantum dots.[42,43] In these last two works, the dot anisotropy has been taken into account within a perturbative scheme, as a correction to the spherical quantum dot spectrum, while the valence-band degeneracy has been properly taken into account. On the other hand, in previous works,[44,45] we have shown that if an effective-mass, single-band model is assumed, the single-particle ellipsoidal quantum dot spectrum can be exactly studied, and the effect of the dot shape on the infrared optical properties taken into account for an arbitrary anisotropy. The exact treatment cannot be performed or becomes very demanding if band mixing and degeneracy are considered. We believe that even if ato-

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mistic calculations are the proper way of describing the band structure of confined structures,[46–48] effective-mass calculations can give realistic descriptions of the quantum dot properties, if the dot dimensions are chosen not too small and if care is taken about the boundary conditions.[49,50] Moreover, it must be stressed that our main interest is in bringing out the relation between the one- and two-electron ground-state properties and the dot shape, rather than band mixing and degeneracy effects which have already been studied.[33,36,51]

In Sec. II we present how, with a suitable coordinate change, we can exactly solve the single-electron confinement in an ellipsoidal quantum dot. Because of the dielectric mismatch between the quantum dot and the surrounding medium, dielectric effects must be included in the electronic spectrum calculation.[33,51] Therefore, in Sec. III we show the analytical calculation of the surface polarization charge potential induced by an electron moving inside an ellipsoidal medium. The study of the two-electron ground state is performed both in the strong confinement regime (correlations effects are supposed negligible in this case) and by using the variational method. A suitable trial wave function, able to account for the electron-electron correlation as well as for its dependence on the dot anisotropy, is made, as shown in Sec. IV. It must be pointed out that by using the curvilinear coordinates proper of the ellipsoidal quantum dot, the choice of this function can be done in a more appropriate way. Moreover, Coulomb and dielectric effects, often evaluated as a first-order correction to the confinement energy, can be taken into account even if their contributions become very relevant. In Sec. V we present our results about the one- and two-electron ground states, showing the different contributions arising from the electron confinement (kinetic energy), Coulomb repulsion, and dielectric effects. It is shown how the electron-electron correlation changes with both the dot anisotropy and the dielectric mismatch. Finally, in Sec. VI, we draw some conclusions.

II. SINGLE-PARTICLE ENERGIES

In previous works[44,45] it has been shown that the effective-mass single-electron problem within an ellipsoidal quantum dot can be exactly treated by performing a suitable coordinates transformation. Let us consider an ellipsoid with azimuthal symmetry around the z axis and let us indicate with a and c its semiaxes in the x-y plane and along the z axis, respectively. If (x,y,z) indicate the Cartesian coordinates, we can define a new set of coordinates (ξ,η,φ) (*prolate spheroidal coordinates*) as follows:

$$\begin{aligned} x&=f\sqrt{(\xi^2-1)(1-\eta^2)}\cos\varphi,\\ y&=f\sqrt{(\xi^2-1)(1-\eta^2)}\sin\varphi,\\ z&=f\xi\eta, \end{aligned} \tag{1}$$

where $1\leqslant\xi<+\infty$, $-1\leqslant\eta\leqslant+1$, $0\leqslant\varphi<2\pi$, and f represents the ellipsoid semifocal distance. Using the transformation (1) the ellipsoid boundary can be represented by an equation like $\xi=\bar{\xi}$. It is not difficult to show that the following relations hold:

$$\begin{cases} f\sqrt{\bar{\xi}^2-1}=a\\ f\bar{\xi}=c \end{cases} \Rightarrow \begin{cases} f=c\sqrt{1-\dfrac{1}{\chi^2}}=ce,\\ \bar{\xi}=\dfrac{1}{\sqrt{1-\dfrac{1}{\chi^2}}}=\dfrac{1}{e}, \end{cases} \tag{2}$$

where $\chi=c/a$ is the ellipsoid anisotropy and $e=f/c$ is its eccentricity. It is evident that Eq. (2) is valid only if $\chi>1$, which follows from the fact that the transformation (1) parametrizes the space with ellipsoidal surfaces which have the semiaxis along the z direction greater than the semiaxes in the x-y plane. Writing the Laplacian operator in the new coordinate system it is possible to show that the solution of the Schrödinger equation

$$-\frac{\hbar^2}{2m^*}\vec{\nabla}^2\psi=E\psi \tag{3}$$

(where m^* is the electron effective mass and E its energy) can be factorized. In other words, it can be written as $\psi(\xi,\eta,\varphi)=je(\xi)S(\eta)\exp(im\varphi)$ where the azimuthal symmetry around the z axis has been taken into account and $je(\xi)$ and $S(\eta)$ are, respectively, solutions of the two separated equations:

$$\frac{d}{d\xi}\left[(\xi^2-1)\frac{dje(\xi)}{d\xi}\right]-\left(A-h^2\xi^2+\frac{m^2}{\xi^2-1}\right)je(\xi)=0, \tag{4a}$$

$$\frac{d}{d\eta}\left[(1-\eta^2)\frac{dS(\eta)}{d\eta}\right]+\left(A-h^2\eta^2-\frac{m^2}{1-\eta^2}\right)S(\eta)=0. \tag{4b}$$

In Eqs. (4a) and (4b), A is a separation constant and $h=f\sqrt{2m^*E/\hbar^2}$. These equations are formally equivalent but must be solved in different ranges of the respective variables. Their solution is more difficult than in spherical coordinates because they are coupled by both the eigenvalue h and the separation constant. Some further mathematical details can be found in Refs. 44 and 45. Here it is enough to say that the hard wall boundary condition [that is, $je(\bar{\xi})=0$] (Ref. 52) leads to a wave function in the form

$$\psi_{n,l,m}(\xi,\eta,\varphi)=je_{l,m}(h_{n,l,m},\xi)S_{l,m}(h_{n,l,m},\eta)\exp(im\varphi), \tag{5}$$

where $h_{n,l,m}$ gives the quantum-dot-confined electronic spectrum. It is important to stress that the particle total angular momentum is no longer a motion constant (as happens in the case of the spherical quantum dot) because of the loss of symmetry with respect to an arbitrary rotational axis. Therefore the ellipsoidally shaped quantum dot constants of motion are its Hamiltonian [with eigenvalues $(\hbar^2/2m^*f^2)h_{n,l,m}^2$], the z component of the particle angular momentum (with eigenvalues $m\hbar$), and the parity operator [with eigenvalues $(-1)^l$]. Let us note that $n=1,2,3,\ldots$, $l=0,1,2,\ldots$, and $m=-l,\ldots,0,\ldots,l$.

III. DIELECTRIC EFFECTS

It is known that if an electron is moving in a quantum dot whose dielectric constant is different from that of the surrounding medium, a surface polarization charge appears. The dielectric potential generated by this surface charge acts on the electron itself and must be taken into account to properly describe the electron motion inside the dot.[56–61] By denoting with I the quantum dot region ($1 \leqslant \xi \leqslant \overline{\xi}$ in our case), with II the surrounding medium ($\xi > \overline{\xi}$), and with ε_I and ε_{II} the respective dielectric constants, the classical calculation of the total electrostatic potential at a given point $\vec{r}$ when the electron is at $\vec{r}_0$ can be performed by solving the Poisson equation with the conditions that (i) the dielectric potential be null at large distances, (ii) it be finite for $\vec{r} \neq \vec{r}_0$, (iii) it be continuous on the surface S which separates the medium I from the medium II, and (iv) its normal derivative be discontinuous on S (the ratio between the external normal derivative to the internal one in each point of S being s if $s = \varepsilon_I/\varepsilon_{II}$ is the dielectric mismatch). Because this total electrostatic potential is obtained as the sum of the surface potential $\Phi(\vec{r},\vec{r}_0)$ (that is, the potential due to the polarization charge which appears on S) and the Coulomb potential of a point charge at $\vec{r}_0$ in the bulk medium, we can write

$$\Phi(\vec{r},\vec{r}_0) = G(\vec{r},\vec{r}_0) - G_b(\vec{r},\vec{r}_0), \tag{6}$$

where $G(\vec{r},\vec{r}_0)$ is the Green function of our problem and $G_b(\vec{r},\vec{r}_0)$ the Green function for a point charge moving in the bulk material (infinite medium with dielectric constant ε_I). The expansion of the first one in prolate spheroidal coordinates is[62]

$$\begin{aligned} G_b(\vec{r},\vec{r}_0) &= \frac{q}{4\pi\varepsilon_0\varepsilon_I}\frac{1}{|\vec{r}-\vec{r}_0|} \\ &= \frac{q}{4\pi\varepsilon_0\varepsilon_I}\frac{1}{f}\sum_{l=0}^{+\infty}(2l+1)\sum_{m=0}^{l}\epsilon_m i^m\left[\frac{(l-m)!}{(l+m)!}\right]^2 \\ &\quad\times P_l^m(\eta_0)P_l^m(\eta)P_l^m(\xi_<)Q_l^m(\xi_>) \\ &\quad\times\cos[m(\varphi-\varphi_0)], \end{aligned} \tag{7}$$

where $\epsilon_0 = 1, \epsilon_1 = \epsilon_2 = \cdots = \epsilon_m = \cdots = 2$, $\xi_< = \min\{\xi,\xi_0\}$, $\xi_> = \max\{\xi,\xi_0\}$, and P_l^m and Q_l^m are, respectively, the first- and second-kind associated Legendre functions. By using the expansion (7) and solving the Poisson equation with the conditions given above, Eq. (6) becomes

$$\begin{aligned} \Phi(\vec{r},\vec{r}_0) &= \frac{q}{4\pi\varepsilon_0\varepsilon_I}\frac{s-1}{f}\sum_{l=0}^{+\infty}(2l+1)\sum_{m=0}^{l}\epsilon_m i^m\left[\frac{(l-m)!}{(l+m)!}\right]^2 \\ &\quad\times\frac{Q_l^m(\overline{\xi})Q_l^{m\prime}(\overline{\xi})}{P_l^m(\overline{\xi})Q_l^{m\prime}(\overline{\xi}) - sQ_l^m(\overline{\xi})P_l^{m\prime}(\overline{\xi})} \\ &\quad\times P_l^m(\xi_0)P_l^m(\eta_0)P_l^m(\xi)P_l^m(\eta)\cos[m(\varphi-\varphi_0)], \end{aligned} \tag{8}$$

where $q = -e$ is the electron charge.

In the calculations we are going to show we have assumed that ε_I has been assumed as the bulk dielectric constant. This could give incorrect results for the dielectric contributions. In fact, many works[9,63–66] have demonstrated that on reducing the dot dimensions the dielectric constant gets lower values. Nevertheless, all these calculations show that for dot dimensions $R > 5$–6 nm the difference between the confined and the bulk dielectric constants is negligible. Therefore, because we are going to consider large dots, no correction is expected to come from a size-dependent dielectric constant.

IV. TWO-ELECTRON GROUND STATE

Let us consider two conduction-band electrons moving inside the ellipsoidal quantum dot. The ground state for the noninteracting system is simply given by the product of two single-particle ground-state wave functions:

$$\begin{aligned} \Psi_0(\vec{r}_1,\vec{r}_2) &= je_{0,0}(h_{1,0,0},\xi_1)S_{0,0}(h_{1,0,0},\eta_1) \\ &\quad\times je_{0,0}(h_{1,0,0},\xi_2)S_{0,0}(h_{2,0,0},\eta_2). \end{aligned} \tag{9}$$

The two-electron Hamiltonian actually contains interaction terms as follows:

$$\begin{aligned} H &= \frac{p_1^2}{2m^*} + \frac{p_2^2}{2m^*} + \frac{e^2}{4\pi\varepsilon_0\varepsilon_I}\frac{1}{|\vec{r}_1-\vec{r}_2|} \\ &\quad - \tfrac{1}{2}e\Phi_s(\vec{r}_1) - \tfrac{1}{2}e\Phi_s(\vec{r}_2) - e\Phi_p(\vec{r}_1,\vec{r}_2), \end{aligned} \tag{10}$$

where $\Phi_s(\vec{r}) = \Phi(\vec{r},\vec{r})$ and $\Phi_p(\vec{r}_1,\vec{r}_2) = \Phi(\vec{r}_1,\vec{r}_2)$. In Eq. (10) it has been considered that the classical energy needed to realize the electrostatic configuration with both electrons inside the dot is given by the sum of their Coulomb repulsion, the interaction of the two electrons with their respective surface charge (being a self-interaction effect, a factor 1/2 arises for these contributions) and the interaction of one electron with the surface charge generated by the second one. These last two will be referred to in the following, respectively, as self-interaction energy and electron-electron surface interaction. It must be pointed out that, if $\varepsilon_I > \varepsilon_{II}$ (that is, $s > 1$), all the electrostatic terms raise the system total energy. Moreover, the Coulomb repulsion and the electron-electron interaction via the surface polarization charge tend to push the electrons far from each other while the self-interaction polarization terms have the opposite effect, pushing both electrons toward the quantum dot center.

In the strong confinement regime the electrostatic terms can be treated as a first-order correction to the kinetic energy because the main contribution to the ground-state energy arises from quantum confinement. Nevertheless, the more the dot dimensions increase, the more both the polarization terms and the Coulomb interaction correlate the two electrons. This means that the wave function (9) realistically describes the two-electron system only in the strong confinement regime, but it is not suitable for studying large dots. Therefore we have investigated the effect of both the dot dimensions and its anisotropy by using the variational method. The trial wave function has been chosen as follows:

$$\Psi(\vec{r}_1,\vec{r}_2)=\Psi_0(\vec{r}_1,\vec{r}_2)\Psi_{\mathrm{corr}}(\vec{r}_1-\vec{r}_2), \tag{11}$$

where Ψ_0 is given in Eq. (9) and the correlated motion of the electrons is described via the factor

$$\Psi_{\mathrm{corr}}(\vec{r}_1-\vec{r}_2)=1-\alpha[1+u(\vec{r}_1-\vec{r}_2)]\exp[-u(\vec{r}_1-\vec{r}_2)], \tag{12a}$$

$$u(\vec{r}_1-\vec{r}_2)=\sqrt{\beta[(x_1-x_2)^2+(y_1-y_2)^2]+\gamma(z_1-z_2)^2}. \tag{12b}$$

The function (11) reflects the system ground-state properties. In fact (i) it depends only on $\varphi_1-\varphi_2$ (that is, it is invariant for rotations of both the electrons of the same angle around the z axis), (ii) it is invariant for reflection of both the electrons [that is, with respect to the transformation $(\vec{r}_1,\vec{r}_2)\rightarrow(-\vec{r}_1,-\vec{r}_2)$], (iii) it is symmetric with respect to the exchange of the two electrons (corresponding to the singlet spin state), (iv) it is null if any of the two electrons is on the ellipsoid boundary, and (v) it is continuous with all its first and second partial derivatives. α, β, and γ are three variational parameters ($0\leqslant\alpha\leqslant1$, $\beta,\gamma\geqslant0$), whose value must be determined by requiring that the energy functional

$$E[\alpha,\beta,\gamma]=\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{13}$$

be minimum. The particular choice of the correlated part of the wave function (11) can be justified by considering that (i) if $\alpha=0$, it becomes the uncorrelated wave function, (ii) if $\alpha\neq0$, it describes the correlated system for which the probability of finding the two electrons at the same position is $1-\alpha$ times smaller than that of finding them far from each other (this probability being null if $\alpha=1$), (iii) if $\beta\neq\gamma$, it can account for the quantum dot anisotropy and therefore for the dependence of the electron-electron correlation on it, and (iv) if the distance between the two electrons is very large, the wave function becomes the uncorrelated one.

V. RESULTS

In this section we want to discuss the main results obtained by using the theoretical background presented in the previous sections.

In the single-particle picture, the electron energy $E^{(1)}$ is the sum of two contributions, the confinement (kinetic) energy K and the self-interaction energy E_s ($E^{(1)}=K+E_s$). They can be written, respectively, as

$$K=\frac{\hbar^2}{2m^*c^2}\kappa(\chi), \tag{14a}$$

$$E_s=\frac{e^2}{4\pi\varepsilon_0\varepsilon_I c}\frac{e_s(\chi)}{2}, \tag{14b}$$

where κ and e_s are two adimensional functions.

TABLE I. The coefficients of Eq. (16) for some values of s.

s	a_0	a_1	a_2	a_3
0.1	−0.473 56	−0.818 60	−0.084 09	+0.009 35
0.5	−0.248 03	−0.434 31	−0.031 75	+0.003 43
3.0	+0.786 34	+1.650 47	−0.048 28	+0.004 94
10.0	+2.758 32	+7.757 76	−0.879 92	+0.081 61
15.0	+2.448 80	+15.131 73	−3.231 84	+0.421 42

Solving with a midpoint shooting method, Eqs. (4a) and (4b), we have calculated the exact[67] single-particle confinement energy for the ellipsoidal quantum dot. A more detailed discussion can be found in Refs. 44 and 45. Here we show only our results concerning the ground-state energy. For the electron kinetic energy we get

$$\kappa(\chi)=2.817\,18+6.478\,45(\chi+0.043\,72)^{1.960\,84}, \tag{15}$$

with $1\leqslant\chi\leqslant5$. Moreover, the self-interaction dielectric shifts have been calculated as a first-order correction (that is, by evaluating the self-interaction mean value on the ground state), for some values of the dielectric mismatch s. A polynomial interpolation of the obtained numerical results has been performed as follows:

$$e_s(\chi)=a_0+a_1\chi+a_2\chi^2+a_3\chi^3, \tag{16}$$

with $1\leqslant\chi\leqslant5$. The coefficients a_i are given in Table I for the considered values of s. All the interpolation formulas we are showing reproduce our numerical data with an error at most of 0.5%. For $\chi\rightarrow1$ and $s=3$ exactly the same result as in Ref. 58 for the Si spherical quantum dot embedded in $\mathrm{SiO_2}$ is obtained. From these results, the dot energy spectrum dependence on χ clearly comes out, showing that if a nonspherical quantum dot is considered, volume confinement can be well described only if related to the actual dot geometry.

Starting from the single-particle picture presented above, the two-electron ground state has been investigated, looking in particular for the dependence of the electron-electron correlation on the dot geometry. The ground-state energy has been first calculated in the strong confinement regime,[68] that is, taking the Coulomb interaction, self-interaction potential, and surface interaction mean values on the uncorrelated ground-state wave function (9). We get

$$E_0^{(2)}=2K+E_c+2E_s+E_p, \tag{17}$$

where

$$E_c=\frac{e^2}{4\pi\varepsilon_0\varepsilon_I c}e_c(\chi), \tag{18}$$

$$E_p=\frac{e^2}{4\pi\varepsilon_0\varepsilon_I c}e_p(\chi). \tag{19}$$

As for the self-energy correction, a polynomial interpolation has been calculated for the surface electron-electron interaction:

$$e_p(\chi)=b_0+b_1\chi+b_2\chi^2+b_3\chi^3, \tag{20}$$

TABLE II. The coefficients of Eq. (20) for some values of s.

s	b_0	b_1	b_2	b_3
0.1	$-0.272\,46$	$-0.633\,40$	$+0.005\,14$	$+0.001\,19$
0.5	$-0.155\,23$	$-0.352\,55$	$+0.008\,01$	$-1.061\,26\times10^{-5}$
3.0	$+0.601\,12$	$+1.528\,15$	$-0.140\,44$	$+0.012\,35$
10.0	$+2.394\,14$	$+7.621\,11$	$-1.105\,27$	$+0.098\,66$
15.0	$+3.553\,29$	$+12.201\,02$	$-1.909\,88$	$+0.167\,19$

with $1\leqslant\chi\leqslant5$. The coefficients b_i are given in Table II. As $\chi\rightarrow1$ the previous formulas give $e_p=s-1$, as it is for the spherical quantum dot.[58] Finally, the Coulomb energy has been calculated, giving

$$e_c(\chi)=1.774\,04+1.117\,55|\chi-1.009\,62|^{0.854\,86}. \quad (21)$$

Even in this case the spherical quantum dot limit[56] is obtained as $\chi\rightarrow1$.

The strong confinement regime description presented above treats the electrostatic contributions to the two-electron ground state as ‘‘small’’ corrections to their kinetic energy. However, it is known[8] that as the dot dimensions increase, this calculation scheme cannot realistically describe the system, because the electrostatic terms become comparable with the electron kinetic energy. Therefore, as explained in Sec. IV, we have performed a variational calculation choosing the trial wave function as shown in Eq. (11) to take into account correlation effects for geometries which cannot be described within the strong confinement picture. The energy functional (13) has been minimized for different values of χ with respect to the three parameters α,β,γ (we will indicate with $\alpha_{\text{min}}, \beta_{\text{min}}, \gamma_{\text{min}}$ their respective values at the minimum point). We are going to show first the results obtained without taking into account the dielectric effects, so that a better understanding of the role played by the Coulomb repulsion can be reached. We will discuss the implications of dielectric effects later. In Fig. 1 we show the result of this calculation performed for CdSe ellipsoidal quantum dots ($m^*/m_e=0.13$, $\varepsilon_I=10.0$), with fixed $a=12$ nm, as a function of $c=a\chi$. The solid line represents the energy functional calculated at its minimum point (that is, $E^{(2)}\equiv E[\alpha_{\text{min}}, \beta_{\text{min}}, \gamma_{\text{min}}]$), the dashed one the same energy but calculated by setting $\beta=0$ (that is, $E[\alpha_{\text{min}}, 0, \gamma_{\text{min}}]$, which takes into account only the electron-electron correlation along the z direction), and the dotted one the ground-state energy in the strong confinement regime [which is given by Eq. (17) and corresponds to set $\alpha=0$ in Eq. (13)]. It comes out that on increasing χ or, equivalently, c, the ground-state energy (solid line) becomes coincident with the energy calculated taking into account only the electron-electron correlation along the z direction (dashed line). This means that for $\chi\gg1$ the electron-electron correlation in the x-y plane is negligible, as expected. In fact, on increasing c with fixed a, we get longer and longer quantum rods. The total ground-state energy arises from the contribution of both the confinement energy, which is minimum if both electrons are in the ellipsoid center, and their Coulomb repulsion, which pushes the electrons far from each other, toward the ellipsoid boundary. The minimum energy configuration is reached with the two electrons placed along the z axis in such a way that they stay as much as possible far from each other and from the ellipsoid boundary. On the contrary, as $\chi\rightarrow1$ (spherical quantum dot limit) we obtain that $E[\alpha_{\text{min}}, 0, \gamma_{\text{min}}]$ becomes coincident with the uncorrelated ground-state energy. In other words, if only the electron-electron correlation along a particular direction (the z axis in our case) is taken into account, the same result as using the strong confinement regime approach is obtained. This reflects the spherical symmetry of the problem, which cannot give rise to a ground-state configuration in which the two electrons are placed along some privileged direction. It is worth noting that a variational approach for the two-electron ground state in CdS spherical quantum dots has been done, using a different trial wave function, in Ref. 56. We have calculated these energies using our variational approach and obtained exactly the same results. A quite important check for our calculation is that we get, in this case, $\beta_{\text{min}}/\gamma_{\text{min}}\simeq1$ within at most 1%.

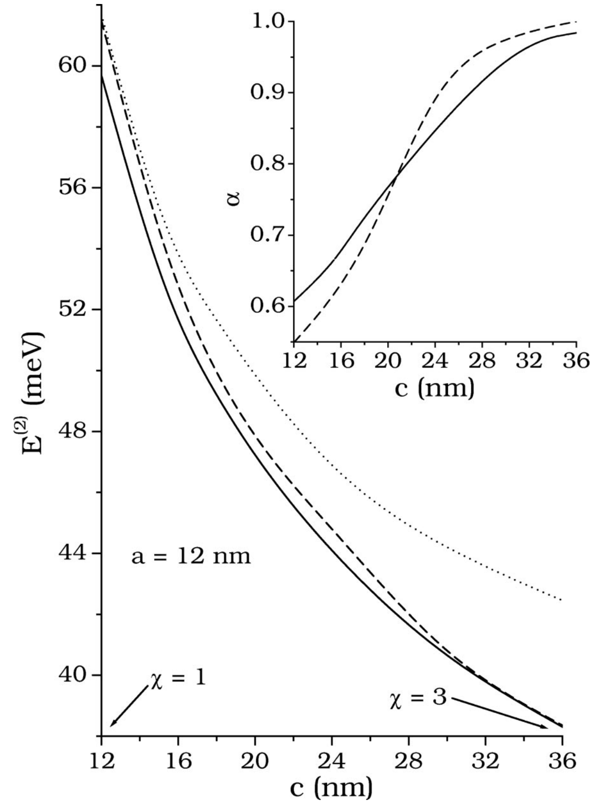

FIG. 1. The ground-state energy calculated using the variational method is shown (solid line) for CdSe quantum dots ($m^*/m_e=0.13$, $\varepsilon_I=10.0$) with fixed $a=12$ nm as a function of c. Dielectric effects have not been included. The energies calculated taking into account only the electron-electron correlation along the z axis ($\beta=0$, dashed line) and for uncorrelated electrons ($\alpha=0$, dotted line) are shown for comparison. The inset shows the value of α at the minimum point as a function of c calculated without ($s=1$, solid line) and with ($s=10$, dashed line) dielectric effects.

The inset of Fig. 1 shows the values of α calculated with fixed $a=12$ nm as a function of c, without ($s=1$, solid line) and with ($s=10$, dashed line) dielectric effects. On increasing c we get $\alpha\rightarrow1$, which corresponds to a null probability

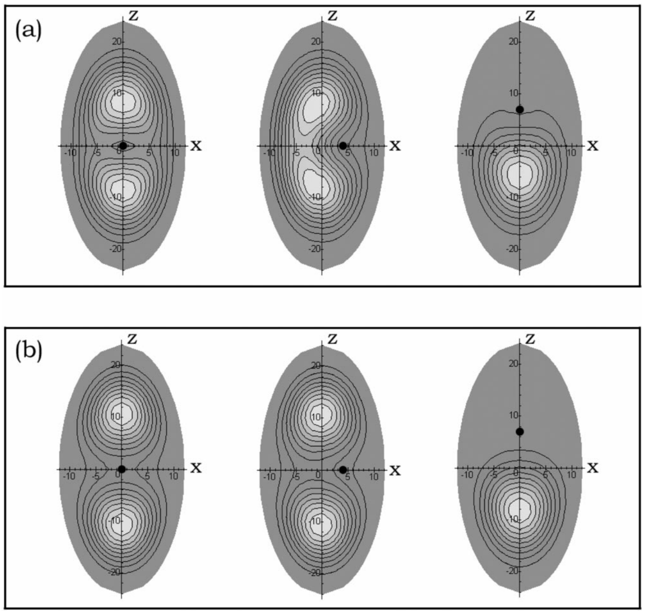

FIG. 2. Projection of the pair correlation function in the x-z plane for a CdSe ellipsoidal quantum dot with $a=12$ nm and $c=24$ nm. The results obtained both without (a) and with (b) dielectric effects are shown. The position of one electron is taken fixed and is indicated with a large dot. The white regions correspond to a maximum of this function. The effect of the dielectric mismatch on the spatial configuration of the two electrons clearly comes out (see text).

of finding the electrons at the same point. This further brings out the strong relation between the electron-electron correlation and the dot geometry.

The projection of the pair correlation function [that is, the probability of finding one electron at $\vec{r}_1$ if the second one is at $\vec{r}_2$ given by $|\Psi(\vec{r}_1,\vec{r}_2)|^2$] in the x-z plane is plotted for a CdSe ellipsoidal quantum dot with $a=12$ nm and $c=24$ nm in Fig. 2. The results obtained both without and with dielectric effects (these last ones will be discussed later) are shown, respectively, in parts (a) and (b) of the figure. The pair correlation function is plotted for different positions of the fixed electron (indicated with a large dot), to better understand the ground-state spatial configuration. The white regions correspond to a maximum of the function. As already stressed previously, the configuration with maximum probability is with the two electrons placed along the ellipsoid major axis.

The electron-electron interaction affects also the correlation energy, defined as $E_{\mathrm{corr}}=E^{(2)}-E_0^{(2)}$ (that is, the difference between the solid line and the dotted one in Fig. 1). In Fig. 3(a) the ratio $E_{\mathrm{corr}}/E^{(2)}$ (that is, the relative error done if the uncorrelated ground-state energy is assumed) for three values of a as a function of χ is shown. It is an increasing function of both a and c. All the obtained results clearly show that for long quantum rods the system description within the strong confinement regime becomes misleading.

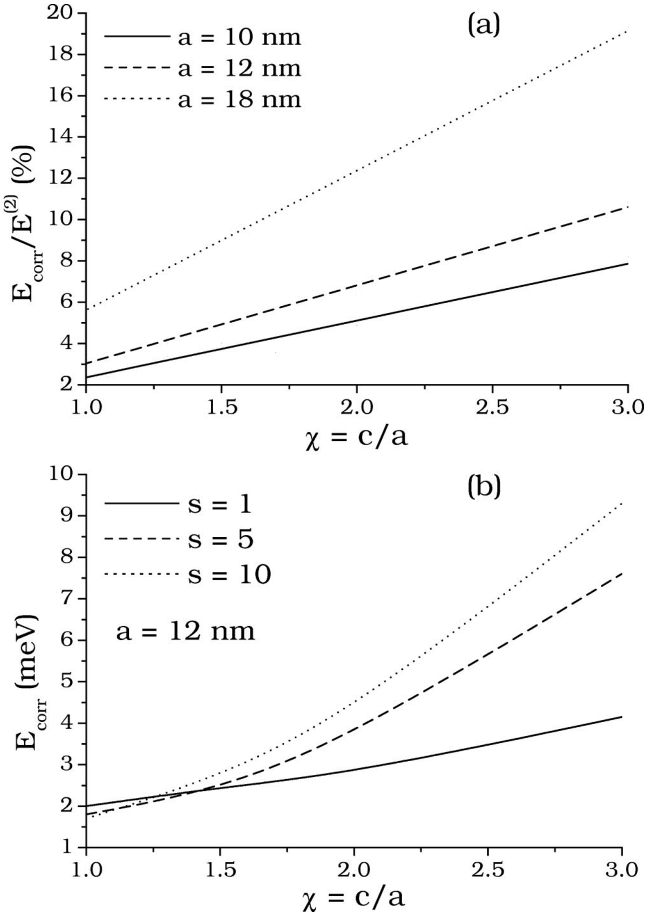

FIG. 3. (a) The ratio $E_{\mathrm{corr}}/E^{(2)}$ (relative error done if the uncorrelated ground-state energy is assumed) for three values of a as a function of χ is shown. Dielectric effects have not been included. The effect of the Coulomb electron-electron correlation becomes relevant on increasing a and/or c. (b) The total correlation energy calculated for $a=12$ nm as a function of χ is shown for three values of the dielectric mismatch s. The contribution of the surface electron-electron interaction clearly comes out on increasing χ.

The same variational technique has been used including dielectric effects for studying how they can affect the electron-electron correlation. The numerical results obtained for the two-electron ground state of CdSe ellipsoidal nanocrystals, with fixed $a=12$ nm and $s=10$ as a function of c, are shown in Table III. For each value of c, the kinetic energy $2K$, the Coulomb repulsion E_c, the self-polarization $2E_s$, and the surface electron-electron interaction E_p are calculated both with the described variational technique and in the strong confinement regime ($\alpha=0$). It comes out that the more the two electrons have the possibility to be far from each other (on increasing c), the more the correlation energy associated with their Coulomb repulsion increases. Moreover, there is a quite relevant contribution to this correlation energy arising from the surface electron-electron interaction for high dot anisotropies. This can be explained by considering that this interaction pushes the electrons far from each other, even if it is less strong than the direct Coulomb repulsion. Therefore this contribution to the correlation energy becomes more significant on increasing c, because in this case the electron quantum confinement decreases and their surface interaction is able to push them far from each other, toward the ellipsoid boundary. This is also supported from the fact that, on the contrary, on increasing c the self-

TABLE III. Two-electron ground-state kinetic $(2K)$, Coulomb (E_c), self-polarization $(2E_s)$, and surface interaction (E_p) energies calculated for CdSe ellipsoidal quantum dots with fixed $a=12$ nm and $s=10$ as a function of c. Both the strong confinement regime and the variational results are shown. It comes out that on increasing the dot major axis a quite relevant contribution to the correlation energy arises from the surface interaction energy.

	$c=12.0012$ nm		$c=18$ nm		$c=24$ nm		$c=36$ nm	
	$\alpha=\alpha_{\min}$	$\alpha=0$	$\alpha=\alpha_{\min}$	$\alpha=0$	$\alpha=\alpha_{\min}$	$\alpha=0$	$\alpha=\alpha_{\min}$	$\alpha=0$
$2K$ (meV)	41.34	40.17	34.12	32.55	33.11	29.65	32.24	27.27
E_c (meV)	18.34	21.53	14.97	19.10	11.02	17.21	6.478	15.18
$2E_s$ (meV)	117.4	116.5	102.8	101.7	94.49	92.35	84.87	81.30
E_p (meV)	107.4	108.0	92.42	93.57	80.22	83.90	62.72	71.90

polarization energy calculated on the uncorrelated wave function becomes smaller and smaller than the one calculated at the minimum point, showing that the electrons are farther and farther from the ellipsoid center. This result is confirmed by comparing the values of $\alpha_{\min}$ in the inset of Fig. 1 calculated without $(s=1$, solid line) and with $(s=10$, dashed line) dielectric effects. It is clear that by including dielectric effects, for nearly spherical quantum dots smaller values are obtained (because the self-polarization potential pushes the electrons toward the ellipsoid center), while on increasing c greater values are obtained, because of the additional contribution to the electron-electron correlation energy due to the surface interaction. The same comparison can be done on the pair correlation function, as in Fig. 2. It comes out that the inclusion of dielectric effects in the minimization of the functional (13) leads to a ground-state wave function where the distance between the two electrons has increased with respect to the case $s=1$. A final check of these results is given in Fig. 3(b), where the correlation energy obtained by taking into account only the Coulomb repulsion $(s=1$, solid line) and the one calculated by including dielectric effects $(s=5$, dashed line, and $s=10$, dotted line) are shown. Only for nearly spherical quantum dots is the correlation energy smaller if dielectric effects are not included.

Finally, in Fig. 4 the energy difference Δ between the one- and two-electron ground-state energies is shown, for CdSe nanocrystals with $a=12$ nm, as a function of χ and for several values of the dielectric mismatch s. It is a decreasing function of χ. This dependence becomes stronger and stronger as $\varepsilon_{II}\rightarrow 1$ $(s=10)$. If we plot Δ as a function of ε_{II}, we get that, in the same limit, a strong increase of Δ is observed, in accordance with the results shown in Ref. 51.

VI. CONCLUSIONS

In this paper we have studied shape effects on the one- and two-electron ground state in ellipsoidal quantum dots. Using a suitable coordinate system which allows us to exactly solve the single-particle effective-mass Hamiltonian, we have calculated the electron energies both in the strong confinement regime and with a variational calculation. The variational wave function has been chosen in such a way to take into account both the electron-electron correlation due to the Coulomb potential and dielectric effects and the anisotropy effects naturally induced by the ellipsoidal boundary. We have shown that if geometry deviations with respect to the spherical quantum dot are considered, quantum confinement effects must be related to the dot shape. The electron-electron correlation is a function of the dot anisotropy. In particular, starting from the spherical quantum dot and considering longer and longer quantum rods, the two electrons are found to be placed along the ellipsoid major axis, with a probability of finding them in the same place which becomes smaller and smaller. It has been shown that for sufficiently anisotropic quantum dots, it is enough to take into account only the correlation along the ellipsoid major axis, the one along the two minor axes becoming negligible.

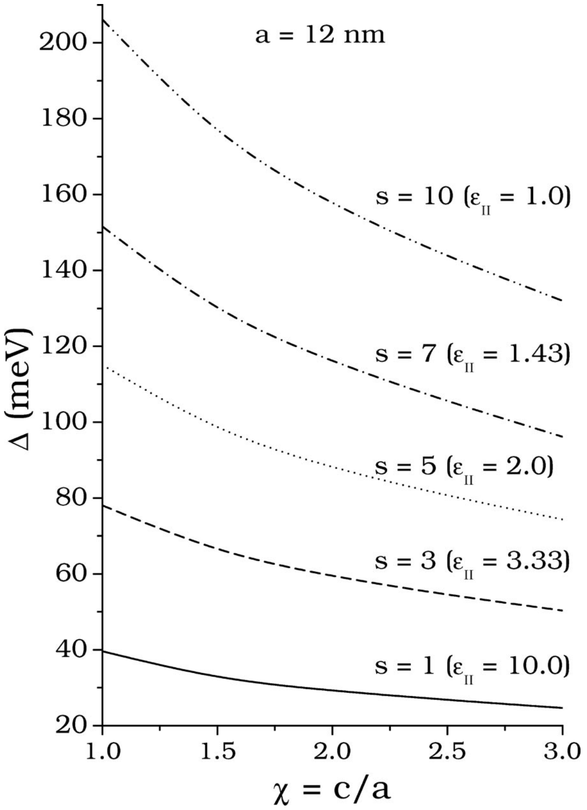

FIG. 4. The difference Δ between the energies of the one- and two-electron ground states is shown for several values of s. It is a decreasing function of χ. This shape dependence becomes very strong as $\varepsilon_{II}\rightarrow 1$.

Dielectric effects have been studied as a function of both the dielectric mismatch between the dot and the surrounding medium and the dot anisotropy. It comes out that on increasing the dot anisotropy significant contributions to the correlation energy are given by the electron-electron surface interaction. The distance between the two electrons increases with respect to the case $s=1$. This shows that neither dielectric effects can be neglected in the one- and two-electron ground-state energy calculation, nor can they be treated perturbatively (losing in this way all information about their effect on the electron-electron correlation). The energy difference Δ between the one- and two-electron ground-state energies has been calculated, showing that the dependence on the dot anisotropy becomes stronger as the external dielectric constant approaches 1.

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[52] About the validity of this infinite barrier model, let us note that it has been shown, for example, for CdSe nanocrystals (Refs. 53 and 54), that in the framework of the Kane model (Ref. 55) it is possible to analytically take into account the finite barrier height at the dot boundary and the nonparabolicity of the conduction band (valence- and conduction-band mixing). It comes out that for either quantum wells deep enough or large quantum dots the electron envelop wave function is null at the boundary, as in the parabolic single-band model we are using. Moreover, a self-consistent equation is derived, which gives the corrections to the confined electrons energy levels with respect to the simple effective-mass model, due to the conduction-band nonparabolicity. These corrections are size dependent. If we use this equation for a spherical quantum dot with radius $R>5$ nm, we find that the single-electron ground-state energy varies at most a few meV. Because here we want to study two-electron correlations effects which become significant only for large dots, we can conclude that the single-band, effective-mass model should not fail for our purposes.

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[67] We must point out that the exact formal solution can be written as a series expansion (Ref. 44), whose coefficients are solutions of suitable recurrence equations. These equations cannot be solved analytically. This means that solutions can be obtained only by using numerical methods, but their accuracy can be controlled. In our case convergence up to 0.01% on the eigenvalues has been achieved.

[68] The strong confinement regime is defined by the condition that the typical dot dimensions be much less than the electron Bohr radius $a_e=4\pi\varepsilon_0\varepsilon_I\hbar^2/m^*e^2$ (Ref. 8). For example, for CdSe we have $a_e\simeq 4$ nm and we must require that $a,c\ll a_e$.