Interplay between quantum confinement and electron-electron interaction in deformed silicon quantum wires

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In this paper we investigate quantum confinement and electron-electron correlation in silicon deformed quantum wires. Starting from the single-particle picture, which shows the possibility of localizing one electron inside the wire deformation, we build a variational *ansatz* for the two-electron ground state. We compare the localizing effect induced by the deformation with the Coulomb repulsion, pointing out the existence of a two-electron confined ground state, depending on the wire geometry. On varying the geometrical parameters characterizing the wire deformation, it is possible to switch from structures dominated by the localization to structures in which the increase of the available volume makes the Coulomb contribution very relevant, as for ordinary quantum dots. The effects induced by the dielectric mismatch between the wire and the surrounding medium are included and discussed.

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I. INTRODUCTION

One of the most attractive aspects of quantum confined systems has been the possibility of obtaining light emission from silicon. Significant advances made since the discovery of porous silicon opened the way toward the use of this material for optoelectronic devices.[1,2]

Among the many, intriguing physical properties are those related to charge transport and sensing properties of porous-silicon-based devices. For example, it has been demonstrated that a large enhancement of the conductivity can be reached via an acceptorlike doping obtained through the adsorption of NO_2 molecules on the porous silicon surface.[3–5]

In the past, many models have been proposed to explain the strong visible luminescence at room temperature,[1] but it is now widely accepted that it is related to quantum confinement effects. A significant role in determining the features of the electronic states can be played by the nanostructure shape. It has been shown[6–8] that the presence of deformations causes the appearance of discrete levels in the miniband structure of a quantum wire. Both the photoluminescence and the Stokes shift between the emission and absorption spectra can be explained in terms of transitions between such states. Moreover, the presence of discrete, localized states can account for porous silicon sensing properties as well.[7]

The geometry-induced electron localization leads to the possibility that such confinement effect can interplay with electron-electron repulsion, giving rise to two-electron confined states. The aim of this paper is the study of the ground state of a two-electron system, in which quantum confinement arises within a deformed quantum wire. We show, under suitable conditions for the wire geometry, the existence of two-electron states localized in correspondence with the deformations. The electron-electron correlation degree is studied as a function of the deformation geometry, showing how it is possible to modify the two-electron ground state, from weakly confined (Coulomb-repulsion dominated) to strongly localized (geometry-induced localization). This can give rise to different charging states for the deformation, leading to the possibility of observing Coulomb-blockade-like effects. We shall not discuss this aspect, because the analysis presented here focuses on the electronic ground-state configuration rather than on transport properties. Nevertheless, it is worth mentioning that the evidence for Coulomb-blockade-related phenomena has been addressed by several authors (see, for example, Refs. 9 and 10).

All the calculations are done in the framework of the effective-mass approximation, using a variational approach that properly takes into account correlation effects. This is shown in Secs. II and III, where the single- and two-particle systems are considered, respectively.

In Sec. IV a detailed discussion of all the electrostatic contributions to the two-electron Hamiltonian is given. We include the dielectric effects arising as a consequence of the dielectric mismatch between the wire and the surrounding medium. The nature of all these contributions is accounted for by a suitable choice of the trial wave function.

Numerical results are shown in Sec. V. The physical aspects involved in the electron localization within the deformation are discussed. In particular we focus on the fundamental difference between quantum confinement and localization, typical of such wires, and discuss the implications on the electron-electron correlation. The results obtained by both neglecting and taking into account the dielectric effects are given (Secs. V A and V B, respectively), to better bringing out the role played by the dielectric mismatch. A semiquantitative evaluation of its influence on the binding of the two-electron system and on the electronic correlation is discussed. Finally, in Sec. VI we draw some conclusions.

II. SINGLE-PARTICLE STATES IN DEFORMED QUANTUM WIRES

In this section we discuss electron localisation in deformed quantum wires. We recall, for completeness, the main points concerning the single-particle ground state. An extended and detailed discussion can be found in Refs. 6–8.

Let us consider a bulged cylindrical quantum wire with its axis along the z direction. Due to the symmetry of the prob-

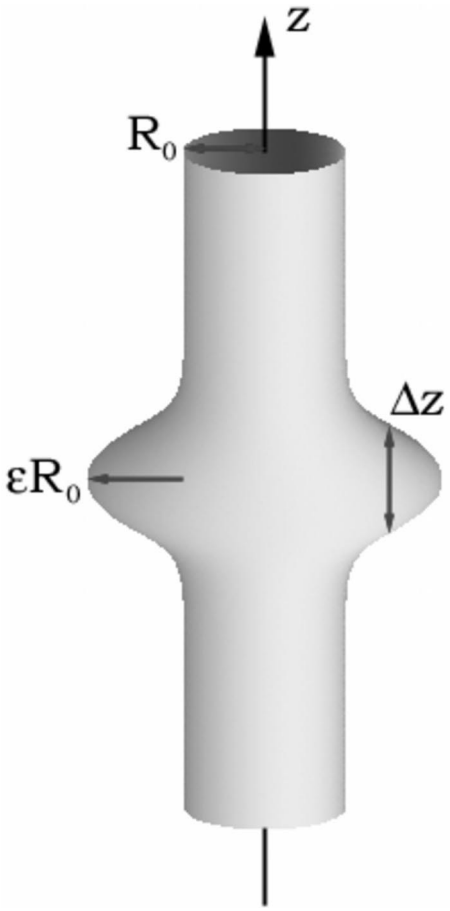

FIG. 1. A bulged quantum wire. R_0 and εR_0 are, respectively, the radius of the undeformed part of the cylinder and the bulge depth (ε positive), while Δz represents the width of the bulge.

lem, in the following we will consider a cylindrical coordinate system (ρ,z,φ) (ρ being the distance from the wire axis, z the position along the axis, and φ the azimuthal angle). The wire bulge can be modeled with a z-dependent radius, which can be chosen as[8]

$$R(z)=R_0\left[1+\varepsilon\exp\left(-\frac{2z^2}{\Delta z^2}\right)\right], \tag{1}$$

where R_0 and εR_0 are, respectively, the radius of the undeformed part of the cylinder and the bulge depth (ε positive), while Δz represents the width of the bulge. A drawing of a bulged wire is shown, together with its geometrical parameters, in Fig. 1.

The motion of an electron within such a structure subject to the external potential U_s can be studied by solving the single-particle Schrödinger equation $-(\hbar^2/2m_{\text{eff}})\nabla^2\psi+U_s(\mathbf{r})\psi(\mathbf{r})=E_s\psi(\mathbf{r})$ assuming the hard-wall boundary condition [namely, $\psi(\mathbf{r})=0$ on the wire boundary]. Here m_{eff} is the particle effective mass. Due to the presence of the deformation, an exact solution cannot be attempted. We follow a functional variational approach, with a suitable choice of the trial wave function. Let us consider the single-particle energy functional

$$\epsilon_s[\psi]=\frac{\int_V d\mathbf{r}[|\nabla_{\mathbf{r}}\psi(\mathbf{r})|^2+u_s(\mathbf{r})|\psi(\mathbf{r})|^2]}{\int_V d\mathbf{r}|\psi(\mathbf{r})|^2}, \tag{2}$$

where $u_s=2m_{\text{eff}}U_s/\hbar^2$ and V is the region inside the wire. It is straightforward to show that the condition that the first functional variation $\delta\epsilon_s$ with respect to ψ is null is equivalent to requiring ψ satisfy both the single-particle Schrödinger equation shown above and the hard-wall boundary condition. Therefore, the problem is reduced to finding a suitable class of trial wave functions and minimizing the functional (2) over the subspace generated by them. This will lead to an upper bound to the ''true'' ground-state energy. We choose

$$\psi(\mathbf{r})=\frac{1}{R(z)}J_0\left(\chi_{0,1}\frac{\rho}{R(z)}\right)F(z), \tag{3}$$

where J_0 is the zero-order Bessel function, $\chi_{0,1}$ its first zero, and $F(z)$ an unknown function of z. Such a choice is motivated by the fact that as the wire profile reduces to the straight wire $[R(z)\rightarrow R_0]$, the corresponding exact ground-state wave function has to be retrieved [in this case $F(z)=1$] as well as that it is expected that the deformation will modify the motion along the z direction. By substituting the wave function (3) into Eq. (2) it is easy to show that the function $F(z)$, which makes it stationary, satisfies a one-dimensional Schrödinger equation that contains the potential u_s (assumed to be dependent only on z for simplicity) and an effective, single-particle potential given (in units of $\hbar^2/2m_{\text{eff}}$) by

$$V_{\text{eff}}(z)=\frac{1}{R^2(z)}\left[\chi_{0,1}^2+\frac{(1+\chi_{0,1}^2)}{3}R'^2(z)\right], \tag{4}$$

which depends on $R(z)$ and its first derivative $R'(z)$, that is, on how the cylinder is deformed. The effect of such a potential on the single-particle motion has been discussed in Ref. 8. It acts as a quantum well in the z direction, which causes electronic localization in the bulge volume. Each localized state corresponds to a new energy level within the miniband gap, thus modifying significantly the electronic spectrum.

The wave function (3) has been shown to be quite a good approximation if $\varepsilon<1$ and $R_0/\Delta z<1$, which is always true for typical geometries involved in porous silicon structures.[6–8]

Finally, it is worth mentioning that the effective one-dimensional Schrödinger equation can be numerically solved, giving the ground-state energy and wave function. Nevertheless, it is useful to find an analytical function that well fits to $F(z)$. It has been shown that

$$f(\alpha,z)=(1+\alpha|z|)e^{-\alpha|z|}, \tag{5}$$

where α is a positive parameter (depending on the geometry), gives quite a good approximation to $F(z)$.

III. THE TWO-ELECTRON GROUND STATE IN DEFORMED QUANTUM WIRES

The effective-mass Schrödinger equation for two interacting electrons confined within a region of volume V is

$$-\frac{\hbar^2}{2m_{\rm eff}}\nabla^2_{\mathbf{r}_1}\Psi(\mathbf{r}_1,\mathbf{r}_2)-\frac{\hbar^2}{2m_{\rm eff}}\nabla^2_{\mathbf{r}_2}\Psi(\mathbf{r}_1,\mathbf{r}_2)+U(\mathbf{r}_1,\mathbf{r}_2)\Psi(\mathbf{r}_1,\mathbf{r}_2)=E\Psi(\mathbf{r}_1,\mathbf{r}_2), \tag{6}$$

where it has been assumed that no external, single-particle potential is present. $U(\mathbf{r}_1,\mathbf{r}_2)$ is the interaction potential, which will be discussed later.

The same functional variational approach depicted in the preceding section can be used for studying the ground state of such a system with hard-wall boundary condition [$\Psi(\mathbf{r}_1,\mathbf{r}_2)=0$ if $\mathbf{r}_1$ or $\mathbf{r}_2$ are on the volume boundary]. First, we define the two-particle energy functional

$$\epsilon[\Psi]=\frac{\int_V d\mathbf{r}_1\int_V d\mathbf{r}_2[|\nabla_{\mathbf{r}_1}\Psi(\mathbf{r}_1,\mathbf{r}_2)|^2+|\nabla_{\mathbf{r}_2}\Psi(\mathbf{r}_1,\mathbf{r}_2)|^2+u(\mathbf{r}_1,\mathbf{r}_2)|\Psi(\mathbf{r}_1,\mathbf{r}_2)|^2]}{\int_V d\mathbf{r}_1\int_V d\mathbf{r}_2|\Psi(\mathbf{r}_1,\mathbf{r}_2)|^2}, \tag{7}$$

where $\epsilon=2m_{\rm eff}E/\hbar^2$, $u(\mathbf{r}_1,\mathbf{r}_2)=(2m_{\rm eff}/\hbar^2)U(\mathbf{r}_1,\mathbf{r}_2)$. The requirement that the first functional variation $\delta\epsilon$ with respect to Ψ be zero leads to the condition that the wave function Ψ satisfies the Schrödinger equation (6) in the volume V together with the hard-wall boundary conditions.[8]

The ground state of the noninteracting system, fulfilling the boundary condition, is simply given by the product of two single-particle ground-state wave functions [see Eq. (3)]

$$\Psi_0(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{R(z_1)}J_0\left(\chi_{0,1}\frac{\rho_1}{R(z_1)}\right)f(\alpha,z_1)\times\frac{1}{R(z_2)}J_0\left(\chi_{0,1}\frac{\rho_2}{R(z_2)}\right)f(\alpha,z_2), \tag{8}$$

where the analytical fit for $F(z)$ has been used.

The wave function (8) cannot actually describe the ground state associated with Eq. (6), because the Hamiltonian contains the interaction potential $U(\mathbf{r}_1,\mathbf{r}_2)$. Since the "true" ground-state wave function describes a correlated system, we consider the product

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\Psi_0(\mathbf{r}_1,\mathbf{r}_2)\Psi_{\rm corr}(\mathbf{r}_1-\mathbf{r}_2), \tag{9}$$

where Ψ_0 is given in Eq. (8) and the correlated motion of the electrons is described by $\Psi_{\rm corr}$.

The trial function (9) must reflect the ground-state properties. Then it must (i) depend only on $\varphi_1-\varphi_2$ (that is, be invariant for rotations of both electrons of the same angle around the z axis), (ii) be invariant for reflections of both electrons [that is, with respect to the transformation $(\mathbf{r}_1,\mathbf{r}_2)\rightarrow(-\mathbf{r}_1,-\mathbf{r}_2)$], (iii) be symmetric with respect to the exchange of the two electrons (corresponding to the singlet spin state), (iv) vanish if any of the two electrons is on the wire boundary, and (v) be continuous together with its first and second partial derivatives. The choice that will be provided fulfills all these conditions.

IV. THE INTERACTION POTENTIAL

It is worth discussing the nature of the interaction potential, the choice of $\Psi_{\rm corr}$ being strongly related to it. We can write

$$\begin{aligned}U(\mathbf{r}_1,\mathbf{r}_2)&=U_{\rm Coul}(\mathbf{r}_1-\mathbf{r}_2)+U^d(\mathbf{r}_1,\mathbf{r}_2)\\&=U_{\rm Coul}(\mathbf{r}_1-\mathbf{r}_2)+U^d_{\rm self}(\mathbf{r}_1)+U^d_{\rm self}(\mathbf{r}_2)+U^d_{e-e}(\mathbf{r}_1,\mathbf{r}_2),\end{aligned} \tag{10}$$

where $U_{\rm Coul}$ is the Coulomb repulsion between the two electrons and U^d a dielectric contribution. This last term arises as a result of the dielectric mismatch between the wire and the surrounding medium.

It is known that an electron moving inside a quantum wire, whose dielectric constant $\varepsilon_{\rm I}$ is different from that of the surrounding medium $\varepsilon_{\rm II}$, causes the appearance of a surface polarization charge.[11–14] A proper description of the electron motion must take into account the interaction between the particle and this surface charge. Making reference to porous silicon nanostructures, all the dielectric interactions are repulsive. In fact, porous silicon is usually surrounded by oxide (SiO_2), whose dielectric constant is smaller than that of silicon ($\varepsilon_{\rm I}=12$, $\varepsilon_{\rm II}=4$). The dielectric interaction for the two-electron system is composed of three terms: (i) two self-interaction terms [$U^d_{\rm self}$ in Eq. (10)] due to the interaction of each electron with the surface charge generated by itself and (ii) the interaction between each electron and the surface charge generated by the second one [U^d_{e-e} in Eq. (10)].

Let us focus first on the self-interaction contribution. An electron moving inside the wire generates a surface polarization charge, as explained above, which is spread out on the whole surface S of the wire. Nevertheless, we expect that the major part of it is localized in a limited region of S, near the electron. The farther the electron from the surface, the smaller the self-interaction energy. Because of the particular geometry of the wire we are considering (see Fig. 1), the interaction of each electron with its relative surface charge is

stronger if the electron is located in the straight part of the wire (having a smaller radius). This means that the self-interaction terms, which are repulsive, tend to push the electrons toward the center of the bulge, favoring in this way a reduction of the electron-electron correlation. On the other hand, the electron-electron interaction term via the surface charge tends to correlate the electrons, each particle being repelled by the polarization charge generated by the other one.[12–14]

Therefore, we can conclude that the full potential contains two repulsive terms (Coulomb and interaction via the surface charge) and a localizing potential that is a self-interaction contribution. The interplay between all such terms, together with the localizing effect induced by the deformation (see Sec. II), will determine the nature of the ground state.

A last point must be stressed here. Given the geometry of the confined system, we can take into account only the electron-electron correlation along the z direction (this means that we consider the dependence of $\Psi_{\rm corr}$ on z_1 and z_2, neglecting all the other coordinates). In fact, it is expected that the minimum energy configuration is reached when the two electrons are placed along the z axis so that the distance between each other and from the wire boundary is as large as possible, in order to minimize both the electrostatic repulsion and the kinetic contribution to the total energy. It has indeed been shown[12] that if we consider more and more elongated quantum rods, for which one of the dimensions gets much longer than the other two, the correlation energy[15] mainly arises from the possibility that the two electrons keep far from each other along the ''long'' direction.

Keeping all this in mind, we can do a suitable choice for $\Psi_{\rm corr}$, as follows:

$$\Psi_{\rm corr}(z_1-z_2)=1-af(\beta,z_1-z_2), \tag{11}$$

where the function $f(\alpha,z)$ is defined in Eq. (5). The trial wave function (9) can be written as

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{R(z_1)}\frac{1}{R(z_2)}J_0\left(\chi_{0,1}\frac{\rho_1}{R(z_1)}\right)\times J_0\left(\chi_{0,1}\frac{\rho_2}{R(z_2)}\right)g(z_1,z_2), \tag{12}$$

where

$$g(z_1,z_2)=(1+\alpha|z_1|)e^{-\alpha|z_1|}(1+\alpha|z_2|)e^{-\alpha|z_2|}\times[1-a(1+\beta|z_1-z_2|)\exp(-\beta|z_1-z_2|)]. \tag{13}$$

a, α, and β are three variational parameters, whose values can be fixed by requiring the energy functional given in Eq. (7) be minimum. Let us note that such a choice fits requirements depicted above well, being able to describe a two-particle system subject to both a repulsive potential and a localizing one. In fact, (i) if $a=0$ or if the distance between the two electrons is very large, the uncorrelated wave function [given in Eq. (8)] is retrieved, and (ii) if $a\neq 0$, it describes the correlated system for which the probability of finding the two electrons at the same position is $(1-a)^2$ times smaller than that corresponding to uncorrelated particles. Then we argue that a represents the electronic correlation degree, so that $0\leqslant a\leqslant 1$. $1/\alpha$ and $1/\beta$ are instead linked to the mean single-electron localization range and to the mean electron-electron distance respectively,[16] so that $\alpha,\beta\geqslant 0$.

Using the trial wave function (12), the energy functional (7) results to be dependent only on the function g:

$$\epsilon[g]=\frac{\int_{-\infty}^{\infty}dz_1\int_{-\infty}^{\infty}dz_2\{[\partial_{z_1}g(z_1,z_2)]^2+[\partial_{z_2}g(z_1,z_2)]^2+V(z_1,z_2)g^2(z_1,z_2)\}}{\int_{-\infty}^{\infty}dz_1\int_{-\infty}^{\infty}dz_2 g^2(z_1,z_2)}. \tag{14}$$

The two electrons move as they were subject to the potential

$$V(z_1,z_2)=V_{\rm eff}(z_1)+V_{\rm eff}(z_2)+V_{\rm el}(z_1,z_2), \tag{15}$$

where $V_{\rm eff}$ has been defined in Eq. (4) and represents the effective, geometry-induced, localizing potential. $V_{\rm el}$ is the potential arising from the electrostatic terms [see Eq. (10)].

The results we are going to show have been obtained assuming the dielectric constant of the bulk material ($\varepsilon_{\rm I}=12$) for the silicon nanostructures. Some works[17,18] have demonstrated that on reducing the average size of the sample (here identified[6] with the geometrical parameter Δz) the dielectric constant decreases. Nevertheless, all these calculations show that the difference between the confined and the bulk dielectric constant is significant only when the average size is reduced approximately down to 15 Å, but becomes really important only when it approaches the lattice constant ($a_0=5.43$ Å for silicon). Therefore, since we are going to consider larger structures, no significant correction is expected to come from a size-dependent dielectric constant.

V. RESULTS

The aim of our calculation is the description of how the electron-electron correlation depends on the geometrical details of the wire deformation as well as the investigation about whether or not a two-electron confined state exists under suitable conditions on the wire deformation geometry.

Before showing the results, some key points must be stressed. It is well known that the three-dimensional confinement within a zero-dimensional system (quantum dot, or QD) gives rise to the appearance of discrete levels, which makes these systems very peculiar because of their atomic-like features. If we look, instead, to quantum confinement within a one-dimensional system (quantum wire, or QWr), the existence of a direction along which there is no confinement is responsible of a miniband structure, that is, one-dimensional bands whose edges are related to quantum confinement along the other two directions (for example, for a cylindrical quantum wire they depend on the inverse square wire radius). In both cases we deal with quantum confinement, the difference being the system dimensionality.

For a deformed quantum wire an intermediate condition holds: discrete energy levels exist in the gap between the one-dimensional bands, corresponding to localized states depending on the bulge geometry. For such a system we must distinguish between the *quantum confinement*, responsible for the position of the miniband edges and whose effect depends on the wire radius, and the *localization* in the z direction, due to the presence of the bulge and origin of the discrete states within the gap.

This ''intermediate'' state (meaning that we find both delocalized and localized states) makes deformed quantum wires very peculiar, giving rise to QD-like or QWr-like systems, depending on the deformation geometrical parameters. This can lead to interesting features for the two-electron system, such as the possibility of observing Coulomb-blockade-like effects, typical of QD's. All the results presented in this section will be described keeping in mind this peculiarity, and in particular the conceptual difference between quantum confinement and localization, in the sense outlined above.

In the strong quantum confinement regime the energy of a two-electron system is nearly exclusively kinetic, and the electrostatic terms can be treated as a perturbative correction. On reducing the quantum confinement (that is, increasing the available volume), the effect of electrostatic terms on the electron motion becomes more and more relevant, and the description within the strong confinement regime (which assumes an uncorrelated ground-state wave function) becomes incorrect. This is not always the case for a deformed quantum wire. In fact, as already pointed out, each electron is subject to a geometrical effective potential $V_{\rm eff}$ [given in Eq. (4)], which pushes the particle toward the center of the bulge, at $z=0$ (localization). We are going to show that it is possible to change the geometry of the bulge in such a way that an increase of the available volume corresponds to both a decrease of the quantum confinement (as for QD's) and an increase of localization, this last effect being dominant. The result is that the electron-electron correlation degree is reduced, because of the action of the z-localizing geometrical potential $V_{\rm eff}$.

A. The effect of the Coulomb interaction

We have minimized the energy functional (14) with respect to the three variational parameters a, α, and β, obtaining, in accordance with the variational principle, an upper bound to the ground-state energy. We first discuss the case in which only the Coulomb repulsion is taken into account [$U(\mathbf{r}_1,\mathbf{r}_2)=U_{\rm Coul}(\mathbf{r}_1-\mathbf{r}_2)$ in Eq. (10)]. The contribution of dielectric effects will be considered later.

The Coulomb contribution can be evaluated through the expansion[19]

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}=\sum_{m=-\infty}^{+\infty}\int_0^{+\infty}e^{im(\varphi_1-\varphi_2)}J_m(k\rho_1)\times J_m(k\rho_2)e^{-k|z_1-z_2|}dk. \tag{16}$$

We obtain [see Eq. (15)]

$$V_{\rm el}(z_1,z_2)=V_{\rm Coul}(z_1,z_2)=\frac{2}{a_B^*}\left[\frac{2}{J_1^2(\chi_{0,1})}\right]^2\int_0^{\infty}e^{-k|z_1-z_2|}\times S[kR(z_1)]S[kR(z_2)]dk, \tag{17}$$

where a_B^* is the material Bohr radius, defined as

$$a_B^*=4\pi\varepsilon_0\varepsilon_{\rm I}\frac{\hbar^2}{m_{\rm eff}e^2}=\varepsilon_{\rm I}\frac{m_e}{m_{\rm eff}}a_B, \tag{18}$$

and the function $S(x)$ is defined through the integral

$$S(x)=\int_0^1 tJ_0^2(\chi_{0,1}t)J_0(xt)dt. \tag{19}$$

The binding energy can be defined by considering that, in the single-particle picture, the effective, geometrical potential (4) has the asymptotic value $\chi_{0,1}^2/R_0^2$, which corresponds to the undeformed wire first miniband edge. This means that single-particle delocalized states correspond to energies above this value, while localized states, if present, to energy levels lying below it. For the two-electron system we can define as a reference state the one with two electrons at $z=-\infty$ and $z=+\infty$, respectively, leading to an energy given by twice the miniband edge. This means that, for a fixed geometry, if $E_{\rm tot}$ is the value of the energy functional at the minimum point, the ground state is confined if $\epsilon<2\chi_{0,1}^2/R_0^2$ and the binding energy can be defined as $E_{\rm B}=(\hbar^2/2m_{\rm eff})(\epsilon-2\chi_{0,1}^2/R_0^2)=(\hbar^2/2m_{\rm eff})\epsilon_B$, where $\epsilon=2m_{\rm eff}E_{\rm tot}/\hbar^2$.

The features of the ground state of the system are presented in Figs. 2–6 as functions of the geometry of the deformation. In the following we indicate with K and C the kinetic and Coulomb contributions to the total energy ($E_{\rm tot}=K+C$). We show (i) the ratios $K/E_{\rm tot}$ and $C/E_{\rm tot}$ (Fig. 2), (ii) the binding energy $E_{\rm B}$ (Fig. 3), (iii) the variational parameter a (Fig. 4) identified with the electron-electron correlation degree (see discussion in Sec. IV), (iv) α^{-1} (Fig. 5), which measures the electron distance from the center of the bulge, and (v) β^{-1} (Fig. 6), which measures the electron-electron distance.[16] In each figure three curves are shown, each corresponding to a fixed value of R_0, as a function of ε [which measures the deformation depth (see Fig. 1)]. Δz (that is, the mean dimension of the sample) is kept fixed at 30 Å.

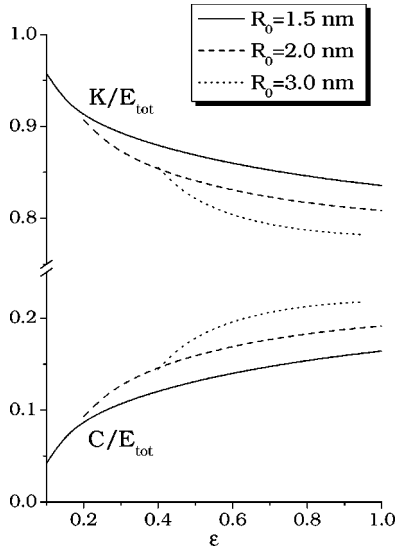

FIG. 2. Ground-state kinetic and Coulomb to total energy ratio as a function of ε for three different values of R_0. Δz has been kept fixed to 30 Å.

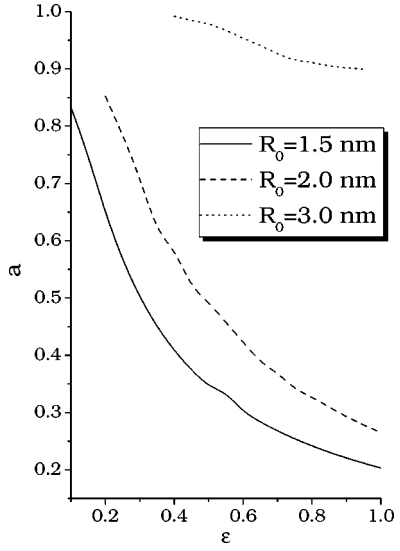

FIG. 4. The variational parameter a for the two-electron ground state and the bulge geometries discussed in Fig. 2. a represents the electron-electron correlation degree.

The shape of the bulge can be substantially changed in two different ways, and the effect of geometry on the electron-electron correlation degree is different in the two cases:

(1) With increasing R_0, keeping ε fixed (that is, moving from the solid to the dashed to the dotted curve, in each of Figs. 2–6), there is an increase of the volume of the bulge, so that the kinetic to total energy ratio is reduced, while the Coulomb to total energy ratio increases,[20] as can be observed in Fig. 2. The modification of the bulge geometry is such to reduce the depth of the localizing effective potential V_{eff} and then the absolute value of binding energy, as Fig. 3 clearly shows. The localization decrease leads to a ground-state configuration in which the effect of the Coulomb repulsion becomes more visible, with the two electrons that tend to keep far from each other along the wire axis. This favors an increase of the electron-electron correlation degree, as shown in Fig. 4. This picture is confirmed by Figs. 5 and 6, where it is shown that with increasing R_0, keeping ε fixed, both the mean localization range α^{-1} of the single-electron wave function and the mean electron-electron distance β^{-1} increase.

(2) With increasing ε, keeping R_0 fixed (that is, moving along each curve from left to right, in each of Figs. 2–6), an increase of the volume of the bulge still causes a

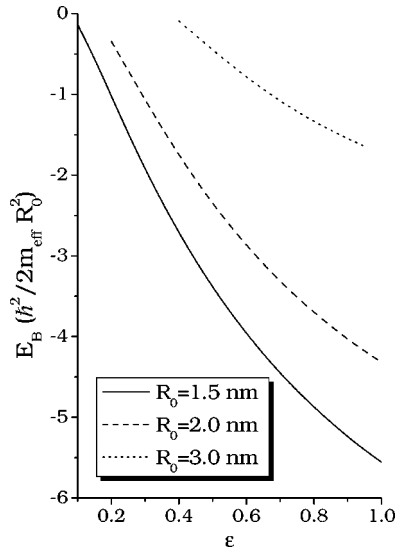

FIG. 3. Binding energies of the two-electron localized ground state, for the same geometries as in Fig. 2. Energy is measured in units of $\hbar^2/2m_{\text{eff}}R_0^2$ ($2m_{\text{eff}}R_0^2E_B/\hbar^2=\epsilon R_0^2-2\chi_{0,1}^2$).

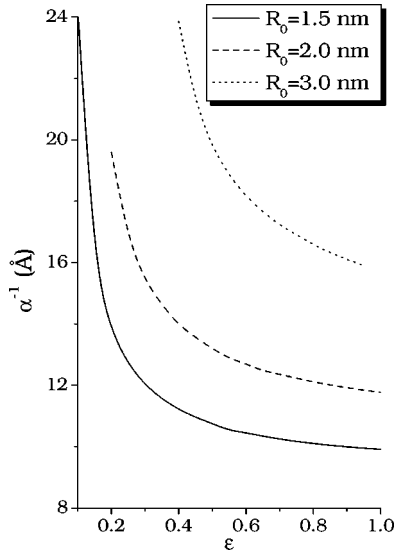

FIG. 5. The variational parameter α^{-1} for the two-electron ground state and the bulge geometries discussed in Fig. 2. α^{-1} is related to the localization range of single-electron wave function.

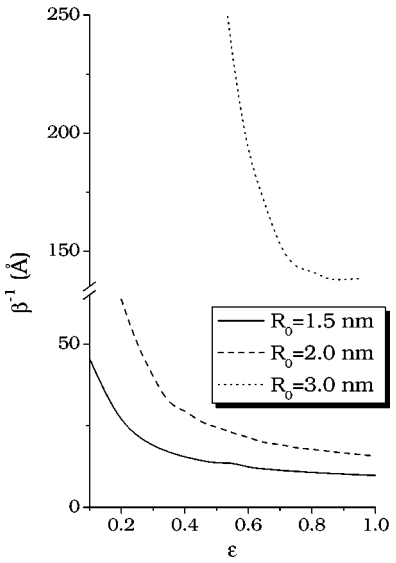

FIG. 6. The variational parameter β^{-1} for the two-electron ground state and the bulge geometries discussed in Fig. 2. β^{-1} is related to the mean electron-electron distance.

reduction of the kinetic to total energy ratio and an increase of the Coulomb to total energy ratio, as seen in Fig. 2. Nevertheless, in this case the binding energy modulus increases, as it is shown in Fig. 3. In fact, with the increase of the deformation depth, the effective potential becomes deeper, and the binding in the bulge stronger, leading to an increased localization of both electrons. Therefore, the electron-electron distance decreases, the contribution of the Coulomb interaction increases, and the leading effect is the localization inside the deeper geometrical potential well. The minimum energy is reached with a lower electron-electron correlation degree *a*, as shown in Fig. 4. The behavior of the spatial extension of the single-particle wave function α^{-1} (Fig. 5) and of the mean electron-electron distance β^{-1} (Fig. 6) confirms this picture.

We can conclude that in both cases the increase of the Coulomb to total energy ratio is observed, but it does not necessarily result in an increase of the electron-electron correlation degree, as expected if the electrons were confined within a quantum dot.[12] This happens only when the geometrical parameter ε is fixed and R_0 increases, leading to a decrease of the binding energy. When it is ε to assume larger values, R_0 being fixed, a reduction of the quantum confinement is still observed (in terms of available volume), which tends to correlate the electrons, but the bulge geometry is such to induce an effective potential V_{eff} whose localizing effects along the *z* direction are stronger than the electrostatic ones. The combined effect of the two opposite trends results in a decrease of the electron-electron correlation degree. In this sense, for a deformed quantum wire, we must distinguish between quantum confinement (that is, the bulge volume) and localization (that is, confinement in the *z* direction) in the bulge, which instead are identified in the case of a true confinement in all three directions. A final check is given in Fig. 7, where the contour plots for the square modulus of the two-electron ground-state wave function (12) are shown. The average with respect to both radial and angular coordinates has been taken. The white regions correspond to a maximum of such function. The three plots are relative to a bulged quantum wire with (a) $R_0=15$ Å, $\varepsilon=0.1$, (b) $R_0=15$ Å, $\varepsilon=0.4$, (c) $R_0=30$ Å, $\varepsilon=0.4$. Δz has been fixed to 30 Å in all cases. The (b) plot can be taken as a reference. It clearly comes out that small values of ε [plot (a)] or large values of R_0 [plot (c)] mean strongly correlated, Coulomb dominated systems, while the opposite limits push toward a localized, bulge-dominated system [plot (b)].

B. A semiquantitative evaluation of dielectric effects

In the preceding section, the shape effects on the two-electron ground state have been described taking into account only the electron-electron Coulomb repulsion [Eq. (17)]. Dielectric effects, due to the dielectric mismatch between the wire and the surrounding medium, have been neglected. In this section we want account for such effects, describing how they can modify the results depicted in the preceding section.

It is worth stressing that the trial wave function choice given in Eq. (12) fits the study of the two-electron system with the inclusion of dielectric effects as well. In fact, as explained in Sec. IV, two further contributions appear (the localizing self-interaction term and the repulsive interaction via the surface charge), whose interplay with the previously

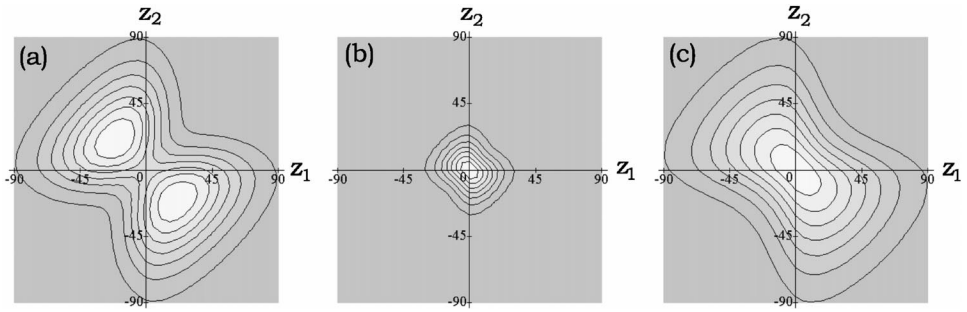

FIG. 7. The contour plots for the square modulus of the two-electron ground-state wave function (12). The average with respect to both radial and angular coordinates has been taken. The white regions correspond to a maximum of such function. The three plots are relative to a bulged quantum wire with (a) $R_0=15$ Å, $\varepsilon=0.1$, (b) $R_0=15$ Å, $\varepsilon=0.4$, (c) $R_0=30$ Å, $\varepsilon=0.4$. Δz has been fixed to 30 Å in all cases. Units for both z_1 and z_2 axes are Å.

considered (kinetic and Coulomb) terms will adjust the variational parameters accordingly. The interesting point is the understanding of whether the overall effect is that of increasing the correlation between the two electrons or that of giving a more localized ground-state configuration.

The calculation of the electrostatic potential associated with the surface polarization charge can be exactly performed for some geometries, such as a cylindrical quantum wire,[13] a spherical quantum dot,[14] or an ellipsoidal quantum dot,[12] for which a proper coordinate system exists. In these special cases it is possible to find elementary solutions of the Poisson equation compatible with the required boundary conditions such that the exact solution can be expressed via a series expansion.

The loss of translational symmetry along the wire axis implies that for the deformed wire it is not possible to exhibit an exact solution for the electrostatic potential generated by the surface charge. This means that only a qualitative or semiquantitative evaluation of dielectric effects on the single- or two-electron ground state can be done.

A good starting point can be the solution of the Poisson equation for one electron inside a straight quantum wire. This will lead to an approximation, which will be worse the sharper the deformation. For the cylindrical quantum wire, the dielectric terms in Eq. (10) can be written as[13]

$$U^d_{\rm self}(\mathbf{r}) = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0\varepsilon_{\rm I}]}(s-1)\frac{2}{\pi} \times \sum_{m=0}^{+\infty}\epsilon_m \int_0^{+\infty} dk d_m(kR_0) I_m^2(k\rho), \tag{20}$$

$$U^d_{e-e}(\mathbf{r}_1,\mathbf{r}_2) = \frac{e^2}{4\pi\varepsilon_0\varepsilon_{\rm I}}(s-1)\frac{2}{\pi}\sum_{m=0}^{+\infty}\epsilon_m \cos[m(\varphi_1-\varphi_2)] \times \int_0^{+\infty} dk \cos[k(z_1-z_2)] \times d_m(kR_0) I_m(k\rho_1) I_m(k\rho_2), \tag{21}$$

with $s=\varepsilon_{\rm I}/\varepsilon_{\rm II}$, I_m and K_m are the modified Bessel functions, $\epsilon_0=1$, $\epsilon_2=\epsilon_3=\cdots=2$, and

$$d_m(kR_0) = \frac{K_m(kR_0)K'_m(kR_0)}{K'_m(kR_0)I_m(kR_0) - sI'_m(kR_0)K_m(kR_0)}. \tag{22}$$

The self-energy relative to the undeformed wire is independent of both z and φ, preserving the rotational and translational symmetry. By averaging this potential on the single-electron ground state of the undeformed wire with respect to ρ and φ, we obtain the total self-interaction energy experimented by one electron at z, moving within the undeformed wire. The result (in units $\hbar^2/2m_{\rm eff}$) is the following:[13]

$$\epsilon^{\infty}_{\rm self}(R_0) = \int_0^{R_0} d\rho \left[\int_0^{2\pi} d\varphi u^d_{\rm self}(\mathbf{r})\phi_0^2(\mathbf{r})\right]\rho = \frac{4}{a_B^*}\frac{s-1}{\pi J_1^2(\chi_{0,1})}\sum_{m=0}^{+\infty}\epsilon_m\int_0^{+\infty} dk d_m(kR_0)p_m(kR_0), \tag{23}$$

where $u^d_{\rm self}(\mathbf{r}) = (2m_{\rm eff}/\hbar^2)U^d_{\rm self}(\mathbf{r})$, $\phi_0(\mathbf{r}) = J_0(\chi_{0,1}\rho/R_0)/\sqrt{\pi}R_0 J_1(\chi_{0,1})$ and the functions $p_m(x)$ are defined through the integral

$$p_m(x) = \int_0^1 t J_0^2(\chi_{0,1}t) I_m^2(xt) dt. \tag{24}$$

For the deformed wire this gives the dielectric contribution to the asymptotic state (in which the two electrons are at $z=-\infty$ and $z=+\infty$, respectively, each one interacting only with its own polarization charge, on the surface of the undeformed part of the cylinder).

If we replace $R(z)$ with R_0 in Eq. (20) we obtain a sort of adiabatic approximation of the self-interaction term in the case of the deformed wire, because we are assuming that the only effect of the deformation is that the electron ''sees'' the same potential as in the straight wire, but with the z-dependent radius $R(z)$. Obviously, this procedure does not exactly introduce the bulge shape. Rather, for each given position z_0 of the electron along the z axis, it is as it felt the self-interaction potential of an undeformed cylinder with a constant radius $R(z_0)$.

Therefore, we assume that a reasonable approximation able to describe at least qualitatively the self-interaction due to the polarization charge is given by the z-dependent potential

$$V^d_{\rm self}(z) = \epsilon^{\infty}_{\rm self}(R(z)). \tag{25}$$

As previously discussed (see Sec. IV), it corresponds to a z-dependent, well-shaped potential that favors the electron localization within the bulge [just like the geometrical effective potential (4)]. The effect of the self-interaction energy can be evaluated by averaging $V^d_{\rm self}(z)$ on the trial wave function (12). This leads to the self-interaction energy

$$\epsilon^d_{\rm self} = \frac{\int_{-\infty}^{+\infty} dz_1 \int_{-\infty}^{+\infty} dz_2 V^d_{\rm self}(z_1) g^2(z_1,z_2)}{\int_{-\infty}^{+\infty} dz_1 \int_{-\infty}^{+\infty} dz_2 g^2(z_1,z_2)}. \tag{26}$$

The results of both the integrals do not change if we exchange z_1 and z_2. Therefore, the total self-interaction contribution to the two-electron ground state is given by $2\epsilon^d_{\rm self}$.

The last term to be evaluated is the electron-electron interaction via the surface charge. We cannot make the same ''adiabatic'' approximation as for the self-interaction energy [that is, to replace R_0 with $R(z)$ in Eq. (21)]. In fact, it can be shown that the integral that appears within Eq. (21) is well defined (that is, not divergent) provided that $k\rho_1, k\rho_2 \leqslant kR_0$. Let us assume that one electron is at z_1 and we want

to find the electrostatic potential due to the surface charge "felt" by the second electron at z_2. If we make the replacement $R_0 \rightarrow R(z_1)$, it is still $k\rho_1 \leqslant kR(z_1)$ but the second electron is free to assume any position because the coordinates z_1 and z_2 can vary independently of each other. This means that if $|z_2| < |z_1|$, we can have $k\rho_2 > kR(z_1)$, because the wire radius is larger for small values of $|z|$. This makes Eq. (21) useless if a z-dependent radius is assumed.

Because the main effect of the electron-electron interaction via the surface charge is due to the repulsive nature of the potential (21) rather than its dependence on the wire shape (as we have seen this is not true, instead, for the self-interaction energy, which gives rise to an extra potential well depending on the bulge depth), we can imagine to give a first approximation as follows. We average the potential (21) on the ground-state wave function for two noninteracting electrons moving inside a straight wire, with respect to ρ and φ. This gives an effective potential, depending on R_0 and $z_1 - z_2$. We assume that this repulsive potential gives at least a qualitative approximation to the electron-electron interaction via the surface charge even in the deformed cylinder. In this way we cannot get any divergence. Moreover we can also say that the error done by doing such an approximation is always negative, namely the contribution to total energy is overestimated. In fact, since $R_0 < R(z)$, the electrons, mostly inside the bulge, are considered closer to the surface charge than they really are.

The electron-electron interaction potential built as depicted above leads to

$$V^d_{e-e}(z_1-z_2) = \int_0^{R_0} d\rho_1 \int_0^{R_0} d\rho_2 \left[\int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_2 \rho_1 \rho_2 \times u^d_{e-e}(\mathbf{r}_1,\mathbf{r}_2)\phi_0^2(\mathbf{r}_1)\phi_0^2(\mathbf{r}_2) \right]$$
$$= \frac{16}{a_B^*} \frac{s-1}{\pi J_1^4(\chi_{0,1})} \int_0^{+\infty} dk \times \cos[k(z_1-z_2)] d_0(kR_0) q^2(kR_0), \quad (27)$$

where $u^d_{e-e}(\mathbf{r}_1,\mathbf{r}_2) = (2m_{\text{eff}}/\hbar^2) U^d_{e-e}(\mathbf{r}_1,\mathbf{r}_2)$ and the function $q(x)$ is defined through the integral

$$q(x) = \int_0^1 t J_0^2(\chi_{0,1} t) I_0(xt) dt. \quad (28)$$

The function represented in Eq. (27) has the shape of a potential barrier centered at $|z_1 - z_2| = 0$ and gives a further contribution to the electron-electron (repulsive) interaction. Thus, the overall effect is that of increasing the correlation between the two electrons. This approximate approach gives correct qualitative information on the effects of the dielectric interaction on the electronic correlation. The contribution to total energy due to this potential is obtained by averaging it on the trial function (12), as follows:

TABLE I. A comparison of binding energies and electron-electron correlation degrees relative to the cases in which dielectric effects are neglected or considered. Binding energies, measured in unit of $\hbar^2/2m_{\text{eff}}R_0^2$, are referred to typical porous silicon geometries [$R_0(\text{Å}) = 5.704 + 0.307\Delta z(\text{Å})$, $\delta = 0.497 - 0.010\Delta z(\text{Å})$ with $\delta = \varepsilon R_0/\Delta z$ (see Ref. 6)]. The superscript d refers to the case in which dielectric effects are included.

Δz (Å)	ϵ_B	ϵ_B^d	a	a^d
15	−3.037	−2.882	0.194	0.265
20	−3.259	−3.111	0.237	0.440
25	−3.118	−2.960	0.309	0.616
30	−2.702	−2.516	0.409	0.830
35	−2.038	−1.817	0.541	0.938
40	−1.139	−1.033	0.713	0.979

$$\epsilon^d_{e-e} = \frac{\int_{-\infty}^{+\infty} dz_1 \int_{-\infty}^{+\infty} dz_2 V^d_{e-e}(z_1-z_2) g^2(z_1,z_2)}{\int_{-\infty}^{+\infty} dz_1 \int_{-\infty}^{+\infty} dz_2 g^2(z_1,z_2)}. \quad (29)$$

The dielectric contributions to the total energy given in Eqs. (26) and (29) must be added to the functional (14) to get the full energy functional [this corresponds to rewriting Eq. (17) as $V_{\text{el}}(z_1,z_2) = V_{\text{Coul}}(z_1,z_2) + V^d_{\text{self}}(z_1) + V^d_{\text{self}}(z_2) + V^d_{e-e}(z_1-z_2)$, using Eqs. (25) and (27)]. This last functional has been minimized for wire geometries typical of porous silicon (see Ref. 6). Even if dielectric effects are included, two-electron localized states are observed. The absolute value of the binding energy of the ground state is smaller than that calculated neglecting dielectric effects, while the corresponding electron-electron correlation degree is larger. This is shown in Table I, where a comparison of the binding energies of the system when dielectric effects are neglected or included, relative to several geometries, is presented. In the same table, an analogous comparison is shown for the electron-electron correlation degrees. The dielectric contribution pushes toward a more correlated system, showing that the effect of the electron-electron interaction via the surface charge [Eq. (27)] is, for the considered geometries, always dominant over the localizing potential associated with the self-interaction terms [Eq. (25)].

The values so obtained are to be considered upper limits to binding energies and electron-electron correlation degrees. In fact, the discussed overestimation of electron-electron interaction potential U^d_{e-e} causes, in our numerical calculation, a systematic decrease of the modulus of the binding energy and an increase of the electron-electron correlation degree with respect to the case in which the analytical form of U^d_{e-e} was exactly evaluated. Nevertheless, this overestimation ensures that the binding energy of the localized states is larger (in modulus) than the calculated energy, and confirms the existence of these states.

VI. CONCLUSIONS

We have pointed out the possibility of binding two electrons within the deformation of a bulged silicon quantum

wire. The interplay between the deformation localizing effect and the repulsive Coulomb potential has been studied and discussed. The result is that under suitable conditions on the wire geometry a two-electron, confined ground state is formed, localized within the deformation. This can have significant consequences on the properties of such systems, relying on the fact that the deformation charging with one, two, or more electrons can give rise to Coulomb-blockade-like effects. The charging energy should be dependent on the deformation geometry and is expected to be larger, the more the Coulomb interaction is significant with respect to the localization. This is what we find if we consider the difference between the two- and single-particle ground-state energies. However, a quantitative analysis of the charging effects requires a more accurate evaluation of dielectric effects, which are known to play a central role.[12,21]

It has been stressed that the localizing effect has quantum-dot-like features, because the increase of the available volume corresponds to an increase of the Coulomb to kinetic energy ratio. Nevertheless, unlike quantum dots, two different regimes can be distinguished concerning the electron-electron correlation. The available volume increase can be followed by an increase or a decrease of the correlation according to whether the localizing effect is decreased (ε fixed, R_0 increasing) or increased (ε increasing, R_0 fixed). The features of the ground-state wave function will be determined by the localization effect [see Fig. 7(b)] or by the electron-electron correlation [see Fig. 7(c)] accordingly.

The contribution due to dielectric mismatch has been semiquantitatively discussed as well, showing how it favors the correlated electron-electron system. Despite this, a two-electron confined ground state is always formed for the considered geometries. An exact treatment of this contribution is expected to confirm this result, because our evaluation of the dielectric contribution to the total energy has been shown to be an overestimation.

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