**D− shallow donor near a semiconductor–metal and a semiconductor–dielectric interface**

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**Abstract**

The ground state energy and the extent of the wavefunction of a negatively charged donor (D−) located near a semiconductor–metal or a semiconductor–dielectric interface are obtained. We apply the effective mass approximation and use a variational two-electron wavefunction that takes into account the influence of all image charges that arise due to the presence of the interface, as well as the correlation between the two electrons bound to the donor. For a semiconductor–metal interface, the D− binding energy is enhanced for donor positions d > 1.5aB (aB is the effective Bohr radius) due to the additional attraction of the electrons with their images. When the donor approaches the interface (i.e. d < 1.5aB) the D− binding energy drops and eventually it becomes unbound. For a semiconductor–dielectric (or a semiconductor–vacuum) interface the D− binding energy is reduced for any donor position as compared to the bulk case and the system becomes rapidly unbound when the donor approaches the interface.

(Some figures in this article are in colour only in the electronic version)

**1. Introduction**

The negatively charged donor center, also called D− system (a hydrogenic donor with a second electron bound to it) has received a lot of interest in the past both from researchers in astrophysics (where it is known as the H− ion [1]) and semiconductor physics [2]. Furthermore, the D− center is one of the simplest ‘many-body’ electronic system that can also be used as a model system to test how well certain theories are able to include electron–electron (e–e) correlations. It has been shown that in the absence of electric and magnetic fields the D− has only one bound state [2]. Experimentally, D− states have been observed in bulk semiconductors [3], in quantum wells [4], and in superlattices [5]. Tunneling through the D− state was reported in [6] for a D− confined in a double-barrier resonant tunneling device. The D− resonance appears in addition to the known resonance due to tunneling through the ground state of the neutral donor D0. It was found that in high magnetic fields the amplitude of the D− resonant peak becomes significantly larger as compared to the amplitude of the D0 peak [6].

Theoretically, the D− center has been investigated using the variational method within the effective mass approach: (i) for the bulk case [7], (ii) the two-dimensional case [8, 9], and (iii) for the superlattice case [10]. In a double-quantum-well device a neutral donor D0 at the center of the quantum well in the presence of a magnetic field can bind a second electron in the other well (a spatially separated D− center) as shown in [11]. In the case of the remote D− center, where donor and electrons are located in different quantum wells, strong electron–electron correlations can give rise to magnetic-field-induced angular-momentum transitions [11, 12]. It has been predicted that electron–phonon interaction in a weakly polar semiconductor leads to a substantial increase of the D− binding
energy [13]. The negatively charged donor center was used as an approximate model system for a trion (charged exciton) to explain the experimental behavior of the two-dimensional electron gas in a quantum well in high magnetic field at high-laser power [14].

In the last few years, there has been renewed interest in the study of dopants in semiconductors due to the possibility to dope the material in a controlled way and to tailor the electronic properties in order to create new functional devices. Because of increased miniaturization, the dopant atoms appear closer and closer to interfaces [15]. Recently, using STM, the binding energy of individual dopants close to a semiconductor interface was measured and found to be substantially increased [15]. In a recent transport experiment on a nanowire surrounded by a metallic gate it was suggested [16] that signatures of the D− state were observed. Due to the closeness of the metallic gate to the donor it was argued that the metallic gate screens the repulsive e−e− interaction which should lead to a larger binding energy. Here we will show that this expectation is only correct if the donor is not too close to the interface. For very close proximity of the donor to the interface the D− binding energy drops and can even become negative, i.e. unbound D− system.

A second motivation for the present study is that the D− system can serve as an entangled pair of electrons which currently is of great interest for quantum information applications [17]. The quantum control of a D0 near a semiconductor–dielectric interface and its possible application for quantum computing has been discussed in [18].

In this paper we study the spin-singlet state of a D− system near a semiconductor–metal (and semiconductor–dielectric) interface within the effective mass approach. As compared to the 3D situation the present problem differs in the following two aspects: (1) the many-particle wavefunction is zero at the interface, and (2) due to the dielectric mismatch at the interface image charges are induced that result in a complicated multicenter Coulomb problem. For the ground state trial function we used a Chandrasekhar type space symmetric wavefunction which we modified in order to satisfy the boundary condition on the semiconductor–insulator interface, and to take into account the contribution of the Coulomb interaction with the image charges in the system. To describe the interaction of the electrons with the images in the insulator or in the metallic gate, we added additional terms to the Chandrasekhar trial function [1]. For the case of a single electron bound to a donor near a metallic or dielectric interface, i.e. the D0 problem, similar terms were introduced recently in [19] which we modified slightly in order to obtain even better results for d > aB. In the present paper, we have calculated the ground state energy of the D− system as a function of the donor position with respect to a semiconductor–metal, a semiconductor–dielectric and a semiconductor–vacuum interface.

The present paper is organized as follows. In section 2 we present the two-electron Hamiltonian and propose trial wavefunctions for the D− center. In section 3 the ground state energy of the D− center near different interfaces is studied as a function of the position of the donor. The extent of the wavefunction and its average position in the direction parallel and perpendicular to the interface are also calculated. Our conclusions and a summary of our results are presented in section 4.

2. The formalism and the variational wavefunction

The Hamiltonian of the D− system, consisting of a donor at a position \( \mathbf{r}_d = (0, 0, d) \) near a semiconductor–metal (semiconductor–dielectric) interface and two electrons, is, in cylindrical coordinates, given by the expression

\[
H = H_1 + H_2 + U(\mathbf{\hat{r}}_1, \mathbf{\hat{r}}_2),
\]

(1)

where

\[
H_i = -\frac{1}{2} \left[ \frac{\partial^2}{\partial r_i^2} + \frac{1}{\rho_i} \frac{\partial}{\partial \rho_i} + \frac{1}{\rho_i^2} \frac{\partial^2}{\partial \theta_i^2} + \frac{\sigma}{\partial z_i^2} \right] + U^0(\mathbf{\hat{r}}_i),
\]

(2)

is the Hamiltonian of a neutral D0 center near an interface, with

\[
U^0(\mathbf{\hat{r}}_i) = \frac{Q}{4\zeta_i} - \frac{1}{\rho_i^2 + (z_i - d)^2} - \frac{Q}{\sqrt{\rho_i^2 + (z_i + d)^2}},
\]

(3)

the Coulomb interaction terms and where dimensionless units of the effective Bohr radius \( a_B = h^2/\epsilon_0 m_e e^2 \) and twice the effective Rydberg energy \( 2R^* = \hbar^2/m_\perp a_B^2 \) were used, and \( \sigma = m_\perp/m_\parallel \) is the ratio between the transverse and longitudinal effective mass (in our numerical calculations we assume \( \sigma = 1 \)).

The first term in \( U^0(\mathbf{\hat{r}}_i) \) describes the interaction between an electron and its image, the second arises due to the attractive interaction between an electron and the donor, and the third term is due to the interaction between an electron and the donor image (as well as the donor and the electron image). See figure 1 for a schematic representation of the different Coulomb terms in the case of a semiconductor–metal interface for which \( Q = -1 \) (i.e. \( \epsilon_0 \to \infty \)). In equation (3) the image charge is given by \( Q = (\epsilon_S - \epsilon_0)/(\epsilon_S + \epsilon_0) \) with \( \epsilon_S (\epsilon_0) \) the permittivity of the semiconductor (dielectric). For the case of a semiconductor–metal interface we assume a very thin oxide layer between the semiconductor and the metal and its only effect is to prevent the electron from penetrating into the metal.
i.e. it provides a very high potential barrier. The two-electron Coulomb potential has the following form:

$$U(\vec{r}_1, \vec{r}_2) = U_{ee}(\vec{r}_1, \vec{r}_2) + U_{el}(\vec{r}_1, \vec{r}_2),$$

with

$$U_{ee}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{\rho_1^2 + \rho_2^2 - 2\rho_1\rho_2 \cos(\theta_1 - \theta_2) + (z_1 - z_2)^2}},$$

$$U_{el}(\vec{r}_1, \vec{r}_2) = \frac{Q}{\sqrt{\rho_1^2 + \rho_2^2 - 2\rho_1\rho_2 \cos(\theta_1 - \theta_2) + (z_1 + z_2)^2}},$$

where $U_{ee}$ describes the electron–electron interaction and $U_{el}$ is the interaction between an electron and the image of the other electron.

The potential energy for the D$^0$ electron along the z-direction for $\rho = 0$ is shown by the dashed curve in figure 2(a) for the semiconductor–metal interface and in figure 2(b) for the semiconductor–dielectric interface. The electron is subject to a $-e/|\vec{r} - \vec{r}_0|$ Coulomb potential near the donor and the potential due to the image charges. When an electron is bound to the positive donor the system becomes neutral and this electron will screen the donor Coulomb potential for a second electron. The mean-field potential seen by the second electron is given by

$$U''(\vec{r}_2) + \langle \psi_D(\vec{r}_1)|U(\vec{r}_1, \vec{r}_2)|\psi_D'(\vec{r}_1) \rangle,$$

where $\psi_D(\vec{r})$ is the normalized ground state wavefunction of the D$^0$ electron which we obtained previously in [19]. This potential is plotted in figures 2(a) and (b) by the solid curve and it is immediately clear that the second electron will feel a strongly screened donor potential. The 1/r Coulomb potential is replaced [8] by the screened potential $(1 + r)e^{-2r}/r$. As a result the second electron can at most only be very weakly bound. Solving this mean-field problem for the second electron will strongly underestimate the D$^+$ binding energy because it neglects (i) exchange, and (ii) electron–electron correlation. The latter will lead to a polarization of the neutral D$^0$ system.

In order to account for exchange and correlation we introduce a Chandrasekhar type space symmetric wavefunction (because we consider the spin-singlet state, i.e. $\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$) which also takes into account the interaction with the image charges in the system, and satisfies the boundary condition at the interface:

$$\psi(\vec{r}_1, \vec{r}_2) = Np(z_1)p(z_2)|g(\vec{r}_1, \vec{r}_2) + g(\vec{r}_2, \vec{r}_1)|\psi(\vec{r}_1, \vec{r}_2),$$

where

$$p(z_i) = z_i/(1 + \alpha z_i),$$

$$g(\vec{r}_1, \vec{r}_2) = \exp(-\lambda_1 r_1 - \lambda_2 r_2) \exp(-\beta_1 p(z_1) - \beta_2 p(z_2)),$$

$$\psi(\vec{r}_1, \vec{r}_2) = 1 + \delta r_{12},$$

with

$$r_{12} = \sqrt{\rho_1^2 + \rho_2^2 - 2\rho_1\rho_2 \cos(\theta_1 - \theta_2) + (z_1 - z_2)^2}.$$
Table 1. The ground state energy of a D$^-$ center near a semiconductor–metal interface at different donor–interface distances $d$, calculated by using two different $p(z_i)$ terms in the wavefunction, equation (7). In the last column we present the results for $\alpha \neq 0$ and including the asymmetric e–e correlation term, equation (9), in the variational wavefunction.

| $d/a_B$ | $p(z_i) = z_i$ | $p(z_i) = \frac{z_i}{(1 + \alpha z_i)}$ | asymmetric e–e |
|--------|----------------|---------------------------------|----------------|
| 2      | $-0.40883$    | $-0.41464$                      | $-0.41464$     |
| 3      | $-0.49106$    | $-0.49783$                      | $-0.49783$     |
| 4      | $-0.51680$    | $-0.52180$                      | $-0.52180$     |
| 5      | $-0.52518$    | $-0.52885$                      | $-0.52885$     |
| 6      | $-0.52768$    | $-0.53061$                      | $-0.53061$     |
| 7      | $-0.52811$    | $-0.53059$                      | $-0.53059$     |
| 8      | $-0.52787$    | $-0.52998$                      | $-0.52998$     |
| 9      | $-0.52747$    | $-0.52922$                      | $-0.52922$     |
| 10     | $-0.52709$    | $-0.52850$                      | $-0.52850$     |

The variational wavefunction includes the asymmetric e–e correlation term, equation (9), in the variational wavefunction. The electron–electron correlation is described by the combination of exponential factors $f(z_i) = \exp(-\beta_i p(z_i))$ that describes the overall interaction of each electron with its image, as well as with the images of the donor and the other electron. Similar functions for the electron–electron repulsive interaction (but with $\alpha = 0$) were used previously for the D$^-$ system in quantum wells [10] and for the two-electron parabolic quantum dot [20].

For a neutral electron–donor D$^0$ problem near an interface [19] we took $\alpha = 0$ and thus $p(z) = z$ which resulted in very good agreement between the results of the variational method and a numerical ‘exact’ finite-element solution. Although the energy was found to be accurate it is clear that the bulk wavefunction is not recovered for $d \to \infty$, which should be spherical symmetry around the donor. The reason why we introduced $p(z_i) = \frac{z_i}{(1 + \alpha z_i)}$ which for $z \to \infty$ approaches the constant value $1/\alpha$ and makes the wavefunction spherical symmetric. In table 1 we compare the obtained variational energy for the D$^-$ using $p(z_i) = z_i$ and $p(z_i) = \frac{z_i}{(1 + \alpha z_i)}$; we see that the latter gives lower energy for all $d$-values, where the difference is a maximum of 1.5%. Thus this extra variational parameter has only a small influence on the energy (we checked that the same conclusion holds for the D$^0$ problem). But we found that quantities such as the average electron position behave much better at large $d$ if we include $\alpha$ as a variational parameter. For $d \to \infty$ we have $p \to 1/\alpha$ and our variational wavefunction reduces to the one proposed by Chandrasekar [1] which has been shown to result in accurate values for the bulk D$^-$ binding energy.

Due to the presence of the interface the e–e correlation term is not necessarily spherically symmetric. In order to check the influence of this asymmetry on the energy we introduced an additional variational parameter $\delta_i$ in the e–e correlation part of equation (7):

$$\psi_D(\mathbf{r}_1, \mathbf{r}_2) = 1 + \delta \sqrt{\rho_1^2 + \rho_2^2 - 2\rho_1 \rho_2 \cos(\theta_1 - \theta_2) + \delta_i(z_1 - z_2)^2}.$$  \hspace{1cm} \text{(9)}$$

The ground state energy of the D$^-$ near a semiconductor–metal interface calculated by using $\psi_D$ in the wavefunction equation (7) is presented in the last column of table 1. Notice that allowing the e–e correlation to be anisotropic does not have a significant influence on the energy, the difference between the energy calculated with and without $\delta_i$ are very small (less than 0.02%). Therefore, in the following we put $\delta_i = 1$ in our calculations.

The D$^-$ binding energy is defined as follows:

$$E_b(d) = E_1 - E_D,$$ \hspace{1cm} \text{Equation (10)}$$

where $E_1$ is the ground state energy of the D$^0$ system [19]. Equation (10) gives the energy that is needed to remove one of the electrons from the donor to infinity. This definition corresponds to the one used for a D$^-$ system in 3D. For a metallic interface, another definition of the binding energy can be used:

$$E_b(d) = E_f + E_1 - E_D,$$ \hspace{1cm} \text{Equation (11)}$$

where $E_f/2R^* = -0.0312$ is the binding energy of an electron with its image near a metallic interface [19, 21]. This is the energy needed to remove one electron from the D$^-$ and bring it to the interface.

The expectation values for the position of electron $i$ in the $z$-direction and in the $\rho$ plane are calculated as $\langle \rho_i \rangle = \int \rho_i \chi_i^2 d\rho$ and $\langle z_i - d \rangle = \int (z_i - d) \chi_i^2 d\rho$, respectively, using only the first part in the total trial function, i.e. $\chi_1 = \psi(z_1) p(z_2) g(\mathbf{r}_1, \mathbf{r}_2) \phi(\mathbf{r}_1, \mathbf{r}_2)$. This allows us to discriminate between the two electrons: one is closely bound to the positive impurity while the other one is very weakly bound. Notice that thanks to our variational wavefunction we are able to separate ‘artificially’ the two electrons. But the variational wavefunction itself considers the two electrons to be indistinguishable because $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1)$.

3. The ground state energy of the D$^-$ center

3.1. Semiconductor–metal interface

The ground state energy, in units of $2R^*$, is shown in figure 3 as a function of the distance of the donor from the interface $d/a_B$. The D$^-$ energy exhibits a shallow minimum around $d \sim 6.5a_B$ and approaches the bulk result $E_{\text{bulk}}/2R^* = -0.5259$ from below for $d \to \infty$. For $d < 6.5a_B$ the D$^-$ energy is a decreasing function of $d$ which is mostly a consequence of the extra constraint that the wavefunction has to be zero at the interface. This can be inferred from the result without image charges (dashed green curve in figure 3). The outer electron of the D$^-$ center becomes bound for $d \geq 1.1a_B$. We considered the second electron bound if the variational parameter $\lambda_2$ is larger than zero and the average position of the electron is not too far from the donor, i.e. $\langle z_2 - d \rangle \ll 10a_B$. For a semiconductor–metal interface, we have two positive image charges from the electrons and only one negative image charge from the donor, so a strengthened electron bound state is expected. This is confirmed by the fact that if we ignore the image charges the second electron becomes only bound when $d \geq 3.2a_B$ (see the dashed green curve in figure 3).

The binding energy is plotted in figure 4 using the two different definitions of the binding energy (equations (10)
The ground state energy (solid red curve) for a $D^-$ system near a semiconductor–metal interface versus the distance of the donor $d/a_B$ from the interface. The dashed green curve represents the results when the image charges are neglected and by black stars we indicate the results when an additional variational parameter $\delta_z$ is included in the e–e correlation term (see equation (9)). For comparison the energies for a neutral donor ($D^0$) (dot-dashed blue curve) and in the absence of the image charges (short-dashed dark red curve) are also shown.

The binding energy (solid red curve) for a $D^-$ center near a semiconductor–metal interface versus the donor–interface distance $d/a_B$. The binding energy in the absence of $E_f$ (the energy of an electron bound to the interface) is shown by the dashed blue curve. The horizontal dashed black line shows the bulk limit of the binding energy. The inset shows the behavior of the binding energy for large $d$ (black circles) which is fitted to the curve $E_b/2R^* = 0.0259 + 0.255a_B/d$ (dashed blue curve).

A clear maximum is found for $d \approx 3.8a_B$ beyond which the binding energy slowly decreases to its $d \rightarrow \infty$ value. This algebraic decrease is due to the interaction with the image charges and is largely a consequence of the $d$-dependence of the $D^0$ energy. For the definition of the binding energy with $E_f = 0$ (blue dashed curve in figure 4) the bulk $D^-$ binding energy $E_{b,\text{bulk}}/2R^* = 0.0259$ is reached from above. Notice that for $d = 3.8a_B$, $E_b/2R^* = 0.0823$ which is a factor 3.18 larger than the bulk $D^-$ binding energy. The large $d$-range is shown in the inset and we found that it can be fitted by the curve $E_b/2R^* = 0.0259 + 0.255a_B/d$.

It is remarkable that in the $D^-$ case the effect of the image charges on its energy almost cancels out for intermediate $d$, while this is not so for the neutral $D^0$ system. In our previous work [19] we found that in the case of a semiconductor–metal interface the contribution of the image terms to the energy of a neutral $D^0$ center is given by $\Delta E = 1/4d$ for large $d$. This is the sum of the contributions arising due to the interaction of the electron with its image (about $-1/4d$) and the interactions of the electron with the donor image as well as the electron image with the donor (each one is about $1/4d$). In figure 1 we show by dashed lines the repulsive interactions between the electrons and the donor image as well as between the donor and the images of the electrons (each line is characterized by the Coulomb energy $1/4d$) and by solid lines the attractive interactions between the electrons and their images (each with the energy $-1/4d$). Now, in the case of the $D^-$, due to the presence of the two electrons (see figure 1), we have twice the energy shift of the single electron problem $2\Delta E = (1/4d)$, and there is also twice a negative shift due to the interaction of each electron with the image of the other electron $2(-1/4d)$ (see equation (5b)). As a result these energy shifts compensate each other, and we find that the energy for $d > 10a_B$ is equal to the energy of the $D^-$ without image charges and is very close to the energy $E_{b,\text{bulk}}/2R^* = -0.5259$ of $D^-$ in the bulk [1]. The same compensation takes place in the case of a semiconductor–dielectric interface where the large $d$ contribution of image terms in the energy of the neutral $D^0$ center is about $-Q/4d$.

The average position of the electrons in the $z$-direction and their extent in the plane parallel to the interface are shown in figures 5(a) and (b), respectively. Notice that one of the electrons, also called the inner electron, follows very closely...
the behavior of the electron bound in the neutral D^0 system. This is very similar to what was found previously for the case of a bulk D^- [7]. The second electron, called the outer electron, is more extended in the \( \rho \)-plane, i.e. its average value \( \langle \rho_2 \rangle \) is about three times larger than for the inner electron. Notice that \( \langle \rho_2 \rangle \) for the outer electron increases rapidly with decreasing \( d \) when \( d < 2a_B \) signaling a rapid decrease of the binding energy and ultimately an unbinding of the outer electron. For \( d > 4.75a_B \) the outer electron is attracted to the interface, i.e. \( \langle z_2 \rangle < d \), as a consequence of the image charges which is responsible for the enhanced D^- binding energy. For smaller \( d \) values we have \( \langle z_2 \rangle > d \) and the outer electron is pushed away from the interface mostly as a consequence of the boundary condition at the interface. This behavior is also illustrated in figure 6 where we show the contour plots of the electron density of the outer and inner electron, i.e. \( |\psi(z, \rho)|^2 = p(z_1)^2 p(z_2)^2 g(\vec{r}_1, \vec{r}_2)^2 \psi(\vec{r}_1, \vec{r}_2)^2 \) with \( r_1, \rho_1 \) and \( (\theta_1 - \theta_2) \) taken as their average value, for \( d/a_B = 2, 5, 9 \). Notice that the electron distribution is asymmetric when the donor is close to the interface and that in such a case a large part of the distribution is found with \( z > d \). In order to illustrate the effect of the electron–electron correlation we show in figure 7 the conditional probability \( P(\vec{r}, \vec{r}_0) = |\psi(\vec{r}, \vec{r}_0)|^2 \). This is the probability to find an electron at position \( \vec{r} \) when the other electron is fixed at position \( \vec{r}_0 \). We fix one of the electrons close to the donor (i.e. it is the inner electron) and put it in three different positions with respect to the interface–donor axis. Notice that the electron (1) has the highest probability to be close to the donor, (2) is repelled by the fixed electron, and (3) has a non-zero probability to be located at \( \vec{r}_0 \). The reason is that the two electrons have opposite spin and therefore the Pauli exclusion principle is not applicable.
Figure 7. The conditional electron probability density of the outer electron where the inner electron is fixed with the D\(^-\) center near a semiconductor–metal interface with \(d/\alpha_B = 3\). The white circles mark out the location of the inner electron, that is (from left to right, in the form \((x/\alpha_B, y/\alpha_B, z/\alpha_B)\) (0, 0, 2), (1, 0, 3) and (0, 0, 4).

Figure 8. The ground state energy (solid red curve) of a D\(^-\) center near a semiconductor–dielectric interface versus the donor–interface distance \(d\). The energy for a neutral donor (D\(^0\)) (dashed blue curve) near a semiconductor–dielectric interface is shown for comparison. The black squares are the \(d\)-values for which we show the electron density in figure 10.

3.2. Semiconductor–dielectric interface

In this subsection we investigate the ground state energy of a D\(^-\) center near a semiconductor–dielectric interface. We used material constants for the semiconductor side corresponding to \(\varepsilon_S = 11.9\) (Si) and for the oxide side \(\varepsilon_O = 3.4\) (SiO\(_2\)).

The potential energy between the particles is still given by equation (1) with corresponding value of \(Q = 0.556\). The results are presented in figure 8 for the ground state energy and in figure 9 for the binding energy. The second electron is bound to the D\(^0\) for \(d \geq 3.5\alpha_B\) which compares to \(d = 3.2\alpha_B\) when we ignore the image charges. This can be explained by the fact that for the D\(^-\) system near a semiconductor–dielectric interface the two electrons induces two negative image charges while they are only attracted by one positive image charge coming from the donor. In figure 8 we also show the energy of the D\(^0\) by the dashed blue curve which corresponds to the situation where the second electron is at infinity. Notice that both curves cross at \(d = 6.3\alpha_B\) and for smaller \(d\)-values the D\(^-\) state has a higher energy and consequently the second electron will be unbound. The binding energy of the second electron to the D\(^0\) is plotted in figure 9 by the solid red curve. This result approaches the bulk result slowly and from below. The inset of figure 9 shows the large \(d\)-behavior which is fitted by the curve \(E_b/2R^* = 0.0259 - 0.145\alpha_B/d\). In figure 10 we show the electron density of the inner and outer electron at \(d/\alpha_B = 5, 6.3\) and 8, corresponding to the black squares marked in figure 8. Notice that the outer electron is much...
Figure 10. The electron density of the $D^-$ center near a semiconductor–dielectric interface at donor distances $d/a_B = 5, 6.3$ and $8$ (see the black squares in figure 8). The top three figures correspond to the inner electron density (when the outer electron is fixed to its average position), whereas the bottom three figures are the densities of the outer electron with the inner electron fixed to its average. Blue (external) and red (central) areas represent low and high probabilities, respectively, and the white area represents almost zero probability.

Figure 11. Similar to figure 8 but now for the $D^-$ and $D^0$ near a semiconductor–vacuum interface.

Further extended in space than the inner electron and is pushed away from the interface.

3.3. Semiconductor–vacuum interface

For the $D^-$ center near a semiconductor–vacuum interface, the material constant is chosen to be $\varepsilon_S = 11.9$ for the semiconductor side and $\varepsilon_O = 1$ for the vacuum side, leading to $Q = 0.845$.

The qualitative behavior for the energy of the $D^-$ and $D^0$ as function of $d$ is similar to the one shown if figure 8. Due to the larger $Q$, the role of the image charges becomes more important and the outer electron becomes bound for $d = 4a_B$. The crossing point between the $D^-$ and $D^0$ curves is pushed to $d = 8.8a_B$ (figure 11). The binding energy is shown in figure 9 by the dashed blue curve. Notice the strongly reduced binding energy as compared to the Si/SiO$_2$ interface and even more so when we compare it with the semiconductor–metal interface case. The large $d$-behavior is shown in the inset which could be fitted by the curve $E_b/2R^* = 0.0259 - 0.218a_B/d$.

4. Conclusion

We proposed a variational approach to investigate the energetics and the wavefunction extent of the spin-singlet ground state of the $D^-$ system that is located near a semiconductor–metal or a semiconductor–dielectric (vacuum) interface. As a trial function we used a modified Chandrasekhar type wavefunction, which differs with the Chandrasekar variational two-electron wavefunction in the following way: (1) it satisfy the boundary condition at the interface and (2) it takes into account all the Coulomb interactions with the image charges. This makes the wavefunction no longer spherical symmetric. This variational approach gives the well-known $d \to \infty$ limit.

We obtained a nonmonotonic behavior of the $D^-$ binding energy as function of donor position near a semiconductor–metal interface with a local maximum for a donor distance from the interface of about $3.8a_B$. For smaller $d$-values the binding energy decreases and for $d < 1.1a_B$ the $D^-$ becomes unbound which is mostly a consequence of the boundary condition of the two-electron wavefunction at the interface. At large $d$ the outer electron is attracted to the interface because of the positive total image charge. For a semiconductor–dielectric (vacuum) interface the $D^-$ binding energy is strongly reduced and is a uniform increasing function of $d$. When the donor moves towards the interface, the energy of the $D^-$ reduces and the system becomes unbound for $d < 3.5a_B$ ($d < 4a_B$) near a Si/SiO$_2$ (Si/vacuum) interface. While for a neutral $D^0$ center near a semiconductor–metal (semiconductor–dielectric)
interference the contribution of the image terms to the binding energy is approximately given by the expression \( \Delta E = 1/4d \left( -Q/4d \right) \) for large \( d \). In the case of the \( D^- \) system, due to the presence of the two electrons, a complete compensation of such terms takes place.

The effect of the dielectric screening on the \( D^- \) binding energy is illustrated in figure 12 where the binding energy is plotted versus \( Q \) for three different positions of the donor from the interface. Here \( Q = (1 - \xi)/(1 + \xi) \) where \( \xi = \varepsilon_O/\varepsilon_S \) is the ratio of the dielectric constants of the material which is located beyond the semiconductor surface and the semiconductor in which the donor is located. Notice that the binding energy decreases with increasing \( Q \). \( Q = -1 \) corresponds to a metal surface and \( Q \approx 1 \) to vacuum. Thus a metallic surface enhances the binding. \( Q = 0 \) corresponds with zero dielectric screening, but note that the result is still influenced by the presence of the interface we imposed that the \( D^- \) wavefunction is zero. Only for \( d \gg a_B \) do we obtain the bulk \( D^- \) binding energy.

After this work was submitted, we found a similar paper [22] very recently published by M J Calderón et al. There the same problem of the \( D^- \) center near an interface was studied theoretically (also experimental measurements were presented) but with a much poorer two-electron wavefunction, where electron–electron correlation was neglected. The authors of [22] cited our work (reference [24] in [22]), which at that moment was available as a preprint arXiv:1005.2315, and mentioned that a more general trial wavefunction for the \( D^- \) system had been proposed in [24] which included Chandrasekhar’s model correlation \( \varphi(r_1, r_2) = (1 + \delta r_{12}) \) and which allows one to obtain more accurate results. In the bulk, the effect of this correlation factor is to increase the binding energy of \( D^- \) from 0.027\( R^* \) obtained in [22] to over 0.052\( R^* \) obtained in our work and in [1]. We should note that this correlation is important also for the small distances \( d \gg a_B \). The account of the factors \( f(z_i) = \exp(-\beta p(z_i)) \) in our trial function which describe the effect of image charges also lead to a strong lowering of the energy as for the \( D^- \) system as well as for the \( D^0 \) [19].

The present calculation was done within the effective mass approximation which is expected to be valid for the considered length scale \( d > a_B \). For a donor very close to the interface, i.e. within three monolayers, the deformation of the lattice close to the interface, i.e. strain relaxation near the donor, may invalidate the effective mass approximation. We also neglected the penetration of the electrons in the metal (and the dielectric) which for the obtained binding energies is expected to be a good approximation. In order to go beyond the present effective mass approximation one can use approaches such as the tight-binding approximation or approaches based on density functional theory.

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