Electronic energy of a hydrogen atom in interaction with an impenetrable surface of a polar crystal

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Abstract. We investigate the behaviour of a hydrogen atom in interaction with the surface of a polar semiconductor. The proton is considered as static and we calculate the binding energy of an electron that cannot penetrate the semiconductor. The interaction of the electron with the surface is described microscopically in terms of electron–phonon and electron–exciton interactions. The electron ground-state energy is calculated using a variational Green function Fock approximation. We find that, when the proton approaches the surface, the electron binding energy decreases dramatically. This decrease is governed by three factors: the deformation of the electron wavefunction that has to vanish at the surface, the screening of the proton charge by the induced dipole moments on the surface and the attraction of the electron to the surface by its image potential. The first effect is found to be the most important when the proton is outside the semiconductor. When the proton is inside the semiconductor, the electron is in a surface image state and the last effect is dominant.

1. Introduction

In this paper, we study the interaction of a hydrogen atom with the surface of a polar semiconductor. We focus more specifically on the long- and medium-range effects of the surface on the electron binding energy. We do not directly investigate the chemisorption itself, the process occurring on the surface involving a mixing of atomic orbitals. The problem is thus modelled as a hydrogen atom interacting with a continuous, polarizable medium occupying half-space. The medium is considered as impenetrable to the electron: the vacuum level lies in the middle of an energy gap. Only the electronic energy is considered. We consider all the possible positions for the proton: inside or outside the crystal. Three effects are analysed: the vanishing of the electron wave function at the boundary, the screening of the proton charge by the semiconductor and the behaviour of the electron in its image potential. Our purpose is to investigate the interrelation between these three effects and to evaluate their relative importance for different positions of the proton. A microscopic approach is used in the paper: the polarization of the crystal is described in terms of an interaction of the electron with the elementary excitations of the crystal that give rise to dipolar moments.

The problem of a hydrogen atom in a semi-infinite space was first studied by Levine in an inert medium for a proton lying on the interface [1]. Later, Shan *et al* solved the problem analytically for an arbitrary position of the proton [2]. More recently, the

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problem was also solved for semi-infinite spaces limited by paraboloidal, hyperboloidal or conical shapes [3]. The more complex problem of a polarizable medium with a plane interface was studied by Babiker and Tilley who used a static point of view [4]. They treated the interaction of the electron and of the proton with the surface in the framework of an electrostatic approach: they used the image potential formalism [5]. They wrote a Schrödinger equation for an electron interacting with its image charge, with the proton and with the image charge of the proton. They then solved this equation numerically for a large static dielectric constant. They obtained the electron ground-state energy and a few excited states for different positions of the proton. They concluded that the surface image states were important for describing the electron behaviour when the electron is in the neighbourhood of the surface.

In this paper, we want to study the interaction of the electron with the proton and with the surface dynamically, from a microscopic point of view. The interaction with the surface is described in terms of electron–phonon and electron–exciton coupling, the two sources of polarization in a polar semiconductor. The proton is treated statically, while the electron, being much lighter, is treated dynamically. The surface effects related to the formation of a chemisorbed state are neglected. The Fock approximation of Matz and Burkey [6] is used to obtain an upper bound to the ground-state energy of the electron. This approximation was previously used to calculate the binding energy of surface states in semiconductors and was found to give good results [7]. Also, in the present case, the electronic recoil effects in the z-direction are neglected and a Gaussian spectrum is used as a variational *ansatz* to simplify the calculations.

In the next section, we derive the microscopic Hamiltonian describing the above system. The Fröhlich Hamiltonian is used as a starting point to describe the electron–phonon and electron–exciton interactions [8, 9]. We then calculate the electron ground-state energy using the Fock approximation. We discuss the limitations of the approach used. In section 3, we present the asymptotic limits of the ground-state energy. Three limits are considered: far inside or outside the crystal and on the surface. In section 4, we present our numerical calculations, the analytical expression for the electron energy being too complicated to be directly interpreted. We give the value of the energy and of the variational parameters as a function of the position of the proton and of the dielectric constants. We also decompose this energy into its three components to understand the different contributions to the ground-state configuration. We finally conclude by summarizing and discussing the above results.

2. The Hamiltonian

We consider an electron and a proton (a hydrogen atom) in interaction with the impenetrable surface of a polar crystal. The surface is thus modelled as an infinite barrier. The interaction of the electron and of the proton with the surface is described microscopically in terms of an electron–surface phonon and of an electron–surface exciton interaction. The electron interaction with the bulk modes does not appear here, the corresponding dipolar moments vanishing outside the crystal [10]. The crystal lies in the $z < 0$ half-space, while for $z > 0$, we have the vacuum. We also consider the proton to be at rest, its mass being much larger than that of the electron. Consequently, only the electronic dynamics is treated in the present paper.

The corresponding Hamiltonian is written in terms of $r = (\rho, z)$, the electronic position,

and of $r_p = (0, 0, z_p)$, the coordinates of the proton [7, 11]:

$$H = p^2 - \frac{2\sqrt{R}}{\sqrt{(z - z_p)^2 + \rho^2}} + \sum_{Q,i} \bar{\omega}_{bi} b^\dagger_{Q,i} b_{Q,i} + \sum_{q,i} \bar{\omega}_{si} a^\dagger_{q,i} a_{q,i} \tag{1}$$

$$+ \sum_{q,i} \left[\bar{\omega}_{si} \, S_{i,q} a_{q,i} \, e^{iq \cdot \rho} \, e^{q|z|} + \mathrm{HC} \right] - \sum_{q,i} \left[\bar{\omega}_{si} \, S_{i,q} a_{q,i} \, e^{-q|z_p|} + \mathrm{HC} \right]$$

$$- \sum_{Q,i} \left[\bar{\omega}_{bi} \, V_{i,Q} b_{Q,i} \sin(q_z z_p) \Theta(-z_p) + \mathrm{HC} \right].$$

In this Hamiltonian, $a_{q,i}$ and $a^\dagger_{q,i}$ are the annihilation and creation operators for surface phonons ($i = 1$, energy $\hbar \omega_{s1}$) and surface excitons ($i = 2$, energy $\hbar \omega_{s2}$ ($\bar{\omega}_{s2} = \omega_{s2}/\omega_{s1}$)) of two-dimensional wavenumber q. The corresponding b operators refer to the bulk excitations of three-dimensional wavevector Q (with energy $\hbar \omega_{b1}$ ($\bar{\omega}_{b1} = \omega_{b1}/\omega_{s1}$) and $\hbar \omega_{b2}$ ($\bar{\omega}_{b2} = \omega_{b2}/\omega_{s1}$)). We use a dimensionless system of units for which the energies are given in terms of $\hbar \omega_{s1}$, the lengths in units of the phonon polaron radius r_{s1} and the masses in units of $2m_e$. $\Theta(z)$ is the step function and, for the surface modes,

$$S_{1,q} = -i \sqrt{2\pi \alpha_{s1} r_{s1}/Sq} \qquad\qquad S_{2,q} = -i \sqrt{2\pi \alpha_{s2} r_{s2}/Sq}$$

$$\alpha_{s1} = e^2 (\bar{\epsilon}_s - \bar{\epsilon}_\infty) \sqrt{m_e/2\hbar^3 \omega_{s1}} \qquad \alpha_{s2} = e^2 \bar{\epsilon}_\infty \sqrt{m_e/2\hbar^3 \omega_{s2}} \tag{2}$$

$$r_{s1} = \sqrt{\hbar/2m_e \omega_{s1}} \qquad\qquad\qquad r_{s2} = \sqrt{\hbar/2m_e \omega_{s2}}$$

$$\bar{\epsilon}_s = (\epsilon_s - 1)/(\epsilon_s + 1) \qquad\qquad \bar{\epsilon}_\infty = (\epsilon_\infty - 1)/(\epsilon_\infty + 1).$$

For the bulk modes, we have

$$V_{1,Q} = -i \sqrt{4\pi \alpha_{b1} r_{b1}/V Q^2} \qquad V_{2,Q} = -i \sqrt{4\pi \alpha_{b2} r_{b2}/V Q^2}$$

$$\alpha_{b1} = e^2 (1/\epsilon_\infty - 1/\epsilon_s) \sqrt{m_e/2\hbar^3 \omega_{b1}} \qquad \alpha_{b2} = e^2 (1 - 1/\epsilon_\infty) \sqrt{m_e/2\hbar^3 \omega_{b2}} \tag{3}$$

$$r_{b1} = \sqrt{\hbar/2m_e \omega_{b1}} \qquad\qquad\qquad r_{b2} = \sqrt{\hbar/2m_e \omega_{b2}}.$$

In these expressions ϵ_s and ϵ_∞ are the static and high-frequency dielectric constants. α_{si} and α_{bi} are the different electron–elementary excitation coupling constants while r_{si} and r_{bi} refer to the different units of length in the polaron problem. V is the volume of the crystal while S is the area of its surface. Finally, we have that the dimensionless Rydberg of the hydrogen atom is given by

$$R = \left(\frac{e^2}{2\hbar \omega_{s1} r_{s1}} \right)^2. \tag{4}$$

The first line of this Hamiltonian contains the electron kinetic energy, the free phonon and free exciton fields and the potential of a single electron interacting with a proton through a Coulomb field. The first term of the second line describes the interaction of the electron with the surface phonon and exciton fields. The second term describes the same interactions for the proton. The last line of H describes the interaction of the proton with the bulk modes. This term is present only if the proton is inside the crystal. The terms containing an interaction of the proton with the excitations of the solid can be diagonalized exactly using the Platzman transform [12]:

$$a_{q,i} = A_{q,i} + S^*_{i,q} \, e^{-q|z_p|}$$

$$b_{Q,i} = B_{Q,i} + V^*_{i,Q} \sin(q_z z_p) \Theta(-z_p). \tag{5}$$

This transform leads to a screening of the proton charge as seen in the resulting Hamiltonian:

$$H' = p^2 + \sum_{Q,i} \bar{\omega}_{bi} B^+_{Q,i} B_{Q,i} + \sum_{q,i} \bar{\omega}_{si} A^+_{q,i} A_{q,i}$$
$$+ \sum_{q,i} \left[\bar{\omega}_{si} S_{i,q} A_{q,i} \, e^{iq\cdot\rho} \, e^{-q|z|} + HC \right] + H_p + H_{im} \tag{6}$$

where

$$H_p = \begin{cases} -\dfrac{2}{\epsilon_s + 1} \dfrac{e^2}{\hbar\omega_{s1} r_{s1} \sqrt{(z-z_p)^2 + \rho^2}} & \text{if } z_p < 0 \\[3mm] -\dfrac{e^2}{\hbar\omega_{s1} r_{s1} \sqrt{(z-z_p)^2 + \rho^2}} + \dfrac{\epsilon_s - 1}{\epsilon_s + 1} \dfrac{e^2}{\hbar\omega_{s1} r_{s1} \sqrt{(z+z_p)^2 + \rho^2}} & \text{if } z_p > 0 \end{cases}$$

and

$$H_{im} = \begin{cases} [(\epsilon_s - 1)/\epsilon_s(\epsilon_s + 1)]e^2/(\hbar\omega_{s1} r_{s1} \, 4|z_p|) & \text{if } z_p < 0 \\[2mm] -[(\epsilon_s - 1)/(\epsilon_s + 1)]e^2/(\hbar\omega_{s1} r_{s1} \, 4|z_p|) & \text{if } z_p > 0. \end{cases}$$

For a defect localized at the surface of the crystal ($z_p = 0$), H' becomes

$$H'(z_p = 0) = p^2 - \frac{2\sqrt{R}}{(\epsilon_s + 1)r} + \sum_{Q,i} \bar{\omega}_{bi} B^+_{Q,i} B_{Q,i} + \sum_{q,i} \bar{\omega}_{si} A^+_{q,i} A_{q,i}$$
$$+ \sum_{q,i} \left[\bar{\omega}_{si} S_{i,q} A_{q,i} \, e^{iq\cdot\rho} \, e^{-q|z|} + CC \right]. \tag{7}$$

For $z = 0$, this Hamiltonian is identical to that studied by Gagnon and Lépine [13].

H' is now the Hamiltonian of an external electron interacting with a proton and with surface phonons and excitons. H_p describes the screened Coulomb potential of the proton if $z_p \leqslant 0$ while for $z_p \geqslant 0$ it consists in the usual vacuum Coulomb potential to which an interaction with the proton image charge has been added. H_{im} describes the interaction of the proton with its image charge [5]. This contribution is a constant for a fixed position of the proton. It does not interfere with the electronic dynamics. Consequently, it will be discarded in the following calculations. We can compare this Hamiltonian to that used by Babiker and Tilley [4]. For $z_p \geqslant 0$, H_p and H_{im} are identical to the corresponding terms found in this paper. However the electron–surface interaction is treated macroscopically by the above authors (image potential approach). In our case, this interaction is treated dynamically, from a microscopic point of view, in terms of electron–phonon and exciton interactions.

The ground-state energy of the above Hamiltonian is calculated using the Fock approximation of Matz and Burkey [6]. This approximation gives an upper bound to the ground-state energy of the Hamiltonian. It is written in terms of the eigenstates ($\{\Psi_\nu(r)\}$) of a model Hamiltonian H_M. This formalism can treat the recoil of the electron interacting with the phonons and the excitons dynamically as has been shown by Elmahboubi and Lépine [7]. It has been previously used to describe an external electron interacting with the surface of a polar crystal [7]. In the present case, this approximation is written as

$$E_0 = \int d^3r \, \Psi_0^*(r) \left[p^2 + H_p \right] \Psi_0(r) + \sum_{\nu,l,q} \int d^3r \, d^3r' \, |\bar{\omega}_{si} S_{i,q}|^2 \, e^{-q(|z|+|z'|)} \, e^{iq\cdot(\rho-\rho')}$$
$$\times \frac{\Psi_\nu(r)\Psi_\nu^*(r')}{E_0 - E_\nu - \bar{\omega}_{si}} \Psi_0(r')\Psi_0^*(r) \tag{8}$$

the summation over ν being a summation over three quantum indices l, m, n.

In the z-direction, the electronic wavefunction is always localized. Far from the surface, it is localized because of the presence of the proton. In the neighbourhood of the surface, it is localized because of its interaction with its image charge. Consequently, the ground-state energy is well separated from the excited states for the z-component of the wavefunction (assuming a model wavefunction that is separable). If the quantum index ν is expanded into three indices l, m, n, the sum over n, the quantum index associated with the z-component of the wavefunction, can then be limited to $n = 0$, the other terms of the summation being much smaller. This is equivalent to neglecting the electronic recoil in the z-direction [7]. It was shown that this approximation can lead to an underestimation of about 10 to 15% for an electron near a surface. In the present case, because of the localizing power of the defect, we expect this approximation to be much better. With this approximation, E_0 is written as

$$
E_0 = \int d^3r \ \Psi_{0,0,0}^*(r) \left[p^2 + H_p \right] \Psi_{0,0,0}(r)
$$

$$
+ \sum_{l,m,i,q} \int d^3r \, d^3r' \, |\bar{\omega}_{si} S_{i,q}|^2 \, e^{-q(|z|+|z'|)} \, e^{iq \cdot (\rho - \rho')}
$$

$$
\times \frac{\Psi_{l,m,0}(r) \Psi_{l,m,0}^*(r')}{E_{0,0,0} - E_{l,m,0} - \bar{\omega}_{si}} \Psi_{0,0,0}(r') \Psi_{0,0,0}^*(r). \tag{9}
$$

To calculate this energy, we write $\Psi_{l,m,0}(r) = \psi_{l,m}(x, y)\phi_0(z)$ and use, for $\psi_{l,m}(x, y)$, a simple two-dimensional harmonic oscillator with β as a variational parameter:

$$
\psi_{l,m}(x, y) = \frac{\beta}{\sqrt{\pi 2^{l+m} l! m!}} H_l(\beta x) H_m(\beta y) \, e^{-\beta^2 \rho^2/2}. \tag{10}
$$

In the z-direction the wavefunction has to vanish at $z = 0$ and $\phi_0(z)$ is written as

$$
\phi_0(z) = N(\delta/\sqrt{\pi})^{1/2} 2\delta z \exp(-\delta^2(z - z_e)^2/2) \tag{11}
$$

where N, the normalization constant is

$$
N = \left[\frac{2\delta z_e}{\sqrt{\pi}} \exp(-\delta^2 z_e^2) + (1 + 2\delta^2 z_e^2)\text{erfc}(-\delta z_e) \right]^{-1/2} \tag{12}
$$

where $\text{erfc}(x)$ is the complementary error function. This wavefunction vanishes for $z \leqslant 0$ because of the infinite barrier at the surface. It corresponds to a bulk harmonic oscillator in its ground state, centred on z_e if the electron is far from the surface (we then expect the electron wavefunction to be centred on the proton ($z_e = z_p$)). If the electron and the proton are close to the surface, or if the proton is inside the semiconductor, we expect to find $z_e = 0$. $\phi_0(z)$ is then the ground-state wavefunction of a half-space harmonic oscillator tied at $z = 0$ and interacting with an infinitely repulsive barrier [7]. In the following, β, δ and z_e are considered as variational parameters. Also, we find for the root mean square distance of the electron from the surface

$$
\langle z^2 \rangle = N^2 \left[\frac{z_e(5 + 2\delta^2 z_e^2)}{\delta \sqrt{\pi}} \exp(-\delta^2 z_e^2) + \frac{1}{2\delta^2}(3 + 12\delta^2 z_e^2 + 4\delta^4 z_e^4)\text{erfc}(-\delta z_e) \right]. \tag{13}
$$

For $z_e = 0$, this is equal to $3/(2\delta^2)$ while for $z_e \to \infty$, we find that it is equal to z_e^2.

With these wavefunctions, E_0 is obtained from equation (9):

$$
E_0 = E_k + E_p + E_s. \tag{14}
$$

In this equation, the kinetic energy (E_k) is

$$E_k = N^2 \left[\frac{\delta z_e}{\sqrt{\pi}} (\delta^2 + 2\beta^2) \exp(-\delta^2 z_e^2) + \frac{1}{2} (2\beta^2 + 3\delta^2 + (4\delta^2\beta^2 + 2\delta^4)z_e^2) \operatorname{erfc}(-\delta z_e) \right].$$

(15)

The contribution of the defect (E_p) is

$$E_p = \begin{cases} -8N^2\beta\delta^3\lambda_0 \displaystyle\int_0^\infty \mathrm{d}z\, z^2 \exp(-\delta^2(z - z_e)^2) \operatorname{erfce}(\beta|z - z_p|) & \text{if } z_p < 0 \\[2ex] -8N^2\beta\delta^3 \displaystyle\sum_\pm \lambda_\pm \int_0^\infty \mathrm{d}z\, z^2 \exp(-\delta^2(z - z_e)^2) \operatorname{erfce}(\beta|z \pm z_p|) & \text{if } z_p > 0 \end{cases}$$

(16)

where

$$\lambda_0 = \frac{2}{\epsilon_s + 1} R^{1/2}$$

(17)

$$\lambda_- = R^{1/2}$$

(18)

$$\lambda_+ = -\frac{\epsilon_s - 1}{\epsilon_s + 1} R^{1/2}.$$

(19)

In the above equations, $\operatorname{erfce}(x) = e^{x^2} \operatorname{erfc}(x)$.

The last component of the ground-state energy is E_s, the energy of interaction of the electron with the excitations of the surface. It is given by

$$E_s = -2\delta^2 N^4 \exp(-2\delta^2 z_e^2) \sum_i \alpha_{si} \sqrt{\bar\omega_{si}^3} \int_0^\infty \mathrm{d}t \int_0^\infty \mathrm{d}q \exp\left(-\bar\omega_{si} t - \frac{2\delta^4 q^2}{B^2}\right)$$

$$\times \left[\frac{2\delta(z_e - q)}{\sqrt{\pi}} + \left(2\delta^2(q - z_e)^2 + 1\right) \operatorname{erfce}(\delta(q - z_e)) \right]^2$$

(20)

where

$$B = \sqrt{\frac{\beta^2}{1 - e^{-2\beta^2 t}}}.$$

For $z_e = 0$, this expression reduces to that previously obtained by Elmahboubi and Lépine to study the electronic surface states near an impenetrable surface [7].

3. Asymptotic limits

It is of interest to estimate a few asymptotic limits of the above expressions to gain an insight into the approximations that have been made. First, we consider the limit when the proton is far from the interface, outside the crystal ($z_p \to \infty$). Then, we expect that $\beta \approx \delta$ and $z_e \approx z_p$. We find

$$E_0 = \frac{3\beta^2}{2} - \frac{4R^{1/2}\beta}{\sqrt{\pi}} + \mathrm{O}\left(\frac{1}{z_p^2}\right)$$

(21)

After minimization, we have

$$E_0 = -\frac{8R}{3\pi} + \mathrm{O}\left(\frac{1}{z_p^2}\right).$$

(22)

where R is the hydrogenic Rydberg (13.6 eV). This energy corresponds to the variational ground-state energy of a hydrogen atom when calculated with a Gaussian wavefunction instead of a coulombic wavefunction ($-8R/3\pi = -11.5$ eV, in dimensional units). The hydrogen atom is unperturbed by the surface, as expected. The corrections to this energy (in $1/z_p^2$) arise from the interaction of the electron with its image charge and with the image charge of the proton.

If the proton is far inside the crystal, E_p becomes ($z_e = 0$ and $z_p \to \infty$):

$$E_p = -\frac{2\lambda_0}{z_p}. \tag{23}$$

This is simply the electrostatic energy between the electron and the proton. It becomes rapidly negligible because of the screening and of the $1/z_p$ behaviour [7]. In this limit, the dominant contribution to the ground-state energy comes from E_s, the surface energy; the electron is bound in a surface image state and the proton has little influence on its energy.

When the proton is on the surface, we expect to have $z_e = z_p = 0$. The ground-state energy then becomes

$$E_0 = \beta^2 + \frac{3}{2}\delta^2 - 8\beta\delta^3\lambda_0 \int_0^\infty dz\, z^2\, e^{-\delta^2 z^2} \text{erfce}(\beta z)$$

$$-2\delta \sum_i \alpha_{si}\sqrt{\bar\omega_{si}^3} \int_0^\infty dt \int_0^\infty dq \exp\left(-\bar\omega_{si}t - \frac{2\delta^2 q^2}{B^2}\right)$$

$$\times \left[\frac{-2q}{\sqrt\pi} + (2q^2 + 1)\,\text{erfce}(q)\right]^2. \tag{24}$$

If the defect is neglected ($\lambda_0 = 0$) and if the strong-coupling limit is taken ($B = \beta$), this expression is identical to that found by Elmahboubi and Lépine [7] for the binding energy of an electron surface state in the strong-coupling limit. If we neglect the interaction of the electron with the polar excitations ($\alpha_{si} = 0$), we find that the minimum lies at $\beta = \delta$. The integration and the final minimization gives

$$E_0 = -\frac{32R}{45\pi}\left(\frac{2}{\epsilon_s + 1}\right)^2 \approx -0.23R\left(\frac{2}{\epsilon_s + 1}\right)^2. \tag{25}$$

If $\epsilon_s = 1$, this is the ground-state energy of a hydrogen atom in a semi-infinite space lying on the interface and calculated variationally with Gaussian wavefunctions. This is to be compared with the exact result: $E_0 = -R/4$ [1, 2].

We also consider, as a reference, the two-dimensional case, when the electron is constrained to move in the plane of the surface ($z = 0$). This limit can be obtained from equation (24) by taking the $\delta \to \infty$ limit and by discarding the z-component of the kinetic energy. We then find

$$E_0 = \beta^2 - 2\sqrt\pi\lambda_0\beta - \sqrt{\frac{\pi}{2}}\beta \sum_i \alpha_{si}\sqrt{\bar\omega_{si}^3} \int_0^\infty dt\, \frac{\exp(-\bar\omega_{si}t)}{\sqrt{1 - \exp(-2\beta^2 t)}}. \tag{26}$$

This expression is identical to that obtained by Gagnon and Lépine [13] for the surface polaron bound to a defect if the excitonic part ($i = 2$), which was not treated in that paper, is discarded.

From these results, we can summarize the behaviour of the above system in the following way. When the proton is far outside the crystal, the ground-state energy is simply that of a hydrogen atom to which a negligible contribution from the surface polarizability (in $1/z_p^2$) is added. When the proton gets nearer to the surface, the electron wavefunction is deformed

in the z-direction, because it has to vanish at $z = 0$. If the crystal is not polarizable, the binding energy ($=-E_0$) is then reduced by a factor of four when the proton is on the surface [1]. If the crystal is polarizable, the electronic energy is further modified, because of two effects: the proton charge is screened by its image charge (this has the effect of reducing the binding energy) and the electron self-energy is increased due to an interaction with its image charge [4, 7]. Finally if the proton is far inside the crystal, the electron is bound into a surface image state [7]; the effect of the proton is then negligible due to screening and to its distance from the electron.

4. Numerical results

The ground-state energy cannot be analysed analytically for the general case. However, equation (14) can be analysed numerically. The following graphs have been calculated for parameters representative of a semiconductor: $\hbar\omega_{s1} = 0.1$ eV, $\hbar\omega_{s2} = 3$ eV and $\epsilon_\infty = 2$. In figure 1, we have plotted the electron ground-state energy as a function of the position of the proton (z_p) for $\epsilon_s = 2.1$, 6.0 and 20. We observe that, when the proton is far outside the crystal, its binding energy depends only weakly on the dielectric constant and is given by equation (22). When the proton approaches the surface, the binding energy decreases rapidly, due to screening effects and because the wavefunction cannot penetrate the surface. This decrease does not depend strongly on the dielectric constants: the distance at which the screening effects occur (at about one Bohr radius from the surface) does not depend on ϵ_s. When the proton is on the surface, the electron energy depends moderately on the static dielectric constant. The screening effects are then at their maximum. Finally when the proton penetrates the solid, the electronic binding energy continues to decrease because the distance between the positive and the negative charge increases. Note that, on this graph, the largest binding energies are obtained for the smallest dielectric constant (2.1) since the screening effects are then smaller. If the curves were extended to larger negative values of z_p, the ground-state energy would tend to the image surface state value as given by Elmahboubi and Lépine [7]. The order of the curves in this limit would be inverted since a large dielectric constant favours the image state.

In figure 2, we plot the two variational parameters β and δ as a function of z_p, for the same set of parameters as in figure 1. We find that far outside the crystal the two parameters are equal. They have the value predicted for a hydrogen atom as obtained from a variational Gaussian spectrum. When the proton approaches the surface, the electron wavefunction in the z-direction is compressed on the surface side of the proton. To reduce the kinetic energy, δ decreases and β increases to maximize the binding energy. This explains the peak in β for z_p near 0.2. This maximum depends only on the distance from the surface and is independent of the dielectric constants. When the proton is on the surface, δ becomes larger than β because the image potential has the same order of magnitude as the Coulomb potential (screened by the surface polarizability) and affects only the value of δ. Note that, if the surface could not be polarized, both parameters would be equal (equation (25)). Finally, when the proton penetrates the crystal, the electronic state tends toward the image state and both parameters decrease, with δ staying larger than β [7].

In figure 3, we plot $\langle z^2 \rangle^{1/2}$ as a function of z_p for the same parameters. It can be seen that $\langle z^2 \rangle^{1/2} \approx z_p$ when the proton is far outside the surface (for $z_p > 0.1$ or one Bohr radius). When the proton approaches the surface (within one Bohr radius), the proton charge screening becomes important and the electron can no longer follow the proton because of the surface barrier. Consequently, $\langle z^2 \rangle^{1/2}$ increases rapidly toward an equilibrium distance determined by the position of the electron with respect to the surface and to the proton.
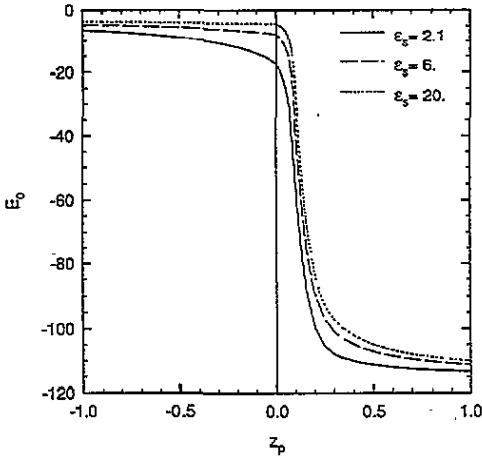
Figure 1. Ground-state energy of the electron as a function of z_p, the distance of the proton from the surface, for $\epsilon_s = 2.1, 6.0$ and 20. Both quantities are in the polaron system of units.
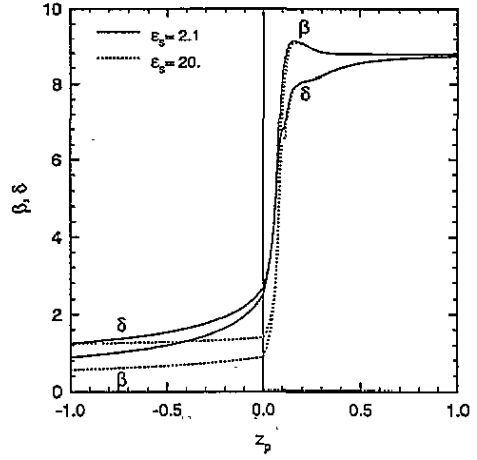
Figure 2. Variational parameters β and δ as a function of z_p, the distance of the proton from the surface, for $\epsilon_s = 2.1$ and 20. All quantities are in the polaron system of units.
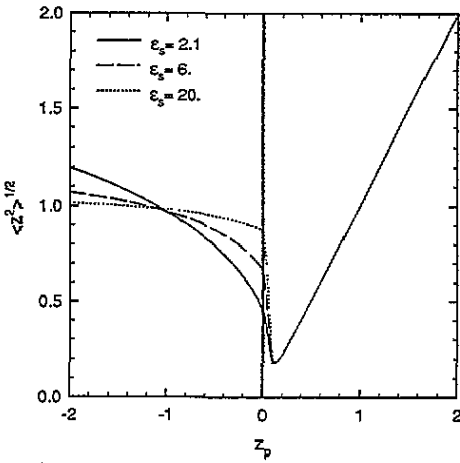

Figure 3. Mean distance of the proton from the surface ($\langle z^2 \rangle^{1/2}$) as a function of z_p, the distance of the proton from the surface, for $\epsilon_s = 2.1, 6.0$ and 20. All quantities are in the polaron system of units.
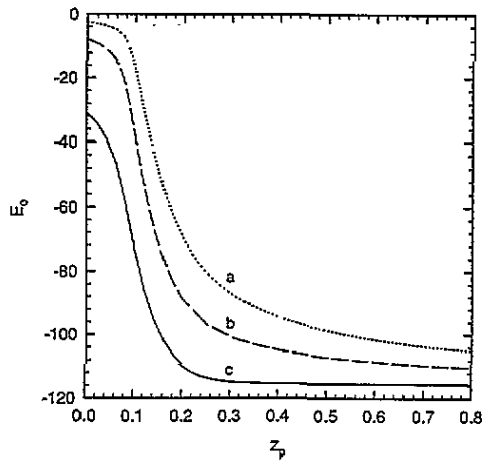
Figure 4. Ground-state energy of the electron as a function of z_p, the distance of the proton from the surface, (a) for $\epsilon_s = 6.0, \epsilon_\infty = 2.0$ with $E_s = 0$ (dotted line), (b) for $\epsilon_s = 6.0, \epsilon_\infty = 2.0$ and $E_s \neq 0$ (dashed line) and (c) for $\epsilon_s = \epsilon_\infty = 1$ (full curve). All quantities are in the polaron system of units.

Finally, when the proton is inside the crystal, the electron is in a bound surface image state at a distance of approximately one polaron radius from the surface (in this case, $\langle z^2 \rangle^{1/2} = \sqrt{3/2}/\delta$). Its position then becomes independent of the position of the proton. Note that for $z_p \lesssim 0.1$, z_e minimizes to zero while for $z_p \gtrsim 0.1$, we find $z_e = z_p$.

These results can be compared to those of Babiker and Tilley who treated the same

problem by solving numerically a Hamiltonian involving an electron in interaction with a proton, with the image charge of the proton and with its own image charge [4]. They found results very similar to ours: a hydrogenic ground-state energy far from the surface and a surface image state when the proton is on the surface. They also found that the electron wavefunction extension was wider in the direction parallel to the plane than in the z-direction, when the proton is on the surface. This is compatible with our result that δ is larger than β when the proton is on the surface.

It is of interest to analyse the different contributions to the ground-state energy of the electron. In figure 4, we plot this energy as a function of z_p, for $z_p > 0$. The curves are drawn for three cases: (a) for $\epsilon_s = 6.0$, $\epsilon_\infty = 2.0$ with $E_s = 0$, (b) for $\epsilon_s = 6.0$, $\epsilon_\infty = 2.0$ and $E_s \neq 0$ and (c) for $\epsilon_s = \epsilon_\infty = 1$. The last case corresponds to a hydrogen atom in half-space. For the three curves, the electronic energy decreases continuously from a value corresponding to the ground state of a hydrogen atom in free space (equation (22)) to that of the ground state of a hydrogen atom on the surface of an impenetrable medium (equation (25)), both calculated with a Gaussian variational spectrum. We note that the effect of the polarizability of the crystal is to decrease the binding energy from case c to case a. These polarizability effects can be divided into two parts: the screening of the proton and the self-energy of the electron in its image potential. The proton screening decreases the electron energy by a factor of about 10 (2.9 eV) for a surface proton as seen if curves a and c are compared. The effect of the electron image energy is to increase the binding energy of the electron as seen from a comparison of curves a and b: the binding energy is increased by 0.4 eV when the proton is on the surface.
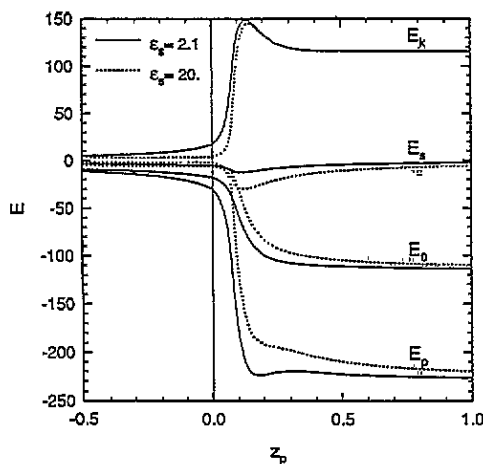

Figure 5. E_0, E_k, E_p and E_s as a function of z_p, the distance of the proton from the surface, for $\epsilon_s = 2.1$ and 20. All quantities are in the polaron system of units.
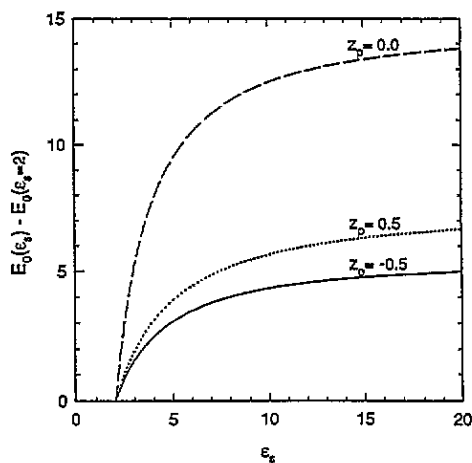
Figure 6. Ground-state energy of the electron as a function of ϵ_s for $z_p = -0.5$, 0.0 and 0.5. All quantities are in the polaron system of units.

In figure 5, we have separated the three different components of the ground-state energy $E_0 = E_k + E_p + E_s$, as a function of z_p. Far outside the crystal, we find that the surface interaction term (E_s) is negligible. The kinetic and the Coulomb terms dominate the electron behaviour. When the proton is far inside the crystal, it is E_s that is the most important term, the electron being trapped in a surface image state. When the proton is in the neighbourhood of the surface, all energies are of the same order of magnitude. Note the maximum in the

kinetic energy around $z_p = 0.1$. This corresponds to the increase in β when the electron wavefunction begins to be compressed by the surface. From that point, when the electron gets nearer to the surface, E_k and E_p decrease rapidly because of the screening of the proton. Corresponding to the maximum of E_k, we also observe a minimum in E_s. This results from the localization of the electron wavefunction and its effect on the image state.

In figure 6, we plot the ground-state energy of the electron as a function of ϵ_s for $z_p = -0.5$, 0.0 and 0.5. We see that the binding energy $(-E_0)$ decreases when the static dielectric constant increases. This is a direct manifestation of the screening effects of the crystal on the charge of the proton. This effect is more pronounced when the proton is on the surface because the screening is then at its maximum. Note that if the proton is far inside the crystal, we have found the binding energy to increase with ϵ_s since in this case the surface energy dominates the Coulomb energy.

5. Conclusions

In this paper, the problem of a hydrogen atom in interaction with the surface of a polar semiconductor is investigated. We assume that the electron cannot penetrate the semiconductor, the vacuum level lying in the middle of an energy gap. The proton is treated as a static particle. We treat the problem from a microscopic point of view, in terms of electron–phonon and electron–exciton interactions. The electron ground-state energy is calculated using the Fock approximation of Matz and Burkey that gives an upper bound to the ground-state energy [6]. This approximation was shown to treat the electron dynamics correctly, to give good results in the calculation of image states and to be valid for any strength of interaction between the electron and the phonons or the excitons [7]. It is expected to give good results as long as the continuum approximation is valid, that is as long as the electron is not too close to the surface. The approach that we use can be compared to that of Babiker and Tilley who treated this problem by numerically solving the Schrödinger equation of an electron in interaction with a proton and with their two image charges [4]. Our results are entirely compatible. In our case we have the advantage of treating the electron interaction with the surface dynamically and being able to analyse the different contributions to the electron binding energy easily.

We have found that three effects are important for the binding of the electron to the proton and to the surface: (1) the reduction in binding energy coming from the screening of the proton charge by its image charge arising from the polarizability of the semiconductor surface, (2) the decrease in binding energy because the electron wavefunction has to vanish at the surface (this increases the kinetic energy of the electron because of the deformation of the wavefunction) and (3) the attraction of the electron by its image charge which has the effect of binding the electron to the surface. Far outside the surface, the electron is strongly bound to the proton. The effect of the surface is negligible. The Coulomb energy between the electron and the proton dominates the binding until the proton reaches a distance of about one Bohr radius from the surface. Then the decrease in Coulomb energy is dramatic (of the order of 95%), the above three effects approaching their maximum. When the proton enters deeply into the semiconductor, the screening of the proton charge is at its maximum and the electron is in a bound surface image state. Note that the electron wavefunction is centred on the external proton until it reaches a distance of about one Bohr radius from the surface.

In conclusion, we have studied the binding energy of a hydrogen atom as a function of the position of the proton with respect to the surface of a semiconductor. We have found that, due to various effects, the ionization energy decreases rapidly when the proton

approaches the surface. When the proton is inside the crystal, the electron becomes bound to the surface while the proton charge is screened by the semiconductor. We have analysed the different components of this reduction in binding energy and found that the deformation of the wavefunction that has to vanish at the surface is determining for the drop in binding energy at one Bohr radius from the surface. This approach is valid as long as the continuum approximation is valid. Thus, it excludes the description of the binding of the hydrogen atom to the surface by the formation of a chemical link. An atomic approach would be necessary to describe the chemisorption. Note also that a guide to the form of the potential curve for hydrogen interacting with the surface of a semiconductor can be obtained by adding the static interaction between the proton and the surface (H_{im}) to the electron binding energy (equation (14)). As the present description is only valid in the continuum approximation and as the proton dynamics is neglected, this approach would only be valid far from the surface.

Acknowledgments

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