

Effect of an image potential on the ground-state energy of shallow-donor impurities near the surface of semi-infinite crystals

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(Received 4 February 1992; revised manuscript received 22 March 1993)*

The effect of image potential on the ground-state energy of a shallow-donor impurity near a sharp surface of a semi-infinite crystal is studied. A simple but realistic trial function is used in the confocal elliptic coordinate system with the foci at the hydrogenic donor impurity and its image point. The ground-state energy of this system is calculated as a function of the impurity position.

I. INTRODUCTION

In recent years, the problems associated with shallow impurities near a sharp planar surface have attracted much attention. Levine¹ investigated theoretically the quantum-mechanical properties for an isolated donor atom located at the surface of a dielectric crystal. Since then, other authors²⁻⁶ have investigated energies and other properties of the donor states. It is important to note that all these authors constrained the impurity atom to lie exactly at the surface.

Realistically, impurities are distributed in the near-interface region, not necessarily localized at the surface. When an impurity atom inside the medium is not too far from the surface, it is no longer possible to solve the Schrödinger equation analytically with proper boundary conditions. A number of authors studied this problem⁷⁻¹¹ variationally; however, they did not consider the effect of the image potential. In this paper, we use a simple but somewhat reasonable trial wave function to study the ground-state energy of shallow-donor impurities near the surface of a semi-infinite crystal. In our calculations, the effect of image potential is taken into account.

II. VARIATIONAL SOLUTIONS OF A HYDROGEN ATOM NEAR AN IMPENETRABLE WALL

Let us first consider a donor impurity embedded in a dielectric crystal. The impurity is near the surface. The distance between the donor impurity and the surface is R . Since the height of the surface barrier is of the order of several eV,¹² and the binding energies of shallow-donor impurities are only of the order of millielectron volts, the surface can be modeled as an infinite potential barrier. This assumption requires that electron wave functions vanish on the surface of the crystal. The effect of finite boundary potentials on the binding energies of donor impurities has been shown to be negligible.^{10,13} Therefore the potential is given by

$$V(r) = \begin{cases} -\frac{e^2}{\epsilon_1 r} & \text{for } r < R \\ \infty & \text{for } r \geq R \end{cases}, \quad (1)$$

where ϵ_1 is the dielectric constant of the crystal, $-e$ is the free-electron charge, and r is the distance of between the electron and the atomic nucleus (Fig. 1), i.e.,

$$r = \sqrt{x^2 + y^2 + (z - R)^2}. \quad (2)$$

In the effective-mass approximation, the Hamiltonian of this system is

$$H = -\frac{\hbar^2}{2m_e^*} \nabla^2 - \frac{e^2}{\epsilon_1 r}. \quad (3)$$

where m_e^* is the electron effective mass.

When an impurity atom is close to the crystal surface, the donor impurity states are also influenced by the distance between the impurity and the surface. As $R \rightarrow \infty$, the solution of the Schrödinger equation should approach the three-dimensional hydrogenic wave function. When $R \rightarrow 0$, it should become the wave function of a hydro-

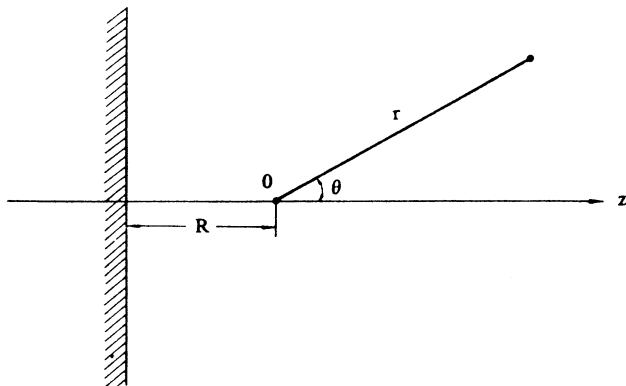


FIG. 1. The coordinate system centered at the hydrogenic impurity. The boundary surface is at $z = -R$.

genlike atom located at the surface of the half-three-dimensional space, i.e., the Levine wave function. Taking these into our consideration, we write the trial wave function of the ground state as

$$\psi(\mathbf{r}, R) = F(\mathbf{r}, R) \phi(\mathbf{r}, \beta), \quad (4)$$

where $\phi(\mathbf{r}, \beta)$ is the ground-state function of a hydrogen atom, i.e.,

$$\phi(\mathbf{r}, \beta) = A \left[\frac{\beta}{a_0^*} \right]^{3/2} \exp \left[-\frac{\beta r}{a_0^*} \right], \quad (5)$$

where $a_0^* = \epsilon_1 \hbar^2 / m_e^* e$, β is the variational parameter, and A is the normalization constant.

Because $V = \infty$ outside the crystal, the wave function satisfies

$$\psi(\mathbf{r}, 0) = 0 \quad \text{when} \quad r \cos \theta = -R. \quad (6)$$

When $r \cos(\theta) = -R$, it equals 0 satisfying the boundary condition Eq. (6). Therefore, $F(\mathbf{r}, R)$ can be selected to be

$$F(\mathbf{r}, R) = R + r \cos(\theta). \quad (7)$$

Thus the trial wave function, Eq. (4) can be written as

$$\psi(\mathbf{r}, R) = A (R + r \cos \theta) \left[\frac{\beta}{a_0^*} \right]^{3/2} \exp \left[-\frac{\beta r}{a_0^*} \right]. \quad (8)$$

In the half-infinite space $z \leq -R$, we have $\psi \equiv 0$, and when $z > -R$, we have a nonvanishing wave function, as expected.

It is convenient at this stage to introduce the confocal elliptic coordinate system. The relations between the confocal elliptic coordinates, (ξ, η, ϕ) , and the cylindrical coordinates read

$$\xi = \{[\rho^2 + (z + 2R)^2]^{1/2} + [\rho^2 + z^2]^{1/2}\} / 2R, \quad (9a)$$

$$\eta = \{[\rho^2 + (z + 2R)^2]^{1/2} - [\rho^2 + z^2]^{1/2}\} / 2R, \quad (9b)$$

$$\phi = \phi, \quad (9c)$$

where

$$z^2 + \rho^2 = r^2, \quad \rho^2 = \chi^2 + y^2, \quad z = r \cos \theta, \quad (10)$$

$$1 \leq \xi \leq \infty, \quad 0 \leq \eta \leq 1, \quad 0 \leq \phi \leq 2\pi. \quad (11)$$

From Eqs. (10) and (11), we obtain

$$r = R(\xi - \eta) \quad (12)$$

and

$$z = R(\xi \eta - 1). \quad (13)$$

Substituting the relations (10)–(13) into the Hamiltonians, H , T , V , and the wave function ψ , we have

$$T = -\frac{\hbar^2}{2m_e^*} \frac{1}{R^2(\xi^2 - \eta^2)} \left[\frac{\partial}{\partial \xi} (\xi^2 - 1) \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta} (1 - \eta^2) \frac{\partial}{\partial \eta} + \frac{\xi^2 - \eta^2}{(\xi^2 - 1)(1 - \eta^2)} \frac{\partial^2}{\partial \phi^2} \right], \quad (14)$$

$$V_1 = -\frac{e^2}{\epsilon_1 R(\xi - \eta)}, \quad (15)$$

$$H = -\frac{\hbar^2}{2m_e^*} \frac{1}{R^2(\xi^2 - \eta^2)} \left[\frac{\partial}{\partial \xi} (\xi^2 - 1) \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta} (1 - \eta^2) \frac{\partial}{\partial \eta} + \frac{\xi^2 - \eta^2}{(\xi^2 - 1)(1 - \eta^2)} \frac{\partial^2}{\partial \phi^2} \right] - \frac{e^2}{\epsilon_1 R(\xi - \eta)}, \quad (16)$$

and

$$\psi = \left[\frac{\beta}{a_0^*} \right]^{3/2} \frac{2\alpha R \xi \eta}{\pi R [4(\alpha^2 + 1) - (\alpha + 2)e^{-2\alpha}]} e^{-\alpha(\xi - \eta)}, \quad (17)$$

where

$$\alpha = \frac{\beta R}{a_0^*}. \quad (18)$$

Using the variational principle, we can obtain the ground-state energies of impurities near the crystal surface as functions of R .

The computed ground-state energies are presently graphically in Fig. 2 [curve (1)], where the energies are in units of effective Rydberg $R_y^* = e^2 / 2a_0^* \epsilon_1$, and R is normalized to the effective Bohr radius a_0^* . From Fig. 2 [curve (1)], it can be seen that the ground-state energy varies remarkably with the distance if R is between a_0^* and $2a_0^*$. For example, the ground-state energy at $R = 0.8a_0^*$ is only one half of that at $R = 0$.

Our results are similar to those obtained by Liu and Lin,⁹ but the physical meaning is clearer and the calculation is simpler. Aside from the effective image potentials, electron-phonon interactions also can be taken into account in our calculations. However, we restrict our dis-

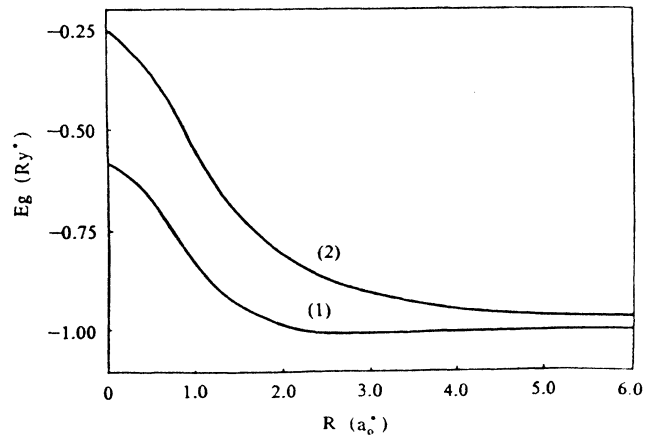


FIG. 2. The ground-state energy of a shallow-donor impurity near the surface as a function of R . Curve (1), the contribution of image potentials is not included. Curve (2), the contribution of the image potentials is included. The energies are in units of the effective Rydberg and distance is in units of the effective Bohr radius.

cussions in this paper only to the effect of image potentials.

III. THE EFFECT OF IMAGE POTENTIALS

We assume that a donor impurity is located at a distance R from the planar interface. The static dielectric constant of the material in the region A , where the impurity atom is contained, is ϵ_1 , and the static dielectric constant in the region B is ϵ_2 . The following calculations are valid for both semiconductor-insulator and semiconductor-vacuum interfaces, if we choose ϵ_1 and ϵ_2 accordingly. The impurity center is chosen as the coordinate origin and the z axis is chosen to be perpendicular to the interface plane. In the effective-mass approximation, the Hamiltonian is

$$H = -\frac{\hbar^2}{2m_e^*} \nabla^2 + V_1 + V_2 + V_3, \quad (19)$$

where V_1 is the screened Coulomb potential, as defined in Eq. (1), V_2 and V_3 are the electron-image-proton interaction and the electron-image-electron interaction, respectively. V_2 and V_3 are found to be

$$V_2 = -\frac{e^2}{\epsilon^*(r^2 + 4R^2 + 4rR \cos\theta)^{1/2}} \quad (20)$$

and

$$V_3 = \frac{e^2}{\epsilon^*(R + r \cos\theta)}, \quad (21)$$

where

$$\epsilon^* = \frac{\epsilon_1(\epsilon_1 + \epsilon_2)}{\epsilon_1 - \epsilon_2}. \quad (22)$$

In the confocal elliptic coordinate system, T and V_1 are expressed by Eqs. (14) and (15), respectively. It is also straightforward to obtain the expressions of V_2 and V_3 in the confocal elliptic coordinate, i.e.,

$$V_2 = -\frac{e^2}{\epsilon^* R (\xi + \eta)} \quad (23)$$

and

$$V_3 = \frac{e^2}{4\epsilon^* R \xi \eta}. \quad (24)$$

Using Eq. (17) as the test wave function, we find the expectation values of the energies are

$$\langle T \rangle = \beta^2, \quad (25)$$

$$\langle V_1 \rangle = -2\beta \frac{\epsilon_1}{\epsilon^*} \frac{1 - 2(1 + \alpha^2)e^{2\alpha}}{2 + \alpha - 4(1 + \alpha^2)e^{2\alpha}}, \quad (26)$$

$$\langle V_2 \rangle = -\beta \frac{\epsilon_1}{\epsilon^*} \frac{(3 + 4\alpha^2)e^{2\alpha} - (3 + 6\alpha + 6\alpha^2 + 2\alpha^3)}{4[4(1 + \alpha^2)e^{2\alpha} - (2 + \alpha)\alpha^3]}, \quad (27)$$

$$\langle V_3 \rangle = \beta \frac{\epsilon_1}{\epsilon^*} \frac{8\alpha e^{2\alpha} + 3 + 2\alpha}{4[4(1 + \alpha^2)e^{2\alpha} - (2 + \alpha)]}, \quad (28)$$

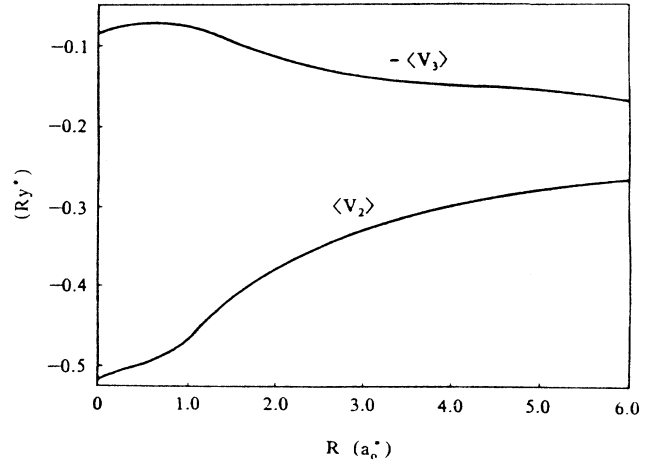


FIG. 3. The interaction energy V_2 (electron-image-nucleus potential) and V_3 (electron-image-electron potential) as functions of the distance from the surface of a symmetric silicon crystal. The energies are in units of the effective Rydberg energy, and R is in units of the effective Bohr radius.

where the energies are in units of effective Rydberg and the distances are given in terms of the effective Bohr radius and $\alpha = \beta R / \alpha_0^*$. Hence the expectation value of the total energy is

$$E = \langle T \rangle + \langle V_1 \rangle + \langle V_2 \rangle + \langle V_3 \rangle. \quad (29)$$

Applying the variational procedures, we obtain the ground-state energies of the impurity atom.

For the sake of simplicity, we assume $\epsilon_1 = 1$. The calculated ground-state energies for a shallow donor near the surface of a symmetric silicon crystal, in which the transverse effective mass equals the longitudinal effective mass, is plotted in Fig. 2 [curve (2)] as a function of the distance of the impurity from the surface, R . Figure 3 shows the contributions of the image potentials, V_2 and V_3 , to the ground-state energy. In Fig. 4, we plot the expectation values of the dipole moment.

From these calculations, we find the following.

(1) Although the contribution of image potentials is small compared with that of the Coulomb interactions, it

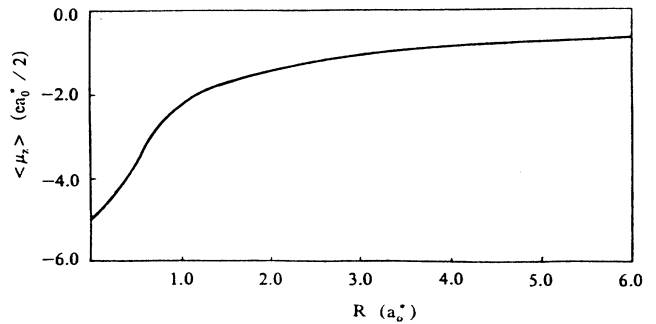


FIG. 4. The expectation value of the dipole moment $\langle \mu_z \rangle$ as a function of R , the distance between the impurity atom and the surface. The dipole moments are in units of $ea_0^*/2$, and R is in units of the effective Bohr radius.

is certainly not negligible, especially when the impurity is very close to the surface. In the case of GaAs, we have $\langle V_2 + V_3 \rangle / \langle V_1 + V_2 + V_3 \rangle = 0.34$, if $R = 0$.

(2) The contribution of the image-proton potential to the ground-state energy is larger than that of the image-electron potential. The former is negative while the latter is positive. Therefore the total contribution of image potentials is equivalent to an increase in the effective nuclear charge.

(3) Because the total contribution of image potentials to the ground-state energy is negative, the presence of the image potentials reduces the ground-state energy and makes the ground-state energy reach the bulk limit $E_g = -E_R^*$ more rapidly.

(4) The effect of the image potential is drastically re-

duced with the increase of the distance from the impurity atom to the interface, as expected. This is because the influence of the interface on the impurity states decreases with the increase of R .

(5) When $R = 0$, the larger the dielectric constant ϵ_1 , the higher the ground-state energy E_g .

(6) When $R = 0$, the expectation value of the dipole moment $|\langle \mu_z \rangle| \neq 0$. This fact indicates that the spherical symmetry of the impurity state is damaged. With increasing R , $|\langle \mu_z \rangle|$ gradually decreases due to the influence of the interface. $|\langle \mu_z \rangle|$ vanishes if R is very large, which means that the deeper the impurity atom, the less the influence of the interface. In other words, when R increases, the ground state of the impurity becomes more spherically symmetric.

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