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Ground states of shallow donor impurities on anisotropic semiconductor surfaces

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Abstract. The surface impurity ground states of anisotropic semiconductors are studied by two different methods, namely the perturbative variational method and the principle of minimal sensitivity which were developed recently. Our treatment is based on (i) a parabolic one-band model and (ii) an infinite-barrier model for electronic states. In spite of the simplicity of the methods, it is found that the calculated energies for Ge and Si are very close to the results obtained by the conventional variational method. The validity of the variational trial wavefunction used in previous calculations is also discussed. A new variational trial function is also proposed for the case of the anisotropic crystals.

1. Introduction

The importance of impurity states in determining the transport and electrical properties of semiconductors has long been recognised. When the donor atom is located on a semiconductor surface the situation is somewhat different from a donor atom located in semiconductor bulk. Levine (1965) introduced this surface shallow impurity problem. He used a Coulombic potential in the material and approximated the work function as being infinite on the vacuum side. The solutions were shown to be the hydrogenic wavefunctions which must satisfy the surface selection rule $l+m=$ odd, where l and m are the orbital and magnetic quantum numbers respectively. Therefore the ground state of a surface donor becomes the 2p state. Later, Bell *et al* (1967) used the same potential but considered the difference between the longitudinal mass and transverse mass. In their work a set of trial functions of the Kohn–Luttinger type (Kohn and Luttinger 1955) were used to calculate the eigen-energies. The importance of image charges was pointed out by Petukhov *et al* (1967) and it was found that the electrostatic-image forces effectively increase the charge of the impurity centre and alter the system of levels. Schechter (1967) pointed out the parameter β used in the image charge potential introduced by Petukhov is too small by a factor of two. Later, several authors (Schechter *et al* 1968, Tefft *et al* 1969, Tefft and Armstrong 1971) calculated the surface effect on shallow impurity states with this altered β and obtained unphysical results. Recently, Jiang and Shan (1985) studied the donor surface impurity states in GaAs and pointed out that the potential energy given originally by Petukhov *et al* (1967) is correct.

The shallow impurity problem is a typical problem in quantum mechanics which cannot be solved exactly. Inevitably properly approximated solutions must be used to obtain quantitative results. Two basic approximation methods are usually used to solve different problems in quantum mechanics, namely the variational method and the perturbation method. In the variational calculation the construction of the trial wavefunction relies heavily on physical intuition. The errors involved are usually difficult to estimate and there is no way to investigate how accurate the trial wavefunction is. On the contrary, the conventional perturbation method can provide a method for systematic corrections of the zeroth-order calculation. However, fast convergence of the perturbation expansion depends strongly on the choice of the small parameter. Frequently, the small parameter is not the obvious one. In this paper we shall exploit two other useful approximation methods which were developed recently to treat the shallow-impurity problem. The first useful method that combines the perturbative method and the variational method was proposed by Lee *et al* (1982), and has been applied to solve the problem of bulk impurity states. Satisfactory results were obtained. The second one is called principle of minimal sensitivity (denoted as PMS), proposed by Stevenson (1981) and is primarily applied to problems in high-energy physics. It asserts that if an approximation depends on parameters of which the true result is known to be independent, then in the absence of

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further information, the approximation is optimised by choosing those parameters so as to minimise the approximation's sensitivity to small variations in their values. Recently Jiang and Shan (1985) applied the perturbative variational method proposed by Lee and co-workers to solve the problem of the shallow states of donor impurity at the surface of isotropic semiconductors and to study the exciton binding energy in superlattice quantum wells (Jiang 1984). Good results were obtained. Although the perturbative variational method, proposed by Lee and co-workers, works very well in the case of isotropic semiconductors, it is still an open question whether this method is feasible to treat the anisotropic case. It is known that the case of impurity on the anisotropic crystal surface is more complicated mathematically and more interesting physically because of the wider possibilities. Therefore, it should be very interesting to extend this method to calculate donor impurity states on the surface of anisotropic semiconductors such as Si and Ge. In order to take into account the anisotropic effect, two parameter trial functions which are products of one-dimensional hydrogenic wavefunctions and two-dimensional hydrogenic wavefunctions are introduced and the principle of minimal sensitivity is exploited.

2. Formulation

The Hamiltonian for the surface-impurity problem is known to be

$$H=-\frac{\hbar^2}{2m_t}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)-\frac{\hbar^2}{2m_l}\frac{\partial^2}{\partial z^2}-\frac{\alpha}{r}+\frac{\beta}{z} \qquad (1)$$

where

$$\alpha=\frac{2e^2}{\varepsilon+1} \qquad \beta=\frac{e^2(\varepsilon-1)}{4\varepsilon(\varepsilon+1)}.$$

The c axis is assumed to be in the z direction, which is normal to the surface. Usually the work function is large compared with the binding energy of the impurity electron and it is approximated as being infinite on the vacuum side. Therefore the wavefunction of the electron must vanish at the surface, i.e.

$$\psi(x, y, z)=0. \qquad (2)$$

It is known that the Schrödinger equation with the Hamiltonian expressed in (1) cannot be solved exactly. Therefore one has to employ some approximation method. As we mentioned in the previous section, we shall apply some novel approximation methods other than the conventional variation or perturbation method to treat the problem.

To make the problem easier to deal with, we first perform a coordinate transformation defined by

$$x=x' \qquad y=y' \qquad z=(m_t/m_l)^{1/2}z'.$$

The Hamiltonian in (1) becomes

$$H=-\frac{\hbar^2}{2m_t}\left(\frac{\partial^2}{\partial x'^2}+\frac{\partial^2}{\partial y'^2}+\frac{\partial^2}{\partial z'^2}\right)$$

$$-\frac{\alpha}{[x'^2+y'^2+(m_t/m_l)z'^2]^{1/2}}+\left(\frac{m_l}{m_t}\right)^{1/2}\frac{\beta}{z'}. \qquad (3)$$

For convenience, we shall drop the prime for the coordinate variables from now on. Then we introduce a parameter λ into H by adding and subtracting a term $\lambda\alpha/r$ to make the Hamiltonian H separate into two parts:

$$H=H_0(\lambda)+H'(\lambda) \qquad (4)$$

where

$$H_0(\lambda)=-\frac{\hbar^2}{2m_t}\nabla^2-\frac{\lambda\alpha}{r}$$

$$H'(\lambda)=\frac{\alpha}{r}\left(\lambda-\frac{1}{(1-\Delta^2\cos^2\theta)^{1/2}}+\frac{\beta'}{\alpha}\frac{1}{\cos\theta}\right)$$

$$\Delta^2=1-(m_t/m_l)$$

$$\beta'=\left(\frac{m_l}{m_t}\right)^{1/2}\beta=(1-\Delta^2)^{-1/2}\beta.$$

The Hamiltonian in (4) contains two parts, i.e. the unperturbed term H_0 and the perturbation term H'. The solutions for the unperturbed Hamiltonian H_0 are the well known hydrogenic wavefunctions. For the H' term one can choose a suitable value λ to make the perturbation expansion converge more quickly.

For illustration, we only consider the ground states here. The excited states can be treated in a similar way. The ground-state wavefunction that satisfies the restriction of (2) can be written as

$$\psi^{(0)}(r;\lambda)=\frac{1}{4\sqrt{\pi}}\left(\frac{\lambda}{a_0}\right)^{5/2}r\cos\theta\exp\left(-\frac{\lambda r}{2a_0}\right) \qquad (5)$$

and the corresponding energy is

$$E_g^{(0)}(\lambda)=-\lambda^2\left(\frac{\alpha}{8a_0}\right) \qquad a_0=\frac{\hbar^2}{m_t\alpha}. \qquad (6)$$

To obtain the total energy for the whole Hamiltonian H, we shall employ two alternative methods to determine the parameter λ.

2.1. The perturbative variational method

We follow the perturbative variational method to find a suitable value of λ which minimises the effect of H'.

The best choice for λ in the calculation of $E_g(\lambda)$ is the one that causes the perturbation series

$$E_g = E_g^{(0)}(\lambda) + \Delta E_g^{(1)}(\lambda) + \Delta E_g^{(2)}(\lambda) + \ldots = E_g^{(0)}(\lambda) + \Delta E_g(\lambda) \quad (7)$$

to converge as fast as possible so that only the first few terms will be used. Hence λ is to be determined by the condition

$$\left| \frac{\Delta E_g(\lambda)}{E_g^{(0)}(\lambda)} \right| = \text{minimum} \quad (8)$$

which can be satisfied by requiring

$$\Delta E_g(\lambda) = 0. \quad (9a)$$

2.2. The principle of minimal sensitivity (PMS)

The main idea of the principle of minimal sensitivity can be stated briefly as follows. In (4), the Hamiltonian H can be divided into two parts $H_0(\lambda)$ and $H'(\lambda)$, where $H_0(\lambda)$ is a function of the parameter λ and can be solved exactly. In spite of the appearance of the parameter λ, the exact result is known to be independent of the choice of the value of λ. However, in most cases only the approximate result is accessible. For instance, if we treat the term H' as a small perturbation, then only a finite number of correction terms can be evaluated. Under this circumstance, in order to obtain the approximation which most closely mimic the exact result's independence of λ, the parameter should be chosen so as to minimise the approximation's sensitivity to small variations in its value. This condition can be satisfied by requiring

$$\frac{\partial A}{\partial \lambda} = 0$$

where A is a physical quantity under consideration. Thus in our case the value of λ can be determined by the condition

$$\frac{\partial E_g}{\partial \lambda} = 0 \quad (9b)$$

where E_g is the total energy given by (7). In actual calculations, only the first-order term (at most up to the second-order term) has to be included in (9*a*) and (9*b*) due to the fast convergence of the perturbation expansion series. For the problem of shallow impurities on the anisotropic semiconductor surface, if we take (5) as our unperturbed ground-state wavefunction. Then the first-order energy correction to the ground state because of the perturbation H' can be calculated as

$$\Delta E_g^{(1)}(\lambda) = \langle \psi_g^{(0)}(r;\lambda) | H'(\lambda) | \psi_g^{(0)}(r;\lambda) \rangle = \tfrac{3}{4}\alpha \left(\frac{\lambda}{a_0}\right) \left(\frac{\lambda}{3} - \frac{1}{2\Delta^3} \times [\sin^{-1}\Delta - \Delta\sqrt{(1-\Delta^2)}] + \frac{\beta'}{2\alpha} \right). \quad (10)$$

The parameter λ can be determined by (9*a*) or (9*b*).

Since the wavefunction in (5) is isotropic while the Hamiltonian given by (1) has highly anisotropic behaviour when the ratio of m_l to m_t is large. The results obtained by the above consideration cannot be expected to be too good. In order to take into account this anisotropic effect, we regroup the Hamiltonian in the following form

$$H = H_{01}(\lambda_1) + H_{02}(\lambda_2) + H'(\lambda_1, \lambda_2) \quad (11a)$$

where

$$H_{01}(\lambda_1) = -\frac{\hbar^2}{2m_t}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \frac{\lambda_1 e^2}{\varepsilon \rho} \qquad \rho = (x^2 + y^2)^{1/2} \quad (11b)$$

$$H_{02}(\lambda_2) = -\frac{\hbar^2}{2m_l}\frac{\partial^2}{\partial z^2} - \frac{\lambda_2 e^2}{\varepsilon z} \quad (11c)$$

$$H'(\lambda_1, \lambda_2) = \frac{\lambda_1 e^2}{\varepsilon \rho} + \frac{\lambda_2 e^2}{\varepsilon z} - \frac{\alpha}{r} + \frac{\beta}{z}. \quad (11d)$$

This is equivalent to dividing the space into a two-dimensional (parallel to the surface) and a one-dimensional (perpendicular to the surface) sub-space. If we take $H_0(\lambda_1, \lambda_2) = H_{01}(\lambda_1) + H_{02}(\lambda_2)$ as the unperturbed Hamiltonian, then the ground-state wavefunction and the energy for the unperturbed system can be written as

$$\psi_g^{(0)}(r;\lambda_1,\lambda_2) = \psi_g^{(01)}(x,y;\lambda_1)\psi_g^{(02)}(z;\lambda_2) \quad (12a)$$

and

$$E_g^{(0)}(\lambda_1,\lambda_2) = E_g^{(01)}(\lambda_1) + E_g^{(02)}(\lambda_2) \quad (12b)$$

respectively, where

$$\psi_g^{(01)}(x,y;\lambda_1) = \left(\sqrt{\frac{2}{\pi}}\right)\gamma \exp(-\gamma\rho) \qquad \gamma = \frac{2m_t e^2}{\varepsilon\hbar^2}\lambda_1 \quad (13a)$$

$$\psi_g^{(02)}(z;\lambda_2) = 2\omega^{3/2} z \exp(-\omega z) \qquad \omega = \frac{m_l e^2}{\varepsilon\hbar^2}\lambda_2 \quad (13b)$$

$$E_g^{(01)}(\lambda_1) = -\frac{2m_t e^4}{\varepsilon^2\hbar^2}\lambda_1^2 \quad (13c)$$

$$E_g^{(02)}(\lambda_2) = -\frac{m_l e^4}{2\varepsilon^2\hbar^2}\lambda_2^2. \quad (13d)$$

The first-order energy correction is now

$$\Delta E_g^{(1)}(\lambda_1,\lambda_2)=\langle\psi_g^{(0)}(r;\lambda_1,\lambda_2)|H'(\lambda_1,\lambda_2)|\psi_g^{(0)}(r;\lambda_1,\lambda_2)\rangle$$
$$=\frac{4m_te^4}{\varepsilon^2\hbar^2}\lambda_1^2+\frac{m_le^4}{\varepsilon^2\hbar^2}\lambda_2^2+\beta\frac{m_le^2}{\varepsilon^2\hbar^2}\lambda_2$$
$$-24\alpha\left(\frac{m_ce^2}{\varepsilon\hbar^2}\right)(a_l\lambda_2)^3(a_t\lambda_1)^2$$
$$\times\int_0^1\frac{u^2\,du}{[a_l\lambda_2u+2a_t\lambda_1(1-u^2)^{1/2}]^4}\quad(14)$$

where $a_t=m_t/m_c$, $a_l=m_l/m_c$ and the total energy is given by

$$E_g(\lambda_1,\lambda_2)=\left(\frac{m_ce^4}{2\varepsilon^2\hbar^2}\right)\left(4a_t\lambda_1^2+a_l\lambda_2^2+\frac{\varepsilon-1}{\varepsilon+1}a_l\lambda_2\right.$$
$$\left.-\frac{96\varepsilon}{\varepsilon+1}(\lambda_2a_l)^3(\lambda_1a_t)^2\int_0^1\frac{u^2\,du}{[\lambda_2a_lu+2\lambda_1a_t(1-u^2)^{1/2}]^4}\right).\quad(15)$$

The best values of λ_1 and λ_2 can be determined by (9).

The above two-parameter approach may implicitly contain a drawback of very small overlapping of the wavefunctions for the x–y plane and the z direction. In other words, the wavefunction of (12a) may over emphasise the anisotropic behaviour of the Hamiltonian. To solve this difficulty, one can turn to the variational approach for help.

To be more specific, let ψ_g and E_g be the wavefunction and the energy of the ground state of the Hamiltonian in (4). Then one can obtain

$$E_g=E_g^{(0)}(\lambda)+E_g(\lambda)\quad(16a)$$

$$\Delta E_g(\lambda)=\frac{\langle\psi_g^{(0)}(r;\lambda)|H'(\lambda)|\psi_g(r)\rangle}{\langle\psi_g^{(0)}(r;\lambda)|\psi_g(r)\rangle}.\quad(16b)$$

If we approximate ψ_g by some variational trial function $\psi_{g,var}$ and substitute it into (16), then the $E_g(\lambda)$ will be improved significantly provided that the variational trial function $\psi_{g,var}$ is constructed very close to the exact wavefunction. The best value of λ can again be determined from (9). Furthermore, the left-hand side of (16a) will be independent of λ when the exact wavefunction is used. Therefore, the variation of

$$E_{g,var}=E_g^{(0)}(\lambda)+\frac{\langle\psi_g^{(0)}(r;\lambda)|H'(\lambda)|\psi_{g,var}(r)\rangle}{\langle\psi_g^{(0)}(r;\lambda)|\psi_{g,var}(r)\rangle}\quad(17)$$

with respect to λ can be used to justify the validity of the variational trial function qualitatively. To test the above statements, we first perform a conventional variation calculation for the Hamiltonian defined in (1) by using an anisotropic trial wavefunction of the Kohn–Luttinger type

$$\psi_{g,var}(r)=N\,z\exp\{-\tfrac{1}{2}[(a_t/a_l)a^2z^2+b^2(x^2+y^2)]^{1/2}/r_0\}\quad(18)$$

where N is the normalisation factor and $r_0=\hbar^2/m_ce^2$. Then using this variational wavefunction as the approximated ground-state wavefunction for H in (17), we can calculate the first-order energy correction to the ground state because of the perturbation Hamiltonian $H'(\lambda)$ as

$$\Delta E_g(\lambda)=\frac{\langle\psi_g^{(0)}(r;\lambda)|H'(\lambda)|\psi_{g,var}(\lambda)\rangle}{\langle\psi_g^{(0)}(r,\lambda)|\psi_{g,var}(r)\rangle}$$
$$=\frac{\alpha}{8a_0}\frac{\lambda F(\lambda)-G(\lambda)+(\beta'/\alpha)I(\lambda)}{K(\lambda)}\quad(19a)$$

where

$$F(\lambda)=\int_0^1\frac{u^2\,du}{(D(u;\lambda))^4}$$
$$G(\lambda)=\int_0^1\frac{u^2\,du}{(1-\Delta^2u^2)^{1/2}(D(u;\lambda))^4}$$
$$I(\lambda)=\int_0^1\frac{u\,du}{(D(u;\lambda))^4}$$
$$K(\lambda)=\int_0^1\frac{u^2\,du}{(D(u;\lambda))^5}$$
$$D(u;\lambda)=\lambda+\{b^2+[(m_t/m_l)a^2-b^2]u^2\}^{1/2}/a_t$$
$$u=\cos\theta.$$

The total energy now is

$$E_{g,var}(\lambda)=E_g^{(0)}(\lambda)+\Delta E_g(\lambda)=-\lambda^2\left(\frac{\alpha}{8a_0}\right)+\Delta E_g(\lambda).\quad(19b)$$

The best value of λ can be determined by setting

$$\Delta E_g(\lambda)=0\quad(20a)$$

or by setting

$$\frac{dE_{g,var}}{d\lambda}=0.\quad(20b)$$

Then the ground-state energy can be obtained by substituting the value of λ in (20).

3. Results and discussion

We consider the shallow impurity problem for the anisotropic semiconductors Si and Ge as a testing example. The physical properties for Si and Ge are listed in table 1. The results of the first-order calculation of the donor impurities on the Si and Ge surface using the isotropic hydrogen wavefunction as the

Table 1. Values of some physical quantities for Si and Ge; m_e represents the true electron mass.

	Mass ratio		Dielectric constant
	$a_t=m_t/m_e$	$a_l=m_l/m_e$	
Si	0.2	1.0	12
Ge	0.082	1.58	16

Table 2. Results of the first-order calculation with λ determined by the perturbative variational criterion and principle of minimal sensitivity.

	Equation for determining λ		Effective Bohr's radius a_0/λ (Å)	Energy (meV)
Si	$E_g(\lambda)=0$	1.098	15.69	−19.41
	$dE_g/d\lambda=0$	1.098	15.69	−19.41
Ge	$E_g(\lambda)=0$	1.043	52.67	−4.201
	$dE_g/d\lambda=0$	1.043	52.67	−4.201

unperturbed wavefunction in both perturbative variational method and the principle of minimal sensitivity are listed in the table 2. It can be seen from the table, both methods yield the same ground-state energies for donor impurities on the surface of Si or Ge semiconductor. The results for the ground state obtained by the anisotropic two-parameter wavefunction defined in (12*a*), (13*a*) and (13*b*) are listed in the fourth column of table 3. Our variational calculation yields better results than those of Tefft *et al* (1969). This is because they used an incorrect image charge potential. From the table one can see the two-parameter perturbative variational method yields worse results than the conventional variational method. This is of course because of the over-emphasis of the anisotropic behaviour of the unperturbed wavefunction. Although the result of the two-parameter case does not supersede that of conventional calculation, however it still gives better results than the one-parameter calculation shown in table 2 as expected. Especially, the result for Ge makes a substantial improvement. This is because that the mass ratio m_l/m_t for Ge is much larger than that for Si. Therefore, the isotropic hydrogenic wavefunctions do yield larger discrepancy in the case of Ge even though the further adjustment has been made via perturbation variational method. On the contrary, since our two-parameter trial function introduces more anisotropic behaviour in the transversal and the longitudinal direction of the system, thus it is able to yield better results than those obtained by the pure hydrogenic wavefunction.

The ground-state energies of the donor impurities on the Si and Ge surface obtained by using the Kohn–Luttinger-type trial wavefunction as the unperturbed wavefunction for both the perturbative variational method and the PMS method are shown in table 4. Although our results and the conventional variational results are very close, it should be noted that compared with the variational method the perturbative variational method and the PMS method are much simpler. The ground-state energies can be calculated quite easily once the value of λ is obtained by (20*a*) or (20*b*). It is interesting to see that the ground-state energies obtained by the method of PMS for both Si and Ge are even lower than the variational results. The results obtained by the perturbative variational method are slightly higher than the variational results and thus no improvement is obtained. This is contrary to the previous results (Lee *et al* 1982) in which Lee and coworkers used the same method to calculate the ground state of the bulk Ge and Si and obtained improved results compared with those obtained by the variational method. This is because our starting Hamiltonian $H_0(\lambda)$ represents a spherical symmetric Hamiltonian which might be very suitable for the case of isotropic semiconductors surface (Jiang and Shan 1985) or for the anisotropic semiconductor bulk (Lee *et al* 1982), however in the anisotropic case such as the surface impurity problems for Ge and Si, the actual Hamiltonian has highly anisotropic behaviour. Furthermore, the trial wavefunction used in (18) might not contain sufficient information for the surface effect. To investigate this problem, we have plotted E_g given in (17) against λ in figure 1. We know that E_g will be independent of λ if the true ψ_g is used to calculate the ground-state energy. Therefore from the flatness of the curves for $E_g(\lambda)$, we can see how good an approximation the trial wavefunction $\psi_{g,var}$ will be compared with the true ψ_g. From figure 1 it is seen that $E_{g,var}$ is found to be constant only over a small range of λ for both Ge and Si. These results suggest that the trial wavefunction used in previous variational calculations is not good enough for calculating the impurity states for anisotropic semiconductor surface. However, it is interesting to note that in figure 1 the curve for Si is flatter than the curve for Ge. It is therefore expected that the results obtained for Si will be better than those for Ge. This is indeed the case as shown in table 4, where the deviation of our calculated energies with the variational result is 2.9% for Ge, but only 0.5% for Si. This is consistent to the fact that the mass anisotropy for Si ($m_l/m_t=5$) is much less than that for Ge ($m_l/m_t=19$). From figure 1 we can also see the reason why the result of the PMS method is better than that of perturbative variational method.

Table 3. Results of variational calculation with the two-parameter trial functions, given by (13).

			Energy (meV)			
				Conventional variational	Effective Bohr radii	
	λ_1	λ_2	Two-parameter	method	1/*A*	1/*B*
Si	0.400	0.273	−19.42	−23.55	11.45	8.083
Ge	0.548	0.136	−6.89	−8.377	26.63	13.60

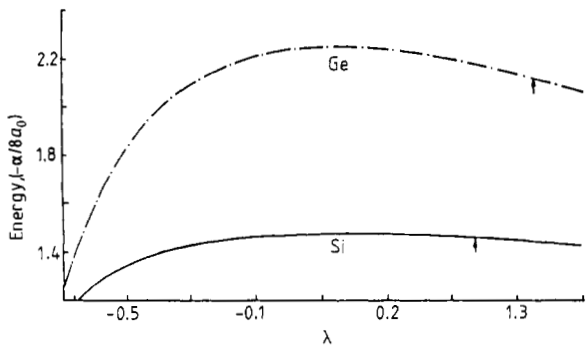

Figure 1. The variation of $E_{g,var}$ in equation (19) with respect to λ for Si and Ge.

The values of λ for the PMS method are the maximum points that will usually fall on the flatness region of the curves, while for the perturbative variational method the values of λ are obtained from (20*a*) which may not fall on the flat ranges as clearly indicated in figure 1.

4. Conclusion

The variational result has been improved by either Lee's approach or Stevenson's principle. The validity of Kohn–Luttinger-type trial functions in the surface impurity problem is also examined in figure 1. They are found to be satisfied in this case, although they do not approximate the exact solutions in the surface case as well as they do in the case of bulk state. The use of three-dimensional hydrogenic wavefunctions yields very poor results for Ge as shown in table 2. However, a substantial improvement can be made by introducing the products of one-dimensional and two-dimensional hydrogenic wavefunctions as our unperturbed wavefunctions. This reveals that the exact solutions for the impurity states in crystals with large anisotropy are no longer three-dimensionally hydrogen-like but somewhat one-dimensionally hydrogen-like in the longitudinal direction and two-dimensionally hydrogen-like in the transverse direction.

In conclusion, we have calculated the surface impurity ground states of anisotropic semiconductors in two novel approximated methods. In this work, the analysis is based on a parabolic one-band model and an infinite-barrier model for electronic states. Thus our treatment neglected any possible effects of the surface-state band structure and assumed the wavefunction of the electron vanishing at the surface. Different trial wavefunctions have been employed. The Kohn–Luttinger-type trial function yielded the best results for different calculations. The simplicity of the perturbative variational method and the principle of minimal sensitivity are exhibited in our calculations.

Table 4. A comparison of the ground-state energies for Si and Ge obtained by the variational method and by the perturbative variational method.

	Equation for determining λ	Values of λ	Energy (meV)	Variational result (meV)
Si	$E_{g,var}(\lambda)=0$	1.206	−23.42	
	$dE_{g,var}/d\lambda=0$	0.487	−23.75	−23.55
Ge	$E_{g,var}(\lambda)=0$	1.451	−8.130	
	$dE_{g,var}/d\lambda=0$	0.461	−8.684	−8.377

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