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Pseudopotential Theory of Shallow-Donor Ground States

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The effective-mass theory of shallow impurity states is given a pseudopotential formulation. A first-principles pseudopotential is constructed accounting for orthogonalization to the impurity core states, spatial dependence of the dielectric constant, and the spatial dependence of the core shielding. Valley-orbit coupling is included, and a correction is made for the energy shift due to the deformation produced by the size difference of the host and impurity atoms. A variational calculation is done for the ground states of P, As, and Sb in Si, and good results are obtained for the lowest ground states (A_1) of P and Sb, poor results for As.

I. INTRODUCTION

The effective-mass theory of shallow impurities given by Kohn and Luttinger[1] agrees well with experiment in the case of the impurity excited states.[2–6] However, there is serious disagreement between theory and experiment in the case of the impurity ground states. The energy levels as determined by far-ir spectroscopy,[7] $|\psi(0)|^2$ as measured by EPR,[8] and also $|\psi(\vec{r}_l)|^2$ as found by electron-nuclear-double-resonance experiments,[8,9] are all poorly predicted by effective-mass theory.

One of the difficulties with the effective-mass theory is that it breaks down if the potential varies rapidly. This is precisely what happens when one tries to account for various central-cell effects,[10] as must be done for the ground state. Morita and Nara[11] have circumvented this difficulty in the case of donors in Si by dividing space about the impurity into two regions. In the outer region, effective-mass theory is valid and in the inner region the complete Schrödinger equation is used, rather than effective-mass theory. They take account of the spatial variation of the dielectric constant, the differing spatial dependence of the core shielding of the host atom and the various impurity atoms, the local distortion of the lattice due to the different size of the host and impurity atoms, of orthogonalization of the impurity wave function to the correct impurity-core wave functions, and of valley-orbit coupling. Their calculated energy levels are a considerable improvement over those calculated by simple effective-mass theory. However, their energy levels are sensitive to the choice of matching radius between the two regions of space, in addition to which there is room for considerable improvement in their values. Furthermore, their calculations do not give wave functions, and hence do not allow analysis of the various resonance experiments. Apart from the first-principles calculations of Morita and Nara, there have also been a number of parametrized treatments of the shallow-donor ground states.[12–14] The advantage of a first-principles treatment is that one can then calculate the real wave functions.

This paper reports on a first-principles calculation using pseudopotential techniques. The corrections to a simple $1/\kappa r$ potential are the same as considered by Morita and Nara, but the screening due to the core electrons is considered far more carefully in this work. In addition, corrections due to the deformation caused by the size differences of the impurity and host atoms are considered. Good results are obtained for P and Sb, but relatively poor agreement with experiment is obtained for As. The near equality of the covalent tetrahedral radii of Si and As suggests that the admixture of higher bands, as proposed by Castner,[15] is responsible. In addition, the large deformation correction for Sb indicates that a more careful treatment of this effect than given here is needed.

In Sec. II the pseudopotential formulation used in this calculation is given. In Sec. III, the impurity potential is developed. The repulsive potential is calculated in Sec. IV, and the results given in Sec. V.

II. PSEUDOPOTENTIAL FORMULATION OF EFFECTIVE-MASS THEORY

The starting point for this calculation is a pseudopotential band calculation for the perfect crystal. The pseudopotential used is similar to the original Phillips–Kleinman pseudopotential[16]

$$V_R\varphi_{n\vec{k}} = -\sum_{c,r_i} E_c[\psi_c(r_i),\ \varphi_{n\vec{k}}]\,\psi_c(r_i), \tag{2.1}$$

where the bottom of the conduction band is taken to have zero energy. V_R is the repulsive potential, $\varphi_{n\vec{k}}$ is a pseudo-band wave function, the E_c are the core energy levels, and the $\psi_c(r_i)$ are the core wave functions of the atom at site r_i. The sum is over the core levels and over the atoms making up the crystal.

This form of pseudopotential is Hermitian and hence the $\varphi_{n\vec{k}}$ form a complete set as they are the eigenfunctions of the Hermitian pseudo-Hamiltonian H_p:

$$H_p\varphi_{n\vec{k}} = (H_0 + V_R)\,\varphi_{n\vec{k}} = E_n(\vec{k})\,\varphi_{n\vec{k}}\ . \tag{2.2}$$

The impurity states are solutions of the Schrödinger equation

$$H\psi = (H_0 + U)\,\psi = E\psi\ , \tag{2.3}$$

where U is the perturbing potential. The wave function can be written in terms of the pseudo-impurity wave function φ:

$$\psi = \varphi - {\sum_{c,r_i}}'[\psi_c(r_i),\ \varphi]\,\psi_c(r_i) - \sum_t (\psi_t,\ \varphi)\,\psi_t\,, \tag{2.4}$$

where the prime on the summation sign denotes the omission of the impurity site in the sum over the host cores, and ψ_t are the impurity-core wave functions. In this manner we have constructed a wave function that is orthogonal to the impurity core states at the impurity site, but orthogonal to the host core states at the other crystal sites. The impurity repulsive potential is

$$V'_R\,\varphi = -{\sum_{c,r_i}}' E_c[\psi_c(r_i),\ \varphi]\,\psi_c(r_i) - \sum_t E_t(\psi_t,\ \varphi)\,\psi_t\,. \tag{2.5}$$

The shallow impurity energies E are much less than the core energies and are therefore neglected. Since the $\varphi_{n\vec{k}}$ form a complete set, φ can be expanded in them:

$$\varphi = \int \sum_n a_n(\vec{k})\,\varphi_{n\vec{k}}\,d\vec{k}\ . \tag{2.6}$$

Therefore

$$\begin{aligned} V'_R\,\varphi &= \int \sum_n a_n(\vec{k})\,V_R\,\varphi_{n\vec{k}}\,d\vec{k} - \sum_t E_t(\psi_t,\ \varphi)\psi_t \\ &\quad + \sum_n \int a_n(\vec{k})\,E_c[\psi_c(0),\ \varphi_{n\vec{k}}]\,\psi_c(0) \\ &= V_R\,\varphi + \sum_c E_c(\psi_c,\ \varphi)\,\psi_c - \sum_t E_t(\psi_t,\ \varphi)\,\psi_t\,, \end{aligned} \tag{2.7}$$

where it is assumed that V_R is not k dependent in the region of k space in which $a_n(\vec{k})$ is nonzero. The final sum over the host core states in (2.7) is for a host atom located at the impurity site. The impurity problem now has been transformed to the solution of the following pseudo-wave equation:

$$\begin{aligned} (H_0 + U + V'_R)\,\varphi &= \left(H_p + U + \sum_c E_c(\psi_c,\ \varphi)\,\frac{\psi_c}{\varphi} - \sum_t E_t(\psi_t,\ \varphi)\,\frac{\psi_t}{\varphi}\right)\varphi \\ &= (H_p + U_p)\,\varphi = E\varphi\ , \end{aligned} \tag{2.8}$$

where U_p is a pseudo-difference potential. If one now proceeds to develop a pseudo-effective-mass equation in complete analogy with the procedures of Kohn and Luttinger,[1] an effective-mass equation is obtained:

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2+U_p\right)F=EF\ , \tag{2.9}$$

$$\varphi=F\,\varphi_{n\vec{k}_i}\ , \tag{2.10}$$

where $\varphi_{n\vec{k}_i}$ is the pseudo-band wave function at the conduction-band minimum located at $\vec{k}=\vec{k}_i$.

If one then includes valley-orbit coupling, following Twose,[17] the following coupled equations are obtained (taking the effective mass to be isotropic):

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2+U_p-E\right)\alpha_j F_j(\vec{r}) +\sum_{l\neq j}\alpha_l e^{i(\vec{k}_l-\vec{k}_j)\cdot\vec{r}}\left(-\frac{\hbar^2}{2m^*}\nabla^2+U_p-E\right)F_l(\vec{r})=0. \tag{2.11}$$

The wave function φ is given by

$$\varphi=\sum\alpha_j F_j(\vec{r})\,\varphi_{n\vec{k}_j}(\vec{r})\ , \tag{2.12}$$

where the sum is over the various degenerate conduction-band minima from which the donor wave functions are constructed. The α_j are determined from symmetry considerations.

III. IMPURITY POTENTIAL

The impurity potential of Nara and Morita[18] is used in this work, but with the core screening approximated more carefully. The impurity potential is

$$U(\vec{r})=\frac{1}{(2\pi)^3}\int d\vec{k}\,e^{-i\vec{k}\cdot\vec{r}}\,\frac{v_d(\vec{k})}{\epsilon(\vec{k})}\ , \tag{3.1}$$

where $v_d(\vec{k})$ is the Fourier transform of the unscreened donor potential and $\epsilon(\vec{k})$ is the wave-number-dependent dielectric constant. Nara and Morita approximate $\epsilon(\vec{k})$ by the function

$$\frac{1}{\epsilon(k)}=\frac{Ak^2}{k^2+\alpha^2}+\frac{Bk^2}{k^2+\beta^2}+\frac{C\gamma^2}{k^2+\gamma^2}\ , \tag{3.2}$$

where

$$\alpha=0.7572,\quad \beta=0.3123,\quad \gamma=2.044,$$
$$A=1.175,\quad B=-0.175,\quad C=1/\epsilon(0)=0.08547,$$

and $\epsilon(0)$ is the static dielectric constant of Si. The unscreened impurity potential is

$$v_d(r)=V(r;\,Z_d^{5+})-V(r;\,Z_{\mathrm{Si}}^{4+}), \tag{3.3}$$

where $V(r;\,Z_j^{n+})$ is the core potential of the n-fold ionized atom with atomic number Z_j. Nara and Morita approximate $V(r;\,Z_j^{n+})$ by

$$V(r;\,Z_j^{n+})=[n+(Z_j-n)e^{-\sigma_j r}](-e^2/r)\ . \tag{3.4}$$

The σ_j are tabulated in Table I.

Castner has calculated a different set of σ_j,[15] obtained by fitting the screening functions calculated from Hartree–Fock calculations with a function of the form (3.4) at $r=0$. These σ_j are also tabulated in Table I. One can express $U(r)$ in the form

$$U(r)=-(2/r)\,Q_d(r). \tag{3.5}$$

The $Q_d(r)$ calculated using both the Nara–Morita and the Castner σ_j are plotted in Figs. 1(a)–1(c) for P, As, and Sb impurities in Si. Since these two sets of screening functions give very different screening functions $Q_d(r)$, it was felt that a more careful approximation of the screening was necessary.

Green, Sellin, and Zachor[19] have developed the following screened potential for neutral atoms:

$$V(r)=-(2/r)\{1+(Z-1)\times[(e^{r/d}-1)H+1]^{-1}\},\quad H=d(Z-1)^{0.4} \tag{3.6}$$

where d is a parameter. They solved the one-electron problem with this potential numerically, and determined d so as to minimize the differences

TABLE I. Core-screening constants σ_j (in units of a_0^{-1}).

	Si	P	As	Sb
Nara and Morita (Ref. 18)	4.28	4.75	3.57	3.29
Castner (Ref. 15)	2.380	2.470	3.225	3.75
This work (small r)	1.933	1.927	2.609	2.697
This work (large r)	1.581	1.546	1.942	1.769
This work (small r)				
$\sigma(1)_j$	4.2625	4.2841	5.6671	5.9686
$\sigma(2)_j$	1.31981	1.26457	1.64524	1.3842
$A(1)_j$	0.443817	0.468068	0.501603	0.59714
$A(2)_j$	0.556183	0.531932	0.498397	0.40286
This work (large r)				
$\sigma(1)_j$	1.233321	1.164342	1.516216	1.171989
$\sigma(2)_j$	3.3353	3.2832	4.2071	3.991520
$A(1)_j$	0.459531	0.426201	0.391577	0.2681860
$A(2)_j$	0.540469	0.573799	0.608423	0.7318140

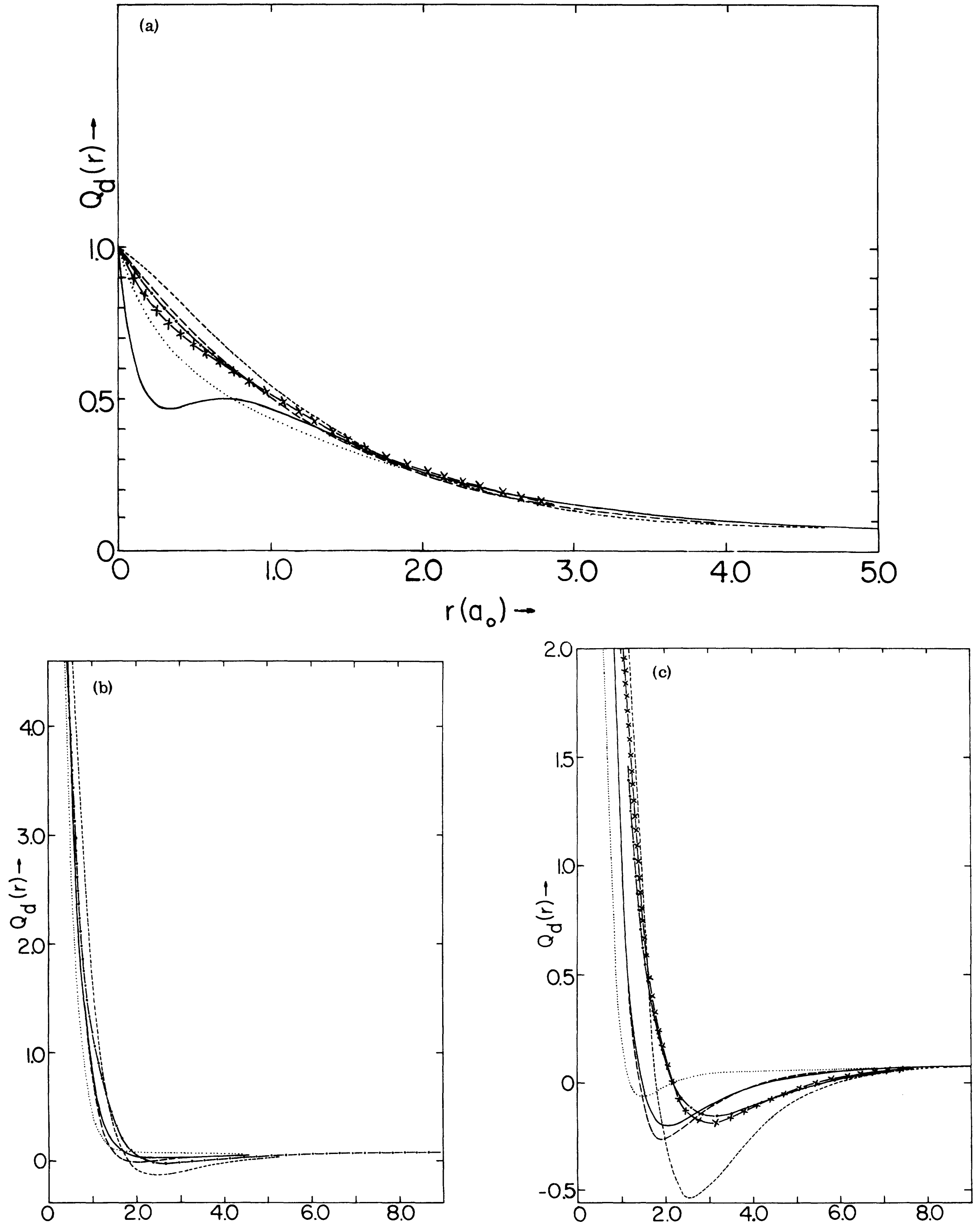


FIG. 1. Impurity potential (a) P in Si, (b) As in Si, and (c) Sb in Si. $Q_d = -rU(r)/e^2$, where $U(r)$ is the impurity potential. ——, Morita and Nara (Ref. 11); • • •, Castner (Ref. 15); — — single exponential (small r); - - -, single exponential (large r); —×—, two exponential (small r); —•—, two exponential (large r). The two exponential fits for As both coincide when drawn to the scale of this graph.

between the one-electron energy levels of this potential and the Hartree-Fock values. (The values of d obtained by Green *et al.* for Si, P, As, and Sb are 0.817, 0.868, 0.663, and 0.870, respectively.) Unfortunately, this potential cannot be Fourier transformed in closed form and hence cannot be directly used to calculate the impurity potential. Thus the approach was adopted of fitting this potential by a simple screening function of the form (3.4), with $n = 1$ for the neutral atom, the assumption being made that the screening constant for the ion in the crystal is the same.

This fit was accomplished in two ways. First, there was the "small-r fit," in which the value of σ_j was adjusted to minimize the function

$$Q = \sum_i \left| e^{-\sigma_j r_i} - [(e^{r_i/d} - 1)H + 1]^{-1} \right| , \tag{3.7}$$

where the r_i ranged from $0.0 \leqslant r \leqslant 3.0a_0$ in steps of $\Delta r = 0.01a_0$. The values of the σ_j so obtained are tabulated in Table I. In addition, there was the "large-r fit," in which σ_j was adjusted to minimize the function

$$Q' = \sum_i \left| \log_{10}(e^{-\sigma_j r_i}) - \log_{10}[(e^{r_i/d} - 1)H + 1]^{-1} \right| , \tag{3.8}$$

where the r_i range from $0.0 \leqslant r \leqslant 3.0a_0$. These values of σ_j are also tabulated in Table I.

Figures 1(a)–1(c) show that the impurity screening functions thus obtained differ greatly for the two fits. This suggested that a two-exponential fit was necessary in order adequately to approximate (3.6) over a wide range of r. Therefore, Eq. (3.4) was replaced by

$$V(r;\ Z_j^{n+}) = \{n + (Z_j - n)[A(1)e^{-\sigma_j(1)r} + A(2)e^{-\sigma_j(2)r}]\}(-e^2/r), \quad A(1) + A(2) = 1. \tag{3.9}$$

TABLE II. Parameters for $Q_d(r)$ (small-r fit) (a_n in units of a_0^{-1}).

	P	As	Sb
A_1	0.880 59	−0.155 19	−5.2749
A_2	−0.172 08	−0.138 15	−0.049 791
A_3	−0.002 121 9	−2.5913	−1.9971
A_4	4.7357	14.1579	27.6713
A_5	9.4889	21.6578	30.5815
A_6	−4.4906	−4.4906	−4.4906
A_7	−9.5259	−9.5259	−9.5259
a_1	0.7572	0.7572	0.7572
a_2	0.3123	0.3123	0.3123
a_3	2.044	2.044	2.044
a_4	4.2841	5.6671	5.9686
a_5	1.264 57	1.645 24	1.3842
a_6	4.2625	4.2625	4.2625
a_7	1.319 81	1.319 81	1.319 81

TABLE III. Parameters for $Q_d(r)$ (large-r fit) (a_n in units of a_0^{-1}).

	P	As	Sb
A_1	0.737 79	−0.164 08	−7.0760
A_2	−0.171 48	−0.136 94	−0.037 165
A_3	0.025 437	−1.3794	−0.293 86
A_4	8.4135	17.2434	24.1285
A_5	5.7972	17.2396	34.0811
A_6	−8.4244	−8.4244	−8.4244
A_7	−5.4636	−5.4636	−5.4636
a_1	0.7572	0.7572	0.7572
a_2	0.3123	0.3123	0.3123
a_3	2.044	2.044	2.044
a_4	1.164 342	1.516 216	1.171 989
a_5	3.2832	4.2071	3.991 52
a_6	1.233 321	1.233 321	1.233 321
a_7	3.3353	3.3353	3.3353

Again, large-r and small-r fits were obtained, analogously to the method outlined in Eqs. (3.7) and (3.8), but with $e^{-\sigma_j r}$ replaced by $A(1)e^{-\sigma(1)r} + A(2)e^{-\sigma(2)r}$, and with the range of r for the large-r fit expanded to $0.0 \leqslant r \leqslant 6.0a_0$. The resulting screening constants are given in Table I. The assumption is again made that this screening function is appropriate for the ionized impurity in the crystal, and the impurity potentials constructed. The resulting screening functions $Q_d(r)$ are also plotted in Figs. 1(a)–1(c) and the two fits can be seen to agree much more closely than the various single-exponential fits. It is evident that the repulsive nature of the impurity potential for Sb for $2.25a_0 < r < 5.5a_0$ is real, and in addition the impurity potential for As in Si, is also repulsive in the range $2.25a_0 < r < 3.25a_0$.

$Q_d(r)$ has the form

$$Q_d(r) = C + \sum_1^7 A_n e^{-a_n r} , \tag{3.10}$$

where $C = 0.08547 = 1/\epsilon(0)$. The A_n and a_n are tabulated in Tables II and III for both fits of two-exponential screening functions.

IV. REPULSIVE POTENTIAL

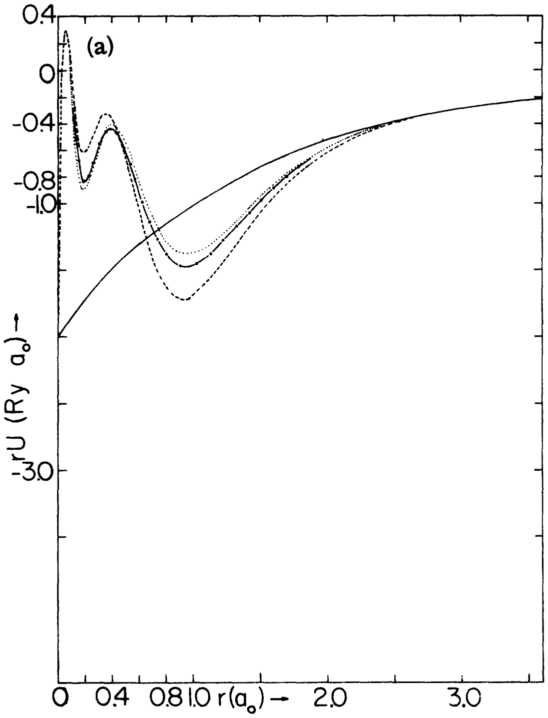
The repulsive potential, from Eq. (2.8), is

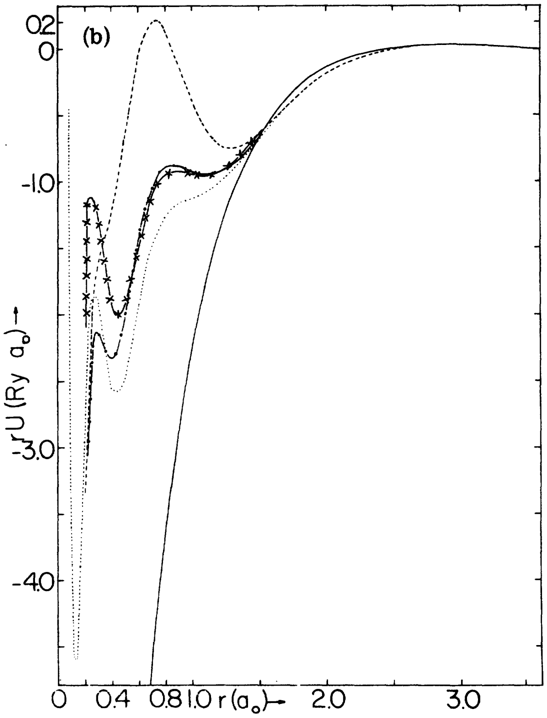
$$V'_R = \sum_c E_c(\psi_c,\ \varphi)\frac{\psi_c}{\varphi} - \sum_t E_t(\psi_t,\ \varphi)\frac{\psi_t}{\varphi} , \tag{4.1}$$

where the ψ_t and E_t are the core wave functions and core energies of the impurity, while the ψ_c and E_c are those of the silicon atom, and φ is the impurity pseudo-envelope function. For the ground state, φ can be well approximated by a constant in the core region. We then have

$$V'_R = \sum_c E_c(\psi_c,\ 1)\psi_c - \sum_t E_t(\psi_t,\ 1)\psi_t. \tag{4.2}$$

The E_c and E_t were obtained from the Hartree-Fock calculations of Mann.[20] The values of $(\psi_c, 1)$





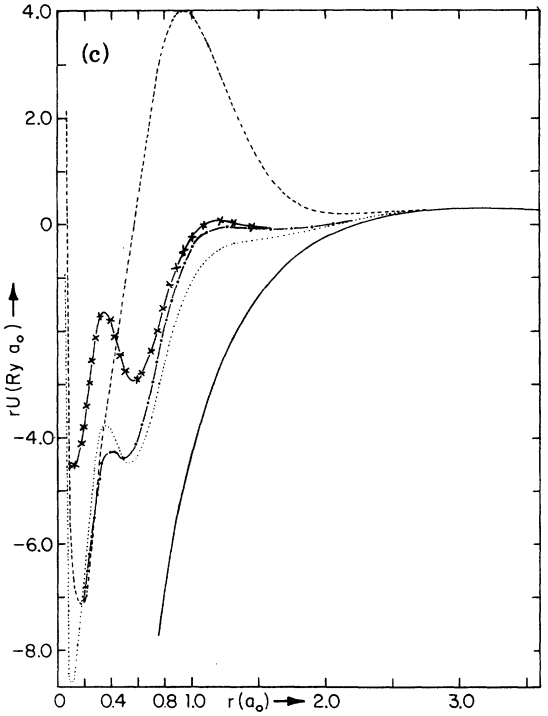


FIG. 2. Pseudopotentials (in Ry-a_0). (a) P in Si, (b) As in Si, and (c) Sb in Si. ——, $rU(r)$; ---, $rU_p(r)$ [approximation (1)]; •••, $rU_p(r)$ [approximation (2)]; —•—, $rU_p(r)$ [approximation (3)]; —×—, $rU_p(r)$ [approximation (4)]. Approximations (3) and (4) coincide for P in Si when drawn to the scale of this graph because of the small relativistic core shifts of P and Si.

and (ψ_t, 1) were obtained by numerically integrating Mann's wave functions.[21]

In the construction of V_R', analytic approximations to ψ_c and ψ_t were used as this greatly simplifies the calculation of the energy. The particular wave functions used are those of Burns,[22] which have the form (for s functions)

$$\psi_n = N r^{n-1} e^{-a_n r}. \tag{4.3}$$

TABLE IV. Hartree-Fock energies of s-like core states E_{ns}, dielectric core shifts of s-like core states ΔE_d, and relativistic core shifts of s-like core states ΔE_r, in Ry.

	Si	P	As	Sb
E_{1s}[a]	−137.64	−159.98	−865.20	−2171.2
ΔE_d	4.79	5.11	8.47	12.7
ΔE_r	−0.35	−0.48	−13.1	−82.6
E_{2s}[a]	−12.326	−15.057	−112.65	−329.54
ΔE_d	3.481	3.805	7.27	11.55
ΔE_r	−0.052	−0.073	−2.93	−20.24
E_{3s}[a]			−16.089	−67.296
ΔE_d			5.013	9.395
ΔE_r			−0.469	−4.185
E_{4s}[a]				−12.150
ΔE_d				6.058
ΔE_r				−0.808

[a] See Ref. 20.

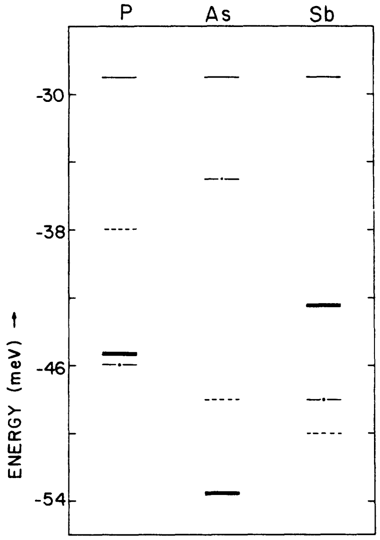


FIG. 3. Ionization energies (in meV) for the lowest (A_1) ground states of P, As, and Sb in Si. ▬, experiment, (Ref. 7); ——, effective-mass theory (Ref. 1); ---, Morita and Nara (Ref. 11); —·—, this work.

The Burns functions differ from Slater functions in that n is an integer, and the values of the a_n are chosen to provide a good approximation to the Hartree-Fock wave functions. The ψ_n were then orthogonalized to each other and these orthogonalized core functions used to compute V_R'.

As a refinement to this V_R', the effect of the dielectric shielding of the medium on the core states was considered by means of a perturbation calculation. The perturbation for the isolated neutral atom was taken to be

$$V' = \frac{1}{(2\pi)^3} \int d\vec{k} \frac{e^{-i\vec{k}\cdot\vec{r}}}{\epsilon(k)} \times \left[\int d\vec{r}' e^{i\vec{k}\cdot\vec{r}'} V(r', Z_j^{\mathrm{H}}) \right] - V(r', Z_j^{\mathrm{H}}) . \quad (4.4)$$

The main effect of this perturbation is a core shift ΔE_d. A somewhat smaller further correction is obtained by calculating perturbed Burns functions for the core states $\psi_c'^B$, and recalculating the integrals $(\psi_c, 1)$. This gives a new repulsive potential

$$V_R'' = \sum_c E_c' (\psi_c^{\mathrm{HF}}, 1) \frac{(\psi_c'^B, 1)}{(\psi_c^B, 1)} \psi_c - \sum_t E_t' (\psi_t^{\mathrm{HF}}, 1) \frac{(\psi_t'^B, 1)}{(\psi_t^B, 1)} \psi_t , \quad (4.5)$$

where $E_c' = E_c + \Delta E_d$, ψ_c^{HF} is the Mann-Hartree-Fock wave function, and the ψ_c^B are the unperturbed Burns wave functions. One further correction was the inclusion of relativistic shifts ΔE_r in the core shifts. In Figs. 2(a)-2(c) are plotted $U(r)$ and $U_p(r)$ for P, As, and Sb impurities in Si, respectively. $U_p(r)$ is plotted in four approximations: (1) unperturbed, (2) dielectric core shifts included, (3) dielectric core shifts and dielectric perturbed wave functions included, and (4) dielectric and relativistic core shifts and dielectric perturbed wave functions included. In Table IV are tabulated the Hartree-Fock energies of the s-core states,[20] the dielectric core shifts ΔE_d calculated from Eq. (4.4) to first order, and the relativistic core shifts ΔE_r calculated by taking $(E_{ns})_{\mathrm{rel}} - (E_{ns})_{\mathrm{nonrel}}$[23,24] in the Herman-Skillman approximation to the Hartree-Fock equations.

V. RESULTS

Using the impurity pseudopotential constructed from Eqs. (3.5), (3.10), and (4.5), and trial functions of the form

$$F = N(e^{-\delta r} + \epsilon e^{-\varphi r}) , \quad (5.1)$$

variational solutions to the effective-mass equations (2.11) were obtained. For the E and T_1 states ($\epsilon = 0$)

$$\begin{aligned} A_1 &: \quad \alpha_j = (1/\sqrt{6})(1, 1, 1, 1, 1, 1) , \\ E &: \quad \alpha_j = \tfrac{1}{2}(1, 1, -1, -1, 0, 0), \qquad (5.2) \\ T_1 &: \quad \alpha_j = (1/\sqrt{2})(1, -1, 0, 0, 0, 0) . \end{aligned}$$

One further correction considered in the calculation of the energies of the A_1 states was that due to the deformation produced by the size difference of the impurity and the Si atom. This was calculated using results of Weinreich.[25] He estimates the first-order correction to the energy to be $E_d = 8 \Xi_u A / r_0 a_0^2$, where Ξ_u is the deformation potential constant, $\Xi_u = 8.5$ eV in Si.[26] r_0 is the tetrahedral covalent radius of the donor atom, a_0 is the radius

TABLE V. Donor-wave-function parameters and energies.

	P	As	Sb
A_1			
δ (a_0^{-1})	0.031 87	0.032 09	0.025 09
ϵ	2.555	−0.630	−0.854
φ (a_0^{-1})	0.0851	0.0527	0.451
E (meV)	−46.0	−35.0	−48.0
E (expt.)[a]	−45.31	−53.51	−42.51
E			
δ (a_0^{-1})	0.024 11	0.023 27	0.021 72
E (meV)	−27.98	−27.29	−25.96
E (expt.)[a]	−32.36	−31.01	−30.37
T_1			
δ (a_0^{-1})	0.024 90	0.022 99	0.020 98
E (meV)	−28.73	−27.13	−25.38
E (expt.)[a]	−33.69	−32.42	−32.67

[a] See Ref. 7.

of the impurity ground state. The constant A may be evaluated from the expression for strain, which in a cubic crystal is

$$u_{xx}=\frac{A}{r^3}\left(1-\frac{3x^2}{r^2}\right) . \tag{5.3}$$

Evaluating the strain along a cubic axis gives

$$u_{xx}=-2A/r^3 . \tag{5.4}$$

Setting $u_{xx}=\Delta r/r$, where Δr is the difference between the tetrahedral covalent radii of the impurity and Si,[27] we then get

$$E_d=-4\Xi_u r_0 \Delta r/a_0^2 . \tag{5.5}$$

Taking $a_0 = 20$ Å (obtained from a simple hydrogenic model), $E_d = 0.007$, -0.001, and -0.019 eV for P, As, and Sb impurities in Si, respectively. This correction is added to the pseudopotential energies for the A_1 states.

The results of these calculations are given in Table V, and plotted in Fig. 3. Agreement is good for P and Sb, but poor for As. Since the tetrahedral covalent radii of Si and As are nearly equal,[27] the lack of agreement with experiment in this case cannot be due to the crude calculation for the size effect. A likely cause is the neglect of admixture of higher bands, as proposed by Castner.[15] In addition, the large value of E_d for Sb suggests that a more careful calculation of the deformation correction is necessary, and that the good result for Sb obtained here is probably fortuitous.

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