

Some New Approaches to Shallow Impurity States*

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A variational calculation of shallow surface impurity states including image-charge and anisotropic mass effects was performed using two different sets of orthogonal functions. The first set was obtained by varying the Bohr radius in the hydrogenic functions, separately for each state. In the second set the Bohr radius was allowed to become anisotropic and the elements were separately treated as variational parameters. In each case it was shown that with certain restrictions on the variational parameters the set remained complete and orthogonal. General expressions for the energy eigenvalues for both the bulk and surface problem obtained from the first set of functions are presented, and numerical results for Si and Ge are given for each set of trial functions. Previously published bulk eigenvalues for Si and Ge were corrected for orthogonality.

I. INTRODUCTION

IN 1965, Levine¹ introduced the problem of shallow donor impurity levels in semiconductors when the ion is on the surface. He used a $(kr)^{-1}$ potential in the material, and approximated the work function as being extremely large on the vacuum side. Bell *et al.*² used this potential and anisotropic wave functions to obtain eigenvalues, effective Bohr radii, and crude transition probabilities. Then Petukhov *et al.*³ showed that image charges were very important, and Schechter *et al.*^{4,5} corrected Petukhov's potential and calculated some eigenfunctions for Si and Ge. All this work showed that for both Si and Ge the problem belonged in the energy range about $\frac{1}{3}$ as large as for the bulk semiconductor shallow donor impurity problem. Also the boundary conditions ruled out the 1s state as the ground state, and introduced polarization effects in any potential electro-magnetic study.

Now it seems necessary for guiding our experimental work to use Schechter's image-charge potential and improved trial functions to obtain more accurate eigenvalues, to learn something of completeness and orthogonality of the wave functions, and generally to see the influence of certain parameters. Our calculation is based on the variational principle as previous calculations have been, but there are two important distinctions.

First, we use a Hamiltonian containing both the image-charge potential correctly introduced by Schechter⁴ and the anisotropic effective mass used by Bell *et al.*² Second, our trial functions form a complete, orthogonal set. The results presented here are therefore more rigorous than previously published results.

Two different sets of functions are used, both being related to the hydrogenic functions. In the first set the Bohr radius is determined by the variational principle separately for each state. Since the variational parameter depends only on the angular momentum quantum numbers and is independent of the principle quantum number, orthogonality and completeness are maintained. This calculation has the advantage of simplicity and is surprisingly accurate except for large mass anisotropies.

The second set of functions is the same as those used by Bell *et al.*² (see also Ref. 5) except that these functions were completely orthogonalized and the resulting set is shown to be complete. This calculation is believed to be very accurate, but it is considerably more complex than the single-parameter calculation.

II. HYDROGENIC WAVE-FUNCTION SOLUTION

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

$$H = \frac{p_x^2 + p_y^2}{2m_t} + \frac{p_z^2}{2m_l} - \frac{\alpha}{r} + \frac{\beta}{z}, \quad (1)$$

where

$$\alpha = \frac{2e^2}{\epsilon + 1}, \quad \beta = \frac{e^2(\epsilon - 1)}{2\epsilon(\epsilon + 1)}. \quad (2)$$

We are assuming here that the c axis is in the z direction and that this direction is normal to the surface, since the

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¹ J. D. Levine, Phys. Rev. **140**, A586 (1965).

² R. J. Bell, W. T. Bousman, Jr., G. M. Goldman, and D. G. Rathbun, Surface Sci. **7**, 293 (1967).

³ B. V. Petukhov, V. L. Pokrovskii, and A. V. Chaplik, Fiz. Tverd. Tela **9**, 70 (1967) [English transl.: Soviet Phys.—Solid State **9**, 51 (1967)].

⁴ D. Schechter, Phys. Rev. Letters **19**, 692 (1967).

⁵ D. Schechter, H. V. Romero, and R. J. Bell, Surface Sci. **11**, 352 (1968).

problem becomes exceedingly complex for other orientations.⁶ The potential-energy terms in Eq. (1) were derived by Schechter.⁴ The first is the potential due to the ion plus its image, while the second term is the repulsion due to the electron image. The kinetic energy is the usual expression for an ellipsoidal effective mass.⁷ The boundary condition $\psi(x, y, 0) = 0$ may be satisfied identically by choosing only those angular momentum eigenfunctions having $l+m = \text{odd}$.¹ In particular, no s states are allowed in the surface-state problem, so the ground state becomes the $2p_0$.

An exact solution for the eigenvalue problem,

$$H\psi = E\psi, \quad (3)$$

cannot be obtained for the Hamiltonian of Eq. (1), so Eq. (3) will be approximately solved using the variational principle. We first split the Hamiltonian into two terms

$$H = H_0 + H', \quad (4)$$

where

$$H_0 = p^2/2m^* - (\alpha - \gamma)/r \quad (5)$$

and

$$H' = \left(\frac{p_x^2 + p_y^2}{2} \right) \left(\frac{1}{m_t} - \frac{1}{m^*} \right) + \frac{p_z^2}{2} \left(\frac{1}{m_l} - \frac{1}{m^*} \right) + \frac{\beta}{z} - \frac{\gamma}{r}, \quad (6)$$

where m^* and γ are parameters to be determined. Clearly, the eigenstates of H_0 are the hydrogenic functions

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(\rho) Y_{lm}(\theta, \phi), \quad (7)$$

where

$$\rho = 2r\hbar^2/nm^*(\alpha - \gamma) \quad (8)$$

and

$$E_n^0 = -m^*(\alpha - \gamma)^2/2\hbar^2n^2. \quad (9)$$

The functions ψ_{nlm} will now be used as approximate eigenstates of the total Hamiltonian H . It appears from the equations above that we have introduced two variational parameters; but that really is not true because the wave functions and the energy depend only on the product $m^*(\alpha - \gamma)$, so the parameters are not independent [see Eq. (10)].

The parameters m^* and γ are chosen to minimize the expectation value of H , separately for each state. This gives only a value for the product $m^*(\alpha - \gamma)$. In order to give a physical meaning to the separate parameters, we also require that m^* be independent of the potential and that γ be independent of the mass anisotropy. Thus, the m^* obtained will be the correct variational choice for any potential, and γ gives the variationally correct potential for any mass.

⁶ Since there are equivalent minima in the conduction bands of Si and Ge in other directions in K space, the Hamiltonian of Eq. (1) will not give all of the surface impurity levels for these materials. Other levels may be obtained by rotating the effective-mass ellipsoid while maintaining the potential as given in Eq. (1). See Sec. IV for further discussion of this point.

⁷ W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257.

Operating with the Hamiltonian of Eq. (1) on the functions ψ_{nlm} and performing the volume integrations gives

$$\begin{aligned} \langle \psi_{nlm} | H | \psi_{nlm} \rangle &= \frac{1}{2} \left[\frac{m^*(\alpha - \gamma)}{\hbar n} \right]^2 \left[\frac{1}{m_t} - \left(\frac{1}{m_t} - \frac{1}{m_l} \right) A_{lm} \right] \\ &\quad + \frac{m^*(\alpha - \gamma)}{\hbar^2 n^2} (\beta C_{lm} - \alpha), \quad (10) \end{aligned}$$

where

$$A_{lm} = \frac{2(l^2 - m^2) + 2l - 1}{(2l - 1)(2l + 3)} \quad (11)$$

and

$$C_{lm} = \langle Y_{lm} | 1/\cos\theta | Y_{lm} \rangle, \quad (12)$$

Y_{lm} being the spherical harmonics.

Minimizing Eq. (10) with respect to $m^*(\alpha - \gamma)$ then gives

$$m^*(\alpha - \gamma) = (\alpha - \beta C_{lm}) \left[\frac{1}{m_t} - \left(\frac{1}{m_t} - \frac{1}{m_l} \right) A_{lm} \right]^{-1} \quad (13)$$

and

$$\begin{aligned} \langle \psi_{nlm} | H | \psi_{nlm} \rangle &= E_{nlm} = - \frac{(\alpha - \beta C_{lm})^2}{2\hbar^2 n^2 \left[\frac{1}{m_t} - \left(\frac{1}{m_t} - \frac{1}{m_l} \right) A_{lm} \right]}. \quad (14) \end{aligned}$$

Equation (14) gives the energy eigenvalues for surface states ($l+m = \text{odd}$) and may also be used for bulk states by letting $\beta = 0$ and $\alpha \rightarrow e^2/\epsilon$.

Clearly, if we choose

$$\gamma = \beta C_{lm} \quad (15)$$

and

$$\frac{1}{m^*} = \frac{1}{m_t} - \left(\frac{1}{m_t} - \frac{1}{m_l} \right) A_{lm}, \quad (16)$$

then Eq. (13) is satisfied, m^* is independent of the potential, and γ is independent of the mass. Values for the parameters C_{lm} and A_{lm} are shown in Table I for some of the low-lying levels.

The effective mass given by Eq. (16) is the correct value to use if one wishes to approximate the anisotropic effective mass in the Hamiltonian by an isotropic effective mass. That is, this approximation gives the correct expectation value for the kinetic energy in any angular momentum eigenstate. It is interesting to note that Eq. (16) reduces to the usual expression

$$\frac{1}{m^*} = \frac{1}{3} \left(\frac{2}{m_t} + \frac{1}{m_l} \right) \quad (17)$$

for spherically symmetric states ($A_{00} = \frac{1}{3}$) but not in general for other states. Thus, the use of Eq. (17) in the Hamiltonian may give energies that are either higher or lower than the true values, depending upon which

TABLE I. Values of the parameters A_{lm} and C_{lm} for a number of low-lying levels. The value of A_{lm} determines the appropriate effective mass for either bulk or surface states. Values of C_{lm} are given only for allowed surface states since this parameter does not appear in the bulk problem.

State	A_{lm}	C_{lm}
s	$\frac{1}{2}$...
p_0	$\frac{1}{2}$	$\frac{3}{2}$
$p_{\pm 1}$	$\frac{1}{2}$...
d_0	$11/21$...
$d_{\pm 1}$	$3/7$	$15/8$
$d_{\pm 2}$	$1/7$...
f_0	$23/45$	$49/24$
$f_{\pm 1}$	$7/15$...
$f_{\pm 2}$	$\frac{1}{2}$	$35/16$
$f_{\pm 3}$	$\frac{1}{2}$...

angular momentum states one is dealing with. The effective mass given by Eq. (16), on the other hand, will never underestimate the kinetic energy, since it was obtained by the variational principle.

It is interesting to note that the combination of Eqs. (14)–(16) yields E_n^0 of Eq. (9). Thus it is clear that the values of γ and m^* given by Eqs. (15) and (16) may also be obtained by the requirement that⁸

$$\langle \psi_{nlm} | H_1' | \psi_{nlm} \rangle = \langle \psi_{nlm} | H_2' | \psi_{nlm} \rangle = 0, \quad (18)$$

where H_1' and H_2' are the kinetic- and potential-energy terms, respectively, in Eq. (6). Thus we have obtained a complete diagonalization of the total Hamiltonian correct to first order in each of the perturbation contributions. Since only second-order perturbations remain, one would expect the results to be unusually accurate. If, for example, we had used the same Hamiltonian, these results would be considerably better than the results obtained by Petukhov *et al.*³ by a perturbation calculation. In fact, it is only the extreme mass anisotropy of Ge which introduces a sizeable error.

A few words are in order at this point concerning the orthogonality and completeness of these wave functions. One may readily show orthogonality by noting the explicit dependence of the wave functions on the variational parameters. This is

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r, \gamma_{lm}, m_{lm}^*) Y_{lm}(\theta, \phi). \quad (19)$$

Clearly, states having different l or m are orthogonal because the spherical harmonics are orthogonal. Furthermore, states having different n are orthogonal because if l and m are the same these are eigenstates of the same hydrogenic Hamiltonian—and such states are known to be orthogonal.

Completeness is shown as follows. Consider an arbitrary function $F(r, \theta, \phi)$. Since the spherical harmonics form a complete set, we may expand this function in the series

$$F(r, \theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l f_{lm}(r) Y_{lm}(\theta, \phi). \quad (20)$$

Now the hydrogenic functions are known to be complete and the spherical harmonics are linearly independent. Therefore, it is always possible to express the coefficients $f_{lm}(r)$ in the form

$$f_{lm}(r) = \sum_{n=l+1}^{\infty} A_{nlm} R_{nl}(r, \gamma_{lm}, m_{lm}^*) \quad (21)$$

for any fixed value of γ and m^* . Clearly, then,

$$\begin{aligned} F(r, \theta, \phi) &= \sum_{n=l+1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^l A_{nlm} R_{nl}(r, \gamma_{lm}, m_{lm}^*) Y_{lm}(\theta, \phi) \\ &= \sum_{n,l,m} A_{nlm} \psi_{nlm}(r, \theta, \phi), \end{aligned} \quad (22)$$

and since F was assumed arbitrary, completeness is established.

III. ANISOTROPIC WAVE-FUNCTION SOLUTION

The solution given in Sec. II is quite accurate except in materials such as Ge with extreme mass anisotropy. In order to test the accuracy of those results and to obtain more accurate results for Ge, we have computed the two lowest-energy levels in Si and Ge by a different method. This method involves the use of the trial functions used by Bell *et al.*² in their calculation of the bulk and some surface eigenstates for Si and Ge (see also Ref. 5). This set of functions is obtained from the hydrogenic functions by the replacements

$$r/a_0 \rightarrow [A^2(x^2 + y^2) + B^2z^2]^{1/2}, \quad (23)$$

$$x/a_0 \rightarrow Ax, \quad (24)$$

$$y/a_0 \rightarrow Ay, \quad (25)$$

and

$$z/a_0 \rightarrow Bz, \quad (26)$$

where a_0 is the Bohr radius, while A and B are variational parameters.

It was noted in Ref. 2 that the first few functions obtained in this manner are orthogonal but that orthogonality is lost at the higher quantum numbers. A way has now been found to make these functions a complete, orthogonal set; therefore, one now has a rigorous justification for the use of the variational principle with these trial functions. Thus the only remaining disadvantage of the use of these functions is that the calculations are very much more cumbersome than those described in Sec. II.

In order to establish orthogonality and completeness, consider the transformations

$$x = A^{-1} \rho \sin \omega \cos \phi, \quad (27)$$

$$y = A^{-1} \rho \sin \omega \sin \phi, \quad (28)$$

$$z = B^{-1} \rho \cos \omega. \quad (29)$$

Then the functions represented by Eqs. (23)–(26) are

⁸ Wayne E. Tefft, Bull. Am. Phys. Soc. 13, 710 (1968).

transformed to the hydrogenic functions;

$$U_{nlm}(x,y,z) = R_{nl}(\rho)Y_{lm}(\omega,\phi). \quad (30)$$

It is obvious from the form of the transformation Eqs. (27)–(29) that for any given point in space the coordinate ρ depends on the values of both A and B , the coordinate ω depends only on the ratio A/B , while the coordinate ϕ is independent of both parameters.

The Jacobian of the transformation is easily shown to be

$$\frac{\partial(x,y,z)}{\partial(\rho,\omega,\phi)} = \frac{\rho^2}{A^2B} \sin\omega. \quad (31)$$

Clearly, then, if A and B were held fixed, we could express the inner product of any pair of these functions as

$$\begin{aligned} \langle U_{n'l'm'} | U_{nlm} \rangle &= \frac{1}{A^2B} \int_0^\infty R_{n'l'}(\rho)R_{nl}(\rho)\rho^2 d\rho \\ &\times \int_0^{2\pi} \int_0^\pi Y_{l'm'}^*(\omega,\phi)Y_{lm}(\omega,\phi) \sin\omega d\omega d\phi. \end{aligned} \quad (32)$$

Note that the upper limit on the ω integration is given as π , which is correct for the bulk problem. This limit becomes $\frac{1}{2}\pi$ for the surface problem because the functions are then assumed identically zero for $z \leq 0$.

Now it is clear that since Eq. (32) is of the same form as the orthogonality integrals for the hydrogen-atom wave functions in spherical coordinates, orthogonality is maintained for any two functions with the same values of A and B and different values of any one of the three quantum numbers n , l , and m . Furthermore, since ϕ is independent of both A and B , any two functions having different values of m are orthogonal even if these parameters are not the same for both functions. For orthogonality with respect to l we must consider two cases. First, if two functions have different parities ($l+m = \text{even}$ for one and odd for the other), they are automatically orthogonal for all positive values of the parameters, and since negative values merely reflect the functions through the origin they are never needed. If two functions have the same values of n and m and values of l differing by an even integer (the same parity), then in general they will be orthogonal only if the ratio A/B is the same for both. And finally, any two functions having the same values of l and m but different values of n will, in general, be orthogonal only if both A and B have the same values for both functions. Thus we can obtain complete orthogonality by requiring that A and B be independent of n and depend on l only within the limitation that the ratios

$$a_m^+ = A_{lm}/B_{lm} \quad (l \text{ even}) \quad (33)$$

and

$$a_m^- = A_{lm}/B_{lm} \quad (l \text{ odd}) \quad (34)$$

depend only on m .

The first requirement (independence of n) is not restrictive since it was shown in Ref. 2 that values of A and B obtained by the variational principle are automatically independent of n . The second restriction actually affects only one of the states (d_0) calculated in Ref. 2 and, as will be shown in Sec. IV, the energy for this state was changed by only a small amount. Furthermore, for either the bulk or the surface-state problem, no state which may be reached from the ground state by an allowed optical transition is affected by this restriction.

The proof of completeness follows in much the same way as for the functions of Sec. II. Consider an arbitrary function $F(r,\theta,\phi)$, which can always be expressed as the sum of two functions

$$F(r,\theta,\phi) = F^+ + F^-, \quad (35)$$

one of which has even parity and the other odd parity. Clearly, either of these functions may be expressed as

$$F^\pm(r,\theta,\phi) = \sum_{m=-\infty}^{\infty} f_m^\pm(r,\theta)e^{im\phi}. \quad (36)$$

Now for a fixed value of m and a definite parity, the transformation from (r,θ) to (ρ,ω) is unique except for the scale of ρ (which is proportional to B_{lm}). Therefore, each of the coefficients in Eq. (36) may be expanded in a series of hydrogenic functions of (ρ,ω) ; consequently,

$$F^\pm(r,\theta,\phi) = \sum_{n=l+1}^{\infty} \sum_{l=|m|}^{\infty} \sum_{m=-\infty}^{\infty} C_{nlm} R_{nl}(\rho) Y_{lm}(\omega,\phi), \quad (37)$$

and therefore completeness is established.

IV. RESULTS AND DISCUSSION

Table II gives a comparison of shallow donor surface-state energy eigenvalues and effective Bohr radii for silicon and germanium obtained by three different methods (see Ref. 7 for constants): the isotropic wavefunction solution using both the isotropic and anisotropic effective-mass approximations, and the anisotropic wavefunction–anisotropic effective-mass solution. Since for each of these calculations the energy is proportional to n^{-2} , one may readily find energy eigenvalues for any state not listed which has the same angular momentum quantum numbers as one of the listed states. Note that the isotropic mass approximation, which is correct for spherically symmetric states, can be in error by as much as 40% for other levels. Although for the levels shown the error is always in the direction of higher energies, this is not true in general. Examination of Eqs. (11) and (14) shows that errors in the opposite direction will always be obtained for states having both l and $|m|$ large, the first such level being $l=4$, $m=3$ in the surface-state problem.

TABLE II. Surface states.

State	Hydrogenic wave function				Aniso. wave function			
	Isot. eff. mass		Aniso. eff. mass		Aniso. eff. mass		Bohr radius (Å)	
	$-E$ (10^{-3} eV)	Bohr radius (Å)	$-E$ (10^{-3} eV)	Bohr radius (Å)	$-E$ (10^{-3} eV)	Bohr radius (Å)	$1/A$	$1/B$
Si	$2p_0$	9.00	20.2	12.75	14.2	13.2	14.7	12.4
	$3p_0$	4.00	20.2	5.67	14.2	5.84	14.7	12.4
	$3d_{\pm 1}$	3.02	23.2	3.35	20.8	3.39	20.0	19.8
	$4p_0$	2.25	20.2	3.19	14.2	3.29	14.7	12.4
	$5p_0$	1.44	20.2	2.04	14.2	2.10	14.7	12.4
	$4d_{\pm 1}$	1.70	23.2	1.90	20.8	1.91	20.0	19.8
	$4f_0$	1.48	24.9	1.84	20.0
	$6p_0$	1.00	20.2	1.42	14.2	1.46	14.7	12.4
	$4f_{\pm 2}$	1.30	26.5	1.30	26.5
	$5d_{\pm 1}$	1.09	23.2	1.22	20.8	1.22	20.0	19.8
Ge	$2p_0$	2.35	58.3	3.74	36.7	4.24	35.8	24.8
	$3p_0$	1.05	58.3	1.66	36.7	1.88	35.8	24.8
	$3d_{\pm 1}$	0.782	67.5	0.901	58.5	0.925	59.2	58.8
	$4p_0$	0.588	58.3	0.934	36.7	1.06	35.8	24.8
	$5p_0$	0.377	58.3	0.598	36.7	0.678	35.8	24.8
	$4d_{\pm 1}$	0.440	67.5	0.507	58.5	0.520	59.2	58.8
	$4f_0$	0.380	67.5	0.505	54.6
	$6p_0$	0.261	58.3	0.415	36.7	0.471	35.8	24.8
	$4f_{\pm 2}$	0.332	77.6	0.332	77.6
	$5d_{\pm 1}$	0.281	67.5	0.324	58.5	0.333	59.2	58.8

One expects a two-parameter calculation, such as the anisotropic wave-function solution, to give better results than a one-parameter calculation, such as the isotropic wave-function solution. An examination of Table II shows that this is indeed the case, the anisotropic wave-function solutions always yielding somewhat lower energies than the isotropic wave-function solutions. Note, however, that for Si, with a mass ratio $m_i/m_e \approx 5$, the difference is at most 3%, while for Ge, with a mass ratio $m_i/m_e \approx 20$, the difference is 12% or less. Thus, one concludes that the simpler calculation is adequate for any material having a mass ratio of 5 or less.

An energy-level diagram based on the anisotropic wave function solution is shown in Fig. 1. Since the selection rules for optical transitions are $\Delta m = \pm 1$ and $\Delta l = \pm 1$, only the $d \pm 1$ levels are accessible from the $2p_0$ ground state. The transition energies for the first few allowed transitions are shown in Fig. 1. A comparison of the

energy levels shown here with the corresponding bulk values of Ref. 2 shows the importance of the image charge in the surface problem. The $2p_0$ energy in Si, for example, goes from 10.7×10^{-3} eV in the bulk to 13.2×10^{-3} eV in the surface because of the image charge potential.

A comparison of the levels shown in Fig. 1 with the results of Refs. 4 and 5 shows that Schechter's method has two serious drawbacks. First, because of the use of an isotropic effective mass, the energy levels have sizeable errors, particularly the ground state. Second, and even more serious, because of the nature of his wave functions, a number of levels are missed entirely by his calculation. One could correct these deficiencies by using a better Hamiltonian and better wave functions, but the calculation would then become extremely complex and the results would probably not be very much better than those obtained here.

A comment is in order concerning central-cell corrections.⁷ Although these are known to be of importance in the ground state for the bulk problem, a way has yet to be found to correctly calculate the effect. Furthermore, since the s states are not allowed in the surface problem, central-cell corrections are expected to be of far less importance here than in the bulk. Consequently, the neglect of these corrections in this calculation should not introduce any serious errors.

In order to further compare the calculations, energy eigenvalues for the bulk states are presented in Table III. The anisotropic wave-function results are those given in Ref. 2, except that the $3d_0$ level was made orthogonal to the ground state as discussed in Sec. III. As expected, this correction increased the energy of this level, although the change was not very large.

TABLE III. Bulk state energies (10^{-3} eV).

State	Hydrogenic wave function aniso. eff. mass		Aniso. wave function aniso. eff. mass	
Si	$1s$	-24.5	-28.6	
	$2p_0$	-8.69	-10.7	
	$2p_{\pm 1}$	-5.35	-5.81	
	$3d_0$	-3.45	-4.47	
	$3d_{\pm 1}$	-3.05	-3.56	
	$3d_{\pm 2}$	-2.25	-2.38	
Ge	$1s$	-6.32	-9.02	
	$2p_0$	-2.51	-4.38	
	$2p_{\pm 1}$	-1.33	-1.59	
	$3d_0$	-0.95	-1.67	
	$3d_{\pm 1}$	-0.81	-1.16	
	$3d_{\pm 2}$	-0.56	-0.62	

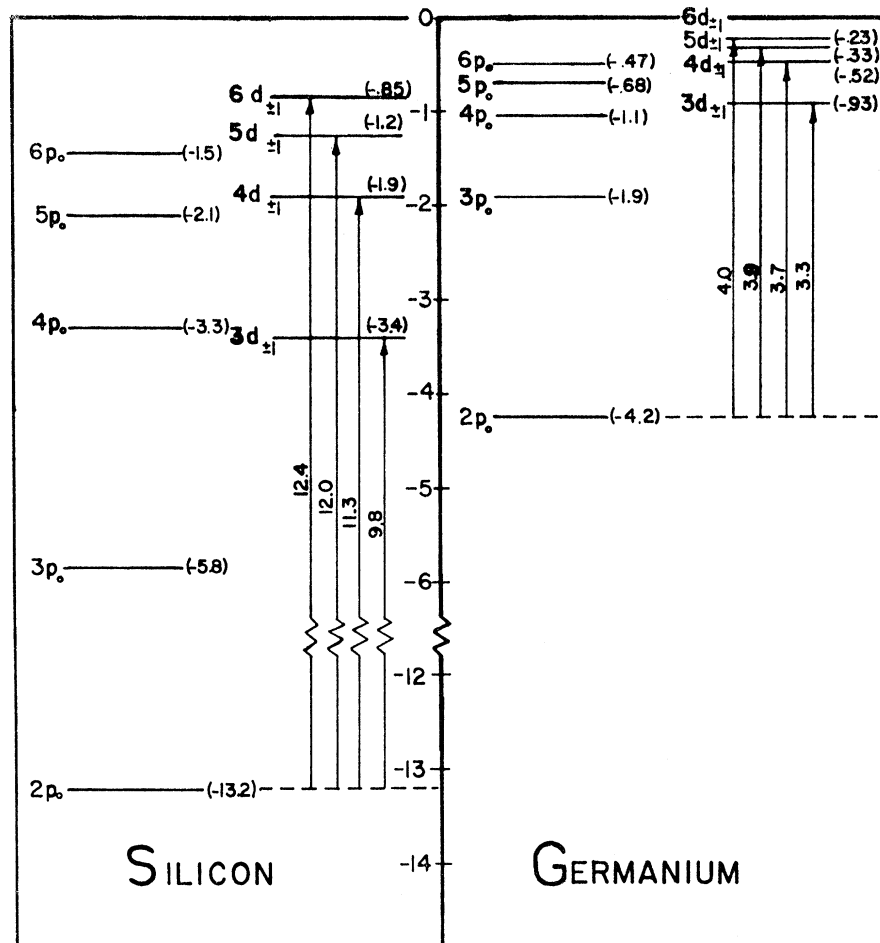


FIG. 1. Energy-level diagram for surface states. The wave function and effective mass are anisotropic. All energies in 10^{-3} eV. Arrows show the allowed optical transitions from the ground state.

Two features should be noted in the bulk results. First, when isotropic wave functions are used, the results for isotropic versus anisotropic mass are in the same ratio as in the surface problem. This was to be expected from the discussion of Sec. II. Second, the errors caused by the use of isotropic wave functions are considerably larger than in the surface problem. The reason for this is that in the surface problem the z^{-1} repulsion tends to cancel the anisotropic mass effect for this particular problem. If the mass anisotropy had been in the opposite direction ($m_i/m_t < 1$), or if the relation between the crystallographic axes and surface had been chosen differently, the surface results with isotropic wave functions would have been less accurate than the bulk results. One has here an important experimental implication for the measurement of surface states. Because of the symmetry of Si,⁹ the surface

⁹ J. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1962), p. 119.

impurity eigenstates include not only solutions of the Hamiltonian of Eq. (1), but also solutions of a Hamiltonian in which the axis of the effective-mass ellipsoid lies in the surface rather than being normal to the surface. From the argument above it is clear that the energies of the latter levels will be considerably different than the energies that we have calculated. In Ge there are eight equivalent directions,⁹ so the problem is even more complicated. Consequently, it may be necessary to extend the calculation to these other states in order to completely interpret experimental results. Such an extension is now being contemplated for a future publication.

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