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CHEMICAL SHIFT PARAMETERS FOR SHALLOW DONORS IN SEMICONDUCTORS*

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Abstract — A model for a shallow donor impurity in a semiconductor is used to calculate two relationships and several conditions involving the chemical shift parameters. The model is based on the standard effective mass form for the donor electron wave function, the existence of a potential in the chemical cell which may be real, pseudo, or rather general in nature, and a few somewhat restrictive approximations. The parameters, Δ, δ and Λ are theoretically calculated and are shown to be related if the approximations are valid. These parameters determine the 1S multiplet level structure and it is shown how properties of the central cell potential can be deduced from a knowledge of this structure. As an example, the inverted structure for Si(Li) is discussed. The often neglected parameter, Λ, is shown to be quite important. A length parameter is determined by the model and is a measure of the effective range of influence of the central cell potential. The model should be useful in determining if choices for the potential and wave function in the central cell region lead to self consistent results. The agreement between the theoretical predictions and the experimental data from both silicon and germanium and five donor impurities from both Group I (lithium) and Group V (arsenic, phosphorus, antimony and bismuth) suggest the model is reasonable.

1. INTRODUCTION

THE HYDROGEN-LIKE energy level spectrum for Group V donor impurities in both silicon and germanium has been known for some time. (For early work and review article, see Ref. [1].) The excited state levels have been calculated to an amazing degree of accuracy [2, 3]. Calculations on the 1S-like levels have not achieved the same success as those on the excited states. This is not because of a lack of effort [4–24] but because of the complexity of the interactions and wave functions which determine the lower energy levels. The purpose of this paper is to provide added physical insight into the lower energy states problem. This insight is gained by using a simplified model calculation. The approach is somewhat novel in that no specifically detailed form for the central cell potential is assumed. Despite this, results relating to the effects of

this potential and its influence on the lower level multiplet structure can be inferred.

A multiplet energy level structure exists for the "1S-like state" because of the many-valley energy degeneracy at the conduction band minimum energy. This structure indicates a breakdown in the effective mass theory. This breakdown occurs because the potential energy that the donor electron experiences near the impurity deviates from the $-(e^2/\kappa r)$ potential used in the effective mass Hamiltonian. Kohn and Luttinger [4] explained how to qualitatively handle the level structure calculations using group theory and other techniques.

The multiplet level structure for silicon and germanium are shown in Figs. 1a and 1b. In silicon the levels are split into a singlet (A_1), a doublet (E), and a triplet (T_2). Because of a difference in the k-space location of the conduction band minimum, germanium has a singlet (A_1) and triplet (T_2) level structure. The non existent levels E_0 and

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C.G. are depicted at the value of the un-modified effective mass value and the center of gravity of the multiplet levels, respectively.

Also in Fig. 1, the energy level structure is described in terms of a set of parameters called the chemical shift parameters. These are shown as Λ, Δ and δ for silicon and as Λ and Δ for germanium. The experimental values for these parameters are given in Table 1.

Theoretical calculations for the chemical shift parameters are also possible. In such calculations, a degenerate perturbation approach is often used and a 'valley-orbit matrix' is introduced[25]. This matrix is the energy matrix in the representation where the wave functions are each associated with a different valley minimum. In silicon the matrix is

$$
\begin{pmatrix}
E_0+\Lambda-E & \Delta(1+\delta) & \Delta & \Delta & \Delta & \Delta \\
\Delta(1+\delta) & E_0+\Lambda-E & \Delta & \Delta & \Delta & \Delta \\
\Delta & \Delta & E_0+\Lambda-E & \Delta(1+\delta) & \Delta & \Delta \\
\Delta & \Delta & \Delta(1+\delta) & E_0+\Lambda-E & \Delta & \Delta \\
\Delta & \Delta & \Delta & \Delta & E_0+\Lambda-E & \Delta(1+\delta) \\
\Delta & \Delta & \Delta & \Delta & \Delta(1+\delta) & E_0+\Lambda-E.
\end{pmatrix}
$$

In germanium the matrix is

$$
\begin{pmatrix}
E_0^-+\Lambda-E & \Delta & \Delta & \Delta \\
\Delta & E_0+\Lambda-E & \Delta & \Delta \\
\Delta & \Delta & E_0+\Lambda-E & \Delta \\
\Delta & \Delta & \Delta & E_0+\Lambda-E.
\end{pmatrix}
$$

Table 1. *Measured chemical shift parameters for shallow donor impurities in silicon and germanium*

Si($E_0 = -31{\cdot}27$ meV)[a]	Λ (meV)	Δ (meV)	δ
As[b]	4·51	3·73	−0·184
P[b]	4·13	2·16	−0·308
Sb[b]	2·53	2·02	−0·586
Li	1·4[c]	−0·30[c]	$\lvert\delta\rvert < 4\times10^{-2[g]}$
Bi($A_1 = -64{\cdot}6$ meV)[d]	?	[e]	[e]
Ge($E_0 = -9{\cdot}81$ meV)[a]			
As[f]	1·21	1·06	—
P[f]	0·97	0·71	—
Sb[f]	0·28	0·08	—
Bi[f]	0·83	0·72	—
Li[f]($E_{\text{gr. state}} = -10{\cdot}0$ meV)	?	?	—

[a] Theoretically computed by FAULKNER R. W., *Phys. Rev.* **184**, 713 (1969).

[b] AGGARAWAL R. L. and RAMDAS A. K., *Phys. Rev.* **140**, A1246 (1965) as modified by Ref. a results.

[c] AGGARWAL R. L., FISHER P., MOURZINE V. and RAMDAS A. K., *Phys. Rev.* **138**, A883 (1965) as modified by Ref. a results.

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[e] CASTNER T. G., Jr., *Phys. Rev. Lett.* **8**, 13 (1962) determined the singlet to triplet separation as (34 ± 2) meV.

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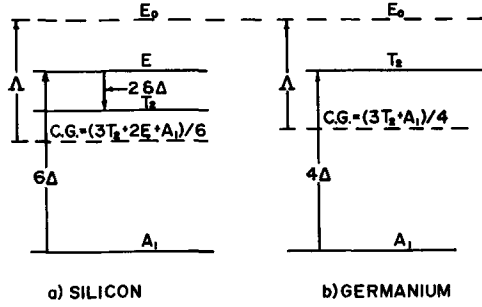
a) SILICON   b) GERMANIUM

Fig. 1. Energy level diagram for 1S-like donor states. Conduction band minima along different symmetry axes cause different level structure schemes for the various semiconductors. Figure 1a is for a $\langle 100 \rangle$ multi-valley semiconductor, such as silicon. Figure 1b is for a $\langle 111 \rangle$ multi-valley semiconductor, such as germanium. Different impurities cause different level separations which are expressed in terms of the chemical shift parameters Λ, Δ and δ. The ground state level for no chemical shift, E_0, and the center of gravity level for the shifted levels, $C.G.$, are of theoretical importance but do not actually exist.

These matrices are of special importance in theoretically calculating the effects of stress on the impurity, e.g., see Ref. [25]. If these matrices are diagonalized, the resulting energy values are those shown for the various levels in Fig. 1.

This paper discusses a model in which (1) the chemical shift parameters would be related to each other, (2) a set of conditions evolve which, if satisfied, place constraints on the parameters and (3) an effective potential radius can be specified. The model is presented in Section 2 with the comparisons to experimental data made in Section 3. Section 4 contains the concluding remarks.

2. THEORETICAL MODEL

(a) Derivation of the two relationships

The wave function for the donor electron can be expressed as

$$\psi(\mathbf{r}) = \sum_n \int_{B.Z.} d^3k \, C_n(\mathbf{k}) \psi_{n,k}(\mathbf{r}), \qquad (1)$$

where $\Psi_{n,k}(\mathbf{r})$ is the Bloch wave function for an electron in the nth band and k^{th} state of the intrinsic crystal; and the $C_n(\mathbf{k})$ coefficients are determined by the Hamiltonian approp-

riate to the crystal containing the impurity. Often a Fourier transform of $C_n(\mathbf{k} - \mathbf{k}_j)$ is of interest and defined as

$$F_{n,j}(\mathbf{r}) = \int d^3k e^{i(\mathbf{k} - \mathbf{k}_j) \cdot \mathbf{r}} \, C_n(\mathbf{k} - \mathbf{k}_j), \qquad (2)$$

where $F_{n,j}(\mathbf{r})$ is referred to as an envelope function and $\mathbf{k}_j$ is at the jth minimum of the several minima in the nth band. If both a one conduction band and slowly varying impurity potential approximations are made, Twose [26] has shown that an effective set of Schroedinger equations for the envelope functions are

$$[H_j - E]\alpha_j F_j(\mathbf{r}) + \sum_{l \neq j} \alpha_l e^{i(\mathbf{k}_l - \mathbf{k}_j) \cdot \mathbf{r}} [H_l - E] \\ \times F_l(\mathbf{r}) = 0, \qquad (3)$$

where E is the energy of one of the multiplet levels relative to the conduction band minima, α_j is the expansion coefficient associated with the jth valley envelope function in the energy state E, and H_j is the jth valley effective mass Hamiltonian. The kinetic energy operator in H_j contains the valley dependent effective mass tensor components.

It is convenient to consider H_j as containing a potential of the form

$$V(\mathbf{r}) = -\frac{e^2}{\kappa r} - W(\mathbf{r}), \qquad (4)$$

where $-e^2/\kappa r$ is the reduced Coulomb potential energy term and $W(\mathbf{r})$ is an effective potential energy term introduced to allow for central cell corrections. The $W(\mathbf{r})$ is the major cause of the 1S-like energy state separation(s). In the past, $W(\mathbf{r})$ has been formulated to account for semi-empirical or empirical central cell potentials, dielectric screening potentials, strain field effects or potentials based on other models [1–23].

If equation (3) is multiplied by $F_j(\mathbf{r})$ and integrated over all space, the secular equation for the eigenvalues E can be obtained. These calculations are performed in Appendix A. This appendix also shows that approximations

can be made to obtain the following for silicon:

$$A_1 = E_0 + \langle F_j|W(\mathbf{r})|F_j \rangle \\ + \langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_l e^{i\mathbf{k}_l \cdot \mathbf{r}} \rangle \\ + 4\langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_m e^{i\mathbf{k}_m \cdot \mathbf{r}} \rangle, \quad (5)$$

$$E = E_0 + \langle F_j|W(\mathbf{r})|F_j \rangle \\ + \langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_l e^{i\mathbf{k}_l \cdot \mathbf{r}} \rangle \\ - 2\langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_m e^{i\mathbf{k}_m \cdot \mathbf{r}} \rangle, \quad (6)$$

$$T_2 = E_0 + \langle F_j|W(\mathbf{r})|F_j \rangle \\ - \langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_l e^{i\mathbf{k}_l \cdot \mathbf{r}} \rangle, \quad (7)$$

and for germanium:

$$A_1 = E_0 + \langle F_j|W(\mathbf{r})|F_j \rangle \\ + 3\langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_m e^{i\mathbf{k}_m \cdot \mathbf{r}} \rangle, \quad (8)$$

$$T_2 = E_0 + \langle F_j|W(\mathbf{r})|F_j \rangle \\ - \langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_m e^{i\mathbf{k}_m \cdot \mathbf{r}} \rangle, \quad (9)$$

where j and l indicate different valleys on the same k-space axis and j and m indicate valleys on different axes. Comparison of these energy levels and those of Fig. 1 show that the chemical shift parameters are related to fundamental matrix elements involving the effective potential. Namely,

$$\Lambda = \langle F_j|W(\mathbf{r})|F_j \rangle, \quad (10)$$

$$\Delta = \langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_m e^{i\mathbf{k}_m \cdot \mathbf{r}} \rangle, \quad (11)$$

and

$$\Delta(1+\delta) = \langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_l e^{i\mathbf{k}_l \cdot \mathbf{r}} \rangle. \quad (12)$$

Thus, Λ is the self valley interaction parameter; Δ is the different axis valley interaction parameter; and $\Delta(1+\delta)$ is the opposite valley interaction parameter. It will now be shown that, if certain assumptions are valid, the integrals in equations (10)–(12) are related and hence the chemical shift parameters will not be independent.

The integral in equations (11) or (12) can be divided into two integrals such that

$$\langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_m e^{i\mathbf{k}_m \cdot \mathbf{r}} \rangle \\ = \langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_m e^{i\mathbf{k}_m \cdot \mathbf{r}} \rangle_{\text{Region }A} \\ + \langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_m e^{i\mathbf{k}_m \cdot \mathbf{r}} \rangle_{\text{Region }B} \quad (13)$$

where Region A is centered on the donor and Region B is the remaining exterior region. Region A is chosen to be the smallest region such that

$$|\langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_m e^{i\mathbf{k}_m \cdot \mathbf{r}} \rangle_{\text{Region }A}| \\ \gg |\langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_m e^{i\mathbf{k}_m \cdot \mathbf{r}} \rangle_{\text{Region }B}|. \quad (14)$$

Thus the Region B integral in equation (13) can be neglected. Note that a Region A can always be found to meet the above definition since $W(\mathbf{r}) \rightarrow 0$ as $|\mathbf{r}| \rightarrow \infty$. For the Group V donors, Region A is likely to be about a Wigner-Seitz cell because (1) $W(\mathbf{r})$ is well localized about the donor and (2) in the Region B integral, the effect of the exponential terms on both the slowly varying envelope and $W(\mathbf{r})$ function is an averaging to zero process because of the slowly damped oscillatory nature of the integrand. The major assumption is now introduced which assumes

$$\langle F_j e^{i\mathbf{k}_j \cdot \mathbf{r}}|W(\mathbf{r})|F_m e^{i\mathbf{k}_m \cdot \mathbf{r}} \rangle_{\text{Region }A} \\ = \langle F_j|W(\mathbf{r})|F_m \rangle_{\text{Region }A} (e^{i(\mathbf{k}_m - \mathbf{k}_j) \cdot \mathbf{r}})_{\text{Ave}} \quad (15)$$

where $(\ )_{\text{Ave}}$ indicates an average over Region A. The extent to which this average value assumption is justified is discussed in Appendix B. It is also assumed that

$$\langle F_j|W(\mathbf{r})|F_m \rangle_{\text{Region }A} \simeq \langle F_j|W(\mathbf{r})|F_j \rangle, \quad (16)$$

which is also discussed in Appendix B. The results of equations (10)–(16) yield directly

$$\frac{\Delta}{\Lambda} = (e^{i(\mathbf{k}_m - \mathbf{k}_j) \cdot \mathbf{r}})_{\text{Ave}} \quad (17)$$

and

$$\frac{\Delta(1+\delta)}{\Lambda} = (e^{i(\mathbf{k}_l - \mathbf{k}_j) \cdot \mathbf{r}})_{\text{Ave}}. \quad (18)$$

Note that these two simple chemical shift relationships depend only on the intrinsic lattice location of the band minima and a suitable choice for the Region A.

(b) *Criteria resulting from the relationships*

The basic relations [equations (17) and (18)]

predict several results which must be satisfied if the approximations are valid. These results can thus be used as test criteria. Criteria 1 and 2 are

$$-1 \leqslant \Delta/\Lambda \leqslant 1 \qquad (19)$$

and

$$-1 \leqslant \Delta(1+\delta)/\Lambda \leqslant 1. \qquad (20)$$

These occur because the exponential terms are bounded. Both criteria are experimentally confirmed for all twelve of the measured donor semiconductor values as shown in Table 2. Other criteria can be developed if it is assumed that Region A is a sphere of radius R. Then the averages indicated in equations (17) and (18) can be evaluated since

$$(e^{i\Delta k \cdot r}) \text{ sphere of radius } R = \frac{3}{(R\Delta k)^3}$$

$$\times [\sin(R\Delta k) - R\Delta k \cos(R\Delta k)]. \qquad (21)$$

Figure 2 shows a plot of this function. As R increases, the function decreases from plus one, goes negative and has a damped oscillatory behavior. The result of equation (21) when combined with the experimental data ratios of equations (17) and (18) determine two radii. These radii are somewhat artificial in that they are used to characterize a particular integral over a tetrahed-

Table 2. *Ratios of measured chemical shift parameters for shallow donor impurities in silicon and germanium. Data obtained from values in Table 1*

Silicon	Δ/Λ	$\Delta(1+\delta)/\Lambda$	$(1+\delta)$
As	0·827	0·674	0·816
P	0·523	0·360	0·692
Sb	0·798	0·330	0·414
Li	−0·22	−0·22	1·0
Germanium			
As	0·876	—	—
P	0·732	—	—
Sb	0·286	—	—
Bi	0·867	—	—

rally symmetric potential. In some sense, however, these radii do characterize the effective range of influence of the potential and are thus referred to as effective potential radii. That these two radii should have reasonably consistent values is the basis for the third criterion. Table 3 shows the value for these radii.

The final three criteria are valid for a small spherical Region A, i.e. $\Delta k \cdot r_{max} < \pi$. Criteria 4 and 5 predict the ratios in equations (19) and (20) should be positive fractions, which can be seen by examining equation (21) or Fig. 2. Criterion 6 is developed from the ratio of equation (18) to equation (17) which yields

$$(1+\delta) < 1 \qquad (22)$$

since $\Delta k(l,j) > \Delta k(m,j)$. Thus δ is expected to be negative for small R values as clearly shown in Fig. 3.

3. COMPARISON WITH EXPERIMENTAL DATA

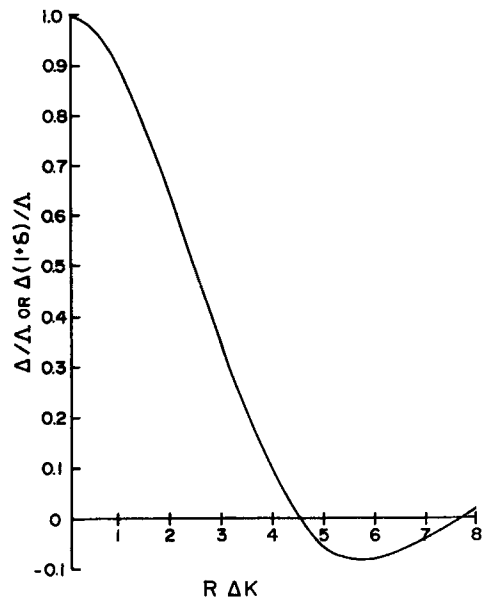### (a) *Group V impurities*

Table 3 shows that the impurity with

Fig. 2. Universal curve for Δ/Λ or $\Delta(1+\delta)/\Lambda$ values. The curve is actually a plot of equation (21).

Table 3. Effective radii obtained from chemical shift relationships and experimental data in Table 1. All radii are given in atomic units

	R from Δ/Λ relation	R from Δ(1 + δ)/Λ relation	Covalent radius[a]
Silicon [R (Wigner–Seitz sphere) = 3·18]			2·22
As	1·9	1·8	2·24
P	3·3	2·8	2·09
Sb	2·0	2·9	2·58
Germanium [R (Wigner–Seitz sphere) = 3·32]			2·32
As	1·3	—	2·24
P	2·0	—	2·09
Sb	3·7	—	2·58
Bi	1·4	—	—

[a] Values obtained from KITTEL C., *Introduction to Solid State Physics*, 4th Edition, Wiley, New York (1971).

approximately the same covalent radius as the host lattice (arsenic for both silicon and germanium) has the smallest effective potential radius as might be expected. The large values of Λ for arsenic show however that the central cell potential is not weak. Thus for this impurity $W(\mathbf{r})$ is a large, well localized potential and is a good case for the approximations of the model. For the other impurities the tetrahedral covalent radii do not match the host lattice radius very well, and larger R values are found. It has been suggested[19] that $W(\mathbf{r})$ for antimony is repulsive for certain $\mathbf{r}$ values. This is consistent with the small Λ(Sb) values since a repulsive region will reduce or could even change the sign of Λ. For bismuth in silicon the doublet has not been experimentally determined. The present calculation, based on the values given in Table 1, suggests it lies 4 ± 2 meV above the triplet and thus has a level ordering similar to the other Group V donors.

(b) Lithium impurity

A lithium donor is a special case because it is located at an interstitial rather than substitutional site. This introduces pronounced changes in the crystal wave functions since the core electrons of the impurity are located in a region of normally low wave function density. (For Group V impurities this is not the case since the impurity core and covalent electrons 'effectively' substitute for the host semiconductor electrons.) This suggests that $W(\mathbf{r})$ should be of a different nature since it must account for orthogonalization of a previously non-existent core of electrons and other changes in the crystal potential and wave function structure.

For lithium in silicon, the two general criteria, equations (19) and (20), are again satisfied. The remaining restrictive criteria are all not met and suggest the small R restriction is not valid in this case. Several features of $W(\mathbf{r})$ can be inferred from the data. The positive Λ value shows the integrated potential produces a net attractive influence. However calculations[28, 29] show that $W(\mathbf{r})$ is a repulsive potential near the lithium nucleus. Thus, to satisfy the inequality of equation (14) a rather large R would be required. A large R value is also indicated by (1) the fact that Δ/Λ and Δ(1 + δ)/Λ ratios are effectively equal, i.e. $\delta \approx 0$ [see Fig. 3], (2) the negative Δ/Λ ratio
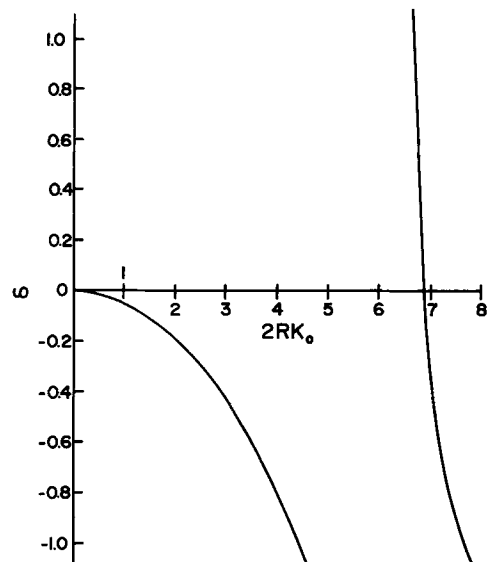

Fig. 3. Curve for δ in ⟨100⟩ multi-valley semiconductors. The curve is obtained from equations (17) and (18).

[see Fig. 2], and (3) the negative $\Delta(1+\delta)/\Lambda$ ratio [see Fig. 2]. [The somewhat large negative ratios for Δ/Λ and $\Delta(1+\delta)/\Lambda$ are partially attributed to negative $W(r)$ values near the core[28, 29].] If the theoretical model is valid for this case, an R value of 6 ± 2 a.u. is obtained from the data. [This value is rather large but $W(r)$ must take into account rather large ($\sim 0\cdot1$ Å) nearest neighbor displacements[30, 29] and associated strain field effects[31].] It is fortunate, however, that one can easily understand why in this special case the A_1 level is not the lowest. This so called 'inverted' level structure occurs when Δ is negative. (See Fig. 1). A negative Δ value occurs because (1) $W(r)$ is negative for small r as previously mentioned and (2) the exponential terms in the integrals of equations (11) and (12) tend to average to zero the positive $W(r)$ values at the more distant r values. Note that this second effect does not occur in equation (10) so that Λ can be positive. It is likely that the case of a lithium donor in germanium will yield a similar structure when the experimental data are obtained.

4. COMMENTS AND SUMMARY

It is certainly possible to choose some $W(r)$ potential and envelope function and perform specific calculations as shown in Appendix B. Such calculations have not been emphasized since quantitative details concerning the potential are probably beyond the validity of the model. However, the purpose of the paper has been met in that a number of new qualitative results concerning the chemical shift parameters have been presented. These considerations were shown to be rather useful in understanding the basic energy level structure as well as features of the central cell potential.

Recent publications by Ning and Sah[23] deserve special comment. These authors have performed a comprehensive calculation for the 1S-like states and wavefunctions.

They determined the three 1S energy levels quite accurately by fitting $W(r)$ with two adjustable parameters for each Group V donor in silicon. Their results agree quite well with experimental data. Note that *if* the present results were exact, the three chemical shift parameters would not be independent and consequently two constants would be sufficient to fit the data. Thus, in areas of overlap between this paper and theirs, there is excellent agreement.

In summary, theoretical calculations based on a simple model have suggested that the chemical shift parameters may be related and would determine effective radii. These calculations required a few assumptions which are believed to be reasonable. There were several consistency criteria predicted by the theory. They were found to be qualitatively satisfied when compared with the experimental data. It was also found that characteristics of the effective potential could be inferred from these comparisons. Comparisons were made with data from two different semiconductors and five different donor impurities from both Groups I and V. Despite the fact that chemical shift parameters vary over more than an order of magnitude, certain ratios of the shift parameters vary only over a small, well defined range as theoretically expected from the model. In addition, the effective model radii for the Group V impurities turned out to be smaller or about equal to the Wigner–Seitz sphere radius and larger than this radius for a lithium impurity. In the past, the center-of-gravity chemical shift potential, Λ, has seldom been mentioned especially in the valley-orbit matrix since it appears as a constant on-diagonal term. But, Λ, which is also the self-valley interaction matrix element, is suggested to be an important parameter in the energy level structure scheme.

APPENDIX A: DERIVATION OF THE ENERGY LEVELS

Equation (3) in the text when multiplied by $F_j(r)$ and integrated over all space yields

$$\alpha_j \langle F_j | H_j | F_j \rangle - E\alpha_j + \sum_{l \neq j} \alpha_l \{ \langle F_l e^{i(k_j - k_l) \cdot r} | H_l | F_l \rangle$$
$$- E \langle F_j e^{i(k_j - k_l) \cdot r} | F_l \rangle \} = 0. \quad (A.1)$$

For convenience define

$$d \equiv \langle F_j | H_j | F_j \rangle, \quad (A.2)$$

$$e \equiv \langle F_j e^{i(k_j - k_l) \cdot r} | H_l | F_l \rangle, \quad (A.3)$$

$$f \equiv \langle F_j e^{i(k_j - k_l) \cdot r} | F_l \rangle, \quad (A.4)$$

$$g \equiv \langle F_j e^{i(k_j - k_m) \cdot r} | H_m | F_m \rangle, \quad (A.5)$$

and

$$h \equiv \langle F_j e^{i(k_j - k_m) \cdot r} | F_m \rangle, \quad (A.6)$$

where j and l represent opposite valleys on the same axis and where j and m represent valleys on different axes. Then in silicon where A_1 has $\vec{\alpha} = 1/\sqrt{6}\,(1,1,1,1,1,1)$, E has an $\vec{\alpha} = 1/2\,(1,1,-1,-1,0,0)$ and T_2 has an $\vec{\alpha} = 1/\sqrt{2}\,(1,-1,0,0,0,0)$, equation (A.1) becomes

$$d - A_1 + e - A_1 f + 4g - 4A_1 h = 0, \quad (A.7)$$

$$d - E + e - Ef - 2g + 2Eh = 0, \quad (A.8)$$

and

$$d - T_2 - e + T_2 f = 0. \quad (A.9)$$

Thus,

$$A_1 = \frac{d + e + 4g}{1 + f + 4h}, \quad (A.10)$$

$$E = \frac{d + e - 2g}{1 + f - 2h}, \quad (A.11)$$

and

$$T_2 = \frac{d - e}{1 - f}. \quad (A.12)$$

In germanium, A_1 has $\vec{\alpha} = 1/2\,(1,1,1,1)$ and T_2 has an $\vec{\alpha} = 1/\sqrt{2}\,(1,-1,0,0)$ so

$$A_1 = \frac{d + 3g}{1 + 3h} \quad (A.13)$$

and

$$T_2 = \frac{d - g}{1 - h} \quad (A.14)$$

as shown by Twose[26]. To the accuracy of the present calculation,

$$H_j | F_j \rangle = E_0 | F_j \rangle + W(r) | F_j \rangle \quad (A.15)$$

and f and h are both $\ll 1$ (actually $< 10^{-4}$ for 1S hydrogenic function in silicon and smaller still in germanium) because of the oscillatory exponential term and the slowly

varying characteristics of the normalized envelope function. These results mean equations ((A.10)–(A.14)) yield equations ((5)–(9)) in the main text.

APPENDIX B: VALIDITY OF THE ASSUMPTIONS

The purpose of this appendix is to examine the assumptions of equations (15) and (16) since the comparisons of the model predictions with the experimental data are possibly limited by the approximate validity of these assumptions. (This is not necessarily true since serious difficulties with the quantitative validity of the effective mass theory for the ground state have been published[32].)

The extent of the approximation of either equations (15) or (16) can be given in terms of 'normalization constants', N_i, defined as

$$L_i = N_i R_i \quad (B.1)$$

where L_i and R_i are the 'true' values for the left and right hand side of equation (15) when $i = 15$ and of equation (16) when $i = 16$. For ideal agreement $N_{15} = N_{16} = 1$.

To calculate N_i a choice for $F(r)$ and $W(r)$ must be made. A naive, but simple, choice is to let $F(r)$ be constant (i.e., exceedingly slowly varying over region A) and $W(r)$ be a spherical potential well of radius R. Inspection of equations (15) and (16) show that the approximations are *exact* (i.e. $N_{15} = N_{16} = 1$).

More complex $W(r)$ have been used by various authors[10–24]. The rather recent results of Ning and Sah[23] suggest for an approximation

$$W(r) = -\frac{e^2}{\kappa r} e^{-br} (1 - Br) \quad (B.2)$$

with b and B donor dependent parameters. Calculations for N_i have been performed for Si(P), Si(As) and Si(Sb) using this potential with the b and B fit parameters[23] and three different forms for $F(r)$. The choices for $F(r)$ were (1) a constant, (2) $\exp(-r/a^*)$, and (3) $1/r$. Choice (2) was chosen because of its resemblance to a hydrogen-like ground state function. Choice (3) is expected in a small r Whittaker function approximation (see Ref. [33] and also Fig. 1 of Ref. [32]). Table B.1 shows these results. It is clear that many of the N values are near one, sometimes differing from one by a factor of about two with no deviations as large as a factor of three. Actually the model is satisfied if only the $N_{15}N_{16}$ product is near one (see discussion in next paragraph). Since the N_{15} values are greater than one while the N_{16} values are less than one, they compliment each other in their product as shown in Table B.1. This improves the agreement of the calculations. Note also that the value of the $N_{15}N_{16}$ product is less than one for $F(r) = $ constant and greater than one for $F(r) \propto 1/r$, i.e. it is one somewhere between the weak and tight bound limits.

These calculations suggest that it would not be very difficult to choose some "reasonable form" for $W(r)$ and $F(r)$ which would make the approximations of equations (15) and (16) very good. On the other hand, this is not the purpose of this paper. For such calculations, it would be desirable to use equations (17) and (18) in the general form

$$\Delta/\Lambda = (e^{i(k_m - k_j) \cdot r})_{Ave} N_{15}(\Delta k_{mj}) N_{16}(\Delta k_{mj}) \quad (B.3)$$

Table B.1. *Normalization constants for various potentials and envelope functions. Potentials used were those of Ref.* [23]

	$F(\mathbf{r}) =$ constant			$F(\mathbf{r}) \propto \exp(-r/a^*)$			$F(\mathbf{r}) \propto 1/r$		
	N_{15}	N_{16}	$N_{15}N_{16}$	N_{15}	N_{16}	$N_{15}N_{16}$	N_{15}	N_{16}	$N_{15}N_{16}$
Phosphorus									
Δk_{mj}	1·24	0·568	0·704	1·26	0·622	0·784	1·74	0·962	1·67
Δk_{lj}	1·37	0·460	0·630	1·41	0·512	0·722	2·35	0·938	2·20
Arsenic									
Δk_{mj}	1·03	0·442	0·455	1·04	0·493	0·513	1·16	0·928	1·08
Δk_{lj}	1·08	0·416	0·449	1·10	0·466	0·564	1·33	0·920	1·22
Antimony									
Δk_{mj}	1·03	0·341	0·351	1·02	0·387	0·395	1·17	0·903	1·06
Δk_{lj}	1·42	0·568	0·806	1·47	0·621	0·913	2·93	0·961	2·82

and

$$\Delta(1+\delta)/\Lambda = (e^{i(\mathbf{k}_i - \mathbf{k}_j)\cdot\mathbf{r}})_{\text{Ave}}N_{15}(\Delta k_{lj})N_{16}(\Delta k_{lj}) \quad (B.4)$$

and solve self-consistently for both $R(\Delta/\Lambda)$ and $N(\Delta[1+\delta]/\Lambda)$.

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