Effect of Potential Correction on the Ground States of P and S^+ Impurities in Silicon: Application of the Cavity Model

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The discrepancies between the observed and the calculated ground state energies of P and S^+ impurities in silicon are discussed on the basis of a cavity model which roughly accounts for the spatial dependence of the inverse dielectric function in the vicinity of the impurity. Applying simple effective mass theory (without reference to the Kohn–Luttinger semi-empirical correction method), it is shown that the model yields energy levels (and also the wave function at the P donor nucleus) in fair agreement with the experiments, if the effective cavity radius r_0 is assumed to resemble the Wigner–Seitz radius r_S rather than the nearest neighbour distance r_d of the Si host lattice.

The result depends critically on the assumption that the effective mass m^* related to the bottom of the conduction band, may be used even for levels as deep as S^+. Application of the cavity model in connection with the free electron mass m_0, gives rise to an almost zero cavity radius which appears to be inconsistent with various estimates yielding $r_S \lesssim r_0 \lesssim r_d$. It is concluded that the effective mass theory rather than a free electron mass equation will be the appropriate starting point for a more refined treatment of the S^+ spectrum and that of related defects.

The paper contains a discussion of various relevant aspects of the problem as well as a review of some different attempts to account for the discrepancies.

It is well known that the ground state of group V impurities [1] in Si and Ge is not in agreement with the prediction of simple effective mass theory [2]. A thorough study has been performed recently by Appel [3] who considers four corrections to the effective mass formalism; namely the deviation of the total perturbing potential U from the potential $U_0 = -e^2/\varkappa r$ ($\varkappa$ = static dielectric constant of the host crystal), and three relativistic effects. He finds that the *potential correction* which lowers the effective mass binding energy and causes the valley-orbit splitting, is the dominant one, at least for donor states in Si. We therefore neglect relativistic effects in this paper and restrict ourselves to Si as host crystal.

Experiments show a splitting of the ground state into two levels, in the case of group V donors [1]. Theoretically, the effective mass ground state is degenerate [2]. If one applies first order perturbation theory the splitting depends on the off-diagonal elements of the potential correction $U - U_0$ between unperturbed states. Since, however, the anisotropic contributions to U are not known, we shall disregard the splitting and restrict our study to the energy shift. Consequently, we shall consider only that part of $U - U_0$ which is spherically symmetrical.

The present investigation is based on the assumption that for both P donors and S^+ impurities in Si the main contribution to the binding energy shift is caused by the breakdown of the dielectric shielding in the vicinity of the impurity [2]. For group V donors other than P individual impurity corrections are not negligible [2, 4]. In the case of S^+ the orbits of the extra electron are more concentrated to the impurity core region than for the shallow donors of group V elements. But similar to the P donor, individual impurity corrections are of minor importance. In particular, the situation becomes quite analogous to the P donor if the sulfur impurities are assumed to occupy substitutional rather than interstitial lattice sites [5]. On the other hand, there is a difficulty connected with the deeper levels such as S^+; namely that the effective mass treatment is less reliable.

[1] For a review of recent measurements see J. H. Reuszer and P. Fisher, Phys. Rev. **135**, A 1125 [1964].
[2] W. Kohn, Solid State Physics, edited by F. Seitz and D. Turnbull, Academic Press Inc., New York 1957, Vol. 5, p. 257.
[3] J. Appel, Phys. Rev. **133**, A 280 [1964].
[4] A. M. K. Müller, Solid State Comm. **2**, 205 [1964].
[5] G. W. Ludwig, Phys. Rev. **137**, A 1520 [1965].

In the absence of a detailed quantitative knowledge of the dielectric polarization effects in the vicinity of the impurity atom, we are forced to introduce further simplifications. A model potential [6, 7] is adopted in Sec. 1 which roughly accounts for the absence of polarisation effects in the central cell region, and which contains only a single somewhat arbitrary parameter, the cavity radius r_0. Sec. 2 is concerned with a qualitative discussion of how this model can be properly incorporated into the formalism of effective mass theory. Since it was felt that a perturbative or a simple variational approach might be inadequate, the resulting SCHRÖDINGER equation was solved exactly [8] for a certain range of r_0. The resulting ionization energy, based on an isotropic effective mass, is shown in Sec. 3. In Sec. 4 the ground state envelope function in the cavity region is considered in detail, and the somewhat cumbersome normalization procedure [5, 9] simplified by the exact solution of a certain integral over confluent hypergeometric functions. A discussion of the results and of the main assumptions is given in Sec. 5, including an estimate of the magnitude of r_0 from comparison with experiments. The r_0-dependence of the binding energy and of the wave function at the lattice site of substitution is compared with the results of different approaches [10–13].

1. The Potential

The HAMILTONian for the extra donor electron in the presence of an isolated impurity atom is given by

$$H = -\frac{\hbar^2}{2\,m_0}\,\nabla^2 + V(\boldsymbol{r}) + U(\boldsymbol{r}), \qquad (1)$$

where $V(\boldsymbol{r})$ is the potential energy of the electron in the effective periodic potential of the undisturbed crystal, and $U(\boldsymbol{r})$ the total perturbing potential. m_0 is the free electron mass.

If one neglects the effect of local strain introduced by the impurity [14], and the effects of lattice vibrations, there remain two corrections to the potential $U_0(r)$:

(1) polarization effects due to a breakdown of the concept of macroscopic dielectric shielding in the vicinity of the impurity;

(2) the deviation due to the self-consistent potential of the impurity ion in the central cell region.

The correction (1) consists of two effects [15]: (a) a local dielectric anisotropy (involving dielectric tensors of order higher than two) which gives rise to non-spherical contributions [3]. Thus on expanding the total potential in terms of cubic harmonics [3],

$$U(\boldsymbol{r}) = f(r) + g(r)\,\frac{x\,y\,z}{r^3} + h(r)\,\frac{x^4+y^4+z^4-3\,r^4/5}{r^4} + \ldots, \qquad (2)$$

one expects the functions $g(r)$, $h(r)$ to be non-vanishing in the vicinity of the impurity. In fact, for simple cubic lattices [where $g(r)$ vanishes under the point group of the lattice site of substitution because of inversion symmetry] contributions to $h(r)$ occur for distances $r \lesssim 3\,d$ (d = lattice constant) [15]. We may tentatively assume that the effect on $g(r)$ and $h(r)$ for the more complex diamond lattice will be of the same order, and neglect all these anisotropy terms [16]. – (b) a local breakdown of the *radial* dielectric lattice shielding [17]. This effect has been estimated to be smaller than (a) [15]: it occurs in the region

$$r \lesssim \tfrac{1}{2}\,d\,. \qquad (3)$$

The correction (1 b) is difficult to obtain since it involves rather lengthy many body calculations. For the case of a Si host crystal, numerical results of PENN [18] were interpolated analytically by AZUMA and SHINDŌ [19] and slightly adjusted by the author [4] to

[6] H. REISS, J. Chem. Phys. **25**, 681 [1956].
[7] A. M. K. MÜLLER, Phys. Letters **12**, 299 [1964].
[8] A. M. K. MÜLLER, Ann. Phys., Lpz. (7) **13**, 351 [1964].
[9] W. KOHN and J. M. LUTTINGER, Phys. Rev. **97**, 883 [1955].
[10] A. GLODEANU, Phys. Letters **14**, 268 [1965].
[11] H. BROOKS, Advances in Electronics and Electron Physics, edited by L. MARTON, Academic Press Inc., New York 1955, Vol. 7, p. 85.
[12] P. E. KAUS, Phys. Rev. **109**, 1944 [1958].
[13] M. BREITENECKER, R. SEXL, and W. THIRRING, Z. Phys. **182**, 123 [1964].
[14] S. SHINOHARA, Nuovo Cim. **22**, 18 [1961].
[15] A. M. K. MÜLLER, Dissertation, Braunschweig 1960, unpublished.
[16] In a calculation of the level splitting these anisotropy terms may prove essential, and must not be neglected *a priori*.
[17] Throughout this paper the concept of "shielding" is used in its usual classical sense of a decrease of the averaged impurity ion potential caused by the multipole contributions due to polarized host crystal atoms. In the language of many body theory this effect is accounted for by collective screening of the external ("bare") impurity potential via the mutually interacting electrons moving under the influence of the effective periodic potential of the undisturbed crystal. See, e. g., J. HUBBARD, Proc. Roy. Soc., London A **240**, 539 [1957]; A **243**, 336 [1957]; A **244**, 199 [1958]. Cf. also Ref. [27].
[18] D. R. PENN, Phys. Rev. **128**, 2093 [1963].
[19] M. AZUMA and K. SHINDŌ, J. Phys. Soc. Japan **19**, 424 [1964].

give, in terms of an inverse spatial dielectric function, $\varepsilon^{-1}(r)$:

$$\varepsilon^{-1}(r) = \begin{cases} e^{-\alpha^* r} + A^*(1 - e^{-\beta^* r}) \\ \qquad + B^*(1 - e^{-\gamma^* r}), & r < r_1, \\ \varkappa^{-1}, & r > r_1, \end{cases} \quad (4)$$

$$\alpha^* = 0.663\, a_0^{-1},\ \beta^* = 8.895\, a_0^{-1},\ \gamma^* = 0.0302\, a_0^{-1},$$
$$A^* = 0.0745, \quad B^* = 0.0110,$$
$$r_1 = 7.127\, a_0, \quad \varkappa = (A^* + B^*)^{-1} = 11.7.$$

The adjustment introduced by the author, consists in cutting that part which would destroy the monotony of the potential (4) [20]. The region of dielectric breakdown is then found to be consistent with the estimate (3) [21]. Very recently a more rigorous calculation of the wave-number-dependent dielectric function for Si has been performed by NARA [22] on the basis of the detailed band structure. The results are in good agreement with those obtained by PENN and interpolated by AZUMA and SHINDŌ, hence the above picture remains unchanged.

For the sake of mathematical convenience a further simplification is introduced. We adopt a rough procedure which partly neglects the continuous distribution of the electronic polarization cloud by setting

$$f(r) = \begin{cases} u(r) + (1/\varkappa - 1)\, u(r_0), & r < r_0, \quad (5\,a) \\ u(r)/\varkappa, & r > r_0, \quad (5\,b) \end{cases}$$

where $u(r)$ is the unshielded or "bare" potential [17], and r_0 the effective radius of a cavity cut out of an otherwise dielectric continuum [6]. In the case of a P donor in Si, one may substitute for $u(r)$ the potential

$$u_0(r) = -e^2/r \quad (6)$$

as the crudest approximation. The choice of (5) combined with (6) permits a rigorous approach to the solution of the corresponding eigenvalue problem (Sec. 3). There is, of course, no strict physical justification to r_0, the effective cavity radius being more or less a phenomenological parameter. However, the model potential (5), (6) may be understood as an approximation to the (averaged, isotropic) field produced by a point dipol model of a cubic lattice which is thought of being polarized under the influence of a point charge $+e$ situated at the lattice site of substitution [7]. This argument leads to a cavity radius of

$$r_0 \leqq \sqrt{3}\, d/4 = r_d. \quad (7)$$

In eq. (7), the in equality sign accounts for the finite range of the polarization clouds produced by the nearest neighbour Si atoms which, of course, cannot be described adequately by strict point dipoles. The radius r_d is the nearest neighbour distance in the diamond lattice. Its numerical value for Si is $4.44\, a_0 = 2.35$ Å.

A separation of the polarization effects (1) from the rest of the total perturbing potential U is, of course, not possible in a strict sense; for an accurate self-consistent treatment would reveal that both the corrections (1) and (2) are mixed in a rather complex way. In the central cell region, however, one may visualize the correction (2) to be determined separately. This can be accomplished by starting the self-consisten calculation from inside, i. e. if one includes the contributions of the impurity ion under the influence of the four surrounding Si atoms only. The polarizing influence from outside (i. e. from the region of shielding) is then manifest in the constant term of (5 a) [12]. Hence the concept of an unshielded or "bare" potential as employed in eq. (5) seems meaningful, and a separation of the effects (1) and (2) thereby posible. Roughly speaking, the bare region should be the central cell region where the shielding mechanism is not effective except that it produces the constant term. This is because the inmost polarization charge clouds are concentrated around the nearest neighbour atoms with only a small overlap into the impurity core region. Hence

$$r_0 \gtrsim r_s \quad (8)$$

where r_s, the radius of the WIGNER–SEITZ sphere, has the value $3.18\, a_0 = 1.68$ Å. Eq. (8) is consistent with an estimate of the effective cavity radius as derived [4] from the many body result (4); namely $r_0 = 3.55\, a_0$ ($a_0 =$ BOHR radius $= 5.29 \cdot 10^{-9}$ cm). It must be emphasized that the relations (7) and (8) are relevant only for substitutional impurities.

The constant term in eq. (5 a) arises from a surface charge which can be visualized as causing the shielding effect of the lattice. This term appears automatically if one requires the continuity of the

[20] Cf. the remark on the monotony of the spatial dielectric function in Ref. [19].

[21] For a graphic representation of the results of Ref. [19] and of eq. (4) see Ref. [4], where ε is identical with ε_3.

[22] H. NARA, J. Phys. Soc. Japan **20**, 778 [1965].

potential at $r=r_0$ in accordance with MAXWELL's theory. One may go a step further and absorb into the surface charge those (continuous) charge contributions which act as to make $u(r)/\varkappa$ different from $u_0(r)/\varkappa$ in the outer region $r>r_0$. As the result one obtains the following modification of (5):

$$f(r)=\begin{cases} u(r)+u_0(r_0)/\varkappa-u(r_0), & r<r_0, \quad (9\,a)\\ u_0(r)/\varkappa, & r>r_0. \quad (9\,b)\end{cases}$$

The cavity model described by (9) will be used as a starting point for what follows. The choice (9) is more convenient than (5), since it allows for a systematic discussion of further simplifications known from actual impurity calculations.

To keep individual impurity corrections to the electronic structure of the silicon crystal as small as possible, only substitutional impurities whose core and valence electron number equals that of Si are taken into consideration. Hence the atomic number Z_D of a donor of ionization degree $Z-1$ is related to the atomic number Z_S of Si by

$$Z_D=Z_S+(Z-1)+1=Z_S+Z. \quad (10)$$

(We consider impurities with a single extra donor electron only.) For $Z=1$, 2 these are the P and S^+ donors, respectively.

The deviation correction (2) in the "bare" region is given by the difference of the self-consistent potential of the impurity ion and the effective periodic potential $V(\boldsymbol{r})$. Near the impurity nucleus these resemble the potential of a free donor ion, $u_{D(Z+)}(\boldsymbol{r})$, and that of a free semiconductor host atom, $u_S(\boldsymbol{r})$, respectively. Therefore, following CSAVINSZKY [23], one may roughly assume that

$$u(\boldsymbol{r})=u_{D(Z+)}(\boldsymbol{r})-u_S(\boldsymbol{r}) \quad (11)$$

holds for $r<r_0$. Eq. (11), with $u(\boldsymbol{r})$ averaged over the angles, can be rewritten as

$$\begin{aligned} u(r)&=u_{D(Z+)}(r)-\left(u_S(r)-\frac{Z e^2}{r}\right)-\frac{Z e^2}{r}\\ &=u_{D(Z+)}(r)-u_{D(Z+)}(r)-\frac{Z e^2}{r}, \end{aligned} \quad (12)$$

where $u_S(r)-Z e^2/r=\tilde{u}_{D(Z+)}(r)$ can be visualized as the potential energy of an artificially introduced „ion" with no interaction between the nuclear excess charge $+Z e$ and the Si-type electron cloud. Both the true and the fictitious ion have equal nuclear charge and similar core and valence electron structure. It is this lack of interaction which leads to a non-zero contribution of the ion difference potential

$$\Delta(r)=u_{D(Z+)}(r)-\tilde{u}_{D(Z+)}(r). \quad (13)$$

On combining (2), (9), (12) and (13) and making all the approximations described above, one obtains

$$U(r)=\begin{cases} -Z e^2/r+\Delta(r)-(1/\varkappa-1)\,Z e^2/r_0-\Delta(r_0), & r<r_0, \quad (14\,a)\\ -Z e^2/\varkappa r, & r>r_0. \quad (14\,b)\end{cases}$$

For a further simplification of the model potential (14) one may proceed in either of two ways. CSAVINSZKY [23] discards the r-independent surface terms [24] of (14) right from the beginning and treats the rest of the potential by first order perturbation theory. In this way his total perturbing potential becomes a step function at $r=r_0$,

$$U(r)=\begin{cases} u_{D(Z+)}(r)-u_S(r)=-Z e^2/r+\Delta(r) & r<r_0, \quad (15\,a)\\ -Z e^2/\varkappa r, & r>r_0, \quad (15\,b)\end{cases}$$

which is then divided in the zero order (slowly varying) term $-Z e^2/\varkappa r$, and the remaining strong perturbation being localized in the cavity region [25]. The potentials $u_{D(+)}(r)$ (corresponding to $Z=1$) and $u_S(r)$ in (15) were approximately determined by a THOMAS–FERMI approach. From the numerical results of CSAVINSZKY's work it is seen that the energy correction which he finally obtains, does not explain the discrepancy between the observed and the effective mass ground state energy for a P donor.

[23] P. CSAVINSZKY, J. Phys. Chem. Solids **24**, 1003 [1963].

[24] The constant V_0 in Ref. [23], eq. (5 a) is due to the THOMAS–FERMI approach of the ion core potential, and must not be identified with the surface term in the above eq. (14). V_0 of Ref. [23] cannot be employed to make $U(r)$ of the present eq. (15) continuous at $r=r_0$.

[25] There appears to be an inconsistency in the perturbation treatment. According to eqs. (11), (12) of Ref. [23] the first order perturbation term should be a difference potential, i. e. the subsequent eq. (13) should read $-e\,\eta(r)+e^2/\varkappa r$.

In fact, his correction turns out too small by one order of magnitude (-1.5 eV as compared with -16 meV) if the cavity radius is taken $r_0 = r_d/2$. Furthermore the energy shift is claimed to be very insensitive to any small increase beyond the r_0 value used. Even if such a conclusion might be doubtful because of a breakdown of perturbation theory in a possible range of rapid change, a more refined approach should include the repulsive effect which would be due to an incorporation of the PAULI principle [4, 23].

CSAVINSZKY has pointed out the difficulty which consists in carrying over the effect of an appropriate core orthogonalization into the effective mass treatment which he needs as a starting point for the perturbation approach. Furthermore, he argues that in a first order perturbation calculation this problem does not arise because the (effective mass) zero order wave function cannot be changed by any orthogonalization since that would amount to changing the unperturbed problem. The situation looks quite different, however, if one thinks of the orthogonalization as being accounted for by an appropriate pseudo-potential [26, 27] („Besetzungsverbotpotential") which could be substituted for *each* of the ion potentials $\tilde{u}_{D(Z+)}(r)$ and $u_{D(Z+)}(r)$. In this case the PAULI principle would operate on the potential energy rather than the wave function, and hence be accessible to first order perturbation theory. Moreover, the pseudo-potential can be carried over into the effective mass formalism without conceptual difficulty since the orthogonalization requirement has been dropped. Proceeding in this way, one may expect from the well known "cancellation effect" [27], that the PAULI repulsion will compensate parts of the ion core attraction thereby reducing the CSAVINSZKY correction and making the remaining discrepancy with the experiment even larger.

The other way in which one may proceed in (14) consists in dropping all terms which depend on $\Delta(r)$, i. e. dropping the ion core and valence correction at all. The potential energy then reads [28]

$$U(r) = \begin{cases} -Z e^2/r - (1/\varkappa - 1)\, Z e^2/r_0\,, & r > r_0\,, \quad (16\,a) \\ -Z e^2/\varkappa r\,, & r > r_0\,. \quad (16\,b) \end{cases}$$

Contrary to (15) one now obtains a continuous function at $r = r_0$. But in using (16), care must be taken that the spectrum of the core and valence states can be eliminated from the treatment of the impurity levels; for a potential like (16) certainly cannot account for the deep lying states of the host crystal. Such a separation is automatically performed by carrying the HAMILTONIAN (1) over in the effective mass formalism (Sec. 2).

Perhaps a more precise way to drop $\Delta(r)$ would be (i) to substitute for it an appropriate pseudo-potential $\Delta_{ps}(r)$, (ii) to transform into effective mass theory, and (iii) to discard the pseudo-potential difference term $\Delta_{ps}(r)$ as a whole. Since the pseudo-potential can be assumed to be a slowly varying function, its appearance in the resulting effective mass HAMILTONIAN can be easier justified than would be possible with $\Delta(r)$ itself. And since $\Delta_{ps}(r)$ exhibits a cancellation effect, its dropping will be less critical than a dropping of $\Delta(r)$ would be.

In comparing the simplifications which lead to either (15) or (16), it is felt that the second kind, namely the dropping of the ion core and valence correction $\Delta(r)$ is at least qualitatively justifyable in terms of the pseudo-potential concept, while it is difficult to see how the abrupt behaviour of the potential (15) could be made plausible on the atomic scale [12]. Therefore it is the model according to (16) that will be employed throughout the rest of this paper.

Finally we mention a third kind of approximation which consists in discarding at the same time both, terms with $\Delta(r)$ *and* the surface terms in eq. (14), thus leading to

$$U(r) = \begin{cases} -Z e^2/r\,, & r < r_0\,, \quad (17\,a) \\ -Z e^2/\varkappa r\,, & r > r_0\,. \quad (17\,b) \end{cases}$$

The SCHRÖDINGER equation corresponding to (17) was studied by BREITENECKER and SEXL [29] using perturbation theory, the WKB method, and a variational treatment with hydrogenic trial functions. In the opinion of the present author, however, the model (17) should be disregarded because of its crudemess. Apart from the physical reasons that speak

[26] P. GOMBAS, Fortschr. Phys. **13**, 137 [1965].

[27] The application of the pseudo-potential method to solid state physics is reviewed by J. M. ZIMAN, Advances Phys. **13**, 89 [1964].

[28] A similar approach was suggested by K. WEISER (private communication). See also K. WEISER, Bull. Amer. Phys. Soc. **6**, 156 [1961].

[29] M. BREITENECKER and R. SEXL, Technical Note Nr. 3, Project Nr. 1098-10 (1961), Institute for Theoretical Physics, University of Vienna, Austria.

against the use of (17), nothing is gained from a pure mathematical point of view if, in an effort to solve the corresponding bound state problem, the constant surface terms in (14) are dropped.

2. Effective Mass Treatment

For shallow levels such as P in Si, the success of the effective mass (EM) theory has been demonstrated on many occasions [2]. In its usual form, the basic potential employed in the formal development of the theory and in the major part of its applications, is $U_0 = -e^2/\varkappa r$. The present potential $U(r)$ of eq. (16), however, is more rapidly varying, in the vicinity of the impurity nucleus, by a factor 12. Moreover, for deeper levels such as S^+, the electron cloud as a whole is much more concentrated to the central cell region. Therefore it is doubtful whether the following corrections to the effective mass formalism are still negligible:

(A) the admixture of BLOCH functions from higher bands into the impurity wave function caused by the strong potential U near the impurity ion; and

(B) possible effects which may be equivalent to a partial replacement of the effective mass m^* by the vacuum electronic mass m_0, preferably in the central cell region.

Concerning (A) the situation is rather fortunate in the case of Si crystals. Recently, APPEL [3] has pointed out that the admixture for shallow donors in Ge is much larger than for shallow donors in Si. For deeper impurity states ($Z = 2$) the work of LUDWIG [5] seems to indicate that other bands yield an important contribution to the impurity wave function. On the other hand, one-dimensional model calculations of BREITENECKER, SEXL, and THIRRING [13] (abbreviated BST in the following) have given strong evidence to the view held by the present author [30], that the effective mass theory is a fairly good approximation even for strong potentials, especially if one is only concerned with the determination of the energy levels. The results of BST show that it is quite reasonable to use the effective mass equation in all space, i. e. not to exclude regions with strongly varying potential as was done in the semi-empirical correction method of KOHN and LUTTINGER [9]. In the present case, with $U(r)$ strongly varying near the origin, one may thus start to a first approximation by applying boundary conditions at $r = \infty$ *and* $r = 0$. It is encouraging that the corrections stemming from the replacement of $E(\boldsymbol{k})$ by $\boldsymbol{k}^2/2\,m^*$, for the example of a deep level embedded in an one-dimensional periodic delta functions potential, are not more than 20 per cent [13]. A second result obtained by BST is already implicit in the perturbative approach of SHINOHARA [14]; namely the replacement of the rapidly varying (say, one-dimensional) potential $U(\xi)$ by a modulated potential

$$U_{\mathrm{mod}}(\xi) = U(\xi)\,|\varphi_0(\xi)|^2, \tag{18}$$

where $\varphi_0(\xi)$ denotes the BLOCH function at the bottom of the conduction band. On FOURIER-analyzing $|\varphi_0|^2$, one obtains from the normalization of the BLOCH wave,

$$|\varphi_0(\xi)|^2 = 1 + \sum_{\substack{\nu=-\infty \\ \nu \neq 0}}^{+\infty} c_\nu \exp\left\{ i \frac{2\pi\nu}{d} \xi \right\},\quad c_\nu^* = c_{-\nu}, \tag{19}$$

and, consequently,

$$U_{\mathrm{mod}}(\xi) = U(\xi) + \text{oscillating terms}, \tag{20}$$

i. e. U appears as the zero term of the modulated potential. Again all the higher terms except the leading U will be discarded in the following [31].

So far no thorough theoretical basis has been established for possible corrections according to (B). In actual impurity calculations, however, such a procedure was employed in several ways. REISS [6] and KAUS [12] used the potential (16) for a determination of the ionization energy of hydrogen interstitial impurities in Si and Ge. REISS solved a simple "vacuum" SCHRÖDINGER equation with the effective mass m^* replaced by m_0, the vacuum electron mass, in all space while BROOKS and FLETCHER [32] as well as

[30] See Ref. [4], Sec. 2.

[31] Eq. (18) holds for a single conduction band minimum. For the impurity ground state of a Si host crystal, the three-dimensional result corresponding to several equivalent minima, is to a lowest approximation

$$U_{\mathrm{mod}}(\boldsymbol{r}) = U(\boldsymbol{r}) \cdot (1/4\,\pi\,N) \int \Big| \sum_{i=1}^{N} \varphi_i(\boldsymbol{r}) \Big|^2 \,\mathrm{d}\Omega \tag{18 a}$$

where $\varphi_i(\boldsymbol{r})$ is the BLOCH wave at the conduction band minimum with wave vector $\boldsymbol{k}_i$, $N = 6$ denotes the number of equivalent minima, and the integration is over the solid angle Ω (unpublished calculations by the author). On expanding (18 a) in analogy with (20), a knowledge of the BLOCH waves is needed to evaluate the correction terms to U. Approximately, the $\varphi_i(\boldsymbol{r})$ can be calculated by the pseudo-potential method [26, 27] (cf. Ref. [22]).

[32] H. BROOKS and N. FLETCHER, unpublished. — N. FLETCHER, Thesis, Harvard University, Cambridge, Massachusetts, 1955, unpublished.

KAUS employed a vacuum SCHRÖDINGER equation with $m = m_0$ inside of a cavity centered around the impurity ion, and an effective mass equation with $m = m^*$, outside [33]. The interior wave function was then matched to the exterior at the matching radius r_m of the cavity. In evaluating the matching condition KAUS [12] introduces a further approximation in that the neglects the contribution of the BLOCH function to the logarithmic derivative at $r = r_m$.

Formally, the treatment of REISS appears as a special case of the more general ansatz of BROOKS and FLETCHER, and of KAUS, namely letting $r_m \to \infty$. KAUS identifies r_m with the formerly introduced cavity radius r_0 of eq. (16) though the points out that such an identification is only a convenience in the computation [34]. The simple effective mass theory is obtained back in the limit $r_m \to 0$.

The question arises whether such a combined procedure of matching a vacuum and an effective mass wave function, can be easily justified. As to the work of REISS, it served for establishing a purely qualitative feature; namely to explain the absence of ionization in the case of hydrogen interstitials in silicon and germanium crystals. Here an explanation requires only a very rough estimate in the order of magnitude of the ionization energy, for which a distinction between m_0 and m^* is quite irrelevant. More recently, GLODEANU [10] has claimed that for rather deep impurity levels in Ge and Si the appropriate choice of the electron mass is $m = m_0$ [35]. Using the simple hydrogen-like model with the potential U_0 for one-electron states and the corresponding helium-like model [37] with

$$U_0(\mathbf{r}_1, \mathbf{r}_2) = -2\,e^2/\varkappa\, r_1 - 2\,e^2/\varkappa\, r_2 + e^2/\varkappa\,|\,\mathbf{r}_1 - \mathbf{r}_2\,| \tag{21}$$

for two-electron states, he was able to account for the impurity levels of S and S^+ in silicon crystals in excellent agreement with experiment. To the author's opinion, however, the striking success is less convincing than it may seem on first sight [38].

At present, both the pure vacuum and the combined EM-vacuum treatment are open to criticism from a more conceptual point of view. For example, it was pointed out by KOHN [41] that because of the PAULI principle the impurity wave function must be a linear combination of BLOCH waves from the conduction band. This condition is not fulfilled *a priori* if the vacuum SCHRÖDINGER equation is incorporated in the treatment of the impurity levels. To avoid such an inconsistency and at the same time bearing in mind that the validity of the effective mass equation goes fairly beyond the range for which it has been rigorously established, it seems promising to assume $m = m^*$ in *all* space, i. e. to employ simple effective mass theory even for deep levels. Our assumption will be confirmed by the results of the numerical calculations (see Sec. 5). This is also in accordance with the present motivation to keep the number of adjustable parameters as small as possible. It is obvious that the matching radius r_m would be such a parameter if one should allow for

[33] The calculations of Ref. [32] hold for substitutional impurities.

[34] In Appendix II of Ref. [12], KAUS argues that the choice of the radius r_m is not critical within certain limits. His argument, however, lacks foundation, since the upper curve in his Fig. 10 is in eror [44], and the corrected curve does not permit such a conclusion.

[35] To the author's knowledge, a detailed acount of GLODEANU's work has not yet been given. CURIE [36], following a suggestion due to FRIEDEL [36a], has studied the conditions under which for deep levels the vacuum mass and not the effective mass may be appropriate.

[36] D. CURIE, J. Phys. Radium **19**, 694 [1958].

[36a] J. FRIEDEL, Physica **20**, 998 [1954]; J. Phys. Radium **15**, 433 [1954].

[37] In the framework of the EM theory the helium-like model was proposed by BST [13] for an explanation of the S level in silicon and the Se level in germanium. So far no calculations have been published. In the corresponding one-electron case of He^+ type, related to S^+ and Se^+ impurities, the result with $m = m^*$ was found in reasonable agreement with experiment only for germanium while in silicon the energy turned out to be too large by a factor 15. The one-electron potential used by BST is identical [51] with eq. (16) of the present work, with $r_0 = r_d$. The large discrepancy for S^+ in Si can be removed by an alternative choice of the cavity radius; namely $r_0 \lesssim r_s$ (see Sec. 5).

[38] The coincidence of GLODEANU's values with the observations is less striking for two reasons. Firstly, his results are based on the "hydrogenic" assumption that $-Z\,e^2/\varkappa\, r$ [or (21), respectively] is the potential all the way to the origin. This corresponds to a vanishing cavity radius r_0 in (16). But a natural assumption would be to choose r_0 of the order of r_s [cf. eq. (8)]. Hence GLODEANU's coincidence is in fact a weak point, because it does not allow for a finite cavity radius. Its occurrence might perhaps be accidental. — Secondly, the experimental value of 370 meV for the ionization energy of the S^+ donor electron is no longer generally accepted but was recently assigned to sulfur pairs [39]. KRAVITZ and PAUL [40] obtained an energy level at −520 meV below the conduction band thereby making the agreement with GLODEANU's result less satisfactory. The cavity radius that would fit this value, though being finite, is still far too small to be physically reasonable (see the discussion, Sec. 5).

[39] See Footnote [17] of Ref. [5].

[40] L. C. KRAVITZ and W. PAUL, to be published.

[41] See p. 681 of Ref. [6].

the above kind of "vacuum mass admixture" in the EM treatment.

From the HAMILTONian (1) one arrives in the usual way at the EM equation

$$\left[-\frac{\hbar^2}{2m^*}\nabla^2-\frac{Ze^2}{r}-\left(\frac{1}{\varkappa}-1\right)\frac{Ze^2}{r_0}-E\right]F_i(\boldsymbol{r})=0\,,\qquad r<r_0\,,\quad (22\,a)$$

$$\left[-\frac{\hbar^2}{2m^*}\nabla^2-\frac{Ze^2}{\varkappa r}-E\right]F_a(\boldsymbol{r})=0\,,\qquad r>r_0\,,\quad (22\,b)$$

with the total perturbing model potential taken from (16). The value of the scalar effective mass m^* is obtained by the energy criterion [12, 42].

3. Ground State Energy

Since the effective cavity radius is not precisely fixed it is convenient to calculate the ionization energy of the donor electron as a function of r_0 in the range $0 \leqq r_0 \leqq r_d$; the radius r_0 can then be determined by fitting the observed energy value. The ground state of an electron with effective mass m^* moving in the potential (16) has been calculated by solving eq. (22) exactly in terms of confluent hypergeometric functions, for the shallow case $Z=1$ [8, 43]. The following values were taken for the effective mass ratio $m^*/m_0=\mu$ and the static dielectric constant [8]:

$$\mu=0.293;\qquad \varkappa=11.7\,. \qquad (23)$$

The resulting ionization energy is shown in Fig. 1 and is expected to be correct to an order of 1 per cent.

On the other hand KAUS [12] seems to have been the first who obtained a solution of a SCHRÖDINGER equation of type (22) by numerical computation (see Appendix II of his paper). In fact what he really did was not to treat (22) directly but to solve for the corresponding equation with m^* replaced by the vacuum mass m_0 (lower curve of Fig. 10, Ref. [12]). The upper curve [12] related to $m=m^*$ was then obtained by a scaling process. His result should by comparable with the exact solution of the author except for a discrepancy stemming from the slightly different parameter values,

$$\mu=0.31;\qquad \varkappa=12\,, \qquad (24)$$

employed in the paper of KAUS. Unfortunately, an error has slipped into the scaling procedure of KAUS so that his upper curve is misleading [44]. The correct scaling is as follows. From the exact solution [8] it is known that for $Z=1$, $\mu=1$ the r_0-dependence of the ground state energy can be described in dimensionless quantities $\bar{\eta}$, C as a function $\bar{\eta}=\bar{\eta}(C)$, where

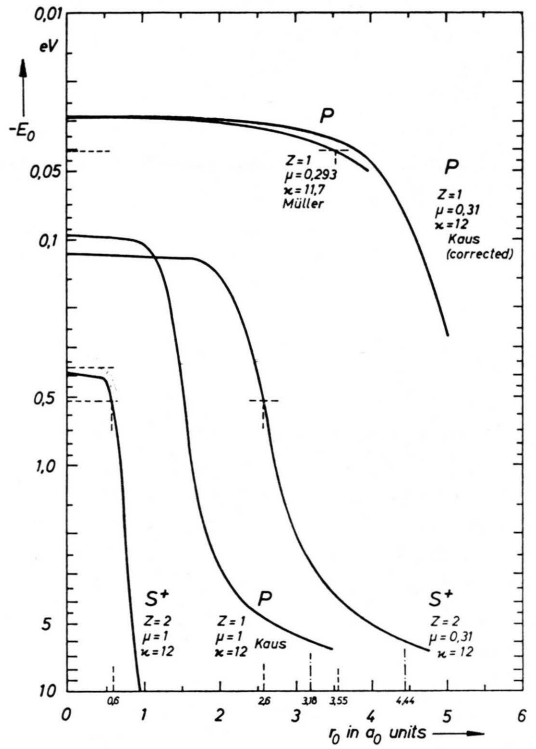

Fig. 1. Ionization energy as a function of the effective cavity radius for donors of nuclear excess charge $+Ze$ ($Z=1$, 2) in silicon ($\varkappa=11.7\ldots12$). Free electron mass: $\mu=1$. Effective mass of the lowest conduction band minimum: $\mu=0.293$ to 0.31. The basic curves are due to KAUS [12, 44] and to MÜLLER [8]. The curves for $Z=2$ are obtained by scaling.

[42] Cf. Footnote [49] of Ref. [2].

[43] The energy is obtained by matching the logarithmic derivatives of the interior and the exterior envelope functions. It was shown by the author that the former can be approximately determined without explicit reference to the energy parameter [8]. The evaluation of the latter which was found to be rather involved, can be simplified in the case of the ground state by calculating the logarithmic derivative from the simple asymptotic expression (31) of the exterior function. It turns out that (31) and the first derivative from it, are valid in a range of $0 \leqq r_0 \leqq 4\,a_0$ within an accuracy of about 3 per cent and less. Formula (31) was employed by KOHN and LUTTINGER in their semi-empirical correction approach to effective mass theory.

[44] P. E. KAUS, private communication. The author is indebted to Dr. KURT WEISER of the IBM Corporation for drawing his attention to the work of Ref. [12].

$$E_0 = -\frac{e^4 m_0}{2\hbar^2 \varkappa^2} \cdot \bar{\eta}\,,$$

$$r_0 = a\,C/2\,, \qquad a = \hbar^2 \varkappa/(e^2 m_0) \tag{25}$$

(E_0 = ground state energy, a = BOHR radius). Transforming $m_0 \to \mu m_0 = m^*$ and the nuclear charge $+e \to +Ze$, one obtains the corresponding solution of the transformed equation by the scaling

$$E_0 \to Z^2 \mu E_0\,, \qquad r_0 \to r_0/Z\mu\,, \tag{26}$$

as is seen by inspection of (25). Applying (26) with $Z=1$, $\mu = 0.31$ to the lower curve of KAUS, one arrives at the corrected curve (Fig. 1). Apart from the difference between the parameter values (23), (24), the various approximations in the calculations of Ref. [8] probably yield a contribution to the remaining discrepancy in Fig. 1. There may also be a deviation due to the errors arising from the graphic representation of Ref. [12] which served as the starting point for the scaling.

In a similar way one obtains the energy curves for $Z=2$ and the vacuum and the effective mass, respectively (Fig. 1). The vacuum results serve for a discussion of GLODEANU's impurity model [10] (see Ref. [38] and Sec. 5).

4. Wave Function for Shallow P Donor

An important tool in testing the validity of the EM equation for strong potentials consists in a comparison of the theoretically determined envelope function at the various lattice sites of the crystal with corresponding information obtained by the Electron Paramagnetic Resonance Method (EPR) [45]. Since the potential (16) is by far strongest near the impurity nucleus interesting information will be gained from the experimental values of $|\Psi|^2$ at the lattice site of substitution. Furthermore, one may ask how rapidly the wave function varies over the central cell region if the EM equation is assumed to be valid all the way to the origin. Hence a careful calculation of the wave function resulting from the cavity model (16), may throw further light on the applicability of the effective mass theory.

In this section we perform the calculation of the EM ground state for $Z=1$, i. e. for the P donor electron, in silicon. The exact ground state envelope function is constructed from two confluent hypergeometric functions; namely [8, 46]

$$F_i(x) = N_i \frac{n}{2x} \mathcal{M}_{\nu,1/2}\left(\Lambda \frac{2x}{n}\right), \quad x < x_0\,, \tag{27 a}$$

$$F_a(x) = N_a \frac{n}{2x} W_{n,1/2}\left(\frac{2x}{n}\right), \quad x > x_0 \tag{27 b}$$

where

$$x = r/a^*, \qquad x_0 = r_0/a^* = C/2,$$
$$a^* = \hbar^2 \varkappa/m^* Z e^2 = a/Z\mu\,, \qquad \nu = \varkappa n/\Lambda\,,$$
$$\Lambda = \left[1 + \frac{4n^2(\varkappa - 1)}{C}\right]^{1/2}.$$

n is the generalized quantum number defined by $\bar{\eta} = 1/n^2$ in eq. (25). The constants N_a, N_i are determined by the requirement of continuity at $x = x_0$, and by normalization over all space:

$$F_i(x_0) = F_a(x_0), \quad 4\pi \int_0^\infty x^2 F^2(x)\,dx = 1\,. \tag{28}$$

Hence
$$N_i = \frac{2x_0}{n} \frac{F_a(x_0)}{\mathcal{M}_{\nu,1/2}(\Lambda \cdot 2x_0/n)}\,. \tag{29}$$

The value of the envelope function at the lattice site of substitution is

$$F_i(0) = \Lambda N_i\,. \tag{30}$$

Thus an evaluation of (30) requires a knowledge of both the WHITTAKER functions $W_{n,1/2}(2x_0/n)$ and $\mathcal{M}_{\nu,1/2}(\Lambda \cdot 2x_0/n)$. For convenience of the computation certain approximations will be introduced whose accuracy was tested; the errors were found not to exceed the order of 1 per cent if r_0 runs in the range of Fig. 1 [47].

In the case of the exterior function $W_{n,1/2}(\varrho)$, the use of the asymptotic expression for $1-n \ll 1$, $2x/n \ll 1$ leads to the approximation [9, 43]

$$F_a(x_0) \approx N_a\, e^{-x_0/n}\left[\frac{1-n}{2x_0} - (1-n)\log(2x_0) + 1\right]. \tag{31}$$

[45] Applications of the EPR method to shallow donors, published up to 1963, are reviewed by L. D. BOGOMOLOVA, V. N. LAZUKIN, and I. V. CHEPELEVA, Usp. Fiz. Nauk **83**, 433 [1964], engl. transl. in Soviet Phys.—Uspekhi **7**, 508 [1965]. For recent work on deeper levels see also Ref. [5].

[46] Notations are due to H. BUCHHOLZ, Die konfluente hypergeometrische Funktion, Springer, Berlin 1957.

[47] For $Z=2$ the range of the validity of the various approximations lies already outside the interval which is of physical interest, so that eqs. (37), (38) are no longer applicable.

The interior function may be approximated by use of the relation [48]

$$\frac{x_0}{x}\frac{\mathcal{M}_{\nu,1/2}(\Lambda\cdot 2x/n)}{\mathcal{M}_{\nu,1/2}(\Lambda\cdot 2x_0/n)} \approx \frac{1-Z_L-\tilde{\tau}x_0}{(1-\tilde{\tau})x_0}e^{x_0}(e^{-x}+q\exp\{-\tilde{\tau}x\}), \quad (32)$$

where

$$Z_L=(1+xF_i'(x)/F_i(x))_{x=x_0}$$
$$=(1+xF_a'(x)/F_a(x))_{x=x_0},$$
$$q=-\frac{1-Z_L-x_0}{1-Z_L-\tilde{\tau}x_0}\exp\{\tilde{\tau}-1)x_0\}, \quad (33)$$
$$\tilde{\tau}=\frac{\tau+\zeta\varkappa}{1+\zeta}, \qquad \tau=\frac{(1-Z_L)(2-x_0)-2x_0}{x_0(1-Z_L-x_0)}.$$

Z_L, the logarithmic derivative of the radial envelope function, is known from earlier work [8] (see Fig. 2 of Ref. [8]). An approximation of the absolute values of the interior WHITTAKER function is readily obtained if one carries out the limit $x\to 0$ in the relation (32),

$$\frac{\Lambda\cdot 2x_0/n}{\mathcal{M}_{\nu,1/2}(\Lambda\cdot 2x_0/n)} \approx \frac{(1-Z_L-\tilde{\tau}x_0)e^{x_0}-(1-Z_L-x_0)\exp\{\tilde{\tau}x_0\}}{(1-\tilde{\tau})x_0}, \quad (34)$$

and this is exactly what is needed in (30).

There remains the determination of the normalization constant N_a. An exact computation according to (27) would be a formidable tast. It can be estimated, however, that the contribution of the interior function to the integral (28) is negligible. Even a replacement of F_i by F_a (singular at the origin) in the interior region, keeps the error in the above limits [9, 50]. Hence we may calculate N_a from a normalization of $F_a(x)$ over *all* space [9] which leads to the integral

$$I_0(n,n;1)=\int_0^\infty W^2_{n,1/2}(\varrho)\,d\varrho. \quad (35)$$

Fortunately, the evaluation of (35) can be performed in closed form as is shown in the Appendix. Making use of eq. (47) one finally arrives at

$$1/N_a^2=\pi n^3\frac{n^2+(1-n)^2(n^2\psi'(2-n)+n+\frac{1}{2})}{[\Gamma(2-n)]^2}. \quad (36)$$

The resulting $F_i(x)$ may be compared with the hydrogenic envelope function of simple effective mass theory, $\{F_i(x)\}_{x_0=0}=e^{-x/\sqrt{\pi}}$, by calculating the ratio

$$Q_i(x)=F_i(x)/\{F_i(x)\}_{x_0=0}\approx m_1+m_2\exp\{-(\tilde{\tau}-1)x\}, \quad (37)$$

where the values of the constants m_1 and m_2 are obtained by combining (27), (29), and (32):

$$m_1=\sqrt{\pi}F_a(x_0)\frac{1}{1-\tilde{\tau}}\left[\frac{1-Z_L}{x_0}-\right]\exp\{x_0\},$$
$$m_2=-\sqrt{\pi}F_a(x_0)\frac{1}{1-\tilde{\tau}}\left[\frac{1-Z_L}{x_0}-1\right]\exp\{\tilde{\tau}x_0\}. \quad (38)$$

For a comparison with the experiment only the case of a P donor ($Z=1$) is considered since it is expected that for the much more concentrated S^+ donor wave function the neglected individual impurity corrections (Sec. 1) play a significant role. In Fig. 2 the ratio $Q_i(x)$ is plotted for a cavity radius $r_0=3.55\,a_0$ (Sec. 1), and values of μ and $\varkappa$ according to (23). It is seen that Q_i varies quite rapidly over the central cell region (increasing by a factor 2).

Our result throws some light on the treatment of BST [13] who start with the same [51] potential (16) but employ a variational trial function of the hydrogen type with the BOHR radius αa_0 as variation parameter. Performing the calculation of these authors for the above values of r_0, $\varkappa$, μ, one arrives at $\alpha=33.2$ for the energy minimum while the value that corresponds to the hydrogenic case of *zero* cavity radius, is $\alpha=a^*/a_0=39.9$. In fact, a plot of both the hydrogen-like ratios for $r_0=0$ and (the

[48] The expression on the right hand side of (32) has the following properties; 1. it is exact for $x=x_0$ and has the exact derivative at this point; 2. in the limit $x_0\to 0$ it becomes asymptotically exact for $0\leqq x\leqq x_0$ thereby approaching the behaviour of the hydrogenic wave function corresponding to U_0; 3. for $x_0\to\infty$ it also becomes asymptotically exact, again resembling hydrogenic behaviour, provided τ is replaced by

$$\tau'=\frac{(1-Z_L)(2-x_0)-2x_0+x_0^2/n^2}{x_0(1-Z_L-x_0)}; \quad (32\,a)$$

the limit of τ' is $\tau'=\varkappa$, coresponding to a potential U_0 with $\varkappa$ replaced by 1. τ' is adjusted to make (32) correct at $x=x_0$ up to the second derivative. τ is obtained from τ' by neglecting the term x_0^2/n^2 which is small in the range of physical interest. A still better result than with τ' is obtainable if the limiting values $\tau'(x_0\to 0)=\tau$, $\tau'(x_0\to\infty)=\varkappa$ are weighted by a factor ζ thus arriving at the average value of eq. (33). By comparing the approximate with the exact values at the points $\nu=0.7$; 0.8; 0.9 (corresponding to $C=0.1532$; 0.2001; 0.2532) as taken from the tables of SLATER [49], a value $\zeta=0.68$ is found to give satisfactory results in the range of $0.15<C<0.25$.

[49] L. J. SLATER, Confluent Hypergeometric Functions, Cambridge University Press, London 1960.

[50] Cf. Footnote [50] of Ref. [2].

[51] Eq. (29) of Ref. [13] is in error and must read identical with eq. (16) of the present paper.

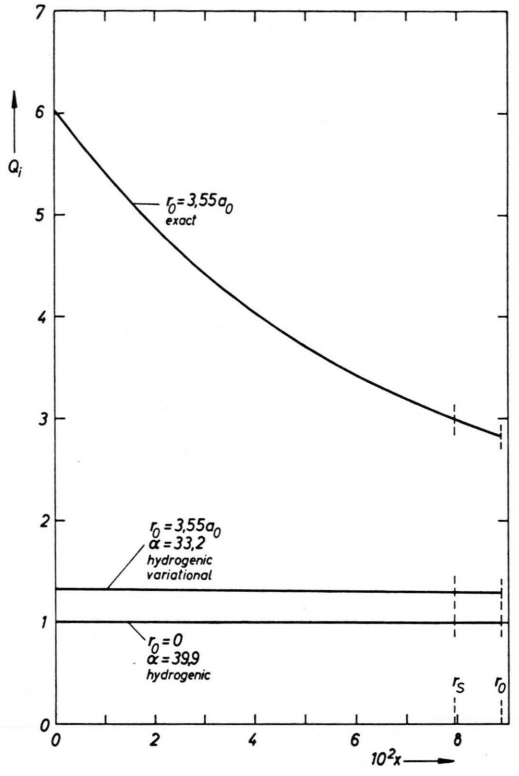

Fig. 2. Ratio $Q_i(x)$ of ground state envelope functions of the P donor in silicon. Comparison of the exact with the hydrogen-like variational result at $r_0 = 3.55\ a_0$ (interior region). According to the definition, $Q_i(x) \equiv 1$ at $r_0 = 0$. α denotes the BOHR radius in units of a_0. The potential energy is due to eq. (16).

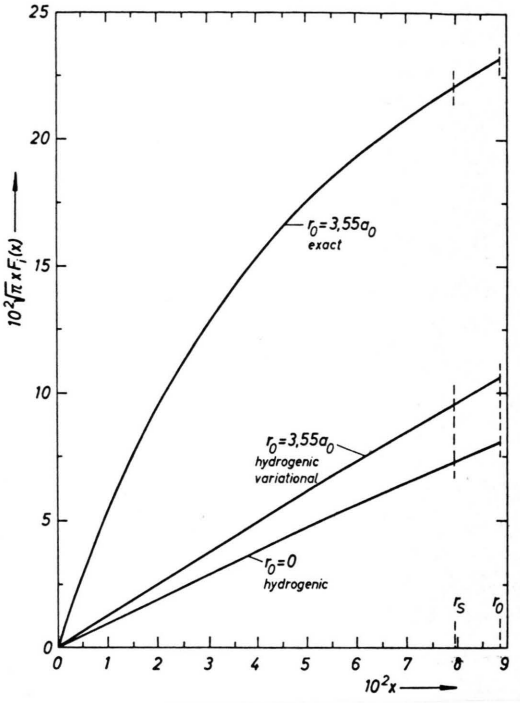

Fig. 3. Absolute radial envelope function of the P donor in Si. Comparison of the exact with the hydrogen-like variational result at $r_0 = 3.55\ a_0$ (interior region). Numerical values: $m_1 = 1.89213$; $m_2 = 4.13504$; $\zeta = 0.68$; $\bar{\tau} = 17.486$; $N_a = 1.3615\ \sqrt{\pi}$; $F_a(x_0)/N_a = 1.9184$; $Q_i(0) = 6.0272$; $Q_i(r_s = 3.0108)$.

variational one) for $r_0 = 3.55\ a_0$ shows that they nearly coincide and are far from resembling the ratio (37) calculated with the *exact* envelope function of the cavity model (16) (Fig. 2). The same can be seen from a comparison of the absolute radial envelope function in Fig. 3. We therefore infer that such a simple variational procedure is quite inadequate [52]. Obviously, the hydrogen-like trial function is not flexible enough to allow for the strong local deformation of the electron cloud under the influence of the unshielded central cell impurity potential (16 a).

From a knowledge of the envelope function at $r = 0$ one arrives in the usual way [2] at the square of the wave function, $|\Psi(0)|^2$, by multiplying $F_i^2(0)$ with the factor $6\eta = 6 \cdot (186 \pm 18)$. It is interesting to compare the result with the observed value as is done in Sec. 5.

[52] This still holds if one is only concerned with the order of magnitude; cf. Sec. 5, Table 1.

5. Discussion

In the preceding Sections the ground state of the SCHRÖDINGER equation with the model impurity potential (16) has been calculated exactly for $Z = 1, 2$, the parameters related to Si ($\varkappa = 11.7$ and $\mu = 0.29\ m_0$ and slightly deviating values; see Fig. 1), and the effective cavity radius r_0 varying from 0 to $4\ a_0$. The underlying assumptions were the following:

(α) the (scalar) effective mass m^* can be used in all space;

(β) the EM equation is fairly valid in all space, i. e. boundary conditions are employed at both $r = \infty$ *and* $r = 0$, to determine the ground state of the donor electron;

(γ) for impurities occupying substitutional lattice sites, r_0 should be bounded, at least in order of magnitude, by $3.2\ a_0 \lesssim r_0 \lesssim 4.5\ a_0$ [eqs. (7), (8)] while the radius of interstitial impurities is known [6] to be $r_0 \approx 2.5\ a_0$.

We are now ready to test these assumptions by comparison with the experiment. The experimental ionization energy of a P donor in Si is 45 meV while the corresponding value for a S^+ impurity may be assumed to be 520 meV [38]. Hence we are concerned with both a shallow and a deep level. While P is substitutional there appears to be no definite evidence that sulfur impurities in Si occupy substitutional rather than interstitial sites [5].

By inspection of the r_0-dependence of the theoretical ground state energies of these impurities in Fig. 1, it is seen that the effective cavity radii fitting the observed values are $r_0 = 3.8\,a_0$ (KAUS: $4.0\,a_0$) and $2.6\,a_0$, respectively, provided the choice $m = m^*$ is made. Theoretically, for impurities which all occupy substitutional lattice sites there should be only a small spread in the corresponding cavity radii owing to the fact that the cavity is not a function of the impurity but rather of the host crystal [53]. Hence, the discrepancy between the P and the S^+ radii being rather significant and the value of $2.6\,a_0$ resembling the interstitial radius, this slightly supports the view that S^+ might be in an *interstitial* position. However, one certainly overestimates the cavity model if one tries to identify the position of occupancy from the experimentally adjusted radii. On the other hand, *for sulfur impurities assumed to be substitutional*, the effective cavity radius resembles the WIGNER–SEITZ radius rather than the nearest neighbour distance and, bearing in mind eq. (8) one may tentatively assume

$$r_0 \approx r_s\,. \tag{39}$$

The existence of a discrepancy between the P and S^+ radii would then reveal the limitations of the cavity model and may be also due to the admixture of BLOCH functions from bands other than the lowest conduction band, as suggested by HAM in the case of S^+ [5]. We conclude that in either case (substitutional or interstitial) the fitting values obtained on choosing $m = m^*$ are fairly consistent with assumption (γ).

Assuming next $m = m_0$ through all space according to GLODEANU [10], one obtains from Fig. 1 a cavity as small as $r_0 = 0.6\,a_0$ for the S^+ defect. On replacing the 520 meV by the alternative level of 370 meV [38] yields even a smaller cavity; in fact according to Fig. 1 the cavity turns out to be zero thereby verifying the striking agreement with the simple hydrogenic model employed by GLODEANU. It becomes thus obvious that this model is inconsistent with our assumption (γ), whether the sulfur impurity may be substitutional or not.

There remains the case of a vacuum mass admixture (Sec. 2) to an otherwise effective mass treatment [11, 12, 32] to be investigated. Here the conclusion is less stringent. For such a treatment would shift the fitted cavity radii to values smaller [54] than in the pure EM case, and hence the S^+ defect would probably violate the lower bound estimate of assumption (γ) at substitutional but not necessarily at interstitial occupancy. It follows that the relevancy of this treatment cannot be excluded from experimental grounds, as far as deeper levels are concerned.

Thus our main conclusion in the case of the S^+ impurity is that assumption (γ) remains consistent with the experiment even if certain modifications should be introduced with respect to (α) and (β). It is expected, however, that these modifications do not alter the tendency of the first two assumptions completely. For example, the coupling with higher bands calls for an extension of the simple EM treatment that is still far from resembling a vacuum mass procedure [cf. assumption (α)] while the unrestricted [55] validity of the modified EM equation(s) probably could be preserved by the inclusion of the modulated potential correction [13] [cf. assumption (β)].

We now turn to the P donor. By comparing the model potential (16) with the approximate many body potential (4), an estimate was performed in a previous note [4] yielding $r_0 \approx 3.55\,a_0 = 1.88$ Å. This would be consistent with our specification (39) for substitutional S^+. On the other hand it contradicts a suggestion of BST [13] according to which $r_0 \approx r_d$ (cf. also the conclusion of Ref. [56]). Apart from this alternative specification of the cavity radius the work of BST rests on the above three assumptions (with P being substitutional and $Z = 1$) and hence

[53] For interstitial impurities this was pointed out by KAUS [12].

[54] The ground state ionization energy will be a monotonously increasing function of the matching radius r_m introduced in Sec. 2. Hence an increase of r_m from zero to a finite value can only by compensated by a decrease of the effective cavity radius r_0.

[55] "Unrestricted" in the sense of assumption (β) of Sec. 5.

[56] M. BREITENECKER and R. SEXL, Technical Note Nr. 2, Project Nr. 1098-10 (1961), Institute for Theoretical Physics, University of Vienna, Austria.

can be directly compared with the present calculations. Since the BST suggestion leads to a variationally calculated ionization energy, $-E_0$, and electron probability, $|\Psi(0)|^2$, which are in fair agreement with the observations, on first sight an inconsistency between assumption (β) and a specification as opposite to BST's as (39) might be expected. At this point, however, one has to bear in mind the lack of flexibility in the BST trial function (Sec. 4). It has been a primary motivation of the present work to improve on this somewhat unsatisfactory situation by checking the BST variational envelope function with an exact calculation. In Table 1 the results are compared for two effective cavity radii; namely the BST value $r_0 = r_d = 4.44\, a_0$, and the above cited $r_0 = 3.55\, a_0$ of the author's estimate.

Let us first consider the ionization energy. For $r_0 = r_d$ there is a significant shift of the energy level (from -50 meV to -72 meV) which destroys the fair agreement of the BST result with the observations (-45 meV). In the case of the smaller radius $r_0 = 3.55\, a_0$, however, the agreement is approximately restored if one now refers to the exact solution (-40 meV). (The BST result corresponding to $3.55\, a_0$ was not calculated because from its variational property of being an upper bound to the exact level, it is *a priori* seen that no improvement towards the observed value would be obtained.)

The wave function at the impurity nucleus exhibits a still more sensitive reaction. If one takes r_0 as large as r_d, its square, $|\Psi(0)|^2$, is increased by about a factor 100 due to the larger flexibility inherent in the exact solution. This enormous value probably goes beyond any validity of the EM equation that may be feasible, and besides overestimates the observed value by a factor 30. We may thus conclude that the unrestricted [55] EM theory is not applicable to a cavity model with a radius being as large as the nearest neighbour distance r_d. Again the fair numerical agreement of the BST variational result which underestimates the observed value $0.44\ \text{Å}^{-3}$ by a factor 3 only, is completely destroyed. Turning now to the smaller radius $3.55\, a_0$ it is interesting to note that the exact solution overestimates the experimental value by only about the same factor 3. Hence again a fair agreement is recovered on the basis of precise calculation and a cavity as small as suggested by (39).

Thus the results of Table 1 support the consistency of assumption (β) with the other two assumptions, and at the same time rule out the specification $r_0 \approx r_d$ as suggested by BST.

One may ask whether there exists an effective cavity radius for the P donor which equally fits *both* the observed energy and the wave function at the donor site. It can be immediately seen from Table 1 that this is not so. This follows from the fact that both $|E_0|$ and $|\Psi(0)|^2$ are monotonously increasing functions of r_0 which for a special radius, namely $r_0 = 3.55\, a_0$ satisfy the inequalities

$$|E_0| < |E_0^{\text{Exp}}| \quad \text{and} \quad |\Psi|^2 > |\Psi^{\text{Exp}}|^2 .$$

This again, of course, demonstrates the limits of applicability for a model of type (16). Moreover, from the opposite signs in the above inequalities and noting that $|E_0|$ and $|\Psi|^2$ are very sensitive to any small change in the effective cavity radius, it can be concluded that $r_0 = 3.55\, a_0$ resembles the value of optimal fitting. This again supports (39).

6. Conclusion

The discrepancy between the observed and the calculated ionization energy of P and S^+ impurities can be essentially accounted for by including the spatial dependence of the shielding of the impurity potential (cf. Refs. [3] and [22]). A simple phenomenological description of the potential correction in terms of the cavity model of eq. (16) emerges from

r_0/a_0	r_0 Å	E_0^{EM} meV	E_0^{BST} meV	$E_0^{\text{Mü}}$ meV	E_0^{Exp} meV	$\lvert\Psi^{\text{EM}}(0)\rvert^2$ Å^{-3}	$\lvert\Psi^{\text{BST}}(0)\rvert^2$ Å^{-3}	$\lvert\Psi^{\text{Mü}}(0)\rvert^2$ Å^{-3}	$\lvert\Psi^{\text{Exp}}(0)\rvert^2$ Å^{-3}
4.44	2.35	-29	(-50)	-72	-45	0.04	0.11 (0.14)	13	0.44
3.55	1.88	-29	> -40	-40	-45	0.04	0.066	1.37	0.44

Table 1. Ionization Energies and Probability Densities at the P Donor Nucleus in Silicon. Calculation are based on the crystal parameters (23). Values in parentheses refer to parameters according to (24). EM: simple effective mass theory. BST: Ref [13], Mü: present author, Exp.: experimental value.

a discussion of the various effects contributing to the total perturbing potential U in the vicinity of the impurity.

On the basis of this model a reasonably fitting of the ionization energy with experiments is obtained if the effective mass m^* rather than the free electron mass m_0 is employed in the SCHRÖDINGER equation. For a P donor the cavity radius fits at $r_0 \approx r_s$, and the application of the unrestricted [55] EM theory yields fair agreement with the observations for both the energy and the wave function at the lattice site of the donor. In the case of a S^+ impurity the cavity radius derived from the experiment, is $r_0 \lesssim r_s$.

A cavity as large as $r_0 = r_d$ appears to be inconsistent with the basic assumptions of EM theory even if it would be physically reasonable.

It is concluded that the interpretation of the S^+ level in terms of a free electron mass model [10] yields satisfactory agreement with experiment only if one would have reason to completely neglect the spatial dependence of the lattice shielding.

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Appendix

Calculation of the integral $\int_0^\infty W_{n,1/2}(\varrho)\, W_{m,1/2}(\varrho)\, \mathrm{d}\varrho$

Starting from the definition

$$I_\nu(n, m; \mu) = \int_0^\infty \varrho^\nu\, W_{n,\mu/2}(\varrho)\, W_{m,\mu/2}(\varrho)\, \mathrm{d}\varrho = I_\nu(m, n; \mu), \tag{40}$$

the integral $I_0(n, n; 1)$ of eq. (35) can be reduced to terms of the type $I_{-1}(n, m; \mu)$ as follows. On multiplying the well known recurrence formula [57]

$$\varrho \frac{\mathrm{d}}{\mathrm{d}\varrho} W_{n,1/2}(\varrho) = \left(\frac{\varrho}{2} - n\right) W_{n,\mu/2}(\varrho) - W_{n+1,\mu/2}(\varrho) \tag{41}$$

by $(1/\varrho)\, W_{m,\mu/2}(\varrho)$ and integrating, yields

$$\int_0^\infty W_{m,\mu/2}(\varrho)\, W'_{n,\mu/2}(\varrho)\, \mathrm{d}\varrho = \tfrac{1}{2} I_0(n, m; \mu) - n\, I_{-1}(n, m; \mu) - I_{-1}(n+1, m; \mu)\,. \tag{42}$$

On interchanging m and n and adding the resulting equation to (42), we arrive at the symmetric relation

$$I_0(n, m; \mu) = (n+m)\, I_{-1}(n, m; \mu) + \{I_{-1}(n+1, m; \mu) + I_{-1}(m+1, n; \mu)\} - W_{n,\mu/2}(0) \cdot W_{m,\mu/2}(0) \tag{43}$$

where use is made of $W_{n,\mu/2}(\varrho) \to 0$ for $\varrho \to \infty$.

The integral $I_{-1}(n, m; \mu)$ was evaluated by BUCHHOLZ [58] who obtained

$$I_{-1}(n, m; \mu) = \frac{1}{n-m} \cdot \frac{\pi}{\sin(\pi\mu)} \left\{ \frac{1}{\Gamma((1+\mu)/2-n)\,\Gamma((1-\mu)/2-m)} - \frac{1}{\Gamma((1+\mu)/2-m)\,\Gamma((1-\mu)/2-n)} \right\}. \tag{44}$$

The integral (44) only exists for $|\mu| < 1$ while we are interested in the case $\mu = 1$. Therefore let $\mu = 1 - \varepsilon$ where ε is a small positive quantity. From the definition of the WHITTAKER function it is then seen that $W_{n,\mu/2}(0) = 0$ for arbitrary n, hence the last term in (43) vanishes. If we now insert the integrals (44) in the relation (43), the limit $\varepsilon \to 0$ can be carried out by means of L'HOSPITAL's rule, and the following expression be obtained with the aid of the functional equation $\Gamma(x+1) = x \cdot \Gamma(x)$:

$$\begin{aligned} I_0(n, m; 1) = {} & \frac{n+m}{n-m} \frac{\partial}{\partial\varepsilon} \left\{ \frac{1}{\Gamma(1-\varepsilon/2-n)\,\Gamma(\varepsilon/2-m)} - \frac{1}{\Gamma(\varepsilon/2-n)\,\Gamma(1-\varepsilon/2-m)} \right\}\Bigg|_{\varepsilon=0} \\ & + \frac{1}{n-m+1} \frac{\partial}{\partial\varepsilon} \left\{ \frac{1}{\Gamma(-\varepsilon/2-n)\,\Gamma(\varepsilon/2-m)} - \frac{1}{\Gamma(\varepsilon/2-n-1)\,\Gamma(1-\varepsilon/2-m)} \right\}\Bigg|_{\varepsilon=0} \\ & + \frac{1}{n-m-1} \frac{\partial}{\partial\varepsilon} \left\{ \frac{1}{\Gamma(1-\varepsilon/2-n)\,\Gamma(\varepsilon/2-m-1)} - \frac{1}{\Gamma(\varepsilon/2-n)\,\Gamma(-\varepsilon/2-m)} \right\}\Bigg|_{\varepsilon=0}. \end{aligned} \tag{45}$$

[57] See Ref. [46], p. 81, eq. (40 a).

[58] See Ref. [46], p. 116, eq. (12). In this equation two signs are in error.

Using the definition $\psi(x) = \frac{\mathrm{d}}{\mathrm{d}x} \log \Gamma(x)$ of the ψ function, (45) can be further transformed to give

$$I_0(n, m; 1) = \frac{1}{[1-(n-m)^2]\ \Gamma(1-n)\ \Gamma(1-m)} \left\{ 1 + n + m + 2\,n\,m\, \frac{\psi(1-m) - \psi(1-n)}{n-m} \right\}. \tag{46}$$

The normalization integral (35) is obtained in the limit $m \to n$. Hence if we apply again L'HOSPITAL's rule the final result is

$$I_0(n, n; 1) = \frac{1 + 2\,n + 2\,n^2\,\psi'(1-n)}{[\Gamma(1-n)]^2} = \frac{2\,n^2 + (1-n)^2\,[1 + 2\,n + 2\,n^2\,\psi'(2-n)]}{[\Gamma(2-n)]^2}. \tag{47}$$

Integrals of the Type $I_\nu(n, m; 1)$ (ν positive, integer) may be evaluated in a similar way by additionally multiplying the recurrence relativn (41) with an appropriate power of ϱ before integrating. Thus ultimately one arrives at $I_0(n, m; 1)$ which is known from eq. (46).

Energietransport zwischen Rekombinationszentren des Mn, Fe, Co, Ni und Cu bei der Elektrolumineszenz von ZnS-Phosphoren

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The transport of energy between Mn, Fe, Co, Ni, and Cu recombination centers in ac-electroluminescence of ZnS-phosphors has been investigated. The exchange of energy is explained to be due to hole migration via the valence band: during any cycle of the voltage electrons and holes are separated temporarily and recombine only after the direction of the electric field is reversed. The delay of recombinations gives rise to a change of the distribution of holes over the activators. Shortly after excitation the holes are distributed according to the capture cross sections. When the field is reversed within this period the recombinations take place in centres with high capture cross section. However when the frequency of the electric field is low and the temperature is so high that holes can be liberated by thermal energy, the holes are distributed following the FERMI-Statistics. The change of hole distribution has been studied by varying frequency, temperature and voltage.

Der Anregungsvorgang, der im DESTRIAU-Effekt durch die Wirkung elektrischer Wechselfelder auf ZnS-Phosphore zur Emission sichtbarer Strahlung führt, ist zwar bis heute in den Einzelheiten noch nicht geklärt, aber alle diskutierten Mechanismen (Feld-Ionisation von Aktivatoren, Stoßionisation durch beschleunigte Elektronen, Trägerinjektion) schließen ein, daß die durch den Anregungsprozeß entstandenen freien Ladungsträger durch die elektrischen Felder zeitweise getrennt werden, bevor sie rekombinieren [1]. Diese Verzögerung der Rekombination wurde u. a. von KUBÁTOVÁ und PATEK [2] experimentell nachgewiesen. Durch die Ladungsträgertrennung finden die Rekombinationsprozesse erst dann statt, wenn sich nach Ablauf einer halben Periodendauer das Feld umkehrt. Der Zeitpunkt der Rekombinationen wird so durch die Frequenz des anregenden Wechselfeldes gesteuert. Da die Beweglichkeit der Elektronen die der Defektelektronen bei weitem übersteigt, wird die Trennung im wesentlichen aktiv von den Elektronen ausgeführt. Der DESTRIAU-Effekt bietet dadurch die Möglichkeit, die energetische Verteilung der Ladungsträger während der Dauer der Trennung zu untersuchen, weil langsame Umlagerungsprozesse von Ladungsträgern zwischen verschiedenartigen Störstellen, die infolge der Abwesenheit von Rekombinationen der Leitungselektronen dem Emissionsakt vorangehen, verfolgt werden können. Werden die die Ladungsträgertrennung bestimmenden Parameter variiert, so äußert sich dies in einer Änderung der Verteilung der Rekombinationen pro Zeit- und Volumeneinheit, z. B. in einer Verschiebung der spektralen Verteilung.

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