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Theory of localized states in semiconductors. II. The pseudo impurity theory application to shallow and deep donors in silicon*†

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A new pseudo impurity theory is developed by combining the general theory of pseudopotentials with effective-mass ideas. It is applicable to a general impurity, both shallow and deep levels, and reduces to the Kohn-Luttinger effective-mass theory in the special cases of isocoric impurities, namely impurities which have isoelectronic cores with the host atoms. The resultant impurity-electron wave function $\psi(\vec{r})$ in the new theory is given by a many-band expansion and has the correct nodal structure in all atomic cells, including the impurity cell. The impurity pseudopotentials are again constructed from fundamental crystal and atomic properties with no adjustable parameters. An application is presented to donors in silicon and excellent agreement is obtained for many shallow and deep, substitutional and interstitial donors. The accuracy of the calculations is investigated. Further conceptual understanding of the effective-mass notion is also attained: it is the "pseudo" electron, described by the smooth pseudo wave function $\phi(\vec{r})$, that may be described by the band-minimum effective mass m^*; whereas the "effective" mass of the real electron, which is described by $\psi(\vec{r})$, is m^* only outside the impurity cell. Inside the impurity cell, the kinetic energy of the real electron is a complicated operator, which reduces to the m^* form in an asymptotic way.

I. INTRODUCTION

In paper I[1] of this series we established the result that, when the impurity potential is constructed from first principles, the effective-mass theory of Kohn and Luttinger (KL-EMT) is valid only for impurities having the same core as the host atoms. For convenience we called such impurities isocoric. The major novel result was that the theory was found to give accurate values for both shallow and deep energy levels of such impurities. Numerical results for the phosphorus and the deep sulfur levels in silicon were found in very good agreement with experimental data. On the other hand, the theory was found to fail completely for the energy levels of nonisocoric donors, such as the shallow arsenic levels in silicon.

These results were understood in the following terms:

(a) The perturbation potential for an isocoric impurity is not responsible for the binding of any additional core states and, as such, it has weak high Fourier components. This, in turn, makes the effective-mass approximation (EMA) applicable. On the other hand, the perturbation potential for a nonisocoric impurity is responsible for the binding of the extra (or less) electrons on the core. It, therefore, has strong high Fourier components which are capable of mixing in more bands and thus invalidate the one-band KL-EMT.

(b) The KL-EMT is a one-band approximation for the expansion of the impurity-electron wave function ψ. This form is good for an isocoric impurity since the nodal structure of this one band's Bloch functions is appropriate in the impurity cell. On the other hand, for a nonisocoric impurity a distinctly different nodal structure must be built for the impurity-cell region, which requires a many-band expansion of ψ.

Including many bands directly in the expansion of ψ in terms of Bloch functions of the perfect crystal proves to be a very tedious process, especially since a many-band expansion is necessary only in the impurity cell and since Bloch functions are not known very accurately. Other possibilities to circumvent these problems are therefore desirable. In this paper, one such alternative approach is presented which makes use of pseudopotential theory. In this approach, the correct nodal structure is built into ψ through a series of rigorous mathematical transformations which amount to reorthogonalizing the Bloch functions in the impurity-cell region so that they are orthogonal to the new core states in that region. Subsequently, the final expression for ψ may be interpreted as a many-band expansion. The important feature of the method is that the impurity cell need not be defined by a boundary for matching purposes. Another feature is that the kinetic energy of the electron is an operator which *asymptotically* becomes equal to the effective-mass form at large distances from the impurity cell. It will be seen that the results may still be *interpreted* in terms of an "effective" mass for the electron, which is equal to the band-minimum effective mass only away from the impurity-cell region. The method can handle nonisocoric substitutional impurities and also interstitial impurities for which the KL-EMT is inapplicable. The present method reduces to the KL-EMT in the special case of isocoric impurities. Accurate numerical calculations can be performed without the use of any adjustable parameters.

In Sec. II of this paper we develop the general pseudo impurity theory (PIT), which is a combination of pseudopotential theory and effective-mass ideas. In Sec. III, numerical applications to donors in silicon are given. Energy levels for shallow and deep, substitutional and interstitial donors are calculated and excellent agreement with available experimental data is obtained. Conclusions are drawn in Sec. IV.

II. GENERAL THEORY

A. Introduction

Pseudopotentials have been used by several authors in the past in connection with the impurity problem, but in distinctly different ways than the present approach. For this reason, we first give a brief account of such previous work, before we embark in the detailed presentation of the present theory.[1a]

The theory of pseudopotentials was developed more than a decade ago in connection with the problem of electronic energy levels of perfect crystals.[2-6] A qualitative analysis of the impurity problem in semiconductors, using pseudopotential ideas, was first attempted by Glodeanu[7] in 1965. In a later paper,[8] in 1969, he made a formal analysis with rather complicated results. No application has been reported. Independently, in 1966, Hermanson and Phillips[9] reported work which had a starting point similar to ours but which followed a different path. Apart from some qualitative results, they used the method to estimate corrections to the hydrogenic model for impurities in rare-gas solids.[10] We will compare their formalism with the present approach as we go along.

In 1965, Abarenkov and Heine[11] formalized[12] the concept of a model potential for atoms or ions and introduced a particular nonlocal form which they fitted to empirical data. Jaros[12,13] used the Abarenkov-Heine potentials for donors in silicon using the EMA. He unfortunately omitted the intervalley mixing, which has been found to be crucially important.[1,14] Recently, Ning and Sah,[14] relying on pseudopotential theory, studied donors in silicon by fitting a two-parameter local potential to the lowest two energy levels of the group-V donors. They then multiplied these potentials by a factor of 2 and predicted energy levels for the corresponding group-VI donors. Their potential is akin to the model potential used by Jaros.[13]

Let us now define our problem. As in paper I,[1] we seek to solve the eigenvalue problem

$$H\psi = [-(\hbar^2/2m)\nabla^2 + V]\psi = E\psi \tag{2.1}$$

where V is the total one-electron self-consistent potential of a crystal containing a point imperfection. In the KL-EMT, to which paper I was devoted, V was written as

$$V = V^0 + U, \tag{2.2}$$

where V^0 is the perfect crystal periodic potential. Perturbation theory was then used to treat U as a perturbation to the perfect system defined by

$$H^0\psi^0_{n\vec{k}} = [-(\hbar^2/2m)\nabla^2 + V^0]\psi^0_{n\vec{k}} = E\psi^0_{n\vec{k}}, \tag{2.3}$$

which was assumed solved. In the present approach we will use the general theory of pseudopotentials (GTP) to transform both systems (2.1) and (2.3) and *then* apply perturbation theory. This leads to new results which not only make numerical calculations possible with rather little computer time, but also yield new physical insights on the impurity problem. Most of these will be arrived at in Sec. II F.

B. General theory of pseudopotentials (GTP)

The GTP was developed by Austin, Heine, and Sham,[4] after the pioneer work of Refs. 2 and 3. It applies to systems such as atoms, molecules, or crystals for which the eigenstates Ψ_n may be grouped into *core states* Ψ_c and *valence states* Ψ_v. All the Ψ_n, $n = c$ or v, satisfy

$$H\Psi_n = [-(\hbar^2/2m)\nabla^2 + V]\Psi_n = E_n\Psi_n. \tag{2.4}$$

(The notation in this section should not be confused with that used for the perturbed crystal in paper I and in Sec. II C.) One then defines a pseudo-Hamiltonian H_Φ by

$$H_\Phi = H + V_R \tag{2.5}$$

and then shows that if V_R is of the general form

$$V_R = \sum_c |\Psi_c\rangle\langle F_c|, \tag{2.6}$$

where F_c are arbitrary functions, then H_Φ has the same valence eigenvalues E_v as H, i.e.,

$$H_\Phi\Phi_v = E_v\Phi_v. \tag{2.7}$$

In Eq. (2.6) the bra-ket notation means that V_R is an integral operator with kernel $V_R(\vec{r}, \vec{r}\,')$ given by

$$V_R(\vec{r}, \vec{r}\,') = \sum_c \Psi_c(\vec{r})F_c^*(\vec{r}\,'), \tag{2.8}$$

so that, when it operates on a state Φ, the result is a function of $\vec{r}$

$$V_R\Phi = \int d^3r'\, V_R(\vec{r}, \vec{r}\,')\Phi(\vec{r}\,'). \tag{2.9}$$

The proof[4] of Eq. (2.7) is simple and is obtained by expanding Φ_v in terms of the Ψ_n. The process yields the following relation between Φ_v and Ψ_v:

$$\Psi_v = \Phi_v - \sum_c \langle\Psi_c|\Phi_v\rangle\Psi_c. \tag{2.10}$$

Each choice of F_c in Eq. (2.6) results in a different set of Φ's, but Eq. (2.10) is always satisfied. This is illustrated schematically in Fig. 1.

For the determination of the energy levels E_v,

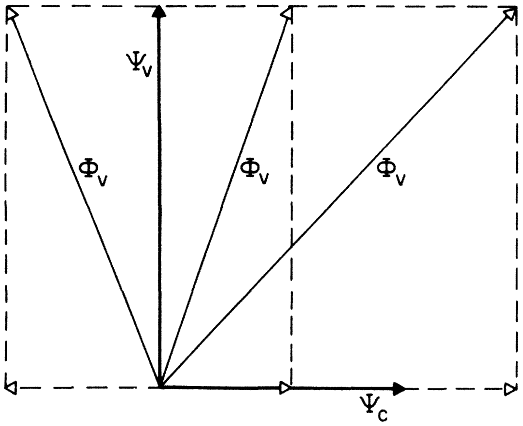

FIG. 1. Illustration of the nonuniqueness of Φ_v by drawing the functions Ψ_v, Ψ_c, and Φ_v as vectors. Ψ_v and Ψ_c are orthogonal. Φ_v can be any vector (within normalization constant). By adding to it its projection on Ψ_c, one always gets Ψ_v.

the system (2.7) has several advantages over (2.4), when the proper choice of F_c is made. Obviously the choice $F_c = 0$ for all c is possible, but it takes us back to Eq. (2.4). It has been shown[3,4] that the choice

$$F_c = -\Psi_c V \tag{2.11}$$

results in nearly optimum cancellation between V_R and V. The resultant total pseudopotential, defined by

$$V_\Phi = V + V_R , \tag{2.12}$$

becomes

$$V_\Phi = (1 - P)V , \tag{2.13}$$

where we defined the projection operator P by

$$P = \sum_c |\Psi_c\rangle\langle\Psi_c| . \tag{2.14}$$

P is an even-parity operator, which would be equal to 1 if the Ψ_c were a complete set of functions. In general, $0 < P < 1$, but the cancellation is such that, as shown in Ref. 4, V_Φ binds no core states, so that the lowest eigenstate of H_Φ is the lowest *valence* state of H. Thus V_Φ has no strong core part or, equivalently, no strong high Fourier components.

The choice of Eq. (2.11) further results in nearly the smoothest pseudo wave functions Φ_v.[3,4] Unlike the corresponding Ψ_v, they are not as rapidly oscillatory in the core region, since there are no core states to which they can be orthogonal.

C. Application to the impurity problem

The GTP may be applied directly to the perfect crystal described by Eq. (2.3). The core states are simply the Bloch functions $\psi^0_{c\vec{k}}$ of the core bands, so the corresponding projection operator P^0 is

$$P^0 = \sum_c \sum_{\vec{k}} |\psi^0_{c\vec{k}}\rangle\langle\psi^0_{c\vec{k}}| . \tag{2.15}$$

The total crystal pseudopotential V^0_Φ is then

$$V^0_\Phi = V^0 + V^0_R , \tag{2.16}$$

where

$$V^0_R = -P^0 V^0 , \tag{2.17}$$

and we have

$$H^0_\Phi \phi^0_{v\vec{k}} = [-(\hbar^2/2m)\nabla^2 + V^0_\Phi]\phi^0_{v\vec{k}} = E^0_v(\vec{k})\phi^0_{v\vec{k}} \tag{2.18}$$

and

$$\psi^0_{v\vec{k}} = (1 - P^0)\phi^0_{v\vec{k}} . \tag{2.19}$$

In order to apply the GTP to the crystal containing a point imperfection, we need an indexing system for the core states. For this we are guided by a tight-binding picture and the fact that at very large distances from the imperfection site, each ψ_c either must reduce to one of the $\psi^0_{c\vec{k}}$ or must vanish. The former kind may be denoted as $\psi_{c\vec{k}}$ even though $\vec{k}$ is no longer a good quantum number. These functions generally have vanishing amplitude in the impurity cell. The latter kind, namely those that vanish far from the impurity site and hence are localized in the impurity cell (they are essentially the core orbitals of the impurity atom), will be labeled by the index c'. Thus, the projector operator P is defined as

$$P = \sum_c \sum_{\vec{k}} |\psi_{c\vec{k}}\rangle\langle\psi_{c\vec{k}}| + \sum_{c'} |\psi_{c'}\rangle\langle\psi_{c'}| \tag{2.20}$$

and the total pseudopotential V_Φ is

$$V_\Phi = V + V_R , \tag{2.21}$$

where

$$V_R = -PV . \tag{2.22}$$

Finally we have

$$H_\Phi \phi = [(\hbar^2/2m)\nabla^2 + V_\Phi]\phi_v = E_v \phi_v , \tag{2.23}$$

where ϕ_v is the pseudo wave function for a perturbed state which either lies in one of the valence or conduction bands and extends throughout the crystal, or is localized around the impurity cell and has its energy in one of the forbidden energy gaps above the valence band. The true wave function ψ_v is related to this via

$$\psi_v = (1 - P)\phi_v . \tag{2.24}$$

We will have a lot more to say about this in Sec. II F.

D. Perturbation pseudopotential U_ϕ: General properties

The method of attack from here on is to write

$$V_\Phi = V^0_\Phi + U_\Phi \tag{2.25}$$

and treat U_Φ as a perturbation to Eq. (2.18). In this section we look at some general properties of U_Φ.

First, using the results of Sec. II D and Eq. (2.25), we have

$$U_\Phi = U + U_R\,, \tag{2.26}$$

where

$$U = V - V^0 \tag{2.27}$$

is the impurity potential of the KL-EMT. It may be referred to as the "true" impurity potential, compared with U_Φ, the impurity pseudopotential. U_R is given by

$$U_R = V_R - V_R^0 = -PV + P^0V^0 \tag{2.28}$$

and, for reasons to be discussed later, will be called the reorthogonalization potential. At this point we can compare with the result of Ref. 9 in which the impurity pseudopotential U_Φ is also given by Eq. (2.26) but in which U_R is given by $U_R = -PU = -P(V - V^0)$ because of an improper choice of unperturbed pseudo-Hamiltonian.[15]

In order to obtain a meaningful interpretation of the present form of U_Φ, we rewrite P^0 and P in terms of Wannier functions. For the perfect crystal we use the well-known relation[16]

$$\psi^0_{c\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_j e^{i\vec{k}\cdot\vec{R}_j}\, w^0_c(\vec{r} - \vec{R}_j)\,, \tag{2.29}$$

where N is the number of atoms and $\vec{R}_j$ are the atomic sites. The Wannier functions $w^0_c(\vec{r} - \vec{R}_j)$ are localized about the sites $\vec{R}_j$[16] and resemble atomic orbitals. For the perturbed crystal, generalized Wannier functions $w_{c'}(\vec{r} - \vec{R}'_j)$ exist[17] and have the same localization properties. For the core states, we have[18]

$$\psi_{c\vec{k}}(\vec{r}) = \frac{1}{(N-1)^{1/2}} \sum_{j\neq 0} e^{i\vec{k}\cdot\vec{R}'_j}\, w_c(\vec{r} - \vec{R}'_j)\,, \tag{2.30a}$$

$$\psi_{c'}(\vec{r}) = w_{c'}(\vec{r} - \vec{R}'_0)\,, \tag{2.30b}$$

where $\vec{R}'_j$ are the new (because of relaxation) lattice sites[19] and $\vec{R}_0$ is the impurity site. In terms of Eqs. (2.29) and (2.30) we get

$$P^0 = \sum_j P^0_j\,; \quad P = \sum_j P_j\,, \tag{2.31}$$

where we defined

$$P^0_j = \sum_c |w^0_{cj}\rangle\langle w^0_{cj}| \tag{2.32a}$$

and

$$P_j = \sum_{c'} |w_{c'j}\rangle\langle w_{c'j}|\,. \tag{2.32b}$$

Finally, we write V^0 and V as

$$V^0 = \sum_j v^0(\vec{r} - \vec{R}_j)\,, \tag{2.33a}$$

$$V = \sum_j v_j(\vec{r} - \vec{R}'_j)\,, \tag{2.33b}$$

where v^0 and v_j are atomiclike potentials, and, using the localization properties of w^0_{cj} and w_{cj}, we get

$$U_\Phi = \sum_j \left[(1 - P_j)v_j(\vec{r} - \vec{R}'_j) - (1 - P^0_j)v^0(\vec{r} - \vec{R}_j)\right]. \tag{2.34}$$

This shows that, in the present approach, U_Φ is simply the change in atomiclike pseudopotentials centered at the atomic sites. In Sec. II E we will see that, via certain valid approximations, this form of U_Φ will prove very useful and easily manageable in numerical calculations. Several important properties of U_Φ can, however, be inferred from general pseudopotential theory. The conclusions will be confirmed numerically in Sec. II E.

As it was seen in Sec. II B, the most fundamental property of the chosen form of the pseudopotential is that it binds no core states. It therefore has no strong short-range part or, equivalently, strong high Fourier components. Recalling the criterion of validity of the effective-mass approximation developed in paper I,[1] we recognize U_Φ as an excellent candidate. One cannot, however, simply use U_Φ in place of U in the effective-mass equation (EME) resulting from the KL-EMT, and carry out calculations. Instead, the EME must be derived in connection with the eigenvalue problems (2.18) and (2.23) of the pseudocrystals. This is done in Sec. II E and it is found to lead to some very significant new results.

Before we finish this discussion, we invoke an additional physical reason that U_Φ does not, in general, have strong high Fourier components. This comes from the assumption that in the case of a substitutional impurity, four of the impurity-atom valence electrons pair-up with electrons from the neighboring host atoms to reconstruct the covalent bonds that hold the crystal together. Now, these bonds in the perfect crystal are generally results of strong $V^0_\Phi(\vec{K}_3)$, where $\vec{K}_3$ is a reciprocal-lattice vector in the [111] direction. Reconstruction of the bonds in the perturbed crystal means that $V_\Phi(\vec{K}_3)$ is about the same magnitude as $V^0_\Phi(\vec{K}_3)$. Consequently $U_\Phi(\vec{K}_3)$ must be very small.

Finally, one last general property of U_Φ is that it depends on the symmetry of the state calculated. It can be shown that, in the sums over c and c' in Eqs. (2.32), only those core states contribute which have the same symmetry as the valence eigenstate for which one is solving. Thus the extent of the effective cancellation depends on the symmetry of the state being calculated. If no core states of a particular symmetry exist, no cancellation will occur for that symmetry. This must be a point of caution and comes up when calculations are performed.

E. Perturbation-theory treatment: The pseudo-EMT

Once we have the eigenvalue problems (2.18) and (2.23) with all quantities defined, we follow a procedure analogous to the KL-EMT. However, instead of expanding $\psi(\vec{r})$ in terms of the $\psi^0_{n\vec{k}}(\vec{r})$, here we expand $\phi(\vec{r})$ in terms of the $\phi^0_{n\vec{k}}(\vec{r})$. We have[19a]

$$\phi(\vec{r})=\sum_n\sum_{\vec{k}} f_n(\vec{k})\phi^0_{n\vec{k}}(\vec{r})\,. \tag{2.35}$$

By substituting this in Eq. (2.23), multiplying on the left-hand side by $\psi^0_{n'\vec{k}'}(\vec{r})$, using the orthogonality relation[4]

$$\langle\psi^0_{n'\vec{k}'}\,|\,\phi^0_{n\vec{k}}\rangle=\delta_{n'n}\delta_{\vec{k}'\vec{k}}$$

and a series of manipulations similar to those for the KL-EMT, one obtains the corresponding EME. The only caution one must exercise in deriving Eq. (2.36) or (2.37) is taking into account the operator nature of U_ϕ. For a spherical minimum at $k=0$, the pseudo EME is

$$-(\hbar^2/2m^*)\nabla^2 f(\vec{r})+\int d^3r'\,U_\phi(\vec{r},\,\vec{r}\,')f(\vec{r}\,')=Ef(\vec{r})\,. \tag{2.36}$$

For a more complicated band and for a two-electron state, corresponding equations can be written. For example, for donors in silicon, we have

$$\sum_{i=1}^{6}\alpha_i\Big(e^{i(\vec{k}_i-\vec{k}_j)\cdot\vec{r}}\,[T_i(-i\nabla)-E]f_i(\vec{r}) +e^{-i\vec{k}_j\cdot\vec{r}}\int d^3r'\,U_\phi(\vec{r},\,\vec{r}\,')f_i(\vec{r}\,')e^{i\vec{k}_i\cdot\vec{r}\,'}\Big). \tag{2.37}$$

We will soon see that in the case of isocoric impurities, U_ϕ is approximately equal to the true impurity potential U and Eq. (2.37) reduces to Eq. (3.4) of paper I. We thus see that the KL-EMT is a special case of the present more general PIT. The validity criterion for Eq. (2.37) has the same form as in paper I, except that the quantities $C^{mm'}_{\vec{k}\vec{k}'}(\vec{K}_h)$ now come from pseudo Bloch functions and are thus much smaller. This shows that the EMA has a wider range of validity than it was originally established (a result discussed also in Refs. 9 and 14) and explains further the success of the KL-EMT in paper I.

F. Some important qualities of the PIT

It may seem that all the transformations and manipulations of the last several sections led simply to the derivation of effective-mass equations, which contain a pseudopotential U_ϕ instead of the true potential U or a screened Coulomb potential. It may be argued that a one-band approximation is still made, whereby there remains a question about its applicability to deep levels. It may be argued further than an effective mass m^* is still used in all space, including the central cell, where some authors have argued the free-electron mass m_0 is more appropriate. None of these objections is valid for our pseudopotential formulation. The discussion that follows is aimed to reinforce the claims and conclusions made thus far with additional physical arguments, clarify the above and other points, and provide new conceptual and physical insights for the effective-mass approach. Section II F 1 is indeed very important in the presentation of the present pseudo impurity theory.

1. Impurity-electron wave function

The first property of the PIT to be noted is that it results in a correct form for the impurity-electron wave function $\psi(r)$ for nonisocoric impurities. This was found in paper I[1] to be the chief failure of the KL-EMT. This is seen as follows.

With the interband coupling neglected through the approximations leading to Eq. (2.36) or (2.37), the impurity-electron pseudo wave function $\phi(\vec{r})$ ends up being constructed from the pseudo Bloch functions $\phi^0_{\vec{k}}(\vec{r})$ of only one band, thus

$$\phi(\vec{r})\simeq\sum_{\vec{k}} f(\vec{k})\phi^0_{\vec{k}}(\vec{r})\,. \tag{2.38}$$

As for the *true* impurity-electron wave function $\psi(\vec{r})$, we recall that it is given by Eq. (2.24), or

$$\psi(\vec{r})=\phi(\vec{r})-\sum_c\sum_{\vec{k}}\langle\psi_{c\vec{k}}\,|\,\phi\rangle\psi_{c\vec{k}}(\vec{r})-\sum_{c'}\langle\psi_{c'}\,|\,\phi\rangle\psi_{c'}(\vec{r})\,. \tag{2.39}$$

[This shows already that a many-band expansion for $\psi(\vec{r})$ is employed—see Sec. II F 2 for a detailed discussion.] No matter what ϕ is, Eq. (2.39) shows that $\psi(\vec{r})$ is by construction orthogonal to the core functions $\psi_{c\vec{k}}$ and $\psi_{c'}$ of the perturbed crystal. More insight may be gained, however, by using the form (2.38) in (2.39) or (2.24) to get

$$\psi=\sum_{\vec{k}} f(\vec{k})(\phi^0_{\vec{k}}-P\phi^0_{\vec{k}})\,. \tag{2.40}$$

Finally, using Eq. (2.19) written as $\phi^0_{\vec{k}}=\psi^0_{\vec{k}}+P^0\phi^0_{\vec{k}}$, we have

$$\psi=\sum_{\vec{k}} f(\vec{k})(\psi^0_{\vec{k}}+P^0\phi^0_{\vec{k}}-P\phi^0_{\vec{k}}) \tag{2.41}$$

or, written out in full,

$$\psi=\sum_{\vec{k}} f(\vec{k})\Big[\psi^0_{\vec{k}}+\sum_c\sum_{\vec{k}'}\langle\psi^0_{c\vec{k}'}\,|\,\phi^0_{\vec{k}}\rangle\psi^0_{c\vec{k}'} -\Big(\sum_c\sum_{\vec{k}'}\langle\psi_{c\vec{k}'}\,|\,\phi^0_{\vec{k}}\rangle\psi_{c\vec{k}'}+\sum_{c'}\langle\psi_{c'}\,|\,\phi^0_{\vec{k}}\rangle\psi_{c'}\Big)\Big]\,. \tag{2.42}$$

The first term in Eq. (2.41) or (2.42) corresponds to what appears in the KL-EMT, where one has only

$$\psi(\vec{r})=\sum_{\vec{k}} F(\vec{k})\psi^0_k(\vec{r})\,. \tag{2.43}$$

The other two terms, which are Schmidt orthogonalization terms, perform a very important role, in that they *reorthogonalize* $\psi^0_{\vec{k}}(\vec{r})$ from being orthogonal to the $\psi^0_{c\vec{k}}$ [oscillations from orthogonality to the $\psi^0_{c\vec{k}}$ are removed by the $P^0\phi^0_{\vec{k}}$ term in Eq. (2.41)] to being orthogonal to the new core functions $\psi_{c\vec{k}}$ and ψ_c (new orthogonality oscillations introduced by the $P\phi^0_{\vec{k}}$ term). This suggests why the term U_R in U_Φ, which is merely a reflection of the last two terms in Eq. (2.41), has been called the *reorthogonalization potential*. At this point we can also see that for an isocoric impurity we have $P \simeq P^0$ whereby Eq. (2.41) reduces to the KL-EMT result. Similarly, for such impurities, $U_R \simeq 0$, showing that the pseudo-EMT reduces completely to the KL-EMT.

It will now be shown that the reorthogonalization terms in Eq. (2.41) are important only in the central cell, where they indeed remedy the old KL-EMT in the case of nonisocoric impurities. This can be seen best by using forms (2.31) and (2.32) for P^0 and P and rearranging the terms somewhat. For a substitutional impurity at $\vec{R}_0$ we get

$$\psi(\vec{r}) = \sum_{\vec{k}} f(\vec{k})\Big(\psi^0_{\vec{k}}(\vec{r}) + \sum_c \langle w^0_{c0} | \phi^0_{\vec{k}}\rangle w^0_{c0}(\vec{r} - \vec{R}_0) - \sum_{c'} \langle w_{c'0} | \phi^0_{\vec{k}}\rangle w_{c'0}(\vec{r} - \vec{R}\,'_0) + \delta\Big), \quad (2.44a)$$

whereas for an interstitial impurity at $\vec{R}_0$ the result is

$$\psi(\vec{r}) = \sum_{\vec{k}} f(\vec{k})\Big(\psi^0_{\vec{k}}(\vec{r}) - \sum_{c'} \langle w_{c'0} | \phi^0_{\vec{k}}\rangle w_{c'0}(\vec{r} - \vec{R}\,'_0) + \delta\Big). \quad (2.44b)$$

In Eqs. (2.44), δ is a small correction given by

$$\delta = \sum_c \sum_{j\neq 0} \langle w^0_{cj} | \phi^0_{\vec{k}}\rangle w^0_{cj}(\vec{r} - \vec{R}_j) - \sum_{c'} \sum_{j\neq 0} \langle w_{c'j} | \phi^0_{\vec{k}}\rangle \times w_{c'j}(\vec{r} - \vec{R}\,'_j). \quad (2.45)$$

It is small because $\vec{R}'_j \simeq \vec{R}_j$ and $w_{cj} \simeq w^0_{cj}$ for $j \neq 0$; physically these approximations mean that lattice relaxation and distortion of host atomic-core orbitals, respectively, are negligibly small (see Sec. III). The smallness of Eq. (2.45) is simply a reflection of the fact that the nodal structure of $\psi(\vec{r})$ is basically the same as that of $\psi^0_{\vec{k}}(\vec{r})$ over the sites $j \neq 0$. Therefore, the important reorthogonalization terms are those written out in Eq. (2.44) which are localized within the impurity cell. The net result is a preferential treatment of the impurity cell, so that the correct form of $\psi(\vec{r})$ is constructed. Take substitutional arsenic in silicon, for example. The second term in (2.44a) removes the 3*s*-3*p*-3*d*-like oscillations that $\psi^0_{\vec{k}}(r)$ had at the impurity site before the arsenic atom was introduced, and the third term builds new 4*s*-4*p*-4*d*-like oscillations to yield an appropriate form for $\psi(\vec{r})$. In the case of an interstitial impurity, the situation is different since $\psi^0_{\vec{k}}(\vec{r})$ has no orthogonality oscillations at interstitial sites, where it is very nearly a plane wave. Hence the expression (2.44b) is such as to simply build appropriate oscillations at the site of interest, depending on the core states of the foreign atom. Finally, with Eq. (2.44a) we see more clearly how the pseudo EMT reduces to the KL-EMT for isocoric substitutional impurities for which $w_{c'0} \simeq w_{c0}$. With Eq. (2.44b), we see that for interstitial impurities the pseudo EMT would reduce to the KL-EMT only when the impurity has no core states at all. This would only be interstitial hydrogen and helium.[20]

On closing this discussion, we might add that an attempt to reorthogonalize $\psi^0_{\vec{k}}$ in a fashion similar to Eq. (2.44a) was used as a *starting point* by the authors of Ref. 21, but their expression contained $\psi^0_{\vec{k}}$ in place of $\phi^0_{\vec{k}}$ in the Schmidt terms. Since $\langle w^0_{c0} | \psi^0_{\vec{k}}\rangle = 0$, it is clear that their expression fails to produce reorthogonalization.

2. *Many-band nature of the pseudo-EMT calculation*

In Sec. II F 2 we saw that even though only one band is retained in the expansion of ϕ in terms of the $\phi^0_{n\vec{k}}$, as in Eq. (2.38), the expression for ψ is the more complicated form given by (2.42), which may be rewritten as

$$\psi(\vec{r}) = \sum_{\vec{k}} \Big(f(\vec{k})\psi^0_{\vec{k}}(\vec{r}) + \sum_c f_c(\vec{k})\psi^0_{c\vec{k}}(\vec{r}) + \sum_{c'} f'_{c'}(\vec{k})\psi_{c\vec{k}}(\vec{r}) + \sum_{c'} f'_{c'}(\vec{k})\psi_{c'}(\vec{r})\Big), \quad (2.46)$$

where we defined

$$f_c(\vec{k}) = \sum_{\vec{k}'} f(\vec{k}\,')\langle \psi^0_{c\vec{k}} | \phi^0_{\vec{k}'}\rangle = f(\vec{k})\langle \psi^0_{c\vec{k}} | \phi^0_{\vec{k}}\rangle, \quad (2.47a)$$

$$f'_c(\vec{k}) = -\sum_{\vec{k}'} f(\vec{k}\,')\langle \psi_{c\vec{k}} | \phi^0_{\vec{k}'}\rangle, \quad (2.47b)$$

$$f'_{c'}(\vec{k}) = -f(\vec{k})\langle \psi_{c'} | \phi^0_{\vec{k}}\rangle. \quad (2.47c)$$

It is easy now to note from Eq. (2.46) that in the construction of $\psi(\vec{r})$ we have three distinct contributions: (a) the $\psi^0_{\vec{k}}$, namely the Bloch functions of the band of interest (conduction band for donors, valence band for acceptors); (b) the $\psi^0_{c\vec{k}}$, which are the core-band Bloch functions of the perfect crystal; and (c) the $\psi_{c\vec{k}}$ and $\psi_{c'}$, which are not perfect-crystal functions. The term involving the $\psi_{c\vec{k}}$ is generally nonzero away from the impurity site and simply cancels the contribution of the $\psi^0_{c\vec{k}}$ term in that region. In any case, the $\psi_{c\vec{k}}$ are accurately expressible in terms of the $\psi^0_{c\vec{k}}$, so that we are still within the subspace of the perfect-crystal core-band Bloch functions. The $\psi_{c'}(\vec{r})$, however, present an interesting contribution: they are essentially the impurity-atom core orbitals. Some of these are still basically within the $\psi^0_{c\vec{k}}$ subspace. But for some impurities, some of these, for example the 4*s*-, the 4*p*-, and 4*d*-like core orbitals of antimony in silicon, belong mainly to the subspace of excited-silicon Bloch functions, particularly those of the 4*s*-, 4*p*-, and 4*d*-like excited conduction bands.

The latter lie above the lowest conduction band on the energy axis.

In summary, in the case of donors, the conduction band contributes through mechanism (a), the core bands through mechanism (b) and partly mechanism (c), and the higher conduction bands, when necessary, contribute through mechanism (c). The net result is the *construction of a trial function with appropriate nodal structure*, as we saw earlier. One may legitimately wonder, however, as to when and how can the valence band contribute. The answer is that it would have to contribute through mechanism (a) on an equal footing with the conduction band. The reason its contribution is generally negligible was discussed in paper I.[1] For one thing, because of the indirectness of the energy gap in silicon, even "deep" levels are close to the conduction band and very far from the valence band (Fig. 11 of paper I[1]). Perturbation theory can show then that valence-band contribution is very small. On the other hand, the symmetry of the top of the valence band is incompatible with the symmetry of the donor ground state.[1] Finally, experimental observations seem to indicate negligible coupling of the donor ground state with the valence band.[1] A similar discussion would apply for contributions of the conduction band to acceptor states.

3. *Real electrons, pseudoelectrons, and effective masses*

In this section we examine the concept of the effective mass. In order to do this we first distinguish between the *real* impurity electron, which is described by the wave function $\psi(\vec{r})$, and the *pseudo*-electron, which is described by the pseudo wave function $\phi(\vec{r})$. These two wave functions are eigenfunctions of different Hamiltonians, have different spatial distributions and hence describe two distinct "particles." The only common point is that they both have the same mass and the same stationary energy. From the development of the present pseudo EMT in Sec. II E, it is clear that it is the pseudo system (2.23) which is transformed into the effective-mass equation. Therefore, it is the pseudoelectron which is described by an equivalent particle of mass m^* which moves in the potential U_Φ; its kinetic energy operator is, in a simple case, given by $-(\hbar^2/2m^*)\nabla^2$. The total effective Hamiltonian, which determines the total energy E, is then given by

$$H_{\text{eff}} = -(\hbar^2/2m^*)\nabla^2 + U + U_R\,, \tag{2.48}$$

where we wrote U_Φ as in Eq. (2.26). This yields to an interpretation from both a "pseudo" and a "real" point of view, so to speak. From the "pseudo" point of view, the contribution to the energy E of the first term in (2.48) is kinetic energy and the rest is potential energy. Hence, the pseudoelectron has an effective mass m^* in all space and move in the potential $U + U_R$ to maintain a constant total energy E. From the "real" point of view, we recall that U is the only true perturbation potential, whereas U_R is *actually kinetic energy in disguise*. Thus, the real electron, which moves in the potential U, has a kinetic energy operator given by $-(\hbar^2/2m^*)\nabla^2 + U_R$. Since U_R turns out to be mainly localized in the impurity-cell region, we see that the real electron, described by $\psi(\vec{r})$, has an effective mass m^* only outside the impurity-cell region. Inside the impurity-cell region, the kinetic energy operator has the complicated form $-(\hbar^2/2m^*)\nabla^2 + U_R$. If one insists on *interpreting* this result in terms of an "effective" mass, one can formally define a mass μ by

$$-(\hbar^2/2\mu)\nabla^2 \equiv -(\hbar^2/2m^*)\nabla^2 + U_R\,. \tag{2.49}$$

μ could then be written formally as

$$\frac{1}{\mu} = \frac{1}{m^*}\left(1 - \frac{2m^* U_R(\vec{r}, \vec{r}\,')}{\hbar^2\nabla^2}\right), \tag{2.50}$$

which shows that it *asympotically* becomes m^*, whereas in the impurity-cell region it is a position-dependent, even nonlocal, complicated function.

We thus conclude that in the pseudo EMT, the real electron is described by a many-band expansion of ψ and by an "effective" mass which is m^* outside the impurity-cell region, but is a complicated function of position within that region. More discussion on this point appears in Sec. III. We note here, however, that all this should not be confused with the fact that m^* comes from an expansion of $E^0(\vec{k})$ to order k^2. The contribution of the k^4 term has been shown to be generally small.[1]

As a last note here, we point out that the concept of pseudoelectrons (and pseudoholes, in the case of acceptors) is not unique to the semiconductor impurity problem. Even though such terminology has not been used, it may be used to illustrate vividly certain properties, wherever pseudopotentials are used. For example, in the case of a metal, such as aluminum, we know that the energy-band structure is very nearly free-electron-like. We also know that the real electrons are described by the true Bloch functions $\psi^0_{n\vec{k}}$, which are *not* plane waves, but orthogonalized plane waves (OPW) with rapid oscillations in atomic-core regions. It is the pseudoelectrons, which are described by the pseudo Bloch functions $\phi^0_{n\vec{k}}$, that are free-particle-like, since the $\phi^0_{n\vec{k}}$ are nearly plane waves. This adds comfort to accepting that the pseudoelectron in the impurity problem can be described by the band-minimum effective mass m^* in all space, even though this cannot generally be done for the real electron.

G. Concluding remarks on the general theory

The pseudo EMT presented in this section in its general form appears to have the power to treat most common impurities in a semiconductor like silicon. The number of approximations involved is sizable in accord with the complexity of the problem. More approximations are made when U_Φ is calculated (Sec. III). Each one must be checked for its validity in specific calculations and estimates of the corresponding accuracy should be made. In comparing with experiment, it must also be borne in mind that the theory calculates the energy states or quantum energy levels at temperature $T = 0\,^\circ\mathrm{K}$ when the lattice is frozen (except for zero-point vibrations), whereas experiment usually measures transitions between states which occur at finite temperatures. The levels then are usually broadened by $\sim k_B T$ and shifted slightly.

In Sec. III the theory is applied to donors in silicon, both shallow and deep, substitutional and interstitial, and, although with varying degree of accuracy, the final results for the ground-state energies agree exceedingly well with the experimental binding energies.

III. APPLICATION TO DONORS IN SILICON

In this section, the pseudo impurity theory (PIT), developed in the previous section will be applied to the study of donors in silicon. These are the group-V elements N, P, As, Sb, Bi at substitutional sites, which act as single donors (conclusive experiment for N is lacking); the group-VI elements O, S, Se, Te, Po also at substitutional sites should be double donors, capable of binding one or two electrons. Experiment has been fairly conclusive only for sulfur.[22,23] Oxygen, on the other hand, has generally been found to form complexes. As for interstitials, lithium (a single donor) and magnesium (a double donor) are the ones identified with certainty. Less accurate information exists on some transition metals.[24,25]

A. Calculation of impurity pseudopotentials

In Sec. II the general expression (2.34) for U_Φ was obtained. For further development, the atomiclike potentials are written as

$$v^0(\vec{r}-\vec{R}_j) = v_0^{+4}(\vec{r}-\vec{R}_j) + v_e^0(\vec{r}-\vec{R}_j)\,, \tag{3.1a}$$

$$v_j(\vec{r}-\vec{R}'_j) = v^{+z_j}(\vec{r}-\vec{R}'_j) + v_e(\vec{r}-\vec{R}'_j)\,. \tag{3.1b}$$

Here, v_0^{+4} and v^{+z_j} are the same ioniclike potentials as the ones appearing in Sec. IV of paper I[1] while v_e^0 and v_e, describing the redistribution of valence electrons, are related to V_e^0 and V_e of Ref. 1 via

$$V_e^0(\vec{r}) = \sum_j v_e^0(\vec{r}-\vec{R}_j)\,, \tag{3.2a}$$

$$V_e(\vec{r}) = \sum_j v_e(\vec{r}-\vec{R}'_j)\,. \tag{3.2b}$$

Then U_Φ can be written as

$$U_\Phi = U_{\phi b} + U_{\phi s}\,, \tag{3.3}$$

where

$$U_\Phi = \sum_j [(1-P_j)v^{+z_j}(\vec{r}-\vec{R}'_j) - (1-P_j^0)v_0^{+4}(\vec{r}-\vec{R}_j)] \tag{3.4}$$

and

$$U_{\phi s} = \sum_j [(1-P_j)v_e(\vec{r}-\vec{R}'_j) - (1-P_j^0)v_e^0(\vec{r}-\vec{R}_j)]\,. \tag{3.5}$$

Clearly, $U_{\phi b}$, the bare impurity pseudopotential, is the result of changes in the ionic pseudopotentials and $U_{\phi s}$ is the result of valence electron redistribution. First we concentrate on $U_{\phi b}$, which, we note, may be written as

$$U_{\phi b} = U_b + U_{Rb}\,, \tag{3.6}$$

where U_b is the same as in Sec. VI of paper I, and U_{Rb} is given by

$$U_{Rb} = \sum_j [1 - P_j v^{+z_j}(\vec{r}-\vec{R}'_j) + P_j^0 v_0^{+4}(\vec{r}-\vec{R}_j)]\,. \tag{3.7}$$

Simple results are obtained, as in paper I, when the following approximations are valid: (a) Lattice relaxation is neglected so that $\vec{R}'_j \simeq \vec{R}_j$; (b) the core electrons at all sites except the foreign atom site remain unperturbed. This means that

$$v^{-z_j}(\vec{r}-\vec{R}'_j) \simeq v_0^{+4}(\vec{r}-\vec{R}_j)\,, \quad j \neq 0 \tag{3.8}$$

$$w_{c'}(\vec{r}-\vec{R}'_j) \simeq w_c^0(\vec{r}-\vec{R}_j)\,, \quad j \neq 0 \tag{3.9}$$

where $\vec{R}_0$ is the impurity site.

Equation (3.8) results in U_b being given as in paper I and (3.9) results in $P_j \simeq P_j^0$ for $j \neq 0$, whereby

$$U_{Rb} = -P_j v^{+z}(\vec{r}) + P_j^0 v_0^{+4}(\vec{r}) \tag{3.10a}$$

for substitutional impurities, and

$$U_{Rb} = -P_j v^{+z}(\vec{r})\,. \tag{3.10b}$$

for interstitial impurities, where the origin of coordinates was taken at $\vec{R}_0$ in both cases.

The potentials $v_0^{+4}(\vec{r})$ and $v^{+z}(\vec{r})$ and hence $U_b(\vec{r})$ may be calculated as in paper I.[1] Using the same approximations, $w_c^0(\vec{r})$ and $w_{c'}(\vec{r})$ may be taken to be free-atom or free-ion core wave functions, with certain reservations when a heavy impurity is studied (see Sec. III D). In this manner, $U_{\phi b}$ is obtainable in numerical form by making use of the Herman-Skillman computer program for atomic structures.[26] Because of the operator nature of U_{Rb}, $U_{\phi b}$ cannot be plotted as was U_Φ in Ref. 1. For plotting purposes only, a local approximation amounts to operating with U_{Rb} on the constant function 1. Thus

$$U_{Rb}^{\text{local}}(\vec{r}) = \int d^3r'\, U_{Rb}(\vec{r}, \vec{r}\,')\,. \tag{3.11}$$

Plots of the local approximants of $U_{\phi b}$ for some typical donors are given in Fig. 2 in tandem with the true potentials U_b in order to exhibit the can-

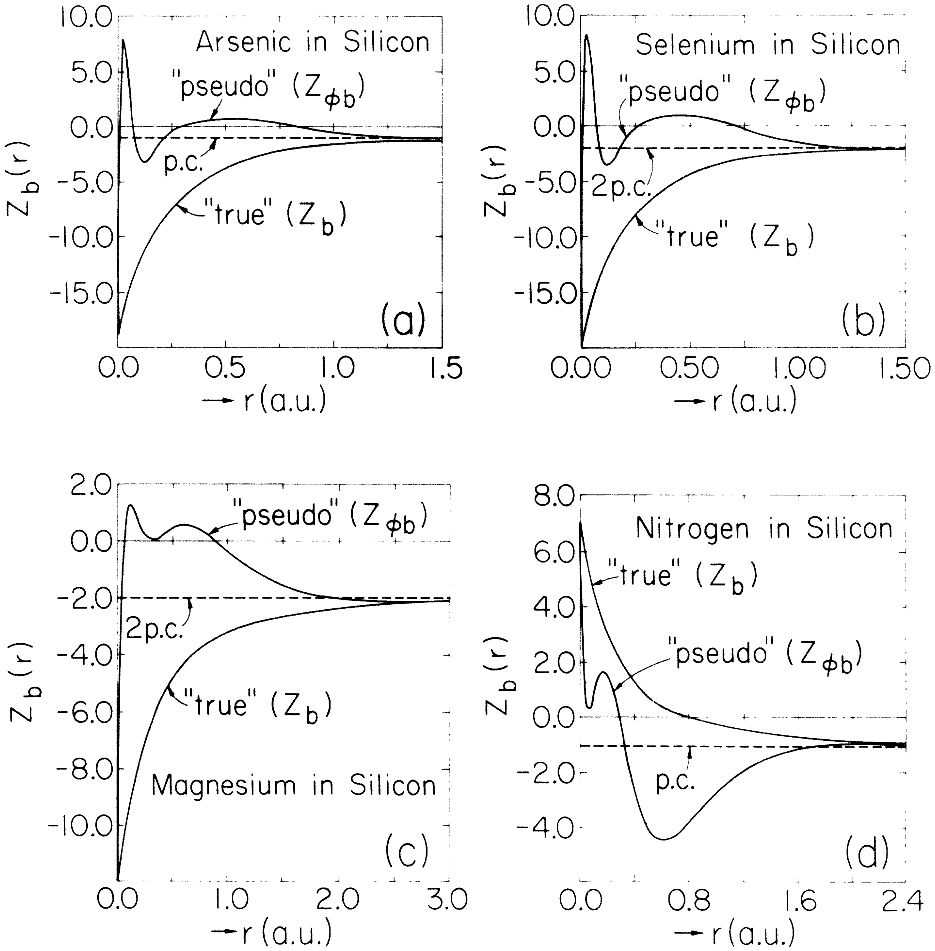

FIG. 2. "True" and "pseudo" impurity potentials for some donors in silicon. Comparison with point-charge potentials (p.c.). The effective charges are the quantities plotted.

cellation generally produced by U_{Rb}. Again, we plot the corresponding effective charges $Z_{\phi b}$ and Z_b. These plots are meant only for qualitative illustration of the cancellation effect and are not appropriate for numerical calculations. For example, use of the local approximant $U_{\phi b}(\vec{r})$ for interstitial magnesium, shown in Fig. 2 (plus its screening $U_{\phi s}$), in the multivalley EME to calculate the ground-state energy yields a value which is about 25% smaller in absolute magnitude than the one obtained by using the full nonlocal pseudopotential.

The bare pseudopotentials can also be displayed Fourier-transformed. Again, however, $\langle\vec{k}+\vec{q}|U_{\phi b}|\vec{k}\rangle$ is not amenable to plotting since it depends on both $\vec{k}$ and $\vec{q}$. Choosing $\vec{k}=0$, we plot the resultant $U_{\phi b}(\vec{q})$ in tandem with the corresponding $U_b(\vec{q})$. Again, the quantities actually plotted are $\rho_{\phi b}(\vec{q})$ and $\rho_b(\vec{q})$, where, for example,

$$\rho_b(\vec{q}) = q^2 U_b(\vec{q})/4\pi . \qquad (3.12)$$

Figure 3 shows such plots for typical donors. Recalling the criterion for the applicability of the EMA, namely

$$R_\phi = \frac{|\rho_{\phi b}(\vec{q}-\vec{K}_h)|}{|\rho_{\phi b}(\vec{q})|} \lesssim 1, \quad h \neq 0 \qquad (3.13)$$

we see that it is generally satisfied. At very large K_h, $\rho_{\phi b}(\vec{q}+\vec{K}_h)$ may be seen to start growing again (no effective cancellation) but this does not invalidate the EMA: We recall[1] that Eq. (3.13) comes from $R_\phi R_{\rm pc} \ll 1$, where $R_{\rm pc}$ is the corresponding ratio for a point-charge potential. Since $R_{\rm pc}$ is vanishingly small at very large K_h, the growth of $\rho_{\phi b}(\vec{q}+\vec{K}_h)$ is neutralized, so that we always have $R_\phi R_{\rm pc} \ll 1$.

For the calculation of $U_{\phi s}$, again we depend on linear-response theory. From the general properties of U_ϕ described in Sec. II, it is expected that the method should be a good approximation in general.[27] Indeed, particularly because of the reconstruction-of-bonds argument of Sec. III D, whereby $U_\phi(\vec{K}_3)$ must be very small, local-field corrections are justifiably left out. Because of the nonlocality of $U_{\phi b}$, however, the prescription

$$\langle\vec{k}+\vec{q}\,|U_\phi\,|\vec{k}\rangle = \frac{\langle\vec{k}+\vec{q}\,|U_\phi\,|\vec{k}\rangle}{\epsilon(\vec{q})} \qquad (3.14)$$

is not strictly valid. Instead, one can show[18] that

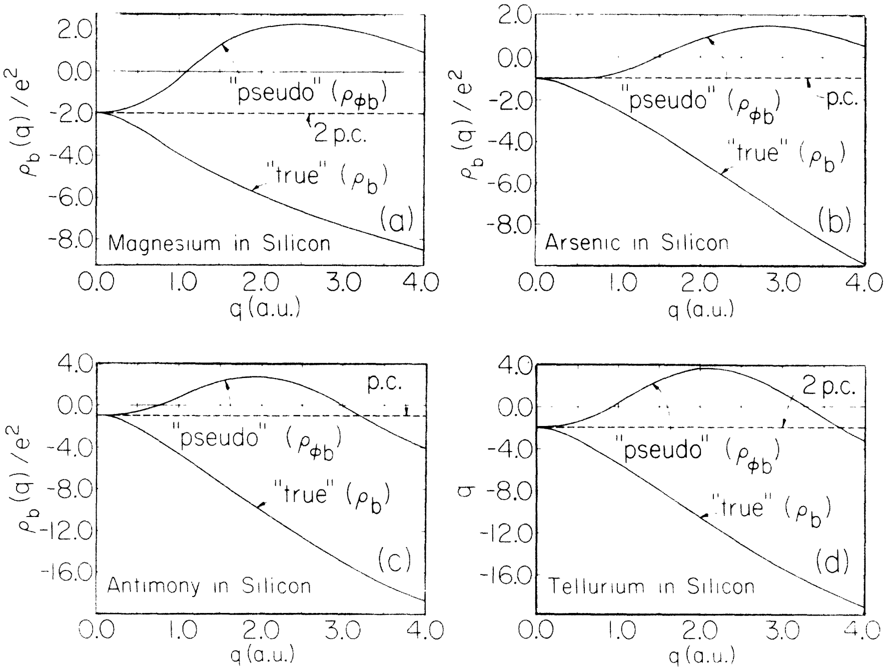

FIG. 3. Fourier transforms of "true" and "pseudo" impurity potentials for some donors in silicon. Comparison with point-charge potentials (p.c.). The effective charge-density transforms $\rho(q)$ are the quantities plotted.

$\langle \vec{k}+\vec{q}|U_\Phi|\vec{k}\rangle$ can be written as

$$\langle \vec{k}+\vec{q}|U_\Phi|\vec{k}\rangle = \frac{\langle \vec{k}+\vec{q}|U_{\Phi b}|\vec{k}\rangle}{\epsilon_{\vec{k}}(\vec{q})}, \tag{3.15}$$

where the function $\epsilon_{\vec{k}}(\vec{q})$ can be written as (see Appendix A)

$$\frac{1}{\epsilon_{\vec{k}}(\vec{q})} = \frac{1}{\epsilon(\vec{q})} + \frac{\Delta_{\vec{k}}(\vec{q})}{\epsilon(\vec{q})}. \tag{3.16}$$

The correction $\Delta_{\vec{k}}(\vec{q})$ depends on how strongly $\langle \vec{k}+\vec{q}|U_{\Phi b}|\vec{k}\rangle$ depends on $\vec{k}$; it is not a general crystal function like $\epsilon(\vec{q})$, but depends on the perturbing potential as well. Indeed for a local potential $\Delta_{\vec{k}}(q) \equiv 0$. Using Eq. (3.6), we have

$$\langle \vec{k}+\vec{q}|U_\Phi|\vec{k}\rangle = \frac{U_b(\vec{q})}{\epsilon(\vec{q})} + \frac{\langle \vec{k}+\vec{q}|U_{Rb}|\vec{k}\rangle}{\epsilon_{\vec{k}}(\vec{q})} \tag{3.17}$$

For the second term in Eq. (3.17) the correction $\Delta_{\vec{k}}(\vec{q})$ in $\epsilon_{\vec{k}}(\vec{q})$ is estimated to contribute only about 1–2% and hence $\epsilon_{\vec{k}}(\vec{q}) \simeq \epsilon(\vec{q})$. Using Eq. (3.17) we can then write the total pseudopotential operator U_Φ as

$$U_\Phi = \tilde{U} + \tilde{U}_R, \tag{3.18}$$

where $\tilde{U}$ is a local term whose Fourier transform is

$$\tilde{U}(\vec{q}) = U_b(\vec{q})/\epsilon(\vec{q}). \tag{3.19}$$

It should be noted that it is not necessarily true that $\tilde{U} = U$ or $\tilde{U}_R = U_R$ except when U_R is very small (phosphorus, sulfur in silicon). This is because the separation (3.18) is purely mathematical, while it is not true that the "true" part (U_b) and the reorthogonalization part (U_{Rb}) of $U_{\Phi b}$ may be screened separately.

From Eq. (3.19), $\tilde{U}(r)$ is obtained directly by inverse-Fourier-transform as $U(r)$ was obtained in paper I.[1] As for $\tilde{U}_R$, even if $\epsilon_{\vec{k}}(\vec{q})$ is approximated by $\epsilon(\vec{q})$, the inverse transformation cannot be carried out in closed form to give $U_R(\vec{r}, \vec{r}\,')$. The difficulty can be circumvented, nevertheless, and the matrix elements of U_R in a variational calculation can be calculated (see Appendix A).

In summary, the bare impurity pseudopotential is calculated as the difference in the pseudopotentials of the impurity and host atoms with their valence electrons removed. All that is necessary for this is a set of core orbitals for the impurity and host atoms. These are obtained in numerical form from a Herman-Skillman program (some of these were displayed in Figs. 9 and 10 in paper I). In terms of these, the "true" potentials of the ions are constructed in the Hartree-Fock-Slater approximation using Eqs. (4.10)–(4.13) of paper I; the "repulsive" terms in the pseudopotentials are constructed by using Eq. (3.10). Again, all that is used are the same core orbitals in order to construct the operators P_j and P_j^0 [Eq. (2.32)], plus the ionic "true" potentials just described. It should be noted that the energies of the core states are not needed in the Austin-Heine-Sham form of the pseudopotential employed here. Finally, the total bare pseudopotential is screened by using the dielectric function computed by Nara as given by Eq. (4.22) of paper I. The details of the evaluation of the various matrix elements are given in the appendixes and the errors introduced by the various

TABLE I. Ionization energies of group-V impurities in silicon using the pseudo impurity theory.

Impurity	Theory a (a.u.)	 c_1	 E (meV)	Experiment E (meV)
point charge[a]	17.80	0.924	48.8	···
phosphorus	21.79	0.977	44.3	45.5[b]
arsenic	14.44	0.922	53.1	53.7[b]
antimony	37.50	0.986	31.7[c]	42.7[b]
Nitrogen (N^0)[d]	7.50	1.0	335.9	···
Nitrogen (N^-)	8.60	1.0	52.5[e]	45.0[f]

[a] Same calculation as in paper I (Ref. 1).

[b] Reference 28.

[c] Discrepancy between theory and experiment is accounted for in Sec. III D.

[d] N^0 center binds one electron like the other group-V elements.

[e] N^- center binds two electrons, both in the $1s(A_1)$ state with an orbit radius of 8.60 a.u. They have a total energy of 388.4 meV, so that the first ionization energy for this center is 52.5 meV.

[f] Reference 29. No identification of the charge state is made in the experimental paper. See also discussion in text.

approximations inherent in this scheme are estimated in Sec. III D.

B. Calculation of ground states

Having constructed the impurity pseudopotentials for the various donors, the multivalley effective-mass approximation (2.37) is used to calculate the ground state. The calculations are similar to those of part I except for the matrix elements of the reorthogonalization potential $\tilde{U}_R$. The same trial functions are used. The matrix elements of $\tilde{U}_R$ are given in Appendix A.

Numerical results for the lowest state of A_1 symmetry for group-V and group-VI substitutional and some interstitial donors in silicon are given in Tables I–III. In all cases, except interstitial lithium, the A_1 state is also the ground state, whence its energy represents the binding or ionization energy of the electron relative to the conduction band as well.

TABLE II. Ionization energies of group-VI impurities in silicon using the pseudo impurity theory.

Impurity	Theory a (a.u.)	 E (meV)	Experiment E (meV)
One-electron centers			
two point charges[a]	5.46	1085.3	···
sulfur (S^+)	6.75	709.8	613.6[b]
selenium (Se^+)	5.58	921.3	···
tellurium (Te^+)	9.32	246.0[c]	···
Two-electron centers			
two point charges[a]	6.43	489.0	···
sulfur (S^0)	7.60	334.4	302.0[d]
selenium (Se^0)	6.53	358.4	···
tellurium (Te^0)	11.56	71.9[c]	140.0[e]

[a] Same calculation as in paper I (Ref. 1).

[b] Reference 22.

[c] Values for Tellurium are corrected in Sec. III D.

[d] Reference 23. The value 302.0 is the thermal activation energy. The ionization energy should be at least 15 meV higher.

[e] Reference 30.

TABLE III. Ionization energies of interstitial impurities in using the pseudo impurity theory.

Impurity	Theory a (a.u.)	 E (meV)	Experiment E (meV)
One-electron centers			
lithium	34.80	33.8[a]	31.0[b]
sodium	32.96	34.6	···
magnesium (Mg^+)	10.13	259.0	256.5[c]
Two-electron centers			
magnesium (Mg^0)	11.70	98.0	107.5[c]

[a] State of A_1 symmetry. Ground state (and thence ionization energy) is T_2+E. See Ref. 31.

[b] State of A_1 symmetry. Reference 31.

[c] Reference 32.

C. Discussion of results

A quick perusal of Tables I–III shows that agreement with experimental data is excellent in all cases, with the exception of antimony and tellurium. The reason for this exception is discussed in Sec. III D and a satisfactory account for the discrepancy is given. For selenium and Te$^+$, there have been no experimental data. Ning and Sah[14] predicted energy levels for these impurities by doubling the parametric potentials fitted to the arsenic and antimony experimental levels, respectively. A comparison is made in Table IV. For nitrogen, which is found to bind up to two electrons, there is scant experimental information. We quoted the result obtained by Zorin *et al.*[29] and assigned it to the N$^-$ center. No identification of the charge state is made in that paper; the paper does mention, however, the existence of deeper levels associated with the same nitrogen center, in agreement with the present theoretical predictions. It should be said, however, that ion implantation, which was used in Ref. 29, generally produces considerable damage and defects with bound states which impede identification of the bound states of the impurity ion.

The accuracy of the calculations will be discussed at length in Sec. III D. For the remainder of this section, we pursue a discussion and analysis of the

TABLE IV. Comparison of present predictions with predictions of Ref. 14.

Impurity	Ionization Energy (meV) Present	 Present corrected[a]	 Ref. 15	 experiment
selenium (Se^+)	921.3	···	1123.0	···
selenium (Se^0)	358.4	···	585.0	···
tellurium (Te^+)	246.0	456.9	539.0	···
tellurium (Te^0)	71.9	136.8	265.0	140.0[b]

[a] See Sec. II D.

[b] Reference 30.

TABLE V. Partial contributions (in meV) to the ground-state energy of donors in silicon to illustrate the cancellation effect between "true" and "reorthogonalization" potentials $\tilde{U}-U_{\text{pc}}+\tilde{W}$ and $\tilde{U}_R$. T denotes kinetic energy. The column marked $2s$ lists the contributions of $2s$ mixing, while all the others list only matrix elements of $f_i^{1s}(r)$.

Impurity	a (a.u.)	T	U_{pc}	$\tilde{W}$	$\tilde{U}_R$	$2s$	E
p. c.	17.80	174.6	−219.9	···	···	−3.5[a]	−48.8
P	21.79	109.9	−157.2	6.7	−2.4	−1.3[a]	−44.3
As	14.44	289.0	−322.2	−174.6	164.0	−9.3[a]	−53.1
Sb	37.50	34.0	−73.3	−24.4	32.0	0.0	−31.7
N	7.50	1564.8	−1227.9	847.8	−1520.6	···	−335.9
Li	34.80	39.8	−80.6	−7.2	14.2	0.0	−33.8
Na	32.96	44.6	−86.5	−22.7	30.0	0.0	−34.6
Mg^+	10.13	706.5	−1307.1	−603.2	944.8	···	−259.0
S^+	6.75	2057.8	−3046.0	328.9	−50.5	···	−709.8
Se^+	5.58	3322.1	−4407.0	−2129.3	2292.9	···	−921.3
Te^+	9.32	879.3	−1556.0	−1394.4	1825.1	···	−246.0

[a] If the point-charge (pc) level is determined variationally using only $f_i^{1s}(r)$, it is found to be −47.3 meV at $a = 21.4$ a.u. (Table III). Hence $2s$ mixing lowers the energy by only 1.5 meV. Similarly for phosphorus the lowering is actually only 0.8 meV and for arsenic it is 3.5 meV.

numerical results for the purpose of illustrating the nature of the method and substantiating the general claims and speculations of Sec. II with specific examples.

As pointed out in Sec. II, the most important feature of the pseudo-EMT method is the cancellation effect, which is present in donors other than phosphorus and sulfur. This was illustrated already in Figs. 2 and 3 and accompanying discussion. Here we examine the actual contributions of the various terms in the total pseudopotential to the total ground-state energy. As seen in the previous subsection, U_Φ consists of $\tilde{U}$ and $\tilde{U}_R$ where $\tilde{U}$ is nearly equal to the true impurity potential U. (Separation of U into $\tilde{U}$ and $\tilde{U}_R$ is not feasible from a computational point of view.) $\tilde{U}$ can then be written as

$$\tilde{U}(\vec{r}) = U_{\text{pc}}(\vec{r}) + \tilde{W}(\vec{r}) \tag{3.20}$$

where $U_{\text{pc}}(\vec{r})$ is the screened point-charge Coulomb potential of paper I[1] and $W(r)$ is a short-range core potential. It was a strong $\tilde{W}(r)$ that invalidated the KL-EMT for most donors in paper I.

The kinetic energy, and the contributions of $U_{\text{pc}}(\vec{r})$, $\tilde{W}(\vec{r})$, and $\tilde{U}_R$ to the total energies of the various donors are listed in Table V. The cancellation between $\tilde{W}$ and $\tilde{U}_R$ is evident in all cases, even for phosphorus and sulfur for which both $\tilde{W}$ and $\tilde{U}_R$ are very small. It should be noted that if $\tilde{U}_R$ were to cancel out $\tilde{W}$ *exactly*, then the donors would be described exactly by a point-charge Coulomb potential. This shows that, in the context of the PIT, the point-charge model can be justified as an approximate or model pseudopotential, whereas in the KL-EMT it was justified as an approximation to the true impurity potential U only for phosphorus and sulfur (two point charges). For the other donors, it had the wrong asymptotic form as $r \to 0$.

In reality $\tilde{W}+\tilde{U}_R$ is not quite zero and accounts for the deviations of the ground state of the different donors from that of the point-charge potential $U_{\text{pc}}(\vec{r})$. It can rightly then be termed *"chemical shift."* With the ground state of $U_{\text{pc}}(\vec{r})$ being at 48.8 meV below the conduction-band edge (N. B., that $U_{\text{pc}}(\vec{r})$ is $\epsilon(\vec{q})$-screened and the calculation includes intervalley interaction), the newly defined chemical shifts[33] are small for phosphorus, arsenic and antimony and larger for lithium. Furthermore, the calculations predict a very large chemical shift for the neutral nitrogen donor, making it a deep level. This is quite noteworthy, especially since the true impurity potential $U(\vec{r})$ for nitrogen in silicon has a repulsive core [Fig. 2(d)]. The binding comes about from the strongly attractive $\tilde{U}_R$. Some insight into this odd behavior of nitrogen may be gained by comparing the free-atom ionization energies for the four group-V elements with the impurity ionization energies in silicon. This is done in Fig. 4. On the free-atom side, the solid

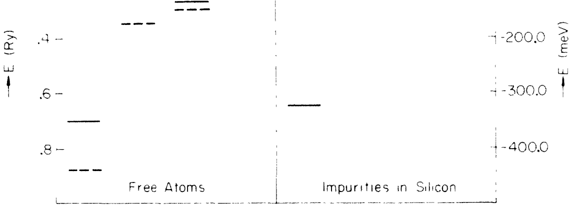

FIG. 4. Comparison of the free-atom ionization energies of nitrogen, phosphorus, arsenic, and antimony with the corresponding ionization energies of the elements as impurities in silicon.

TABLE VI. Demonstration of the importance of the intervalley mixing.

Impurity		T (meV)	U_{pc} (meV)	$\tilde{W}$ (meV)	$\tilde{U}_R$ (meV)
	Intravalley	218.4	−186.4	−17.2	5.4
arsenic[a]	Intervalley	70.6	−135.8	−157.4	158.6
	Total	289.0	−322.2	−174.6	164.0
	Intravalley	443.9	−596.5	−70.0	31.2
magnesium	Intervalley	262.6	−710.6	−533.2	913.6
	Total	706.5	−1307.1	−603.2	944.8
	Intravalley	761.5	−440.0	104.8	−50.4
nitrogen	Intervalley	803.3	−787.9	743.0	−1470.2
	Total	1564.8	−1227.9	847.8	−1520.6

[a] As in Table V, only the 1s contribution is listed here.

lines are theoretical,[26] and the dashed lines are experimental.[34] In both cases, nitrogen turns out to bind its outer electron stronger than the other three group-V elements. It should also be recalled that the nitrogen isoelectronic trap in GaP is strong enough to bind an electron. Finally, the comparison of Fig. 4 shows that the relative position of the phosphorus-arsenic-antimony levels is a very subtle effect resulting from the delicate balancing of attractive and repulsive forces of both electrostatic and quantum-mechanical origin.

Chemical shifts for the double donors have not been analyzed previously. They should be defined with respect to the two-point-charge model U_{pc}, which has a very deep level at 1085 meV from the bottom of the conduction band. This level is probably too deep for our approximations to hold, and lies below the top of the valence band. In the KL-EMT such shifts would be measured relative to a value of about 125 meV, which is the one-valley ground state of $-2e^2/\epsilon r$. As Tables II and III show, the experimental results span the entire range between the two extremes. An interesting comparison can be made, however, between substitutional sulfur and interstitial magnesium, which illustrates once more the power of the pseudo EMT. For both of these, we have $U(\vec{r}) = -2e^2/\epsilon r$ at values of r away from the imperfection site. On the other hand, as $r \to 0$ we have $U(r) \to -2e^2/\epsilon r$ for sulfur and $U(\vec{r}) \to -12e^2/r$ for magnesium; however, this strong attraction is so effectively cancelled that the Mg levels come out quite shallower than those of sulfur, in excellent agreement with experiment (Tables II and III).

Going back to Table V and the values of $\tilde{U}_R$, we recall that $\tilde{U}_R$ is actually kinetic energy for the real electron and can be looked upon as a modification of the electron's effective mass in the central cell. It is seen from Table V that $\tilde{U}_R$ is in general positive. For phosphorous and sulfur, U_R is negative but too small to be important (~ 2% of kinetic energy). Most notably, however, $\tilde{U}_R$ is negative and very large for nitrogen in silicon. This means that the real electron's "effective" mass is highly *reduced* in the central cell. Indeed, comparing the value of $\langle\tilde{U}_R\rangle$ with that of the kinetic energy and recalling that $\langle\tilde{U}_R\rangle$ comes entirely from the central cell while the kinetic energy comes from all space, we conclude that the "effective" mass of the real electron is *negative* in the central cell! This seems to contradict intuition which claims an "effective" mass equal to m_0 as $r \to 0$.[10,13] A closer examination, however, reminds us that the true potential $U(\vec{r})$ for nitrogen in silicon is repulsive to an electron at small r. Therefore, the real electron, while being bound at the center, avoids the core region. In other words, the electron acts as a hole in the core region and hence has a negative "effective" mass. This makes clear the distinction between the real electron and the pseudoelectron. The latter has an effective mass m^* throughout space.

Another aspect of the calculation that should be illustrated is the role of the intervalley interaction. In Table VI three examples are used to demonstrate the relative magnitudes of the intravalley and intervalley terms. It is clear that the intervalley mixing is very important. Finally it may be of interest to see how much of the potential energy comes from the Kohn-Luttinger potential $-e^2/\epsilon r$, as was done in paper I.[1] For arsenic, its contribution is −165.2 meV. Adding this to the intravalley kinetic energy term, we get a *positive* 53.2 meV to the energy. All the rest of the contributions, the "central cell corrections," account for −106.3 meV, so that the total energy is −53.1 meV below the bottom of the conduction band. This illustrates once more *that central cell contributions cannot be equated with the discrepancy between experiment and Faulkner's value of* −31.27 meV.

D. Investigation of the accuracy of the calculations—corrections

As in paper I,[1] the accuracy of the calculations depends on (a) the approximations made in deriving the multivalley effective-mass equation and (b) the approximations made in constructing the impurity pseudopotential. For the first item, the discussion in Sec. V C of paper I applies here as well, since the only difference between the two methods is the exact pseudopotential transformation of the eigenvalue problems (2.1) and (2.3). This of course is crucial, as it results in a weak perturbation pseudopotential which makes the EMA applicable to nonisocoric impurities. Indeed for isocoric impurities, as noted earlier, where the KL-EMT is applicable,[1] the present pseudo impurity theory reduces to the same results (since U_R turns out to be negligibly small). The accuracy estimates of paper I apply both to the present general theory and to its special case, the KL-EMT of paper I. Here then, we present some studies on the approximations made in constructing the impurity pseudopotential itself for the various cases. This again will apply to the special case of paper I. Fuller discussion of all the approximations was made in Ref. 18.

The first approximation made in obtaining a working expression for U_ϕ was the neglect of lattice relaxation, namely $\vec{R}_j' \simeq \vec{R}_j$. Lattice relaxation is expected to be small in the case of donors when the Jahn-Teller effect is not present. It is sufficient to say here that the correction to the energy would be proportional to $(\vec{R}_j' - \vec{R}_j)^2$ and hence small. It will be discussed further elsewhere. It should be noted, however, that even though the magnitude of $\vec{R}_j' - \vec{R}_j$ may be related to an effective "size" of the donor atom, it is not true that the present calculation has neglected to incorporate a "size effect." This is obvious from Figs. 2 and 3, where one notices that the pseudopotentials for the various impurities have different effective radii of non-$(-e^2/\epsilon r)$ behavior in the impurity cell. This is, of course, incorporated automatically in the calculation.

The second approximation, the independent-core assumption, was seen to imply Eqs. (3.8) and (3.9). The accuracy of this approximation can be estimated by assuming that $w_{c'}(\vec{r} - \vec{R}_j)$ varies slightly from $w_c^0(\vec{r} - \vec{R}_j)$, which implies that $v^{+zj}(\vec{r} - \vec{R}_j)$ varies slightly from $v_0^{+4}(\vec{r} - \vec{R}_j)$. Instead of using the numerical potentials we write

$$v_0^{+4}(\vec{r}) = -e^2 Z(\vec{r})/r \tag{3.21}$$

and approximate

$$Z(\vec{r}) = 10 + 4e^{-\sigma r}, \tag{3.22}$$

which has the correct asymptotic form. The constant σ is about 4.3 a.u. (compare Ref. 21). Then we can vary $v_0^{+4}(\vec{r} - \vec{R}_j)$ by changing σ to $\sigma + \delta\sigma$. This would result in an additional potential ΔU be present in the perturbation. Treating $\delta\sigma$ as a small quantity, it is easily shown that

$$\Delta U(\vec{r}) \simeq 10\delta\sigma e^2 e^{-\sigma|\vec{r}-\vec{R}_j|}, \tag{3.23}$$

where the contribution of only the atomic site R_j is included. The contribution to the energy level is given by

$$\langle \Delta U \rangle \simeq \int d^3r \, |F(\vec{r})|^2 \Delta U(\vec{r}) \tag{3.24}$$

and, since $\Delta U(\vec{r})$ is localized about R_j and $F(r)$ is nearly constant in that region, we get

$$\langle \Delta U \rangle \simeq |F(\vec{R}_j)|^2 \int d^3r \, \Delta U(\vec{r}). \tag{3.25}$$

This can be evaluated in a straightforward manner. Including only nearest neighbors as being perturbed, this gives an estimate of

$$\langle \Delta U \rangle \simeq 17\delta \text{ meV} \tag{3.26}$$

for a state of orbit radius $a = 10$ a.u. which is a fairly deep level (close to the Mg^+ level). For shallower levels it is even less. Now, the value of δ cannot reasonably be expected to be more than 0.1 (namely a 10% change in the nearest-neighbor-core charge density), whereby the correction is about 1–2 meV even for deep levels, and less for shallow levels.

Next in the series of approximations is in the construction of $v^{+z}(\vec{r})$ and $v_0^{+4}(\vec{r})$ for which free-atom core orbitals were used, as described in Appendix B. The calculations were repeated by using free-ion core orbitals and the change in the resultant energy level was negligible. For the pseudo-EMT, the effect of the uncertainty in w_c^0 and $w_{c'}$ in the reorthogonalization potential U_R was found to be more pronounced. For the shallow levels and the average-depth magnesium levels the uncertainty is not more than 1%, while for the deep selenium levels it is about 5%. For this same reason, the nitrogen levels may actually be even deeper than reported here. In order to study further these uncertainties in the choice of core wave functions and core charge densities for the potentials v^{+z} and v_0^{+4}, we calculated distorted core wave functions by the prescription

$$x_c'(\vec{r}) = x_c(\vec{r} + \tfrac{1}{100}\eta\vec{r}),$$

renormalized them, and used them to calculate the ground-state energy level. Results for magnesium are displayed in Fig. 5 and show that a 1% uncertainty in the core wave function translates to about 2.5% uncertainty in the energy level. Positive η implies pulling the electron distribution toward the origin where the impurity is located, i.e., the wave function is "squeezed." As expected, "squeezing" the wave functions makes the level deeper. A 100% "squeeze" would reduce the center to a two-point-charge center. Similar results were

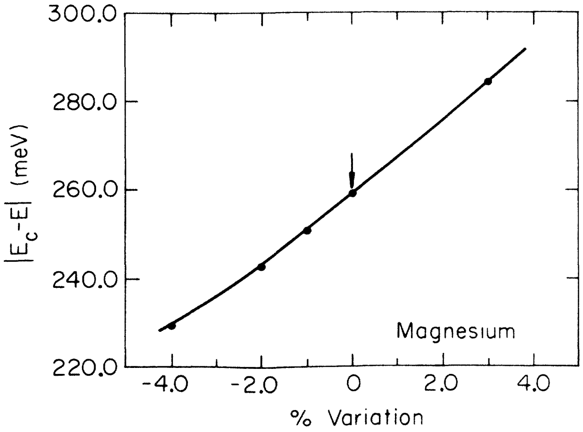

FIG. 5. Effect of varying the core wave functions on the energy levels. Positive variation corresponds to "squeezing" the wave functions.

obtained for the other cases.

Next, a number of approximations are involved in using linear dielectric screening to calculate $U_{\Phi s}$ from the bare $U_{\Phi b}$. First of all, the applicability of linear screening is justified from the fact that $U_{\Phi b}$ (or U_b in paper I,[1] when applicable) does not have strong high Fourier components, since it does not bind any core electrons. This was also illustrated earlier through the ratio R_Φ and Fig. 3. Two approximations in the use of linear screening for $U_{\Phi s}$ are discussed in Appendix A. Finally, uncertainties exist in the function $\epsilon(q)$. The function used here is the one given by Eq. (4.22) of paper I.[1] The effect of uncertainties in $\epsilon(q)$ on the energy levels was investigated by first varying $\epsilon(0)$ in Eq.

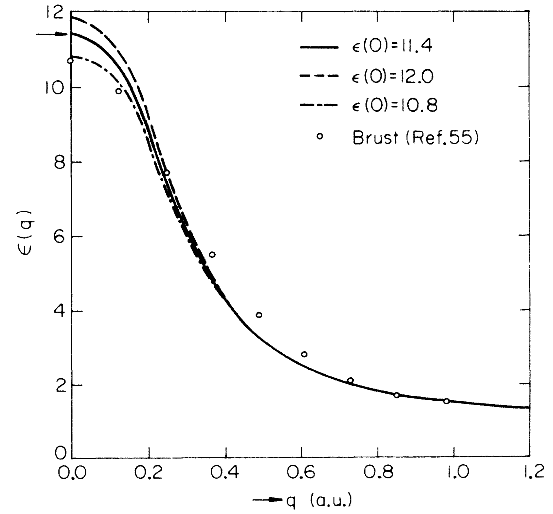

FIG. 6. Forms of $\epsilon(q)$ as functions of $\epsilon(0)$. Energy levels obtained with these and intermediate forms are displayed in Fig. 8.

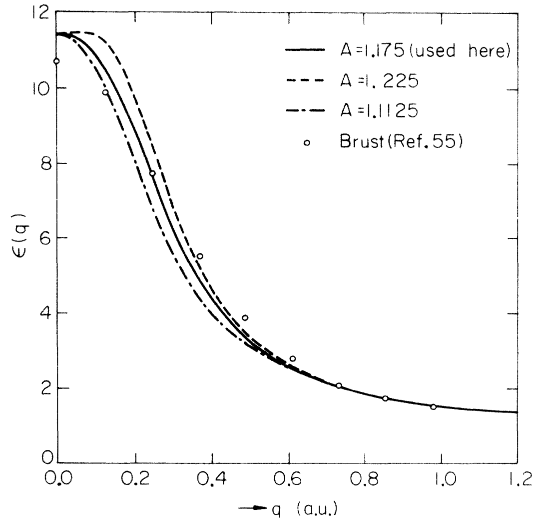

FIG. 7. Forms of $\epsilon(q)$ as functions of the parameter A Eq. (4.22) of paper I (Ref. 1). Energy levels obtained with these and intermediate forms are displayed in Fig. 9.

(4.22) of paper I and then by varying the parameter A. The resultant functions are plotted in Figs. 6 and 7, respectively, and the energy levels for certain impurities as functions of $\epsilon(0)$ and A are displayed in Figs. 8 and 9. In both cases, the levels become deeper with reduced screening, as expected.

Summarizing, we can safely say that the accuracy of the present calculations for donors in silicon is about 5% for shallow levels and about 10% for deep levels. A look at Tables I–III shows that the agreement with experiment is excellent in all cases with the exception of antimony and tellurium. For antimony, for which experiment is very accurate, the discrepancy is about 25%. A check of all the approximations involved revealed that the discrepancy should be caused by the large size of the cores of these impurities. One possibility is to assume

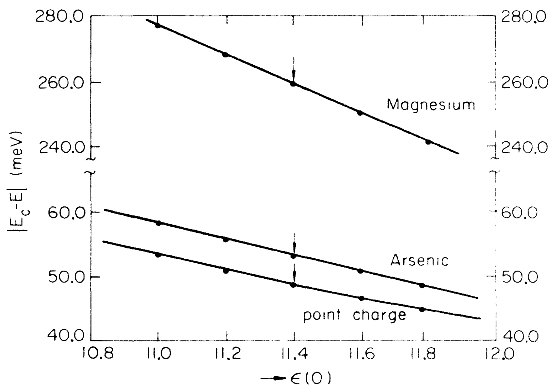

FIG. 8. Donor energy levels as functions of $\epsilon(0)$.

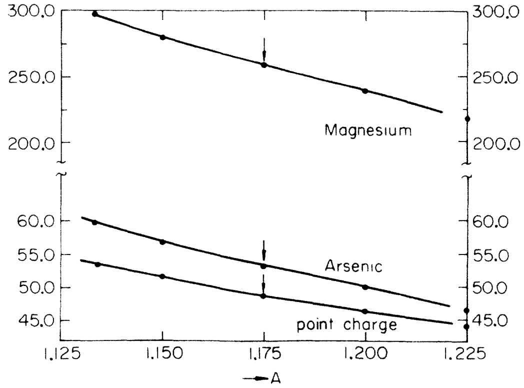

FIG. 9. Donor energy levels as functions of the parameter A of $\epsilon(q)$, Eq. (4.22) of paper I (Ref. 1).

that the smeared-out d-like core states of these impurities extend out appreciably and push away the nearest neighbors. Another possibility is that the core wave functions of the impurity are squeezed by the surrounding crystal. Comparing with our findings for magnesium (Fig. 5), we expect about 10% squeeze to account for the discrepancy in the energy level. Various amounts of "squeezing" were indeed applied to the antimony core wave functions and the result on the energy level is shown in Fig. 10. It is seen that a 9.15% squeeze would give the correct energy level. The reliability of this correction is enhanced when we apply the same "squeezing" on the tellurium core wave functions, recalling that Te and Sb have almost identical cores. The results are shown in Table VII, which show an excellent improvement in the agreement with experiment. This also brings the S-Se-Te levels more in line with the pattern of P-As-Sb levels.

E. Excited states

A word should be said about the excited states. As seen in paper I,[1] nothing further is to be said

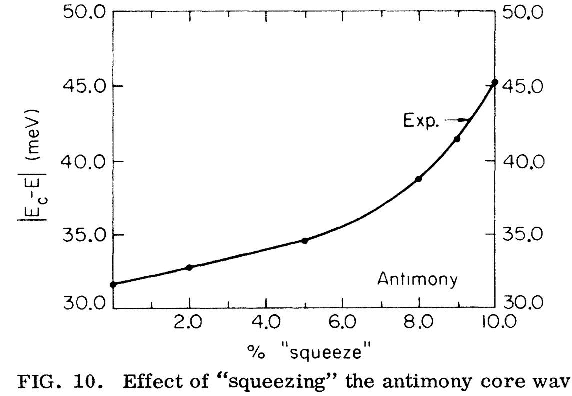

FIG. 10. Effect of "squeezing" the antimony core wave functions on the ground-state energy. The experimental value is obtained with a 9.15% "squeeze."

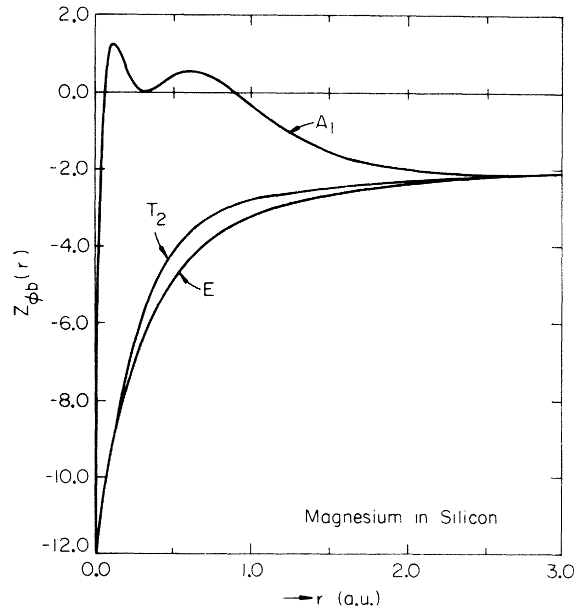

FIG. 11. Bare pseudopotentials for the A_1, the T_2, and the E states of interstitial magnesium in silicon. Due to the absence of E-like (d-like) core states, the pseudopotential for the E state is equal to the true impurity potential.

about the p-like, d-like, etc., states which are determined entirely by the Coulomb tail of the potential and a one-valley calculation. For the "other members of the split ground state"—namely the T_2 and E levels of s-like envelopes—the pseudo impurity theory faces the same difficulty described in paper I, namely the inadequacy of the spherical-effective-mass approximation. The calculation is very instructive, however, since the reorthogonalization potentials are different from those of the A_1-level potentials. The sums over c and c' are over the p and d core orbitals for the T_2 state and over the d core orbitals for the E state. This generally results in little or no cancellation at all, as is illustrated in Fig. 11, and raises additional questions about the applicability of linear screening and even the EMA itself! The detailed expressions for the energy are given in Appendix B and numerical results for the various donors given in Table VIII. The agreement with experiment is still good,

TABLE VII. Corrected tellurium donor levels in silicon.

	a (a.u.)	E (meV)$_{\text{theory}}$	E (meV)$_{\text{expt.}}$
Te^+	7.33	456.9	···
Te^0	8.22	136.8	140.0[a]

[a] Reference 30.

TABLE VIII. Energy levels of E and T_2 symmetry of donors in silicon. Reference point is the bottom of the conduction band.

Impurity	Symmetry	Theory a (a.u.)	Theory E (meV)	Experiment E (meV)
nitrogen	E	38.2	−31.0	...
	T_2	35.6	−32.6	...
phosphorus	E	39.0	−30.5	−32.6[a]
	T_2	37.8	−31.3	−33.9[a]
arsenic	E	40.6	−29.6	−31.2[a]
	T_2	40.6	−29.8	−32.6[a]
antimony	E	42.8	−28.5	−30.5[a]
	T_2	44.0	−27.8	−32.9[a]
sulfur	E	19.6	−118.2	...
	T_2	17.2	−130.4	−188.3[b]
selenium	E	20.8	−113.2	...
	T_2	19.8	−118.6	...
tellurium	E	22.5	−107.3	...
	T_2	23.2	−106.0	...
lithium	E	40.2	−30.0	−32.8[c]
	T_2	39.2	−30.5	−32.8[c]
sodium	E	41.6	−29.1	...
	T_2	42.0	−29.0	...
magnesium	E	21.6	−110.8	...
	T_2	21.0	−113.6	...

[a] Reference 28. Corrected using theoretical value for $3p_\pm$ from Ref. 21.

[b] See Ref. 23. The identification of this level is somewhat uncertain due to the weakness of the transition.

[c] Reference 31.

the average discrepancy being about 10%. One interesting result is that nigrogen falls in line with the other donors, and magnesium has T_2 and E levels close to the one-valley estimate of 125 meV using $-2e^2/\epsilon r$. Ho and Ramdas[32] searched for these levels but were unable to observe them. Finally, it is noted that the experimentally observed inversion of the relative positions of the A_1 and $E+T_2$ of interstitial lithium[31] did not materialize from the calculations presented here. This is a very subtle effect and inversion can be obtained by slightly changing the perturbation pseudopotential.[18] This and other aspects of interstitial impurities will be the subject of a future paper.

F. Comparison with previous theoretical work

In this section we discuss briefly previous theoretical work on the donors in silicon in order to bring our results into perspective and for further comparison.

Since the development of the original effective-mass theory by Kohn and Luttinger and others, many attempts have been made to improve the calculation. These can be divided into two classes: those which included intervalley mixing and those which did not. Since with the work of Refs. 14, 44, and the present results, it has been established that intervalley mixing is very important and cannot be omitted, no direct comparison can be made with any papers that used a one-valley approximation.[12,13,35–40] Any agreement with experiment obtained in these papers may be considered fortuitous.

The papers that included intervalley mixing are very few. Baldereschi[45] was the first to do it using a point-charge model for the impurity potential. The intervalley contribution was computed from perturbation theory using wave functions from a one-valley calculation. A direct not-perturbation-theory calculation of the point-charge model was done in paper I,[1] showing an improvement over the results of Ref. 45. The chemical nature of donors was not considered in Ref. 45, and deep levels were not treated at all.

Ning and Sah[14] carried out a study of donors in silicon including intervalley mixing. For the group-V shallow donors, they fitted a two-parameter phenomenological potential to the two lowest 1S states, A_1, and T_2 states. For the group-VI deep donors, they used the same fitting procedure for sulfur and the obtained potential was very nearly the same as the one obtained for phosphorus, except for a factor of 2. This led them to double the arsenic potential to predict levels for selenium and, similarly, to double the antimony potential to predict levels for tellurium. These predictions are compared with the present work in Table IV. The results of Ref. 14 obtained by the "doubling" technique are not as reliable as the present results obtained from first-principles potentials. The fact that "doubling" works for sulfur is easily understood, since

$$Z_S - Z_{Si} = 2(Z_P - Z_{Si}) \tag{3.27}$$

on account of the position of Si, P, and S in the Periodic Table, i.e., S and P are isocoric to Si. Here Z_X is the atomic number (nuclear charge) of element X. No such equalities hold even approximately for the nonisocoric Se and Te impurities in Si, for which the "doubled" potential is probably deeper than it should be.

A cellular approach is taken by Morita and Nars.[21] They used EMT only outside a central cell of radius r_0 and solved the full Hamiltonian within the well. Application of the theory was made to the shallow P, As, Sb, and interstitial lithium. As pointed out at the end of Sec. II F 1, the theory expression used to reorthogonalize $\psi^0_{\vec{k}_i}$ to the impurity core states does not accomplish the desired effect. Their numerical results may thus not be reliable.[41]

Recently, Schechter[42] published a pseudopotential calculation of the *shallow* P, As, and Sb donors including intervalley mixing. There are three main differences between the present work and that

TABLE IX. Comparison of present predictions with those of Schechter (Ref. 14a), before strain fields are included.

Impurity	Ionization energy (meV) Schechter	Present	Expt.
phosphorus	53.0	44.3	45.5[a]
arsenic	34.0	53.1	53.7[a]
antimony	29.0	31.7	42.7[a]

[a] Reference 28.

of Schechter. First, Schechter uses a local approximation to the pseudopotential. As pointed out earlier, our calculations showed that a local approximation could introduce an error in the range of 20%. In the present work, a local approximation is not used. Second, Schechter employed dielectric screening for the *true* impurity potential. Since this potential is very strong in the cases of nonisocoric impurities—when it is capable of binding a number of core states—dielectric screening may not be valid.[1] This was first pointed out by Cohen and Phillips,[43] who showed that only the *total* pseudopotential, which is weak, can be calculated using dielectric screening. This is the procedure used in the present work. Finally, Schechter uses the same pseudopotential for the states of A_1, T_2, and E symmetry. Pseudopotentials are, however, known to be symmetry dependent: The core states used in constructing the "repulsive" terms must be the ones of the same symmetry as the state being calculated. This was done here (see, for example, Fig. 11 and Appendix B). In Table IX we compare our results for the ground state of P, As, and Sb with those of Schechter before corrections due to strain fields are added. (For the comparison in Table IX, it should also be noted that Schechter uses $\epsilon(0) = 11.7$—we used $\epsilon(0) = 11.4$ and checked the effect of this uncertainty in Figs. 6 and 8—and that the value of m^* used by Schechter (not given in Ref. 42) may not coincide with the one used here.)

Finally, in conclusion, we remark that except for the parametric calculations for Se and Te of Ref. 14 discussed earlier, there exists no other previous theoretical calculation of the deep levels which we treat here. No other theory exists, for example, for magnesium, for which we obtained excellent agreement with experiment. For our predictions for the deep nitrogen level there is neither experimental nor previous theoretical results for comparison.

IV. CONCLUSIONS

We have presented an alternative approach to the problem of energy states localized at point imperfections in semiconductors. The new pseudo impurity theory combines pseudopotential theory with effective-mass ideas. Its main feature is that the impurity-electron wave function is expressed in terms of many bands in such a way that the appropriate nodal structure, required by the Pauli exclusion principle, is built-in automatically. Furthermore, the kinetic energy of the electron is given by a complicated operator which asymptotically reduces to the effective-mass expression $-(\hbar^2/2m^*)\nabla^2$ outside the impurity cell. The theory has been found applicable to a variety of shallow and deep, substitutional and interstitial donors in silicon and excellent agreement with available experimental data has been obtained. The theory reduces to the KL-EMT of paper I in the special case of isocoric impurities, namely impurities whose cores are isoelectronic with the host cores.

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APPENDIX A: DIELECTRIC SCREENING FOR A NON-LOCAL PERTURBATION

Due to the absence of strong high Fourier components in the bare pseudopotential $U_{\phi b}$, the corresponding screening potential $U_{\phi s}$ may be calculated by linear-response theory. In other words, the change in the valence pseudoelectron charge density caused by the presence of $U_{\phi b}$ may be calculated to first order in $U_{\phi b}$. A complication arises, however, due to the nonlocal nature of $U_{\phi b}$ whereby $\langle \vec{k}+\vec{q} | U_{\phi b} | \vec{k} \rangle$ depends on both $\vec{k}$ and $\vec{q}$. This effect was studied by Harrison[6] and by Animalu.[44] It was shown in Ref. 18 that the terms can be arranged to obtain Eqs. (3.15) and (3.16), where

$$\Delta_{\vec{k}}(\mathrm{q}) = \frac{8\pi e^2}{q} \sum_n \sum_{\vec{k}'} \frac{|\langle \psi^0_{n,\vec{k}'+\vec{q}} | e^{i\vec{q}\cdot\vec{r}} | \phi^0_{v\vec{k}'} \rangle|^2}{E^0_n(\vec{k}'+\vec{q}) - E^0_v(\vec{k}')} \times \left(1 - \frac{\langle \vec{k}'+\vec{q} | U_{\phi b} | \vec{k}' \rangle}{\langle \vec{k}+\vec{q} | U_{\phi b} | \vec{k} \rangle} \right), \tag{A1}$$

which shows that $\Delta_{\vec{k}}(\vec{q}) \equiv 0$ if $\langle \vec{k}+\vec{q} | U_{\phi b} | \vec{k} \rangle$ does not depend on $\vec{k}$. The magnitude of $\Delta_k(q)$ may be estimated by assuming an average deviation of $\langle \vec{k}'+\vec{q} | U_{\phi b} | \vec{k}' \rangle$ from $\langle \vec{k}+\vec{q} | U_{\phi b} | \vec{k} \rangle$. It was thus found[18] that the approximation $\epsilon_{\vec{k}}(\vec{q}) \simeq \epsilon(\vec{q})$ introduces a small uncertainty of a few percent in the potential matrix element.

APPENDIX B: ENERGY EXPRESSIONS

For variational calculations the matrix elements of the effective Hamiltonian are calculated between

TABLE X. Decomposition of the $(2l+1)$-dimensional representations of the spherical harmonics into the irreducible representations of the T_d group.

Label	l	Dimension $(2l+1)$	Decomposition
s	0	1	A_1
p	1	3	T_2
d	2	5	$E+T_2$
f	3	7	$A_1+T_1+T_2$

the trial functions given in paper I.[1] Explicit expressions for the kinetic energy terms, for the local part of the perturbation potential, and for the electron-electron interaction for two-electron centers were given in Appendix B of Ref. 1 and are identical for the present calculations. In this appendix we give explicit expressions for the matrix elements of the nonlocal term in the impurity pseudopotential, namely the reorthogonalization potential $\tilde{U}_R$.

The first difficulty is that $\tilde{U}_R$ is not obtainable directly in the form $\tilde{U}_R(\vec{r}, \vec{r}\,')$. Instead, it is known in its Fourier-transformed form

$$\langle \vec{k}+\vec{q}\,|U_R|\,\vec{k}\rangle = \langle \vec{k}+\vec{q}\,|U_{Rb}|\,\vec{k}\rangle/\epsilon(\vec{q})\,. \tag{B1}$$

For this reason, Eq. (B3b) of Ref. 1 cannot be used directly. The integral may still be evaluated by sandwiching complete sets of plane waves on either side of U_{Rb}. The result is

$$(\tilde{U}_R)_{mn} = \sum_i \sum_j \alpha_j^* \alpha_i \sum_{\vec{k}} \sum_{\vec{k}'} F_j^{ms*}(\vec{k}) \times \frac{\langle \vec{k}\,|U_{Rb}|\,\vec{k}\,'\rangle}{\epsilon(|\vec{k}-\vec{k}\,'|)} F_i^{ns}(\vec{k}\,') \tag{B2}$$

where $F_j^{ms}(\vec{k})$ is the Fourier transform of $F_j^{ms}(\vec{r})$ given by

$$F_j^{ms}(\vec{k}) = \int d^3r\, F_j^{ms}(\vec{r})\, e^{-i(\vec{k}-\vec{k}_j)\cdot\vec{r}} \tag{B3}$$

for $m=1, 2$. Noting that $F_j^{ms}(\vec{k})$ is localized about $\vec{k}=\vec{k}_j$ and $F_i^{ns}(\vec{k}\,')$ is localized about $\vec{k}\,'=\vec{k}_i$, we can approximate $\epsilon(|\vec{k}-\vec{k}\,'|)$ by $\epsilon(|\vec{k}_j-\vec{k}_i|)$. This was essentially the approximation used by Baldereschi[45] for the point-charge model. The accuracy depends on the value of a. It was found[18] that this approximation would go bad for values of a smaller than any obtained in the present calculations.

Expression (B2) can then be transformed back to coordinate space, yielding

$$(\tilde{U}_R)_{mn} = \frac{1}{\epsilon(|\vec{k}_j-\vec{k}_i|)} \int d^3r\, F_j^{ms*}(\vec{r})\, e^{-i\vec{k}_j\cdot\vec{r}} \times \int d^3r'\, U_{Rb}(\vec{r}, \vec{r}\,')\, F_i^{ns}(\vec{r}\,')\, e^{i\vec{k}_i\cdot\vec{r}\,'}\,. \tag{B4}$$

Now a typical term of U_{Rb} is of the form

$$U_{Rb}^{\text{typ}} = |w_c\rangle\langle w_c|v\,, \tag{B5}$$

so that

$$U_{Rb}^{\text{typ}}(\vec{r}, \vec{r}\,') = w_c(\vec{r})\, w_c^*(\vec{r}\,')\, v(\vec{r}\,')\,. \tag{B6}$$

Using this in (B4), we get for the typical term

$$(U_R^{\text{typ}})_{mn} = \sum_{i=1}^{6} \sum_{j=1}^{6} \frac{\alpha_j^{\mu*}(\Gamma)\alpha_i^{\mu}(\Gamma)}{\epsilon(|\vec{k}_j-\vec{k}_i|)} \times \int d^3r\, F_j^{ms*}(\vec{r})\, w_c(\vec{r})\, e^{-i\vec{k}_j\cdot\vec{r}} \times \int d^3r'\, w_c(\vec{r}\,')\, v(\vec{r}\,')\, F_i^{ns}(\vec{r}\,')\, e^{i\vec{k}_i\cdot\vec{r}\,'}. \tag{B7}$$

The result, as usual, will depend on Γ but not on μ.

In order to proceed further we recall (Sec. II D) that only the w_c of the same symmetry as the state being calculated have nonvanishing contributions. In order to check which atomic-core orbitals should be included, we must find linear combinations of them that transform according to irreducible representations of T_d. This amounts to decomposing the spherical harmonics Y_{lm} of the spherical-symmetry group to the Kubic harmonics of the point group T_d. The decomposition for values up to $l=3$ is shown in Table X.[45]

This shows that for the state of A_1 symmetry we must include only s-like core states (if one were to treat bismuth in silicon, the f-like core states should also be included. Bismuth has, however, too large a core for our approximations to be valid (Sec. III D). For T_2 states we must include p- and d-like core orbitals and for E states we must include d-like core orbitals.

Before the integrals and summations in Eqs. (B7) can be performed, the correct Kubic harmonics must be constructed which correspond to the set of α_i chosen in Appendix B of Ref. 1. In general, then, each w_c should actually bear three indexes $w_{cl\Gamma}$ and can be written as

$$w_{cl\Gamma}(\vec{r}) = R_{cl}(\vec{r})\, K_l^{(\Gamma)}(\theta, \phi)\,, \tag{B8}$$

where $K_l^{(\Gamma)}(\theta, \phi)$ is the Kubic harmonic (abbreviated KH) of Γ symmetry and angular momentum l.

TABLE XI. Constants $c_m^{\mu}(\Gamma)$ for $\Gamma=A_1$, T_2, E. [Note: $c_m^{\mu}(\Gamma)$ is not defined for the entries left blank, since m ranges from $-l$ to $+l$.]

			m				
Γ	l	μ	-2	-1	0	$+1$	$+2$
A_1	0	1			1		
T_2	1	1		$1/\sqrt{2}$	0	$-1/\sqrt{2}$	
		2		$-i/\sqrt{2}$	0	$-i/\sqrt{2}$	
		3		0	1	0	
	2	1	0	$-1/\sqrt{2}$	0	$-1/\sqrt{2}$	0
		2	0	$-i/\sqrt{2}$	0	$i/\sqrt{2}$	0
		3	$1/\sqrt{2}$	0	0	0	$-1/\sqrt{2}$
E	2	1	$1/\sqrt{2}$	0	0	0	$1/\sqrt{2}$
		2	$1/2\sqrt{2}$	0	$-\sqrt{3}/2$	0	$1/2\sqrt{2}$

There should actually be one more index to number the KH that form a basis for the Γ representation of the symmetry group. When necessary, we will use the additional index μ. There is a direct analogy in the terminology with that of free atoms. The index c is simply the principal quantum number, normally called n, l is the angular momentum quantum number, and μ corresponds to the magnetic quantum number m. μ replaces m because T_d symmetry has replaced spherical symmetry. Indeed, we have

$$K_l^{(\Gamma)\mu}(\theta, \phi) = \sum_m c_m^\mu(\Gamma) Y_{lm}(\theta, \phi). \tag{B9}$$

The constants $c_m^\mu(\Gamma)$, which also depend on l, must be determined,[47,48] so that the $K_l^{(\Gamma)\mu}(\theta, \phi)$ transform among them (in the index μ) in the same manner as the constants $\alpha_i^\mu(\Gamma)$, in the index μ, under the operations of T_d. The radial functions $R_{cl}(r)$ are the same as those of the atomic-core wave functions.

Before we determine the constants $c_m^\mu(\Gamma)$ for the cases of interest, we obtain a general expression for $(\tilde{U}_R^{\text{typ}})_{mn}$ by substituting Eq. (B9) in (B7) and using the expansion

$$e^{i\vec{k}\cdot\vec{r}} = 4\pi \sum_{l'} \sum_{m'} i^{l'} j_{l'}(kr) Y^*_{l'm'}(\theta_k, \phi_k) Y_{l'm'}(\theta_r, \phi_r) \tag{B10}$$

for the exponentials $e^{i\vec{k}_i\cdot\vec{r}}$, where $j_l(kr)$ are the cylindrical Bessel functions. Then, using the orthonormality of spherical harmonics, we get

$$(\tilde{U}_R^{\text{typ}})_{mn} = (4\pi)^2 \sum_{i=1}^{6} \sum_{j=1}^{6} \frac{\alpha_j^{\mu *}(\Gamma)\alpha_i^\mu(\Gamma)}{\epsilon(|\vec{k}_j - \vec{k}_i|)} \sum_m \sum_{m'} c_m^{\mu *}(\Gamma) c_{m'}^\mu(\Gamma) Y_{lm'}(\theta_j, \phi_j) Y^*_{lm}(\theta_i, \phi_i)$$
$$\times \int_0^\infty r^2\, dr\, F_j^{ms*}(r) R_{cl}(r) j_l(k_0 r) \int_0^\infty r'^2\, dr'\, R^*_{cl}(r') F_i^{ns}(r') j_l(k_0 r') v(r'). \tag{B11}$$

The constants $c_m^\mu(\Gamma)$ for the cases of interest were found[49] and are given in Table XI. The integrals and summations can then be done, though laboriously, particularly for the E symmetry. Naturally, since the energy depends only on Γ and not the index μ, any μ can be chosen for each Γ. The contribution of $l = 2$ to the T_2 state turns out to be zero. The final results can be written in the compact form

$$(\tilde{U}_R^{\text{typ}})_{mn} = 4\pi G(\Gamma)\left(\sum_{\lambda=1}^{3} \frac{|g_\lambda(\Gamma)|}{\epsilon(\Delta_\lambda)}\right)$$
$$\times \int_0^\infty F_j^{ms*}(r) P_{cl}(r) j_l(k_0 r) r\, dr$$
$$\times \int_0^\infty F_i^{ns}(r') P^*_{cl}(r') j_l(k_0 r') v(r') r'\, dr', \tag{B12}$$

where we wrote

$$P_{cl}(r) = r R_{cl}(r) \tag{B13}$$

and the constants $G(\Gamma)$ are

$$G(A_1) = 1, \quad G(T_2) = 3, \quad G(E) = \tfrac{15}{8}. \tag{B14}$$

The constant g_λ are the same as those of Appendix B of Ref. 1. It is to be remembered that $l = 0$ for A_1, $l = 1$ for T_2 and $l = 2$ for E. Then expressions like (B12) can be directly evaluated numerically by the computer, once the P_{cl} and v are known. This result is, of course, for a typical term (C29) of $U_{Rb}(\vec{r}, \vec{r}\,')$, so that for a particular impurity a number of them is summed up.

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