Scattering-theoretic method for defects in semiconductors. I. Tight-binding description of vacancies in Si, Ge, and GaAs

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A technique for an accurate and efficient calculation of point-defect-induced changes in the electronic structure of an otherwise perfect crystal is described. It is based on the Green's-function method introduced by Koster and Slater and developed further by Callaway and coworkers, and achieves its efficiency and convenience by *avoiding* the use of Wannier functions. The efficiency and accuracy of the method is exhibited by calculating the states of a widely studied model system, namely, the ideal vacancy in covalent solids, using semiempirical, but realistic, host energy-band structures. Results for the vacancy in Si, Ge, and GaAs compare favorably with those obtained previously. In addition, a wealth of new information is obtained. It is argued that the present method is the most efficiency stemming from an exploitation of both the short-range nature of the defect potential and the translational symmetry of the host crystal.

I. INTRODUCTION

The electronic structure of shallow impurities is by now well understood in the framework of the effective-mass theory.¹ Recent extensions of that theory allow the use of more realistic impurity potentials and pseudopotentials and make possible the study of moderately deep levels as well.²⁻⁴ The latter have energy levels which lie deep in the gap, but their wave functions are still appreciably delocalized so that effective-mass-like approximations apply. There exists, however, a large class of impurities and defects with energy levels which are deep in the gap and whose wave functions have most of their amplitude in the vicinity of the central cell. Effective-mass theory is not adequate for such deep levels.

A large number of techniques have been proposed for the study of deep impurities and other point defects.^{17,18} We use a brief review⁵ of some of these as a vehicle for presenting the essential aspects of the physical problem which a successful theory must accommodate. The first such aspect is the local environment of the impurity site. The *defect-molecule* model for a vacancy in diamond was introduced by Coulson and Kearsley⁶ for just this purpose. In this model, the vacancy wave function was formed from the four dangling sp^3 hybrid orbitals on the four nearest neighbors. The model was for a long time the only available description of the electronic structure of defects and was used for several applications.⁷⁻⁹

The contemporary descendent of the defectmolecule model is the use of finite molecular clusters to simulate the impurity or defect and its immediate environment. The most extensive studies using such clusters were those of Messmer and Watkins and co-workers^{10,11} who investigated the vacancy, substitutional nitrogen, and the selfinterstitial in diamond. A wealth of information was obtained. In particular, it was confirmed that the wave function of a deep defect such as the vacancy may decay rather slowly, even if the defect potential is very localized. As a consequence, it was found for these systems that even clusters of 71 atoms were not large enough to contain the wave function sufficiently so as to eliminate undesirable surface-defect interactions which introduce uncertainty in the determination of the position of the bound-state energy levels.

Attempts to deal with the problems posed by the cluster surfaces were made by a number of authors¹²⁻¹⁴ by saturating the dangling bonds with hydrogen atoms. The surface states then move out of the band gap into the bands, making the identification of defect levels in the gap somewhat easier. The most successful such calculations were carried out using the self-consistent $X\alpha$ -scattered-wave method.¹⁴⁻¹⁶ An alternative way to deal with cluster surfaces is to impose periodic boundary conditions, which correspond to an infinite crystal with a "superlattice" of defects.^{17,18} The surface-defect interactions are thus replaced by defect-defect interactions, which result in broadening of the defect level into a band.

The possibility of increasing the size of the simulating molecular cluster to accommodate the poorly localized bound-state wave function increased greatly with the advent of continued-fraction¹⁹ and other moment-based techniques for the calculation of specialized properties, such as partial state densities, of very large clusters (2500 atoms and more). In such large clusters, the defect and the surfaces are decoupled. The defect states appear in the local density of states as sharp, δ -function-like peaks, from which their

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energies can be obtained. Applications have so far been made to ideal vacancies in germanium²⁰ and silicon.²¹

All the methods discussed above have the common characteristic that they do not make use of the fact that the energy levels and wave functions of the unperturbed crystal can be conveniently obtained in terms of a band-structure calculation. An alternative method, which exploits the availability of perfect-crystal solutions, was orginally proposed by Koster and Slater.²² Letting H^0 be the perfect crystal Hamiltonian and V the defect potential, one has for the perturbed crystal

$$(H^0 + V)\psi = E\psi.$$
⁽¹⁾

For levels in the gaps, Eq. (1) may be written in terms of the perfect-crystal Green's function $G^{0}(E)$ as

$$\psi = G^0(E) V \psi \,. \tag{2}$$

Equation (2) is then expanded in localized orbitals, such as Wannier functions, in order to exploit the restricted range of V. For a localized potential, only a finite number of the potential matrix elements will be different from zero. Koster and Slater showed that in order to find the energy of a bound state, it is sufficient to expand Eq. (2) in the finite basis in which the matrix V is nonzero, i.e., the size of the matrix is determined by the range of the perturbation potential not by the range of its wave function, in contrast to all the methods described above. This is the principal advantage of the Koster-Slater approach, since, as mentioned above, for many deep defects the wave function is more extended than the perturbing potential. For example, the range of the potential of a vacancy in silicon is¹⁸ \sim 3 Å as compared to the range of its wave function, which is ~6 Å. Another major advantage of the method is that it automatically yields bound states measured from the perfectcrystal band edges, in contrast to cluster methods in which band edges are not defined in an unambiguous manner. Finally, this method yields directly all the *changes* of the electronic properties (e.g., changes in densities of states, charge densities, total energies, etc.), as compared with the other methods in which the changes must be obtained by subtracting the corresponding perturbedcrystal and perfect-crystal quantities.

The method of Koster and Slater²² has been described more thoroughly in terms of the general theory of Green's functions by Callaway.²³ The first numerical applications of the method using the full band structure of the host crystal were made by Callaway and Hughes²⁴ for an unrelaxed vacancy and divacancy in silicon. The calculations consisted of two major steps, the evaluation of the matrix elements of the Green function and of the potential. The Green's-function matrix elements have a rather simple form in the Wannier representation, but the calculation of the matrix elements of V require an explicit knowledge of the Wannier functions. The numerical determination of Wannier functions turned out to be very tedious and difficult. For this reason, only a few subsequent applications have been made.²⁵⁻²⁷

More recently, Jaros and Brand²⁸ have carried out numerical calculations²⁹ using a method similar in spirit to the Koster-Slater Green's function method, namely, the method originally introduced by Bassani, Iadonisi, and Preziosi.³⁰ The precise relationship between the two methods as well as their relative merits will be discussed in the Appendix.

In this paper we turn to reexamine and generalize the Koster-Slater method and show that solutions of the impurity problem can be obtained efficiently if one foregoes the construction of Wannier functions but, instead, uses a conveniently chosen basis set of localized states. We describe a generalized version of the Koster-Slater-Callaway equations using arbitrary localized basis sets and apply the method to a widely studied model problem, namely, the ideal vacancy in Si, Ge, and GaAs, in order to make possible unambiguous comparisons with other methods. A similar model was first studied by Lannoo and Lenglart³¹ for a highly simplified host band structure. In the present work we use the more realistic tight-binding parametrization of the host energy bands obtained by Pandey and Phillips.³² Overall, the approximations used in constructing the Hamiltonian are identical in spirit with those used with success by Pandey and Phillips³² and by Pandey *et al.*^{33,34} in their study of surface states. Comparison with experiment is still not feasible because lattice relaxation is not taken into account in this paper. but from the point of view of methodology, the present work describes in detail a method which provides an exact and computationally efficient solution to the problem of the ideal vacancy which has been studied extensively in terms of small and large clusters.

The outline of the development is as follows. In Sec. II, the Green's-function method is described. This section is mainly based on papers of Koster and Slater²² and Callaway,²³ and is included here primarily for completeness, but all results are explicitly given in terms of any complete orthonormal set of states. Section III contains material specific to ideal vacancies in the tight-binding approximation. Numerical solutions are obtained for Si, Ge, and GaAs and compared to other calculations. Our main conclusions are summarized in Sec. IV.

II. GREEN'S-FUNCTION METHOD

The Green's function method is based on formal scattering theory. In this section, the basic equations of the method will be given in a generalized form in terms of arbitrary basis set of localized functions. This form will be used in the remainder of the paper for numerical calculations.

We concentrate first on states within the band gaps, where the Green's operator for the perfect crystal is real and unambiguously defined by

$$G^{0}(E) = (E - H^{0})^{-1}.$$
 (3)

The Schrödinger equation for the imperfect crystal, namely, Eq. (1), can then be written as

$$\psi = (E - H^{0})^{-1}V\psi = G^{0}(E)V\psi$$
(4)

or, equivalently,

$$[1 - G^{0}(E)V]\psi = 0.$$
 (5)

This last equation indicates that nontrivial solutions exist only when the operator $1 - G^0 V$ does not have an inverse, i.e., when its determinant is zero. This requirement may be seen by expanding ψ in any complete orthonormal set of states ϕ_{α} in the form

$$\psi = \sum_{\alpha} C_{\alpha} \phi_{\alpha} \tag{6}$$

and taking matrix elements of G^0 and V in the same basis. Equation (5) becomes a set of linear algebraic equations

$$\sum_{\alpha'} \left[\delta_{\alpha \, \alpha'} - \sum_{\alpha''} G^0_{\alpha \, \alpha''}(E) V_{\alpha'' \alpha'} \right] C_{\alpha'} = 0 , \qquad (7)$$

which has nontrivial solutions when

$$\det \left\| \delta_{\alpha \alpha'} - \sum_{\alpha''} G^{0}_{\alpha \alpha''}(E) V_{\alpha'' \alpha'} \right\| = 0.$$
(8)

The Green's function matrix $G^0_{\alpha\alpha'}(E)$ is given by

$$G^{0}_{\alpha\alpha'}(E) = \langle \alpha | (E - H^{0})^{-1} | \alpha' \rangle.$$
(9)

or, more conveniently, by

$$G^{0}_{\alpha \alpha'}(E) = \sum_{n\vec{k}} \frac{\langle \alpha | n\vec{k} \rangle \langle n\vec{k} | \alpha' \rangle}{E - E^{0}_{n\vec{k}}} , \qquad (10)$$

where E_{nk}^{0} are the eigenvalues of H^{0} , i.e., the perfect-crystal energy bands.

Equation (8) is the condition that must be satisfied for a bound state to exist. If the functions ϕ_{α} are localized about atomic sites and the perturbation potential V has a finite range, the matrix element $V_{\alpha\alpha'}$ will be nonzero only if both ϕ_{α} and $\phi_{\alpha'}$ overlap with the potential. The potential matrix can then be schematically written as

$$\underline{V} = \begin{pmatrix} V & 0 \\ 0 & 0 \end{pmatrix}, \tag{11}$$

where V denotes the nonvanishing part of the matrix. After writing the matrix of the Green function G^0 as

$$\underline{G}^{0}(E) = \begin{pmatrix} G_{11}^{0}(E) & G_{12}^{0}(E) \\ G_{21}^{0}(E) & G_{22}^{0}(E) \end{pmatrix}$$
(12)

the matrix of the operator $1 - G^{0}(E)V$ becomes

$$1 - \underline{G}_{0}(E)\underline{V} = \begin{pmatrix} 1 - G_{11}^{0}(E)V & 0 \\ G_{21}^{0}(E)V & 1 \end{pmatrix}.$$
 (13)

From (13) it is now evident that

$$\det \|\mathbf{1} - \underline{G}_0(E)\underline{V}\| = \det \|\mathbf{1} - G_{11}^0(E)V\|$$
(14)

so that the size of the determinant reduces to the size of the nonzero part of the potential matrix.²²

Solution of the corresponding subset of linear algebraic equations yields a subset of the coefficients C_{α} . The remaining coefficients are given by

$$C_{\beta} = \sum_{\alpha} \sum_{\alpha'} G^{0}_{\beta\alpha}(E_{\nu}) V_{\alpha\alpha'} C_{\alpha'}, \qquad (15)$$

where E_{ν} is the energy of the ν th bound state in the gap.

We turn now to examine the effect of the perturbation V on the states within the energy bands of the perfect crystal. The definition of G^0 is now generalized to

$$G^{0}(E) = \lim_{\epsilon \to 0^{+}} \left(E - H_{0} + i\epsilon \right)^{-1}, \qquad (16)$$

and Eq. (4) is replaced by the Lippmann-Schwin- ger^{35} equation

$$\psi_{n\vec{k}} = \psi_{n\vec{k}}^{0} + \lim_{\epsilon \to 0^{+}} G^{0}(E+i\epsilon) V \psi_{n\vec{k}}, \qquad (17)$$

where $\psi_{n\mathbf{k}}^0$ is a perfect-crystal Bloch function, namely, a solution of

$$H^{0}\psi_{n\vec{k}}^{0} = E_{n\vec{k}}^{0}\psi_{n\vec{k}}^{0}.$$
 (18)

(*n* and \bar{k} are not conserved in the perturbed crystal, but are convenient labels for the scattering states.) In turn, Eq. (5) is replaced by

$$[1 - G^{0}(E)V]\psi_{n\vec{k}} = \psi_{n\vec{k}}^{0}.$$
⁽¹⁹⁾

Because of the presence of $\psi_{n\vec{k}}^0$ on the right-hand side of Eq. (19), solutions exist at all energies within the energy bands of the perfect crystal. The wave function ψ corresponding to a solution at $E = E_{n\vec{k}}^0$ is not, of course, equal to $\psi_{n\vec{k}}^0$. Similarly, the density of states is altered in the vicinity of the defect. If we let D(E) denote the determinant defined by Eq. (14), i.e.,

$$D(E) = \det \| \mathbf{1} - G^{0}(E) V \| \,. \tag{20}$$

it may be shown that the change in the density of states is given by

$$\Delta N(E) = \frac{1}{\pi} \frac{d\delta(E)}{dE}, \qquad (21)$$

where the quantity $\delta(E)$, known as the phase shift, is defined by

$$\delta(E) = -\tan^{-1}[\operatorname{Im} D(E)/\operatorname{Re} D(E)].$$
(22)

It is clear from Eq. (22) that $\delta(E)$ goes through an odd multiple of $\frac{1}{2}\pi$ every time $\operatorname{Re} D(E) = 0$. $\delta(E)$ may then be expanded about such an energy, which we label E_0 . The result is²³

$$\tan\delta(E) \approx -\Gamma/2(E - E_0) \tag{23}$$

where

$$\Gamma = 2 \operatorname{Im} D(E_0) / \operatorname{Re} D'(E_0) . \tag{24}$$

In (24), the prime denotes differentiation with respect to energy. In the region close to E_0 , $\Delta N(E)$ becomes

$$\Delta N(E) = \frac{\Gamma}{2\pi} \frac{1}{(E - E_0)^2 + \frac{1}{4}\Gamma^2} .$$
 (25)

This characteristic Breit-Wigner form indicates that for $\Gamma > 0$ one has a *resonance* or a peak in $\Delta N(E)$ with a half-width Γ , whereas for $\Gamma < 0$ one has an *antiresonance* or a dip in $\Delta N(E)$ with a halfwidth $|\Gamma|$.

From the analytical properties of D(E), one can deduce³⁶ the important sum rule

$$\int_{-\infty}^{\infty} \Delta N(E) = 0 .$$
 (26)

When the states in the gaps are counted separately from changes in the density of states within the bands, (26) becomes

$$\int_{\text{bands}} \Delta N(E) = -N_b, \qquad (27)$$

where N_b is the total number of bound states in the gaps. The relations (26) and (27) are the solid-state analog of Levinson's theorem.³⁶

III. IDEAL VACANCIES IN Si, Ge, AND GaAs

In this section, we will apply the Green's-function method described in the previous section to study the ideal vacancy in Si, Ge, and GaAs. The term "ideal" will be defined more precisely in subsection B below.

A. Perfect crystal

In the empirical tight-binding method, the Hamiltonian H^0 describing the perfect crystal is defined directly in terms of its matrix elements with respect to a basis set of atomiclike functions $\phi_{\alpha}(\mathbf{\tilde{r}} - \mathbf{\tilde{R}}_{j})$:

$$H^{0} = \sum_{\alpha j} \sum_{\alpha' j'} \left| \phi_{\alpha j} \right\rangle H^{0}_{\alpha \alpha' j j'} \left\langle \phi_{\alpha' j'} \right|.$$
(28)

 \vec{R}_{j} denotes the atomic positions and α labels atomiclike orbitals on each atom. The Bloch functions are then expanded in terms of the $\phi_{\alpha}(\vec{r}, \vec{R}_{j})$. Translational symmetry reduces the size of the resultant secular matrix to the number of orbitals in the unit cell. The secular matrix depends on the wave vector \vec{k} and is entirely defined in terms of the $H^{0}_{\alpha\alpha' jj'}$, without the need for explicit forms for the ϕ_{α} . The eigenvalues of the secular matrix at each \vec{k} are the energy bands.

In the present study, s and p atomiclike orbitals were used, which, combined with the fact that Si, Ge, and GaAs have two atoms in the unit cell, yield an 8×8 secular matrix at each \vec{k} . Four valence bands and the four lowest conduction bands are, therefore, obtained. In such a representation, the most accurate parameterization of the energy bands of those materials available in the literature is that of Pandey and Phillips.³²⁻³⁴ which retains only first- and second-nearest-neighbor interactions and neglects all the overlap matrix elements. This parametrization has been very successful in describing surface states of the same materials.³²⁻³⁴

B. Ideal-vacancy equations

Let us denote the perturbed-crystal Hamiltonian by H, and the perfect-crystal Hamiltonian by H^0 , as in Sec. II. The ideal vacancy is then defined in a manner identical to that used in the various extended-Hückel calculations,^{10,13,17} and in the tightbinding method using large clusters.^{20,21} To wit, an atom is removed from the perfect crystal, leaving all other atoms at the same positions; the atomiclike orbitals are retained on all other atoms, and their interactions are assumed *unaltered*.

A useful illustration of the model is given in Fig. 1(a), where the matrix H^0 of the infinite perfect crystal is partitioned in four blocks. The size of H_X^0 is equal to the number of n_0 of orbitals on the atom to be removed, which we refer to as atom X. In the present case of s and p orbitals on each atom, $n_0 = 4$ so that H_X^0 is a 4×4 submatrix. The matrix H for the ideal vacancy is defined by (see Fig. 1)

$$\underline{H} \equiv \underline{H}_{B}^{0} \,. \tag{29}$$

The cluster calculations that were discussed in Sec. I correspond to truncating H_B^o . In the present method, H_B^o will be retained as an infinite matrix.

In order to cast the above model in a form suitable for the Green's-function equations described

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FIG. 1. Schematic illustration for the derivation of the matrix \underline{V} for ideal vacancies. See text.

in Sec. II, we must identify V, which is defined by the operator equation

$$V = H - H^{\circ} . \tag{30}$$

In order to obtain a matrix representation for V_{\star} one must define H to be of the same dimension as H^{0} . One such possibility is to take H to be \hat{H}_{1} , defined schematically in Fig. 1(b). E_0 is an arbitrary energy and I is the unit matrix of the same order as H_X^0 . Note that \hat{H}_1 has exactly the same eigenvalues as H_B^0 , plus an n_0 -fold degenerate eigenvalue at E_0 which is to be ignored as spurious except for purposes of satisfying Levinson's theorem. $(E_0$ would best be chosen outside the range of interest). This form of H would allow one to construct V and proceed with the solution of the Green's function equations. The size of V would, however, be determined by the form of H_{A}^{0} , which in turn depends on the number of nearest-neighbor interactions one includes in H^0 . In the case of the Pandey-Phillips³² parameterization, the resultant V would be 56×56 . Note that the physical meaning of V is to cut off the interactions of atom X with all other atoms in the crystals, which is equivalent to removing it.

An alternative and more advantageous way to obtain a matrix representation of V is to take H equal to \hat{H}_2 , as defined schematically in Fig. 1(c), where E_0 and I are as before. In the limit as $E_0 \rightarrow \infty$, \hat{H}_2 has precisely the same eigenvalues as H_B^0 , plus an n_0 -fold degenerate eigenvalue at infinity, which is again to be ignored as spurious except for satisfying Levinson's theorem. The perturbation matrix V is now diagonal and only $n_0 \times n_0$, i.e., 4×4 , which is a substantial reduction. Physically, V, instead of cutting off the interactions of atom \overline{X} with the other atoms, places the energies of the orbitals on atom X at infinity so that the interactions represented in Fig. 1 by H_A^0 produce no coupling whatsoever. (V is an infinite potential perturbation at the site of the atom to be removed. It does not affect any other Hamiltonian matrix elements. This assumption is equivalent to removing an atom without altering the nearby matrix elements, as commonly done in cluster calculations of the vacancy.) By symmetry the s and p orbitals on the central atom do not mix so that the relevant "X" block of the matrix $1 - G^0(E)V$ is diagonal. Consequently, the determinant of $1 - G^0(E)V$ is zero whenever

$$G^0_{\alpha\alpha}(E) = 1/E_0, \qquad (31)$$

where α is any of the orbitals on atom X. In the limit of $E_0 \rightarrow \infty$, (31) becomes

$$G^0_{\alpha\alpha}(E) = 0. \tag{32}$$

When α is the *s* orbital on atom *X*, the zeros of $G^{0}_{\alpha\alpha}(E)$ in the regions of the band gaps correspond to bound states of A_1 symmetry, whereas when α is one of three *p* orbitals on atom *X*, the zeros of $G^{0}_{\alpha\alpha}(E)$ in the regions of the band gaps correspond to bound states of T_2 symmetry. Furthermore, the ideal vacancy in the *s*-*p* approximation (no *d* or *f* orbitals) introduces no bound states of symmetry other than A_1 and T_2 .

As for the regions within the energy bands, the zeros of $\operatorname{Re} G^0_{\alpha\alpha}(E)$ correspond to resonances and antiresonances. The complete change in the density of states is given by (21) where

$$\delta(E) = -\tan^{-1}[\operatorname{Im} G^0_{\alpha\alpha}(E)/\operatorname{Re} G^0_{\alpha\alpha}(E)].$$
(33)

Once more, the changes in the density of A_1 and T_2 states are given separately by $G^0_{ss}(E)$ and $G^0_{pp}(E)$, whereas the states of other T_d symmetries remain unchanged.

Finally, the coefficients C_i of the ν th bound-state wavefunctions are given by

$$C_{l} = G_{l0}(E_{\nu}) \left(\sum_{l} G_{l0}^{2}(E_{\nu}) \right)^{-1/2}, \quad l \neq 0$$
(34)

where $l = (\lambda, j)$ is a composite index and l = 0 denotes orbitals on atom X. C_0 is identically zero for all bound states. The index λ stands for an appropriately symmetrized combination of orbitals on the shells surrounding atom X.

Before concluding this subsection, it is important to emphasize that the zeros of $G^0_{\alpha\alpha}(E)$ are the *exact* bound-state eigenvalues of the *infinite* matrix H^0_B . As we shall see in the next subsection, they can be obtained numerically to arbitrary accuracy with relatively small and rather modest computational effort.

C. Calculations

For numerical calculations of the energy levels of the ideal vacancy, we need to compute the

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Green's-function matrix elements $G_{ss}^{0}(E)$ and $G_{pp}^{0}(E)$ on the atom X. We let $\alpha = s$ or p and address the issue of computing $G_{\alpha\alpha}^{0}(E)$ for energies both within the energy bands and the band gaps. Equation (10) is then generalized to read

$$G^{0}_{\alpha\alpha}(E) = \lim_{\epsilon \to 0^{+}} \sum_{n\bar{k}} \frac{\langle \alpha | nk \rangle \langle nk | \alpha' \rangle}{E - E^{0}_{n\bar{k}} + i\epsilon} .$$
(35)

This expression may also be written as

$$G^{0}_{\alpha\alpha'}(E) = \lim_{\epsilon \to 0^{+}} \int \frac{dE'}{E - E' + i\epsilon} A_{\alpha\alpha'}(E'), \qquad (36)$$

where the quantity A(E), known as the spectraldensity operator,³⁶ is defined by

$$A(E) = \sum_{n\vec{k}} \left| n\vec{k} \right\rangle \delta(E - E_{n\vec{k}}^{0}) \langle n\vec{k} \right|$$
(37)

so that its matrix elements appearing in (36) are given by

$$A_{\alpha\alpha'}(E) = \sum_{n\vec{k}} \langle \alpha | n\vec{k} \rangle \langle n\vec{k} | \alpha' \rangle \delta(E - E_{n\vec{k}}^{\circ}).$$
(38)

Finally, using the Dirac identity

$$\lim_{\epsilon \to 0^+} \int \frac{f(t) dt}{t + i\epsilon} = \mathbf{P} \int \frac{f(t) dt}{t} - i\pi f(0) , \qquad (39)$$

where P stands for "principal value," (36) becomes

$$G^{0}_{\alpha\alpha}(E) = \mathbf{P} \int \frac{A_{\alpha\alpha'}(E')}{E - E'} dE' - i\pi A_{\alpha\alpha'}(E) .$$
(40)

For our present purposes, $A_{ss}(E)$ and $A_{pp}(E)$ are standard s-like and p-like partial densities of states, respectively, and therefore positive definite quantities. A_{pp} is identical for p_x , p_y , and p_z . The sum over the Brillouin zone is reduced by symmetry to a sum over the irreducible $\frac{1}{48}$ th of the zone and can be evaluated using one of several standard techniques. For the present calculations, the method of Gilat and Raubenheimer^{37, 38} was used.

Once $A_{ss}(E)$ and $A_{pp}(E)$ were evaluated, the real parts of $G_{ss}^0(E)$ and $G_{pp}^0(E)$ were obtained by carrying out the principal-value integrals, as indicated in Eq. (40). Principal-value integrals were evaluated using the identity³⁹

$$\mathbf{P} \int_{a}^{b} \frac{f(t')}{t-t'} dt' = \int_{a}^{b} \frac{f(t') - f(t)}{t-t'} dt' - f(t) \ln \frac{b-t}{t-a},$$
(41)

which is valid for a < t < b. The integral on the right-hand side of (41) is now regular and can be computed by Simpson's rule. In evaluating the real part of the Green's functions by carrying out the principal-value integral in Eq. (40), the integrals must be evaluated over the whole range of the eight energy bands in order for the theory to

be internally consistent. Having evaluated $\operatorname{Re} G_{ss}^{0}(E)$ and $\operatorname{Re} G_{pp}^{0}(E)$, their zeros within the band gaps were located and identified as bound states. The changes in the densities of states within the energy bands were then evaluated using Eqs. (21) and (33).

A general result of these calculations is particularly interesting. As we just saw, the bound states in the gap are determined by

$$\int \frac{A_{\alpha\alpha}(E')}{E-E'} dE' = 0, \qquad (42)$$

where $\alpha = s$ or p and $A_{\alpha\alpha}(E')$ is positive definite. The integral is over all the bands, so that, for bound states in the fundamental gap, (42) becomes

$$\int_{\text{valence}} \frac{A(E')}{E - E'} dE' = \int_{\text{conduction}} \frac{A(E')}{E' - E} dE, \qquad (43)$$

where both integrals are positive for all values of E. Equation (43) reveals that, for the ideal vacancy, the bound states in the gap arise from a sensitive balance between valence- and conduction-band quantities, so that both sets of bands are needed with equal accuracy. Note that if the conduction bands were left out, no bound states would result. This conclusion is of course specific to the model of the ideal vacancy used in this work, and does not necessarily remain true for other types of perturbation.

Calculations have been carried out for the ideal vacancy in Si, Ge, and GaAs. Figure 2 shows the real and imaginary parts of the Green's functions for Si. The positions of the bound states within the gaps of all three materials are given in Table I. The corresponding changes in the densities of states are given in Figs. 3-6. In the case of GaAs, no bound states were found in the so-called antisymmetric gap of the valence bands in the case of the As vacancy. The Ga vacancy in GaAs, however, introduces A_1 and T_2 bound states at -10.05 and -10.02 eV, respectively. (The gap begins at -10.09 eV.) In all cases, Levinson's theorem is satisfied, if the states at infinity discussed in Sec. III B are taken into account. In particular, when the changes of densities of states of all symmetries are summed up, the integral of $\Delta N(E)$ over the entire energy range, including the bound states is -8 (including spin degeneracy), corresponding to the +8 states at infinity. The Fermi level E_F in the perturbed crystal is then determined from

$$\int_{-\infty}^{E_F} \Delta N(E) \, dE = -M \,, \qquad (44)$$

where M is the number of valence electrons that were removed, i.e., 4 for Si and Ge, 3 for a Ga vacancy in GaAs, and 5 for an As vacancy in GaAs. Using (44), it was determined that the T_2



FIG. 2. Real and imaginary parts of $G^{0}_{ss}(E)$ and $G^{0}_{pp}(E)$ of Si.

level in the gaps of Si and Ge is occupied by two electrons, an indication that a Jahn-Teller distortion is inevitable in agreement with experimental observations.⁴⁰ In the case of the Ga vacancy in GaAs, the T_2 level in the gap (almost coincident with the valence-band top) is occupied by three electrons and is again unstable with respect to Jahn-Teller distortions. In the case of the As vacancy, the T_2 level is very near the bottom of the conduction band and would contain only one electron.

TABLE I. Bound-state energies introduced in the fundamental gap by the ideal vacancy in Si, Ge, and GaAs. Energies in eV and measured from the top of the valence bands. A_1 and T_2 denote the symmetries of the bound state.

	A ₁	T_2
Si	• • •	0.27
Ge	• • •	0.11
$GaAs:V_{Ga}$	• • •	0.02
GaAs:VAs	0.71	1.47



FIG. 3. Changes in the density of states induced by an ideal vacancy in Si. (Bound states in the gap not shown. See Table I.)

D. Comparison with other methods

As we stated in Sec. I, the results of the present calculations cannot be compared with experimental data, largely because the crystal surrounding a vacancy undergoes Jahn-Teller distortions, which have not been included in the theory. We therefore turn to a comparison of our results with those obtained by others for ideal vacancies. A direct comparison can be made with the results of Kauffer, Pêcheur, and Gerl²¹ and of Joannopoulos and Mele.²⁰ These authors define the ideal vacancy in an identical way (see Sec. III B), except that they use different parameterization for the energy bands, and of course, different methods for computing the vacancy-induced changes in the electronic structure of the host. In order to compare the relative accuracy and merits of different methods, we have repeated our calculations using the parameters employed by Kauffer et al. for Si. We have obtained the same T_2 bound state in the gap (0.18 eV compared 41 with 0.12 eV of Kauffer et al.) and A_1 resonances (at -0.80 and -7.27 eV compared with -0.88 and -7.27 eV, respectively, of Kauffer et al.) but we also obtain an antiresonance at 6.45 eV and other structure (Fig. 7). Note



FIG. 4. Changes in the density of states induced by an ideal vacancy in Ge. (Bound states in the gap not shown. See Table I.)

that the antiresonances required to satisfy Levinson's theorem are not identified by Kauffer *et al*.

Furthermore, the present method is considerably more straightforward. Note that the three methods, ours, that of Kauffer et al., and that of Joannopoulos and Mele, all require the evaluation of a single matrix element of a Green's function as a function of energy. In the present method, the relevant Green's function is that of the *perfect* crystal, which can be calculated by the very efficient Brillouin-zone integration routines, exploiting translational symmetry. In contrast, in the methods of Refs. 20 and 21, the relevant Green's function is that corresponding to the *im*perfect crystal. The latter is a much more complicated quantity and requires the use of more cumbersome techniques originally developed for amorphous materials, which lack periodicity altogether. Furthermore, the present technique yields directly the defect-induced change in the density of states $\Delta N(E)$, whereas the other two techniques yield the total local density of states of the perturbed crystal and $\Delta N(E)$ must be obtained by subtracting two rather similar quantities, which increases the inherent uncertainty.

Finally, we should remark that the above numer-



FIG. 5. Changes in the density of states induced by an ideal Ga vacancy in GaAs. (Bound states in the gap not shown. See Table I.)

ical results for the ideal vacancy were obtained using tight-binding Hamiltonians which give a good description of the bulk valence bands and a rather poor description of the conduction bands. Since both sets of bands play an important role in determining the bound states in the gap [cf. Eq. (43)], such tight-binding Hamiltonians do not necessarily provide a realistic description of the vacancy states. Nevertheless, the present results compare qualitatively very well with the results obtained for similar systems by Louie et al.¹⁸ and by Jaros and Brand,²⁸ who used more rigorous pseudopotential band structures. In particular, the number and positions of the band states in the gaps are very similar. On the other hand, the present method produces a more detailed picture of resonances and antiresonances.

IV. CONCLUSIONS

The main conclusion of this paper is that the Koster-Slater Green's-function technique, which was found to be very cumbersome by Callaway and co-workers who used the Wannier representation, becomes very efficient and accurate when



FIG. 6. Changes in the density of states induced by an ideal As vacancy in GaAs. (Bound states in the gap not shown. See Table I.)

conventional LCAO representations are used. The method has substantial advantages over small- or large-cluster techniques, primarily because it exploits both the short-range nature of defect potentials and the translational symmetry of the host crystal. These advantages are also present when first-principles LCAO energy-band calculations are used to describe the host crystal. The results of such calculations will be reported elsewhere.

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APPENDIX

In this Appendix, we discuss the method introduced by Bassani, Iadonisi, and Preziosi,³⁰ which has recently been used extensively by Jaros and Brand.²⁸ The basic determinantal relationship of the method was originally derived by expanding



FIG. 7. Changes in the density of states of an ideal vacancy in Si using the tight-binding parametrization of Kauffer *et al.* (Ref. 21). Notice the similarities between this figure and Fig. 3.

the impurity wave function ψ in terms of Bloch functions and following with a number of transformations. We show here that the same determinant may be obtained by starting with the general Green's function results of Sec. II. As we saw in that section, bound states in the band gaps correspond to zeros of

$$D(E) = \det \| \mathbf{1} - G^{0}(E)V \|.$$
 (A1)

Let now $V = V_1 V_2$ as in the method of Bassani *et al.* (Originally, Bassani *et al.* assumed $V_1 = V_2 = V^{1/2}$, but Jaros and Brand generalized the theory to arbitrary V_1 and V_2 satisfying $V = V_1 V_2$.) Substituting in (A1), we observe immediately that the determinant

$$\tilde{D}(E) = \det \| \mathbf{1} - V_2 G^0 V_1 \|$$
(A2)

has the same zeros as D(E). If we express $\tilde{D}(E)$ in terms of a set of functions g_m , so that

$$\tilde{D}(E) = \det \left\| \delta_{mm'} - \langle m \left| V_2 G^0 V_1 \left| m' \right\rangle \right\|, \tag{A3}$$

and note that

$$\langle m \mid V_2 G^0 V_1 \mid m' \rangle = \sum_{n\vec{k}} \frac{\langle m \mid V_2 \mid n\vec{k} \rangle \langle n\vec{k} \mid V_1 \mid m' \rangle}{E - E_{n\vec{k}}^0}$$
(A4)

we recover the determinant obtained by Bassani et al. This derivation establishes a direct relationship between the method of Bassani et al. and the standard Green's-function formulation, and at the same time it reveals an inherent drawback of the former. Note that in Eq. (A4) the sums over \vec{k} depend on the perturbation and must be repeated for each impurity or defect. In contrast, Eq. (10)

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shows that in the standard Green's-function formulations, the sums over \vec{k} do not depend on the perturbation and must, therefore, be done only once for each material. Since these sums are by far the most time-consuming aspect of the calculations, the standard Green's-function technique appears to be more convenient for numerical work.

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