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Critique of the tight-binding method: Ideal vacancy and surface states

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We have investigated the dependence of the calculated energy eigenvalues for gap states, introduced by ideal vacancies and surfaces, on the choice of localized basis functions in the tight-binding method. In this method the Hamiltonian describing the system with an ideal vacancy is defined by removing all the Hamiltonian matrix elements between orbitals localized about the central atom with all basis states describing the system; the remaining atoms are assumed to have their positions unaltered, the atomiclike orbitals are retained on these atoms, and their Hamiltonian matrix elements are assumed unaltered. We find, using a Green's-function analysis, that if Wannier functions are employed as a basis there are no ideal vacancy-gap states. In addition, if the atomic orbitals of the isolated atoms are taken as the basis set, no ideal vacancy-gap states exist in the limit as the number of orbitals on the atom to be removed approaches infinity although spurious solutions for gap states can exist in a finite band model. Since the Green's-function analysis is exactly equivalent to finding the solutions of the Schrödinger equation with the Hamiltonian described above, these results obtain for all other techniques of solving the eigenvalue equation when the tight-binding Hamiltonian for an ideal vacancy in a crystal is employed. We find the reason for these surprising results is the fact that the tight-binding method is not equivalent to removing the potential of the removed atom. We demonstrate this by solving a two-atom problem by both the tight-binding method and by the Koster-Slater method, with only the latter method yielding the exact result. Moreover, we show that if the size of the basis set is allowed to increase without limit, the tight-binding method yields the same eigenvalues for the isolated atom as it does for the two-atom Hamiltonian. This result is generalized to the many-atom case and explains why no gap states are found if a complete basis is employed. This result is independent of the method used to solve the eigenvalue equation. The analysis is extended to surface-state calculations where it is shown that no gap states exist in the tight-binding method when Wannier functions are used as the basis set. Finally, using a Green's-function technique, we show how ideal vacancy-gap states may be calculated if the change in the potential, and consequently in the tight-binding matrix elements, is incorporated.

I. INTRODUCTION AND CONCLUSIONS

In the last few years there has been considerable interest in calculating the electronic states introduced in the band gaps of semiconductor crystals by vacancies and surfaces. Excellent reviews of the various methods have been published by Pantelides[1] for vacancy-state calculations and by Pollmann[2] for surface-state calculations. In this paper we critically examine the tight-binding method as applied to both problems.[3,4] The application of this method, employing a Green's-function analysis, has been generalized and extended to the study of the electrical properties of interfaces[5] and more recently to superlattices[6] and has become an important technique in semiconductor calculations.

The basis for the method is the early work of Koster and Slater,[7] who showed that the electronic energy levels introduced in the band gaps by a localized perturbation could be calculated from a knowledge of the Green's function for the perfect crystal and the matrix elements of the potential, both calculated in the Wannier representation. Moreover, the rank of the determinant required for the calculation of the energy eigenvalues was shown to be equal to the rank of the nonzero elements of the perturbing potential matrix in this representation.

Further amplification of this method has been given by Callaway[8] and calculations of the electronic states in the band gap have been performed for the vacancy[9] and divacancy[10] of Si in the Wannier representation. The calculations turned out to be difficult because of the complexity inherent in calculating the Wannier functions and few subsequent calculations have been performed in this representation.[11]

However, Lannoo and Lenglart[12] observed that the Green's-function method is not limited to employing Wannier functions as a basis, but can be applied using some other localized basis set. They used a set of s and p orbitals on each atom and performed a linear combination of atomic orbitals (LCAO) band-structure calculation for Si assuming nearest-neighbor interactions only. The Hamiltonian matrix elements were treated as parameters and fitted to known energy bands. The ideal vacancy in the tight-binding method is then defined by removing all the Hamiltonian matrix elements between orbitals localized about the central atom with all basis states describing the system; the remaining atoms are assumed to have their positions unaltered (no lattice relaxation), the atomic-like orbitals are retained on these atoms, and their Hamiltonian matrix elements are assumed unaltered. We shall refer to this procedure as the orbital-removal method since the resulting Hamiltonian matrix from which the eigenvalues and eigenvectors of the vacancy state are derived is identical to the Hamiltonian matrix that would be obtained if the orbitals on the central atom were removed from the basis set and no other changes were made in the Hamiltonian matrix. This method has been extended by Bernholc and Pantelides,[3] who showed using the same model of an ideal vacancy that in an arbitrary localized representation the gap states introduced by the vacancy are given by the zeros of the determinant of $G^0_{\alpha\alpha'}$ where G^0 is the perfect-crystal Green's function and α, α' are the atomiclike orbitals on the atom to be removed. Using symmetry considerations they find that if s, p orbitals are employed, states of A_1 symmetry are given by the zeros of G^0_{ss} and states of T_2 symmetry are given by the zeros of G^0_{pp}. For Si, they find a bound state of T_2 symmetry 0.27 eV above the valence-band edge using the tight-binding parametrization of the best energy bands obtained by Pandey and Phillips.[13] Earlier calculations of this quantity by Callaway and Hughes[9] using the Koster-Slater method in the Wannier representation yielded no gap states unless the vacancy potential was made stronger than the negative of the atomic potential that was removed. Kauffer *et al.*,[14] employing an identical definition of the ideal vacancy as given in Ref. 3 but using a different parametrization of the energy bands, find a bound state 0.12 eV above the valence-band edge.

Calculations of the Si vacancy states directly employing the vacancy potential have also been performed. Louie *et al.*,[15] employing a periodically spaced vacancy in a pseudopotential calculation which involved the self-consistently determined potential near the defect, find a bound state at approximately 0.5 eV above the valence-band edge. More recently, other calculations directly employing the vacancy potential have been performed by Bernholc, Lipari, and Pantelides[16] and by Baraff and Schluter,[17] who find the unrelaxed vacancy state 0.76 and 0.7 eV above the valence band, respectively. When self-consistency is included the eigenvalue is lowered by about 0.1 eV.[16] In comparing the results of Refs. 3 and 16, Bernholc *et al.*[16] speculate that the level obtained in the tight-binding method is too low because the conduction bands are not adequately represented by the tight-binding parameters. Support for this argument has been given by Papaconstantopoulos and Economou,[18] who used 20 adjustable parameters in an sp^3 basis which include first-, second-, and third-neighbor interactions to fit a band structure obtained from a pseudopotential calculation. Performing the same calculation given in Ref. 3 they find a bound state of T_2 symmetry 0.75 eV above the top of the valence band.

In applying the orbital-removal method, certain questions naturally arise which have not previously been systematically studied. One such question is whether the calculated binding energy of a vacancy state (or a surface state) depends on the choice of localized basis states used to parametrize the Hamiltonian matrix, i.e., we could employ s, p, etc., atomiclike orbitals, or Wannier functions or the true atomic orbitals. In each case the matrix elements appearing in the Hamiltonian will be different but can correspond to the same energy-band eigenvalues. Recent work by Das Sarma and Madhukar[19] has shown that for three different choices of tight-binding parameters such that the fitting of the energy bands appears "equally good", the A_1 vacancy energy levels for GaAs calculated by this method are significantly different, essentially covering the entire band gap, but scaled with the ionicity of the material implied by the particular set of tight-binding orbitals employed. Similar variations are found for the other vacancy states as well. A second question involves the convergence of the solutions for gap states as the number of orbitals and hence the number of bands is increased, i.e., can spurious solutions exist for gap states in a finite-band approximation which will disappear (merge into the bands) as the number of bands is increased.

Our analysis is based on the Green's-function technique developed by Bernholc and Pantelides.[3] This technique is exactly equivalent to finding the eigenvalues and eigenfunctions of the vacancy states in the orbital-removal method as defined above. Moreover, the Green's-function method provides a useful analytic technique for studying the implications of the definition of the vacancy in the tight-binding method. We wish to stress that our analysis is therefore not a critique of the Green's-function method but rather of the tight-binding method and is equally applicable to whatever technique is employed to solve the Schrödinger equation when the tight-binding definition of the vacancy is employed.

In Sec. II we employ Wannier functions as our basis set in the orbital-removal method for vacancy states. Since the orbital-removal method does not require the calculations of the matrix elements of the perturbing potential, the problems encountered by Callaway and Hughes[9] are eliminated and the perfect-crystal Green's function is easily evaluated.[8] We find no vacancy-gap states in this model independent of the number of bands included in the calculation.

In Sec. III we examine the solutions employing the true atomic orbitals (which are not orthogonal between different atoms) as a basis set. There too we find that as the number of orbitals on the atomic species to be removed increases without limit, there are no vacancy-gap states.

Section IV is devoted to the study of a two-band model, and the matrix elements of the Green's function on the vacancy cell are explicitly given in terms of matrix elements of the Hamiltonian and the energy-band functions. When the Green's function is evaluated with Wannier functions chosen as a basis, the eigenvalue equation reduces to that given in Sec. II and there are no bound states in the gap. However, if the basis functions are changed to other localized functions so the Bloch sums are the usual basis functions used in $\vec{k}\cdot\vec{p}$ perturbation theory, we find that spurious solutions for gap states may be found.

Section V is devoted to explaining these surprising results. It is argued that the orbital-removal method cannot entirely represent the effect of removing an atom from the crystal. As an illustration we show that if we start with only two atoms (the Green's-function method is still valid once some minor notational changes are made) the orbital-removal method does not yield the correct energy eigenvalues when one atom is removed, i.e., the average value of the potential of the removed atom still appears in the eigenenergy of the remaining isolated atom. Furthermore, we show that if we assume a continually larger set of orbitals on each atom and remove the matrix elements involving orbitals localized about the atom to be removed, as required by the definition of the vacancy in the tight-binding method, the eigenvalues of the resulting Hamiltonian matrix approach the eigenvalues of the two-atom problem and not those of the isolated atom. This result follows from the fact that in the orbital-removal method the Hamiltonian matrix elements between orbitals not on the removed atom are retained unchanged as if the removed atom were still present. We generalize our arguments to the multiatom case and conclude that as the number of orbitals on each atom is allowed to become continually larger, the eigenvalues obtained in the tight-binding (orbital-removal) method for the vacancy approach those of the unperturbed system. This conclusion is independent of any Green's-function analysis and is applicable to all methods of solving the Schrödinger equation when the tight-binding definition of the vacancy is employed, i.e., when the Hamiltonian matrix elements between orbitals not on the removed atom are retained unchanged. In particular, it explains the results of Secs. II and III when the Green's-function technique was employed as well as the results of Sec. IV, since the eigenvalues of the tight-binding Hamiltonian with or without the vacancy can be different if a finite basis set is employed. However, if the negative of the potential of the removed atom is treated as the perturbation and the Koster-Slater equation is solved, we recover the exact ground-state energy for the isolated atom in the two-atom problem.

In Sec. VI we study the implications of these results for surface state calculations in the layer-orbital-removal method.[4] We show explicitly, employing Wannier functions as the localized basis set, that for one atom per unit cell this method yields no gap states for both nearest- and also next-nearest-neighbor interactions. In addition, we show that in the limit of removing many layers, no gap states exist. We are thus led to the conclusion that the orbital-removal method cannot yield reliable and unambiguous results for the electronic energy levels for vacancies or surfaces and that the potential of the removed atom or atoms must be included if accurate results are to be obtained.[16,17,20]

Finally, in Sec. VII, using a Green's-function technique we show how ideal vacancy states may be calculated using the orbital-removal method if the change in the potential, and consequently the change in the tight binding matrix elements with orbitals on other atoms, is incorporated.

II. ORBITAL-REMOVAL METHOD IN THE WANNIER REPRESENTATION FOR VACANCY STATES

The bound-state energy eigenvalues for ideal vacancy states in the band gaps of the perfect crystal are given by the solutions of

$$\det G^0_{\alpha\alpha'}(E) = 0, \tag{1}$$

where $\{\phi_\alpha\}$ denote the orthonormal set of orbitals associated with the atom to be removed creating the vacancy.[3] Here

$$G^0_{\alpha\alpha'} = \sum_{n,\vec{k}} \frac{\langle \alpha | n\vec{k}\rangle\langle n\vec{k} | \alpha'\rangle}{E - E^0_{n\vec{k}}}, \tag{2}$$

where the matrix elements of the perfect-crystal Green's function G^0 are given in terms of the Bloch states of the perfect crystal, $|n\vec{k}\rangle$, and the corresponding energy bands $E^0_{n\vec{k}}$ and the $\{\phi_\alpha\}$ are the set of orbitals which are localized about the site of the atom to be removed.

A. Case of one atom per unit cell

Suppose the ϕ_α are Wannier functions, $A_n(\vec{r}-\vec{R}_j)$, where

$$A_{nj} = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}_j} \psi_{n\vec{k}}(\vec{r}), \tag{3}$$

so

$$\langle A_{n'j}|\psi_{n\vec{k}}\rangle = \frac{1}{\sqrt{N}}\, e^{i\vec{k}\cdot\vec{R}_j}\,\delta_{nn'}, \tag{4}$$

Then removing an atom at R_j yields

$$(G^0_{jj})_{n'n''} = \sum_{n,\vec{k}} \frac{\langle A_{n'j}|n\vec{k}\rangle\langle n\vec{k}|A_{n''j}\rangle}{E-E^0_{n\vec{k}}} = \frac{1}{N}\,\delta_{n'n''}\sum_{\vec{k}}\frac{1}{E-E^0_{n'\vec{k}}}. \tag{5}$$

Thus in this representation $(G^0_{jj})_{n'n''}$ is diagonal, so

$$\det G^0_{jj}(E) = \prod_n \frac{1}{N}\sum_{\vec{k}}\frac{1}{E-E^0_{n\vec{k}}}, \tag{6}$$

and the solutions of Eq. (1) are the solutions of

$$\frac{1}{N}\sum_{\vec{k}}\frac{1}{E-E^0_{n\vec{k}}} = 0 \tag{7}$$

for some n. But if E is in a band gap, for a given $n, E-E^0_{n\vec{k}}$ always has the same sign for all $\vec{k}$. Therefore there are no solutions of Eq. (7) in the band gaps. The discussion above is also valid for removing an entire cell of a crystal with more than one atom per unit cell and therefore leads to the result that there are no gap states for the divacancy of Si or Ge, etc., predicted by this calculation.

We observe, however, that in the Kronig-Penney model, the removal of one "atom," i.e., one delta function, can be treated exactly. It is well known that in such a model one gap state is introduced between every two successive bands[21] which is a counter example to the result given by Eq. (7).

We also note that in the empirical tight-binding method, it is not necessary to know the functional forms of the Wannier functions. In this method the matrix elements of the Hamiltonian between localized atomiclike orbitals are adjusted to reproduce the band structure obtained from other methods. If the Wannier functions are taken as this set of localized orbitals then the matrix elements of the unperturbed Hamiltonian are given by $\langle A_{n'j'}|H^0|A_{nj}\rangle = \epsilon_{n,j-j'}\delta_{n,n'}$, where

$$\epsilon_{n,j} = \frac{1}{N}\sum_{\vec{k}}\epsilon_n(\vec{k})e^{-i\vec{k}\cdot\vec{R}_j}.$$

Thus for any given band structure $\epsilon_n(\vec{k})$ we can make the eigenvalues of the empirical Hamiltonian approximate $\epsilon_n(\vec{k})$ as closely as we desire with the resulting Bloch states satisfying Eq. (4) exactly, from which Eq. (7) immediately follows.

B. Case of p atoms per unit cell

For p atoms in a unit cell of the crystal and S_i orbitals on atom $i=1,\ldots,p$ we have $Q=\sum_i S_i$ bands. Corresponding to each band there is a Wannier function $A_n(\vec{r}-\vec{l})$, $n=1,2,\ldots,Q$.

We note that because the Bloch waves are determined only up to an overall phase factor $e^{i\Theta_n}$ where Θ_n can be chosen to be a function of $\vec{k}$, the Wannier functions for a given band defined by Eq. (3) are not unique.[22] We can make use of this nonuniqueness to shift the Wannier functions in space so they are each centered about the separate atoms of the cell, i.e., in the trivial case where we are dealing with free electrons we could take $\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot(\vec{r}-\vec{b})}$, where $\vec{b}$ is arbitrary corresponding to $\Theta(\vec{k}) = \vec{k}\cdot\vec{b}$. Then the Wannier function in the $j=0$ cell is centered at $\vec{r}=\vec{b}$. The precise choice of the phase $\Theta_n(\vec{k})$ will also determine the form of the decay of the Wannier functions.[22] In the following discussion we assume that the $\Theta_n(\vec{k})$ have been appropriately chosen so each Wannier function in each cell is centered about a particular atom. In the spirit of the tight-binding approximation, that atom could be chosen as the one having the orbital which has the greatest overlap integral with the Bloch functions belonging to a given band, i.e., has the maximum value for $\sum_{\vec{k}}|\langle n\vec{k}|\phi_i\rangle|^2$, where ϕ_i is the atomic orbital. (For a solid having two identical atoms per unit cell, this procedure would require modification.)

Denoting the Wannier functions related in this way to the jth atom as $A_{\alpha j}(\vec{r})$ we have for a vacancy of atom j in the $\vec{l}=0$ cell

$$(G^0_{jj})_{\alpha\alpha'} = \sum_{n,\vec{k}}\frac{\langle\alpha,j|n\vec{k}\rangle\langle n\vec{k}|\alpha',j\rangle}{E-E^0_{n\vec{k}}}. \tag{8}$$

But since

$$\psi_{n\vec{k}} = \frac{1}{\sqrt{N}}\sum_{\vec{l}} e^{i\vec{k}\cdot\vec{l}}A_n(\vec{r}-\vec{l}) \tag{9}$$

with

$$\langle A_{n'l'}|A_{nl}\rangle = \delta_{nn'}\delta_{ll'}, \tag{10}$$

we again have

$$G^0_{n'n''} = \frac{1}{N}\sum_{\vec{k}}\frac{1}{E-E^0_{n\vec{k}}}\,\delta_{n'n''}, \tag{11}$$

where n', n'' are composite subscripts for α, j with α varying from 1 to S_j and j denotes the atom removed in the cell. Thus

$$\det G^0 = \prod_n \frac{1}{N}\sum_{\vec{k}}\frac{1}{E-E^0_{n\vec{k}}}, \tag{12}$$

so there are no solutions in the energy band gaps with this set of localized states.

We have thus shown that a set of localized states exists which can be associated with the atoms in a cell such that when used as a basis to construct the Hamiltonian matrix, result in no band gap states when the orbital-removal method is employed to calculate the energy spectrum of vacancy states.

It can, of course, be argued that such localized states are not the true atomic orbitals that should be removed but rather a combination of many orbitals not only from the atom to be removed, but from other atoms as well. However, the same argument can be made as well in the cases in which this method has been employed. In such cases the orthonormal set of atomiclike functions that are removed are constructed, using Lowdin's method,[23] by taking linear combinations of the atomic orbitals from different atoms in different cells. This is necessary because the actual atomic orbitals on two atoms will not in general be orthogonal to each other. When this orthogonalization process is completely carried out the resulting atomiclike orbitals include contributions from essentially all atomic orbitals in the system. It thus appears that if unambiguous results are to be obtained, the orbitals that should be removed are the true atomic orbitals related to the removed atom rather than some set which has been obtained by taking linear combinations of orbitals which include contributions from other atoms.

III. ORBITAL-REMOVAL METHOD USING ATOMIC ORBITALS

We consider the basis functions $\{\phi_{\alpha j}\}$ to be the true atomic orbitals where j denotes the jth atom in the crystal. Then since orbitals on the same atomic site are eigenfunctions of the same atomic Hamiltonian we can take

$$\langle \phi_{\alpha j} | \phi_{\alpha' j} \rangle = \delta_{\alpha\alpha'} \tag{13}$$

but

$$\langle \phi_{\alpha j} | \phi_{\alpha' j'} \rangle \neq 0, \quad j \neq j' . \tag{14}$$

Employing the same arguments as Bernholc and Pantelides (see the Appendix) it can be shown that in the orbital-removal method the energy levels in the band gaps introduced by the ideal vacancy are given by the solutions of

$$\det \tilde{G}^0_{11} = 0 , \tag{15}$$

where

$$\tilde{G}^0 = S^{-1} G^0 S^{-1} \tag{16}$$

and S is the overlap matrix, i.e.,

$$S_{\alpha j, \alpha' j'} = \langle \phi_{\alpha j} | \phi_{\alpha' j'} \rangle . \tag{17}$$

It follows from Eq. (13) that

$$\underline{S} = \begin{bmatrix} I & S_{12} \\ S_{21} & S_{22} \end{bmatrix} . \tag{18}$$

It is convenient to take linear combinations of the $\{\phi_{\alpha j}\}$ to form a set $\{\phi'_{\alpha j}\}$ such that

$$\phi'_{\alpha 0} = \phi_{\alpha 0}$$

$$\text{and} \tag{19}$$

$$\langle \phi_{\alpha 0} | \phi'_{\alpha' j'} \rangle = \delta_{\alpha\alpha'} \delta_{jj'} ,$$

where $j = 0$ denotes the atom to be removed. Thus the orbitals on the atom to be removed are still the atomic orbitals and in this representation S has the form

$$\underline{S} = \begin{bmatrix} I & 0 \\ 0 & S_{22} \end{bmatrix} . \tag{20}$$

Then

$$\underline{S}^{-1} = \begin{bmatrix} I & 0 \\ 0 & S_{22}^{-1} \end{bmatrix} , \tag{21}$$

and it follows from Eqs. (16) and (21) that

$$\tilde{G}^0_{11} = G^0_{11} \tag{22}$$

with matrix elements

$$\tilde{G}^0_{\alpha\alpha'} = G^0_{\alpha\alpha'} = \sum_{n, \vec{k}} \frac{\langle \alpha | n\vec{k} \rangle \langle n\vec{k} | \alpha' \rangle}{E - E^0_{n\vec{k}}} , \tag{23}$$

where α, α' are orthonormal atomic orbitals on the $j = 0$ atom. In a finite-band approximation there will be r orbitals $\alpha = 1, \ldots, r$. We can make a unitary transformation to another set of r orthonormal functions A'_α without changing the value of the determinant, i.e.,

$$\det G^{0\prime} = \det U G^0 U^\dagger = \det U U^\dagger \det G^0 = \det G^0 . \tag{24}$$

We choose the A'_α as follows. Let A'_1 be that linear combination of the $\phi_{\alpha 0}$ which gives the maximum overlap with the Wannier function A_1 belonging to the lowest energy band and centered in the cell of the atom $j = 0$. Similarly, let A'_2 be that linear combination of the $\phi_{\alpha 0}$ which is orthogonal to A'_1 and gives the maximum overlap with the Wannier function A_2 belonging to the next highest energy band, etc. For any finite set of r atomic orbitals these functions cannot, in general, be made identical to the Wannier functions. However, as r increases the fit can be made better until in the limit as $r \to \infty$ $A'_n \to A_n$ for $n \leq r$ because the $\{\phi_{\alpha 0}\}$ then span a complete orthonormal set for any square integrable function since they are the eigenfunctions of an atomic Hamiltonian.

Thus in the limit of large r

$$\langle A'_\alpha | n\vec{k} \rangle \to \langle A_\alpha | n\vec{k} \rangle = \frac{1}{\sqrt{N}} \delta_{\alpha n} , \quad n \leq r . \tag{25}$$

For one atom per cell there are only r bands if there are r orbitals taken as the basis on each atom. For more than one atom per cell the number of bands equals r plus the number of orbitals on the other atoms in a cell. We keep the number of these orbitals on other atoms in the unit cell fixed and finite throughout the calculation. Then the contribution from these higher-lying bands to $G^0_{\alpha\alpha'}$ is

$$G^{0(r)}_{\alpha\alpha'}(E)=\sum_{n>r,\vec{k}}\frac{\langle\alpha|n\vec{k}\rangle\langle n\vec{k}|\alpha'\rangle}{E-E^0_{n\vec{k}}}. \tag{26}$$

However, as $r\rightarrow\infty$, $E_{n\vec{k}}\rightarrow\infty$ for $n\geq r$ and since there are a finite number of such bands and the matrix elements appearing in $G^{0(r)}_{\alpha\alpha'}$ are nonsingular we have that for any finite energy E,

$$G^{0(r)}_{\alpha\alpha'}\rightarrow 0 \quad \text{as } r\rightarrow\infty. \tag{27}$$

Substituting the results of Eqs. (23)–(27) into Eq. (15) yields a diagonal matrix with the resulting eigenvalue equation

$$\frac{1}{N}\sum_{\vec{k}}\frac{1}{E-E^0_{n\vec{k}}}=0 \tag{28}$$

which has no solution for E in an energy gap. Equation (28) results only in the limit $r\rightarrow\infty$. This result also obtains if any complete set of basis functions is employed and is not limited to the use of the true atomic orbitals. In a finite-band model solutions for E can exist in the energy gaps (as shown in Sec. IV) depending on the choice of basis functions, but Eq. (28) implies that these solutions will disappear (the energy level will move into a band) when a complete set of basis functions is employed.

IV. VACANCY STATES IN A FINITE BAND MODEL

The sensitivity of the calculated energy eigenvalues to the choice of basis functions can be most easily seen in a two-band model. If we take two orthonormal orbitals per unit cell ϕ_1 and ϕ_2, the eigenvalue-eigenvector equation for the energy bands and Bloch functions can be written

$$\sum_j A_{ij}C_j=EC_i, \tag{29}$$

where

$$A_{ij}(\vec{k})=\langle\chi_i|H^0|\chi_j\rangle, \tag{30}$$

$$\psi_{n\vec{k}}=\sum_i C_i^{(n)}(\vec{k})\chi_i(\vec{r},\vec{k}), \tag{31}$$

and χ_i is the Bloch sum arising from the ϕ_i orbital.

Taking only two orbitals per unit cell results in Eq. (29) being a 2×2 matrix equation which can be solved analytically for the energy bands and the Bloch functions. Employing these results we find

$$\langle\phi_i|G^0|\phi_j\rangle=\begin{pmatrix}\frac{1}{N}\sum_{\vec{k}}\frac{E-A_{22}}{(E-E^0_{1\vec{k}})(E-E^0_{2\vec{k}})} & \frac{1}{N}\sum_{\vec{k}}\frac{A_{12}}{(E-E^0_{1\vec{k}})(E-E^0_{2\vec{k}})}\\ \frac{1}{N}\sum_{\vec{k}}\frac{A_{21}}{(E-E^0_{1\vec{k}})(E-E^0_{2\vec{k}})} & \frac{1}{N}\sum_{\vec{k}}\frac{E-A_{11}}{(E-E^0_{1\vec{k}})(E-E^0_{2\vec{k}})}\end{pmatrix}. \tag{32}$$

If we take $\phi_n=A_n$, the Wannier function belonging to the nth band for $n=1, 2$, then

$$\chi_{n,\vec{k}}=\psi_{n,\vec{k}}=\frac{1}{\sqrt{N}}e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}(\vec{r}) \tag{33}$$

and

$$A_{nn'}=E^0_{n\vec{k}}\,\delta_{nn'}. \tag{34}$$

Substituting Eqs. (33) and (34) into Eq. (32) yields

$$\langle\phi_i|G^0|\phi_j\rangle=\begin{pmatrix}\frac{1}{N}\sum_{\vec{k}}\frac{1}{E-E^0_{1\vec{k}}} & 0\\ 0 & \frac{1}{N}\sum_{\vec{k}}\frac{1}{E-E^0_{2\vec{k}}}\end{pmatrix}, \tag{35}$$

which is just a special case of the result obtained in Sec. II yielding no vacancy states in the gap.

However, if instead of Eq. (33) we take

$$\chi_{n\vec{k}}=\frac{1}{\sqrt{N}}e^{i\vec{k}\cdot\vec{r}}u_{n0}(\vec{r}),\quad n=1, 2 \tag{36}$$

corresponding to atomiclike orbitals

$$\phi_{nl}=\phi_n(\vec{r}-\vec{l})=\frac{1}{\sqrt{N}}\sum_{\vec{k}}e^{-i\vec{k}\cdot\vec{l}}\chi_{n\vec{k}}=\frac{1}{\sqrt{N}}u_{n0}(\vec{r})\sum_{\vec{k}}e^{i\vec{k}\cdot(\vec{r}-\vec{l})} \tag{37}$$

then, as with the case of Wannier functions, the functions $\phi_n(\vec{r}-\vec{l})$ are localized[24] about the cell $\vec{l}$ and satisfy

$$\langle\phi_{nl}|\phi_{n'l'}\rangle=\delta_{nn'}\delta_{ll'}. \tag{38}$$

Then

$$A_{nn}=\epsilon_n+\frac{\hbar^2k^2}{2m}\,,\quad n=1,\,2 \tag{39}$$

where

$$H^0u_{n0}=\epsilon_n u_{n0} \tag{40}$$

and

$$A_{nn'}=\frac{\hbar}{m}\vec{\mathrm{k}}\cdot\vec{\mathrm{p}}_{nn'}\,,\quad n\neq n' \tag{41}$$

where

$$\vec{\mathrm{p}}_{nn'}=\langle u_{n0}|\vec{\mathrm{p}}\,|u_{n'0}\rangle\,. \tag{42}$$

Substituting Eqs. (38)–(41) into Eq. (32) we see immediately that the off-diagonal terms in G^0 are zero because A_{12} is odd in $\vec{\mathrm{k}}$ and $E_{1\vec{\mathrm{k}}}$ and $E_{2\vec{\mathrm{k}}}$ are both even and

$$G^0_{11}=\sum_{\vec{\mathrm{k}}}\frac{E-\epsilon_2-\hbar^2k^2/2m}{(E-E^0_{1\vec{\mathrm{k}}})(E-E^0_{2\vec{\mathrm{k}}})}\,, \tag{43}$$

$$G^0_{22}=\sum_{\vec{\mathrm{k}}}\frac{E-\epsilon_1-\hbar^2k^2/2m}{(E-E^0_{1\vec{\mathrm{k}}})(E-E^0_{2\vec{\mathrm{k}}})}\,, \tag{44}$$

with

$$E_{\frac{1}{2}}=\frac{\hbar^2k^2}{2m}+\frac{(\epsilon_1+\epsilon_2)\pm[(\epsilon_1-\epsilon_2)^2+4|\vec{\mathrm{k}}\cdot\vec{\mathrm{p}}_{12}|^2]^{1/2}}{2}\,. \tag{45}$$

If the two orbitals refer to two different atoms in the unit cell, then the eigenvalues for states in the gap are given by $G^0_{11}=0$ if atom 1 is removed or $G^0_{22}=0$ if atom 2 is removed. In either case $(E-E_{1\vec{\mathrm{k}}})(E-E_{2\vec{\mathrm{k}}})<0$ for E in the gap. Then for any E in the gap $E-(\epsilon_1+\hbar^2k^2/2m)\leq 0$ because $(E_1)_{\min}=\epsilon_1$ so $G^0_{22}\neq 0$ for such E. However, the term $E-(\epsilon_2+\hbar^2k^2/2m)$ can change sign for E in the gap, so removing atom 1 (i.e., the one associated with the conduction band) can lead to gap states. A more careful analysis shows that for sufficiently large p_{12}, the energy of this vacancy state can be made as close to the top of the valence band as desired, and as p_{12} is decreased the energy of this state can be made to rise to the bottom of the conduction band. In addition, if the two orbitals refer to the same atom (there is thus one atom per unit cell) then the condition for a gap state is

$$\det G^0=0=G^0_{11}G^0_{22}$$

so the above analysis still obtains, i.e., depending on the magnitude of p_{12} there can be a gap state corresponding to $G^0_{11}=0$. Thus the results depend on the choice of localized orbitals describing the atomiclike states to be removed, i.e., if Wannier functions are employed there will be no gap states, but with another similar, but not identical, choice of a localized basis set we can obtain gap states in a finite-band model even though the energy bands in both cases are the same.

V. DISCUSSION OF ASSUMPTIONS IN IDEAL VACANCY CALCULATIONS

The results of Sec. II lead to the conclusion that either there are no gap states introduced in a crystal by an ideal vacancy, i.e., that some relaxation must be assumed if any gap states are to exist, or there is some fundamental problem with the orbital-removal method. We examine the latter possibility.

There are two fundamental assumptions from which Eq. (1) directly follows. The first asserts that when an atom is removed from a perfect crystal all the other atoms retain their original positions. This essentially defines the ideal vacancy and, although it may not be true in practice, yields a well defined problem that can fruitfully be used as a starting point for vacancy calculations.

The second assumption is the atomiclike orbitals are retained on all other atoms and their interactions are assumed unaltered. However, the matrix elements of the full Hamiltonian between any two orbitals (in the single-particle approximation) depend in principle on the potential throughout the solid and not merely on the contribution of these two atoms to the crystal potential. Thus this assumption is not equivalent to asserting that each atom continues to make the same contribution to the crystal potential as it did originally (except of course for the vacancy atom) but rather is equivalent to assuming that the crystal potential has not changed at all anywhere in the solid. For example, the second assumption requires that the matrix elements of the potential between orbitals from atoms adjacent to, but on opposite sides of, the vacancy be unchanged. This clearly cannot be true except when all interactions except those from nearest neighbors are neglected. Even in the case of nearest-neighbor interactions only, the matrix elements of the potential between states on a single atom adjacent to the vacancy will change because these states will partially overlap the vacancy site.

This point is most simply illustrated by the following model calculation. We first observe that the orbital-removal method is not restricted to a crystal but can be applied to any multiatom system provided that the Bloch states in the Green's function are replaced by the complete set of quantum states q, with energy E_q, of the unperturbed system. Here q denotes all the quantum numbers associated with a given state. Equation (1) then is valid for states not degenerate with any E_q with

$$G^0_{\alpha\alpha'}=\sum_q\frac{\langle\alpha|q\rangle\langle q|\alpha'\rangle}{E-E_q}\,. \tag{46}$$

Consider two identical atoms separated by a finite distance. For simplicity we take one orbital on each atom ϕ_1 and ϕ_2, each of which is an eigenfunction of the Hamiltonian of the isolated atom and assume they are orthonormal for the given separation distance. It is then trivial to calculate the Green's function given by Eq. (46). The resulting eigenvalue when atom 1 is removed is then obtained from $G_{11}^0(E)=0$ which results in

$$E=\epsilon+\langle\phi_2|V_1|\phi_2\rangle \tag{47}$$

with wave function $\psi=\phi_2$, where ϵ is the eigenvalue for the isolated atom and V_1 is the potential due to the presence of atom 1. We thus see that even though atom 1 has been removed, its contribution through the potential, V_1, remains and leads to an incorrect energy eigenvalue for an electron in the presence of the remaining atom 2.

An even simpler way of seeing that this must happen is to first recognize that the eigenvalues obtained from setting the determinant of the appropriate block of the Green's function equal to zero are identical to the eigenvalues obtained from the Hamiltonian matrix when all rows and columns involving matrix elements with the removed orbitals are set equal to zero, and E_0 (which is allowed to approach infinity) is placed on the diagonal of this part of the matrix. In our two-atom, one orbital per atom model the initial Hamiltonian matrix is only 2 × 2 and setting the matrix elements involving ϕ_1 equal to zero immediately yields

$$\begin{aligned}E=H_{22}^0=\langle\phi_2|H^0|\phi_2\rangle&=\langle\phi_2|[(P^2/2m+V_2)+V_1]|\phi_2\rangle\\&=\epsilon+\langle\phi_2|V_1|\phi_2\rangle\end{aligned} \tag{48}$$

as obtained from the Green's-function calculation. Moreover, it is clear that if we assume a continually larger set of orbitals on each atom and set the matrix elements involving orbitals from atom 1 equal to zero, the resulting Hamiltonian matrix is composed of matrix elements of the full Hamiltonian $H^0=P^2/2m+V_1+V_2$ between all the states of the isolated atom 2. Then since the atomic orbitals on isolated atom 2 span a complete set, as the number of these orbitals increases without limit, the eigenvalues of the Hamiltonian matrix approach the eigenvalues of $H^0=P^2/2m+V_1+V_2$, of which Eq. (48) is the first approximation, and not the eigenvalues of $H=P^2/2m+V_2$.

This is also what happens in the case of the ideal vacancy in an otherwise perfect crystal. The orbital-removal method yields the same eigenvalues as obtained from setting to zero the matrix elements involving the orbitals from the atom to be removed but not modifying the other matrix elements. Thus the other elements of the Hamiltonian matrix involve matrix elements of the full Hamiltonian including the potential of the atom that was removed. Then, as the number of orbitals is allowed to approach infinity and the set becomes complete, the resulting eigenvalues become those of the perfect crystal with no vacancy present. This is the reason why in Sec. III we found no gap states when we allowed the number of orbitals to approach infinity and assumed completeness of the set of orbitals.

Thus, although the orbital-removal method is very appealing, it cannot be correct because it does not actually change the potential from that of the perfect crystal. At best it will result in spurious results for a finite-band model as indicated by Eq. (48) for the two-atom problem and these solutions must ultimately converge to the band energies of the perfect crystal when the method is made fully convergent. Since the cluster calculation[25] employing the orbital-removal method is an approximation to treating the vacancy in an infinite crystal, it too suffers from the same defect as well as do other non-Green's-function techniques employing the tight-binding (orbital removal) definition of the vacancy.[26]

Nothing stated above, however, should be construed as implying that the original Koster-Slater method is incorrect. When this latter method is employed in the case of a vacancy, orbitals are not removed but rather the crystal Hamiltonian is perturbed by adding a term that represents the change in the potential due to the removal of the atom.

In terms of the Green's-function approach this yields[7]

$$(I-G^0U)\psi=0\,, \tag{49}$$

where U is the pertubation potential, G^0 is the Green's function for the unperturbed Hamiltonian, and ψ is the wave function for the electron state. If Eq. (49) is written in terms of its matrix elements with respect to a complete orthonormal basis $\{\phi_\alpha\}$ then

$$\sum_{\alpha',\beta}(\delta_{\alpha\alpha'}-G_{\alpha\beta}^0U_{\beta\alpha'})C_{\alpha'}=0\,, \tag{50}$$

where

$$\psi=\sum_\alpha C_\alpha\phi_\alpha \tag{51}$$

and the energy eigenvalues are given by

$$\det(I-G^0U)=0\,. \tag{52}$$

In the two-atom model discussed above $U=-V_1$ for the removal of atom 1. We have exactly solved Eqs. (50) and (52) assuming only one atomic orbital on each atom where each orbital is the true atomic state in the absence of the other atom. We find for the ground state

$$E=\epsilon$$

and

$$\psi=\phi_2$$

exactly. Thus, unlike the orbital-removal method, the original Koster-Slater method yields the exact result both for the energy and the wave function when the perturbation created by the vacancy is treated correctly.

VI. IMPLICATIONS FOR SURFACE-STATE CALCULATIONS

The orbital-removal method has been extended to the problem of surface-state calculations.[4] In this case a whole plane of atoms is removed if only nearest-neighbor interactions are included, two planes if next-nearest-neighbor interactions are included, etc. Since this method is equivalent to creating a "planar vacancy" or a "multiplanar vacancy" by the orbital-removal method without taking into consideration any change in the matrix elements of the Hamiltonian between orbitals on atoms that are not removed, it must suffer from the same difficulties as the orbital-removal method in the vacancy calculation.

We can show this directly by demonstrating that as in the case of the vacancy calculation there are no surface-state energy eigenvalues in the band gaps when Wannier functions are employed as the localized atomiclike orbitals. For simplicity we consider the case of one atom per unit surface cell. Then the energy eigenvalues for surface states in the energy band gaps are given by the solutions of[4]

$$\det\|G^0_{ll'}(E,\vec{q})\|=0\,, \tag{53}$$

where $G^0_{ll'}$ is the Green's function in the layer-orbital representation, i.e.,

$$G^0_{ll'}(E,\vec{q})=\langle\phi^{\alpha m}_{\vec{q}}|G^0|\phi^{\alpha' m'}_{\vec{q}}\rangle\,, \tag{54}$$

where l is a composite subscript for the orbital α on the atomic plane m, and l, l' in Eq. (53) run only over those layers to be removed creating the two-noninteracting surfaces. Here the layer orbitals $\phi^{\alpha m}_{\vec{q}}$ are defined by[4]

$$\phi^{\alpha,m}_{\vec{q}}=\frac{1}{\sqrt{N_2}}\sum_j e^{i\vec{q}\cdot\vec{\rho}^m_j}\phi_\alpha(\vec{r}-\vec{\rho}^m_j)\,, \tag{55}$$

where $\vec{\rho}^m_j$ are the two-dimensional lattice vectors connecting sites occupied by the atoms with orbital type α on the mth lattice plane and $\vec{q}$ is a vector in the two-dimensional Brillouin zone defined by a surface cell. Let

$$\phi_\alpha(\vec{r}-\vec{\rho}^m_j)=A_\alpha(\vec{r}-\vec{\rho}^m_j)\,.$$

Then the layer orbitals can be written

$$A^{\alpha,m}_{\vec{q}}=\frac{1}{\sqrt{N_2}}\sum_j e^{i\vec{q}\cdot\vec{\rho}^m_j}A_\alpha(\vec{r}-\vec{\rho}^m_j)$$

and

$$\psi_{n\vec{k}}=\frac{1}{\sqrt{N}}\sum_{j,m} e^{i\vec{k}\cdot\vec{\rho}^m_j}A_n(\vec{r}-\vec{\rho}^m_j) \tag{56}$$

so

$$\langle\psi_{n\vec{k}}|A^{\alpha' m'}_{\vec{q}}\rangle=\frac{\sqrt{N_2}}{\sqrt{N}}e^{-im'k_\perp a}\delta_{n\alpha'}\delta_{\vec{q},\vec{k}_\parallel}\,,$$

where we have used $\vec{\rho}^m_j=\vec{\rho}_j+m\vec{a}$ and $\vec{k}_\parallel$ is the projection of $\vec{k}$ on the surface, and $k_\perp$ is the projection of $\vec{k}$ on $\vec{a}$. Then

$$\begin{aligned}G^0_{ll'}(E,\vec{q})&=\sum_{n,\vec{k}}\frac{\langle A^{\alpha,m}_{\vec{q}}|n\vec{k}\rangle\langle n\vec{k}|A^{\alpha' m'}_{\vec{q}}\rangle}{E-E_{n\vec{k}}}\\&=\frac{N_2}{N}\sum_{k_\perp}\frac{e^{ik_\perp a(m-m')}}{E-E_\alpha(\vec{q},k_\perp)}\delta_{\alpha\alpha'}\,,\end{aligned} \tag{57}$$

which is diagonal in band index so Eq. (53) becomes $\prod_\alpha \det G^{0\alpha\alpha}_{mm'}=0$ where $G^{0\alpha\alpha}_{mm'}$ are the elements of G^0 belonging to band α.

In the case where only one layer is to be removed (i.e., nearest-neighbor interactions only) $m=m'=1$ so $G^{0\alpha\alpha}_{mm'}$ is a 1×1 matrix and the eigenvalue condition is

$$\sum_{k_\perp}\frac{1}{E-E_\alpha(\vec{q},k_\perp)}=0\,, \tag{58}$$

which yields no gap solutions.

If we must remove two layers (i.e., next-nearest-neighbor interactions), then $G^{0\alpha\alpha}_{mm'}$ is a 2×2 matrix, and the eigenvalue condition is

$$\det G^{0\alpha\alpha}_{mm'}=\left(\frac{N_2}{N}\right)^2\begin{vmatrix}\displaystyle\sum_{k_\perp}\frac{1}{E-E_\alpha(\vec{q},k_\perp)} & \displaystyle\sum_{k_\perp}\frac{e^{ik_\perp a}}{E-E_\alpha(\vec{q},k_\perp)}\\ \displaystyle\sum_{k_\perp}\frac{e^{-ik_\perp a}}{E-E_\alpha(\vec{q},k_\perp)} & \displaystyle\sum_{k_\perp}\frac{1}{E-E_\alpha(\vec{q},k_\perp)}\end{vmatrix}=0 \tag{59}$$

or

$$\left|\sum_{k_\perp}\frac{1}{E-E_\alpha(\vec{q},k_\perp)}\right|^2-\left|\sum_{k_\perp}\frac{e^{ik_\perp a}}{E-E_\alpha(\vec{q},k_\perp)}\right|^2=0\,,$$

But for E in an energy band gap $E-E_\alpha$ always has the same sign for a given α so the first term is always larger than the second. Thus for the case of next-nearest-neighbor interactions there are no gap states.

In general, if we have a Hamiltonian with n nearest-neighbor interactions we can remove n layers to decouple the two solids to create two noninteracting ideal surfaces. Since $G^0_{ll}(E,\vec{q})$ is diagonal in band index in the Wannier representation, the ideal surface-state energy spectrum is obtainable from the zeros of $\det G^{0\alpha\alpha}_{mm'}=0$ where, for a given α, $G^{0\alpha\alpha}_{mm'}$ has rank n. For $n>2$ it is difficult to proceed as above to show no solutions exist in the gap by direct evaluation of the determinant.

Consider the case where we take an infinite solid in all directions and take the limit

$$\frac{N_2}{N}\sum_{k_\perp} \to \frac{a}{2\pi}\int dk_\perp .$$

Then

$$G^{0\alpha\alpha}_{mm'} = \frac{a}{2\pi}\int f_{\alpha\vec{q}}(k_\perp) e^{ik_\perp a(m-m')} dk_\perp ,$$

where

$$f_{\alpha\vec{q}}(k_\perp) = \frac{1}{E - E_\alpha(\vec{q}, k_\perp)} .$$

For interactions between n nearest neighbors we can decouple the two solids to create two noninteracting surfaces by removing any number of layers greater than or equal to n. If we let the number of layers removed become increasingly large, i.e., $m, m' = M \gg n$, then $G^{0\alpha\alpha}_{mm'}$ looks the same as the Hamiltonian matrix in the Wannier representation of a one-dimensional problem with energy-band function $f_{\alpha\vec{q}}(k_\perp)$, i.e., if $f_{\alpha\vec{q}}(k_\perp)$ is the energy-band function of some Hamiltonian h, then in terms of the Wannier functions $\tilde{A}_{\alpha m}$,

$$\langle \tilde{A}_{\alpha m} | h | \tilde{A}_{\alpha m'} \rangle = f_{\alpha\vec{q}, m'-m} ,$$

where

$$f_{\alpha,\vec{q},m} = \frac{a}{2\pi}\int f_{\alpha\vec{q}}(k_\perp) e^{-ik_\perp am} dk_\perp .$$

In the limit of large M, the matrix representation of h in the Wannier representation can be diagonalized by a unitary transformation to a Bloch representation

$$\det G^{0\alpha\alpha}_{mm'} = \det \tilde{G}^{0\alpha\alpha}_{ii'} = \prod_i \tilde{G}^{0\alpha\alpha}_{ii} ,$$

where $\tilde{G}^{0\alpha\alpha}_{ii}$ is the ith eigenvalue of $\tilde{G}^{0\alpha\alpha}_{mm'}$ but since $G^{0\alpha\alpha}_{mm'}$ is the Hamiltonian matrix of h with eigenvalues $f_{\alpha q}(k_\perp)$, we have

$$\tilde{G}^{0\alpha\alpha}_{ii'} = \frac{1}{E - E_\alpha(\vec{q}, k_\perp)} \delta_{ii'}$$

so $\det G^{0\alpha\alpha}_{mm'}$ can never be equal to zero for E in the gap.

Despite the results above for vacancy states and surface states, the orbital-removal method may be applicable to problems involving overlayers, heterojunctions, and superlattices. This is due to the fact that in these cases not only is a plane or planes of atoms removed, but they are replaced by another set of atoms having interactions with the other atoms in the crystal and thus the potential is actually changed. The analysis of Sec. V, however, suggests that if accurate quantitative results are to be obtained, the matrix elements of the Hamiltonian between states that are near the removed layers must be adjusted to take account of the change in potential due to the existence of the interface.

VII. ATOM REMOVAL EMPLOYING ORBITAL-REMOVAL TECHNIQUE

In Sec. V we showed that the reason why the orbital-removal method leads to no gap states when a complete set of basis states is employed is because the matrix elements of the Hamiltonian between orbitals not on the removed atom have not been modified to take into account the changes in the potential resulting from the atom removal.

However, it is easy to see by comparing the Hamiltonian matrix with and without the removed atom that the perturbation representing the atom removal (assuming no changes in the potential from redistribution of charge on the other atoms) can be written[5]

$$\underline{V} = \begin{bmatrix} E_0 I & 0 \\ 0 & -V_a \end{bmatrix} , \tag{60}$$

where I has the rank of the number of orbitals on the atom to be removed and V_a represents the matrix elements of the potential of the atom to be removed with all other orbitals in the system and $E_0 \to \infty$.

If V_a is assumed to be appreciable for only some finite set of orbitals then we can write

$$\underline{V} = \begin{bmatrix} V & 0 \\ 0 & 0 \end{bmatrix}$$

so the eigenvalue condition is

$$0 = \det|\underline{I} - \underline{G}^0 \underline{V}| = \det|\underline{I} - G^0_{AA} \underline{V}| , \tag{61}$$

where G^0_{AA} denotes only the matrix elements of G^0 with those orbitals which have nonzero matrix elements with V.

Equation (60) can be written

$$V = U_1 U_2 , \tag{62}$$

where

$$U_1 = \begin{bmatrix} I & 0 \\ 0 & -V_a \end{bmatrix} , \quad U_2 = \begin{bmatrix} E_0 I & 0 \\ 0 & I \end{bmatrix}$$

and substituting Eq. (62) into Eq. (61) yields

$$0 = \det|I - G^0_{AA} U_1 U_2| = \det|U_2^{-1} - G^0_{AA} U_1| . \tag{63}$$

Writing

$$G^0_{AA} = \begin{bmatrix} G^0_{11} & G^0_{12} \\ G^0_{21} & G^0_{22} \end{bmatrix} ,$$

where G_{11}^0 has the same rank as $E_0 I$ and G_{22}^0 has the same rank as V_a and letting $E_0 \to \infty$ we obtain from Eq. (63)

$$\det |U_2^{-1} - G_{AA}^0 U_1| = \begin{vmatrix} G_{11}^0 & G_{12}^0 V_a \\ G_{21}^0 & I + G_{22}^0 V_a \end{vmatrix} = 0 \qquad (64)$$

as the eigenvalue equation. It is trivial to show that in the two-atom case the solution of Eq. (64) gives the exact energy ϵ for the isolated atom 2 when atom 1 is removed.

Equation (64) gives a partial explanation of the results of Ref. 19 where it was found that the energy of the vacancy gap states depended on the choice of tight-binding parameters. Different choices of such parameters are equivalent to different choices of basis states which will affect the values of the elements of the Green's function as well as the elements of V_a. This will lead to different values of the energy eigenvalues when Eq. (1) is employed, but should lead to consistent results if Eq. (64) is employed until convergence is reached, i.e., if the matrix V_a is made progressively larger until the eigenvalue calculated is no longer changing.

We note that as in the case of the orbital-removal method, the atom-removal method as discussed here succeeds in removing from the problem the large matrix elements of the potential associated with the orbitals on the atom to be removed which are required in the usual Koster-Slater treatment of the problem.[9] This in turn leads to the result that the gap states' energies as calculated employing the atom removal should not be as sensitive to the strength of the atomic potential as in the Koster-Slater treatment. Nevertheless, although the matrix elements of V_a are much smaller than the on-site matrix elements of the atomic potential, their inclusion can change the calculated energy of the vacancy states of a semiconductor by a significant fraction of the band gap even if the magnitudes of these matrix elements are only tenths of an electron volt because these contributions to the binding energy can add coherently. This can easily be seen by solving a linear triatomic problem for the vacancy state produced by the removal of the middle atom. If a basis containing only one orbital per atom is chosen the problem can be solved both exactly and in the approximation that the off-diagonal elements of the potential of the removed atom be neglected.

The calculation of the energy eigenvalue for the vacancy state may be further simplified by noting that in Sec. V we found for the two-atom case that if the perturbation matrix V_a was neglected, the derived unperturbed wave function was still exact. The exact energy could then be obtained by calculating the expectation value of the perturbation, $-V_a$, with the unperturbed wave function.

If one assumes that for a finite-band model the wave function calculated by initially neglecting V_a is a good approximation to the vacancy-state wave function, then the approximate energy eigenvalue can be calculated using first-order perturbation theory. It has previously been shown[3] that if a basis $\{\phi_{l,j}\}$ is employed that ensures that the matrix $G_{00jj'}^0$ is diagonal (e.g., an sp^3 basis on each atom for an Si vacancy) then

$$\psi^0(E_\nu) = \sum_\lambda C_\lambda \phi_\lambda , \qquad (65)$$

where $\lambda = (l, j)$ is a composite index and

$$C_\lambda = G_{\lambda 0}^0(E_\nu) \Big(\sum_\lambda |G_{\lambda 0}^0|^2 \Big)^{-1/2} \qquad (66)$$

and

$$C_\lambda = 0 , \quad l = 0 \quad \text{for all } j$$

with the value of j' corresponding to $\lambda' = 0$ in Eq. (66) given by the orbital that makes $G_{00j'j'}^0(E_\nu) = 0$.

The perturbed energy corresponding to including the matrix elements of V_a is then given in first-order perturbation theory as

$$E'_\nu = E_\nu - \frac{\sum_{\lambda\lambda'} G_{\lambda 0}^{0*}(E_\nu)(V_a)_{\lambda\lambda'} G_{\lambda' 0}^0}{\sum_\lambda' |G_{\lambda 0}^0|^2} , \qquad (67)$$

the primed sum indicating all orbitals with $l = 0$ are excluded. It should be noted, however, that whether Eq. (64) or Eq. (67) is employed to calculate the eigenenergy, the matrix elements of V_a are required and these are not given directly from a tight-binding fit to the band structure since such a fit is generally equivalent to parametrizing the matrix elements of the full Hamiltonian and not those of the atomic potentials separately.

Similarly, the inclusion of the matrix elements of the potential of removed atomic planes may be used in the surface-state calculation. This would make the orbital-removal method equivalent to the effect of removing the atoms.

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APPENDIX: GREEN'S-FUNCTION METHOD WITH A NONORTHOGONAL BASIS

Let $\{\phi_\alpha\}$ be a complete set of functions with overlap matrix

$$S_{\alpha\alpha'} = \langle \phi_\alpha | \phi_{\alpha'} \rangle \, .$$

The Schrödinger equation for the energy and eigenfunction of a state in a band gap can be written

$$[\underline{1} - G^0(E)\underline{V}]\psi = 0 \, , \tag{A1}$$

where V is the perturbation potential on the unperturbed Hamiltonian H^0 and $G^0 = (E - H^0)^{-1}$. Since the set $\{\phi_\alpha\}$ is complete we may expand ψ in terms of its elements:

$$\psi = \sum_{\alpha'} C_{\alpha'} \phi_{\alpha'} \, . \tag{A2}$$

Substituting Eq. (A2) into Eq. (A1), multiplying both sides of the resultant equation by ϕ_α^*, and integrating yields

$$\sum_{\alpha'} [S_{\alpha\alpha'} - (G_0 V)_{\alpha\alpha'}] \, C_{\alpha'} = 0 \, . \tag{A3}$$

If the $\{\phi_\alpha\}$ were a complete orthonormal set, then

$$\sum_{\alpha''} |\alpha''\rangle\langle\alpha''| = \underline{1}$$

from which it immediately follows that

$$(G^0 V)_{\alpha\alpha'} = \sum_{\alpha''} G^0_{\alpha\alpha''} V_{\alpha''\alpha'} \, .$$

In general, for a nonorthonormal set $\{\phi_\alpha\}$,

$$\underline{1} = \sum_{\beta,\gamma} |\phi_\gamma\rangle\langle\phi_\beta| (S^{-1})_{\gamma\beta} \, . \tag{A4}$$

Equation (A4) follows from noting that since $\{\phi_\alpha\}$ is complete,

$$|f\rangle = \sum_\alpha f_\alpha |\phi_\alpha\rangle \, .$$

Therefore,

$$\langle \phi_\beta | f \rangle = \sum_\alpha f_\alpha S_{\beta\alpha} \, ,$$

and multiplying by $S^{-1}_{\gamma\beta}$ and summing over β gives

$$\sum_\beta S^{-1}_{\gamma\beta} \langle \phi_\beta | f \rangle = \sum_{\alpha,\beta} f_\alpha S^{-1}_{\gamma\beta} S_{\beta\alpha} = \sum_\alpha f_\alpha \delta_{\gamma\alpha} = f_\gamma \, .$$

Therefore

$$|f\rangle = \sum_\gamma f_\gamma |\phi_\gamma\rangle = \sum_{\gamma,\delta} S^{-1}_{\gamma\beta} |\phi_\gamma\rangle\langle\phi_\beta | f \rangle \, ,$$

from which Eq. (A4) immediately follows.

Using Eq. (A4) we obtain

$$(G^0 V)_{\alpha\alpha'} = \sum_{\beta,\gamma} G^0_{\alpha\beta} (S^{-1})_{\beta\gamma} V_{\gamma\alpha'} \tag{A5}$$

and substituting (A5) into Eq. (A3) and multiplying both sides of Eq. (A3) by $(S^{-1})_{\delta\alpha}$ and summing over α yields

$$\sum_{\alpha'} \Bigl(\delta_{\delta\alpha'} - \sum_{\alpha,\beta,\gamma} S^{-1}_{\delta\alpha} G^0_{\alpha\beta} S^{-1}_{\beta\gamma} V_{\gamma\alpha'} \Bigr) C_{\alpha'} = 0$$

which has nontrivial solutions if and only if

$$\det \Bigl\| \delta_{\alpha\alpha'} - \sum_{\alpha''} \tilde{G}^0_{\alpha\alpha''} V_{\alpha''\alpha'} \Bigr\| = 0 \, , \tag{A6}$$

where

$$\tilde{G}^0_{\alpha\alpha''} \equiv \sum_{\beta,\gamma} S^{-1}_{\alpha\beta} G^0_{\beta\gamma} S^{-1}_{\gamma\alpha''} \, . \tag{A7}$$

We may now proceed in exactly the same manner as given in Ref. 3, i.e., we write for a potential having only a finite number of nonzero matrix elements with the basis states $\{\phi_\alpha\}$,

$$\underline{V} = \begin{bmatrix} V & 0 \\ 0 & 0 \end{bmatrix} \, ,$$

and partition $\underline{\tilde{G}}^0$ so that it is written

$$\underline{\tilde{G}}^0 = \begin{bmatrix} \tilde{G}^0_{11} & \tilde{G}^0_{12} \\ \tilde{G}^0_{21} & \tilde{G}^0_{22} \end{bmatrix} \, .$$

It then follows that

$$\det \| \underline{I} - \underline{\tilde{G}}^0 \underline{V} \| = \det \| \underline{I} - \tilde{G}^0_{11} \underline{V} \| \, . \tag{A8}$$

Again using the arguments of Ref. 3, the eigenvalues of the Hamiltonian for which all matrix elements with orbitals in the atom to be removed are set equal to zero are the same as those obtained by $V = E_0 I$ and letting $E_0 \to \infty$. We obtain from Eqs. (A6) and (A8)

$$\det \| \tilde{G}^0_{11} \| = 0 \, . \tag{A9}$$

[1] S. T. Pantelides, Rev. Mod. Phys. 50, 797 (1978).

[2] J. Pollmann, in *Festkörperprobleme* (*Advances in Solid State Physics*) edited by J. Treusch (Vieweg, Braunschweig, 1980), Vol. XX, p. 117.

[3] J. Bernholc and S. T. Pantelides, Phys. Rev. B 18, 1780 (1978).

[4] J. Pollmann and S. T. Pantelides, Phys. Rev. B 18, 5524 (1978).

[5] J. Pollmann and S. T. Pantelides, Solid State Commun. 30, 621 (1979); Phys. Rev. B 21, 709 (1980).

[6] I. Ivanov and J. Pollmann, Solid State Commun. 32, 869 (1979).

[7] G. F. Koster and J. C. Slater, Phys. Rev. 95, 1167 (1954); 96, 1208 (1954); G. F. Koster, *ibid.* 95, 1436 (1954).

[8] J. Callaway, J. Math. Phys. 5, 783 (1964); Phys. Rev. 154, 515 (1967).

[9] J. Callaway and A. J. Hughes, Phys. Rev. 156, 860 (1967).

[10] J. Callaway and A. J. Hughes, Phys. Rev. 164, 1043 (1967).

[11] N. J. Parada, Phys. Rev. B 3, 2042 (1971); J. Callaway, *ibid.* 3, 2556 (1971); S. P. Singhal, *ibid.* 4, 2497 (1971); 5, 4203 (1972).

[12] M. Lannoo and P. Lenglart, J. Phys. Chem. Solids 30, 2409 (1969).

[13] K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. 32, 1433 (1974); Phys. Rev. B 13, 750 (1976).

[14] E. Kauffer, P. Pecheur, and M. Gerl, J. Phys. C 9, 2319 (1976); Phys. Rev. B 15, 4107 (1977).

[15] S. G. Louie, M. Schluter, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 13, 1654 (1976).

[16] J. Bernholc, N. O. Lipari, and S. T. Pantelides, Phys. Rev. B 21, 3545 (1980).

[17] G. A. Baraff and M. Schluter, Phys. Rev. B 19, 4965 (1979).

[18] D. A. Papaconstantopoulos and E. N. Economou, Phys. Rev. B 6, 2903 (1980).

[19] S. Das Sarma and A. Madhukar, Solid State Commun. (in press).

[20] D. Kalkstein and P. Soven, Surf. Sci. 26, 85 (1971).

[21] A. Haug, *Theoretical Solid State Physics* (Pergamon, New York, 1972), Vol. 2, p. 158.

[22] W. Kohn, Phys. Rev. B 7, 4388 (1973).

[23] P. O. Lowdin, J. Chem. Phys. 18, 365 (1950). S. T. Pantelides and J. Pollmann, J. Vac. Sci. Technol. 16, 1349 (1979).

[24] J. M. Ziman, *Principles of the Theory of Solids*, 2nd ed. (Cambridge University Press, Cambridge, 1972), p. 174.

[25] G. D. Watkins and R. P. Messmer, Phys. Rev. B 7, 2568 (1973).

[26] J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B 10, 5075 (1974); D. J. Chadi and M. L. Cohen, *ibid.* 11, 732 (1975); T. F. Lee and T. C. McGill, J. Phys. C 6, 3438 (1973).