Reduced Hamiltonian method for solving the tight-binding model of interfaces

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A new method is presented for solving the tight-binding equations for interfaces and surfaces. The method can be applied to a variety of interfacial situations including heterojunctions and superlattices in which disruptions occur over many atomic layers away from the interfaces. The method features an expansion of the total wave function in terms of bulk states with complex wave vectors in regions where there is no interfacial disruption, and transfer matrices in regions where there is interfacial disruption. It is simple to implement and computationally more efficient than any previous method of solving the interface tight-binding equations.

I. INTRODUCTION

The empirical tight-binding model has been used extensively to calculate the electronic properties of semiconductor interfaces (surfaces being considered as a special case). Its popularity is due to ease in implementation and its ability to produce realistic band structures (with appropriate choices for the empirical parameters). Typical results from calculations using the model include the energies, orbital characteristics, and decay lengths of interface states, and energy densities of states per layer.[1] Complications in addition to the presence of an interface can be included by suitable modifications of the tight-binding parameters. Examples include defects,[2] compositional grading across interfaces,[3] lattice distortions,[4] and electrostatic potential gradients.[5]

There is one major computational difficulty that must be overcome in the implementation of the method. In general the tight-binding method, or any other method which employs a local orbital basis, produces a Hamiltonian matrix whose dimension increases with the size of the repeated unit cell. The dimension equals the number of orbitals per atom times the number of atoms in the unit cell. The presence of the interface destroys translational symmetry in the perpendicular direction, and thus the unit-cell size becomes infinite. The original solution to this problem for interfaces was to limit the size of the unit cell in the perpendicular direction by either creating a slab with a finite thickness sandwiched between the vacuum (for surfaces or interfaces),[6] or by repeating the slab in the perpendicu-

lar direction to create an artificial supercell (for interfaces).[7] The resulting inaccurate boundary conditions limited the usefulness of the method to physical situations in which the deviation of the electronic properties of interest from bulklike occurred within a few atomic layers away from the interface.

Subsequently, as reviewed in Ref. 1, methods were developed which correctly incorporated the semi-infinite nature of the problem. This was done in a variety of ways, including the use of bulk and surface Green's functions, and/or transfer matrices. A major recent advance was the rediscovery of a simple method for deriving the transfer matrix and its application to the calculation of the surface Green's function.[8]

In this paper we present a new method for solving the tight-binding equations exactly and with the correct boundary conditions. It has three major components: transfer matrices, an expansion in bulk states with complex wave-vector values, and a quickly convergent iterative method for finding energy eigenvalues. The transfer matrices relate the electronic wave function on neighboring atomic planes in non-bulklike regions, i.e., regions in which there is interfacial disruption. Sufficiently far from the interface, the tight-binding Hamiltonian is bulklike and, therefore, the wave function can be expressed as a linear combination of bulk states. In addition to the familiar oscillating Bloch bulk states, the presence of the interface requires that bulk states which grow or decay exponentially away from the interface be included in the expansion. These are bulk states which have complex wave-vector values.

The transfer matrices and complex wave-vector bulk states are then used in the formation of a "reduced" tight-binding Hamiltonian matrix for the system. Diagonalizing it produces the energy eigenvalues and the electronic wave function. As will be shown, however, the transfer matrices and bulk-state expansion are found assuming an initial guess for the energy. Thus, this method must be iterated until the assumed energy agrees with a final energy eigenvalue of the Hamiltonian matrix. Convergence occurs rapidly, typically within five iterations for millivolt precision.

Parts of this method have been either presented or used for calculations on specific systems as follows. Reference 9 describes in detail a general and convenient method for obtaining the bulk states with complex wave vectors within the tight-binding formalism (also for $\vec{k}\cdot\vec{p}$ and pseudopotential formalisms). Reference 10 is a study of the GaAs-AlAs (100) superlattice which uses an expansion of the superlattice wave function in terms of bulk GaAs and AlAs states. It also uses the iterative technique to find the eigenvalues of a reduced Hamiltonian. Reference 5 demonstrates the full method to be described here for two systems: the Si(111)-(2×1) reconstructed surface including second-layer relaxation, and the GaAs-AlAs (100) heterojunction with a doping-induced potential gradient extending over ten GaAs layers.

In this paper we present in detail the reduced Hamiltonian method for solving the tight-binding model of interfaces. The systems of interest here are those which preserve lattice periodicity parallel to the interface. Any interfacial disruption, such as compositional grading, lattice relaxation, potential gradients, or foreign overlayers, are assumed to be uniform parallel to the interface. Perturbations which do break the parallel periodicity, such as point defects, are probably best handled using a hierarchical Green's-function approach.[1] In this context also the transfer matrix[8] or complex wave-vector bulk-state[9,11] concepts provide substantial improvements over conventional methods for obtaining tight-binding Green's functions.

The method will be described in the following three sections. Section II discusses the derivation and application of the transfer matrix. As derived here, the transfer matrix is slightly simpler than that of Ref. 8 in that a smaller fundamental layer is used.[9] Section III briefly describes how the transfer matrix is used to obtain the complex wave-vector bulk states. Section IV describes how the transfer matrices and the complex wave-vector bulk states are used to form the reduced Hamiltonian. Section V describes a refinement to the method needed when the region of interfacial disruption is large.
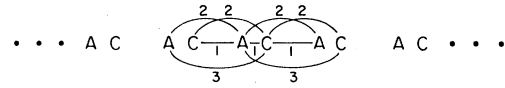

FIG. 1. Zinc-blende (111) atomic planes. A and C represent anion and cation planes, respectively. First-, second-, and third-nearest-neighbor interactions with two of the planes are shown.

II. THE TRANSFER MATRIX

The transfer matrix relates the electronic wave function on different planes parallel to an interface. In fact, if the wave function is known on a small number of adjacent planes (depending on the orientation of the planes and the number of neighbor overlaps included), the transfer matrices give the wave function on all other planes. An explicit form for the transfer matrix is simple to derive.

First, it is necessary to carefully define a "sublayer" ("layers" will be defined subsequently). A sublayer consists of the smallest number of adjacent atomic planes parallel to the interface such that each sublayer interacts (has nonzero tight-binding overlaps) with the same number of other sublayers on each side. Consider, for example, (111) oriented planes in zinc-blende material. Let A represent anion atomic planes and C represent cation atomic planes in Fig. 1. It illustrates the interactions between planes including first-, second-, and third-nearest-neighbor overlaps. Redundant overlaps, such as third-nearest-neighbor interactions between adjacent planes, are not indicated. Note that the distance between planes alternates. If only nearest-neighbor overlaps are considered, each atomic plane is a sublayer, because each only has interactions with adjacent planes on each side (even though the interactions are unequal). Similarly, when second-nearest-neighbor overlaps are included, a sublayer is still a single atomic plane because each plane has overlaps with adjacent and next-to-adjacent planes on each side. Including third-neighbor interactions changes the situation. Now, each anion plane has an interaction with the second cation plane to its right, but not with the second cation plane to its left. The reverse is true for each cation plane. It is, therefore, necessary to define a sublayer as consisting of the closely spaced anion-plane—cation-plane pair. Each sublayer then only has interaction with adjacent sublayers on each side.[12]

The next step is to write the total tight-binding electronic wave function, Ψ as a sum over functions, Ψ_m, on each sublayer:

$$\Psi(\vec{r}) = \sum_m \Psi_m(\vec{r} - md\hat{e}_z) \ . \tag{1}$$

Each Ψ_m is a two-dimensional Bloch function with wave vector $\vec{k}_t$ in the plane of the sublayers, d being the sublayer spacing in the z direction:

$$\Psi_m(\vec{r}) = \sum_{j=1}^{J} C_j(m) \left[\sum_n e^{i\vec{k}_t \cdot \vec{R}_n} \alpha_j(\vec{r} - \vec{R}_n - \vec{R}_j) \right] .$$

(2)

The index n labels the unit cells located by the two-dimensional vector $\vec{R}_n$. The index j labels the J orbitals per unit cell, α_j, centered at $\vec{R}_n + \vec{R}_j$ and contributing with an amplitude $C_j(m)$. The summation within the parentheses can be abbreviated by Ψ_{mj} so that

$$\Psi = \sum_m \sum_j C_j(m) \Psi_{mj} .$$

(3)

The Ψ_{mj}, which will be called "sublayer orbitals," are the most convenient basis in which to derive the transfer matrix. The Ψ_{mj} are not restricted to be

orthonormal.

Schrödinger's equation, $H\Psi = E\Psi$, can be written in matrix form

$$\sum_{m=-M}^{M} \underline{H}_{l,l+m} \underline{C}(l+m) = 0 ,$$

(4)

where $\underline{H}_{lm}$ is the $J \times J$ matrix with elements

$$(\underline{H}_{lm})_{ij} = (\Psi_{li} \mid H - E \mid \Psi_{mj}) ,$$

(5)

and $\underline{C}(m)$ is the column vector of $C_j(m)$'s on the mth sublayer (matrices and column vectors are indicated by underlining). M is the number of sublayers which interact with any given sublayer (on one side). Equation (4) can be solved for $\underline{C}(l+M)$ by multiplying by $(\underline{H}_{l,l+M})^{-1}$:

$$\underline{C}(l+M) = -(\underline{H}_{l,l+M})^{-1}$$
$$\times \sum_{m=-M}^{M-1} \underline{H}_{l,l+m} \underline{C}(l+m) .$$

(6)

Including the trivial equations $\underline{C}(l+m) = \underline{C}(l+m)$ produces the matrix equation

$$\begin{bmatrix} \underline{C}(l-M+1) \\ \underline{C}(l-M+2) \\ \vdots \\ \underline{C}(l+M) \end{bmatrix} = \begin{bmatrix} \underline{0} & \underline{1} & \underline{0} & \underline{0} \\ \underline{0} & \underline{0} & \underline{1} & \underline{0} \\ \underline{0} & \underline{0} & \underline{0} & \cdots & \underline{0} \\ \underline{0} & \underline{0} & \underline{0} & \underline{0} \\ \vdots & \vdots & \vdots & \vdots \\ \underline{0} & \underline{0} & \underline{0} & \cdots & \underline{1} \\ -\underline{H}_{l,l+M}^{-1} \underline{H}_{l,l-M} & -\underline{H}_{l,l+M}^{-1} \underline{H}_{l,l-M+1} & \cdots & -\underline{H}_{l,l+M}^{-1} \underline{H}_{l,l+M-1} \end{bmatrix}$$

$$\times \begin{bmatrix} \underline{C}(l-M) \\ \underline{C}(l-M+1) \\ \vdots \\ \underline{C}(l+M-1) \end{bmatrix} .$$

(7)

The net result is that the coefficients on the $(l+M)$th sublayer (and thus the wave function there) can be found if the coefficients on the previous $2M$ sublayers are known. Similarly, the wave function on sublayers at greater z can be found in terms of the wave function on the original $2M$ sublayers by repeated multiplications by transfer matrices of the same form as in Eq. (7). The same is true for the wave function on sublayers at lesser z.

III. COMPLEX WAVE-VECTOR BULK STATES

The complex wave-vector bulk states are easily obtained once the transfer matrix is known.[13] They result from the analysis of the previous section with the additional fact that for a bulk crystal (no interface) the electronic wave function is a Bloch state in

the z direction also. Thus, if the unit cell in the z direction contains L sublayers, the wave function repeats every L sublayers with a phase factor $e^{ik_z Ld}$. Labeling a given transfer matrix by $\underline{T}_n$, where n is

the sublayer on which the transfer matrix gives the new coefficients $[n = l + M$ in Eq. (7)], and sucessively multiplying the transfer matrices produces the eigenvalue equation

$$
\begin{bmatrix} \underline{C}(l-M+L) \\ \underline{C}(l-M+1+L) \\ \vdots \\ \underline{C}(l+M+L-1) \end{bmatrix} = \underline{T}_{l+M+L-1} \cdots \underline{T}_{l+M+1}\underline{T}_{l+M}
\begin{bmatrix} \underline{C}(l-M) \\ \underline{C}(l-M+1) \\ \vdots \\ \underline{C}(l+M-1) \end{bmatrix} = e^{ik_z Ld}
\begin{bmatrix} \underline{C}(l-M) \\ \underline{C}(l-M+1) \\ \vdots \\ \underline{C}(l+M-1) \end{bmatrix}
\tag{8}
$$

Diagonalizing the matrix resulting from the product of transfer matrices in Eq. (8) produces $J \times 2M$ complex k_z wave vectors and associated propagating (k_z real) and evanescent (k_z complex) bulk states. If L is less than $2M$, a particular bulk state is determined by the first $J \times L$ components of the eigenvector in Eq. (8). The remaining components describe sublayers L over from the first ones and are thus redundant.

IV. THE REDUCED HAMILTONIAN METHOD

A. Heterojunction

This section will describe the use of transfer matrices and bulk-state expansions in forming the reduced Hamiltonian. For definiteness, the system to be considered will consist of a heterojunction in which three regions are clearly identifiable. Region I (see Fig. 2) is the region far enough to the left of the interface so that it is essentially bulklike and can be described by the bulk Hamiltonian of semiconductor A. Similarly, the Hamiltonian of semiconductor B describes region III. Region II is the transition region in which the Hamiltonian is non-bulklike.

The interfacial disruption which characterizes region II is any which can be modeled in terms of tight-binding parameters. For example, an electrostatic potential variation can be represented by a layer-dependent shift in the on-site energy parameter between an orbital and itself.[5] Compositional grading from semiconductor A to B can be represented by a layer-dependent weighted average of the tight-binding parameters which describe A and B.[3] There are also simple rules which allow for the adjustment of the parameters due to lattice relaxation and thus it too can be modeled.[14,15] It is assumed here that the disruption is such that at least one bound state exists. The method to be described is designed to find the energies and wave functions of the bound states.

The single heterojunction system with bound states is a representative system to which the reduced Hamiltonian method can be applied. Other systems, with bound or continuum states, are handled by straightforward modifications. Examples include surfaces with reconstruction,[5] quantum wells (two heterojunctions back to back), and superlattices (repeated heterojunctions).[10]

B. Description of the electronic state

The electronic state is described in one of two ways, depending on the region. A local orbital point of view for the wave function is used in region II where the Hamiltonian is varying, and bulk-state expansions are used in regions I and III where bulk Hamiltonians prevail. Representing the bulk states in regions I and III by F_i^I and F_i^{III}, where i labels the $J \times 2M$ solutions to Eq. (8), the total wave function Ψ can be written

$$
\Psi = \sum_i f_i^I F_i^I , \tag{9a}
$$

in region I, and

$$
\Psi = \sum_i f_i^{III} F_i^{III} , \tag{9b}
$$

in region III. Equation (1) gives the form of Ψ in region II, with the understanding that the Ψ_m can be
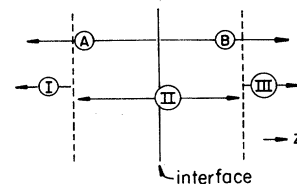

FIG. 2. Heterojunction with semiconductors labeled A and B. The Hamiltonian is bulklike in regions I and III. Region II is the region of interfacial disruption.

related using the transfer matrices [Eq. (7)].

Before proceeding, it is convenient to define a "layer" and to carefully specify to which region

each layer belongs. Iterating Eq. (7) $2M$ times gives the $2M$ coefficients $\underline{C}(l+M)$ to $\underline{C}(l+3M-1)$ in terms of the original $\underline{C}(l-M)$ to $\underline{C}(l+M-1)$:

$$
\begin{bmatrix}
\underline{C}(l+M) \\
\underline{C}(l+M+1) \\
\vdots \\
\underline{C}(l+3M-1)
\end{bmatrix}
= \underline{T}_{l+3M-1} \cdots \underline{T}_{l+M+1} \underline{T}_{l+M}
\begin{bmatrix}
\underline{C}(l-M) \\
\underline{C}(l-M+1) \\
\vdots \\
\underline{C}(l+M-1)
\end{bmatrix} .
\tag{10}
$$

The two column vectors in Eq. (10) now have no sublayers in common and the transfer may be envisioned as being between two adjacent blocks of sublayers. These blocks will from here on simply be called "layers" (equivalent to the principal layers of Ref. 8), and the product of transfer matrices in Eq. (10) will be the new transfer matrix which relates adjacent layers. Thus, Eq. (10) can be written $\underline{C}(l+1)=\underline{T}_{l+1}\underline{C}(l)$ with these new definitions. A layer orbital is the straightforward extension of the sublayer orbital of Eq. (3).

There is a simple relationship between the description of the wave function in terms of bulk states and in terms of layer orbitals. It is obtained by using both descriptions of the wave function on the layer which bounds regions I and II and that between regions II and III. Figure 3 illustrates the heterojunction by representing the layers by circles—filled in region II and open in regions I and III. Layers 0 and $N+1$ are the boundary layers. The wave function on layer $N+1$, for example, can be written using either Eq. (3) or Eq. (9). Equating the two gives

$$
\sum_j C_j(N+1)\Psi_{N+1,j} = \sum_i f_i^{\mathrm{III}}F_i^{\mathrm{III}}(N+1) , \tag{11}
$$

where the $\Psi_{N+1,j}$ are now the layer orbitals on layer $N+1$ and $F_i^{\mathrm{III}}(N+1)$ is the ith bulk-state solution to Eq. (8) evaluated on layer $N+1$. The F_i^{III} can also be expressed in terms of the $\Psi_{N+1,j}$:

$$
F_i^{\mathrm{III}}(N+1) = \sum_m S_{mi}^{\mathrm{III}}\Psi_{N+1,m} , \tag{12}
$$

where the columns of the matrix $\underline{S}^{\mathrm{III}}$ are the eigenvectors of Eq. (8), and the origin of the bulk states in region III is chosen to be on layer $N+1$. Substituting this in Eq. (11) produces the matrix equation

$$
\underline{C}(N+1)=\underline{S}^{\mathrm{III}}\underline{f}^{\mathrm{III}} . \tag{13a}
$$

Similarly,

$$
\underline{C}(0)=\underline{S}^{\mathrm{I}}\underline{f}^{\mathrm{I}} . \tag{13b}
$$

The transfer matrices relate $\underline{C}(0)$ and $\underline{C}(N+1)$, and thus $\underline{f}^{\mathrm{I}}$ and $\underline{f}^{\mathrm{III}}$:

$$
\underline{C}(N+1)=\underline{T}_{N+1}\underline{T}_N \cdots \underline{T}_2\underline{T}_1\underline{C}(0) , \tag{14}
$$

and Eq. (13) imply

$$
\underline{S}^{\mathrm{III}}\underline{f}^{\mathrm{III}}=\underline{U}_{N+1}\underline{S}^{\mathrm{I}}\underline{f}^{\mathrm{I}} , \tag{15}
$$

where $\underline{U}_{N+1}$ represents the product of transfer matrices in Eq. (14). Thus,

$$
\underline{f}^{\mathrm{III}}=(\underline{S}^{\mathrm{III}})^{-1}\underline{U}_{N+1}\underline{S}^{\mathrm{I}}\underline{f}^{\mathrm{I}} . \tag{16}
$$

C. Determinantal solution

As will be shown in this subsection, Eq. (16) already provides a theoretically simple, but numerically impractical, method for finding the allowed energy levels. The condition to be used to determine the energies of bound states is that the wave function in regions I and III remains finite. This implies that the f_i in Eq. (9) are zero for the bulk states which grow exponentially away from the interface. In regions I, these states have $\mathrm{Im}k_z > 0$, and in region III, $\mathrm{Im}k_z < 0$. There are the same number of growing and decaying bulk states in each region.[9]

Let the column vectors $\underline{f}^{\mathrm{I}}$ and $\underline{f}^{\mathrm{III}}$ be organized such that the coefficients of the bulk states with $\mathrm{Im}k_z > 0$ are above those with $\mathrm{Im}k_z < 0$:

$$
\underline{f}^{\mathrm{I}}=
\begin{bmatrix}
\underline{f}_+^{\mathrm{I}} \\
\underline{f}_-^{\mathrm{I}}
\end{bmatrix}, \quad
\underline{f}^{\mathrm{III}}=
\begin{bmatrix}
\underline{f}_+^{\mathrm{III}} \\
\underline{f}_-^{\mathrm{III}}
\end{bmatrix} . \tag{17}
$$

The matrix in Eq. (16) can be written as four square blocks:

$$
\underline{M}=(\underline{S}^{\mathrm{III}})^{-1}\underline{U}_{N+1}\underline{S}^{\mathrm{I}}=
\begin{bmatrix}
\underline{M}_{++} & \underline{M}_{+-} \\
\underline{M}_{-+} & \underline{M}_{--}
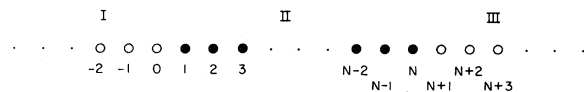\end{bmatrix} , \tag{18}
$$

FIG. 3. Heterojunction with layers numbered. Open circles, regions I or III, filled circles, region II.

which connect the growing and decaying components of f^{I} and f^{III}. Since $\underline{f}^{I}_{+}$ and $\underline{f}^{III}_{-}$ must be zero, Eq. (16) becomes

$$\underline{f}^{III}_{+} = M_{+-}\underline{f}^{I}_{-} \tag{19a}$$

and

$$\underline{0} = \underline{M}_{--}\underline{f}^{I}_{-} \; . \tag{19b}$$

Equation (19b) is satisfied only if $\det(\underline{M}_{--})=0$. Since $\underline{M}$ depends on energy, the energies which cause the determinant to be zero are the allowed levels. Then, Eqs. (19a) and (19b) can be used to find the coefficients of the bulk states and thus the wave function.

The major deficiency of this method is that it is difficult and time consuming to carry out the indicated energy scanning procedure for realistic tight-binding models with several (≥ 4) orbitals per atom. The determinants, which are sums and differences of very large numbers, are ill-behaved numerically using conventional techniques. An alternative is to diagonalize $\underline{M}_{--}$ and search for eigenvalues equal to zero. This is substantially more time consuming than evaluating determinants, but it is feasible. A better strategy is provided by the reduced Hamiltonian method. It avoids energy scans altogether. Instead, an iterative procedure is introduced which produces successively more accurate energy levels.

If only continuum states are of interest, Eq. (16) is sufficient and it is a convenient route to follow to obtain the total wave function. The reduced Hamiltonian method, in fact, cannot be used, as shown shortly. Continuum states are distinguished from bound states in that they include bulk states in regions I and III with purely real values of k_z. The amplitudes of incoming bulk states with real k_z ($k_z \geq 0$ in region I, $k_z \leq 0$ in region III) must be specified and the amplitudes of the outgoing bulk states found from Eq. (16). Let $\underline{f}^{I}_{+}$ and $\underline{f}^{III}_{-}$ include the amplitudes of the incoming states. Thus, $\underline{f}^{III}_{+}$ and $\underline{f}^{I}_{-}$ remain to be found. Using Eqs. (17) and (18) in Eq. (16) produces

$$\underline{f}^{I}_{-} = (\underline{M}_{--})^{-1}(\underline{f}^{III}_{-} - \underline{M}_{-+}\underline{f}^{I}_{+}) \tag{20a}$$

and

$$\underline{f}^{III}_{+} = M_{+-}\underline{f}^{I}_{-} + \underline{M}_{++}\underline{f}^{I}_{+} \; . \tag{20b}$$

D. Reduced Hamiltonian

The goal here is to construct a Hamiltonian matrix using the transfer matrices and the bulk states. Its eigenvalue closest to the energy assumed in its construction will then be the next approximation to the bound-state electron energy. A new Hamiltoni-

an is constructed using this energy, and the process is repeated until convergence is achieved.

The basis functions of the Hamiltonian matrix will now be described. On the lth layer the ith basis function, ϕ_i, can be written

$$\phi_i(l) = \sum_j C^i_j(l)\Psi_{lj} \; , \tag{21}$$

where Ψ_{lj} is the jth layer orbital on the lth layer. Let us choose the ϕ_i so that on layer 1 (see Fig. 3) the $C^i_j(l)$ have the simple form $C^i_j(1)=\delta_{ij}$. The $C^i_j(l)$, and thus ϕ_i, on other layers within region II can then be found by using the transfer matrices:

$$\underline{C}^i(l) = \underline{T}_l\underline{T}_{l-1}\cdots\underline{T}_2\underline{C}^i(1) \; . \tag{22}$$

On layers within regions I and III, ϕ_i is expressed as linear combinations of the bulk solutions F^{I}_j and F^{III}_j. The linear combination is not, however, given by Eq. (13) (after multiplying by $(\underline{S}^{III})^{-1}$ or $(\underline{S}^{I})^{-1}$) as might be expected. The reason is that this would introduce bulk states which do not decay exponentially away from the interface. Thus, some Hamiltonian matrix elements would be infinite. Since unbound, continuum states necessarily contain bulk states which do not decay, the infinite matrix elements prohibit the use of the reduced Hamiltonian method for them, as mentioned in the preceding section.

To remedy this for bound states, the ϕ_i in regions I and III are *defined* to be the linear combinations of bulk states which result from Eq. (13), but with the exponentially growing bulk states explicitly omitted. Then, in regions I or III,

$$\phi_i(l) = \sum_j \bar{f}^{I,III}_{ij}F^{I,III}_j(l) \tag{23}$$

with

$$\underline{\bar{f}}^{I}_{i} = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ \underline{f}^{I}_{i-} \end{bmatrix} \; , \quad \underline{\bar{f}}^{III}_{i} = \begin{bmatrix} \underline{f}^{III}_{i+} \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$

where the $F^{I,III}_j$ are the bulk states in regions I or III, and $\underline{f}^{I}_{i-}$ and $\underline{f}^{III}_{i+}$ are column vectors defined similarly to those in Eq. (17).

With the ϕ_i known on all layers, it is a simple matter to calculate the Hamiltonian matrix. Since the ϕ_i are not orthonormal, it is also necessary to calculate the overlap between them. The overlap matrix is given by

$$o_{ij} = (\phi_i \mid \phi_j)$$

$$= \sum_{l=-\infty}^{\infty} \sum_{m,n} \sum_{k=-1,0,1} [C_m^i(l)]^* C_n^j(l+k)$$

$$\times (\Psi_{lm} \mid \Psi_{l+k,n}) \qquad (24a)$$

and the Hamiltonian matrix by

$$h_{ij} = (\phi_i \mid H \mid \phi_j)$$

$$= \sum_{l=-\infty}^{\infty} \sum_{m,n} \sum_{k=-1,0,1} [C_m^i(l)]^* C_n^j(l+k)$$

$$\times (\Psi_{lm} \mid H \mid \Psi_{l+k,n}) . \qquad (24b)$$

The Appendix contains details concerning the evaluation of these sums.

The Schmidt orthogonalization procedure is then used to find orthonormal combinations $\bar{\phi}_i$ of the original ϕ_i,

$$\bar{\phi}_i = \sum_n G_{ni} \phi_n , \qquad (25)$$

and the transformed Hamiltonian matrix

$$\underline{\bar{h}} = \underline{G}^\dagger \underline{h} \underline{G} . \qquad (26)$$

Diagonalizing $\underline{\bar{h}}$ produces the energy eigenvalues, one of which is chosen for the recalculation of the transfer matrices and bulk states. A new $\underline{\bar{h}}$ is found, and the whole process is repeated until an energy eigenvalue coincides with the input energy from the previous iteration.

An example of the rapid convergence of this method is provided by the calculation reported in Ref. 5. There, the bound-state energy of an electron in a GaAs-AlAs heterojunction was found. The electron was confined by the large GaAs-AlAs conduction-band discontinuity on one side and a superimposed, linearly increasing electrostatic potential (14 meV/Å) over ten GaAs layers on the other. A bound-state energy of 0.374 eV above the bottom of the triangular potential well was found. Starting with an initial guess slightly above the well bottom (0.001 eV), the relevant eigenvalues of $\underline{\bar{h}}$ produced in successive iterations were 0.255, 0.101, 0.366, 0.381, 0.377, 0.374, and 0.374. Thus, seven iterations were needed in this case. Physical intuition and experience reduce the number of iterations substantially in most cases.

Unfortunately, it cannot be guaranteed that all bound-state energies in a given system will be detected starting from arbitrary initial-energy guesses. If the initial guess is sufficiently far off from a specific bound-state energy, the iteration procedure may converge to another bound state or to the continuum.

To ensure that all bound states are found, it is necessary to survey a range of initial energies. Again, experience as well as simple models of the system of interest provide guides in finding the bound-state energies.

V. REFINEMENT FOR MANY-LAYER TRANSFERS

The procedure outlined in the preceding sections is limited in the number of disrupted layers that can be included. The limitation is caused by the finite precision of the digital computer. The problem occurs in Eq. (22) in the repeated multiplication of transfer matrices. Each transfer matrix in Eq. (22) has eigenvalues, λ_i, that are on the order of the exponential eigenvalues in Eq. (8). The eigenvalues of the product of n transfer matrices will therefore be on the order of λ_i^n. Since some of the $|\lambda_i|$ are less than 1 and some greater than 1 (for $\mathrm{Im}k_z$ greater than and less than 0, respectively) the repeated multiplication in Eq. (22) will eventually cause information concerning the smaller eigenvalues, and their respective eigenvectors, to be lost. For example, the maximum number of layers that could be transferred over in Ref. 5 was fifteen (using double precision with an IBM 370 computer). The potential gradient variation was thus restricted to this number of layers.

There is a simple refinement that can extend the method to a larger number of layers. It consists of changing the basis set from the ϕ_i basis of Eq. (21) to a basis set designed to counteract the appearance of very large and very small eigenvalues in the product of transfer matrices in Eq. (22).

The new basis set is constructed as follows. Let N' be the number of layers which can be transferred over without a loss of precision. The product of the N' transfer matrices is diagonalized and its eigenvectors found. The eigenvectors are used to define new basis states ϕ_j':

$$\phi_j' = \sum_i B_{ij} \phi_i , \qquad (27)$$

where B_{ij} is the ith component of the jth eigenvector. The normalization of the jth eigenvector is chosen to be $1/|\gamma_j|^2$, where γ_j is the jth eigenvalue. This ensures that after transferring the basis states over N' layers, the amplitudes on layer N' will be on the order of one. The Hamiltonian in the new basis is then $\underline{B}^\dagger \underline{h} \underline{B}$ and the new overlap matrix is $\underline{B}^\dagger \underline{o} \underline{B}$. In practice, this has been found to be an effective technique for extending the number of layers which can be transferred over. Even larger numbers of layers can be accommodated by repeating the above procedure each time precision is about to be lost.

VI. CONCLUSIONS

A new method for solving the tight-binding model of interfaces has been developed. It is easily implemented and computationally efficient. Time-consuming diagonalizations of large matrices, as in slab or supercell calculations, or integrals over Brillouin zones, as in conventional Green's-function methods, are avoided. The computation time involved in the calculation grows only linearly with the number of disrupted layers. Bound-state energies of typical systems can be computed quickly in the time-sharing mode of moderate-sized computers. In addition, the ability to present the total wave function in the bulklike regions (regions I and III) as linear combinations of bulk states facilitates the understanding of the relationship between bulk and interface electronic structures.

The variety of problems to which the tight-binding model can be applied is greatly extended. A large range of interface systems with two-dimensional translational symmetry can be investigated. The main restriction is that the system must be bounded on each side by either the vacuum or by a bulk material with no disruption (e.g., an electrostatic potential gradient, as in Ref. 5, must eventually become constant far enough away from the interface) or periodic. A few examples of systems of current interest which are ideally suited for treatment by the reduced Hamiltonian method include superlattices, quantum wells, two-dimensional electronic systems at heterojunctions, and the determination of bound states and of tunneling properties in multicomponent heterojunctions. In addition, the effects of reconstruction, electrostatic potentials, compositional grading, or other features which can be modeled within the tight-binding formalism can be included.

APPENDIX

This section presents a summary of the manipulations needed to evaluate the sums over layers in Eq. (24). It is assumed that the matrix elements between layer orbitals in Eqs. (24a) and (24b), with and without the Hamiltonian, are similar in that there are the same type and number of nonzero interactions. Thus the procedure is the same for both sums. The sums can be split into three parts, in regions I, II, and III. The contributions from the two boundaries between regions also need special analyses.

First, the sum over region II is done. Let $\underline{W}_m$ represent the matrix of Hamiltonian matrix elements between layer orbitals within the mth layer, and V_m the matrix between orbitals on the mth layer and the $(m+1)$th layer. Then, the contribution from region II to $\underline{h}_{ij}$ can be written

$$\underline{h}_{ij}^{\mathrm{II}} = \sum_{m=1}^{N} \underline{C}^{i\dagger}(m)\underline{W}_m \underline{C}^j(m)$$
$$+ \sum_{m=1}^{N-1} [\underline{C}^{i\dagger}(m)\underline{V}_m \underline{C}^j(m+1)$$
$$+ \underline{C}^{i\dagger}(m+1)\underline{V}_m^{\dagger} \underline{C}^j(m)] . \qquad \text{(A1)}$$

In practice, this sum is done incrementally, with $\underline{C}^i(m+1)$ found from the preceding $\underline{C}^i(m)$ by multiplying by $\underline{T}_{m+1}$.

Note that the sum omits the interaction between layers N and $N+1$. This is because $\phi_i(N+1)$ is expressed as a sum of bulk states without the exponentially growing ones [Eq. (23)]. Thus $\underline{C}^i(N+1)$ is not obtained from $\underline{C}^i(N)$ by multiplying by $\underline{T}_{N+1}$. By introducing the projection operator, $\underline{P}^{\mathrm{III}}$, which projects out the growing bulk states, $\underline{C}^i(N+1)$ can be written

$$\underline{C}^i(N+1)=\underline{S}^{\mathrm{III}}\underline{P}^{\mathrm{III}}(\underline{S}^{\mathrm{III}})^{-1}\underline{T}_{N+1}\underline{C}^i(N) . \qquad \text{(A2)}$$

Here, $\underline{T}_{N+1}$ acting on $\underline{C}^i(N)$ produces $\underline{C}^i(N+1)$ as if the growing bulk states were included, $(\underline{S}^{\mathrm{III}})^{-1}$ transforms this into the bulk-state basis [see Eq. (13)], $\underline{P}^{\mathrm{III}}$ projects out the growing states, and $\underline{S}^{\mathrm{III}}$ transforms back into the layer orbital basis. $\underline{P}^{\mathrm{III}}$ has the simple form

$$\underline{P}^{\mathrm{III}}= \begin{bmatrix} \underline{1} & \underline{0} \\ \underline{0} & \underline{0} \end{bmatrix} , \qquad \text{(A3)}$$

where each element is actually a block matrix which acts on the growing or decaying bulk-state coefficients organized such that the decaying states are on top [as in Eq. (17)]. The contribution to h from this interaction can be written $\underline{h}^{\mathrm{II,III}}$ and has the same form as a term in the second sum in Eq. (A1) with $m=N$ and with $\underline{C}^i(N+1)$ given by Eq. (A2).

The interaction between layers 0 and 1 have the same complication. $\underline{C}^i(0)$ must contain no exponentially growing states to the left. It can be written

$$\underline{C}^i(0)=\underline{S}^{\mathrm{I}}\underline{P}^{\mathrm{I}}(\underline{S}^{\mathrm{I}})^{-1}\underline{T}_1^{-1}\underline{C}^i(1) , \qquad \text{(A4)}$$

with

$$\underline{P}^{\mathrm{I}}= \begin{bmatrix} \underline{0} & \underline{0} \\ \underline{0} & \underline{1} \end{bmatrix} .$$

This is similar to Eq. (A2), except that $\underline{T}_1^{-1}$ transfers from $\underline{C}^i(1)$ to $\underline{C}^i(0)$ instead of $\underline{T}_{N+1}$ transferring from $\underline{C}^i(N)$ to $\underline{C}^i(N+1)$. Its contribution to $\underline{h}$ can be written $\underline{h}^{\mathrm{I,II}}$ and it also has the same form as a term in the second sum in Eq. (A1), but with $m=0$.

All that remains is to calculate the contributions from regions I and III. This is easily done in the bulk-state basis, and then transformed back into the ϕ_i basis. Since the Hamiltonian is constant within region I (or III), the Hamiltonian matrix elements between two bulk states, F_i^{I} and F_j^{I}, can be written

$$h'_{ij}=(\underline{S}_i^{\mathrm{I}})^{\dagger}(e^{-ik_j a}\underline{Q}+\underline{R}+e^{ik_i^* a}\underline{Q}^{\dagger})$$
$$\times(\underline{S}_j^{\mathrm{I}})(1-e^{-i(k_j-k_i^*)a})^{-1} . \qquad (A5)$$

Here, (S_i^{I}) is the ith column of the matrix $\underline{S}^{\mathrm{I}}$, $\underline{R}$ is similar to $\underline{W}_m$ except that it represents interactions between layer orbitals within a unit cell instead of within a layer, $\underline{Q}$ represents interactions between a unit cell and the one to its left, and k_i and k_j are the perpendicular complex wave vectors of the ith and jth bulk states. The sum over unit cells separated by the distance a forms a geometric series of exponential terms whose sum is the last factor in Eq. (A5). This equation can be further simplified by using

Schrödinger's equation for the bulk material to eliminate $\underline{Q}$ in terms of R and exponentials, if desired. Transforming to the ϕ_i basis gives

$$\underline{h}^{\mathrm{I}}=[\underline{P}^{\mathrm{I}}(\underline{S}^{\mathrm{I}})^{-1}\underline{T}_1^{-1}]^{\dagger}\underline{h}'\underline{P}^{\mathrm{I}}(\underline{S}^{\mathrm{I}})^{-1}\underline{T}_1^{-1} , \qquad (A6)$$

with similar reasoning that lead to Eq. (A4).

Region III is dealt with similarly. The formula for $\underline{h}''$, the Hamiltonian between bulk states in region III, is similar so that in Eq. (A5) with k_i and k_j replaced by $-k_i$ and $-k_j$, and with $\underline{Q}$ replaced by $\underline{Q}^{\dagger}$ (left interactions replaced by right ones). Then, the transformations to the ϕ_i basis can be accomplished by

$$\underline{h}^{\mathrm{III}}=[\underline{P}^{\mathrm{III}}(\underline{S}^{\mathrm{III}})^{-1}\underline{U}'_{N+1}]^{\dagger}\underline{h}''\underline{P}^{\mathrm{III}}(\underline{S}^{\mathrm{III}})^{-1}\underline{U}'_{N+1} , \qquad (A7)$$

where $\underline{U}'_{N+1}$ connects layers 1 and $N+1$:

$$\underline{U}'_{N+1}=\underline{T}_{N+1}\underline{T}_N\cdots\underline{T}_2 . \qquad (A8)$$

Finally, the total Hamiltonian in the ϕ_i basis is written

$$\underline{h}=\underline{h}^{\mathrm{I}}+\underline{h}^{\mathrm{I,II}}+\underline{h}^{\mathrm{II}}+\underline{h}^{\mathrm{II,III}}+\underline{h}^{\mathrm{III}} , \qquad (A9)$$

and similarly for the overlap matrix [Eq. (24a)].

[1]J. Pollmann, in Festkörperprobleme, Advances in Solid State Physics, edited by J. Treusch (Vieweg, Braunschweig, 1980), Vol. 20, p. 117.

[2]M. S. Daw and D. L. Smith, Phys. Rev. B 20, 5150 (1979).

[3]G. C. Osbourn, J. Vac. Sci. Technol. 17, 1104 (1980).

[4]D. J. Chadi, J. Vac. Sci. Technol. 15, 631 (1978).

[5]Y. C. Chang and J. N. Schulman, J. Vac. Sci. Technol. 21, 540 (1982).

[6]K. Hirabayashi, J. Phys. Soc. Jpn. 27, 1475 (1969).

[7]J. N. Schulman and T. C. McGill, Phys. Rev. B 19, 6341 (1979).

[8]D. H. Lee and J. D. Joannopoulos, Phys. Rev. B 23, 4988 (1981); B 23, 4997 (1981). Also, see J. Vac. Sci. Technol. 21, 351 (1982) by the same authors for a method related to the reduced Hamiltonian method.

[9]Y. C. Chang and J. N. Schulman, Phys. Rev. B 25, 3975 (1982).

[10]J. N. Schulman and Y. C. Chang, Phys. Rev. B 24, 4445 (1981).

[11]R. E. Allen, Phys. Rev. B 19, 917 (1979); B 20, 1454 (1979).

[12]A principal layer, as defined in Ref. 8, would consist of the two closely spaced anion-plane—cation-plane pair with either second- or third-nearest-neighbor interactions included.

[13]The derivation given here is equivalent to, but simpler than, the derivation in Ref. 9. See Ref. 9 and Y. C. Chang, Phys. Rev. B 25, 605 (1982) for detailed discussions of complex band structures.

[14]W. A. Harrison, Electronic Structure and the Properties of Solids (Freeman, San Francisco, 1980), p. 48.

[15]G. C. Osbourn, J. Appl. Phys. 53, 1586 (1982).