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Difference-equation approach to the electronic structures of surfaces, interfaces, and superlattices

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A method for calculating the electronic structure of surfaces, interfaces, quantum wells, and superlattices in the tight-binding (TB) theory is presented. This method fully takes advantage of the repeated layer structure of these systems. The TB equations in the repeated regions are solved in terms of the characteristic solutions, and the final problem is reduced to a small set of boundary equations. This approach applies to both the eigenvalue problem and Green's functions with various boundary conditions. A one-dimensional model is used to display the mathematical structure. Several analytical results are derived to illustrate the application of the method. The theory is then extended to three dimensions with multiple orbitals. The possibility of using this method for a first-principles self-consistent calculation is also considered.

I. INTRODUCTION

Recently, considerable attention has been paid to the study of surfaces, interfaces, quantum wells, and superlattices because of their relevance to modern device and materials applications.[1,2] Although the electronic-structure calculations for these systems have progressed very rapidly,[2-16] they have not been carried out as rigorously as the conventional bulk-band calculations. The difficulty arises from the fact that superlattices in general have too large unit cells, and the other structures do not possess the full crystal periodicity. However, all these structures contain repeated layers inside a large portion of the bulk. One should be able to take advantage of this special feature. The main purpose of this paper is to show how this special feature is utilized in the electronic-structure calculation using the tight-binding (TB) theory. The equations for the eigenvalue problem and the Green's functions in the TB theory are reduced to difference equations coupling the layers. These difference equations in the repeated regions are solved in terms of the characteristic solutions, and the remaining problem is to match these solutions on the boundaries.

Although the present method is related to other previous TB approaches to these structures,[7-10] the mathematical structure of the difference equations, the systematic solutions, and the capability of this method for dealing with both the eigenvalue problem and the Green's functions with various boundary conditions have not been uniformly and clearly described before.

To introduce the idea, we start with a one-dimensional model in Sec. II. The methods for calculating the band energies and the Green's functions for the bulk, surface, interface, and superlattice are described. Several analytical results are derived to demonstrate the usefulness of this method. Section III then generalizes the method to three dimensions with multiple orbitals. Section IV contains a summary and discussion. The possibility of applying this method to a self-consistent first-principles calculation is also considered.

II. ONE-DIMENSIONAL MODEL

The basic idea of the difference-equation approach can be best illustrated via the following one-dimensional model. Once the results of this model are understood, it is straightforward to generalize to three dimensions.

A. Eigenvalue problems

Consider the following one-dimensional chain consisting of S segments of A and B atoms sitting on N lattice sites labeled by the numbers:

$$\begin{array}{l} A\,A\,A\,A\,A\,A\,A\,A\,B\,B\,B\,B\,A\,A\,A\,A\,A\,B\,B\,B\,B\,B\,B\,B\cdots\cdots A \\ 1\;2\;3\;4\;5\;6\;7\;8\;9\cdots\cdots n\cdots\cdots\cdots\cdots\cdots\cdots\cdots N\,. \end{array}$$

The tight-binding model to be used assumes one local orbital per atom, denoted by $|n\rangle$ for the orbital at the nth site, and that these local orbitals are orthonormal: $\langle n|m\rangle=\delta_{nm}$. It further assumes that the only nonzero matrix elements of the one-electron Hamiltonian are the term values $\varepsilon_n=\langle n|H|n\rangle$ and the first-neighbor interactions $t_{nm}=\langle n|H|m\rangle$ for $m=n+1$ and $m=n-1$. Let the values of ε_n be ε_A or ε_B depending on whether an A

or B atom is located at the nth site. Similarly, let t_{nm} be t_A, t_B, or t, respectively, for the A-A, B-B, and A-B interactions. The eigenvalue problem, $(H-E)|\psi\rangle=0$, becomes the following N coupled difference equations, if $|\psi\rangle$ is expanded as $\sum_n c_n|n\rangle$:

$$t_{nn-1}C_{n-1}+(\varepsilon_n-E)C_n+t_{nn+1}C_{n+1}=0 \ . \tag{1}$$

We note that Eq. (1) repeats itself, if n is not any of the boundary sites. The general solution of this second-order difference equation inside a segment, for example, an A segment, takes the form

$$c_n=a_1r_1^n+a_2r_2^n \ , \tag{2}$$

where a_1 and a_2 are arbitrary constants and r_1 and r_2 are the two roots of the following characteristic equation:

$$t_A+(\varepsilon_A-E)r+t_Ar^2=0 \ . \tag{3}$$

Note that $r_1r_2=1$ in this model. If $r_1=r_2=r$, then the solution becomes $c_n=(a_1+a_2n)r^n$. After the general solutions of the form of Eq. (2) are substituted into Eq. (1), the N coupled equations are reduced to $2S$ boundary equations, where S is the total number of segments.

For a pure crystal, if the Born–von Kármán periodic boundary condition is applied, the two boundary equations are

$$t_Ac_N+(\varepsilon_A-E)c_1+t_Ac_2=0 \ , \tag{4}$$

$$t_Ac_{N-1}+(\varepsilon_A-E)c_N+t_Ac_1=0 \ . \tag{5}$$

After Eqs. (2) and (3) are used in Eqs. (4) and (5), one finds $r_1^N=1$ or $r_2^N=1$ for nontrivial solutions. If we set $r_1=e^{ik\alpha}$, where α is the lattice constant, we immediately obtain the familiar quantization for the wave vector: $k=2m\pi/Na$ with m being integers. Then the band energies are given by $E(k)=\varepsilon_A+2t_A\cos(ka)$.

The eigenvalue problem for a slab with surfaces differs from that for a bulk pure crystal only in the boundary equations. Consider a simple case where the surface effect only causes a change in the term value on the surface sites. The two boundary equations then become

$$t_Ac_2+(\varepsilon_A+\Delta-E)c_1=0 \ , \tag{6}$$

$$(\varepsilon_A+\Delta-E)c_N+t_Ac_{N-1}=0 \ , \tag{7}$$

where Δ is the difference between the surface and bulk term values. If r_1 is set to be $e^{i\theta}$, then Eqs. (6) and (7) reduce to

$$e^{i(N+1)\theta}(\Delta e^{-i\theta}-t_A)^2-e^{-i(N+1)\theta}(\Delta e^{i\theta}-t_A)^2=0 \ . \tag{8}$$

With the presence of Δ, localized surface states or the Tamm states[17] may be allowed, depending on the strength of Δ. These surface states have their wave functions decaying exponentially from the surface into the bulk. For these localized states to exist, θ must have a finite imaginary part. For the case $|e^{i\theta}|>1$, the second term of Eq. (8) becomes negligible, and the bound-state energy is determined by $\Delta e^{-i\theta}-t_A=0$, or $e^{i\theta}=\Delta/t_A$, which requires $|\Delta|>|t_A|$. Similarly, if $|e^{i\theta}|<1$, the first term of Eq. (8) can be ignored, then $e^{i\theta}=t_A/\Delta$, which again requires $|\Delta|>|t_A|$. In either case, if $|\Delta|>|t_A|$ is satisfied, the surface-state energy is given by $E_s=\varepsilon_A+\Delta+t_A^2/\Delta$. All the other solutions correspond to the extended states with energies lying within the band of the pure crystal, i.e., $|E-\varepsilon_A|<2|t_A|$. These extended-state energies are still given by $E=\varepsilon_A+2t_A\cos\theta$, but the quantum number θ is now determined by Eq. (8).

The interface problem corresponds to the case with two different segments. After the general solutions are matched on the boundaries, four coupled linear equations are obtained, from which the eigenenergies and eigenkets can be solved. For a quantum well, two more boundary equations are needed.

For a superlattice, consider a chain consisting of repeated double segments of n A atoms and m B atoms. In other words, the superlattice has a periodicity of $D=(n+m)a$. For the eigenvalue problem, it is most convenient to use the Born–von Kármán boundary condition or equivalently the Bloch theorem for the superlattice, i.e., $c_0=c_{n+m}e^{-iKD}$ and $c_{n+m+1}=c_1e^{iKD}$, where K is a superlattice wave vector. Then only four boundary equations are required:

$$te^{-iKD}c_{n+m}+(\varepsilon_A-E)c_1+t_Ac_2=0 \ , \tag{9}$$

$$t_Ac_{n-1}+(\varepsilon_A-E)c_n+tc_{n+1}=0 \ , \tag{10}$$

$$tc_n+(\varepsilon_B-E)c_{n+1}+t_Bc_{n+2}=0 \ , \tag{11}$$

$$t_Bc_{n+m-1}+(\varepsilon_B-E)c_{n+m}+te^{iKD}c_1=0 \ . \tag{12}$$

After the general solution of Eq. (2) for the A segment for c_j with j from 1 to n and a similar form for the B segment for c_{n+j} with j from 1 to m are used, Eqs. (9)–(12) reduce to four coupled homogeneous linear equations.

B. Green's functions

The one-electron Green's function, $G(E)=(E-H)^{-1}$, is useful for calculating many electronic properties, e.g., the density of states and the electronic density, of a solid without actually computing the eigenenergies and eigenfunctions. It will be shown below that the Green's functions for the layer structures can be obtained directly from the solutions to the difference equations without performing the Brillouin-zone intergration usually employed in such calculations. We shall consider pure crystals first, then surfaces and interfaces.

The Green's function by definition satisfies the following equation:

$$(H-E)G=-I \ , \tag{13}$$

where I is the identity operator. For a pure A chain, taking the site-diagonal (the nn) matrix element of Eq. (13) yields

$$t_Ag_{n-1n}+(\varepsilon_A-E)g_{nn}+t_Ag_{n+1n}=-1 \ . \tag{14}$$

Taking the off-diagonal matrix element (the mn element for $m\neq n$) gives

$$t_Ag_{m-1n}+(\varepsilon_A-E)g_{mn}+t_Ag_{m+1n}=0 \ . \tag{15}$$

In the above equations, g_{mn} is $\langle m|G(E)|n\rangle$. Note that g_{mn} in Eq. (15) as a function of m for a given n obeys the same equation as Eq. (1), so the general solution can be written as $g_{mn}=a_1 r_1^{m-n}+a_2 r_2^{m-n}$. However, different a_1 and a_2 are needed, depending on whether $m>n$ or $m<n$. In this connection, we note that the solution for the Green's functions in the present difference-equation form is similar to that in the usual differential-equation form: we match the right-side Green's function g_{mn}^R ($m\geq n$) on the right boundary and the left-side Green's function g_{mn}^L ($m\leq n$) on the left boundary, and then the two Green's functions are matched at $m=n$. Finally, the discontinuity condition, Eq. (14) in the present case, determines the final solution. In doing so, we also keep in mind that the energy for the Green's function has an infinitesimal imaginary part, which we choose to be $E+i\delta$, so the two characteristic roots can always be chosen such that $|r_1|>1$ and $|r_2|<1$. For a bulk crystal with a large N, g_{mn} should approach zero as m approaches both extreme ends while n lies in the middle of the bulk. To satisfy this condition, we require that $g_{mn}^R=a_2 r_2^{m-n}$ and $g_{mn}^L=a_1 r_1^{m-n}$. The condition $g_{nn}^R=g_{nn}^L=g_{nn}$ implies that $g_{nn}=a_1=a_2$, so that

$$g_{mn}^R=g_{nn} r_2^{m-n} \ , \tag{16}$$

and

$$g_{mn}^L=g_{nn} r_1^{m-n} \ . \tag{17}$$

Substituting these two results into Eq. (14), one obtains

$$g_{nn}=(E+i\delta-\varepsilon_A-t_A/r_1-t_A r_2)^{-1} \ . \tag{18}$$

Using the fact that $r_2=1/r_1$ and the explicit forms of r_2, we find

$$g_{nn}=\begin{cases}-1/[(E-\varepsilon_A)^2-4t_A^2]^{1/2} & \text{for } E-\varepsilon_A<-2|t_A| \\ -i/[4t_A^2-(E-\varepsilon_A)^2]^{1/2} & \text{for } |E-\varepsilon_A|<2|t_A| \\ 1/[(E-\varepsilon_A)^2-4t_A^2]^{1/2} & \text{for } E-\varepsilon_A>2|t_a| .\end{cases} \tag{19}$$

With g_{nn} available, all the off-diagonal Green's function can also be evaluated explicitly from Eqs. (16) and (17). The density of states per atom given by $\rho(E)=-\operatorname{Im}g_{nn}/\pi$ is also readily available from Eq. (19).

The above results can be easily extended to surfaces. Assume that the site index $n=1$ corresponds to the surface, then Eq. (14) becomes

$$(\varepsilon_A+\Delta-E)g_{11}+t_A g_{21}=-1 \ . \tag{20}$$

Equation (16) still holds, so $g_{m1}=g_{11}r_2^{m-1}$. Then Eq. (20) yields

$$g_{11}=(E+io-\varepsilon_A-\Delta-t_A r_2)^{-1} \ , \tag{21}$$

which has the following explicit forms:

$$g_{11}=\begin{cases}2/\{E+i\delta-\varepsilon_A-2\Delta-[(E-\varepsilon_A)^2-4t_A^2]^{1/2}\} & \text{for } E-\varepsilon_A<-2|t_A| \\ 2/\{E-\varepsilon_A-2\Delta-i[4t_A^2-(E-\varepsilon_A)^2]^{1/2}\} & \text{for } |E-\varepsilon_A|<2|t_A| \\ 2/\{E+i\delta-\varepsilon_A-2\Delta+[(E-\varepsilon_A)^2-4t_A^2-4t_A^2]^{1/2}\} & \text{for } E-\varepsilon_A>2|t_A| .\end{cases} \tag{22}$$

The contribution from the surface to the density of states, $\rho_1(E)=-\operatorname{Im}g_{11}/\pi$, can now be evaluated explicitly. The bound surface-state energies can also be found from Eq. (22) by setting the denominator in the first or the third line of this equation to zero, which yields $E_b=\varepsilon_A+\Delta+t_A^2/\Delta$ provided that $|\Delta|>|t_A|$, a result already obtained based on the eigenvalue problem. The other Green's functions, such as g_{22} and g_{33}, etc., can be obtained in a similar fashion.

To obtain the interface Green's function, one can either modify the above procedure slightly or use Dyson's equation. To digress onto this point, let us evaluate the interface Green's function.[2,18] Let the A segment occupy the sites for $n\geq 1$ and the B segment the sites for $n\leq 0$, and let us evaluate g_{11}. The characteristic roots for the a segment are chosen such that $|r_1|>1$ and $|r_2|<1$, and similarly for the B segment, $|x_1|>1$ and $|x_2|<1$. Then following Eqs. (16) and (17) and the way they were derived, $g_{m1}^R=g_{11}r_2^{m-1}$ for $m\geq 1$, and $g_{m1}^L=b_1 x_1^{m-1}$ for $m\leq 0$. The boundary equations for the Green's functions that we are after are the 01 and 11 matrix elements of Eq. (13) given by

$$t_B g_{-11}+(\varepsilon_B+\Delta_B-E)g_{01}+t g_{11}=0 \ , \tag{23}$$

$$t g_{01}+(\varepsilon_A+\Delta_A-E)g_{11}+t_A g_{21}=-1 \ , \tag{24}$$

where Δ_A and Δ_B are the surface perturbations. From Eqs. (23) and (24) the interface Green's function g_{11} is found to be

$$g_{11}=1/[E+io-\varepsilon_A-\Delta_A-t_A r_2-t^2/(t_B x_1-\Delta_B)] \ . \tag{25}$$

This result can also be obtained using Dyson's equation. Let G be the Green's function for the whole system containing the interface and G^0 be the Green's function for the two independent A and B crystals. The Dyson's equation connects G to G^0 by

$$G=G^0+G^0VG \ , \tag{26}$$

where V is the difference between the Hamiltonians of the connected and disconnected chains. In the present model, V takes the form

$$V=|0\rangle t\langle 1|+|1\rangle t\langle 0| \ . \tag{27}$$

Then the 11 and 01 matrix elements of Eq. (26) are given by $g_{11}=g^0_{11}+g^0_{11}tg_{01}$ and $g_{01}=g^0_{00}tg_{11}$, respectively, which yield

$$g_{11}=(1-g^0_{11}tg^0_{00}t)^{-1}g^0_{11} \ . \tag{28}$$

Note that in deriving g_{11} we have used the fact that g^0_{01} and g^0_{10} are zero.[18] The g^0_{11} in Eq. (28) is the surface Green's function for the A segment given by Eq. (21). Similarly,

$$g^0_{00}=1/(E+io-\varepsilon_B-\Delta_B-t_Bx_2)$$

is the surface Green's function for the B segment. When these expressions are used, Eq. (28) reduces to Eq. (25).

This section has displayed the basic mathematical structure of the difference-equation approach to the eigenvalue problems and the Green's functions in one dimension. This approach will be generalized to three-dimensional layer structures in Sec. III.

III. THREE-DIMENSIONAL LAYER STRUCTURES

We define a three-dimensional (3D) layer structure as a system having the same two-dimensional crystal periodicity for all the layer units. The extension needed from the one-dimensional model to the the 3D structures is to replace each atom in the chain by a plane of atoms.

Since each planar unit is a two-dimensional lattice, one can construct from the tight-binding orbitals the planar Bloch functions:

$$|n,\alpha;\mathbf{k}_\parallel\rangle=\frac{1}{\sqrt{N_s}}\sum_{l_\parallel}e^{i\mathbf{k}_\parallel\cdot\boldsymbol{l}_\parallel}|n,\alpha;\boldsymbol{l}_\parallel\rangle \ , \tag{29}$$

where n is the label of the planar unit, $\mathbf{k}_\parallel$ is a wave vector inside the two-dimensional Brillouin zone associated with the planar lattice represented by the lattice vectors $\boldsymbol{l}_\parallel$, N_s is the total number of unit cells in each plane, and α is the label for the local orbitals. The number of local orbitals n_s, which is the same as the number of independent planar Bloch bases defined in Eq. (29), is equal to the number of orbitals per atom times the number of atoms per unit cell in each planar unit. The plane label n in general can represent a set of layers. Since the whole system has the two-dimensional lattice translational symmetry represented by the lattice vectors $\{\boldsymbol{l}_\parallel\}$, all functions of the Hamiltonian are diagonal in blocks of $\mathbf{k}_\parallel$. In terms of the basis functions defined in Eq. (29), all the matrix elements of the Hamiltonian between any two basis functions with different $\mathbf{k}_\parallel$ are zero. Thus $\mathbf{k}_\parallel$ can be used as a set of the quantum numbers to simplify the eigenvalue problem and the calculation of the Green's functions.

Below we will assume that the local orbitals are orthonormal and the Hamiltonian matrix element are not zero only between those orbitals residing in the same plane unit or in two nearest planar units. The longer-range interactions can be handled within the present formalism either by using a larger planar unit or by generalizing the difference equations to higher order.

The one-dimensional chain in Sec. II can be used to represent a system consisting of slabs of A and B atoms by letting each atom in the chain represent a plane of atoms. When the eigenfunction for a $\mathbf{k}_\parallel$ is expanded in terms of the planar basis of Eq. (29) as

$$|\psi\rangle=\sum_n\sum_\alpha C_\alpha(n)|n\alpha,\mathbf{k}_\parallel\rangle \ , \tag{30}$$

the eigenvalue problem $(H-E)|\psi\rangle=0$ in the present model becomes a set of coupled difference equations:

$$\begin{aligned}&\sum_{\alpha'}H_{\alpha\alpha'}(n,n-1)C_{\alpha'}(n-1)\\&\quad+\sum_{\alpha'}[H_{\alpha\alpha'}(n,n)-E\delta_{\alpha\alpha'}]C_{\alpha'}(n)\\&\qquad+\sum_{\alpha'}H_{\alpha\alpha'}(n,n+1)C_{\alpha'}(n+1)=0 \ .\end{aligned} \tag{31}$$

Inside an A slab, Eq. (31) may be written in the matrix form

$$\mathbf{F}^\dagger_A C_{n-1}+\mathbf{A}C_n+\mathbf{F}_A C_{n+1}=0 \ , \tag{32}$$

where the C's are column matrices and the bold capital letters $\mathbf{F}$ and $\mathbf{A}$ are square matrices of order n_s. Explicitly, the matrix elements in Eqs. (31) and (32) are defined as

$$\mathbf{F}_{\alpha\alpha'}=H_{\alpha\alpha'}(n,n+1)$$

and

$$\begin{aligned}\mathbf{A}_{\alpha\alpha'}&=H_{\alpha\alpha'}(n,n)-E\delta_{\alpha\alpha'}\\&=\langle n,\alpha;\mathbf{k}_\parallel|(H-E)|n,\alpha';\mathbf{k}_\parallel\rangle \ .\end{aligned}$$

The difference equation (32) has the following general solution:

$$C_n=\sum_j a_j r_j^n \boldsymbol{\alpha}_j \ , \tag{33}$$

for the column matrix of the nth plane in an A slab, where r_j and $\boldsymbol{\alpha}_j$ are, respectively, the eigenvalue and eigenvector of the jth solution to the following characteristic equation:

$$(\mathbf{F}^\dagger_A+r\,\mathbf{A}+r^2\mathbf{F}_A)\boldsymbol{\alpha}=0 \ . \tag{34}$$

The a_j's in Eq. (33) are constants to be determined by the boundary conditions and the normalization of the wave function. The quadratic matrix eigenvalue problem of Eq. (34) can be cast into a linear eigenvalue problem so that the eigenvalues and eigenvectors can be easily obtained.[19] There are in general a total of $2n_s$ characteristic roots from Eq. (34), with r and $1/r^*$ forming pairs of roots. Although $\mathbf{F}_A$ is generally not Hermitian, r^* and

$1/r$ were also found to be the roots in all the cases that we have studied.[20] After the characteristic solutions $\{r_j, \boldsymbol{\alpha}_j\}$ are obtained, the remaining problem is to match these solutions on the boundaries. Having considered the one-dimensional model in detail in Sec. II, we will simply write down the expressions for the corresponding three-dimensional cases.

A. Surface and interface states

While the extended-state electronic structure in a system with surfaces and interfaces may be treated more efficiently using the Green's functions as will be considered later, the eigenvalue problem is more transparent for dealing with states which are localized on the surfaces and interfaces. Extending the boundary equation of Eq. (6) to the present case, we have

$$(\mathbf{A}+\mathbf{V})C_1+\mathbf{F}_A C_2=0 \ , \tag{35}$$

where $\mathbf{V}$ is the surface perturbation. Since the wave function of a surface state decays exponentially into the bulk, the C_n in Eq. (33) should only include those solutions with the characteristic roots $|r_j|<1$. Let the number of r_j satisfying this condition be n_b; then the n_b expansion coefficients a_j in Eq. (33) of the surface states obey the following equation:

$$\sum_j (\mathbf{V}\boldsymbol{\alpha}_j r_j - \mathbf{F}_A^\dagger \boldsymbol{\alpha}_j) a_j = 0 \ . \tag{36}$$

A similar technique can be used to treat the interface states, for which the allowed characteristic solutions are those that decay exponentially from the interface into both sides of the bulk. These solutions are then connected by two boundary equations coupling the two surfaces.

B. Superlattice band structure

The boundary equations for a three-dimensional superlattice with multiple orbitals take forms similar to Eqs. (9)–(12), except that the c's are to be replaced by the column matrices and the interaction parameters are to be replaced by the $\mathbf{k}_\parallel$-dependent square matrices. After the general solutions in Eq. (33) for both A and B slabs are substituted into these boundary equations, a set of $4n_s \times 4n_s$ homogeneous linear equations are obtained and are to be solved for the band energies and wave functions.

We note that, if the superlattice is treated as a bulk, then a direct application of the TB theory will require a Hamiltonian matrix with a dimension $(n+m)n_s$ that increases linearly with the number of layers in the slabs.[21,22] In contrast, the present approach only needs to deal with matrices of a fixed dimension $4n_s$ regardless of the thickness of the slabs. Th price paid is that the matrices are now energy dependent. The numerical aspects of the application of this method to semiconductor superlattices will be reported separately.[20]

C. Green's functions

The Green's functions for the layer structures for a given $\mathbf{k}_\parallel$ and energy $E+i\delta$ in the present model are defined as

$$g_{n\alpha,m\alpha'}(\mathbf{k}_\parallel, E+i\delta) = \langle n,\alpha;\mathbf{k}_\parallel|(E+i\delta-H)^{-1}|m\alpha';\mathbf{k}_\parallel\rangle \ . \tag{37}$$

Unless stated otherwise, we will be working on fixed $\mathbf{k}_\parallel$ and $E+i\delta$, so these two parameters will be suppressed. We will use $\mathbf{G}_{nm}$ for a given pair of plane indices n and m to denote a square matrix of dimension n_s such that the $g_{n\alpha,m\alpha'}$ in Eq. (37) is the $\alpha\alpha'$ matrix element of $\mathbf{G}_{nm}$.

Consider the pure-crystal Green's functions first. The one-dimensional Eqs. (13) and (14) now become

$$\mathbf{F}_A^\dagger \mathbf{G}_{n-1n} + \mathbf{A}\mathbf{G}_{nn} + \mathbf{F}_A \mathbf{G}_{n+1n} = -I \ , \tag{38}$$

$$\mathbf{F}_A^\dagger \mathbf{G}_{m-1n} + \mathbf{A}\mathbf{G}_{mn} + \mathbf{F}_A \mathbf{G}_{m+1n} = 0 \ . \tag{39}$$

Note that Eq. (39) can be solved in the same way as Eq. (32). Since the energy is $E+i\delta$, one-half of the characteristic roots of Eq. (34), denoted as r_j for $j=1$ to n_s, have magnitudes less than 1 and the other half, to be denoted by $x_j = r_{j+n_s}$ for $j=1$ to n_s, have $|x_j|>1$. The eigenvectors of Eq. (34) corresponding to r_j are denoted as $\boldsymbol{\alpha}_j$ and those corresponding to x_j are denoted as $\boldsymbol{\beta}_j$. In terms of these solutions, the Green's function column by column can be written as

$$\mathbf{G}_{mn}^{R(i)} = \sum_j a_j^{(i)} r_j^{m-n} \boldsymbol{\alpha}_j \ , \tag{40}$$

$$\mathbf{G}_{mn}^{L(i)} = \sum_j b_j^{(i)} x_j^{m-n} \boldsymbol{\beta}_j \ , \tag{41}$$

where i indicates the ith column. These two equations correspond to Eqs. (16) and (17), respectively, for the one-dimensional model. It is more convenient to write these equations in terms of square matrices. Let us define $a_j^{(i)}$ and $b_j^{(i)}$ as the ij matrix elements of $\mathcal{A}$ and $\mathcal{B}$, respectively, and let $\mathbf{P}$ and $\mathbf{Q}$ be, respectively, the square matrices formed by the column matrices $\{\boldsymbol{\alpha}_j\}$ and $\{\boldsymbol{\beta}_j\}$. Then $\mathbf{G}_{mn}^R = \mathbf{P}\mathbf{R}^{m-n}\mathcal{A}$, $\mathbf{G}_{mn}^L = \mathbf{Q}\mathbf{X}^{m-n}\mathcal{B}$, and $G_{nn} = G_{nn}^R = G_{nn}^L = \mathbf{P}\mathcal{A} = \mathbf{Q}\mathcal{B}$ with G_{nn} given by

$$\mathbf{G}_{nn} = [\mathbf{F}_A(\mathbf{Q}\mathbf{X}\mathbf{Q}^{-1} - \mathbf{P}\mathbf{R}\mathbf{P}^{-1})]^{-1} \ , \tag{42}$$

where $\mathbf{R}_{ij} = r_i\delta_{ij}$ and $\mathbf{X}_{ij} = x_i\delta_{ij}$. The other Green's functions for the bulk can then be calculated from $\mathbf{G}_{mn}^R = \mathbf{P}\mathbf{R}^{m-n}\mathbf{P}^{-1}\mathbf{G}_{nn}$ and $\mathbf{G}_{mn}^L = \mathbf{Q}\mathbf{X}^{m-n}\mathbf{Q}^{-1}\mathbf{G}_{nn}$.

The surface and interface Green's functions are not much more complicated, once the above results for the bulk pure crystals are available. For example, the surface Green's function can be obtained either from Dyson's equation or from matching $\mathbf{G}_{m1}^R$ to the surface boundary equation,

$$(\mathbf{A}+\mathbf{V})\mathbf{G}_{11} + \mathbf{F}_A \mathbf{G}_{21} = -I \ . \tag{43}$$

Both ways lead to the following surface Green's function:

$$\mathbf{G}_{11} = -(\mathbf{A}+\mathbf{V}+\mathbf{F}_A\mathbf{P}\mathbf{R}\mathbf{P}^{-1})^{-1} \ . \tag{44}$$

Note that the poles of $\mathbf{G}_{11}$ yield the surface states when they exist outside the energy spectra of the bulk. This result is equivalent to Eq. (36) from the eigenvalue consideration.

To conclude this section, we point out that the key to our approach is to solve the difference equations in the repeated regions in terms of the characteristic solutions given by Eqs. (33) and (34). Once this is done, the eigenvalue problem and the Green's functions can be cast into boundary equations. The information contained in this and previous sections is sufficient for one to generalize to other cases.

IV. SUMMARY AND DISCUSSION

This paper concerns the calculation of the electronic structure of surfaces, interfaces, quantum wells, and superlattices. As mentioned earlier, it is difficult to apply the conventional band techniques to these systems, because superlattices in general have too large unit cells and other systems do not have the complete crystal periodicity. Although useful information about surfaces and interfaces has been obtained using artificial periodic supercells,[3,4,13,15,16] it remains to be quantified how large these supercells are needed to be and how accurately the surface and interface effects are represented by these supercells. A direct comparison between the results from the supercell calculation with those based on the true boundaries will help resolve these questions.

This paper presents a difference-equation approach to treating these layer structures. This method fully takes advantage of the symmetry of the repeated regions by solving the difference equations in terms of the characteristic solutions. Both the eigenvalue problem and the Green's functions are then reduced to a small set of boundary equations. A one-dimensional model was used to display the basic mathematical structure and to derive analytical examples. The formalism is then extended to the three-dimensional cases with multiple orbitals. The ability to calculate the layer Green's functions such as those given in Eqs. (42) and (44) without requiring the Brillouin-zone integration along the $k_\perp$ perpendicular to the layers may also be useful for studying the defect and alloy problems of surfaces[23] and interfaces.

The most immediate application of the present method to realistic systems is to utilize the empirical tight-binding (ETB) method. The ETB method has been useful for calculating the band structure[24–26] and structural properties[27] for the pure and alloy bulks. The present method will make ETB readily applicable to surfaces, interfaces, quantum wells, and superlattices.[20]

Although all the formulas derived in this paper assume that the interactions are truncated up to the first-neighboring planes, these formulas can handle the longer-range interactions by using multilayer planar units. For example, if a double-layer unit is used for the zinc-blende semiconductor superlattices,[20] all the ETB Hamiltonians with interactions up to the second neighbors can be directly applied to these formulas. Another way to handle the longer-range interactions is to generalize the quadratic difference equation to higher orders. The number of the characteristic roots $\{r_j\}$, or the number of the complex-k values defined by $r_j = e^{ik_j a}$, depends not only on the number of orbitals n_s but also on the range of interactions. For a first-neighbor model with n_s orbitals per planar cell, there are $2n_s$ characteristic roots. Including the second-neighbor interactions, this number increases to $4n_s$. The final size of the matrices is then fixed by the number of $\{r_j\}$ and by the number of the boundary equations required.

Because our method facilitates the calculation of the Green's functions and hence the local charge densities, it points to the possibility for a first-principles self-consistent calculation using the density-functional theory.[3,4] This is desired so that the structural properties of these layer structures can be studied as rigorously as those for the bulk. One essential step in this undertaking is to find a set of efficient and compact local orbitals, namely, the number of orbitals n_s required has to be kept to a minimum and the extension of these orbitals has to be limited to the first few neighbors. The tight-binding orbitals derived from the linearized muffin-tin orbitals (LMTO) method by Andersen and Jepsen[28] and the truncated atomic orbitals[29] may be useful in this connection. One may also consider using the energy-dependent orbitals which satisfy Schrödinger's equation locally but truncate in short distances. This energy dependence in the basis should not cause too much concern, because, after all, the Green's functions and the characteristic solutions of the difference equations have to be calculated as functions of the energy.

Finally, there is one important problem involving interfaces that cannot be handled by the present approach. This is the case in which the two surfaces involved contain no commensurate two-dimensional lattice, as is often found in antiboundaries and grain boundaries. Whether or not the present approach can be extended to treat this problem requires a further study.

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