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Elementary excitations in the surface region of a semi-infinite solid

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An exact method is described for calculating the electronic or vibrational excitations in the surface region of a semi-infinite solid, starting from an orthogonal tight-binding or linear-combination-of-atomic-orbitals model for electrons or a Born–von Kármán model for phonons. A combination of matrix continued fraction and conventional Green's function techniques is used; this separates the effects of termination or cleavage of the perfect bulk crystal from effects arising from changes in the interactions in the surface region. Many ordered overlayers and a restricted class of interfaces can be treated by the same methods.

I. INTRODUCTION

A variety of methods have been proposed for calculating the properties of elementary excitations at solid surfaces. Kalkstein and Soven[1] (KS), for example, have presented an exact Green's function theory based on the tight-binding or linear-combination-of-atomic-orbitals (LCAO) formalism. Within the tight-binding framework, several approximate methods have been employed for surfaces. Slab calculations, for example, have proven to be useful for both electronic[2] and vibrational[3] states. The real-space recursion method of Haydock, Heine, and Kelly[4] can be applied to surfaces; in fact, approximate alloy surface densities of states have been calculated by this technique.[5] Dempsey and Kleinman[6] have recently compared results of slab and real-space recursion calculations for iron surfaces.

The method we will describe shares some elements of the three approaches mentioned above. The starting point is an orthogonal tight-binding or LCAO Hamiltonian for electrons, or a Born–von Kármán model for phonons. The only other assumption made is that the various planes of atoms parallel to the surface share a common two-dimensional translational symmetry, so that a two-dimensional transform with respect to surface or planar wave vectors can be performed. We emphasize that, unlike slab or real-space recursion calculations, the method is exact within the confines of these starting assumptions. An overlayer ordered in a commensurate superlattice of the substrate surface net can also be treated, as can interfaces when the constituents share a common two-dimensional Bravais lattice.

After taking the transform with respect to surface wave vectors, the desired elements of the Green's function are developed in terms of a matrix continued fraction. An exact termination of the continued fraction can be performed when a level is reached at which the planar transforms of the Hamiltonian or dynamical matrix settle down to their bulk values. For electrons, the Green's function that terminates the continued fraction is that appropriate for the surface region of a cleaved perfect bulk crystal, and it can be determined either by the methods outlined by KS or by using standard numerical techniques for solving coupled second-order equations. For phonons, the same procedures apply, but the correspondence of the Green's function terminating the matrix continued fraction with that for a perfect cleaved crystal is not precisely the same, as will be discussed later.

The combination of matrix continued fraction and conventional Green's function approaches naturally separates effects arising from termination of the perfect bulk crystal from effects due to perturbed interactions in the surface region. The computationally difficult part of the problem is to calculate the Green's function for the terminated bulk over the desired mesh of wave vectors in the two-dimensional Brillouin zone (BZ). Once this is done, the effects of changes in the interactions in the surface region on such quantities as spectral functions and dispersion relations in the surface region can be found by straightforward matrix manipulation, and layer-dependent densities of states can be calculated by integrating the appropriate spectral functions over the surface BZ.

The method is exact, given an appropriate starting Hamiltonian. Furthermore, it is not limited to density-of-states calculations, but can also be used to determine other quantities of physical interest. In special cases, e.g., for single electronic bands[7] and decoupled phonons[8] at the (100) surface of a simple cubic crystal, the matrix equations reduce to the familiar scalar equations for a linear chain with first-nearest-neighbor interactions. In general, however, finite matrix equations must be solved. We will illustrate the method for a case for which the matrices involved are 2×2's rather than scalars.

II. THEORY

For simplicity, we consider only surfaces of monatomic crystals with one atom per unit cell in the two-dimensional Bravais lattice, although it is straightforward to extend the method to more complicated systems. Let L index the layers in the semi-infinite crystal and l denote the unit cell (atom) within a layer. The interaction between sites L,l and L',l' is described by a Hamiltonian or force constant matrix $\underline{H}(L,l;L',l')$, and the inverse of the one-particle Green's function has elements

$$\underline{G}^{-1}(L,l;L',l';z)=z\underline{I}\,\delta(L,L')\delta(l,l')-\underline{H}(L,l;L',l'),\tag{1}$$

where $\underline{I}$ is the unit matrix of the same dimension as $\underline{H}$, and $z=E+i\epsilon$ for electrons, $z=M(\omega^2+i\epsilon)$ for phonons. Note that we do not assume a single-band Hamiltonian or any other simple form for $\underline{H}(L,l;L',l')$ which will lead eventually to some kind of decoupling. To give two examples, the interatomic force constant matrices for lattice vibrations are Cartesian 3×3's, while for electrons described by an s-p-d tight-binding model, the Hamiltonian matrices $\underline{H}(L,l;L',l')$ are 9×9's. Layer spectral density matrices can be defined by

$$\underline{\rho}(L;z)=-\frac{1}{\pi}\,\mathrm{Im}\lim_{\epsilon\to 0}\underline{G}(L,l;L,l;z),\tag{2}$$

and are independent of the particular site l within the layer.

To determine the Green's function, we take the two-dimensional transform

$$\underline{G}(L,l;L',l';z)=\frac{1}{N_s}\sum_{\vec{q}_s}e^{-i\vec{q}_s\cdot[\vec{R}(L,l)-\vec{R}(L',l')]}\,\underline{G}(L,L';\vec{q}_s,z),\tag{3}$$

$$\underline{G}(L,L';\vec{q}_s,z)=\frac{1}{N_s}\sum_{l,l'}e^{i\vec{q}_s\cdot[\vec{R}(L,l)-\vec{R}(L',l')]}\,\underline{G}(L,l,L',l';z).\tag{4}$$

Here $\vec{q}_s$ is a wave vector in the two-dimensional reciprocal lattice, N_s is the number of atoms in a layer ($N_s\to\infty$), and $\vec{R}(L,l)$ is the position of the atom at L,l.

The important thing to note, now, is that with the assumption that the interplanar interactions have finite range, the transform of the Hamiltonian and hence of the inverse Green's function is always a block tridiagonal matrix, that is,

$$\underline{G}^{-1}(\vec{q}_s,z)=\begin{bmatrix} z\underline{1}-\underline{A}_1 & -\underline{B}_1 & \underline{0} & \underline{0} & \\ -\underline{B}_1^{\dagger} & z\underline{1}-\underline{A}_2 & -\underline{B}_2 & \underline{0} & \\ \underline{0} & -\underline{B}_2^{\dagger} & z\underline{1}-\underline{A}_3 & -\underline{B}_3 & \\ \underline{0} & \underline{0} & -\underline{B}_3^{\dagger} & z\underline{1}-\underline{A}_4 & \\ & & & & \ddots \end{bmatrix}\tag{5}$$

The matrices $\underline{A}_i(\vec{q}_s)$ and $\underline{B}_i(\vec{q}_s)$ are $(n-1)\times(n-1)$ square blocks of matrices $\underline{H}(L,L';\vec{q}_s)$, where n specifies the range of the interplanar interactions: atoms in plane 1 interact with atoms in planes 1 to n, those in plane 2 with atoms in planes 2 to $n+1$, etc. In Eq. (5), $\underline{1}$ is the unit matrix of the same dimension as $\underline{A}_i$, $\underline{B}_i$. As an illustration of the form of the $\underline{A}_i$ and $\underline{B}_i$ matrices,

$$\underline{A}_1(\vec{q}_s)=\begin{bmatrix} \underline{H}(1,1;\vec{q}_s) & \underline{H}(1,2;\vec{q}_s) & \cdots & \underline{H}(1,n-1;\vec{q}_s) \\ \underline{H}(2,1;\vec{q}_s) & \underline{H}(2,2;\vec{q}_s) & \cdots & \underline{H}(2,n-1;\vec{q}_s) \\ \vdots & \vdots & & \vdots \\ \underline{H}(n-1,1;\vec{q}_s) & \underline{H}(n-1,2;\vec{q}_s) & \cdots & \underline{H}(n-1,n-1;\vec{q}_s) \end{bmatrix},\tag{6}$$

$$\underline{B}_1(\vec{q}_s)=\begin{bmatrix} \underline{H}(1,n;\vec{q}_s) & \underline{0} & \cdots & \underline{0} \\ \underline{H}(2,n;\vec{q}_s) & \underline{H}(2,n+1;\vec{q}_s) & \cdots & \underline{0} \\ \vdots & \vdots & & \vdots \\ \underline{H}(n-1,n;\vec{q}_s) & \underline{H}(n-1,n+1;\vec{q}_s) & \cdots & \underline{H}(n-1,2n-2;\vec{q}_s) \end{bmatrix};\tag{7}$$

To illustrate the size of $\underline{A}_i$ and $\underline{B}_i$ more graphically, consider the (110) surface of an fcc crystal with first- or first- and second-neighbor interactions. The range n of the interplanar interactions is three for either case, so $n-1=2$. For lattice vibrations, the matrices $\underline{A}_i, \underline{B}_i$ are thus 2×2 blocks of Cartesian 3×3's, so that $\underline{A}_i$ and $\underline{B}_i$ are 6×6's in overall size. For electrons described by an s-p-d tight binding model, $\underline{A}_i$ and $\underline{B}_i$ would be 18×18 matrices.

While the inverse Green's function is a block tridiagonal matrix, the Green's function itself is not, but, blocked in the same way as in Eq. (5), has the form

$$\underline{G}(\vec{q}_s,z)=\begin{bmatrix} \underline{G}_{11}(\vec{q}_s,z) & \underline{G}_{12}(\vec{q}_s,z) & \underline{G}_{13}(\vec{q}_s,z) & \\ \underline{G}_{21}(\vec{q}_s,z) & \underline{G}_{22}(\vec{q}_s,z) & \underline{G}_{23}(\vec{q}_s,z) & \\ \underline{G}_{31}(\vec{q}_s,z) & \underline{G}_{32}(\vec{q}_s,z) & \underline{G}_{33}(\vec{q}_s,z) & \\ & & & \ddots \end{bmatrix}. \tag{8}$$

Note that the subscripts ij in $\underline{G}_{ij}(\vec{q}_s,z)$ do not refer to individual planes but to sets of $(n-1)$ planes, from $(i-1)(n-1)+1$ to $i(n-1)$ and from $(j-1)(n-1)+1$ to $j(n-1)$, respectively.

Suppose that we wish to find the upper left block, $\underline{G}_{11}(\vec{q}_s,z)$, of the Green's function, from which we could determine the layer spectral density functions $\underline{\rho}(L;z)$ defined in Eq. (2) for planes 1 to $n-1$. Let us redefine the upper left block of $\underline{G}$ as $\underline{g}_1$, that is,

$$\underline{g}_1=\underline{G}_{11}(\vec{q}_s,z). \tag{9}$$

Using matrix identities for inverting blocked matrices as shown in Appendix A, we find that $\underline{g}_1$ is given by the series of equations

$$\underline{g}_1=(z\underline{1}-\underline{A}_1-\underline{B}_1\cdot\underline{g}_2\cdot\underline{B}_1^\dagger)^{-1}, \tag{10a}$$

$$\underline{g}_2=(z\underline{1}-\underline{A}_2-\underline{B}_2\cdot\underline{g}_3\cdot\underline{B}_2^\dagger)^{-1}, \tag{10b}$$

$$\vdots$$

This series of equations can be terminated when the matrices $\underline{A}_i$ and $\underline{B}_i$ settle down to their bulk values, which we shall denote by $\underline{A}_b(\vec{q}_s)$ and $\underline{B}_b(\vec{q}_s)$. Suppose that this occurs m blocks down, so that $\underline{A}_i=\underline{A}_b$ and $\underline{B}_i=\underline{B}_b$ for $i\geq m$. Note that this settling down to bulk values of the Hamiltonian or force constant matrices $\underline{H}(L,l;L',l')$ occurs after $(m-1)\times(n-1)$ planes, so m will usually be small. Starting at level m, the equations for $\underline{g}_i$ are

$$\underline{g}_m=(z\underline{1}-\underline{A}_b-\underline{B}_b\cdot\underline{g}_{m+1}\cdot\underline{B}_b^\dagger)^{-1}, \tag{11a}$$

$$\underline{g}_{m+1}=(z\underline{1}-\underline{A}_b-\underline{B}_b\cdot\underline{g}_{m+2}\cdot\underline{B}_b^\dagger)^{-1}, \tag{11b}$$

$$\vdots$$

Since these equations for $\underline{g}_i$, $i\geq m$, all have the same structure, we can solve exactly for $\underline{g}_m=\underline{g}_{m+j}$.

$$\underline{g}_m=\underline{g}_b=(z\underline{1}-\underline{A}_b-\underline{B}_b\cdot\underline{g}_b\cdot\underline{B}_b^\dagger)^{-1}. \tag{12}$$

Together with Eqs. (10a), (10b), . . . , which we restate as

$$\underline{g}_i=(z\underline{1}-\underline{A}_i-\underline{B}_i\cdot\underline{g}_{i+1}\cdot\underline{B}_i^\dagger)^{-1},\quad 1\leq i\leq m-1, \tag{13}$$

this provides an exact formal solution for $\underline{g}_1=\underline{G}_{11}(\vec{q}_s,z)$.

While Eqs. (12) and (13) are those appropriate for numerical calculations, an alternative expression for $\underline{g}_1$ may provide additional insight. We define a notation for premultiplication and postmultiplication of a matrix inverse, $\underline{M}_1\underline{M}_2//\underline{M}=\underline{M}_1\cdot\underline{M}^{-1}\cdot\underline{M}_2$. Then from Eqs. (12) and (13), $\underline{g}_1$ can be expressed as a matrix continued fraction.

$$\underline{g}_1=\underline{1}/(z\underline{1}-\underline{A}_1-\underline{B}_1\underline{B}_1^\dagger//(z\underline{1}-\underline{A}_2-\underline{B}_2\underline{B}_2^\dagger//\ldots. \tag{14}$$

This equation has the same form as that for the Green's function at the end of a semi-infinite linear chain; if the matrices in Eq. (15) were 1×1's (scalars), it would correspond to a linear chain with nearest-neighbor interactions only.

In order to determine $\underline{g}_1$ from Eqs. (12) and (13), we must be able to calculate the Green's function $\underline{g}_b$ that terminates the continued fraction. Before outlining how this can be done, we digress briefly to discuss what $\underline{g}_b$ represents. From inspection of Eqs. (5), (8), (9), (10a), and (10b), $\underline{g}_b$ is the upper left or 1, 1 block of a Green's function whose inverse is like that in Eq. (5), but with all elements $\underline{A}_i$, $\underline{B}_i$ replaced by the bulk quantities $\underline{A}_b$, $\underline{B}_b$. For electrons, $\underline{g}_b$ thus corresponds to the Green's-function transform in the surface region of a cleaved bulk crystal. For phonons, however, $\underline{g}_b$ does not correspond in precisely the same way to the Green's function at the surface of a cleaved crystal with no changes in the interatomic force constants. For such a cleaved crystal, the self force constants at the surface would differ from those in the bulk in order to give overall translational invariance, i.e., to satisfy

$$\underline{H}(L,l;L,l)=-\sum_{L',l'}{}' \underline{H}(L,l;L',l'),$$

where the prime on the sum excludes the term $L',l'=L,l$. For $\underline{g}_b$, the self force constants at the surface do not satisfy this relationship, but are the same as in the bulk. Hence for phonons, $\underline{g}_b$ is the Green's function in the surface region of one half of a cleaved perfect crystal which is still connected by springs to the immobile, other half crystal.

Several methods can be used to calculate $\underline{g}_b$. First, Eq. (12) can be rewritten

$$\underline{0}=\underline{B}_b\cdot\underline{g}_b\cdot\underline{B}_b^{\dagger}\cdot\underline{g}_b-(z\underline{1}-\underline{A}_b)\cdot\underline{g}_b+\underline{1}\,. \tag{15}$$

This equation is quadratic in the elements of $\underline{g}_b$, and can be solved directly by iterative numerical techniques. In the simplest cases, Eq. (15) reduces to a scalar equation whose solution is

$$g_b=\frac{1}{2|B_b|^2}\{z-A_b-[(z-A_b)^2-4|B_b|^2]^{1/2}\}, \tag{16}$$

where the branch of the square root function is chosen to give the proper $(1/z)$ behavior for $z\rightarrow\pm\infty$. The scalar case, which corresponds to a linear chain with nearest-neighbor interactions, has been recognized as describing s electrons and decoupled phonons at the (100) surface of simple cubic crystals.[7,8] Kalkstein and Soven[1] (KS) used scalar examples for all of their illustrative calculations. We have tested one technique for a direct numerical solution of Eq. (15) for s electrons at the (110) surface of a face-centered cubic crystal, for which the matrices in Eq. (15) are 2×2's, and found it possible to achieve good accuracy with reasonable amounts of computer time.

A second method of calculating the terminated bulk function $\underline{g}_b$ is that of KS. Let $\underline{G}_0(L-L';\vec{q}_s,z)$ denote the interplanar transform of the Green's function in the infinite, perfect bulk crystal. $\underline{G}_0(L-L';\vec{q}_s,z)$ can be found by taking the full three-dimensional transform $\underline{G}_0(\vec{q}_s,q_\perp\hat{e}_\perp;z)$ of the bulk Green's function, where $q_\perp$ is the wave vector in the surface normal direction $\hat{e}_\perp$, multiplying by $\exp\{-iq_\perp\hat{e}_\perp\cdot[\vec{R}(L)-\vec{R}(L')]\}$, and integrating over $q_\perp$ from 0 to $2\pi/a_\perp$, where $a_\perp$ is the interplanar spacing. $\underline{g}_b$ can then be determined from $\underline{G}_0$ and the "missing" interactions $(-\underline{H}_b)$ in the surface region of the terminated bulk; schematically,

$$\hat{\underline{g}}_b=(\underline{1}+\underline{G}_0\cdot\underline{H}_b)^{-1}\cdot\underline{G}_0\,. \tag{17}$$

There is one feature of the treatment of KS that is not apparent in the preceding very brief summary, and that should be mentioned: namely, Eq. (17) really represents an equation of twice the dimension as Eqs. (12) and (13) of our matrix continued fraction approach. We have indicated this in Eq. (17) by adding a carat over $\underline{g}_b$. The reason for this increase in dimension is that KS show how to find the Green's function in the surface region of one half of a cleaved crystal, and the perturbations arising from cleavage extend through the surface regions of both halves. For example, cleavage cuts the interactions between an atom in plane 1 and its former neighbors in planes -1 to $-(n-1)$ in the other half crystal (as in Appendix B, we have no plane 0). Thus if Eq. (12) is of order $[n_H(n-1)]\times[n_H(n-1)]$, where n_H is the rank of the interatomic Hamiltonian or force constant matrices $\underline{H}(L,l;L',l')$, then Eq. (17) is of order $[2n_H(n-1)]\times[2n_H(n-1)]$. If the approach of KS is used to calculate not just the recursion Green's function, but also the true Green's function in the surface region in the presence of additional surface perturbations, then matrices of twice the dimension $n_H(n-1)$ must be manipulated at every stage of the calculations.

We have described a method for calculating $\underline{g}_1(\vec{q}_s,z)=\underline{G}_{11}(\vec{q}_s,z)$, the upper left block of the Green's function for the semi-infinite solid as defined in Eq. (5). We want to emphasize that the method is not limited to calculating $\underline{g}_1$. Similar equations can be derived for other blocks of the Green's function which may be of interest. For example, the 2, 1 block of $\underline{G}$ is $\underline{G}_{21}=\underline{g}_2\cdot\underline{B}_1^{\dagger}\cdot\underline{g}_1$. We thus have a general procedure for determining the Green's function in the surface region.

For situations in which the interplanar forces in the surface region are of longer range than in the bulk, the ability to determine other blocks of the Green's function can be used to simplify the calculations. Suppose, for example, that atoms in plane 1 interact with atoms in planes 1 to $2n-1$, and that the range of the interplanar interactions decreases on going down into the bulk, until finally atoms in a bulk plane k interact with atoms in planes $k-n+1$ to $k+n-1$. For this case, the matrices in Eqs. (12) and (13) are of size $[2(n-1)]\times[2(n-1)]$. Now, however, the terminated bulk Green's function $\underline{g}_b$ can be partitioned into four $(n-1)\times(n-1)$ blocks that can all be expressed in terms of an $(n-1)\times(n-1)$ Green's function $\underline{\gamma}_b$,

$$\underline{g}_b=\begin{pmatrix}\underline{\gamma}_b & \underline{\gamma}_b\cdot\underline{\beta}_b\cdot\underline{\gamma}_b\\ \underline{\gamma}_b\cdot\underline{\beta}_b^{\dagger}\cdot\underline{\gamma}_b & -\underline{\beta}_b^{-1}\cdot(z\underline{1}-\underline{\alpha}_b)\cdot\underline{\gamma}_b\cdot\underline{\beta}_b\cdot\underline{\gamma}_b\end{pmatrix}, \tag{18}$$

$$\underline{\gamma}_b=(z\underline{1}-\underline{\alpha}_b-\underline{\beta}_b\cdot\underline{\gamma}_b\cdot\underline{\beta}_b^{\dagger})^{-1}\,. \tag{19}$$

$\underline{\gamma}_b$ can be found either by direct solution of Eq. (19) or by the method of KS. For this example, the range of the interplanar interactions at the surface was exactly twice that in the bulk, but similar procedures can be used for other cases in which the range of interactions is greater in the surface region.

To illustrate how ordered overlayers can be treated if their structure is commensurate with that of the substrate, consider a 2×1 overlayer on an fcc (100) surface. The two-dimensional BZ for the overlayer is a rectangle equal to half of the square BZ for the substrate. The theory presented carries through unchanged if the larger, square BZ is used to define the two-dimensional transforms. Interfaces can be treated by similar methods if a common two-dimensional symmetry is maintained parallel to the interface; since more notation is need to define this problem, the solution is outlined in Appendix B.

Before ending this section, we want to distinguish clearly our exact, matrix continued fraction approach from the approximate recursion procedure of Haydock, Heine, and Kelly.[4] Their method is designed to calculate particular scalar elements of the Green's function in real space. By use of the Lanczos algorithm, a scalar continued fraction is generated for the desired element of the Green's function. This is then terminated approximately by a function of the form given in Eq. (16), with the coefficients A and B chosen to give the proper bandwidth. This procedure works reasonably well for a restricted number of situations. In contrast, our matrix continued fraction equations (12) and (13) are exact, and are not limited to cases where one continuous band occurs, or where hybridization between multiple bands is ignored.

Another variation of the recursion method which could be applied to surface problems would be to perform recursion calculations after transforming with respect to surface wave vectors $\vec{q}_s$. This would yield approximate solutions for particular elements, $G_{ii}(L,L;\vec{q}_s,z)$, of the transform of the Green's function. Like real space recursion, this method would give approximate rather than exact results.

III. ILLUSTRATIVE RESULTS AND DISCUSSION

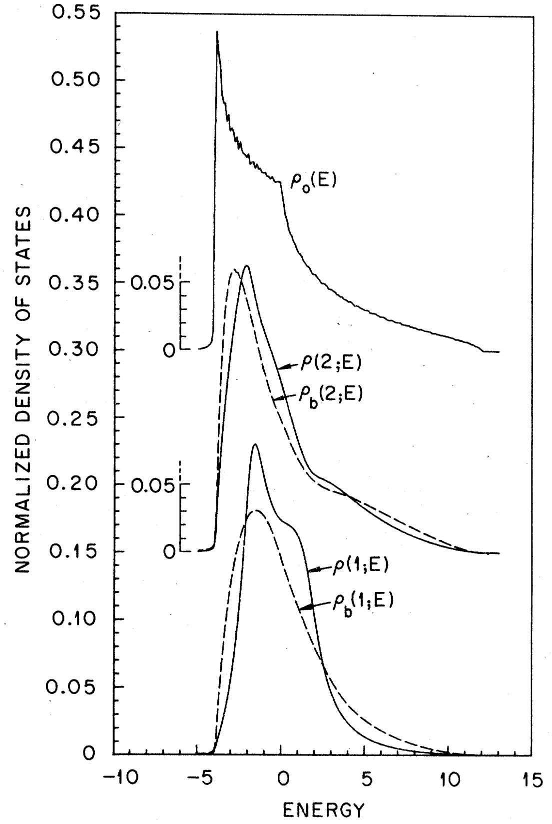

FIG. 1. Surface region, terminated bulk, and infinite bulk densities of states for s electrons, in an fcc (110) crystal. Plane 1 and plane 2 results in the surface region [full curves, $\rho(L;E)$] and in the terminated bulk [dashed curves, $\rho_b(L;E)$] are at the bottom and middle; the infinite crystal density of states $\rho_0(E)$ is at the top.

To test some of the computational aspects of our approach, we have performed calculations for several simple model electronic systems, namely, s electrons at various surfaces of cubic crystals, with first- and second-neighbor interactions allowed. Although s-band tight-binding calculations are not of intrinsic interest, these systems provide the simplest cases for which Eqs. (12) and (13) do not reduce to scalar equations, but instead are 2×2 or 3×3 matrix equations. Applications to more realistic problems such as lattice vibrations or electrons in d-band metals would involve larger matrices, but the structure of the calculations would remain the same.

In our calculations, the terminated bulk Green's functions $g_b(\vec{q}_s,z)$ were found by the method outlined by KS, but in its general matrix form. A small but finite imaginary part of z was included throughout the calculations; this makes it possible to use very simple and direct procedures to evaluate the necessary integrals.

Figure 1 gives illustrative results for s electrons in an fcc (110) crystal with first-nearest-neighbor (1nn) interactions. The range n of the interplanar interactions is three for this case, so the matrices $\underline{A}_i$, $\underline{B}_i$, $\underline{g}_i$, and $\underline{g}_b$ are 2×2's; adding second-nearest-neighbor (2nn) interactions would not change the range n for this surface. The two-dimensional real and reciprocal lattices for an fcc (110) crystal are rectangular. For the results shown, all site-diagonal elements of the Hamiltonian were set equal to zero, while the interactions $h_{1\text{nn}}(L,L')$ between first neighbors in planes L and L' were assigned the following values: $h_{1\text{nn}}(L,L)=h_{1\text{nn}}(\text{bulk})=1.0$; $h_{1\text{nn}}(1,2)=0.6$; $h_{1\text{nn}}(1,3)=0.8$. The imaginary part of z used was 0.02.

The curves in Fig. 1 exhibit some expected features. The density of states in the surface layer differs significantly from the terminated bulk results (bottom) because of the 40% and 20% reductions in the 1nn interactions between planes 1,2, and 1,3, respectively. In the second layer (middle), the surface region and terminated bulk results are more similar to one another, and both are closer to the infinite bulk density of states (top). No surface bound states appear for this example.

As already noted, we have used relatively simple numerical integration techniques. The integrals over $q_\perp$ needed to evaluate the interplanar transforms $G_0(L-L';\vec{q}_s,z)$ of the infinite bulk Green's function were performed by expanding the numerator and denominator of the integrands to first order in each of a relatively small number of $q_\perp$ integrals (for Fig. 1,80), integrating, and summing. The surface BZ integrals were calculated by summation over a regular mesh of points (for Fig. 1,2500 points in the full surface BZ). With the integration procedures used, the infinite bulk density of states curve in Fig. 1 exhibits some noise, although the singularities at $E=-4$ and 0 show up rather well. A computationally interesting point is that the noise in G_0 does not produce uncertainties of the same magnitude in the surface region or terminated bulk results. In fact, somewhat coarser integration meshes, e.g., summing over 900 or 1600 rather than 2500 $\vec{q}_s$ values in the surface BZ, gave almost identical results for the Green's functions in the surface region, while the oscillations in the infinite crystal Green's functions increased substantially.

Although we have shown only density of states results, we can of course also calculate other quantities such as spectral functions $A(L,L;\vec{q}_s,E) \propto \operatorname{Im}G(L,L;\vec{q}_s,E)$ for elementary excitations in the surface region. To generate the curves in Fig. 1, in fact, constant-$\vec{q}_s$ results for $G(L,L';\vec{q}_s,E)$ for $(L,L')=(1,1)$, (1,2), and (2,2) were calculated as functions of E for 2500 $\vec{q}_s$ values in the surface BZ.

Our calculations for these simple electronic models have demonstrated the advantage of separating the effects of cleavage or termination from those produced by additional perturbations in the surface region. Almost all of the computer time required for the calculations is spent in evaluating the infinite and terminated bulk Green's functions, which can be calculated once and stored; a relatively small amount of time is needed to perform the matrix multiplications and inversions in Eq. (13) that yield the Green's function in the surface region. We believe that our calculations for these simple models also demonstrate the feasibility of performing similar calculations for more realistic models for electrons or phonons in the surface region of semi-infinite crystals.

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APPENDIX A: DERIVATION OF EQUATIONS (10a), (10b),...

Equations (10a), (10b),. . . are derived by using an identity for inverting blocked matrices.[9] Let a matrix $\underline{S}$ be defined in terms of blocks $\underline{\alpha}_1$, $\underline{\alpha}_2$, $\underline{\beta}_1$, $\underline{\beta}_2$ by

$$\underline{S}=\begin{pmatrix} \underline{\alpha}_1 & \underline{\beta}_1 \\ \underline{\beta}_2 & \underline{\alpha}_2 \end{pmatrix} \tag{A1}$$

$\underline{\alpha}_1$ and $\underline{\alpha}_2$ are assumed to be square matrices whose inverses exist. The inverse of $\underline{S}$, blocked in the same way, is

$$\underline{S}^{-1} \quad \begin{pmatrix} \underline{\gamma}_1^{-1} & -\underline{\alpha}_1^{-1}\cdot\underline{\beta}_1\cdot\underline{\gamma}_2^{-1} \\ -\underline{\alpha}_2^{-1}\cdot\underline{\beta}_2\cdot\underline{\gamma}_1^{-1} & \gamma_2^{-1} \end{pmatrix} \tag{A2}$$

where

$$\underline{\gamma}_1=\underline{\alpha}_1-\underline{\beta}_1\cdot\underline{\alpha}_2^{-1}\cdot\underline{\beta}_2\,, \tag{A3a}$$

$$\underline{\gamma}_2=\underline{\alpha}_2-\underline{\beta}_2\cdot\underline{\alpha}_1^{-1}\cdot\underline{\beta}_1\,. \tag{A3b}$$

To apply this identify to calculating $\underline{g}_1=\underline{G}_{11}(\vec{q}_s,z)$, the upper left block of the Green's function in Eq. (8), we block the inverse Green's function in Eq. (5) as follows:

$$\underline{G}^{-1}=\begin{pmatrix} z\underline{1}-\underline{A}_1 & \underline{\beta}_1 \\ \underline{\beta}_1^\dagger & \underline{G}_2^{-1} \end{pmatrix} \tag{A4}$$

$$\underline{\beta}_1=(-\underline{B}_1 \;\; \underline{0} \;\; \underline{0} \;\; \cdots) \tag{A5}$$

$$\underline{G}_2^{-1}=\begin{bmatrix} z\underline{1}-\underline{A}_2 & -\underline{B}_2 & 0 & \\ -\underline{B}_2^\dagger & z\underline{1}-\underline{A}_3 & \underline{B}_3 & \\ 0 & -\underline{B}_3^\dagger & z\underline{1}-\underline{A}_4 & \\ & & & \ddots \end{bmatrix}\,. \tag{A6}$$

Then from Eqs. (A1), (A2), and (A3a), the upper left block of $\underline{G}$ is given by

$$\begin{aligned} \underline{g}_1 &= (z\underline{1}-\underline{A}_1-\underline{\beta}_1\cdot\underline{G}_2\cdot\underline{\beta}_1^\dagger)^{-1} \\ &= (z\underline{1}-\underline{A}_1-\underline{B}_1\cdot\underline{g}_2\cdot\underline{B}_1^\dagger)^{-1}\,, \end{aligned} \tag{A7}$$

where $\underline{g}_2$ is in turn the upper left block of $\underline{G}_2$. Equation (A7) is the same as Eq. (10a); Eqs. (10b) and the others in the series follow on repeated application of the matrix identify (A2).

APPENDIX B: INTERFACES

As stated in the main text, interfaces can be treated by the matrix continued fraction approach if a common two-dimensional symmetry is maintained parallel to the interface, allowing a two-dimensional transform to be performed. Consider an interface between two materials for which this condition is satisfied, e.g., a Au-Ag interface. Let the planes in material M_+ on one side of the interface be labeled $1, 2, 3, \ldots$, and let n_+ give the range of the interactions in M_+; atoms in plane 1 interact with atoms in planes 1 to n_+, etc. In material M_- on the other side of the interface, the planes are labeled $-1, -2, -3, \ldots$, and the range of the interplanar interaction is n_-. Assume finally the atoms in planes 1 to $n_+ - 1$ in M_+ can interact with atoms in planes -1 to $-(n_- - 1)$ in M_-. This last assumption affects only the blocking we use, not the basic approach.

After transforming with respect to $\vec{q}_s$, the inverse Green's function can be written as an infinite, block tridiagonal matrix, which we partition initially as follows:

$$\underline{G}^{-1} = \begin{pmatrix} \underline{G}^{-1}(M_-) & -\underline{\beta}_I \\ -\underline{\beta}_I^\dagger & \underline{G}^{-1}(M_+) \end{pmatrix} \tag{B1}$$

$$\underline{G}^{-1}(M_-) = \begin{bmatrix} \ddots & & & \\ & z\underline{1}_- - \underline{A}_{3-} & -\underline{B}_{2-}^\dagger & \underline{0} \\ & -\underline{B}_{2-} & z\underline{1}_- - \underline{A}_{2-} & -\underline{B}_{1-}^\dagger \\ & \underline{0} & -\underline{B}_{1-} & z\underline{1}_- - \underline{A}_{1-} \end{bmatrix}, \tag{B2}$$

$$\underline{G}^{-1}(M_+) = \begin{bmatrix} z\underline{1}_+ - \underline{A}_{1+} & -\underline{B}_{1+} & \underline{0} & \\ -\underline{B}_{1+}^\dagger & z\underline{1}_+ - \underline{A}_{2+} & -\underline{B}_{2+} & \\ \underline{0} & -\underline{B}_{2+}^\dagger & z\underline{1}_+ - \underline{A}_{3+} & \\ & & & \ddots \end{bmatrix}, \tag{B3}$$

$$\underline{\beta}_I = \begin{bmatrix} & & & \iddots \\ \underline{0} & \underline{0} & \underline{0} & \\ \underline{0} & \underline{0} & \underline{0} & \\ \underline{B}_I & \underline{0} & \underline{0} & \end{bmatrix}, \tag{B4a}$$

$$\underline{\beta}_I^\dagger = \begin{bmatrix} & \underline{0} & \underline{0} & \underline{B}_I^\dagger \\ & \underline{0} & \underline{0} & \underline{0} \\ & \underline{0} & \underline{0} & \underline{0} \\ \iddots & & & \end{bmatrix} \tag{B4b}$$

Here $\underline{1}_-$, $\underline{A}_{i-}$, and $\underline{B}_{i-}$ are $(n_- - 1) \times (n_- - 1)$ blocks whose components are matrices (e.g., 3×3's for phonons in monatomic Bravais lattices); $\underline{1}_+$, $\underline{A}_{i+}$, and $\underline{B}_{i+}$ are $(n_+ - 1) \times (n_+ - 1)$'s; $\underline{B}_I$ and $\underline{B}_I^\dagger$, describing interactions across the interface, are $(n_- - 1) \times (n_+ - 1)$ and $(n_+ - 1) \times (n_- - 1)$ blocks, respectively. Note that we have defined the matrices above the diagonal as $\underline{B}_{i+}$ in M_+ and $\underline{B}_{i-}^\dagger$ in M_-; this notational choice yields equations which are most similar in form to those in the main text.

Suppose that we want to find the Green's function in the interfacial region in material M_+, specifically in the $(n_+ - 1) \times (n_+ - 1)$ block of $\underline{G}$ which occupies the same location as $z\underline{1}_+ - \underline{A}_{1+}$ does in the inverse. To do this, we first block $\underline{G}$ like its inverse in Eq. (B1),

$$\underline{G} = \begin{pmatrix} \underline{G}(-,-) & \underline{G}(-,+) \\ \underline{G}(+,-) & \underline{G}(+,+) \end{pmatrix}, \tag{B5}$$

then use the matrix identity in Appendix A to determine the semi-infinite matrix $\underline{G}(+,+)$,

$$\underline{G}(+,+)=[\underline{G}^{-1}(M_+)-\underline{\beta}_J^\dagger\cdot\underline{G}(M_-)\cdot\underline{\beta}_J]^{-1}. \tag{B6}$$

Substituting for $\underline{\beta}_J$ and $\underline{\beta}_J^\dagger$ from Eqs. (B4a) and (B4b) and carrying out the matrix multiplication, we obtain

$$\underline{\beta}_J^\dagger\cdot\underline{G}(M_-)\cdot\underline{\beta}_i=\begin{bmatrix}\underline{B}_J^\dagger\cdot\underline{g}_{1-}\cdot\underline{B}_J & 0 & 0 & \\ 0 & 0 & 0 & \\ 0 & 0 & 0 & \\ & & & \ddots\end{bmatrix} \tag{B7}$$

$$\underline{g}_{1-}=\underline{G}_{-1,-1}(M_-). \tag{B8}$$

$\underline{g}_{1-}$ is the lower right block of $\underline{G}(M_-)$; if only material M_- were present, so that we had a surface rather than an interface, $\underline{g}_{1-}$ would be the surface region block of the Green's function for M_-. As such, it can be found by the methods described in the main text and Appendix A.

From Eqs. (B6)–(B8), we are left with the problem of evaluating the upper left or 1, 1 block of $\underline{G}(+,+)$, whose inverse is given by

$$\underline{G}^{-1}(+,+)=\begin{bmatrix} z\underline{1}_+-\underline{A}_{1+}-\underline{B}_J^\dagger\cdot\underline{g}_{1-}\cdot\underline{B}_J & -\underline{B}_1 & \underline{0} & \\ -\underline{B}_{1+}^\dagger & z\underline{1}_+-\underline{A}_{2+} & -\underline{B}_2 & \\ \underline{0} & -\underline{B}_2^\dagger & z\underline{1}_+-\underline{A}_{3+} & \\ & & & \ddots \end{bmatrix}. \tag{B9}$$

Except for the added term $-\underline{B}_J^\dagger\cdot\underline{g}_{1-}\cdot\underline{B}_J$ in $\underline{G}_{1,1}^{-1}(+,+)$, this is identical to Eq. (5). If we call the desired block of the Green's function $\underline{G}_{11}$, the following equations provide a complete formal solution:

$$\underline{G}_{11}=(z\underline{1}_+-\underline{A}_{1+}-\underline{B}_J^\dagger\cdot\underline{g}_{1-}\cdot\underline{B}_J-\underline{B}_{1+}\cdot\underline{g}_{2+}\cdot\underline{B}_{1+}^\dagger)^{-1}, \tag{B10}$$

$$\underline{g}_{i\pm}=(z\underline{1}_\pm-\underline{A}_{i\pm}-\underline{B}_{i\pm}\cdot\underline{g}_{i+1,\pm}\cdot\underline{B}_{i\pm}^\dagger). \tag{B11}$$

The two series of equations (B11) can be terminated when $\underline{A}_{i\pm}$ and $\underline{B}_{i\pm}$ settle down to their bulk values.

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