

Simple scheme for surface-band calculations. I

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(Received 21 August 1980)

A simple, efficient scheme for calculating the electronic structure of a surface is presented. The scheme is applicable to any general Hamiltonian that can be described within a localized-orbital basis. The method is much faster than the current techniques available. The basic concept is that of wave-function matching through a transfer matrix. The eigensolutions of this matrix then provide all the information concerning the projected band structure, surface-state energies, orbital character, and decay lengths. A rather detailed discussion of the formalism is presented for a general surface system. A comprehensive and illustrative example is also presented for readers who are interested in using the scheme but not in the details of the theory.

I. INTRODUCTION

During the past decade there have been many methods developed for calculating surface states with Hamiltonians based on localized orbital representations.¹ Three very successful techniques include the "slab method,"²⁻⁵ the "effective-field method,"⁶⁻⁸ and the "Slater-Koster method."⁹⁻¹¹ The first approximates the surface system as a slab and generally requires rather large matrix diagonalization. The latter two treat the semi-infinite surface system and involve Green's-function formalisms. They are rather time consuming, involving self-consistent continued-fraction expansions and bulk Green's-function calculations, respectively.

In this paper we introduce a simple and efficient scheme that complements these methods for calculating surface band structures. It gives the projected band structure of the bulk crystal and the dispersion curves, character, and decay lengths of surface states. The method is conceptually simple and not very time consuming. Test calculations¹² on identical surface systems with the aforementioned techniques indicate that our scheme is, in fact, faster by about an order of magnitude.

The essential idea of our method is rather trivial: Generate wave-function matching conditions to solve for the eigenstates of the system. This can be done very effectively using transfer-matrix techniques. The transfer-matrix approach¹³ has been used successfully with various Hamiltonians involving plane-wave-like basis functions.¹⁴⁻¹⁶ With these Hamiltonians the transfer-matrix links (though a partial integration of the Schrödinger equation) the wave function and its derivative across any region. The problem simplifies considerably, however, for localized-orbital Hamiltonians. One can now define a trans-

fer matrix that directly links the wave function on pairs of neighboring layer orbitals. The eigenvalues and eigenvectors of this transfer matrix then provide all the information necessary to calculate the electronic structure of the system.

The format of this paper is as follows: In Sec. II we discuss the basic formalism of our method. This is done for a general surface system and is rather detailed. It includes a discussion of the bulk crystal, the ideal surface, the relaxed surface, and the reconstructed surface. For the reader who is not interested in the specific details of the general formalism we have included a self-contained sample calculation in Sec. III. This provides a step-by-step example, illustrating the use of the method. Finally in Sec. IV we make some concluding remarks.

II. FORMALISM

A. Bulk crystal

Consider a three-dimensional crystal. We wish to think of it as an infinite stack of principal layers. A principal layer is defined as the smallest group of atomic layers such that only nearest-neighbor interactions between principal layers exist. The periodicity parallel to the layers further reduces the system to that of noninteracting one-dimensional chains. (There is one chain for each wave vector \vec{k}_\parallel along the layer.) This is shown schematically in Fig. 1(a), where the circles, triangles, squares, etc., represent inequivalent principal layers. The interactions between neighboring principal layers are also, in general, different. The principal layers can form a *periodic* array of "superlayers."¹⁷ This is shown in Fig. 1(b). Let us now assume there are μ "layer orbitals" in each principal layer and m principal layers in each superlayer. The Bloch state of any orbital ϕ_α , in any principal layer l , in any

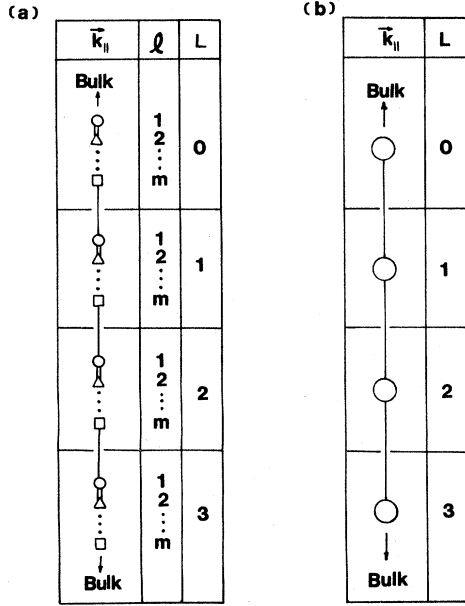


FIG. 1. Schematic representation of (a) an ideal bulk crystal as an infinite one-dimensional chain for each \bar{k}_{\parallel} . The circles, triangles, squares, etc., are different principal layers. The indices l and L are for principal layers and superlayers, respectively. (b) An ideal bulk crystal in terms of superlayers shown as circles.

superlayer L is given by

$$\psi_{L, l, \alpha}(\bar{k}_{\parallel}) = \frac{1}{\sqrt{N_{\parallel}}} \sum_{\bar{R}_{\parallel}} e^{i\bar{k}_{\parallel} \cdot \bar{R}_{\parallel}} \phi_{\alpha}(L, l, \bar{R}_{\parallel}), \quad (1)$$

where $\alpha = 1, \dots, \mu$, $l = 1, \dots, m$, and \bar{R}_{\parallel} is a lattice vector. The total wave function for the system is then

$$\Psi(\bar{k}_{\parallel}, E) = \sum_{L, l, \alpha} [C_l^L(\bar{k}_{\parallel}, E)]_{\alpha} \psi_{L, l, \alpha}(\bar{k}_{\parallel}). \quad (2)$$

The Schrödinger equation can then be written as¹⁸

$$\begin{bmatrix} C_{l+2}^L \\ C_{l+1}^L \end{bmatrix} = t_{l+2, l}^{L, L} \begin{bmatrix} C_{l+1}^L \\ C_l^L \end{bmatrix}, \quad (3a)$$

and

$$\begin{bmatrix} C_1^{L+1} \\ C_m^L \end{bmatrix} = t_{1, m-1}^{L+1, L} \begin{bmatrix} C_m^L \\ C_{m-1}^L \end{bmatrix}, \quad (3b)$$

$$\begin{bmatrix} C_2^{L+1} \\ C_1^{L+1} \end{bmatrix} = t_{2, m}^{L+1, L} \begin{bmatrix} C_1^{L+1} \\ C_m^L \end{bmatrix}, \quad (3c)$$

where the C_l^L are column vectors of length μ . The transfer matrices $t_{i', i}^{L', L}$ are given by the following expressions. The "intrasuperlayer" transfer matrix is

$$t_{i+2, i}^{L, L} = \begin{bmatrix} H_{i+1, i+2}^{L, L-1}(E - H_{i+1, i+1}^{L, L}) - H_{i+1, i+2}^{L, L-1} H_{i+1, i}^{L, L} & \\ & 1 \end{bmatrix}, \quad (4a)$$

and the "intersuperlayer" transfer matrices are

$$t_{1, m-1}^{L+1, L} = \begin{bmatrix} H_{m, 1}^{L+1, L}(E - H_{m, m}^{L, L}) - H_{m, 1}^{L+1, L} H_{m, m-1}^{L, L} & \\ & 1 \end{bmatrix}, \quad (4b)$$

$$t_{2, m}^{L+1, L} = \begin{bmatrix} H_{1, 2}^{L+1, L+1}(E - H_{1, 1}^{L+1, L+1}) - H_{1, 2}^{L+1, L+1} H_{1, m}^{L+1, L} & \\ & 1 \end{bmatrix}, \quad (4c)$$

where the matrix element of the Hamiltonian between states $\psi_{L_1, l_1, \alpha}(\bar{k}_{\parallel})$ and $\psi_{L_2, l_2, \beta}(\bar{k}_{\parallel})$ is given by

$$[H_{l_1, l_2}^{L_1, L_2}(\bar{k}_{\parallel})]_{\alpha \beta} = \sum_{\bar{R}_{\parallel}} e^{i\bar{k}_{\parallel} \cdot \bar{R}_{\parallel}} \langle \phi_{\alpha}(L_1, l_1, \bar{0}) | H | \phi_{\beta}(L_2, l_2, \bar{R}_{\parallel}) \rangle. \quad (5)$$

From Eqs. (4) we can construct a composite transfer matrix T , which links two adjacent principal layers in one superlayer to the two corresponding principal layers in the adjacent superlayer, for example,

$$\begin{bmatrix} C_2^{L+1} \\ C_1^{L+1} \end{bmatrix} = T_{L+1, L} \begin{bmatrix} C_2^L \\ C_1^L \end{bmatrix}, \quad (6)$$

where

$$T_{L+1, L} = (t_{2, m}^{L+1, L} t_{1, m-1}^{L+1, L}) \left(\prod_{i=3}^m t_{i, i-2}^{L, L} \right). \quad (7)$$

Now in a crystal we must have $H_{l_1, l_2}^{L_1, L_2} = H_{l_1, l_2}^{L_1+1, L_2+L}$; therefore $T_{L+1, L} = T_{L+2, L+1} = \dots = T$ and

$$\begin{bmatrix} C_2^M \\ C_1^M \end{bmatrix} = T^M \begin{bmatrix} C_2^0 \\ C_1^0 \end{bmatrix}. \quad (8)$$

Substituting (3) and (8) into Eq. (2) we get

$$\Psi(\bar{k}_{\parallel}, E) = \sum_{L=-\infty}^{\infty} \sum_{\beta=1}^{\mu} \left(\sum_{n=3}^m \left\{ \vec{u}_{\beta} \cdot T^L \prod_{i=3}^n t_{i, i-2}^{L, L} \begin{bmatrix} C_2^0 \\ C_1^0 \end{bmatrix} \right\} \psi_{L, n, \beta} \right. \\ \left. + \vec{u}_{\beta} \cdot T^L \begin{bmatrix} C_2^0 \\ C_1^0 \end{bmatrix} \psi_{L, 2, \beta} \right. \\ \left. + \vec{v}_{\beta} \cdot T^L \begin{bmatrix} C_2^0 \\ C_1^0 \end{bmatrix} \psi_{L, 1, \beta} \right), \quad (9)$$

where \vec{u}_{β} and \vec{v}_{β} , $\beta = 1, \dots, \mu$, are 2μ -dimensional column vectors with components given by $(\vec{u}_{\beta})_i = \delta_{\beta, i}$ and $(\vec{v}_{\beta})_i = \delta_{\beta+\mu, i}$. Thus $\Psi(\bar{k}_{\parallel}, E)$ is determined completely from a knowledge of the C^0 vector on neighboring principal layers 1 and 2.¹⁹

The composite transfer matrix T is the key quantity of the present scheme. It contains the information about the bulk projected band struc-

ture, the eigenenergies of surface states, their character, and decay lengths. The rest of this section is devoted to extracting this information from T .

The composite transfer matrix T has a very general and interesting property. It can be easily proved from Eqs. (4) and (7) that

$$T^{-1} = \begin{bmatrix} 0 & -H_{2,1}^{1,1} \\ H_{1,2}^{1,1} & 0 \end{bmatrix} T \begin{bmatrix} 0 & H_{2,1}^{1,1} \\ -H_{1,2}^{1,1} & 0 \end{bmatrix}. \quad (10)$$

This implies that if λ is an eigenvalue of T then λ^{-1} is also an eigenvalue of T .

Consider now $\vec{e}_\beta(\vec{k}_\parallel, E)$, $\beta=1, \dots, 2\mu$ to be the 2μ -normalized eigenvectors of the transfer ma-

trix T with eigenvalues λ_β . Then it follows from (9) that

$$\Psi(\vec{k}_\parallel, E) = \sum_\alpha A_\alpha \chi(\lambda_\alpha, \vec{k}_\parallel, E), \quad (11)$$

where

$$\chi(\lambda_\alpha, \vec{k}_\parallel, E) = \sum_{L=-\infty}^{\infty} \lambda_\alpha^L \sum_{\beta=1}^{\mu} \left\{ \left[\sum_{n=3}^m (\vec{u}_\beta \cdot \prod_{l=3}^n t_{l,l-2}^{L,L} \vec{e}_\alpha) \psi_{L,n,\beta} \right] + (\vec{u}_\beta \cdot \vec{e}_\alpha) \psi_{L,2,\beta} + (\vec{v}_\beta \cdot \vec{e}_\alpha) \psi_{L,1,\beta} \right\} \quad (12)$$

and

$$A_\alpha = \frac{\begin{vmatrix} (\vec{e}_1 \cdot \vec{e}_1) \cdots (\vec{e}_1 \cdot \vec{F}) \cdots (\vec{e}_1 \cdot \vec{e}_{2\mu}) \\ \vdots \\ (\vec{e}_{2\mu} \cdot \vec{e}_1) \cdots (\vec{e}_{2\mu} \cdot \vec{F}) \cdots (\vec{e}_{2\mu} \cdot \vec{e}_{2\mu}) \end{vmatrix}}{\begin{vmatrix} (\vec{e}_1 \cdot \vec{e}_1) \cdots (\vec{e}_1 \cdot \vec{e}_\alpha) \cdots (\vec{e}_1 \cdot \vec{e}_{2\mu}) \\ \vdots \\ (\vec{e}_{2\mu} \cdot \vec{e}_1) \cdots (\vec{e}_{2\mu} \cdot \vec{e}_\alpha) \cdots (\vec{e}_{2\mu} \cdot \vec{e}_{2\mu}) \end{vmatrix}}, \quad \vec{F} = \begin{pmatrix} C_2^0 \\ C_1^0 \end{pmatrix}. \quad (13)$$

In Eq. (11) only the α 's with $|\lambda_\alpha(E)| = 1$ are included in the summation because the C_1^0 and C_2^0 are chosen to give $A_\alpha = 0$ when $|\lambda_\alpha| \neq 1$. This guarantees an extended and normalizable solution.

The projected band structure is therefore obtained by diagonalizing $T(\vec{k}_\parallel, E)$ for a given \vec{k}_\parallel and

a set of energies E . The allowed bulk solutions are then obtained if there exists at least one α such that $|\lambda_\alpha(E)| = 1$. This procedure allows for an accurate determination of the projected band edges without the need for diagonalizing the bulk Hamiltonian at many \vec{k}_\parallel 's.

B. The ideal surface

We define an ideal surface as a sudden truncation of an otherwise perfect crystal. It can be represented schematically by a semi-infinite chain as shown in Fig. 2(a). For simplicity, we have assumed that the surface is in the 1st principal layer of the 0th superlayer. Proceeding as before we can write the total wave function for the surface system $\Psi_s(\vec{k}_\parallel; E)$ as

$$\Psi_s(\vec{k}_\parallel, E) = \sum_{L=0}^{\infty} \sum_{\beta=1}^{\mu} \left(\sum_{n=3}^m \left\{ (\vec{u}_\beta \cdot T^L \prod_{l=3}^n t_{l,l-2}^{L,L} \begin{bmatrix} C_2^0 \\ C_1^0 \end{bmatrix}) \psi_{L,n,\beta} \right\} + (\vec{u}_\beta \cdot T^L \begin{bmatrix} C_2^0 \\ C_1^0 \end{bmatrix}) \psi_{L,2,\beta} + (\vec{v}_\beta \cdot T^L \begin{bmatrix} C_2^0 \\ C_1^0 \end{bmatrix}) \psi_{L,1,\beta} \right). \quad (14)$$

In terms of the eigensolutions of T we again obtain

$$\Psi_s(\vec{k}_\parallel, E) = \sum_\alpha A_\alpha \chi_s(\lambda_\alpha, \vec{k}_\parallel, E), \quad (15)$$

where

$$\chi_s(\lambda_\alpha, \vec{k}_\parallel, E) = \sum_{L=0}^{\infty} \lambda_\alpha^L \sum_{\beta=1}^{\mu} \left\{ \left[\sum_{n=3}^m \left[(\vec{u}_\beta \cdot \prod_{l=3}^n t_{l,l-2}^{L,L} \vec{e}_\alpha) \psi_{L,n,\beta} \right] + (\vec{u}_\beta \cdot \vec{e}_\alpha) \psi_{L,2,\beta} + (\vec{v}_\beta \cdot \vec{e}_\alpha) \psi_{L,1,\beta} \right] \right\}. \quad (16)$$

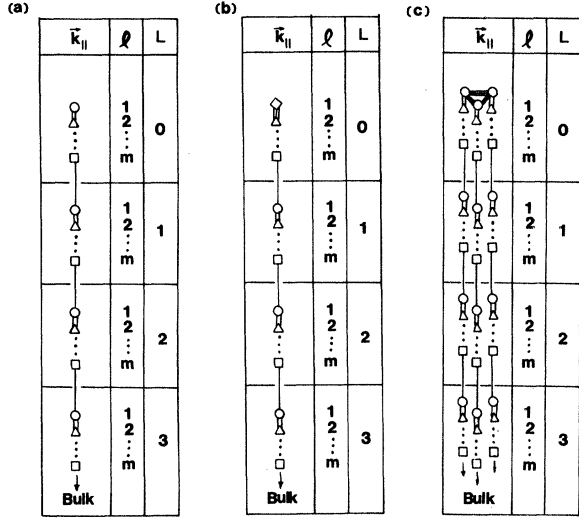


FIG. 2. Schematic representation of (a) an ideal semi-infinite crystal, where the surface termination occurs at the 1st principal layer of the 0th superlayer. (b) A relaxed surface, where the relaxed principal layer is represented as a diamond and the triple line indicates a relaxed interlayer coupling. (c) A reconstructed surface for each \vec{k}_{\parallel} shown as a system of coupled unreconstructed ideal chains with wave vector $\vec{k}_{\parallel} + \vec{G}$. The inter-chain coupling is only through the 1st principal layer.

In order to obtain physically meaningful and normalizable solutions, we must restrict the summation in (15) so that $|\lambda_{\alpha}| \leq 1$.

The Schrödinger equation at the surface is given by

$$(E - H_{1,1}^{0,0})C_1^0 = H_{1,2}^{0,0}C_2^0. \quad (17)$$

Since

$$\begin{bmatrix} C_2^0 \\ C_1^0 \end{bmatrix} = \sum_{\alpha, |\lambda_{\alpha}| \leq 1} A_{\alpha} \begin{bmatrix} P_2 \cdot \vec{e}_{\alpha} \\ P_1 \cdot \vec{e}_{\alpha} \end{bmatrix}, \quad (18)$$

$$(P_2)_{\alpha\beta} \equiv (\vec{u}_{\alpha})_{\beta}, \quad (P_1)_{\alpha\beta} \equiv (\vec{v}_{\alpha})_{\beta},$$

the A_{α} 's can be determined by substituting (18) into (17). This gives

$$(-H_{1,2}^{0,0}, (E - H_{1,1}^{0,0})) \sum_{\alpha, |\lambda_{\alpha}| \leq 1} A_{\alpha} \begin{bmatrix} P_2 \cdot \vec{e}_{\alpha} \\ P_1 \cdot \vec{e}_{\alpha} \end{bmatrix} = 0. \quad (19)$$

If E is within the bulk region, then (19) gives the coefficient A_{α} for the resonant or extended states in the system. If E is in the gap then there are only μ values of $|\lambda_{\alpha}| < 1$ and Eq. (19) must be conditionally satisfied. That is, a solution exists only if

$$\det[(E_s - H_{1,1}^{0,0})S_1 - H_{1,2}^{0,0}S_2] = 0, \quad (20)$$

where

$$\begin{aligned} [S_1(\vec{k}_{\parallel}, E)]_{\alpha\beta} &= [\vec{v}_{\alpha} \cdot \vec{e}_{\beta}(\vec{k}_{\parallel}, E)], \\ [S_2(\vec{k}_{\parallel}, E)]_{\alpha\beta} &= [\vec{u}_{\alpha} \cdot \vec{e}_{\beta}(\vec{k}_{\parallel}, E)]. \end{aligned} \quad (21)$$

This equation then determines the bona fide surface states of the system. The allowed surface-state energies can then be substituted back into Eq. (19) to solve for A_{α} 's, and the A_{α} 's can in turn be substituted into Eq. (13) to get the orbital character. The decay length of any surface state with energy E_s (in units of superlayer spacing) can be obtained from

$$D = - \frac{1}{\ln |\lambda(\vec{k}_{\parallel}, E_s)|_{\max}}, \quad (22)$$

where

$$|\lambda|_{\max} = \max_{|\lambda| \leq 1} (|\lambda_1|, \dots, |\lambda_{\mu}|). \quad (23)$$

C. The relaxed surface

For a relaxed surface the symmetry remains unchanged and is the same as in the ideal case. The system therefore can again be represented as a semi-infinite one-dimensional chain as shown in Fig. 2(b). The only difference is that now the 0th superlayer is not equivalent to all others. In terms of the transfer matrix this means

$$T_1 \equiv T_{1,0} \neq T_{2,1} = T_{3,2} = \dots \equiv T_2.$$

The total wave function $\Psi_{s,r}(\vec{k}_{\parallel}, E)$ is now given by

$$\begin{aligned} \Psi_{s,r}(\vec{k}_{\parallel}, E) &= \sum_{L=1}^{\infty} \sum_{\beta=1}^{\mu} \left(\sum_{n=3}^m \left\{ \left(\vec{u}_{\beta} \cdot T_2^{L-1} \prod_{i=3}^n T_{i,i-2}^{L,L} \begin{bmatrix} C_2^1 \\ C_1^1 \end{bmatrix} \right) \psi_{L,n,\beta} \right\} + \left(\vec{u}_{\beta} \cdot T_2^{L-1} \begin{bmatrix} C_2^1 \\ C_1^1 \end{bmatrix} \right) \psi_{L,2,\beta} + \left(\vec{v}_{\beta} \cdot T_2^{L-1} \begin{bmatrix} C_2^1 \\ C_1^1 \end{bmatrix} \right) \psi_{L,1,\beta} \right) \\ &+ \sum_{\beta=1}^{\mu} \left(\sum_{n=3}^m \left\{ \left(\vec{u}_{\beta} \cdot \prod_{i=3}^n T_{i,i-2}^{0,0} T_1^{-1} \begin{bmatrix} C_2^1 \\ C_1^1 \end{bmatrix} \right) \psi_{0,n,\beta} \right\} + \left(\vec{u}_{\beta} \cdot T_1^{-1} \begin{bmatrix} C_2^1 \\ C_1^1 \end{bmatrix} \right) \psi_{0,2,\beta} + \left(\vec{v}_{\beta} \cdot T_1^{-1} \begin{bmatrix} C_2^1 \\ C_1^1 \end{bmatrix} \right) \psi_{0,1,\beta} \right). \end{aligned} \quad (24)$$

In terms of the eigensolutions of T_2 we can write

$$\Psi_{s,r}(\vec{k}_{\parallel}, E) = \sum_{\alpha, |\lambda_{\alpha}| \leq 1} A_{\alpha} \chi_{s,r}(\lambda_{\alpha}), \quad (25)$$

where

$$\begin{aligned} \chi_{s,r}(\lambda_\alpha) = & \sum_{L=1}^{\infty} \lambda_\alpha^L \sum_{\beta=1}^{\mu} \left\{ \prod_{n=3}^m \left[\left(\vec{u}_\beta \cdot \prod_{l=3}^n t_{l,l-2}^{L,L} \vec{e}_\alpha \right) \psi_{L,n,\beta} \right] + (\vec{u}_\beta \cdot \vec{e}_\alpha) \psi_{L,2,\beta} + (\vec{v}_\beta \cdot \vec{e}_\alpha) \psi_{L,1,\beta} \right\} \\ & + \sum_{\beta=1}^{\mu} \left\{ \sum_{n=3}^m \left[\left(\vec{u}_\beta \cdot \prod_{l=3}^n t_{l,l-2}^{0,0} T_1^{-1} \vec{e}_\alpha \right) \psi_{0,n,\beta} \right] + (\vec{u}_\beta \cdot T_1^{-1} \vec{e}_\alpha) \psi_{0,2,\beta} + (\vec{v}_\beta \cdot T_1^{-1} \vec{e}_\alpha) \psi_{0,1,\beta} \right\}. \end{aligned} \quad (26)$$

Since this wave function is determined through the vector C^1 it is convenient to transfer the surface boundary condition (17) into the 1st superlayer.

Using

$$\begin{bmatrix} c_2^0 \\ c_1^0 \end{bmatrix} = T_1^{-1} \begin{bmatrix} c_2^1 \\ c_1^1 \end{bmatrix} \quad (27)$$

we obtain

$$\left(-H_{1,2}^{0,0}, (E - H_{1,1}^{0,0}) \right) T_1^{-1} \begin{bmatrix} c_2^1 \\ c_1^1 \end{bmatrix} = 0. \quad (28)$$

Now, from (25) and (26) we have

$$\begin{bmatrix} c_2^1 \\ c_1^1 \end{bmatrix} = \sum_{\alpha, |\lambda_\alpha| \leq 1} A_\alpha \begin{bmatrix} P_2 \cdot \vec{e}_\alpha \\ P_1 \cdot \vec{e}_\alpha \end{bmatrix}, \quad (29)$$

and (28) becomes

$$\left[\left(-H_{1,2}^{0,0}, (E - H_{1,1}^{0,0}) \right) T_1^{-1} \right] \sum_{\alpha, |\lambda_\alpha| \leq 1} A_\alpha \begin{bmatrix} P_2 \cdot \vec{e}_\alpha \\ P_1 \cdot \vec{e}_\alpha \end{bmatrix} = 0. \quad (30)$$

The condition for allowed surface states is then given by

$$\det[(E_{s,r} - H_{1,1}^{0,0}) T_1^{-1} S_1 - H_{1,2}^{0,0} T_1^{-1} S_2] = 0. \quad (31)$$

The solutions of Eq. (31) can again be substituted into (30) to determine A_α 's and the orbital character. The decay length of any surface state with energy $E_{s,r}$ is again obtained from (22) and (23).

D. The reconstructed surface

When a surface undergoes reconstruction, the surface unit cell is enlarged. Consequently, the 1st Brillouin zone of the surface becomes smaller. Thus each \vec{k}_\parallel chain in the new zone must be coupled to all other $\vec{k}_\parallel + \vec{G}$ chains in the old zone. (Here \vec{G} represents a reciprocal-lattice vector of the reconstructed surface.) This is shown schematically in Fig. 2(c). As a result of this coupling the eigenstate of the reconstructed system characterized by \vec{k}_\parallel will be a linear combination of all the eigenstates of the unreconstructed $\vec{k}_\parallel + \vec{G}$ chains. Therefore

$$\Psi_{s,RC}(\vec{k}_\parallel, E) = \sum_{\vec{G}, E'} C_{\vec{G}}^\alpha(E') \Psi_s(\vec{k}_\parallel + \vec{G}, E'). \quad (32)$$

This can be simplified, however, in the case where the surface states of the unreconstructed system are very localized. Now the coupling between a surface state at $\vec{k}_\parallel + \vec{G}$ and a bulk continuum state at $\vec{k}_\parallel + \vec{G}'$ is very small. Thus the eigenstates of the reconstructed system can be divided into those which derive purely from gap states and those which derive purely from bulk continuum states. Since our main interest is in the behavior of surface states under surface reconstruction we may write

$$\Psi_{s,RC}(\vec{k}_\parallel, E) = \sum_{\vec{G}, \alpha} C_{\vec{G}}^\alpha \Psi_s^\alpha(\vec{k}_\parallel + \vec{G}), \quad (33)$$

where $\Psi_s^\alpha(\vec{k}_\parallel + \vec{G})$ is the α^{th} gap state of the $\vec{k}_\parallel + \vec{G}$ chain, and $\Psi_{s,RC}(\vec{k}_\parallel, E)$ is the total wave function of the reconstructed system. Substitution of (33) into the Schrödinger equation for the reconstructed system then gives the required secular equation.

III. AN EXAMPLE

In this section we are going to illustrate the use of the techniques described in this paper by calculating the surface properties of a simple and in-

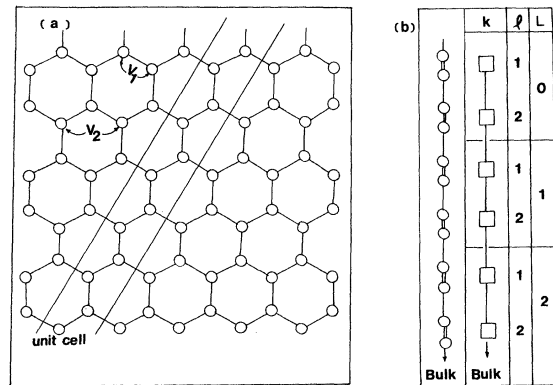


FIG. 3. (a) Semi-infinite two-dimensional honeycomb lattice with the surface line indicated by dangling bonds. The unit cell for this semi-infinite system is also shown. The atoms interact through V_1 and V_2 . (b) Schematic representation of the honeycomb lattice as a one-dimensional chain, where the circles are atomic layers, and the squares principal layers. l and L are principal and superlayer indices, respectively.

structive system. Consider a semi-infinite two-dimensional honeycomb lattice as shown in Fig. 3(a). For simplicity we assume there is only one s -like orbital on each atom. We further assume there are only 1st neighbor (V_1) and 2nd neighbor (V_2) interactions between the atoms. The s -like orbitals are taken to be orthonormal.

In what follows we will set up the transfer matrix T , obtain the projected band structure, calculate the surface bands, and find the wave functions and decay lengths of the surface states.

A. The transfer matrix

To set up the transfer matrix we must first identify the principle layers which only interact through nearest neighbors. Since the atoms interact through 2nd neighbors, each principle layer must contain two atomic layers as shown in Fig. 3. We may now define superlayers which will contain two equivalent principle layers¹⁷ as shown in Fig. 3(b). This is useful since the transfer matrix T couples adjacent superlayers.

$$T(k, E) = \begin{bmatrix} H_1^{-1}(E - H_0)H_1^{-1}(E - H_0) - H_1^{-1}H_1^\dagger & -H_1^{-1}(E - H_0)H_1^{-1}H_1^\dagger \\ H_1^{-1}(E - H_0) & -H_1^{-1}H_1^\dagger \end{bmatrix}, \quad (37)$$

where H_0 is the interaction of a principal layer with itself and H_1 is the interaction between adjacent principal layers. They are given by

$$H_0 = \begin{bmatrix} V_2(\eta + \eta^*) & V_1(1 + \eta) \\ V_1(1 + \eta^*) & V_2(\eta + \eta^*) \end{bmatrix}, \quad (38)$$

$$H_1 = \begin{bmatrix} V_2(1 + \eta) & 0 \\ V_1 & V_2(1 + \eta) \end{bmatrix}, \quad (39)$$

where $\eta = e^{ika}$ and a is the lattice constant in the surface line.

B. The projected band structure

The projected band structure can immediately be obtained from a knowledge of the eigenvalues of $T(k, E)$. As shown in (10) the eigenvalues will always fall into two groups: the set $\{\lambda\}$ and $\{\lambda^{*-1}\}$. A bulk solution will be allowed at (k, E) if any $|\lambda(k, E)| = 1$.

As an example, in Table I we have listed the modulus of the eigenvalues of T at $k=0$ for a series of energies. We have chosen $V_1 = -1.0$ and $V_2 = -0.1$. Notice a gap is clearly visible within -0.8 and 1.2 . Note also that in this region two $|\lambda| < 1$ and two $|\lambda| > 1$. Performing a similar oper-

There are two s -like orbitals in the unit cell of each principle layer. Therefore the Bloch-state basis function for the l th principle layer of the L th superlayer is given by a two-component vector:

$$\psi_{L, l}(k) = \frac{1}{\sqrt{N}} e^{ikna} \begin{bmatrix} S_1(L, l, na) \\ S_2(L, l, na) \end{bmatrix}. \quad (34)$$

The total wave function is then given by

$$\Psi(k, E) = \sum_{L, l} [C_l^L(k, E)\psi_{L, l}(k)], \quad (35)$$

where the coefficients C_l^L are two-component column vectors. The transfer matrix $T(k, E)$ is defined from

$$\begin{bmatrix} C_2^L \\ C_1^L \end{bmatrix} = T^L(k, E) \begin{bmatrix} C_2^0 \\ C_1^0 \end{bmatrix}, \quad (36)$$

where T is a 4×4 matrix. The components of T are obtained from the matrix elements of the Hamiltonian between principal layers. Thus

for several k points we obtain the projected band structure shown in Fig. 4(a). We are now in a position to search for the surface states in the gaps.

C. Surface bands

The allowed energies of surface states for a given k are obtained from (2) by satisfying

$$\det[(E_s - H_0)S_1 - H_1 S_2] = 0, \quad (40)$$

TABLE I. The eigenvalues of T for several energies at $k=0.0$. Note that $|\lambda_1| = |\lambda_4|^{-1}$ and $|\lambda_2| = |\lambda_3|^{-1}$.

E	$ \lambda_1(E) $	$ \lambda_2(E) $	$ \lambda_3(E) $	$ \lambda_4(E) $
1.5	1190.1611	1.0	1.0	0.00084
1.4	1273.0781	1.0	1.0	0.00079
1.3	1357.0171	1.0	1.0	0.00074
1.2	1441.9956	1.0	1.0	0.00069
1.1	1528.0203	1.9667	0.5087	0.00065
1.0	1615.0960	2.4975	0.4005	0.00062
-0.6	3151.3489	2.1858	0.4574	0.00032
-0.7	3256.1641	1.7605	0.5670	0.00031
-0.8	3361.9915	1.0	1.0	0.00030
-0.9	3468.8291	1.0	1.0	0.00029
-1.0	3576.6724	1.0	1.0	0.00028
-1.1	3685.5160	1.0	1.0	0.00027

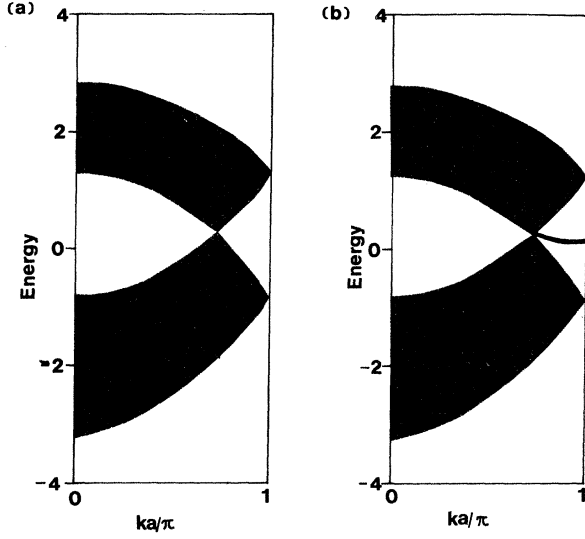


FIG. 4. (a) Projected band structure of the system shown in Fig. 3, where the energy is plotted in units of $|V_1|$. (b) A band of surface states is found for $k \geq 2\pi/3a$ for energies near 0.2.

where

$$S_1 = \begin{bmatrix} e_3^\alpha & e_3^\beta \\ e_4^\alpha & e_4^\beta \end{bmatrix}, \quad S_2 = \begin{bmatrix} e_1^\alpha & e_1^\beta \\ e_2^\alpha & e_2^\beta \end{bmatrix}. \quad (41)$$

Here $e_1^\alpha, e_2^\alpha, \dots, e_4^\alpha$ and $e_1^\beta, e_2^\beta, \dots, e_4^\beta$ are the components of the α and β eigenvectors of T which have $|\lambda_\alpha| < 1$ and $|\lambda_\beta| < 1$.

TABLE II. The determinant in Eq. (40) as calculated for several energies at $k=0.0, \pi/2a$, and $0.99\pi/a$.

E	$k=0.0$ det	$k=\pi/2a$ det	$k \sim \pi/a$ det
1.1	1.222 22		0.022 97
1.0	1.611 47		0.021 43
0.9	1.955 60		0.019 08
0.8	2.267 96		0.016 92
0.7	2.549 99	0.682 19	0.014 42
0.6	2.799 85	1.043 06	0.011 79
0.5	3.014 87	1.305 26	0.009 03
0.4	3.192 13	1.460 35	0.006 14
0.3	3.329 25	1.562 81	0.003 17
0.2	3.424 38	1.592 11	0.000 00
0.1	3.476 30	1.539 04	0.003 24
0.0	3.484 32	1.390 10	0.006 20
-0.1	3.448 12		0.010 15
-0.2	3.367 34		0.013 70
-0.3	3.241 33		0.017 50
-0.4	3.068 23		0.021 30
-0.5	2.843 61		0.024 97
-0.6	2.556 61		0.028 86
-0.7	2.175 67		0.032 66

In Table II we list various values of the determinant in (40) for a series of gap energies at $k=0, \pi/2a$, and $\sim\pi/a$. We notice that no surface state can be identified at $k=0$ and $\pi/2a$. Near π/a , however, we obtain a surface state where the $|\det| \approx 0$ at $E_s=0.2$. Performing a similar search for many k points, we obtain the surface band shown in 4(b).²⁰

Note at $k=\pi/a$ the outer atomic surface layer is decoupled from the rest of the system. Consequently, the transfer matrix is not defined. The energy of the surface state is then given exactly by $E_s = V_2(\eta + \eta^*) = 0.2$.

D. Wave function and decay length

From (35) and (36) we can write

$$\Psi_s(k, E_s) = \sum_{L=0}^{\infty} (\psi_{L,1}, \psi_{L,2}) T^L(k, E_s) \begin{bmatrix} C_1^0 \\ C_2^0 \end{bmatrix}, \quad (42)$$

where C_1^0 and C_2^0 represents four unknowns to be determined. In terms of the eigensolutions of T we obtain

$$\Psi(k, E_s) = \sum_{L=0}^{\infty} \sum_{\alpha=1}^4 \left((\psi_{L,1}, \psi_{L,2}) \begin{bmatrix} S_1 \\ S_2 \end{bmatrix} \right)_\alpha \lambda_\alpha^L A_\alpha, \quad (43)$$

where the four coefficients A_α are given by (13). Note, however, that in (43) two of the A_α 's with $|\lambda_\alpha| > 1$ must be identically zero for a meaningful solution. This leaves the other two A_α 's to be determined by (19) and (21) with

$$[(E_s - H_0)S_1 - H_1S_2] \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = 0. \quad (44)$$

The C_1^0 and C_2^0 are then obtained by inverting (13).

In Table III we show the normalized orbital character of several surface states at (k, E_s) ,

TABLE III. The energy, character, and decay length (in units of superlayer spacing) for various surface states. Charge-density projections are given in the character column, where l_n stands for the n th atomic layer in the l th principal layer.

$\frac{ka}{\pi}$	E_s	Character				Decay length
		1_1	1_2	2_1	2_2	
0.720	0.273	0.565	0.004	0.428	0.003	3.16
0.765	0.253	0.633	0.003	0.362	0.002	1.55
0.810	0.234	0.749	0.003	0.248	0.001	0.95
0.855	0.220	0.834	0.002	0.164	0.000	0.63
0.900	0.210	0.910	0.001	0.089	0.000	0.43
0.945	0.203	0.971	0.000	0.029	0.000	0.28

where (40) is satisfied. The decay length (in units of superlayer spacing) of each surface state is also listed. These are obtained directly from the eigenvalues of $T(k, E_s)$ with maximum modulus less than 1 as in (22) and (23).

We note that the surface states are primarily localized on the 1st atomic layer of each principal layer. This is a consequence of E_s being near the self-energy of an atomic layer [i.e., $V_2(\eta + \eta^*)$]. For a one-dimensional system of atomic layers the nodal structure of the state near this energy is of the form (+, 0, -, 0, +, ...) with a wavelength close to the superlayer spacing. Note, in addition, that as $k \rightarrow \pi/a$ the surface state is approaching complete localization on the surface layer as discussed earlier.

IV. CONCLUSION

We have presented a simple and efficient scheme for calculating surface band structures with Hamiltonians described within localized orbital basis functions. The specific advantages of this technique are the following.

(1) It is conceptually simple, avoiding Green's functions and placing the bulk solid and a surface-terminated solid on an equal footing. This is particularly appealing from a pedagogical point of view.

(2) It saves a considerable amount of computational effort as compared to techniques presently available. The matrices that need to be diagonalized are smaller than those in slab calculations. This difference in size overcompensates the larger number of diagonalizations needed in this scheme. Moreover, time-consuming calculations of bulk Green's functions or effective fields are avoided. An example of typical matrix sizes of T for a few representative low-index surfaces is given in Table IV.

(3) It is accurate in the sense that no approxi-

TABLE IV. The size of the transfer matrix T for various representative elemental surfaces using N basis orbitals per atom and up to 3rd neighbor interactions.

Surfaces	n th-neighbor interactions		
	1st	2nd	3rd
bcc (100)	$2N$	$4N$	$4N$
fcc (100)			
fcc (111)	$2N$	$2N$	$4N$
Diamond (111)	$2N$	$4N$	$6N$
Diamond (100)			
Diamond (110)	$4N$	$8N$	$8N$

mations have been made in constructing the quantities required in the main formalism. The Slater-Koster method, for example, requires knowledge of the bulk Green's function which is obtained by integrating over a finite grid of \vec{k}_\perp 's.

(4) Once the T matrix is obtained for a given solid it need not be calculated again for studying surface relaxations, reconstructions, or interfaces between surface systems. In this sense it is as efficient as the Slater-Koster scheme or the effective-field approach.

(5) The decay lengths and orbital character of the surface states are direct by-products of the method.

ACKNOWLEDGMENTS

We should like to thank Dr. E. Mele, D. Vanderbilt, and D. Allan for helpful comments. One of us (J.J.) would like to thank the Alfred P. Sloan Foundation for a fellowship. This work was supported in part by JSEP Contract No. DAAG-29-78-C-0020.

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¹²For example, we studied the ZnO(10 $\bar{1}$ 0) surface with 13 orbitals per molecule and nearest-neighbor interactions. The "Slater-Koster method" was faster than the "effective-field" method by about 1.2, our scheme was faster than the Slater-Koster method by about 11.0.

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¹⁷A superlayer is defined as a stack of inequivalent principal layers. For the special case where all principal layers are equivalent the superlayer must be de-

finied as *two* adjacent principal layers.

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¹⁹Note the similarity to the plane-wave-like basis system where one needs to know the wave function and its derivative on the *same* layer.

²⁰A similar surface feature has been observed in Ref. 7 where the honeycomb lattice was studied using sp^2 -like orbitals with nearest-neighbor interactions.