

Green's-function formalism suitable for studying chemisorption on real semi-infinite systems*

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A new formalism for obtaining the Green's functions suitable for studying the surface properties and chemisorption properties of real crystals is presented. The method has a number of calculational advantages which make it possible to examine the problem of chemisorption on the surface of crystals which are represented by realistic and complex band structures. The method is illustrated by applying it first to a linear monatomic chain, second to a simple cubic *s*-band crystal, and third to a two-band fcc crystal. The first two well-known examples are presented to verify the method. The last example has not been considered before and shows the importance of including in the model calculation all of the crystal bands, even those not involved directly in the chemisorption bond.

I. INTRODUCTION

The Green's-function formalism for studying the surface properties of semi-infinite systems and the chemisorption properties of these systems has been well known for a number of years.¹⁻³ To date, however, most of the work has been directed toward simple model systems because of the computational complexity of the method.⁴⁻¹⁰ Even those papers which deal with "real" systems, necessarily make a number of approximations regarding the electronic properties of the bulk crystal in order to simplify the calculation to the point where it becomes tractable.¹¹⁻¹³ Many useful qualitative conclusions regarding the behavior of the change in the density of states during chemisorption have been made with these model calculations. Quantitative comparisons, however, are not presently possible due to the absence of a numerical procedure which is practical for considering real systems with complex band structures.

Two schemes have evolved which are directed toward solving this problem. The first is the method of generating the Green's function as a continued fraction as reported by Haydock, Heine, and Kelly.^{14,15} This method is closely related to the method of moments which has been exploited by Cyrot-Lackmann, Gaspard, and others.¹⁶⁻¹⁸ Whether this method can be practically applied to a real system such as Ni where the full Ni band structure is considered carefully is yet to be demonstrated, although rather complicated model systems have been studied.

The other scheme has recently been used by Fassaert, Liebmann, and van der Avoird.^{19,20} By a clever numerical procedure, they solve for the chemisorption energy of an atom on a semi-infinite

slab without the step of determining the appropriate Green's function. Their method does not permit the calculation of the change in the density of states,²¹ but it is the first attempt to describe accurately the substrate with a realistic and complex model.

The numerically difficult step in those chemisorption calculations which give the change in the density of states is the determination of either the bulk or the surface Green's function in a mixed representation (one depending on wave vector parallel to the surface and on layer index perpendicular to the surface). In this paper, we present a new way to determine this Green's function which has the characteristic that it is no more difficult to consider complex band structures than to consider model bands. We illustrate the method by applying it first to two well-known situations, a monatomic linear chain made up of atoms with one *s*-like orbital and the logical extension to the (001) surface of a simple cubic crystal made up of the same type of atoms.⁴⁻¹⁰ Finally, we apply the method to the nontrivial situation, never before considered, of chemisorption of a one-level adatom on the (001) surface of a fcc metal made up of two interacting bands. This last example shows all the steps of the procedure and also demonstrates the importance in chemisorption calculations of including all of the substrate bands.

II. FORMALISM

In this section, we will discuss the Green's functions for four different subsystems. Whereas only the last of the four contains the desired information regarding the chemisorbed system, our method is based on the fact that the first Green's

function is easy to determine, and through a series of steps the other three can be found sequentially. Hence, we will encounter G^0 the Green's function for a single two-dimensional layer of atoms having the structure of a layer in the bulk crystal; G , the Green's function for the bulk crystal; G^s , the Green's function for a crystal with a surface; and G^a , the Green's function for a crystal with a surface and an adsorbed atom. The first, G^0 , is relatively easy to determine; the last, G^a , contains the desired information about the chemisorbed system. In what follows, we will specialize to consider the (001) surface of a monatomic cubic crystal. However, this in no way restricts the usefulness of the method since it is an easy matter to generalize to other surfaces of solids with different crystal structures.

A. Layer Green's function

We write the one-electron wave function for the infinite crystal in a mixed Bloch-Wannier representation using atomiclike orbitals as

$$\psi(\vec{r}) = \sum_{i, m, n, l} a_i^l e^{i(k_1 n + k_2 m)} \phi_i(\vec{r} - \vec{R}_{n, m, l}), \quad (1)$$

where n , m , l label the lattice cell, $\vec{R}_{n, m, l}$ is the position vector for that cell, and i denotes the type of atomic state on each site. The terms k_1 and k_2 are dimensionless wave vectors (ranging from $-\pi$ to π) in the [100] and [010] directions, respectively. The choice of the wave function to be in this form is made anticipating the fact that the surface destroys the periodicity in one direction, here the [001] direction, but retains the periodicity in the other two directions.

Using this wave function in Schrödinger's equation results in a matrix equation which is of the form

$$\sum_{j'} H_{ij}(l, \vec{k}) a_{j'}^i = E_i(\vec{k}) a_i^i, \quad (2)$$

where E_i is the energy of the i th band, a_i^i is the ei-

genvector of the Hamiltonian, and the matrix $H_{ij}(l, \vec{k})$ is the Hamiltonian matrix element between the i th and j th-type orbitals in layers l and l' , respectively.

For this first step in our solution, we ignore all interactions between layers. Thus, the Schrödinger matrix equation becomes

$$\sum_j H_{ij}(l, \vec{k}) a_j^i = \epsilon_i(\vec{k}) a_i^i, \quad (3)$$

where the matrix now is independent of l and has the dimension $(N \times N)$, and where N is the number of orbitals on each atom. Even for complex systems, this matrix is not very large. With the solution to this equation, we can construct the Green's function for a two-dimensional plane of atoms not interacting with any of its neighboring planes as

$$G_{ij}^0(l, \vec{k}, E) = \sum_k \frac{a_i^{ik} a_j^{jk}}{E - \epsilon_k(\vec{k})} \delta_{il}. \quad (4)$$

Using this Green's function as a starting point, we now proceed to solve sequentially for the other Green's functions in the overall calculation.

B. Bulk Green's function

To obtain the Green's function for the bulk crystal *with interacting planes*, we write the Dyson equation as

$$G_{ij}(l, l') = G_{ij}^0(l, l') + \sum_{l''} G_{il'}^0(l, l'') V_{l''} G_{jj}(l'', l'), \quad (5)$$

where the perturbation comes from the terms in the Hamiltonian matrix of Eq. (2) for $l \neq l'$, i.e., those which connect the planes. This Green's function satisfies the symmetry conditions

$$G_{ij}(l, l') = G_{ji}(l, l') = G_{ij}(l', l). \quad (6)$$

In addition, the Green's function depends only on the difference $l - l'$. Restricting our attention to those Green's functions with positive arguments, Eq. (5) can be written as

$$G_{ij}(l) = G_{ij}^0(l) \delta_{l0} + \sum_{j'} G_{ij'}^0(l) \left(\sum_{l'=0}^{l-1} (1 - \frac{1}{2} \delta_{l'0}) [V_{l'j'}(l - l') + V_{l'j'}(l + l')] G_{j'j}(l') + \sum_{l'=M-l+1}^{M-l} V_{l'j'}(l - l') G_{j'j}(l') \right), \quad 0 \leq l < M \quad (7)$$

$$G_{ij}(l) = \sum_{j'} G_{ij'}^0(l) \sum_{l'=l-M}^{l+M} V_{l'j'}(l - l') G_{j'j}(l'), \quad l \geq M \quad (8)$$

where M is the largest integer for which $V_{ij}(M) \neq 0$. Remember that every function in these equa-

tions depends upon k_1 and k_2 .

In order to solve Eqs. (7) and (8), we proceed as follows. First, we solve Eq. (8) making the assumption that it is valid for all l , even $l < M$. This will give us a set of homogeneous solutions. Second, we form a general solution by constructing a

linear combination of the homogeneous solutions using arbitrary coefficients. Third, we substitute into Eq. (7) to obtain an equation for the coefficients. By solving for the coefficients, we obtain the Green's function which we desire. These steps will be worked out below in detail.

By assuming Eq. (8) is valid for all l , we can represent the solution in the form

$$G_{ij}(l) = q^l G_{ij}(0), \quad (9)$$

where q is a complex quantity to be determined. By substituting into Eq. (8), we obtain, after dividing by q^l (note that the case $q=0$ is not allowed since that corresponds to noninteracting planes),

$$G_{ij}(0) = \sum_{i'j'} G_{i'i'}^0(0) \sum_{l'=-M}^M V_{i'j'}(-l') q^{l'} G_{j'j}(0). \quad (10)$$

For each index j , there are N equations in the set of Eqs. (10), where N is the number of bands in the crystal. With some simple manipulations, Eq. (10) can be rewritten in matrix form as

$$\sum_{j'} (P_{ij'} - \delta_{ij'}) G_{j'j}(0) = 0, \quad (11a)$$

where

$$P_{ij'} = \sum_{i'} \sum_{l'=-M}^M G_{i'i'}^0(0) V_{i'j'}(-l') q^{l'}. \quad (11b)$$

The condition that Eq. (11a) has a solution is that

$$\det(P_{ij'} - \delta_{ij'}) = 0, \quad (12)$$

and this condition determines the values of q which satisfy Eq. (9). Note that this condition is independent of the subscript j in Eq. (11a). From the several solutions for q which result from Eq. (12), we choose those which satisfy the condition

$$|q| \leq 1, \quad (13)$$

since the Green's function in Eq. (9) must satisfy the condition

$$|G_{ij}(l+1)| \leq |G_{ij}(l)|. \quad (14)$$

The determination of the q 's which satisfy Eqs. (13) and (14) for a general case is complicated, so it is convenient at this point to restrict our discussion to the case where $V_{ij}(l) = V_{ij}(-l)$ and $V_{ij}(l) = 0$ for $l > 1$ (i.e., $M=1$). For this case, Eq. (11a) can be written

$$\sum_{j'} (A_{ij'} - Q \delta_{ij'}) G_{j'j}(0) = 0, \quad (15a)$$

where

$$A_{ij'} = \sum_{i'} G_{i'i'}^0(0) V_{i'j'}(1), \quad (15b)$$

and

$$Q = (q + q^{-1})^{-1} = q / (1 + q^2). \quad (16)$$

Here Q is the eigenvalue of the matrix A_{ij} . From Eq. (16), then, we have for the α th eigenvalue

$$q_\alpha = \min \left(\frac{1}{2Q_\alpha} \pm \frac{1}{2Q_\alpha} (1 - 4Q_\alpha^2)^{1/2} \right). \quad (17)$$

From these solutions, we can construct a general expression for the Green's function, namely,

$$G_{ij}(l) = \sum_{\alpha=1}^N b_\alpha q_\alpha^l G_{ij}^\alpha(0), \quad (18)$$

where the quantities b_α are unknown coefficients, and the $G_{ij}^\alpha(0)$ is determined from Eq. (15a) (it is the i th component of the α th eigenvector of the matrix A_{ij}). By substituting Eq. (18) into Eq. (7), we obtain a set of N equations for the unknowns b_α which can be written as (to remove the arbitrariness in the index j , we set $j=i$, although other choices would also suffice)

$$\sum_{\alpha=1}^N B_{i\alpha} b_\alpha = G_{ii}^0(0), \quad (19)$$

where

$$B_{i\alpha} = \sum_{j'} (\delta_{ij'} - 2q_\alpha A_{ij'}) G_{j'i}^\alpha(0). \quad (20)$$

By solving the set of linear equations in Eq. (19) numerically, we find the Green's function for the bulk through Eq. (18). This procedure for finding the bulk Green's function is the difficult step in considering chemisorption. The method we have presented holds a number of advantages over other methods when it comes to the application to a system with a large number of orbitals per atom. We will illustrate the method below, but first we complete the formalism of the chemisorption problem by presenting the method for obtaining the surface Green's function, and then the Green's function for the chemisorbed system.

C. Surface Green's function

Now we proceed to determine the Green's function appropriate for the (001) surface. This is done by writing Dyson's equation for the perturbed bulk system where the perturbation eliminates the bulk interactions between the $l=0$ and $l=-1$ planes. This equation is

$$\begin{aligned} G_{ij}^s(l, l') \\ = G_{ij}(l - l') - \sum_{i', j'} G_{i'i'}(l - l' - 1) V_{i'j'}(1) G_{j'j}^s(0, l), \end{aligned} \quad (21)$$

where the superscript "s" means that the Green's function is for the surface, and the matrix $V_{ij}(1)$ is the same as used above. Note that the minus sign in Eq. (21) eliminates the bulk interactions and

that all the quantities depend upon k_1 and k_2 . For the consideration of chemisorption to follow, we only need the surface Green's function for the surface layer. Thus, choosing $l=l'=0$ in Eq. (21) gives

$$G_{ij}^s(0,0) = G_{ij}(0) - \sum_{i'j'} G_{ii'}(1) V_{i'j'}(1) G_{j'j}^s(0,0). \quad (22)$$

Upon rearrangement, this equation gives

$$G_{ij}^s(0,0) = \sum_{j'} (D^{-1})_{ij'} G_{j'j}(0), \quad (23)$$

where D_{ij} is a matrix which is given by

$$D_{ij} = \delta_{ij} + \sum_{i'} G_{ii'}(1) V_{i'j}(1). \quad (24)$$

Thus, the Green's function for the surface layer is specified completely once the bulk Green's functions for a layer, $G_{ij}(0)$, and for nearest-neighbor layers, $G_{ij}(1)$, are known. Note, again, that the quantities in Eq. (23) all depend on k_1 and k_2 .

D. Chemisorption Green's function

Finally, we arrive at the formalism necessary to consider chemisorption. We want to find the diagonal matrix elements of the Green's function matrix for the composite system schematically given by

$$G^a = \begin{bmatrix} G_{aa'}^a & G_{aj}^a \\ G_{ia'}^a & G_{ij}^a \end{bmatrix}, \quad (25)$$

where the indices a and a' range over the levels on the adatom and the indices i and j range over the bands of the substrate. This matrix is determined from a Dyson equation

$$G^a = G^s + G^s V^a G^a, \quad (26)$$

where the matrix G^s is

$$G^s = \begin{bmatrix} G_{aa'}^0 & 0 \\ 0 & G_{ij}^s \end{bmatrix}. \quad (27)$$

This represents the composite of the free atom and the free surface with no interaction. The matrix V^a in Eq. (26) represents the interaction due to chemisorption and contains terms connecting the adatom levels to the substrate orbitals. The free-atom Green's-function matrix is given by

$$G_{aa'}^0 = (E - E_a)^{-1} \delta_{aa'}. \quad (28)$$

Symbolically, the solution to Eq. (26) is given by

$$G^a = (I - G^s V^a)^{-1} G^s, \quad (29)$$

where I is the identity matrix. In some simple cases, this matrix inversion can be done analytically; for more realistic cases, numerical methods

must be used. The desired information regarding the chemisorbed system is contained in the imaginary part of the diagonal matrix elements of G^a . This imaginary part is the density of states. Of more interest is the change in the density of states due to chemisorption. This can be found by taking the difference of the imaginary parts of the new Green's function and the old as follows:

$$\Delta n_r = \text{Im}(G_{rr}^a - G_{rr}^s), \quad r = a, i. \quad (30)$$

Alternatively, the change in the density of states could be found from the phase shift function by^{4,9,10}

$$\Delta n = -\frac{1}{\pi} \frac{d\eta}{dE}, \quad (31)$$

where

$$\eta(E) = -\tan^{-1}[\det(I - V^a G^s)]. \quad (32)$$

In the first instance, the change in the density of states of each type orbital is found, whereas in the second instance, the total change in the density of states is obtained without the need of determining explicitly the Green's function for the chemisorbed system.

In summary, the following computational steps are required in this method to obtain the change in the density of states (see Table I). First, we must find the eigenvalues and eigenvectors of the Hamiltonian matrix in Eq. (3) to construct the first Green's function G^0 in Eq. (4). Second, the eigenvalues and eigenvectors of matrix A in Eq. (15) must be found and the terms q_α determined in Eq. (17) from the eigenvalues. Third, matrix B must be constructed in Eq. (20) and the set of linear equations in Eq. (19) solved for b_α . Fourth, the bulk Green's function is constructed from Eq. (18) and explicitly obtained for a single layer $G_{ij}(0)$ and for first neighbor layers $G_{ij}(1)$. Fifth, the matrix

TABLE I. Labeling of the four Green's-function matrices considered along with the perturbation matrices that relate them to each other and their dimensions. The essence of the method is that the first Green's function can be determined easily and the others can be found in sequence.

Matrix	Dimension	Definition
G^0	N^a	Layer Green's function
V	N	Layer-layer interaction
G	N	Bulk Green's function
$-V$	N	Perturbation creating surface
G^s	N	Surface Green's function
V^a	$N+n^b$	Adatom-surface interaction
G^a	$N+n$	Chemisorption Green's function

^a N is the number of bands.

^b n is the number of adatom levels.

D in Eq. (24) is constructed, inverted, and used in Eq. (23) to obtain the surface Green's function. All of the above matrix manipulations are done with $(N \times N)$ matrices where N is the number of bands in the bulk crystal. Sixth, a larger Green's-function matrix of dimension $(N+n) \times (N+n)$ is constructed where n is the number of molecularlike orbitals on the admolecule involved in forming the chemisorption bond. Finally, if only the total change in the density of states is desired, then the phase shift function in Eq. (32) is determined which leads to the total change in the density of states through Eq. (31). Alternatively, the matrix Eq. (21) can be used which requires inverting an $(N+n) \times (N+n)$ matrix along with a simple matrix multiplication. Then by forming the difference in Eq. (30), the partial change in the density of states for each band can be determined.

III. RESULTS AND DISCUSSION

Here we consider three examples to illustrate the formalism of the previous section. They are (i) a monatomic linear chain of atoms with one orbital per atom, (ii) a simple cubic crystal with one s band, and (iii) a two-band crystal with the fcc structure. For the first two examples, we only carry them as far as the determination of the bulk Green's function. For the third example, which is both new and the most complicated of the three, we consider all stages of the chemisorption problem.

A. Linear chain

We start with a very simple case of a linear chain of atoms with one electronic state per atom at energy $E=0$. The Green's function of the uncoupled atoms corresponding to Eq. (4) is simply

$$G^0(E) = E^{-1}, \quad (33)$$

where the subscripts i and j are dropped since there is only one band. We assume that the interaction between atoms is limited to nearest neighbors and is of magnitude β . Then the matrix A_{ij} in Eq. (15b) only has one element, and the eigenvalue in Eq. (16) is

$$Q = A = \beta/E. \quad (34)$$

Upon rearrangement, this becomes

$$\beta q^2 - E q + \beta = 0. \quad (35)$$

Using Eq. (17), the solution for q divides into two cases depending on the magnitude of E . For the case $|E| > |2\beta|$, we have

$$q = E/2\beta - \text{sgn}(E/\beta)(E^2/4\beta^2 - 1)^{1/2}, \quad E^2 > 4\beta^2. \quad (36)$$

Note that q^{-1} is given by

$$q^{-1} = E/2\beta + \text{sgn}(E/\beta)(E^2/4\beta^2 - 1)^{1/2}, \quad E^2 > 4\beta^2. \quad (37)$$

For the case $|E| < |2\beta|$, we have

$$q = E/2\beta \pm i(1 - E^2/4\beta^2)^{1/2}, \quad E^2 < 4\beta^2 \quad (38)$$

and

$$q^{-1} = q^*. \quad (39)$$

For this case, the sign is ambiguous, but we cannot determine the sign uniquely until later in the calculation.

Since for this linear-chain example, $N=1$, the sum in Eq. (15a) only has one term and therefore $G^\alpha(0) = 1$. Eq. (20) then reduces to a trivial case and becomes

$$B = (E - 2q\beta)/E. \quad (40)$$

Consequently, the Green's function using Eqs. (18) and (19) takes the simple form

$$G(0) = b = G^0(0)/B. \quad (41)$$

By substituting Eqs. (36), (38), and (40) into Eq. (41), we obtain for both energy ranges

$$G(0) = \frac{\text{sgn}(E/\beta)}{2\beta(E^2/4\beta^2 - 1)^{1/2}}, \quad E^2 > 4\beta^2, \quad (42)$$

$$G(0) = \frac{\pm i}{2\beta(1 - E^2/4\beta^2)^{1/2}}, \quad E^2 < 4\beta^2. \quad (43)$$

To determine the proper sign in Eq. (43), we impose the condition that the imaginary part of the Green's function (which is proportional to the density of states) be positive. Hence, we choose the upper sign²² both in Eqs. (43) and (38). The Green's functions in Eqs. (42) and (43) are the correct result for the case of a linear chain. (*Note that this result was obtained very easily without the necessity of performing an integral over \vec{k} space.*⁹)

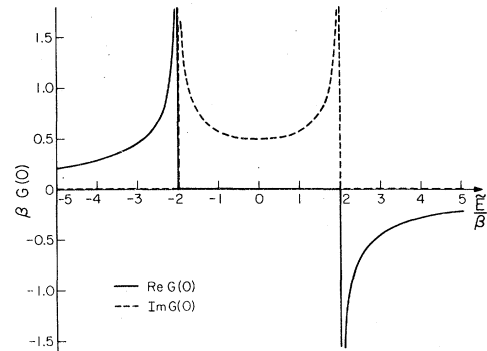


FIG. 1. Real and imaginary parts of the bulk Green's function for cases A and B. For the linear-chain case, $\vec{E} = E$. For the three-dimensional "cubium" case, $\vec{E} = E - 2\beta(\cos k_1 + \cos k_2)$.

This Green's function is shown in Fig. 1. The solid line is the real part of the Green's function which for this simple case is nonzero only outside of the band which has a width of 4β . The imaginary part of the Green's function is shown with the dashed line and is nonzero only inside the band. It is proportional to the density of states.

B. *s*-band cubium

The second example we consider is the tight-binding model of a monatomic simple cubic crystal with one orbital per atom. This corresponds to "cubium" and has been studied extensively by other authors.⁴⁻⁸ In formulating the problem to discuss the (001) surface, the bulk partial Green's function $G(U', \vec{k}, E)$ is needed in Eq. (4). Again, we can drop the subscripts i and j since there is only one band for this system. The energy for the noninteracting layers is given simply by

$$\epsilon(\vec{k}) = 2\beta(\cos k_1 + \cos k_2), \quad (44)$$

where β is the nearest-neighbor hopping integral, and, again, we have set the energy of the atomic level equal to zero (as for the linear-chain case). The Green's function in Eq. (4) for the noninteracting planes is given by

$$G^0(\vec{k}, E) = [E - 2\beta(\cos k_1 + \cos k_2)]^{-1}. \quad (45)$$

The perturbation potential which gives the interaction between adjacent planes is simply β , the same as in the linear-chain case. Consequently, the results for the linear-chain case presented in Eqs. (42) and (43) can be carried over directly to the case of "cubium" if we make the identification of variables

$$E \rightarrow E - 2\beta(\cos k_1 + \cos k_2). \quad (46)$$

Thus, the Green's function for each value of k_1 and k_2 is also shown in Fig. 1 as long as the identification of the energy axis in the figure is given by Eq. (46).

This particular bulk Green's function has been derived by others by several different methods.^{4, 17, 22} The method we present here is not simpler than some of these previous derivations. However, our method does have the advantage of being applicable directly to complex systems.

C. Two-band fcc metal

Now we will apply the formalism to a model two-band system. The reason for doing this is that the present calculation will illustrate all of the steps needed in performing a chemisorption calculation, namely, determination of the bulk Green's func-

tions, finding the appropriate surface Green's functions, and finally obtaining the change in the density of states due to chemisorption on this surface. We choose the system to be a simple tight-binding crystal with the fcc structure and with two electronic states per atom. We will examine the chemisorption of a one-level adatom in the on-site configuration on the (001) surface. These choices specify a problem that has not been solved before by any method. Even though the model is simple, it will illustrate all of the numerical steps that must be performed for more complex and realistic problems.

The model is specified in the linear-combination-of-atomic-orbitals (LCAO) tight-binding (TB) scheme. The on-site energy integrals are given by α_i ($i=1, 2$ distinguish the bands of the solid), and the nearest-neighbor resonance or hopping integrals are given by β_{ij} ($i, j=1, 2$). In all the calculations presented in this example, we use $\alpha_1 = 0.0$, $\alpha_2 = -0.2$, $\beta_{11} = -1.0$, $\beta_{22} = -0.25$, and $\beta_{12} = -0.25$ (note that β_{11} defines the units of energy). The bulk band structure for this fcc model, determined by standard techniques, is shown in Fig. 2. The solid line in the figure is for noninteracting bands which cross (i.e., for $\beta_{12} = 0.0$). The dashed line shows the model we use with interacting bands. The modeling of a broad band and a narrow band is to simulate a transition metal with an *s* band and a *d* band.

For the bulk crystal, the matrix Schrödinger Eq. (3) can be written as

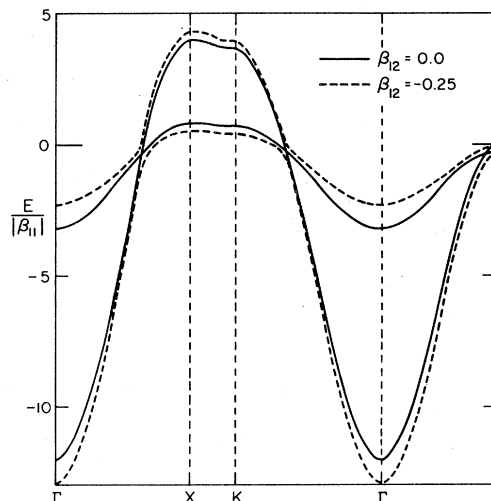


FIG. 2. Bulk band structure for the two-band fcc model described in the text. For $\beta_{12} = 0.0$, the two bands are independent. For $\beta_{12} = -0.25$, the two bands interact and repel each other. The wave-vector notation is that appropriate for the bulk Brillouin zone of a fcc crystal.

$$[\alpha_i - \epsilon_\kappa(\vec{k})]a_i^i + \sum_j 4\beta_{ij}(\cos k_1)(\cos k_2)a_i^j + \sum_j 2\beta_{ij}(\cos k_1 + \cos k_2)(a_{i-1}^j + a_{i+1}^j) = 0. \quad (47)$$

Since we first want the Green's function for the l th layer noninteracting with the other layers, we neglect the last summation in Eq. (47) which connects different layers. The band energies for this noninteracting layer are given by

$$\epsilon_\kappa(\vec{k}) = \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \left[\frac{1}{4}(\epsilon_1 - \epsilon_2)^2 + \epsilon_{12}^2 \right]^{1/2}, \quad (48)$$

where

$$\epsilon_1 = \alpha_1 + 4\beta_{11}f(\vec{k}), \quad (49)$$

$$\epsilon_2 = \alpha_2 + 4\beta_{22}f(\vec{k}), \quad (50)$$

$$\epsilon_{12} = 4\beta_{12}f(\vec{k}), \quad (51)$$

$$f(\vec{k}) = \cos k_1 \cos k_2. \quad (52)$$

The label $\kappa = 1, 2$ denotes the choice of sign in Eq. (48). By substituting Eq. (48) into the truncated form of Eq. (47), we obtain

$$[\alpha_i - \epsilon_\kappa(\vec{k})]a_i^{\kappa} + \sum_j 4\beta_{ij}(\cos k_1)(\cos k_2)a_i^{\kappa} = 0, \quad (53)$$

where the label κ has been added to the coefficients a_i^i since their values depend upon which value of ϵ_κ is used. In general, the values of the coefficients a_i^{κ} must be found by using numerical techniques. For this model problem, however, they can be found analytically with the result being

$$a_i^{\kappa} = \epsilon_{12} D_\kappa, \quad (54)$$

$$a_i^{2\kappa} = -(\epsilon_1 - E_\kappa) D_\kappa, \quad (55)$$

where

$$D_\kappa = \{ \epsilon_{12}^2 + [\epsilon_1 - \epsilon_\kappa(\vec{k})]^2 \}^{-1/2}. \quad (56)$$

Note that all quantities depend upon the wave vectors k_1 and k_2 . Now all the quantities needed to define the Green's function for the layer in Eq. (4) are known.

To obtain the Green's function for our model bulk crystal with interacting planes, we examine Eq. (47) to determine the interaction matrix between layers. It is given by

$$V_{ij}(l, l') = 2\beta_{ij}(\cos k_1 + \cos k_2)\delta_{l', l \pm 1}. \quad (57)$$

Using this matrix in Eq. (12) and then substituting into Eq. (11) gives for each value of j

$$(c_1 - Q)G_{1j} + c_2 G_{2j} = 0, \quad (58)$$

$$c_3 G_{1j} + (c_4 - Q)G_{2j} = 0, \quad (59)$$

where

$$c_1 = G_{11}^0 V_{11} + G_{12}^0 V_{21}, \quad (60)$$

$$c_2 = G_{11}^0 V_{12} + G_{12}^0 V_{22}, \quad (61)$$

$$c_3 = G_{21}^0 V_{11} + G_{22}^0 V_{21}, \quad (62)$$

$$c_4 = G_{21}^0 V_{12} + G_{22}^0 V_{22}. \quad (63)$$

The parameters c_1 , c_2 , c_3 , and c_4 are complicated, but completely specified and trivial to express numerically. To solve for the eigenvalues Q , we have from Eq. (14)

$$\det \begin{vmatrix} c_1 - Q & c_2 \\ c_3 & c_4 - Q \end{vmatrix} = 0, \quad (64)$$

which yields

$$Q_\alpha = \frac{1}{2}(c_1 + c_4) \pm \left[\frac{1}{4}(c_1 - c_4)^2 + c_2 c_3 \right]^{1/2}, \quad (65)$$

where $\alpha = 1, 2$ depending upon the choice of sign.

Following the assumption of Eq. (18), Eq. (19) for the two unknowns b_α becomes

$$\sum_{\alpha=1}^2 [G_{11}^\alpha - 2(c_1 G_{11}^\alpha + c_2 G_{21}^\alpha)q_\alpha] b_\alpha = G_{11}^0, \quad (66)$$

$$\sum_{\alpha=1}^2 [G_{22}^\alpha - 2(c_3 G_{12}^\alpha + c_4 G_{22}^\alpha)q_\alpha] b_\alpha = G_{22}^0, \quad (67)$$

where q_α is given by Eqs. (17) and (65), and the quantities G_{ij}^α are found numerically by solving Eqs. (58) and (59) for a particular choice of q_α (i.e., G_{ij}^α are the eigenvectors associated with the eigenvalue Q_α). Again, we solve these equations numerically for the unknowns, in this case the two b_α . Then we substitute into Eq. (18) to obtain the desired bulk Green's functions.

In the consideration of chemisorption, these bulk Green's functions, which at this stage depend on k_1 and k_2 , represent an intermediate step. However, for purposes of illustration, we present in Fig. 3 the imaginary parts of G_{11} and G_{22} summed over the two-dimensional Brillouin zone. The details of how this sum is performed will be discussed later. These curves are proportional to the density of states for electrons in bands 1 and 2, respectively. The effect of the coupling of the two bands is seen by the feature at $E=0$ in the imaginary part of G_{11} and the feature at $E=4$ in the imaginary part of G_{22} . When the bands are uncoupled, i.e., when $\beta_{12} = 0$, then these two features are absent.

We now proceed to determine the Green's function appropriate for the (001) surface. We generate the matrix D_{ij} in Eq. (24) numerically which is 2×2 in this example. The inverse can be written analytically in terms of the matrix components, and the matrix product in Eq. (23) is easily performed.

For the chemisorption calculation which we have chosen, it is only necessary that we know the surface Green's function as a function of energy and not as a function of k_1 and k_2 . This is true because

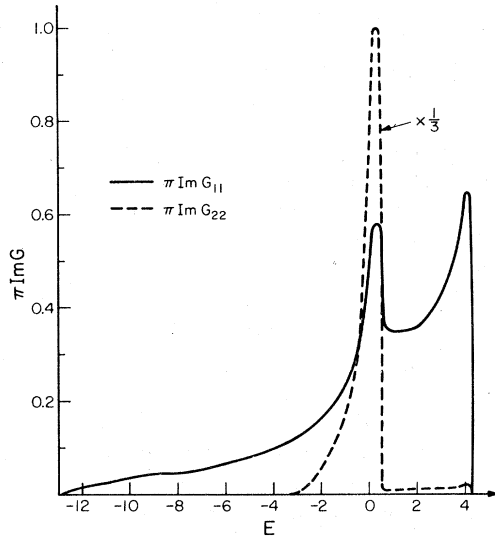


FIG. 3. Density of electronic states in each of the two bands for an atom in the bulk showing the effects of the interaction of the two bands.

we are choosing the chemisorbed site to be directly above the surface atom so that the perturbation which causes the chemisorption does not depend upon k_1 and k_2 . Therefore, our calculation of chemisorption becomes simpler if we sum the surface Green's function over the two-dimensional Brillouin zone and thereby eliminate the k_1 and k_2 dependence. Due to the form of the Green's func-

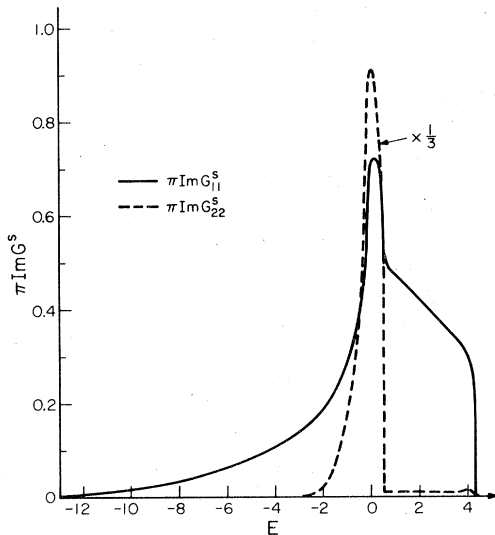


FIG. 4. Density of electronic states in each of the two bands for an atom at the surface. This represents the two contributions to the density of states as might be observed by surface sensitive photoemission. Note the differences between this figure and the bulk results in Fig. 3.

tion chosen in Eq. (4), this sum over the Brillouin zone is

$$\begin{aligned} \bar{G}_{ij}(n, m, l, l', E) \\ = \int_{-\pi}^{\pi} dk_1 \int_{-\pi}^{\pi} dk_2 \cos(nk_1 + mk_2) G_{ij}^s(l, l', k_1, k_2, E). \end{aligned} \quad (68)$$

To obtain the density of states on a surface atom, we must obtain $\bar{G}_{ij}(0, 0, 0, 0, E)$ so that Eq. (36) becomes merely a sum over the Brillouin zone. In this work, the sum is performed by sampling²³ a mesh of special points in the two-dimensional zone. The results shown in the figures are for a sample of 1275 points in the irreducible $\frac{1}{8}$ of the square-surface Brillouin zone.

In Fig. 4, we present the densities of states for the two types of bands for the surface layer of atoms. On comparing Figs. 3 and 4, we see that the density of states for band 1 is significantly changed between the bulk and the surface. Band 2 is also different, but in a more subtle way.

We are now in a position to consider chemisorption explicitly. For illustration purposes, we choose one of the simplest cases. We choose the adatom to have one atomic level at energy E_a . The atom sits in the on-site configuration where the adatom level interacts only with the two orbitals on the nearest substrate atom below it with resonance integrals of V_{a1} and V_{a2} between adatom and atomic levels 1 and 2, respectively. The Green's function G_{aa}^0 for the free atom is given simply by Eq. (28). We wish to find the diagonal matrix elements of the Green's-function matrix for the composite system given by

$$G^a = \begin{bmatrix} G_{aa}^a & G_{a1}^a & G_{a2}^a \\ G_{a1}^a & G_{11}^a & G_{12}^a \\ G_{a2}^a & G_{12}^a & G_{22}^a \end{bmatrix}. \quad (69)$$

To obtain these, we solve the matrix Eq. (29) numerically, where the matrix G^s is

$$G^s = \begin{bmatrix} G_{aa}^0 & 0 & 0 \\ 0 & G_{11}^s & 0 \\ 0 & 0 & G_{22}^s \end{bmatrix}, \quad (70)$$

and the interaction matrix V is given in our simple case by

$$V = \begin{bmatrix} 0 & V_{a1} & V_{a2} \\ V_{a1} & 0 & 0 \\ V_{a2} & 0 & 0 \end{bmatrix}. \quad (71)$$

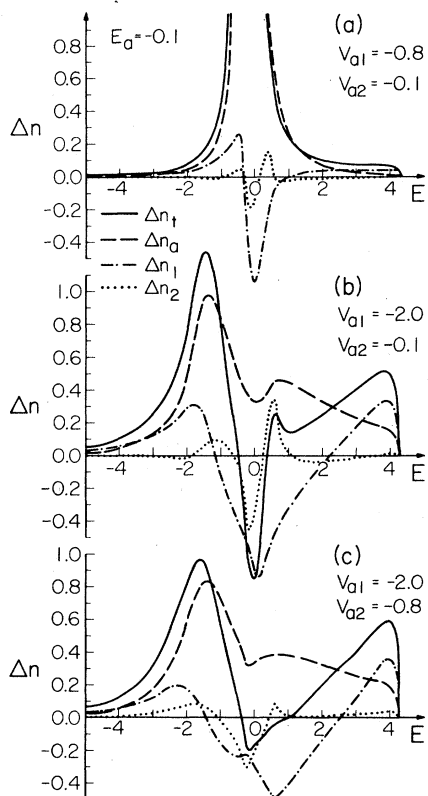


FIG. 5. Change in the density of states Δn due to chemisorption of an adatom with energy level $E_a = -0.1$. For three different values of the interaction strengths between adatom and the two bands, the total change in the density of states as well as the partial changes due to the electrons in band 1, band 2, and on the adatom are shown.

It is the fact that the V matrix does not depend on k_1 and k_2 which allows us to use the Green's functions which have been summed over the surface Brillouin zone.

We have obtained the change in the density of states on the adatom and in both bands on the surface atom by the method given in Eq. (30). In Fig. 5, we present results for the case $E_a = -0.1$, and for several choices of the parameters V_{a1} and V_{a2} . We show the changes in the density of states of the electrons in band 1, Δn_1 ; of the electrons in band 2, Δn_2 ; and the change in the density of states of electrons on the adatom, Δn_a . Also shown is the total change in the density of states Δn_t , where each change is equally weighted in the sum. This total change is related to the results of a photoemission measurement. These curves show the familiar bonding and antibonding resonances in the surface density of states and how these resonances are affected by changes in the strength of coupling. Of importance is the observation that increasing the

strength of coupling of the adatom to one band has an effect on the electrons in the other band. Comparing Δn_2 between Figs. 5(a) and 5(b) shows that increasing the coupling between the adatom and band 1 perturbs band 2. Hence, there are important effects due to the interaction of substrate electrons even though those electrons may not participate directly in the bonding process.

In Fig. 6, we show similar results for the case $E_a = 2.9$. Again we see the important effect of bands being perturbed even though they are not strongly involved in the chemisorption bond. Here Δn_2 is considerably larger in Fig. 6(b) than in 6(a), while only the coupling to band 1 is increased. Also, for larger coupling strengths, a localized antibonding state is split-off above the metal bands.

IV. CONCLUSIONS

A new method has been presented for finding the Green's function for a bulk material in a mixed representation depending upon wave vector parallel to an imaginary plane and layer number perpendicular to the plane. The calculation of this bulk

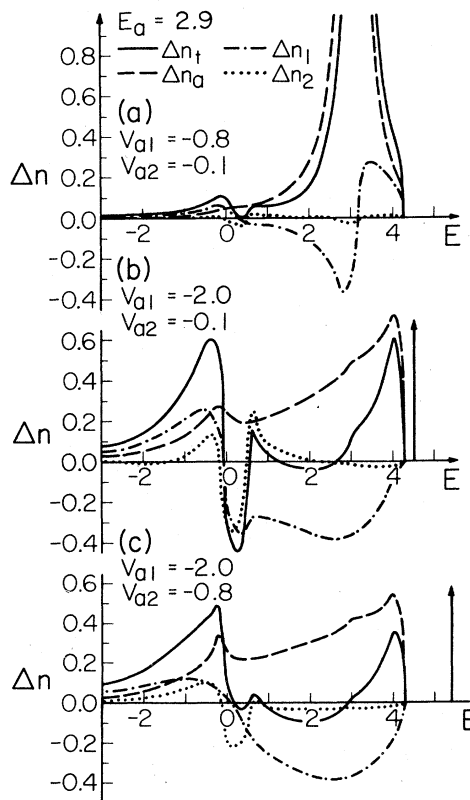


FIG. 6. Same as in Fig. 5 where the energy of the adatom level is $E_a = 2.9$. Note the fact that changing the interaction strength with only one band affects the results in the other band significantly.

Green's function is the most important intermediate step in studying systems wherein the imaginary plane becomes the surface of the crystal and upon which additional atoms may be chemisorbed. The value of this new method lies in the fact that it is numerically practical for studying crystals with complex band structures where the bands can be calculated in a LCAO scheme. Calculations of chemisorption on Ni, for example, can now be attempted using realistic bands rather than relying on simplifying assumptions.²⁴

The method has been demonstrated by analytically solving for the bulk Green's functions for a monatomic linear chain and for the (001) surface of s-band "cubium" (two well-known results). Finally, a new system was considered, the (001) surface of a two-band fcc metal, to demonstrate in detail the numerical steps required for more complex cases.

In addition, the chemisorption of a one-level ad-

atom on the two-band fcc metal was presented. Here, all the steps of a chemisorption calculation were demonstrated on a system not heretofore considered. It was shown that the familiar bonding and antibonding resonances can be recognized although additional structure is present. For the first time, it was specifically demonstrated that when a single level interacts with a multiple band substrate, increasing the interaction between the adatom and only one band significantly affects the electron density in the other bands.

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