Multiple-scattering solutions to the Schrödinger equation for semi-infinite layered materials

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The electronic structure of a layered system, such as a bulk, its surface, or internal interface, is formulated solely in terms of the angular-momentum matrix elements of the isolated layer scattering operators and structural Green's functions that couple the layers together. In contrast to the traditional layer-doubling technique, based on plane-wave expansions, the scattering matrix of the semi-infinite solid is constructed from the solution of a self-consistent equation using the real-space multiple-scattering theory approach. Results of calculations using this new technique are presented and compared with those based on layer coupling with plane-wave expansions.

I. INTRODUCTION

Defects in solids, despite forming only a small percentage of the total of a bulk material, can have a profound influence on macroscopic properties. Specifically, planar defects, such as surfaces and interfaces, are important in determining properties as diverse as catalytic activity,[1] mechanical stability, and deformation behavior.[2] In addition, novel interfacial magnetism found in artificially layered materials may lead to technological improvements in data-storage and -retrieval media.[3] These materials can now be fabricated with great control using techniques capable of producing atomistically sharp interfaces, such as molecular-beam epitaxy. Theories which can help us understand and predict such properties will clearly require a detailed knowledge of the ground-state electronic structure, as well as the bonding and the atomistic structure of these low-dimensional systems.

In practice, techniques capable of yielding the electronic structure of surfaces and interfaces with accuracy similar to that existing for perfect crystals have only recently been realized.[4–6] The difficulties arising from the reduced symmetry and infinite number of unique atoms in the two-dimensional (2D) unit cell has slowed down progress in the development of suitable methods. As a result, innovative uses of perfect-crystal techniques using films[7] or supercells[8] have been adopted by many groups. Systems with large numbers of atoms in a unit cell often need to be considered in order to reduce the effects induced by the artificial boundaries, and thus, calculations on the more complicated structures become extremely demanding computationally. Calculations for semi-infinite solids circumvent the problem of an infinite number of atoms in the 2D unit cell by embedding a finite slab, representing the region of interest, in an otherwise perfect crystal. The matrix Green's-function formalism of Williams *et al.*[9] formulates the perturbation induced by the defect in terms of the perfect-crystal Green's function and the perturbing potential, which is then most easily solved within a localized basis set. This method has the flexibility to study a wide range of problems, and, for example, was successfully used by Feibelman[10] in a study of the chemisorption of an isolated Si atom on an Al monolayer. Two other embedding techniques are those of wave-function matching[4,11] or Green's-function matching[5,6,12–14] and both rely on the fact that electronic screening ensures that the perturbations induced by the defect are localized within a finite distance. Perhaps the most flexible of the Green's-function matching methods for treating 2D defects are those based upon multiple-scattering theory and are collectively known as layer-Korringa-Kohn-Rostoker (LKKR) approaches. LKKR methods have been applied not only to studies of the electronic properties of surfaces[12,14] and interfaces,[6,13] but also to the interpretation of photoemission[15] and low-energy electron diffraction[16] (LEED) experiments. Green's-function matching methods have also been developed for isolated impurities. This technique has been successfully applied to studies of local-moment formation.[17]

II. MULTIPLE-SCATTERING THEORY

The electronic properties of the solid are determined from the charge density which is found from the imagi-

nary part of the trace of the one-electron Green's function. A multiple-scattering analysis of the Dyson equation for G, at a given energy and 2D wave vector $\mathbf{k}$ in the 2D Brillouin zone (BZ), leads to the following expansion about atom α in layer i, labeled α_i, in terms of the atomic Green's function G^{α_i}, atomic (cell) t operator, and the site-diagonal blocks of the scattering-path operator τ,[12,13,18]

$$G=\frac{1}{\Omega}\{G_0+G_0t^{\alpha_i}G_0+(1+G_0t^{\alpha_i})(t^{\alpha_i})^{-1}\times[\tau^{\alpha_i\alpha_i}(\mathbf{k})-t^{\alpha_i}](t^{\alpha_i})^{-1}\times(1+t^{\alpha_i}G_0)\}\ , \tag{1}$$

where Ω is the area of the BZ. In order to calculate $\tau^{\alpha_i\alpha_i}$, we partition the solid into a finite number of layers where the potentials are allowed to relax in a self-consistent-field calculation, bounded on either side by two half-solids in the case of a bulk or interface calculation, and one half-space and a surface barrier in the case of a surface. The exact number of layers included is determined by electronic screening and is chosen so that the potentials of the outermost layers are bulklike to within some prescribed accuracy. Each half-space is characterized by semi-infinite periodicity (SIP),[19] defined as the regular repetition of a basic scattering unit, e.g., a monolayer, along a given direction. Scattering operators for systems characterized by SIP can be found using the recently developed real-space multiple-scattering theory (RS MST) approach.[19] This technique equates the problem of solving the Schrödinger equation for a system with an infinite number of scatterers to one of a finite number in which boundary scatterers are renormalized to represent the infinite half-solid. A self-consistent equation for the determination of either the total-scattering operator or the site components of the scattering-path operator is found by using the property of removal invariance, which states that the scattering properties of a system with SIP remain unchanged when a finite number of basic repeating units is removed from the free end of the system.[19] The resulting equation is expanded, and solved, in the angular-momentum basis set.

At any given $\mathbf{k}$ point in the 2D BZ, a half-solid can be viewed as a semi-infinite chain of scatterers, represented by the layer t matrices, whose inverse (m_i) is given by

$$m_i=(t^{\alpha_i})^{-1}-G_{ii}(\mathbf{k})\ , \tag{2}$$

where $G_{ii}(\mathbf{k})$ are the intralayer structure constants. The layers are coupled together by the interlayer structure constants $G_{ij}(\mathbf{k})$, which can be evaluated using formulas given by Kambe.[20] Here all quantities are matrices in angular-momentum space. We wish to represent the scattering-path operator, τ, which has an infinite number of site indices, by an effective matrix, $\bar{\tau}$, with a finite number of site indices with the boundary sites renormalized. The self-consistent equation for $\bar{\tau}$ is given by

$$\bar{\tau}=\begin{bmatrix} I & 0 & \cdots & 0 & 0 \\ 0 & I & \cdots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & I & g(\mathbf{R}_{01}) \end{bmatrix} \begin{bmatrix} m & -\mathcal{G} \\ -\mathcal{G}' & \bar{\tau}^{-1} \end{bmatrix}^{-1} \begin{bmatrix} I & 0 & \cdots & 0 \\ 0 & I & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & I \\ 0 & 0 & \cdots & g(\mathbf{R}_{10}) \end{bmatrix}\ , \tag{3}$$

where m^{-1} is the scattering operator of the repeat unit and $g(\mathbf{R}_{ij})$ is the angular-momentum representation of the translation operator associated with the vector $\mathbf{R}_{ij}$ which connects the origins of the layers i and j. The quantities $\mathcal{G}$ ($\mathcal{G}'$) are matrices formed from the interlayer structure constants between the layer represented by m and those represented by $\bar{\tau}$, and are given by

$$\mathcal{G}=(G_{01},G_{02},\ldots,G_{0n}) \tag{4}$$

and

$$\mathcal{G}'=\begin{bmatrix} G_{10} \\ G_{20} \\ \vdots \\ G_{n0} \end{bmatrix}\ . \tag{5}$$

It can be shown[21] that the multiple-scattering expansion of (3) gives the exact Green's function up to nth-nearest neighbors, i.e., G_{0n} and G_{n0}, where n is the number of site indices in $\bar{\tau}$. Green's functions connecting sites further apart are given by the matrix products of G_{0n} or G_{n0} with appropriate powers of the translation operator g. They involve internal summations of angular-momentum states which are truncated at a finite l in practical calculations. The translation operator g is determined by the requirement that the Green's function propagating between $(n+1)$th neighbors is also exactly given regardless of the l truncation, leading to the expression of the $\mathbf{k}$-dependent effective translation operator,

$$g(\mathbf{R}_{01})=[G_{0n}(\mathbf{k})]^{-1}G_{0,n+1}(\mathbf{k}) \tag{6}$$

with an analogous construct for $g(\mathbf{R}_{10})$. The scattering-path operator of an interface can then be found using (3) to determine scattering operators for left and right half-spaces, $\bar{\tau}_l$ and $\bar{\tau}_r$, and then inverting the multiple-scattering matrix

$$\tau=\begin{bmatrix} \bar{\tau}_l^{-1} & -\mathcal{G}_{li} & -\mathcal{G}_{lr} \\ -\mathcal{G}_{il} & m_i & -\mathcal{G}_{ir} \\ -\mathcal{G}_{rl} & -\mathcal{G}_{ri} & \bar{\tau}_r^{-1} \end{bmatrix}^{-1} \tag{7}$$

and inserting the appropriate blocks into (1). The subscript i labels the interfacial layers. More interfacial layers can be included in embedding problems involving lattice relaxation or impurities. In the case of a surface calculation, the quantity $\bar{\tau}_l$ would represent the scattering from the surface barrier.

III. RESULTS

In the following calculations, we use the muffin-tin approximation to the crystal potential. Within this model the angular-momentum expansion of (1) in Hartree atomic units is given by

$$G(\mathbf{r},\mathbf{r}')=-\frac{4i\kappa}{\Omega}\left[\sum_{L}\bar{R}_L^{\alpha_i}(\mathbf{r}_<)R_L^{(1)\alpha_i}(\mathbf{r}>)+\sum_{LL'}R_L^{\alpha_i}(\mathbf{r}')(t_l^{\alpha_i})^{-1}[\tau_{iLL'}^{\alpha\alpha}(\mathbf{k})-\delta_{LL'}t_{l'}^{\alpha_i}](t_{l'}^{\alpha_i})^{-1}R_{L'}^{\alpha_i}(\mathbf{r})\right], \tag{8}$$

where $R_L^{\alpha_i}(\mathbf{r}_<)$ and $R_L^{(1)\alpha_i}(\mathbf{r}_>)$ are products of the regular and irregular solutions to the radial Schrödinger equation, respectively, and a complex spherical harmonic. The overtilde is used to denote complex conjugation of the spherical harmonic only and $r_{>(<)}$ is the greater (lesser) of r and r'. The $\mathbf{k}$-resolved density of states, $n(E,\mathbf{k})$, is found from the imaginary part of (8) in the usual manner and was calculated with a constant imaginary energy of 1 mRy at $k_x=0, k_y=0$, i.e., at the Γ point of the 2D BZ. The energy zero was chosen to be the muffin-tin zero, the angular-momentum expansion was truncated at $l=2$, and in the LKKR calculations 25 planes waves were used in the interlayer scattering. All potentials were assumed to be those of the self-consistent bulk solid, and in surface calculations no account was taken of the barrier. Figure 1 shows $n(E,\mathbf{0})$ on a surface atom in three- and nine-layer slabs representing a Cu(100) surface.[22] The rate of convergence in system size of $n(E,\mathbf{0})$ is slow, illustrating that in this case a film calculation of $n(E,\mathbf{0})$ for a semi-infinite surface is inappropriate (compare to Fig. 2). Integrated quantities, of course, will show smaller differences; however, such differences may be important for certain total-energy calculations. Figure 2(a) shows the converged $n(E,\mathbf{0})$ for a surface atom in a semi-infinite surface obtained with the old LKKR method. Figure 2(b) shows the corresponding $n(E,\mathbf{0})$ found with the new algorithm, with the site dimension of $\bar{\tau}$ equal to 1 and 2. We find that (1) increasing the site dimension of $\bar{\tau}$ to 3 changes $n(E,\mathbf{0})$ in the fifth decimal place, (2) the values calculated agree with the old LKKR calculation to three significant figures, and (3) the angular-momentum convergence is comparable between old and new methods in this geometry.

Bulk Cu was simulated as an interface between two ideal (100) surfaces. The results of this calculation are shown in Fig. 3, which compares $n(E,\mathbf{0})$ obtained with the old LKKR method with the new approach. As in the surface calculation, the values agree to the same accuracy and the rate of convergence in the site size of $\bar{\tau}$ is similar. We have also tested the algorithm at $\mathbf{k}=(k_x,k_y)\cong(0.3,0.3)$ (not shown) and found identical behavior in convergence rates. Further, we believe the new approach is converged to greater accuracy than the old LKKR method since the interlayer structure constants are calculated to machine accuracy rather than truncated at 25 plane waves. This is supported by calculations which show that the LKKR results converge towards those obtained with the new technique as the number of plane waves is increased. The CPU times of both approaches are similar, with each $(E,\mathbf{k})$ point in this (100) geometry taking $\cong 1$ to 2 s on a Cray 2.

The LKKR method is capable of providing solutions to the one-electron Schrödinger equation which are accurate enough for total-energy calculations.[6] Self-consistent, spin-polarized, total-energy calculations using the new method are at present underway on a Σ 3 tilt boundary in Fe, and will be reported in a future publication. The details of the self-consistent cycle and the total-energy calculation in the semi-infinite geometry are discussed in more detail in Ref. 13.

Finally, we note that in the RS MST approach the equations of multiple-scattering theory are applied to a finite-size cluster representing a semi-infinite solid. In these calculations, while the bare sites are represented by muffin-tin scattering matrices, the boundary cells are in fact associated with cell t matrices representing semi-

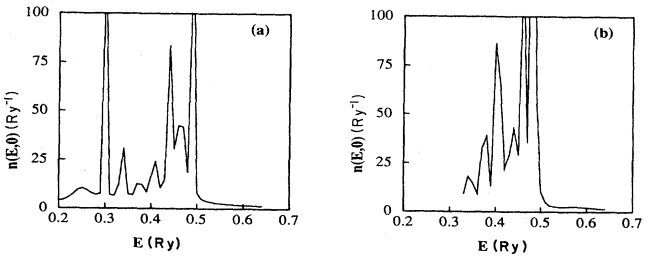

FIG. 1. k-resolved density of states $[n(E,\mathbf{0})]$ for Cu(100) slabs of (a) three layers, and (b) nine layers.

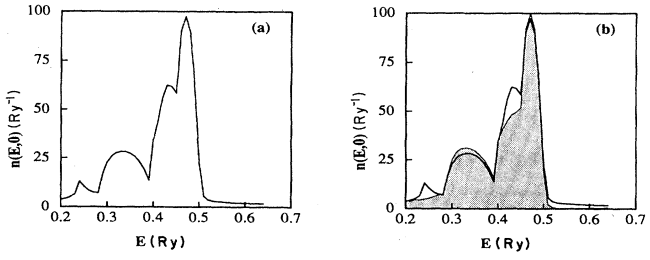

FIG. 2. k-resolved density of states $[n(E,\mathbf{0})]$ for an atom at a Cu(100) surface. (a) LKKR results and (b) new approach: shaded curve, one layer; solid line, two layers in the repeat unit.

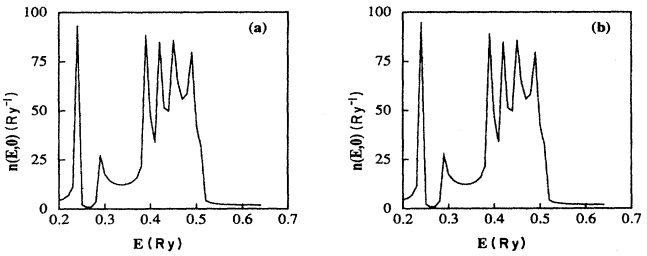

FIG. 3. k-resolved density of states $[n(E,0)]$ for an atom in bulk Cu(100). (a) LKKR results and (b) new approach with a two-layer repeat unit.

infinite chains. This folding of the half-space, i.e., use of a single cell to represent a semi-infinite chain, is not valid if so-called near-field corrections (NFC's) exist.[23] The rapid convergence in the angular-momentum expansions and the excellent agreement with the results obtained with the layer-doubling technique provide strong numerical evidence of the vanishing of the NFC's and the validity of multiple-scattering formalism for the case of space-filling nonoverlapping cell potentials.[24]

IV. CONCLUSIONS

An efficient extension to the LKKR algorithm has been presented which treats all multiple-scattering events in a spherical wave basis. The technique, unlike the usual LKKR formulations, is equally applicable to both high- and low-Miller-index surfaces and interfaces because the Bloch Green's functions for close-spaced places can be treated using Kambe's methods.[20] In addition to applications in electronic-structure calculations, the methods described here should be applicable to treating the LEED problem from high-Miller-index surfaces, such as found at stepped surfaces. Initial work on this problem is presently underway and preliminary results indicate that comparable accuracies are possible in LEED intensities up to 300 eV above the muffin-tin zero, when the angular-momentum expansion is truncated at the appropriate atomic value.[25]

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