Closed-form solutions to surface Green's functions

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We obtain closed-form analytic solutions for surface Green's functions within arbitrary multiorbital models. The formulation is completely general, and is equally valid for empirical tight binding, linear-muffin-tin-orbital tight binding, screened Korringa-Kohn-Rostoker and other Green's-function equivalent formalisms, where the Hamiltonian can be put into a localized (i.e., block-band) form. The solutions are applicable to finite or semi-infinite surface systems, with quite general substrate and overlayers, or even to superlattices. This is achieved by solving Dyson's equations by means of a matrix-valued extension of the Möbius transformation. The analytical properties of the solutions are discussed, and by considering their asymptotic limit, a simple closed form for the exact (semi-infinite) surface Green's function is obtained. The numerical calculation of the surface Green's function (or of observable quantities such as the density of states) using this closed form is compared with previously known iterative procedures. We find that it is far faster, far more stable, and more accurate than the best iterative method. [S0163-1829(97)03804-6]

I. INTRODUCTION

There are a wide variety of interesting and important physical models which correspond to a class of systems which are quasi-one-dimensional, i.e., translationally invariant in two dimensions, but with the translational symmetry broken in the third dimension. We can think of them as a set of (possibly nonidentical) atomic planes, stacked parallel to a chosen crystallographic orientation. The stack may be finite, semi-infinite, or infinite. Such systems are referred to as multilayers. Metallic, semiconductor, and, in particular, magnetic multilayers[1] are currently the subject of intense research, both experimental and theoretical.

There are a wide variety of theoretical treatments of such systems, including empirical tight binding,[2] linear-muffin-tin-orbital (LMTO) tight binding,[3] and screened Korringa-Kohn-Rostoker (KKR),[4] where the Hamiltonian assumes a localized (i.e., block-band) form. Within such schemes, the fundamental problem is to calculate the surface Green's function, which can then be related to the physical properties of the system (such as the density of states). All the methods currently used for calculating the surface Green's function of a finite or semi-infinite system are recursive[5] or iterative,[6,7] and therefore, the surface Green's function can be obtained only numerically.

Numerical calculation of the Green's function has a number of disadvantages. Firstly, for semi-infinite systems, the convergence becomes slow when the imaginary part of the complex energy is small (which is required, for example, in transport applications), or near van Hove singular k points. Second, a purely numerical calculation gives little or no insight into the behavior of the surface Green's function, and ultimately to the behavior of the system. For example, in applications to magnetic multilayers, the explicit dependence of the Green's function on the number of atomic planes in a stack is required if one is to understand the origin of the oscillatory coupling or giant magnetoresistance (GMR).[8,9] All these problems are eliminated, and the computational effort is greatly reduced when one can use a closed-form expression for the surface Green's function which has (to date) been available only for simple single-orbital models of layered structures.[10–12]

In this paper, we show that for any model with a local (i.e., block-band) Hamiltonian–arbitrary lattice, N orbitals, and hopping to Rth nearest neighbors (hereafter referred to as an N band, Rth-order local Hamiltonian model)—it is always possible to obtain closed-form solutions to the surface Green's function for a general surface system composed of n adlayers on an arbitrary (finite or semi-infinite) substrate.

We begin by defining the general local Hamiltonian model for an arbitrary multilayer system in a mixed $\{\mathbf{k}_\parallel, R\}$ basis. We then introduce matrix-valued extensions of the Möbius or bilinear transformations, familiar from complex variable theory. Central to these transformations are the ''Möbius transformation matrices'' $\mathbf{X}$ and $\mathbf{Y}$, which are simple functions of the on-site layer self-energy ($\mathbf{u}$) and hopping ($\mathbf{t}$) matrices. These transformations are then used to solve Dyson's adlayering equations, for the n adlayer surface Green's function $\mathbf{G}_{nn}^{(n)}$. We show that the solution is expressible in closed form (even for fractional n), in terms of the eigenvalues and eigenvectors of the Möbius transformation matrices. These eigenvalues and eigenvectors are related to the eigenstates of the bulk adlayer material. For a given energy ε, we show that the surface Green's functions $\mathbf{G}_{nn}^{(n)}(\varepsilon)$ are asymptotically quasiperiodic in n, with periods determined by the bulk adlayer propagating states. (This agrees with the intuitive view that, as we grow an overlayer on top of any substrate, eventually the surface characteristics are governed by the overlayer.) Further, by taking the asymptotic limit $n \to \infty$, we are able to determine simple closed formulas for the left- and right-surface Green's functions of a semi-infinite crystal. Finally, we compare the time taken to compute these surface elements using the closed forms presented here, with the fastest iterative technique previously available.

The core of this paper is contained in Sec. III, where we develop a mathematical construct—the $[N]$-dimensional

Möbius transformation. These transformations and all the results following from their application are (to the best of our knowledge) entirely new. Although many results have been known for the relatively trivial case of a single-band ($N=1$) model.[13] This paper is somewhat mathematically dense, so it may help the reader if I point out some of the key features contained herein.

(i) A mathematical technique — the $[N]$-dimensional Möbius transformation (Sec. III) — is introduced, and applied to the solution of the surface Green's function adlayering equations (Secs. IV and IX).

(ii) Easy to evaluate closed forms for the surface Green's function of finite and semi-infinite systems are obtained (Secs. VII and VIII).

(iii) For thick-finite, or semi-infinite multilayer (or superlayer) surfaces, these forms are more accurate and faster to calculate than previous techniques (Sec. X).

(iv) For adlayers of thickness n, on top of an arbitrary substrate, these closed forms have a (asymptotically) simple and physical n dependence. This simple dependence is the key to understanding many physical features of multilayer systems (Sec. VII).

In the first part of this paper, an analysis is performed for the special case of nearest-neighbor interaction only ($R=1$). However, in the second part, we show that it is extendible to arbitrary Rth-order interactions, and explain why the results derived in the $R=1$ case are true generally. For the sake of clarity, the main text of this paper is devoted solely to the case of the left-hand surface Green's function, while the right-hand case is dealt with in the Appendixes.

II. MULTIORBITAL LOCAL-HAMILTONIAN FORMULATION

Consider a general surface system composed of a stack of n homogeneous atomic planes (adlayers) on top of an arbitrary finite or semi-infinite substrate (grown in the $+\mathbf{d}$ direction). Then for a large class of physical models, including empirical tight-binding[2] layered LMTO tight binding[3] and screened KKR (Ref. 4) formulations, the Hamiltonian for this system can be expressed (in a mixed $\{\mathbf{k}_\parallel, R\}$ basis) in the form

$$(\mathbf{H}^{(n)})_{ij} = \begin{cases} \mathbf{H}^0_{ij}, & i,j \leqslant 0 \\ \mathbf{u}, & i=j; i=1,\ldots,n \\ \mathbf{t}_\alpha, & j=i+\alpha; i=1-\alpha,\ldots,n-\alpha; \alpha=1,\ldots,R \\ \mathbf{t}^\dagger_\alpha, & i=j+\alpha; j=1-\alpha,\ldots,n-\alpha; \alpha=1,\ldots,R \\ 0, & \text{otherwise} \end{cases} \tag{1}$$

which we call local, or block-band. Here $\mathbf{H}^{(0)}_L$ is the left-hand ($+\mathbf{d}$) finite or semi-infinite substrate Hamiltonian, while $\mathbf{u}$ and $\mathbf{t}_\alpha$ are the $N\times N$ self-energy and (αth order) hopping matrices for the bulk adlayer.

We will use suffixes L and R (left and right) to denote overlayers grown in the $+\mathbf{d}$ and $-\mathbf{d}$ directions, respectively. As mentioned above, we will deal solely with the left-hand case here, while the right-hand case will be dealt with in the Appendix.

For realistic three-dimensional systems, these matrices will depend on the in-plane momentum $\mathbf{k}_\parallel$, but the form of this dependence is immaterial to this communication, and we will therefore ignore this parameter. Clearly this form of Hamiltonian is somewhat idealized, since the true self-energies and hoppings of such a system may vary from plane to plane.[14] However, from the study of self-consistent density-functional calculations,[14–18] it is known that such variation is localized to within one or two planes of the substrate/adlayer interface. Therefore this Hamiltonian is a very good approximation of the true one, so long as we take the interface to be inside $\mathbf{H}^0_{ij}$,[19,20] i.e., we consider adlayers of more than a few planes thickness. A similar Hamiltonian is available for a right-hand adlayer grown in the $-\mathbf{d}$ direction.

III. N-DIMENSIONAL MÖBIUS TRANSFORMATIONS

In this section we present a matrix-valued extension of the ''Möbius'' or ''bilinear'' transformation. We recall that, in complex variable theory,[21] the most general rigid conformal transformation of the complex plane $\mathbf{C}$ is given by the Möbius transformation $z\rightarrow(az+b)/(cz+d)$ for $\{a,b,c,d\}\in\mathbf{C}$, and $ad-bc\neq 0$. These transformations form a group — the Möbius group — which can be represented by 2×2 matrices $\mathbf{A}=\left(\begin{smallmatrix} a & b \\ b & d \end{smallmatrix}\right)$ — in which successive transformations are represented by matrix multiplication.

Now, let $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, $\mathbf{d}$, and $\mathbf{z}$ be $N\times N$ matrices over the complex plane $\mathbf{C}$, and let $\mathbf{A}$ be a $2N\times 2N$-dimensional matrix given by

$$\mathbf{A}=\begin{pmatrix} \mathbf{a} & \mathbf{b} \\ \mathbf{c} & \mathbf{d} \end{pmatrix}. \tag{2}$$

Then, if we define the ''left-hand'' and ''right-hand'' N-dimensional Möbius transformation (LHMT, RHMT) of $\mathbf{z}$ by $\mathbf{A}$ as

$$\mathbf{A}_\bullet\mathbf{z}\equiv(\mathbf{az}+\mathbf{b})(\mathbf{cz}+\mathbf{d})^{-1} \quad [N]\ \text{LHMT}, \tag{3}$$

$$\mathbf{z}^\bullet\mathbf{A}\equiv(\mathbf{a}+\mathbf{zc})^{-1}(\mathbf{b}+\mathbf{zd}) \quad [N]\ \text{RHMT}. \tag{4}$$

Then it is not difficult to show that these transformations are associative with respect to multiplication,

$$\mathbf{A}_\bullet(\mathbf{B}_\bullet\mathbf{z})=(\mathbf{AB})_\bullet\mathbf{z}, \tag{5}$$

$$(\mathbf{z}^\bullet\mathbf{A})^\bullet\mathbf{B}=\mathbf{z}^\bullet(\mathbf{AB}). \tag{6}$$

When $N=1$, the LHMT and RHMT are equal, and reduce to the usual Möbius transformation of complex variable theory.

It is clear that the $[N]$ LHMT and $[N]$ RHMT form realizations [or nonlinear representations of $GL(2N,\mathbf{C})$ on $M(N,\mathbf{C})$ — the algebra of $N\times N$ matrices]. We are unaware of any reference to these N-dimensional extensions in the mathematical literature.

IV. LEFT-HAND, N-BAND ADLAYERING PROBLEM FOR $R=1$

Consider a one-dimensional system of n adlayers on top of a finite or semi-infinite substrate, grown in the $+\mathbf{d}$ direction. Then the local (block-band) Hamiltonian with first-nearest-neighbor hoppings ($R=1$) looks like

$$(\mathbf{H}_L^{(n)})_{ij}=\begin{cases}(\mathbf{H}_L^{(0)})_{ij}, & i,j\leqslant 0\\ \mathbf{u}, & i=j;i=1,\ldots,n\\ \mathbf{t}, & j=i+1;i=0,\ldots,n-1\\ \mathbf{t}^\dagger, & i=j+1;j=0,\ldots,n-1\\ 0, & \text{otherwise.}\end{cases} \tag{7}$$

The Green's function for this system (at energy ε) is defined by $\mathbf{G}_L^{(n)}\equiv(\varepsilon-\mathbf{H}_L^{(n)})^{-1}$. Now, if we deposit an extra adlayer on the surface of this system, then the Hamiltonian becomes $\mathbf{H}_L^{(n+1)}=\mathbf{H}_L^{(n)}+\mathbf{\Delta H}$, where

$$(\mathbf{\Delta H})_{ij}=\begin{cases}\mathbf{u}, & i=j=n+1\\ \mathbf{t}, & i=n;j=n+1\\ \mathbf{t}^\dagger, & i=n+1;j=n\\ 0, & \text{otherwise.}\end{cases} \tag{8}$$

We can, therefore, use Dyson's equations to relate the surface Green's-function element[22] for this system $(\mathbf{G}_L^{(n+1)})_{n+1,n+1}$ to the surface Green's-function element for the system with n adlayers $(\mathbf{G}_L^{(n)})_{n,n}$,

$$\mathbf{g}_{n+1}^L=(\varepsilon-\mathbf{u}-\mathbf{t}^\dagger\mathbf{g}_n^L\mathbf{t})^{-1} \quad \text{where} \quad \mathbf{g}_n^L\equiv(\mathbf{G}_L^{(n)})_{n,n}. \tag{9}$$

Clearly we can use the $[N]$ LHMT to obtain

$$\mathbf{g}_{n+1}^L=(\mathbf{X}_L)\bullet\mathbf{g}_n^L \quad \text{where} \quad \mathbf{X}_L\equiv\begin{pmatrix}\mathbf{0} & \mathbf{t}^{-1}\\ -\mathbf{t}^\dagger & \mathbf{v}\mathbf{t}^{-1}\end{pmatrix} \tag{10}$$

and where we define $\mathbf{v}\equiv\varepsilon-\mathbf{u}$. Hence by associativity we deduce that

$$\mathbf{g}_n^L=(\mathbf{X}_L)^n\bullet\mathbf{g}_0^L \quad \text{where} \quad \mathbf{X}_L\equiv\begin{pmatrix}\mathbf{0} & \mathbf{t}^{-1}\\ -\mathbf{t}^\dagger & \mathbf{v}\mathbf{t}^{-1}\end{pmatrix}, \tag{11}$$

where $\mathbf{g}_0^L$ is the surface Green's function element for the system with no adlayers, i.e., $\mathbf{H}_L^{(0)}$. Similarly using the $[N]$ RHMT we obtain the alternative form

$$\mathbf{g}_n^L=\mathbf{g}_0^L\bullet(\mathbf{Y}_L)^n \quad \text{where} \quad \mathbf{Y}_L\equiv\begin{pmatrix}\mathbf{t}^{\dagger-1}\mathbf{v} & \mathbf{t}^{\dagger-1}\\ -\mathbf{t} & \mathbf{0}\end{pmatrix}. \tag{12}$$

Thus Eqs. (11) and (12) provide the solution to the Dyson adlayering equations for the left-hand surface Green's function (9). It is important to note that for non-Hermitian $\mathbf{t}$, the $2N\times 2N$ matrices $\mathbf{X}$ and $\mathbf{Y}$ cannot in general be block diagonalized (although this is certainly algebraically possible for $N=1$, and probably also for $N=2$). For Hermitian $\mathbf{t}$ however, it is always possible to reduce these solutions to algebraic formulas in $N\times N$ matrices. For example, for $\mathbf{X}_L$, we have

$$\mathbf{S}^{-1}\mathbf{X}_L\mathbf{S}=\begin{pmatrix}\mathbf{x}_- & \mathbf{0}\\ \mathbf{0} & \mathbf{x}_+\end{pmatrix} \quad \text{where} \quad \mathbf{S}=\begin{pmatrix}\mathbf{t}^{-1}\mathbf{x}_+ & \mathbf{t}^{-1}\mathbf{x}_-\\ \mathbf{1} & \mathbf{1}\end{pmatrix},$$

$$\mathbf{S}^{-1}=\delta_1^{-1}\begin{pmatrix}\mathbf{t} & -\mathbf{x}_-\\ -\mathbf{t} & \mathbf{x}_+\end{pmatrix}. \tag{13}$$

Here $\delta_n\equiv(\mathbf{x}_+^n-\mathbf{x}_-^n)$, and $\mathbf{x}_\pm$ are the solutions to the quadratic matrix equation

$$\mathbf{x}^2-\mathbf{v}\mathbf{t}^{-1}\mathbf{x}+\mathbf{1}=\mathbf{0}\Rightarrow\mathbf{x}_\pm=\tfrac{1}{2}(\mathbf{v}\mathbf{t}^{-1}\pm\sqrt{\mathbf{v}\mathbf{t}^{-1}\mathbf{v}\mathbf{t}^{-1}-4}). \tag{14}$$

Hence we obtain[23]

$$\mathbf{g}_n^L=\mathbf{t}^{-1}\delta_1^{-1}(\delta_n-\delta_{n-1}\mathbf{t}\mathbf{g}_0)(\delta_{n+1}-\delta_n\mathbf{t}\mathbf{g}_0)^{-1}\delta_1. \tag{15}$$

For the remainder of the main text, we will deal with the $[N]$ LHMT solution to the left-hand adlayering equations (11). The results for the other three possible cases will be presented in the Appendix.

V. CONNECTION BETWEEN THE SPECTRUM OF $\mathbf{X}_L$ AND THE BULK BAND STRUCTURE

In order to understand the analytic and asymptotic properties of our Green's-function elements, we need to discuss some features of the spectrum and eigenvectors of the Möbius transformation matrices. It is not difficult to deduce that (for $\mathbf{t}$ nonsingular[24])

$$\det(\mathbf{X}_L-\lambda\mathbf{1})=(-1)^N\det(\lambda\mathbf{t}^{-1})\det(\mathbf{v}-\lambda\mathbf{t}-\lambda^{-1}\mathbf{t}^\dagger) \tag{16}$$

and hence (taking $\lambda=0$) $\det(\mathbf{X}_L)=\det(\mathbf{t})^*/\det(\mathbf{t})\in\mathbf{C}^1$—i.e., lies on the unit circle in the complex plane. That is, $\mathbf{X}_L$ has no zero eigenvalues and is therefore invertible. We assume hereafter that it is also diagonalizable.

Hence by taking the Hermitian conjugate of Eq. (16), we obtain

$$\det(\mathbf{v}-\lambda\mathbf{t}-\lambda^{-1}\mathbf{t}^\dagger)=\det(\mathbf{v}^\dagger-\lambda^{*-1}\mathbf{t}-\lambda^*\mathbf{t}^\dagger)=0 \tag{17}$$

as a necessary and sufficient condition for λ to be an eigenvalue of $\mathbf{X}_L$. Hence (for ε real), if λ is an eigenvalue of $\mathbf{X}_L$, then so is λ^{*-1}.[25] *Therefore there are $N-P$ eigenvalues λ inside $\mathbf{C}^1$, $N-P$ outside $\mathbf{C}^1$, and $2P$ on $\mathbf{C}^1$ (for some integer P).*

Now, we can rewrite Eq. (17) as

$$\det(\mathbf{C}(\lambda)-\varepsilon\mathbf{1})=0 \quad \text{where} \quad \mathbf{C}(\lambda)\equiv\mathbf{u}+\lambda\mathbf{t}+\lambda^{-1}\mathbf{t}^\dagger \tag{18}$$

as being a necessary and sufficient condition for λ to be an eigenvalue of $\mathbf{X}_L$.

Now for $\lambda\equiv e^{ikd}\in\mathbf{C}^1$, then $\mathbf{C}(\lambda)=\mathbf{E}(k)$ — the ''energy matrix'' of the bulk adlayer system. Hence we have shown that *if an energy band (of the bulk adlayer system) cuts ε at k' [i.e., $\det(\mathbf{E}(k')-\varepsilon\mathbf{1})=0$], then $\lambda=e^{ik'd}$ is a $\mathbf{C}^1$ eigenvalue of $\mathbf{X}_L$ — and vice versa.* We will see in Sec. VII that this is a crucially important result, since it implies that for an adlayer system, the behavior of the surface Green's function (for thick adlayers) is entirely determined by the bulk adlayer system.

VI. DIAGONALIZATION OF $\mathbf{X}_L$

The $2N\times 2N$ matrix $\mathbf{X}_L$ can (in general) only be diagonalized numerically. Let us assume that this has been performed, so that its eigenvalue and eigenvector matrices are $\mathbf{\Lambda}$ and $\mathbf{O}_L$ (i.e., $\mathbf{O}_L^{-1}\mathbf{X}_L\mathbf{O}_L=\mathbf{\Lambda}$). Then let us define six new $N\times N$ submatrices as follows. Let $\mathbf{\Lambda}_1$ and $\mathbf{\Lambda}_2$ be the $N\times N$ upper-left and lower-right submatrices of $\mathbf{\Lambda}$. Let $\mathbf{o}_1$ and $\mathbf{o}_2$ be the $N\times N$ upper-left and upper-right submatrices of $\mathbf{O}_L$. Let ω_1 and ω_2 be the $N\times N$ upper-right and lower-right submatrices of $\mathbf{O}_L^{-1}$. Then it is easy to show that $\mathbf{\Lambda}$, $\mathbf{O}_L$, and $\mathbf{O}_L^{-1}$ have the form

$$\mathbf{O}_L^{-1}\mathbf{X}_L\mathbf{O}_L=\mathbf{\Lambda} \quad \text{where} \quad \mathbf{\Lambda}\equiv\mathrm{diag}(\lambda_1,\lambda_2,\ldots,\lambda_{2N})=\begin{pmatrix}\mathbf{\Lambda}_1 & \mathbf{0}\\ \mathbf{0} & \mathbf{\Lambda}_2\end{pmatrix}, \quad \mathbf{O}_L\equiv\begin{pmatrix}\mathbf{o}_1 & \mathbf{o}_2\\ \mathbf{to}_1\mathbf{\Lambda}_1 & \mathbf{to}_2\mathbf{\Lambda}_2\end{pmatrix}, \quad \mathbf{O}_L^{-1}\equiv\begin{pmatrix}-\mathbf{\Lambda}_1^{-1}\omega_1\mathbf{t}^\dagger & \omega_1\\ -\mathbf{\Lambda}_2^{-1}\omega_2\mathbf{t}^\dagger & \omega_2\end{pmatrix}. \tag{19}$$

Thus, once $\mathbf{\Lambda}$ and $\mathbf{O}_L$ have been calculated numerically, we can simply read off the $N\times N$ submatrices $\mathbf{\Lambda}_1$, $\mathbf{\Lambda}_2$, $\mathbf{o}_1$, $\mathbf{o}_2$, ω_1, and ω_2.

Now these submatrices are not independent, since their ansatz form (19) must satisfy the demands that $\mathbf{O}_L\mathbf{O}_L^{-1}=\mathbf{O}_L^{-1}\mathbf{O}_L=\mathbf{1}$ and $\mathbf{O}_L^{-1}\mathbf{X}_L\mathbf{O}_L=\mathbf{\Lambda}$. This leads to four independent constraints that the numerical form of the submatrices satisfy identically:

$$\mathbf{o}_1\omega_1+\mathbf{o}_2\omega_2=\mathbf{0}, \tag{20}$$

$$\mathbf{o}_1\mathbf{\Lambda}_1\omega_1+\mathbf{o}_2\mathbf{\Lambda}_2\omega_2=\mathbf{t}^{-1}, \tag{21}$$

$$\mathbf{o}_1\mathbf{\Lambda}_1^{-1}\omega_1+\mathbf{o}_2\mathbf{\Lambda}_2^{-1}\omega_2=-\mathbf{t}^{\dagger-1}, \tag{22}$$

$$\mathbf{o}_1\mathbf{\Lambda}_1^2\omega_1+\mathbf{o}_2\mathbf{\Lambda}_2^2\omega_2=\mathbf{t}^{-1}\mathbf{v}\mathbf{t}^{-1}. \tag{23}$$

We will see in Appendix A, Sec. 3 that once $\mathbf{X}_L$ has been diagonalized, and the $N\times N$ submatrices read off, then it becomes immediately possible to diagonalize the remaining Möbius transformation matrices $\mathbf{X}_R$, $\mathbf{Y}_L$, and $\mathbf{Y}_R$ in terms of these submatrices.

VII. SURFACE GREEN'S-FUNCTION SOLUTION AND ASYMPTOTIC PERIODICITY

The solution to the $[N]$ adlayering problem for the surface Green's functions $\mathbf{g}_n^L$ and $\mathbf{g}_n^R$ is now given by Eqs. (11) and (19),

$$\begin{aligned}\mathbf{g}_n^L&=(\mathbf{O}_L\mathbf{\Lambda}^n\mathbf{O}_L^{-1})_\bullet\mathbf{g}_0^L\\ &=\mathbf{O}_L{}_\bullet(\mathbf{\Lambda}_1^n\mathbf{f}_0^L\mathbf{\Lambda}_2^{-n}), \quad \text{where} \quad \mathbf{f}_0^L\equiv\mathbf{O}_L^{-1}{}_\bullet\mathbf{g}_0^L,\end{aligned} \tag{24}$$

and hence by Eq. (3) we obtain

$$\mathbf{g}_n^L=\mathbf{\Delta}_n^L{\mathbf{\Delta}_{n+1}^L}^{-1}\mathbf{t}^{-1}$$

where

$$\mathbf{\Delta}_n^L\equiv\mathbf{o}_1\mathbf{\Lambda}_1^n\mathbf{f}_0^L+\mathbf{o}_2\mathbf{\Lambda}_2^n \quad \text{and} \quad \mathbf{f}_n^L\equiv\mathbf{O}_L^{-1}{}_\bullet\mathbf{g}_n^L. \tag{25}$$

This solution explicitly demonstrates the n (i.e., adlayer thickness) dependence of the surface Green's function. This expression can be used to deduce closed forms for the other Green's-function elements, for both surface systems and infinite multilayers.

We note that since $\mathbf{\Lambda}_1$ and $\mathbf{\Lambda}_2$ are diagonal, then $\mathbf{\Lambda}_1^n$ and $\mathbf{\Lambda}_2^n$ and hence $\mathbf{g}_n^L$ and $\mathbf{g}_n^R$ are defined for noninteger n. These solutions have been used recently to determine continuous underlying curves for the magnetic-coupling and magnetoresistance of magnetic multilayers.[8,9].

Furthermore, the matrix $\mathbf{f}^L$ defined above, which is the bilinearly transformed surface Green's function, has a particularly simple dependence upon n:

$$\mathbf{f}_n^L=\mathbf{\Lambda}_1^n\mathbf{f}_0^L\mathbf{\Lambda}_2^{-n}. \tag{26}$$

Let us examine the asymptotic (i.e., thick adlayer) behavior of the surface Green's function. Let the eigenvalues λ of $\mathbf{X}_L$ be ordered such that

$$|\lambda_1|\leqslant|\lambda_2|\leqslant\cdots\leqslant|\lambda_{2N}|, \tag{27}$$

then, considering the restrictions on their positions in the complex plane as discussed in Sec. V, let us say that $\{\lambda_1,\lambda_2,\ldots,\lambda_{N-P}\}$ lie inside $\mathbf{C}^1$, $\{\lambda_{N+P+1},\lambda_{N+P+2},\ldots,\lambda_{2N}\}$ lie outside $\mathbf{C}^1$, and $\{\lambda_{N-P+1},\lambda_{N-P+2},\ldots,\lambda_{N+P}\}\equiv\{e^{idk_{N-P+1}},e^{idk_{N-P+2}},\ldots,e^{idk_{N+P}}\}$ lie on $\mathbf{C}^1$. Now let us consider the bilinearly transformed surface Green's functions $\mathbf{f}^L$. It is clear [from Eq. (26)] that, as n increases, many of the elements of this matrix die away, and that in the limit $n\to\infty$,

$$\lim_{n\to\infty}(\mathbf{f}_n^L)_{rs}=\begin{cases}e^{idnk_r}(\mathbf{f}_0^L)_{rs}e^{-idnk_{N+s}} & \text{for } r=N-P+1,\ldots,N, \quad s=1,\ldots,P\\ 0, \quad \text{otherwise}\end{cases} \tag{28}$$

so that (in the asymptotic limit) the elements of the matrix $\mathbf{f}_n^L$ are functions of $2P$ plane waves $\{e^{idnk_\alpha};\alpha=N-P+1,\ldots,N+P\}$ with periods $\{p_\alpha=2\pi/dk_\alpha\}$.[26]

Now, we can define an extended matrix function of $2N$ parameters $\{n_r;r=1,\ldots,2N\}$ by

$$(\tilde{\mathbf{f}}^L_{n_1\ldots n_{2N}})_{rs}\equiv\left(\frac{\lambda_r^{n_r}}{\lambda_{N+s}^{n_{N+s}}}\right)(\mathbf{f}_0^L)_{rs}. \tag{29}$$

Then, in the asymptotic limit $\{n_r\}\to\infty$, this whole matrix is periodic in n_α with period p_α (α as defined above). Hence if we define the extended surface Green's function by $\tilde{\mathbf{g}}^L_{n_1\ldots n_{2N}}\equiv\mathbf{O}_L\bullet\tilde{\mathbf{f}}^L_{n_1\ldots n_{2N}}$. Then (in the asymptotic limit $\{n_r\}\to\infty$) this matrix must also be periodic in n_α, with period p_α. Now clearly, if we set $n_1=\cdots=n_{2N}=n$, then $\tilde{\mathbf{g}}^L_{n\ldots n}=\mathbf{g}_n^L$, and hence we obtain the following important result: *For large n, $\mathbf{g}_n^L$ is a matrix whose elements are quasiperiodic functions of $2P$ plane waves, with periods $2\pi/dk_\alpha$. By Sec. V, we see that these periods are dictated by the k-point values at which the bulk adlayer energy bands cut ε.*[27,28]

This is what is expected physically, and is the multiband generalization of a conjecture by Mathon *et al.*,[20] made for the very special case of $P=1$. As the thickness of the overlayer increases, the surface states are increasingly represented by the bulk adlayer system. The decaying states (represented by the eigenvalues of $\mathbf{X}$ not lying on $\mathbf{C}^1$) die away, leaving only the propagating states ($\mathbf{C}^1$ eigenvalues of $\mathbf{X}$).

This result is crucially important if one wishes to develop analytic expressions for the asymptotic behavior of multilayered systems. Using Eq. (29), one can perform multidimensional Fourier decompositions of arbitrary scalar functions of the surface Green's function, such as the spectral density and conductivity. Such a procedure has recently been developed in order to obtain analytic expressions for the magnetic coupling of realistic (multiband) magnetic multilayer systems.[8,9] Furthermore, this asymptotic behavior is the key to understanding many physical features of realistic multilayered systems.

VIII. SEMI-INFINITE SURFACE GREEN'S FUNCTIONS

In Sec. VII we saw that (for ε real) for n large, the surface Green's function is an oscillatory function of $2P$ plane waves, and is therefore not defined in the $n\to\infty$ limit. However, if we add a small imaginary part to the energy ($\varepsilon\to\varepsilon+i\delta$), then the degeneracies of the eigenvalues λ of $\mathbf{X}$ are lifted so that $|\lambda_1|<|\lambda_2|<\cdots<|\lambda_{2N}|$. Then for any $N\times N$ matrix $\mathbf{x}$: $\lim_{n\to\infty}\mathbf{\Lambda}_1^n\mathbf{x}\mathbf{\Lambda}_2^{-n}=\mathbf{0}$. Hence defining the semi-infinite surface Green's function by $\mathbf{g}_\infty=\lim_{n\to\infty}\mathbf{g}_n$, we obtain the following simple closed forms for the semi-infinite left-hand surface Green's function:

$$\mathbf{g}_\infty^L=\mathbf{O}_L\bullet\mathbf{0}=\mathbf{o}_2\mathbf{\Lambda}_2^{-1}\mathbf{o}_2^{-1}\mathbf{t}^{-1}. \tag{30}$$

We note that $\mathbf{g}_\infty$ does not depend on $\mathbf{g}_0$ — i.e., all memory of the substrate is lost in the infinite limit.

IX. EXTENSION TO *R*TH-ORDER NEIGHBOR INTERACTIONS

So far we have considered adlayering in the local Hamiltonian model with only first-nearest-neighbor interactions. Higher-order interactions can of course always be reduced to first-nearest-neighbor form by the method of principal layering.[29,30] In particular, if we have Rth-order nearest neighbor interactions, then the adlayered Hamiltonian for n adlayers (1), can always be reduced to form (7), by defining $\mathbf{u}$ and $\mathbf{t}$ to be the $NR\times NR$ matrices $\mathbf{U}$ and $\mathbf{T}$:

$$\mathbf{u}\to\mathbf{U}\equiv\begin{pmatrix}\mathbf{u}&\mathbf{t}_1&\cdots&\mathbf{t}_{R-1}\\ \mathbf{t}_1^\dagger&\mathbf{u}&&\mathbf{t}_{R-2}\\ \vdots&&\ddots&\vdots\\ \mathbf{t}_{R-1}^\dagger&\mathbf{t}_{R-2}^\dagger&\cdots&\mathbf{u}\end{pmatrix},$$

$$\mathbf{t}\to\mathbf{T}\equiv\begin{pmatrix}\mathbf{t}_R&\mathbf{0}&\cdots&\mathbf{0}\\ \mathbf{t}_{R-1}&\mathbf{t}_R&&\mathbf{0}\\ \vdots&&\ddots&\vdots\\ \mathbf{t}_1&\mathbf{t}_2&\cdots&\mathbf{t}_R\end{pmatrix}. \tag{31}$$

The $[NR]$-M.T's will then provide solutions to the surface Green's functions $\mathbf{G}_{nn}^{(n)}$, which are correct for $n=0,R,2R,\ldots$ — i.e., an integral number of principal layers,

$$\mathbf{G}_{Rn,Rn}^{(Rn)}=\mathbf{X}_\bullet^n\mathbf{G}_{00}^{(0)}\quad\text{for } n=1,2,\ldots. \tag{32}$$

The question arises, however, as to whether we can extend this solution to fractional numbers of principal layers, and in particular to single layers; i.e., does $\mathbf{G}_{11}^{(1)}=(\mathbf{X}^{1/R})_\bullet\mathbf{G}_{00}^{(0)}$? However, for $\mathbf{X}$ nondegenerate there are R^{2NR} roots of $\mathbf{X}^{1/R}$, leading to R^{2NR-1} different solutions to $\mathbf{G}_{11}^{(1)}$. Worse still, for $\mathbf{X}$ degenerate (such as might occur at the Brillouin-zone boundary of a three-dimensional system) there are an infinite number of solutions. Only one of these solutions might represent a single adlayer.

In this section we show that it is always possible to obtain the surface Green's function $\mathbf{G}_{11}^{(1)}$ for a single adlayer within an Rth-order local Hamiltonian model, by means of a suitable Möbius transformation, and we construct the corresponding Möbius transformation matrix. Let us consider adlayering a single adlayer on top of a (left-hand) substrate with Rth-order interactions. Let the adlayer self-energy be $\mathbf{u}$ and the adlayer-substrate hoppings be $\{\mathbf{t}_\alpha;\alpha=1,\ldots,R\}$. Now, because of the finite range of the interaction, the $N\times N$ surface Green's function $\mathbf{G}_{n+1,n+1}^{(n+1)}$ can be obtained by solving a reduced Dyson's matrix-equation, which involves only the $NR\times NR$ bottom right-hand submatrix of $\mathbf{G}^{(n)}$,

$$\widetilde{\mathbf{J}}^{(n+1)}=(\mathbf{1}-\mathbf{J}^{(n)}\boldsymbol{\Delta}\mathbf{H})^{-1}\mathbf{J}^{(n)}, \tag{33}$$

where $\mathbf{J}^{(n)}$, $\widetilde{\mathbf{J}}^{(n+1)}$, and $\boldsymbol{\Delta}\mathbf{H}$ are $N(R+1)\times N(R+1)$ matrices, given by

$$\mathbf{J}^{(n)}=\begin{pmatrix} \begin{pmatrix} & \mathbf{g}_L^{(n)} & \end{pmatrix} & \begin{pmatrix} \mathbf{0} \end{pmatrix} \\ \begin{pmatrix} \mathbf{0} \end{pmatrix} & \frac{1}{\varepsilon}\mathbf{1} \end{pmatrix},$$

$$\boldsymbol{\Delta}\mathbf{H}=\begin{pmatrix} \begin{pmatrix} & \mathbf{0} & \end{pmatrix} & \begin{matrix} \mathbf{t}_R \\ \vdots \\ \mathbf{t}_1 \end{matrix} \\ \begin{matrix} \mathbf{t}_R^{\dagger} \cdots \mathbf{t}_1^{\dagger} \end{matrix} & \mathbf{u} \end{pmatrix}, \tag{34}$$

$$\widetilde{\mathbf{J}}^{(n+1)}=\begin{pmatrix} \mathbf{G}_{n+1-R,n+1-R}^{(n+1)} & \cdots \mathbf{G}_{n+1-R,n+1}^{(n+1)} \\ \vdots & \begin{pmatrix} & \mathbf{g}_L^{(n+1)} & \end{pmatrix} \\ \mathbf{G}_{n+1,n+1-R}^{(n-1)} & \end{pmatrix}. \tag{35}$$

Here $\mathbf{g}_L^{(n)}$ and $\mathbf{g}_L^{(n+1)}$ are the $NR\times NR$ bottom right-hand submatrices of the total Green's functions $\mathbf{G}^{(n)}$ and $\mathbf{G}^{(n+1)}$,

$$\mathbf{g}_L^{(n)}\equiv\begin{pmatrix} \mathbf{G}_{n+1-R,n+1-R}^{(n)} & \cdots & \mathbf{G}_{n+1-R,n}^{(n)} \\ \vdots & \ddots & \vdots \\ \mathbf{G}_{n,n+1-R}^{(n)} & \cdots & \mathbf{G}_{n,n}^{(n)} \end{pmatrix}. \tag{36}$$

Now it is clear from the reduced Dyson equation (33) that $\mathbf{G}_{n+1,n+1}^{(n+1)}$ is a function of all the elements of $\mathbf{g}_L^{(n)}$. What we require, therefore, is an iterative equation (in n) for $\mathbf{g}_L^{(n+1)}$ (and hence $\mathbf{G}_{n+1,n+1}^{(n+1)}$) in terms of $\mathbf{g}_L^{(n)}$. However, the reduced Dyson equation does not fit the bill, since $\mathbf{J}^{(n)}$ and $\widetilde{\mathbf{J}}^{(n+1)}$ do not have the same form. Such an equation does exist, however, in terms of the $[NR]$-M.T. In particular, the following can be shown: *For the N-band local Hamiltonian model with Rth-order neighbor interaction, the $NR\times NR$ bottom right-hand submatrix of the total Green's function $(\mathbf{g}_L^{(n)})$, for the n (left-hand) adlayer system is given by the Möbius transformation*

$$\mathbf{g}_L^{(n)}=(\boldsymbol{\Xi}_L)^n\bullet\mathbf{g}_L^{(0)} \quad \text{where} \quad \boldsymbol{\Xi}_L\equiv\begin{pmatrix} \mathbf{a} & \mathbf{b} \\ \mathbf{c} & \mathbf{d} \end{pmatrix}, \tag{37}$$

and where $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, and $\mathbf{d}$ are $NR\times NR$ matrices given by

$$\mathbf{a}=\begin{pmatrix} \begin{pmatrix} \mathbf{0} \end{pmatrix} & \begin{pmatrix} & \mathbf{1} & \end{pmatrix} \\ \mathbf{0} & \begin{pmatrix} & \mathbf{0} & \end{pmatrix} \end{pmatrix}, \quad \mathbf{b}=\begin{pmatrix} \begin{pmatrix} \mathbf{0} \end{pmatrix} & \begin{pmatrix} & \mathbf{0} & \end{pmatrix} \\ \mathbf{t}_R^{-1} & \begin{pmatrix} & \mathbf{0} & \end{pmatrix} \end{pmatrix},$$

$$\mathbf{c}=\begin{pmatrix} \begin{pmatrix} \mathbf{0} \end{pmatrix} & \begin{pmatrix} & \mathbf{0} & \end{pmatrix} \\ -\mathbf{t}_R^{\dagger} & (-\mathbf{t}_{R-1}^{\dagger}\ldots-\mathbf{t}_1^{\dagger}) \end{pmatrix}, \tag{38}$$

$$\mathbf{d}=\begin{pmatrix} \begin{pmatrix} -\mathbf{t}_{R-1}\mathbf{t}_R^{-1} \\ -\mathbf{t}_{R-2}\mathbf{t}_R^{-1} \\ \vdots \end{pmatrix} & \begin{pmatrix} & \mathbf{1} & \end{pmatrix} \\ (\varepsilon-\mathbf{u})\mathbf{t}_R^{-1} & \begin{pmatrix} & \mathbf{0} & \end{pmatrix} \end{pmatrix},$$

The verification of this fundamental result is rather lengthy, but follows straightforwardly by substitution of Eq. (37) into the reduced Dyson equation (33).

For $R=1$, we have $\mathbf{a}=\mathbf{0}$, $\mathbf{b}=\mathbf{t}^{-1}$, $\mathbf{c}=-\mathbf{t}^{\dagger}$, and $\mathbf{d}=(\varepsilon-\mathbf{u})\mathbf{t}^{-1}$, so that we clearly recover the matrix (11). Since, by construction, $\boldsymbol{\Xi}_L$ is proportional to an Rth root of the first order, principal layer, interaction matrix $\mathbf{X}_L$ [with $\mathbf{u}$ and $\mathbf{t}$ matrices given by Eq. (31)], then all the results about $\mathbf{X}$ derived so far readily generalize to $\boldsymbol{\Xi}$: its eigenvalues $\{\mu_i=\lambda_i^{1/R}\}$ are the appropriate Rth roots of those belonging to $\mathbf{X}$, with $N-P$ lying inside $\mathbf{C}^1$, $N-P$ outside $\mathbf{C}^1$, and $2P$ on $\mathbf{C}^1$; it is not difficult to show that these eigenvalues satisfy the equation [cf. Eq. (18)]

$$\det(\mathbf{C}(\mu)-\varepsilon\mathbf{1})=0$$

where

$$\mathbf{C}(\mu)\equiv\mathbf{u}+\mu\mathbf{t}_1+\mu^{-1}\mathbf{t}_1^{\dagger}+\cdots+\mu^R\mathbf{t}_R+\mu^{-R}\mathbf{t}_R^{\dagger}; \tag{39}$$

therefore the $\mathbf{C}^1$ eigenvalues $\{\mu=e^{ikd/R}\}$ (Ref. 31) correspond to the $2P$ k points at which ε crosses the bulk adlayer energy bands, as defined in the *principal* Brillouin zone $-\pi R/d\geqslant k\geqslant\pi R/d$ (with d/R being the interatomic-plane distance); the diagonalization matrices $\mathbf{O}_L$ and $\mathbf{O}_L^{-1}$ and the diagonalized forms (19)–(23) are correct, the only alteration being in the matrix $\boldsymbol{\Lambda}$ (i.e., its correct Rth root $\mathcal{M}=\mathrm{diag}(\mu_1,\ldots,\mu_{2\mathrm{NR}})$ must be taken);[32] the asymptotic periodicity properties of the surface Green's functions as discussed in Sec. VII still hold true; the forms for the semi-infinite surface Green's functions (30) remain correct.

X. COMPUTATIONAL ADVANTAGES AND APPLICATION TO SUPERLATTICES

To date, the most efficient computational method for calculating the semi-infinite surface Green's-function elements has been the decimation technique.[7] This is an iterative scheme, where, at the ith iteration, one has calculated the surface Green's function for a finite slab of width 2^i layers. The computational effort is therefore proportional to the total number of iterations required, and hence is a function of both the accuracy imposed and the convergence rate. The convergence rate itself depends in the imaginary part of the energy parameter (Im$[\varepsilon]$), and the proximity of any singular values of the Green's function.[6] In contrast, the present method, based on Eq. (30), is independent of all these parameters, and

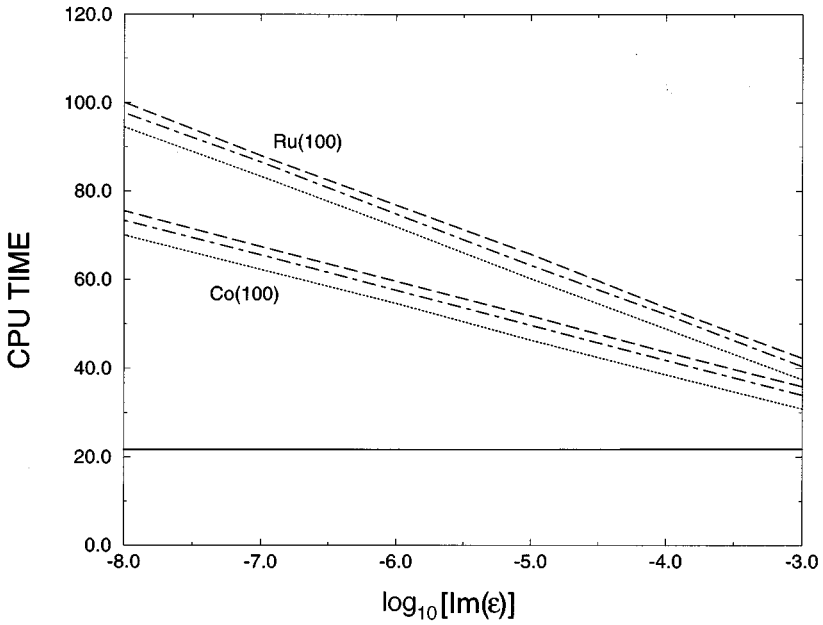

FIG. 1. CPU time (arbitrary units) to calculate the semi-infinite surface Green's function, vs $\log_{10}[\mathrm{Im}(\varepsilon)]$, for fcc Cu(100) and Rh(100). The decimation method is depicted for three convergence criteria: ·····, $\xi=10^{-3}$; ·–·–·–, $\xi=10^{-6}$; and – – – –, $\xi=10^{-9}$, while the analytic Mobius technique is seen to be constant: ———.

in addition provides machine value accuracy. It is therefore somewhat unfair simply to compare the CPU times for the two procedures. However, in Fig. 1, we depict the times to compute the surface spectral density (i.e., summed over $\mathbf{k}_\parallel$) for various accuracies (ξ) and $\mathrm{Im}[\varepsilon]$, for the case of fcc Co(100) and Ru(100) with s, p, and d tight-binding parameters taken from Ref. 33.

We observe that the CPU time for the decimation technique (t_{dec}) depends logarithmically on the $\mathrm{Im}[\varepsilon]$ ($t_{\mathrm{DEC}}\sim-\ln(\mathrm{Im}[\varepsilon])$) but only weakly on the accuracy ξ. Our analytic method is constant, and faster for $\mathrm{Im}[\varepsilon]<10^{-2}$ Ry.

Now, although the present technique is already significantly faster than decimation for pure materials, its real computational power is in its application to superlattices. Consider, for example, the case of a superlattice, composed of S different principal layers $A_1, A_2, \ldots, A_S$, so that schematically the semi-infinite left-hand system looks like $\ldots(A_1A_2\ldots A_S)(A_1A_2\ldots A_S)(A_1A_2\ldots A_S)$. Then the Hamiltonian for this system can be written like Eq. (7), where the self-energy and hopping matrices are given by the $NS\times NS$ matrices

$$\mathbf{u}=\begin{pmatrix} \mathbf{u}_{A_1} & \mathbf{t}_{A_1A_2} & & & \\ \mathbf{t}^{\dagger}_{A_1A_2} & \mathbf{u}_{A_2} & & 0 & \\ & & \ddots & & \\ & & & \mathbf{u}_{A_{S-1}} & \mathbf{t}_{A_{S-1}A_S} \\ & 0 & & \mathbf{t}^{\dagger}_{A_{S-1}A_S} & \mathbf{u}_{A_S} \end{pmatrix},$$

$$\mathbf{t}=\begin{pmatrix} \mathbf{0} & & \\ \vdots & \begin{pmatrix} & \\ \mathbf{0} & \end{pmatrix} & \\ \mathbf{0} & & \\ \mathbf{t}_{A_SA_1} & \mathbf{0}\cdots\mathbf{0} & \end{pmatrix}. \tag{40}$$

Now, since the decimation technique scales as N^3 (where N is the order of the $\mathbf{u}$ and $\mathbf{t}$ matrices), then for fixed ξ, $\mathrm{Im}[\varepsilon]$, and $\mathbf{k}_\parallel$, the time to calculate the semi-infinite surface Green's function in this case will be $T_{\mathrm{DEC}}(SN)\sim S^3T_{\mathrm{DEC}}(N)$ [where $T_{\mathrm{DEC}}(N)$ is the time to calculate the semi-infinite surface Green's function for $N\times N$ self-energy and hopping matrices].

On the other hand, we can write the semi-infinite superlattice surface Green's function as

$$\mathbf{g}_\infty=\lim_{n\to\infty}(\mathbf{X}_{12\ldots S})^n_{\bullet}\mathbf{g}_0 \quad \text{where } \mathbf{X}_{12\ldots S}\equiv\mathbf{X}_S\mathbf{X}_{S-1}\ldots\mathbf{X}_1, \tag{41}$$

where $\mathbf{X}_{12\ldots S}$ is an $N\times N$ matrix.

Now, we assume that $\mathbf{X}_{12\ldots S}$ is diagonalizable,

$$\mathbf{X}_{12\ldots S}=\mathbf{O}_{12\ldots S}\mathbf{\Lambda}_{12\ldots S}\mathbf{O}^{-1}_{12\ldots S}. \tag{42}$$

Then for $\mathrm{Im}[\varepsilon]\neq0$, its eigenvalues $\{\lambda_i\}$ can be ordered such that $|\lambda_1|<|\lambda_2|<\cdots<|\lambda_{2N}|$. Hence we may use the arguments of Sec. VIII to deduce that

$$\mathbf{g}_\infty=\mathbf{O}_{12\ldots S}{}_{\bullet}\mathbf{0}. \tag{43}$$

Since the time taken to diagonalize a matrix $\sim 6\times$ the time taken to multiply two such matrices, then the time to calculate the semi-infinite surface Green's function in this case is $T_{\mathrm{MOB}}(SN)\sim(6+S)T_{\mathrm{MOB}}(N)$ [where $T_{\mathrm{MOB}}(N)$ is the time taken to calculate the semi-infinite surface Green's function using the Möbius transformation technique, for $N\times N$ self-energy and hopping matrices]. In other words, the time to calculate the semi-infinite surface Green's function for S layers per superlayer scales as S^3 using the decimation method, but only (weakly) as S using the closed form.

XI. CONCLUSION

We have shown that there are two realizations of $GL(2N,\mathbf{C})$ on $M(N,\mathbf{C})$, which are matrix-valued extensions of the Möbius transformation familiar from complex variable theory. We have used these transformations to solve the general Green's-function adlayering problem (arbitrary growth direction, lattice, and number of bands) within a local Hamiltonian model. We have shown that (for a given value of the energy parameter ε) the surface Green's functions are as-

ymptotically quasiperiodic, with the number of periods and their values dictated by the k points at which the bulk adlayer energy bands cut ε. We have given closed form solutions for the finite and semi-infinite surface Green's functions in terms of the eigenvalues and eigenvectors of the Möbius transformation matrices. Finally we have shown that the time to calculate the semi-infinite surface Green's functions using the closed form is (for $\mathrm{Im}[\varepsilon]<10^{-2}$ Ry) faster than the previously known decimation technique, and scales linearly with the complexity of the multilayer. We have developed similar techniques to obtain closed-form solutions to all Green's function elements, for general local Hamiltonian multilayers (for both bulk and surface systems). This will be the subject of a forthcoming publication.

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APPENDIX: FURTHER RESULTS

The results of the main text are for the left-hand surface Green's function, whose adlayering equations (11) are solved by use of the $[N]$ LHMT, i.e., by use of the Möbius transformation matrix $\mathbf{X}_L$. In this appendix, we briefly describe the corresponding results for the remaining three cases: the left-hand surface Green's function solved by use of the $[N]$ RHMT; and the right-hand surface Green's function solved by use of the $[N]$ LHMT and RHMT.

1. Right-hand, N-band adlayering problem for $R=1$

For the case of the right-hand system, the surface Green's-function adlayering equations are [cf. Eq. (9)]

$$\mathbf{g}^R_{n+1}=(\varepsilon-\mathbf{u}-\mathbf{t}\mathbf{g}^R_n\mathbf{t}^\dagger)^{-1} \quad \text{where } \mathbf{g}^R_n\equiv(\mathbf{G}^{(n)}_R)_{n,n}. \tag{A1}$$

These equations relate the surface Green's function for a right-hand system with $n+1$ adlayers, to the surface Green's function for a system with n adlayers.

They can be solved (as in Sec. IV) in terms of the $[N]$ LHMT and RHMT. Analogous expressions to Eqs. (11) and (12) are obtained for $\mathbf{g}^R_n$ in terms of $2N\times 2N$ Möbius transformation matrices $\mathbf{X}_R$ and $\mathbf{Y}_R$ — which are obtained from $\mathbf{X}_L$ and $\mathbf{Y}_L$ by interchanging $\mathbf{t}\leftrightarrow\mathbf{t}^\dagger$.

2. Connection between the spectrum of $\mathbf{X}_R$, $\mathbf{Y}_L$, $\mathbf{Y}_R$ and the bulk band structure

It is easy to show that if $\{\lambda_i\}$ are the eigenvalues of $\mathbf{X}_L$, then they are also the eigenvalues of $\mathbf{Y}_R$, while $\{\lambda_i^{-1}\}$ are the eigenvalues of $\mathbf{X}_R$ and $\mathbf{Y}_L$. It follows that the results of Sec. V are immediately applicable to the eigenvalues of $\mathbf{X}_R$, $\mathbf{Y}_L$, and $\mathbf{Y}_R$.

3. Diagonalization of $\mathbf{X}_R$, $\mathbf{Y}_L$, and $\mathbf{Y}_R$

Once the matrix $\mathbf{X}_L$ has been diagonalized numerically, and one has read off the $N\times N$ submatrices $\mathbf{\Lambda}_1$, $\mathbf{\Lambda}_2$, $\mathbf{o}_1$, $\mathbf{o}_2$, ω_1, and ω_2, as described in Sec. VI. Then it is immediately possible to diagonalize the remaining Möbius transformation matrices $\mathbf{X}_R$, $\mathbf{Y}_L$, and $\mathbf{Y}_R$ in terms of these and the $2N\times 2N$ transposition matrix $\mathbf{P}\equiv\left(\begin{smallmatrix}\mathbf{0} & \mathbf{1}\\ \mathbf{1} & \mathbf{0}\end{smallmatrix}\right)$ via

$$\mathbf{O}_R^{-1}\mathbf{X}_R\mathbf{O}_R=\mathbf{P}\mathbf{\Lambda}^{-1}\mathbf{P} \quad \text{where } \mathbf{O}_R\equiv\begin{pmatrix}\mathbf{o}_2 & \mathbf{o}_1\\ \mathbf{t}^\dagger\mathbf{o}_2\mathbf{\Lambda}_2^{-1} & \mathbf{t}^\dagger\mathbf{o}_1\mathbf{\Lambda}_1^{-1}\end{pmatrix}, \quad \mathbf{O}_R^{-1}\equiv\begin{pmatrix}\mathbf{\Lambda}_2\omega_2\mathbf{t} & -\omega_2\\ \mathbf{\Lambda}_1\omega_1\mathbf{t} & -\omega_1\end{pmatrix}, \tag{A2}$$

$$\mathbf{Q}_L^{-1}\mathbf{Y}_L\mathbf{Q}_L=\mathbf{\Lambda}^{-1} \quad \text{where } \mathbf{Q}_L\equiv\begin{pmatrix}-\mathbf{o}_1 & -\mathbf{o}_2\\ \mathbf{t}\mathbf{o}_1\mathbf{\Lambda}_1 & \mathbf{t}\mathbf{o}_2\mathbf{\Lambda}_2\end{pmatrix}, \quad \mathbf{Q}_L^{-1}\equiv\begin{pmatrix}\mathbf{\Lambda}_1^{-1}\omega_1\mathbf{t}^\dagger & \omega_1\\ \mathbf{\Lambda}_2^{-1}\omega_2\mathbf{t}^\dagger & \omega_2\end{pmatrix}, \tag{A3}$$

$$\mathbf{Q}_R^{-1}\mathbf{Y}_R\mathbf{Q}_R=\mathbf{P}\mathbf{\Lambda}\mathbf{P} \quad \text{where } \mathbf{Q}_R\equiv\begin{pmatrix}\mathbf{o}_2 & \mathbf{o}_1\\ -\mathbf{t}^\dagger\mathbf{o}_2\mathbf{\Lambda}_2^{-1} & -\mathbf{t}^\dagger\mathbf{o}_1\mathbf{\Lambda}_1^{-1}\end{pmatrix}, \quad \mathbf{Q}_R^{-1}\equiv\begin{pmatrix}\mathbf{\Lambda}_2\omega_2\mathbf{t} & \omega_2\\ \mathbf{\Lambda}_1\omega_1\mathbf{t} & \omega_1\end{pmatrix}. \tag{A4}$$

Equations (A2)–(A4) can be verified using constraints (20)–(23).

4. Surface Green's-function solution and asymptotic periodicity

Using Eqs. (11), (12), and (A2)–(A4), we can deduce similar closed-forms to Eq. (25) for the surface Green's functions

$$\mathbf{g}^L_n=\mathbf{t}^{\dagger-1}{\mathbf{\Omega}^L_{n+1}}^{-1}\mathbf{\Omega}^L_n \quad \text{where } \mathbf{\Omega}^L_n\equiv\mathbf{\Lambda}_1^{-n}\omega_1+\mathbf{h}^L_0\mathbf{\Lambda}_2^{-n}\omega_2 \quad \text{and} \quad \mathbf{h}^L_n\equiv\mathbf{g}^L_n{}^{\bullet}\mathbf{Q}_L, \tag{A5}$$

$$\mathbf{g}^R_n=\mathbf{\Delta}^R_n{\mathbf{\Delta}^R_{n+1}}^{-1}\mathbf{t}^{\dagger-1} \quad \text{where } \mathbf{\Delta}^R_n\equiv\mathbf{o}_2\mathbf{\Lambda}_2^{-n}\mathbf{f}^R_0+\mathbf{o}_1\mathbf{\Lambda}_1^{-n} \quad \text{and} \quad \mathbf{f}^R_n\equiv\mathbf{O}_R^{-1}{}_{\bullet}\mathbf{g}^R_n, \tag{A6}$$

$$\mathbf{g}^R_n=\mathbf{t}^{-1}{\mathbf{\Omega}^R_{n+1}}^{-1}\mathbf{\Omega}^R_n \quad \text{where } \mathbf{\Omega}^R_n\equiv\mathbf{\Lambda}_2^{n}\omega_2+\mathbf{h}^R_0\mathbf{\Lambda}_1^{n}\omega_1 \quad \text{and} \quad \mathbf{h}^R_n\equiv\mathbf{g}^R_n{}^{\bullet}\mathbf{Q}_R, \tag{A7}$$

where the bilinearly transformed surface Green's-function matrices $\mathbf{f}$ and $\mathbf{h}$ have a particularly simple dependence upon n:

$$\mathbf{h}_n^L=\mathbf{\Lambda}_1^n\mathbf{h}_0^L\mathbf{\Lambda}_2^{-n} \quad \mathbf{f}_n^R=\mathbf{\Lambda}_2^{-n}\mathbf{f}_0^R\mathbf{\Lambda}_1^n \quad \mathbf{h}_n^R=\mathbf{\Lambda}_2^{-n}\mathbf{h}_0^R\mathbf{\Lambda}_1^n. \tag{A8}$$

Because we can solve the surface adlayering equations using either the LHMT or the RHMT, then we obtain two forms for both $\mathbf{g}_n^L$ [Eqs. (25) and (A5)] and $\mathbf{g}_n^R$ [Eqs. (A6) and (A7)]. The equivalence of these two forms can be demonstrated using the constraints (20)–(23). The argument which was used in Sec. VII to obtain the asymptotic (i.e., thick adlayer) properties of $\mathbf{f}_n^L$ can now be directly applied to $\mathbf{h}_n^L$, $\mathbf{f}_n^R$, and $\mathbf{h}_n^R:\mathbf{g}_n^R$ is a matrix whose elements are quasiperiodic functions of $2P$ plane waves, with periods $2\pi/dk_\alpha$. The k_α are the k-point values at which the bulk adlayer energy bands cut ε.

5. Semi-infinite surface Green's functions

The analysis of Sec. VIII can be applied to the remaining three cases, giving an alternative closed form for the semi-infinite left-hand surface Green's function $\mathbf{g}_\infty^L$, and two forms for the semi-infinite right-hand surface Green's function $\mathbf{g}_\infty^R$:

$$\begin{aligned}\mathbf{g}_\infty^L&=\mathbf{0}^{\bullet}\mathbf{Q}_L^{-1}=\mathbf{t}^{\dagger-1}\omega_1^{-1}\mathbf{\Lambda}_1\omega_1,\\ \mathbf{g}_\infty^R&=\mathbf{O}_{R\bullet}\mathbf{0}=\mathbf{o}_1\mathbf{\Lambda}_1\mathbf{o}_1^{-1}\mathbf{t}^{\dagger-1},\\ \mathbf{g}_\infty^R&=\mathbf{0}^{\bullet}\mathbf{Q}_R^{-1}=\mathbf{t}^{-1}\omega_2^{-1}\mathbf{\Lambda}_2^{-1}\omega_2.\end{aligned} \tag{A9}$$

Once again, the equivalence of the two forms for $\mathbf{g}_\infty^L$ and $\mathbf{g}_\infty^R$ can be deduced from the constraints (20)–(23).

6. Extension to Rth-order neighbor interactions

Consider a right-hand adlayer — grown in the $-\mathbf{d}$ direction. Let $\mathbf{g}_R^{(n)}$ be the $NR\times NR$ top left-hand submatrix of the total Green's function $\mathbf{G}^{(n)}$ for this system,

$$\mathbf{g}_R^{(n)}\equiv\begin{pmatrix}\mathbf{G}_{n,n}^{(n)} & \cdots & \mathbf{G}_{n,n+1-R}^{(n)}\\ \vdots & \ddots & \vdots\\ \mathbf{G}_{n+1-R,n}^{(n)} & \cdots & \mathbf{G}_{n+1-R,n+1-R}^{(n)}\end{pmatrix}. \tag{A10}$$

Then this submatrix can be deduced from the right-hand substrate Green's function via a $[2NR]$ LHMT [cf. Eqs. (37) and (38)],

$$\mathbf{g}_R^{(n)}=(\mathbf{\Xi}_R)^n{}_{\bullet}\mathbf{g}_R^{(0)} \quad \text{where } \mathbf{\Xi}_R\equiv\begin{pmatrix}\mathbf{a} & \mathbf{b}\\ \mathbf{c} & \mathbf{d}\end{pmatrix}, \tag{A11}$$

and where $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, and $\mathbf{d}$ are $NR\times NR$ matrices given by

$$\mathbf{a}=\begin{pmatrix}\begin{pmatrix}\mathbf{0}\end{pmatrix} & \mathbf{0}\\ \begin{pmatrix}\mathbf{1}\end{pmatrix} & \begin{pmatrix}\mathbf{0}\end{pmatrix}\end{pmatrix},\quad \mathbf{b}=\begin{pmatrix}\begin{pmatrix}\mathbf{0}\end{pmatrix} & \mathbf{t}_R^{\dagger-1}\\ \begin{pmatrix}\mathbf{0}\end{pmatrix} & \begin{pmatrix}\mathbf{0}\end{pmatrix}\end{pmatrix},$$

$$\mathbf{c}=\begin{pmatrix}(-\mathbf{t}_1\ \ldots\ -\mathbf{t}_{R-1}) & -\mathbf{t}_R\\ \begin{pmatrix}\mathbf{0}\end{pmatrix} & \begin{pmatrix}\mathbf{0}\end{pmatrix}\end{pmatrix}, \tag{A12}$$

$$\mathbf{d}=\begin{pmatrix}\begin{pmatrix}\mathbf{0}\end{pmatrix} & (\varepsilon-\mathbf{u})\mathbf{t}_R^{\dagger-1}\\ \begin{pmatrix}\mathbf{1}\end{pmatrix} & \begin{pmatrix}-\mathbf{t}_1^{\dagger}\mathbf{t}_R^{\dagger-1}\\ \vdots\\ -\mathbf{t}_{R-1}^{\dagger}\mathbf{t}_R^{\dagger-1}\end{pmatrix}\end{pmatrix}.$$

Similar forms to Eqs. (38) and (A12) can also be derived for generalizations to the right-hand Möbius transformation matrices $\mathbf{Y}_L$ and $\mathbf{Y}_R$.

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[14] Under such circumstances, with random self-energies and hoppings, and for a finite system, a fast numerical method for calculating the Green's-function elements has been developed by Godfrin (Ref. 5).

[15] See, for example, Refs. 16 and 17 for the case of semiconductors, Ref. 18 for the case of metals, and references within.

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[18] A. J. Freeman and Ru-qian Wu, J. Magn. Magn. Mater. **100**, 497 (1991).

[19] In fact, such Hamiltonians have been used with great success recently in the study of the coupling and magnetoresistance ef-

fects of magnetic-multilayers (see, for example, Refs. 8, 9, 11, and 20).

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[21] L. V. Ahlfors, *Complex Analysis*, 3rd ed. (McGraw-Hill, New York, 1979).

[22] By the surface Green's-function element, we mean the $N\times N$ bottom-right-hand submatrix of the total Green's function $\mathbf{G}_L$, or the $N\times N$ top-left submatrix of $\mathbf{G}_R$.

[23] For this special case of $\mathbf{t}=\mathbf{t}^\dagger$, this solution can also be derived more directly, by a straightforward generalization of the $N=1$ case. For $\mathbf{t}\neq\mathbf{t}^\dagger$ $(N\neq 1)$ the adlayering equations resist such an obvious solution, and one must proceed as above with $2N\times 2N$ matrices.

[24] For some specific multilayer models [e.g., sc(100) and fcc(111) lattices with hopping to both first- and second-nearest neighbors] there may be certain points $(\mathbf{k}_\parallel^0)$ in the two-dimensional Brillouin zone at which the hopping matrix $\mathbf{t}(\mathbf{k}_\parallel^0)$ is singular or near singular. Our analysis fails at these specific points. However, in the neighborhood of these points we find that the algorithms developed here are numerically very stable. Typically, for $|\mathbf{k}-\mathbf{k}_\parallel^0|>10^{-6}$ times the length of the Brillouin zone, the error in the surface Green's function $[\mathbf{g}(\mathbf{k})]$ is less than $<10^{-5}$%. Such points can easily be tested for, so that if the surface Green's function is continuous in the neighborhood, it may be determined at $\mathbf{k}_\parallel^0$ by numerical interpolation. In practice, however, one is extremely unlikely to encounter such points during any numerical calculation.

[25] If in addition the elements of **u** and **t** are real (as is usually the case in tight-binding models with certain adlayer growth directions), then $\det(\mathbf{v}-\lambda\mathbf{t}-\lambda^{-1}\mathbf{t}^T)=\det(\mathbf{v}^T-\lambda^{-1}\mathbf{t}-\lambda\mathbf{t}^T)$ and hence for **v** symmetric, if λ is an eigenvalue so is λ^{-1}.

[26] In practice, the spread of eigenvalues is usually such that a good approximation to periodicity is obtained for $n\approx 10$.

[27] We note that for the case of a single band cutting ε $(P=1)$, Eq. (28) implies that there is only one nonzero element of $\mathbf{g}_n^L$, and that this is a function of a single period $2\pi/d(k_N-k_{N+1})$.

[28] For the case of real **u** and **t** matrices, this reduces to a quasiperiodic function of P plane waves, with periods $\{2\pi/dk_\alpha;\alpha=N-P+1,\ldots,N\}$.

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[30] D. H. Lee and J. D. Joannopoulos, Phys. Rev. B **23**, 4997 (1981).

[31] d is the inter-principal-layer distance, so that d/R is the interlayer distance.

[32] N.B. If **X** has degenerate eigenvalues, then $\mathcal{M}$ is diagonal only if a suitable basis of degenerate eigenvectors is chosen in **O**.

[33] D. A. Papaconstantopoulus, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).