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# Surface Green's function calculations: A nonrecursive scheme with an infinite number of principal layers

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A novel computational method for a surface Green's function matrix is introduced for the calculation of electrical current in molecular wires. The proposed nonrecursive approach includes an infinite number of principal layers and yields the second-order matrix equation for the transformed Green's function matrix. The solution is found by the direct diagonalization of the auxiliary matrix without any iteration process. As soon as complex roots of the auxiliary matrix ($\simeq \hat{G}_S$) are calculated, the gaps and the bands in the surface electronic structure are found. It is shown that the solution of a second-order matrix equation determines the spectral density matrix, that is, the density of states for noninteracting electrons. Single and double principal layer models are studied both analytically and numerically. The energy interval for nonvanishing spectral matrices is determined. This method is applicable to matrices of any rank. © *2007 American Institute of Physics*.
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Design and fabrication of nanoscale electronic circuits and devices have inspired much of the last decade's thorough research into the electronic properties of a molecular bridge placed between electrodes. In theoretical studies, the electrical current through a metal-molecule-metal junction is usually investigated in the framework of Green's function methods, and the effects of contacts are described by coupling matrices $\gamma$.[1,2] Thus, correct calculations of contacts become an important problem in the evaluation of electrical current. To find $\gamma$, one needs to determine the matrix elements of interaction between the molecule and surface states of metal electrodes and multiply by the surface spectral function matrix, that is, proportional to the imaginary part of the surface Green's function.[2,3] The latter determines the surface density of states for noninteracting electrons.[4]

Density functional theory is commonly used in the calculations of the electrical current.[5–7] For many molecular bridges, where electron correlation is important, advanced electron propagator methods should be employed.[8–10] In these methods, the electrical current can be expressed in terms of pole strengths $a_j$, poles $\varepsilon_j$, and the Fermi functions of the electrodes $f_{L,R}(\varepsilon_j)$,[8–10]

$$J = \frac{e}{\hbar}\sum_j \frac{\gamma^L(j)\gamma^R(j)a_j[f_L(\varepsilon_j) - f_R(\varepsilon_j)]}{|\gamma^L(j) + \gamma^R(j)|}, \tag{1}$$

where coupling matrices for left and right electrodes are given by

$$\gamma^L(j) = \sum_{i=1}^{n_l} c_i^2(j)\gamma_i^L(j), \quad \gamma^R(j) = \sum_{i=n_l+1}^{n} c_i^2(j)\gamma_i^R(j).$$

The index $i$ denotes active terminal orbitals with corresponding partial interactions $\gamma_i$ and contributions to Dyson orbitals $c_i(j)$ in which the Green's function matrix is diagonal. In the derivation of Eq. (1), we have assumed that linewidth (coupling) matrices are in diagonal forms. Meir and Wingreen[2] found the expression for coupling matrices,

$$\gamma_i^{L,R} = \sum_{\mathbf{k},\alpha} V_{i,\mathbf{k}\alpha}^* V_{\mathbf{k}\alpha,i} A_\alpha^{L,R}(\mathbf{k}), \tag{2}$$

where $V_{\mathbf{k}\alpha,i}$ is an interaction matrix element between surface states and molecular bridge states and $A_\alpha(\mathbf{k})^{L,R}$ is a surface spectral function such that $A_\alpha(\mathbf{k})^{L,R} = -2\,\Im\mathrm{Tr}\{G_\alpha^{L,R}(\mathbf{k},E)\}$.

Because the elements of the coupling matrices in Eq. (1) can vanish with respect to the voltage applied to nanoscale devices,[10] electronic properties play an important role in molecular wires, determining negative differential resistance,[11,12] rectification,[13] and switching.[14] Molecular devices with these properties could perform functions in electronic circuits that are analogous to those of transistors.[1]

The main goal of this work is to properly calculate the spectral function or the imaginary part of the surface Green's function. There are several competing methods. The most commonly used is a renormalization-group technique proposed by López-Sancho and Lopez-Sancho[15] that proceeds through a finite number of recursive computations. In this procedure, an auxiliary, imaginary parameter $i\varepsilon$ is introduced in the initial step[5–7,16,17] and, after several iterations, the finite imaginary part of the surface Green's function is found. However, the imaginary part of the matrix is not clearly defined. In general, the Green's function should be diagonal-

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ized first, the imaginary part of the matrix should be separated subsequently, and finally a unitary transformation should restore the matrix to the initial form. Such a procedure will be implemented in this work. For correlated electrons, the density of states and the imaginary part of the Green's function are two different quantities that are equal to each other only for noninteracting fermions.[4] Thus, for correlated electrons in electrodes, the previous approaches should be substantially improved and new methods should be developed. In this paper, we reconsider a renormalization-group technique for the surface Green's functions,[18] reducing the problem to a second-order matrix equation that will be solved analytically and numerically for gold surfaces. In particular, we study single and double atomic layer models. In the proposed approach no artificial parameter $\varepsilon$ is required and the imaginary part of the Green's function appears naturally. Analytical solutions for special cases will be presented to provide an intuitive understanding of the proposed method.

The nearly diagonal Hamiltonian matrix for a semi-infinite electrode is given by

$$\mathbf{H}_R = \begin{pmatrix} \mathbf{H}_{00} & \mathbf{H}_{01} \\ \mathbf{H}_{01}^{\dagger} & \mathbf{H}_R \end{pmatrix}, \tag{3}$$

where $\mathbf{H}_{00}$ represents the couplings between the atoms within the surface layer and $\mathbf{H}_{01}$ stands for the interaction between surface and bulk layers. A three-dimensional metal electrode is considered to be infinite in two directions along the surface plane and semi-infinite in the normal direction. Thus, the electrode is divided into a semi-infinite stack of principal layers, where the latter term is defined as the smallest set of atomic layers that reflects the symmetry of a crystal with nearest-neighbor interactions between them.[15] Hence, periodic boundary conditions in two surface directions reduce the system to noninteracting one-dimensional chains, with one chain for each wave vector $\mathbf{k}_{\|}$ in the plane of the layer. This form of the Hamiltonian exhibits the property that after the removing of a surface layer, the Hamiltonian remains unchanged. The matrix (3) can be presented as a semi-infinite matrix in the following manner:

$$\mathbf{H}_R = \begin{pmatrix} \mathbf{H}_{00} & \mathbf{H}_{01} & 0 & 0 & 0 & \cdots \\ \mathbf{H}_{01}^{\dagger} & \mathbf{H}_{00} & \mathbf{H}_{01} & 0 & 0 & \cdots \\ 0 & \mathbf{H}_{01}^{\dagger} & \mathbf{H}_{00} & \mathbf{H}_{01} & 0 & \cdots \\ 0 & 0 & \mathbf{H}_{01}^{\dagger} & \mathbf{H}_{00} & \mathbf{H}_{01} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \tag{4}$$

Here the square matrices $\mathbf{H}_{00}$ and $\mathbf{H}_{01}$ have rank $n$, where $n$ is the number of atomic layers in the principal layer multiplied by the number of atomic orbitals under consideration. $\mathbf{H}_{00}$ describes interactions within the principal layer. (Here we assume that the surface layer is identical to the bulk layers.) $\mathbf{H}_{01}$ accounts for interactions between two nearest-neighbor principal layers. This matrix appears on both sides of the diagonal (as a Hermitian one on a bottom side) because of a general requirement for Hamiltonians to be Hermitian. In this work, we study a gold lattice oriented in the

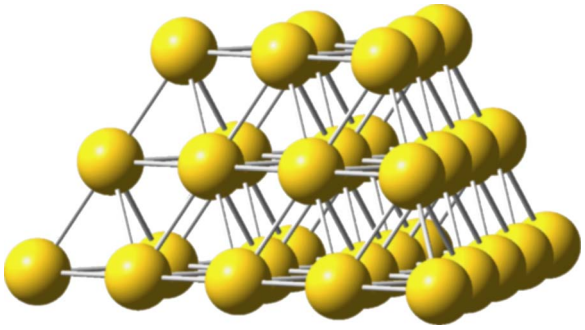

FIG. 1. fcc-lattice structure of gold.

$\langle 111 \rangle$ direction. $\mathbf{H}_{00}$ and $\mathbf{H}_{01}$ are, in general, matrix functions of a surface wave vector $\mathbf{k}_{\|}$.

A surface Green's function, i.e., the projection of the electrode Green's function $\mathbf{G}$ onto the surface electronic states, is given by the following expression:[6,18]

$$\mathbf{G}_S(E) = [E - \mathbf{H}_{00} - \mathbf{H}_{01}\mathbf{G}_S(E)\mathbf{H}_{01}^{\dagger}]^{-1}. \tag{5}$$

In general, $\mathbf{G}_S$ is a matrix where the $(i,j)$ element is a local retarded Green's function that connects atomic layers $i$ and $j$ within a principal layer.

To evaluate $\mathbf{G}_S$, we employ a scheme by López-Sancho and Lopez-Sancho,[15] where the electrode Hamiltonian is represented as a block-tridiagonal matrix. Eq. (5) for the surface Green's function matrix can be rewritten as a second-order matrix equation in the following way:[20]

$$\mathbf{H}_{01}\mathbf{Y}^2 + (\mathbf{H}_{00} - E)\mathbf{Y} + \mathbf{H}_{01}^{\dagger} = 0, \tag{6}$$

where $\mathbf{Y} = \mathbf{G}_S\mathbf{H}_{01}^{\dagger}$. Employing a resolvent matrix method,[19] we numerically solve matrix Eq. (6) for fixed $\mathbf{k}_{\|}$.

In a *single layer model*, we assume that the principal layer of the (111)-fcc gold structure (see Fig. 1) consists of a single atomic layer. In the perpendicular direction, there are semi-infinite chains of atoms connected by $s$ orbitals. In this case, the matrix elements $\mathbf{H}_{00}$ and $\mathbf{H}_{01}$ become simple $(1 \times 1)$ numbers: $H_{00} = Vg_1(\mathbf{k}_{\|})$, $H_{01} = Vg_2(\mathbf{k}_{\|})$, $V$ is a coupling between $s$ orbitals of the nearest-neighbor atoms, $g_1(\mathbf{k}_{\|})$ determines phase shifts between $s$ orbitals of atoms inside the atomic layer, and $g_2(\mathbf{k}_{\|})$ stands for phase shifts between $s$ orbitals of atoms in neighboring atomic layers. $s$ orbitals are assumed to be orthonormal. The coupling constants $V$ are taken from Ref. 21. For gold, $V = -0.908$ eV. The functions $g_1(\mathbf{k}_{\|})$ and $g_2(\mathbf{k}_{\|})$ are found in the tight-binding approximation.[22] In this model, the matrix expression (6) for the surface Green's function results in a simple quadratic equation with the solution,

$$G_S(\mathbf{k}_{\|}) = \frac{H_{00}(\mathbf{k}_{\|}) - E}{2|H_{01}(\mathbf{k}_{\|})|^2} \pm i\frac{\sqrt{(2|H_{01}(\mathbf{k}_{\|})|)^2 - (H_{00}(\mathbf{k}_{\|}) - E)^2}}{2|H_{01}(\mathbf{k}_{\|})|^2}. \tag{7}$$

The imaginary part of $G_S(\mathbf{k}_{\|})$ exists for energies in the interval: $H_{00} - 2|H_{01}| \leqslant E \leqslant H_{00} + 2|H_{01}|$. Consequently, the local spectral function, $A(\mathbf{k}_{\|}, E) = -2\,\Im\mathrm{Tr}\{G_S(\mathbf{k}_{\|}, E)\}$, can also be found. The integral spectral function $A(E)$ is determined from integration of the local spectral function over $\mathbf{k}_{\|}$ in the first Brillouin zone. Figure 2 shows the integral spectral

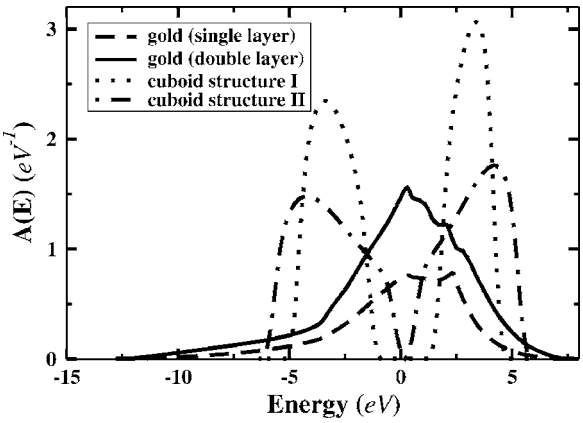


FIG. 2. Integral spectral function. The dashed line corresponds to the single layer model of gold described by Eq. (7), the solid line determines the integral spectral function for two layers in the gold principal layer, the dotted line stands for the cuboid model where the intralayer interaction is $h_{21}^1=-1.0$ eV (structure I), and the dashed-dot line determines the cuboid structure (II) where the intralayer interaction is $h_{21}^1=-2.0$ eV.

function for a (111)-gold surface versus energy $E$ (see the dashed line in Fig. 2).

In the more realistic *double layer model*, we assume that there are only two layers in a principal layer in which the gold atoms interact with both their nearest neighbors ($V_1=-0.908$ eV) and their second nearest neighbors ($V_2=0.038$ eV). In this case, $\mathbf{H}_{00}$ is a $2\times2$ matrix,

$$\mathbf{H}_{00}=\begin{pmatrix} h_{11}^0(\mathbf{k}_\parallel) & h_{12}^0(\mathbf{k}_\parallel) \\ h_{12}^{0*}(\mathbf{k}_\parallel) & h_{22}^0(\mathbf{k}_\parallel) \end{pmatrix}. \tag{8}$$

$h_{11}^0(\mathbf{k}_\parallel)$ and $h_{22}^0(\mathbf{k}_\parallel)$ determine the intralayer interactions in the first and second atomic layers, respectively, while $h_{12}^0(\mathbf{k}_\parallel)$ stands for the interaction between the first and second atomic layers within the principal layer. The $2\times2$ Hamiltonian matrix $\mathbf{H}_{01}$ in Eq. (4) determines the interaction between two neighboring principal layers,

$$\mathbf{H}_{01}=\begin{pmatrix} h_{11}^1(\mathbf{k}_\parallel) & h_{12}^1(\mathbf{k}_\parallel) \\ h_{21}^1(\mathbf{k}_\parallel) & h_{22}^1(\mathbf{k}_\parallel) \end{pmatrix}. \tag{9}$$

$h_{11}^1(\mathbf{k}_\parallel)$ stands for the interaction between the first atomic layer in the upper principal layer and the first atomic layer in the lower principal layer. $h_{12}^1(\mathbf{k}_\parallel)$ determines the interaction between the first atomic layer in the upper principal layer and the second atomic layer in the lower principal layer and its value is rather small. $h_{21}^1(\mathbf{k}_\parallel)$ corresponds to the interaction between the second atomic layer in the upper principal layer and the first atomic layer in the lower principal layer. Finally, $h_{22}^1(\mathbf{k}_\parallel)$ determines the interaction between the second layer in the upper principal layer and the second layer in the lower principal layer. For these terms, the tight-binding coupling constants $V_1$ and $V_2$, and phase shifts $g(\mathbf{k}_\parallel)$ between atomic layers are chosen in the same manner as for the single layer model described above. Now Eq. (6) for the surface Green's function matrix is a second-order, $2\times2$ matrix problem. We solve Eq. (6) both numerically and analytically. The former approach is necessary for solving Eq. (6) for higher rank matrices where an analytical solution is impossible.

*Numerical solution.* Employing the resolvent matrix method,[19] we have written an original FORTRAN 90 code to compute $\hat{G}_S$ for different $\mathbf{k}_\parallel$ points in a two-dimensional Brillouin zone of a (111)-gold surface (see Fig. 1). Both the surface Green's function matrix, $\mathbf{G}_S=\mathbf{Y}(\mathbf{H}_{01}^\dagger)^{-1}$, and the surface local spectral function, $A(\mathbf{k}_\parallel,E)=-2\Im\,\mathrm{Tr}\{\mathbf{G}_S(\mathbf{k}_\parallel,E)\}$, have been calculated.

An *analytical solution* is possible only in a particular case where all the elements of the matrix (9) vanish except $h_{21}^1(\mathbf{k}_\parallel)$. If we assume that $h_{11}^0=h_{22}^0$ (i.e., the first and second atomic layers are the same), the analytical solution for the (1, 1) element of the surface Green's function matrix yields

$$g_{11}=\frac{(h_{11}^0-E)^2-|h_{12}^0|^2+|h_{21}^1|^2\pm i\sqrt{D}}{2(E-h_{11}^0)|h_{21}^1|^2}, \tag{10}$$

where $D=2(|h_{12}^0|^2+|h_{21}^1|^2)(h_{11}^0-E)^2+2|h_{12}^0|^2|h_{21}^1|^2-(h_{11}^0-E)^4-|h_{12}^0|^4-|h_{21}^1|^4$. Consequently, the imaginary part of $g_{11}$ is given by

$$\Im g_{11}=-\frac{\sqrt{D}}{2(E-h_{11}^0)|h_{21}^1|^2}. \tag{11}$$

Similarly

$$\Im g_{22}=-\frac{(h_{11}^0-E)\sqrt{D}}{2|h_{21}^1|^2|h_{12}^0|^2}. \tag{12}$$

Therefore, the surface local spectral function is obtained in a standard way: $A(E,\mathbf{k}_\parallel)=-2(\Im g_{11}+\Im g_{22})$ where the surface local spectral function is nonvanishing when $D>0$. The four roots of $D=0$ determine the proper intervals for the allowed energy: $E_{1,2,3,4}=h_{11}^0\pm(|h_{21}^1|\pm|h_{12}^0|)$. At a particular $\mathbf{k}_\parallel$ point in a two-dimensional Brillouin zone, the surface local spectral function has an energy gap if there are four different roots (see Fig. 4) for the local spectral function.

The width of the energy gap is equal to $2|(|h_{12}^0|-|h_{21}^1|)|$. Note that if $|h_{12}^0|=|h_{21}^1|$ (atomic layers inside the principal layer interact with the same strength as neighboring atomic layers in adjacent principal layers), then the model becomes the single layer model that has been described above. The surface integral spectral function for the gold electrode oriented in the ⟨111⟩ direction is depicted in Fig. 2 (the solid line). The integral spectral function calculated for a double layer model resembles the behavior of the integral spectral function calculated for a single layer model, but the numerical values are different. Indeed, in both cases the integral spectral functions vanish at the same values of energy.

To demonstrate the potential of our method, we find spectral functions of the cuboid structure with the following parameters: $h_{11}^0=-0.1$ eV, $h_{12}^0=-2.0$ eV, and $h_{11}^1=-0.1$ eV (see the structure in Fig. 3). Two different structures (I and II) differ by the intraprinciple layer coupling: $h_{21}^1=-1.0$ eV for structure I and $h_{21}^1=-2.0$ eV for structure II. As shown in Fig. 2, the integral spectral function of structure I exhibits a well-pronounced gap ($\simeq2$ eV) with two high bands. If the intraprincipal layer interaction is changed to $-2.0$ eV ($|h_{12}^0|=|h_{21}^1|$), the gap vanishes. In addition to the calculations of the integral spectral function, we have found a local surface spectral density function along the high-symmetry line of the

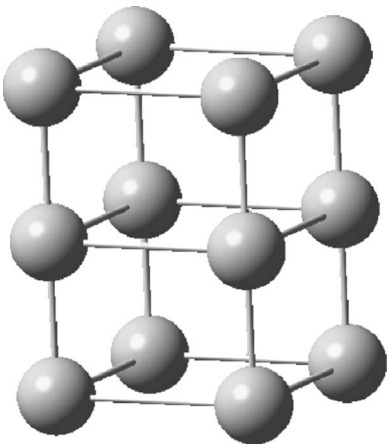

FIG. 3. Cuboid crystal structure. This structure is chosen to demonstrate a gap in a spectral density.

surface Brillouin zone in the $\bar{\Gamma}\bar{X}$ direction (see Fig. 4). In this figure, we have fixed the projection such that $k_y=0$ and calculated the dependence of the imaginary part of the Green's function on $k_x$ and $E$. For the calculations, we have chosen the following values of the parameters: $h_{11}^0=-2.0$ eV, $h_{12}^0=-2.0$ eV, $h_{11}^1=-0.1$ eV, and $h_{21}^1=-1.0$ eV. For the definition of the parameters see Eqs. (8) and (9). Figure 4 demonstrates how the width of the gap (the valley) and the heights of the bands depend on the wave vector $k_x$ and the energy $E$.

For the calculation of electric current in molecular tunnel junctions it is necessary to find coupling matrices connecting a bridge with metal electrodes [see Eq. (2)]. A spectral density of the leads plays an important role in the energy dependence and therefore, in the current-voltage characteristics of a molecular device. Usually this matrix is considered to be energy independent, thus assuming that the whole voltage dependence is owing to the bridge. In this work we have challenged this assumption and have shown how the energy dependence of the spectral density of the metal electrodes can be crucial for a voltage dependence in electric current. The problem under consideration is numerical rather than analytical because each particular case can lead to different energy dependences in $\gamma(E)$. In this work we have proposed a novel method for nonrecursive calculations of the surface Green's function matrices using an infinite number of principal layers. This method is truly *ab initio*, for it has no adjustable parameter for finding the nonvanishing imaginary part of the surface spectral Green's function matrix. A renormalization-group scheme has been employed that leads to the second-order matrix equation for the surface Green's matrix. The solutions of this equation exhibit imaginary parts in a diagonalized form that represents the imaginary parts of the Green's matrix or the spectral function matrix that is the density of states for noninteracting electrons. For current calculations in molecular wires, it is important to use the imaginary part of the Green's function rather than the density of states. In our calculations, we have obtained both gap and nongap solutions for the spectral function (see the curves for structures I and II in Fig. 2) for different values of the parameters of the Hamiltonian. For realistic values of the parameters of the Hamiltonian of the gold structure (see Fig. 1), single and double layer models for the principal layer have been studied. Despite some qualitative similarities between them (no gap), the single layer model exhibits a broader, nonstructured peak in the spectral function with half the peak/valley ratio. From our calculations, we have obtained the integral spectral density for the (111)-fcc gold structure depicted in Fig. 1. To demonstrate the capabilities of the proposed numerical method, we have studied cuboid structures (see Fig. 3) with different sets of parameters (see the graphs for structures I and II in Figure 2). For structure I, a well-pronounced gap and band peaks have been found (for this structure the intraprincipal layer coupling $h_{21}^1=-1.0$ eV), while for $h_{21}^1=-2.0$ eV (structure II), the gap shrinks to zero. In addition to the integral spectral function, we have studied the local spectral function along the high-symmetry line of the surface Brillouin zone in the $\bar{\Gamma}\bar{X}$ direction. The gap width and the band peaks substantially depend on the wave vector $k_x$.

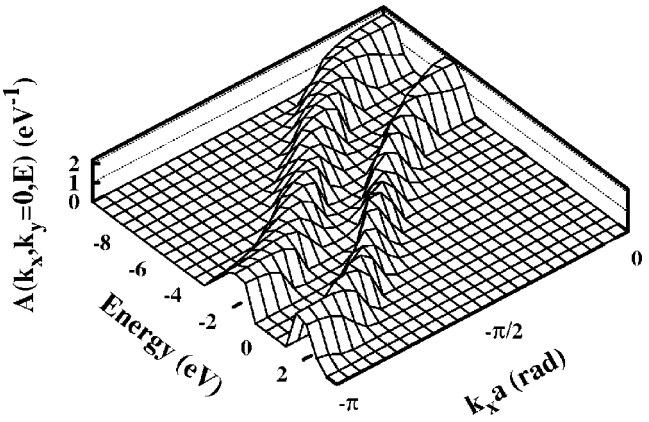


FIG. 4. Three-dimensional picture of the local spectral function. Here $k_y=0$. The energy gap is presented by the valley.

In addition, an analytical solution has been found for a double layer model where the interaction between the principal layers is only due to the coupling between neighboring layers. This solution [see Eqs. (10)–(12)] demonstrates the origination of the complex Green's function matrix for some particular energy intervals corresponding to the bands of the surface electronic structure. In the future, this model will be extended to higher-rank matrix calculations that include more gold orbitals.

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