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## On the calculation of the surface Green function by the tight-binding linear muffin-tin orbital method

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**Abstract.** In this paper, we report the development of a simple and very efficient method for the determination of the Green function of an ideal semi-infinite crystal within the frame of the tight-binding linear muffin-tin orbital method. As a test of the method, we calculate the  $k_{\parallel}$ -resolved layer densities of states for Cu(001) and Cu(111) surfaces.

In the last few years a number of theoretical methods have been developed to study the electronic structure of solid surfaces. The methods can be divided into two groups:

- (i) an eigenvalue technique applied to a finite slab;
- (ii) a Green function (GF) formalism for a semi-infinite system.

The powerful film linear augmented plane-wave method [1] is advantageous in film problems, and it even allows us to include effects of non-muffin-tin potentials. The linear muffin-tin orbital (LMTO) method [2] has been applied to the finite film recently [3]. The GF methods are not limited to films or slabs, the minimal basis set is used, and the formalism can be developed either in real space using the layer Korringa–Kohn–Rostoker (KKR) method [4], or in the tight-binding (TB) representation [5]. The advantage of the TB methods in comparison with the layer KKR method is their simplicity, but they are usually limited to semi-empirical treatments. This situation has been changed with the development of the first-principles TB approach based on the LMTO method. This TB LMTO method [6] retains the simplicity of the empirical schemes but combines it with an accuracy comparable with other first-principles methods.

The presence of the surface is included in the TB formalism via the so-called natural boundary condition: no hopping is allowed out of the sample. To formulate this mathematically, we introduce the notion of the principal layer [7]: any crystal with a surface can be described by a semi-infinite stack of principal layers with only nearest-neighbour interactions between them. The projection of the GF of the ideal semi-infinite crystal onto the top principal layer is the surface Green function (SGF), which is a central quantity for applications of the GF method to surfaces, overlayers and interfaces [7].

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One group of methods for the determination of the SGF starts from the infinite crystal and introduces a surface-localised ‘pseudopotential’ which decouples the sample into two parts by compensating for the undesired hoppings [8, 9] or by surrounding the fragment by an infinitely high barrier [5, 10]. The latter approach is advantageous because the perturbation is explicitly symmetrical and extends only over one principal layer [10]. A common feature of these approaches is the determination of the SGF via integration of certain expressions containing the bulk GF over the surface-normal component  $k_{\perp}$  of the  $\mathbf{k}$ -vector in the Brillouin zone. The TB LMTO method has been applied to the evaluation of the SGF using both methods in recent papers [9, 11]. Here we present a new approach, which allows us to evaluate the SGF directly, avoiding  $k_{\perp}$  integration and bulk resolvent. The method has been proposed by us recently [12], and here we implement it practically.

The LMTO Hamiltonian in the orthogonal representation [6] is

$$H_{RL,R'L'} = C_{RL} \delta_{RR'} \delta_{LL'} + \Delta_{RL}^{1/2} [\mathbf{S}^0 (1 - \boldsymbol{\gamma} \mathbf{S}^0)^{-1}]_{RL,R'L'} \Delta_{R'L'}^{1/2} \tag{1}$$

where  $\mathbf{X} = \mathbf{C}, \Delta, \boldsymbol{\gamma}$  are the potential parameter matrices, diagonal with respect to the site ( $\mathbf{R}$ ) and orbital ( $L = l, m$ ) indices and describing the scattering properties of atoms. The lattice structure enters the problem via the structure constant matrix  $\mathbf{S}^0$ . The Hamiltonian acts in the space spanned by the projector

$$\Pi = \sum_{i=0} \Pi_i \quad \Pi_i = \sum_{\mathbf{R}_{\parallel}} \sum_{\{R_{\perp}\}_i} \sum_L |\chi_{RL}\rangle \langle \chi_{RL}| \tag{2}$$

Here,  $|\chi_{RL}\rangle$  is the muffin-tin orbital (MTO),  $\mathbf{R} = (\mathbf{R}_{\parallel}, R_{\perp})$  and  $\{R_{\perp}\}_i$  denote the group of atomic layers forming the  $i$ th principal layer.

We wish to determine the quantity  $G_{00}(z) = \Pi_0 G(z) \Pi_0$ ,  $G(z) = (z - H)^{-1}$ . To this end we change from the original MTO representation (1) to the most-localised representation [11, 12]. For  $G(z)$  we obtain

$$\begin{aligned} G_{RL,R'L'}(z) &= \lambda_{RL}^{\beta}(z) \delta_{RR'} \delta_{LL'} + \mu_{RL}^{\beta}(z) g_{RL,R'L'}^{\beta}(z) \mu_{R'L'}^{\beta}(z) \\ g_{RL,R'L'}^{\beta}(z) &= \{[P^{\beta}(z) - S^{\beta}]^{-1}\}_{RL,R'L'} \\ S_{RL,R'L'}^{\beta} &= [S^0 (1 - \beta S^0)^{-1}]_{RL,R'L'} \\ \lambda_{RL}^{\beta}(z) &= \Delta_{RL}^{-1/2} (\gamma_{RL} - \beta_{RL}) \mu_{RL}^{\beta}(z) \quad \mu_{RL}^{\beta}(z) = (\dot{P}_{RL}^{\beta}(z))^{1/2} \\ P_{RL}^{\beta}(z) &= (z - C_{RL}) / [\Delta_{RL} + (\gamma_{RL} - \beta_{RL})(z - C_{RL})]. \end{aligned} \tag{3}$$

The quantities  $\beta$  and  $P^{\beta}(z)$ , which are diagonal with respect to the indices  $\mathbf{R}$  and  $L$ , characterise the most-localised LMTO representation and the potential function; the quantity  $\dot{P}^{\beta}(z)$  denotes the energy derivative of  $P^{\beta}(z)$ . The most-localised structure constant matrix  $\mathbf{S}^{\beta}$  has the shortest possible spatial extent [6]. The problem is reduced to the evaluation of  $g_{00}^{\beta}(z) = \Pi_0 g^{\beta}(z) \Pi_0$ , for which we obtain the exact equation using a simple idea; we add a principal layer of bulk atoms to the semi-infinite crystal in such a way that we recover the same semi-infinite crystal. After the Bloch transformation for sites of the principal layers has been performed, the equation reads [12]

$$g_{00}^{\beta}(z, \mathbf{k}_{\parallel}) = [P_{00}^{\beta}(z) - S_{00}^{\beta}(\mathbf{k}_{\parallel}) - S_{01}^{\beta}(\mathbf{k}_{\parallel}) g_{00}^{\beta}(z, \mathbf{k}_{\parallel}) S_{10}^{\beta}(\mathbf{k}_{\parallel})]^{-1} \tag{4}$$

In this expression,  $P_{00}^{\beta}(z) = \Pi_0 P^{\beta}(z) \Pi_0$ ,  $S_{00}^{\beta} = \Pi_0 S^{\beta} \Pi_0$ ,  $S_{01}^{\beta} = \Pi_0 S^{\beta} \Pi_1$  and  $S_{10}^{\beta} = (S_{01}^{\beta})^+$ . Note that, for a perfect crystal,  $P_{ii}^{\beta}(z) = P_{00}^{\beta}(z)$ ,  $S_{i,i+1} = S_{01}$ , etc. The equation can be derived using the partitioning technique developed for surface-related

problems in [10, 13]. Equation (4) is exact, can be solved easily by iterations and conserves the Herglotz property of  $g_{00}(z)$ . We note that equation (4) is formally similar to the self-consistent equation for the transfer matrix appearing in the transfer matrix method of [14]. For an s-cubium model, equation (4) is reduced to the quadratic equation whose solution, when substituted back into equation (3), gives the well known result obtained first in [8]. The equation similar to (4) could be derived also directly in the orthogonal LMTO representation in which the Hamiltonian (1) is written. The transformation (3) to the most-localised LMTO representation has, however, great practical importance in reducing the dimensionality of the problem owing to the above-mentioned shortest possible spatial extent of the structure constant  $\mathbf{S}^\beta$  (e.g. only its first-nearest neighbours are sufficient for the FCC lattice [6]).

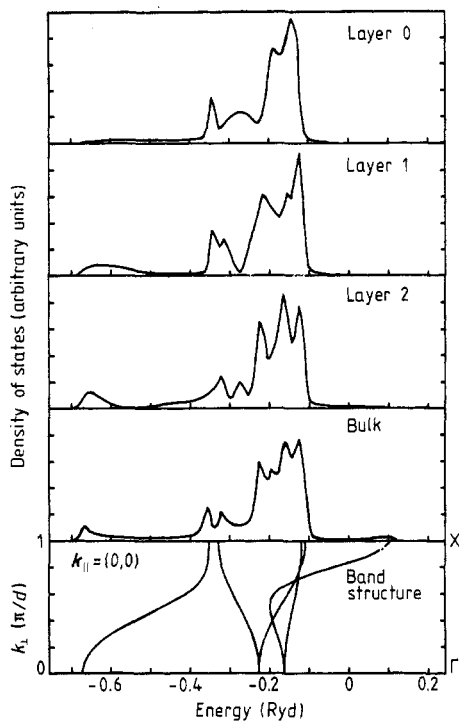
We note that equation (4) can be obtained by letting the potential function  $P^\beta(z)$  go to infinity within the principal layer surrounding the sample. This is less restrictive than a hard-wall potential used in conventional TB approaches. As discussed in [11], it is simple to go beyond this approximation for a free surface by coupling to it a few layers or even the semi-infinite crystal with potential parameters corresponding to a flat potential [6]. This is equivalent to a certain surface barrier in the vacuum. Conveniently, added atoms can form a periodic continuation of the sample, so that we have got an ideal infinite crystal with the bulk structure constant matrix  $\mathbf{S}^\beta$  and an abrupt change in the potential functions  $P^\beta(z)$  at the sample boundary. In practice, a single layer of added atoms has almost the same effect as a full added space. The corresponding expression for this new SGF, which we denote by  $\tilde{g}_{00}^\beta(z, \mathbf{k}_\parallel)$ , is

$$\begin{aligned} \tilde{g}_{00}^\beta(z, \mathbf{k}_\parallel) = & \{P_0^\beta(z) - S_{00}^\beta(\mathbf{k}_\parallel) - S_{01}^\beta(\mathbf{k}_\parallel)g_{00}^\beta(z, \mathbf{k}_\parallel)S_{10}^\beta(\mathbf{k}_\parallel) \\ & - S_{10}^\beta(\mathbf{k}_\parallel)[P_1^\beta(z) - S_{00}^\beta(\mathbf{k}_\parallel)]^{-1}S_{01}^\beta(\mathbf{k}_\parallel)\}^{-1}. \end{aligned} \quad (5)$$

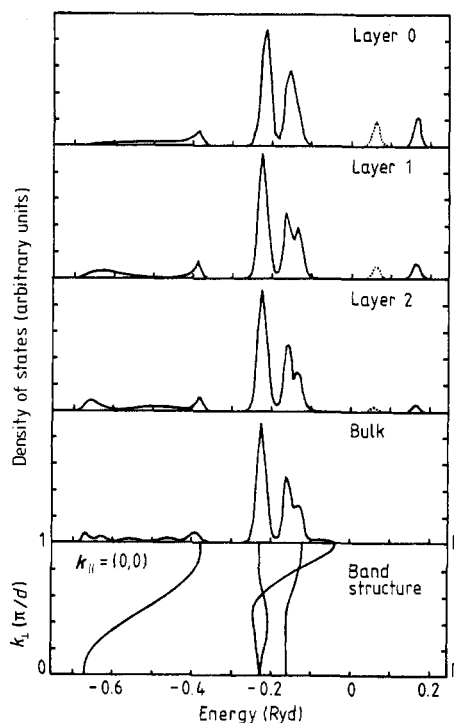
This equation can be again obtained by the partitioning technique of [13];  $P_0^\beta(z)$  denotes the vacuum potential function, and  $g_{00}^\beta(z, \mathbf{k}_\parallel)$  is the SGF defined in equation (4). Note that  $\tilde{g}_{00}^\beta$  is simply the subsurface GF for a system consisting of an overlayer of added atoms on the semi-infinite substrate. The other subsurface elements of  $g^\beta(z)$ , given by  $g_{ii}^\beta(z) = \Pi_i g^\beta(z) \Pi_i$ , can be found similarly [13].

We apply our formalism to the evaluation of electronic structure of FCC Cu(001) and Cu(111) surfaces, using the  $sp^3d^5$  basis set and the self-consistent bulk potential parameters, and taking into account nearest-neighbour interactions to determine the elements of  $\mathbf{S}^\beta(\mathbf{k}_\parallel)$  [6]. A principal layer consists of a single atomic layer in both cases. We solve equation (4) for  $(g_{00}^\beta)^{-1}$  rather than for  $g_{00}^\beta$ , shift the energy into the complex plane and perform an analytical deconvolution back onto the real axis at the end of calculations. The use of  $[g_{00}^\beta(z, \mathbf{k}_\parallel)]^{-1}$  as an input value for  $[g_{00}^\beta(z + \delta z, \mathbf{k}_\parallel)]^{-1}$  speeds up the calculations appreciably.

The layer- and  $\mathbf{k}_\parallel$ -resolved densities of states, denoted by  $\rho(E, \mathbf{k}_\parallel) \propto \sum_L \dot{P}_L^\beta(E) \text{Im}[g_{00}^\beta(E + i0, \mathbf{k}_\parallel)]_{L,L}$  are plotted in figures 1 and 2. We note the overall good agreement of our results with those obtained by the layer KKR method for the same systems [15]. The bulk-derived peaks coincide with corresponding bulk bands; the peaks damped into the bulk are surface states. The layer of added atoms representing a surface barrier, lying at  $\Phi(111) \approx 5$  eV ( $\Phi(111)$  is the work function) above the bulk Fermi level, shifts the surface state on Cu(111) towards the Fermi level, leaving the bulk states essentially unchanged (figure 2). The lowering of the above surface barrier by 2.5 eV shifts the surface state onto the Fermi level in accordance with experiment [16].



**Figure 1.** Layer- and  $k_{\perp}$ -resolved densities of states for the FCC Cu(001) surface ( $k_{\parallel} = (0, 0)$ ). The Fermi level is the energy zero. The bottom row gives the corresponding bulk band structure along the surface normal, which is  $\Gamma$ -X. The inter-layer spacing is  $d$ .



**Figure 2.** Layer- and  $k_{\perp}$ -resolved densities of states for the FCC Cu(111) surface ( $k_{\parallel} = (0, 0)$ ). The Fermi level is the energy zero. The bottom row gives the corresponding bulk band structure along the surface normal, which is  $\Gamma$ -L. The inter-layer spacing is  $d$ . The changes after adding one layer of additional atoms are indicated by a broken line.

We have presented a new method for determination of the SGF, which is physically transparent, reliable and inexpensive concerning computer time, memory and programming requirements. It yields a solution for an ideal semi-infinite solid to which non-ideal layers can be added in order to determine the electronic structure of more complex systems, such as disordered or partially covering overlayers on the perfect substrate, with possible changes in inter-layer spacings.

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