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Theory of surface electronic states in metallic superlattices

B. Djafari-Rouhani* and L. Dobrzynski
Laboratoire d'Etude des Surfaces et Interfaces, Associé au Centre National de la Recherche Scientifique,
Faculté Libre des Sciences, 13 rue de Toul, F-59046 Lille Cédex, France

P. Masri†
Laboratoire d'Etude des Surfaces, Interfaces et Composants, E.R.A. N1022 Associé au Centre National de la Recherche Scientifique,
U.S.T.L., Place E. Bataillon, F-34060, Montpellier Cédex, France

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We report the existence of surface-localized electronic states for a superlattice consisting of alternating slabs (parallel to the surface) of two different metals. The superlattice has a larger periodicity in the direction perpendicular to the slabs and therefore many electronic branches in the folded Brillouin zone. In the gaps existing between these bulk branches appear the surface-localized modes. The theory is developed on an *s*-band model of a simple-cubic crystal. The simplicity of this model allows one to obtain in closed form the bulk and (001) surface Green's functions for this superlattice. The analytic knowledge of these functions enables us to study easily all the bulk and surface electronic properties of this metallic superlattice, which otherwise would require huge numerical calculations. We give here the analytic expression we obtained for the folded bulk electronic bands and also the expression that gives the surface electronic states. A few figures for specific cases illustrate these results.

I. INTRODUCTION

A superlattice consists of alternating thin layers of two deposited compounds. In particular, in recent years there has been great interest in the fabrication and measurement of properties of bimetallic superlattices[1] such as Nb-Cu, Mo-Ni, Ta-Mo, Nb-Ta, Nb-Al, etc. Model calculations of the electronic structure and of the local electron densities of states in bimetallic superlattices have also appeared recently.[2-4]

In this paper, we report, for the first time to our knowledge, the existence of localized electronic states at the free surface of a bimetallic superlattice. The surface is taken to be parallel to the interfaces between the two metals from which the superlattice is built. Such systems have a new periodicity in the direction x_3 perpendicular to the interfaces. This produces a folding of the electronic bands in a reduced Brillouin zone, and the opening of new gaps in which surface states may exist.

Previously, we presented a theory of surface phonons in superlattices[5] based on a well-known phonon model of a simple-cubic crystal, for which the Green's functions can be worked out in closed form. The mathematical similarities of this model[6] with a corresponding classical tight-binding model for the study of electronic properties of surfaces[7,8] are well known.

Each unit cell of this model contains a single nondegenerate Wannier orbital. The electrons hop from site to site via a nearest-neighbor overlap integral of strength γ_i. Thus, the bulk-electronic-energy band consists of a single band of tight-binding form. The superlattice under study here is built up from, alternately, L_1 and L_2 (001) atomic planes of two such simple-cubic lattices having the same lattice parameter, a_0, and characterized by the overlap integrals (γ_1 and γ_2) and occupation numbers (Z_1 and Z_2) of their respective electronic bands. These alternating thin layers are bound together by an overlap integral $\tilde{\gamma}$ between the interface atoms. This simple model enables one to obtain, in closed form, the bulk and (001) surface Green's function for this superlattice. Only the diagonal element of the bulk Green's function was given before, through a different procedure, and it was used for the calculation of local electron densities of states in infinite superlattices.[3]

We obtain here for the first time—and in closed form—a simple analytic expression for the folded bulk electronic bands of this superlattice, taking into account the effect of self-consistency at the interfaces. Then we show the existence of localized electronic states at (001) surfaces of this superlattice, discussing the effect of the physical parameters defined above. The surface states also depend on the kind of layer (1 or 2) and its thickness near the (001) free surface.

In Sec. II we obtain the bulk and surface Green's function for the superlattice defined above, and in Sec. III these results are used for the calculation of the bulk and surface electronic bands.

II. BULK AND SURFACE ELECTRONIC GREEN'S FUNCTION FOR A SUPERLATTICE

A. Tight-binding model

The *d* bands of transition metals are well described by the tight-binding model. The *d* states of the free atom give rise to a complex array of five bands of *d* symmetry in the crystalline state, and these five bands may contain at most ten electrons. In this paper we study a much simpler model which includes only a single *s* band of tight-binding character. We assume each energy level is fivefold degenerate in order to make a crude model of the *d* bands of transition metals. The resulting set of bands is then filled by ten electrons.

The crystal will be taken to be simple cubic. The tight-binding band described above will be generated from a model which assumes all hopping integrals to be zero, except for nearest-neighbor sites. The Hamiltonian of the system is

$$H_0=E_1\sum_{l}C^\dagger(l)C(l)-\gamma_1\sum_{l,\delta}C^\dagger(l+\delta)C(l)\ , \tag{1}$$

where E_1 is the energy of the atomic level and $C^\dagger(l)$ and $C(l)$ are, respectively, the creation and the annihilation operators for the site l. In this Hamiltonian, l ranges over all sites in the crystal, and δ ranges over the sites which form the nearest neighbors of l.

In the infinitely extended crystal, the energy bands are described by

$$E(\mathbf{k})=E_1-2\gamma_1[\cos(k_1a_0)+\cos(k_2a_0)+\cos(k_3a_0)]\ , \tag{2}$$

where a_0 is the lattice parameter and $\mathbf{k}$ is the wave vector.

This model, while highly oversimplified, can account for trends present in the physical properties of transition metals. Values were extracted[7] for γ_1 by comparing measured values of the cohesion energy with those predicted by this model: $\gamma_1\simeq\frac{5}{12}$ eV for the 3*d* series, $\frac{1}{2}$ eV for the 4*d* series, and $\frac{7}{12}$ eV for the 5*d* series. For our purposes, the virtue of this admittedly simple model is that we can carry the calculation by analytic methods.

B. Green's function for a film

For the semi-infinite crystal with Hamiltonian $\underline{H}$, the electronic properties can be discussed by employing the Green's function $G^{(s)}(l,l';E)$ defined by

$$G^{(s)}(l,l';E)=\langle l\,|\,[(E+i\epsilon)\underline{I}-\underline{H}]^{-1}\,|\,l'\rangle\ , \tag{3}$$

where by this equation we mean the matrix element of the indicated operator between the Wannier functions associated with the two states l and l'. Particularly convenient is the function $G(\mathbf{k}_{\|};l_3,l_3';E)$ related to $G(l,l';E)$ by a partial Fourier transform,

$$G^{(s)}(l,l';E)=\frac{1}{N_s}\sum_{\mathbf{k}_{\|}}G^{(s)}(\mathbf{k}_{\|};l_3,l_3';E)e^{i\mathbf{k}_{\|}\cdot(l_{\|}-l'_{\|})a_0}\ , \tag{4}$$

where N_s is the number of atoms in the surface of the crystal, $\mathbf{k}_{\|}$ is a two-dimensional wave vector parallel to the surface, and the sum over $\mathbf{k}_{\|}$ covers the two-dimensional Brillouin zone. This surface Green's function may be readily obtained in closed analytic form for the present model,[5-7]

$$G^{(s)}(k_{\|};l_3,l_3';E)=\frac{1}{\gamma_1}\frac{1}{t_1^2-1}(t_1^{|l_3-l_3'|+1}-t_1^{l_3+l_3'+1})\ ,\qquad l_3,l_3'\geq 1 \tag{5}$$

where

$$t_1=\begin{cases}\zeta_1-(\zeta_1^2-1)^{1/2}, & \zeta_1>1\\ \zeta_1+i(1-\zeta_1^2)^{1/2}, & -1<\zeta_1<+1\\ \zeta_1+(\zeta_1^2-1)^{1/2}, & \zeta_1<-1\end{cases} \tag{6a}$$

and where

$$\zeta_1=\frac{E_1-E}{2\gamma_1}-\cos(k_1a_0)-\cos(k_2a_0)\ . \tag{6b}$$

Let us now create a film by removing all overlap integrals between the atoms situated in the $l_3=L_1$ and L_1+1 planes of the above semi-infinite crystal. The corresponding Green's function $\underline{U}_1$ can be easily worked out with the help of the Dyson equation and the above surface Green's function. We find

$$U_1(k_{\|};l_3,l_3';E)=\frac{1}{\gamma_1}\frac{1}{t_1^2-1}\left[t_1^{|l_3-l_3'|+1}-t_1^{l_3+l_3'+1}+t_1^{2L_1+3}\frac{(t_1^{l_3}-t_1^{-l_3})(t_1^{l_3'}-t_1^{-l_3'})}{t_1^{2L_1+2}-1}\right]\ , \tag{7a}$$

where

$$1\leq l_3,l_3'\leq L_1\ . \tag{7b}$$

Let us remark that the above surface and film Green's functions do not take into account any self-consistent rearrangement of the electrons near the free surfaces. We will return to this question later.

In the same manner we construct another film of L_2 (001) layers. In order to distinguish one of these two films from the other, we will use an index $K=1$ or 2. The corresponding Green's function $\underline{U}_2$ can be obtained from Eqs. (7) and (6) by changing all indices 1 to 2. Let us also remark that, for this $K=2$ film, one has $1\leq l_3,l_3'\leq L_2$.

C. Bulk Green's function for the superlattice

Let us now set this $K=2$ film in epitaxy with the $K=1$ film, but without any binding between the interface atoms. We characterize this uncoupled double film by another integer n. An infinite repetition $-\infty<n<+\infty$ without coupling of this double film gives us our starting point for our model of a superlattice. One easily sees that the corresponding Green's function is

$$U(\mathbf{k}_{\|};n,K,l_3;n',K',l_3';E)=\delta_{nn'}\delta_{KK'}U_K(\mathbf{k}_{\|};l_3,l_3';E)\ . \tag{8}$$

We now couple all of these alternating $K=1$ and $K=2$ films together in order to obtain an infinite superlattice via the following procedure.[9]

(1) We set the uncoupled films 1 and 2, respectively, to potentials V_1 and V_2 in order to align the Fermi energies in all of the slabs. This only translates the origins E_1 and E_2 of the energies, and in what follows we include these potentials V_1 and V_2 in E_1 and E_2. We will explain later how we determine E_1 and E_2 as functions of the occupa-

tions of the occupations Z_1 and Z_2 of each band and of its shape in order to align the Fermi energies.

(2) We then couple all of the films by using a hopping integral $\tilde{\gamma}$ between the corresponding interface atoms. In order to satisfy self-consistency we introduce the self-consistent intra-atomic potentials Δ_1 and Δ_2 to the surface atoms. The matrix elements of this perturbation potential that couple all of the alternating films together are then

$$\begin{aligned}\delta V(nKl_3;n'K'l_3') = &-\tilde{\gamma}\sum_m(\delta_{nm}\delta_{K2}\delta_{l_3L_2}\delta_{n',n+1}\delta_{K'1}\delta_{l_3'1}+\delta_{n,m+1}\delta_{K1}\delta_{l_31}\delta_{n'm}\delta_{K'2}\delta_{l_3'L_2})\\ &-\tilde{\gamma}\sum_m(\delta_{nm}\delta_{K1}\delta_{l_3L_1}\delta_{n'm}\delta_{K'2}\delta_{l_3'1}+\delta_{nm}\delta_{K2}\delta_{l_31}\delta_{n'm}\delta_{K'1}\delta_{l_3'L_1})\\ &-\Delta_2\sum_m\delta_{nm}\delta_{K2}\delta_{n'm}\delta_{K'2}(\delta_{l_3L_2}\delta_{l_3'L_2}+\delta_{l_31}\delta_{l_3'1})\\ &-\Delta_1\sum_m\delta_{K1}\delta_{K'1}(\delta_{n,m+1}\delta_{l_31}\delta_{n',m+1}\delta_{l_3'1}+\delta_{nm}\delta_{l_3L_1}\delta_{n'm}\delta_{l_3'L_1})\ .\end{aligned} \tag{9}$$

We can now work out in closed form the elements $D(\mathbf{k}_{\|};n,K,l_3;n',K',l_3';E)$ of the Green's function $\underline{D}$ of this infinite superlattice, with the help of the Dyson equation

$$\underline{D}=\underline{U}+\underline{U}\delta\underline{V}\,\underline{D}\ . \tag{10}$$

In what follows, and for simplicity, we will no longer write explicitly the dependence on $\mathbf{k}_{\|}$ and E in the elements of $\underline{U}$ and $\underline{D}$.

After some algebra (see the Appendix for more details) we can obtain the elements of $\underline{D}$ as functions of the q_K defined in terms of the t_K of Eq. (6a) by

$$t_K=e^{q_K},\quad K=1\text{ or }2 \tag{11}$$

and a new variable t defined by

$$t=\begin{cases}\eta-(\eta^2-1)^{1/2}, & \eta>1\\ \eta+i(1-\eta^2)^{1/2}, & -1<\eta<1\\ \eta+(\eta^2-1)^{1/2}, & \eta<-1\end{cases} \tag{12}$$

with

$$\begin{aligned}2\eta=&-2\frac{\sinh(q_1L_1)\sinh(q_2L_2)}{\sinh q_1\sinh q_2}\left[1-\frac{\Delta_1}{\gamma_1}\frac{\sinh[q_1(L_1-1)]}{\sinh(q_1L_1)}\right]\left[1-\frac{\Delta_2}{\gamma_2}\frac{\sinh[q_2(L_2-1)]}{\sinh(q_2L_2)}\right]\\ &+\frac{\gamma_1\gamma_2}{\tilde{\gamma}^2}\frac{\sinh[q_1(L_1+1)]\sinh[q_2(L_2+1)]}{\sinh q_1\sinh q_2}\left[1-2\frac{\Delta_1}{\gamma_1}\frac{\sinh(q_1L_1)}{\sinh[q_1(L_1+1)]}+\frac{\Delta_1^2}{\gamma_1^2}\frac{\sinh[q_1(L_1-1)]}{\sinh[q_1(L_1+1)]}\right]\\ &\times\left[1-2\frac{\Delta_2}{\gamma_2}\frac{\sinh(q_2L_2)}{\sinh[q_2(L_2+1)]}+\frac{\Delta_2^2}{\gamma_2^2}\frac{\sinh[q_2(L_2-1)]}{\sinh[q_2(L_2+1)]}\right]+\frac{\tilde{\gamma}^2}{\gamma_1\gamma_2}\frac{\sinh[q_1(L_1-1)]\sinh[q_2(L_2-1)]}{\sinh q_1\sinh q_2}\ .\end{aligned} \tag{13}$$

This expression is directly related to the bulk electronic bands of our superlattice. We will show this in the next section and study the effect of the self-consistent interface potentials Δ_1 and Δ_2 on the position of these bands. We will see that the effect of Δ_1 and Δ_2 is small, and that the bulk bands of superlattice can be described with a good precision when taking Δ_1 and Δ_2 to be zero in the above expression. With this approximation, η has the following simple form:

$$2\eta=-2\frac{\sinh(q_1L_1)\sinh(q_2L_2)}{\sinh q_1\sinh q_2}+\frac{\gamma_1\gamma_2}{\tilde{\gamma}^2}\frac{\sinh[q_1(L_1+1)]\sinh[q_2(L_2+1)]}{\sinh q_1\sinh q_2}+\frac{\tilde{\gamma}^2}{\gamma_1\gamma_2}\frac{\sinh[q_1(L_1-1)]\sinh[q_2(L_2-1)]}{\sinh q_1\sinh q_2}\ , \tag{14}$$

and the elements of the superlattice Green's functions will be given here within this approximation.

First, we give the elements of $\underline{D}$ between different $K=1$ and $K=2$ films:

$$D(n1l;n'2l')=\frac{1}{\sinh q_1\sinh q_2}\frac{t}{t^2-1}\left[\left[\frac{1}{\tilde{\gamma}}\sinh[q_1(L_1+1-l_3)]\sinh(q_2l'_3)-\frac{\tilde{\gamma}}{\gamma_1\gamma_2}\sinh[q_1(L_1-l_3)]\sinh[q_2(l'_3-1)]\right]t^{|n-n'-1|}+\left[\frac{1}{\tilde{\gamma}}\sinh[q_2(L_2+1-l'_3)]\sinh(q_1l_3)-\frac{\tilde{\gamma}}{\gamma_1\gamma_2}\sinh[q_2(L_2-l'_3)]\sinh[q_1(l_3-1)]\right]t^{|n-n'|}\right] \tag{15}$$

and

$$D(n2l;n'1l')=\frac{1}{\sinh q_1\sinh q_2}\frac{t}{t^2-1}\times\left[\left[\frac{1}{\tilde{\gamma}}\sinh[q_2(L_2-l_3+1)]\sinh(q_1l'_3)-\frac{\tilde{\gamma}}{\gamma_1\gamma_2}\sinh[q_1(l'_3-1)]\sinh[q_2(L_2-l_3)]\right]t^{|n-n'|}+\left[\frac{1}{\tilde{\gamma}}\sinh(q_2l_3)\sinh[q_1(L_1-l'_3+1)]-\frac{\tilde{\gamma}}{\gamma_1\gamma_2}\sinh[q_1(L_1-l'_3)]\sinh[q_2(l_3-1)]\right]t^{|n-n'+1|}\right]. \tag{16}$$

The elements of $\underline{D}$ between the same K films are

$$D(n1l_3;n'1l'_3)=\delta_{nn'}U_1(l_3l'_3)-\tilde{\gamma}[U_1(l_31)D(n-1,2,L_2;n'1l'_3)+U_1(l_3L_1)D(n21;n'1l'_3)] \tag{17}$$

and

$$D(n2l_3;n'2l'_3)=\delta_{nn'}U_2(l_3l'_3)-\tilde{\gamma}[U_2(l_3L_2)D(n+1,1,1;n'2l'_3)+U_2(l_31)D(n1L_1;n'2l'_3)]\ , \tag{18}$$

where

$$U_K(l_3l'_3)=\frac{1}{2\gamma_K}\frac{\cosh[q_K(L_K+1-l_3-l'_3)]-\cosh[q_K(L_K+1-|l_3-l'_3|)]}{\sinh q_K\sinh[q_K(L_K+1)]}\ , \tag{19}$$

$$U_K(l_31)=-\frac{1}{\gamma_K}\frac{\sinh[q_K(L_K+1-l_3)]}{\sinh[q_K(L_K+1)]}\ , \tag{20}$$

and

$$U_K(l_3L_K)=-\frac{1}{\gamma_K}\frac{\sinh(q_Kl_3)}{\sinh[q_K(L_K+1)]}\ . \tag{21}$$

Only the diagonal elements $D(nKl;nKl)$ of this Green's function were given before[3] in a different form. These authors[3] first coupled together two different films $K=1$ and $K=2$ and then constructed out of this bifilm the superlattice. The method of Menon and Arnold[3] introduces in the denominator of the superlattice Green's function the poles of the bifilm, which, of course, are no longer good poles for the superlattice, and therefore they must also appear in the numerator of their Green's function. This is the main reason why a direct comparison between the $D(nKl;nKl)$ of Menon and Arnold and ours is not easy. Let us note also that in both their way and our way of deriving the superlattice Green's function, in the denominator one has the poles of the two single films $K=1$ and $K=2$ (given by $\sinh[q_K(L_K+1)]$), which must also appear in the numerator of the superlattice Green's function. In Eqs. (15) and (16) we divided out these common factors appearing in the numerator and denominator of the nondiagonal elements of $\underline{D}$. In the elements of $D(nKl_3;n'Kl'_3)$ given by Eqs. (17) and (18), we left one of these common factors, namely $\sinh[q_K(L_K+1)]$, in the numerator and one in the denominator, as these enable us to write these results in a more compact form.

D. Surface Green's function for the superlattice

We will consider here two different cases, depending on the thickness of the last film near the free surface.

1. Surface film with same width as corresponding bulk films

We create two free surfaces by equating to zero all overlap integrals $\tilde{\gamma}$ between atoms in the plane

$(n=0, K=2, l_3=L_2)$ and atoms in the plane $(n=1, K=1, l_3=1)$. The corresponding perturbation to the potential is

$$\delta V^{(s)}(nKl_3;n'K'l'_3)=\tilde{\gamma}(\delta_{n0}\delta_{K2}\delta_{l_3L_2}\delta_{n'1}\delta_{K'1}\delta_{l'_31}+\delta_{n1}\delta_{K1}\delta_{l_31}\delta_{n'0}\delta_{K'2}\delta_{l'_3L_2}) \; . \tag{22}$$

Let us call $\underline{G}$ the Green's function of these two semi-infinite superlattices. Its elements can be obtained with the help of the Dyson equation and are, for n and $n'\geq 1$,

$$G(nKl_3;n'K'l'_3)=D(nKl_3;n'K'l'_3)+\tilde{\gamma}\frac{D(nKl_3;02L_2)D(111;n'K'l'_3)}{1-\tilde{\gamma}D(111;02L_2)} \; , \tag{23}$$

and, in particular,

$$G(111;111)=\frac{D(111;111)}{1-\tilde{\gamma}D(111;02L_2)} \; , \tag{24}$$

where $D(111;111)$ and $D(111;02L_2)$ can be obtained with the help of Eqs. (17) and (15) in the following form:

$$D(111;111)=\frac{1}{\gamma_1}\frac{t}{t^2-1}\frac{1}{\sinh q_1\sinh q_2}\left[-\sinh[q_1(L_1-1)]\sinh(q_2L_2)+\frac{\gamma_1\gamma_2}{\tilde{\gamma}^2}\sinh(q_1L_1)\sinh[q_2(L_2+1)]\right] \tag{25}$$

and

$$D(111;02L_2)=\frac{t}{t^2-1}\frac{1}{\sinh q_1\sinh q_2}\left[\frac{1}{\tilde{\gamma}}\sinh(q_1L_1)\sinh(q_2L_2)-\frac{\tilde{\gamma}}{\gamma_1\gamma_2}\sinh[q_1(L_1-1)]\sinh[q_2(L_2-1)]+\frac{t}{\tilde{\gamma}}\sinh q_1\sinh q_2\right] \; . \tag{26}$$

The poles of $G(111;111)$ given by Eq. (24) will enable us to study the appearance of localized surface states in the next section. Expression (24) does not include the effect of self-consistency on the surface atoms. We will see on the examples of the next section that these effects are small.

2. *Surface film with width smaller than corresponding bulk films*

We now create two other free surfaces by equating to zero all interactions between atoms in plane $(n=1, K=1, l_3=l_0<L_1)$ and in plane $(n=1, K=1, l_3=l_0+1)$.

As above, one obtains the surface Green's function, which, for n and $n'\geq 1$, $l_3\geq l_0+1$ when $n=1$, and $l'_3\geq l_0+1$ when $n'=1$, is

$$G(nKl_3;n'K'l'_3)=D(nKl_3;n'K'l'_3)+\frac{\gamma_1 D(nKl_3;1,1,l_0)D(1,1,l_0+1;n'K'l'_3)}{1-\gamma_1 D(1,1,l_0;1,1,l_0+1)} \; , \tag{27}$$

and, in particular,

$$G(1,1,l_0+1;1,1,l_0+1)=\frac{D(1,1,l_0+1;1,1,l_0+1)}{1-\gamma_1 D(1,1,l_0;1,1,l_0+1)} \; . \tag{28}$$

The elements of $\underline{D}$ can be calculated as above with the help of Eq. (17).

The poles of the above surface Green's function [Eqs. (24) and (28)] will enable us to study in the next section the corresponding surface states.

III. BULK AND SURFACE ELECTRONIC BANDS OF A METALLIC SUPERLATTICE

The bulk electronic bands of our metallic superlattice can be obtained from the knowledge of the bulk Green's functions. Let us first recall that for the infinite simple-cubic lattice described by Eqs. (1) and (2), the bulk electronic band given by Eq. (2) can also be presented as

$$\zeta_1=\cos(k_3a_0) \; , \tag{29}$$

where ζ_1 is given by Eq. (6b). In the same manner, for the infinite superlattice, we obtain the bulk electronic bands from

$$\eta=\cos[k_3(L_1+L_2)a_0] \; , \tag{30}$$

where η is given by Eqs. (13) and (14), respectively, with or without interface self-consistency, and because the periodicity in the direction x_3 is now given by $(L_1+L_2)a_0$, one has

$$-\pi<k_3(L_1+L_2)a_0<+\pi \; . \tag{31}$$

Because of this larger periodicity in the direction x_3, one has a folding of the electron dispersion curves in a reduced Brillouin zone and opening of new gaps between these folded dispersion curves. In these gaps, new surface states may appear; they can be found from the new poles in the surface Green's functions [Eqs. (24) and (28)] due to the creation of the free surface.

All of these expressions, which give us the bulk and surface electronic bands of the superlattice, are functions of the atomic levels E_1 and E_2. As explained in Sec. II C, we will translate these energies E_1 and E_2 in order to align the Fermi energy in all uncoupled films of the superlattice. The calculation of E_F-E_1 and E_F-E_2 requires the knowledge of the bulk density of states of each metal. These energies can, however, be obtained in closed form by approximating the local density of states of atom i by a rectangular band[10] of width W_i. The second moment of the density of states is within this approximation

$$\mu_{2i}=\frac{W_i^2}{12}=\sum_j \gamma_{ij}^2 , \tag{32}$$

where the γ_{ij} stands for the overlap integrals between the atom i and its first-nearest neighbors. Then one easily obtains

$$E_i-E_F=(\tfrac{1}{2}-Z_i)\left[12\sum_j \gamma_{ij}^2\right]^{1/2} , \tag{33}$$

where Z_i $(0\leq Z_i\leq 1)$ is the electronic occupation number for the atom i. For d electrons in a transition metal, Z_i is the number of d electrons divided by 10.

In what follows we will take E_F as the origin of the energies. Thus, once the occupation numbers Z_1 and Z_2 for the two metals are given, Eq. (33) gives us E_1 and E_2.

Following the procedure outlined in Sec. II C, we now couple all the films together by use of the overlap integral $\tilde{\gamma}$ and of the self-consistency potentials Δ_1 and Δ_2 on the interface atoms [Eq. (9)]. The self-consistency in metallic systems where the charge screening is short ranged is well realized by assuming the charge neutrality of each atom.[10] Then in the same way that we derived Eq. (2), one obtains, for the atoms of planes 1 and L_1 of the simple-cubic films 1,

$$E_1-\Delta_1-E_F=(\tfrac{1}{2}-Z_1)[12(5\gamma_1^2+\tilde{\gamma}^2)]^{1/2} , \tag{34}$$

and, for the atoms of planes $2\leq l_3\leq L_1-1$,

$$E_1-E_F=(\tfrac{1}{2}-Z_1)\gamma_1\sqrt{72} . \tag{35}$$

In the same way, one obtains the energies E_2 and $E_2-\Delta_2$ for the films 2.

For the surface atoms (having five rather than six first-nearest neighbors) of a semi-infinite superlattice, one can introduce self-consistency potentials Δ_s on the surface atoms. Δ_s is calculated from an expression similar to Eq. (34), with $\tilde{\gamma}=0$ and Δ_1 replaced by Δ_s. The surface Green's functions given by Eqs. (24) and (28) are also modified in a straightforward manner.

On the figures which follow we represent only the results for $\Delta_1=\Delta_2=\Delta_s=0$, as the effects of self-consistency were found to be small for these cases. However, we will discuss separately the effects of Δ_1 and Δ_2, and those of Δ_s, on the results.

The first five figures correspond to two-atomic-plane-thick films $(L_1=L_2=2)$, in order to avoid the complexity of too many bands. Figure 6 will show the effects due to greater values of L_1 and L_2. In all of these examples the interface-overlap integral $\tilde{\gamma}$ was taken to be equal to $(\gamma_1+\gamma_2)/2$.

First, we consider the case of half-filled bands, namely $Z_1=Z_2=0.5$, for which the self-consistency is automatically achieved.[7] Figure 1 displays the corresponding bulk bands and surface states for the metallic superlattice. In this example, the ratio $\gamma_1/\gamma_2=2$, greater than the order of magnitude given in Sec. II A, was chosen mostly for increased clarity of the figure as the gaps were smaller for $\gamma_1/\gamma_2=1.4$. However, for both values of γ_1/γ_2 above, we obtained the same number of surface states. This example represents, qualitatively, a superlattice made from one transition metal of the $3d$ series and the one from the $5d$ series. We remark that the surface states are very different depending on the nature and the number l_0 of atomic planes (here, 1 or 2) of the film 1 or 2 near the surface. One can also notice the symmetry of the bulk and surface bands with respect to the origin of the figure $(E=0$ and $S=0)$, where

$$S=\cos(k_1a_0)+\cos(k_2a_0) . \tag{36}$$

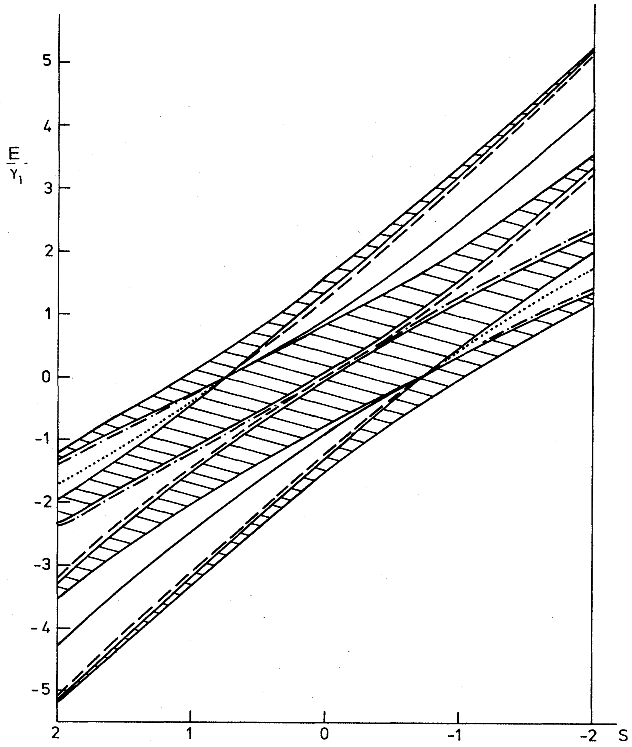

FIG. 1. Bulk and surface electronic states for a metallic superlattice made of films with $L_1=L_2=2$ atomic planes. The ratio between the overlap integrals is taken to be $\gamma_1/\gamma_2=2$ and the occupation numbers $Z_1=Z_2=\frac{1}{2}$; then, $E_1=E_2=0$. The origin in energy is taken at the Fermi energy E_F. The bands are drawn as functions of $S=\cos(k_1a_0)+\cos(k_2a_0)$. The hatched areas correspond to the bulk bands of the superlattice. The surface states are given, respectively, for the metal 1 at the surface with a number of planes $l_0=2$ (dashed line) or $l_0=1$ (solid line), and for the metal 2 at the surface with $l_0=2$ (dashed-dotted line) or $l_0=1$ (dotted line). The quantities presented on both axes are dimensionless.

Figure 2 represents a case for which the overlap integrals γ_1, γ_2, and $\tilde{\gamma}$ are equal (metals of the same transition series), but the occupation numbers Z_1 and Z_2 are

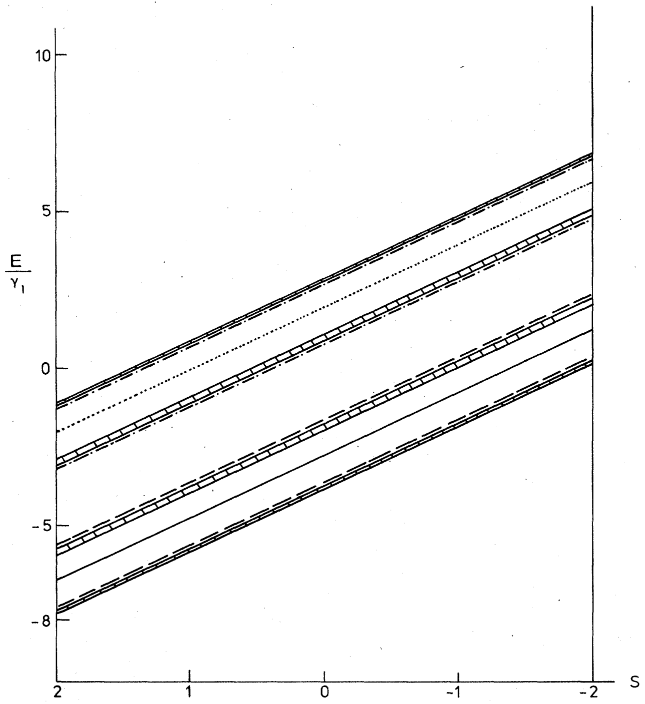

FIG. 2. Same as in Fig. 1, but with $L_1=L_2=2$, $\gamma_1=\gamma_2$, $Z_1=0.8$, and $Z_2=0.3$.

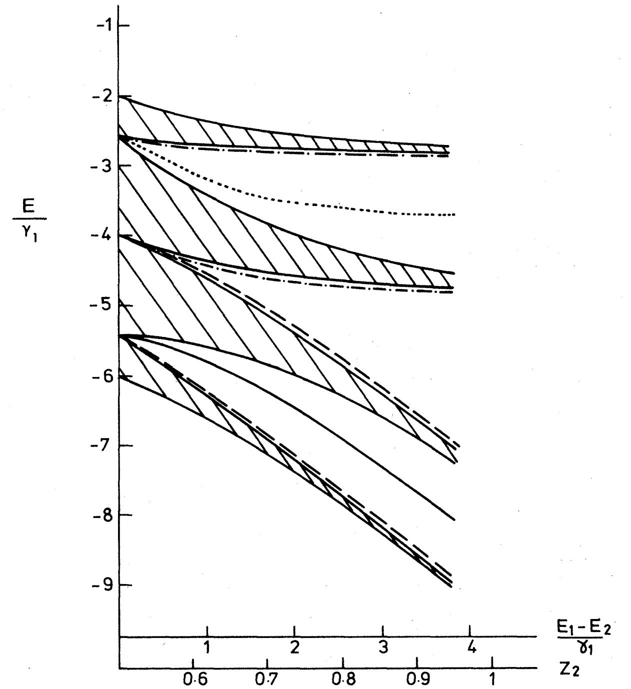

FIG. 3. Bulk and surface electronic bands of a metallic superlattice for $L_1=L_2=2$, $\gamma_1=\gamma_2$, and $Z_1=\frac{1}{2}$ as functions of E_2 or Z_2, at the point $k_1=k_2=0$ of the two-dimensional Brillouin zone. The lines representing the bulk and surface states have the same meanings as in Fig. 1.

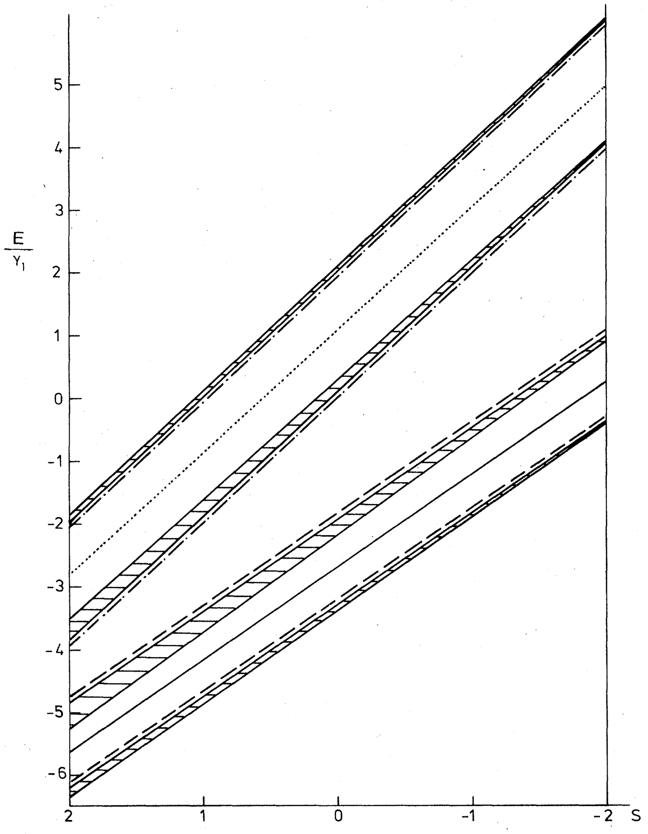

FIG. 4. Same as in Fig. 1 for a superlattice having qualitatively the parameters of the Nb-Cu system. These parameters are given in the text.

different, namely $Z_1=0.8$ and $Z_2=0.3$. This gives, with the help of Eq. (35), $E_1-E_F=-2.546\gamma_1$ and $E_2-E_F=1.697\gamma_1$. For this case, as $\gamma_1=\gamma_2=\tilde{\gamma}$, the interface self-consistency potentials Δ_1 and Δ_2 are zero, but the surface self-consistency potentials Δ_s differ from zero and slightly affect the position of the surface states given in Fig. 2 for $\Delta_s=0$. For film 1 near the surface, we found $\Delta_s\simeq-0.222\gamma_1$, and the effect of Δ_s is to increase the energies of the surface states, as well as for $l_0=2$ and 1, by an amount too small to be represented on the scale of this figure. For film 2 near the surface, we found $\Delta_s\simeq0.148\gamma_2$ and a small decrease of the energies of the surface states. These shifts of the surface states were found to be, at most, of the same order of magnitude as the values of Δ_s. We also notice in Fig. 2 the small width of the bulk bands; this is mostly due to the fact that the bulk bands of the two infinite metals are well separated in energy, because of the difference between E_1 and E_2. One can also remark that in this figure all bulk and surface dispersion curves are straight lines with a slope of 2. Indeed, for $\gamma_1=\gamma_2=\tilde{\gamma}$, ζ_1 and ζ_2 [Eq. (6b)] and then η [Eqs. (13) and (14)] are functions of the same parameter, $E/2\gamma_1+S$, as well as the superlattice Green's functions. Thus, the results given in Fig. 2 can be obtained by performing the calculation for only one value of S or (k_1,k_2).

Keeping in mind this property due to $\gamma_1=\gamma_2=\tilde{\gamma}$, we

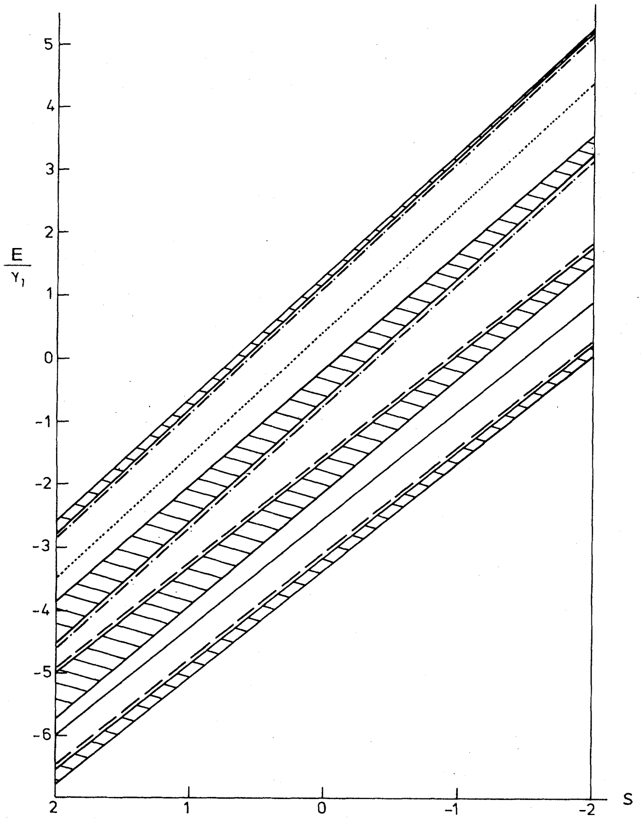

FIG. 5. Same as in Fig. 1 for a superlattice having qualitatively the parameters of the Mo-Ni system. These parameters are given in the text.

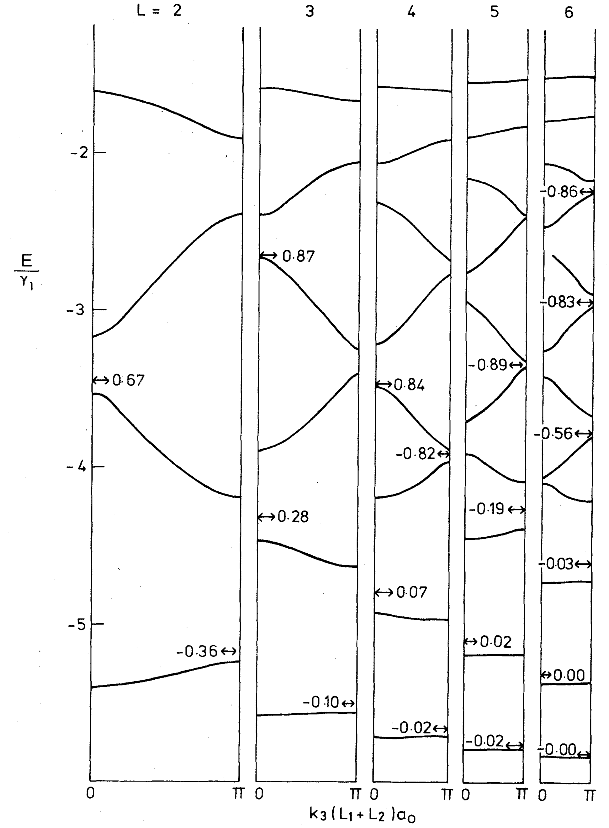

FIG. 6. Dispersion of the bulk bands in function of k_3, for several film widths, namely $L_1=L_2$ varies here from 2 to 6; $\gamma_1=1.4\gamma_2$, $Z_1=Z_2=\frac{1}{2}$ $(E_1=E_2=0)$, and $k_1=k_2=0$. The energies of the surface states are indicated by double-headed arrows (↔). The numbers near the position of the surface states give the decay factor t_s [Eq. (12)] of the corresponding wave function from one elementary cell $[(L_1+L_2)a_0]$ to another.

represented in Fig. 3 the bulk and surface states for $k_1=k_2=0$, as functions of E_1-E_2 (origin at $E_1=E_F$) and of the difference between the occupation numbers Z_1 and Z_2 (origin at $Z_1=\frac{1}{2}$). When $E_1=E_2$, the two metals are identical and we observe only a folding of the bulk bands within a smaller Brillouin zone, without any gaps. When E_2 becomes different of E_1, the bulk bands shift apart and surface modes appear within the gaps. We emphasize the result that when E_1-E_2 increases (the bulk bands of the two metals having a decreasing overlap in energy), the width of the bulk bands decreases and these bulk states become more and more localized within each film. The effects of self-consistency were neglected.

We also considered examples which can depict qualitatively two metallic superlattices already realized. Figure 4 was drawn for parameters corresponding to the order of magnitude of those of the Nb-Cu superlattice within the frame of the simple model studied here: $\gamma_{\mathrm{Nb}}=1.4\gamma_{\mathrm{Cu}}$, $Z_{\mathrm{Nb}}=0.4$, and $Z_{\mathrm{Cu}}=0.9$; this implies that $E_{\mathrm{Nb}}-E_F=0.849\gamma_{\mathrm{Nb}}$ and $E_{\mathrm{Cu}}-E_F\simeq-2.424\gamma_{\mathrm{Nb}}$. Figure 5 can, in the same manner, represent qualitatively the Mo-Ni superlattice, with $\gamma_{\mathrm{Mo}}=1.2\gamma_{\mathrm{Ni}}$, $Z_{\mathrm{Mo}}=0.5$, and $Z_{\mathrm{Ni}}=0.8$, implying that $E_{\mathrm{Mo}}-E_F=0$ and $E_{\mathrm{Ni}}-E_F=-2.121\gamma_1$. On these two figures the bulk and surface states are represented for $\Delta_1=\Delta_2=\Delta_s=0$. The values of these self-consistent potentials were found to be at the interface: $\Delta_{\mathrm{Nb}}=0.019\gamma_{\mathrm{Nb}}$, $\Delta_{\mathrm{Cu}}=0.122\gamma_{\mathrm{Cu}}$, and $\Delta_{\mathrm{Mo}}=0$, $\Delta_{\mathrm{Ni}}=0.044\gamma_{\mathrm{Ni}}$. Their effect is to decrease the energies of the surface states by an amount smaller than the values of Δ_1 and Δ_2 and one not noticeable on these figures.

Finally, in Fig. 6 we show the effect of an increase of the thickness of films 1 and 2 on the bulk and surface states. This study was done for $\gamma_1=1.4\gamma_2$ and $Z_1=Z_2=0.5$, implying that $E_1=E_2=E_F$, and by varying $L_1=L_2$ from 2 to 6. Letting $k_1=k_2=0$, we represent the dispersion of the bulk bands of the superlattice as a function of the wave vector k_3 perpendicular to the layers. The dispersion of the bulk bands of the superlattice is important in the energy regions for which the bulk bands of the two metals overlap; outside these regions the superlattice bands are almost flat. We indicated in Fig. 6, by double-headed arrows (↔), the energies of the surface states, for $k_1=k_2=0$, when a complete film 1 is near the surface $(l_0=L_1)$. The number appearing near the position of each surface state gives the value of the parameter t_s [value of t given by Eq. (12) for the surface state]. This number t_s is the decay factor of the Green's function [Eqs. (15)—(18)], and then also the decay factor of the wave function associated to the surface state, from one elementary cell $[(L_1+L_2)a_0]$ to the other. The surface state can be very localized near the surface (small t_s) or it can decay slowly inside the bulk (t_s close to 1) when it lies close to a bulk band in a narrow gap between two wide bulk bands.

IV. DISCUSSION

In this paper we obtained, for the first time, surface electronic states on a simple three-dimensional atomic model of a metallic superlattice. The simplicity of this model enables us to derive, in closed form, the bulk and surface Green's functions for this superlattice. From the poles of these Green's functions we obtained simple expressions for the bulk and surface electronic bands of this metallic superlattice. We also analyzed the case for which the width of the last surface film was smaller than that of the corresponding bulk films. A few specific examples illustrate these general results. Of course, the results given on these examples are qualitative, since real transition metals are not simple cubic, as in our model, and they have $5d$ electrons, s-d coupling, etc. However, some general trends can be expected to remain true for more realistic models. The bulk bands of a superlattice are expected to be almost nondispersive in energy regions, while the bulk bands of the two constitutive metals do not overlap. The existence of rather wide gaps between the bulk bands of a superlattice should also remain for more sophisticated models, as well as the existence of surface states (and even more general defect states) within these gaps.

ACKNOWLEDGMENTS

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APPENDIX: BULK GREEN'S FUNCTION FOR THE SUPERLATTICE

In this appendix we will show how one can obtain the bulk Green's function $\underline{D}$ of the metallic superlattice under study in this paper. We start with the Dyson equation (10) relating $\underline{D}$ to the Green's function $\underline{U}$ of the same infinite set of uncoupled films. $\underline{U}$ was obtained in closed form [Eqs. (7) and (8)]. The perturbation $\underline{\delta V}$ which couples all these films together is given by Eq. (9), but, since we saw in Sec. III that the self-consistent potentials Δ_1 and Δ_2 can be neglected to a good approximation, we set, for what follows, $\Delta_1=\Delta_2=0$ in Eq. (9).

When use is made of the Dyson equation (10), we obtain

$$D(nKl_3;n'K'l_3')=\delta_{nn'}\delta_{KK'}U_K(l_3,l_3')-\tilde{\gamma}\{\delta_{K1}[U_1(l_31)D(n-1,2,L_2;n'K'l_3')+U_1(l_3L_1)D(n,2,1;n',K'l_3')]$$
$$+\delta_{K2}[U_2(l_31)D(n,1,L_1;n'K'l_3')+U_2(l_3L_2)D(n+1,1,1;n'K'l_3')]\}\ , \tag{A1}$$

where the

$$U_K(l_3l_3')\equiv U_K(\mathbf{k}_{\parallel};l_3,l_3';E)$$

are given by Eq. (7). In order to solve this system of equations, it is useful to define

$$f(n,n')=D(n21;n'K'l_3')\ , \tag{A2}$$

$$g(n,n')=D(n2L_2;n'K'l_3')\ , \tag{A3}$$

$$v(n,n')=D(n11;n'K'l_3')\ , \tag{A4}$$

$$w(n,n')=D(n1L_1;n'K'l_3')\ , \tag{A5}$$

and also to rewrite Eq. (A1) as the following set of four equations:

$$v(n,n')=\delta_{nn'}\delta_{1K'}U_1(1l_3')$$
$$-\tilde{\gamma}[U_1(11)g(n-1,n')+U_1(1L_1)f(n,n')]\ , \tag{A6}$$

$$w(n,n')=\delta_{nn'}\delta_{1K'}U_1(L_1l_3')$$
$$-\tilde{\gamma}[U_1(L_11)g(n-1,n')+U_1(11)f(n,n')]\ , \tag{A7}$$

$$f(n,n')=\delta_{nn'}\delta_{2K'}U_2(1l_3')$$
$$-\tilde{\gamma}[U_2(1L_2)v(n+1,n')+U_2(11)w(n,n')]\ , \tag{A8}$$

$$g(n,n')=\delta_{nn'}\delta_{2K'}U_2(L_2l_3')$$
$$-\tilde{\gamma}[U_2(11)v(n+1,n')+U_2(L_21)w(n,n')]\ . \tag{A9}$$

Using the values of $f(n,n')$ and $g(n,n')$ given by Eqs. (A8) and (A9) in Eqs. (A6) and (A7), one obtains

$$\Delta v(n,n')+Av(n+1,n')+Bw(n,n')$$
$$+Cw(n-1,n')=K_1(n,n')\ , \tag{A10}$$

$$\Delta w(n,n')+Aw(n-1,n')+Bv(n,n')$$
$$+Cv(n+1,n')=K_2(n,n')\ , \tag{A11}$$

where

$$\Delta=1-\tilde{\gamma}^2U_1(11)U_2(11)\ , \tag{A12}$$

$$A=-\tilde{\gamma}^2U_1(1L_1)U_2(1L_2)\ , \tag{A13}$$

$$B=-\tilde{\gamma}^2U_1(1L_1)U_2(11)\ , \tag{A14}$$

$$C=-\tilde{\gamma}^2U_1(11)U_2(L_21)\ , \tag{A15}$$

$$K_1(n,n')=\delta_{nn'}[\delta_{1K'}U_1(1l_3')-\tilde{\gamma}\delta_{2K'}U_1(1L_1)U_2(1l_3')]$$
$$-\delta_{n-1,n'}\tilde{\gamma}\delta_{2K'}U_1(11)U_2(L_2l_3')\ , \tag{A16}$$

and

$$K_2(n,n') = \delta_{nn'}[\delta_{1K'}U_1(L_1 l'_3) - \tilde{\gamma}\delta_{2K'}U_1(11)U_2(1l'_3)] - \delta_{n-1,n'}\tilde{\gamma}\delta_{2K'}U_1(L_1 1)U_2(L_2 l'_3)\ . \tag{A17}$$

Now, the value of $v(n+1)$ given by Eq. (A11) can be inserted into Eq. (A10), which yields $v(n)$ as a function of $w(n)$ and $w(n-1)$. This last expression of $v(n)$, and also $v(n+1)$, is used again in Eq. (A10) and finally provides

$$w(n+1,n') + w(n-1,n') - 2\eta w(n,n') = F_1\delta_{n-1,n'} + F_2\delta_{nn'} + F_3\delta_{n+1,n'}\ , \tag{A18}$$

where

$$2\eta = \frac{1 - 2\tilde{\gamma}^2 U_1(11)U_2(11) + \tilde{\gamma}^4[U_2^2(11) - U_2^2(1L_2)][U_1^2(11) - U_1^2(1L_1)]}{\tilde{\gamma}^2 U_1(1L_1)U_2(1L_2)} \tag{A19}$$

and

$$F_1 = \frac{\delta_{2K'}}{\tilde{\gamma}}\frac{U_2(L_2 l'_3)}{U_2(L_2 1)}\ , \tag{A20}$$

$$F_2 = \delta_{1K'}\left[\frac{-U_1(L_1 l'_3)}{\tilde{\gamma}^2 U_1(1L_1)U_2(1L_2)} - \frac{U_2(11)}{U_2(1L_2)}\left[U_1(1l'_3) - \frac{U_1(11)U_1(L_1 l'_3)}{U_1(1L_1)}\right]\right] + \delta_{2K'}\left[\frac{1}{\tilde{\gamma}}\frac{U_1(11)U_2(1l'_3)}{U_1(1L_1)U_2(1L_2)} - \tilde{\gamma}\left[\frac{U_1^2(11)}{U_1(1L_1)} - U_1(1L_1)\right]\left[\frac{U_2(11)U_2(1l'_3)}{U_2(1L_2)} - U_2(L_2 l'_3)\right]\right]\ , \tag{A21}$$

$$F_3 = -\delta_{1K'}\left[\frac{U_1(11)U_1(1l'_3)}{U_1(1L_1)} - U_1(L_1 l'_3)\right]\ . \tag{A22}$$

Equation (A18) can be solved, remembering that the solution of

$$h(n+1,n') + h(n-1,n') - 2\eta h(n,n') = \delta_{nn'} \tag{A23}$$

is

$$h(n,n') = \frac{t^{|n-n'|+1}}{t^2-1}\ , \tag{A24}$$

where

$$t = \begin{cases} \eta - (\eta^2-1)^{1/2}, & \eta > 1 \\ \eta + i(1-\eta^2)^{1/2}, & -1 < \eta < 1 \\ \eta + (\eta^2-1)^{1/2}, & \eta < -1\ . \end{cases} \tag{A25}$$

Returning to Eq. (A18), one obtains

$$w(n,n') = F_1\frac{t^{|n-n'-1|+1}}{t^2-1} + F_2\frac{t^{|n-n'|+1}}{t^2-1} + F_3\frac{t^{|n-n'+1|+1}}{t^2-1}\ . \tag{A26}$$

In the same manner, one can obtain each of the four elements of $\underline{D}$ appearing in the second member of Eq. (A1), or even, directly, their linear combination. Finally, one obtains the elements of the superlattice Green's function as given by Eqs. (15)–(18), and once use is made of expression (7) for the films Green's functions $\underline{U}_K$, the value of 2η given by Eq. (A19) reduces to that given by Eq. (14).

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[*] New permanent address: Laboratoire de Physique et de Spectroscopie Electronique, Université de Haute Alsace, 4 rue des Frères Lumière, 68093 Mulhouse Cédex, France.

[†] On attachment to Theoretical Physics Division, A.E.R.E. Harwell and to the Department of Theoretical Physics, University of Oxford.

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