

Band structure of thin films*Nikhiles Kar and Paul Soven[†]*Department of Physics and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174*

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We present the formalism of a multiple-scattering technique for computing the bound energy eigenstates in a thin film. The potential is of the muffin-tin variety within the film and is a function of the normal coordinate in the exterior region. An application to a monolayer film of copper is presented, and the results compared to previous calculations.

I. INTRODUCTION

The object of this paper is to present a formalism for calculating the band structure of thin films. We also present some preliminary results for a monolayer film of copper. The motivation for our work is to develop a method of calculating the surface electronic structure of transition metals. There is considerable evidence that the healing length of the surface of a solid (the distance into the bulk beyond which the potential effectively resembles that of the infinite solid) is relatively short. Jellium calculations¹ seem to indicate that a self-consistently calculated potential approaches the bulk limit within a few angstroms, as would be expected on the basis of the short screening length of metals. On the other hand, the local density of states on the (100) face of nickel has been calculated in a tight-binding approximation by Davenport² using a scheme which views the surface as being the actual top layer of a semi-infinite system. The same quantity has been calculated by Terakura³ who views the surface as simply the top layer of a 13-layer film. The results of these calculations for the surface density of states is remarkably similar, a fact which justifies our hope that the film geometry will be adequate for dealing with surfaces of actual solids.

Kleinman and co-workers⁴ have performed similarly motivated calculations on films of aluminum and lithium. Unfortunately, we cannot simply carry over their formalism to the cases of interest to us, since it is based on pseudopotential ideas and consequently is applicable only to simple metals. Appelbaum and Hamann⁵ have carried out pseudopotential-based calculations for the surfaces of semi-infinite sodium and silicon. Again, the implicit assumption of a weak ionic potential prevents their formalism from being applied to transition metals. Recently, Cooper⁶ and Kasowski⁷ have presented calculational schemes that are, in principle, applicable to the case of transition-metal films. These are discussed in Sec. III of the paper, where we compare some of their results to ours. For the

sake of completeness, we merely note at this point that the formalism of Cooper would appear to be rather oversimplified in that it does not take into account the exterior of the film in a reasonable manner. Kasowski's method and ours can be viewed as differently cast versions of the same basic technique, although we feel that the formalism presented here is rather more amenable to self-consistent solution.

The only practical way of dealing with transition metals is to approximate the potential by one of muffin-tin form. In such a scheme the potential is taken to be spherically symmetric within a sphere of typical atomic size surrounding each nuclear position. The potential in the interstitial region between the spheres is taken to be a constant, which can be chosen as zero with the appropriate choice of energy origin. For an infinite system these are the only regions that exist and nothing more need be specified about the structure of the potential. For a molecule or a film there is an additional region in which the potential must be defined. Johnson's⁸ scattered wave scheme for molecular calculations surrounds the molecule with a large sphere outside of which the potential is taken to be spherically symmetric. The obvious generalization to a film geometry is to take the potential outside of the planar boundaries of the film to be a function of the normal coordinate only. Three distinct regions of space are thus defined, in each of which the form of the potential is sufficiently simple that rapid solution to the Schrödinger equation for the combined system is practical.

Our calculational scheme is a direct generalization of the Korringa-Kohn-Rostoker (KKR)⁹ formalism for band calculations of infinite systems and of Johnson's⁸ scattered-wave formalism for molecular calculations. The Schrödinger equation is numerically integrated in regions I and III (which is an easy procedure owing to the simple geometry and one-dimensional nature of the potentials in those regions) and the resulting solutions combined to yield an eigenfunction for the system. The conditions that the solution to the Schrödinger equation

in the interstitial region smoothly connect the solutions in all regions I and III yields a secular equation of the usual multiple-scattering type. A film is periodic in directions parallel to its surfaces, which implies that \vec{k}_\parallel , a two-dimensional wave vector parallel to the surface, is a good quantum number. Each eigenfunction is then characterized by such a wave vector (the eigenfunctions are Bloch-like in directions parallel to the film but are molecularlike in the third direction), and one must solve the secular equation repeatedly for every wave vector in the appropriate two-dimensional Brillouin zone. Self-consistency in the potential is possibly a very important part of any surface calculation. The copper calculations reported here do not include it, and consequently we do not present at this point the appropriate extensions of our formalism to yield the correctly normalized eigenfunctions.

II. FORMALISM

The physical system is periodic in two dimensions (referred to as the parallel directions) and nonperiodic (molecularlike) in the third dimension. The film may be divided into unit cells with the position of each cell being specified by a two-dimensional vector \vec{R}_n . The α th type of atom within each cell has the coordinate vector \vec{r}_α (in general three dimensional) with respect to the position. The radius of the α th muffin-tin sphere is a_α , and the sides of the film are at $z = z_1$ and $z = z_2$, $z_2 < z_1$. Position with respect to the center of the sphere at $\vec{R}_{n\alpha} = \vec{R}_n + \vec{r}_\alpha$ is measured by $\vec{r}_{n\alpha}$, i. e., $\vec{r}_{n\alpha} = \vec{r} - \vec{R}_{n\alpha}$.

In accord with the nature of the film geometry, the crystalline potential is periodic in directions parallel to the film surfaces. As was discussed in the Introduction, we make the further approximations that (i) the potential is spherically symmetric within each muffin-tin sphere; (ii) that it depends only upon the normal (z) coordinate in the region of space outside of the planes defining the film; and (iii) that it is a constant (taken to be zero for convenience) in the interstitial region. It is thus completely defined by the relations

$$\begin{aligned} V(\vec{r}) &= V_\alpha(r_{\alpha n}) & \text{if } |\vec{r}_{\alpha n}| < a_\alpha \\ &= V_1(z) & \text{if } z > z_1 \\ &= V_2(z) & \text{if } z < z_2 \\ &= 0, & \text{otherwise.} \end{aligned} \quad (1)$$

The structure of any energy eigenfunctions is partially dictated by the periodic nature of the system. The two-dimensional lattice defined by the vectors $\{\vec{R}_n\}$ has a reciprocal lattice with vectors $\{\vec{g}_m\}$, and a corresponding two-dimensional surface Brillouin zone (SBZ). Any eigenfunction of the system is characterized by a two-dimensional wave

vector which may be restricted to lie within the SBZ. Owing to the special nature of the muffin-tin potential each eigenfunction has a particularly simple representation in those regions where the potential is nonzero. Let $\psi(\vec{r})$ be an energy eigenfunction of two-dimensional wave vector \vec{k} and energy E . Within the sphere centered at $\vec{R}_{n\alpha}$ it has the representation

$$\psi(\vec{r}) = \sum_L e^{i\vec{k} \cdot \vec{R}_{n\alpha}} A_{\alpha L} \frac{J_{\alpha l}(r_{n\alpha})}{J_{\alpha l}(a_\alpha)} Y_L(\vec{r}_{n\alpha}), \quad (2)$$

where L denotes the quantum numbers (l, m), and $J_{\alpha l}(r)$ is the radial solution for angular momentum l in the central potential $V_\alpha(r)$. In the region outside of the film the same eigenfunction has the representation

$$\psi(\vec{r}) = \sum_m e^{i(\vec{k} + \vec{g}_m) \cdot \vec{r}} A_{km} \frac{u_{km}(z)}{u_{km}(z_k)}, \quad (3)$$

where $k = 1, 2$ corresponds to $z = z_1, z_2$, respectively, and the function $\exp[i(\vec{k} + \vec{g}_m) \cdot \vec{r}] u_{km}(z)$ is a solution to the Schrödinger equation with the potential $V_k(z)$. The function $u_{km}(z)$ satisfies the one-dimensional Schrödinger equation

$$\left(|\vec{k} + \vec{g}_m|^2 - \frac{\partial^2}{\partial z^2} + V_k(z) \right) u_{km}(z) = E u_{km}(z) \quad (4)$$

together with the boundary condition that it vanish at infinity (since only bound states are being considered). The representation of the function in the interstitial region is very complex. Fortunately, it is not needed at all in solving the eigenvalue problem, and at our present level of sophistication it is not needed in the self-consistency procedure either.

The secular equation is determined by finding the relation between the amplitudes $A_{\alpha L}$, A_{km} which ensure that ψ is actually a solution to the complete Schrödinger equation for the system. The starting point is Green's theorem, which in the present context states that if ψ is a bound solution to the Schrödinger equation with energy E , then it satisfies the integral equation

$$\psi(\vec{r}) = \int \left(\psi(\vec{r}') \frac{\partial G(\vec{r}, \vec{r}')}{\partial n'} - G(\vec{r}, \vec{r}') \frac{\partial \psi(\vec{r}')}{\partial n'} \right) dS', \quad (5)$$

where the surface integral is taken over all surfaces bounding the region of constant (zero) potential. $G(\vec{r}, \vec{r}')$ is the free-electron Green's function at energy E . (Since only bound states of the system are being sought, one is at liberty to use the real, i. e., not complex, free-electron Green's function. This is the form employed in the detailed calculations presented in the Appendix.) The scattered-wave secular equation is derived from (5) by requiring that the function on the left-hand side reduces as one approaches the surfaces to the func-

tion appearing under the integral on the right-hand side of the expression.

It follows from Eq. (2) that on the surface of the sphere centered at the function and its normal derivative take the form

$$\begin{aligned}\psi &= e^{i\vec{k}\cdot\vec{r}_{n\alpha}} \sum_L A_{\alpha L} Y_L(\vec{r}_{n\alpha}), \\ \frac{\partial\psi}{\partial n} &= -e^{i\vec{k}\cdot\vec{r}_{n\alpha}} \sum_L \gamma_{\alpha l} A_{\alpha L} Y_L(\vec{r}_{n\alpha}),\end{aligned}\quad (6)$$

where $\gamma_{\alpha l}$ is the logarithmic derivative of $J_{\alpha l}(\gamma)$ evaluated at $\gamma = a_{\alpha}$. In the same way, on the planar boundaries

$$\begin{aligned}\psi &= \sum_m A_{km} \exp[i(\vec{k} + \vec{g}_m) \cdot \vec{r}], \\ \frac{\partial\psi}{\partial n} &= \pm \sum_m \gamma_{km} A_{km} \exp[i(\vec{k} + \vec{g}_m) \cdot \vec{r}],\end{aligned}\quad (7)$$

where γ_{km} is the logarithmic derivative of $u_{km}(z)$ at $z = z_k$, and the minus or plus sign is taken as $k = 1$ or 2 , respectively.

The secular equation itself is derived by recognizing that

$$a_{\alpha}^2 e^{i\vec{k}\cdot\vec{r}_{\alpha}} A_{\alpha L} = \int \psi(\vec{r}) Y_L(\vec{r}_{\alpha}) dS_{\alpha}, \quad (8)$$

where the integral is taken over the surface of the α th sphere in the central unit cell, while

$$S_0 A_{km} = \int \psi(\vec{r}) \exp[-i(\vec{k} + \vec{g}_m) \cdot \vec{r}] dS_k, \quad (9)$$

where S_0 is the unit cell area and the integral is taken over a unit cell on the plane $z = z_k$.

It is clear from the structure of Eq. (5) that upon substitution of expressions (6)–(9) one will find a set of linear relations among the amplitudes. For example,

$$\begin{aligned}a_{\alpha}^2 e^{i\vec{k}\cdot\vec{r}_{\alpha}} A_{\alpha L} &= \sum_{\beta L'} \left[\sum_n e^{i\vec{k}\cdot\vec{r}_{n\beta}} \int dS_{\alpha} dS'_{n\beta} Y_L(\vec{r}_{\alpha}) \left(\frac{\partial G(\vec{r}, \vec{r}')}{\partial n'} + \gamma_{\beta L} G(\vec{r}, \vec{r}') \right) Y_L(\vec{r}'_{\beta n}) A_{\beta L'} \right] \\ &+ \sum_{mp} \left[\int dS_{\alpha} dS'_p Y_L(\vec{r}_{\alpha}) \left(\frac{\partial G(\vec{r}, \vec{r}')}{\partial n'} \pm \gamma_{pm} G(\vec{r}, \vec{r}') \right) e^{i(\vec{k} + \vec{g}_m) \cdot \vec{r}_1} \right] A_{pm}.\end{aligned}\quad (10)$$

The evaluation of these integrals and their analogs in the expressions for A_{pm} is straightforward, but very tedious. We discuss it in the Appendix. The result is a system of equation of the form

$$\begin{aligned}\sum_{\beta L'} M_{LL'}^{\alpha\beta} A_{\beta L'} + \sum_{pm} \langle \alpha L | M | pm \rangle A_{pm} &= 0, \quad (11a) \\ \sum_{\beta L'} \langle pm | M | \beta L' \rangle A_{\beta L'} + \sum_{p'm} \langle pm | M | p'm \rangle A_{p'm} &= 0.\end{aligned}\quad (11b)$$

The condition for having an eigenvalue at energy E and wave vector \vec{k} is, of course, that the determinant of the coefficients vanish. There are several points to be made. The first is that this secular equation is of exceedingly high order, even when allowance is made for the rapid convergence of the sums. The order of the system is the number of atoms per unit cell (at least the number of atomic layers in the film) times the number of important angular-momentum components (typically nine for transition metals), plus the number of reciprocal-lattice vectors needed to describe the wave function outside of the film. The second point is that there is no direct coupling between the A_{pm} corresponding to different reciprocal-lattice vectors. This follows from the translational invariance of the free-electron Green's function. There is, of course, an indirect coupling between the A_{pm} for different m arising from their individual couplings to the $A_{\alpha L}$.

Both of these observations suggest that the natural way to proceed is to solve Eq. (11a) for A_{1m} and A_{2m} in terms of the $A_{\alpha L}$ and then substitute the expressions back into Eq. (11b). One finds in this way a much smaller system of equations involving only the amplitudes $A_{\alpha L}$. In addition, it is found that all formulas are considerably simplified if one introduces quantities $B_{\alpha L}$, defined by the expression

$$B_{\alpha L} = a_{\alpha}^2 \{ E^{1/2} j'_l [a_{\alpha}(E)^{1/2}] - \gamma_{\alpha l} j_l [a_{\alpha}(E)^{1/2}] \} A_{\alpha L}, \quad (12)$$

where j_l is the usual spherical Bessel functions.

The result of these manipulations is the following set of equations:

$$\cot(\delta_{\alpha l}) B_{\alpha L} + \sum_{\beta L'} S_{LL'}^{\alpha\beta} B_{\beta L'} + \sum_{\beta L'} T_{LL'}^{\alpha\beta} B_{\beta L'} = 0. \quad (13)$$

$\delta_{\alpha l}$ is the phase shift in the potential $V_{\alpha}(\gamma)$ for angular momentum l and energy E . As is shown in the Appendix, the S matrix is a purely geometrical quantity. It is essentially the matrix introduced by Kambe,¹⁰ and may be described as either the two-dimensional version of the KKR structure constants or the periodic extension of the structure constants used by Johnson⁸ in the molecular scattered-wave approach. Its evaluation is awkward, requiring Ewald-type summations, and in fact forms the most time-consuming element of the computations. The matrix T represents an indirect interaction between two spheres via multiple scatterings from the

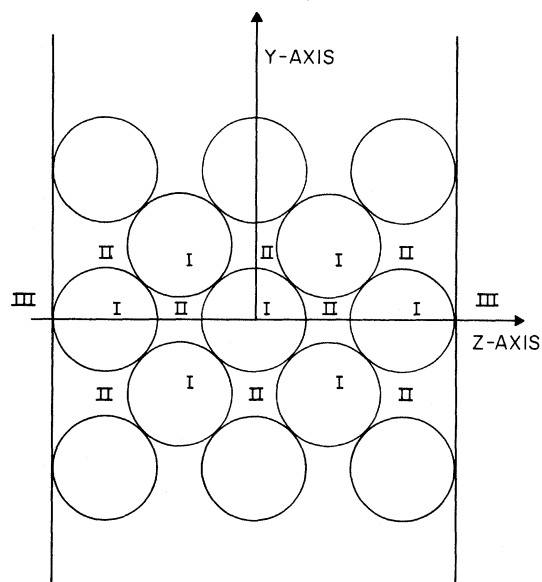


FIG. 1. Schematic representation of a five-layer film along y - z plane. (Note: the results presented in the paper are for a *single* layer, although the formalism is for a multilayer system.)

walls of the film. Its evaluation requires a very rapidly converging reciprocal-lattice summation. T may be shown to have whatever symmetry is possessed by S . It has simple poles at the eigenvalues of the "empty film" in which all interior potentials are set equal to zero.

III. APPLICATION TO A COPPER MONOLAYER

In this part of the paper we present the result of a non-self-consistent calculation of the electronic spectrum of a monoatomic film of copper. The po-

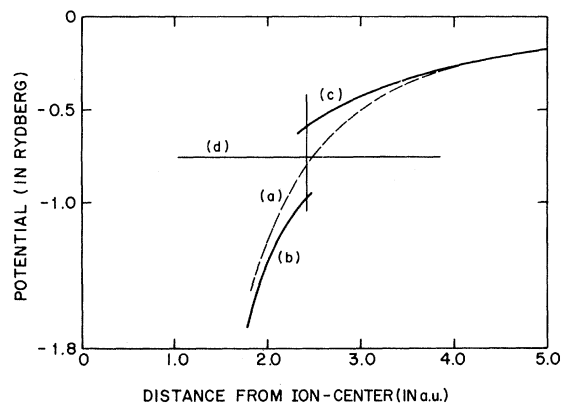


FIG. 2. Potential for single-layer copper film: (a) atomic potential, (b) spherically averaged potential inside muffin-tin, (c) planar-averaged potential outside film boundaries, (d) volume-averaged constant potential in the interstitial region.

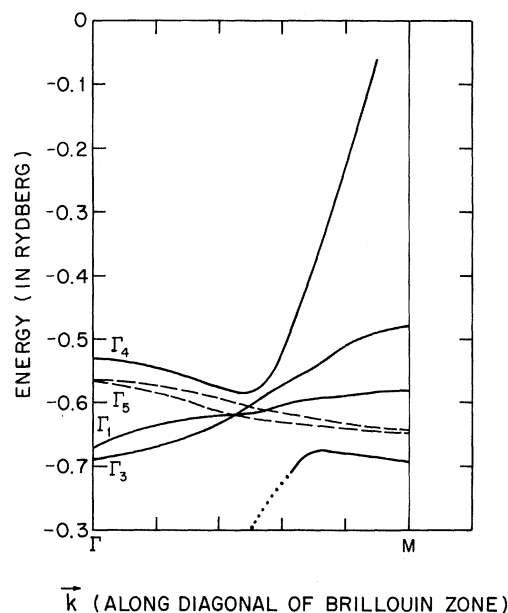


FIG. 3. Band structure along diagonal of Brillouin zone for a single-layer film (100) face. Dashed lines represent states odd under reflection on the plane of the film.

tential for our calculation was constructed using a generalization of the Mattheiss¹¹ prescription for generating approximate one-electron potentials for infinite systems. One assumes that the total Coulomb potential and charge density of the film can be represented as a superposition of atomic potentials and charge densities. The atomic quantities were in our case derived from Herman-Skillman-type¹² wave functions for atomic copper, which were calculated with an exchange parameter (the α of $X\alpha$ theory) of 0.707. The atomic charge densities and Coulomb potentials were then overlapped and spherically averaged within each muffin-tin sphere, volume averaged in the interstitial region between the spheres, and planar averaged over a unit cell in the exterior region. The exchange-correlation potential for the film was constructed from the overlapped-averaged charge density using statistical exchange and the value of α employed in the atomic calculations. A sketch of the potential employed in the calculations is shown in Fig. 2. The discontinuities at the boundaries of the various regions are typical of what occurs in most muffin-tin constructions.

The calculations described here were carried out for a monolayer having the structure of the (100) face of fcc copper. The two-dimensional Brillouin zone is a square corresponding to the square net structure of the (100) face. In Fig. 3 we present the result of our calculations for wave vectors along the diagonal of the Brillouin zone. The band

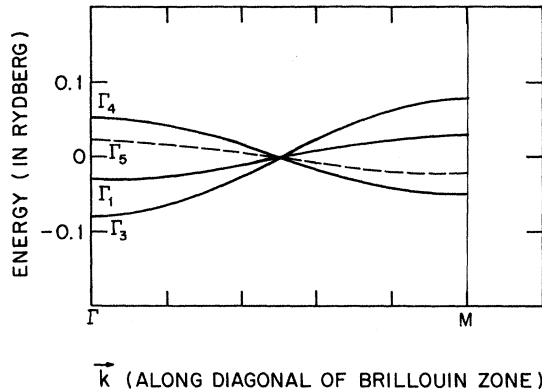


FIG. 4. Tight-binding band structure for d bands of a single layer of copper (100) face with bulk parameters of Mueller. The dashed line represents a twofold degenerate band odd under reflection on the plane of the film.

structure may be described as a tight-binding-type complex of five predominantly d -type bands, hybridizing if symmetry permits with a plane-wave-type band of sp character. The ordering of levels, especially at the Γ point in the center of the surface Brillouin zone looks rather odd when compared to the levels in bulk copper. The " t_{2g} -type" states (which we label Γ_4 and Γ_5 following the notation of Heine¹³) lie above the " e_g -type" levels, contrary to what occurs in the bulk case. The point, of course, is that the band structure we calculate is in fact that of a monolayer film and not that of a bulk system, and consequently there is no reason to expect a similar ordering in the two cases. To convince ourselves of the essential correctness of our results, we carried out an elementary tight-binding calculation for a d -band complex in the film geometry. The two-center integrals ($dd\sigma$), ($dd\pi$), and ($dd\delta$) were those derived by Mueller¹⁴ by fitting to the band structure calculated by Burdick¹⁵ using the augmented-plane-wave method. Our results are presented in Fig. 4. It is clear that the band structure shown in Fig. 3 is exactly what would be expected on the basis of the tight-binding model coupled with a hybridizing plane wave threading through the d -band complex. In the direction shown, the plane wave would have symmetry Σ_1^+ (the superscript + referring to parity under the mirror operation) and would hybridize with only two of the tight-binding d bands. The degeneracy of the Σ_1^+ , Σ_2^- states shown in Fig. 4 is a consequence of our having included only nearest-neighbor tight-binding interactions. The small splitting of these states shown in Fig. 3 is indicative of the fact that second-neighbor interactions are small, but not entirely negligible. The splittings of the states are not the same in the two calculations, as would be expected since the LCAO parameters were derived

from a fit to a bulk band structure, whereas in the film that different d orbitals sample the vacuum region to varying extents.

It is clear too, that our guess at the potential is not very wrong, in that a reasonable filling of the band would place the Fermi level at roughly the correct place insofar as the work function of bulk copper is concerned. One would expect that self-consistency would make only qualitative changes in the band structure.

It is possible to make contact with various other calculations that have appeared recently. The results of Davenport² and of Terakura³ for the local density of states on the (100) surface of nickel suggest the existence of a large peak in the density of states near the center of the band. It is clear on inspection of the band structure shown in Fig. 3 that this peak exists for the two-dimensional structure as well. In a tight-binding scheme based on nearest-neighbor hopping only and neglecting sd hybridization the d -band complex shown in the figure is completely degenerate half way out to the zone corner. (There is some degeneracy in other directions as well.) It is clear from our calculations that the inclusion of sd hybridization reduces but does not destroy completely the near-degeneracy and consequent large peak in the density of states.

Cooper⁶ has recently published a set of calculations on thin films of copper some of which should be directly comparable to our work. The boundaries of the film in his case are planes upon which the wave function is constrained to vanish. Although the position of the plane can vary with energy (thereby simulating the varying amounts of leakage into the vacuum that wave functions of different energy would experience), we believe that the problem Cooper solves is in fact not the problem of a thin film in vacuum. There appears to be too many states in his result, and the concomitant lowering of the Fermi level to cause a partial emptying of the d -band complex would seem to be very unlikely. Kasowski⁷ has reported some work on surface states in copper which is based upon a thin-film calculation. One of the calculations he reports is for a monolayer film, although from the published work it is difficult to understand exactly how the vacuum interface is treated. We disagree with his results, at least insofar as the ordering of the levels at Γ is concerned. At the moment we can offer no explanation for this disagreement. The tight-binding-type calculations discussed above were performed to verify the level ordering predicted by us on the basis of the more nearly completely scattered wave calculations.

APPENDIX

In this section of the paper we sketch out the derivation of the matrix elements entering into both

forms of the secular equations. The derivations are only meant to indicate the nature of the calculations, although complete expressions for the matrix elements are presented.

All of the matrix elements entering into Eqs. (11) are essentially various projections of the free-electron Green's function. Since only bound states are being sought, it is appropriate and convenient to work with the real form of the Green's function, although in fact if one used the complex (outgoing wave) form then the additional parts of the resulting expressions would vanish in any event. The Green's function that we employ has the representation

$$G(\vec{r} - \vec{r}') = (16\pi^3)^{-1} \int d\vec{q} e^{i\vec{q}\cdot\vec{R}} [(E - q^2 + i\delta)^{-1} + (E - q^2 - i\delta)^{-1}] \quad (\text{A1})$$

with

$$\vec{R} = \vec{r} - \vec{r}'.$$

There are various alternative representations which are useful in calculating the matrix elements. If we decompose the vector \vec{q} appearing in (A1) according to $\vec{q} = \vec{q}_{\parallel} + \vec{q}_{\perp}$, where \vec{q}_{\parallel} (\vec{q}_{\perp}) is parallel (perpendicular) to the plane of the film, then one can perform the q_{\perp} integration independently to yield the representation

$$G(\vec{r} - \vec{r}') = (2\pi)^{-2} \int d\vec{q}_{\parallel} e^{i\vec{q}_{\parallel}\cdot(\vec{r}-\vec{r}')} g(z, z' | \vec{q}_{\parallel}). \quad (\text{A2})$$

If $Q^2 = E - \vec{q}_{\parallel}^2 > 0$, then

$$g(z, z' | \vec{q}_{\parallel}) = (2Q)^{-1} \sin(Q|z - z'|), \quad (\text{A3})$$

while if $\bar{Q}^2 = \vec{q}_{\parallel}^2 - E > 0$, then

$$g(z, z' | \vec{q}_{\parallel}) = -(2\bar{Q})^{-1} \exp(-\bar{Q}|z - z'|). \quad (\text{A4})$$

Since

$$\langle pm | M | p'm \rangle = S_0^{-1} \int dS_p dS_p' \exp[i\vec{K}_m \cdot (\vec{r} - \vec{r}')] \times \left(\pm \frac{\partial G(\vec{r} - \vec{r}')}{\partial z'} \mp \gamma_{p'm} G(\vec{r} - \vec{r}') \right)_{z=z_p, z'=z_p'}, \quad (\text{A5})$$

where the upper (lower) sign is taken for $z = z_1$ (z_2), and the integrals are over a unit cell, it is easy to show that

$$\langle pm | M | p'm \rangle = \pm \left(\frac{\partial}{\partial z_p} - \gamma_{p'm} \right) g(z_p, z_p' | \vec{K}_m) \quad (\text{A6})$$

with

$$\vec{K}_m = \vec{k} + \vec{g}_m,$$

where the orthogonality of the functions $e^{i\vec{K}_m \cdot \vec{r}}$ over a single unit cell has been exploited. To present our results, we employ the notation $Q_m^2 = |E - \vec{K}_m^2|$, $D = z_1 - z_2$, and $\bar{\gamma}_{pm} = \gamma_{pm}/Q_m$, and make the convention in what follows that the upper or lower form is

applicable depending upon whether E is greater than or less than K_m^2 . Our result is

$$\langle 1m | M | 1m \rangle = \begin{cases} \frac{1}{2} \\ \frac{1}{2}(1 - \bar{\gamma}_{1m}) \end{cases}, \quad (\text{A7a})$$

$$\langle 1m | M | 2m \rangle = \begin{cases} -\frac{1}{2}[\cos(Q_m D) + \bar{\gamma}_{2m} \sin(Q_m D)] \\ -\frac{1}{2}(1 - \bar{\gamma}_{2m}) e^{-Q_m D} \end{cases}, \quad (\text{A7b})$$

$$\langle 2m | M | 1m \rangle = \begin{cases} -\frac{1}{2}[\cos(Q_m D) - \bar{\gamma}_{1m} \sin(Q_m D)] \\ -\frac{1}{2}(1 + \bar{\gamma}_{1m}) e^{(-Q_m D)} \end{cases}, \quad (\text{A7c})$$

$$\langle 2m | M | 2m \rangle = \begin{cases} \frac{1}{2} \\ \frac{1}{2}(1 + \bar{\gamma}_{2m}) \end{cases}. \quad (\text{A7d})$$

Matrix elements of the form $\langle pm | M | \alpha L \rangle$ involve surface integrals over the surface $z = z_p$, as well as integrals over the surface of all α -type spheres in the film. Owing to the Bloch character of the wave functions, all integrals of the latter type differ by only a phase factor. Substitution of Eqs. (6) and (7) into (5), and use of the relation $\partial/\partial n' = -\partial/\partial a_{\alpha}$ which is valid on the surface of the α -type sphere, leads to the expression

$$\langle pm | M | \alpha L \rangle = -\frac{a_{\alpha}^2}{S_0} \sum_n e^{i\vec{k}\cdot\vec{R}_{n\alpha}} \int dS_p e^{-i(\vec{k}+\vec{g}_m)\cdot\vec{r}} \times \int d\Omega'_{n\alpha} \left(\frac{\partial}{\partial a_{\alpha}} + \gamma_{\alpha L} \right) G(\vec{r} - \vec{r}') Y_L(\vec{r}'_{n\alpha}), \quad (\text{A8})$$

where $d\Omega_{n\alpha}$ is an element of solid angle with respect to $\vec{R}_{n\alpha}$. Use of representation (A2) for the free-electron Green's function allows (A8) to be cast into the form

$$\langle pm | M | \alpha L \rangle = -\frac{a_{\alpha}^2}{S_0} \int d\Omega'_{n\alpha} \left(\frac{\partial}{\partial a_{\alpha}} + \gamma_{\alpha L} \right) e^{-i\vec{K}_m \cdot \vec{r}} g(z_p, z' | \vec{K}_m) Y_L(\vec{r}'_{n\alpha}). \quad (\text{A9})$$

In deriving (A9), we have used the fact that the sum over all unit cells can be used to transform the restricted surface integral into one over the entire plane, which then picks out a single component of $g(z, z' | \vec{q}_{\parallel})$. Further reduction of this expression is accomplished with the aid of the conventional expansion

$$e^{i\vec{k}\cdot\vec{r}} = \sum_L 4\pi i^L Y_L(\vec{r}) Y_L(\vec{k}) j_L(kr) \quad (\text{A10})$$

the use of which allows evaluation of the remaining integrals in (A9). One should note in this context that (A10) is valid for complex as well as real \vec{k} . In the former case the spherical harmonic $Y_L(\vec{k})$ is most easily interpreted as a polynomial in the complex variables k_x/k , k_y/k and k_z/k , where $k = (k_x^2 + k_y^2 + k_z^2)^{1/2}$. To shorten the forthcoming expressions we introduce the notation $Z_L(\vec{K}_m) = Y_L(\vec{K}_m)$, $(E - K_m^2)^{1/2}$ in which $(E - K_m^2)^{1/2} = +i(K_m^2 - E)^{1/2}$ if $K_m^2 > E$.

Our results for the plane-sphere matrix elements are as follows:

$$\langle 1m | M | \alpha L \rangle = \frac{2\pi a_\alpha^2 (-i)^l}{S_0 Q_m} e^{-i\vec{k}_m \cdot \vec{\tau}_\alpha} J_{\alpha l} Z_L(\vec{K}_m) \times \begin{cases} \{\exp[iQ_m(z_1 - \tau_{\alpha z})] - (-1)^L \\ \times \exp[-iQ_m(z_1 - \tau_{\alpha z})]\} , \\ \exp[-Q_m(z_1 - \tau_{\alpha z})] , \end{cases}$$

with

$$J_{\alpha L} = E^{1/2} j'_L[a_\alpha(E)^{1/2}] - \gamma_{\alpha L} j_l[a_\alpha(E)^{1/2}], \quad (A11)$$

where $(-1)^L \equiv (-1)^{l+m}$.

Matrix elements of the form $\langle 2m | M | \alpha L \rangle$ are obtained from expression (A11) by replacing $z_1 - \tau_{\alpha z}$ by $\tau_{\alpha z} - z_2$ and multiplying by $(-1)^L$.

Sphere-plane matrix elements of the form $\langle \alpha L | M | \beta m \rangle$ are evaluated in a very similar manner. For the sake of brevity we omit details of the derivation and merely present our results.

$$\langle \alpha L | M | 1m \rangle = -\pi i^l j_l[a_\alpha(E)^{1/2}] e^{i\vec{k}_m \cdot \vec{\tau}_\alpha} Z_L(\vec{K}_m) \times \begin{cases} \{(-1)^L(1 + i\bar{\gamma}_{1m}) \exp[iQ_m(z_1 - \tau_{\alpha z})] \\ + (1 - i\bar{\gamma}_{1m}) \exp[iQ_m(\tau_{\alpha z} - z_1)]\} , \\ (1 + \bar{\gamma}_{1m}) \exp[-Q_m(z_1 - \tau_{\alpha z})] . \end{cases} \quad (A12)$$

Our results for the analogous matrix elements involving plane 2, those of the form $\langle \alpha L | M | 2m \rangle$, are obtained from (A12) by replacing $z_1 - \tau_{\alpha z}$ by $\tau_{\alpha z} - z_2$, and $\bar{\gamma}_{1m}$ by $\bar{\gamma}_{2m}$. For the case $E < K_n^2$ it is also necessary to change the sign in front of the logarithmic derivative.

Matrix elements of the form $\langle \alpha L | M | \beta L' \rangle$ are quite similar to those occurring in the molecular scattered wave and KKR formalisms. From Eq. (8) it is clear that the quantity to be evaluated is

$$\langle \alpha L | M | \beta L' \rangle = -\delta_{\alpha\beta} \delta_{LL'} - e^{i\vec{k} \cdot \vec{\tau}_\alpha} \int d\Omega_\alpha \times Y_L(\vec{r}_\alpha) \alpha_\beta^2 \left(\frac{\partial}{\partial a_\beta} - \gamma_{\beta L'} \right) \times \int d\Omega'_\beta \sum_n e^{i\vec{k} \cdot \vec{R}_{n\beta}} G(\vec{r} - \vec{r}' - \vec{R}_{n\beta}) . \quad (A13)$$

One needs to invoke the standard one- and two-center expansions of the free-electron Green's function. In particular, we use the representation

$$G(\vec{r} - \vec{r}') = \kappa \sum_L Y_L(\vec{r}) Y_L(\vec{r}') j_l(\kappa r_<) n_l(\kappa r_>) , \quad (A14)$$

where $\kappa = |E|^{1/2}$, and $r_<$ is the smaller and $r_>$ the greater of r and r' . To evaluate those terms in (A13) with $\vec{R}_{n\beta} \neq 0$, we use the two-center expansion

$$G(\vec{r} - \vec{r}' - \vec{R}) = \kappa \sum_{L, L', L''} i^{l-l'-l''} Y_L(\vec{r}) Y_{L'}(\vec{r}') Y_{L''}(\vec{R})$$

$$\times j_l(\kappa r) j_{l'}(\kappa r') n_l(\kappa R) C(L, L', L') . \quad (A15)$$

In this expression C is the Gaunt coefficient $C(L, L', L'') = 4\pi \int Y_L(\Omega) Y_{L'}(\Omega) Y_{L''}(\Omega) d\Omega$ and the sum is over all angular momenta for which these do not vanish.

Representations (A14) and (A15) are valid for positive energies only. For E less than zero, the correct expansion are obtained by replacing κ by $i\kappa$ in the arguments of the Bessel functions, and replacing the Neumann functions n_l by the Hankel function $h_l = j_l + in_l$.

Evaluation of (A13) is quite straightforward with the aid of the various expansions of G . We find the result:

$$\langle \alpha L | M | \beta L' \rangle = \kappa a_\alpha^2 j_l(\kappa a_\alpha) [\delta_{\alpha\beta} \delta_{LL'} N_{\alpha l} + S_{LL'}^{\alpha\beta} J_{\beta L'}] , \quad (A16)$$

where

$$J_{\alpha l} = \left(\frac{\partial}{\partial a_\alpha} - \gamma_{\alpha l} \right) j_l(\kappa a_\alpha) , \quad (A17)$$

$$N_{\alpha l} = \left(\frac{\partial}{\partial a_\alpha} - \gamma_{\alpha l} \right) n_l(\kappa a_\alpha) .$$

The structure constants are given by

$$S_{LL'}^{\alpha\beta} = \sum_{L''} i^{l-l'-l''} C(L, L', L'') D_{LL'}^{\alpha\beta} , \quad (A18)$$

where

$$D_L^{\alpha\beta} = \sum_n \exp[i\vec{k} \cdot (\vec{R}_n + \vec{\tau}_\beta - \vec{\tau}_\alpha)] \times Y_L(\vec{R}_n + \vec{\tau}_\beta - \vec{\tau}_\alpha) n_l(\kappa |\vec{R}_n + \vec{\tau}_\beta - \vec{\tau}_\alpha|) \quad (A19)$$

in which the term $n=0$ is omitted for the site-diagonal case $\alpha = \beta$. For the case of E less than zero we find a similar formula. In particular, the expression for the structure constant is unchanged except for the omission of the factor $i^{l-l'-l''}$ in (A18) and the replacement $n_l(\kappa R) \rightarrow h_l(i\kappa R)$ in (A19).

We indicated in the text that it is more convenient to reduce the size of the secular equation by solving for the $A_{\beta m}$ and then reinserting the resulting expressions in the remainder of the secular equation. The result of this procedure is a secular equation referring only to the amplitudes of the wave function of the surface of the spheres. For the sake of completeness we present at this point our result for the matrix T appearing in (13):

$$T_{LL'}^{\alpha\beta} = -\frac{8\pi^2 i^{l-l'}}{S_0 \kappa} \sum_m \frac{Y_L(\vec{Q}_m) Y_{L'}(\vec{Q}_m) e^{i\vec{k}_m \cdot (\vec{\tau}_\alpha - \vec{\tau}_\beta)} M_{LL'}^{\alpha\beta}(m)}{\Delta_m Q_m} . \quad (A20)$$

The quantity Δ_m is

$$\Delta_m = \begin{cases} (1 + \bar{\gamma}_{1m} \bar{\gamma}_{2m}) \sin(Q_m D) + (\bar{\gamma}_{1m} - \bar{\gamma}_{2m}) \cos(Q_m D) \\ (1 - \bar{\gamma}_{1m})(1 + \bar{\gamma}_{2m}) - (1 + \bar{\gamma}_{1m})(1 - \bar{\gamma}_{2m}) e^{-2Q_m D} . \end{cases} \quad (A21)$$

For $K_m^2 > E$,

$$M_{L'L'}^{\alpha\beta}(m) = (1 + \bar{\gamma}_{1m})(1 - \bar{\gamma}_{2m})e^{-Q_mD} \{ \exp[Q_m(\tau_{\beta z} - \tau_{\alpha z})] + (-1)^{L+L'} \exp[Q_m(\tau_{\alpha z} - \tau_{\beta z})] \} \\ + (-1)^L(1 + \bar{\gamma}_{1m})(1 + \bar{\gamma}_{2m}) \exp[Q_m(\tau_{\alpha z} + \tau_{\beta z})] + (-1)^{L'}(1 - \bar{\gamma}_{1m})(1 - \bar{\gamma}_{2m}) \exp[-Q_m(\tau_{\alpha z} + \tau_{\beta z})], \quad (A22)$$

while for $K_m^2 < E$, (i) with $L+L'$ odd:

$$M_{L'L'}^{\alpha\beta}(m) = -(-1)^L(\bar{\gamma}_{1m} + \bar{\gamma}_{2m}) \cos[Q_m(\tau_{\alpha z} + \tau_{\beta z})] + (-1)^L(1 - \bar{\gamma}_{1m}\bar{\gamma}_{2m}) \sin[Q_m(\tau_{\alpha z} + \tau_{\beta z})] \\ + \{ (\bar{\gamma}_{1m} - \bar{\gamma}_{2m}) \sin(Q_mD) - (1 + \bar{\gamma}_{1m}\bar{\gamma}_{2m}) \cos(Q_mD) \} \sin[Q_m(\tau_{\alpha z} - \tau_{\beta z})];$$

(ii) with $L+L'$ even:

$$M_{L'L'}^{\alpha\beta}(m) = -(-1)^L(\bar{\gamma}_{1m} + \bar{\gamma}_{2m}) \sin[Q_m(\tau_{\alpha z} + \tau_{\beta z})] - (-1)^L(1 - \bar{\gamma}_{1m}\bar{\gamma}_{2m}) \cos[Q_m(\tau_{\alpha z} + \tau_{\beta z})] \\ + \{ (\bar{\gamma}_{1m} - \bar{\gamma}_{2m}) \sin(Q_mD) - (1 + \bar{\gamma}_{1m}\bar{\gamma}_{2m}) \cos(Q_mD) \} \cos[Q_m(\tau_{\alpha z} - \tau_{\beta z})]. \quad (A23)$$

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