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Method for calculating surface electronic structure of noble and transition metals

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We present a new method for the calculation of the electronic structure of noble and transition-metal surfaces that is based upon the linear combination of muffin-tin orbitals (LCMTO) technique. We adopt the by now common technique of using film calculations to accurately simulate the electronic structure at the surface of bulk d-band metals. A central feature of our method is the introduction of a new basis consisting of (a) muffin-tin orbitals plus (b) additional functions we call "plane-wave orbitals," which are constructed from the exact solutions of Schrödinger's equation in the regions exterior to the film. This method has the virtue of being able to treat non-muffin-tin potentials, yet reproduces, in the limit of a muffin-tin potential, exactly the same results as the more conventional film Green's-function method of Kar and Soven and of Kohn. This parallels the relationship of the bulk LCMTO method to the Korringa-Kohn-Rostoker method, and we conclude, therefore, that our method is the proper generalization (for films) of the bulk LCMTO technique. We also outline a linearization scheme, based on one successfully used in recent bulk LCMTO calculations, to achieve the computational speed necessary for self-consistent film calculations.

I. INTRODUCTION

The surface electronic behavior of noble and transition metals plays a dominant role in determining a number of the most important observable properties of these metals. With this in mind, we have developed a practical technique for rapid and accurate calculations of the electronic energies and wave functions and the related charge-density distribution at the surface. In this paper we present the formal development of this method. We adopt the basic philosophy proposed in our own earlier work,[1-4] and in that of other authors,[5-12] of using film calculations to accurately simulate the electronic structure at the surfaces of bulk d-band metals. Since the "healing length" for surface perturbations on d-band behavior is only a few layer thicknesses, self-consistent calculations for moderately thick films, say about 15 or 20 layers thick, should accurately yield the surface charge density for the metals of interest.

There are several features of film calculations which tend to increase the difficulties beyond those encountered in physically realistic bulk-metal calculations. Substantial changes are expected in the charge-density distribution on approaching the surface as compared to that prevailing within the bulk of the metal. The results of non-self-consistent calculations (especially Refs. 1, 2, 4, 7, 9) enforce our expectation that the correct nature of this surface charge distribution, and the related potential, can only be found through performing self-consistent calculations. Such self-consistent calculations can be carried out in a physically realistic way provided one has an accurate and practical technique for treating non-muffin-tin contributions to the potential, since such non-muffin-tin effects are expected to become quite important on approaching the surface. The lack of translational symmetry (i.e., periodic behavior) in the direction of the film normal is another difficulty. This, of course, is associated with the physical requirement that the electronic wave functions must vanish on going to infinity in a direction normal to the film. Thus from the technical point of view there are three requirements for any calculational technique to be used in performing practical, physically realistic computations of film electronic structure for d-band metals: (i) It must be capable of treating non-muffin-tin contributions to the potential. (ii) The technique must properly take into account the periodic symmetry within the plane of the film and the lack of periodic symmetry in the normal direction. This means that the wave functions must exhibit oscillatory propagating behavior in the plane of the film while decaying normal to the film, so as to vanish at large distances from the film. (iii) It must be possible to achieve the computational speed necessary, in practice, to iterate to self-consistency.

We have developed a technique satisfying these requirements that is based upon the linear combination of muffin-tin-orbitals (LCMTO) technique.[13-15] Previous methods suggested for the film problem have either been limited in their capability to treat point (i) the non-muffin-tin contributions,[7,8] or have relied on awkward devices (such as treating a hypothetical solid consisting of thin metal films separated by appreciable regions of vacuum) to treat point (ii) the differing character of the electronic motion parallel and perpendicular to the film.[12] A central feature of our technique is the introduction of a new basis consisting of (a) the usual muffin-tin-orbitals[13] (MTO's) plus (b) additional functions we call "plane-wave-orbitals" (PWO's) which are constructed from the exact solutions of Schrödinger's equation in the regions exterior to the film. This basis has allowed us to develop a variational technique that satisfies the physical requirements, under (ii), for describing the electronic behavior both inside and outside the film. This is in distinction to another LCMTO technique for films that has been developed recently by Kasowski,[12] and that, as discussed in Sec. II, appears to have significant practical difficulties in satisfying requirement (ii). Furthermore, our technique shares the virtue, common to LCMTO-type techniques in general,[13,14] of being particularly suitable for treating non-muffin-tin potentials, thus satisfying requirement (i). On the other hand, in the limit of a film muffin-tin potential, our technique reproduces exactly the same results as the more conventional film Green's-function treatment.[7,8] This parallels the relationship of the bulk LCMTO method[13,14] to the Korringa-Kohn-Rostoker (KKR)[16] method, and further strengthens our confidence in the computational scheme presented here. With regard to point (iii), we plan to achieve the desired computational speed through the use of a linearized version of our method. The linearization scheme is based[17] on one used very successfully in recent[18] bulk LCMTO calculations. In the remainder of this paper we present the formal development of our method, and discuss the features of interest and primary advantages of this technique over earlier ones. The formal development is presented for the case of the monolayer. The extension to more than one layer is straightforward and is given in the Appendix. The outline of the paper is as follows:

In Sec. II, we introduce the mixed basis of muffin-tin orbitals (MTO's) and plane-wave orbitals (PWO's), the use of which is central to our calculations. This mixed MTO-PWO basis represents the fundamental difference between the theory we have developed and Kasowski's[12] MTO formalism for films. In the limit of a muffin-tin potential inside specified boundary "surfaces" and a z-varying (z is the film normal direction) potential outside, there are three "tail cancellation"[13] conditions to be satisfied in order for a linear combination of MTO's and PWO's to be a solution of the Schrödinger equation. One cancellation condition is for correct behavior inside the muffin-tin spheres and two for the exterior regions, one on either side of the film. In Kasowski's[12] work, the wave function is a linear combination of MTO's only; and there is just a single cancellation condition within the muffin-tin spheres. This creates great practical difficulties in obtaining a physically reasonable description of the difference in behavior of the wave function in a direction parallel to the film as compared to a direction normal to the film.

In Sec. III we discuss the relationship of our method to the Green's-function method for films and surfaces of Kar and Soven[7] and of Kohn.[8] In particular we show that the relationship of our method to that of Kar and Soven and of Kohn is analogous to the relationship of Andersen and Kasowski's[13,14] bulk LCMTO method to the KKR[16] method for bulk band calculations. For a muffin-tin potential within the film and a potential varying only in the normal direction outside the film (a "film muffin-tin potential"), our method yields the same results as that of Refs. 7 and 8, in the limit of an exact solution. Our method, however, has the same advantage with regard to rapidity of convergence that the bulk LCMTO method[14] has with respect to the KKR[16] method. This is because, for a given size secular determinant, our method, like the bulk LCMTO method, includes higher-order angular momentum components in an approximate manner (this is discussed further in Sec. IV). Even more important with regard to our objectives, our method has the advantage, with respect to that of Refs. 7 and 8, of being able to treat non-muffin-tin contributions to the potential. This is also the case[19] for the bulk LCMTO method[13,14] with respect to the KKR[16] method. This shared advantage follows from the fact that both our LC(MTO-PWO) method and the bulk LCMTO method can treat non-muffin-tin effects through the use of a variational principle.

In Sec. IV we present our approach, using a variational method, for treating deviations in the potential from muffin-tin form. That is, the LC(MTO-PWO) wave functions, while exact only for a film muffin-tin potential, are used to approximate the wave functions of a more general Hamiltonian through application of the Rayleigh-Ritz variational method. As already stated, this is analogous to the way such effects are treated in bulk LCMTO calculations. We also discuss, for a film muffin-tin-potential, the relative rates of convergence (mentioned above) of our LC(MTO-PWO) method as compared to the film Green's-function method[7,8]; and we remark on the implications of this with regard to treating non-muffin-tin potentials. We expect[4] important physical effects to be associated with the variation of the charge density and the associated potential in the direction parallel to the plane of the surface, in the region immediately outside the nominal surface layer. The treatment of Sec. IV involves having a strictly z-dependent (film normal direction) potential outside two boundary "surfaces." However, these "surfaces" can be chosen at any desired distance from the surface layers of the film. Thus we can use the full power of our method for treating non-muffin-tin effects (associated with the variation of the potential parallel to the plane) in the region between the surface layers and the boundary "surfaces."

In Sec. V we discuss some points of practical consequence related to the implementation of our method. To deal with the orthogonality requirement[15] between the LC(MTO-PWO) wave functions and the core states of a single muffin-tin potential, we follow a device introduced by Andersen and Wooley[20] in their LCMTO method for molecular calculations. This has the advantage of eliminating the necessity of calculating core states. This device is particularly convenient when linearizing the computational scheme. The linearization scheme we outline enables us to obtain the electronic eigenvalues and eigenstates for our LC(MTO-PWO) variational method by solving an ordinary secular determinant,

$$\det |H_{LL'} - EO_{LL'}| = 0 , \tag{1}$$

where H is the Hamiltonian matrix and O is the overlap matrix. The computational speed gained by this linearization is of great value in self-consistent calculations involving iterations or in calculations for thicker films, requiring larger basis sets and correspondingly larger determinants.

The generalization of the formalism to thicker films is given in the Appendix.

II. DEFINITION OF THE BASIS

Within the context of the independent-particle approximation, the only assumption we have made regarding the film potential is that it is periodic in the plane of the film (the x-y plane) and nonperiodic in a direction normal to the film (the z direction). For the purpose of defining our basis functions, however, we specialize to the case of a muffin-tin potential inside boundary "surfaces" at $z = z_1$ and z_2, and a z-varying potential outside these "surfaces." Throughout this paper we refer to this special case as a film muffin-tin potential.[21] Subsequently, we shall use these basis functions to treat more general film potentials (Sec. IV).

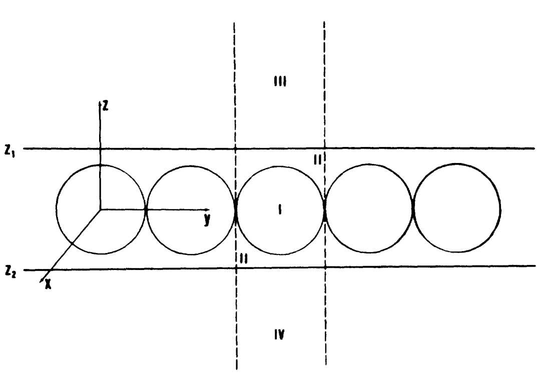

FIG. 1. Schematic representation of a monolayer film with one atom per unit cell. The unit cell, indicated by the dashed lines, extends from $z = -\infty$, to $+\infty$, and there are two boundary "surfaces," one at $z = z_1$ and one at $z = z_2$.

In view of its two-dimensional periodicity, the film can always be divided into unit cells which extend to ±∞ in the z direction. To simplify the following discussion, however, we restrict ourselves to a monolayer film with one atom per unit cell. (The generalization to thicker films is straightforward and is given in the Appendix.) For the special case of a film muffin-tin potential, this is schematically depicted in Fig. 1. Referring to this figure, the potential $V(\vec{r})$ is defined as follows. $V(\vec{r})$ is spherically symmetric within spheres (region I) of radius S centered at each atomic site $\vec{R}$, and, in the interstitial region (region II), $V(\vec{r})$ is constant. Thus $V(\vec{r})$ has the usual muffin-tin form in regions I and II (i.e., between the boundary "surfaces" at $z = z_1$ and z_2). In the exterior regions III and IV, $z > z_1$ and $z < z_2$, respectively, the potential depends only on the z coordinate. The film muffin-tin potential is then specified by the following equation:

$$V(\vec{r}) = \begin{cases} V_{\mathrm{MT}}(|\vec{r} - \vec{R}|), & |\vec{r} - \vec{R}| \le S \\ V_1(z), & z > z_1 \\ V_2(z), & z < z_2 \\ V_{\mathrm{MTZ}}, & \vec{r} \in \text{interstitial} \end{cases} \tag{2}$$

where the constant V_{MTZ} is usually chosen as the zero of energy [the "muffin-tin zero" (MTZ)].

The periodic nature of the film potential implies that the wave functions depend on a two-dimensional crystal momentum vector $\vec{k}$, which can be restricted to lie within the first Brillouin zone of the two-dimensional reciprocal lattice. We therefore let $\Psi_{\vec{k}}(E, \vec{r})$ denote a solution of Schrödinger's equation for the potential given by Eq. (2). We then express the wave function $\Psi_{\vec{k}}(E, \vec{r})$ as a linear combination of suitably chosen basis functions. In analogy with the LCMTO method[13,14] for bulk solids, these basis functions are constructed from the exact solutions in regions I, III, and IV. We now proceed to define this basis.

A. Muffin-tin orbitals (MTO)

The partial wave

$$\phi_L(E, \kappa, \vec{r}) = i^l Y_L(\hat{r}) \times \begin{cases} u_l(E, \vec{r}), & |\vec{r}| < S \\ -s_l[-\kappa^{l+1} n_l(\kappa r)] \\ -c_l[\kappa^{-l} j_l(\kappa r)], & S < |\vec{r}| \end{cases} \tag{3}$$

is a solution at energy E of the Schrödinger equation for a single muffin-tin potential $V_{\mathrm{MT}}(r)$ embedded in the flat potential, $V_{\mathrm{MTZ}}=(E-\kappa^2)$, where $\kappa=(E-V_{\mathrm{MTZ}})^{1/2}$ or $i(V_{\mathrm{MTZ}}-E)^{1/2}$ for $E>V_{\mathrm{MTZ}}$ or $E<V_{\mathrm{MTZ}}$, respectively. We use the notation $Y_L(\vec{r})$ for the spherical harmonic, where L denotes the angular momentum quantum numbers l and m. $u_l(E,\vec{r})$ is a solution of the radial Schrödinger equation, and j_l and n_l are the spherical Bessel and Neumann functions. The coefficients s_l and c_l are chosen so that ϕ_L and its first derivative are continuous at $r=S$. For $\kappa^2>0$ ϕ is δ function normalizable, but for $\kappa^2<0$ ϕ diverges. Only if $c_l/\kappa^{2l+1}s_l=\cot\delta_{l,E}=i$ (where $\delta_{l,E}$ is the phase shift) is ϕ a bound state. It is possible, however, to construct a basis function which is normalizable at all energies. This is done by adding onto ϕ_L a solution of the homogeneous Schrödinger equation which is regular at the origin. In this way, we obtain the muffin-tin-orbital[13] basis function (MTO), which is defined as

$$\chi_L(E,\kappa,\vec{r})=i^l Y_L(\vec{r})\begin{cases} u_l(r)+(c_l-is_l\kappa^{2l+1}) \\ \times J_l(\kappa r)\,, & |\vec{r}|\le S \\ -s_l K_l(\kappa r)\,, & S<|\vec{r}| \end{cases} \tag{4a}$$

where the functions

$$J_l(\kappa r)=\kappa^{-l}j_l(\kappa r) \tag{4b}$$

$$\begin{aligned} K_l(\kappa r)&=i\kappa^{l+1}h_l^{(1)}(\kappa r)\,,\\ &=i\kappa^{l+1}[j_l(\kappa r)+in_l(\kappa r)] \end{aligned} \tag{4c}$$

are regular at $\kappa=0$.

B. Plane-wave orbitals (PWO)

For a potential that is given by $V_1(z)$ in the semi-infinite region $z_1<z$ (region III of Fig. 1), and by $V_{\mathrm{MTZ}}=E-\kappa^2$ in the remainder of space, a solution at energy E of Schrödinger's equation is

$$\phi_{1,m}(E,\kappa,\vec{r})=e^{i(\vec{k}+\vec{g}_m)\cdot\vec{r}} \times\begin{cases} \overset{(1)}{u}_{\vec{k},m}(E,z)\,, & z_1\le z \\ s_{1,m}e^{-iQ_m z}-c_{1,m}e^{iQ_m z}\,, & z<z_1 \end{cases} \tag{5}$$

where $\vec{g}_m$ is a two-dimensional reciprocal lattice vector and $Q_m=[\kappa^2-(\vec{k}+\vec{g}_m)^2]^{1/2}$ or $i[(\vec{k}+\vec{g}_m)^2-\kappa^2]^{1/2}$ for $\kappa^2>(\vec{k}+\vec{g}_m)^2$ or $\kappa^2<(\vec{k}+\vec{g}_m)^2$, respectively. $\overset{(1)}{u}_{\vec{k},m}$ is a solution of the one-dimensional Schrödinger equation.[7,8]

$$\left((k+g_m)^2-\frac{\partial^2}{\partial z^2}+V_1(z)\right)\overset{(1)}{u}_{\vec{k},m}=E\overset{(1)}{u}_{\vec{k},m}\,. \tag{6}$$

The coefficients $s_{1,m}$ and $c_{1,m}$ are chosen so that $\phi_{1,m}$ and its first derivative are continuous at $z=z_1$. Similarly, for a potential that is given by $V_2(z)$ when $z<z_2$ (region IV of Fig. 1), and by V_{MTZ} in the remainder of space, a solution of Schrödinger's equation is

$$\phi_{2,m}(E,\kappa,\vec{r})=e^{i(\vec{k}+\vec{g}_m)\cdot\vec{r}}\begin{cases} \overset{(2)}{u}_{\vec{k},m}(E,z)\,, & z\le z_2 \\ s_{2,m}e^{iQ_m z}-c_{2,m}e^{-iQ_m z}\,, & z_2<z \end{cases} \tag{7}$$

where $\overset{(2)}{u}_{\vec{k},m}$ is a solution of a one-dimensional equation similar to (6). For $\kappa^2>(\vec{k}+\vec{g}_m)^2$, $\phi_{1,m}$ and $\phi_{2,m}$ are δ function normalizable, but for $\kappa^2<(\vec{k}+\vec{g}_m)^2$ they diverge unless $c_{1,m}$ and $c_{2,m}$ are both zero. Again, basis functions which are normalizable at all energies can be obtained by adding onto the ϕ functions appropriate solutions of the homogeneous Schrödinger equation, thus defining the plane-wave orbitals (PWO)

$$\chi_{1,m}(E,\kappa,\vec{r})=e^{i\vec{K}_m\cdot\vec{r}}\begin{cases} \overset{(1)}{u}_{k,m}+c_{1,m}e^{iQ_m z}\,, & z_1\le z \\ s_{1,m}e^{-iQ_m z}\,, & z<z_1 \end{cases} \tag{8a}$$

$$\chi_{2,m}(E,\kappa,\vec{r})=e^{i\vec{K}_m\cdot\vec{r}}\begin{cases} u_{k,m}^{(2)}+c_{2,m}e^{-iQ_m z}\,, & z\le z_2 \\ s_{2,m}e^{iQ_m z}\,, & z_2<z \end{cases} \tag{8b}$$

where $\vec{K}_m\equiv\vec{k}+\vec{g}_m$.

C. Expansion of the wave function

The wave function $\Psi_{\vec{k}}(E,\vec{r})$ is now expressed as a linear combination of MTO's [Eq. (4)] and PWO's [Eqs. (8a) and (8b)]

$$\begin{aligned} \Psi_{\vec{k}}(E,\vec{r})=&\sum_L A_L(\vec{k})\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\chi_L(E,\kappa,\vec{r}-\vec{R})\\ &+\sum_{i,m}A_{i,m}\chi_{i,m}(E,\kappa,\vec{r})\,, \end{aligned} \tag{9}$$

where $\vec{R}$ is a two-dimensional direct lattice vector and the index i takes on the values 1 or 2. Two features of the expansion (9) should be noted. First, $\Psi_{\vec{k}}$ is always a solution of Schrödinger's equation in the interstitial region (region II of Fig. 1) regardless of the values of the coefficients A_L and $A_{i,m}$. This follows from the definitions of χ_L and $\chi_{i,m}$. Second, for $\Psi_{\vec{k}}$ to be a solution inside the muffin-tin spheres (region I of Fig. 1) and in the exterior regions (regions III and IV of Fig. 1), all the terms proportional to solutions of the homogeneous Schrödinger equation should destructively interfere in these three regions (this is the three region "tail cancellation" condition referred to in Sec. I). This is because the u_l and $\overset{(i)}{u}_{\vec{k},m}$ functions are the exact solutions there.

The mixed MTO-PWO basis leading to Eq. (9) represents the fundamental difference between the theory presented here and Kasowski's[12] MTO formalism for films. In Kasowski's work, the wave function is a linear combination of MTO's only, and there is just a single interference condition — inside the muffin-tin spheres. As a consequence, the κ^2 parameter in Kasowski's MTO's must be restricted to being negative in order to satisfy the physical requirement that the electronic wave function vanish on going to infinity in a direction normal to the film. One is thus forced to use localized basis functions. This restriction in his theory can only be overcome by treating a hypothetical solid consisting of thin films each separated by several vacuum layers from a neighboring film. In this way, periodicity in the normal direction is restored, and an associated bulk problem must be solved. In practice, however, this method has great practical difficulties associated with the requirement that the long-range oscillating tails of the ($\kappa^2>0$) MTO's must cancel in the vacuum. In the particular case of calculating surface states, for example, Kasowski concludes that, in comparison to using localized basis functions, "a thicker film is required so that the long-range oscillating tails can cancel in vacuum."[12] Many layers may be required with the number of basis functions increasing with the number of layers. The vacuum cancellation condition is, however, an intrinsic feature of our method for *any* film thickness. Kasowski's approach, therefore, seems questionable to us. On the other hand, Kasowski[12] claims that the alternative of choosing $\kappa^2<0$ leads to good[22] results for close-packed metals such as Ni and Cu. This choice, however, leads to exponentially decaying basis functions. While the wave function does decay exponentially in a direction normal to the film, we expect oscillatory propogating behavior for the valence-band electrons in directions which are in the plane of the film. This raises the question of the accuracy of the resulting wave functions when the localized basis is used. By contrast, the theory presented here correctly describes the variation of the wave function in all space without the necessity of introducing a hypothetical solid with all the attendant difficulties. In addition, we will show in the next two sections that, for a film muffin-tin potential, our method gives the same results as a more conventional Green's-function theory.[7,8] For all these reasons we feel that our method is preferable to that developed by Kasowski.

III. RELATIONSHIP TO THE GREEN'S-FUNCTION METHOD FOR FILMS AND SURFACES

In this section we consider the relationship between our theory, which uses the mixed MTO-PWO basis described in Sec. II, and the Kar and Soven[7] and Kohn[8] generalizations of the KKR formalism. In particular, we show that, for a film muffin-tin potential [Eq. (2)], the three region tail-cancellation condition, discussed above, leads to the secular equations obtained by the method of Kar and Soven[7] and Kohn.[8] We conclude, therefore, that our three region tail-cancellation condition is the proper generalization (for films) of Andersen's[13] single tail-cancellation condition which, he shows, leads to the familiar KKR[16] equation for a bulk muffin-tin potential.

The proof of equivalence proceeds as follows. Corresponding to each of the three tail-cancellation conditions, we extract from Eq. (9) an equation containing only those terms which are proportional to a solution of the homogeneous Schrödinger equation. From these three equations, we obtain a system of linear equations for the A_L and $A_{i,m}$ coefficients of Eq. (9). This system of equations, in turn, is equivalent to those obtained by Kar and Soven[7] and Kohn.[8] A simplification of these equations is achieved by eliminating the $A_{i,m}$ coefficients in favor of the A_L coefficients. The result is a much smaller system of equations (identical to those obtained by Kar and Soven[7]) which are structurally very similar to the usual KKR equations.

To begin, we consider the interference condition in the muffin-tin spheres (for simplicity, the one at $\vec{R}=0$). For $\Psi_{\vec{k}}(E,\vec{r})$ [Eq. (9)] to be a solution in the muffin-tin spheres, we require [from Eqs. (4), (8), and (9)] that

$$\sum_L A_L(\vec{k})\left((c_l - is_l\kappa^{2l+1})J_L(\kappa,\vec{r}) - s_l\sum_{\vec{R}\neq 0}\exp(i\vec{k}\cdot\vec{R})K_L(\kappa,\vec{r}-\vec{R})\right)$$

$$+\sum_m\{A_{1,m}s_{1,m}\exp[i(\vec{K}_m\cdot\vec{r}-Q_mz)]+A_{2,m}s_{2,m}\exp[i(\vec{K}_m\cdot\vec{r}+Q_mz)]\}=0\,, \qquad (10)$$

where $J_L(\kappa,\vec{r})=i^lY_L(\hat{r})J_l(\kappa r)$ and $K_L(\kappa\vec{r})=i^lY_L(\hat{r})K_l(\kappa r)$. The summation over the direct lattice in Eq. (10) can be expressed in terms of the film structure functions $B_{L'L}(\kappa,\vec{k})$

$$-s_l\sum_{\vec{R}\neq 0}\exp(i\vec{k}\cdot\vec{R})K_L(\kappa,\vec{r}-\vec{R})=\begin{cases}-\sum_{L'}J_{L'}(\kappa,\vec{r})[s_lB_{L'L}(\kappa,\vec{k})]\,, & \kappa^2<0\\ is_l\kappa^{2l+1}J_L(\kappa,\vec{r})-\sum_{L'}J_{L'}(\kappa,\vec{r})[s_lB_{L'L}(\kappa,\vec{k})-s_lD_{L'L}(\kappa,\vec{k})]\,, & 0<\kappa^2\end{cases} \qquad (11a)$$

where

$$B_{L'L}(\kappa,\vec{k}) = 4\pi \sum_{\vec{R}\neq 0} \exp(i\vec{k}\cdot\vec{R}) \times \sum_{L''} C_{LL'L''}\kappa^{l+l'-l''} K^{A*}_{L''}(\kappa,\vec{R}), \tag{11b}$$

the auxilliary quantity $D_{L'L}$ is defined as

$$D_{L'L}(\kappa,\vec{k}) = -4\pi i\kappa^{2l+1} \sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R}) \times \sum_{L''} C_{LL'L''}\kappa^{-l+l'-l''} J^{*}_{L''}(\kappa,\vec{R}) \tag{11c}$$

and $C_{LL'L''}$ is the Gaunt coefficient

$$C_{LL'L''} = \int Y_L(\hat{r}) Y_{L'}(\hat{r}) Y_{L''}(\hat{r})\, d\Omega_{\hat{r}} . \tag{11d}$$

Here $K^A_L(\kappa,\vec{r})$ is defined as in Ref. 14

$$K^A_L(\kappa,\vec{r}) = i^l Y_L(\vec{r})\kappa^{l+1} \begin{cases} ih^{(1)}_l(\kappa r), & \kappa^2<0 \\ -n_l(\kappa r), & 0<\kappa^2 \end{cases} \tag{11e}$$

and the lattice summation in Eq. (11c) includes the site at the origin. Equations (11) were obtained with the aid of the addition theorems[13, 14]

$$K^A_L(\kappa,\vec{r}-\vec{R}) = 4\pi \sum_{L',L''} C_{LL'L''}\kappa^{l+l'-l''} \times J_{L'}(\kappa,\vec{r}) K^{A*}_{L''}(\kappa,\vec{R}), \quad |\vec{r}|<|\vec{R}| \tag{12a}$$

and

$$J_L(\kappa,\vec{r}-\vec{R}) = 4\pi \sum_{L',L''} C_{LL'L''}\kappa^{-l+l'+l''} \times J_{L'}(\kappa,\vec{r}) J^{*}_{L''}(\kappa,\vec{R}) . \tag{12b}$$

It is worth noting that, for a three-dimensional lattice, $D_{L'L}$ would vanish except on the free-electron parabola, $E=(\vec{k}+\vec{g}_m)^2$. This is not true for the two-dimensional lattice sum in Eq. (11c). The last two terms in Eq. (10) can be rewritten by expanding[23] the exponentials

$$\exp[i(\vec{K}_m \pm \vec{Q}_m)\cdot\vec{r}] = 4\pi \sum_L i^l \kappa^l J_l(\kappa r)\, Y_L(\vec{r}) Y_L(\vec{K}_m \pm \vec{Q}_m), \tag{13}$$

where we have defined $\vec{Q}_m = Q_m\hat{z}$. Substituting (11a) and (13) into (10) we obtain the system of equations

$$\sum_L A_L(\vec{k})[(c_l - is_l\kappa^{2l+1})\delta_{LL'} - s_l B_{L'L}] + \sum_L [S^{(1)}_L(\kappa,\vec{k}) + S^{(2)}_L(\kappa,\vec{k})]\delta_{LL'} = 0, \quad \kappa^2<0 \tag{14a}$$

$$\sum_L A_L(\vec{k})[c_l\delta_{LL'} - s_l B_{L'L} + s_l D_{L'L}] + \sum_L [S^{(1)}_L(\kappa,\vec{k}) + S^{(2)}_L(\kappa,\vec{k})]\delta_{LL'} = 0, \quad 0<\kappa^2 \tag{14b}$$

where the quantities $S^{(1)}_L$ and $S^{(2)}_L$ are defined in terms of the $A_{1,m}$ and $A_{2,m}$ as

$$S^{(1)}_L(\kappa,\vec{k}) = 4\pi\kappa^l \sum_m A_{1,m} s_{1,m} Y_L(\vec{K}_m - \vec{Q}_m), \tag{14c}$$

$$S^{(2)}_L(\kappa,\vec{k}) = 4\pi\kappa^l \sum_m A_{2,m} s_{2,m} Y_L(\vec{K}_m + \vec{Q}_m) . \tag{14d}$$

Note that, for an infinite three-dimensional crystal $D_{L'L}=0$, the quantities $S^{(1)}_L$ and $S^{(2)}_L$ are dropped, and Eqs. (14a) and (14b) are just the usual KKR equations. The new feature in these equations are the terms (proportional to the coefficients $A_{1,m}$ and $A_{2,m}$) which contain information about scattering from the film boundary surfaces at $z=z_1$ and z_2.

We now turn to the interference condition in the exterior regions (regions III and IV of Fig. 1). For $\Psi_{\vec{k}}(E,\vec{r})$ [Eq. (9)] to be a solution in regions III and IV, we require [from Eqs. (4), (8), and (9)] that for $z_1<z$

$$\sum_L A_L(\vec{k})\Big[-s_l \sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R}) K_L(\kappa,\vec{r}-\vec{R})\Big] + \sum_m [A_{1,m}c_{1,m} + A_{2,m}s_{2,m}] \times \exp[i(\vec{K}_m\cdot\vec{r} + Q_m z)] = 0 \tag{15a}$$

and for $z<z_2$

$$\sum_L A_L(\vec{k})\Big[-s_l \sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R}) K_L(\kappa,\vec{r}-\vec{R})\Big] + \sum_m [A_{1,m}s_{1,m} + A_{2,m}c_{2,m}] \times \exp[i(\vec{K}_m\cdot\vec{r} - Q_m z)] = 0, \tag{15b}$$

where the lattice summations include the site at the origin. It is straightforward but tedious to show that[23(a)]

$$\sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R}) K_L(\kappa,\vec{r}-\vec{R}) = \frac{2\pi i}{A} \sum_m \kappa^l \exp(i\vec{K}_m\cdot\vec{r})/Q_m \times \begin{cases} Y_L(\vec{K}_m + \vec{Q}_m)\exp(iQ_m z), & z_1<z \\ Y_L(\vec{K}_m - \vec{Q}_m)\exp(-iQ_m z), & z<z_2 \end{cases} \tag{16}$$

where A is the cross-sectional area of the unit cell. Substituting from Eq. (16) into Eqs. (15a) and (15b), we obtain the following system of equations:

$$-\frac{2\pi i}{A}\sum_{L} A_L s_l \kappa^l Y_L(\vec{K}_m+\vec{Q}_m)/Q_m + A_{1,m}c_{1,m}+A_{2,m}s_{2,m}=0\,, \tag{17a}$$

$$-\frac{2\pi i}{A}\sum_{L} A_L s_l \kappa^l Y_L(\vec{K}_m-\vec{Q}_m)\big/Q_m + A_{1,m}s_{1,m}+A_{2,m}c_{2,m}=0\,. \tag{17b}$$

The secular equations (14) and (17) are essentially equivalent to Eqs. (11a) and (11b) of Kar and Soven,[7] and Eqs. (23), (28), and (29) of Kohn.[8] Thus the zeros of the determinant of the coefficients A_L, $A_{1,m}$, and $A_{2,m}$ in these equations determine the eigenvalues $E_{\vec{k}}$ of the film.

Following Ref. 8 we further simplify this system of equations by eliminating the coefficients $A_{i,m}$ in favor of the A_L coefficients. This is done by first solving Eqs. (17a) and (17b) for the $A_{i,m}$ in terms of the A_L, and then substituting into Eqs. (14a) and (14b). The result is the much smaller system of equations

$$\sum_{L} s_l A_L \Lambda_{L'L}=0\,, \tag{18a}$$

where we have defined the quantity

$$\Lambda_{L'L}=\kappa^{l+l'+1}(i)^{l'-l} \times\begin{cases}(\cot\delta_{l,E})\delta_{LL'}+S_{L'L}+T_{L'L}\,, & 0<\kappa^2\\ (\cot\delta_{l,E}-i)\delta_{LL'}+S_{L'L}+T_{L'L}\,, & \kappa^2<0\end{cases} \tag{18b}$$

and $S_{L'L}=-\kappa^{-l-l'-1}(i)^{-l'+l}B_{L'L}$. The functions $T_{L'L}$ are given by Eqs. (A6) of the Appendix (after setting $\tau_\alpha=\tau_\beta=0$). The secular equations (18a) are essentially identical[24] to those obtained by Kar and Soven [Eq. (13) of Ref. 7].

We close this section with a few remarks regarding Eq. (18b). The matrix (18b) is formally similar to the KKR matrix for bulk materials. As in the bulk case, the structure functions $S_{L'L}$ depend only on the film crystal structure, i.e., they are independent of the film potential. By contrast, the $T_{L'L}$ functions contain information about the scattering from the boundary "surfaces," and they depend on the exterior potentials [$V_1(z)$ and $V_2(z)$] through the logarithmic derivatives at the boundary "surfaces" (Appendix). Kar and Soven[7] have discussed some technical details regarding the evaluation of both $S_{L'L}$ and $T_{L'L}$, and they have successfully applied Eqs. (18a) and (18b) to calculating the band structure of a copper monolayer.

IV. LC(MTO-PWO) METHOD FOR NON-MUFFIN-TIN POTENTIALS

An important advantage of the formalism presented here is its ability to treat deviations in the potential from the muffin-tin form. Such non-muffin-tin Hamiltonians have been successfully treated in bulk solids[14,15,20] using the LCMTO method, and the approach developed in this section is basically similar. The MTO-PWO expansion (9) is used to approximate the wave functions of a more general Hamiltonian through application of the Rayleigh-Ritz variational method[25]

$$\langle\delta\Psi\,|H-E\,|\Psi\rangle=0\,, \tag{19}$$

where the potential in Eq. (19) is not restricted to the special form (2). The trial wave functions Ψ are chosen to have the LC(MTO-PWO) form (9) for the obvious reason that, in the special case of a film muffin-tin potential, they are the exact wave functions.

A difficulty arises, however, if $\kappa^2>0$ in Eq. (9). In this case the basis functions do not decrease fast enough at infinity to make integrals [in Eq. (19)] over the potential in the exterior regions converge. This problem can be overcome if we neglect deviations in the exterior potential from the special form (2). Thus, if we continue to demand that the exterior potential depends only on the z coordinate, we can impose the exterior interference conditions [Eqs. (17a) and (17b)] as a set of linear variational constraints.[26] In this case, the integrals in the exterior regions vanish identically, since the $u^{(i)}_{\vec{k},m}$ functions [Eqs. (5) and (7)] are the exact solutions there. This restriction is not a serious limitation of our methods, since the boundary "surfaces" can be chosen at any desired distance (Fig. 1) from the surface layers of the film. We can then use the full power of the variational method to treat non-muffin-tin effects associated with the variation of the potential parallel to the plane.

In view of the preceding discussion, the trial wave functions have the following simple form within the unit cell[27] [from Eqs. (9), (12a), (12b), (17a), and (17b)]

$$\Psi_{\vec{k}}(r)=\sum_{L}A_L\phi_L(\vec{r}) + \sum_{L'}J_{L'}(\kappa,\vec{r})\Big[\sum_{L}s_lA_L\Lambda_{L'L}\Big]\,,\quad z_2<z<z_1 \tag{20a}$$

$$\Psi_{\vec{k}}(\vec{r})=\sum_{m}\exp(i\vec{K}_m\cdot\vec{r})\begin{cases}A_{1,m}u^{(1)}_{\vec{k},m}\,, & z_1<z\\ A_{2,m}u^{(2)}_{\vec{k},m}\,, & z<z_2\end{cases} \tag{20b}$$

where $\phi_L(\vec{r})$ is given by Eq. (3) and $\Lambda_{L'L}$ is given by Eq. (18b). In obtaining this representation of the wave function, we have taken advantage of the equations of constraint [Eqs. (17a) and (17b)] discussed above. This is particularly evident in Eq. (20b), i.e., Eq. (9) reduces to Eq. (20b) in the exterior regions, when the exterior interference conditions (17a) and (17b) are applied. It is also worth noting that the secular equation (18a) is nothing more than the requirement that the quantity in square brackets in Eq. (20a) vanishes, i.e., it is just the interference condition within the muffin-tin spheres. In the variational treatment of the problem, however, we do not impose this condition on the trial wave functions. Instead, for a film muffin-tin potential, this interference condition is a result of the variational calculation (as shown below). Finally, we point out that we need only Eq. (20a) in evaluating the integrals in Eq. (19), since all of the integrals in the exterior regions are constrained to vanish identically. Once a solution of Eq. (19) is found, however, and the A_L coefficients are determined, the $A_{i,m}$ coefficients can then be obtained from Eqs. (17a) and (17b). In this way, the wave function $\Psi_{\vec{k}}(\vec{r})$ is specified throughout the unit cell.

Substituting from Eqs. (20a) and (20b) into Eq. (19) we obtain, in the usual way,[28] the secular equations

$$\begin{aligned}0=\sum_L A_L\Big(&\sum_{L''}(\delta_{L'L''}+\Lambda^{\dagger}_{L'L''}t_{l''})\Lambda_{L''L}s_{l'}s_l\\&+\langle\phi_{L'}|\Delta V|\phi_L\rangle\\&+\sum_{L''}(s_l\langle\phi_{L'}|\Delta V|J_{L''}\rangle\Lambda_{L''L}+\text{h.c.})\\&+\sum_{L'',\bar{L}}s_{l'}s_l\langle J_{\bar{L}}|\Delta V|J_{L''}\rangle\Lambda^{\dagger}_{L'\bar{L}}\Lambda_{L''L}\Big),\end{aligned}\tag{21a}$$

where

$$t_l=\langle J_L(\kappa,\vec{r})|-\nabla^2+V_{\text{MT}}(r)-E\,|J_L(\kappa,\vec{r})\rangle_{\text{MT}}\,,\tag{21b}$$

and h.c. means complex conjugation plus interchange of the L and L' indices. We have defined the cellular potential as

$$V(\vec{r})=\begin{cases}V_{\text{MT}}(r)+\Delta V(\vec{r})\,, & |\vec{r}|<S\\ (E-\kappa^2)+\Delta V(\vec{r})\,, & \vec{r}\in\text{interstitial}\end{cases}\tag{22}$$

where κ may be treated as an additional variational parameter (otherwise $E-\kappa^2=V_{\text{MTZ}}$). In Eq. (22), $\Delta V(\vec{r})$ is the non-muffin-tin part of the cellular potential.

For a film muffin-tin potential $\Delta V(\vec{r})=0, E-\kappa^2=V_{\text{MTZ}}$, and the secular equations (21a) have a solution if

$$\det[(\delta_{L'L''}+\Lambda^{\dagger}_{L'L''}t_{l''})\Lambda_{L''L}]=0\,.\tag{23}$$

Since $\Lambda_{L''L}$ is a factor, the LC(MTO-PWO) secular determinant (23) yields the same energies as (18a) provided that $\Lambda_{L''L}$ is square rather than rectangular. In this case, Eq. (23) implies that $\det\Lambda=0$, which, in turn, is just the interference condition in the muffin-tin spheres [i.e., the requirement that the quantity in square brackets in Eq. (20a) vanishes]. We have thus shown that, in the limit of a film muffin-tin potential, the variational method employing the energy dependent MTO-PWO basis yields the same results as the film Green's-function method[7,8] [Eqs. (18a) and (18b)]. On the other hand, the full LC(MTO-PWO) matrix in Eqs. (21a) provides a variational estimate of the energies for non-muffin-tin Hamiltonians.

We end this section with a brief discussion of the relative rates of convergence (for a film muffin-tin potential) of the LC(MTO-PWO) method and the film Green's-function method. This is based on the above remarks regarding Eq. (23) and the equivalence of the two methods when $\Lambda_{L'L}$ is square. In an approximate calculation using the Green's-function method, only a finite number of partial waves $\phi_l(E,\vec{r})$ [Eq. (3)] are included, and higher angular momentum components are neglected. This is also true for the LC(MTO-PWO) method if $\Lambda_{L'L}$ in Eq. (23) is square rather than rectangular. When $\Lambda_{L'L}$ is rectangular, however, the LC(MTO-PWO) method includes higher angular momentum components in an approximate manner. Thus, for a given size secular determinant, we expect the energies and wave functions determined by the LC(MTO-PWO) method (23) to be better converged than those given by the Green's-function method (18a) and (18b). A direct treatment of these higher partial waves by the Green's-function method would require a secular determinant of greater size. In this connection, Williams, Janak, and Moruzzi[29] have shown that the LCMTO method[14] (for a bulk muffin-tin potential) is, essentially, just an application of Lowdin's[30] perturbation theory to the usual KKR equation, and it is in this sense that higher partial waves are approximately treated. To illustrate these considerations, we take, for example, a case where the summation over L in the trial wave function (20a) includes terms up to $l=2$ only. The summation over L', however, is usually extended to include higher angular momenta, $l'_{\text{max}}>2$. In this way, the wave function (20a) contains, in an approximate way, the contributions of higher partial waves. A direct treatment of these by the Green's-function method would require a secular determinant of greater size ($l>2$).

In view of similar considerations in the bulk case, Andersen and Kasowski[14] have argued that the LCMTO wave functions show better convergence than the KKR wave functions, especially in the outer parts of the unit cell where non-muffin-tin effects are expected to be large. They have, in fact, demonstrated the consequent advantage of the LCMTO technique in silicon[15] where the structure is open and non-muffin-tin effects are important. Similarly, we believe that, for treating general film potentials with substantial non-muffin-tin contributions, the LC(MTO-PWO) method is preferable to the Green's-function method, since the wave functions are expected to be more accurate just where the non-muffin-tin effects are apt to be strongest.

V. DISCUSSION OF CORE ORTHOGONALIZATION AND THE LINEARIZATION OF THE METHOD

There are a number of points of practical consequence related to the implementation of Eqs. (21). The first is related to the required orthogonality between the wave functions (20a) and the core states of a single muffin-tin potential. The resolution of this question is related to the linearization of the variational approach, which is necessary in order to gain computational speed for self-consistent calculations and calculations for thicker films.

Since we are no longer imposing the interference condition in the muffin-tin-spheres.

$$\sum_L s_l A_L \Lambda_{L'L} = 0 \tag{18a}$$

there is no guarantee that the wave functions (20a) will be orthogonal to the core states of the muffin-tin potential $V_{\mathrm{MT}}(r)$. As noted by Andersen and Kasowski,[14,15] this can introduce "false zeros" in the secular determinant. The inconvenience of having to identify these false zeros can be avoided by a redefinition of the MTO's and PWO's inside the muffin-tin spheres. Following Ref. 20, we replace J_L in Eq. (4a) by $\tilde{J}_L$, which is orthogonal to the core states, matches onto J_L with continuous first derivative, but is otherwise unspecified so far. In addition, we replace K_L in all the other muffin-tin spheres by $\tilde{K}_L$

$$\tilde{K}_L(\kappa, \vec{r}) = \begin{cases} 4\pi \sum\limits_{L', L''} C_{LL'L''} \kappa^{l+l'-l''} \tilde{J}_L(\kappa, \vec{r}-\vec{R}) K^*_{L''}(-\vec{R}), & |\vec{r}-\vec{R}| \le S \text{ and } \vec{R} \ne 0 \\ K_L(\kappa, \vec{r}), & \text{otherwise} \end{cases} \tag{24}$$

where we have used the addition theorems (12a) and (12b) to define $\tilde{K}_L$. From its definition, we note that $\tilde{K}_L$ matches onto K_L with continuous first derivative at the surface of all other muffin-tin spheres. Finally, we redefine the PWO [Eqs. (8a) and (8b)] within the muffin-tin spheres. Instead of

$$\begin{aligned} \chi_{1,m} &= s_{1,m} \exp[i(\vec{K}_m - \vec{Q}_m) \cdot (\vec{r} - \vec{R})] \\ &= s_{1,m}\Bigg(4\pi \sum_L i^l \kappa^l J_l(\kappa |\vec{r}-\vec{R}|) \\ &\qquad \times Y_L(\vec{r}-\vec{R}) Y_L(\vec{K}_m - \vec{Q}_m)\Bigg), \\ &\qquad\qquad |\vec{r}-\vec{R}| < S \end{aligned}$$

we define $\tilde{\chi}_{1,m}$ as

$$\begin{aligned} \tilde{\chi}_{1,m} = s_{1,m}\Bigg(4\pi \sum_L i^l \kappa^l \tilde{J}_l(\kappa |\vec{r}-\vec{R}|) Y_L(\vec{r}-\vec{R}) \\ \times Y_L(\vec{K}_m - \vec{Q}_m)\Bigg), \quad |\vec{r}-\vec{R}| < S \end{aligned} \tag{25}$$

and similarly for $\tilde{\chi}_{2,m}$. Again we note that $\tilde{\chi}_{i,m}$ ($i = 1, 2$) matches onto $\chi_{i,m}$ with continuous first derivative at the surface of the muffin-tin spheres. The net effect of all these changes is to replace J_L by $\tilde{J}_L$ in Eq. (20a) and in the muffin-tin integrals of Eqs. (21). For the special case of a film muffin-tin potential, the only change in Eq. (23) occurs in t_l. In view of the discussion after Eq. (23), the eigenvalues in this case are therefore still equal to the Green's-function eigenvalues [Eqs. (18a) and (18b)], regardless of the choice of the $\tilde{J}_L$ functions. In Refs. 12 and 15, $\tilde{J}_L$ is obtained by orthogonalizing J_L to the core states. We prefer an alternative choice proposed in Ref. 20. In that work, $\tilde{J}_l$ is proportional to the energy derivative of the partial wave $(\partial/\partial E)u_l(E, r)$, which satisfies all the requirements on $\tilde{J}_l$ but eliminates the necessity of calculating core states. This choice is particularly convenient when going over to a linearized version of Eq. (21).[31]

The linearization of the MTO method has been extensively discussed by Andersen for bulk solids[17] and molecules.[20] The procedure is basically similar for the film problem and will now be briefly outlined. The basic idea is to neglect, over a certain energy range, the energy dependence of the MTO's and PWO's. The resulting secular matrix thus becomes linear in energy

$$\det|H(\kappa)_{LL'} - EO(\kappa)_{LL'}| = 0, \tag{26}$$

where H is the Hamiltonian matrix and O is an overlap matrix. The parameter κ is treated as an energy-independent variational parameter, and Andersen[20] has found that relatively few values of κ are needed to accurately determine the minima of $E_i(\kappa)$, where i denotes the roots of the secular determinant. The eigenvalues and eigenvectors of (26) can then be simultaneously found by a simple diagonalization procedure.

APPENDIX: GENERALIZATION TO THICKER FILMS

In general, the unit cell contains more than one atom, and we denote by $\vec{\tau}_\alpha$ the spatial coordinate of the αth atom within each cell. We associate MTO basis functions $\chi_{\alpha,L}(E,\kappa,\vec{r})$ [defined as in Eq. (4a)] with each of these, and the LC(MTO-PWO) wave function (9) then becomes

$$\Psi_{\vec{k}}(E,\vec{r})=\sum_{\alpha,L}A_{\alpha,L}(\vec{k})\sum_{\vec{R}}\exp(i\vec{k}\cdot\vec{R})\times\chi_{\alpha,L}(E,\kappa,\vec{r}-\vec{R}-\vec{\tau}_\alpha)+\sum_{i,m}A_{i,m}\chi_{i,m}(E,\kappa,\vec{r})\,. \tag{A1}$$

As in Sec. III, the three region tail-cancellation condition leads to a system of linear equations for the $A_{\alpha,L}$ and $A_{i,m}$ coefficients in Eq. (A1). Thus the cancellation condition inside the muffin-tin spheres (14a) and (14b) becomes

$$\sum_{\alpha,L}A_{\alpha,L}(\vec{k})[(c_{\alpha,L}-is_{\alpha,l}\kappa^{2l+1})\delta_{L,L'}\delta_{\alpha,\beta}-s_{\alpha,l}B^{\beta\alpha}_{L'L}]+\sum_{\alpha,L}[S^{(1)}_{\alpha,L}(\kappa,\vec{k})+S^{(2)}_{\alpha,L}(\kappa,\vec{k})]\delta_{L,L'}\delta_{\alpha,\beta}=0\,,\quad \kappa^2<0 \tag{A2a}$$

$$\sum_{\alpha,L}A_{\alpha,L}(\vec{k})[c_{\alpha,l}\delta_{L,L'}\delta_{\alpha,\beta}-s_{\alpha,l}B^{\beta\alpha}_{L'L}+s_{\alpha,l}D^{\beta\alpha}_{L'L}]+\sum_{\alpha,L}[S^{(1)}_{\alpha,L}(\kappa,\vec{k})+S^{(2)}_{\alpha,L}(\kappa,\vec{k})]\delta_{L,L'}\delta_{\alpha,\beta}=0\,,\quad 0<\kappa^2 \tag{A2b}$$

and the exterior cancellation conditions (17a) and (17b) become

$$-\frac{2\pi i}{A}\sum_{\alpha,L}A_{\alpha,L}s_{\alpha,L}\kappa^l Y_L(\vec{K}_m+\vec{Q}_m)\exp(-i\vec{K}_m\cdot\vec{\tau}_\alpha)\times\exp(-iQ_m\tau_{\alpha z})Q_m^{-1}+A_{1,m}c_{1,m}+A_{2,m}s_{2,m}=0\,, \tag{A3a}$$

$$-\frac{2\pi i}{A}\sum_{\alpha,L}A_{\alpha,L}s_{\alpha,L}\kappa^l Y_L(\vec{K}_m-\vec{Q}_m)\exp(-i\vec{K}_m\cdot\vec{\tau}_\alpha)\times\exp(iQ_m\tau_{\alpha z})Q_m^{-1}+A_{1,m}s_{1,m}+A_{2,m}c_{2,m}=0\,, \tag{A3b}$$

where

$$B^{\beta\alpha}_{L'L}=4\pi\sum_{\vec{R}}\exp(i\vec{k}\cdot\vec{R})\sum_{L''}C_{LL'L''}\kappa^{l+l'-l''}K^{A*}_{L''}(\kappa,\vec{R}+\vec{\tau}_\alpha-\vec{\tau}_\beta)(1-\delta_{\alpha,\beta}\delta_{\vec{R},\vec{0}})\,, \tag{A4a}$$

$$D^{\beta\alpha}_{L'L}=-4\pi i\kappa^{2l+1}\sum_{\vec{R}}\exp(i\vec{k}\cdot\vec{R})\sum_{L''}C_{LL'L''}\kappa^{-l+l'+l''}J^{*}_{L''}(\kappa,\vec{R}+\vec{\tau}_\alpha-\vec{\tau}_\beta)\,, \tag{A4b}$$

$$S^{(1)}_{\alpha,L}=4\pi\kappa^l\sum_m A_{1,m}s_{1,m}Y_L(\vec{K}_m-\vec{Q}_m)\exp(i\vec{K}_m\cdot\vec{\tau}_\alpha)\exp(-iQ_m\tau_{\alpha z})\,, \tag{A4c}$$

$$S^{(2)}_{\alpha,L}=4\pi\kappa^l\sum_m A_{2,m}s_{2,m}Y_L(\vec{K}_m+\vec{Q}_m)\exp(i\vec{K}_m\cdot\vec{\tau}_\alpha)\exp(iQ_m\tau_{\alpha z})\,, \tag{A4d}$$

and $\tau_{\alpha z}$ is the z component of $\vec{\tau}_\alpha$. Eliminating the $A_{i,m}$ coefficients in favor of the $A_{\alpha,L}$ coefficients in Eqs. (A2a) and (A2b) we obtain the smaller system of equations

$$\sum_{\alpha,L}s_{\alpha,L}A_{\alpha,L}\Lambda^{\beta\alpha}_{L'L}=0\,, \tag{A5a}$$

where

$$\Lambda^{\beta\alpha}_{L'L}=\kappa^{l+l'+1}(i)^{l'-l}\exp[i\vec{k}\cdot(\vec{\tau}_\beta-\vec{\tau}_\alpha)]\begin{cases}(\cot\delta^{\alpha}_{l,E})\delta_{L,L'}\delta_{\alpha,\beta}+S^{\beta\alpha}_{L'L}+T^{\beta\alpha}_{L'L}\,, & 0<\kappa^2\\ (\cot\delta^{\alpha}_{l,E}-i)\delta_{L,L'}\delta_{\alpha,\beta}+S^{\beta\alpha}_{L'L}+T^{\beta\alpha}_{L'L}\,, & \kappa^2<0\end{cases} \tag{A5b}$$

The quantity

$$S^{\beta\alpha}_{L'L}=-\kappa^{-l-l'-1}(i)^{-l'+l}\exp[i\vec{k}\cdot(\vec{\tau}_\alpha-\vec{\tau}_\beta)]B^{\beta\alpha}_{L'L}\,,$$

and the functions $T^{\beta\alpha}_{L'L}$ are defined as

$$\begin{aligned}T^{\beta\alpha}_{L'L}=\frac{8\pi^2 i^{l-l'+1}}{A\kappa}\sum_m[Q_m(s_{1,m}s_{2,m}-c_{1,m}c_{2,m})]^{-1}Y_L(\vec{K}_m+\vec{Q}_m)Y_{L'}(\vec{K}_m+\vec{Q}_m)\exp[i\vec{g}_m\cdot(\vec{\tau}_\beta-\vec{\tau}_\alpha)]\\ \times(-s_{1,m}c_{2,m}(-1)^{L'}\exp[-iQ_m(\tau_{\alpha z}+\tau_{\beta z})]-s_{2,m}c_{1,m}(-1)^{L}\exp[iQ_m(\tau_{\alpha z}+\tau_{\beta z})]\\ +\{\exp[iQ_m(\tau_{\beta z}-\tau_{\alpha z})]+(-1)^{L+L'}\exp[iQ_m(\tau_{\alpha z}-\tau_{\beta z})]\}W(m))\,,\end{aligned} \tag{A6a}$$

where the quantity $W(m)$ is defined as

$$W(m)=\begin{cases}\frac{1}{2}(c_{1,m}c_{2,m}+s_{1,m}s_{2,m})\,, & K_m^2<\kappa^2\\ s_{1,m}s_{2,m}\,, & \kappa^2<K_m^2\end{cases}\tag{A6b}$$

and the coefficients $s_{i,m}$ and $c_{i,m}$ [Eqs. (8a) and (8b)] are given by

$$\begin{aligned}s_{j,m}&=[\exp(\pm iQ_m z_j)]\,(iQ_m\mp\gamma_{j,m})/(2iQ_m)\,,\quad j=1,2\\ c_{j,m}&=[\exp(\mp iQ_m z_j)]\,(-iQ_m\mp\gamma_{j,m})/(2iQ_m)\,,\end{aligned}\tag{A6c}$$

and the upper (lower) sign is taken for $j=1$ (2). The $\gamma_{j,m}$ are the logarithmic derivatives at the boundary surfaces

$$\gamma_{j,m}=(\partial/\partial z)u_{\vec{k},m}^{(j)}\big|_{z=z_j}\tag{A6d}$$

and we have set $u_{\vec{k},m}^{(j)}(z_j)=1$. $T_{L'L}^{\beta\alpha}$ thus depends on the exterior potential through the logarithmic derivatives at the boundary surfaces.

Equation (A6a) can also be written

$$\begin{aligned}T_{L'L}^{\beta\alpha}=\frac{-8\pi^2 i^{l-l'}}{A\kappa}&\\ \times\sum_m Y_L(\vec{K}_m+\vec{Q}_m)Y_{L'}(\vec{K}_m+\vec{Q}_m)&\\ \times\exp[i\vec{g}_m\cdot(\vec{\tau}_\beta-\vec{\tau}_\alpha)]\,M_{L'L}^{\beta\alpha}(m)/\Delta_m Q_m&\end{aligned}\tag{A7}$$

which has the same form as Eq. (A20) of Kar and Soven.[7] The quantity Δ_m is identical to that given by Eq. (A21) of Ref. 7, and the quantity $M_{L'L}^{\beta\alpha}$ is identical to that given by Eqs. (A22) and (A23) of Ref. 7. There appear to be some minor errors of transcription in Ref. 7. Thus

$$M_{L'L}^{\beta\alpha}(m)=i\bar{M}_{L'L}^{\beta\alpha}(m)\,,\quad K_m^2<\kappa^2, L+L'\ \text{odd}$$

$$M_{L'L}^{\beta\alpha}(m)=i\,\exp(-Q_m D)\bar{M}_{L'L}^{\beta\alpha}(m)\,,\quad \kappa^2<K_m^2$$

where $\bar{M}$ is given by Eqs. (A22) and (A23) of Ref. 7 and $D=z_1-z_2$.

Finally, we display the generalization of Eqs. (21a) and (21b), the secular equation used to treat general potentials including non-muffin-tin effects:

$$\begin{aligned}0=\sum_{\alpha,L}A_{\alpha,L}\Big(&\sum_{\beta,L''}(\delta_{\alpha',\beta}\delta_{L',L''}+\Lambda_{L'L''}^{\dagger\alpha'\beta}t_{l''}^{\beta})\Lambda_{L'',L}^{\beta\alpha}s_{\alpha',l}s_{\alpha,l}+\langle\phi_{\alpha',L'}|\Delta V^{\alpha'}|\phi_{\alpha,L}\rangle\delta_{\alpha',\alpha}\\ &+\sum_{L''}(s_{\alpha,l}\langle\phi_{\alpha',L'}|\Delta V^{\alpha'}|J_{L''}\rangle\Lambda_{L''L}^{\alpha'\alpha}+\text{h.c.})+\sum_{\beta,L'',\bar{L}}s_{\alpha',l'}s_{\alpha,l}\langle J_{\bar{L}}|\Delta V^{\beta}|J_{L''}\rangle\Lambda_{L'\bar{L}}^{\dagger\alpha'\beta}\Lambda_{L''L}^{\beta\alpha}\Big)\,,\end{aligned}\tag{A8a}$$

where

$$t_l^{\alpha}=\langle J_l(\kappa,\vec{r})|-\nabla^2+V_{\text{MT}}^{\alpha}(r)-E|J_l(\kappa,\vec{r})\rangle_{\text{MT}}\tag{A8b}$$

and h.c. means complex conjugation plus interchange of the α, L indices with the α', L' indices. We have defined a cellular potential

$$V(\vec{r})=\sum_{\beta,\vec{R}}V^{\beta}(\vec{r}-\vec{R}-\vec{\tau}_\beta)\,,$$

where V^β is nonzero only within the atomic Wigner-Seitz (AWS) cell centered at $\vec{\tau}_\beta$ In analogy with Eq. (22) V^β is defined as

$$V^{\beta}(\vec{r})=\begin{cases}V_{\text{MT}}^{\beta}(r)+\Delta V^{\beta}(\vec{r})\,, & |\vec{r}|<S_\beta\\ (E-\kappa^2)+\Delta V^{\beta}(\vec{r})\,, & S_\beta<|\vec{r}|\,.\end{cases}$$

Thus the angular brackets $\langle X|\Delta V^{\alpha}|Y\rangle$ in Eq. (A8a) denote one center cellular integrals

$$\int X^*(\vec{r})\Delta V^{\alpha}(\vec{r})Y(\vec{r})\,d^3r\,,\quad \text{AWS cell at } \vec{\tau}_\alpha$$

and the integral in Eq. (A8b) extends only over the muffin-tin sphere in the αth AWS cell.

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[16] W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954); J. Korringa, Physica (Utr.) 13, 392 (1947).

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κ vanishes in the interstitial region. As pointed out in this reference, this is a poor assumption for open structures.

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[19] See, for example, Refs. 14 and 15. Particularly noteworthy, is the successful calculation of the electronic band structure of silicon, reported in Ref. 15.

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[21] This film potential is the same as that of Refs. 7 and 8.

[22] There is, however, a substantial discrepancy between his energy eigenvalues for a copper monolayer and those of Kar and Soven (Ref. 7) and of Cooper (Refs. 1, 2, and 4) both of which are in close agreement (Ref. 4) with each other.

[23] As noted in Ref. 7, this expansion is valid for both real and imaginary $\vec{Q}_m$. (a) When $L=0$ ($l=0$, $m=0$), Eq. (16) becomes an identity for the two-dimensional Green's function previously derived by Kambe in Z. Naturforsch. A 22, 422 (1967) [Eqs. (34), (42), (A11)]. Equation (16) is derived by making use of the following relationship:

$$\int_{r=\eta}^{\infty} \exp(-i\vec{k}\cdot\vec{r})K_L(\kappa+i\delta,\,\vec{r})\,d^3r$$

$$=[k^2-(\kappa+i\delta)^2]^{-1}$$

$$\times\int_{r=\eta}^{\infty}[\exp(-i\vec{k}\cdot\vec{r})\nabla^2 K_L(\kappa+i\delta,\vec{r})$$

$$-K_L(\kappa+i\delta,\vec{r})\nabla^2\exp(-\vec{k}\cdot\vec{r})]\,d^3r$$

$$=\frac{4\pi Y_L(\vec{k})}{k^2-(\kappa+i\delta)^2}\{K_l[(\kappa+i\delta)\eta],j_l(k\eta)\}$$

and thus

$$K_L(\kappa,\vec{r}-\vec{R})=\lim_{\substack{\eta\to 0\\ \delta\to 0}}(2\pi)^{-3}\int\exp[i\vec{k}\cdot(\vec{r}-\vec{R})]\frac{4\pi Y_L(\vec{k})}{k^2-(\kappa+i\delta)^2}$$

$$\times\{K_l[(\kappa+i\delta)\eta],j_l(k\eta)\}\,d^3k$$

$$=(2\pi)^{-2}\int\exp[i\vec{k}_{\parallel}\cdot(\vec{r}\cdot\vec{R})]$$

$$\times\left[2\pi i\kappa^l\exp(iQ_{\parallel}|z|)Q_{\parallel}^{-1}Y_L\left(\vec{k}_{\parallel}+Q_{\parallel}\frac{z}{|z|}\hat{z}\right)\right]d^2k_{\parallel}\ ,$$

where

$$\{K_l(\kappa r),j_l(kr)\}\equiv r^2\left(K_l(\kappa r)\frac{\partial}{\partial r}j_l(kr)-j_l(kr)\frac{\partial}{\partial r}K_l(\kappa r)\right)$$

$\vec{k}=\vec{k}_{\parallel}+\vec{k}_z$, and $Q_{\parallel}=(\kappa^2-k_{\parallel}^2)^{1/2}(i(k_{\parallel}^2-\kappa^2)^{1/2})$ when $\kappa^2>k_{\parallel}^2$ $(\kappa^2<k_{\parallel}^2)$.

[24] There appear to be some minor errors of transcription in Ref. 7. This is discussed in the Appendix.

[25] A. Messiah, *Quantum Mechanics*, Vol. 2 (North-Holland, Amsterdam, 1968), p. 762.

[26] These difficulties were handled in an analogous manner by Andersen and Wooley (Ref. 20) in developing their MTO molecular formalism.

[27] Since the addition theorem (12a) holds only for $|\vec{r}|<|\vec{R}|$, we have implicitly assumed that $|\vec{r}|$ is less than the nearest-neighbor distance in deriving Eq. (20b). This is not a necessary assumption, since there exist alternative representations for the wave function in the interstitial region. One of these, a reciprocal lattice representation, may in fact prove more convenient for evaluating the interstitial integrals occurring in Eq. (19) (see, for example, the discussion on p. 3072 of Ref. 17).

[28] See Ref. 20, for example.

[29] A. R. Williams, J. F. Janak, and V. L. Moruzzi, Phys. Rev. B 6, 4509 (1972), Appendix C.

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[31] For a detailed discussion of such a linearized scheme see Refs. 17 and 20. This choice $\tilde{J}_L$ was successfully used in Ref. 18.