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Generalized non-muffin-tin band theory

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A new way of applying the non-spherically-symmetric phase-functional method of Williams and van Morgan to the band-structure problem is derived that results in a generalized (non-muffin-tin) Green's-function band theory that is variationally stationary and exact in the single-electron, local-potential approximation. The "near-field" correction, believed to destroy the separability of Green's-function band theories, is implicitly included in the non-spherically-symmetric phase-functional basis. This basis is discussed in some detail as we correct an error in the previous work of Williams and van Morgan. Using this basis to expand the crystal wave function, we obtain an equation that is the most general expression of Green's-function band theory. This equation contains a sum over the structure constants of the Korringa-Kohn-Rostoker method and two "phase functions" (corresponding to the cosine and sine of the nondiagonal partial-wave phase shifts) that are independently calculable; hence the effects of structure and cellular potential completely separate. The variational procedure of Kohn and Rostoker then yields a secular determinant that can be solved for the non-muffin-tin bands and wave functions; the resulting theory is suitable for self-consistent-field applications.

I. INTRODUCTION

One of the principal requirements for performing a calculation of the macroscopic properties of a crystalline solid is an adequate knowledge of the microscopic quantum states of the crystal. This is because the bulk properties seem to depend, occasionally quite sensitively, on the details of the electronic states rather than the average over those details. Various approximational schemes have been developed to determine the quantum states and their associated energy spectra (the electron bands), but most of these theories rely heavily on the so-called muffin-tin (MT) potential. In this approximation, the potential is assumed to be nonzero only inside a spherical domain inscribed in the Wigner-Seitz (WS) cells of the crystal, and is often assumed to be spherically symmetric as well, though that requirement has been softened in the last ten years.[1]

Even for those crystals where the MT approximation seems to be well justified *a posteriori*, it is not a desirable restriction. In atomic physics, the "best" solutions to the single-electron time-independent Schrödinger equation are the variationally stationary self-consistent field (SCF) solutions that result in an electronic charge distribution that reproduces the potential used.[2] SCF band-structure calculations are indeed possible in the MT approximation; however, it is well known that the results do not adequately describe any system where there is substantial anisotropy in either the potential or the charge density distribution. A useful review article by Koelling[3] discusses the SCF energy-band techniques and their shortcomings; two of the weak spots in virtually all the techniques currently used are the lack of a generally usable basis set and the muffin-tin approximation. We wish to quote a phrase from Koelling's paper that emphasizes this latter point: "So, although the inclusion of non-muffin-tin effects has often been discussed, the additional calculational effort involved has often caused them to be neglected in practice."[4]

In order to perform the highly desirable non-muffin-tin SCF band-structure calculations, it is first necessary to have a theory that allows the calculation of energy bands from non-muffin-tin (NMT) crystal potentials in a straightforward, economically feasible manner. It is this need that primarily motivates our work. As a bonus, the basis used is quite generally applicable and should go a long way towards eliminating the guesswork from a calculation (i.e., does the basis used adequately approximate this particular problem? etc.).

This paper develops a generalized (NMT) band theory corresponding to the Korringa-Kohn-Rostoker[5,6] (KKR) or Green's-function technique for separating the structure-linked and potential-linked aspects of the problem. It is based on solving Schrödinger's differential equation via an inhomogeneous Fredholm integral equation of the second kind with the appropriate Green's function. The crystal solution is directly constructed from a multiple-scattering equation so that it satisfies Bloch boundary conditions on the surface of the WS cell, and the matrix elements of the Hamiltonian never explicitly appear.

The method of solution is to expand the crystal wave function sought in a set of basis functions that are themselves integral equation solutions to Schrödinger's equation. These basis functions are the so-called "phase functional" solutions to the Schrödinger equation with the correct, non-spherically-symmetric potential supported on the smallest sphere circumscribing the cell (called the bounding or circumscribing sphere in the text). The result is a secular determinant with all the advantages of the KKR determinant, i.e., independent calculation of the structure constants and the scattering matrix, and a spherical harmonic representation. This method of calculation does not require the MT approximation as it matches the boundary conditions imposed on the solution at the surface of the circumscribed, rather than the inscribed sphere.

The phase-functional solutions used as a basis are non-spherically-symmetric generalizations of the phase-functional solutions of Calogero,[7] Babikov,[8] and others. Nonspherical phase-functional (PF) solutions similar to the ones we derive were first used by Williams and van Morgan (WM),[9] who used multiple scattering off the full cellular potential to derive a secular determinant of the same general form as our own. They obtained preliminary results that were quite promising in several artificial problems; however, as was pointed out by Ziesche[10] and Faulkner,[11] they neglected what has been called the "near-field" correction that arises from the region where the bounding sphere overlaps the nearest-neighbor cell. Inclusion of this effect has always led to the elimination of the clean separation of the effects of structure and potential, which is the principle desirable feature of Green's-function band theories. Our procedure differs from WM's in the following three ways:

(a) Our PF solutions are constructed using the crystal potential throughout the bounding sphere. We demonstrate that these solutions form a complete, linearly independent set of functions in terms of which an "arbitrary" solution (to Schrödinger's equation at the same energy) can be uniquely expanded, subject to an easily verified determinantal condition. We were unable to construct a similar completeness argument for the basis functions of WM, and it seemed to us that they were not the best functions to use to expand the solutions sought.

(b) We avoid the use of their three-center expansions of the Green's function from which they obtain the structure constants. In WM's derivation they reorder an infinite sum; we were able to extend their argument and show that such a reordering implies that the standard expansion of the Green's function in free spherical waves [see Eq. (2.13)] can be written with the arguments in either order. While this may be algebraically true, the infinite sums so expressed no longer converge, which suggests that WM's terms containing the structure constants might be divergent when summed (see Appendix A). We were able to manipulate the equation arising from matching solutions on the bounding sphere (which *does not* diverge when summed) into a form that appears to match solutions on the surface of the cell but contains the effects of structure and potential in a completely separable form.

(c) We use the full variational procedure of Kohn and Rostoker (KR) to ensure that our energy bands are correct to second order in the error in our wave functions. While we could have used a projective argument similar to that of WM and obtained essentially the same secular determinant, such an approach would not guarantee us second-order accuracy, nor would it explicitly check for completeness and orthogonality to core states as the variational procedure does. Finally, a projective argument involving spherical harmonics is not generally valid when applied to an equation derived only for $\vec{r}$ restricted to a nonspherical domain.

To summarize our procedure, we use a set of PF expansion functions defined on the bounding sphere (see Sec. II). They are computable by solving a set of coupled ordinary differential equations from the origin to the bounding sphere. They can easily be shown to be complete and linearly independent subject to a determinantal condition; therefore, they already contain the effects of the near field. We use these functions to solve a second set of ordinary differential equations in parallel with the first solution (see Sec. III). They are derived from the integral equation solution to Schrödinger's equation for the whole crystal. This equation, after suitable manipulation, becomes the fundamental equation of Green's-function (or multiple-scattering) band theory and contains the structure constants of KKR in a completely separable form. It is converted (via the variational procedure of KR) into a secular determinant; the energies for which this determinant is zero are the band energies $\epsilon(\vec{k})$. The secular equation can then be solved for the expansion coefficients of the actual crystal wave function on the cell and the results stored for a SCF calculation in, for example, the local density functional formalism of Kohn and Sham.[12]

The computational advantages of the theory are that the structure constants are the readily accessible, well-understood ones of KKR. They can either be tabulated or dynamically computed in the course of an actual calculation,[13,14] and carry all the information inherent in the lattice structure. For $\vec{k}$ vectors possessing some symmetry, the secular determinant can be quite small, yet the convergence should still be good due to the angular momentum cutoff intrinsic to scattering off a domain with bounded support. Two sets of coupled differential equations must be solved once at each energy. However, as we shall explain in Appendix B, much of the integration can be done in parallel, and the whole thing should not take much more time than solving a single set of coupled equations. Finally, the possibility exists of constructing a linearized version of this theory along the lines of the existing linearized muffin-tin-orbital[15] or the linearized-KKR (Ref. 16) theories which may substantially reduce the storage required to perform a SCF calculation and reduce the time necessary to calculate the bands, but only experience can determine the accuracy of the results so obtained. We defer the development of such a theory to the time when the algebraic results of this paper are thoroughly tested.

Two points of potential numerical difficulty are discussed in the text. First of all, a term that would diverge if summed independently is added and subtracted under the summation of our secular equation. It is folded into two terms so that it is ultimately cancelled out; however, one of the two terms is a summation over the structure constants, the other is an independently obtained number. This cancellation (*before* the equation is summed) must therefore depend, in a nontrivial manner, on the convergence of the sum over the structure constants. We feel, because of the angular-momentum cutoff, that this sum will converge rapidly enough to eliminate the divergence in all but pathological cases (this is discussed in substantially more detail at the end of Sec. III). This feeling is borne out by the test cases of WM which checked, among other things, the convergence properties of secular determinants of the same form as our own. However, only testing the theory in actual applications will determine if and when trouble may result. We expect, for physical reasons, that our theory will be sufficiently rapidly convergent to be of use in most cases of physical interest. The second problem is related to the first and concerns the decomposition of the crystal potential in spherical harmonics. This can be done numerically with a quadrature, and will converge rapidly enough to ensure good results if the potential is sufficiently smooth (this also was verified by WM) inside the bounding sphere. Geometrical considerations indicate that the bounding sphere only penetrates about 20% of the distance from the cell boundary to the nearest-neighbor nucleus in an fcc or bcc lattice; this is sufficiently far away from the nearest-neighbor nucleus that the potential in the outer part of the sphere should be largely screened from the deep nuclear potential of the neighboring atom, and hence we expect its expansion to converge at an acceptable rate.

This paper is intended to indicate that non-muffin-tin Green's-function band-structure calculations, previously thought to be impractical because the near-field correction seemed to destroy the separation between structure and potential, may in fact be economically and numerically feasible. The reasons are detailed in the paper and are linked to a technique for extending a "boundary-value problem" on the WS cell to the bounding sphere using the phase-functional approach to multiple scattering. We are currently engaged in the necessary process of testing this approach numerically in a variety of cases of increasing difficulty and hope to report on our results in the near future.

II. THE PHASE-FUNCTIONAL BASIS

We seek solutions to Schrödinger's equation,

$$(\nabla^2+\kappa^2)\phi(\vec{r})=V(\vec{r})\phi(\vec{r}) \;, \tag{2.1}$$

defined on some domain Ω with bounded support. Using a Green's function for the inhomogeneous equation (2.1) that satisfies the differential equations

$$\begin{aligned}(\nabla_0^2+\kappa^2)G(\vec{r},\vec{r}_0)&=(\nabla^2+\kappa^2)G(\vec{r},\vec{r}_0)\\ &=\delta(\vec{r}-\vec{r}_0) \;,\end{aligned} \tag{2.2}$$

we construct the integral-equation solution to Schrödinger's equation,[17]

$$\phi(\vec{r})=-\int_{\partial\Omega}[G(\vec{r},\vec{r}_0)\vec{\nabla}_0\phi(\vec{r}_0)-\phi(\vec{r}_0)\vec{\nabla}_0G(\vec{r},\vec{r}_0)]\cdot d\vec{S}_0+\int_{\Omega}G(\vec{r},\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0 \;. \tag{2.3}$$

We define

$$\chi(\vec{r})=-\int_{\partial\Omega}[G(\vec{r},\vec{r}_0)\vec{\nabla}_0\phi(\vec{r}_0)-\phi(\vec{r}_0)\vec{\nabla}_0G(\vec{r},\vec{r}_0)]\cdot d\vec{S}_0 \tag{2.4}$$

to be the *boundary* or *inhomogeneous term* of the Fredholm integral equation of the second kind [Eq. (2.3)]. $\chi(\vec{r})$ is generally a complicated functional of the boundary conditions and the shape of the boundary; we therefore seek a simpler representation that is more appropriate to quantum theory. We let Ω go to all space and choose zero boundary conditions on the boundary $\partial\Omega$. Then

$$\phi(\vec{r})=\int_{R^3} G(\vec{r},\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0 \tag{2.5}$$

is the solution over all space (Euclidean 3-space). We can break the integral into two distinct pieces and write

$$\phi(\vec{r})=\int_{R^3-\Omega} G(\vec{r},\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0+\int_{\Omega} G(\vec{r},\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0 \; . \tag{2.6}$$

If we restrict $\vec{r}\in\Omega$, then we see that

$$\begin{aligned}\chi(\vec{r})&=-\int_{\partial\Omega}[G(\vec{r},\vec{r}_0)\vec{\nabla}_0\phi(\vec{r}_0)-\phi(\vec{r}_0)\vec{\nabla}_0 G(\vec{r},\vec{r}_0)]\cdot d\vec{S}_0\\ &=\int_{R^3-\Omega} G(\vec{r},\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^2r_0\end{aligned} \tag{2.7}$$

must satisfy the Helmholtz equation for $\vec{r}\in\Omega$,

$$(\nabla^2+\kappa^2)\chi(\vec{r})=0 \; . \tag{2.8}$$

We know from Fredholm's theorems[18,19] that $\chi(\vec{r})$ uniquely determines the solution $\phi(\vec{r})$ (except at eigenenergies). We are limited in our choice of $\chi(\vec{r})$ by the requirements of quantum theory; only those $\chi(\vec{r})$ that lead to solutions $\phi(\vec{r})$ that are square integrable over all space are candidates. Equation (2.7) implicitly contains this restriction via $\phi(\vec{r})V(\vec{r})$ integrated over all space while (2.4) does not. For this reason we will work exclusively with this (multiple-scattering) formulation rather than the "boundary-value" formulation implicit in (2.3). The axioms of quantum mechanics always apply to the "global" wave function while for obvious reasons we prefer to work within "local" regions of space. However, we really do not have that much freedom to choose boundary conditions on a domain with bounded support in quantum mechanics and should work with equations that directly reflect that fact. The advantages of the PF basis is that it explicitly spans *all* the axiomatically allowed solutions on a finite domain without requiring detailed information about the potential or wave function outside the domain (except to know that they exist and are reasonably well behaved).

We will work with the stationary wave Green's function

$$\begin{aligned}G_0(\vec{r},\vec{r}_0)&=\tfrac{1}{2}[G_+(\vec{r},\vec{r}_0)+G_-(\vec{r},\vec{r}_0)]\\ &=-\frac{1}{4\pi}\frac{\cos(\kappa\,|\,\vec{r}-\vec{r}_0\,|\,)}{|\,\vec{r}-\vec{r}_0\,|} \; ,\end{aligned} \tag{2.9}$$

where G_+ and G_- are the usual outgoing and incoming wave Green's functions.[20] Note the implicit energy dependence ($\epsilon=\kappa^2$). All the results of this section can easily be extended to more general problems by using a more general form of the Green's function with the time dependence appropriate to the particular problem of interest, expanded in the free spherical waves defined by the regular and irregular solutions to

$$(\nabla^2+\kappa^2)F_L(\vec{r})=0 \; . \tag{2.10}$$

We will work in spherical coordinates and index our solutions with the composite label $L=(l,m)$; the usual regular and irregular solutions are then

$$J_L(\vec{r})=j_l(\kappa r)Y_L(\hat{r}) \tag{2.11a}$$

and

$$N_L(\vec{r})=n_l(\kappa r)Y_L(\hat{r}) \; , \tag{2.11b}$$

where $j_l(\kappa r)$ is the regular spherical Bessel function and $n_l(\kappa r)$ is the irregular spherical Neumann function of the lth order. We see that

$$G_0(\vec{r},\vec{r}_0)=-\frac{\kappa}{\sqrt{4\pi}}N_0(\vec{r}-\vec{r}_0) \tag{2.12}$$

from which we may conclude, via the addition theorems for spherical harmonics[21] and Bessel functions,[22] that

$$G_0(\vec{r},\vec{r}_0)=-\kappa\sum_L N_L(\,|\,\vec{r}_>\,|\,)J_L^*(\,|\,\vec{r}_<\,|\,) \; , \tag{2.13}$$

where $|\,\vec{r}_>\,|$ is the greater of the two arguments and $|\,\vec{r}_<\,|$ is the lesser. The restriction on the size of the arguments is *absolutely necessary* in order for the expansion to converge.

Now let us examine $\chi(\vec{r})$ for $\vec{r}\in\Omega$. By Eq. (2.7) with the use of expansion (2.13),

$$\begin{aligned}\chi(\vec{r})&=\int_{R^3-\Omega} G_0(\vec{r},\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0\\ &=-\kappa\sum_L\left[J_L(\vec{r})\int_{r\atop(R^3-\Omega)}^{\infty} N_L^*(\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0+N_L(\vec{r})\int_{0\atop(R^3-\Omega)}^{r} J_L^*(\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0\right]\end{aligned} \tag{2.14}$$

or

$$\chi(\vec{r})=\sum_L[C^{\omega}_{\chi L}(r)J_L(\vec{r})+S^{\omega}_{\chi L}(r)N_L(\vec{r})]\ , \quad (2.15)$$

where we define

$$C^{\omega}_{\chi L}(r)=-\kappa\int_{r\ (R^3-\Omega)}^{\infty} N_L^*(\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0\ , \quad (2.16a)$$

$$S^{\omega}_{\chi L}(r)=-\kappa\int_{0\ (R^3-\Omega)}^{r} J_L^*(\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0\ . \quad (2.16b)$$

The condition $R^3-\Omega$ on the integral indicates the restriction of the domain of integration to $\vec{r}_0\in R^3-\Omega$; the limits of the integrals are constructed so that the Green's-function expansions *converge* for any $\vec{r}\in\Omega$. (Note that, in practice, restricting the domain of the integration means multiplying the potential by a unit step function with the shape of the domain and then integrating over all angles in the expressions above, leaving us with the radial integral whose limits are indicated explicitly.)

This is the variable-phase, or phase-functional (PF), construction. It always involves two radially-dependent functions called the "phase functions" $C^{\omega}_{\chi L}(r)$ and $S^{\omega}_{\chi L}(r)$, that arise from the breakup of the integral equation required for the expansion of the Green's function appearing under the integral sign to converge. We shall treat it in more detail momentarily for the integral over Ω, where it is more relevant.

Let us examine Eqs. (2.15) and (2.16). The phase function $S^{\omega}_{\chi L}(r)$ must be zero when $r\rightarrow 0$ so that $\chi(\vec{r})$ remains regular (and hence square integrable) on Ω. It will remain zero out to the radius of the inscribed sphere. The phase function $C^{\omega}_{\chi L}(r)$ as $r\rightarrow 0$ has been integrated over all space outside Ω, and so becomes a constant, not generally equal to zero, for r inside the inscribed sphere. Both $C^{\omega}_{\chi L}(r)$ and $S^{\omega}_{\chi L}(r)$ will continuously *vary* for all r between the inscribed sphere and ∞. Therefore, no form simpler than (2.15) exists for $\chi(\vec{r})$ if r is greater than the radius of the inscribed sphere, and (2.15), with its varying coefficients, is very difficult to work with. Recall that we wish to use $\chi(\vec{r})$ to uniquely determine $\phi(\vec{r})$ for $\vec{r}\in\Omega$; if $\chi(\vec{r})$ is an expansion with variable coefficients [i.e., (2.15)] for some $\vec{r}\in\Omega$, we will not be able to use linear algebra to find the correct solution.

The situation simplifies if the surface $\partial\Omega$ and the inscribed sphere coincide. If Ω is a spherical domain, then we may conclude from the arguments above that

$$\chi(\vec{r})=\sum_L C^{s}_{\chi L}(\infty)J_L(\vec{r}) \quad (2.17)$$

for *all* $\vec{r}\in\Omega$. (The coefficient is a constant for a spherical domain. The reason for the ∞ designation will shortly be apparent.) *Only* for a spherical domain Ω or a domain where the *actual potential* defined on all space, $V(\vec{r})$, is *zero* in the region between the bounding sphere and Ω [see Eqs. (2.16) and Fig. 1] can we write $\chi(\vec{r})$ in the form (2.17).

We find that the integral equation solution to an "arbitrary" boundary value problem in quantum mechanics is [from (2.5) and (2.7)] for $\vec{r}\in\Omega$

$$\phi(\vec{r})=\chi(\vec{r})+\int_{\Omega}G_0(\vec{r},\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0 \quad (2.18)$$

or

$$\phi(\vec{r})=\sum_L C^{s}_{\phi L}(\infty)J_L(\vec{r}) + \int_S G_0(\vec{r},\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0 \quad (2.19)$$

if S is a spherical domain and $\vec{r}\in S$. Note that the simple form of (2.19) arises from the spherical shape of S, and $V(\vec{r})$ in this expression must be the *same* $V(\vec{r})$ appearing in (2.1) everywhere in S. This is an error made by WM in Eq. (2.5) of Ref. 9. They constructed a set of solutions with the form of (2.19) where they truncated the Schrödinger potential at the edge of some nonspherical domain, expecting to obtain the effect of the potential and wave function outside the domain from multiple scattering. However, as we have seen, this effect is phase functional (i.e., the phase functions vary) for various $\vec{r}$ *inside* the domain and *cannot* in general be represented by a linear combination like (2.17). Thus their equations appear to be unable to represent *any* solutions to (2.1) (where the potential is defined over all space and the wave function is a permissible one) restricted to a nonspherical domain, as those solutions (except for the trivial one) cannot have the form of (2.19). The correct form of (2.18) for a nonspherical domain must be

$$\phi(\vec{r})=\sum_L[C^{\Omega}_{\phi L}(r)J_L(\vec{r})+S^{\Omega}_{\phi L}(r)N_L(\vec{r})] + \int_{\Omega}G_0(\vec{r},\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0 \quad (2.20)$$

for $\vec{r}\in\Omega$, where the phase functions $C^{\Omega}_{\phi L}(r)$ and $S^{\Omega}_{\phi L}(r)$ must contain the information in $V(\vec{r})$ and $\phi(\vec{r})$ integrated over all $R^3-\Omega$. [Alternatively, they contain functionally the boundary conditions imposed on $\phi(\vec{r})$ at $\partial\Omega$, which is equivalent to the other from integrating by parts twice over $R^3-\Omega$, with suitable asymptotic conditions at ∞.]

We are now ready to define and construct the PF basis on a spherical domain S. By basis we mean a set of solutions to the Schrödinger equation (2.1) at a given energy ϵ, restricted to the domain S, which is complete in the sense that any allowed solution to

(2.1) at the same energy also restricted to S can be expanded as a unique linear combination of these solutions.[23] We require the domain S to be spherical so that we can exploit the simplicity of $\chi(\vec{r})$ in (2.19); once we construct the PF basis we will be able to seek a particular solution working only with the $\chi(\vec{r})$'s. Thus it is very important to obtain a simple, linear expression like (2.17) to work with.

The PF basis will consist of those solutions of the form (2.19) that behave like free, regular spherical waves at the origin. We index the solutions with the label L such that

$$\lim_{r\to 0}\phi_L(\vec{r})=J_L(\vec{r}) \tag{2.21}$$

and

$$\phi_L(\vec{r})=\sum_{L'}C^s_{LL'}(\infty)J_{L'}(\vec{r}) + \int_S G_0(\vec{r},\vec{r}_0)V(\vec{r}_0)\phi(\vec{r}_0)d^3r_0 \,. \tag{2.22}$$

As before, we use expansion (2.13) and break the integral in (2.22) into two parts to ensure the convergence of the Green's-function expansion. We get

$$\phi_L(\vec{r})=\sum_{L'}\left[C^s_{LL'}(\infty)J_{L'}(\vec{r})-\kappa J_{L'}(\vec{r})\int_{\substack{r\\(S)}}^{\infty}N^*_{L'}(\vec{r}_0)V(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0-\kappa N_{L'}(\vec{r})\int_{\substack{0\\(S)}}^{r}J^*_{L'}(\vec{r}_0)V(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0\right] \tag{2.23}$$

or

$$\phi_L(\vec{r})=\sum_{L'}[C^s_{LL'}(r)J_{L'}(\vec{r})+S^s_{LL'}(r)N_{L'}(\vec{r})] \tag{2.24}$$

with

$$C^s_{LL'}(r)=C^s_{LL'}(\infty)-\kappa\int_{\substack{r\\(S)}}^{\infty}N^*_{L'}(\vec{r}_0)V(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0 \,, \tag{2.25a}$$

$$S^s_{LL'}(r)=-\kappa\int_{\substack{0\\(S)}}^{r}J^*_{L'}(\vec{r}_0)V(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0 \,, \tag{2.25b}$$

where our use of the notation $C^s_{LL'}(\infty)$ is manifestly justified. Equation (2.24) defines the PF basis, and Eqs. (2.25) define the phase functions. It is now easy to see that the $C^s_{LL'}(r)$ and $S^s_{LL'}(r)$ are the nondiagonal equivalents of the cosine and sine of the partial-wave-phase shift of ordinary scattering theory. They are defined so the partial-wave phases are zero at the origin, so that the condition (2.21) appears as the boundary conditions

$$C^s_{LL'}(0)=\delta_{LL'} \tag{2.26a}$$

and

$$S^s_{LL'}(0)=0 \,. \tag{2.26b}$$

The "scattering matrix" defined by Eqs. (2.25) is nondiagonal because a non-spherically-symmetric potential mixes partial waves with different L. These equations [(2.22)–(2.26)] provide a marvelously flexible framework in terms of which a problem in quantum mechanics can be expressed and solved.

Let us prove the conditional completeness and independence of the PF basis. This can be done by noting that an arbitrary solution to Schrödinger's equation on S can be written [via (2.19)]

$$\psi(\vec{r})=\sum_{L}C^s_{\psi L}(\infty)J_L(\vec{r}) + \int_{(S)}G_0(\vec{r},\vec{r}_0)V(\vec{r}_0)\psi(\vec{r}_0)d^3r_0 \,. \tag{2.27}$$

We seek a set of coefficients $\{a_L\}$ such that

$$\psi(\vec{r})=\sum_{L}a_L\phi_L(\vec{r}) \,. \tag{2.28}$$

But then [with the use of (2.22)]

$$\begin{aligned}\psi(\vec{r})&=\sum_{L}a_L\phi_L(\vec{r})=\sum_{L}a_L\left[\sum_{L'}C^s_{LL'}(\infty)J_{L'}(\vec{r})+\int_{(S)}G_0(\vec{r},\vec{r}_0)V(\vec{r}_0)\phi_L(\vec{r})d^3r_0\right]\\&=\sum_{L'}\left[\sum_{L}a_LC^s_{LL'}(\infty)\right]J_{L'}(\vec{r})+\int_{(S)}G_0(\vec{r},\vec{r}_0)V(\vec{r}_0)\psi(\vec{r}_0)d^3r_0 \,,\end{aligned} \tag{2.29}$$

which can be true only if (relabeling the indices)

$$C^s_{\psi L}(\infty)=\sum_{L'}a_{L'}C^s_{L'L}(\infty) \,. \tag{2.30}$$

The last step is essentially a restatement of Fredholm's theorem that $\chi(\vec{r})$ uniquely determines $\psi(\vec{r})$ via the integral equation (see Refs. 18 and 19). The conditions from Fredholm's theorem appear here in slightly different form. From linear algebra, we know that (2.30) uniquely determines a set of

$\{a_L\}$'s that solve the problem via (2.28) if and only if $C^s_{LL'}(\infty)$ is invertible, i.e.,

$$\det|C^s_{LL'}(\infty)|\neq 0 \; . \tag{2.31}$$

This is the condition that must be satisfied if the $\phi_L(\vec{r})$'s are to form a "basis" in the sense we discussed earlier. If condition (2.31) is violated, it implies the existence of an energy eigenvalue or a peculiar angular degeneracy that amounts to the same thing. (The determinant will be zero if one or more of the rows or columns are directly proportional to each other or if a diagonal element of the diagonalized matrix is zero.) This energy eigenstate will have a well-defined angular behavior, and this particular mix of partial waves will not participate directly in scattering processes. Once this particular state is determined, however, the rest of the partial waves are still available to construct a scattering solution. This point is discussed again in Sec. III in the context of the band-structure problem.

Before we go on to the next section and a specific application along the lines of (2.27)–(2.30), we should note that the phase functions (2.25) can be calculated by solving a set of coupled ordinary differential equations implied by (2.25). This is discussed in Appendix B, and an algorithm for obtaining the more specific solutions required for the application to the band-structure problem is given. These differential equations cannot be solved for a completely arbitrary potential. As one might expect, the potential must be less singular than an inverse cube for the solution to be well defined.[24] Furthermore, we would prefer that the potential be spherically symmetric in the vicinity of the origin so that the solution can be expressed in spherical harmonics there. Finally, for practical (i.e., numerical) reasons we would prefer that the potential be reasonably smooth and spherically decomposable in the region of interest. Fortunately, all of these conditions can usually be satisfied for some cellular division in the band-structure problem, and even in the cases where they cannot something can still be done at the cost of some accuracy.

In order to apply this theory, we see that a way must be found to determine the $C^s_{\psi L}(\infty)$'s for the spherical domain and Green's function chosen. In some cases (like the ordinary scattering problem) these can be determined *a priori;* in other cases both they and the energies for which they are defined must be determined by constructing and solving a secular equation. In Sec. III we will discuss the specific application to the band-structure problem[25] which is an example of the latter kind of problem. However, we feel that the PF basis has a number of possible applications in quantum physics that have not been fully exploited, and we hope that this treatment is sufficient to suggest new lines of application in other problems of interest as well as this one.

III. THE MULTIPLE-SCATTERING APPROACH TO THE BAND-STRUCTRE PROBLEM

Let us briefly review the relevant aspects of the band-structure problem. We seek a solution to Schrödinger's equation

$$(\nabla^2+\kappa^2)\psi_{\vec{k}}(\vec{r})=V_c(\vec{r})\psi_{\vec{k}}(\vec{r}) \; , \tag{3.1}$$

where the crystal potential possesses the symmetry of some infinite regular lattice,

$$V_c(\vec{r})=V_c(\vec{r}+\vec{Z}_\mu) \; , \tag{3.2}$$

for any $\vec{Z}_\mu$ that is a basic lattice vector. For simplicity we will assume that identical atoms are located at the $\vec{Z}_\mu$; more complex crystals can be treated in this theory but we do not discuss them at this time. It is a well-known result of group theory that a solution to (3.1) for potentials (3.2) must satisfy Bloch's theorem; that is,

$$\psi_{\vec{k}}(\vec{r})=e^{-i\vec{k}\cdot\vec{Z}_\mu}\psi_{\vec{k}}(\vec{r}+\vec{Z}_\mu) \; , \tag{3.3}$$

where $\vec{k}$ is a vector in the reciprocal lattice that labels the particular solution to (3.1) satisfying (3.3).[26] Only certain energies ϵ are compatible with a given $\vec{k}$ in the reciprocal lattice; we seek these energies and their dependence on $\vec{k}$. These functions $\epsilon(\vec{k})$ occur in bands and form the energy spectra of electrons interacting with the crystal potential.

We wish to calculate the bands and their associated wave functions using a mechanizable procedure derived from a NMT theory that can be made self-consistent. This theory should, ideally, augment our understanding of the physics of a given problem rather than confuse it. Furthermore, in order to be of practical use, the theory (which will involve the truncation of some infinite set of expansion functions) should be rapidly convergent.

Let us expand the desired solution to (3.1) in terms of the PF basis derived in the last section. We seek a set of coefficients $\{a_L(\epsilon,\vec{k})\}$ such that (for $\vec{r}\in S$)

$$\psi_{\vec{k}}(\vec{r})=\sum_L a_L(\epsilon,\vec{k})\phi_L(\vec{r}) \; , \tag{3.4}$$

where (also for $\vec{r}\in S$)

$$\phi_L(\vec{r})=\sum_{L'}C^s_{LL'}(\infty)J_{L'}(\vec{r}) + \int_{(S)}G_0(\vec{r},\vec{r}_0)V_c(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0 \tag{3.5}$$

is the PF basis for the domain consisting of the

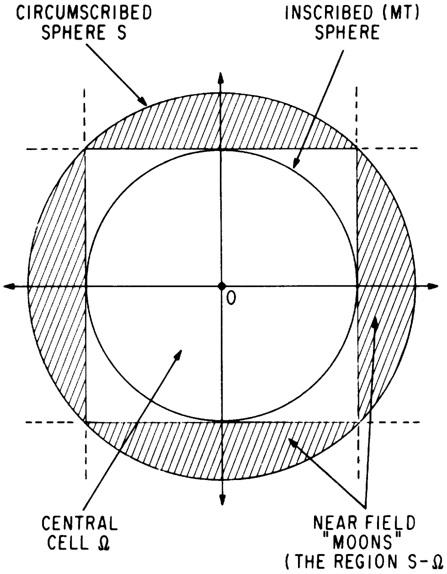

FIG. 1. Schematic representation of a typical central cell, showing the limiting spheres and the separation of the domains (the near-field region). Note that the bounding sphere does not penetrate deeply into the nearest-neighbor cells.

sphere circumscribing the central crystal cell (Fig. 1). The function $\psi_{\vec{k}}(\vec{r})$ and the potential $V_c(\vec{r})$ must satisfy (3.1)–(3.3). We write the integral equation solution to (3.1) as

$$\psi_{\vec{k}}(\vec{r})=\int_{R^3}G_0(\vec{r},\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0 \tag{3.6}$$

or

$$\psi_{\vec{k}}(\vec{r})=\int_{(R^3-S)}G_0(\vec{r},\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0 + \int_{(S)}G_0(\vec{r},\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0 \,. \tag{3.7}$$

Let us, as usual, define

$$\begin{aligned}\chi_{\vec{k}}(\vec{r})&=\int_{(R^3-S)}G_0(\vec{r},\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0\\ &=\sum_L C^s_{\chi L}(\infty)J_L(\vec{r})\,,\end{aligned} \tag{3.8}$$

where the last equality is justified by (2.14) and (2.17). We will now examine this term in greater detail. If we expand the Green's function via (2.13) we obtain

$$\chi_{\vec{k}}(\vec{r})=-\kappa\sum_L J_L(\vec{r})\int_{(R^3-S)}N^*_L(\vec{r}_0)V_c(\vec{r}_0)\times\psi_{\vec{k}}(\vec{r}_0)d^3r_0\,, \tag{3.9}$$

which serves to define the $\{C^s_{\chi L}(\infty)\}$'s.

Let us add and subtract a term to the integral *under the summation:*

$$\chi_{\vec{k}}(\vec{r})=-\kappa\sum_L J_L(\vec{r})\left[\int_{(R^3-S)}N^*_L(\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0+\int_{(S-\Omega)}N^*_L(\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0 - \int_{(S-\Omega)}N^*_L(\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0\right]. \tag{3.10}$$

The integral over $(S-\Omega)$ is well defined; it is just some number (though we will never have to explicitly evaluate it) and the sum (3.10) converges as rapidly as the sum (3.9). We combine the first two terms (under the summation) and obtain

$$\chi_{\vec{k}}(\vec{r})=-\kappa\sum_L J_L(\vec{r})\left[\int_{(R^3-\Omega)}N^*_L(\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0-\int_{(S-\Omega)}N^*_L(\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0\right]. \tag{3.11}$$

Let us examine the first term in the large parentheses. If we change variables from $\vec{r}_0\rightarrow\vec{r}_0+\vec{Z}_\mu$ and integrate over $R^3-\Omega$ by integrating over each WS cell separately, we obtain

$$\chi_{\vec{k}}(\vec{r})=-\kappa\sum_L J_L(\vec{r})\left[\sum_{\mu\neq0}\int_{(\Omega_\mu)}N^*_L(\vec{r}_0+\vec{Z}_\mu)V_c(\vec{r}_0+\vec{Z}_\mu)\psi_{\vec{k}}(\vec{r}_0+\vec{Z}_\mu)d^3r_0 - \int_{(S-\Omega)}N^*_L(\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0\right]. \tag{3.12}$$

With the use of (3.2) and (3.3), this becomes

$$\chi_{\vec{k}}(\vec{r})=-\kappa\sum_L J_L(\vec{r})\left[\sum_{\mu\neq0}\int_{(\Omega_\mu)}N^*_L(\vec{r}_0+\vec{Z}_\mu)V_c(\vec{r}_0)e^{+i\vec{k}\cdot\vec{Z}_\mu}\psi_{\vec{k}}(\vec{r}_0)d^3r_0 - \int_{(S-\Omega)}N^*_L(\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0\right]. \tag{3.13}$$

For all lattices such that $|\vec{Z}_\mu|_{\min} > |\vec{r}_0|_{\max}$ [$\vec{r}_0$ is restricted by Eq. (3.13) to lie in the cell; this condition and its limitations are discussed in detail below], we can expand[27]

$$N_L^*(\vec{r}_0+\vec{Z}_\mu)=\sum_L\sum_{L''} I_{LL'L''}J_{L'}^*(\vec{r}_0)N_{L''}(\vec{Z}_\mu)\ , \tag{3.14a}$$

where

$$I_{LL'L''}=\int Y_L^*(\hat{r})Y_{L'}(\hat{r})Y_{L''}(\hat{r})d^2\hat{r} \tag{3.14b}$$

and perform the sum over L'' and μ, using the fact that

$$D_{LL'}(\vec{k})=\sum_{\mu\neq 0}\left[\sum_{L''} I_{LL'L''}N_{L''}(\vec{Z}_\mu)e^{i\vec{k}\cdot\vec{Z}_\mu}\right] \tag{3.15}$$

are the structure constants of KKR. Then

$$\chi_{\vec{k}}(\vec{r})=-\kappa\sum_L J_L(\vec{r})\left[\sum_{L'} D_{LL'}(\vec{k})\int_{(\Omega_\mu)}J_{L'}^*(\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0-\int_{(S-\Omega)}N_L^*(\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0\right]. \tag{3.16}$$

Note that the term we added and subtracted in Eq. (3.10) is now folded into a sum over the structure constants of KKR, and thus its cancellation is contingent upon the convergence of that sum.

We now write (3.7) as

$$\psi_{\vec{k}}(\vec{r})=-\kappa\sum_L J_L(\vec{r})\left[\sum_{L'} D_{LL'}(\vec{k})\int_{(\Omega)}J_{L'}^*(\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0-\int_{(S-\Omega)}N_L^*(\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0\right]$$
$$+\int_{(S)}G_0(\vec{r},\vec{r}_0)V_c(\vec{r}_0)\psi_{\vec{k}}(\vec{r}_0)d^3r_0 \tag{3.17}$$

and substitute (3.4) for $\psi_{\vec{k}}(\vec{r})$ everywhere it appears in (3.17) (which is now justified since $\vec{r},\vec{r}_0$ are both restricted to lie within S). Subtracting everything to the left and relabeling the indices, we obtain

$$\sum_L a_L(\epsilon,\vec{k})\left[\left[\left[\phi_L(\vec{r})-\int_{(S)}G_0(\vec{r},\vec{r}_0)V_c(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0\right]\right.\right.$$
$$-\kappa\sum_{L'}J_{L'}(\vec{r})\left[\int_{(S-\Omega)}N_{L'}^*(\vec{r}_0)V_c(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0\right.$$
$$\left.\left.\left.-\sum_{L''}D_{L'L''}(\vec{k})\int_{(\Omega)}J_{L''}^*(\vec{r}_0)V_c(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0\right]\right]\right]=0\ . \tag{3.18}$$

Using the definition of the $\phi_L(\vec{r})$'s, Eq. (3.5), we get

$$\sum_L a_L(\epsilon,\vec{k})\left[\sum_{L'}J_{L'}(\vec{r})\left[C_{LL'}^s(\infty)-\kappa\int_{(S-\Omega)}N_{L'}^*(\vec{r}_0)V_c(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0\right.\right.$$
$$\left.\left.+\kappa\sum_{L''}D_{L'L''}(\vec{k})\int_{(\Omega)}J_{L''}^*(\vec{r}_0)V_c(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0\right]\right]=0\ . \tag{3.19}$$

We now fold the remaining integral term into the $C_{LL'}^s(\infty)$'s and *define* the quantities

$$C_{LL'}^\Omega(\infty)=C_{LL'}^s(\infty)-\kappa\int_{(S-\Omega)}N_{L'}^*(\vec{r}_0)V_c(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0=-\kappa\int_{(R^3-\Omega)}N_{L'}^*(\vec{r}_0)V_c(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0 \tag{3.20a}$$

and

$$S_{LL'}^\Omega(\infty)=S_{LL'}^s(\infty)+\kappa\int_{(S-\Omega)}J_{L'}^*(\vec{r}_0)V_c(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0=-\kappa\int_{(\Omega)}J_{L'}^*(\vec{r}_0)V_c(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0\ , \tag{3.20b}$$

in terms of which Eq. (3.19) becomes

$$\sum_{L} a_L(\epsilon,\vec{k}) \left[\sum_{L'} J_{L'}(\vec{r}) \left[C^{\Omega}_{LL'}(\infty) - \sum_{L''} D_{L'L''}(\vec{k}) S^{\Omega}_{LL''}(\infty) \right] \right] = 0 \,, \tag{3.21}$$

which is almost our secular equation. This is the fundamental equation of Green's-function band theory and is exact.

Let us now construct, from (3.21), the secular determinant to be solved for the bands $\epsilon(\vec{k})$. We use the variational procedure of KR, as this will yield bands correct to second order in the error in the wave function. It has been noted (by Faulkner) that the variational procedure *per se* plays little, if any, role in the derivation of the secular determinant; we disagree, for reasons we shall discuss below.

Equation (3.21) is valid for all $\vec{r} \in S$ (*not* just $r \in \Omega$) and so we multiply by $-\kappa V_c(\vec{r}) \phi^{*}_{L0}(\vec{r})$ and integrate over S to obtain

$$\sum_{L} a_L(\epsilon,\vec{k}) \left[\sum_{L'} -\kappa \int_{(S)} J_{L'}(\vec{r}) V_c(\vec{r}) \phi^{*}_{L0}(\vec{r}) d^3 r \left[C^{\Omega}_{LL'}(\infty) - \sum_{L''} D_{L'L''}(\vec{k}) S^{\Omega}_{LL''}(\infty) \right] \right] = 0 \tag{3.22}$$

or

$$\sum_{L} a_L(\epsilon,\vec{k}) \left[\sum_{L'} [S^{s}_{L0L'}(\infty)]^{*} \left[C^{\Omega}_{LL'}(\infty) - \sum_{L''} D_{L'L''}(\vec{k}) S^{\Omega}_{LL''}(\infty) \right] \right] = 0 \,. \tag{3.23}$$

This will have a unique solution [a set of normalizable $a_L(\epsilon,\vec{k})$'s] if and only if

$$\det \left| \sum_{L'} [S^{s}_{L0L'}(\infty)]^{*} \left[C^{\Omega}_{LL'}(\infty) - \sum_{L''} D_{L'L''}(\vec{k}) S^{\Omega}_{LL''}(\infty) \right] \right| = 0 \,. \tag{3.24}$$

This is the secular determinant. However, it is very difficult to solve in its present form. If we can show that

$$\det | [S^{s}_{L0L'}(\infty)]^{*} | \neq 0 \tag{3.25}$$

[a condition related to the condition (2.31) for the completeness and independence of the $\phi_L(\vec{r})$'s], then we can use $\det|AB| = \det|A| \det|B|$ to require

$$\det \left| C^{\Omega}_{LL'}(\infty) - \sum_{L''} D_{L'L''}(\vec{k}) S^{\Omega}_{LL''}(\infty) \right| = 0 \,. \tag{3.26}$$

This is the "usual" secular determinant. [In KKR the diagonal $S^{\Omega}_{LL''}(\infty)$, evaluated on the MT restricted potential, is inverted and separated from the structure constants to form the cotangent of the partial wave phase shifts; a similar procedure is followed in Appendix C.] It can be solved for the energy bands $\epsilon(\vec{k})$ by the procedure of fixing ϵ (or κ in the phase functions) and varying $\vec{k}$ (and hence the structure constants) until (3.26) is satisfied. Alternatively, the reverse procedure can also be used. One can then solve the set of linear equations

$$\sum_{L} \left[C^{\Omega}_{LL'}(\infty) - \sum_{L''} D_{L'L''}(\vec{k}) S^{\Omega}_{LL''}(\infty) \right] a_L(\epsilon,\vec{k}) = 0 \tag{3.27}$$

[again, using condition (3.25)] for the $a_L(\epsilon,\vec{k})$'s, from which one can reconstruct the wave function $\psi_{\vec{k}}(\vec{r})$ if it is required for, e.g., a SCF calculation.

We can now see why a variational procedure is preferred over the projective approach. First of all, it guarantees the second-order accuracy of the bands, which the projective argument, even if it leads to the same determinant and bands, does not. Second, as we have seen, a variational derivation implies an additional condition, Eq. (3.25), that would have been missed by a projective argument. Equation (3.25) is an explicit check for the completeness and independence of the $\phi_L(r)$'s. Furthermore, it checks for the energy eigenvalues of the spherical potential, which will correspond to the localized core states of the modified atomic potential. Should the test associated with (3.25) [or equivalently, Eq. (2.31)] fail, then the full equation (3.24) must be used to obtain the band states, which will be properly orthogonal to the core states. Finally, the projective argument is actually invalid in the case where the solution obtained does not correctly extend into the "moons"; in order to project out against a spherical harmonic, one must be able to integrate the function to be decomposed through all angles for any radius r.

At this point we wish to discuss several potentially troublesome aspects of this derivation. First of all, the integral term added and subtracted in Eq. (3.10) has been folded into the $C^{\Omega}_{LL'}(\infty)$ and the sum over the structure constants and the $S^{\Omega}_{LL'}(\infty)$ (hence we never have to evaluate it independently). Its cancellation depends now upon the numerical accuracy of the phase functions and upon the convergence of the sum over the structure constants. This point might concern us because this integral term, multiplied by $J_L(\vec{r})$ and summed over L will in general diverge for $|\vec{r}|$ greater than the MT radius. Thus Eq. (3.21) contains two terms which, if summed *independently* over L, would also diverge for these $\vec{r}$'s.

We do not expect any difficulty, numerical or otherwise, to arise from this observation. This is for two reasons. First, the angular-momentum cutoff inherent to scattering theories (and one of the prime advantages of KKR) should guarantee that our sum over the structure constants will converge sufficiently rapidly to effectively cancel the divergence before the sum over L is performed. Equation (3.21) converges as rapidly as (3.9) from which it was derived; only residual errors arising from truncating the basis set can produce any problems. Second, if Eq. (3.25) is satisfied *the terms in (3.21) separate.* That is, the sum over L is *never* performed and a set of independent equations (3.27) result. We believe this to be the reason that WM obtained meaningful results in spite of the divergences in their multiple-scattering equation. Whether or not their projective argument was valid, it succeeded in producing a secular determinant that effectively separated the terms in their fundamental equation. The strong convergence properties of Green's-function band theory then yielded the best results their basis was capable of though it was incomplete and though their expansion for the Green's function for the crystal was divergent for certain r. This is a powerful argument in favor of using the Green's-function method in band-structure calculations; it is so strongly convergent that flaws in the implementation of the method produce minimal errors.

A second point to discuss is the restriction $|\vec{Z}_\mu|_{\min} > |\vec{r}_0|_{\max}$ on the crystal lattice required for Eq. (3.15) to converge. There are clearly many lattices (i.e., the cubic or any close-packed lattice) where this requirement is always met. There are certainly other lattices where it may or may not be met, depending on the substance studied. The requirement that the crystal potential be decomposable in spherical harmonics in the bounding sphere (see Appendix B) produces a slightly stronger restriction of the same sort. The deep nuclear potential of the nearest-neighbor atoms must be far enough beyond the edge of the bounding sphere that the numerical decomposition of the potential can proceed without difficulty. If it is not possible to satisfy either or both of these related requirements for a particular substance, it may be necessary to introduce a basis (of empty cells) and work with the more complex problem thus formed. The extension of this theory to this sort of problem is deferred to some later time; those interested might proceed along the lines indicated by WM, who included a site label on their cellular potentials.

A great deal of the structure of this method derives from the earlier work of WM. Occasionally, this paper may seem quite critical of their paper; however, it is generally details of their method that we are criticizing, not the overall approach. Indeed, the authors are indebted to WM, for by isolating the weak points of their derivation from a point of view slightly different from those of Ziesche and Faulkner, we were able to fix them up and so recover an exact theory of essentially the same form. We were motivated by the feeling that WM's results certainly "look right"; that is, they have the form one would expect the exact NMT theory to have. At this point we would like to briefly compare and constrast the two theories to emphasize their simularities and differences.

Both approaches begin with the phase-functional basis. However, WM incorrectly represent the inhomogeneous term of the integral equation for the phase-functional solution on the cell, neglecting the near-field contribution from the moons between the cell boundary and the bounding sphere. We correct this by working with a basis defined throughout the sphere which includes the near-field effects explicitly and has a simple representation for the inhomogeneous term.

Both approaches then evaluate the integral equation solution to Schrodinger's equation for the entire crystal, using the PF basis. WM break the volume integral into an integral over the cell and an integral over the outside of the cell. We break the volume integral into an integral over the bounding sphere and an integral over the region outside the sphere. We do this to avoid working with a phase-functional representation of the exterior integral. By adding and subtracting a term under the summation over $J_L(\vec{r})$, we effectively repartition the integral to recover the usual structure constants and modify the $C^s_{LL'}(\infty)$ coefficients accordingly. The result is the multiple-scattering equation that would result if one scattered the *complete* set of functions $\phi_L(\vec{r})$ off the truncated cellular potential for all the cells of the crystal.

WM derive the structure constants by examining the three-argument expansion of the Green's function for the crystal. Their argument concerning the cell partitionings for which their equations separate is invalid, as it involves the reordering of an infinite sum. This point is quite important and is covered in detail in Appendix A. As a result their term containing the structure constants, when summed against the $J_L(\vec{r})$'s, does not always converge. This is by itself not necessarily bad; our equivalent term does the same thing. However, their coefficients

$C^{\Omega}_{LL'}(\infty)$ do not contain the term (that we added and subtracted termwise to emphasize the point) that *cancels* this divergence. Hence their multiple-scattering equation does not *formally* converge. As we noted, this does not seem to make the theory unusable because obtaining the secular equation effectively decouples each term in the sum from the others anyway; the angular-momentum cutoff then ensures convergence to an answer. The answer simply contains an error that is very difficult to estimate.

We finally obtain, from a slightly different procedure, a secular determinant that looks very much like WM's. In fact, the only differences are in how we calculate the $C^{\Omega}_{LL'}(\infty)$ and $S^{\Omega}_{LL'}(\infty)$ (and hence the nondiagonal scattering matrix) and the variational approach to the secular determinant. As a result, we feel that our secular equation has the form one would expect a NMT Green's-function band theory to have. For this reason, and the reasons detailed above, we believe this to be a viable generalized theory suitable for use in SCF band-structure calculations and the most general statement of Green's-function band theory made to date.

IV. CONCLUSIONS

In this paper we have presented the derivation of a general technique, based on multiple scattering in the phase-functional formalism, for solving the band-structure problem. The results presented are valid for lattices without a basis; the results can be extended to a complex lattice (i.e., a lattice with a basis) by adding a species index (label) to the quantities $C^{\Omega}_{LL'}(\infty)$, $S^{\Omega}_{LL'}(\infty)$, $V_c(\vec{r})$, $\phi_L(\vec{r})$, and $a_L(\epsilon,\vec{k})$. The structure constants would then be modified in Eq. (3.15), since $\psi_{\vec{k}}(\vec{r})$ [through the $a_L(\epsilon,\vec{k})$] satisfies Bloch's theorem on the lattice but not the basis. We do not present the actual equations in this work, as they can be obtained from WM's paper, changing their basis functions $C^{\Omega}_{LL'}(\infty)$ and $S^{\Omega}_{LL'}(\infty)$ to ones calculated along the lines suggested in this paper. The results presented in this paper suffice for studies of pure metallic crystals, including the transition metals, in a self-consistent manner.

At this time we are engaged in the application of these results to a variety of test cases. We intend to study a number of metals, including several treated in some detail in the MT approximation for purposes of comparison. Initially we will not do a SCF calculation to avoid obscuring the direct utility of the method, but eventually we hope to make the entire procedure self-consistent. It is too early to report on these results (though preliminary work shows some promise), but we hope to complete at least one calculation in the near future for demonstration purposes.

We feel that the phase-functional solutions developed by WM and in this work have not been exploited as fully as they might be in physics. In particular, they appear to have possible applications in ordinary scattering theory and atomic physics where the Born approximation or other methods turn out to be too expensive or inappropriate.

To conclude, we hope that this work fills the need for a reliable, reasonably cost-effective method for calculating SCF electronic energy bands without recourse to the MT approximation.

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APPENDIX A: THE GREEN'S-FUNCTION EXPANSION

In this appendix we discuss the convergence properties of the Green's-function expansion. In particular, we will examine the algebraic consequences of reordering the sums in the three-point expansion of $G_0(\vec{r},\vec{r}_0+\vec{Z})$, as was done by WM, and show that it leads to a diverging result. As usual we will work with the stationary Green's function; the arguments are trivially extendable to include the other Green's functions for incoming or outgoing waves.

We begin by examining [via (2.13)]

$$G_0(\vec{r},\vec{r}_0+\vec{Z})=-\kappa\sum_L N_L^*(\vec{r}_0+\vec{Z})J_L(\vec{r}),\quad (|\vec{r}|<|\vec{r}_0+\vec{Z}|) \tag{A1a}$$

$$=-\kappa\sum_L N_L(\vec{r}-\vec{Z})J_L^*(\vec{r}_0),\quad (|\vec{r}-\vec{Z}|>|\vec{r}_0|) \tag{A1b}$$

$$=-\kappa\sum_L N_L(\vec{Z})J_L^*(\vec{r}-\vec{r}_0),\quad (|\vec{Z}|>|\vec{r}-\vec{r}_0|)\,, \tag{A1c}$$

which are the three ways of expanding the three-point function so that $\vec{Z}$ is part of the argument of N_L. (A1c) is the usual muffin-tin requirement and expansion and we will not discuss it further. (A1a) and (A1b) can both be expanded again if $|\vec{Z}| > |\vec{r}_0|$ and $|\vec{Z}| > |\vec{r}|$, respectively. We have

$$G_0(\vec{r},\vec{r}_0+\vec{Z}) = -\kappa\sum_{L}\left[\sum_{L'}\sum_{L''} I_{LL'L''}N_{L'}(\vec{Z})J^*_{L''}(\vec{r}_0)\right]\times J_L(\vec{r}) \qquad \text{(A2a)}$$

from (A1a) and Eq. (3.14a), and

$$G_0(\vec{r},\vec{r}_0+\vec{Z}) = -\kappa\sum_{L}\left[\sum_{L'}\sum_{L''} I_{LL'L''}N_{L'}(\vec{Z})J_{L''}(\vec{r})\right]\times J^*_L(\vec{r}_0) \qquad \text{(A2b)}$$

from (A1b). The parentheses are necessary to maintain the order of the sum. Suppose, now, we attempt to reorder the sum, that is, claim that (A2b) is *equivalent* to

$$G_0(\vec{r},\vec{r}_0+\vec{Z}) = -\kappa\sum_{L''}\left[\sum_{L}\sum_{L'} I_{LL'L''}N^*_{L'}(\vec{Z})J_{L}(\vec{r}_0)\right]\times J_{L''}(\vec{r})\,, \qquad \text{(A3)}$$

which is just (A2a) if we relabel the indices. ($I_{LL'L''}$ is completely symmetric.) We can then contract (A5) according to (3.14a) and find that (assuming $|\vec{Z}| > |\vec{r}|$ *and* $|\vec{Z}| > |\vec{r}_0|$)

$$G_0(\vec{r},\vec{r}_0)+\vec{Z}) = -\kappa\sum_{L''} N^*_{L''}(\vec{r}_0+\vec{Z})J_{L''}(\vec{r}) \qquad \text{(A1a')}$$

if the requirement on (A1b) ($|\vec{r}-\vec{Z}| > |\vec{r}_0|$) is satisfied. But this is *not convergent for all* $\vec{r},\vec{r}_0$ *such that this condition is met.* We already know that (A1a) will *only* converge if *its* conditions are met, and there clearly exist $\vec{r},\vec{r}_0$ that will violate the condition on (A1a) but satisfy the condition on (A1b). We can make the contradiction more apparent by changing variables so that $\vec{r}\,'_0=\vec{r}_0+\vec{Z}$. Then

$$G_0(\vec{r},\vec{r}\,'_0) = -\kappa\sum_{L} N^*_L(\vec{r}\,'_0)J_L(\vec{r}) \qquad \text{(A4a)}$$

is the equivalent of (A1a) and *requires* that $|\vec{r}\,'_0| > |\vec{r}|$. If $|\vec{r}| > |\vec{r}\,'_0|$, then

$$G_0(\vec{r},\vec{r}\,'_0) = -\kappa\sum_{L} N_L(\vec{r})J^*_L(\vec{r}\,'_0)\,, \qquad \text{(A4b)}$$

but we can always find *some* $|\vec{Z}|\rightarrow 0$ such that $|\vec{r}-\vec{Z}| > |\vec{r}_0|$. For that $\vec{Z}$, (A1b) implies (A1a), which implies (A4a), and we find that our reordering of the sum in (A2b) leads us to the contradictory result that the Green's function can be expressed as (A4a) *or* (A4b) for *any* $\vec{r},\vec{r}\,'_0$ without regard to the relative size of their arguments. This is algebraically *true.* The terms in the sums (A2a) and (A2b) have a one-to-one correspondence, but those sums will converge *only* if added in the order indicated by the parentheses.

This is why we were careful in Sec. III to perform all of our algebraic manipulations under the summation over $J_L(\vec{r})$. If we treated the integral term over the moons around the cell independently, it would not sum in a convergent manner. This would necessitate treating diverging sums numerically, and, while the sums would still cancel to produce a converging result, the requisite subtraction of large numbers would introduce an unacceptable error. By working *within* the sum over $J_L(\vec{r})$ we *never have to subtract a pair of diverging partial sums.* We subtract only the terms that *if summed* would diverge, but are perfectly well-defined *numbers* otherwise, and thus avoid the necessity of working with large numbers. In practice we do not even do this subtraction; we actually invert the matrix $S^{\Omega}_{LL'}(\infty)$, multiply the result into the $C^{\Omega}_{LL'}(\infty)$ and then subtract off the completely separate structure-constant matrix (as seen in Appendix B).

APPENDIX B: EVALUATION OF THE PHASE-FUNCTIONAL BASIS

The integral equations for the phase functions are (from Sec. II)

$$C^s_{LL'}(r) = C^s_{LL'}(\infty) - \kappa\underset{(S)}{\int_r^{\infty}} N^*_{L'}(\vec{r}_0)V(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0 \qquad \text{(2.25a)}$$

and

$$S^s_{LL'}(r) = -\kappa\underset{(S)}{\int_0^{r}} J^*_{L'}(\vec{r}_0)V(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0 \qquad \text{(2.25b)}$$

on the spherical domain S. We also must evaluate in parallel the phase functions

$$C^{\Omega}_{LL'}(r) = C^{\Omega}_{LL'}(\infty) - \kappa\underset{(\Omega)}{\int_r^{\infty}} N^*_{L'}(\vec{r}_0)V(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0 \qquad \text{(3.20a')}$$

and

$$S^{\Omega}_{LL'}(r) = -\kappa\underset{(\Omega)}{\int_0^{r}} J^*_{L'}(\vec{r}_0)V(\vec{r}_0)\phi_L(\vec{r}_0)d^3r_0 \qquad \text{(3.20b')}$$

on the cell Ω for use in the secular equation (3.26). Recalling that $\phi_L(\vec{r})$ is given by

$$\phi_L(\vec{r}) = \sum_{L'}[C^s_{LL'}(r)J_{L'}(\vec{r}) + S^s_{LL'}(r)N_{L'}(\vec{r})] \qquad \text{(2.24)}$$

for $\vec{r}\in S$ (note that the phase functions on the *sphere* must be used, *not* the phase functions on the cell) we define the following decompositions:

$$V_s(\vec{r})=\sum_L V_{sL}(r)Y_L(\hat{r}) \tag{B1}$$

with

$$V_{sL}(r)=\int_{(4\pi)}V_s(\vec{r})Y_L^*(\hat{r})d^2\hat{r}\ , \tag{B2}$$

where

$$V_s(\vec{r})\begin{cases}V(\vec{r}), & \vec{r}\in S\\ 0, & \vec{r}\notin S\end{cases} \tag{B3}$$

$$\phi_L(\vec{r})=\sum_{L'}\phi_{LL'}^s(r)Y_{L'}(\hat{r})\quad\text{for } \vec{r}\in S \tag{B4}$$

with

$$\phi_{LL'}^s(r)=[C_{LL'}^s(r)j_{l'}(r)+S_{LL'}^s(r)n_{l'}(r)]\ , \tag{B5}$$

and

$$V_\Omega(\vec{r})=\sum_L V_{\Omega L}(r)Y_L(\hat{r}) \tag{B6}$$

with

$$V_{\Omega L}(r)=\int_{(4\pi)}V_\Omega(\vec{r})Y_L^*(\hat{r})d^2\hat{r}\ , \tag{B7}$$

where

$$V_\Omega(\vec{r})\begin{cases}V(\vec{r}), & \vec{r}\in \Omega\\ 0, & \vec{r}\notin \Omega .\end{cases} \tag{B8}$$

From the integral equations for the phase functions we obtain the following coupled ordinary differential equations:

$$\frac{dC_{LL'}^s}{dr}=\kappa r^2\int_{(4\pi)}N_{L'}^*(\vec{r})V_s(\vec{r})\phi_L(\vec{r})d^2\hat{r}\ , \tag{B9a}$$

$$\frac{dS_{LL'}^s}{dr}=-\kappa r^2\int_{(4\pi)}J_{L'}^*(\vec{r})V_s(\vec{r})\phi_L(\vec{r})d^2\hat{r}\ , \tag{B9b}$$

and

$$\frac{dC_{LL'}^\Omega}{dr}=\kappa r^2\int_{(4\pi)}N_{L'}^*(\vec{r})V_\Omega(\vec{r})\phi_L(\vec{r})d^2\hat{r}\ , \tag{B10a}$$

$$\frac{dS_{LL'}^\Omega}{dr}=-\kappa r^2\int_{(4\pi)}J_{L'}^*(\vec{r})V_\Omega(\vec{r})\phi_L(\vec{r})d^2\hat{r}\ . \tag{B10b}$$

Integrating over angles (using the decompositions just given), we obtain

$$\frac{dC_{LL'}^s}{dr}=\kappa r^2\sum_{L''}\sum_{L'''}n_{l'}(r)V_{sL''}(r)\phi_{LL'''}^s(r)I_{L'L''L'''}\ , \tag{B11a}$$

$$\frac{dS_{LL'}^s}{dr}=-\kappa r^2\sum_{L''}\sum_{L'''}j_{l'}(r)V_{sL''}(r)\phi_{LL'''}^s(r)I_{L'L''L'''}\ , \tag{B11b}$$

and

$$\frac{dC_{LL'}^\Omega}{dr}=\kappa r^2\sum_{L''}\sum_{L'''}n_{l'}(r)V_{\Omega L''}(r)\phi_{LL'''}^s(r)I_{L'L''L'''}\ , \tag{B12a}$$

$$\frac{dS_{LL'}^\Omega}{dr}=-\kappa r^2\sum_{L''}\sum_{L'''}j_{l'}(r)V_{\Omega L''}(r)\phi_{LL'''}^s(r)I_{L'L''L'''}\ , \tag{B12b}$$

where

$$I_{L'L''L'''}=\int_{(4\pi)}Y_{L'}^*(\hat{r})Y_{L''}(\hat{r})Y_{L'''}(\hat{r})d^2\hat{r} \tag{3.14b'}$$

describes the angular mixing. The boundary conditions on the differential equations (B11) are

$$C_{LL'}^s(0)=\delta_{LL'} \tag{2.26a}$$

and

$$S_{LL'}^s(0)=0\ , \tag{2.26b}$$

and they can be numerically integrated out from the origin to r equal to radius of S, where the phase functions become constant. Solving (B11) alone allows one to obtain $\phi_L(\vec{r})$, but we also require the phase functions on the cell, which depend on $\phi_L(\vec{r})$ on the sphere. These functions [the solutions to (B12) with the *same* boundary conditions (2.26)] will be identical to the $C_{LL'}^s(r)$ and $S_{LL'}^s(r)$ out to the radius of the inscribed sphere, at which point the $V_{\Omega L}(r)$ begin to differ from the $V_{sL}(r)$. An efficient algorithm for evaluating the two kinds of phase functions in parallel is thus as follows:

(a) Integrate the phase functions $C_{LL'}^s(r)$ and $S_{LL'}^s(r)$ from the origin to the inscribed sphere. [This can be done only after a routine to generate the $V_{sL}(r)$, $V_{\Omega L}(r)$, etc., has been written.] The matrix must be truncated at some $L_{\max}$, and need not be saved at intermediate values of r unless one wishes to reconstruct the wave function.

(b) Using the values of $C_{LL'}^s(r)$ and $S_{LL'}^s(r)$ on the inscribed sphere as boundary conditions, one integrates *both* (B11) and (B12) out from the origin. Since both differential equations require the *same* $\phi_{LL'}^s(r)$ and only (B11) generates a new $\phi_{LL'}(r+\Delta r)$ a step further out, the routine integrating (B11) must be kept a step or two ahead of the routine integrating (B12). In this way one can avoid storing the intermediate $C_{LL'}^s(r)$ and $S_{LL'}^s(r)$ for more than the one or two values of r needed to integrate first (B11) and then (B12) the next step out.

When r reaches the circumscribed spheres, both sets of phase functions become constant. The $C^s_{LL'}(\infty)$ or $S^s_{LL'}(\infty)$ matrices can be determinantally checked to see if they satisfy the variational-completeness test (2.31) or (3.25) and then discarded.

The $C^\Omega_{LL'}(\infty)$ and $S^\Omega_{LL'}(\infty)$ can be used in Eq. (3.26) to solve for the bands $\epsilon(\vec{k})$ after making the following simplifications.

We take

$$\sum_L a_L(\epsilon,\vec{k})\left[\sum_{L'}[S^s_{L0_{L'}}(\infty)]^*\left[C^\Omega_{LL'}(\infty)-\sum_{L''}D_{L'L''}(\vec{k})S^\Omega_{LL''}(\infty)\right]\right]=0 \tag{3.23}$$

and simplify it to

$$\sum_L\left[C^\Omega_{LL'}(\infty)-\sum_{L''}D_{L'L''}(\vec{k})S^\Omega_{LL''}(\infty)\right]a_L(\epsilon,\vec{k})=0 \tag{3.23'}$$

with the use of the condition (3.25). To solve this equation we define (see WM)

$$b_{L'}(\epsilon,\vec{k})=\sum_L S^\Omega_{LL'}(\infty)a_L(\epsilon,\vec{k}) \tag{B13}$$

and

$$C^\Omega_{LL'}(\infty)=\sum_{L''}\eta^\Omega_{L'L''}(\infty)S^\Omega_{LL''}(\infty)\ . \tag{B14}$$

Then (3.23′) becomes

$$\sum_L[\eta^\Omega_{LL'}(\infty)-D_{LL'}(\vec{k})]b_{L'}(\epsilon,\vec{k})=0\ , \tag{B15}$$

and the secular determinant is just

$$\det|\eta^\Omega_{LL'}(\infty)-D_{LL'}(\vec{k})|=0\ . \tag{B16}$$

The $\eta^\Omega_{LL'}(\infty)$ is the analog of the nondiagonal scattering matrix for the single-site potential. If we use the spherical phase functions

$$C^s_{LL'}(\infty)=\sum_{L''}\eta^s_{L'L''}(\infty)S^s_{LL''}(\infty)\ , \tag{B17}$$

then the $\eta^s_{LL'}(\infty)$ *is* the scattering matrix for the spherical domain S, related to the cotangent of the partial-wave phase shifts but nondiagonal due to the nonspherical symmetry of the potential $V_s(\vec{r})$. (B14) and (B17) are defined as they are to avoid the question of left versus right inverses [since the $C_{LL'}(\infty)$ and $S_{LL'}(\infty)$ are not necessarily Hermitian]. If we define $S^{-1}_{LL'}(\infty)$ by (for the domain S or Ω)

$$\sum_{L''}S^{-1}_{L'L''}(\infty)S_{LL''}(\infty)=\delta_{LL'} \tag{B18}$$

then

$$\eta_{L'L''}(\infty)=\sum_L C_{LL'}(\infty)S^{-1}_{LL''}(\infty) \tag{B19}$$

in the order shown. This allows us to complete the algorithm for evaluating the bands $\epsilon(\vec{k})$, which requires that $D_{LL'}(\vec{k})$ be available for arbitrary $\epsilon,\vec{k}$. When steps (a) and (b) above are completed, we construct $\eta^\Omega_{LL'}(\infty)$ from (B14) or (B18) and (B19). We then vary $\vec{k}$ for the given ϵ until determinantal condition (B16) is satisfied. This yields the band structure $\epsilon(\vec{k})$ at a point in the reciprocal lattice, which can be carried to several other points using the symmetry transformations of the point group. Repeating this procedure for different ϵ's, we ultimately generate the entire band structure $\epsilon(\vec{k})$ for the crystal. Once condition (B16) is satisfied, the set of equations (B15) can be solved for the $\{b_L(\epsilon,\vec{k})\}$'s and the $\{a_L(\epsilon,\vec{k})\}$'s, if desired.

We strongly recommend that those interested in performing a band-structure calculation consult WM's appendixes and proceed with some caution. We have simplified the notation somewhat for clarity, but if one wishes, for example, to use real spherical harmonics and avoid using complex numbers (which can be done if the lattice and cellular potential possess inversion symmetry), then care must be taken to use the appropriate phases so that the addition theorems used extensively in the analysis work correctly. (This is the major function of the spherical harmonics *per se* in the formalism of the paper and arises because the Green's function involves only $|\vec{r}-\vec{r}_0|$.) Ham and Segall also make many relevant observations concerning imaginary phases in the free spherical waves (that we have omitted in the interest of clarity) in their table of structure constants for Green's-function band-structure calculations.[28] These are important when $\epsilon<0$ and can introduce confusion when applying the method described herein unless caution is used.

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[1] See, for example, R. Evans and J. Keller, J. Phys. C 4, 3155 (1971).

[2] E. Merzbacher, *Quantum Mechanics*, 2nd ed. (Wiley, New York, 1971), pp. 535—540.

[3] D. D. Koelling, Rep. Prog. Phys. 44, 139 (1981).

[4] D. D. Koelling, Rep. Prog. Phys. 44, 187 (1981). The discussion on pp. 164—172 and 185—187 is especially relevant to the motivation of this work.

[5] J. Korringa, Physica 13, 392 (1947).

[6] W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1967).

[7] F. Calogero, *Variable Phase Approach to Potential Scattering* (Academic, New York, 1967).

[8] V. V. Babikov, Usp. Fiz. Nauk 93, 3 (1967) [Sov. Phys.—Usp. 92, 271 (1967)].

[9] A. R. Williams, and J. van W. Morgan, J. Phys. C 7, 37 (1974).

[10] P. Ziesche, J. Phys. C 7, 1085 (1974).

[11] J. S. Faulkner, Phys. Rev. B 19, 6186 (1979).

[12] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965). This is based upon the density functional theorem of Hohenberg and Kohn that is the basis of the density functional approach to SCF theory; it is the local-potential approximation.

[13] B. Segall and F. Ham, in *Methods in Computational Physics, Energy Bands of Solids,* edited by B. Adler, S. Fernbach, and M. Rotenberg (Academic, New York, 1968), Vol. 8.

[14] B. Segall and T. W. Yang, Phys. Rev. B 21, 3737 (1980).

[15] O. K. Andersen, Phys. Rev. B 12, 3061 (1975).

[16] Faulkner (Ref. 11) derives a linearized KKR in his work, based on what he calls pivoted multiple scattering. It is reasonable to believe that the results of this paper can be similarly linearized, but doing so might wash out the details in the electronic structure that this theory is intended to explore. Segall and Yang have shown that the structure constants themselves are "linearizable" and it may be that this approach is more reasonable to those wishing to optimize cost effectiveness.

[17] P. M. Morse and H. Feshbach, *Method of Theoretical Physics* (McGraw-Hill, New York, 1953), part I, pp. 803—806. The "density" $\rho(\vec{r}_0)$ must be replaced by the quantum source term $V(\vec{r}_0)\psi(\vec{r}_0)$. Virtually any good mathematical physics book [see for example Wyld) (Ref. 21) will derive this result.

[18] Fredholm's theorems are concerned with the structure and degeneracy of integral equations (of the second kind) and link these solutions with the appropriate kernel to the usual structure of quantum theory. Because of the importance of this connection, we give two references: R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1953), Vol. I, pp. 112—122, and Ref. 19.

[19] V. S. Vladimirou, *Equations of Mathematical Physics* (Dekker, New York, 1971), pp. 217—231.

[20] P. M. Morse and H. Feshbach, Ref. 17, pp. 804—811, especially p. 811.

[21] H. W. Wyld, *Mathematical Methods for Physics* (Benjamin, Reading, Massachusetts, 1976), pp. 99—103.

[22] H. W. Wyld, *Mathematical Methods for Physics,* Ref. 21, pp. 187—192.

[23] We do *not* mean that the $\phi_L(\vec{r})$ are eigenfunctions of some self-adjoint operator with real eigenvalues that commutes with the Hamiltonian. There may in fact be such a operator (that would project out of the whole solution a particular mixture corresponding to some conserved quantity such as its angular behavior at the origin), but we do not wish to discuss it at this time. The point is, that this is not an expansion in energy eigenstates and hence the secular determinant we derive is quite different from the usual one.

[24] See the comments in Morse and Feshbach (Ref. 17), Vol. II, pp. 1665—1667. The inverse-cube force law produces a curious quantum structure that appears (for negative potentials) to discretize the energy levels and fixes them relative to one another, but leaves their overall magnitude variable. This lack of uniqueness is what we see in the phase-functional method as an infinitely rapidly varying phase at the origin, resulting in an overall random phase *between* components of different L that are uniformly coupled and shifted by the potential in a well-defined way out from the origin (where everything is smooth). However, this problem is unimportant in most applications; even in those fields where an inverse-cube force law exists (such as the nuclear potential) it does not extend to the singularity at the origin. While inverse-cube laws may still be treatable, we feel (for numerical reasons) that extreme caution should be exercised for anything beyond an inverse square.

[25] Those interested in alternative applications may wish to consult one author's (R. G. B.) dissertation (unpublished). The author develops the results of this paper for more general lattices and discusses the application of the PF formalism to problems including ordinary and multiple scattering off of a nonspherically symmetric, NMT potential. The conclusions briefly speculate on other possible applications without developing them.

[26] J. F. Cornwall, in *Group Theory and Electronic Energy Bands in Solids,* edited by E. P. Wohlforth (Wiley, New York, 1969), pp. 74—77.

[27] A. R. Williams, S. M. Hu, and D. W. Jepsen, *Computational Methods in Band Theory* (Plenum, New York, 1970), pp. 169—171. It is interesting to note that this addition theorem, while correct, is incorretly derived by the authors. Matching the coefficients in the sums as they did is equivalent to claming that $\sum_L a_L b_L = \sum_L a_L c_L$ implies that $b_L = c_L$, which is just not true. Actually, the correct procedure would have been to multiply by a spherical harmonic and project out a single term in the sum. This may seem like a trivial point to raise, but confusion on this issue caused the authors to waste a great deal of time and energy. This mistake is also related to the similar one made by WM in constructing their secular equation.

[28] F. Ham and L. J. Segall, General Electric Company Report No. 61-RL-(2876G) (unpublished). This table can still be obtained from the authors of Ref. 13 and contains the structure constants for the fcc and bcc lattices for a limited number of points on the symmetry axes.