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Multiple-scattering theory for space-filling cell potentials

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The multiple-scattering theory (MST) method of Korringa, and of Kohn and Rostoker for determining the electronic structure of solids, originally developed in connection with potentials bounded by nonoverlapping spheres (muffin-tin potentials), is generalized to the case of space-filling potential cells of arbitrary shape. Both variational and nonvariational formalisms are used in effecting this generalization. In contrast to the case of muffin-tin potentials, different forms of MST exhibit different convergence rates for the energy and the wave function. Numerical results are presented that illustrate the differing convergence rates of the variational and nonvariational forms of MST for space-filling potentials. The generalized MST described here should be useful quite generally for constructing global solutions to linear partial differential equations from sets of locally exact solutions.

I. INTRODUCTION

The method proposed by Korringa[1] and by Kohn and Rostoker[2] (KKR) provides a convenient way for calculating the electronic structure of solids. The method was originally formulated for periodic systems and for use with potentials of muffin-tin (MT) form, i.e., potentials that are nonzero only within a sphere inscribed inside the Wigner-Seitz cell and that are also spherically symmetric. Its numerical applications have been confined almost exclusively to such potentials. Although this MT approximation is quite appropriate in many cases, e.g., reasonably close-packed crystalline metals,[3] it cannot properly describe a number of physical systems, e.g., semiconductors and surface and interface regions. The atomic (cell) potentials in such systems often deviate significantly from their spherical average, and the contributions from regions outside the inscribed spheres are generally non-negligible. Thus a proper treatment of such systems within the KKR method requires the extension of the method to non-MT, space-filling cells.

Much work[4–30] has been devoted to the question of the applicability of the KKR method to space-filling potential cells. It is impossible to summarize this large and complex body of work in a meaningful way in the space available here, although we hope to do so in a later publication.[31] Unfortunately, the topic of full-cell KKR theory has been confused by the subtleties associated with the problem and by several controversies. Recently, however, several groups have begun to report good results in applications to real materials.[24,25,28,30] The objectives of the present paper are to provide a firm theoretical foundation for this work and to explicate some of the subtleties that may be encountered when multiple-scattering theory (MST) is extended to treat non-muffin-tin, generally shaped potentials.

In this paper we will discuss five basic issues. In the past much attention has been paid to the issue of "near-field corrections," a term used to indicate a belief that MST cannot be applied without modification if the potentials have shapes and positions such that their circumscribing spheres overlap.[7,10] For muffin-tin potentials (with nonoverlapping circumscribing spheres), it is relatively easy to derive the MST secular equation from a knowledge of the positions of the scatterers and their scattering amplitudes. The details of the wave function or even the potential within the scatterer need not even be mentioned. It is only necessary to know how a scatterer converts an incoming partial wave into an outgoing one. For non-muffin-tin scatterers this simple derivation is inadequate because the scattered wave expressed as a linear combination of spherical waves does not achieve its asymptotic form until it is outside a sphere which circumscribes the potential. Therefore it appears to be necessary to treat the interaction of this scattered wave with neighboring atoms before it has achieved its asymptotic form, and it is only the asymptotic form which is describable in terms of the scattering amplitude. Ziesche[7] and later Faulkner[10] proposed altering the structure constants of KKR theory to account for these "near-field" effects.

A second issue closely related to the issue of "near-field corrections" is that of the convergence of the partial-wave expansions that occur in full-cell MST. Several partial wave expansions are involved in full-cell MST and care must be taken to ensure that all are convergent. The partial-wave expansion of the Helmholtz equation Green function $G_0(\mathbf{r},\mathbf{r}') = \sum_L J_L(\mathbf{r}_<)H_L(\mathbf{r}_>)$ can be particularly troublesome in full-cell MST because it is difficult to maintain the condition (necessary for convergence) that the argument of the Green function, which is smaller in absolute value, be associated with the regular solution to the Helmholtz equation (J_L) and the larger with the irregular solution (H_L).

A third issue is that of representablity.[32,33] In deriving the muffin-tin KKR equations following the method of Kohn and Rostoker,[2] the crystal wave function within each cell is expanded as a linear combination of solutions to the Schrödinger equation for that cell alone,

$$\psi(\mathbf{r}) = \sum_L a_L R_l(r, E) Y_L(\hat{r}). \tag{1.1}$$

It is generally assumed that an expansion of this type is valid and convergent. In deriving MST for nonspherical potentials a similar representation of the wave function is used, but with the role of the local solutions to the separable spherical problem, $R_l(r)Y_L(\hat{r})$, being played by more complicated functions $\phi_L(\mathbf{r})$, which are local solutions to the Schrödinger equation for a nonspherical potential that are usually calculated using a procedure[6,11,22] which we shall describe in Sec. III. The propriety of the expansion appears much more questionable in this case. Recently a closely related issue has been raised by Newton,[34] who pointed out that the Williams-Morgan procedure for calculating $\phi_L(\mathbf{r})$ may involve a term which is singular at the origin with the result that the functions $\phi_L(\mathbf{r})$ would not be well defined.

A fifth issue is whether or not the characteristic energies obtained from the MST secular equation are variational with respect to the wave function.[29] If the characteristic energy is variational with respect to the wave function, a first-order error in the trial wave function yields only a second-order error in the energy. When Kohn and Rostoker derived the KKR equations for muffin-tin potentials they were careful to do so within the context of a variational principle. The secular matrix that they derived in this way differed from other versions by a multiplicative factor which did not affect the variational nature of the result. Thus all versions of MST for muffin-tin potentials are variational. We shall show that this is not necessarily true for full-cell MST. In this case some versions are variational and others are not. The existence of a variational form of MST is of practical importance in, for example, the determination of the total energy using density-functional theory.

A brief plan of the paper may be helpful. Section II contains a brief description of the Kohn-Rostoker variational principle. Section III is devoted to the issue of representability and to the related issue raised by Newton of a possible singularity at the origin. We show that it is indeed possible to express the total system wave function as an expansion of the form $\psi(\mathbf{r}) = \sum_L a_L \phi_L(\mathbf{r})$, where the functions $\phi_L(\mathbf{r})$ are local solutions to the Schrödinger equation which may be obtained using the potential in a single cell only. In order to show that an expansion of this type is valid for representing the system wave function, we found it necessary to derive an angular momentum expansion for the Green function for a nonspherical potential. This derivation is given in an appendix. We also show that the functions ϕ_L are well defined and that no singularity arises at the origin in their calculation.

Section IV of the paper contains a generalization of the Kohn-Rostoker derivation of MST that applies to nonperiodic systems and to nonspherical muffin-tin potentials (i.e., nonspherical potentials whose circumscribing spheres do not overlap). This derivation is quite simple and serves to highlight the difficulties that must be overcome in Sec. V where we present a variational derivation of full-potential MST. A nonvariational derivation of full-potential MST is presented in Sec. VI and is shown to yield a closely related version of MST which does not have the variational property of the version derived in Sec. V.

Section VII contains some numerical examples which illustrate the main points of the paper. Both the variational and nonvariational derivations as well as the numerical examples demonstrate that near-field corrections are not needed. However, care and prudence must be exercised in converging certain internal angular momentum sums for full-cell MST. Section VIII contains a brief discussion of our results and their implications for applications to real materials.

II. THE VARIATIONAL PRINCIPLE OF KOHN AND ROSTOKER

The time independent Schrödinger equation

$$[-\nabla^2 + V(\mathbf{r}) - E]\psi(\mathbf{r}) = 0 \tag{2.1}$$

may, for bound states, be written in the integral form

$$\psi(\mathbf{r}) - \int d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi(\mathbf{r}') = 0, \tag{2.2}$$

where $G_0(\mathbf{r}, \mathbf{r}')$ is the Green function for the Helmholtz equation

$$(\nabla^2 + E) G_0(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \tag{2.3}$$

Kohn and Rostoker[2] showed that Eq. (2.2) is equivalent to the variational principle $\delta\Lambda[\psi] = 0$ where the functional Λ is defined by the expression

$$\Lambda = \int d\mathbf{r}\, \psi^*(\mathbf{r}) V(\mathbf{r}) \times \left(\psi(\mathbf{r}) - \int d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi(\mathbf{r}') \right). \tag{2.4}$$

This variational principle can be used to obtain a secular equation determining the wave function. Upon using a trial function of the form $\psi = \sum_{j=0}^n a_j \phi_j$, with a_j a complex coefficient and ϕ_j an element of some basis set, and substituting into Eq. (2.4) we obtain

$$\Lambda = \sum_{i,j=0}^{n} a_i^* \Lambda_{ij} a_j, \tag{2.5}$$

where

$$\Lambda_{ij} = \int \phi_i^*(\mathbf{r}) V(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} - \int d\mathbf{r} \int d\mathbf{r}' \phi_i^*(\mathbf{r}) V(\mathbf{r}) G_0(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \phi_j(\mathbf{r}') \tag{2.6}$$

is a Hermitian matrix. The application of the variational principle $\delta\Lambda/\delta a_i = 0$ to Eq. (2.5) yields the set of homogeneous linear equations

$$\sum_{j=1}^{n} \Lambda_{ij} a_j = 0, \quad i = 1, 2, \ldots, n \tag{2.7}$$

which has nontrivial solutions only if its determinant vanishes. This requirement leads to the secular equation

$$\det |\Lambda_{ij}(E)| = 0, \tag{2.8}$$

which determines the energy. The energy dependence of Λ comes from the energy dependence of the Green function and possibly from the energy dependence of the basis functions. Since the energy is determined from a secular equation based on a variational principle, the error in the energy will be of second order with respect to the error in the wave function.

There are three important differences between the Kohn-Rostoker variational principle and the more common variational procedure that is usually associated with the names of Rayleigh[35] and Ritz,[36] namely, $\delta\Omega[\psi] = 0$, where

$$\Omega = \int d\mathbf{r}\, \psi^*(\mathbf{r})[E - H]\psi(\mathbf{r}). \tag{2.9}$$

First, the Kohn-Rostoker secular equation (2.8) is not linear in the energy even if the basis functions ϕ_j are energy independent. Thus, since the convenience of a secular equation that is linear in energy is lost from the beginning, there is no further loss in convenience if the basis functions are chosen to be energy dependent. The second important difference is that since the Kohn-Rostoker variational functional $\Lambda[\psi]$ only involves integral operators rather than the differential operator that occurs in the Rayleigh-Ritz procedure, it remains valid in the presence of discontinuities in the basis functions which would lead to singularities in Eq. (2.9). This makes it possible to choose basis functions that are piecewise combinations of locally exact solutions to the Schrödinger equation.

Thus, although Kohn and Rostoker could have chosen almost any set of functions ϕ_j in which to expand their trial wave function, they chose functions which took best advantage of their variational principle. They divided space into cells, approximated the potential within each cell by a muffin-tin potential, and used as basis functions the exact local solutions to the Schrödinger equation (for the muffin-tin potential) within each cell. The use of locally exact solutions has the important benefit of allowing the volume integrals within each cell that occur in Eq. (2.4) to be reduced by means of Green's theorem to surface integrals which turn out to be trivial to evaluate for muffin-tin potentials. In the following we shall extend their derivation to the case of nonoverlapping potentials of general shape.

A final difference between the Rayleigh-Ritz and Kohn-Rostoker variational principles is that the energy obtained from the secular equation of the Rayleigh-Ritz procedure is not only stationary but a *minimum* (at least for the lowest energy state), and thus provides an upper bound to the exact ground-state energy. The characteristic energies of the Kohn-Rostoker variational procedure are only stationary with respect to errors in the trial wave functions, and therefore it is not possible using the Kohn-Rostoker variational principle to establish a rigorous upper or lower bound even to to the lowest energy state.

III. EXPANSION OF THE WAVE FUNCTION IN BASIS FUNCTIONS OF A NONSPHERICAL POTENTIAL

An important step implicit in the derivation of KKR theory given by Kohn and Rostoker is the assumption that the wave function within any given cell can be expanded in terms of functions which satisfy the Schrödinger equation for a single spherical potential,

$$\psi(\mathbf{r}) = \sum_{L,n} a_L^n R_l(E, r_n) Y_L(\hat{r}_n) \Theta_n(\mathbf{r}). \tag{3.1}$$

We shall show in this section that the above expansion is valid and is a special case of a similar relation

$$\psi(\mathbf{r}) = \sum_{L} a_L^n \phi_L^n(E, \mathbf{r}_n) \Theta_n(\mathbf{r}), \tag{3.2}$$

which holds for nonspherical potentials. Here $\Theta_n(\mathbf{r})$ is unity for $\mathbf{r}$ inside cell n and vanishes otherwise, and $\phi_L^n(E, \mathbf{r}_n)$ is a solution of the Schrödinger equation for energy E, corresponding to the potential in cell n.

We note that the proposition we have undertaken to demonstrate is not a completeness relation in the usual sense of the term. We do not require that *any* function be expandable in terms of the basis functions ϕ_L, only functions that satisfy the Schrödinger equation need be expandable. Furthermore, it should be noted that we cannot simply invoke a theorem from Sturm-Liouville theory to establish the result we seek because the functions ϕ_L are not eigenfunctions of a Sturm-Liouville eigenvalue problem. Our proof is, however, similar to a proof[37] that any function of a complex variable $f(z)$, which is analytic in a domain including the origin, can be expanded in terms of cylindrical Bessel functions $f(z) = \sum_{l=0}^{\infty} a_l J_l(z)$.

The functions $\phi_L^n(\mathbf{r})$ which play a role in this theory analogous to that played by the radial wave functions $R_l(r)Y_L(\hat{r})$ in muffin-tin MST may be determined within a sphere circumscribing cell n. In the remainder of this section we shall omit the superscript n since we are dealing with the basis functions for a single cell. The wave function $\psi(\mathbf{r})$ within the sphere circumscribing this cell is determined by the equation

$$\psi(\mathbf{r}) = \int_{\Omega_S} d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi(\mathbf{r}') - \int_S dS' \hat{\mathbf{n}}' \cdot [G_0(\mathbf{r}, \mathbf{r}') \nabla' \psi(\mathbf{r}') - \nabla' G_0(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}')], \tag{3.3}$$

which may be derived by applying Green's theorem to Eq. (2.2) and assuming that the wave function and its derivative vanish for $\mathbf{r} \to \infty$. In the above equation, the first integral extends over the volume of the sphere and the second over its surface. A relation of this type is valid for any closed surface S, as long as $\mathbf{r}$ is restricted to the enclosed integration volume Ω_s. In Eq. (3.3) and later equations where similar notation is used, the operator ∇' is understood to operate only on the function to its immediate right.

Thus for values of $\mathbf{r}$ within the sphere circumscribing cell n, $\psi(\mathbf{r})$ is determined by the potential within the sphere and by the value and normal gradient of $\psi(\mathbf{r})$ on its surface. (The value and gradient cannot both be *arbitrarily* specified over the entire boundary for then the system will be overdetermined.) This expression can be simplified by use of the standard multipole expansion of the Green function

$$G_0(\mathbf{r},\mathbf{r}') = \sum_L J_L(\mathbf{r}) H_L(\mathbf{r}') \qquad (r' > r), \tag{3.4}$$

where $J_L(\mathbf{r}) = j_l(\kappa r) Y_L(\hat r)$ is a solid harmonic which is regular at the origin, $H_L(\mathbf{r}) = -i\kappa h_l(\kappa r) Y_L(\hat r)$ is an irregular solid harmonic, and $\kappa = E^{1/2}$. The origin that is the center of the sphere can, in principle, be taken anywhere within the cell; however, if there is a singularity in the potential, e.g., from a nucleus, the derivations are simplified if the origin is taken at the singularity. We shall assume in the following that there is no more than one singularity within the cell and that the origin (and the center of the circumscribing sphere) is taken at the singularity if there is one. We shall also assume that any singularities are sufficiently mild that $r^2 v(\mathbf{r})$ is integrable, i.e., that the integral

$$\int_0^{\epsilon} r^2 dr \int d\hat r \, v(\mathbf{r}) \tag{3.5}$$

is finite.

Using the identities $V(\mathbf{r})\psi(\mathbf{r}) = (\nabla^2 + E)\psi(\mathbf{r})$ and $\psi(\mathbf{r}) = \int d\mathbf{r}' (\nabla'^2 + E) G_0(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')$ followed by Green's theorem we have

$$\psi(\mathbf{r}) = \sum_L \{ H_L(\mathbf{r}) [J_L, \psi]_r - J_L(\mathbf{r}) [H_L, \psi]_r \}, \tag{3.6}$$

where the Wronskians $[J_L, \psi]_r$ and $[H_L, \psi]_r$ are defined in terms of integrals over a sphere of radius r surrounding the origin

$$[J_L, \psi]_r = r^2 \int_r d\hat r' \cdot [J_L(\mathbf{r}')\nabla' - \nabla' J_L(\mathbf{r}')]\psi(\mathbf{r}'), \tag{3.7}$$

$$[H_L, \psi]_r = r^2 \int_r d\hat r' \cdot [H_L(\mathbf{r}')\nabla' - \nabla' H_L(\mathbf{r}')]\psi(\mathbf{r}'). \tag{3.8}$$

We know on physical grounds that $\psi(\mathbf{r})$ must be bounded everywhere in space and in particular at the cell center so it can be expanded there in terms of regular solid harmonics,

$$\psi(\mathbf{r}) \to \sum_L a_L J_L(\mathbf{r}) \;\; \text{for} \;\; \mathbf{r} \to 0. \tag{3.9}$$

We therefore define local basis functions $\phi_L^n(\mathbf{r})$ which satisfy the Schrödinger equation (2.1) throughout the sphere circumscribing cell n, which behave as $J_L(\mathbf{r})$ near the origin, and which satisfy Eqs. (3.13) and (3.14) below. If we assume that relation (3.2) is valid, it follows from Eqs. (3.6)–(3.8) that ϕ_L is given by

$$\phi_L(\mathbf{r}) = \sum_{L'} [J_{L'}(\mathbf{r}) C_{L'L}(r) + H_{L'}(\mathbf{r}) S_{L'L}(r)], \tag{3.10}$$

where

$$\begin{aligned} C_{L'L}(r) &= -[H_{L'}, \phi_L]_r \\ &= -r^2 \int_r d\hat r' \cdot [H_{L'}(\mathbf{r}')\nabla' - \nabla' H_{L'}(\mathbf{r}')]\phi_L(\mathbf{r}') \end{aligned} \tag{3.11}$$

and

$$\begin{aligned} S_{L'L}(r) &= [J_{L'}, \phi_L]_r \\ &= r^2 \int_r d\hat r' \cdot [J_{L'}(\mathbf{r}')\nabla' - \nabla' J_{L'}(\mathbf{r}')]\phi_L(\mathbf{r}'). \end{aligned} \tag{3.12}$$

Equations (3.11) and (3.12) may be converted via Green's theorem into volume integrals from which it is easy to see that the basis functions ϕ_L may be obtained by integrating the equations,[6]

$$\frac{dC_{L'L}(r)}{dr} = -r^2 \int_r d\hat r' H_{L'}(\mathbf{r}') V(\mathbf{r}') \phi_L(\mathbf{r}'), \tag{3.13}$$

$$\frac{dS_{L'L}(r)}{dr} = r^2 \int_r d\hat r' J_{L'}(\mathbf{r}') V(\mathbf{r}') \phi_L(\mathbf{r}'). \tag{3.14}$$

These equations are coupled through ϕ_L [Eq. (3.10)]. The boundary condition at the origin is $S_{L'L}(0) = 0$ and $C_{L'L}(0) = \delta_{L'L}$.

In light of recent criticisms[34] it is important to verify that the functions defined by the above procedure are well behaved at the origin. It appears that the generalized cosine function

$$C_{L'L}(r) = \delta_{L'L} - \int_0^r d\mathbf{r}' H_{L'}(\mathbf{r}') V(\mathbf{r}') \phi_L(\mathbf{r}') \tag{3.15}$$

contains a *possible* divergence near the origin arising from the singularity in $H_{L'}$, which is proportional to $r^{-(l'+1)} Y_{L'}(\hat r)$ near the origin. If the potential is spherically symmetric near the origin (and less singular than r^{-2}), the singularity of $H_{L'}$ will be eliminated by the r dependence of ϕ_L which varies as $r^l Y_L(\hat r)$. One may be concerned that a nonspherical potential will couple $H_{L'}$ and ϕ_L for different values of l and l' in such a way that the integrand of Eq. (3.15) will have a nonintegrable singularity.

No such singularity will occur, however, if the potential has the usual form for electronic-structure calculations

$$V(\mathbf{r}) = Z/r + \tilde V(\mathbf{r}), \tag{3.16}$$

where $\tilde V(\mathbf{r})$ has a convergent Taylor-series expansion around the origin

$$\begin{aligned} \tilde V(\mathbf{r}) = a &+ \sum_i b_i x_i + \sum_{i,j} c_{ij} x_i x_j \\ &+ \sum_{i,j,k} d_{ijk} x_i x_j x_k + \cdots . \end{aligned} \tag{3.17}$$

An expansion of this form can be written as

$$\tilde V(\mathbf{r}) = \sum_L r^l f_L(r^2) Y_L(\hat r), \tag{3.18}$$

where f_L is a function of r^2 which is regular at the origin. To see that this is the case, consider one of the terms of order l in Eq. (3.17),

$$x^m y^n z^{l-m-n} = r^l \sum_{l',\mu'} \beta_{l'\mu'} Y_{l'\mu'}(\hat{r}). \tag{3.19}$$

The coefficients $\beta_{l'\mu'}$ are given by

$$\beta_{l'\mu'} = \int d\hat{r}\, Y_{l'\mu'}(\hat{r})(x/r)^m (y/r)^n (z/r)^{l-m-n}, \tag{3.20}$$

from which it is obvious that $\beta_{l'\mu'} = 0$ if $l' > l$. Furthermore, $\beta_{l'\mu'} = 0$ unless the parity of $Y_{l'\mu'}$ is the same as that of $x^m y^n z^{l-m-n}$, which implies that when the expansion (3.17) is converted into an expansion in powers of r and spherical harmonics, the second-order term of (3.17) will generate terms which have r^2 multiplying spherical harmonics with l equal to either 2 or 0. Similarly, the third-order term will generate terms which have r^3 multiplying spherical harmonics with l equal to either 3 or 1, the fourth-order term will generate terms which have r^4 multiplying spherical harmonics with values of l equal to 4, 2, or 0, and so on.

Because each Y_L which enters V in Eq. (3.11) is multiplied by a function which vanishes at least as fast as r^l as $r \to 0$, each term in the integrand of $C_{L'L}(r)$ will be proportional near the origin to

$$f_L(r^2) r^{(l+l''-l'+1)} C(L, L', L''), \tag{3.21}$$

where $C(L, L', L'')$ is an integral of three spherical harmonics over solid angles which vanishes if $l + l'' < l'$. Thus potentials of the form described by Eqs. (3.16) and (3.17) do not cause problems at the origin. Although potentials can be imagined which violate the condition (3.17), and for which the integrand of $C_{L'L}$ might have a nonintegrable singularity at the origin, such potentials do not appear to us to be relevant to electronic-structure calculations.

In order to demonstrate that the wave function within a sphere S surrounding cell n can be expanded in terms of the functions $\phi_L(\mathbf{r})$, we use the result, shown in the Appendix, that the Green function for the Schrödinger equation within the bounding sphere of a cell supporting a potential of the form of Eq. (3.16) has a convergent expansion of the form

$$G(\mathbf{r}, \mathbf{r}') = \sum_L \phi_L(\mathbf{r}_<) F_L(\mathbf{r}_>). \tag{3.22}$$

Here $F_L(\mathbf{r})$ is proportional to a linear combination of irregular solid harmonics for points outside the range of the potential. Within the range of the potential it is an irregular solution to the Schrödinger equation.

By virtue of the definition of the Green function and the fact that $\psi(\mathbf{r})$ satisfies the Schrödinger equation by assumption we can write

$$\psi(\mathbf{r}) = \int d\mathbf{r}'[\nabla'^2 + E - V(\mathbf{r}')]G(\mathbf{r}, \mathbf{r}')\psi(\mathbf{r}') - \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}')[\nabla'^2 + E - V(\mathbf{r}')]\psi(\mathbf{r}'), \tag{3.23}$$

which can be converted by Green's theorem into

$$\psi(\mathbf{r}) = \int_S dS'\, \hat{\mathbf{n}}' \cdot [\nabla' G(\mathbf{r}, \mathbf{r}') - G(\mathbf{r}, \mathbf{r}')\nabla']\psi(\mathbf{r}'), \tag{3.24}$$

where the integral is over the surface of the sphere S. Using the expansion (3.22) in this integral gives, for points $\mathbf{r}$ *within* this sphere,

$$\psi(\mathbf{r}) = \sum_L \phi_L(\mathbf{r}) a_L, \tag{3.25}$$

where a_L is given by

$$a_L = \int_S dS'\, \hat{\mathbf{n}} \cdot [\nabla' F_L(\mathbf{r}') - F_L(\mathbf{r}')\nabla']\psi(\mathbf{r}'). \tag{3.26}$$

In the limit as $l \to \infty$, the angular momentum term in the kinetic energy $l(l+1)/r^2$ dominates the potential energy so that $\phi_L(\mathbf{r}) \to J_L(\mathbf{r})$, and $F_L(\mathbf{r}') \to H_L(\mathbf{r}')$ and since $\mathbf{r}' > \mathbf{r}$, by assumption, the expansion is convergent.

The result for a_L, Eq. (3.26), agrees with a result obtained by Brown and Ciftan.[11] We can rewrite their Eq. (2.30) in terms of Wronskian integrals over the surface of the sphere,

$$[H_L, \psi]_S = \sum_{L'} [H_L, \phi_{L'}]_S\, a_{L'}, \tag{3.27}$$

whereas Eq. (3.26) above is equivalent to $a_L = -[F_L, \psi]_S$, and from Eq. (A3) we have

$$\sum_{L'} [H_L, \phi_{L'}]_S F_{L'} = -H_L. \tag{3.28}$$

We believe, however, that their derivation is incomplete because in their Eq. (2.29) a sum and an integral were interchanged without justification.

The functions $\phi_L^n(\mathbf{r})$ have the interesting and useful property that for points within cell n their value is unaffected if the potential is modified outside cell n. In particular the potential outside cell n can be set to zero without affecting the value of the functions within the cell where they are used to expand the wave function.[22] Thus the functions $\phi_L^n(E, \mathbf{r})$ can, for points $\mathbf{r}$ inside cell n, be assumed to have been calculated using a potential which is equal to $v_n(\mathbf{r})$ inside cell n and which vanishes outside that cell and thus to be independent of the potentials in neighboring cells.

IV. MST FOR NONSPHERICAL MUFFIN-TIN POTENTIALS

In this section we present a variational derivation of the secular equation of MST for potentials which are nonspherical but which vanish outside a circumscribing sphere. Thus the potentials considered in this section have the form $V(\mathbf{r}) = \sum_n v_n(\mathbf{r}_n)$, where the individual potentials $v_n(\mathbf{r})$ vanish outside a radius R_n. This derivation generalizes the Kohn-Rostoker derivation by allowing the atoms to assume arbitrary positions (subject to the constraint that their circumscribing spheres do not overlap) and by allowing the potentials to be nonspherical within the circumscribing spheres. It also helps to highlight the difficulty that must be faced in the general case (treated in Sec. V) in which the circumscribing spheres do overlap.

For potential functions of the type considered in this section, the Kohn-Rostoker variational functional, $\Lambda[\psi]$ can be written as a sum over individual potentials

$$\Lambda = \sum_n \Lambda^n = \sum_n \int_{R_n} d\mathbf{r}\, \psi^*(\mathbf{r}) v_n(\mathbf{r}) B^n(\mathbf{r}), \tag{4.1}$$

where the integral extends over the sphere of radius R_n centered at site n. The function $B^n(\mathbf{r})$ is given by

$$B^n(\mathbf{r}) = \psi(\mathbf{r}) - \int d\mathbf{r}\, G_0(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}'), \tag{4.2}$$

where the integral is over all of space and the superscript n on $B^n(\mathbf{r})$ reminds us that the argument $\mathbf{r}$ of B^n lies within the muffin-tin in cell n. $B^n(\mathbf{r})$ satisfies the Helmholtz equation, i.e., $(\nabla^2 + E)B^n(\mathbf{r}) = 0$, so that we can use Green's theorem to write Λ^n as a surface integral over the surface of the sphere which encloses potential n:

$$\Lambda^n = R_n^2 \int d\hat{r} \left(\frac{\partial}{\partial r}\psi^*(\mathbf{r}) - \psi^*(\mathbf{r})\frac{\partial}{\partial r} \right) B^n(\mathbf{r}). \tag{4.3}$$

The function $B^n(\mathbf{r})$, written above as an integral over all of space, can also be written as a sum of integrals over the individual cells. Using the facts that $\psi(\mathbf{r}) = \int d\mathbf{r}'(\nabla'^2 + E)G_0(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')$ and $V(\mathbf{r})\psi(\mathbf{r}) = (\nabla^2 + E)\psi(\mathbf{r})$, we can write it in the form

$$B^n(\mathbf{r}) = \sum_m \int_{S_m} dS'\, \hat{\mathbf{n}}' \cdot [\nabla' G_0(\mathbf{r},\mathbf{r}') - G_0(\mathbf{r},\mathbf{r}')\nabla']\psi(\mathbf{r}'). \tag{4.4}$$

Since the argument $\mathbf{r}$ of $B(\mathbf{r})$ in Eq. (4.3) is on the surface of a sphere of radius R_n and the integration is over cell surfaces S_m, we know that $r < r'$ for all points in all of the integrals in Eq. (4.4). This is a crucial point that facilitates the derivation of MST because it allows us to expand the Green functions in Eq. (4.4) in the form $G(\mathbf{r},\mathbf{r}') = \sum_L J_L(\mathbf{r}H_L(\mathbf{r}')$. Note that this is only true if the potentials have the geometry assumed here. It is not true if any of the circumscribing spheres overlap, e.g., for full cell potentials.

Using the expansion of the Green function we have

$$\Lambda_n = \sum_{mL} [\psi^*, J_L^n]_{R_n} [H_L^n, \psi]_{S_m}, \tag{4.5}$$

where

$$[\psi^*, J_L^n]_{R_n} = R_n^2 \int_{R_n} d\hat{r}_n \left[\psi^*(\mathbf{r}_n)\frac{\partial}{\partial r}J_L(\mathbf{r}_n) - \left(\frac{\partial}{\partial r}\psi^*(\mathbf{r}_n)\right) J_L(\mathbf{r}_n) \right] \tag{4.6}$$

and

$$[H_L^n, \psi]_{S_m} = \int_{S_m} dS' \hat{\mathbf{n}}' \cdot \{ H_L(\mathbf{r}_n')\nabla'\psi(\mathbf{r}_m') - [\nabla' H_L(\mathbf{r}_n')]\psi(\mathbf{r}_m')\}. \tag{4.7}$$

The notation $\mathbf{r}_n'$, for example, means $\mathbf{r}' - \mathbf{R}_n$. For $n \neq m$, the irregular solid harmonics centered on site n, $H_L(\mathbf{r}_n')$, can be expanded in terms of regular solid harmonics centered on site m

$$H_L(\mathbf{r}_n') = \sum_{L'} G_{LL'}(\mathbf{R}_{nm}) J_L(\mathbf{r}_m'), \tag{4.8}$$

where

$$G_{LL'}(\mathbf{R}_{nm}) = 4\pi \sum_{L''} \mathbf{i}^{l-l'-l''} C(LL'L'') H_{L'}(\mathbf{R}_{nm}), \tag{4.9}$$

with $C(LL'L'')$ being a Gaunt number (integral of three spherical harmonics), so that,

$$\Lambda = \sum_{m,n,L_1,L_2} [\psi^*, J_{L_1}^n]_{R_n} \{ [H_{L_1}^n, \psi]_{R_n} \delta_{mn} \delta_{L_1 L_2} + G_{L_1 L_2}(R_{mn}) [J_{L_2}^n, \psi]_{R_m} \}. \tag{4.10}$$

Substitution for ψ and ψ^* by their expansions in terms of the local basis functions discussed in the preceding section yields

$$\Lambda = - \sum_{m,n,L,L',L_1,L_2} a_L^{n*} \tilde{S}_{LL_1}^n \{ C_{L_1 L_2}^n \delta_{L_1 L_2} - G_{L_1 L_2}(R_{mn}) S_{L_2 L'}^m \} a_L^m . \tag{4.11}$$

Variation with respect to the coefficients a yields the generalized KKR secular matrix

$$\tilde{S}\{C - GS\}a = 0. \tag{4.12}$$

This result can be cast into a more familiar form by omitting the factor $\tilde{S}$ and by defining a new set of coefficients $b = S^{-1}a$,

$$\{CS^{-1} - G\}b = 0. \tag{4.13}$$

As will be discussed in the following section, however, the removal of the transposed sine matrix $\tilde{S}$ may destroy the variational nature of the solutions, and the inversion of the sine matrix may not always be possible.

V. VARIATIONAL DERIVATION OF MST FOR SPACE-FILLING CELLS

In this section we treat the general case of potentials which may be nonzero throughout the Wigner-Seitz cell. For convenience of exposition we treat the case where the total potential $V(\mathbf{r})$ is confined to a finite region of space. Our final formulas will, however, be applicable to infinite systems as well. We divide this region into nonoverlapping but otherwise arbitrarily shaped cells, denoting by Ω_n the volume occupied by cell n, and by $v_n(\mathbf{r})$ the potential within that cell. As in the preceding section, Λ will be written in the form $\Lambda = \sum_n \Lambda^n$, where

$$\Lambda^n = \int_{\Omega_n} d\mathbf{r}\, \psi^*(\mathbf{r}) v_n(\mathbf{r}) B^n(\mathbf{r}) \tag{5.1}$$

and where $B^n(\mathbf{r})$ is again given by Eq. (4.2) with the small but important difference that $\mathbf{r}$ can now be any point within cell n. Just as in the preceding section, Green's theorem can be used to convert $B^n(\mathbf{r})$ into surface integrals over each of the cells m,

$$B^n(\mathbf{r}) = \sum_m \int_{S_m} dS'\, \hat{\mathbf{n}}' \cdot [\nabla' G_0(\mathbf{r},\mathbf{r}') - G_0(\mathbf{r},\mathbf{r}')\nabla']\psi(\mathbf{r}'). \tag{5.2}$$

Similarly, the identities $(\nabla^2 + E)B^n(\mathbf{r}) = 0$ and $\psi^*(\mathbf{r})v_n(\mathbf{r}) = (\nabla^2 + E)\psi^*(\mathbf{r})$ can be used with Green's theorem to write Λ^n as

$$\Lambda^n = \int_{S_n} dS\, \hat{\mathbf{n}} \cdot [\nabla\psi^*(\mathbf{r}) - \psi^*(\mathbf{r})\nabla] B^n(\mathbf{r}) \tag{5.3}$$

$$= \int_{S_n} dS\, \hat{\mathbf{n}} \cdot [\nabla\psi^*(\mathbf{r}) - \psi^*(\mathbf{r})\nabla] \sum_m \int_{S_m} dS'\, \hat{\mathbf{n}}' \cdot [\nabla' G_0(\mathbf{r},\mathbf{r}') - G_0(\mathbf{r},\mathbf{r}')\nabla']\psi(\mathbf{r}'). \tag{5.4}$$

In order to derive a useful formula for Λ^n, we must separate the integrals in Eq. (5.4). This can be done by using the Green-function expansion $G_0(\mathbf{r},\mathbf{r}') = \sum_L J_L(\mathbf{r}) H_L(\mathbf{r}')$ centered about a point in cell n, but in order to be certain that this expansion is convergent, we require that all points $(\mathbf{r}')$ on the surface S_m be farther from the expansion center in cell n than all points $(\mathbf{r})$ on the surface S_n of cell n. If cells n and m are not near neighbors, this condition is satisfied, but if $n = m$ or if cells n and m are neighbors, this condition appears to be violated and these cases must be given further consideration. Let us write Eq. (5.2) as

$$B^n(\mathbf{r}) = \sum_{m,L'} B^{nm}_{L'}(\mathbf{r}) a^m_{L'}, \tag{5.5}$$

where we have expanded $\psi(\mathbf{r}')$ in terms of the local basis functions Eq. (3.2) within each of the cells m so that

$$B^{nm}_{L'}(\mathbf{r}) = \int_{S_m} dS' \hat{\mathbf{n}}' \cdot [\nabla' G_0(\mathbf{r},\mathbf{r}') - G_0(\mathbf{r},\mathbf{r}')\nabla'] \phi^m_{L'}. \tag{5.6}$$

If cells n and m are not near neighbors, it is clear that $B^{nm}_{L'}$ can be written in the form

$$B^{nm}_{L'}(\mathbf{r}) = -\sum_{L_1} J_{L_1}(\mathbf{r}_n)[H^n_{L_1}, \phi^m_{L'}]_{S_m}, \tag{5.7}$$

where the square brackets are used as in the preceding section [Eq. (4.7)] to denote a Wronskian-type surface integral over the surface of cell m of an irregular solid harmonic centered in cell n and a basis function centered in cell m.

It is slightly less obvious but equally true that $B^{nm}_{L'}$ can be written in this form when n and m are the same cell or near neighbors. First consider the case where $m = n$. In this case the surface S_m in Eq. (5.6) can be expanded to a sphere which circumscribes the cell without changing the value of $B^{mm}_{L'}$. This can be seen by using Green's theorem to convert Eq. (5.6) into a volume integral

$$B^{mm}_{L'}(\mathbf{r}) = \phi^m_{L'}(\mathbf{r}) - \int_{\Omega_m} d\mathbf{r}' G_0(\mathbf{r},\mathbf{r}') v_m(\mathbf{r}') \phi^m_{L'}(\mathbf{r}') \tag{5.8}$$

from which it is clear that Ω_m can be *any* volume which includes cell m, i.e., the region where v_m is nonzero, and therefore S_m can be any surface which encloses cell m. Expanding S_m to a sphere circumscribing cell m allows the use of the Green-function expansion to obtain Eq. (5.7).

When m and n are neighbors we can again expand the surface S_m so that all points on its surface are farther from the expansion center in cell n than all points on the surface S_n (Fig. 1). In performing this expansion, however, it is necessary to enclose the expansion center in cell n with the result that the value of the surface integral is changed. Let $\tilde{S}_m$ represent the expanded surface and let $\tilde{B}^{nm}_{L'}$ represent the value of the surface integral over the expanded surface. It is clear that

$$\tilde{B}^{nm}_{L'}(\mathbf{r}) = \phi^m_{L'}(\mathbf{r}) - \int d\mathbf{r}' G(\mathbf{r},\mathbf{r}') v_m(\mathbf{r}') \phi^m_{L'}(\mathbf{r}'), \tag{5.9}$$

while

$$B^{nm}_{L'}(\mathbf{r}) = -\int d\mathbf{r}' G(\mathbf{r},\mathbf{r}') v_m(\mathbf{r}') \phi^m_{L'}(\mathbf{r}'). \tag{5.10}$$

Thus $\tilde{B}^{nm}_{L'}(\mathbf{r}) = B^{nm}_{L'}(\mathbf{r}) + \phi^m_{L'}(\mathbf{r})$. Now $\tilde{B}^{nm}_{L'}$ can be written as

$$\tilde{B}^{nm}_{L'}(\mathbf{r}) = -\sum_{L_1} J_{L_1}(\mathbf{r}_n)[H^n_{L_1}, \phi^m_{L'}]_{\tilde{S}_m}. \tag{5.11}$$

Consider the surface integrals $[H^n_{L_1}, \phi^m_{L'}]_{\tilde{S}_m}$. Each of these may be split into an integral over S_m and an integral over the the surface bounding the remainder of $\tilde{\Omega}_m$. This latter surface integral may be reduced to the integral over a small sphere centered at the the expansion center in cell n. Thus

$$[H^n_{L_1}, \phi^m_{L'}]_{\tilde{S}_m} = [H^n_{L_1}, \phi^m_{L'}]_{S_m} + [H^n_{L_1}, \phi^m_{L'}]_{S^0_n}, \tag{5.12}$$

where S^0_n is a small sphere surrounding the expansion center in cell n, i.e., the singularity of $H_{L_1}(\mathbf{r}_n)$.

Now $\phi^m_{L'}$ satisfies the Helmholtz equation $(\nabla^2 + E)\phi^m_{L'}(\mathbf{r}) = 0$ for $\mathbf{r}$ outside of cell m. For this reason, by arguments analogous to those of Sec. III, $\phi^m_{L'}$ can be expanded in regular solid harmonics about the point $\mathbf{r}_n = 0$,

$$\phi^m_{L'}(\mathbf{r}) = \sum_{L_2} J^n_{L_2}(\mathbf{r}_n) \alpha^{nm}_{L_2 L'}. \tag{5.13}$$

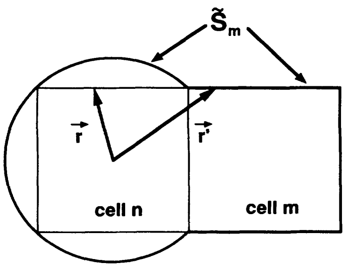

FIG. 1. The surface integral over cell m may be expanded to enclose a sphere which circumscribes cell n.

Then using the relation $[H_L, J_{L'}] = -\delta_{LL'}$ we have

$$[H^n_{L_1}, \phi^m_{L'}]_{S^0_n} = -\alpha^{nm}_{L_2L'} \tag{5.14}$$

and

$$-\sum_{L_2} J^n_{L_2}(\mathbf{r}_n)[H^n_{L_2}, \phi^m_{L'}]_{S^0_n} = \phi^m_{L'}(\mathbf{r}), \tag{5.15}$$

which is valid so long as $\mathbf{r}$ is inside a sphere inscribed within cell n. However, this relation defines a boundary condition for the wave function represented by the above summation and its derivative on the surface of this sphere. This, together with the fact that the same wave function satisfies the Helmholtz equation, uniquely determines its values throughout the cell, and in fact throughout the region where $v_m = 0$. Consequently summation (5.15) gives $\phi^m_{L'}(\mathbf{r})$ everywhere in cell n.

Thus $\tilde{B}^{nm}_{L'}(\mathbf{r})$ can be written as

$$\tilde{B}^{nm}_{L'}(\mathbf{r}) = -\sum_{L_1} J_{L_1}(\mathbf{r}_n)[H^n_{L_1}, \phi^m_{L'}]_{S_m} + \phi^m_{L'}(\mathbf{r}), \tag{5.16}$$

which implies [upon comparison with Eqs. (5.9)–(5.11)] that B^{nm} can be written in the form

$$B^{nm}_{L'}(\mathbf{r}) = -\sum_{L_1} J_{L_1}(\mathbf{r}_n)[H^n_{L_1}, \phi^m_{L'}]_{S_m} \tag{5.17}$$

even if cells n and m are near neighbors.

Using these results to separate the integrals over S_n and S_m in Eq. (5.4), the integral over S_n becomes

$$\sum_L a^{n*}_L \int_{S_n} dS\,\hat{\mathbf{n}} \cdot [\nabla\phi^{n*}_L(\mathbf{r}) - \phi^{n*}_L(\mathbf{r})\nabla] J_{L''}(\mathbf{r}_n). \tag{5.18}$$

Thus Λ can be written in the form

$$\Lambda = \sum_n \Lambda^n = \sum_{n,n',L,L'} a^{n*}_L \lambda^{nn'}_{LL'} a^{n'}_{L'}, \tag{5.19}$$

where

$$\lambda^{nn'}_{LL'} = \sum_{L''} \int_{S_n} dS\,\hat{\mathbf{n}} \cdot [\nabla\phi^{n*}_L(\mathbf{r}_n) - \phi^{n*}_L(\mathbf{r}_n)\nabla] J_{L''}(\mathbf{r}_n) \times \int_{S_{n'}} dS'\hat{\mathbf{n}}' \cdot [\nabla' H_{L''}(\mathbf{r}'_n) - H_{L''}(\mathbf{r}'_n)\nabla']\phi^{n'}_{L'}(\mathbf{r}'_{n'}). \tag{5.20}$$

Note that it is now *necessary* that the surface integrals be performed *before* the sum over L''. Otherwise the sum would diverge whenever r'_n is smaller than r_n, a situation that will occur for general potentials, but which can be avoided for muffin-tin potentials. The reason for the lack of commutivity of the sums and integrals in the last equation is the fact that one may replace complete sums or integrals by complete sums or integrals of the same value, but one may not necessarily be allowed to rearrange the individual terms of infinite sums.

The generalized KKR equations are obtained by minimizing Eq. (5.19) with respect to the coefficients a^n_L, with the result

$$\sum_{n',L'} \lambda^{nn'}_{LL'}(E) a^{n'}_{L'} = 0. \tag{5.21}$$

The eigenvalues of Eq. (2.1) are found among those values of E for which the determinant of the Hermitian matrix $\lambda^{nn'}_{LL'}$ vanishes. This matrix is the product of the generalized sine and cosine matrices $S^n_{LL'}$, and $C^{nn'}_{LL'}$ defined by the expressions

$$S^n_{LL'}(E) = \int_{S_n} dS\,\hat{\mathbf{n}} \cdot [J_L(\mathbf{r}_n)\nabla - \nabla J_L(\mathbf{r}_n)]\phi^n_{L'}(\mathbf{r}_n) \tag{5.22}$$

and

$$C^{nn'}_{LL'} = \int_{S_{n'}} dS'\hat{\mathbf{n}}' \cdot [\nabla' H_L(\mathbf{r}'_n) - H_L(\mathbf{r}'_n)\nabla']\phi^{n'}_{L'}(\mathbf{r}'_{n'}), \tag{5.23}$$

so that

$$\lambda^{nn'}_{LL'} = \sum_{L''} \tilde{S}^n_{LL''} C^{nn'}_{L''L'}, \tag{5.24}$$

with a tilde denoting the transpose of a matrix. Note that in $C^{nn'}_{LL'}$ the integral extends over the surface of cell $\Omega_{n'}$ but that the Hankel function is expanded about the center of cell Ω_n. We see that $S^n_{LL'}$ and $C^n_{LL'} = C^{nn}_{LL'}$ are, respectively, the generalized sine and cosine matrices for cell n defined in Sec. III.

If the shape of the cell is such that the intercell vectors which connect the expansion centers of each cell are larger than all of the intracell vectors between a cell center and its boundary, the generalized cosine matrix $C^{nn'}_{LL'}$ can be be expanded using the addition theorem for the irregular solid harmonics, Eq. (4.8), allowing the generalized cosine matrix to be written, for $n \neq n'$, as

$$C^{nn'}_{LL'} = -\sum_{L''} G_{LL''}(\mathbf{R}_{nn'}) S^{n'}_{L''L}. \tag{5.25}$$

For periodic materials, the Fourier transform of $G_{LL'}(\mathbf{R}_{nn'})$ yields the well-known structure constants of the KKR method. With the use of Eq. (5.25), the secular equation which determines the allowed energies can be written in the form

$$\det\left|\underline{\tilde{S}}^n\,\underline{C}^n - \underline{\tilde{S}}^n\{\underline{G}^{nm}\underline{S}^m\}\right| = 0. \tag{5.26}$$

Here, underlined quantities denote matrices in L space, and the curly brackets indicate that for nearby cells, e.g., nearest neighbors, the product of the structure constants and one of the sine matrices must be carried to convergence before the other sine matrix is multiplied by the resulting product.

The last expression shows that the secular equation for MST for space filling, even nonconvex but nonoverlapping cells, has the same form as the secular equation for MT potentials. In particular the separation of structure and potential, i.e., the structure constants and the sine and cosine matrices, that characterizes MST in the MT case remains a feature of the non-MT case subject to the constraint mentioned above, namely that the expansion of the generalized cosine matrix Eq. (5.25) into a structure constant matrix and a sine matrix requires that the distances between expansion centers in different cells exceed the distances between the expansion center for a given cell and all points on its boundary.

It is important to realize moreover that the rate of convergence of the expansion Eq. (4.8) depends on L as well as on the ratio $r_{n'}/R_{nn'}$ with larger values of L requiring that the summation over L' be truncated at higher values. For muffin-tin potentials of equal radii, the ratio $r_{n'}/R_{nn'}$ never exceeds 0.5 and the convergence of this sum is seldom a critical consideration, but as this ratio approaches unity great care must be exercised to maintain convergence. The usual practice of treating all matrices as square and truncating them at a common cutoff ($l_{\max}$) can easily lead to a sequence of solutions that as a function of $l_{\max}$ appears to converge for low values of $l_{\max}$ but actually diverges. The importance of converging any internal summation has been noted previously.[23,27]

Formally, Eq. (5.26) can be written in a number of equivalent forms which, however, exhibit different convergence characteristics. As is shown in Sec. VI it is possible, for example, to derive rigorously a version of the MST equations which omits the $\tilde{S}$, i.e.,

$$\sum_{n',L'} C^{nn'} a_{L'}^{n'} = 0, \tag{5.27}$$

but the energies for which this equation is satisfied will not be variational with respect to the wave function as are those obtained from Eqs. (5.21) or (5.26). The result that some forms of the KKR secular equation are variational while others are not is a new feature which distinguishes non-muffin-tin MST from the muffin-tin limit and is due to the conditional convergences associated with non-muffin-tin MST and the consequent necessity of converging internal angular momentum sums. The practical consequence of this is that it is not strictly correct to view Eq. (5.26) or $\lambda_{LL'}^{nn'}$ in Eq. (5.24) as the products of *square* matrices $\tilde{S}^n$ and $C^{nn'}$.

VI. NONVARIATIONAL DERIVATION OF MST FOR SPACE-FILLING CELLS

In this section we provide a nonvariational derivation of the secular equation of multiple-scattering theory. This derivation is considerably simpler than that of the preceding section and is valid in the case of arbitrarily shaped and even interpenetrating cells, provided the following two restrictions are satisfied: First, it is assumed that there exists a finite neighborhood around the origin of a cell that lies in the domain of the cell. Second, it is assumed that the shortest intercell vector (nearest-neighbor vector) is larger than any intracell vector. Under these two fairly broad conditions that are easily satisfied in the case of most realistic materials, the secular equation of MST takes the MT form. In the event that the first condition is satisfied, but one or more of the intercellular vectors violates the second condition, MST is still valid, but its form is slightly different from that of muffin-tin MST.

We begin with the Lippmann-Schwinger equation (2.2),

$$B(\mathbf{r}) = \psi(\mathbf{r}) - \int G_0(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}')d\mathbf{r}' = 0. \tag{6.1}$$

Thus we are looking for the bound states of the potential $V(\mathbf{r})$ or for the states that exist even in the absence of an incident wave. Using Eqs. (2.3) and (2.1) we have

$$\begin{aligned} 0 &= \int \{G_0(\mathbf{r},\mathbf{r}')\nabla'^2\psi(\mathbf{r}') - [\nabla'^2 G_0(\mathbf{r},\mathbf{r}')]\psi(\mathbf{r}')\}d\mathbf{r}' \\ &= \sum_n \int_{\Omega_n} \{G_0(\mathbf{r},\mathbf{r}')\nabla'^2\psi(\mathbf{r}') - [\nabla'^2 G_0(\mathbf{r},\mathbf{r}')]\psi(\mathbf{r}')\}d\mathbf{r}'. \end{aligned} \tag{6.2}$$

The second line of this equation follows upon partitioning the volume of integration into the volumes of individual cells, with a subsequent summation over cells. Through the use of Green's theorem, this equation can be converted to a sum of surface integrals

$$\sum_n \int_{S_n} dS'\hat{\mathbf{n}}\cdot[G_0(\mathbf{r},\mathbf{r}'_n)\nabla' - \nabla' G_0(\mathbf{r},-\mathbf{r}')]\psi(\mathbf{r}') = 0, \tag{6.3}$$

where now $\hat{\mathbf{n}}\cdot\nabla'$ denotes the outward derivative over the surface S_n of the cell at n. Upon substituting the expansion in local basis functions, Eq. (3.2), for $\psi(\mathbf{r})$ in Eq. (6.3), and writing

$$G_0(\mathbf{r},\mathbf{r}') = \sum_L G_L(\mathbf{r},\mathbf{r}'), \tag{6.4}$$

with

$$G_L(\mathbf{r},\mathbf{r}') = \begin{cases} J_L(\mathbf{r})H_L(\mathbf{r}') & \text{if } r' > r \\ H_L(\mathbf{r})J_L(\mathbf{r}') & \text{if } r > r', \end{cases} \tag{6.5}$$

we can cast Eq. (6.3) in the form

$$\begin{aligned} 0 = \sum_n \int_{S_n} dS'\hat{\mathbf{n}}\cdot \sum_{L',L} [\, & G_{L'}(\mathbf{r},\mathbf{r}'_n)\nabla'\phi_L^n(\mathbf{r}'_n) \\ & -\phi_L^n(\mathbf{r}'_n)\nabla' G_{L'}(\mathbf{r},\mathbf{r}'_n)]a_L^n. \end{aligned} \tag{6.6}$$

Now, consider $G_0(\mathbf{r},\mathbf{r}')$ with $\mathbf{r}$ in cell Ω_p and $\mathbf{r}'$ on the *surface* of cell Ω_n. Upon restricting $\mathbf{r}$ to lie inside a sphere inscribed within cell Ω_p, we have, $G_L(\mathbf{r}_p,\mathbf{r}'_n) = J_L(\mathbf{r}_p)H_L(\mathbf{r}'_n)$, and Eq. (6.6) takes the form

$$0 = \sum_{L'} J_{L'}(\mathbf{r}_p) \sum_n \int_{S_n} dS'\hat{\mathbf{n}}\cdot \sum_L [H_{L'}(\mathbf{r}'_p)\nabla' - \nabla' H_{L'}(\mathbf{r}'_p)]\, \phi_L^n(\mathbf{r}'_n)a_L^n. \tag{6.7}$$

Finally, using the expression Eq. (5.23) we obtain

$$-\sum_{L'} J_{L'}(\mathbf{r}_p)\sum_{L,n} C^{pn}_{L'L} a^n_L = 0. \tag{6.8}$$

The secular equation determining the coefficients a^n_L now follows from Eq. (6.8). Since $J_L(\mathbf{r}_p)$ does not vanish identically, we must have

$$\sum_{L,n} C^{pn}_{L'L} a^n_L = 0, \tag{6.9}$$

which has a nontrivial solution for the a^n_L only if the determinant vanishes,

$$\det C^{pn}_{LL'} = 0. \tag{6.10}$$

This equation is a computationally tractable, MST secular equation that is valid for arbitrary cell shapes, subject, so far as we can ascertain, only to the requirement that there be a finite region surrounding the origin of each cell that is within the domain of that cell so that the argument connecting Eqs. (6.8) and (6.9) is valid.

If the cell geometries are such that $|\mathbf{R}_{pn}| > |\mathbf{r}'_n|$ for all values of $\mathbf{r}'_n$, we can expand $H_{L'}(\mathbf{r}'_p)$ using Eq. (4.8) and use Eqs. (5.24) and (5.22) to write

$$C^{pn}_{LL'} = C^n_{LL'}\delta_{np} - \sum_{L} G_{LL''}(\mathbf{R}_{pn}) S^p_{L''L'}(1-\delta_{np}). \tag{6.11}$$

Upon substitution into Eq. (6.10), the last expression leads immediately to the usual form of the secular equation of MST.

VII. NUMERICAL RESULTS

In order to demonstrate the validity of Eq. (5.26) and the variational nature of the energy for its solutions, we have calculated the energy and the wave function for some of the $\mathbf{k} = 0$ states of a two-dimensional square lattice. In this test the individual potentials $v_n(\mathbf{r})$ were taken as a constant V_0 within cell n and zero outside. The cells were squares arranged so as to completely fill the plane. Thus, although the total crystal potential was V_0, a constant which allowed us to trivially calculate the exact wave function and eigenenergies of the Schrödinger equation, MST was faced with the formidable task of representing these functions using the free-space Green function. Details of the the two-dimensional "empty lattice test" such as the two-dimensional versions of $H_L(\mathbf{r})$, $J_L(\mathbf{r})$, and $G_{LL'}(\mathbf{R})$ can be found in papers by Butler and Nesbet[27] and Faulkner.[15] Note, however, that our conclusions concerning the validity of MST as determined by the empty lattice test differ from those of Faulkner, who obtained extremely poor convergence in angular momentum and was not able to decide whether or not near-field corrections are necessary.

Results for the empty lattice test are shown in Table I. The column denoted by $l_{\max}$ shows the maximum value of the orbital angular momentum used in the expansion of the wave function. We emphasize, however, that it is necessary to converge all internal sums if one is to obtain meaningful results in a test such as this. Thus internal sums were not truncated at $l_{\max}$, but carried to full convergence by means of calculating the quantities $C^{nn'}_{LL'}$ through direct integration for the first two nearest-neighbor shells of a given site. Since the state being investigated was a state with full square symmetry, only values of orbital angular momentum evenly divisible by 4 entered the calculation. The column denoted by E_{calc} contains the energies for which the secular Eq. (5.26) is satisfied. We also show the ratio of the error in the energy ($E_{\text{calc}} - E_{\text{exact}}$) to mean-square error in the wave function (MSWFE) defined as

$$\int d\mathbf{r}|\psi_{\text{calc}}(\mathbf{r}) - \psi_{\text{exact}}(\mathbf{r})|^2 \Big/ \int d\mathbf{r}|\psi_{\text{exact}}|^2, \tag{7.1}$$

where the calculated value of the wave function ψ_{calc} was obtained from Eq. (3.10) using the coefficients a^n_L obtained from Eq. (5.21). Finally, we show E_{var}, a variationally refined value of the energy, calculated by using the Rayleigh-Ritz variation principle with the calculated wave function

$$E_{\text{var}} = \frac{\int d\mathbf{r}\, \psi^*_{\text{calc}}(\mathbf{r}) H \psi_{\text{calc}}(\mathbf{r})}{\int d\mathbf{r}|\psi_{\text{calc}}(\mathbf{r})|^2}. \tag{7.2}$$

TABLE I. Calculated energies and wave-function errors for the second and third $k = 0$ states of a square lattice. The depth of the potential in this example is taken as $V_0 = -9$, and the side of the square is π. The energy is measured in units of l^{-2} where l is the unit length. The maximum angular momentum used in the calculation is denoted by $l_{\max}$, while E_{exact} and E_{calc} denoted the exact and calculated energies and MSWFE denotes the mean-square error in the wave function. E_{var} denotes the energy calculated by using the calculated MST wave function in the Rayleigh-Ritz variational expression for the energy. These calculations employed the variational version of MST, Eq. (5.21).

$l_{\max}$	E_{exact}	E_{calc}	MSWFE	$\frac{E_{\text{calc}} - E_{\text{exact}}}{\text{MSWFE}}$	E_{var}
0	-5.0	-5.9291847	6.91×10^{-3}	-3.58	-4.906345
4	-5.0	-4.9999550	7.97×10^{-6}	5.65	-4.999792
4	-1.0	-0.994071	1.15×10^{-3}	5.15	-0.978936
8	-1.0	-0.99999989	1.55×10^{-8}	7.02	-0.9999989

TABLE II. Calculated energies and wave-function errors for the second and third $k = 0$ states of a square lattice. The parameters are the same as for Table I. These calculations employed a nonvariational version of MST, Eq. (5.27).

$l_{\max}$	E_{exact}	E_{calc}	MSWFE	$\frac{E_{\text{calc}} - E_{\text{exact}}}{\text{MSWFE}}$	E_{var}
0	-5.0	-4.0386580	1.88×10^{-1}	5.12	-4.2449788
4	-5.0	-5.0125155	3.39×10^{-5}	-369.22	-4.9996807
4	-1.0	-0.8783834	1.87×10^{-3}	65.10	-0.9704981
8	-1.0	-0.9992260	1.33×10^{-7}	5811.48	-0.9999960

The calculated $\mathbf{k} = 0$ wave functions can be used in the Rayleigh-Ritz procedure because they are continuous across the cell boundaries due to their symmetry. Although their derivatives are not continuous, the contribution to the Rayleigh-Ritz integral from the discontinuity of the wave-function derivatives can be accounted for by a formula due to Kohn[39] and Schlosser and Marcus.[40]

The important point to notice is that the error in the energy is of the same order as the mean-square error of the wave function, even though both of these vary over eight orders of magnitude for the different values of $l_{\max}$. Furthermore, it is clear that the variational procedure does not improve the energy over the value obtained from the secular equation itself. These results may be contrasted with similar calculations using the version of the MST equations without the $\tilde{S}$, Eq. (5.27), which are shown in Table II. The energy for this version improves with increasing $l_{\max}$, but not as fast as the mean-square error of the wave function. For this version, however, the Rayleigh-Ritz refinement does greatly improve the energy. The wave functions are of comparable accuracy in the two versions of MST.

VIII. DISCUSSION

The subject of near-field corrections has caused confusion and controversy for nearly twenty years. It is relatively easy to derive the MST equations for nonspherical muffin-tin potentials and to postulate that the same form remains valid for space-filling cells. A more careful consideration of the problem, however, reveals several reasons for doubting that this could be the case. Approaching the problem from the point of view of scattering theory, one soon realizes that a partial wave which is scattered off of a nonspherical scatterer does not attain its asymptotic form within a sphere which circumscribes the potential. Moreover, if one attempts to use the asymptotic form within this circumscribing sphere, it can be found to diverge. On the other hand, if one approaches the problem from the point of view of the Lippmann-Schwinger equation, one quickly faces the problem of expanding the Green function in partial waves while rigorously maintaining the proper conditions on its arguments to ensure convergence.

It is clear however, that although the considerations of the preceding paragraph indicate the conceptual difficulties that must be faced in extending MST to treat full cell potentials, they do not constitute a proof of the existence of near-field corrections. We plan to show elsewhere[38] how the conceptual difficulties in the scattering theory approach can be resolved. In the meantime we hope that the two derivations of full-cell MST presented here are sufficiently simple and convincing that the issue of near-field corrections may finally be laid to rest. Our conclusions in this regard agree with those of several previous workers.[20–22,24–26]

We have addressed the question of whether or not the basis functions ϕ_L introduced by Williams and Morgan[4,6] as analogs to the radial wave functions of muffin-tin MST can be used to represent the physical wave function of the system. We were able to answer this question in the affirmative. In answering this question it was necessary to derive the form of the angular momentum expansion of the Green function for a single nonspherical potential. We also investigated a question raised recently[34] concerning the behavior of the basis functions near the origin and demonstrated that there is no problem for potentials likely to be used in electronic structure calculations.

We have pointed out a new feature of full-cell MST. Some versions of the theory are variational and others are not. This result is closely related to the issue of internal angular momentum summations since the various forms of the MST secular equations can be obtained by multiplying the variational form $\tilde{S}[C-GS]a = 0$, derived in Sec. V by the sine and cosine matrices or their inverses. For example, the nonvariational form derived in Sec. VI is obtained by omitting the $\tilde{S}$ from the above relation. Other forms such as $[1 - Gt]b = 0$, $[t^{-1} - G]c = 0$, and $[t - tGt]d = 0$, where $t = CS^{-1}$, can be derived by (formal) multiplication of $[C-gS]$ by the appropriate factors of the sine and cosine matrices. We speculate that *if* the internal summations are converged, the forms of the secular matrix which are symmetric will yield a variational energy and the others will not.

It is important to realize that the inverses of sine and cosine matrices must be interpreted in the generalized sense, e.g.,

$$\sum_{L_i} C_{LL_i} C^{-1}_{L_iL'} = \delta_{LL'}, \tag{8.1}$$

where the internal sum (over L_i) is carried high enough to ensure convergence. In our experience the inversion of $C_{LL'}$ calculated for the empty lattice test in two dimensions is difficult, but possible. We expect the inversion of $S_{LL'}$ to be much more difficult and probably not even possible for some potentials. One alternative to inverting these matrices is to calculate the t matrix directly. This should be straightforward at positive energies by a simple modification of the procedure used to calculate C and S. The direct calculation of t^{-1}, which would be very useful for the application of the CPA, seems to us to be much more difficult.

Since the objective of this paper is to establish a firm theoretical foundation for full-potential MST we have emphasized some of the subtleties that can arise when the potential deviates greatly from the muffin-tin form. In many practical calculations that use potentials that are nearly of the muffin-tin form and that use relatively small values of $l_{\max}$ the effect of subtleties such as the convergence of internal sums and nonvariational energies may be quite small. This is especially true if the zero of the potential can be chosen to lie at the corners of the cells so that the potential is very small for those points at greatest distances from the origin. Even when this is not done the results may be quite acceptable. Faulkner[10] compared the energies calculated for a muffin-tin potential for paramagnetic fcc nickel with the energies obtained after the potential had been shifted by a constant Δ. The root-mean-square error expressed as a fraction of this shift was approximately 5%. More recently Nicholson and Faulkner[28] applied a similar test to a potential for bcc Nb. For the three energies that were compared the maximum error (again expressed as a fraction of the shift) was approximately 1%. These calculations used square matrices and $l_{\max} = 4$.

Finally we would like to remark that the procedures that we have described here should be very generally useful for solving linear partial differential equations. MST can be viewed as a technique for fitting together local solutions to a partial differential equation to obtain a proper global solution satisfying all boundary conditions. The procedure has already been used to solve the Poisson equation[41] and it is clear that it could be used to solve the inhomogeneous wave equation. In order to apply this technique to a linear partial differential equation one needs to be able to generate local solutions to the equation and one needs a Green function for a related simpler equation which can be expanded in spherical harmonics at any point in space.

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APPENDIX

Here we show that the Green function for a nonspherical potential can be constructed in the form

$$G(\mathbf{r},\mathbf{r}') = \sum_L [\,\phi_L(\mathbf{r}) F_L(\mathbf{r}')\Theta(r'-r) + \phi_L(\mathbf{r}') F_L(\mathbf{r})\Theta(r-r')], \tag{A1}$$

where $\phi_L(\mathbf{r})$ is a solution to the Schrödinger equation, which equals $J_L(\mathbf{r})$ as $r \to 0$. This is the only boundary condition which we apply to $\phi_L(\mathbf{r})$ that is calculated within a sphere of radius R using Eqs. (3.10), (3.13), and (3.14).

The function $F_L(\mathbf{r})$ is also a solution to the Schrödinger equation which is, however, irregular at the origin. In order to determine the function F we investigate the form of the Green function. If the potential vanishes for $r > R$, we know that the Green function can be written, for $r > R$, $r' > R$, and $r' > r$, as

$$G(\mathbf{r},\mathbf{r}') = \sum_L J_L(\mathbf{r}) H_L(\mathbf{r}') + \sum_{L,L'} H_L(\mathbf{r}) t_{LL'} H_{L'}(\mathbf{r}'), \tag{A2}$$

which by comparison with Eqs. (3.10) and (3.22) yields, for $r' \geq R$,

$$F_L(\mathbf{r}') = \sum_{L'} [C^{-1}(R)]_{LL'} H_{L'}(\mathbf{r}') \quad (r' \geq R), \tag{A3}$$

where the t matrix $t_{LL'}$ is given by $S(R)C^{-1}(R)$. We assume here that the cosine matrix $C_{L'L}(R,E)$ can be inverted. This should be possible if E is not a bound-state energy for a single potential. F_L satisfies the integral equation

$$F_L(\mathbf{r}) = \alpha_L H_L(\mathbf{r}) + \int_0^R d\mathbf{r}' G_0(\mathbf{r},\mathbf{r}') V(\mathbf{r}') F_L(\mathbf{r}'), \tag{A4}$$

where α is to be determined so that the boundary condition Eq. (A3) is satisfied. The result is that $F_L(\mathbf{r})$ may be written in a form analogous to Eq. (3.10)

$$F_L(\mathbf{r}) = \sum_{L'} [\bar{C}_{LL'}(r) J_{L'}(\mathbf{r}) + \bar{S}_{LL'}(r) H_{L'}(\mathbf{r})], \tag{A5}$$

where $\bar{C}$ and $\bar{S}$ are given by

$$\bar{C}_{LL'}(r) = \int_r^R d\mathbf{r}' F_L(\mathbf{r}') V(\mathbf{r}') H_{L'}(\mathbf{r}'), \tag{A6}$$

$$\bar{S}_{LL'}(r) = C^{-1}_{LL'}(R) - \int_r^R d\mathbf{r}' F_L(\mathbf{r}') V(\mathbf{r}') J_{L'}(\mathbf{r}'). \tag{A7}$$

For reference we also give the analogous expressions for $C_{L'L}$ and $S_{L'L}$ which are used to represent $\phi_L(\mathbf{r})$ in Eq. (3.10),

$$C_{L'L}(r) = \delta_{L'L} - \int_0^r d\mathbf{r}' H_{L'}(\mathbf{r}') V(\mathbf{r}') \phi_L(\mathbf{r}'), \tag{A8}$$

$$S_{L'L}(r) = \int_0^r d\mathbf{r}' J_{L'}(\mathbf{r}') V(\mathbf{r}') \phi_L(\mathbf{r}'). \tag{A9}$$

Thus if Eq. (A1) is to be valid, the Green function for a nonspherical potential must be expressible in the form

$$\begin{aligned} G(\mathbf{r},\mathbf{r}') = \sum_{L,L'} \{ & J_L(\mathbf{r})[C(r)\bar{C}(r')]_{LL'}J_{L'}(\mathbf{r}') \\ & +J_L(\mathbf{r})[C(r)\bar{S}(r')]_{LL'}H_{L'}(\mathbf{r}') \\ & +H_L(\mathbf{r})[S(r)\bar{C}(r')]_{LL'}J_{L'}(\mathbf{r}') \\ & +H_L(\mathbf{r})[S(r)\bar{S}(r')]_{LL'}H_{L'}(\mathbf{r}')\}, \end{aligned} \qquad \text{(A10)}$$

where the square brackets with the LL' subscripts indicate the LL' matrix element of the product of two sine and cosine matrices. Now we know that the Green function may be expressed quite generally in the form

$$\begin{aligned} G(\mathbf{r},\mathbf{r}') = {} & G_0(\mathbf{r},\mathbf{r}') \\ & +\int d\mathbf{r}_1 \int d\mathbf{r}_2\, G_0(\mathbf{r},\mathbf{r}_1)t(\mathbf{r}_1,\mathbf{r}_2)G_0(\mathbf{r}_2,\mathbf{r}'), \end{aligned} \qquad \text{(A11)}$$

which leads directly to

$$\begin{aligned} G(\mathbf{r},\mathbf{r}') = \sum_{L,L'} [& J_L(\mathbf{r})g^{JJ}_{LL'}(r,r')J_{L'}(\mathbf{r}') \\ & +J_L(\mathbf{r})g^{JH}_{LL'}(r,r')H_{L'}(\mathbf{r}') \\ & +H_L(\mathbf{r})g^{HJ}_{LL'}(r,r')J_{L'}(\mathbf{r}') \\ & +H_L(\mathbf{r})g^{HH}_{LL'}(r,r')H_{L'}(\mathbf{r}')], \end{aligned} \qquad \text{(A12)}$$

where (for $r' > r$)

$$g^{JJ}_{LL'}(r,r') = \int_r^R d\mathbf{r}_1 \int_{r'}^R d\mathbf{r}_2 H_L(\mathbf{r}_1)t(\mathbf{r}_1,\mathbf{r}_2)H_{L'}(\mathbf{r}_2), \qquad \text{(A13)}$$

$$\begin{aligned} g^{JH}_{LL'}(r,r') = {} & \int_r^R d\mathbf{r}_1 \int_0^{r'} d\mathbf{r}_2 H_L(\mathbf{r}_1)t(\mathbf{r}_1,\mathbf{r}_2)J_{L'}(\mathbf{r}_2) \\ & +\delta_{LL'}, \end{aligned} \qquad \text{(A14)}$$

$$g^{HJ}_{LL'}(r,r') = \int_0^r d\mathbf{r}_1 \int_{r'}^R d\mathbf{r}_2 J_L(\mathbf{r}_1)t(\mathbf{r}_1,\mathbf{r}_2)H_{L'}(\mathbf{r}_2), \qquad \text{(A15)}$$

$$g^{HH}_{LL'}(r,r') = \int_0^r d\mathbf{r}_1 \int_0^{r'} d\mathbf{r}_2 J_L(\mathbf{r}_1)t(\mathbf{r}_1,\mathbf{r}_2)J_{L'}(\mathbf{r}_2). \qquad \text{(A16)}$$

Thus the validity of the Green-function expansion, Eq. (A1), will be established if the following can be verified:

$$[C(r)\bar{C}(r')]_{LL'} = g^{JJ}_{LL'}(r,r'), \qquad \text{(A17)}$$

$$[C(r)\bar{S}(r')]_{LL'} = g^{JH}_{LL'}(r,r'), \qquad \text{(A18)}$$

$$[S(r)\bar{C}(r')]_{LL'} = g^{HJ}_{LL'}(r,r'), \qquad \text{(A19)}$$

$$[S(r)\bar{S}(r')]_{LL'} = g^{HH}_{LL'}(r,r'). \qquad \text{(A20)}$$

The following relations will be useful in working with $C\bar{C}$, $C\bar{S}$, $S\bar{C}$, and $S\bar{S}$:

$$F_L(\mathbf{r}) = H_L(\mathbf{r}) + \int_0^R d\mathbf{r}' H_L(\mathbf{r}')V(\mathbf{r}')G(\mathbf{r}',\mathbf{r}), \qquad \text{(A21)}$$

$$\begin{aligned} Z_L(\mathbf{r}) & = \sum_{L'} \phi_{L'}(\mathbf{r})C^{-1}_{L'L}(R) \\ & = J_L(\mathbf{r}) + \int_0^R d\mathbf{r}' G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')J_L(\mathbf{r}'). \end{aligned} \qquad \text{(A22)}$$

These may be derived by verifying that they satisfy the Schrödinger equation and the correct boundary condition at R and at the origin, respectively. We will also use Eq. (A1).

We use a shorthand notation since the manipulations are lengthy. We also take $r' > r$:

$$C\bar{C} = \left(1 - \int_0^r HV\phi\right)\left(\int_{r'}^R FVH\right), \qquad \text{(A23)}$$

$$C\bar{C} = \int_{r'}^R FVH - \int_0^r \int_{r'}^R HVGVH, \qquad \text{(A24)}$$

$$\begin{aligned} C\bar{C} = {} & \int_{r'}^R HVH + \int_0^R \int_{r'}^R HVGVH \\ & -\int_0^r \int_{r'}^R HVGVH, \end{aligned} \qquad \text{(A25)}$$

$$C\bar{C} = \int_r^R \int_{r'}^R HtH = g^{JJ}, \qquad \text{(A26)}$$

$$C\bar{S} = \left(C_R + \int_r^R HV\phi\right)\left(C_R^{-1} - \int_{r'}^R FVJ\right), \qquad \text{(A27)}$$

$$\begin{aligned} C\bar{S} = 1 + {} & \int_r^R HVZ - \int_{r'}^R FVJ + \int_0^R \int_{r'}^R HVGVJ \\ & -\int_r^R \int_{r'}^R HVGVJ, \end{aligned} \qquad \text{(A28)}$$

$$C\bar{S} = 1 + \int_r^R HVJ - \int_{r'}^R HVJ \qquad \text{(A29)}$$

$$\begin{aligned} & +\left(\int_r^R \int_0^R - \int_0^R \int_{r'}^R \right. \\ & \left. + \int_0^R \int_{r'}^R - \int_r^R \int_{r'}^R\right) HVGVJ, \end{aligned} \qquad \text{(A30)}$$

$$C\bar{S} = 1 + \int_r^R \int_0^{r'} HtJ = g^{JH}, \qquad \text{(A31)}$$

$$S\bar{C} = \int_0^r JV\phi \int_{r'}^R FVH, \qquad \text{(A32)}$$

$$S\bar{C} = \int_0^r \int_{r'}^R JVGVH, \qquad \text{(A33)}$$

$$S\bar{C} = \int_0^r \int_{r'}^R JtH = g^{HJ}, \qquad \text{(A34)}$$

$$S\bar{S} = \int_0^r JV\phi\left(C_R^{-1} - \int_{r'}^R FVJ\right), \qquad \text{(A35)}$$

$$S\bar{S} = \int_0^r JVZ - \int_0^r \int_{r'}^R JVGVJ, \qquad \text{(A36)}$$

$$S\bar{S} = \int_0^r JVJ + \int_0^r \int_0^R JVGVJ - \int_0^r \int_{r'}^R JVGVJ, \tag{A37}$$

$$S\bar{S} = \int_0^r JVJ + \int_0^r \int_0^{r'} JVGVJ, \tag{A38}$$

$$S\bar{S} = \int_0^r \int_0^{r'} JtJ = g^{HH}. \tag{A39}$$

We have also verified directly that $[\nabla^2 + E - V(\mathbf{r})]$ applied to the Green function in the form of Eq. (A1) yields $\delta(\mathbf{r}-\mathbf{r}')$. Using the fact that both ϕ_L and F_L satisfy the Schrödinger equation we have

$$\begin{aligned}
[\nabla^2 + E - V(\mathbf{r})]G(\mathbf{r},\mathbf{r}') &= \sum_L F_L(\mathbf{r}')\nabla \cdot [\nabla\phi_L(\mathbf{r})\Theta(r'-r) + \phi_L(\mathbf{r})\nabla\Theta(r'-r)] \\
&\quad + \sum_L \phi_L(\mathbf{r}')\nabla \cdot [\nabla F_L(\mathbf{r})\Theta(r-r') + F_L(\mathbf{r})\nabla\Theta(r-r')] \\
&= \sum_L F_L(\mathbf{r}')[2\nabla\phi_L(\mathbf{r}) \cdot \nabla\Theta(r'-r) + \phi_L(\mathbf{r})\nabla^2\Theta(r'-r)] \\
&\quad + \sum_L \phi_L(\mathbf{r}')[2\nabla F_L(\mathbf{r}) \cdot \nabla\Theta(r-r') + F_L(\mathbf{r})\nabla^2\Theta(r-r')] \\
&= \sum_L F_L(\mathbf{r}')\left(-2\frac{\partial}{\partial r}\phi_L(\mathbf{r})\delta(r-r') - \phi_L(\mathbf{r})\frac{2}{r}\delta(r-r') - \phi_L(\mathbf{r})\delta'(r-r')\right) \\
&\quad + \sum_L \phi_L(\mathbf{r}')\left(2\frac{\partial}{\partial r}F_L(\mathbf{r})\delta(r-r') + F_L(\mathbf{r})\frac{2}{r}\delta(r-r') + F_L(\mathbf{r})\delta'(r-r')\right).
\end{aligned} \tag{A40}$$

Consider the two terms involving $\frac{2}{r}\delta(r-r')$. Substitution for ϕ_L and F_L from Eqs. (3.10) and (A5) yields

$$\begin{aligned}
&\frac{2}{r}\delta(r-r') \sum_{L_1,L_2} Y_{L_1}(\hat{r}')Y_{L_2}(\hat{r})\{j_{l_1}(\kappa r)j_{l_2}(\kappa r)[C\bar{C} - \bar{C}^T C^T]_{L_1L_2} + h_{l_1}(\kappa r)h_{l_2}(\kappa r)[S\bar{S} - \bar{S}^T S^T]_{L_1L_2} \\
&\qquad + j_{l_1}(\kappa r)h_{l_2}(\kappa r)[C\bar{S} - \bar{C}^T S^T]_{L_1L_2} + h_{l_1}(\kappa r)j_{l_2}(\kappa r)[S\bar{C} - \bar{S}^T C^T]_{L_1L_2}\},
\end{aligned} \tag{A41}$$

where C, $\bar{C}$, S, and $\bar{S}$, are evaluated at argument r, and we have used the superscript T to denote the matrix transpose. We have also incorporated a factor of $-i\kappa$ into the spherical Hankel functions $h_l(\kappa r)$. From the above expressions for these quantities it is clear that $C\bar{C} - \bar{C}^T C^T$ and $S\bar{S} - \bar{S}^T S^T$ vanish and that $C\bar{S} - \bar{C}^T S^T = \delta_{L_1L_2}$. Thus this term vanishes.

Now consider the term involving the derivative of the δ function. This generalized function is only meaningful when it appears as a factor in the integrand of an integral. Thus we investigate the integral

$$\int dr\, r^2 f(r) \sum_L [\phi_L(\mathbf{r}')F_L(\mathbf{r}) - \phi_L(\mathbf{r})F_L(\mathbf{r}')]\delta'(r-r'). \tag{A42}$$

Integration by parts gives

$$\begin{aligned}
&\int dr\, r^2 f(r) \sum_L [\phi_L(\mathbf{r}')F_L(\mathbf{r}) - \phi_L(\mathbf{r})F_L(\mathbf{r}')]\delta(r-r') - \int dr \frac{\partial}{\partial r}[r^2 f(r)] \sum_L [\phi_L(\mathbf{r}')F_L(\mathbf{r}) - \phi_L(\mathbf{r})F_L(\mathbf{r}')]\delta(r-r') \\
&\qquad - \int r^2 f(r) \sum_L \left(\phi_L(\mathbf{r}')\frac{\partial}{\partial r}F_L(\mathbf{r}) - \frac{\partial}{\partial r}\phi_L(\mathbf{r})F_L(\mathbf{r}')\right)\delta(r-r').
\end{aligned} \tag{A43}$$

The first two integrals above vanish for the same reasons as expression (A41), with the result that the term involving $\delta'(r-r')$ in Eq. (A40) is equivalent to $-\frac{1}{2}$ of the first term in that equation.

Thus we have

$$[\nabla^2 + E - V(\mathbf{r})]G(\mathbf{r},\mathbf{r}') = \sum_L \left(\phi_L(\mathbf{r}')\frac{\partial}{\partial r}F_L(\mathbf{r}) - \frac{\partial}{\partial r}\phi_L(\mathbf{r})F_L(\mathbf{r}')\right)\delta(r-r'). \tag{A44}$$

Substituting for ϕ_L and F_L in terms of C, S, $\bar{C}$, and $\bar{S}$, as was done in the evaluation of (A41), and using again the relations $C\bar{C} - \bar{C}^T C^T = 0$, $S\bar{S} - \bar{S}^T S^T = 0$, and $C\bar{S} - \bar{C}^T S^T = \delta_{L_1L_2}$, together with the Wronskian relation satisfied by the spherical Bessel and Hankel functions, we obtain

$$[\nabla^2 + E - V(\mathbf{r})] \sum_L \phi_L(\mathbf{r}_<)F_L(\mathbf{r}_>) = \sum_L Y_L(\hat{r})Y_L(\hat{r}')\delta(r-r') = \delta(\mathbf{r}-\mathbf{r}'). \tag{A45}$$

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