PHYSICAL REVIEW B VOLUME 46, NUMBER 23 15 DECEMBER 1992-I

Green-function cellular method for the electronic structure of molecules and solids

X.-G. Zhang
Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0045

W. H. Butler and D. M. Nicholson
Metals and Ceramics Division, Oak Ridge National Laboratory, P.O. Box 2008,
Oak Ridge, Tennessee 37831-6114

R. K. Nesbet
IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

(Received 17 June 1992)

A technique for obtaining rigorous solutions to the single-electron Schrödinger equation for solids and molecules, the Green-function cellular method (GFCM), is described. The technique is similar to full-potential multiple-scattering theory in that basis functions which are locally exact solutions to the Schrödinger equation within each potential cell are used to represent the wave function. Unlike multiple-scattering theory, however, the coefficients of expansion for the wave function are determined by a secular matrix which couples only nearest-neighbor cells. The matrix elements are Wronskian-like integrals over cell surfaces which may be chosen independently for each atomic cell. Similarly to multiple-scattering theory, the GFCM can be used to calculate the system Green function directly. As a special case, the GFCM formalism can be used to calculate the structure constants of Korringa-Kohn-Rostoker theory without using Ewald sums. Numerical calculations of the energy bands of fcc Cu illustrate the speed and flexibility of the method. A simple linearization scheme which allows the use of multiple energy panels without introducing discontinuities in the energy bands is used in these calculations.

I. INTRODUCTION

Multiple-scattering theory (MST) was first applied to calculate the electronic structure of periodic solids by Korringa.[1] Somewhat later Kohn and Rostoker[2] derived the same secular equation as Korringa by use of a variational technique that can be used with discontinuous trial wave functions. In this paper we shall use the term MST to describe the application of multiple-scattering theory or equivalent techniques to assemblies of atoms of arbitrary configuration and reserve the more familiar term Korringa-Kohn-Rostoker (KKR) theory for its application to periodic solids. Although MST was originally developed for potentials which are spherically symmetric within nonoverlapping spheres and constant outside these spheres, i.e., muffin-tin potentials, it has been generalized so that it can be applied to general space-filling potentials.[3]

One important aspect of MST is its representation of the system wave function by a linear combination of basis functions which are locally exact solutions of the Schrödinger equation in nonoverlapping regions of space. Although an arbitrary linear combination of these solutions is an exact solution to the Schrödinger equation it will not, in general, be a physically acceptable solution because there will be discontinuities both in value and in normal gradient when one passes from one region to another. Continuity of the wave function and of its normal gradient across boundaries between different cells is achieved, however, in the limit of completeness, by solving the MST equations which determine the correct linear combination of these locally exact basis functions and the characteristic energy. Compared with other methods, MST requires a rather small set of basis functions, as few as nine for the transition metals. It can also be used to calculate the Green function directly without resort to a poorly convergent spectral representation.

In this paper we present a technique for solving the Schrödinger equation which we call the Green-function cellular method (GFCM). This method is different from but closely related to full-potential MST and to full-potential KKR theory. Some of the advantages of the GFCM over full-potential MST are that it does not require structure constants, yields a secular equation with couplings only between nearest-neighbor atoms, is more easily linearized, and does not require the definition of polyhedral cells. The GFCM like MST can be used to calculate the Green function directly.

Although the GFCM is a cellular method it differs fundamentally from previous cellular methods, such as that of Wigner and Seitz,[4] that of Slater,[5,6] or the variational cellular method (VCM) of Ferreira and Leite.[7] The GFCM is based on an integral form of the Schrödinger equation and is closely related to MST, whereas previous cellular methods have been based on the variational principles of Rayleigh and Ritz[8] or of Schlosser and Marcus.[9]

Although the GFCM does not use structure constants, it can be used to calculate them as the coefficients which make an irregular solution to the Helmholtz equation join smoothly and continuously to regular solutions in adjacent cells. It can be used in a similar manner to calculate the Green function of the Schrödinger equation. The calculation of structure constants and the Green function will be discussed in Sec. III. In Sec. V we demonstrate that the GFCM is a practical and rapidly convergent technique for electronic structure calculations by using it to calculate the electronic structure of Cu. These calculations use a linearized version of the theory which is discussed in Sec. IV.

II. THE GFCM SECULAR EQUATION

Zhang and Butler[10] derived the GFCM secular equation by matching the wave function and its normal gradient across cell boundaries. Here we present a more rigorous derivation of this secular equation from the Lippmann-Schwinger equation. This derivation is along the same lines as a derivation of MST in Ref. 3. A preliminary account of this derivation was given previously.[10,11]

The single-particle Schrödinger equation for a system with the potential function $V(\mathbf{r})$, in Rydberg units, can be expressed as a modified Helmholtz equation,

$$\{\nabla^2 + \epsilon\}\,\psi(\mathbf{r}) = V(\mathbf{r})\psi(\mathbf{r}). \tag{1}$$

Using the Green function G_0 for the free-particle Helmholtz equation, the Schrödinger equation is converted into the Lippmann-Schwinger integral equation for the wave function ψ,

$$\psi(\mathbf{r}) = \chi(\mathbf{r}) + \int_{\Re^3} d\mathbf{r}' G_0(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}'). \tag{2}$$

The potential function $V(\mathbf{r})$ is assumed to be defined everywhere in the coordinate space $\Re^3$. Eigenfunctions which satisfy the boundary conditions of the Green function are defined by the condition that the function χ should vanish identically. The free-particle Green function G_0 satisfies the differential equation

$$\{\nabla^2 + \epsilon\}\,G_0(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'). \tag{3}$$

$\Re^3$ is subdivided into space-filling cells Ω_n, which do not overlap. This is equivalent to partitioning V into cell potentials, $V(\mathbf{r}) = \sum_n v_n(\mathbf{r}_n)$, where $v_n(\mathbf{r}_n)$ takes the value of $V(\mathbf{r})$ for $\mathbf{r}$ inside cell n and vanishes elsewhere. The Lippmann-Schwinger equation for an eigenfunction ψ can be rewritten as a sum of integrals over individual cells Ω_n,

$$\sum_n \int_{\Omega_n} d\mathbf{r}'\,\{G_0(\mathbf{r},\mathbf{r}')V(\mathbf{r}') - \delta(\mathbf{r}-\mathbf{r}')\}\,\psi(\mathbf{r}') = 0. \tag{4}$$

The explicit occurrence of V in the integrand can be eliminated using Eqs. (1) and (3), and we use Green's theorem to convert the volume integrals to Wronskian integrals over the surfaces of the individual cells to obtain

$$\sum_n \int_{S_n} d\mathbf{S}'\,\{G_0(\mathbf{r},\mathbf{r}')\nabla'\psi(\mathbf{r}') - \psi(\mathbf{r}')\nabla' G_0(\mathbf{r},\mathbf{r}')\} = 0. \tag{5}$$

We suppose that $\mathbf{r}$ is in cell m, and use the notation $\mathbf{r}_m$ to denote $\mathbf{r}-\mathbf{R}_m$, where $\mathbf{R}_m$ represents the coordinate of the center of cell m. We can expand $G_0(\mathbf{r},\mathbf{r}')$ about the center of that cell,

$$G_0(\mathbf{r},\mathbf{r}') = \sum_L \{\, J_L(\mathbf{r}_m)N_L^*(\mathbf{r}'_m)\theta(r'_m - r_m) + N_L(\mathbf{r}_m)J_L^*(\mathbf{r}'_m)\theta(r_m - r'_m)\}. \tag{6}$$

Here $\theta(x)$ represents the step function which is unity for $x>0$ and zero for $x<0$. The generalized solid-harmonic functions J_L and N_L are constructed as products of regular and irregular spherical Bessel functions (e.g., spherical Hankel functions), respectively, with spherical harmonic angular factors. Angular quantum numbers (ℓ, m) are combined here into a single index L. Various conventions are used in the literature to define irregular solid harmonics. Here the notation N_L will be used for a generic irregular function, to be defined more precisely in a particular context, but with normalization always chosen so that the Wronskian surface integrals

$$\int_{S_m} d\mathbf{S}\,\{J_L^*(\mathbf{r}_m)\nabla N_{L'}(\mathbf{r}_m) - N_{L'}(\mathbf{r}_m)\nabla J_L^*(\mathbf{r}_m)\} = \delta_{L,L'} \tag{7}$$

satisfy the indicated Kronecker δ relation. By Green's theorem, the corresponding integrals vanish for any two J functions, and will be assumed to vanish between any two N functions by construction. In the following we shall use the notation $[J_L^m, N_{L'}^m]_m$ to represent the Wronskian integral in the above equation. The normal gradient on a closed cell surface is defined to be directed outwards. To derive the secular equation from Eq. (5), we can restrict $\mathbf{r}_m$ to be confined within a sphere inscribed inside cell m without losing generality, and use the expansion of the Green function to obtain $\sum_{nL} J_L(\mathbf{r}_m)[N_L^m,\psi]_n = 0$. Since the functions $J_L(\mathbf{r}_m)$ are linearly independent, this implies

$$\sum_n [N_L^m,\psi]_n = 0 \qquad \text{all } m, L. \tag{8}$$

In full-potential MST and in the GFCM the wave function is expanded in each local cell n as a linear combination of basis functions defined uniquely within that cell,[3,12]

$$\psi(\mathbf{r}) = \sum_L \phi_L^n(\mathbf{r}_n)a_L^n, \tag{9}$$

for $\mathbf{r}$ inside cell n or on its boundary surface. Here the $\phi_L^n(\mathbf{r}_n)$ are regular solutions of the one-electron Schrödinger equation in cell n,

$$\{\nabla^2 + \epsilon - v_n(\mathbf{r}_n)\}\,\phi_L^n(\mathbf{r}_n) = 0, \tag{10}$$

where the subscript L specifies the boundary condition at the origin, $\phi_L^n(\mathbf{r}_n)|_{r_n<r_{\text{cutoff}}} = J_L^n(\mathbf{r}_n)$ for $r_{\text{cutoff}} \to 0$. If $\psi(\mathbf{r})$ is expanded within cell n, using Eq. (9), and the result is substituted into Eq. (8), the secular equation obtained from this expansion is

$$\sum_{nL}[N_{L'}^m, \phi_L^n]_n a_L^n = 0 \qquad \text{all } m, L'. \tag{11}$$

The full-potential MST secular equation is obtained, as pointed out by Butler and Nesbet,[13] by computing Wronskian surface integrals that define the cosine matrix, $C_{L'L}^n = -[N_{L'}^n, \phi_L^n]$, and the sine matrix, $S_{L'L}^n = [J_{L'}^n, \phi_L^n]$, and, for $m \neq n$, expanding the irregular solid harmonics centered at m in terms of regular solid harmonics centered at n, $N_{L'}^{m*} = \sum_{L_1} g_{L'L_1}^{nm} J_{L_1}^{n*}$,

$$\sum_{nL}\left\{C_{L'L}^n\delta_{mn} - \sum_{L_1} g_{L'L_1}^{mn} S_{L_1 L}^n\right\} a_L^n = 0 \qquad \text{all } m, L', \tag{12}$$

which is the familiar nonvariational secular equation of full-potential multiple-scattering theory.[14]

The GFCM secular equation can be derived from Eq. (8) by a geometrical argument. We can write Eq. (8) as

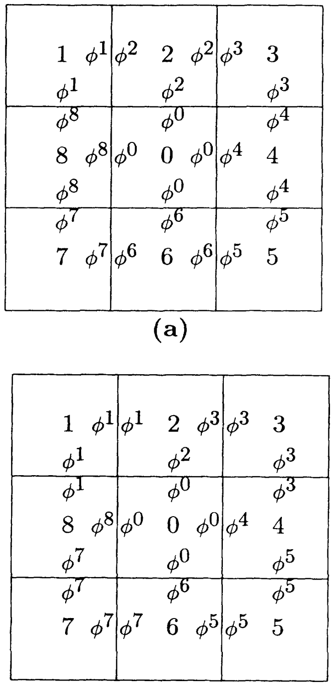
$$\sum_{n} \sum_{p=\substack{\text{neighbors}\\ \text{of } n}} [N_L^m, \psi]_{S_{np}} = 0 \qquad \text{all } m, L, \tag{13}$$

which states the fact that the surface of cell n is made up of the interfaces S_{np}, which separate cell n from each of its nearest-neighbor cells labeled by p. Because the expansions in both cells p and n are representations of a trial wave function ψ which becomes continuous and smooth across the boundary between the two cells in the limit of convergence of the expansions in both cells, the expansions from either cell are equally valid on their interface. Consequently, as indicated in Fig. 1, one can eliminate all surface integrals except for those involving the cell m, in which the irregular harmonic function N_L^m is centered. This choice of local expansions, as indicated by Fig. 1(b), eliminates all Wronskian integrals except for cell m and its interfaces with adjacent cells, implying the secular equation,

$$\sum_{p=\substack{\text{neighbors}\\ \text{of } m}} \sum_{L}\{[N_{L'}^m, \phi_L^m]_{S_{mp}} a_L^m - [N_{L'}^m, \phi_L^p]_{S_{mp}} a_L^p\} = 0$$
$$\text{all } m, L', \tag{14}$$

where S_{mp} denotes the interface between adjacent cells m and p. This is the defining equation of the GFCM.

The result of this analysis is a cellular method based on multiple-scattering theory through the Lippmann-Schwinger equation, in which structure constants are not used and which yields a secular matrix with strictly nearest-neighbor couplings. Practical problems associated with structure constants are avoided, e.g., poor convergence in either $\mathbf{r}$ or $\mathbf{k}$ space, free-electron singularities, etc. Another feature of the GFCM is the fact that the surface which defines the integrals in Eq.(14) is not restricted to be a cell boundary. If the basis functions from each cell are integrated out into the regions inside neighboring cells, the expansion of the wave function in terms of these basis functions may still be valid. It is assumed that the potential is not singular in these regions, so long as atomic nuclei are excluded. In addition, because the matching conditions of the wave function on the boundaries between nearest neighbors are independent of the matching between other cells, one can deform the boundaries of the cell and evaluate the surface integrals over spheres instead of polyhedra. In short, the surface of integration may be chosen differently for each cell, and this choice can be made to minimize the computational effort. Of course using such a surface may introduce additional error in the ℓ truncation because the basis functions ϕ_L^n must be computed somewhat further from their local origins.



(a)

(b)

FIG. 1. (a) Choice of basis functions in expanding the wave function ψ in the integrals $\sum_n [N^0, \psi]_{S_n}$ to obtain multiple-scattering theory. Here, for example, the basis functions ϕ_L^2 and ϕ_L^3 are used on the sides of interface S_{23} corresponding to cells 2 and 3, respectively. (b) Choice of basis functions in expanding the wave function in the same integrals as above to obtain the Green-function cellular method. Here, the basis functions ϕ_L^3 are used on *both* sides of the interface S_{23}, leading to the cancellation of the integrals over S_{23}.

The GFCM secular equation bears a strong formal resemblance to that of the VCM.[7] The VCM secular equation can be written in the form

$$\sum_{p=\substack{\text{neighbors}\\ \text{of } m}} \sum_{L}\{[\phi_{L'}^m, \phi_L^m]_{S_{mp}} a_L^m - [\phi_{L'}^m, \phi_L^p]_{S_{mp}} a_L^p\} = 0$$
$$\text{all } m, L', \tag{15}$$

and can be seen to differ from that of the GFCM by the use of the local basis function ϕ_L^m which occurs on the left-hand side of the Wronskian-like surface integrals instead of the generic irregular solution to the Helmholtz equation, N_L^m. The VCM converges rapidly and is variational in the sense that the errors in the energy are of second order with respect to errors in the trial wave function. It has, however, a significant drawback; it produces as many false roots as true roots. Although these false roots can be identified and ignored, they cause problems in, for example, the direct calculation of the Green function. The origin of these false roots lies in the fact that if the VCM equations are satisfied for a particular choice of coefficients a_L^n, they will also be satisfied for another choice of coefficients which switches the sign of the function value and of the normal gradient on one side of a cell boundary. Thus the false roots correspond to a "maximum mismatch" at the cell boundaries.

III. STRUCTURE CONSTANTS AND THE GREEN FUNCTION

It was pointed out in the Introduction and in the preceding section that both MST and the GFCM can be viewed as schemes for achieving continuity and smoothness of a wave function which consists of a linear combination of solutions to the Schrödinger equation which are locally exact within individual cells. So far, we have used these procedures on regular functions. They can, however, be applied to irregular functions as well. Consider as an example an irregular solution to the Helmholtz equation centered on site n, $N_L(\mathbf{r}_n)$. This function can also be expressed as $\tilde{N}^n$ which equals $N_L(\mathbf{r}_n)$ within cell n but is expressed as an expansion of regular functions in all other cells. Thus within cell p, $\tilde{N}^n$ will be expressed as

$$\tilde{N}_L^n(\mathbf{r}_n) = N_L^p(\mathbf{r}_p)\delta_{pn} + \sum_{L''} J_{L''}^p(\mathbf{r}_p) g_{L''L}^{pn}(1-\delta_{pn}). \tag{16}$$

The expansion, in terms of regular solutions to the Helmholtz equation, will converge if the distance between the centers n and p exceeds r_p. The coefficients $g_{L''L}^{pn}$ are the well-known structure constants used in MST, linearized muffin-tin orbital (LMTO),[15] or atomic-cell orbital[16,17] (ACO) theory. However, we can view them as unknown coefficients to be determined by the requirement that the solution to the Helmholtz equation $\tilde{N}^n$ be smooth and continuous across all cell boundaries.

Substituting the above expression for $\tilde{N}^n$ into the MST secular equation (11) in place of $\sum_L \phi_L a_L$, we obtain

$$g_{L'L}^{mn} = [N_{L'}^m, N_L^n]_n = -[N_{L'}^m, N_L^n]_m. \tag{17}$$

This equation is obviously correct as can be verified by expanding $N_{L'}^{m*}$ as $\sum_{L''} g_{L'L''}^{mn} J_{L''}^{n*}$ and using the Wronskian relation Eq. (7). The corresponding GFCM formula, obtained by substituting $\tilde{N}^n$ into Eq. (14) in place of $\sum_L \phi_L a_L$, may be computationally useful,

$$g_{L'L}^{mn} + \sum_{\substack{p\neq n, L'' \\ p=\text{neighbors of } m}} [N_{L'}^m, J_{L''}^p]_{S_{mp}} g_{L''L}^{pn} = -\sum_{p=\substack{\text{neighbors} \\ \text{of } m}} [N_{L'}^m, N_L^p]_{S_{mp}} \delta_{pn}. \tag{18}$$

These equations have been verified for a fcc lattice by using them to calculate zero-energy structure constants along the Γ-K line, and comparing with results calculated from the structure-constant program STR published by Skriver.[15]

We can extend this logic to obtain formulas for calculating the Green function of the Schrödinger equation by direct analogy. Consider a solution to the Schrödinger equation which is irregular in cell n. This function can be represented in cell p by analogy with Eq. (16),

$$\tilde{\xi}_L^n(\mathbf{r}_n) = \xi_L^p(\mathbf{r}_p)\delta_{pn} + \sum_{L'} \phi_{L'}^p(\mathbf{r}_p) G_{L'L}^{pn}(1-\delta_{pn}). \tag{19}$$

Here the regular and irregular solutions of the Helmholtz equation J and N, respectively, have been replaced by regular and irregular solutions of the Schrödinger equation, denoted here by ϕ and ξ, respectively. The function, Eq. (19), determines the Green function for the Schrödinger equation through

$$\begin{aligned} G(\mathbf{r}_m, \mathbf{r}_n') &= \sum_L \tilde{\xi}_L^m(\mathbf{r}_m)\phi_L^{n*}(\mathbf{r}_n') \\ &= \sum_L \left\{ \xi_L^m(\mathbf{r}_m)\delta_{mn} + \sum_{L'} \phi_{L'}^m(\mathbf{r}_m) G_{L'L}^{mn} \right\} \\ &\quad \times \phi_L^{n*}(\mathbf{r}_n'). \end{aligned} \tag{20}$$

Here it is assumed that $r_m > r_n'$ if $m = n$. It was shown in Ref. 3 that the Green function for a finite nonspherical scatterer can be written in the form $G_n(\mathbf{r}, \mathbf{r}') = \sum_L \xi_L^n(\mathbf{r}_n)\phi_L^{n*}(\mathbf{r}_n')$. Equation (20) can be viewed as a simple generalization of that result which will be valid if we can find the coefficients $G_{LL'}^{mn}$ which make the irregular function smooth and continuous.

Thus the MST expression for the structure constants, Eq. (17), generalizes to an expression for the Green-function coefficients of the form

$$\sum_p [N^m, \phi^p]_p G^{pn} = -[N^m, \xi^n]_n. \tag{21}$$

The corresponding GFCM expression for the Green function coefficients analogous to Eq. (18) is

$$[N^m, \phi^m]_m G^{mn} - \sum_{\substack{p\neq n \\ p=\text{neighbors of } m}} [N^m, \phi^p]_{S_{mp}} G^{pn} = -[N^m, \xi^m]_m \delta_{mn} + \sum_{p=\substack{\text{neighbors} \\ \text{of } m}} [N^m, \xi^p]_{S_{mp}} \delta_{np} \tag{22}$$

for all cells m. These equations must be valid for generic irregular functions ξ, required only to satisfy Kronecker δ relations analogous to Eqs. (7),

$$[\phi_L^m, \xi_{L'}^m]_m = \delta_{L,L'}, \quad [\xi_L^m, \xi_{L'}^m]_m = 0. \tag{23}$$

As in the case of the KKR structure constants, numerical values of the structural matrix G^{mn} depend on the particular representation of irregular functions that is used and on the boundary conditions imposed on the extended irregular functions defined in Eq. (19).

The preceding derivations of Green functions were based on the idea of achieving continuity and smoothness of an irregular solution to the Schrödinger or Helmholtz equation. They seem to imply that a general formula for the Green function might have the form

$$\sum_p M^{mp}[\phi^p]G^{pn} = -M^{mn}[\xi^n]. \tag{24}$$

Here $M[\phi]$ is the secular matrix whose elements are linear functionals of the local regular solutions, and $M[\xi]$ is the secular matrix with the regular solution replaced by an irregular solution for each site. In the following we derive a general formula for the Green function of just this type based on the fact that the variation of a wave function due to a change ΔV in the potential function is determined by the Schrödinger Green function through the Lippmann-Schwinger equation for the perturbed wave function $\tilde{\psi}$,

$$\tilde{\psi}(\mathbf{r}) = \psi(\mathbf{r}) + \int_{\Re^3} d\mathbf{r}' G(\mathbf{r},\mathbf{r}')\Delta V(\mathbf{r}')\tilde{\psi}(\mathbf{r}'). \tag{25}$$

Applied to an infinitesimal variation of V at a point $\mathbf{r}'$, such that $\Delta V d\mathbf{r}' = \delta v(\mathbf{r}')$, this implies

$$\delta\psi(\mathbf{r}) = G(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')\delta v(\mathbf{r}'), \tag{26}$$

which can be taken as the fundamental definition of the Green function as the functional derivative of ψ with respect to variations of V. We shall use this definition to construct G.

If $\mathbf{r}$ is in cell m and if the variation of V is restricted to $\delta v_n(\mathbf{r}'_n)$ in cell n, only the basis functions in that cell are modified. The variation in the wave function as given by Eq. (9) due to the change in the potential is given by

$$\frac{\delta\psi(\mathbf{r})}{\delta v(\mathbf{r}')} = \sum_L \frac{\delta\phi_L^n(\mathbf{r}_n)}{\delta v_n(\mathbf{r}'_n)} a_L^n \delta_{mn} + \sum_L \phi_L^m(\mathbf{r}_m)\frac{\delta a_L^m}{\delta v_n(\mathbf{r}'_n)}, \tag{27}$$

where $\mathbf{r}$ is in cell m and $\mathbf{r}'$ is in cell n. Applying Eq. (26) to an isolated cell n, we obtain

$$\frac{\delta\phi_L^n(\mathbf{r}_n)}{\delta v_n(\mathbf{r}'_n)} = G_n(\mathbf{r},\mathbf{r}')\phi_L^n(\mathbf{r}'_n) - \left[G_n(\mathbf{r},\mathbf{r}''), \frac{\delta\phi_L^n(\mathbf{r}''_n)}{\delta v_n(\mathbf{r}'_n)}\right]_{\mathbf{r}''}, \tag{28}$$

where the first term represents a special solution and the second term is a Wronskian surface integral,

$$\oint_{\text{cell}} d\mathbf{S}''[G_n(\mathbf{r},\mathbf{r}'')\nabla'' - \nabla'' G_n(\mathbf{r},\mathbf{r}'')]\delta\phi_L^n(\mathbf{r}''_n)/\delta v_n(\mathbf{r}'_n),$$

which reflects the arbitrariness of G_n on the cell boundary, as explained below. For coordinate values within cell n, the single-site Green function is

$$G_n(\mathbf{r},\mathbf{r}') = \sum_L \{\phi_L^n(\mathbf{r}_n)\xi_L^{n*}(\mathbf{r}'_n)\theta(r'_n - r_n) + \xi_L^n(\mathbf{r}_n)\phi_L^{n*}(\mathbf{r}'_n)\theta(r_n - r'_n)\}. \tag{29}$$

The only boundary condition imposed on a basis function ϕ is its limiting behavior at the cell origin. The boundary conditions satisfied by the local Green function G_n are determined by an arbitrary choice of boundary values of the functions ξ^n on or outside the cell surface S_n, subject to the Kronecker δ relations of Eqs. (23). Hence Eq. (29) satisfies all defining conditions for an on-site Green function.

Determination of $\delta a_L^m/\delta v_n$ can be accomplished by consideration of the particular secular equation being used. In the remainder of this section we assume that the secular equation has the form

$$\sum_{mL} M_{L'L}^{pm}[\phi_L^m]a_L^m = 0. \tag{30}$$

We further assume that the elements of the secular matrix depend linearly on the locally exact solutions of the Schrödinger equation, ϕ_L^m, so that Eq. (30) includes both the cases of MST and of the GFCM, but not the VCM which depends bilinearly on the basis functions. The variation of Eq. (30) with respect to v_n yields

$$\sum_{mL} M_{L'L}^{pm}\left[\frac{\delta\phi_L^m}{\delta v_n(\mathbf{r}'_n)}\right] a_L^m + \sum_{mL} M_{L'L}^{pm}[\phi_L^m]\frac{\delta a_L^m}{\delta v_n(\mathbf{r}'_n)} = 0. \tag{31}$$

The first term in this equation can be evaluated using Eqs. (28) and (29),

$$\sum_{mL} M_{L'L}^{pm}\left[\frac{\delta\phi_L^m}{\delta v_n(\mathbf{r}'_n)}\right] a_L^m = \sum_L M_{L'L}^{pn}[\xi_L^n]\phi_L^{n*}(\mathbf{r}'_n)\psi(\mathbf{r}'_n) - \sum_{LL''} M_{L'L}^{pn}[\phi_L^n]\left[\xi_L^n, \frac{\delta\phi_{L''}^n}{\delta v_n(\mathbf{r}'_n)}\right]_{S_n} a_{L''}^n. \tag{32}$$

From this equation and from Eq. (31) it follows that $\delta a_L^m/\delta v_n(\mathbf{r}'_n)$ is determined by

$$\sum_{Lm} M_{L'L}^{pm}[\phi_L^m]\frac{\delta a_L^m}{\delta v_n(\mathbf{r}'_n)} = -\sum_L M_{L'L}^{pn}[\xi_L^n]\phi_L^{n*}(\mathbf{r}'_n)\psi(\mathbf{r}'_n) + \sum_{LL''} M_{L'L}^{pn}[\phi_L^n]\left[\xi_L^n, \frac{\delta\phi_{L''}^n}{\delta v_n(\mathbf{r}'_n)}\right]_{S_n} a_{L''}^n. \tag{33}$$

Using this result in Eq. (27) and comparing with Eq. (26) we have

$$G(\mathbf{r}_m,\mathbf{r}'_n)=\sum_L \xi_L^m(\mathbf{r}_m)\phi_L^{n*}(\mathbf{r}'_n)\delta_{mn}+\sum_{LL'}\phi_L^m(\mathbf{r}_m)G_{LL'}^{mn}\phi_{L'}^{n*}(\mathbf{r}'_n), \qquad (34)$$

where the Green-function coefficients $G_{LL'}^{mn}$ satisfy Eq. (24). This relation gives the Green-function coefficients for any secular matrix which is linear in the locally exact solutions ϕ_L.

It is clear in the above derivation that the definition of the irregular solutions ξ of the Schrödinger equation in each local cell is arbitrary so long as the Kronecker δ conditions of Eqs. (23) are satisfied. It can easily be verified that any transformation of the set of functions ξ by adding linear combinations of regular functions ϕ with a Hermitian matrix of coefficients simply moves the corresponding term between the two parts of the local representation of the Schrödinger Green function indicated in Eq. (34), leaving it invariant. The present derivation is covariant with respect to the group of such transformations. Of course, for particular applications, it may be desirable to specify a particular representation. This can be done freely subject to the Kronecker δ conditions.

The relation, Eq. (24), which gives the Green function for any valid secular matrix which is linear in the locally exact basis functions, can be used to obtain a formal relation between the secular matrix of the GFCM, Eq. (14), and that of MST, Eqs. (11) or (12). The major difference between the two, of course, is that the secular matrix of the GFCM contains only nearest-neighbor coupling, whereas that of MST contains couplings between all sites through the structure constants. Let us denote the secular matrix of MST by $M[\phi]$ and the secular matrix of GFCM by $P[\phi]$. From Eq. (24) it follows that

$$G^{-1}=-P[\xi]^{-1}P[\phi]=-M[\xi]^{-1}M[\phi]. \qquad (35)$$

Thus the GFCM secular matrix can be obtained (at least formally) from that of MST by means of the transformation

$$P[\phi]=P[\xi]M[\xi]^{-1}M[\phi]. \qquad (36)$$

We have not yet tested this relation in a numerical calculation and it is not yet clear to us if it has more than formal significance in three dimensions because it requires the inversion of $M[\xi]$ which is essentially the structure constant matrix.

IV. PIVOTED GFCM AND LINEARIZATION

Pivoted MST or the pivoted GFCM can be derived from the Lippmann-Schwinger equation, Eq. (2), using a Green function at a different energy from that of the wave function. The usual Lippmann-Schwinger equation, Eq. (2), rewritten to include energy dependencies and pivoted to energy ϵ_0, is

$$\psi(\mathbf{r},\epsilon)=\int d\mathbf{r}'G_0(\mathbf{r},\mathbf{r}';\epsilon_0)\left\{V(\mathbf{r}')-\epsilon+\epsilon_0\right\}\psi(\mathbf{r}',\epsilon), \qquad (37)$$

where $\left\{\nabla^2+\epsilon_0\right\}G(\mathbf{r},\mathbf{r}';\epsilon_0)=\delta(\mathbf{r},\mathbf{r}')$, provides an equally good solution to Eq. (1).

One can follow the derivations in Secs. II and III step by step, starting from Eq. (37) rather than Eq. (2) to obtain secular equations and expressions for the Green function which are quite similar to those derived previously. The only difference is that the functions N_L^m on the left of all the Wronskian surface integrals are now calculated at the pivoted energy ϵ_0 instead of ϵ. For the particular case of $\epsilon_0=0$, this function becomes

$$N_L(\mathbf{r}_m)\sim r_m^{-\ell-1}Y_L(\hat{\mathbf{r}}_m), \qquad (38)$$

which is completely independent of the energy parameter. This not only greatly simplifies the computational procedure, it also allows a technique in which both the secular matrix and the basis functions can be linear in energy.

The use of $r_m^{-\ell-1}Y_L(\hat{\mathbf{r}}_m)$ in place of $N(\mathbf{r}_m)$ is standard practice in LMTO theory[18] and is analogous to the use of zero-energy structure constants in "pivoted" MST.[21] However, there is one important difference. Although the basis functions are independent of the pivoting energy, the generalized sine and cosine matrices are not. In pivoted MST one uses structure constants evaluated at the pivoting energy, therefore the potential used in calculating C and S matrices must be shifted in energy by the appropriate amount to make the arguments of the relevant regular and irregular Bessel functions used in calculating C and S equal to the pivoting energy, usually zero. This has the effect of putting a step into the potential at the cell boundary equal to the difference between the pivoting energy and the actual energy. This relatively large step at the cell boundary can cause significant problems in ℓ convergence, especially in the internal sum between the structure constant matrix and the sine matrix in Eq. (12). The pivoted GFCM, on the other hand, does not have this problem primarily because only the irregular functions on the left of the Wronskians are calculated at the pivoting energy, whereas the other quantities are all calculated at the physical energy; thus the potential does not need to be shifted. In addition, there are no structure constants and hence no internal ℓ sum in the GFCM.

Because of the close relationship established here between GFCM and MTO/ACO theory, this method can be extended to an energy-linearized variational theory very simply, e.g., following in detail the linearized ACO methodology (LACO).[16] This linearized theory will be presented in later publications. We describe here a simple linearization scheme which nevertheless allows the use of multiple energy panels without introducing discontinuities in the energy bands. We assume that the secular matrix of the GFCM can be well approximated over the energy range of interest by a form which is linear in energy,

$$M(\epsilon)=A\epsilon+B, \qquad (39)$$

where matrices A and B are energy independent and ϵ is the energy parameter. Now if we do calculations at two energies ϵ_1 and ϵ_2, we can find the matrices A and B as

$$A = \frac{M(\epsilon_1) - M(\epsilon_2)}{\epsilon_1 - \epsilon_2}, \quad B = \frac{M(\epsilon_2)\epsilon_1 - M(\epsilon_1)\epsilon_2}{\epsilon_1 - \epsilon_2}. \tag{40}$$

It is easy to verify that the energy eigenvalues are given by the eigenvalues of the matrix

$$A^{-1}B = \{M(\epsilon_1) - M(\epsilon_2)\}^{-1} \{M(\epsilon_2)\epsilon_1 - M(\epsilon_1)\epsilon_2\}. \tag{41}$$

To minimize the error introduced by linearization, one can use multiple energy panels and keep only those eigenvalues which lie within each panel. Unlike the conventional linearization scheme which uses only one pivoting energy for each energy panel, this approach does not introduce discontinuities in the energy bands because the error due to linearization vanishes at both ends of the energy panel (i.e., when $\epsilon = \epsilon_1$ or $\epsilon = \epsilon_2$). The present simplified linearized method defines a band-structure theory with a secular matrix that has only nearest-neighbor couplings. This rigorous formalism is then computationally analogous to the use of an approximate tight-binding Hamiltonian matrix.

Because N_L^m, used either in the unpivoted or the pivoted GFCM form, is independent of atom type, the site off-diagonal matrix elements M^{mn} depend only on the atom type on site n. This feature and the fact that the matrix is of nearest-neighbor form may facilitate the application of the GFCM to the solution of the impurity problem and to applications of the coherent-potential approximation (CPA) to disordered systems. Detailed studies of these features will be presented in a separate publication.

V. NUMERICAL STUDIES

Initial tests of the GFCM formalism[10] included a two-dimensional empty-lattice test and an application to the diatomic $H_2{}^+$ ion. The empty-lattice test provides a rigorous test of any full-potential band-structure theory and has been used extensively to study full-potential multiple-scattering theory.[13,22] It was shown[10,11] that the energy eigenvalues and the mean-square error of the wave functions converge with respect to the ℓ truncation at about the same rate, with similar convergence behaviors for calculations done with surfaces defined on the cell boundaries, in circumscribing spheres, and on inscribed (muffin-tin) spheres. The results of $H_2{}^+$ compared well with the exact results.[23]

In this paper we present a calculation of energy bands of fcc Cu. The calculation uses a non-muffin-tin potential obtained from using the self-consistent quadratic KKR. The secular matrix given by Eq. (14) is calculated using matching conditions on the Wigner-Seitz sphere, and the linearization scheme discussed in the previous section is used with energy panels defined by the end points at 0.225 Ry intervals from −0.10 to 0.80 Ry. The calculation was carried out along the Γ-X and the Γ-L directions.

It should be noted that the Wronskian surface integrals required in practical calculations can be evaluated outside the loop over points in **k** space. The **k** dependence of the secular matrix in the GFCM is in the form of a phase factor multiplying a fixed integral for each interface surface,

$$M_{L'L}(\mathbf{k}) = \sum_{p=\substack{\text{neighbors}\\ \text{of } m}} \{ [N_{L'}^m, \phi_L^m]_{S_{mp}} - [N_{L'}^m, \phi_L^p]_{S_{mp}} e^{i\mathbf{k}\cdot\mathbf{R}_{mp}} \}. \tag{42}$$

Therefore, for each energy the required **k**-independent Wronskian integrals are calculated and stored, and are used subsequently for all **k** points. Thus the computational effort of surface quadrature is not proportional to the number of **k** points. The present scheme may be especially efficient in following details of a complicated Fermi surface because arbitrary search paths can be followed in **k** space without computing structure constants.

The calculation was carried out on an IBM RISC/6000 model 320. For the case of $\ell_{\max} = 4$, calculation of the whole energy range with 100 **k** points required less than 7 min of CPU time. Nearly half of this time was spent

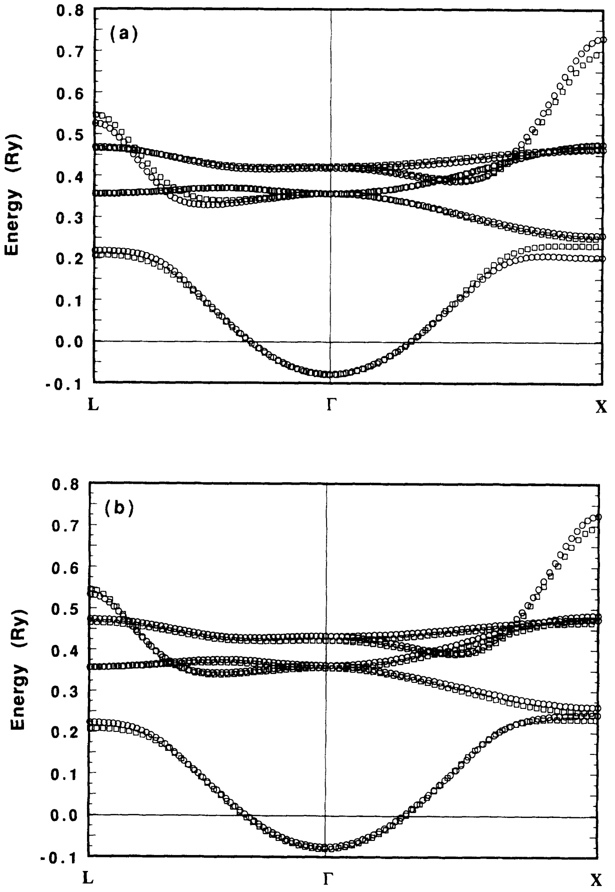


FIG. 2. Energy bands of fcc Cu along the Γ-X and the Γ-L directions, calculated with linearized GFCM. (a) Using $\ell_{\max} = 4$ for the GFCM, and (b) using $\ell_{\max} = 6$. In both panels the results of the quadratic KKR with $\ell_{\max} = 4$ are indicated by squares and the results of the GFCM by open circles.

calculating the basis functions within the unit cell and the surface integrals between cells. These parts of the calculation scale as N, the number of atoms.

The preliminary results of the Cu band calculation are shown in Fig. 2, and are compared with the corresponding bands calculated by the quadratic KKR technique using $\ell_{\max} = 4$. The GFCM calculations used a sphere of radius 2.8 a.u. as the surface for the Wronskian surface integrals in Eq. (14). The lattice constant is 6.76 a.u. Overall, the results are in good agreement. We note especially that the errors due to linearization are negligible. In appraising the convergence of the GFCM it should be noted that because it does not yield a variational secular equation, errors in the band energies are the *same* order as those of the wave functions. Furthermore, unlike MST, the GFCM cannot produce converged energies with wave functions that are converged only near the nucleus (i.e., for very short-ranged potentials). This implies that relative to most other techniques the GFCM wave functions will be better converged for the same level of convergence of the band energies. If highly converged band energies are desired a variational correction can be applied. For most purposes, however, the charge density which is determined by the wave functions is the more useful quantity. We plan a more detailed comparison with other full-potential calculations as well as a study of the convergence of both the energy bands and the charge density with respect to the number of basis states in a later publication.

VI. DISCUSSION AND CONCLUSIONS

The Green-function cellular method can be viewed as a form of multiple-scattering theory in which the structure constants that couple different sites are resummed into nearest-neighbor couplings. In addition to its nearest-neighbor nature, the GFCM has the advantage that it can readily be linearized in energy, and in the case of periodic systems, the **k** dependence is trivial. As discussed here, an extension of the GFCM formalism is capable of producing the Schrödinger Green function directly. GFCM can be readily combined with the CPA for the treatment of substitutionally disordered systems. It provides an alternative to the ACO and/or KKR formalism as a direct full-potential extension of KKR theory, and can be equally well developed into an energy-linearized theory.

Both the GFCM and the KKR method are derived from the same principles. The numerical behavior of the GFCM and nonvariational KKR are also similar. The expression we derive for the structure constants in terms of Wronskian cellular integrals further shows the relationship between the two methods. It is unclear to us whether the Kohn-Rostoker variational principle can be related to the GFCM and used to derive a variational version of the theory. The nonvariational nature of the theory may result in less accurate band energies. However, one can certainly use the GFCM as an alternative to ACO and/or KKR to construct basis functions that are valid over the range of an energy panel, following LMTO and/or LACO methodology, and then use them in the Rayleigh-Ritz variational technique or more precisely in the Schlosser-Marcus technique. The ability of the GFCM to compute the Green function directly should make the computation of the energy bands unnecessary in many applications.

We expect that the methods which we describe here should be generally useful for solving linear partial-differential equations. The closely related ACO and/or KKR method has already been implemented for solving the Poisson equation.[24] Computational techniques require only minor modifications of existing methodology built into LACO programs. These methods are advantageous for parallel processing because the computational effort of obtaining the local basis functions can be done independently for each atom or cell. The computations can be organized in terms of surface integrals that are evaluated outside the symmetry loop or **k** loop. The required surface integrals are weighted computationally by nearest-neighbor pairs of inequivalent atoms, not quadratically by the full number of atoms. The step of the calculation in which the local solutions are matched to form the global solution reduces to solving a system of linear equations corresponding to a matrix with only nearest-neighbor couplings.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge helpful discussions with G. M. Stocks and A. Gonis. Research sponsored in part by Division of Materials Science, Office of Basic Energy Sciences, and by the High Performance Computing and Communication Program, U.S. Department of Energy under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

---

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

[2] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[3] The problem of generalizing MST to general potentials has an extensive literature, much of which is referenced in W. H. Butler, A. Gonis, and X.-G. Zhang, Phys. Rev. B **45**, 11 527 (1992).

[4] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[5] J. C. Slater, Phys. Rev. **45**, 794 (1934).

[6] W. Kohn, Phys. Rev. **87**, 472 (1952).

[7] L. G. Ferreira and J. R. Leite, Phys. Rev. Lett. **40**, 49 (1978); Phys. Rev. A **18**, 335 (1978); **20**, 689 (1979); A. C. Ferraz, E. K. Takahashi, and J. R. Leite, Phys. Rev. B **26**, 690 (1982).

[8] J. W. Strutt (Lord Rayleigh), *Theory of Sound* (Dover, New York, 1945), Vol. I, Sec. 88; W. Ritz, J. Reine Angew. Math. **135**, 1 (1908).

[9] H. Schlosser and P. M. Marcus, Phys. Rev. **131**, 2529 (1963).

[10] X.-G. Zhang and W. H. Butler, Phys. Rev. Lett. **68**, 3753 (1992).

[11] W. H. Butler and X.-G. Zhang, in *Application of Multiple Scattering Theory to Materials Science*, edited by W. H. Butler, A. Gonis, P. H. Dederichs, and R. Weaver, MRS Symposia Proceedings No. 253 (Materials Research Society, Pittsburgh, 1992).

[12] R. K. Nesbet, Phys. Rev. B **41**, 4948 (1990).

[13] W. H. Butler and R. K. Nesbet, Phys. Rev. B **42**, 1518 (1990).

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

[15] H. L. Skriver, *The LMTO Method* (Springer-Verlag, New York, 1984).

[16] R. K. Nesbet, Phys. Rev. B **33**, 8027 (1986).

[17] R. K. Nesbet and Tjet Sun, Phys. Rev. B **36**, 6351 (1987).

[18] O. K. Andersen, in *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971).

[19] A. R. Williams and J. van W. Morgan, J. Phys. C **47**, 37 (1974).

[20] A. B. Chen (unpublished).

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

[22] J. S. Faulkner, Phys. Rev. B **38**, 1690 (1988).

[23] P. R. Bates, K. Kedsham, and A. L. Stewart, Philos. Trans. R. Soc. **246**, 216 (1953).

[24] R. K. Nesbet, Bull. Am. Phys. Soc. **35**, 418 (1990).