Validity, accuracy, and efficiency of multiple-scattering theory for space-filling scatterers

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

R. K. Nesbet
IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099
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The equations of multiple-scattering theory (MST) are solved for the case of a lattice of square-well potentials in the shape of squares that fill the plane. We find that multiple-scattering theory is exact within reasonably achievable numerical accuracy. There *is* a problem with the convergence of MST in its traditional formulation that has obscured the fact that it is an exact theory even for non-muffin-tin, space-filling potentials. We show that this problem can be easily circumvented and describe a rapidly convergent, exact formulation of MST.

I. INTRODUCTION

Multiple-scattering theory[1-4] (MST) is a powerful and useful technique for solving the wave equation. This power and utility result from the following capabilities. (1) It provides an efficient basis for expanding solutions and yields smaller secular equations than other techniques. (2) It can be used to generate the Green function directly, by-passing the need to generate it through a poorly convergent spectral sum. (3) It allows a separation between structure and potential which is not possible with other techniques.

The primary limitation of MST as a means of calculating electronic states in condensed matter has been its restriction to potentials of "muffin-tin" form, i.e., to potentials that consist of a sum of spherically symmetrical, nonoverlapping "atomic" potentials. Until fairly recently this restriction was not a severe impediment to the application of this technique since the actual potential for many interesting problems, especially in crystalline metals, could be well approximated by this form. Today, however, the state of the art of electronic-structure calculations requires that a technique be capable of treating molecules, surfaces, grain boundaries, and other systems whose potentials are not well approximated by muffin tins.

Much has been written in recent years concerning the application of MST to non-muffin-tin potentials. It is not difficult to write down formally the scattering matrix for a nonspherical scatterer,[5-8] and there is little doubt[9] that MST can be rigorously applied to nonspherical potentials, *provided* they are sufficiently separated that if each were circumscribed by a sphere none of these "bounding spheres" would overlap. Considerable controversy has raged, however, over whether or not MST can be rigorously applied to solve the wave equation in the more interesting situation in which the bounding spheres do overlap, and, in particular, over the situation in which the atomic potentials consist of cells which fill all of space.

Ziesche[10] and Faulkner[11] claimed that there are "near-field corrections" which must be included for a rigorous treatment of systems in which the bounding spheres overlap. This view has been challenged by Gonis and co-workers,[12,13] by Zeller,[14,15] by Molenaar,[16,17] and by Nesbet.[18] Although several analytic proofs have been advanced to demonstrate that multiple-scattering theory is correct, even for space-filling scatterers, the subject remains contentious and previous numerical tests have proved ambiguous. Nevertheless, a consensus appears to be emerging that the "near-field corrections" vanish for nonpathological geometries. This consensus is strongly supported by the numerical tests reported here.

As the controversy over "near-field corrections" is being resolved, a second controversy is rising over whether or not the Williams-Morgan[5-7] approach to calculating the scattering matrix is correct. Brown and Ciftan[19-21] have proposed an alternative formulation which has been challenged by Faulkner[22] and by Zeller.[15] The numerical tests reported here strongly support Nesbet's[18] formal demonstration that the two approaches give identical results when and *if* both are carried to convergence in the partial-wave expansions. The Williams-Morgan approach, however, converges much more slowly than that of Brown and Ciftan for the test case considered here, and, in fact, we were not able to conclusively demonstrate the convergence of the former.

Perhaps a more important issue than the question of whether or not near-field corrections exist is the issue of whether or not MST remains an efficient technique for electronic-structure calculations when it is extended to treat non-muffin-tin potentials. Recent numerical results by Faulkner[23,24] are extremely disturbing in this

regard. Faulkner studied the empty-lattice problem in two dimensions. He used multiple-scattering theory to solve the wave equation for a system of square atomic potentials each of side a arranged in a square lattice so that they filled all of space. The depth of the potentials was a constant, V_0, so that the total potential was uniform, allowing the exact result for the dispersion relation, $E = V_0 + (K_n + k)^2$, to be known trivially.

Because he treated a two-dimensional system, Faulkner could include a large number of partial waves in his expansions of the wave functions. The parameter $\ell_{\max}$, the number of different radial functions used to expand the wave function within a cell, provides a convenient measure of the number of partial waves used to represent the wave functions. In one dimension[25] $\ell_{\max}$ may be zero or one and the size of the secular equation for a general symmetry is equal to the number of atoms times $\ell_{\max}$. In two and three dimensions, there is no *a priori* upper limit to $\ell_{\max}$. It is typically increased until a tolerably small error is achieved. For a two-dimensional system of general symmetry the size of the secular equation that determines the energy eigenvalues is $2\ell_{\max} + 1$. In three dimensions this size is $(\ell_{\max} + 1)^2$. Faulkner found that the energies of most states were well converged for $\ell_{\max} = 34$, but one state was not converged, even for $\ell_{\max} = 56$.

Faulkner's result is disturbing for two reasons. The fact that he found one state that did not appear to converge could be interpreted as indicating that MST is not exact for non-muffin-tin scatterers unless "near-field corrections" are included. More importantly, the fact that extremely large numbers of partial waves appeared to be necessary would seem to negate any possible advantage of non-muffin-tin MST for routine calculations in condensed-matter systems. It is not precisely clear what Faulkner's two-dimensional results portend for three dimensions, although we will argue later that the problems he uncovered will, in many cases, be worse in three dimensions than in two. It should be noted that an $\ell_{\max}$ value of 35 in three dimensions would imply, for a system of general symmetry, a secular equation of size 1225 times the number of scatterers.

Here the two-dimensional empty-lattice test is performed carefully and it is demonstrated that the standard formulas of MST are correct for this system, albeit slowly and conditionally convergent. The origin of the poor convergence will be elucidated and it will be shown that it can be corrected by a slight modification of the MST equations so that rapid convergence in the number of partial waves can be obtained.

II. MULTIPLE-SCATTERING THEORY IN TWO DIMENSIONS FOR SPACE-FILLING SCATTERERS

The basic idea of multiple-scattering theory is that the wave equation can be solved in a piecewise fashion by dividing space into separate regions. Solutions to the wave equation are first obtained for each region independently and then these solutions are matched at the boundaries that separate the regions to form a solution that is valid throughout the region of interest. The wave equation is given by

$$[-\nabla^2 + V(\mathbf{r}) - E]\Psi(\mathbf{r}, E) = 0 \; . \tag{1}$$

Generally, in problems in condensed-matter physics $V(\mathbf{r})$ is the potential due to atomic scatterers located at positions $\mathbf{R}_n$. In the following it is assumed that space can be divided into regions that are associated with each scatterer. Usually, points closer to $\mathbf{R}_n$ than to any other scattering center will belong to scatterer n. For definiteness we find it convenient to give explicit results for two dimensions since that is the case for which we have performed numerical tests. The extension to one or three dimensions is straightforward. We also will write our equations assuming that the energy parameter is negative, as would be appropriate for studying the bound states of a finite system. For an infinite system with space-filling scatterers the energy zero is arbitrary and the calculation could also be performed at positive energy. The translation to positive energy is straightforward, basically requiring that ordinary cylindrical Bessel functions be substituted for the modified ones used here.

The wave function inside region n can be expanded in terms of partial waves, which are functions of $\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$ [or equivalently of $r_n = |\mathbf{r}_n|$ and $\phi_n = \tan^{-1}(y_n/x_n)$],

$$\Psi_{\mathrm{I}n}(\mathbf{r}) = \sum_{\ell=-\infty}^{\infty} c_\ell^n R_\ell(r_n) e^{i\ell\phi_n} \; . \tag{2}$$

Here each partial wave is a solution to the wave equation and is distinguished by its behavior in the vicinity of the origin where $R_\ell(r) \Rightarrow I_\ell(\alpha r)$, where $I_\ell(\alpha r)$ is a modified cylindrical Bessel function of the type that is regular at the origin[26] and $\alpha = \sqrt{-E}$. Since the radial wave functions labeled by $+\ell$ and $-\ell$ are not linearly independent, Eq.(2) might better be written as

$$\Psi_{\mathrm{I}n}(\mathbf{r}) = c_0^n R_0(r_n)\cos\phi_n + \sum_{\ell=1}^{\infty} \sum_{m=-1,1} c_{\ell m}^n R_\ell(r_n) e^{i\ell m\phi_n} \; , \tag{3}$$

which makes the expression appear more similar to the three-dimensional case than the original form. The latter form also makes it obvious that the exponential functions can be eliminated in favor of sines and cosines for computations. For simplicity of notation, however, we will use the form (2).

Even if the scatterers fill all of space, we can imagine that there is an infinitesimal region along the boundary separating the scatterers where the potential is zero. Since this region occupies zero volume, we are free to choose the potential there to be whatever we desire. We will call this interstitial volume region II and assume the potential there to be zero. The wave function in region II can be expanded as a multicenter expansion involving

"outgoing" waves from all of the scatterers

$$\Psi_{\rm II}(\mathbf{r}) = \sum_n \sum_{\ell=-\infty}^{\infty} b_\ell^n K_\ell(\alpha r_n) e^{i\ell\phi_n} . \quad (4)$$

Here K_ℓ is a modified cylindrical Bessel function that vanishes exponentially at large values of its argument.[26] In the vicinity of scatterer n the wave function in region II can also be expanded as a single-center expansion that involves both "incoming" waves, regular at R_n, and "outgoing" waves, irregular at R_n,

$$\Psi_{{\rm II}n}(\mathbf{r}) = \sum_{\ell=-\infty}^{\infty} [a_\ell^n I_\ell(\alpha r_n) + b_\ell^n K_\ell(\alpha r_n)] e^{i\ell\phi_n} . \quad (5)$$

Our strategy will be to match the solutions $\Psi_{{\rm I}n}$ and $\Psi_{{\rm II}n}$ at the boundary of cell n. In the linear atomic-cell orbitals method (LACO), based on a variational solution to the wave equation in space-filling atomic cells,[27] boundary matching between cells is carried out in terms of surface integrals. In the present case the relevant matching condition is

$$\int dS\, \hat{\mathbf{n}} \cdot (\Psi_{{\rm II}n}^* \nabla \Psi_{{\rm I}n} - \nabla \Psi_{{\rm II}n}^* \Psi_{{\rm I}n}) = 0 . \quad (6)$$

This relation is a generalization of the step in the derivation of muffin-tin MST in which the logarithmic derivatives of the radial wave functions inside the muffin tin are matched to the logarithmic derivatives of those outside to determine the scattering phase shifts or t matrices. Equation (6) takes the form of a Green's-theorem surface integral, and can be derived by partial integration of volume integrals of the standard variational form for the wave equation. It clearly reduces to the matching condition for radial logarithmic derivatives if the local potential has spherical symmetry within a spherical atomic cell and it is clearly a necessary condition for consistency.

Using Eqs. (2) and (5) in Eq. (6) yields

$$\sum_{\ell=-\infty}^{\infty} \sum_{\ell'=-\infty}^{\infty} (a_\ell^n W_{\ell\ell'}^I + b_\ell^n W_{\ell\ell'}^K) c_{\ell'}^n = 0 . \quad (7)$$

where

$$W_{\ell\ell'}^I = \int dS\, \hat{\mathbf{n}} \cdot [I_\ell(\alpha r_n) e^{-i\ell\phi_n} \nabla (R_{\ell'}(r_n) e^{i\ell'\phi_n}) - \nabla (I_\ell(\alpha r_n) e^{-i\ell\phi_n}) R_{\ell'}(r_n) e^{i\ell'\phi_n}] . \quad (8)$$

and

$$W_{\ell\ell'}^K = \int dS\, \hat{\mathbf{n}} \cdot [K_\ell(\alpha r_n) e^{-i\ell\phi_n} \nabla (R_{\ell'}(r_n) e^{i\ell'\phi_n}) - \nabla (K_\ell(\alpha r_n) e^{-i\ell\phi_n}) R_{\ell'}(r_n) e^{i\ell'\phi_n}] . \quad (9)$$

The requirement that the single-center expansion of the wave function in region II ($\Psi_{{\rm II}n}$) be consistent with the multicenter expansion ($\Psi_{\rm II}$) leads to the requirement that

$$\sum_{\ell=-\infty}^{\infty} a_\ell^n I_\ell(\alpha r_n) e^{i\ell\phi_n} = \sum_{n'\neq n} \sum_{\ell'=-\infty}^{\infty} b_{\ell'}^{n'} K_{\ell'}(\alpha r_{n'}) e^{i\ell'\phi_{n'}} . \quad (10)$$

This relation is fundamental to MST and may be expressed in words as the requirement that the "incoming" wave on any scatterer equals the sum of the "outgoing" waves from all of the other scatterers.

The next step in the usual derivation of the MST equations requires that partial waves (regular at infinity) be expandable in terms of partial waves (regular at the origin) centered at another site. For our case of two dimensions at negative energy this relation is

$$K_{\ell'}(\alpha r_{n'}) e^{i\ell'\phi_{n'}} = \sum_{\ell=-\infty}^{\infty} g_{\ell'\ell}(\mathbf{R}_{n'n}) I_\ell(\alpha r_n) e^{i\ell\phi_n} , \quad (11)$$

where the structure constants $g_{\ell'\ell}(\mathbf{R}_{n'n})$ are given by[24,28–30]

$$g_{\ell'\ell}(\mathbf{R}_{n'n}) = g_{\ell\ell'}(\mathbf{R}_{nn'}) = K_{\ell-\ell'}(\alpha R_{nn'})(-1)^{\ell'} e^{i(\ell'-\ell)\phi_{nn'}} , \quad (12)$$

with $\mathbf{R}_{n'n} = \mathbf{R}_n - \mathbf{R}_{n'}$ and $\phi_{nn'} = \phi_{n'} - \phi_n$. Using this expansion (11) in Eq. (10) allows the coefficients of the "incoming" waves, a_ℓ^n, to be eliminated in favor of the coefficients of the "outgoing" waves,

$$a_\ell^n = \sum_{\ell'=-\infty}^{\infty} \sum_{n'\neq n} b_{\ell'}^{n'} g_{\ell'\ell}(\mathbf{R}_{n'n}) . \quad (13)$$

The multiple-scattering equations can then be written as

$$\sum_{n'} (g_{nn'} W_{n'}^I + W_n^K \delta_{nn'}) c_{n'} = 0 , \quad (14)$$

a notation in which the angular momentum indices are suppressed.

For an infinite periodic system, the site dependence can be eliminated by the ansatz $c_n = e^{i\mathbf{k}\cdot\mathbf{R}_n} c_0(\mathbf{k})$, which yields the generalized Korringa-Kohn-Rostoker (KKR) equations[2,3]

$$[g(\mathbf{k}, E) W^I(E) + W^K(E)] c_0(\mathbf{k}, E) = 0 , \quad (15)$$

$$g_{\ell\ell'}(\mathbf{k}, E) = \sum_{n'\neq n} e^{i\mathbf{k}\cdot\mathbf{R}_{nn'}} g_{\ell\ell'}(\mathbf{R}_{nn'}, E) . \quad (16)$$

The condition that determines the characteristic values of the energy, i.e., the bound-state energies for a finite system of scatterers or the dispersion relation for an infinite periodic system, is obtained by setting the determinant of the matrix $gW^I + W^K$ to zero.

III. THE EMPTY-LATTICE TEST IN TWO DIMENSIONS

The empty lattice test in two dimensions requires (1) the generation of matrices W^I and W^K, (2) the calculation of the structure-constant matrix g, and (3) the determination of the values of the energy parameter that allow solutions of the linear system (14).

The first step is straightforward once the radial wave function for a single scatterer $R_\ell(r_n) e^{i\ell\phi_n}$ is known. Ac-

cording to the original Williams-Morgan development,[5] the radial wave equation which results from the separation of variables in spherical polar coordinates for the case of spherically symmetrical potentials (actually circularly symmetrical in our case) is replaced by a coupled set of differential equations:

$$\frac{dC_{\ell'\ell}(r)}{dr} = -rK_{\ell'}(\alpha r)\sum_{\ell''=-\infty}^{\infty} V_{\ell''\ell'}(r)\Phi_{\ell''\ell}(r) ,$$

$$\frac{dS_{\ell'\ell}(r)}{dr} = rI_{\ell'}(\alpha r)\sum_{\ell''=-\infty}^{\infty} V_{\ell''\ell'}(r)\Phi_{\ell''\ell}(r) ,$$

$$\Phi_{\ell'\ell} = I_{\ell'}(\alpha r)C_{\ell'\ell}(r) + K_{\ell'}(\alpha r)S_{\ell'\ell}(r) , \tag{17}$$

$$V_{\ell'\ell}(r) = \frac{1}{2\pi}\int_0^{2\pi} d\phi\, e^{i(\ell'-\ell)\phi}V(r,\phi) ,$$

$$R_\ell(r)e^{i\ell\phi} = \sum_{\ell'=-\infty}^{\infty} e^{i\ell'\phi}\Phi_{\ell'\ell} ,$$

with initial conditions

$$C_{\ell'\ell}(0) = \delta_{\ell'\ell} ,$$
$$S_{\ell'\ell}(0) = 0 . \tag{18}$$

The matrices $C_{\ell'\ell}(r)$ and $S_{\ell'\ell}(r)$ when evaluated at the radius of the circumscribing sphere provide the sine and cosine matrices necessary to form the KKR matrix.

At this stage we encounter our first controversy. In the original formulation[5] $V(r,\phi)$ is a truncated potential that vanishes when $\mathbf{r}$ lies outside the cell at the origin which we denote by Ω_0,

$$V(r,\phi) = \begin{cases} V(\mathbf{r}) & \text{if } \mathbf{r}\in\Omega_0 \\ 0 & \text{otherwise} . \end{cases} \tag{19}$$

Brown and Ciftan, however,[19–21] have suggested that the potential should not be truncated and that the coupled differential equations [Eqs. (17)] be integrated out to the radius of the bounding sphere using the full untruncated potential $V(\mathbf{r})$, with integrals being performed over the truncated potentials to determine $C_{\ell'\ell}$ and $S_{\ell'\ell}$ only after the radial wave function has been determined:

$$C^{\mathrm{BC}}_{\ell'\ell} = \delta_{\ell'\ell} - \int_{\Omega_0} K_{\ell'}(\alpha r)e^{-i\ell'\phi}V(r,\phi)R_\ell(r)e^{i\ell\phi}r\,dr\,d\phi \tag{20}$$

and

$$S^{\mathrm{BC}}_{\ell'\ell} = \int_{\Omega_0} I_{\ell'}(\alpha r)e^{-i\ell'\phi}V(r,\phi)R_\ell(r)e^{i\ell\phi}r\,dr\,d\phi . \tag{21}$$

We solved these equations both ways and found that the results for the wave function calculated for $\mathbf{r}\in\Omega_0$ are essentially the same. This result is presented in Fig. 1, which shows the difference between the wave functions calculated by the two techniques, along the line connecting the center of the square with one of its corners, as

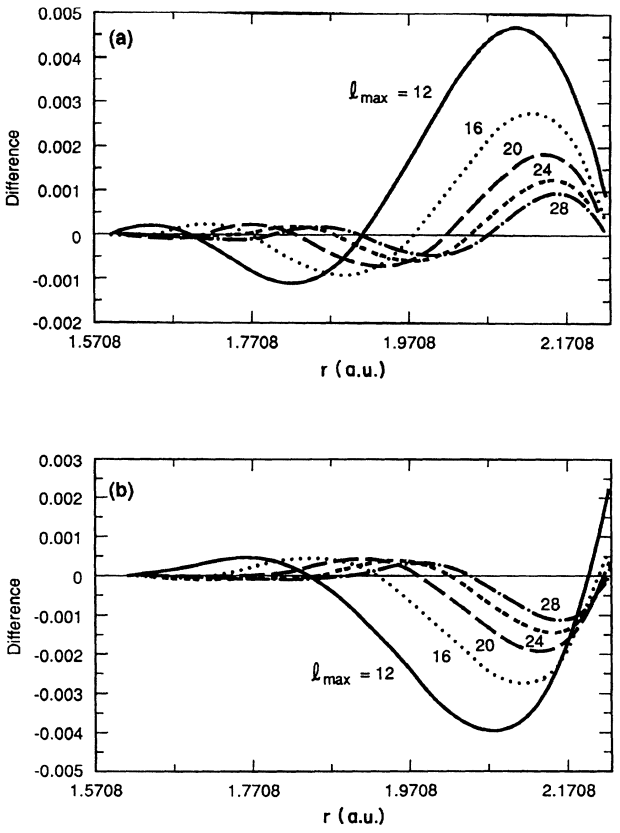

FIG. 1. Difference between the Williams-Morgan and Brown-Ciftan wave functions. (a) $\ell = 0$ and $\ell'_{\max} = 12, 16, 20, 24, 28$. (b) $\ell = 4$ and $\ell'_{\max} = 12, 16, 20, 24, 28$. The Brown-Ciftan wave function for the empty-lattice test is $J_\ell(\sqrt{E+V}r)\cos(\ell\phi)$.

a function of the number of partial waves included in the expansion of $R_\ell(r)e^{i\ell\phi}$. Only the portion outside the muffin tin is shown since the wave functions are identical within the muffin tin. For the empty-lattice test, the Brown-Ciftan wave function is obtained trivially,

$$R_\ell(r) = (\alpha/\beta)^\ell J_\ell(\beta r) , \tag{22}$$

where $\beta = \sqrt{E+V}$. From Fig. 1 it appears that the differences between the Williams-Morgan approach and the Brown-Ciftan approach are small and tend to zero as the number of partial waves is increased, at least for this example and for $l_{\max}$ less than 28. However, preliminary calculations using values of $l_{\max}$ up to 48, not shown here, show behavior that may be indicative of conditional convergence typical of asymptotic series. Implications of such behavior will be discussed below.

A technique for calculating the wave function that avoids truncation of the potential, such as that of Brown and Ciftan, seems to us to be advantageous. Truncation of the potential only causes convergence problems and offers no advantage or simplification. The Brown-Ciftan technique has been criticized by Faulkner[24] because he found in his numerical tests that the matrix $C^{\mathrm{BC}}(S^{\mathrm{BC}})^{-1}$ was not symmetric. We suspect, but have not proved, that $C^{\mathrm{BC}}(S^{\mathrm{BC}})^{-1}$ is, in fact, symmetric if properly cal-

TABLE I. Calculated energy of lowest state for an "empty lattice" filled with potentials of side $a = \pi$ and depth $V = -5$ as a function of the internal ℓ-sum cutoff, ℓ_i^{co}. The exact energy is $E = -5$. All calculations use $\ell_{max} = 0$.

ℓ_i^{co}	Eq. (15)	Eq. (29)
0	−5.500 59	−4.984 63
4	−4.959 16	−4.999 21
8	−5.004 88	−4.999 97
12	−4.999 352	−4.999 998 6
16	−5.000 094	−4.999 999 941
20	−4.999 985	−4.999 999 999

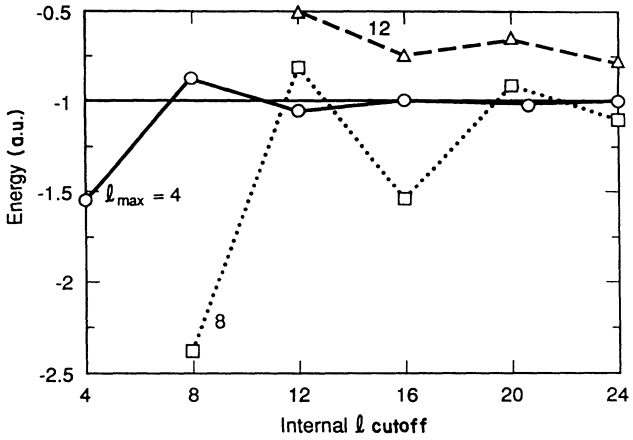

FIG. 2. Convergence of Eq. (15) as a function of the cut-off of the internal sum in the matrix product $(gW^I)_{\ell\ell'} = \sum_{\ell''} g_{\ell\ell''} W^I_{\ell''\ell}$ for a state at $E = V_0 + (2\pi/a)^2$. A similar plot using the results of Eq. (29) would be indistinguishable from the exact energy on the scale of this figure.

culated. It should be noted that this is a rather strange mathematical object, because, as observed by Faulkner, S^{BC} is an infinite-dimensional matrix with vanishing determinant. Its inversion and the subsequent multiplication of the inverse should be approached with circumspection. We have verified that all of the eigenvalues that we calculated are real. It has been pointed out to us[31,32] that the Brown-Ciftan approach might be inappropriate for cases in which the crystal potential has real, physical discontinuities, e.g., a "checkerboard" potential consisting of alternating positive and negative square-well potentials, each in the shape of a square. Fortunately, the effective one-electron potentials of real materials are continuous.

The volume integrals, Eqs. (20) and (21), can be integrated by parts and reduced to the surface integrals,[27] Eqs. (9) and (8), so that

$$W^K_{\ell\ell'} = -C_{\ell\ell'} , \tag{23}$$

$$W^I_{\ell\ell'} = S_{\ell\ell'} . \tag{24}$$

We will use the notations W^K, W^I, and C, S interchangeably in the remainder of this paper and we will not distinguish between the Brown-Ciftan and Williams-Morgan versions of (C, S). We solved the multiple-scattering equations (14) for a potential which was constant, $V_0 = -5$, and for lattice constant $a = \pi$. For these choices the lowest-lying states of full square symmetry are at $E = -5$ (corresponding to a wave function which is a constant) and at $E = -1$ [corresponding to wave function $\sum_\ell c_\ell R_\ell(r) \cos \ell\phi = \cos 2x + \cos 2y$]. We evaluated W^K and W^I using the wave function corresponding to the Brown-Ciftan prescription, Eqs. (20)–(22), and we evaluated the structure constants by summing over points on a square lattice exactly as indicated by Eqs. (12) and (16). For purposes of comparison we also solved the MST equations in the atomic-sphere approximation (ASA). In the ASA the space-filling cell is replaced by a sphere (circle) of equal volume. In this case the sine and cosine matrices are diagonal.

The results are shown in Table I for the lowest state and in Table II and Fig. 2 for the next-highest state. Our results show that Eq. (14) gives the lowest-energy state essentially *exactly* for $\ell_{max} = 0$, and that the state at $E = -1$ is in error by less than 1% using $l_{max} = 4$. In order to achieve this excellent convergence, however, it was necessary to carry the internal partial-wave sum involved in the matrix product gW^I, equivalent to gS in Eq. (14) to relatively high values of ℓ. This problem is worse for larger values of ℓ_{max}. For $\ell_{max} = 12$, for example, the internal partial-wave sum had to be taken to 56 in order to obtain an energy within 1% of the correct result. Although the energy levels converge rapidly with

TABLE II. Energy calculated using Eq. (15) of second-lowest state with full square symmetry for an "empty lattice" filled with potentials of side $a = \pi$ and depth $V = -5$ as a function of ℓ_{max} and the internal ℓ-sum cutoff, ℓ_i^{co}. The exact energy is $E = -1$.

	ℓ_{max}			
ℓ_i^{co}	0	4	8	12
0	−0.306 14			
4	−0.277 44	−1.555 82		
8	−0.278 89	−0.877 05	−2.405 8	
12	−0.278 78	−1.058 16	−0.789 65	−0.490 45
16	−0.278 79	−0.992 65	−1.552 15	−0.752 25
20	−0.278 79	−1.011 94	−0.891 94	−0.648 37
24	−0.278 79	−1.006 15	−1.084 08	−0.780 61

TABLE III. Energy calculated using Eq. (29) of second-lowest state with full square symmetry for an "empty lattice" filled with potentials of side $a = \pi$ and depth $V = -5$ as a function of ℓ_{max} and the internal ℓ-sum cutoff, ℓ_i^{co}. The exact energy is $E = -1$. Note the vast improvement in convergence with respect to ℓ_i^{co} compared to Table II.

	ℓ_{max}			
ℓ_i^{co}	0	4	8	12
0	−0.273 02			
4	−0.278 71	−0.993 09		
8	−0.278 79	−1.006 71	−0.998 254	
12	−0.278 79	−1.007 38	−0.999 752	−0.999 528
16	−0.278 79	−1.007 44	−0.999 959	−0.999 910
20	−0.278 79	−1.007 44	−0.999 987	−0.999 984
24	−0.278 79	−1.007 44	−0.999 990	−0.999 997
ASA	−0.328 50	−0.330 55	−0.330 66	−0.330 67

ℓ_{max}, this convergence is only obtained if the internal partial-wave sum is converged first. Confusing results and serious errors can result from using the same l_{max} for the internal sum as for the parameter that determines the size of the secular equation. This can be seen by examining the first entry in each column of Table II.

The results for the ASA, which is widely used in the linear muffin-tin orbitals (LMTO) method, are given as the last line in Table III. The accuracy of the ASA is poor for the empty-lattice test, but it *is* apparently stable. One might have expected unphysical results at high values of ℓ_{max} due to the unphysical nature of the approximation which utilizes overlapping spheres to represent the potential.

IV. SOLUTIONS TO THE INTERNAL-SUM PROBLEM

The results of the preceding section are encouraging in some respects and discouraging in others. They are encouraging in that they demonstrate that MST is essentially exact for this problem, if it is carried to convergence. We did not encounter the problems seen by Faulkner in his two-dimensional empty-lattice tests. Although the reason for this is not entirely clear to us, we suspect it is related to Faulkner's use of the truncated potential in solving the coupled equations for the radial wave function. Faulkner also encountered great difficulties in inverting the sine matrix, $S_{\ell\ell'}$. This inversion is, of course, unnecessary for obtaining the eigenvalues and eigenfunctions, although it does yield a symmetrical secular equation so that the eigenvalues are manifestly real and it does simplify the calculation of the Green function. Our results are consistent with and extend those of Zeller,[15] who showed that MST for the two-dimensional empty-lattice test is exact in the limit of vanishing potential, whereas the "near-field error" found by Faulkner was first order in the strength of the potential.

The discouraging aspect of the results presented in Fig. 2 and Tables I and II is the apparent necessity for an extremely large cutoff in the internal ℓ sum. Fortunately, this difficulty can be overcome. The problem arises from the attempt to expand an "outgoing" wave centered on a neighboring site in terms of "incoming" waves centered at the origin. This can be seen from an examination of gW^I of Eq. (14), which may be expanded using the definition of $g_{\ell\ell'}$ [Eq. (12)] and the volume-integral representation of W^I [Eq. (21)] as

$$(gS)_{\ell\ell''} = \sum_{\ell'=-\infty}^{\infty} \sum_{n' \neq n} K_{\ell-\ell'}(\alpha R_{nn'})(-1)^{\ell'} e^{i(\ell'-\ell)\phi_{nn'}} \int_{\Omega_n} I_{\ell'}(\alpha r) e^{-i\ell'\phi_n} V(\mathbf{r}) R_{\ell''}(r) e^{i\ell''\phi_n} . \tag{25}$$

Note that the summand of the ℓ' sum involves the product $K_{\ell+\ell'}(\alpha R) I_{\ell'}(\alpha r)$. For large values of ℓ' this product tends to

$$(\ell' + \ell)!(\alpha r/2)^{\ell'} / [\ell'!(\alpha R/2)^{\ell'+\ell}] . \tag{26}$$

It is well known that the sum [Eq. (25)] will diverge when $r = R$, and it should not be surprising that the number of terms required for convergence increases rapidly as r/R increases. The somewhat surprising result that convergence in the empty-lattice test cannot be achieved with the usual MST procedure of using a single parameter, ℓ_{max}, to govern the size of the C, S, and g matrices can be understood by observing that increasing ℓ and ℓ' simultaneously does not guarantee that (26) will become small.

On the one hand, it is clear from Eq. (25) that this problem is accentuated for the empty-lattice test and may be much less severe for a potential that is much smaller in the corners of the cell, where r is relatively large, than in those parts of the cell where r is small.

This observation indicates one procedure for reducing the problem, namely choosing the zero of the potential to coincide with the corners of the cell. This procedure is not a panacea, however, since it lacks generality and since one reason for pursuing MST for space-filling potentials is the hope that the energy parameter can be fixed (for example, at $E=0$) and the characteristic values obtained by shifting the potential zero. The technique of shifting the potential so that the energy may remain fixed is a vital aspect of the ASA-LMTO (Ref. 33) method, the quadratic Korringa-Kohn-Rostoker method,[8,11] and the LACO method.[27,34–36]

It might be hoped that this convergence problem is less severe in three dimensions than in two; however, we know of no clear evidence to sustain this hope. The most important parameter is the ratio of the distance from the origin to the corner of the cell and the distance from the origin to the center of a neighboring cell. For the square lattice in two dimensions this ratio is $\sqrt{2}/2 = 0.707$. Exactly the same ratio is obtained for a fcc lattice and a larger ratio, $\sqrt{3}/2 = 0.866$, is obtained for simple cubic. For the bcc lattice, however, this ratio is smaller, $\frac{1}{2}\sqrt{5/3} = 0.6455$. We suspect that errors in a three-dimensional empty-lattice test would be relatively larger for simple cubic, followed by fcc, followed by bcc, and that the errors for the fcc case would be comparable to those observed for the square lattice in two dimensions.[37]

Fortunately, there is a general and effective procedure for dealing with this problem. One can avoid it entirely by eschewing the expansion of the outgoing waves from nearby sites. This simply requires elimination of nearest-neighbor sites in the calculation of the structure constants,

$$g'_{\ell\ell'}(\mathbf{k},E) = \sum_{n'\neq n,n+\delta} e^{i\mathbf{k}\cdot\mathbf{R}_{nn'}} g_{\ell\ell'}(\mathbf{R}_{nn'},E) , \tag{27}$$

where $n+\delta$ labels a neighbor to site n, and the addition of a second term, $C'_{\ell\ell'}$, analogous to $C_{\ell\ell'}$ [Eq. (9)], except that the outgoing waves are centered on neighboring sites rather than the origin,

$$C'_{\ell\ell'} = \int_{\Omega_n} dS\,\hat{\mathbf{n}}\cdot \sum_{n'=n+\delta} [K_\ell(\alpha r_{n'})e^{-i\ell\phi_{n'}} \nabla(R_{\ell'}(r_n)e^{i\ell'\phi_n}) - \nabla(K_\ell(\alpha r_{n'})e^{-i\ell\phi_{n'}})R_{\ell'}(r_n)e^{i\ell'\phi_n}] . \tag{28}$$

The modified secular equation,

$$(C + C' + g'S)c = 0 , \tag{29}$$

converges much faster than the original MST equation [Eq. (14)] as is shown in Fig. 2 and Tables I–III.

These results make clear that two separate partial-wave expansions are important in multiple-scattering theory and both must be accurately converged if MST is to give an accurate result. Firstly, the radial wave-function expansion, Eq. (2), must contain enough partial waves to adequately represent the wave function within a cell. This is not difficult to achieve because the angular momentum barrier [$V_\ell = \ell^2/r^2$ in two dimensions and $V_\ell = \ell(\ell+1)/r^2$ in three dimensions] is effective in eliminating partial waves with ℓ values much in excess of

$$\ell_c = \sqrt{E + V_c}\, r_c , \tag{30}$$

where r_c and V_c are, respectively, the distance to the corner of the cell and the value of the potential there.

Secondly, in the traditional formulation of MST, it is necessary that irregular wave functions centered on neighboring sites be accurately expanded in terms of regular wave functions centered at the origin. This second requirement may be much more severe than the first, as can be seen from expression (26). Fortunately, it is possible to use the alternative formulation described above to eliminate the need for ℓ values much greater than ℓ_c.

The procedure we have outlined is quite flexible. As many neighbor shells can be removed from the structure constants as are necessary to make the expansions of the irregular waves easy to deal with. In fact, one can eliminate the structure constants altogether. In this case the MST equations can be converted into a form that has the appearance of a tight-binding Hamiltonian,

$$\sum_m \sum_{\ell'=-\infty}^{\infty} H^{nm}_{\ell\ell'} c^m_{\ell'} = 0 , \tag{31}$$

where

$$H^{nm}_{\ell\ell'} = \int_{\Omega_m} dS\,\hat{\mathbf{n}}(K^n_\ell \nabla R^m_{\ell'} - \nabla K^n_\ell R^m_{\ell'}) , \tag{32}$$

which by Green's theorem is equivalent to

$$H^{nm}_{\ell\ell'} = \int_{\Omega_m} dv\, K^n_\ell V(\mathbf{r}) R^m_{\ell'} . \tag{33}$$

Here we have used K^n_ℓ to represent $K_\ell(\alpha r_n)e^{i\ell\phi_n}$ and R^m_ℓ to represent $R_\ell(\alpha r_m)e^{i\ell\phi_m}$.

V. CONCLUSIONS

The results of the two-dimensional empty-lattice test are consistent with and strongly support the following propositions. (1) Multiple-scattering theory is exact for space-filling scatterers. The "near-field corrections" postulated by Ziesche and Faulkner are zero. (2) In the calculation of the sine and cosine matrices which describe scattering by a single cell, abrupt truncation of the potential can lead to convergence problems in the partial-wave expansion. A technique which avoids this truncation, such as that of Brown and Ciftan, is preferable to the original prescription of Williams and Morgan, although

the two prescriptions appear to give the same results if the latter can be taken to convergence. (3) In formulating the MST equations it is critical that certain internal partial-wave sums (representing irregular wave functions expanded about an adjacent site in terms of regular wave functions expanded about the origin) be adequately converged. For non-muffin-tin scatterers this will often require that the internal sum include more partial waves than appear in the secular equation. (4) This difficulty can be avoided by reformulating the MST equations to use the irregular wave functions directly without reexpanding them about the origin.

The question of the convergence of the Williams-Morgan prescription for calculating the sine and cosine matrices needs further study. Unpublished results of Brown[38] and preliminary calculations that we have performed using high values of l_{max} indicate that the series expansions obtained by the method of Williams and Morgan[5,6] may be asymptotic in nature. This postulated asymptotic behavior is not in conflict with previous results obtained by one of us,[18] demonstrating the equivalence of basis functions within the cell as long as it is understood that numerical evaluation of the functions defined by the method of Williams and Morgan may require a more sophisticated method of summation, such as a conversion to continued fractions.

A second issue which needs further study is whether or not the sine matrix can be reliably and efficiently inverted so that the standard MST expressions for the Green function that are needed for impurity calculations and for alloy theory can be recovered.

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