Basis functions for arbitrary cells in multiple-scattering theory

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We present a formal and numerical study of the solutions of the Schrödinger equation associated with spatially bounded, but otherwise arbitrarily shaped potentials. We show that the scattering matrix (t-matrix), is sufficient to represent the solution everywhere outside the cell, not just outside a sphere bounding the cell. We also show that the basis function in the interior of the cell is independent of the potential surrounding the cell. We illustrate our formal results with the results of numerical calculations and discuss the implications of these results to multiple-scattering theory and to the calculation of the electronic structure of solids.

I. INTRODUCTION

The multiple-scattering theory (MST) method, which was first applied to periodic solids by Korringa[1] and by Kohn and Rostoker[2] (KKR), has been used extensively to calculate the electronic structure of materials. Because of perceived technical and conceptual difficulties associated with the use of general space-filling potentials in MST, however, most of the numerical applications of MST have been confined to potentials of the muffin-tin (MT) form, i.e., potentials that are bounded by nonoverlapping spheres and that are also spherically symmetric. In spite of the fact that the MT approximation has led to successful applications of the KKR method in many cases,[3] it cannot describe properly a great number of physical systems, e.g., open lattices, 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 often non-negligible. Thus, a proper treatment of such systems within the KKR method requires its extension to non-MT, space-filling cells.

The attempts to extend the MST method to general potentials have generated controversies, and a large body of work[4-34] has been devoted to deciding the question of the applicability of the KKR method to space-filling potential cells. Originally, the question centered on the existence of "near-field corrections," which were additional terms suggested by Ziesche and Faulkner,[7,10] to be added to the MST structure constants in order to correct for the (presumed) fact that for full cell potentials the "scattering by one site does not end before the scattering from a neighboring site begins." Recently, it has become clear that there is no need for these postulated corrections to the structure constants.[16,18-22,24-27,30,34] We refer the reader to the last of these references for the current state of our understanding of full potential MST. It should

also be emphasized that the formal and conceptual foundations of MST for space-filling potentials are of more than academic interest since work is proceeding at several institutions[31,35-37] on full potential electronic-structure calculations based on multiple-scattering theory.

Although the results of Ref. 34 are rigorous and are supported by numerical tests and examples, some questions of a conceptual and intuitive nature remain unanswered. For example, one of the reasons that the need for near-field corrections seemed so plausible was the perception that the single-cell basis functions could not be fully described at all points within the bounding sphere of a cell by the t matrix for that cell. The evidence for this perception was the observation that the usual expression for the basis function (in terms of a sum over angular momentum involving the cell t matrix) which is valid outside the bounding sphere actually diverges for points inside the bounding sphere but outside the potential. We believe it is this observation which led to the idea that near-field corrections are needed. One of the objectives of this paper is to show that (this divergence notwithstanding) the t matrix *does* contain all of the information necessary to describe the basis function at any point outside the cell.

In addition to the controversy over near-field corrections, another controversy has arisen and has sometimes been confused with it. The question has been raised[11,14,32,33] as to whether the method proposed by Williams and Morgan[6] for solving the Schrödinger equation associated with the potential of a single cell is valid. Brown and Ciftan suggested that the method of Williams and Morgan, which requires that the potential be truncated at the cell boundary, leads to wrong or divergent results, and that correct solutions can only be obtained if one includes the potential in the "moon" region of a cell, i.e., outside the cell but inside the (smallest) sphere about a given center bounding the cell.

In addressing this issue from a formal standpoint, Nesbet[22] argued that the two approaches were formally equivalent. Subsequent calculations by Butler and Nesbet[27] for the two-dimensional square lattice showed that the differences between the Brown-Ciftan and Williams-Morgan prescriptions for calculating the basis functions were small and decreased as the convergence of the Williams and Morgan prescription was improved by using more cylindrical harmonics in the calculation of each basis function. Later calculations by Butler, Brown, and Nesbet[29] found a divergence in the Williams-Morgan procedure for the two-dimensional square lattice which only became apparent when extremely large numbers of cylindrical harmonics were used to expand the basis functions.

In this paper we focus on the solution to the Schrödinger equation for a single nonspherical cell. We believe that our results give additional insight into the issue of near-field corrections and resolve the issue of whether one should use truncated or nontruncated potentials. The objectives of this paper are as follows: (1) to show how basis functions for nonspherical potentials can be defined and calculated. Different authors use different definitions for the basis functions and there are subtle differences in their properties and physical significance; (2) to demonstrate that the Williams-Morgan basis functions at points within the scatterer depend only on the value of the potential within the scatterer; (3) to demonstrate that the t matrix for a single scatterer contains all of the information necessary to construct the scattered wave function at all points outside the potential; (4) to show how MST for space-filling potentials can be derived by means of an analytic continuation of the (divergent) expression for the t matrix in the moon regions.

A brief plan of the paper may be helpful to the reader. Section II contains a description of two types of basis functions that are commonly used in full-potential multiple-scattering theory. This section also discusses the calculation of the t matrix for a nonspherical scatterer. Finally, it is shown in this section that for points inside a cell, the basis functions introduced by Williams and Morgan depend only on the potential within that cell. Section III shows how the t matrix can (at least in principle) be used to compute the basis function (or scattered wave function) at all points outside the potential including those within the circumscribing sphere. This section also contains a derivation of full-potential MST in terms of an analytic continuation of the divergent expression for the basis functions in the moon region. In Sec. IV most of the formal results are illustrated with numerical examples calculated for a two-dimensional square cell. In Sec. V we summarize the conclusions and discuss some of their implications.

II. BASIS FUNCTIONS AND WAVE FUNCTIONS FOR NONSPHERICAL POTENTIALS

A. Basis functions and t matrix

In this section, we discuss the solutions of the Schrödinger equation, or (equivalently) the Lippmann-

Schwinger equation, for the case of a single, spatially bounded potential cell. It is important to make a distinction at the outset between *basis* functions and *wave* functions. We shall use the term *basis* function to mean a function which satisfies the Schrödinger equation within a finite region of space containing the origin. A basis function, as we use the term, is the analog for nonspherical scatterers of what is informally called the "radial wave function" in MST for spherical scatterers. A basis function may not be a physically meaningful wave function, but a set of basis functions can be used to expand a wave function as will be shown below. Keeping this distinction between basis functions and wave functions in mind may make some properties of basis functions, such as Nesbet's result that the Williams-Morgan basis functions for points within a cell are independent of the value of the potential for points outside the cell, seem more reasonable.

We also caution the reader who is familiar with other electronic-structure techniques that the basis functions used in MST differ from those used in most other methods in that they are energy dependent and that each basis function is an exact solution to the Schrödinger equation in a local region of space.

Functions that satisfy the Schrödinger equation for a single potential

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

can be obtained from the Lippmann-Schwinger equation

$$\phi_L^n(\mathbf{r}) = J_L(\mathbf{r}) + \int d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}') v_n(\mathbf{r}') \phi_L^n(\mathbf{r}'). \tag{2.2}$$

Here $J_L(\mathbf{r})$ is a solution to the Helmholtz equation which is regular at the origin. It is expressed as a product of a spherical Bessel function and a spherical harmonic $J_L(\mathbf{r}) = j_\ell(\sqrt{E}r)Y_L(\hat{r})$. The subscript L represents both orbital and azimuthal quantum numbers, i.e., $L \equiv (\ell, m)$. We shall also use solutions to the Helmholtz equation which are irregular at the origin, $H_L(\mathbf{r}) = -i\sqrt{E}h_\ell(\sqrt{E}r)Y_L(\hat{r})$. The Green function for the Helmholtz equation can, for example, be represented by the multipolar expansion

$$G_0(\mathbf{r}, \mathbf{r}'; E) = -\frac{e^{i\sqrt{E}|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r} - \mathbf{r}'|}$$

$$= \begin{cases} \sum_L J_L(\mathbf{r})H_L(\mathbf{r}') & \text{for } r' > r \\ \sum_L H_L(\mathbf{r})J_L(\mathbf{r}') & \text{for } r' < r. \end{cases} \tag{2.3}$$

Equation (2.2) is a Fredholm equation of the second kind[39,40] and is known to have a unique solution which can be obtained by iteration,

$$\phi_L^n(\mathbf{r}) = J_L(\mathbf{r}) + \int d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}') v_n(\mathbf{r}') J_L(\mathbf{r}')$$

$$+ \int d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}') v_n(\mathbf{r}') \int d\mathbf{r}'' G_0(\mathbf{r}', \mathbf{r}'') v_n(\mathbf{r}'')$$

$$\times J_L(\mathbf{r}'') + \cdots. \tag{2.4}$$

The conditions under which this series converges have been discussed by Newton.[41] Expanding the Green function G_0 in Eq. (2.2), we have

$$\phi_L^n(\mathbf{r}) = J_L(\mathbf{r}) + \sum_{L'} J_{L'}(\mathbf{r}) \int_r^{R_n} d\mathbf{r}' H_{L'}(\mathbf{r}') v_n(\mathbf{r}') \phi_L^n(\mathbf{r}')$$
$$+ \sum_{L'} H_{L'}(\mathbf{r}) \int_0^r d\mathbf{r}' J_L(\mathbf{r}') v_n(\mathbf{r}') \phi_L^n(\mathbf{r}'), \quad (2.5)$$

where we assume that the potential vanishes for $r > R_n$.

For values of r outside the range of the potential we have

$$\phi_L^n(\mathbf{r})|_{r > R_n}$$

$$= J_L(\mathbf{r}) + \sum_{L'} H_{L'}(\mathbf{r}) \int d\mathbf{r}' J_{L'}(\mathbf{r}') v_n(\mathbf{r}') \phi_L^n(\mathbf{r}'), \quad (2.6)$$

which can be written in terms of the t matrix,

$$\phi_L^n(\mathbf{r})|_{r > R_n} = J_L(\mathbf{r}) + \sum_{L'} H_{L'}(\mathbf{r}) t_{L'L}^n. \quad (2.7)$$

Here the t matrix is given by

$$t_{L'L}^n = \int d\mathbf{r}' J_{L'}(\mathbf{r}') v_n(\mathbf{r}') \phi_L^n(\mathbf{r}') \quad (2.8)$$

which can, by use of the Lippmann-Schwinger equation, be shown to be equivalent to the well-known expression

$$t_{L'L}^n = \int d\mathbf{r} \int d\mathbf{r}' J_{L'}(\mathbf{r}) t^n(\mathbf{r}, \mathbf{r}') J_L(\mathbf{r}') \quad (2.9)$$

where

$$t^n(\mathbf{r}, \mathbf{r}') = v_n(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') + v_n(\mathbf{r}) G_0(\mathbf{r}, \mathbf{r}') v_n(\mathbf{r}')$$
$$+ v_n(\mathbf{r}) \int d\mathbf{r}'' G_0(\mathbf{r}, \mathbf{r}'') v_n(\mathbf{r}'') G_0(\mathbf{r}'', \mathbf{r}') v_n(\mathbf{r}')$$
$$+ \cdots. \quad (2.10)$$

Near the origin, the basis function can be written as a linear combination of regular solid harmonics,

$$\phi_L^n(\mathbf{r})|_{r \to 0} = \sum_{L'} J_{L'}(\mathbf{r}) B_{L'L}^n \quad (2.11)$$

where the coefficients $B_{L'L}^n$ are given by

$$B_{L'L}^n = \delta_{L'L} + \int d\mathbf{r}' H_{L'}(\mathbf{r}') v_n(\mathbf{r}') \phi_L^n(\mathbf{r}'). \quad (2.12)$$

Note that the *basis* functions $\phi_L^n(\mathbf{r})$ are proper *wave* functions for the case of a scattering problem involving a single potential in vacuum at positive energy with a single incident spherical wave of unit amplitude and boundary conditions specifying outgoing scattered waves at large distances.

B. The Williams-Morgan form of the basis functions

The basis functions defined above are closely related to basis functions introduced by Williams and Morgan. The Williams-Morgan basis functions are defined by a

Lippmann-Schwinger equation with a different inhomogeneous term

$$\phi_L^{\mathrm{WM}}(\mathbf{r}) = \sum_{L'} J_{L'}(\mathbf{r}) C_{L'L}^n$$
$$+ \int_\Omega d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}') v_n(\mathbf{r}') \phi_L^{\mathrm{WM}}(\mathbf{r}'), \quad (2.13)$$

where the matrix $C_{L'L}^n$ is determined uniquely by first setting $\phi_L^{\mathrm{WM}}(\mathbf{r}) = J_L(\mathbf{r})$ for $r < r_0$ and then taking the limit $r_0 \to 0$. This implies that $C_{L'L}^n$ is given by

$$C_{L'L}^n = \delta_{L'L} - \int_\Omega d\mathbf{r}' H_{L'}(\mathbf{r}') v_n(\mathbf{r}') \phi_L^{\mathrm{WM}}(\mathbf{r}'). \quad (2.14)$$

In these equations Ω is the volume occupied by the cell. The relation between the basis functions ϕ_L^n and those of Williams and Morgan can be determined by comparing them near the origin where we have

$$\phi_L^{\mathrm{WM}}(\mathbf{r})|_{r \to 0} = J_L(\mathbf{r}),$$
$$\phi_L^n(\mathbf{r})|_{r \to 0} = \sum_{L'} J_{L'}(\mathbf{r}) B_{L'L}^n. \quad (2.15)$$

Generally, we have

$$\phi_L^{\mathrm{WM}}(\mathbf{r}) = \sum_{L'} \phi_{L'}^n(\mathbf{r}) C_{L'L}^n \quad (2.16)$$

and

$$\phi_L^n(\mathbf{r}) = \sum_{L'} \phi_{L'}^{\mathrm{WM}}(\mathbf{r}) B_{L'L}^n. \quad (2.17)$$

The advantage of the Williams-Morgan basis functions is that they can be obtained by integrating a pair of coupled differential equations starting from a simple boundary condition near the origin, $\phi_L^{\mathrm{WM}}(\mathbf{r}) = J_L(\mathbf{r})$. From Eq. (2.13) we have

$$\phi_L^{\mathrm{WM}}(\mathbf{r}) = \sum_{L'} [J_{L'}(\mathbf{r}) c_{L'L}(r) + H_{L'}(\mathbf{r}) s_{L'L}(r)] \quad (2.18)$$

where

$$c_{L'L}(r) = C_{L'L}^n + \int_r^{R_n} d\mathbf{r}' H_{L'}(\mathbf{r}') v_n(\mathbf{r}') \phi_L^{\mathrm{WM}}(\mathbf{r}')$$
$$= \delta_{L'L} - \int_0^r d\mathbf{r}' H_{L'}(\mathbf{r}') v_n(\mathbf{r}') \phi_L^{\mathrm{WM}}(\mathbf{r}') \quad (2.19)$$

and

$$s_{L'L}(r) = \int_0^r d\mathbf{r}' J_{L'}(\mathbf{r}') v_n(\mathbf{r}') \phi_L^{\mathrm{WM}}(\mathbf{r}'). \quad (2.20)$$

The functions ϕ_L^n are sometimes more convenient for formal manipulations while the Williams-Morgan basis functions ϕ_L^{WM}, may be easier to calculate numerically. In contrast to the basis functions ϕ_L^n, the Williams-Morgan basis functions are generally not wave functions since they only satisfy a single boundary condition at the origin.

For the basis functions ϕ_L^n, the boundary conditions are determined by the choice of the irregular functions that are used to expand the Green function. For the

Williams-Morgan basis functions, on the other hand, a choice can be made concerning the irregular functions to be used. If ϕ_L^{WM} were a physical wave function, the irregular function occurring in the Green function would be determined by the boundary condition at $r \to \infty$ or on some bounding surface. However, since no external boundary condition is applied, there is an arbitrariness in the choice of irregular function.

Thus the Williams-Morgan basis functions, for example, can also be obtained starting from Eq. (2.13) but with the Green function expansion (2.3) replaced by

$$G_0(\mathbf{r}, \mathbf{r}'; E) = -\frac{\cos\sqrt{E}|\mathbf{r} - \mathbf{r}'|}{4\pi|\mathbf{r} - \mathbf{r}'|}$$
$$= \begin{cases} \sum_L J_L(\mathbf{r})N_L(\mathbf{r}') & \text{for } r' > r \\ \sum_L N_L(\mathbf{r})J_L(\mathbf{r}') & \text{for } r' < r, \end{cases} \quad (2.21)$$

where $N_L(\mathbf{r}) = \sqrt{E}n_\ell(\sqrt{E}r)Y_L(\mathbf{r})$. In this case Eqs. (2.18)–(2.20), are unchanged except that H_L is replaced by N_L. This latter form is most closely related to the sine and cosine of the phase shift that can be defined for muffin-tin potentials. For muffin-tin potentials, we have, using N_L for the irregular function,

$$c_{L'L}(r) = \delta_{L'L}\left[1 - \int_0^r r^2\sqrt{E}n_\ell(\sqrt{E}r)v_n(r)\phi_\ell^n(r)dr\right]$$
$$= \delta_{L'L}A_\ell(r)\cos\eta_\ell(r) \quad (2.22)$$

and

$$s_{L'L}(r) = \delta_{L'L}\int_0^r r^2 j_\ell(\sqrt{E}r)v_n(r)\phi_\ell^n(r)dr$$
$$= -\delta_{L'L}E^{-1/2}A_\ell(r)\sin\eta_\ell(r). \quad (2.23)$$

Finally, we comment on a point that may have troubled a careful reader. In deriving the second line of Eq. (2.19) we appear to be using a "wrong order Green-function expansion" in the sense that the first term in Eq. (2.18) seems to contain a divergent sum over L', $\sum_{L'} J_{L'}(\mathbf{r})H_{L'}(\mathbf{r}')$ where $r > r'$. The sum in Eq. (2.18) is conditionally convergent. The integral must be performed first. The integral $c_{L'L}(r)$ can be shown by use of Green's theorem to be equivalent to a surface integral,

$$c_{L'L}(r) = -\int_{S_n} d\mathbf{S}\cdot[H_{L'}(\mathbf{r}')\nabla' - \nabla'H_{L'}(\mathbf{r}')]\phi_L^{\text{WM}}(\mathbf{r}'),$$
$$(2.24)$$

where S_n is any surface which encloses a sphere of radius r or cell n, whichever is smaller. Since the surface integral in the above equation can be evaluated on a sphere with any radius greater than r without changing its value, the apparent divergence of the angular momentum expansion can be avoided.

We showed above that the t matrix can be obtained from the basis function $\phi_L^n(\mathbf{r})$ using Eq. (2.8). It can also be obtained from the generalized cosine and sine matrices $C_{L'L}^n$ and $S_{L'L}^n$, which are calculated from the Williams-Morgan basis functions using Eq. (2.14) and

$$S_{L'L}^n = \int d\mathbf{r}' J_{L'}(\mathbf{r}')v_n(\mathbf{r}')\phi_L^{\text{WM}}(\mathbf{r}'). \quad (2.25)$$

Thus, using Eq. (2.16), we have

$$t_{L'L}^n = \sum_{L''} S_{L'L''}^n [C^n]_{L''L}^{-1}. \quad (2.26)$$

Nesbet[42] recently pointed out that the formula

$$t^n = S^n[S^{n\dagger}C^n]^{-1}S^{n\dagger} \quad (2.27)$$

is helpful in calculating the t matrix from the generalized sine and cosine matrix. Calculations by one of us[43] confirmed that this approach is more efficient than use of Eq. (2.26).

C. Independence of Williams-Morgan basis functions within a cell of the potential in the moon region

In Eqs. (2.19) and (2.20) the integrals over $\mathbf{r}'$ will, for sufficiently large values of r, include regions of space which are outside the cell, but within the bounding sphere $r < R_n$. Usually the purpose of calculating the basis functions will be the solution of a multiple-scattering problem involving more than one potential v_n. There has been some controversy[14,15] over whether the correct procedure is to use a v_n which is truncated at the cell boundary as implied in the original work of Williams and Morgan[4,6] or to use the value of the potential that is present in the physical multiple-cell problem as suggested by Brown and Ciftan.[11,14,23,32,33] Note that Brown and Ciftan as well as Williams and Morgan use the *truncated* potential in calculating $C_{L'L}^n$ from Eq. (2.14).

In this subsection, we show, following Nesbet,[22] that the potential in the moon region does not affect the basis functions evaluated at points inside the cell. Consider basis functions $\phi_L^\Omega(\mathbf{r})$ and $\phi_L^S(\mathbf{r})$ which satisfy the Schrödinger equation for potentials V^Ω and V^S, respectively, where V^Ω and V^S coincide inside the cell Ω and where V^Ω vanishes outside the cell. In this subsection we omit the superscript WM, but it should be understood that we are dealing with the Williams-Morgan form of the basis functions. Basis functions for the truncated and nontruncated potentials are given by

$$\phi_L^\Omega(\mathbf{r}) = \chi_L^\Omega(\mathbf{r}) + \int_\Omega d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}')V^\Omega(\mathbf{r}')\phi_L^\Omega(\mathbf{r}') \quad (2.28)$$

and

$$\phi_L^S(\mathbf{r}) = \chi_L^S(\mathbf{r}) + \int_S d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}')V^S(\mathbf{r}')\phi_L^S(\mathbf{r}') \quad (2.29)$$

where χ^Ω and χ^S are solutions of the Helmholtz equation. The subscripts on the integration signs indicate the region of integration in each case.

Subtracting Eq. (2.28) from Eq. (2.29), we obtain the general expression

$$\phi_L^S(\mathbf{r}) - \phi_L^\Omega(\mathbf{r})$$

$$= \chi_L^S(\mathbf{r}) - \chi_L^\Omega(\mathbf{r})$$
$$+ \int_\Omega d\mathbf{r}' G_0(\mathbf{r},\mathbf{r}')V^\Omega(\mathbf{r}') \left[\phi_L^S(\mathbf{r}') - \phi_L^\Omega(\mathbf{r}')\right]$$
$$+ \int_M d\mathbf{r}' G_0(\mathbf{r},\mathbf{r}')V^S(\mathbf{r}')\phi_L^S(\mathbf{r}'). \tag{2.30}$$

Here M indicates the moon region external to the cell but within the sphere. Now, with the vector $\mathbf{r}$ in Ω, we apply the Helmholtz (free-particle) differential operator $\nabla^2 + E$ to both sides of this expression to obtain

$$\left(\nabla^2 + E\right)\left[\phi_L^S(\mathbf{r}) - \phi_L^\Omega(\mathbf{r})\right] = V^\Omega(\mathbf{r})\left[\phi_L^S(\mathbf{r}) - \phi_L^\Omega(\mathbf{r})\right], \tag{2.31}$$

since the χ's are solutions of the homogeneous $(V = 0)$ equation and the last integral vanishes under this operator as the arguments of G_0 lie in different domains. Now, it follows from Eq. (2.31) that the difference function is a regular solution of the Schrödinger equation inside the cell Ω. It is obvious from the procedure by which they are constructed [Eqs. (2.18)–(2.20)], that the Williams-Morgan basis functions calculated with the truncated and nontruncated $v_n(\mathbf{r})$, $\phi_L^\Omega(\mathbf{r})$, and $\phi_L^S(\mathbf{r})$ are identical for points $\mathbf{r}$ within a sphere inscribed inside the cell. However, since $\phi_L^S - \phi_L^\Omega$ is a solution to the Schrödinger equation for all points inside Ω and since it vanishes at all points within the inscribed sphere it follows[38] that it vanishes for all points within Ω. Because of the controversial nature of this result we have performed a numerical test which is described in Sec. IV. Note that the functions ϕ_L^n calculated using the truncated and nontruncated v_n are *not* equal for points within the cell and that Eqs. (2.16) and (2.17) pertain to basis functions $\phi^{\rm WM}$ calculated using truncated potentials.

III. THE SCATTERED WAVE FUNCTION INSIDE THE BOUNDING SPHERE

As mentioned in the preceding section, the basis function $\phi_L^n(\mathbf{r})$ becomes a physical wave function for a scattering problem at positive energy with an incident spherical wave of unit amplitude. For points outside the bounding sphere of the scattering potential, it is clear that the scattered wave function is completely determined by the t matrix. In this section we address the question of whether or not the t matrix is sufficient to determine the wave function in the moon region (outside the potential but inside the bounding sphere).

It could be argued on intuitive, physical grounds that the t matrix should provide a complete description of the scattered wave function everywhere outside a potential cell. However, it is no longer obvious that this is the case when scattering theory is cast in the angular momentum representation because the multipole expansion of the wave function in terms of the t matrix, Eq. (2.7), is only guaranteed to converge *outside* a sphere bounding the cell. If this expression is used at points inside the sphere, the term $\sum_{L'} H_{L'}(\mathbf{r})t_{L'L}$ will generally diverge.

This behavior led some to suspect that the wave function in the moon region surrounding a cell, i.e., outside the cell but inside a bounding sphere, is not described completely in terms of the cell t matrix, and led to the further conjecture that the scattering off of two adjacent, generally shaped cells whose bounding spheres overlap cannot be described in terms of the cell scattering matrices. Instead, according to this conjecture, one should take account of the so-called *near-field corrections*,[7,12,15] arising from the presence of a nonvanishing potential inside the moon region of a given cell.

In this section we show that the wave function in the moon region *is* completely determined by the t matrix. There is a simple, intuitive argument, based on viewing the cell potential as a collection of nonoverlapping spheres, which leads directly to this result.[25] Here we present two additional arguments based, respectively, on a shifted-center and a shifted-cell approach. Both arguments highlight the nature of the problem as one associated with geometry alone, being quite independent of the nature of the potential in the region close to a given cell. The first line of argument, that of the shifted center, is simpler and more intuitive than that of the shifted cell. However, it is less well suited for computations and less general than the shifted-cell approach. For example, it is only valid in the case of convex cells while the shifted-cell argument applies to cells of arbitrary shape.

A. Displaced-center approach: Convex cells

From its derivation, it is clear that Eq. (2.7) is only guaranteed to converge for points $\mathbf{r}$ outside a sphere which bounds the potential, i.e., for $r > R_n$. For a point inside this sphere, such as point P in Fig. 1, it is clear that the restriction $r > r'$ necessary for the convergence of the angular momentum sum in Eq. (2.6) will be violated for some parts of the range of integration. Thus it is not surprising that $\sum_{L'} H_{L'}(\mathbf{r})t_{L'L}$ has been observed in numerical examples to diverge for points $\mathbf{r}$ inside the bounding sphere.

In spite of these difficulties, a convergent expression for the wave function at P in terms of the cell t matrix can be obtained along the following lines. First, we note that the point P which lies *inside* a sphere centered at O,
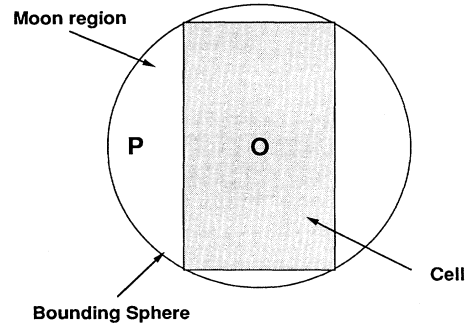

FIG. 1. A nonspherical cell, a bounding sphere circumscribing the cell, and a point P in the moon region.

taken to be the geometric center of the cell shown in Fig. 1, lies *outside* a sphere centered at a point O', displaced from O by a vector $\mathbf{a}$, as is shown in Fig. 2. Denoting the cell t matrix obtained in terms of angular momentum expansions about O' by $t_{L'L}(\mathbf{a})$, we can write the wave function at P in the form

$$\phi_L(\mathbf{r}_0') = J_L(\mathbf{r}_0') + \sum_{L'} H_{L'}(\mathbf{r}_0')t_{L'L}(\mathbf{a}) \qquad (3.1)$$

where $\mathbf{r}_0' = -\mathbf{a} + \mathbf{r}_0$ is the radius vector from the shifted center at O' to P. But, under a displacement of the origin, the spherical Bessel functions transform according to the rule[44]

$$J_L(\mathbf{r} - \mathbf{a}) = \sum_{L'} g_{LL'}(\mathbf{a})J_{L'}(\mathbf{r}) \qquad (3.2)$$

so that the t matrix, which, is defined by Eq. (2.9), transforms under a displacement of the origin of expansion of the Bessel functions according to the relation

$$t_{LL'}(\mathbf{a}) = \sum_{L_1 L_2} g_{LL_1}(\mathbf{a}) \, t_{L_1 L_2} \, g_{L_2 L'}(-\mathbf{a}) \qquad (3.3)$$

where $t_{L_1 L_2}$ is the cell t matrix evaluated about the original center at O, and $g_{LL_1}(\mathbf{a})$ is the matrix of the translation operator in the angular momentum representation, given by

$$g_{LL'}(\mathbf{a}) = 4\pi \sum_{L''} i^{\ell-\ell'+\ell''} J_{L''}(\mathbf{a}) \int d\mathbf{r} Y_L(\mathbf{r})Y_{L'}(\mathbf{r})Y_{L''}(\mathbf{r}).$$

$$(3.4)$$

Now, Eq. (3.1) takes the form

$$\phi_L(\mathbf{r}_0') = J_L(\mathbf{r}_0')$$
$$+ \sum_{L'} H_{L'}(\mathbf{r}_0') \left[\sum_{L_1 L_2} g_{L'L_1}(\mathbf{a})t_{L_1 L_2}g_{L_2 L}(-\mathbf{a}) \right],$$
$$(3.5)$$

which expresses explicitly the wave function at a point inside the moon region of a cell in terms of the cell t ma-
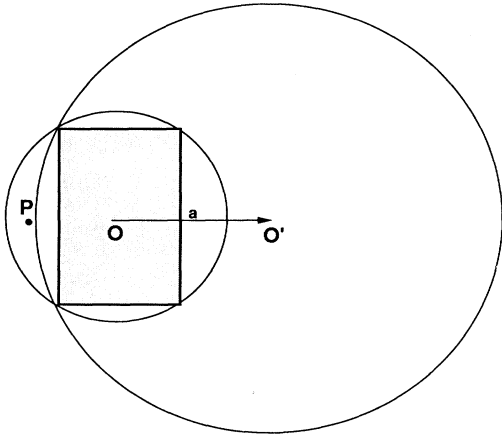

FIG. 2. A point P which lies inside the bounding sphere of a cell centered at O falls outside the bounding sphere centered at O', displaced from O by the vector $\mathbf{a}$.

trix. It is important to realize that the sums inside the brackets in Eq. (3.5) must be performed before those outside in order for the summation to be convergent. Thus the sum over L_1 must precede that over L'. If the order of these two sums is reversed, the resulting expression reduces to Eq. (2.7), which in the present case diverges.

In the construction just described, we can take the point P to lie arbitrarily close to the cell boundary by allowing the vector $\mathbf{a}$ to become very large (essentially approaching infinity as the point moves right against the face of the cell). Therefore, at least formally, the t matrix in the angular momentum representation yields a complete description of the wave function *everywhere* outside a spatially bounded potential cell. We point out that the basic feature characterizing the shifted-center construction just described is the replacement of a *single*, divergent sum, that over L' in Eq. (2.7), by a *double*, conditionally convergent sum, that over L_1 and L' in Eq. (3.5). Note that this replacement is based *purely* on the underlying geometry, i.e., ratios of vectors and the shape of a potential cell, and does not involve the potential in the moon region.

It is clear that the shifted-center argument can only be used with potential cells of convex shape. Also, its numerical implementation becomes increasingly cumbersome as the point P approaches the face of a cell, and the length of the vector $\mathbf{a}$ becomes very large. The method described in the next subsection removes the first limitation and also yields a more convenient expression for computations.

B. Displaced-cell approach

Our starting point is again the Lippmann-Schwinger equation in the form of Eq. (2.2). We seek a convergent, multipole expression of the wave function in the moon region, point P in Fig. 1, in terms of the cell t matrix. Such an expression can be obtained as follows. We note that for all points confined to the moon region adjacent to a face of a convex polyhedral cell there exist vectors $\mathbf{b}$ that satisfy the inequalities

$$|\mathbf{b}| < |\mathbf{r}_0 - \mathbf{r} + \mathbf{b}| \qquad (3.6)$$

and

$$|\mathbf{r}| < |\mathbf{r}_0 + \mathbf{b}| \qquad (3.7)$$

for all vectors $\mathbf{r}$ inside the cell. We can readily establish the existence of these vectors. Any vector $\mathbf{b}$ that is perpendicular to the face of the cell, directed outward, and larger than the largest vertical distance from the bounding sphere to the face satisfies the inequalities above.

We now add and subtract such a vector $\mathbf{b}$ in the argument of G_0 in Eq. (2.2) and use the first inequality above to obtain the expression

$$\phi_L(\mathbf{r}_0) = J_L(\mathbf{r}_0)$$
$$+ \sum_{L'} J_{L'}(\mathbf{b}) \left[\int d\mathbf{r} H_{L'}(\mathbf{r} - \mathbf{r}_0 + \mathbf{b})v(\mathbf{r})\phi_L(\mathbf{r}) \right].$$
$$(3.8)$$

Here the sum and integral *can* be interchanged since $|\mathbf{r} - \mathbf{r_0} + \mathbf{b}| > |\mathbf{r_0}|$. In view of the second inequality above, the Hankel function in the last equation can be further expanded to yield the result

$$\phi_L(\mathbf{r}_0) = J_L(\mathbf{r}_0) + \sum_{L'} J_{L'}(\mathbf{b}) \left[\sum_{L''} G_{L'L''}(\mathbf{r}_0 + \mathbf{b}) \int d\mathbf{r} J_{L''}(\mathbf{r}) v(\mathbf{r}) \phi_L(\mathbf{r}) \right]$$

$$= J_L(\mathbf{r}_0) + \sum_{L'} J_{L'}(\mathbf{b}) \left[\sum_{L''} G_{L'L''}(\mathbf{r}_0 + \mathbf{b}) t_{L''L} \right]. \qquad (3.9)$$

This equation is an expression for the wave function at a point inside the moon region explicitly in terms of the cell t matrix. It should be kept in mind that the brackets in Eq. (3.9) indicate the proper order in which the sums should be performed in order to yield converged results. In particular, the sum over L'', corresponding to the *second* expansion, must be carried out before the sum over L' that arose as a result of the *first* expansion.

There are obvious similarities between Eqs. (3.5) and (3.9). In both a divergent sum has been replaced by a conditionally convergent double sum. Both derivations highlight the geometric nature of the problem. However, the expression in Eq. (3.9) holds two advantages over that in Eq. (3.5). First, it can be generalized to the case of concave cells, as we argue below. Second, it only involves sums over values of L that are not excessively large and vectors of finite, and usually small, length in contrast to the large values of L and the infinite vectors that could occur in Eq. (3.5). The calculations presented in the next section indicate that converged results can be obtained over a broad range of the outside sum L' when the internal sum L_1 is taken to values about twice as large as those of the outer sum L'. Also the value of b for which optimal convergence rates can be expected was found numerically to be of the order of the radius of the circumscribing sphere. The convergence properties of the double sum in Eq. (3.9) have been discussed at length in a previous publication,[45,46] which treated the three-dimensional Poisson equation.

In addition, Eq. (3.9) has a physical interpretation which is distinct from that of Eq. (3.5). The effect of the double expansion in that equation was to shift the position of the cell center. In Eq. (3.9), the points inside the moon region are shifted to positions outside through the addition of the vector $\mathbf{b}$. Then, the wave function is calculated at these shifted positions and brought inside the moon region by means of the outer sum involving $J_L(\mathbf{b})$. Alternatively, we may think of the points in the moon region as being kept in place but with the entire cell being shifted by $-\mathbf{b}$. In contrast to the shifted-center approach of the preceding subsection, during the shifting operations in the present argument, the center of the cell remains fixed with respect to the cell boundary leading to expressions which involve the original cell t matrix.

The shifted-cell approach can be generalized to treat *concave* cells. For parts of the moon region around a concave cell there may be no single vector $\mathbf{b}$ that satisfies the inequalities in (3.6) and (3.7). However, it is possible to replace the single vector $\mathbf{b}$ by a sum of N vectors, $\mathbf{b} = \sum_{\alpha=1}^{N} \mathbf{b}_\alpha$, so chosen that for all α the following inequality holds:

$$|\mathbf{b}_n| < \left| \sum_{\alpha=1}^{n} \mathbf{b}_\alpha - \mathbf{r} + \mathbf{r}_0 \right|. \qquad (3.10)$$

This allows a *series* of consecutive expansions of the type used in Eq. (3.8) by which the point at $\mathbf{r}_0$ is moved outside the bounding sphere or the cell is displaced in the opposite direction in a number of steps rather than in a single step.

C. Derivation of MST equations

One may view Eq. (3.9) as a technique for performing an analytic continuation of Eq. (2.7) (which is only convergent for $r > R_n$) into the moon region ($r < R_n$) corresponding to a particular face of the cell. This approach can be used to derive the secular equations of MST for space-filling cells. We imagine that the space-filling cells are separated by narrow corridors of vanishing potential whose width will ultimately be set to zero. We follow the original approach of Korringa[1] and attempt to match wave functions along the boundaries of the cells. We write the wave function in the corridor surrounding a given cell as the sum of "incoming and outgoing waves" which are regular and irregular at the origin, respectively. If the potentials were confined within nonoverlapping spheres we could write, for example,

$$\psi^n = \sum_L \left[J_L^n + \sum_{L'} H_{L'}^n t_{L'L}^n \right] a_L^n. \qquad (3.11)$$

For full cell potentials, however, the sum over L' in the above equation will generally diverge inside the bounding sphere so that it cannot be used within the narrow corridor of zero potential. We know, however, from the discussion of the preceding subsection that there is an analytic continuation of the second term in this equation such that the outgoing term can be written as

$$\psi^n = \sum_L [J_L^n + \phi_L^{n,\text{out}}] a_L^n, \qquad (3.12)$$

where

$$\phi_L^{n,\text{out}}(\mathbf{r}_n)|_{r_n > R_n} = \sum_{L'} H_{L'}^n(\mathbf{r}_n) t_{L'L}^n. \qquad (3.13)$$

The usual derivation of the MST equations equates the "incoming" wave on site n with the sum of the "outgoing" waves from all of the other sites,

$$\sum_L J_L^n(\mathbf{r}_n) a_L^n = \sum_{n' \neq n, L'} \phi_{L'}^{n',\text{out}}(\mathbf{r}_{n'}) a_{L'}^{n'}. \qquad (3.14)$$

If cells n' and n adjoin then the expansion of $\phi_{L'}^{n',\text{out}}$ using Eq. (3.13) cannot be applied in the zero-potential region separating these cells. The expansion of this function centered at the center of cell n given by Eq. (3.9) does converge, however, provided that the distance between the centers of the cells exceeds the radius of the bounding sphere. This provides exactly the analytic continuation needed to complete the derivation of the MST secular matrix,

$$\phi_{L'}^{n',\text{out}}(\mathbf{r}_{n'}) = \sum_L J_L^n(\mathbf{r}_n) \left[\sum_{L''} G_{LL''}(\mathbf{R}_{nn'}) t_{L''L'}^{n'} \right].$$

(3.15)

This equation when substituted in Eq. (3.14) yields the MST secular equation for space-filling potentials,

$$a_L^n = \sum_{n' \neq n} \sum_{L'L''} G_{LL''}(\mathbf{R}_{nn'}) t_{L''L'}^{n'} a_{L'}^{n'}.$$

(3.16)

It is a simple generalization of Korringa's[1] result and is currently being used by several groups to calculate the electronic structure of solids. We only caution that workers should be careful to converge the internal sum (over L'') for potentials whose bounding spheres overlap significantly. Note that the analytic continuation described by Eq. (3.9) never has to be evaluated in a practical calculation. Its existence is sufficient to allow the above derivation of the KKR secular matrix.

We believe the above to be a rigorous derivation of the full cell MST equations subject to the constraint (which can be easily removed if necessary) that the distance between expansion centers of adjacent cells should exceed the radii of the bounding spheres. We have not proved here, however, that a solution to the MST equations allows us to reconstruct the wave function everywhere in space. Thus, although the basis functions converge or have well-defined analytic continuations, we have not shown that in all cases the wave function, which consists of a sum of these basis functions with coefficients determined by the secular equation $\sum_L \phi_L^n a_L^n$ converges. This convergence *was* shown, however, for the case in which the system potential is analytic (aside from a term proportional to $1/r$) within each of the bounding spheres.[34] Fortunately this case is the one that is important for most physical applications.

IV. NUMERICAL RESULTS

In this section, we provide numerical examples of the formalism presented in the preceding sections by examining explicitly the case of a two-dimensional square cell. In particular, we illustrate by means of explicit calculations (i) that the t matrix suffices to determine completely the basis function everywhere outside a potential cell, even in the moon region; (ii) that the solution of the coupled-channel equations depends critically on the convergence of the internal sums defining the basis function; and (iii) that the values of the cell basis functions evaluated at points inside the cell are independent of the value of the

potential in the moon region around the cell. Before presenting the results of the numerical calculations, we quote a few relevant formulas for the case of scattering theory in two dimensions.[15,27]

A. The two-dimensional square cell

The Green function for the two-dimensional Helmholtz equation is

$$G(\mathbf{r},\mathbf{r}') = \begin{cases} -\dfrac{i}{4} H_0(\kappa|\mathbf{r}-\mathbf{r}'|) & \text{if } E \geq 0 \\ -\dfrac{1}{2\pi} K_0(\kappa|\mathbf{r}-\mathbf{r}'|) & \text{if } E < 0, \end{cases}$$

(4.1)

where $\kappa = \sqrt{|E|}$ and where H_0 is a Bessel function of the third kind and K_0 is a modified Bessel function.[46] The Green function can be expanded in cylindrical harmonics as

$$G(\mathbf{r},\mathbf{r}') = -\frac{1}{2\pi} \sum_{L=-\infty}^{\infty} I_L(\kappa r_<) K_L(\kappa r_>) e^{iL(\theta-\theta')}$$

(4.2)

for $E < 0$. The Green function for $E \geq 0$ may be obtained from the relations[46]

$$I_L(z) = i^{-L} J_L(iz),$$

(4.3)

$$K_L(z) = \frac{\pi}{2} i^{L+1} H_L(iz).$$

(4.4)

Using these Green-function expansions in the equations that determine $\phi_L(\mathbf{r})$, Eqs. (2.18)–(2.20), and omitting in this section the superscript WM, we obtain

$$\phi_L(r) e^{iL\theta} = \sum_{L'=-\infty}^{\infty} [\, I_{L'}(\kappa r) e^{iL'\theta} c_{L'L}(r)$$
$$+ K_{L'}(\kappa r) e^{iL'\theta} s_{L'L}(r)]$$

(4.5)

with the explicit expressions for the elements of the phase function matrices

$$c_{L'L}(r) = \delta_{L'L} + \frac{1}{2\pi} \int_0^r K_{L'}(\kappa r') V_{L-L'}(r') \phi_L(r') r' dr',$$

(4.6)

and

$$s_{L'L}(r) = -\frac{1}{2\pi} \int_0^r I_{L'}(\kappa r') V_{L-L'}(r') \phi_L(r') r' dr' d\theta'.$$

(4.7)

Note that we have used the normalization $\bar{C} = \underline{1}$, the factor $-1/2\pi$ in Eq. (4.2) has been absorbed into $s_{L'L}(r)$, and $V_L(r)$ is defined by

$$V_L(r) = \frac{1}{2\pi} \int_0^{2\pi} d\theta V(r,\theta) e^{iL\theta}.$$

(4.8)

If V is symmetrical about the x axis so that $V(r,-\theta) = V(r,\theta)$, then $V_L(r) = V_{-L}(r)$ and the relations $c_{L'L} = c_{-L'-L}$ and $s_{L'L} = s_{-L'-L}$ hold. In this case the states will be either odd or even with respect to $\theta \rightarrow -\theta$. For even states (symmetric about the x−axis), we have

$$\phi_L(\mathbf{r}) = \sum_{l'=-\infty}^{\infty} [I_{L'}(\kappa r)\cos L'\theta\, c_{L'L}(r) + K_{L'}(\kappa r)\cos L'\theta\, s_{L'L}(r)]$$

$$= \sum_{L'=0}^{\infty} \epsilon_{L'}\cos L'\theta\, I_{L'}(\kappa r)[c_{L'L}(r) + c_{-L'L}(r)] + \sum_{L'=0}^{\infty} \epsilon_{L'}\cos L'\theta\, K_{L'}(\kappa r)[s_{L'L}(r) + s_{-L'L}(r)] \qquad (4.9)$$

where $\epsilon_{L'} = 1$ if $L' \neq 0$ and $\epsilon_0 = 0.5$.

We can define $\tilde{c}_{L'L}(r) = c_{L'L}(r) + c_{-L'L}(r)$ and similarly $\tilde{s}_{L'L}(r) = s_{L'L}(r) + s_{-L'L}(r)$, which allows us to write the equations for calculating basis functions for symmetric states in the form

$$\tilde{c}_{L'L}(r) = \delta_{LL'}$$
$$+ \sum_{L''=0}^{\infty} \epsilon_{L''} \int_0^r r'dr' K_{L'}(\kappa r')$$
$$\times [V_{L''-L'} + V_{L''+L'}]\phi_{L''L}(r'), \qquad (4.10)$$

$$\tilde{s}_{L'L}(r) = -\sum_{L''=0}^{\infty} \epsilon_{L''} \int_0^r r'dr' I_{L'}(\kappa r')$$
$$\times [V_{L''-L'} + V_{L''+L'}]\phi_{L''L}(r'), \qquad (4.11)$$

and

$$\phi_L(\mathbf{r}) = \sum_{L'=0}^{\infty} \epsilon_{L'}\cos L'\theta\, \{\, I_{L'}(\kappa r)\tilde{c}_{L'L}(r)$$
$$+ K_{L'}(\kappa r)\tilde{s}_{L'L}(r)\}. \qquad (4.12)$$

B. Sufficiency of the asymptotic forms of $C_{L'L}$ and $S_{L'L}$

First we illustrate the point made in Sec. III that it is possible to represent the basis function in the moon region using only the asymptotic form of the matrices $C_{L'L}$ and $S_{L'L}$. Figure 3 shows the value of a symmet-
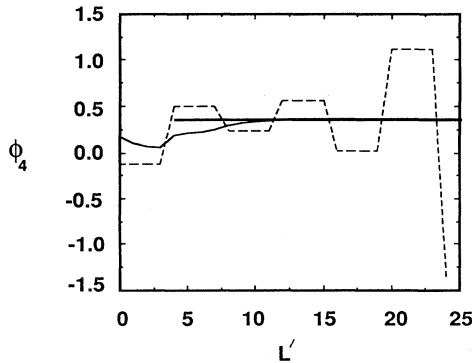

FIG. 3. The basis function $\phi_4(\mathbf{r})$ at the midpoint on the boundary of a square cell as a function of the internal summation index. The thick solid line is the exact result, the dashed line represents the divergent expansion resulting from Eq. (4.13), and the thin solid line represents the convergent double summation of Eq. (4.15).

ric $L = 4$ basis function calculated for a two-dimensional square cell of side equal to π and with a constant potential $V = -5$ Ry. The basis function is evaluated at a point in the moon region, specifically at the center of one of the faces. The thick solid line shows the exact result which in this case is a Bessel function corresponding to a shifted energy $E' = E + 5$. This basis function was also calculated using the single expansion in Eq. (4.12), but with the asymptotic values of the generalized sine and cosine matrices

$$\phi_L(E,\mathbf{r}) = \sum_{L'} [J_{L'}(\mathbf{r})C_{L'L} + H_{L'}(\mathbf{r})S_{L'L}], \qquad (4.13)$$

which is valid *outside* a sphere (here a circle), bounding the cell. The results as a function of the internal summation index L' are shown by the dashed line in the figure. Of the two terms inside the brackets in Eq. (4.13), the first yields a convergent expression *everywhere* outside the cell. This is because the product $\sum_{L'} J_{L'}(\mathbf{r})C_{L'L}$ converges for all values of $\mathbf{r}$, as discussed in Sec. II, Eq. (2.24). However, the second term diverges. This divergence arises because the term containing $S_{L'L}$ is the result of an integral, Eq. (4.11), over cell vectors some of which have magnitudes larger than the argument $\mathbf{r}$ of the Neumann function. Thus the summation over L' in this term includes an incorrect expansion of the free-particle propagator of the form

$$\sum_L J_L(\mathbf{r})H_L(\mathbf{r}') \quad \text{for } r > r', \qquad (4.14)$$

leading to the divergent behavior exhibited in Fig. 3.

The figure also shows the results obtained when the second sum in Eq. (4.13) is replaced by a double expansion of the type indicated in Eq. (3.8). Now, the basis function in the moon region takes the form

$$\phi_L(E,\mathbf{r}) = \sum_{L'} J_{L'}(\mathbf{r})C_{L'L}$$
$$+ \sum_{L'} J_{L'}(\mathbf{b}) \left[\sum_{L''} G_{L'L''}(\mathbf{r}+\mathbf{b})S_{L''L}\right]. \qquad (4.15)$$

Taking $b = 1$ and carrying the sum over L'' to a maximum value of $L''_{\max} = 60$ yields a rapidly converging expansion as L' increases, as is indicated by the thin solid curve.

As mentioned above, it is necessary to carry out the sum over L'' prior to that over L'. If the order of summations is interchanged, one obtains the divergent expansion of Eq. (4.13). If the upper limit on the L' sum approaches $L''_{\max}$ even the double summation in Eq. (4.15) will become an inaccurate representation of the function $\phi_L(E,\mathbf{r})$. We have found numerically that choosing $L''_{\max}$

about twice as large as the largest value of the outer sum over L', coupled with a value of b about the size of the radius of the bounding sphere, usually leads to convergence over a wide range of values of L'.

Clearly, both L''_{max} and the maximum value of L' depend on the value of L that characterizes the basis function. Both must increase sufficiently fast as L increases in order to maintain convergence. Finally, note that the behavior exhibited by the various sums in Eqs. (4.13) and (4.15) has a purely geometric origin, depending only on the lengths of vectors in the argument of the free-particle propagator and not on the details of the potential in the cell. The results shown here illustrate the fact that the asymptotic values of the generalized sine and cosine matrices, and hence of the t matrix, suffice to determine the basis function everywhere outside the boundary of a cell, even inside the moon region.

C. Coupled-channel equations for truncated potentials

In the numerical studies reported here, we consider the solution $\phi_L^\Omega(\mathbf{r})$ of the Schrödinger equation associated with a two-dimensional cell in the shape of a square and having a constant potential $V_0 = -5.0$ Ry. This solution can be found in either of two ways. The first method of solution involves the straightforward application of the formalism presented above, namely the solution of the coupled-channel equations, Eqs. (4.5)–(4.7) or (4.10)–(4.12). In this method, for this example, the potential that enters the coupled channel equations is V_0 everywhere within the square cell and zero outside. We call this the truncated potential. An alternative method, proposed by Brown and Ciftan,[11,14,32,33,23] who believed the first method to be incorrect, consists in using the true crystal potential everywhere inside the sphere which bounds the potential in solving the coupled channel equations. For this example, the Brown-Ciftan approach yields coupled channel equations which are trivial to solve since they correspond to a constant potential.

Our experience with the first method (truncated potentials) indicates that it is a viable procedure, but its successful implementation depends on the convergence of the internal sums in the expression for the basis function, Eq. (4.12). In that expression, one must carry the summation on the right-hand side of the equation to values of L', which in general must exceed the value of the of the basis function index L in order to yield converged results. The magnitude of this internal index depends in general on the value of the outer index L. It is important to note the interplay of these two indices and how it affects the convergence of the basis function. In solving for the basis function $\phi_L^\Omega(\mathbf{r})$, corresponding to a given value of L, one can determine the phase functions $c_{L'L}$ and $s_{L'L}$ through Eqs. (4.10) and (4.11) to arbitrarily high values of L'. As the basis function is not known exactly and is itself being determined through the coupled-channel equations, the values of the phase functions become less and less reliable with increasing L'. This is because the exact evaluation of the phase functions requires the exact value of the basis function, which in turn is given only if these phase

functions are known exactly. Thus one may obtain fairly stable, apparently convergent results as a function of the internal summation index, but as that index approaches its cutoff value (where the phase functions are not very accurately known) the basis function may begin to show signs of instability. This behavior is illustrated in Fig. 4 in connection with the two-dimensional square cell for the basis function corresponding to $L = 0$ and with a cutoff value of the internal sum $L' = 64$.

The figure shows the difference between the calculated and exact basis functions for $L = 0$, $\phi_0^\Omega(\mathbf{r})$, at various distances r from the center of the cell, indicated in the figure, along a ray from the center to a corner of the square. The values $r = 3.145\,38$, $3.475\,25$, and $4.442\,88$ correspond, respectively, to a point on the MT sphere inscribed in the cell, to a point between this sphere and the cell corner, and to the cell corner. In each case the internal summation in the basis function Eq. (4.5) was carried to $L = 64$, and the phase functions $\underline{c}$ and $\underline{s}$ were also determined to that value. As is seen in this figure, $\phi_0^\Omega(\mathbf{r})$ converges with increasing L' for points $\mathbf{r}$ well inside the cell (away from the corner), but at the corner, it can be seen to diverge when L' approaches 64, its cutoff value. Thus, when the basis function used in the determination of the phase functions is also determined by the calculation (as will be the case in all but the simplest model calculations), the coupled-channel equations may yield divergent values for the phase functions and the basis function. The divergences can, however, be pushed farther and farther away from the region of interest by solving these equations for higher and higher values of the internal summation index.

We have verified that the solutions to the coupled-channel equations with truncated potential are finite and correct by substituting the correct solution

$$\phi_L^S(\mathbf{r}) = \left(\frac{\kappa}{\sqrt{E+V_0}}\right)^L J_L(\beta r)e^{iL\theta} \qquad (4.16)$$
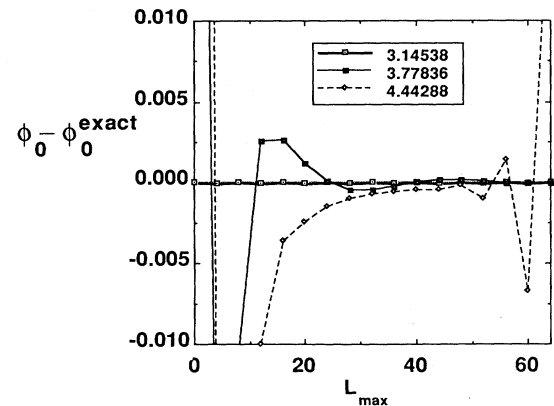
FIG. 4. The difference between the calculated and the exact basis function for $L = 0$ as a function of internal summation index at various points along a ray from the center of a square cell of side equal to π to a corner of the cell. The curves correspond to various distances along this ray as indicated in the legend. The point $r = 3.145\,38$ lies on the MT sphere, while $r = 4.442\,88$ is at the corner.

into the left-hand side of Eqs. (4.6) and (4.7). The correct result is generated on the right-hand side of Eq. (4.5) as the internal limit of the summation on L' is increased. These results indicate that the coupled-channel equations with truncated potential are correct, but must be used with care in cases such as the empty lattice test in which the truncated potential is extremely nonspherical. In other words, these equations are indeed satisfied by the exact basis functions and are not inherently divergent, but the sum over L' in Eq. (4.5) may diverge if the internal summation used to represent $\phi_L(r')$ in Eqs. (4.6) and (4.7) is truncated at too small a value. On the other hand, when these equations are applied to realistic potentials, whose strength is often concentrated inside the MT sphere, reliable results may be obtained even when all expansion variables, even those corresponding to internal summations, are truncated at fairly small values.

D. Independence of basis functions of potential in the moon region

The second approach which can be followed in solving for the cell basis functions is based on the formal results of Sec. II C. We saw there that the basis function for points r inside the cell is independent of the potential in the moon region of the cell and that it coincides there with the basis function for a sphere (circle, in this case), which contains the potential in the moon region. This affords one the possibility of solving first for the basis function of the sphere and then determining the cell phase functions through an additional integration over the moon region; see Eq. (2.30). For the case of the square cell with a constant potential $-V_0$, the obvious choice for the potential in the moon region is also $-V_0$, leading to a spherically symmetric potential inside the sphere (circle) and a straightforward determination of the sphere basis function, Eq. (4.16). In realistic cases the choice of the potential to be used in the moon region may be less obvious.

In the present case, Eq. (4.16) yields an exact expression for the basis function of the sphere and thus for the cell basis function inside the domain of the cell where the two coincide. The fact that these two basis functions ϕ_L^{WM} do indeed coincide over the domain of the cell is illustrated in Figs. 5 and 6 for the case of the square cell. It follows from Eq. (2.30) that inside the domain of a cell Ω the cell basis function differs from that of the sphere by an integral over the moon region, so that we must have $\int_{moon} G_0(\mathbf{r} - \mathbf{r}')V(\mathbf{r}')d^3r' = 0$. For the case at hand, we have explicitly

$$\phi_L^\Omega(\mathbf{r}) = \left(\frac{\kappa}{\beta}\right)^L J_L(\beta r)e^{iL\theta} - \left(\frac{\kappa}{\beta}\right)^L \sum_{L'} e^{iL\theta'} V_0 \int_{moon} \frac{d^2r}{2\pi}\left[K_{L'}(\kappa r')e^{-iL'\theta'}J_L(\beta r')e^{iL\theta'}I_{L'}(\kappa r) \right.$$

$$\left. -I_{L'}(\kappa r')e^{-iL'\theta'}J_L(\beta r')e^{iL\theta'}K_{L'}(\kappa r)\right], \qquad (4.17)$$

where the various functions occurring here have been introduced above. Note that the second term inside the brackets in this expression involves the "wrong order" expansion of the Green function so that if the sum over L' were carried out before the integral were evaluated the sum would diverge [the argument r' in the regular

solution $I_{L'}(\kappa r')$ lies in the moon region and can become larger than the length r of the argument of the irregular function $K_{L'}(\kappa r)$, which lies inside the cell]. However, as argued above, performing the integral first always leads to converged results.

Now, if the functions $\phi_L^\Omega(\mathbf{r})$ and $\phi_L^S(\mathbf{r})$ are to coincide
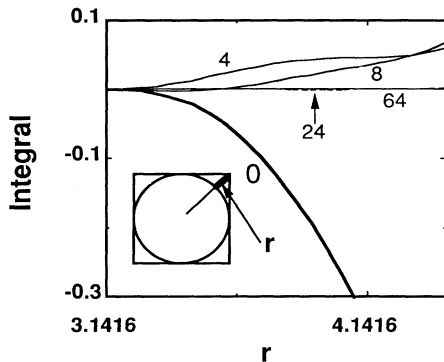

FIG. 5. The integral over the moon region of the cell that represents the difference between the cell and sphere basis functions when the argument of the basis function lies at various positions along a ray from the center of a square cell of side π to the corner of the cell. Note that convergence is essentially complete for $L > 24$, where L is the internal summation index.
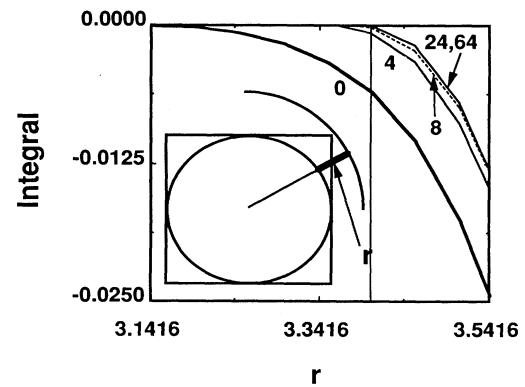

FIG. 6. Results analogous to those of Fig. 5, but along a ray making an angle of $\pi/8$ with the horizontal axis. Note that now the moon region does contribute when the argument of the basis function lies outside the cell, so that the cell basis function and the sphere basis function are no longer identical there.

when r lies in the cell, then the second term on the right-hand side of Eq. (4.17) must vanish. That this is indeed the case is demonstrated in Figs. 5 and 6. These figures show the value of that term as a function of the internal angular momentum summation index, indicated along the curves, and as a function of the length r along two different directions: In Fig. 5, r varies along a line from the MT radius to the corner of the cell, while in Fig. 6 the direction of r makes an angle of $\pi/8$ with the positive x axis, and the vertical line indicates the point where this ray crosses the cell boundary. In both cases, the integral, and hence the difference between the cell and sphere basis functions, approaches zero with increasing L'. We also note that when r lies in the moon region rather than inside the cell, i.e., to the right of the vertical line in Fig. 6, the integral over the moon region no longer vanishes as the two basis functions are no longer identical there.

V. DISCUSSION AND CONCLUSIONS

In this paper, we have examined the formal and computational aspects of the solutions of the Schrödinger equation associated with nonspherical potentials. The main results of our study can be summarized as follows. First, we have shown that the t matrix associated with a spatially bounded but otherwise arbitrarily shaped potential (provided that the t matrix exists) suffices to determine the wave function everywhere outside the cell boundary, and not only outside a sphere circumscribing the cell. Second, we showed that the methods proposed by Williams and Morgan, on one hand, and by Brown and Ciftan, on the other, yield identical results when both are carried to convergence.

The fact that the cell basis functions do not depend on the potential outside the cell has interesting computational implications. For example, it affords one the freedom to place any potential in the moon region of a cell that allows the Schrödinger equation for the entire sphere to be solved more easily than that for the cell alone. We used this feature above to set the wave function inside a cell of constant potential equal to that of a sphere containing the same potential. In that case it was easy to assign a potential to the moon region, i.e., the cell potential itself, that greatly simplified the calculation of the sphere wave function. In realistic cases, the choice of moon potential may be less obvious.

Brown and Ciftan[11,14,32,33] have suggested that the cell potentials to be used in the calculation of electronic structure must be the physical potential contained inside a sphere that is circumscribed around a given cell. In other words, the potential in the moon region of a cell depends on the potentials of the neighboring atoms. They argued

that this procedure provided an exact and convergent treatment of cell scattering, while that of Williams and Morgan was inherently divergent. They supported their conclusions with numerical results based on the empty lattice. The discussion just given allows us to interpret the results of Brown and Ciftan as follows.

Both procedures, that of Williams and Morgan[6] and of Brown and Ciftan,[14] are indeed inherently convergent if all summations are properly carried out, but either may yield divergent results for particular truncations of sums for certain potentials. In fact, the latter may have worse convergence problems than the former if moon potentials contributed by the cells adjacent to a given cell deviate greatly from spherical symmetry. Consider as a first example, a square lattice of square well muffin-tin potentials. In this case, the Williams-Morgan method is trivial and the Brown-Ciftan method would be expected to have convergence difficulties similar to those observed in Sec. IV for the Williams-Morgan method.

Consider as a second example, a checkerboard lattice, with potentials $+U$ and $-U$ distributed in alternate cells of a square lattice. In this case, the straightforward application of the Williams-Morgan procedure requires the solution of the coupled-channel equations for two nonspherical potentials equal to $\pm U$ inside the square cell and zero outside. The Brown-Ciftan procedure requires the solution of these equations for two nonspherical potentials equal to $\pm U$ inside the cell and $\mp U$ outside, respectively. We expect the Williams-Morgan version to be marginally easier to solve. Even better would be to recognize that the potential outside the cell is irrelevant so the basis functions can be trivially solved for constant potentials $\pm U$.

It appears, then, that in realistic calculations one should consider carefully the choice of the potential that should be placed in the moon region of a cell, as a proper choice may greatly reduce computational labor. It is not expected that the potential of nearby cells would always constitute the best choice.

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