Multiple Scattering Theory for Space Filling Potentials

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ABSTRACT

Multiple scattering theory (MST) provides an efficient technique for solving the wave equation for the special case of muffin-tin potentials. Here MST is extended to treat space filling non- muffin tin potentials and its validity, accuracy and efficiency are tested by application of the two dimensional empty lattice test. For this test it is found that the traditional formulation of MST does not converge as the number of partial waves is increased. A simple modification of MST, however, allows this problem to be solved exactly and efficiently.

INTRODUCTION

Multiple Scattering Theory (MST) is a powerful tool for treating problems involving the interaction of waves with matter. When it is applied to the problem of calculating the electronic structure of materials it yields the Korringa Kohn Rostoker band theory technique[1,2] for treating periodic crystals and the Scattered Wave Method[3,4] for treating clusters of atoms. It is the extremely efficient set of basis functions provided by multiple scattering theory and the variational nature of the formalism that are responsible for the rapid convergence and small set of secular equations that characterize these methods. The popular and efficient linear combination of muffin-tin orbitals technique for band structure calculations can be viewed (at its simplest level) as an approximation to MST[5].

Multiple scattering theory is sometimes called the Green function method because it greatly facilitates the calculation of the single particle Green function for the system under consideration. The Green function, which is extremely useful for calculating the effect on the system of a perturbation such as an impurity or an applied field is generated by the inverse of the MST secular matrix. Another important feature of multiple scattering theory is its ability to separate the potential aspect of a problem from the structural aspects. It is this feature together with its facility for generating the Green function that makes MST so suitable for calculating the electronic structure of alloys.

The primary limitation of MST has been its restriction to potentials of muffin-tin form. A muffin-tin potential is one which vanishes outside a set of non-overlapping spheres. Within each muffin-tin, the potential is generally assumed to be spherically symmetrical about the center of the sphere but this restriction is not difficult to remove. The requirement that the potential vanish outside of non-overlapping spherical regions has, however, proven to be very troublesome. If this restriction could be removed, it would be possible to apply MST to problems which are currently of great interest in solid state physics and materials science.

After many false starts and a large amount of work by a number of authors over the past fifteen years, a consensus seems to be emerging that MST is not, in fact, restricted to muffin-tin scatterers and is rigorously correct at least in principle, for space filling potentials. The calculations presented here strengthen this consensus. There are, however, some

subtleties associated with this increased generality which are just now becoming apparent. Fortunately, once these subtleties are understood, they are relatively easy to overcome. We demonstrate here that MST for space filling scatterers works very well indeed for the stringent test of a square lattice of space filling potentials each of which is a step function shaped like a square.

MULTIPLE SCATTERING THEORY

Multiple Scattering theory for space filling scatterers can be derived from scattering theory[6], from an identity in integral equation theory[7], from the Kohn Variational principle[8], from a variational principle applied to the reaction matrix[9], and from wave matching arguments. The last method is perhaps the least rigorous, but in our opinion, the most intuitive. The short derivation sketched below is intended to be applicable to one, two, or three dimensions. Table I shows how the equations derived in this section should be modified for various dimensionalities[10,11]

Table I: Translation Table for One, Two and Three Dimensions

generic symbol	one dimension	two dimensions	three dimensions
$J_\ell(z)$	$\cos(z - \ell\pi/2)$	$J_\ell(z)$	$j_\ell(z)$
$H_\ell(z)$	$i^{-\ell}e^{iz}$	$J_\ell(z) + iN_\ell(z)$	$h_\ell(z)$
$\sum_L$	$\sum_{\ell=0,1}$	$\sum_{\ell=0,\infty}\sum_{m=-1,1}$	$\sum_{\ell=0,\infty}\sum_{m=-\ell,\ell}$
$Y_L(\hat{r})$	$sign(x)^\ell/\sqrt{2}$	$e^{i\ell m\phi}$	$Y_{\ell m}(\theta, \phi)$

In order to derive the basic equations of MST, we imagine that space is divided into cells which surround each atom. Generally we will call that volume or space which is closer to the center of atom n than to any other atom, cell n. The potential inside this cell can be written as $V(\mathbf{r_n})$ where $\mathbf{r_n} = \mathbf{r} - \mathbf{R_n}$ is a vector originating from $\mathbf{R_n}$, the center of cell n. We further imagine that there is a region of infinitesimally small volume surrounding each potential where the potential is constant. We will call this volume region II to distinguish it from the region where the potential is equal to the true crystal potential which we call region I. This is not really an approximation since region II has zero volume. One way to view multiple scattering theory is that it allows one to solve the Schrödinger equation (SE) in a piecewise fashion, finding solutions for one cell (or scatterer) at a time, and then using the superposition principle to fit the pieces together in such a manner that all of the boundary conditions are satisfied.

Within region In the total wave function can be written in terms of functions which satisfy the Schrödinger equation and behave like regular bessel functions at the origin,

$$\Psi_{In}(E,\mathbf{r}) = \sum_L c_L^n(E)R_\ell(E,r_n)Y_L(\hat{r_n}). \tag{1}$$

In the part of region II surrounding atom n the wave function can be expanded in terms of wave functions which satisfy the free electron SE. These are $J_\ell(\kappa r)$ which is a solution of the radial part of the SE for energy $E = \kappa^2$ that is regular at the origin (varying as r^ℓ), and $H_\ell(\kappa r)$ which is a solution that satisfies outgoing wave boundary conditions at large distances.

$$\Psi_{IIn}(E,\mathbf{r}) = \sum_L [a_L^n(E)J_\ell(\kappa r_n) + b_L^n(E)H_\ell(\kappa r_n)]Y_L(\hat{r_n}). \tag{2}$$

It is clear that Eq.(2) cannot be a solution for very large values of r_n because $J_\ell(z)$ does not behave properly at infinity. However, a multi-center expansion based on outgoing waves whcih behave properly at large distances can be valid throughout region II,

$$\Psi_{II}(E, \mathbf{r}) = \sum_n \sum_L b_L^n(E) H_\ell(\kappa r_n) Y_L(\hat{r_n}). \tag{3}$$

The two representations for the wave function in region II, Ψ_{IIn} and Ψ_{II} will agree if (in the vicinity of cell n),

$$\sum_L a_L^n(E) J_\ell(\kappa r_n) Y_L(\hat{r_n}) = \sum_{n' \neq n} \sum_{L'} b_{L'}^{n'}(E) H_{L'}(\kappa r_{n'}) Y_{L'}(\hat{r_{n'}}). \tag{4}$$

This equation provides a means of eliminating the coefficients a_L^n in favor of the coefficients b_L^n. This is facilitated by an addition theorem of the form

$$H_{L'}(\kappa r_{n'}) Y_{L'}(\hat{r_{n'}}) = \sum_L g_{L'L}(E, \mathbf{R}_n - \mathbf{R}_{n'}) J_L(\kappa r_n) Y_L(\hat{r}_n) \tag{5}$$

which can be used in Eq.(4) to obtain

$$a_L^n(E) = \sum_L \sum_{n' \neq n} b_{L'}^{n'}(E) g_{L'L}(E, \mathbf{R}_n - \mathbf{R}_{n'}). \tag{6}$$

In addition we need to ensure that the wave function "inside" potential n, Ψ_{In} matches on smoothly to the potential "outside", Ψ_{IIn}. A necessary condition for this matching is that the following surface integral over the surface of cell n vanish

$$\int_{\Omega_n} dS\hat{n} \cdot [\Psi_{IIn}^* \nabla \Psi_{In} - \nabla \Psi_{IIn}^* \Psi_{In}] = 0. \tag{7}$$

This relation is a straight-forward 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 in order to determine the scattering phase shifts or t-matrix. It can also be derived from a variational principle.

The MST equations are obtained by using Eq.(1) for Ψ_{In} and Eq.(2) for Ψ_{IIn} in Eq.(7) which yields

$$\sum_L \sum_{L'} [-a_L^n C_{LL'}^n + b_L^n S_{LL'}^n] c_{L'}^n = 0 \tag{8}$$

where

$$C_{LL'}^n = -\int_{\Omega_n} dS\hat{n} \cdot [H_\ell(\kappa r_n) Y_L(\hat{r}_n) \nabla(R_\ell(r_n) Y_{L'}(\hat{r}_n)) - \nabla(H_\ell(\kappa r_n) Y_L(\hat{r}_n)) R_{\ell'}(r_n) Y_{L'}(\hat{r}_n)] \tag{9}$$

$$= \delta_{LL'} - \int_{\Omega_n} dv H_\ell(\kappa r_n) Y_L(\hat{r}_n) V(\mathbf{r_n}) R_{\ell'}(r_n) Y_{L'}(\hat{r}_n) \tag{10}$$

and

$$S_{LL'}^n = \int_{\Omega_n} dS\hat{n} \cdot [J_\ell(\kappa r_n) Y_L(\hat{r}_n) \nabla(R_\ell(r_n) Y_{L'}(\hat{r}_n)) - \nabla(J_\ell(\kappa r_n) Y_L(\hat{r}_n)) R_{\ell'}(r_n) Y_{L'}(\hat{r}_n)] \tag{11}$$

$$= \int_{\Omega_n} dv J_\ell(\kappa r_n) Y_L(\ddot{r}_n) V(\mathbf{r_n}) R_{\ell'}(r_n) Y_{L'}(\hat{r}_n). \tag{12}$$

Use of Eq.(6) in Eq.(8) gives the extended MST equations

$$\sum_{L'} \sum_{n'} [\sum_{L''} g_{LL''}^{nn'} S_{L''L'}^{n'} - C_{LL'}^n \delta_{nn'}] c_{L'}^{n'} = 0. \tag{13}$$

We shall see below that although Eq.(5) converges if the ratio $z = r_n/|\mathbf{R_n} - \mathbf{R_{n'}}|$ is less than unity, it may converge very slowly if z is not small enough. For muffin-tin scatterers z can be no larger than $1/2$, the maximum value being obtained for a point at the muffin tin radius of atom n and n' being a touching muffin-tin. For square scatterers z may be as large as $1/\sqrt{2}$. In this case it may be better to avoid the use of the addition theorem (Eq. 5). Its use is not necessary since Eq.(4) is almost as convenient for eliminating the coefficients a_L^n in favor of the coefficients b_L^n. Thus the extended MST equations, Eq.(13) can also be written (in a notation which omits the angular momentum indices) as

$$\sum_{n' \neq n+\delta} [g^{nn'} S^{n'} - \tilde{C}^{nn'} - C^n \delta_{nn'}] c^{n'} = 0 \tag{14}$$

where $n + \delta$ labels the nearest neighbors to cell n and where

$$\tilde{C}_{LL'}^{nn'} = - \int_{\Omega_n} dv \, H_\ell(\kappa r_n') Y_L(\hat{r}_{n'}) V(\mathbf{r_n}) R_{\ell'}(r_n) Y_{L'}(\hat{r}_n). \tag{15}$$

TWO DIMENSIONAL EMPTY LATTICE TEST

Faulkner[11] has pointed out that the two dimensional empty lattice test provides a stringent and effective test of a multiple scattering theory which has been generalized to treat non-muffin tin potentials. In this test the total crystal potential is represented as the sum of "atomic" potentials each of which is shaped like a square (or other space filling polygon) and has depth V_0. Since the total crystal potential is uniform, the exact band structure and wave functions are known trivially. On the other hand MST will be strongly challenged to construct these free electron wave functions from "atomic" states of square atoms.

The formalism of the last section did not describe how the radial wave functions, $R_\ell(\kappa r)$, used to expand Ψ_{In} are obtained. There is, in fact, a small controversy over how they should be calculated. The basic procedure for solving for the wave function in a partial wave basis for a non-spherical scatterer was laid out by Williams and Morgan[12,13] who derived a coupled set of differential equations for the wave function (here generalized for use in d dimensions where $d = 1, 2 \, or \, 3$),

$$\frac{dC_{L'L}(r)}{dr} = r^{d-1} H_{\ell'}(\kappa r) \sum_{L''} V_{L''L'}(r) \phi_{L''L}(r)$$

$$\frac{dS_{L'L}(r)}{dr} = -r^{d-1} J_{\ell'}(\kappa r) \sum_{L''} V_{L''L'}(r) \phi_{L''L}(r)$$

$$\phi_{L'L} = J_{\ell'}(\kappa r) C_{L'L}(r) + H_{\ell'}(\kappa r) S_{L'L}(r)$$

$$V_{L'L}(r) = \int d\hat{r} \, Y_{L'}(\hat{r}) V(\mathbf{r}) Y_L(\hat{r}) / \int d\hat{r}$$

$$R_\ell(r) Y_L(\hat{r}) = \sum_{L'} Y_{L'}(\hat{r}) \phi_{L'L}(r)$$

$$\tag{16}$$

with initial conditions

$$C_{L'L}(0) = \delta_{L'L}$$

$$S_{L'L}(0) = 0 \tag{17}$$

In the original formulation[12] $V(\mathbf{r})$ is a truncated potential that vanishes when $\mathbf{r}$ lies outside the cell at the origin which we denote by Ω_0

$$V(\mathbf{r}) = \left\{ \begin{array}{ll} V(\mathbf{r}) & \text{if } \mathbf{r} \in \Omega_0 \\ 0 & \text{otherwise} \end{array} \right\} \tag{18}$$

Brown and Ciftan[7], however, have suggested that the potential should not be truncated and that the coupled differential equations (Eqs.16) be integrated out to the radius of the bounding sphere using the full untruncated potential $V(r)$, with integrals being performed over the truncated potentials to determine $C_{L'L}$ and $S_{L'L}$ only after the radial wave function has been determined.

$$C_{L'L}^{BC} = \delta_{L'L} - \int_{\Omega_0} H_{\ell'}(\kappa r) Y_{L'}(\hat{r}) V(\mathbf{r}) R_{\ell}(r) Y_L(\hat{r}) d\mathbf{r} \tag{19}$$

and

$$S_{L'L}^{BC} = \int_{\Omega_0} J_{\ell'}(\kappa r) Y_{L'}(\hat{r}) V(\mathbf{r}) R_{\ell}(r) Y_L(\hat{r}) d\mathbf{r}. \tag{20}$$

Recently, Nesbet has shown formally that both procedures should lead to the same wave function within a particular cell *provided* both procedures converge[14].

RESULTS

We have solved the coupled channel equations both ways. Of course, the Brown-Ciftan procedure is trivial in this instance since the total potential is a constant. In general, for physical potentials we expect that the Brown-Ciftan version of the equations(16- 20) will be easier to solve and will converge faster because of the absence of the singular step function. In fact we have found that for the present test case, the Williams-Morgan procedure does not converge. Although the divergence is rather mild and does not become apparent until extremely large numbers of partial waves are included in the calculation, we are confident that the observed divergence is real and not merely a numerical artifact. A detailed study of this problem will be reported elsewhere[15].

The eigenvalues found in the empty lattice test using Eq.(13) and the Brown-Ciftan prescription for the wave function for the second lowest energy level with full square symmetry are given in Table II. The columns correspond to different values of ℓ_{max} which is the number of different radial wave functions used in the calculation. It is traditional in MST to work with square matrices so that the upper limit in the sum on L'' used to multiply the structure constant matrix $g_{LL''}$ by the sine matrix $S_{L''L'}$ would be equal to the upper limits on L and L'. Surprisingly, this procedure does not converge for the two dimensional empty lattice test as can be seen by comparing the first entries in each column of Table II. Non-muffin tin MST only converges for this test if the internal sum on L'' is taken quite high. In fact, the cut-off of this internal sum (ℓ_i^{co}) must be taken higher for higher values of ℓ_{max}, the cut-off used for the outer sums. To obtain an energy within 1% of the exact energy for $\ell_{max} = 12$, for example, it was necessary to use an internal cut-off, ℓ_i^{co}, of 56.

The necessity for the large internal sum cut-off arises from the slow convergence of the expansion of an "outgoing" wave in terms of "incoming" waves centered on an adjacent site (Eq. 5) in situations where the distance from the center of the cell to a corner is a large fraction of the separation between centers. If that expansion is avoided for near neighbors, (Eq.14) the convergence is greatly improved as is shown in Table III.

CONCLUSIONS

Our results are consistent with the following propositions: (1) MST is exact for space filling scatterers. (2) In solving for the wave functions for a single scatterer, abrupt truncation of the potential can lead to convergence problems in the partial wave expansions. A technique which avoids this truncation such as that of Brown and Ciftan is preferable to the original prescription of Williams and Morgan. (3) If the potential is strong in the corner of a space filling cell in two or three dimensions the internal angular momentum sum associated

Table II: Energy calculated using Eq.(13) of the 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 cut-off, ℓ_i^{co}. The exact energy is $E = -1$.

ℓ_i^{co}	ℓ_{max}			
	0	4	8	12
0	-.30614			
4	-.27744	-1.55582		
8	-.27889	-.87705	-2.4058	
12	-.27878	-1.05816	-.78965	-.49045
16	-.27879	-.99265	-1.55215	-.75225
20	-.27879	-1.01194	-.89194	-.64837
24	-.27879	-1.00615	-1.08408	-.7806l

Table III: Energy calculated using Eq.(14) 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 cut-off, 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_i^{co}	ℓ_{max}			
	0	4	8	12
0	-.27302			
4	-.27871	-.99309		
8	-.27879	-1.00671	-.998254	
12	-.27879	-1.00738	-.999752	-.999528
16	-.27879	-1.00744	-.999959	-.999910
20	-.27879	-1.00744	-.999987	-.999984
24	-.27879	-1.00744	-.999990	-.999997

with the expansion of an irregular (H_L) function in terms of regular (J_L) functions centered on an adjacent site will converge slowly and more partial waves must be included in this sum than appear in the secular equation. (4) This difficulty can be avoided by reformulating the MST equations so that the H_L functions are used directly without being re- expanded about neighboring sites.

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