KORRINGA-KOHN-ROSTOKER ELECTRONIC STRUCTURE METHOD FOR SPACE-FILLING CELL POTENTIALS

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ABSTRACT

The multiple scattering theory (MST) method of Korringa, and of Kohn and Rostoker for determining the electronic structure of solids, originally developed in connection with potentials bounded by non-overlapping spheres (muffin-tin (MT) potentials), is generalized to the case of space-filling potential cells of arbitrary shape through the use of a variational formalism. This generalized version of MST retains the separability of structure and potential characteristic of the application of MST to MT potentials. However, in contrast to the MT case, different forms of MST exhibit different convergence rates for the energy and the wave function. Numerical results are presented which illustrate the differing convergence rates of the variational and nonvariatonal forms of MST for space-filling potentials.

INTRODUCTION

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

Much work[4-25] has been devoted to the question of the applicability of the KKR method to space-filling potential cells. In this work, a great deal of attention has was been paid to the issue of "near field corrections", a term used to indicate that MST cannot be applied without modification to potentials with shapes and positions such that their circumscribing spheres overlap. This, in turn, would imply that the separability of structure and potential, so convenient for computations in the case of MT potentials, would be lost with the result that the application of MST to space-filling cells would become a much more arduous undertaking, both conceptually and in practical terms.

In this paper we present a derivation of the secular equation of multiple scattering theory for non-MT potentials within a variational formalism. The existence of a variational form of MST has a number of important implications. First, it is of practical importance, in, for example, the determination of the total energy in charge-self-consistent calculations of the electronic structure. Second, it is of formal importance because it provides a complete justification of the validity of MST in the case of space-filling cells. In addition, the formalism of this paper shows clearly that the problems encountered in generalizing MST to space-filling potentials are primarily geometrical in nature involving the convergence of the angular momentum expansion of the free particle propagator.

This derivation also shows explicitly that MST retains the desirable seperability of potential and structure even in the case of non-MT, space-filling cells. However, in contrast to the case of MT potentials, the variational nature of the eigenvalues of the secular equation determining the band structure is greatly affected by the particular form in which that equation is written. This feature is borne out by numerical calculations whose results are presented in a later section. This feature is new in the sense that in the case of muffin-tin MST all of the various forms of the muffin-tin MST secular equation yield energies that are variational with respect to the wave function.

THE VARIATIONAL PRINCIPLE OF KOHN AND ROSTOKER

The time independent Schrödinger equation,

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

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

$$\psi(\mathbf{r}) = \int d\mathbf{r}' G_0(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}'), \tag{2}$$

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

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

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

$$\Lambda = \int d\mathbf{r}\, \psi^*(\mathbf{r})V(\mathbf{r})\psi(\mathbf{r}) - \int d\mathbf{r} \int d\mathbf{r}' \psi^*(\mathbf{r})V(\mathbf{r})G_0(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}'). \tag{4}$$

This variational principle can be used to obtain a secular equation determining the wave function. Upon using a trial function of the form,

$$\psi = \sum_{j=0}^{n} a_j\phi_j, \tag{5}$$

with a_j a complex coefficient and ϕ_j an element of some basis set, and substituting into Eq. (4) we obtain,

$$\Lambda = \sum_{i,j=0}^{n} a_i^*\Lambda_{ij}a_j, \tag{6}$$

where

$$\begin{aligned} \Lambda_{ij} &= \int \phi_i^*(\mathbf{r})V(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r} \\ &- \int\int \phi_i^*(\mathbf{r})V(\mathbf{r})G_0(\mathbf{r}-\mathbf{r}')V(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r}d\mathbf{r}', \end{aligned} \tag{7}$$

is a Hermitian matrix. The application of the variational principle to Eq. (6),

$$\frac{\delta\Lambda}{\delta a_i} = 0 \quad i = 1,2,...,n, \tag{8}$$

yields the set of homogeneous linear equations,

$$\sum_{j=1}^{n} \Lambda_{ij}a_j = 0, \quad i = 1,2,...,n, \tag{9}$$

which has non-trivial solutions only if its determinant vanishes. This requirement leads to the secular equation,

$$\det |\Lambda_{ij}(E)| = 0, \tag{10}$$

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

There are two important differences between the Kohn-Rostoker variational principle and the more common variational procedure that is usually associated with the names of Rayleigh[26] and Ritz[27], $\delta\Omega[\psi] = 0$, where

$$\Omega = \int d\mathbf{r}\ \psi^*(\mathbf{r})[E - H]\psi(\mathbf{r}). \tag{11}$$

Firstly, the Kohn-Rostoker secular Eq. (10) is not linear in the energy even if the basis functions ϕ_j are energy independent. Thus, since the convenience of a secular equation that is linear in energy is lost from the beginning there is no further loss in convenience if the basis functions are chosen to be energy dependent. The second important difference is that since the Kohn-Rostoker variational functional, $\Lambda[\psi]$, only involves integral operators rather than the differential operator that occurs in the Rayleigh-Ritz procedure, it remains valid in the presence of discontinuities in the basis functions which would lead to singularites in Eq. (11). This makes it possible to choose basis functions that are piecewise combinations of locally exact solutions to the Schrödinger equation.

Thus, although Kohn and Rostoker could have chosen almost any set of functions, ϕ_j, in which to expand their trial wave function, they chose functions which took best advantage of their variational principle. They divided space into cells, approximated the potential within each cell by a muffin-tin potential, and used as basis functions the exact local solutions to the Schrödinger equation (for the muffin- tin potential) within each cell. The use of locally exact solutions has the important benefit of allowing the volume integrals within each cell that occur in Eq. (4) to be reduced by means of Green's theorem to surface integrals which turn out to be trivial to evaluate for muffin-tin potentials. In the following we shall extend their derivation to the case of non-overlapping potentials of general shape.

VARIATIONAL DERIVATION OF MST FOR SPACE-FILLING CELLS

For convenience of exposition we treat the case where the total potential $V(\mathbf{r})$ is confined to a finite region of space. Our final formulae will, however, be applicable to infinite systems as well. We divide this region into non-overlapping, but otherwise arbitrarily shaped cells, denoting by Ω_n the volume occupied by cell n, and by $v_n(\mathbf{r})$ the potential within that cell. Thus Λ will be written as $\Lambda = \sum_n \Lambda^n$ where

$$\Lambda^n = \int_{\Omega_n} d\mathbf{r}\ \psi^*(\mathbf{r})v_n(\mathbf{r})B(\mathbf{r}) \tag{12}$$

and where $B(\mathbf{r})$ is given by the expression

$$B(\mathbf{r}) = \psi(\mathbf{r}) - \int d\mathbf{r}' G_0(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}'). \tag{13}$$

By use of the identities,

$$V(\mathbf{r}')\psi(\mathbf{r}') = (\nabla'^2 + E)\psi(\mathbf{r}') \tag{14}$$

and

$$\psi(\mathbf{r}) = \int d\mathbf{r}'(\nabla'^2 + E)G_0(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}') \tag{15}$$

together with Green's theorem, Eq. (13) can be converted to a surface integral,

$$B(\mathbf{r}) = \int_{S'} dS'\ \hat{n}' \cdot [\nabla' G_0(\mathbf{r},\mathbf{r}') - G_0(\mathbf{r},\mathbf{r}')\nabla']\psi(\mathbf{r}'). \tag{16}$$

Similarly, the identities,

$$(\nabla^2 + E)B(\mathbf{r}) = 0 \tag{17}$$

and

$$\psi^*(\mathbf{r})v_n(\mathbf{r}) = (\nabla^2 + E)\psi^*(\mathbf{r}) \tag{18}$$

can be used with Green's theorem to write Λ^n as

$$\Lambda^n = \int_{S_n} dS\, \hat{n} \cdot [\nabla\psi^*(\mathbf{r}) - \psi^*(\mathbf{r})\nabla]B(\mathbf{r}) \tag{19}$$

$$= \int_{S_n} dS\, \hat{n} \cdot [\nabla\psi^*(\mathbf{r}) - \psi^*(\mathbf{r})\nabla] \times \int_{S'} dS'\, \hat{n}' \cdot [\nabla' G_0(\mathbf{r},\mathbf{r}') - G_0(\mathbf{r},\mathbf{r}')\nabla']\psi(\mathbf{r}') \tag{20}$$

The surface S' may be any surface that encloses the region where $V(\mathbf{r}) \neq 0$, and the surface S_n is the surface enclosing Ω_n, that region of space where $v_n(\mathbf{r})$ is nonzero (Fig. 1).

In order to derive a useful formula for Λ^n, we must separate the integrals in Eq. (20). This can be done by using the Green function expansion,

$$G_0(\mathbf{r},\mathbf{r}') = \sum_L J_L(\mathbf{r}_n)H_L(\mathbf{r}'_n), \quad \text{for } r'_n > r_n \tag{21}$$

where $\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$ is centered about a point in cell n. In order for this expansion to be convergent, it is only necessary that all points on the surface S' be further from the expansion center in cell n than all points on the surface, S_n, of cell n (Fig.1). The choice of these surfaces provides one way of obtaining a valid, convergent expansion of G_0 in terms of intracell vectors in adjacent cells that can be integrated independently over the cell surfaces. Thus Λ^n is given by

$$\Lambda^n = \sum_{L''} \int_{S_n} dS\, \hat{n} \cdot [\nabla\psi^*(\mathbf{r}) - \psi^*(\mathbf{r})\nabla]J_{L''}(\mathbf{r}_n) \times \int_{S'} dS'\, \hat{n}' \cdot [\nabla' H_{L''}(\mathbf{r}'_n) - H_{L''}(\mathbf{r}'_n)\nabla']\psi(\mathbf{r}'), \tag{22}$$

where the sum over L'' could be moved outside the integrals because it is convergent for every value of the integrand.

At this stage it is convenient to employ local sets of basis functions to expand our trial wave function in the form,

$$\psi(\mathbf{r}) = \sum_n \psi_n(\mathbf{r})\Theta_n(\mathbf{r}) = \sum_{nL} A^n_L \phi^n_L(E,\mathbf{r}_n)\Theta_n(\mathbf{r}) \tag{23}$$

where $\Theta_n(\mathbf{r})$ is unity for $\mathbf{r}$ inside cell n and vanishes otherwise, and where $\phi^n_L(E,\mathbf{r}_n)$ is a solution of the Schrödinger equation for energy E, corresponding to the potential in cell n. The functions ϕ_L have the form

$$\phi_L(\mathbf{r}) = \sum_{L'}[J_{L'}(\mathbf{r})C_{L'L}(r) + H_{L'}(\mathbf{r})S_{L'L}(r)] \tag{24}$$

where

$$C_{L'L}(r) = -[H_{L'},\phi_L]_r = -r^2 \int_r d\hat{r}' \cdot [H_{L'}(\mathbf{r}')\nabla'\phi_L(\mathbf{r}') - \nabla' H_{L'}(\mathbf{r}')\phi_L(\mathbf{r}')] \tag{25}$$

and

$$S_{L'L}(r) = [J_{L'},\phi_L]_r = r^2 \int_r d\hat{r}' \cdot [J_{L'}(\mathbf{r}')\nabla'\phi_L(\mathbf{r}') - \nabla' J_{L'}(\mathbf{r}')\phi_L(\mathbf{r}')]. \tag{26}$$

and where $[f,g]$ denotes the Wronskian of the two functions f and g.

Using these local solutions, the integral over S_n becomes

$$I_{S_n} = \sum_L A^{n*}_L \int_{S_n} dS\hat{n} \cdot [\nabla\phi^{n*}_L(\mathbf{r}) - \phi^{n*}_L(\mathbf{r})\nabla]J_{L''}(\mathbf{r}_n). \tag{27}$$

Now, consider the surface integral over S',

$$I_{S'} = \int_{S'} dS'\hat{n}' \cdot [\nabla' H_{L''}(\mathbf{r}'_n) - H_{L''}(\mathbf{r}'_n)\nabla']\psi(\mathbf{r}'). \tag{28}$$

This integral can be written as a sum of surface integrals over the surfaces of each of the cells in the system. Using the expansion in terms of local basis functions, Eq. (24), we have

$$I_{S'} = \sum_{n'L'} A^{n'}_{L'} \int_{S'} dS'\hat{n}' \cdot [\nabla' H_{L''}(\mathbf{r}'_n) - H_{L''}(\mathbf{r}'_n)\nabla']\phi^{n'}_{L'}(\mathbf{r}'_{n'}). \tag{29}$$

At first glance, it might appear that the surface of integration can be *either* S' or any surface bounding cell n', such as the surface $S_{n'}$ of the cell itself because the functions ϕ^{n}_{L} are local functions that satisfy the Schrödinger equation for the cell potential $v_n(\mathbf{r})$. A conceivable reason for this is that, by the use of Green's theorem, the integrals in Eq. (29) can be written as volume integrals

$$\delta_{nn'}\delta_{LL'} - \int_{\Omega_{n'}} dv' H_L(\mathbf{r}'_n) v_{n'}(\mathbf{r}')\phi^{n'}_{L'}(\mathbf{r}'_{n'}) \tag{30}$$

where $\Omega_{n'}$ is the volume contained within surface $S_{n'}$. Clearly this integral is independent of the volume of integration as long as it includes all of the volume in which $v_{n'}$ is nonvanishing. However, the integral over the surface, S', of the large sphere always includes the singularity of the Hankel function, while the integral over the surface of a cell may not. This is true when the Hankel function is expanded about the center of an adjacent cell. Even though the contribution of this singularity is non vanishing, it is still true that the replacement of one surface integral by the other does not affect the expansion for Λ. That this is indeed the case is shown in the appendix.

Thus Λ can be written in the form,

$$\Lambda = \sum_{n} \Lambda^{n} = \sum_{nn'LL'} A^{n*}_{L} \lambda^{nn'}_{LL'} A^{n'}_{L'} \tag{31}$$

where

$$\begin{aligned} \lambda^{nn'}_{LL'} = \sum_{L''} \int_{S_n} & dS\hat{n} \cdot [\nabla \phi^{n*}_{L}(\mathbf{r}_n) - \phi^{n*}_{L}(\mathbf{r}_n)\nabla] J_{L''}(\mathbf{r}_n) \\ \times \int_{S_{n'}} & dS'\hat{n}' \cdot [\nabla' H_{L''}(\mathbf{r}'_n) - H_{L''}(\mathbf{r}'_n)\nabla']\phi^{n'}_{L'}(\mathbf{r}'_{n'}), \end{aligned} \tag{32}$$

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

The generalized KKR equations are obtained by minimizing Eq. (31) with respect to the coefficients A^{n}_{L}, with the result

$$\sum_{n'L'} \lambda^{nn'}_{LL'}(E) A^{n'}_{L'} = 0. \tag{33}$$

The eigenvalues of Eq. (1) are found among those values of E for which the determinant of the Hermitian matrix $\lambda^{nn'}_{LL'}$ vanishes. This matrix is the product of the generalized sine and cosine matrices, $S^{n}_{LL'}$, and $C^{nn'}_{LL'}$, defined by the expressions

$$S^{n}_{LL'}(E) = \int_{S_n} dS\hat{n} \cdot [\nabla J_L(\mathbf{r}_n) - J_L(\mathbf{r}_n)\nabla]\phi^{n}_{L'}(\mathbf{r}_n) \tag{34}$$

and

$$C^{nn'}_{LL'} = \int_{S_{n'}} dS'\hat{n}' \cdot [\nabla' H_L(\mathbf{r}'_n) - H_L(\mathbf{r}'_n)\nabla']\phi^{n'}_{L'}(\mathbf{r}'_{n'}), \tag{35}$$

so that

$$\lambda^{nn'}_{LL'} = \sum_{L''} \tilde{S}^{n}_{LL''} C^{nn'}_{L''L'}. \tag{36}$$

with a tilde denoting the transpose of a matrix. Note that in $C^{nn'}_{LL'}$ the integral extends over the surface of cell $\Omega_{n'}$ but that the Hankel function is expanded about the center of cell Ω_n. We see that $C^{n}_{LL'} = C^{nn}_{LL'}$.

If the shape of the cell is such that the intercell vectors which connect the expansion centers of each cell are larger than all of the intracell vectors between a cell center and its boundary, the generalized cosine matrix, $C^{nn'}_{LL'}$, can be be expanded using the addition theorem[29] for the spherical Hankel functions

$$H_L(\mathbf{r}_n) = \sum_{L'} G_{LL'}(\mathbf{R}_{nn'}) J_{L'}(\mathbf{r}_{n'}), \quad \text{for } R_{nn'} > r'_n, \tag{37}$$

allowing the generalized cosine matrix to be written, for $n \neq n'$, as

$$C^{nn'}_{LL'} = \sum_{L''} G_{LL''}(\mathbf{R}_{nn'}) S^{n'}_{L''L}, \tag{38}$$

where $G_{LL'}(\mathbf{R}_{nm})$ is the real-space structure constant between the centers of the two cells, and is given explicitly by the expression,

$$G_{LL'}(\mathbf{R}) = 4\pi \sum_{L''} i^{\ell-\ell'-\ell''} C\,(LL'L'')\; H_{L''}(\mathbf{R}), \tag{39}$$

with $C(LL'L'')$ being a Gaunt number, (integral of three spherical harmonics). For periodic materials, the Fourier transform of $G_{LL'}(\mathbf{R}_{nn'})$ yields the well-known structure constants of the KKR method. With the use of Eq. (38), the secular equation which determines the allowed energies can be written in the form,

$$\det \left| \tilde{\mathbf{S}}^{n} \mathbf{C}^{n} - \tilde{\mathbf{S}}^{n} \left[\mathbf{G}^{nm} \mathbf{S}^{m} \right] \right| = 0. \tag{40}$$

Here, quantities in bold type denote matrices in L-space, and the brackets indicate that for nearby cells, e.g., nearest neighbors, the product of the structure constants and one of the sine matrices must be caried to convergence before the other sine matrix is multiplied by the resulting product. The last expression shows that the secular equation for MST for space filling, even non-convex but non- overlapping cells has the same form as the secular equation for MT potentials. In particular the separation of structure and potential, i.e., the structure constants and the sine and cosine matrices, that characterizes MST in the MT remains a feature of the non-MT case subject to the constraint mentioned above, namely that the expansion of the generalized cosine matrix Eq. (38) into a structure constant matrix and a sine matrix requires that the distances between expansion centers in different cells exceed the distances between the expansion center for a given cell and all points on its boundary.

Formally, Eq. (40) can be written in a number of equivalent forms which, however, exhibit different convergence characteristics. It is possible, for example, to derive rigorously a version of the MST equations which omits the $\tilde{S}$, i.e.

$$\sum_{n'L'} C^{nn'} A^{n'}_{L'} = 0 \tag{41}$$

but the energies for which this equation is satisfied will not be variational with respect to the wave function as are those obtained from eqs.(33 or 40). The result that some forms of the KKR secular equation are variational while others are not is a new feature which distinguishes non-muffin tin MST from the muffin- tin limit and is due to the conditional convergences associated with non muffin-tin MST and the consequent necessity of converging internal angular momentum sums. The practical consequence of this is that one may not view Eq. (40) or $\lambda^{nn'}_{LL'}$ in Eq. (36) as the products of *square* matrices $\tilde{S}^n$ and $C^{nn'}$.

Table I: Calculated energies and wave function errors for the second and third $k = 0$ states of a square lattice. These calculations employed the variational version of MST, Eq. (31).

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

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NUMERICAL RESULTS

In order to demonstrate the validity of Eq. (40) and the variational nature of the energy for its solutions, we have calculated the energy and the wave function for some of the $\mathbf{k} = 0$ states of a two dimensional square lattice. In this test the individual potentials $v_n(\mathbf{r})$ were taken as a constant V_0 within cell n and zero outside. The cells were squares arranged so as to completely fill the plane. Thus, although the total crystal potential was, V_0, a constant which allowed us to trivially calculate the exact wave function and eigenenergies of the Schrödinger equation, MST was faced with the formidable task of representing these functions using the free space Green function. Details of the the two dimensional "empty lattice test" such as the two dimensional versions of $H_L(\mathbf{r})$, $J_L(\mathbf{r})$, and $G_{LL'}(\mathbf{R})$ can be found in papers by Butler and Nesbet[30] and Faulkner[14]. Note, however, that our conclusions concerning the validity of MST as determined by the empty lattice test differ from those of Faulkner, who obtained extremely poor convergence in angular momentum and was not able to decide whether or not near field corrections are necessary.

Results for the empty lattice test are shown in Table I. The depth of the potential in this example is taken as $V_0 = -9$, and the side of the square is π. The energy is measured in units of l^{-2} where l is the unit length. The maximum angular momentum used in the calculation is denoted by ℓ_{max}, while E_{exact} and E_{calc} denoted the exact and calculated energies and MSWFE denotes the mean square error in the wave function. E_{var} denotes the energy calculated by using the calculated MST wave function in the Rayleigh-Ritz variational expression for the energy. The column denoted by ℓ_{max} shows the maximum value of the orbital angular momentum used in the expansion of the wave function. We emphasize, however, that it is necessary to converge all internal sums if one is to obtain meaningful results in a test such as this. Thus, internal sums were not truncated at ℓ_{max}, but carried to full convergence by means of calculating the quantities $C^{nn'}_{LL'}$ through direct integration for the first two nearest neighbor shells of a given site. Since the state being investigated was a state with full square symmetry, only values of orbital angular momentum evenly divisible by four entered the calculation. The column denoted by E_{calc} contains the energies for which the secular Eq. (40) is satisfied. We also show the ratio of the error in the energy $(E_{calc} - E_{exact})$ to mean square error in the wave function (MSWFE) defined as

$$\int d\mathbf{r}|\psi_{calc}(\mathbf{r}) - \psi_{exact}(\mathbf{r})|^2 / \int d\mathbf{r}|\psi_{exact}|^2, \tag{42}$$

where the calculated value of the wave function, ψ_{calc}, was obtained from Eq. (24) using the coefficients a^n_L obtained form Eq. (33). Finally, we show E_{var}, a variationally refined value of the energy calculated by using the Rayleigh-Ritz variation principle with the calculated wave function,

$$E_{var} = \frac{\int d\mathbf{r}\psi^*_{calc}(\mathbf{r})H\psi_{calc}(\mathbf{r})}{\int d\mathbf{r}|\psi_{calc}(\mathbf{r})|^2} \tag{43}$$

The important point to notice is that the error in the energy is of the same order as the mean square error of the wave function, even though both of these vary over eight orders of magnitude for the different values of ℓ_{max}. Furthermore, it is clear that the variational procedure does not improve the energy over the value obtained from the secular equation itself. These results may be contrasted with similar calculations using the version of the MST equations without the $\tilde{S}$,

Table II: Calculated energies and wave function errors for the second and third $k = 0$ states of a square lattice. The parameters are the same as for the previous table. These calculations employed a non- variational version of MST, Eq. (41).

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

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Eq. (41), which are shown in Table II. The energy for this version improves with increasing ℓ_{max} but not as fast as the mean square error of the wave function. For this version, however, the Rayleigh-Ritz refinement does greatly improve the energy. The wave functions are of comparable accuracy in the two versions of MST.

DISCUSSION

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

It is clear however, that although the considerations of the previous paragraph indicate the conceptual difficulties that must be faced in extending MST to treat full cell potentials they do not constitute a proof of the existence of "near field corrections". The formalism presented above makes it apparent that MST can be applied to space-filling cell potentials provided that care is taken to guarantee the convergence of sums over angular momentum states. In this regard, MST assumes identical forms in the MT and non-MT cases. However, we have also established that the variational properties of MST depend strongly on the particular form of the secular equation. Depending on that form, the eigenvalues of the secular equation may or may not be variational with respect to changes in the wave function. This and other features of non-MT scattering theory will be explored in greater detail in a future publication[28].

APPENDIX

We pointed out above that the replacement of an integral over the surface, S', of the sphere bounding an assembly of scattering cells by an integral over the surface of one of these cells may not be justified because the former includes the singularity of the Hankel function whereas the latter may not. To see that this circumstance does not affect the value of the functional Λ, we calculate and compare the values obtained for the surface integral in the two cases.

We begin by writting Eq. (12) in the form,

$$\Lambda^n = \int_{\Omega_n} d\mathbf{r}\psi^*(\mathbf{r})v_n(\mathbf{r})B^n(\mathbf{r}), \tag{44}$$

where

$$B^n(\mathbf{r}) = \sum_m \int_{S_m} dS'\,\hat{n}'\cdot[\nabla' G_0(\mathbf{r},\mathbf{r}') - G_0(\mathbf{r},\mathbf{r}')\nabla']\psi(\mathbf{r}'). \tag{45}$$

Using the expansion of $\psi(\mathbf{r})$ in terms of basis functions, Eq. (24), we can write

$$B^n(\mathbf{r}) = \sum_{mL'} B^{nm}_{L'}(\mathbf{r})a^m_{L'}, \tag{46}$$

where

$$B^{nm}_{L'}(\mathbf{r}) = \int_{S_m} dS'\hat{n}'\cdot[\nabla' G_0(\mathbf{r},\mathbf{r}') - G_0(\mathbf{r},\mathbf{r}')\nabla']\phi^m_{L'} \tag{47}$$

If cells n and m are neighbors far enough apart the surface S_m can be expanded so that the conditions for the expansion of the free-particle propagator are satisfied. In that case, $B^{nm}_{L'}$ can be written in the form,

$$B^{nm}_{L'}(\mathbf{r}) = -\sum_{L_1} J_{L_1}(\mathbf{r}_n)[H^n_{L_1},\phi^m_{L'}]_{S_m}, \tag{48}$$

where the square brackets denote a Wronskian type surface integral over the surface of cell m of an irregular solid harmonic centered in cell n and a basis function centered in cell m.

It is slightly less obvious but equally true that $B^{nm}_{L'}$ can be written in this form when n and m are the same cell or near neighbors. First consider the case where $m = n$. In this case the surface S_m in Eq. (47) can be expanded to a sphere which circumscribes the cell without changing the value of $B^{nm}_{L'}$. This can be seen by using Green's theorem to convert Eq. (47) into a volume integral,

$$B^{mm}_{L'}(\mathbf{r}) = \phi^m_{L'}(\mathbf{r}) - \int_{\Omega_m} d\mathbf{r}' G_0(\mathbf{r},\mathbf{r}')v_m(\mathbf{r}')\phi^m_{L'}(\mathbf{r}') \tag{49}$$

from which it is clear that Ω_m can be *any* volume which includes cell m, i.e. the region where v_m is non-zero, and therefore S_m can be any surface which encloses cell m. Expanding S_m to a sphere circumscribing cell m allows the use of the Green function expansion to obtain Eq. (48).

When m and n are neighbors we can again expand the surface S_m so that all points on its surface are farther from the expansion center in cell n than all points on the surface S_n, (Fig. 2). In performing this expansion, however, it is necessary to enclose the expansion center in cell n with the result that the value of the surface integral is changed. Let $\tilde{S}_m$ represent the expanded surface and let $\tilde{B}^{nm}_{L'}$ represent the value of the surface integral over the expanded surface. It is clear that

$$\tilde{B}^{nm}_{L'}(\mathbf{r}) = \phi^m_{L'}(\mathbf{r}) - \int d\mathbf{r}' G(\mathbf{r},\mathbf{r}')v_m(\mathbf{r}')\phi^m_{L'}(\mathbf{r}') \tag{50}$$

while

$$B^{nm}_{L'}(\mathbf{r}) = -\int d\mathbf{r}' G(\mathbf{r},\mathbf{r}')v_m(\mathbf{r}')\phi^m_{L'}(\mathbf{r}'). \tag{51}$$

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

$$\tilde{B}^{nm}_{L'}(\mathbf{r}) = -\sum_{L_1} J_{L_1}(\mathbf{r}_n)[H^n_{L_1},\phi^m_{L'}]_{\tilde{S}_m}. \tag{52}$$

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

$$[H^n_{L_1},\phi^m_{L'}]_{\tilde{S}_m} = [H^n_{L_1},\phi^m_{L'}]_{S_m} + [H^n_{L_1},\phi^m_{L'}]_{S^0_n} \tag{53}$$

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

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

$$\phi^m_{L'}(\mathbf{r}) = \sum_{L_2} J^n_{L_2}(\mathbf{r}_n)a^{nm}_{L_2L'}. \tag{54}$$

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

$$[H^n_{L_1}, \phi^m_{L'}]_{S^0_n} = -\alpha^{nm}_{L_2 L'}, \tag{55}$$

and

$$-\sum_{L_2} J^n_{L_2}(\mathbf{r}_n)[H^n_{L_2}, \phi^m_{L'}]_{S^0_n} = \phi^m_{L'}(\mathbf{r}). \tag{56}$$

which is valid so long as $\mathbf{r}$ is inside a sphere inscribed within cell $\boldsymbol{n}$. However, this relation defines a boundary condition for the wave function represented by the above summation and its derivative on the surface of this sphere. This together with the fact that the same wave function satisfies the Helmholtz equation, uniquely determines its values throughout the cell, and in fact throughout the region where $v_m = 0$. Consequently summation(56) gives $\phi^m_{L'}(\mathbf{r})$ everywhere in cell n.

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

$$\tilde{B}^{nm}_{L'}(\mathbf{r}) = -\sum_{L_1} J_{L_1}(\mathbf{r}_n)[H^n_{L_1}, \phi^m_{L'}]_{S_m} + \phi^m_{L'}(\mathbf{r}). \tag{57}$$

which implies (upon comparison with Eqs.(50) to (52)), that B^{nm} can be written in the form,

$$B^{nm}_{L'}(\mathbf{r}) = -\sum_{L_1} J_{L_1}(\mathbf{r}_n)[H^n_{L_1}, \phi^m_{L'}]_{S_m} \tag{58}$$

even if cells n and m are near neighbors. Th value of $\tilde{B}^{nm}_{L'}$ does not change when the surface of integration is expanded from that in Fig. 2 to S' in Fig. 1. Thus, an integral over S' in Eq. (29) can be replaced by an integral over a cell surface in all cases, which justifies Eq. (31).

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REFERENCES

1. J. Korringa, Physica **13**, 392 (1947).
2. W.Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954)
3. V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon Press, New York, 1978)
4. A. R. Williams and J. van W. Morgan, J. Phys. C **7**, 37 (1974).
5. R. G. Brown and M.d Ciftan, Phys. Rev. B **27**, 4564 (1983).
6. W. John, G. Lehmann, and P. Ziesche, Phys. Status Sol. B **53**, 287 (1972).
7. P. Ziesche and G. Lehmann, *Ergebnisse in der Electronentheorie der Metalle* (Akademie-Verlag, Berlin, (1983), p. 151.
8. P. Ziesche, J. Phys. C **7**, 1085 (1974).
9. L. G. Ferreira, A. Agostino, and D. Lida, Phys. Rev. B **14**, 354 (1976).

10. L. Scheire, Physica A **81**, 613 (1975).

11. R. G. Brown and M. Ciftan, Phys. Rev. B **32**, 3454 (1985).

12. E. Badralexe and A. J. Freeman, Phys. Rev. B **36**, 1378 (1987); **36**, 1389 (1987); **36**, 1401 (1987); **38**, 10469 (1988).

13. B. D. Keister, Am. J. Phys. **149**, 162 (1983).

14. J. S. Faulkner, Phys. Rev. B **32**, 1339 (1985); **38**, 1686 (1988).

15. A. Gonis, Phys. Rev. B **33**, 5914 (1986).

16. R. Zeller, J. Phys. C **20**, 2347 (1987).

17. R. Zeller, Phys. Rev. B **38**, 5993 (1988).

18. J. Molenaar, J. Phys. C **21**, 1455 (1988).

19. R. K. Nesbet, Phys. Rev. B **30**, 4230 (1984); **33** , 3027 (1986).

20. R. K. Nesbet, Phys. Rev. B **41**, 4948 (1990).

21. A. Gonis, X.-G. Zhang, and D. M. Nicholson, Phys. Rev. B **38**, 3564 (1988).

22. A. Gonis, X.-G. Zhang, and D. M. Nicholson, Phys. Rev. B **40**, 947 (1989).

23. X.-G. Zhang and A. Gonis, Phys. Rev. B **39**, 10373 (1989).

24. W. H. Butler and R. K. Nesbet, Phys. Rev. **42**, 1518 (1990).

25. Chin-Yu Yeh, A.-B. Chen, D. M. Nicholson, and W. H. Butler, Phys. Rev. B **42**, 10976, (1990)

26. J. W. Strutt (Lord Rayleigh), *Theory of Sound*, Volume I, sec.88, reprinted by Dover Publications, New York, (1945).

27. W. Ritz, J. Reine Angew. Math. **135**, 1 (1908).

28. W. H. Butler, A. Gonis and X.-G. Zhang, to be submitted.

29. M. Danos and L. C. Maximon, J. Math. Phys. bf 6, 766 (1965).

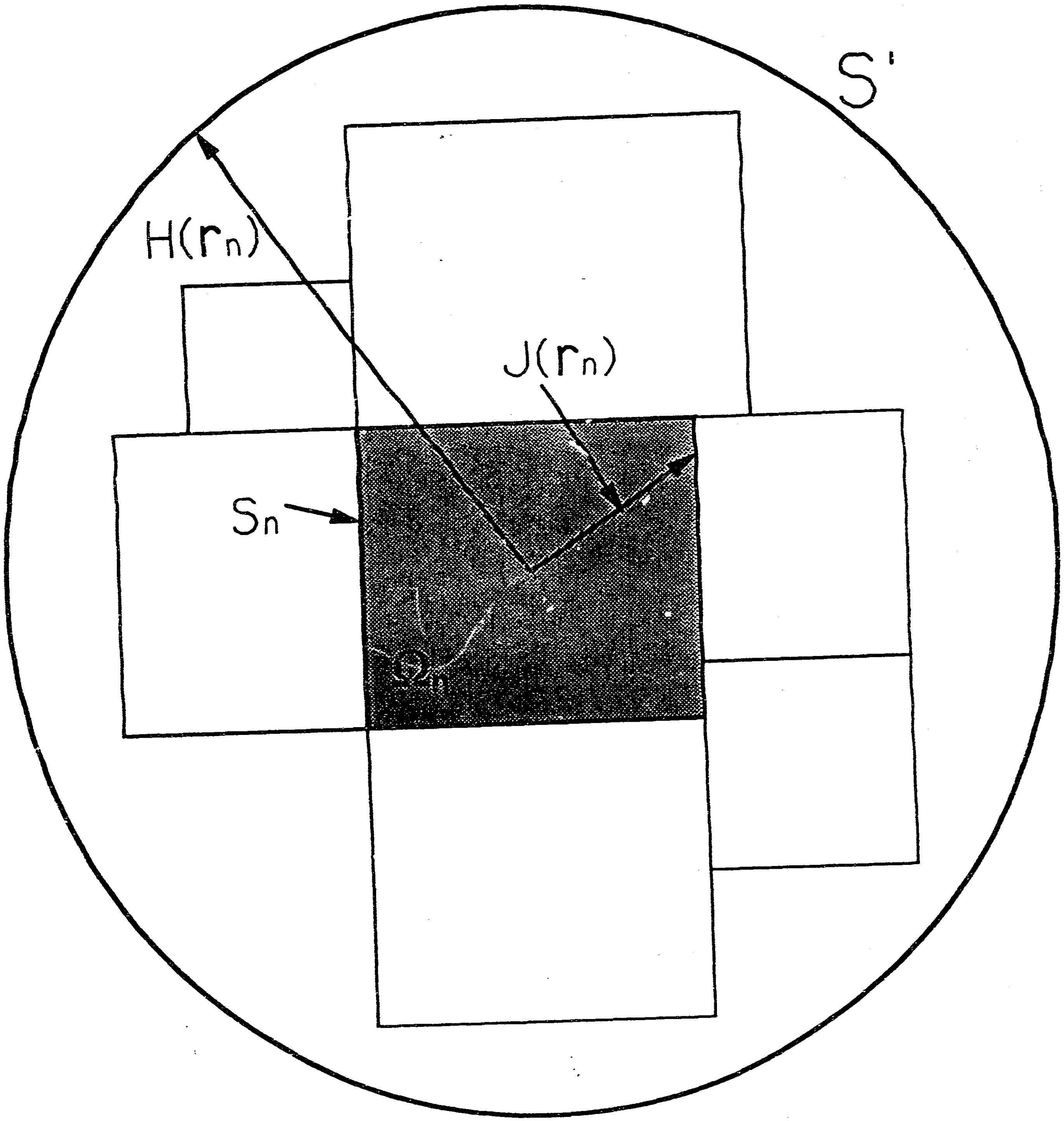
[*] The value and gradient cannot both be *arbitrarily* specified over the entire boundary for then the system will be overdetermined.

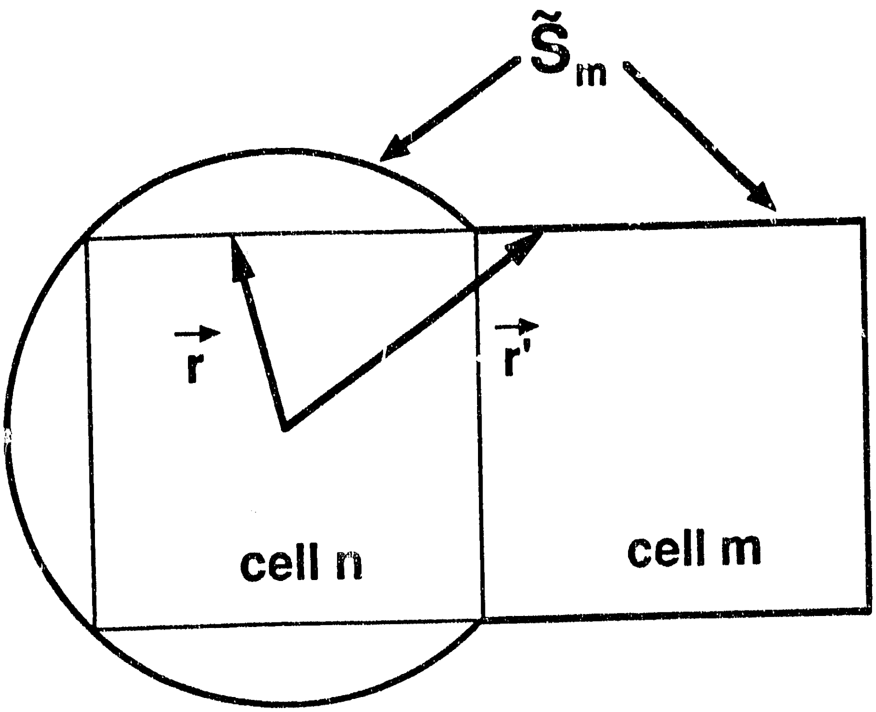
30. W. H. Butler and R. K. Nesbet, Phys. Rev. **42**, 1518 (1990).

Figure Captions

Fig. 1 The surface of integration S' of a sphere bounding a scattering assembly.

Fig. 2 The surface integral over cell m may be expanded to enclose an adjacent cell, n.


S'
H(r_n)
J(r_n)
S_n
Ω_n



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