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Multiple-scattering approach to band theory

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Some new developments in multiple-scattering theory are described in connection with the problem of band theory. Functions that are the logical extension of incoming and outgoing waves are defined for points within the sphere that bounds the range of an atomic scattering potential. Taking these functions into account, a multiple-scattering equation for band theory with general non-muffin-tin potentials is derived. This equation contains terms that were not included in earlier formulations of this problem. A new set of formulas for calculating the scattering from an atomic potential is introduced. It is shown that, among other things, these formulas can be used to derive simplified and linearized band-theory equations entirely within the multiple-scattering framework. Both algebraically and numerically, it is shown that these linearized equations work well. In particular, for the special case of a muffin-tin potential, they will give exactly the same results as a fully converged Korringa-Kohn-Rostoker calculation at any chosen energy. Linearized band-theory equations derived earlier by combining the variational and multiple-scattering approaches are obtained by manipulating the equations from this study.

I. INTRODUCTION

The first use of the mathematical technique known today as multiple-scattering theory to solve a physics problem was reported in 1892 in a paper by Rayleigh.[1] The major early steps in the development of this theory were by Ewald[2] and Kasterin.[3] The theory was first used for the calculation of stationary electronic states by Korringa.[4] It has been developed for many purposes within the area of solid-state physics by Lax,[5] Kohn and Rostoker,[6] Morse,[7] Slater and Johnson,[8] and others.

This paper describes some new developments in this theory. The problem considered is the calculation of the electronic states in an ordered solid, but the methods can clearly be applied to other problems as well.

Section II briefly reviews the multiple-scattering formalism and arrive at the form of the equations that is most useful for the derivations in this paper. In Sec. III, the Korringa-Kohn-Rostoker (KKR) equations are rederived in such a way as to highlight the aspects of these equations to be discussed.

The first completely new results appear in Sec. IV, where certain functions are introduced and it is argued that they can usefully be looked upon as the extension of the incoming and outgoing waves inside of the sphere that bounds the range of the potential. A knowledge of the properties of these functions is very useful in multiple-scattering derivations. In particular, they are used in Sec. V in a derivation of band-theory equations for the case of non-muffin-tin potentials. It is shown that certain terms that involve these functions were left out in previous derivations of these equations.[9,10]

In Sec. VI, a new set of formulas are presented that are very useful for the calculation of the scattering from either a muffin-tin or non-muffin-tin potential. These formulas could usefully be inserted in the standard multiple-scattering equations or they can be used to derive simplified and even linearized versions of these equations.

The recent interest in linearized band-theory expressions has been inspired by the successes of the linearized-muffin-tin-orbital (LMTO) formalism of Andersen.[11] More recently, the linearized-augmented-spherical-wave (LASW) formalism of Williams *et al.*[12] has had similar success. Both of these approaches rely on multiple-scattering theory results, but they also use the Rayleigh-Ritz variational method. In this sense, they can be looked upon as hybrid techniques.

In Sec. VI, I point out that the multiple-scattering equations can be reformulated so that the incoming waves always appear to have the same energy, E_0. From this starting point, using the quantities introduced in the preceding sections and making certain clearly defined approximations, I obtain a set of equations that I call pivoted-multiple-scattering (PMS) equations because all of the calculations necessary for a full band-theory study can be done at one pivotal energy, E_0. It is an easy step to go from the PMS equations to a linearized Korringa-Kohn-Rostoker (LKKR) band theory by expanding them in energy measured relative to an arbitrary origin, E_ν, and ignoring terms of higher order than linear.

The resulting LKKR equations have much in common with the LMTO and LASW equations, but they also have some distinct differences. For example, if a muffin-tin potential is used in the calculations the LKKR equations will lead to exactly the same results as a completely converged KKR calculation for one value of the energy which can be chosen at will. These results are illustrated by a numerical example in which the bands are calculated for a typical transition metal. The way that the calculations can be done for non-muffin-tin potentials is indicated.

In Sec. VIII, I show how the PMS equations can be manipulated into the same form as the LASW and then the LMTO equations. Since the PMS equations are derived entirely on the basis of multiple-scattering theory, a general investigation of the question as to what advantages should accrue from the addition of a variational step is made. It is shown by a numerical example that at least in the areas covered in this paper, the multiple-scattering equations are sufficient.

The various sections in this paper are more or less self-contained, so the reader who is primarily interested in one question might go directly to the relevant section. In my view, however, the arguments in the different sections support each other and should be considered as a whole.

II. MULTIPLE-SCATTERING EQUATIONS

In present-day terminology, the multiple-scattering equations are just another way of writing the Lippmann-Schwigner equation[13]

$$|\psi\rangle = |\chi\rangle + G_0 V |\psi\rangle \,, \tag{2.1}$$

for the special case that the potential may be written as a sum of potentials

$$V = \sum v_n \,. \tag{2.2}$$

The operator G_0 in (2.1) is defined by

$$G_0 = \lim_{\epsilon \to 0} (E + i\epsilon - H_0)^{-1} \,. \tag{2.3}$$

It is useful to recall that the Lippman-Schwinger equation has the property that if $|\chi\rangle$ is a solution of

$$H_0 |\chi\rangle = E |\chi\rangle \,, \tag{2.4}$$

then $|\psi\rangle$ is a solution of

$$(H_0 + V) |\psi\rangle = E |\psi\rangle \,, \tag{2.5}$$

corresponding to exactly the same energy, E.

The Lippmann-Schwinger equation is frequently rewritten in the form

$$|\psi\rangle = |\chi\rangle + G_0 T |\chi\rangle \,, \tag{2.6}$$

by introducing the t matrix

$$T = V(1 + G_0 T) \,. \tag{2.7}$$

For the potential defined in (2.2) it can be shown that this t matrix takes the form

$$T = \sum Q_n \,, \tag{2.8}$$

where

$$Q_n = t_n \Big(1 + G_0 \sum_{m \neq n} Q_m \Big) \,, \tag{2.9}$$

and t_n is the t matrix for scattering from one of the individual potentials

$$t_n = v_n (1 + G_0 t_n) \,. \tag{2.10}$$

Defining an incoming wave $|\psi_n^i\rangle$ by

$$Q_n |\chi\rangle = t_n |\psi_n^i\rangle \,, \tag{2.11}$$

makes it possible to rewrite (2.6) and (2.9) as

$$|\psi\rangle = |\chi\rangle + \sum_n G_0 t_n |\psi_n^i\rangle \,, \tag{2.12}$$

and

$$|\psi_n^i\rangle = |\chi\rangle + \sum_{m \neq n} G_0 t_m |\psi_m^i\rangle \,. \tag{2.13}$$

These have been called the fundamental equations of multiple-scattering theory.[14] They can be used to describe the scattering of a particle by a collection of potentials, but they can also be used to look for stationary states. Korringa[4] was apparently the first to do this. Stationary states occur for the energies at which the t matrix, T is singular because at those energies the scattering equations have nontrivial solutions in the limit that $|\chi\rangle$ approaches zero. Another way to find the energies and wave functions of stationary states is to set

$$|\chi\rangle = 0 \,, \tag{2.14}$$

and look for solutions of the resulting homogeneous equations. This will be done in the following.

It is frequently useful to define an outgoing wave by

$$|\psi_n^o\rangle = G_0 t_n |\psi_n^i\rangle \,, \tag{2.15}$$

and rewrite (2.12) in the equivalent forms

$$|\psi\rangle = \sum_m |\psi_m^o\rangle \,, \tag{2.16}$$

which says that the total solution is the sum of the outgoing waves from all of the scatterers, or

$$|\psi\rangle = |\psi_n^i\rangle + |\psi_n^o\rangle \,, \tag{2.17}$$

the solution is the sum of the incoming and outgoing wave associated with any scatterer n. It should be noted that these solutions are valid for all $\vec{r}$ and not just the region of space in the neighborhood of one scatterer. They are equivalent because according to (2.13) the incoming wave on a given site is the sum of the outgoing waves from all the other sites

$$|\psi_n^i\rangle = \sum_{m\neq n} |\psi_m^0\rangle \,. \tag{2.18}$$

These equations can be given concrete form in the position representation assuming that the potentials v_n are local, $\langle \vec{r}|v_n|\vec{r}'\rangle = v_n(\vec{r})\delta(\vec{r}-\vec{r}')$, and that $v_n(\vec{r})=0$ outside of some bounding sphere of radius S_n. The potential $v_n(\vec{r})$ describes the scattering due to an atom in our applications, and we will assume that the position of the nucleus is at the center of the sphere, $\vec{R}_n$. By the standard methods of scattering theory it can be shown that when $\vec{r}_n = \vec{r} - \vec{R}_n$, and $r_n > S_n$, the solution in the neighborhood of the nth scatterer may be written as the linear combination

$$\psi(E,\vec{r}) = \sum_L \psi_L^n(E,\vec{r}_n) d_L^n \,, \tag{2.19}$$

where

$$\psi_L^n(E,\vec{r}_n) = Y_L(\vec{r}_n) j_l(\alpha r_n) - i\alpha \sum_{L'} Y_{L'}(\vec{r}_n) h_{l'}^{+}(\alpha r_n) T_{L'L}^n(E) \,. \tag{2.20}$$

In this function L stands for the pair of indices l, m, $Y_L(\vec{r})$ is a real spherical harmonic, $j_l(\alpha r)$ and $h_l^{+}(\alpha r)$ are spherical Bessel and Hankel functions, $\alpha=\sqrt{E}$, and $T_{L'L}^n$ are the elements of the t matrix in the angular momentum representation, $\underline{T}^n$, which describe the scattering due to v_n.

The Wigner reaction matrix[15] $\underline{R}^n$ is related to the t matrix

$$\underline{R}^n = \underline{T}^n(\underline{I} - i\alpha\underline{T}^n)^{-1} \,. \tag{2.21}$$

Another function that can be used to expand the solution in the neighborhood of the nth scatterer as in (2.19),

$$\psi(E,\vec{r}) = \sum_L Z_L^n(E,\vec{r}_n) C_L^n \,, \tag{2.22}$$

is

$$Z_L^n(E,\vec{r}_n) = \alpha Y_L(\vec{r}_n) n_l(\alpha r_n) - \sum_{L'} Y_{L'}(\vec{r}_n) j_{l'}(\alpha r_n) X_{L'L}^n \,. \tag{2.23}$$

The quantities that appear in this equation were identified in connection with (2.20) with the exception of the spherical Neumann function $n_l(\alpha r)$, and the matrix $\vec{X}^n$ which is defined as minus the reciprocal of the reaction matrix

$$\underline{X}^n = -(\underline{R}^n)^{-1} \,. \tag{2.24}$$

Using Eq. (2.20) it is easy to show that

$$\psi_L^n(E,\vec{r}_n) = \sum_{L'} Z_{L'}^n(E,\vec{r}_n) T_{L'L}^n \,. \tag{2.25}$$

If follows that the solution, $\psi(E,\vec{r})$, can equally well be expanded according to (2.19) or (2.22) as long as the expansion coefficients are related by

$$C_L^n = \sum_{L'} T_{LL'}^n d_{L'}^n \,. \tag{2.26}$$

From (2.17) and the expansion in (2.19) it follows that the incoming and outgoing waves near the nth scatterer can be identified as

$$\psi_n^i(E,\vec{r}_n) = \sum_L Y_L(\vec{r}_n) j_l(\alpha r_n) d_L^n \,, \tag{2.27}$$

and

$$\psi_n^0(E,\vec{r}_n) = -i\alpha \sum_{L'L} Y_{L'}(\vec{r}_n) h_{l'}^{+}(\alpha r_n) T_{L'L}^n d_L^n \,. \tag{2.28}$$

This is perhaps the most natural way to express the picture of incoming and outgoing waves from the scattering theory point of view, but the equivalence of the expansion in (2.19) and (2.22) has the effect that it is equally proper to write the incoming and outgoing waves as

$$\psi_n^i(E,\vec{r}_n) = -\sum_{L'} Y_{L'}(\vec{r}_n) j_{l'}(\alpha r_n) X_{L'L}^n C_L^n \,, \tag{2.29}$$

and

$$\psi_n^0(E,\vec{r}_n) = \alpha \sum_L Y_L(\vec{r}_n) n_l(\alpha r_n) C_L^n \,. \tag{2.30}$$

This last form is the one that we will use in Secs. III–IX.

III. BAND THEORY FROM MULTIPLE-SCATTERING THEORY

The multiple-scattering equations are particularly easy to solve when all of the potentials $v_n(\vec{r}_n)$ are the same, the scattering centers $\vec{R}_n$ form a Bravais lattice, and the bounding spheres outside of which $v_n(\vec{r})=0$ do not overlap. A simple example of such a lattice is pictured in Fig. 1. This is a reasonable representation of the potential field seen by an electron in a crystal that has one atom per unit cell, and the extension to more than one atom per unit cell is obvious. Inserting the incoming and outgoing waves from (2.29) and (2.30) into (2.18) leads to

$$-\sum_{L',L} Y_{L'}(\vec{r}) j_{L'}(\alpha r) X_{L'L} C_L = \alpha \sum_{n\neq 0}\sum_L Y_L(\vec{r}_n) n_l(\alpha r_n) C_L^n \,, \tag{3.1}$$

where the superscript has been left off of the

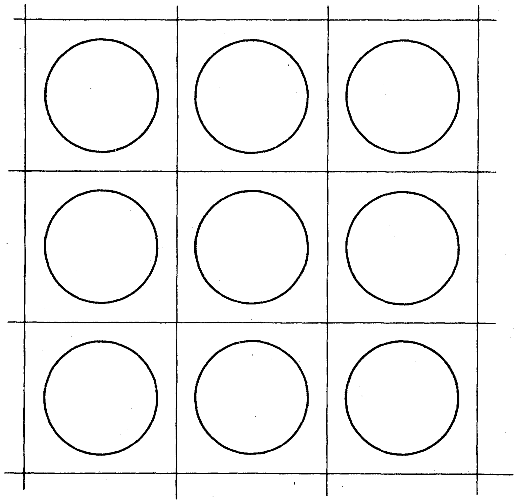

FIG. 1. Illustration of a lattice for which multiple-scattering theory can be applied most easily. There is one atom per unit cell, and the bounding spheres do not overlap.

matrix $\underline{X}$ defined in (2.24) because all of the scatterers are the same. In writing this equation, we have assumed that the point $\vec{r}$ is within the central unit cell but outside the bounding sphere of the potential in that cell. We have also set $C_L^0 = C_L$.

The periodicity of the system can be used to derive Bloch's theorem, which in the language being used here takes the form

$$C_L^n = e^{i\vec{k}\cdot\vec{R}_n} C_L \,. \tag{3.2}$$

Inserting this into the right side of (3.1) leads to an expression of the form $\sum f_L^{\vec{k}}(E,\vec{r})C_L$, where

$$f_L^{\vec{k}}(E,\vec{r}) = \alpha \sum_{n\neq 0} Y_L(\vec{r}_n) n_l(\alpha r_n) e^{i\vec{k}\cdot\vec{R}_n} \,. \tag{3.3}$$

Since the Neumann functions have no singularities except for the points $\vec{R}_n$, the $f_L^{\vec{k}}(E,\vec{r})$ are regular within the central unit cell and it must be possible to expand them in that region in terms of spherical Bessel functions

$$f_L^{\vec{k}}(E,\vec{r}) = \sum_{L'} Y_{L'}(\vec{r}) j_{l'}(\alpha r) B_{L'L}(E,\vec{k}) \,. \tag{3.4}$$

The development of the mathematical expressions for calculating the expansion coefficients $B_{L'L}(E,\vec{k})$ in a numerically efficient way is one of Ewald's major theoretical contributions. These coefficients are called structure constants in band theory, and formulas for them are available in the literature for both one atom per unit cell[16] and several atoms per unit cell.[17]

Inserting (3.4) into (3.1) and equating coefficients of the Bessel functions leads to a set of homogeneous equations for the C_L,

$$\sum_L M_{L'L} C_L = 0 \,, \tag{3.5}$$

where

$$M_{L'L}(E,\vec{k}) = X_{L'L}(E) + B_{L'L}(E,\vec{k}) \,. \tag{3.6}$$

This result was first obtained by Korringa[4] with essentially the same derivation that is used here. In that work, the further assumption was made that the potentials $v_n(\vec{r})$ are spherically symmetric in which case the matrix $X_{L'L}$ becomes diagonal with elements

$$X_{L'L} = \alpha \cot\eta_l \delta_{L'L} \,, \tag{3.7}$$

where η_l are the well-known phase shifts of scattering theory.

The spherically symmetric potentials that lead to (3.7) are usually referred to as muffin-tin potentials. The more general potentials used in deriving (3.6) might be described as anisotropic muffin-tin potentials because their bounding spheres cannot overlap and the potential must be a constant (which we have chosen to be zero) in the interstitial region outside the spheres. The generalization of the band-theory equations to anisotropic muffin-tin potentials is straightforward and has been discussed by other authors.[18]

Equations (3.5) and (3.6) [with the condition (3.7)] are generally referred to as the KKR equations because they were derived independently by Kohn and Rostoker[6] using the Kohn variational technique. In this approach, the function $\psi(E,\vec{r})$ that minimizes the functional

$$\Lambda(\psi) = \int \psi(E,\vec{r})^* V(\vec{r}) F(\vec{r})\, dv \,, \tag{3.8}$$

where

$$F(\vec{r}) = \psi(E,\vec{r}) - \int G_0(E,\vec{r},\vec{r}\,') V(\vec{r}\,') \psi(E,\vec{r}\,')\, dv' \,, \tag{3.9}$$

is sought. In this particular application, the minimization principle plays no role because the derivation is unchanged if one carries out their manipulations to obtain *a* $\psi(E,\vec{r})$ that causes $F(\vec{r})$ to be identically zero. Since this amounts to solving the Lippmann-Schwinger equation (2.1) formulated as an integral equation [with $\chi(\vec{r}) = 0$],

$$\psi(E,\vec{r}) = \int G_0(E,\vec{r},\vec{r}\,') V(\vec{r}\,') \psi(E,\vec{r}\,')\, dv' \,, \tag{3.10}$$

it is not surprising that the results are identical with the ones that arise from the multiple-scattering equations (2.12) and (2.13).

The KKR matrix $\underline{M}$ in (3.5) can be made finite by ignoring contributions that correspond to an angular momentum greater than $l_{\max}$. The dimension of $\underline{M}$ should then be $(2l_{\max}+1)^2$, but there is a standard technique that can be used to reduce it. This is the partitioning technique[19] in which the elements of the matrix $\underline{M}$ that correspond to $l=0, 1, \ldots, l_1$ are used to form a submatrix $\underline{M}_{11}$ and the coefficients C_L corresponding to the same l are written as a column matrix $\underline{C}_1$, while the elements of $\underline{M}$ and the coefficients C_L that correspond to $l = l_1+1,\ l_1+2, \ldots,\ l_{\max}$ are used to form $\underline{M}_{22}$ and $\underline{C}_2$. Using the elements of $\underline{M}$ that couple the small l's to the large ones to form $\underline{M}_{12}$ and $\underline{M}_{21}$, it is easy to see that (3.5) can be rewritten

$$(\underline{M}_{11} - \underline{M}_{12}\underline{M}_{22}^{-1}\underline{M}_{21})\underline{C}_1 = 0\,, \tag{3.11}$$

and

$$\underline{C}_2 = -\underline{M}_{22}^{-1}\underline{M}_{21}\underline{C}_1\,. \tag{3.12}$$

These equations are exact and are simply another way of writing (3.5).

If the scattering is small in the angular momentum channels $l_1 < l \leq l_{\max}$ the corresponding elements of $X_{LL'}$ are much larger than the structure constants $B_{LL'}(E,\vec{k})$. Therefore, a good approximation to (3.11) and (3.12) is

$$(\underline{M}_{11} + \underline{M}_{12}\underline{R}_{22}\underline{M}_{21})\underline{C}_1 = 0\,, \tag{3.13}$$

and

$$\underline{C}_2 = \underline{R}_{22}\underline{M}_{21}\underline{C}_1\,, \tag{3.14}$$

where we have made use of (2.24).

This partitioned form of the KKR equations makes it possible to find eigenvalues that are very well converged in l using matrices of dimension $(2l_1+1)^2$ rather than $(2_{l_{\max}}+1)^2$. A numerical example that illustrates this convergence is shown in Sec. VIII. The coefficients corresponding to $l_1 < l \leq l_{\max}$ can then be found from (3.14).

The wave function can be expressed within the interstitial region using (2.16) and (2.30) as a multicenter expansion

$$\psi_{\vec{k}}(E,\vec{r}) = \alpha \sum_L Y_L(\vec{r}) n_l(\alpha r) C_L(E,\vec{k}) + \alpha \sum_L \sum_{n\neq 0} Y_L(\vec{r}_n) n_l(\alpha r_n) e^{i\vec{k}\cdot\vec{R}_n} C_L(E,\vec{k})\,. \tag{3.15}$$

From (3.3) and (3.4) it can be seen that the second term in this equation can be written as a one-center expansion, so that an alternative form for the expression is

$$\psi_{\vec{k}}(E,\vec{r}) = \alpha \sum_L Y_L(\vec{r}) n_l(\alpha r) C_L(E,\vec{k}) + \sum_{L',L} Y_{L'}(\vec{r}) j_{l'}(\alpha r) B_{L'L}(E,\vec{k}) C_L(E,\vec{k})\,. \tag{3.16}$$

The sums over L in these last two equations correspond to $0 \leq l \leq l_{\max}$, but there is no limit on the sum over L' in (3.16). Thus, starting from a KKR matrix of dimension $(2l_1+1)^2$ we have seen how to obtain eigenvalues that are converged as well as if we had included l's up to $l_{\max}$, and wave functions corresponding to arbitrarily large values of l.

IV. WHAT'S INSIDE THE BOUNDING SPHERES?

In the derivation in Sec. III, we focused our attention on the interstitial region outside the bounding spheres where the potential function can be taken to be zero. This is the normal approach in multiple-scattering theory because it is in this region that the incoming and outgoing solutions correspond to our intuitive picture. It is shown in this section that there are practical advantages in constructing solutions inside of the bounding spheres that are the logical extensions of the incoming and outgoing waves. To do this, I consider solutions of the differential equation

$$(-\nabla^2 + v(\vec{r}) - E)\psi(E,\vec{r}) = 0\,, \tag{4.1}$$

in the central unit cell where $v(\vec{r})$ is a single anisotropic muffin-tin potential.

The solutions of (4.1) that I want to introduce are generalizations of solutions that were used by Jost[20] in his fundamental studies on scattering theory. By direct substitution it can be seen that the function $\phi_{L_0}(E,\vec{r})$ that satisfies the integral equation

$$\phi_{L_0}(E,\vec{r}) = Y_{L_0}(\vec{r}) j_{l_0}(\alpha r) + \int \tilde{G}(E,\vec{r},\vec{r}\,') v(\vec{r}\,') \phi_{L_0}(E,\vec{r}\,')\, dv'\,, \quad |\vec{r}\,'| \leq |\vec{r}|\,, \tag{4.2}$$

is a solution of (4.1) if

$$\tilde{G}(E,\vec{r},\vec{r}\,') = -\alpha \sum_L Y_L(\vec{r})[j_l(\alpha r) n_l(\alpha r') - n_l(\alpha r) j_l(\alpha r')] Y_L(\vec{r}\,')\,, \tag{4.3}$$

and the integration is over a region bounded by a sphere of radius r. Real spherical harmonics $Y_L(\vec{r})$ are used in (4.3). It can similarly be seen that the functions

$$f_{L_1}^{\pm}(E,\vec{r}) = Y_{L_1}(\vec{r}) h_{l_1}^{\pm}(\alpha r) - \int \tilde{G}(E,\vec{r},\vec{r}\,') v(\vec{r}\,') f_{L_1}^{\pm}(E,\vec{r}\,')\, dv'\,, \quad |\vec{r}\,'| \geq |\vec{r}|\,, \tag{4.4}$$

are solutions of (4.1) when the integration is over all space except for the spherical region described above.

The function $\phi_{L_0}(E,\vec{r})$ approaches $Y_{L_0}(\vec{r})j_{l_0}(\alpha r)$ in the limit as r approaches zero, and hence $\phi_{L_0}(E,\vec{r})$ is regular at the origin. The angular momentum subscript L_0 refers to this asymptotic behavior. In general, the function could be written

$$\phi_{L_0}(E,\vec{r})=\sum_{L} Y_L(\vec{r})\phi_{LL_0}(E,r)\,. \tag{4.5}$$

The functions $f^{\pm}_{L_1}(E,\vec{r})$ become equal to $Y_{L_1}(\vec{r})\times h^{\pm}_{l_1}(\alpha r)$ as soon as r becomes greater than S, the radius of the bounding sphere. They will contain many angular momentum components when $r<S$, and they will be singular at the origin except for special values of the energy E.

The usefulness of the functions $\phi_{L_0}(E,\vec{r})$ and $f^{\pm}_{L_1}(E,\vec{r})$ stems from the fact that the integral equations that they satisfy, (4.2) and (4.4), are of the Volterra form, whereas the Lippmann-Schwinger equation (2.1) leads to an integral equation of the Fredholm form[21] (3.10). The existence and properties of these solutions of the Volterra equations is manifest, whereas the Fredholm equation is more difficult to deal with mathematically. A useful technique for studying the solution of the more complicated equation is to relate them to the solutions of the simpler one. It was for this purpose that Jost introduced functions similar to $\phi_{L_0}(E,\vec{r})$ and $f^{\pm}_{L_1}(E,\vec{r})$ for the special case of spherically symmetric potentials.[20]

The functions $f^{\pm}_{L_1}(E,\vec{r})$ are linearly independent solutions of (4.1) and hence it is possible to write any solution as a linear combination of them, in particular

$$\phi_{L_0}(E,\vec{r})=\frac{1}{2}\sum_{L_1}[f^{+}_{L_1}(E,\vec{r})a_{L_1L_0}(E)+f^{-}_{L_1}(E,\vec{r})b_{L_1L_0}(E)]\,. \tag{4.6}$$

Convenient expressions for calculating the coefficients $a_{L_1L_0}$ and $b_{L_1L_0}$ are discussed in Sec. V, but it can be shown for the special case of spherically symmetric potential that

$$a_{L_1L_0}(E)=\mathcal{L}^{-}_{l_1}(\alpha)\delta_{L_1L_0},\quad b_{L_1L_0}(E)=\mathcal{L}^{+}_{l_1}(\alpha)\delta_{L_1L_0}\,,$$

where $\mathcal{L}^{\pm}_{l_1}(\alpha)$ are the well-known Jost functions[22] of scattering theory.

The coefficients $a_{L_1L_0}(E)$ and $b_{L_1L_0}(E)$ may be looked on as elements of matrices $\underline{a}$ and $\underline{b}$. If $b^{-1}_{LL'}$ is an element of the inverse of $\underline{b}$, then the function

$$\psi^{+}_{L}(E,r)=\sum_{L_0}\phi_{L_0}(E,\vec{r})b^{-1}_{L_0L}\,, \tag{4.7}$$

may be written

$$\psi^{+}_{L}(E,\vec{r})=\tfrac{1}{2}[f^{-}_{L}(E,\vec{r})+\sum_{L'}f^{+}_{L'}(E,\vec{r})S_{L'L}(E)]\,, \tag{4.8}$$

where the matrix whose elements are $S_{L'L}(E)$ is

$$\underline{S}=\underline{ab}^{-1}\,. \tag{4.9}$$

Defining a matrix T by

$$\underline{T}=(i/2\alpha)(\mathrm{S}-\mathrm{I})\,, \tag{4.10}$$

and a function $J_L(E,\vec{r})$ by

$$J_L(E,\vec{r})=\tfrac{1}{2}[f^{+}_{L}(E,\vec{r})+f^{-}_{L}(E,\vec{r})]\,, \tag{4.11}$$

we can write

$$\psi^{+}_{L}(E,\vec{r})=J_L(E,\vec{r})-i\alpha\sum_{L'}f^{+}_{L'}(E,\vec{r})T_{L'L}(E)\,. \tag{4.12}$$

Clearly, $J_L(E,\vec{r})=Y_L(\vec{r})j_l(\alpha r)$ when $\vec{r}$ is outside the bounding sphere. Comparing (4.12) for such $\vec{r}$ with (2.20), it can be seen that the matrix T is the on-the-energy-shell t matrix that was introduced in Sec. II. Similar arguments show that S is the s matrix that can be used in an alternative description of the scattering.

The interesting point about (4.12) is that the coefficients that must be used to couple the solution $J_L(E,\vec{r})$ and $f^{+}_{L}(E,\vec{r})$ to obtain the physically acceptable solution $\psi^{+}_{L}(E,\vec{r})$ are just the elements of the t matrix that are normally only used in connection with coupling the incoming and outgoing waves in the asymptotic region. This fact, coupled with their asymptotic behavior leads me to claim that $J_L(E,\vec{r})$ is the logical extension of the incoming wave into the region inside the bounding sphere, and $f^{+}_{L}(E,\vec{r})$ is the extension of the outgoing wave.

From the point of view of the person who is primarily interested in solving differential equations, what is accomplished by scattering theory is to produce a set of coefficients such that two functions that are singular at the origin [f^{+}_{L} and f^{-}_{L} in (4.6) or J_L and f^{+}_{L} in (4.12)] can be combined to obtain a function that is regular at the origin.

In the same manner as in (2.23) we can introduce the solution

$$Z_L(E,\vec{r})=\alpha N_L(E,\vec{r})-\sum J_{L'}(E,\vec{r})X_{L'L}(E)\,, \tag{4.13}$$

where the matrix X is the negative of the inverse of the Wigner reaction matrix R defined in (2.21). The function $N_L(E,\vec{r})$ is defined by

$$N_L(E,\vec{r})=(1/2i)[f^{+}_{L}(E,\vec{r})-f^{-}_{L}(E,\vec{r})]\,, \tag{4.14}$$

and it becomes $Y_L(\vec{r})n_l(\alpha r)$. This is clearly the extension of the function defined in (2.23) to values of $\vec{r}$ that fall within the bounding sphere, and the relation in (2.22) is now true for all $\vec{r}$. The extension of the incoming wave is $-\sum J_{L'}(E,\vec{r})X_{L'L}(E)$

and of the outgoing wave is $\alpha N_L(E,\vec{r})$.

The condition (2.18) that an incoming wave is the sum of outgoing waves from the other sites can now be used to write an equation of the form (3.1), but dropping the condition that the point $\vec{r}$ must be outside the bounding sphere,

$$-\sum_{L'L} J_{L'}(E,\vec{r})X_{L'L}(E)C_L = \alpha \sum_{n\neq 0}\sum_{L} N_L(E,\vec{r}_n)e^{i\vec{k}\cdot R_n}C_L\,. \tag{4.15}$$

The derivation of the KKR equations for anisotropic muffin-tin potentials goes through just as before, but the function $f_L^{\vec{k}}(E,\vec{r})$ defined in (3.3) must be written

$$f_L^{\vec{k}}(E,\vec{r}) = \sum_{L'} J_{L'}(E,\vec{r})B_{L'L}(E,\vec{k})\,, \tag{4.16}$$

where $\vec{r}$ is inside the bounding sphere. The multiple-scattering equations are true for any $\vec{r}$, so it must be possible to derive formulas from them without such a requirement as $\vec{r}$ being outside the bounding sphere. Indeed, Eqs. (4.16) and (4.15) lead to exactly the same expression for the KKR matrix as has already been written in (3.6).

The physical implication of (4.16) is obvious in retrospect. The outgoing solution from the nth lattice site illustrated in Fig. 1 is given by the function

$$f_L^n(E,\vec{r}) = \alpha N_L(E,\vec{r}_n)\,. \tag{4.17}$$

When $\vec{r}$ is outside any of the other bounding spheres, for example, the one in the central cell, this outgoing solution must be a linear combination of the solution defined in (4.11) and (4.4),

$$f_L^n(E,\vec{r}) = \sum_{L'} J_{L'}(E,\vec{r})B_{L'L}^n(E)\,. \tag{4.18}$$

The coefficients $B_{L'L}^n$ are just the ones that may be used to expand the singular solution $Y_L(\vec{r}_n)n_l(\alpha r_n)$ in terms of the nonsingular ones $Y_L(\vec{r})j_l(\alpha r)$ when $\vec{r}$ is in the central cell

$$Y_L(\vec{r}_n)n_l(\alpha r_n) = \sum Y_{L'}(\vec{r})j_{l'}(\alpha r)B_{L'L}^n\,. \tag{4.19}$$

These coefficients can be shown to be

$$B_{L'L}^n = 4\pi i^{(l'-l)}\sum_{L''} i^{-l''}C_{L'L}^{L''}n_{l''}(\alpha R_n)Y_{L''}(\vec{R}_n) \tag{4.20}$$

where $C_{L'L}^{L''}$ are Gaunt factors. The connection between these coefficients and the structure constants is formally

$$B_{L'L}(E,\vec{k}) = \sum_{n\neq 0} B_{L'L}^n(E)e^{ik\cdot R_n}. \tag{4.21}$$

In other words, the outgoing or incoming waves propagating through a lattice such as the one illustrated in Fig. 1 must be expanded in terms of the solutions of differential equation (4.1) when $\vec{r}$ is inside one of the bounding spheres, and not solutions of the Helmholtz equation that is obtained by setting $v(\vec{r})=0$. This observation has not been emphasized in previous discussions of multiple-scattering theory and has implications that appear to have been overlooked.

V. NON-MUFFIN-TIN POTENTIALS

When the bounding spheres outside of which $v(\vec{r})=0$ are nonoverlapping as shown in Fig. 1, we have seen that the KKR equations follow from the multiple-scattering equations whether we use the considerations of Sec. IV or not. Suppose that $v(\vec{r})\neq 0$ within the shaded areas shown in Fig. 2. A bounding sphere is indicated by the dotted line in that figure, and clearly the spheres associated with the different cells will overlap. The solutions $N_L(E,\vec{r})$ and $J_L(E,\vec{r})$ must be used within the entire region surrounded by the sphere, not just the shaded region, in order for the incoming and outgoing waves to be related by the asymptotic form of a scattering matrix such as the inverse of the reaction matrix in (4.13).

We can still use the condition (2.18) to write an equation just like (4.15), but we cannot use the ordinary structure constants of KKR theory in an expression for $f_L^{\vec{k}}(E,\vec{r})$ like (4.16). This

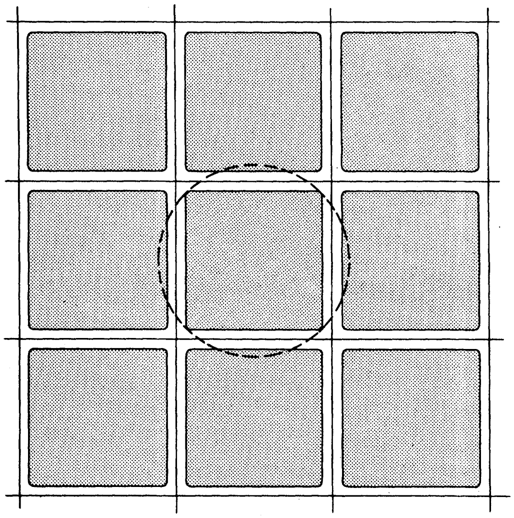

FIG. 2. Illustration of a lattice for which multiple-scattering theory becomes more difficult to apply. The potential functions have nonzero values within the shaded regions, and the bounding spheres indicated by the dotted line will overlap.

expression relies on the fact that the coefficients $B^n_{L'L}$ in (4.18) can be found by considering the transformation properties of solutions of the Helmholtz equation. Then, formally, $B_{L'L}(E,\vec{k})$ is given by (4.21) although it is necessary to go to the paper by Ewald[2] to get a rigorous discussion of this equation. For the case shown in Fig. 2, an expansion like (4.18) can be used only for cells, n, such that their spheres do not overlap the one associated with the central cell.

The problem for the nearest-neighbor cells is to find a set of coefficients $\hat{B}^n_{L'L}$ such that

$$\alpha N_L(E,\vec{r}_n)=\sum_{L'} J_{L'}(E,\vec{r})\hat{B}^n_{L'L}(E)\,, \tag{5.1}$$

for $\vec{r}$ in the central cell. Such coefficients exist, but it appears that it would be very difficult to find them. It would require not only the calculation of the off-diagonal elements of the reaction matrix $R_{L'L}(E)$ but also the solutions of the integral equations (4.4) for many values of $\vec{r}$. They will, of course, depend on the potential $v(\vec{r})$, and it therefore follows that the nice separation between atomic scattering and structural quantities in the ordinary KKR is lost when non-muffin-tin effects are properly taken into account.

In an earlier discussion of this problem, Williams and van Morgan[9] obtained a set of KKR equations just like the ones for anisotropic muffin-tin potentials, (3.5) and (3.6), except that the reaction matrix is evaluated at the bounding sphere that will overlap its neighbors like the one shown in Fig. 2. From the point of view of the present work, the error in this derivation arose in assuming at a certain stage [Eq. (2.10) in Ref. 9] that $J_L(E,\vec{r})=Y_L(\vec{r})j_l(\alpha r)$ and $N_L(E,\vec{r})=Y_L(\vec{r})n_l(\alpha\vec{r})$ in the region outside the shaded area but within the bounding sphere. In a later study, Ziesche eliminated the assumption about $N_L(E,\vec{r})$, but he still assumed $J_L(E,\vec{r})=Y_L(\vec{r})j_l(\alpha r)$ in that region [Eq. (2.10) in Ref. 10]. Ziesche was thus led to a critique based on questions about the convergence of the equations used in translating the solutions of the Helmholtz equation, rather than the more general problem of finding the $\hat{B}^n_{L'L}(E)$ in (5.1). He emphasized the point that the treatment of outgoing waves from neighboring sites must be handled differently from the others, but his near-field corrections differ from the ones that arise in the present work. The conclusion that I arrive at is that the problem of carrying out a rigorous multiple-scattering calculation for potentials that cannot be put in the form of anisotropic muffin-tin potentials is more difficult than it appeared to be in previous discussions.

Perhaps the most straightforward way out of this difficulty is simply to ignore the near-field corrections and do the calculation that was suggested by Williams and van Morgan.[9] For reasonably close-packed systems in which the non-muffin-tin corrections are not too large, for example most metals or ordered metallic alloys, it should work rather well. This is because the functions $J_L(E,\vec{r})$ and $N_L(E,\vec{r})$ must link smoothly to their asymptotic forms at the radius of the bounding sphere so they must be nearly equal to $Y_L(\vec{r})j_l(\alpha r)$ and $Y_L(\vec{r})n_l(\alpha r)$ for some distance inside the sphere. Their singularities at $r=0$ are not too serious because it is not usually necessary to consider such small values of r. Certain test calculations on systems of the type described here indicate that the approach has promise.[9] It will be shown in a later section that the new computational schemes[11,12] that have been put forward with the idea of simplifying non-muffin-tin calculations (among other things) make an assumption that is equivalent to ignoring the near-field effects at the start, so they can never give a better approximation except by happenstance.

A possible approach to a more rigorous treatment of the multiple-scattering equations would be to construct the bounding spheres so that they do not overlap, as illustrated in Fig. 1, and then include the part of the potential function that is outside the bounding spheres, $v_{\text{ext}}(\vec{r})$, in the Hamiltonian H_0 which is used in (2.3). The Green's function $G_0(E,\vec{r},\vec{r}\,')$ will then describe the propagation of an electron through the potential $v_{\text{ext}}(\vec{r})$ rather than through free space. Of course, the solutions of the Helmholtz equation could no longer be used to describe the waves in the interstitial region. This approach has not been used in any serious way to my knowledge, but the idea can be used to explain what might appear to be a serious inconsistency in this discussion.

In an apparent contradiction to the remarks in this section there exists a type of potential function that cannot be forced into the form of a simple anisotropic muffin-tin potential but for which the multiple-scattering equations can be used to derive easily solvable band-theory equations. This is a potential in which there are several bounding spheres in each unit cell. It would arise in the description of an ordered compound or even a crystal structure like hcp that has more than one atom per unit cell.

The resolution of this apparent contradiction is illustrated in Figs. 3(a) and 3(b). Suppose we first use the simple KKR equations to calculate a $G_0(E,\vec{r},\vec{r}\,')$ which describes the propagation through a lattice that contains one muffin tin per

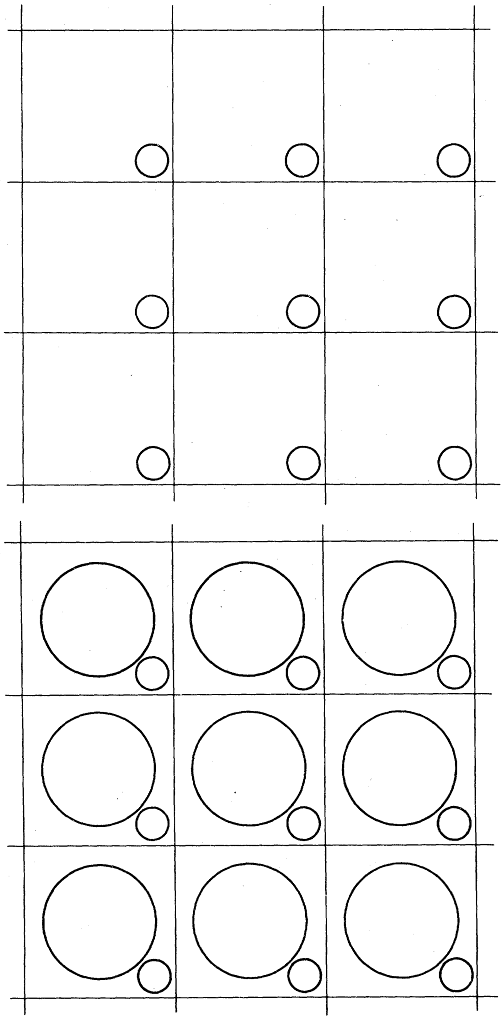

FIG. 3. Simple lattice illustrated in (a) may be combined with the one in Fig. 1 to obtain the complex lattice in (b) that has two atoms per unit cell.

unit cell as shown in Fig. 3(a). This G_0 is then used in a calculation for a potential function like the one indicated in Fig. 1. The resulting solutions will then describe the electronic states in a crystal with the potential function shown in Fig. 3(b). Of course, in practice it is not necessary to go through this step-by-step process to solve the problem as the KKR equations for such complex lattices are well known.[17]

The point to this discussion of complex lattices is to show that the difficulties inherent in going beyond the anisotropic muffin-tin potential are quite real and cannot be brushed aside by invoking this counterexample.

Of course, the reasons that spheres play such a central role in this discussion stems from the use of the solutions of the Helmholtz equation in spherical coordinates $Y_L(\vec{r})j_l(\alpha r)$ and $Y_L(\vec{r})n_l(\alpha r)$. If we could replace these with solutions in coordinates that are commensurate with the shape of a Wigner-Seitz cell, then the potential functions would only have to be bounded by nonoverlapping Wigner-Seitz cells and the problem would be solved. It is not clear how this could be achieved at the present time.

As I pointed out, the direct calculation of the $\hat{B}^n_{L',L}(E)$ in (5.2) will be difficult, but the necessary mathematical tools for doing it have been developed in this section and in Sec. IV. This could become a useful approach in future developments of high-precision band-theory techniques.

A final point concerning the non-muffin-tin problems should be emphasized. We have been assuming that the constant value of $V(\vec{r})$ in the interstitial region, the unshaded region in Fig. 2, is zero. We could assign any value to this constant potential, V_{con} and the parameter α would become the square root of $E - V_{\text{con}}$. If the boundaries of the shaded regions expand to fill the interiors of the unit cells, the volume of the interstitial region will be zero. The results of any band-theory calculations must then be independent of V_{con}. This point appears trivial, but it is the basis for many of the derivations in later sections of this paper.

VI. CALCULATION OF SCATTERING MATRICES

In Sec. IV, it was shown that the t matrix of scattering theory can be written in terms of the matrices a and b whose elements are the coefficients that appear in the expression (4.6) for $\phi_{L_0}(E,\vec{r})$. Inserting (4.9) into (4.10) and the result into (2.21) leads to the following expression for the Wigner reaction matrix:

$$\underline{R} = -(1/i\alpha)(\underline{a}-\underline{b})(\underline{a}+\underline{b})^{-1}\,. \tag{6.1}$$

It follows that the problem of calculating any of the scattering matrices comes down to the calculation of the coefficients $a_{L_1L_0}(E)$ and $b_{L_1L_0}(E)$. By taking the Wronskian of $\phi_{L_0}(E,\vec{r})$ with $f^{\pm}_{L_1}(E,\vec{r})$ and passing to the limit that r goes to infinity it can be shown that

$$\begin{aligned} a_{L_1L_0}(E) &= \delta_{L_1L_0} - i\alpha\int h^{-}_{l_1}(\alpha r)Y_{L_1}(\vec{r})v(\vec{r})\phi_{L_0}(E,\vec{r})\,dv\,, \\ b_{L_1L_0}(E) &= \delta_{L_1L_0} + i\alpha\int h^{+}_{l_1}(\alpha r)Y_{L_1}(\vec{r})v(\vec{r})\phi_{L_0}(E,\vec{r})\,dv\,. \end{aligned} \tag{6.2}$$

Since the spherical harmonics $Y_L(\vec{r})$ are real it is clear that

$$a_{L_1L_0}=b^*_{L_1L_0}\,. \tag{6.3}$$

If we define matrices $\underline{c}=-\mathrm{Re}\underline{b}$ and $\underline{s}=\mathrm{Im}\underline{b}$ so that

$$\underline{b}=\underline{c}+i\,\underline{s} \tag{6.4}$$

it is clear that the matrix $\underline{X}=-\underline{R}^{-1}$ which we have been using can be written

$$\underline{X}=\alpha\underline{cs}^{-1}. \tag{6.5}$$

The elements of the matrices $\mathbf{c}$ and $\mathbf{s}$ are, from (6.2)

$$c_{LL_0}=\alpha\int n_l(\alpha r)Y_L(\vec{r})v(\vec{r})\phi_{L_0}(E,\vec{r})\,dv-\delta_{LL_0}\,, \tag{6.6}$$

and

$$s_{LL_0}=\alpha\int j_l(\alpha r)Y_L(\vec{r})v(\vec{r})\phi_{L_0}(E,\vec{r})\,dv\,. \tag{6.7}$$

These equations could be used in their present form to calculate the scattering matrix. The Volterra equation (4.2) can easily be solved to find $\phi_{L_0}(E,\vec{r})$ in the region within which $v(\vec{r})\neq 0$, and the integrals (6.6) and (6.7) carried out. This process can be converted into essentially the same computational technique as the one suggested by Williams and van Morgan.[9]

The equation for c_{LL_0} and s_{LL_0} can be put into another form by inserting

$$v(\vec{r})\phi_{L_0}(E,\vec{r})=(\nabla^2+E)\phi_{L_0}(E,\vec{r}) \tag{6.8}$$

into (6.6) and (6.7) and using Green's theorem. If the integral is extended to the radius S of the bounding sphere, it can be shown that

$$c_{LL_0}=\alpha S^2\,[n_l\,,\,\phi_{LL_0}] \tag{6.9}$$

and

$$s_{LL_0}=\alpha S^2\,[j_l\,,\,\phi_{LL_0}] \tag{6.10}$$

where $\phi_{LL_0}(E,r)$ is defined in (4.5) and the square bracket indicates the quantity

$$[f,g]=f(r)\frac{dg(r)}{dr}-\frac{df(r)}{dr}g(r)\,, \tag{6.11}$$

evaluated at $r=S$.

For the special case of muffin-tin potentials

$$\phi_{LL_0}(E,r)=\phi_l(E,r)\delta_{LL_0}\,, \tag{6.12}$$

and the previous equations can be written

$$c_{LL_0}=A_l\cos\eta_l\delta_{LL_0},\quad s_{LL_0}=A_l\sin\eta_l\delta_{LL_0}\,, \tag{6.13}$$

where η_l is the scattering phase shift that can be calculated from

$$\cot\eta_l=[n_l\,,\,\phi_l]/[j_l\,,\,\phi_l], \tag{6.14}$$

a result well known to band-theory practitioners. The constant, A_l, could be evaluated using scattering theory, but is plays no important role in this discussion. Inserting (6.13) into (6.5) leads to the standard expression for $X_{LL'}$ for muffin-tin potentials already quoted in (3.7).

Probably the most useful formulas for c_{LL_0} and s_{LL_0} are obtained with the help of certain auxilliary functions $\tilde{J}_L(\alpha,\vec{r})=Y_L(\vec{r})\tilde{J}_l(\alpha,r)$ and $\tilde{N}_L(\alpha,\vec{r})=Y_L(\vec{r})\tilde{N}_l(\alpha,r)$ that are obtained by solving a rather strange-appearing eigenvalue equation. Let us write the potential $v(\vec{r})$ as the sum of a spherically symmetric part $v_0(r)$ and a nonspherically symmetric part $\hat{v}(\vec{r})$

$$v(\vec{r})=v_0(r)+\hat{v}(\vec{r})\,. \tag{6.15}$$

Then $\tilde{J}_L(\alpha,\vec{r})$ is defined to be a solution of

$$[-\nabla^2+v_0(r)]\tilde{J}_L(\alpha,\vec{r})=E_l^J\,\tilde{J}_L(\alpha,\vec{r})\,, \tag{6.16}$$

which is regular at the origin and satisfies the boundary conditions

$$\tilde{J}_l(\alpha,S)=j_l(\alpha S),\quad \tilde{J}_l'(\alpha,S)=j_l'(\alpha S)\,, \tag{6.17}$$

at the bounding sphere. There are many such functions corresponding to different eigenvalues E_l^J, but we will choose a particular one in our later applications using a criterion that will be obvious in context. The function $\tilde{N}_L(\alpha,\vec{r})$ is a solution of

$$[-\nabla^2+v_0(r)]\tilde{N}_L(\alpha,\vec{r})=E_l^NN_L(\alpha,\vec{r})\,, \tag{6.18}$$

that is regular at the origin and satisfies the conditions

$$\tilde{N}_l(\alpha,S)=n_l(\alpha S),\quad \tilde{N}_l'(\alpha,S)=n_l'(\alpha S)\,. \tag{6.19}$$

The eigenvalues are functions of $E=\alpha^2$ and could be written $E_l^J(E)$ and $E_l^N(E)$.

The boundary conditions (6.17) make it possible to replace $j_l(\alpha r)$ with $\tilde{J}_l(\alpha,r)$ in (6.10). Using the differential equations (6.16) and (6.18) and applying Green's theorem in reverse leads to

$$s_{LL_0}=(E_l^J-E)\alpha\int\tilde{J}_L(\alpha,\vec{r})\phi_{L_0}(E,\vec{r})\,dv+\alpha\int\tilde{J}_L(\alpha,\vec{r})\hat{v}(\vec{r})\phi_{L_0}(E,\vec{r})\,dv\,. \tag{6.20}$$

Similar arguments applied to the other function leads to

$$c_{LL_0}=(E_l^N-E)\alpha\int\tilde{N}_L(\alpha,\vec{r})\phi_{L_0}(E,\vec{r})\,dv+\alpha\int\tilde{N}_L(\alpha,\vec{r})\hat{v}(\vec{r})\phi_{L_0}(E,\vec{r})\,dv\,. \tag{6.21}$$

The integrals are over the volume of the bounding sphere. Since the functions $\tilde{N}_L(\alpha,\vec{r})$ and $\tilde{J}_L(\alpha,\vec{r})$ will later be used in connection with an approximate band theory scheme[12] in which connection they have been given the name augmented spherical waves (ASW) it should perhaps be emphasized that Eqs. (6.20) and (6.21) are exact.

The only connection that ASW's have with the energy E is through the conditions (6.17) and (6.19). In principle, it does not matter which of the allowed eigenvalues and corresponding eigenfunctions are used in (6.20) and (6.21), but in practice, it would probably be a good idea to use the E_l^J and E_l^N closest to E.

In Secs. VII and VIII, these equations will be used to discuss several approximate schemes in band theory, but they could be made the basis of a very serious calculation of the scattering matrices. The method proposed here is to find just the diagonal part of $\phi_{L_0}(\vec{r})$, $Y_{L_0}(\vec{r})\phi_{L_0L_0}(E,r)$, by solving (4.1) with the approximation $v(\vec{r})=v_0(r)$. The function $\phi_{L_0L_0}(E,r)$, which may more simply be called $\phi_{l_0}(E,r)$, is thus obtained merely by solving a radial differential equation rather than the integral equation (4.2). It must be normalized so that it approaches $j_{l_0}(\alpha r)$ as r approaches zero, but of course it has no preset value at $r=s$. We then get the approximate equations

$$s_{LL_0}=(E_l^J-E)\alpha\int_0^s r^2\tilde{J}_{l_0}(\alpha,r)\phi_{l_0}(E,r)\,dr\,\delta_{LL_0}$$

$$+\alpha\int_0^s r^2\tilde{J}_l(\alpha r)\hat{v}_{LL_0}(r)\phi_{l_0}(E,r)\,dr\,, \tag{6.22}$$

and

$$c_{LL_0}=(E_l^N-E)\alpha\int_0^s r^2\tilde{N}_{l_0}(\alpha,r)\phi_{l_0}(E,r)\,dr\,\delta_{LL_0}$$

$$-\alpha\int_0^s r^2\tilde{N}_l(\alpha,r)\hat{v}_{LL_0}(r)\phi_{l_0}(E,r)\,dr\,, \tag{6.23}$$

where

$$\hat{v}_{LL_0}(r)=\int Y_L(\vec{r})\hat{v}(\vec{r})Y_{L_0}(\vec{r})\,d\Omega\ . \tag{6.24}$$

VII. PIVOTED MULTIPLE-SCATTERING EQUATIONS AND LINEARIZED KKR

Up to this point, the usefulness of the quantities derived in Secs. II–VI has been described within the context of the standard multiple-scattering approach. Following the work of Andersen[11] there has been a recent trend toward the introduction of approximations which somewhat reduce the precision of the calculations but allow them to be carried out much more rapidly. The derivations of these techniques all involve the addition of a variational step. In this section, it will be shown how the quantities derived above can be used to obtain a simplified band-theory technique entirely within the framework of multiple-scattering theory. This section shows how the resulting equations can be used for very precise calculations with very little computational effort. Section VIII compares this formalism with the ones that include a variational step in some detail.

The basic observation that leads to the simplified equations is the one that was made at the end of Sec. V: if the boundaries of the interstitial region in which the potential $V(\vec{r})$ is taken to be a constant, V_{con}, are allowed to expand until they coincide with the cell boundaries, then the band-theory calculation must not depend on the choice of V_{con}. This simply follows from the fact that the volume of the interstitial region has shrunk to zero.

The freedom to vary V_{con} can be used to arrange matters so that the energy of the incoming wave is always the same, E_0. If the energy would change from E_0 to E, then it is brought back to the reference value by adding $\Delta=E-E_0$ to V_{con}. This is equivalent to subtracting Δ from the potential $v(\vec{r})$. Neglecting the near-field contributions to the structure constants that were described in Sec. V, the KKR matrix for a general non-muffin-tin potential thus may be written

$$M_{L'L}(E,\vec{k})=X^{\Delta}_{L'L}(E_0)+B_{L'L}(E_0,\vec{k})\,. \tag{7.1}$$

The matrix $\vec{X}^{\Delta}(E_0)$ describes the scattering from the shifted potential

$$v^{\Delta}(\vec{r})=v(\vec{r})-\Delta\sigma(\vec{r})\,, \tag{7.2}$$

where $\sigma(\vec{r})=1$ if $\vec{r}$ is inside the unit cell and $\sigma(\vec{r})=0$ otherwise. The structure constants $B_{L'L}(E_0,\vec{k})$ are just the ones used in (3.6). It should be emphasized that this reformulation would be exact if we had not left out the near-field corrections.

The most useful form for the matrix $\underline{X}^{\Delta}(E_0)$ is obtained with the help of the $\underline{c}$ and $\underline{s}$ matrices in the form that they take in (6.20) and (6.21). Although the results are independent of the precise way that the function $\Delta\sigma(\vec{r})$ is subtracted from $v_0(r)+\hat{v}(\vec{r})$, perhaps the easiest way is

$$\begin{aligned}
v^{\Delta}(\vec{r})&=v_0^{\Delta}(r)+\hat{v}^{\Delta}(\vec{r})\,,\\
v_0^{\Delta}(r)&=v_0(r)\,,\\
\hat{v}^{\Delta}(\vec{r})&=\hat{v}(\vec{r})-\Delta\sigma(\vec{r})\,.
\end{aligned} \tag{7.3}$$

That is, the shift is associated with the non-muffin-tin part of the potential, and thus the quantities $E_l^J(E_0)$, $\tilde{J}_l(\alpha_0,r)$, $E_l^N(E_0)$, and $\tilde{N}_l(\alpha_0,r)$ are unaffected. Then (6.20) and (6.21) become

$$s^{\Delta}_{LL_0}(E_0)=[E_l^J(E_0)-E_0]\alpha_0\int\tilde{J}_L(\alpha_0,\vec{r})\phi^{\Delta}_{L_0}(E_0,\vec{r})\,dv$$

$$-(E-E_0)\alpha_0\int\sigma(\vec{r})\tilde{J}_L(\alpha_0,\vec{r})\phi^{\Delta}_{L_0}(E_0,\vec{r})\,dv$$

$$+\alpha_0\int\tilde{J}_L(\alpha_0,\vec{r})\hat{v}(\vec{r})\phi^{\Delta}_{L_0}(E_0,\vec{r})\,dv\,, \tag{7.4}$$

and

$$c_{LL_0}(E_0)=[E_l^N(E_0)-E_0]\alpha_0\int \tilde{N}_L(\alpha_0,\vec{r})\phi^{\Delta}_{L_0}(E_0,\vec{r})\,dv$$
$$-(E-E_0)\alpha_0\int \sigma(\vec{r})\tilde{N}_L(\alpha_0,\vec{r})\phi^{\Delta}_{L_0}(E_0,\vec{r})\,dv$$
$$+\alpha_0\int \tilde{N}_L(\alpha_0,\vec{r})\hat{v}(\vec{r})\phi^{\Delta}_{L_0}(E_0,\vec{r})\,dv\,. \qquad (7.5)$$

The function $\phi^{\Delta}_{L_0}(E_0,\vec{r})$ is the solution of (4.1) obtained by solving the integral equation (4.2) for the potential $v^{\Delta}(\vec{r})$.

Equations (7.4) and (7.5) are still exact and no further approximation has been made if they are used in (6.5) to calculate the $X^{\Delta}_{L',L}(E_0)$ for (7.1), but it is useful to make approximations to simplify the calculations. All three of the integrals in each of these equations are over the volume enclosed by the bounding sphere, but the functions $\sigma(\vec{r})$ and $\hat{v}(\vec{r})$ are zero outside the unit cell. Let us split the difference and change the range of integration of the first two integrals to the region enclosed by the Wigner-Seitz sphere and remove the function $\sigma(\vec{r})$ from the second integral. Further, the off-diagonal elements of $\phi^{\Delta}_{L_0}(E_0,\vec{r})$ should be ignored as in the argument that led to (6.22) and (6.23). It is easy to see that when the exact shape of the unit cell is ignored, the function $\phi^{\Delta}_{L_0}(E_0,\vec{r})$ become $Y_{L_0}(\vec{r})\phi_{l_0}(E,r)$, the solution of (4.1) for the original potential $v_0(\vec{r})$ that corresponds to the energy E. The combination of these approximations leads to

$$s^{\Delta}_{LL_0}=(E_l^J-E)I_l^J(E,E_0)\delta_{LL_0}+U^J_{LL_0}(E,E_0)\,, \qquad (7.7)$$

and

$$c^{\Delta}_{LL_0}=(E_l^N-E)I_l^N(E,E_0)\delta_{LL_0}+U^N_{LL_0}(E,E_0)\,. \qquad (7.8)$$

The first set of integrals has become

$$I_l^J(E,E_0)=\alpha_0\int_0^W r^2\tilde{J}_l(\alpha_0,r)\phi_l(E,r)\,dr\,, \qquad (7.9)$$

and

$$I_l^N(E\,,E_0)=\alpha_0\int_0^W r^2\tilde{N}_l(\alpha_0,r)\phi_l(E,r)\,dr\,, \qquad (7.10)$$

where W is the Wigner-Seitz radius. The second set is

$$U^J_{LL_0}(E,E_0)=\alpha_0\int_0^S r^2\tilde{J}_l(\alpha_0,r)\hat{v}_{LL_0}(r)\phi_{l_0}(E,r)\,dr\,, \qquad (7.11)$$

and

$$U^N_{LL_0}(E,E_0)=\alpha_0\int_0^S r^2\tilde{N}_l(\alpha_0,r)\hat{v}_{LL_0}(r)\phi_{l_0}(E,r)\,dr\,, \qquad (7.12)$$

where the elements $\hat{v}_{LL_0}(r)$ are written in (6.24). In the following, E_l^J and E_l^N refer to $E_l^J(E_0)$ and $E_l^N(E_0)$.

It is much easier to calculate the elements $X^{\Delta}_{L',L}(E_0)$ for use in (7.1) from (7.7) and (7.8) particularly as it turns out that the integrals in (7.9)–(7.12) may easily be parametrized. If these integrals are calculated for a number of energies and fit to a power series in E, the only sizable terms are the constant and linear terms.

In order to clarify the preceding discussion, calculations for an actual potential function have been made. A muffin-tin potential has been chosen so that the eigenvalues could be compared with the values obtained from ordinary KKR equations. The potential describes paramagnetic nickel, but it can be looked upon as just a typical transition metal.

For this example, the integrals $U^J_{LL_0}(E,E_0)$ and $U^N_{LL_0}(E,E_0)$ are zero. The integrals in (7.9) and (7.10) were carried out and it was found that they could be written very accurately as

$$I_l^J(E,E_0)=I_l^J(E_0)[1+S_l^0(E-E_0)]\,, \qquad (7.13)$$

and

$$I_l^N(E,E_0)=I_l^N(E_0)[1+C_l^0(E-E_0)]\,, \qquad (7.14)$$

where $I_l^J(E_0)=I_l^J(E_0,E_0)$, S_l^0 is the logarithmic derivative of $I_l^J(E,E_0)$ evaluated at $E=E_0$, while $I_l^N(E_0)$ and C_l^0 are defined similarly.

The KKR matrix of (7.1) can now be written

$$M_{L',L}(E,k)$$
$$=\frac{(E_l^N-E)}{(E_l^J-E)}\frac{[1+C_l^0(E-E_0)]}{[1+S_l^0(E-E_0)]}\alpha_0\rho^0\delta_{L',L}$$
$$+B_{L',L}(E_0,\vec{k})\,, \qquad (7.15)$$

where

$$\rho_l^0=I_l^N(E_0)/I_l^J(E_0)\,. \qquad (7.16)$$

This is a special case of the pivoted multiple-scattering (PMS) equation. Clearly the matrix in (7.15) is exactly the KKR matrix for $E=E_0$ and all values of $\vec{k}$ when the potential is of the muffin-tin form. The errors introduced by the approximations made so far will thus be a minimum at the pivotal energy E_0, and will increase as $|E-E_0|$ gets larger. PMS equations can be written down for non-muffin-tin potentials, but they will be discussed later. The PMS equations are interesting because obtaining them is the major step in deriving linearized KKR equations, and it will be seen that they have other uses as well.

Using the same partitioning technique that led to (3.13), it is easy to write the elements of the PMS matrix as

$$M_{L',L}=\frac{(E_l^N-E)[1+C_l^0(E-E_0)]}{(E_l^J-E)[1+S_l^0(E-E_0)]}\alpha_0\rho_l^0\delta_{L',L}+C_{L',L}\,, \qquad (7.17)$$

where

$$C_{L'L}=B_{L'L}-\sum_{L''}{}' B_{L'L''}\frac{(E^J_{l''}-E)[1+S^0_{l''}(E-E_0)]}{(E^N_{l''}-E)[1+C^0_{l''}(E-E_0)]}\times\frac{1}{\alpha_0\rho^0_{l''}}B_{L''L}\,. \tag{7.18}$$

In these equations l and l' may take on the values $0,\ 1,\ldots,l_1$ while l'' is $l_1+1,\ l_1+2,\ldots,l_{\max}$.

The PMS matrix may be put into a linearized form by multiplying through on both sides by the denominator of the diagonal term in (7.17), expanding the result in powers of E, and neglecting terms beyond the linear term. That is

$$M^S_{L'L}=(E^J_{l'}-E)[1+S^0_{l'}(E-E_0)]M_{L'L}\times(E^J_l-E)[1+S^0_l(E-E_0)]\,, \tag{7.19}$$

is, to terms linear in E,

$$M^S_{L'L}\cong H^S_{L'L}(\vec{\mathrm{k}})-EO^S_{L'L}(\vec{\mathrm{k}})\,. \tag{7.20}$$

The symmetric matrices $H^S_{L'L}(\vec{\mathrm{k}})$ and $O^S_{L'L}(\vec{\mathrm{k}})$ depend only on $\vec{\mathrm{k}}$ and the parameters in the PMS equation. They play the role of the Hamiltonian and overlap matrices from a variational calculation although $\underline{O}^s(\vec{\mathrm{k}})$ need not be positive definite.

These matrices will arise again in Sec. VIII, but as a basis for a linearized band theory they suffer from two defects.

The first defect is that the determinant of the matrix $\underline{M}^s$ is clearly zero whenever E is equal to any of the E^J_l, and these zeros are spurious in the sense that they do not represent eigenvalues. The linearized equation (7.20) will thus yield some true eigenvalues of the system but they will also give as solutions some of the spurious roots. For some choices of E_0 the E^J_l are outside the range of the bands of interest, but in general these spurious roots are a problem.

The second defect arises in the linearization process. In general, the coefficients of E^2, $E^3,\ldots$ in the expansion of the elements in (7.19) are of the order of one, so (7.20) is only true when the magnitude of E is rather small, in our example less than 0.2 in appropriate units.

This second defect can be gotten around by noting that E appears in (7.17) only as the difference between two energies. It is, therefore, possible to introduce an energy parameter E_ν about which the expansion will be made. If we introduce the new variable $E^{N'}_l=E^N_l-E_\nu$, $E^{J'}_l=E^J_l-E_\nu$, and $E'_0=E_0-E_\nu$, then the expansion can be made in powers of $E-E_\nu$ which can be made small by a proper choice of E_ν.

The problem of spurious roots can be eliminated by multiplying only on the left by the denominator of the diagonal part of (7.17) rather than on both sides before expanding to obtain

$$M^U_{L'L}=[E^{N'}_l-(E-E_\nu)][1+C^0_l(E-E_\nu-E'_0)]\delta_{L'L}+[E^{J'}_{l'}-(E-E_\nu)][1+S^0_{l'}(E-E_\nu-E'_0)]C_{L'L} \tag{7.21}$$

where $C_{L'L}$ is given in (7.18). It is a straightforward matter to multiply out these functions and collect the terms that are independent of energy and the coefficients of $(E-E_\nu)$ to write

$$M^U_{L'L}\cong H^U_{L'L}(\vec{\mathrm{k}})-(E-E_\nu)O^U_{L'L}(\vec{\mathrm{k}})\,. \tag{7.22}$$

Clearly the Hamiltonian and overlap matrices that arise from this process are asymmetrical. Operationally this poses no difficulty because the numerical procedures for diagonalizing a system like (7.22) go through essentially as fast as the ones for a system like (7.20) for the relatively small matrices involved. There is a mathematical possibility that these procedures could lead to complex eigenvalues, but this does not occur in practice.

The unlinearized PMS equations can now be seen to take on an added significance. The zeroes of the determinant of the matrix $\underline{M}(\vec{\mathrm{k}})$ whose elements are defined in (7.15) are the best values that can be obtained for the eigenvalues of the system from

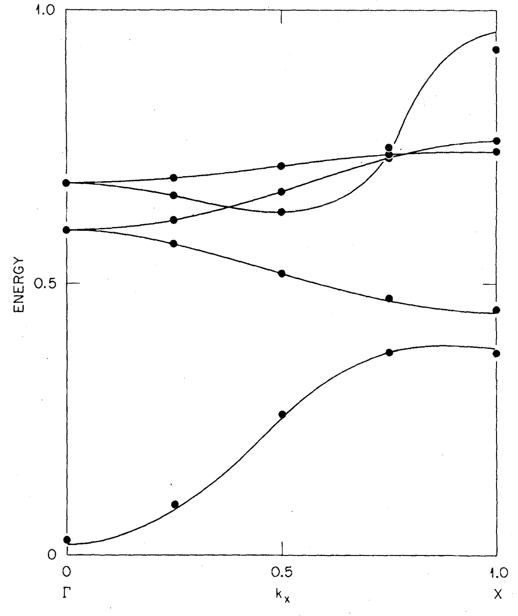

FIG. 4. Comparison of PMS values for the energies for various $\vec{\mathrm{k}}$ (dots) with the results of an $l_{\max}=4$ KKR band-theory calculation for a paramagnetic nickel muffin-tin potential. The vectors $\vec{\mathrm{k}}$ lie on the line that connects the center of the fcc Brillouin zone (Γ) to the midpoint of the square face (X). The energy is in dimensionless units and must be multiplied by 0.897 55 to obtain values in rydbergs.

linearized KKR equations as long as the pivotal energy E_0 is not changed. In principle, it would be necessary to diagonalize the equations many times using different values for E_ν, but it will be seen in the numerical example that satisfactory approximations to the PMS eigenvalues can be obtained using two or three values for E_ν. An approximation that is adequate for some purposes can be obtained using only one E_ν.

The PMS eigenvalues for the paramagnetic nickel muffin-tin potential that I have used as an example are compared in Fig. 4 with the results of an $l_{\max}=4$ KKR calculation. Partitioning was used in the PMS equations, as in (7.17), but the KKR eigenvalues were obtained without partitioning. All of the energies quoted in connection with this example are in dimensionless units. They must be multiplied by 0.897 55 to obtain energies in rydbergs. In these dimensionless units the pivotal energy E_0 is 0.6.

The PMS eigenvalues agree with the ones from the KKR calculation to four figures for energies sufficiently near to 0.6. It is clear from Fig. 4 that the PMS eigenvalues are quite accurate over the whole range of energies considered. The rms deviation of these eigenvalues from the KKR eigenvalues is 0.0068.

The parameters calculated from the nickel potential for the PMS equations are shown in Table I. It is clear that spurious roots arising from $E_0^J=0.7572$ and $E_1^J=0.5619$ would cause problems if we did not use the asymmetrical formulation of (7.21) and (7.22). The error involved in replacing the ratio $\rho_l(E,E_0)=I_l^N(E,E_0)/I_l^J(E,E_0)$ with the approximation $\rho_l^0[1+C_l^0(E-E_0)]/[1+S_l^0(E-E_0)]$ is less than one percent at both $E=0.01$ and $E=0.90$ except for $l=2$ for which the linearized prediction is about five percent too high at either end of the range. It follows from this that the relatively large error in the PMS eigenvalue corresponding to the $X_{4'}$ symmetry does not arise from this approximation since this state is mostly s and p. It presumably reflects the neglect of near-field corrections on the $B_{L'L}(E_0,\vec{k})$ and the replacement of the actual cell boundary with a Wigner-Seitz sphere.

In Table II, I list some of the eigenvalues I calculated from the KKR equations and the PMS equations. I also list some of the eigenvalues I calculated from the linearized KKR equations of (7.22) for $E_\nu=0.6$, 0.4, 0.3, and 0.2.

Of course, when $E_\nu=E_0=0.6$ the LKKR equations will yield the same eigenvalues as the PMS and hence the KKR equations for energies near 0.6. The errors increase for eigenvalues that are farther away, reaching a maximum of about 0.1 at the bottom of the band. If the band theory program is being used for a calculation that requires great accuracy only in the neighborhood of some energy, say the Fermi energy, then the best choice of E_0 and E_ν would be the Fermi energy and one diagonalization will be sufficient.

Overall, the rms error of the eigenvalues from the LKKR calculation with $E_\nu=0.6$ is 0.0272 relative to the PMS eigenvalues and 0.0266 relative to the KKR eigenvalues. These errors can be reduced to 0.0072 and 0.0088 by doing two diagonalizations using $E_\nu=0.3$ as well as $E_\nu=0.6$. The rms errors could be reduced still further to 0.0048 and 0.0081 by doing diagonalizations at values of E_ν of 0.2, 0.4, and 0.6, but this would not be useful in most cases.

It is possible to get a good feeling for the errors caused by the linearization process by comparing the PMS eigenvalues in Table II with the ones calculated from the LKKR. Roughly, the errors become significant when the magnitude of $E-E_\nu$ exceeds 0.2.

There seems to be no advantage in using more than one pivotal energy E_0 for a fcc structure like the one in this example, but for a more open structure there might be.

TABLE I. Parameters for the PMS equations calculated from the paramagnetic nickel muffin-tin potential with $E_0=0.6$, in dimensionless units.

$l=$	0	1	2	3	4
E_l^J	0.7572	0.5619	−0.0168	0.4500	0.5125
E_l^N	4.1783	1.8703	0.6015	4.5234	7.3183
$I_l^N(E_0)$	0.0169	−0.0097	−0.0185	−1.4600	−27.2400
C_l^0	0.1143	−0.1218	−0.6989	−0.3122	−0.2402
$I_l^J(E_0)$	−0.0848	0.0071	0.0010	0.0263	0.0317
S_l^0	−0.2358	−0.1545	−1.5110	−0.3441	−0.2634
ρ_l^0	−0.1991	−1.364	−19.16	−55.49	−859.0

TABLE II. Eigenvalues for the paramagnetic nickel muffin-tin potential calculated for various values of $\vec{k}$ lying on the line Δ that connects the center of the fcc Brillouin zone to the midpoint of the square face.

	$l_{\max}^{\text{KKR}}=4$	PMS $E_0=0.60$	LKKR $E_0=0.60$ $E_\nu=0.60$	LKKR $E_0=0.60$ $E_\nu=0.40$	LKKR $E_0=0.60$ $E_\nu=0.30$	LKKR $E_0=0.60$ $E_\nu=0.20$	$l_{\max}^{\text{KKR}}=2$
$k=0.00$							
Γ_1	0.0188	0.0271	−0.0670	−0.0087	0.0089	0.0201	0.0188
Γ_{12}	0.6840	0.6834	0.6799	0.6499	0.6270	0.6005	0.6846
$\Gamma_{25'}$	0.5977	0.5979	0.5979	0.5769	0.5552	0.5288	0.5988
$k=0.25$							
Δ_1	0.0837	0.0928	0.0217	0.0694	0.0827	0.0902	0.0837
Δ_1	0.6622	0.6619	0.6598	0.6315	0.6089	0.5824	0.6635
Δ_5	0.6165	0.6163	0.6161	0.5926	0.5707	0.5445	0.6179
Δ_2	0.6925	0.6920	0.6878	0.6574	0.6346	0.6082	0.6932
$\Delta_{2'}$	0.5740	0.5747	0.5742	0.5574	0.5366	0.5108	0.5758
$k=0.50$							
Δ_1	0.2526	0.2591	0.2164	0.2529	0.2586	0.2581	0.2526
Δ_1	0.6301	0.6298	0.6293	0.6061	0.5859	0.5621	0.6328
Δ_5	0.6680	0.6674	0.6650	0.6368	0.6148	0.5891	0.6700
Δ_2	0.7133	0.7136	0.7072	0.6761	0.6536	0.6276	0.7140
$\Delta_{2'}$	0.5194	0.5213	0.5159	0.5119	0.4937	0.4693	0.5214
$k=0.75$							
Δ_1	0.3743	0.3735	0.3283	0.3729	0.3703	0.3581	0.3744
Δ_1	0.7494	0.7404	0.7315	0.6984	0.6762	0.6513	0.7541
Δ_1	1.8503	1.6642	2.0480	2.0350	2.0220	2.0060	1.8681
Δ_5	0.7320	0.7309	0.7241	0.6939	0.6725	0.6480	0.7332
Δ_2	0.7345	0.7338	0.7267	0.6956	0.6736	0.6482	0.7349
$\Delta_{2'}$	0.4679	0.4718	0.4547	0.4680	0.4531	0.4304	0.4689
$k=100$							
X_1	0.3810	0.3714	0.3168	0.3781	0.3740	0.3585	0.3811
X_1	1.5186	1.3655	1.6320	1.6440	1.6390	1.6280	1.5193
$X_{4'}$	0.9593	0.9282	0.9288	0.9285	0.9275	0.9253	0.9695
X_2	0.7435	0.7426	0.7349	0.7039	0.6821	0.6571	0.7436
X_3	0.4474	0.4522	0.4281	0.4501	0.4369	0.4151	0.4476
X_5	0.7637	0.7622	0.7533	0.7234	0.7026	0.6789	0.7639

A rather different approach to solving the PMS equations in the form they take in (7.21) is to note that they are essentially quadratic in E. Higher powers of E arise in the expansion of the denominator times the second term in (7.18), but that whole term is small in general. Therefore, rather than linearizing the PMS equations about several values of E_ν, it might be better to quadraticize them about one value. The numerical procedures for taking advantage of this form of the equations are not as available as they are for linearized equations, but we are investigating this approach.

VIII. COMPARISONS WITH PREVIOUS WORK

The first band-theory technique that was linearized in the sense in which that term has been used in this paper is the LMTO technique of Andersen.[11] The LASW technique of Williams *et al.*[12] came later, but for the purposes of making a comparison with the developments in this paper it turns out to be easier to first establish the connection with the LASW and then the LMTO.

The ASW method is a Rayleigh-Ritz variational calculation based on a particular choice of basis functions, $\Phi_L^n(\vec{r})$. When the point $\vec{r}$ is in the neighborhood of the nth scatterer,

$$\Phi_L^n(\vec{r})=\alpha_0\tilde{N}_L(\alpha_0,\vec{r}_n)\,, \tag{8.1}$$

where $\alpha_0=\sqrt{E_0}$ and $\tilde{N}_L(\alpha,\vec{r})$ is the function introduced in Sec. VI. The function $\Phi_L^n(\vec{r})$ is defined to be given by the combination

$$\Phi_L^n(\vec{r})=\sum_{L'}\tilde{J}_{L'}(\alpha_0,\vec{r})B_{L'L}^n(E_0)\,, \tag{8.2}$$

when $\vec{r}$ is, for example, near the scatterer in the central cell. The function $\tilde{J}_L(\alpha,\vec{r})$ is the other ASW introduced in Sec. VI. The coefficients $B_{L'L}^n(E)$ are given in (4.20). The Bloch sum of these trial functions

$$\chi_L^{\vec{k}}(\vec{r}) = \sum_n e^{i\vec{k}\cdot\vec{R}_n}\Phi_L^n(\vec{r}) , \tag{8.3}$$

is then

$$\chi_L^{\vec{k}}(\vec{r}) = \alpha_0\tilde{N}_L(\alpha_0, \vec{r}) + \sum_{L'} \tilde{J}_{L'}(\alpha_0, \vec{r})B_{L'L}(E_0, \vec{k}) , \tag{8.4}$$

because of (4.21).

It should be pointed out that the relation (8.2) is simply part of the definition of $\Phi_L^n(\vec{r})$ and does not follow from mathematical necessity as does the relation between the $N_L(E, \vec{r}_n)$ and $J_L(E, \vec{r})$ in (4.18) and (4.17).

For a muffin-tin potential the elements of the Hamiltonian matrix

$$\int \chi_{L'}^{\vec{k}}(\vec{r})^*[-\nabla^2 + v_0(r)]\,\chi_L^{\vec{k}}(\vec{r})\,dv = H_{L'L}(\vec{k}) , \tag{8.5}$$

are given by

$$\begin{aligned} H_{L'L}(\vec{k}) = {} & \alpha_0^2\langle\tilde{N}_l^2\rangle E_l^N\delta_{L'L} \\ & + [\alpha_0\langle\tilde{N}_{l'}\tilde{J}_{l'}\rangle E_{l'}^J + \alpha_0\langle\tilde{N}_l\tilde{J}_l\rangle E_l^N]B_{L'L} \\ & + \sum_{L''} B_{L'L''}E_{l''}^J\langle\tilde{J}_{L''}^2\rangle B_{L''L} . \end{aligned} \tag{8.6}$$

The integrals

$$\langle\tilde{N}_l^2\rangle = \int_0^w r^2\tilde{N}_l(\alpha_0, r)^2\,dr , \tag{8.7}$$

and

$$\langle\tilde{J}_l^2\rangle = \int_0^w r^2\tilde{J}_l(\alpha_0, r)^2\,dr , \tag{8.8}$$

should be over the central unit cell, but are normally taken over a Wigner-Seitz sphere. By an application of Green's theorem, it can be shown that

$$\alpha_0\langle\tilde{N}_l\tilde{J}_l\rangle = 1/(E_l^J - E_l^N) . \tag{8.9}$$

Inserting this into (8.6) leads to ASW equations essentially identical with Eqs. (29) or (A13) of Ref. 12 except they do not contain the so-called combined corrections which will be discussed later. The elements of the overlap matrix

$$\int \chi_{L'}^{\vec{k}}(\vec{r})^*\chi_L^{\vec{k}}(\vec{r})\,dv = O_{L'L} , \tag{8.10}$$

may be obtained from (8.6) by setting E_l^J and E_l^N equal to unity.

These matrices should be compared with the symmetrical Hamiltonians and overlap matrices in (7.20). Let us forget for the moment about the derivatives S_l^0 and C_l^0 and carry out the multiplication indicated in (7.19). It is convenient to pre- and post-multiply by $(E_l^J - E)/(E_l^J - E_l^N)$ rather than just $E_l^J - E$. The result may be simplified to

$$\begin{aligned} M_{L'L}^S \cong {} & \frac{(E_l^N - E)}{(E_l^J - E_l^N)}\alpha_0\rho^0\delta_{L'L} \\ & + \left[1 + \frac{E_{l'}^N - E}{(E_{l'}^J - E_{l'}^N)} + \frac{E_l^N - E}{(E_l^J - E_l^N)}\right]B_{L'L} \\ & + \sum_{L''} B_{L'L''}\frac{E_{l''}^J - E}{E_{l''}^J - E_{l''}^N}\,\frac{1}{\alpha_0\rho_{l''}^0}B_{L''L} , \end{aligned} \tag{8.11}$$

if we assume that E is approximately equal to E_l^N for $l = 0, 1, \ldots, l_1$ and E is approximately equal to E_l^J for $l = l_1 + 1, l_1 + 2, \ldots, l_{\max}$. In this equation, we have ignored products like $(E_l^N - E)(E_{l'}^N - E)$, $(E_l^N - E)(E_{l''}^J - E)$, or $(E_{l''}^J - E)^2$. Carrying through this philosophy, for $l = 0, 1, \ldots, l_1$, we will replace $\phi_l(E_0, r)$ with $\tilde{N}_l(\alpha_0, r)$ in the integrals that are used to obtain ρ_l^0 from (7.16). For $l = l_1 + 1, l_1 + 2, \ldots, l_{\max}$ we replace $\phi_l(E_0, r)$ by $\tilde{J}_l(\alpha_0, r)$ in those integrals. Using (8.9) it can then be shown that within these approximations

$$\alpha_0\rho_l^0 = \alpha_0^2\langle\tilde{N}_l^2\rangle(E_l^J - E_l^N) ,$$
$$l = 0, 1, \ldots, l_1 , \tag{8.12}$$

and

$$1/\alpha_0\rho_l^0 = \langle\tilde{J}_l^2\rangle(E_l^J - E_l^N) ,$$
$$l = l_1 + 1, l_1 + 2, \ldots, l_{\max} . \tag{8.13}$$

Inserting these expressions into (8.11) leads to

$$\begin{aligned} M_{L'L}^S = {} & \alpha_0^2\langle\tilde{N}_l^2\rangle(E_l^N - E)\delta_{L'L} + [\alpha_0\langle\tilde{N}_{l'}\tilde{J}_{l'}\rangle(E_{l'}^J - E) \\ & + \alpha_0\langle\tilde{N}_l\tilde{J}_l\rangle(E_l^N - E)]B_{L'L} \\ & + \sum_{L''} B_{L'L''}\langle\tilde{J}_{L''}^2\rangle(E_{l''}^J - E)B_{L''L} . \end{aligned} \tag{8.14}$$

Clearly, the Hamiltonian and overlap matrices that arise in the ASW approach are the energy-independent terms and the terms that multiply minus E in this matrix. It is also easy to see how the energy can be replaced by $E - E_\nu$ as in the PMS equations by reinterpreting E_l^N and E_l^J as $E_l^{N'}$ and $E_l^{J'}$.

The only remaining difference between this approximation to the PMS equations and the ASW is that the summation index L'' ranges only over $l'' = l_1 + 1, l_1 + 2, \ldots, l_{\max}$ in (8.14). This difference is typical of the difference in formulas arrived at by partitioning a multiple-scattering result and those obtained by a variational approach. This point will be discussed in more detail below, but the extra terms have relatively little effect on the final calculations and one could just arbitrarily extend the range of summation.

By the set of approximations and maneuvers outlined above, it is possible to start with the PMS equations and arrive at the basic ASW equations.

The MTO equations[11] are obtained by making a further approximation. Andersen introduces a function $\phi_l(E_\nu, r)$ that is a solution of a radial equation

$$[-D_r^l + v_0(r) - E_\nu]\,\phi_l(r) = 0\,, \tag{8.15}$$

with D_r^l the usual operator

$$D_r^l = -r^{-2}\frac{d}{dr}r^2\frac{d}{dr} + l(l+1)r^{-2}\,. \tag{8.16}$$

The only boundary condition on this function is that it is regular at the origin so it can be calculated for any energy E_ν. The function is normalized within the Wigner-Seitz sphere

$$\langle\phi_l^2\rangle = 1\,, \tag{8.17}$$

and from this it follows that

$$\langle\phi_l\dot{\phi}_l\rangle = 0\,, \tag{8.18}$$

where the function $\dot{\phi}_l(r)$ is obtained by taking the partial derivative with respect to energy of $\phi_l(r)$ point by point. It is a solution of the inhomogeneous equation

$$[-D_r^l + v_0(r) - E_\nu]\dot{\phi}_l(r) = \phi_l(r)\,. \tag{8.19}$$

In the MTO approach the radial functions that enter the theoretical development are all expanded as linear combinations of $\phi_l(r)$ and $\dot{\phi}_l(r)$ in a sort of functional Taylor's series expansion, retaining only the first two terms.

Let us express the functions that appear in the ASW development as such a Taylor's expansion,

$$\alpha_0\tilde{N}_l(\alpha_0, r) \cong a_l(\alpha_0)^{-1}[\phi_l(r) - \omega_l^N(\alpha_0)\dot{\phi}_l(r)] \tag{8.20}$$

and

$$\tilde{J}_l(\alpha_0, r) \cong a_l(\alpha_0)\frac{\phi_l(r) - \omega_l^J(\alpha_0)\dot{\phi}_l(r)}{\omega_l^J(\alpha_0) - \omega_l^N(\alpha_0)}\,. \tag{8.21}$$

The way the fitting parameters $a_l(\alpha_0)$, $\omega_l^J(\alpha_0)$, and $\omega_l^N(\alpha_0)$ have been inserted in these equations is for convenience in writing the answer we will obtain. Using (8.17) and (8.18) it follows that:

$$\begin{aligned}
&\alpha_0^2\langle\tilde{N}_l^2\rangle = a_l^{-2}(1 + \omega_l^{N^2}\langle\dot{\phi}_l^2\rangle)\,,\\
&\langle\tilde{J}_l^2\rangle = \frac{1 + \omega_l^{J^2}\langle\dot{\phi}_l^2\rangle}{(\omega_l^J - \omega_l^N)^2}a_l^2\,,\\
&\alpha_0\langle\tilde{N}_l\tilde{J}_l\rangle = \frac{1 + \omega_l^J\omega_l^N\langle\dot{\phi}_l^2\rangle}{\omega_l^J - \omega_l^N}\,.
\end{aligned} \tag{8.22}$$

The functions on the right of (8.20) and (8.21) are not eigenfunctions of the radial equation like true ASW's, but the expectation value of their energy can be interpreted as an approximation to the eigenvalue

$$\alpha_0\langle\tilde{N}_l^2\rangle(E_l^N - E_\nu) = \alpha_0^2\langle\tilde{N}_l\,|\,-D_r^l + v_0(r) - E_\nu\,|\tilde{N}_l\rangle\,, \tag{8.23}$$

or

$$\alpha_0^2\langle\tilde{N}_l^2\rangle(E_l^N - E_\nu) = a_l^{-2}\omega_l^N\,. \tag{8.24}$$

Similarily

$$\langle\tilde{J}_l^2\rangle(E_l^J - E_\nu) = a_l^2\omega_l^J\,, \tag{8.25}$$

and an analogous argument leads to

$$\alpha_0\langle\tilde{N}_l\tilde{J}_l\rangle(E_l^J - E_\nu) = \omega_l^J/(\omega_l^J - \omega_l^N)\,, \tag{8.26}$$

and

$$\alpha_0\langle\tilde{N}_l\tilde{J}_l\rangle(E_l^N - E_\nu) = \omega_l^N/(\omega_l^J - \omega_l^N)\,. \tag{8.27}$$

Multiplying through the matrix in (8.14) on both sides by a_l and using (8.22) through (8.27) leads to

$$\begin{aligned}
a_{l'}M^S_{L'L}a_l = {}&[\omega_l^N - (E - E_\nu)(1 + \omega_l^{N^2}\langle\dot{\phi}_l^2\rangle)]\delta_{L'L} + \left(\frac{\omega_{l'}^J - (E - E_\nu)(1 + \omega_{l'}^J\omega_{l'}^N\langle\dot{\phi}_{l'}^2\rangle)}{\omega_{l'}^J - \omega_{l'}^N} + \frac{\omega_l^N - (E - E_\nu)(1 + \omega_l^J\omega_l^N\langle\dot{\phi}_l^2\rangle)}{\omega_l^J - \omega_l^N}\right)\\
&\times a_{l'}B_{L'L}a_l + \sum_{L'} a_{l'}B_{L'L''}a_{l''}\frac{\omega_{l''}^J - (E - E_\nu)(1 + \omega_{l''}^{J^2}\langle\dot{\phi}_{l''}^2\rangle)}{(\omega_{l''}^J - \omega_{l''}^N)^2}a_{l''}B_{L''L}a_l\,.
\end{aligned} \tag{8.28}$$

The pivotal energy E_0 is always zero in the MTO approach. Passing to the limit, we can identify the quantities that appear in Andersen's MTO equations.

$$\begin{aligned}
&\lim_{E_0\to 0} a_{l'}(\alpha_0)B_{L'L}(E_0, \mathbf{k})a_l(\alpha_0) = S^{\mathbf{k}}_{L'L}\,,\\
&\lim_{E_0\to 0} \omega_l^J(\alpha_0) = \omega(l)\,,\\
&\lim_{E_0\to 0} \omega_l^N(\alpha_0) = \omega(-l-1)\,.
\end{aligned} \tag{8.29}$$

Carrying out this operation on (8.28) and picking out the usual terms leads to Eqs. (4.9) and (4.10) of Ref. 11 for the Hamiltonian and overlap matrices of the LMTO formalism for the case $D_L = -l - 1$.

One difference between the MTO approach and both the PMS and ASW approaches is that in the latter all of the essential calculations are carried out for $E = E_0$ and the transformation of the energy variable to $E - E_\nu$ is trivial. In the MTO, at least in principle, the functions $\phi_l(E_\nu, r)$ and $\dot{\phi}_l(E_\nu, r)$ must be recalculated for each choice of E_ν. The approximation being made is that the functions on the left of (8.20) and (8.21) can be approximated as indicated for any E_ν.

The manipulations that I have gone through have produced what Andersen has called the important matrices of the LMTO formalism.[11] They are the results obtained in the most straightforward way by the application of the Rayleigh-Ritz variational method to the MTO or ASW trial functions, but so called combined correction terms must be added to them in actual applications. The derivatives C_l^0 and S_l^0 were ignored in Eq. (8.11). It is easy to see from Table I that this is not a good approximation. These quantities can be included in the discussion, and they will lead to terms analogous to the combined corrections of MTO or ASW theory. Some tedious and not very informative algebra leads to the result that, as with the more important terms described above, the proper manipulations of the PMS equations lead to results that are similiar to but not identical with the ones obtained from the other approaches.

It is clear that the asymmetrical Hamiltonian and overlap matrices used in the calculations in Sec. VII have no counterpart in the MTO or ASW approaches. The reason for this is that E_0 in the MTO formalism is always zero while in the ASW calculations reported[12] it was -0.01. The E_l^J are very small or negative for such values of E_0. With the other approximations that are made the spurious zeros that arise from them are probably not too noticeable in the results since they lie outside the range of the bands of interest. It is expected on this basis that the ASW equation derived for positive E_0[(A13) of Ref. 12] would have a rather small region of convergence.

For the muffin-tin potential and fcc structure used in the numerical example in the preceding section the $l_{\text{max}} = 4$ KKR calculations are exact to within the significant figures reported. The PMS equations lead to those same results at E_0, and are seen to diverge from the exact results very slowly as $|E - E_0|$ increases. From this point of view, the further approximations that must be made to obtain the ASW or MTO equations will not be helpful. The addition of actual non-muffin-tin terms in the potential is also quite easy within the PMS framework, although the approximation being made is more apparent than it is in the other formalisms.

It should be obvious that the derivations in Sec. VII were inspired by the very real successes of the MTO and ASW formalisms. There is a significant difference in the philosophy of the various derivations that is worth investigating, however. The question is whether it is better to add a variational step or to stay within the multiple-scattering formalism when deriving simplified band-theory equations. This question is not well posed from a mathematical point of view, but we have shown by example that it is not necessarily better to add such a step. Perhaps some further remarks on this question will be helpful.

The most frequently quoted authority for the idea that the inclusion of a variational step will bring improvements to the multiple-scattering equations is a paper by Andersen and Kasowski[23] (AK) in which an early version of the MTO formalisms was compared with the results of a KKR calculation. The conclusions were that both the convergence of the eigenvalues was improved and the wave functions were more accurately represented. From the point of view of a KKR practitioner the version of that theory that was considered by AK is a highly simplified one. In particular, it did not include the partitioning or treatment of the wave functions described in Sec. III.

Indeed, it has already been pointed out by Williams[24] that the AK equations for a muffin-tin potential can be obtained by replacing the phase shifts in the matrix $\underline{R}_{22}$ in (3.13) with their Born approximation values and then extending the sum from $l'' = 0$ to l_{max}. That is, the matrix in (3.13) is replaced by

$$\underline{M} = \underline{M}_{11} + \underline{M}_{12}\underline{R}_{22}^B\underline{M}_{21} + \underline{M}_{11}\underline{R}_{11}^B\underline{M}_{11}, \tag{8.30}$$

where

$$R_{L',L}^B = -(1/\alpha)\tan\eta_l^B\,\delta_{L',L}\,. \tag{8.31}$$

In order to appreciate what this means it is best to look at some actual calculations.

Figure 5 shows the results of a calculation of

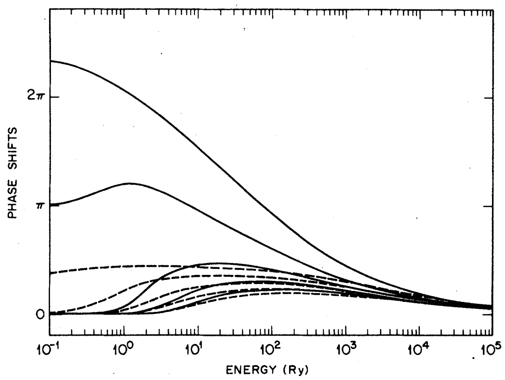

FIG. 5. Phase shifts, η_l, calculated for an aluminum muffin-tin potential as a function of energy in rydbergs. The solid lines are the η_l from (6.14) and the dotted lines are the η_l^B calculated with the Born approximation. Note the logarithmic energy scale. The magnitude of the phase shift for a given energy decreases as l increases from its minimum value of zero to its maximum of four.

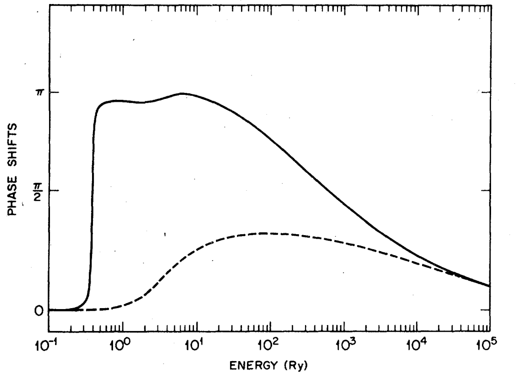

FIG. 6. *d*-phase shift η_2 calculated for a copper muffin-tin potential as a function of energy. The Born approximation η_2^B is shown with a dotted line. Note the logarithmic energy scale.

the phase shifts for an aluminum muffin-tin potential over a very wide range of energies. The logarithmic energy scale should be noted. The phase shifts all go to zero for very high energies and they have the values near zero energy that they should have by Levinson's theorem. It can be seen that the Born phase shifts indicated by the dotted lines in this figure become really good approximations only for energies in the range of 10 000–100 000 Ry. The Born approximation is not too bad at low energies for large enough l because the behavior of the phase shifts is dominated by the asymptotic form of their energy dependence which the Born approximation gets right. For lower values of l, however, the approximation is not good even if we ignore the additive multiples

TABLE III. Eigenvalues for various muffin-tin potentials calculated for $\vec{k}=(0.0, 0.0, 0.5)$. The truncated KKR results are the zeros of the determinant of the matrix in (3.6) with $l_{\max}=2$ for Nb and Rb and $l_{\max}=1$ for Al. The partitioned KKR results are obtained from the matrix in (3.13) with $l_{\max}=4$ and $l_1=2$ for Nb and Rb and $l_1=1$ for Al. The calculations of the results labeled Born made use of the first two terms in (8.30), while the Andersen-Kasowski (AK) calculations made use of all three, the values of $l_{\max}$ and l_1 being the same as above. The errors relative to the KKR eigenvalues calculated with $l_{\max}=4$ appear below the approximate eigenvalues. These errors are calculated from (8.32). The dimensionless energy units used in this table can be converted to rydbergs by multiplying the Nb, Rb, and Al values by 1.0173, 0.3423, and 0.6741.

	$l_{\max}^{\mathrm{KKR}}=4$	KKR partitioned	Born	AK	KKR truncated
Niobium					
	0.4683	0.4683	0.4684	0.4684	0.4686
		4.3	17.4	21.7	
	0.5288	0.5292	0.5334	0.5332	0.5436
		2.2	30.7	29.9	
	0.6862	0.6863	0.6898	0.6898	0.6974
		0.5	31.3	31.3	
	0.7872	0.7870	0.7919	0.7918	0.8016
		−1.1	32.7	32.2	
	0.9549	0.9552	0.9568	0.9567	0.9598
		7.6	39.3	38.1	
Rubidium					
	0.0674	0.0674	0.0674	0.0674	0.0675
		0.0	−41.7	−41.7	
	0.2615	0.2617	0.2603	0.2601	0.2660
		2.9	−28.6	−32.7	
	0.3030	0.3034	0.3024	0.3020	0.3062
		12.2	−19.8	−33.5	
	0.3763	0.3763	0.3753	0.3752	0.3802
		−0.4	−27.7	−29.8	
	0.3817	0.3820	0.3813	0.3811	0.3846
		10.9	−13.2	−19.9	
Aluminum					
	−0.0825	−0.0822	−0.0822	−0.0823	−0.0798
		10.2	10.2	8.7	
	1.0989	1.0993	1.0988	1.0973	1.1690
		0.6	−0.1	−2.3	
	1.1606	1.1954	1.2052	1.2021	1.2263
		52.9	67.9	63.2	

of π. Another case for which the Born approximation must be bad at low energies is illustrated in Fig. 6. The $l=2$ phase shift for a copper muffin-tin is plotted there. This potential has a d-scattering resonance at about 0.3 Ry that appears as a rapid rise in the phase shift that clearly cannot be reproduced by the Born approximation. These calculations demonstrate that the Born approximation will be particularly bad at low energies for $l=0$, 1, and 2 when dealing with a transition metal and 0 and 1 for a nontransition metal.

Table III shows the results of KKR calculations done with $l_{\max}=4$ and $l_{\max}=l_1$ where $l_1=2$ for Nb and Rb and $l_1=1$ for Al. The values shown are calculated with the various approximations that have been described. Since the eigenvalues calculated with $l_{\max}=l_1$, E_{l_1} are uniformly larger than those for $l_{\max}=4$, E_4, the deviation of any approximate eigenvalue from E_4, $\mathcal{E}$, is given as a percent of the error introduced by simply truncating the KKR matrix,

$$\mathcal{E}=\frac{E_{\text{app}}-E_4}{E_{l_1}-E_4}\times 100\% . \tag{8.32}$$

The results designated as partitioned were obtained using just (3.12). The ones called Born were obtained from (3.12) but replacing the phase shifts for l_1+1, $l_1+2,\ldots,l_{\max}$ with their Born approximation values. That is, using the first two terms in (8.30). Finally, the AK results are gotten by extending the sum in the partitioned term over all l, the full matrix in (8.30).

It can be seen from Table III that, as claimed, the AK eigenvalues are an improvement over the truncated KKR. However, the eigenvalues would have been slightly better if they had not included the last term in (8.30), and much better results are obtained using the actual phase shifts in a partitioned KKR calculation rather than the Born approximation.

From the point of view of multiple scattering it is surprising that the AK eigenvalues are as good as they are. The resolution of this dilemma was also indicated by Williams *et al.*[24] Since the Born approximation matrix $\underline{R}^B_{11}$ is bracketed by the KKR matrices $\underline{M}_{11}$, it does not make much difference what is in it.

The purpose of these numerical studies is not to attack the Andersen-Kasowski theory which is no longer used in any case. The calculations show that improvements in multiple-scattering results obtained by introducing a variational step can sometimes be more apparent than real. They also justify an earlier assertion in this section, that it does not matter very much if the sums in a partitioned term are extended to low l.

I do not claim to have answered in general the question of whether Rayleigh's variational method needs to be brought to the aid of one of his other inventions, the multiple scattering method. I do claim, however, that simplified and linearized band-theory equations with very desirable features can be found without that step.

IX. CONCLUSIONS

The multiple-scattering theory will never play as central a role in quantum physics as does the Rayleigh-Ritz variational method or the Rayleigh-Schrödinger perturbation theory, but there are classes of problems for which it is uniquely well suited. I hope I have demonstrated that the singular functions described in Sec. IV are a useful addition to this theory. These functions were introduced and discussed from a different point of view in a previous publication.[25]

The usefulness of the PMS equations and the linearized KKR should be obvious from the example shown. The fact that these equations yield exactly the same results as a completely converged KKR calculation at any one energy is very attractive to those of us who have been utilizing the constant-energy-search KKR method.[26] By choosing the pivotal energy to be the Fermi energy, we can reap the advantages of a linearized band theory without introducing unacceptable errors into the calculations of the states on and near the Fermi surface.

One of the avenues of research I hope to see pursued is the development of techniques to take advantage of the fact that the PMS equations are almost exactly quadratic in the energy.

It will be interesting to see how effective these equation are in dealing with non-muffin-tin potentials. Of course, the linearized KKR should work at least as well as any of the other linearized band theories for this case. A point to bear in mind is that although the calculation of the near-field corrections to the structure constant might be too time consuming in the usual band-theory approach, it should be possible to calculate them for one or two energies. This would be one way to improve the calculations if they are not satisfactory.

Finally, it is interesting to consider how these methods might be used in coherent-potential-approximation (CPA) calculations on alloys. The atomic sphere approximation (ASA) idea of Andersen[11] has already been used in this connection,[27] but it was not too helpful. The structure constants were only calculated at one energy but the equation for the self-energy had to be solved iteratively for many energies. Since this process requires many Brillouin zone integrals, the relatively small amount of time saved on structure constant calculations is unimportant. It is for this reason that the muffin-tin CPA equations are now solved without this approximation.[28] If the parameterization of the reaction matrix that leads to the PMS equations could be used to reduce the number of energies at which iterations must be carried out, there would be a considerable saving of time.

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