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Comments

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Non-muffin-tin band theories of the multiple-scattering type

J. S. Faulkner
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
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Numerical calculations on an empty-lattice model are used to illustrate the fact that the greatest improvement in the accuracy of the eigenvalues for a non-muffin-tin potential comes from the inclusion of the off-diagonal elements of the scattering matrices. The eigenvalues calculated with a recently proposed formulation are seen to be no better than those obtained with other schemes that ignore near-field corrections.

The band-theory equations derived from multiple-scattering theory[1-4] by Korringa[5] and from an equivalent integral formulation by Kohn and Rostoker[6] have played a central role in calculations of the properties of solids using the local-density approximation. These Korringa-Kohn-Rostoker (KKR) equations are well adapted to digital computers, and they can be applied with equal accuracy to simple metals, transition metals, or rare earths. The multiple-scattering approach has proved useful in deriving fast-band-theory equations[7-10] that have the speed of interpolation schemes and the accuracy of first-principles methods. Also, the KKR coherent-potential-approximation equations for calculating the electronic[11-13] states of substitutional solid-solution alloys are derived from multiple-scattering theory.

In their original form, the KKR equations were worked out for a crystal potential $V(\mathbf{r})$ that has the muffin-tin form. Such a potential is spherically symmetric within a set of nonoverlapping spheres, and is constant outside these spheres. The energy scale is always adjusted so that the potential in the region between the spheres, called the interstitial region, is equal to zero. Although muffin-tin models have proved to be accurate enough in many applications, there are cases for which more accuracy is needed. Much effort has been made over the years to derive band-theory equations from multiple-scattering theory without using the muffin-tin approximation.[9,14-21] Some of the resulting equations were investigated numerically, but in other studies the only justification for the equations are the algebraic virtues that they are perceived to have by their authors. The purpose of the present paper is to comment on some questions concerning non-muffin-tin effects in band theory that have recently arisen and to illustrate these comments with some specific calculations. The remarks are relevant to the other applications of multiple-scattering theory as well.

The empty-lattice model is a simple non-muffin-tin model for which the exact eigenvalues are known. It has been used by band theorists since the 1930s. The crystal potential for this model can be written

$$V(\mathbf{r}) = -\Delta \sum_i \sigma(\mathbf{r}-\mathbf{R}_i) \ , \tag{1}$$

where $\mathbf{R}_i$ are the lattice vectors for the chosen lattice. The function $\sigma(\mathbf{r})$ is a step function which has the value one when $\mathbf{r}$ is inside the unit cell and zero when $\mathbf{r}$ is outside. The unit cells are most conveniently viewed as the Wigner-Seitz cells that show the symmetry of the crystal. Since the unit cells that are being summed over in (1) fill all space, it is equally accurate to say that $V(\mathbf{r})$ is a constant $-\Delta$. The eigenvalues $E(\mathbf{k})$ that should be obtained from a band-theory calculation with this potential are obviously the free-electron eigenvalues $E_0(\mathbf{k})$ measured from $-\Delta$. When $V(\mathbf{r})$ is taken to be the sum of nonoverlapping potentials, as in (1), the volume of the interstitial region has shrunk to zero. The interstitial region is just the part of space that is within the distance ϵ of the surface of the unit cells, in the limit as ϵ approaches zero.

The KKR equations for a non-muffin-tin potential that I derived[9] may be written as a set of simultaneous algebraic equations

$$\sum_{L'} M_{LL'} C_{L'} = 0 \ , \tag{2}$$

in which the indices L represent the pair of angular momentum quantum numbers l and m. The eigenvalues $E(\mathbf{k})$ are the values for which the determinant of the matrix of coefficients is zero

$$\det \underline{M}(E,\mathbf{k}) = 0 \ . \tag{3}$$

The matrix $\underline{M}(E,\mathbf{k})$ is shown to be

$$\underline{M}(E,\mathbf{k}) = \underline{X}(E) + \underline{B}(E,\mathbf{k}) + \underline{N}(E,\mathbf{k}) \ , \tag{4}$$

where $\underline{X}(E)$ is a matrix that describes the scattering from the potential in the central cell $v(\mathbf{r})$ as if it were embedded in a vacuum, and the $\underline{B}(E,\mathbf{k})$ are certain structure constants that may be calculated for a given crystal structure[22] using a technique invented by Ewald. The elements of $\underline{N}(E,\mathbf{k})$ were dubbed near-field corrections by Ziesche.[17] The formula that I derived for them differs from Ziesche's, and I will soon publish yet another version, but the nomenclature is still apt because the lattice sums are over only a

few sites in the neighborhood of the central one. As was mentioned before, the energy E that appears in these matrices is measured relative to the constant value that $V(\mathbf{r})$ takes on in the interstitial region. There must always be an interstitial region in order to apply multiple-scattering theory, even though its volume may go to zero.

The potential function for the central cell in the empty-lattice model,

$$\underline{v}(\mathbf{r}) = -\Delta\sigma(\mathbf{r}), \tag{5}$$

is highly aspherical since it has the sharp corners typical of a Wigner-Seitz cell. It can be expanded for lattices that have cubic point-group symmetry as

$$v(\mathbf{r}) = -\Delta \sum_l \omega_l(r) K_l(\mathbf{r}) \ , \tag{6}$$

where $K_l(\mathbf{r})$ is a cubic harmonic. There is only one cubic harmonic for each l of value 0, 4, 6, or 8 and higher angular momenta will be ignored. The scattering matrix $\underline{X}(E)$ is written

$$\underline{X}(E) = \kappa \underline{c}(E) \underline{s}(E)^{-1} \ , \tag{7}$$

with κ being the square root of E. The elements of the cosine and sine matrices are

$$c_{LL_0}(E) = -\kappa\Delta \sum_{L_1} \int_0^s n_l(\kappa r)\omega_{LL_1}(r)\phi_{L_1L_0}(E,r)r^2dr - \delta_{LL_0} \ ,$$
$$s_{LL_0}(E) = -\kappa\Delta \sum_{L_1} \int_0^s j_l(\kappa r)\omega_{LL_1}(r)\phi_{L_1L_0}(E,r)r^2dr \ , \tag{8}$$

where

$$\omega_{L_1L_2}(r) = \sum_l C^l_{L_1L_2}\omega_l(r) \ , \tag{9}$$

and the constants in this expression are the Gaunt factors

$$C^l_{L_1L_2} = \int Y_{l_1m_1}(\mathbf{r}) K_l(\mathbf{r}) Y_{l_2m_2}(\mathbf{r}) d\Omega \ , \tag{10}$$

the $Y_{lm}(\mathbf{r})$ being real spherical harmonics. The functions $\phi_{LL_0}(E,r)$ are solutions of the integral equations

$$\phi_{LL_0}(E,r) = j_l(\kappa r)\delta_{LL_0} - \Delta \sum_{L_1} \int_0^r g_l(E,r,r')\omega_{LL_1}(r') \times \phi_{L_1L_0}(E,r')r'^2dr' \ , \tag{11}$$

where

$$g_l(E,r,r') = -\kappa[j_l(\kappa r)n_l(\kappa r') - n_l(\kappa r)j_l(\kappa r')] \ . \tag{12}$$

These equations for $\underline{c}(E)$ and $\underline{s}(E)$ are essentially the ones in Calogero's[23] book, and they appear much more complicated than they are. If one replaces the spherical harmonics in (10) with the linear combinations that can serve as basis functions for the point group of the crystal, many of the elements of $\underline{c}(E)$ and $\underline{s}(E)$ are zero and many of the remaining elements are equal to each other. For example, when the angular momenta l and l' in the matrix indices L and L' are allowed to range from zero to $l_{\max}=4$, the matrices in (4) will have the dimension 25. For a cubic crystal, however, only 19 of the possible 625 elements of $\underline{c}(E)$ or $\underline{s}(E)$ must be calculated.

The results of all the calculations to be discussed in this paper are summarized in Table I. The near-field corrections $\underline{N}(E,\mathbf{k})$ are set equal to zero in all of them. These corrections will be treated in a later paper. The matrices are made finite by considering only those elements for which the angular momenta satisfy $0 \leq l \leq 4$, and it follows from this that only terms corresponding to $l \leq 8$ need to be included in (6) because the Gaunt factors defined in (10) are identically zero when $l > l_1 + l_2$. This is a large number of l values for a KKR calculation. The l convergence is illustrated for this model in the calculations published by Williams and van Morgan.[16] All of the calculations are carried out on the body-centered-cubic Bravais lattice.

Attention is focused on two sets of eigenvalues. One is the set of 12 eigenvalues at the point Γ in the Brillouin zone, i.e., $\mathbf{k}=\mathbf{0}$. In the free-electron case these eigenvalues would be degenerate with energy equal to 2 in dimensionless units. In the empty-lattice model they should remain degenerate with energy $2-\Delta$, but because of the neglect of $\underline{N}(E,\mathbf{k})$ and the truncation in angular momentum this set of eigenvalues is split into five subsets corresponding to the

TABLE I. Collection of rms errors for approximate empty-lattice calculations as a function of Δ, the amount that the potential has been lowered. Dimensionless energy units are used throughout. These units are about the same as rydbergs for metallic systems. Briefly, the approximations considered are as follows: case 1—multiple-scattering formula ignoring near-field corrections; case 2—same as case 1 but scattering matrices are approximated; case 3—formula from Ref. 21; case 4—potential is replaced by its spherical average; case 5—Wigner-Seitz cell replaced by Wigner-Seitz sphere.

Δ	Exact energy	Case 1 rms error	Case 2 rms error	Case 3 rms error	Case 4 rms error	Case 5 rms error
			Eigenvalues from point Γ			
0.2	1.80	0.005 06	0.005 13	0.005 11	0.023 48	0.024 97
0.4	1.60	0.008 81	0.008 75	0.009 01	0.047 39	0.050 31
0.6	1.40	0.011 39	0.011 18	0.011 82	0.072 28	0.076 25
0.8	1.20	0.013 01	0.012 66	0.013 70	0.098 52	0.103 03
			Eigenvalues from point H			
0.2	0.8	0.000 37	0.000 42	0.000 44	0.015 12	0.016 16
0.4	0.6	0.000 87	0.001 03	0.000 58	0.030 61	0.032 63
0.6	0.4	0.003 56	0.003 92	0.002 86	0.046 83	0.049 55
0.8	0.2	0.007 73	0.008 39	0.006 46	0.064 04	0.067 07

symmetry types $\Gamma_1, \Gamma_{15}, \Gamma_{12}, \Gamma_{25'}$, and Γ_{25}. The other eigenvalues that are considered correspond to a $\mathbf{k}$ point at the corner of the Brillouin zone that is called the H point. There are six eigenvalues that have the energy 1 in the free-electron case. In these empty-lattice calculations they break up into the three sets with symmetries H_1, H_{12}, and H_{15}. The three energies that result from these empty-lattice calculations are clustered about the exact value of $1-\Delta$. The rms errors in Table I are all calculated relative to the appropriate exact value. The energies can be converted from dimensionless units to rydbergs by multiplying by the factor $(2\pi/a)^2$, where a is the lattice constant expressed in Bohr radii. This factor is about 1 for most metals, so the dimensionless units are about the same as rydbergs.

The only approximation in the calculations called case 1 in Table I is the neglect of the near-field corrections $\underline{N}(E,\mathbf{k})$. The functions $\phi_{LL_0}(E,r)$ are calculated from the coupled integral equations in (11), and then inserted in the equations in (8) to obtain the scattering matrices $\underline{c}(E)$ and $\underline{s}(E)$. The structure constants $\underline{B}(E,\mathbf{k})$ are calculated with our standard computer programs. The rms errors may not seem so small at first sight, but it should be noted that the potentials in this model calculation are much more aspherical than the potentials that appear in non-muffin-tin calculations on real metals. It was found in calculations in Rb, Nb, and Pd,[24,25] for example, that the potential differed from zero in the region between the muffin-tin sphere and the cell boundary by approximately 0.1 Ry or less. The values of Δ used in this calculation were chosen to be very much larger than that just to emphasize the point that the near-field corrections for this case are extremely small.

The calculations for case 2 are simpler than those for case 1 in that the function $\phi_{LL_0}(E,r)$ is calculated only approximately. The spherical average of the potential $v(\mathbf{r})$ in (5) will be called $v_0(r)$. It is just a constant times $\omega_0(r)$, the component of the step function for $l=0$. I calculated the solutions $F_l(E,r)$ from a radial Schrödinger equation using the potential $v_0(r)$. The normalization was chosen so that

$$\lim_{r\to 0} F_l(E,r) = j_l(\kappa r). \tag{13}$$

The scattering matrices $\underline{c}(E)$ and $\underline{s}(E)$ were calculated from (8) with the substitution

$$\phi_{LL_0}(E,r) \to F_l(E,r)\delta_{LL_0} \ . \tag{14}$$

The rms errors for this case are essentially the same as the ones for case 1. This illustrates that the error in the eigenvalues does not depend sensitively on the accuracy of the calculation of $\underline{c}(E)$ and $\underline{s}(E)$.

It might seem strange at first that some of the rms errors are smaller for case 2 than for case 1. The answer is easily found by looking at the eigenvalues. Four of the five eigenvalues corresponding to the point Γ and $\Delta=0.4$ are calculated to be greater than 1.60 in case 1. The approximation used in case 2 causes all of the eigenvalues for this $\mathbf{k}$ to be a little smaller, so it appears to diminish this particular error. The only meaningful interpretation of the results in Table I comes from looking at the overall trends.

The calculations in case 3 were done to test the equations in a recent paper by Brown and Ciftan (BC).[21] Their assertion is that the expression in (4) should be replaced by one in which $\underline{N}(E,\mathbf{k})$ is zero but the matrices $\underline{c}(E)$ and $\underline{s}(E)$ that make up $\underline{X}(E)$ should be calculated from formulas that are slightly different from the ones in (8). They would replace the solutions $\phi_{LL_0}(E,r)$ in those equations with solutions of integral equations like the ones in (11) except that the potential $v(\mathbf{r})$ is replaced by another one $u(\mathbf{r})$. Rather than going to zero at the cell boundary, the potential $u(\mathbf{r})$ is equal to the total potential $V(\mathbf{r})$ in (1) all the way to the boundary of the sphere that circumscribes the unit cell. In the empty-lattice model $u(\mathbf{r})$ is just a constant $-\Delta$, so the BC prescription is to calculate $\underline{c}(E)$ and $\underline{s}(E)$ from equations like (8) except that the replacement

$$\phi_{LL_0}(E,r) \to \left(\frac{E}{E+\Delta}\right)^{l/2} j_l(\sqrt{E+\Delta}\, r)\delta_{LL_0} \tag{15}$$

is made. The rms errors listed in Table I for case 3 are not essentially lower than those for cases 1 or 2, so the BC assertion that calculating the scattering matrices differently will reproduce the effect of near-field corrections is not justified by these calculations.

It might be thought from the rms errors for cases 1, 2, and 3 that almost any approximation will lead to about the same level of accuracy, but this is not the case. The crucial point for reducing the errors into the mRy range is to represent the off-diagonal elements in the scattering matrices $\underline{c}(E)$ and $\underline{s}(E)$ with reasonable accuracy. For example, suppose the potential $v(\mathbf{r})$ in (5) is actually approximated by its spherical average $v_0(r)$. Instead of using the solution $F_l(E,r)$ to calculate the matrix elements of $\underline{c}(E)$ and $\underline{s}(E)$ for the total $v(\mathbf{r})$, these matrices would contain only the diagonal elements

$$\begin{aligned} c_{LL_0}(E) &= \kappa S^2[n_l,F_l]\delta_{LL_0} \ , \\ S_{LL_0}(E) &= \kappa S^2[j_l,F_l]\delta_{LL_0} \ , \end{aligned} \tag{16}$$

where S is the radius of the sphere that circumscribes the potential and

$$[f,g] = f(r)\frac{dg(r)}{dr} - \frac{df(r)}{dr}g(r) \ , \tag{17}$$

evaluated at $r=S$. The results of calculations done with these formulas are shown as case 4 in Table I. The rms errors for this case are orders of magnitude larger than for the preceding cases.

The simplest calculations that I did were with an empty-lattice version of the spherical model[7] in which the unit cell is replaced by a Wigner-Seitz sphere that has the same volume. The potential $v(\mathbf{r})$ is approximated by a function that has the value $-\Delta$ when $|\mathbf{r}|$ is less than the Wigner-Seitz radius r_{WS}, and is zero otherwise. The cosine and sine matrices have only values on the diagonal elements. They are given by formulas like the ones in (16) except that S is replaced by r_{WS} and $F_l(E,r)$ is replaced by the function in (15). The rms errors for this model, referred to as case 5 in Table I, are extremely large, as would be expected.

DISCUSSION

These calculations demonstrate that a large fraction of the errors caused by ignoring the non-muffin-tin parts of a potential function can be eliminated by the simple expedient of including the nondiagonal parts of the scattering matrix. Similar, but less extensive calculations encouraged Williams

and van Morgan[16] in their belief that an equation like (4) with $\underline{N}(E,\mathbf{k})$ set equal to zero should be exact. It was later recognized that multiple-scattering theory requires near-field corrections.

Brown and Ciftan[21] did some algebra that convinced them that the effect of the near-field corrections can be completely absorbed into a scattering operation in a way that is computationally very simple. Their specific proposal was outlined in the discussion of case 3 in the preceding section. The variational step that they use on page 4573 of their paper to transform their equations into a tractable form plays a different role from the one in Ref. 6. Although Kohn and Rostoker chose to use the language of the Kohn variational theorem in the body of their paper, they prove in their Appendix 1 that the same equations can be obtained nonvariationally. It would be a reasonable assumption that the introduction of a true variational step would not help the convergence of the theory. The numerical results in Table I provide evidence for this assumption. The empty-lattice model is not very physical, but it is the only three-dimensional model of a non-muffin-tin potential that I am aware of for which the exact eigenvalues are known. As in any calculation, the series are approximated by a finite number of terms. If Brown and Ciftan's equations were truly superior to the others, however, it is reasonable to expect that they would have begun to demonstrate some systematic reduction in the error at the level of convergence attained in these calculations.

To sum up, it is my belief that the mathematical problem of finding a set of band-theory equations from multiple-scattering theory for a non-muffin-tin potential that is computationally tractable is still unsolved. However, many physically interesting problems can be treated by simply ignoring the near-field corrections.

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