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Exact eigenvalue equation for a finite and infinite collection of muffin-tin potentials

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The integral eigenvalue equation of the Hamiltonian with a finite-range potential is transformed so as to explicitly take into account the particular structure of a potential consisting of a finite collection of nonoverlapping, muffin-tin–type individual potentials (scatterers). The separation between structure and potential, thought to be obtained as an exact result in the framework of multiple-scattering theory, is found to represent an approximation which originates in having considered what is only a necessary condition to be both necessary and sufficient. As an application, the equation for the energy levels of a muffin-tin periodic potential is discussed and shown to be represented by the Korringa-Kohn-Rostoker equation only as an approximate result.

I. INTRODUCTION

Since the pioneering work of Korringa,[1] it has been traditional to study the quantum mechanics of a collection of nonoverlapping, muffin-tin–type potentials by using the multiple-scattering approach irrespective of whether the collection is finite or not.[2–7] Essentially, this approach separates the effect of the geometry (i.e., the relative positions of the scatterers) from the effect of the particular, single-scatterer potential. Aside from considerable computational advantages,[8] it has generated a rich series of developments [e.g., the Korringa-Kohn-Rostoker (KKR) equation,[1] the relativistic KKR equation, the KKR-CPA (coherent-potential-approximation) method, the rigid-muffin-tin approximation and others] in solid-state physics.[2]

Our purpose is to reconsider this separation obtained by the widely used[2–7] multiple-scattering theory for the eigenvalue equation of a finite collection of nonoverlapping (i.e., muffin-tin type) potentials and moreover (as an application obtained by modifying the boundary conditions) for an infinite collection as well. The paper is organized as follows: We first recall the (algebraic) homogeneous system of equations for the multipole coefficients of the eigenfunction of a Hamiltonian with a finite-range (and regular enough) potential—as obtained in the framework of the variable-phase method.[9] Further, we consider that the potential consists of a finite collection of identical, nonoverlapping, muffin-tin–type potentials and gradually transform the system of equations so as to reflect this particular structure of the potential. In doing so, care is taken to preserve the equivalence with the initial (integral) eigenvalue equation. Finally, as an application obtained by modifying the boundary conditions (i.e., by introducing Bloch periodicity), we discuss the case of the muffin-tin periodic potential and show that the KKR equation represents only an approximation to the integral eigenvalue equation and not an exact result.[1]

II. FINITE-RANGE POTENTIAL

Consider the eigenvalue equation for Hamiltonians with a finite-range potential $U(r)$,

$$\Psi(E,\mathbf{r})=\int G(E,\mathbf{r},\mathbf{r}')U(\mathbf{r}')\Psi(E,\mathbf{r}')d\mathbf{r}' , \tag{1}$$

where

$$G(E,\mathbf{r},\mathbf{r}')=\frac{-1}{4\pi}\frac{\cos(E^{1/2}|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} =\frac{\pi E^{1/2}}{2}\sum_L j_L(E,\mathbf{r}_<)n_L^*(E,\mathbf{r}_>) , \tag{2}$$

with the usual notation for the Bessel (j) and Neumann (n) functions multiplied with spherical harmonics, and $\mathbf{r}_>=\mathbf{r}$ and $\mathbf{r}_<=\mathbf{r}'$ if $r=\max\{|\mathbf{r}|,|\mathbf{r}'|\}$, or $\mathbf{r}_>=\mathbf{r}'$ and $\mathbf{r}_<=\mathbf{r}$ if $r'=\max\{|\mathbf{r}|,|\mathbf{r}'|\}$.[10] ($L\equiv\{l,m\}$ is a collective angular momentum index.) Hereafter, we denote the solutions of Eq. (1) by $\Psi(E_n,\mathbf{r})$, $n=1,2,\ldots$. If the potential $U(\mathbf{r})$ is regular enough,[11] then Eq. (1) can be solved as follows: From Eqs. (1) and (2) we find the boundary conditions at the origin

$$\Psi(E_n,\mathbf{r})\rightarrow\sum_L j_L(E_n,\mathbf{r})A_L^0(E_n) \quad \text{as } r\rightarrow 0 , \tag{3}$$

where the A^0 coefficients are functionals of the eigenfunction

$$A_L^0(E_n)=\int n_L^*(E_n,\mathbf{r})U(\mathbf{r})\Psi(E_n,\mathbf{r})d\mathbf{r} . \tag{4}$$

Then, the (integral) eigenvalue equation, Eq. (1), is now equivalent to solving the (Schrödinger) equation

$$(\Delta+E_n)\Psi(E_n,\mathbf{r})=U(\mathbf{r})\Psi(E_n,\mathbf{r}) , \tag{5}$$

with the boundary conditions given by Eqs. (3) and (4). Thus, by constructing the coupled-channel equation for Eq. (5), we easily find

$$\Psi(E_n,\mathbf{r})=\sum_L \Phi_L^0(E_n,\mathbf{r})A_L^0(E_n) , \tag{6}$$

where the functions $\Phi_L^0(E,\mathbf{r})$ are defined as solution of

$$\begin{aligned}&(\Delta+E)\Phi_L^0(E,\mathbf{r})=U(\mathbf{r})\Phi_L^0(E,\mathbf{r}) ,\\ &\Phi_L^0(E,\mathbf{r})\to j_L(E,\mathbf{r}) \text{ as } r\to 0 .\end{aligned} \tag{7}$$

Since the $\Phi_L^0(E,\mathbf{r})$ can be computed (relatively easily) at any energy E by solving Volterra-type integral equations,[9] we continue the analysis in terms of these functions. Then, by introducing Eq. (6) into Eq. (4), we find

$$\sum_{L'}\left[\delta_{LL'}-\frac{\pi E_n^{1/2}}{2}\int n_L^*(E_n,\mathbf{r})\times U(\mathbf{r})\Phi_{L'}^0(E_n,\mathbf{r})\right]A_{L'}^0(E_n)d\mathbf{r}=0 , \tag{8}$$

which, by construction, represents a necessary condition for the A^0 coefficients. Apparently, this condition is also sufficient since the solution of Eqs. (5) and (3) is unique [or, alternatively, because the $A_L^0(E_n)$ are not subject to conditions other than Eq. (8)]. We, therefore, conclude that the eigenvalues E_n and the corresponding $A_L^0(E_n)$ are given by the solution of

$$\sum_{L'}\left[\delta_{LL'}-\frac{\pi E^{1/2}}{2}\int n_L^*(E,\mathbf{r})U(\mathbf{r})\Phi_{L'}^0(E,\mathbf{r})d\mathbf{r}\right]A_{L'}^0=\sum_{L'}C_{LL'}(E)A_{L'}^0=0 , \tag{9}$$

where the unknowns are E and A_L^0. Thus, the solution of Eq. (1) can be found as follows: (i) solve Eq. (7) at any energy E, (ii) calculate the matrix $C_{LL'}(E)$, (iii) find the levels E_n from the equation

$$\det\mathbf{C}(E)=0 , \tag{10}$$

and finally, (iv) find from Eq. (9) the corresponding $A_L^0(E_n)$ which, by means of Eq. (6), uniquely determine the solution of Eq. (1).

III. FINITE COLLECTION OF MUFFIN-TIN–TYPE POTENTIALS

Suppose now that the potential $U(\mathbf{r})$ has a particular structure as given by a finite collection,

$$U(\mathbf{r})=\sum_{\mathbf{R}}^{N}\mathcal{V}^{\mathbf{R}}(\mathbf{r}) , \tag{11}$$

of muffin-tin–type scatterers (but not necessarily identical or arranged regularly),

$$\mathcal{V}^{\mathbf{R}}(\mathbf{r})=\begin{cases}\mathcal{V}^{\mathbf{R}}(\boldsymbol{\rho}) & \text{if } \mathbf{r}=\boldsymbol{\rho}+\mathbf{R}\\ 0 & \text{otherwise} ,\end{cases} \tag{12}$$

with $\mathcal{V}^{\mathbf{R}}(\rho)=0$ for $\rho\geq\mu^{\mathbf{R}}$ as in Fig. 1 and the functions $\mathcal{V}^{\mathbf{R}}(\boldsymbol{\rho})$ are regular everywhere.[11] Clearly, this particular structure will be reflected somehow in Eqs. (9) and (10) and we now address this point.

Specifically, the question is whether Eqs. (9) and (10) can be expressed in terms of a geometrical factor describing the relative positions $\mathbf{R}$ and the solution of Eq. (7) for each single muffin-tin potential $\mathcal{V}^{\mathbf{R}}(\boldsymbol{\rho})$ [hence avoiding the integration of Eq. (7) over the whole potential U]. Thus, we introduce the function $\Phi_L^{\mathbf{R}}(E,\rho)$ as defined by Eq. (7) but around the center $\mathbf{R}$ (see Fig. 1),

$$\begin{aligned}&(\Delta+E)\Phi_L^{\mathbf{R}}(E,\rho)=U(\rho+\mathbf{R})\Phi_L^{\mathbf{R}}(E,\rho) ,\\ &\Phi_L^{\mathbf{R}}(E,\rho)\to j_L(E,\rho) \text{ as } \rho\to 0 .\end{aligned} \tag{13}$$

In particular, for $\rho=\rho\leq\mu^{\mathbf{R}}$ i.e., inside the muffin-tin sphere, we have

$$\Phi_L^{\mathbf{R}}(E,\boldsymbol{\rho})=\phi_L^{\mathbf{R}}(E,\boldsymbol{\rho}) , \tag{14}$$

where the functions $\phi_L^{\mathbf{R}}(E,\boldsymbol{\rho})$ are determined only by the cell potential $\mathcal{V}^{\mathbf{R}}(\boldsymbol{\rho})$. Moreover, if the potentials $\mathcal{V}^{\mathbf{R}}(\boldsymbol{\rho})$ are identical, then the index $\mathbf{R}$ in Eq. (14) becomes irrelevant. [We also notice that if the potential U in Eq. (13) is periodic, i.e., it consists in an infinite collection of identical scatterers, then the index $\mathbf{R}$ in Eq. (13) becomes irrelevant as well.[12]]

In terms of the functions defined by Eq. (13), we easily find, aside from the expansion defined by Eq. (6), that there is also a multipole expansion around each $\mathbf{R}$,

$$\Psi(E_n,\mathbf{R}+\rho)=\sum_L \Phi_L^{\mathbf{R}}(E_n,\rho)A_L^{\mathbf{R}}(E_n) \tag{15}$$

and, in view of our purpose [i.e., to find in what way the structure of the potential, Eq. (11), is reflected in Eqs. (9)

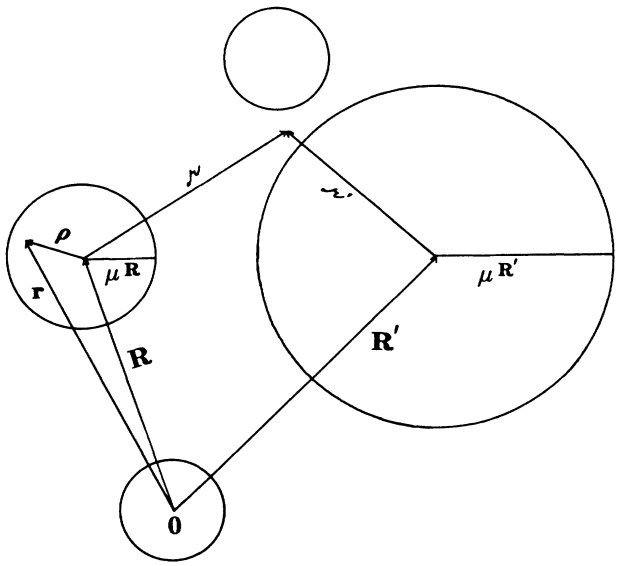

FIG. 1. Finite collection of muffin-tin–type scattering centers.

and (10)], we now focus on finding all the $A^{\mathbf{R}}$ coefficients [not only A^0 as in Eq. (8)]. To do this, we now look for the necessary *and* sufficient conditions satisfied by these coefficients.

Thus, since Eq. (15) gives the multipole expansion of the same function Ψ, the solution of Eq. (1), these coefficients should satisfy

$$\sum_L \Phi_L^0(E_n,\boldsymbol{\rho}+\mathbf{R})A_L^0(E_n)=\sum_L \Phi_L^{\mathbf{R}}(E_n,\boldsymbol{\rho})A_L^{\mathbf{R}}(E_n)\ , \tag{16}$$

for any $\boldsymbol{\rho}$, and $\mathbf{R}$.[13] Also, by using the translation property[14]

$$n_L^*(E,\mathbf{R}+\boldsymbol{\rho})=\sum_L N_{LL'}(E,-\mathbf{R})j_{L'}^*(E,\boldsymbol{\rho}),\quad \rho<R\ , \tag{17}$$

in Eq. (8), we obtain

$$\sum_{\mathbf{R}}^{N}\sum_{L'}\left[\mathcal{C}_{LL'}^{\mathbf{R}}(E_n)\delta_{0\mathbf{R}}-\sum_{L''}N_{LL''}(E_n,-\mathbf{R})\mathcal{S}_{L''L'}^{\mathbf{R}}(E_n)\right]A_{L'}^{\mathbf{R}}(E_n)=0\ , \tag{18}$$

where, by convention, $N_{LL'}(E,\mathbf{0})\equiv 0$ and we recall the $\mathcal{C}$ and $\mathcal{S}$ matrices of the variable phase method[9] corresponding to the cell potential $\mathcal{V}^{\mathbf{R}}$ (with all the other centers absent),

$$\mathcal{C}_{LL'}^{\mathbf{R}}(E)=\delta_{LL'}-\frac{\pi E^{1/2}}{2}\int n_L^*(E,\boldsymbol{\rho})\mathcal{V}^{\mathbf{R}}(\boldsymbol{\rho})\phi_{L'}(E,\boldsymbol{\rho})d\boldsymbol{\rho}\ ,$$
$$\mathcal{S}_{LL'}^{\mathbf{R}}(E)=\frac{\pi E^{1/2}}{2}\int j_L^*(E,\boldsymbol{\rho})\mathcal{V}^{\mathbf{R}}(\boldsymbol{\rho})\phi_{L'}(E,\boldsymbol{\rho})d\boldsymbol{\rho}\ . \tag{19}$$

Apparently, Eqs. (16) and (18) represent necessary conditions for the $A^{\mathbf{R}}$ coefficients. By construction, these equations are also sufficient [for by introducing Eq. (16) into Eq. (18) one obtains Eq. (9) which was shown to be equivalent to Eq. (1)]. Thus, the system of equations obtained by putting together

$$\sum_L \Phi_L^0(E,\boldsymbol{\rho}+\mathbf{R})A_L^0=\sum_L \Phi_L^{\mathbf{R}}(E,\boldsymbol{\rho})A_L^{\mathbf{R}}\ , \tag{20}$$

taken for all the points $\boldsymbol{\rho}$ and $\mathbf{R}$ and

$$\sum_{\mathbf{R}}^{N}\sum_{L'}\left[\mathcal{C}_{LL'}^{\mathbf{R}}(E)\delta_{0\mathbf{R}}-\sum_{L''}N_{LL''}(E,-\mathbf{R})\mathcal{S}_{L''L'}^{\mathbf{R}}(E)\right]A_{L'}^{\mathbf{R}}=0\ , \tag{21}$$

with the unknown E, A_L^0 and $A_L^{\mathbf{R}}$ are equivalent to the system of equations defined by Eq. (9) and hence to Eq. (1).

Since Eq. (16) is rather difficult to handle, however, the question arises if one can possibly absorb these equations (or at least part of them) into a set of more convenient equations. Thus, it is easy to see that the system

$$\sum_{\mathbf{R}'}^{N}\sum_{L'}\left[\mathcal{C}_{LL'}^{\mathbf{R}}(E)\delta_{\mathbf{R}\mathbf{R}'}-\sum_{L''}N_{LL''}(E,\mathbf{R}-\mathbf{R}')\mathcal{S}_{L''L'}^{\mathbf{R}'}(E)\right]A_{L'}^{\mathbf{R}'}=0\ , \tag{22}$$

obtained by writing Eq. (21) for each of the N centers, $\mathbf{R}$, already contains a part of Eq. (20). More precisely, we are going to show that the wave function obtained by introducing the solution of Eq. (22) into Eq. (15) satisfies some—but not all—parts of Eq. (16).

Actually, assume, for simplicity, the case of only two scattering centers in Eq. (1) as shown in Fig. 2. Then, the corresponding system obtained from Eq. (22) is given by

$$\sum_{L'}\left[\mathcal{C}_{LL'}^{0}(E)A_{L'}^{0}-\sum_{L''}N_{LL''}(E,-\mathbf{R})\mathcal{S}_{L''L'}^{1}(E)A_{L'}^{1}\right]=0\ , \tag{23a}$$

$$\sum_{L'}\left[\mathcal{C}_{LL'}^{1}(E)A_{L'}^{1}-\sum_{L''}N_{LL''}(E,\mathbf{R})\mathcal{S}_{L''L'}^{0}(E)A_{L'}^{0}\right]=0\ , \tag{23b}$$

and, in view of checking Eq. (16), we recall the form of the solutions of Eq. (13),[9]

$$\Phi_L^{\mathbf{R}}(E,\boldsymbol{\rho})=\sum_L j_{L'}(E,\boldsymbol{\rho})C_{L'L}^{\mathbf{R}}(E,\boldsymbol{\rho})+n_{L'}(E,\boldsymbol{\rho})S_{L'L}^{\mathbf{R}}(E,\boldsymbol{\rho})\ , \tag{24}$$

where

$$C_{L'L}^{\mathbf{R}}(E,\boldsymbol{\rho})=\delta_{L'L}-\frac{\pi E^{1/2}}{2}\int_{\boldsymbol{\rho}'\le\boldsymbol{\rho}} n_{L'}^*(E,\boldsymbol{\rho}')U(\boldsymbol{\rho}'+\mathbf{R})\times\Phi_L^{\mathbf{R}}(E,\boldsymbol{\rho}')d\boldsymbol{\rho}'\ ,$$
$$S_{L'L}^{\mathbf{R}}(E,\boldsymbol{\rho})=\frac{\pi E^{1/2}}{2}\int_{\boldsymbol{\rho}'\le\boldsymbol{\rho}} j_{L'}^*(E,\boldsymbol{\rho}')U(\boldsymbol{\rho}'+\mathbf{R})\times\Phi_L^{\mathbf{R}}(E,\boldsymbol{\rho}')d\boldsymbol{\rho}'\ . \tag{25}$$

[Note that these coefficients are constant and equal to $\mathcal{C}_{L'L}^{\mathbf{R}}(E)$ and $\mathcal{S}_{L'L}^{\mathbf{R}}(E)$ of Eq. (19) respectively, in the sphere up to the next muffin-tin potential, i.e., for those $\boldsymbol{\rho}$ with $\mu^{\mathbf{R}}\le\boldsymbol{\rho}\,|\,\mathbf{R}-\mathbf{R}'\,|-\mu^{\mathbf{R}'}$.]

If we now consider a point $\boldsymbol{\rho}$ with $\mu^0\le\boldsymbol{\rho}\le R-\mu^1$, e.g., the point C in Fig. 2, then by multiplying Eq. (23) with $j_L(E,\boldsymbol{\rho})$ and $j_L(E,\boldsymbol{\rho}-\mathbf{R})$ respectively, and using Eq. (17), we have

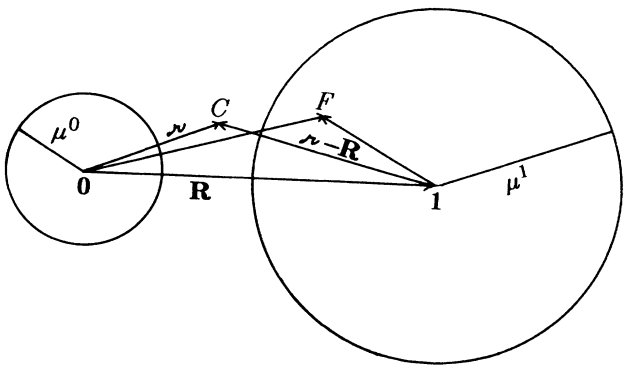

FIG. 2. Two scattering centers.

$$\sum_{L,L'}[j_L(E,\kappa)\mathcal{C}^0_{LL'}(E)A^0_{L'}-n_L(E,\kappa-\mathbf{R})\mathcal{S}^1_{LL'}(E)A^1_{L'}]=0\ , \tag{26a}$$

$$\sum_{L,L'}[j_L(E,\kappa-\mathbf{R})\mathcal{C}^1_{LL'}(E)A^1_{L'}-n_L(E,\kappa)\mathcal{S}^0_{LL'}(E)A^0_{L'}]=0\ , \tag{26b}$$

and hence (by subtracting the two equations) we further obtain

$$\sum_{L,L'}[j_L(E,\kappa)\mathcal{C}^0_{LL'}(E)+n_L(E,\kappa)\mathcal{S}^0_{LL'}(E)]A^0_{L'} = \sum_{L,L'}[j_L(E,\kappa-\mathbf{R})\mathcal{C}^1_{LL'}(E) + n_L(E,\kappa-\mathbf{R})\mathcal{S}^1_{LL'}(E)]A^1_{L'}\ , \tag{27}$$

where we recall Eqs. (24), (25) and (19). Thus, the wave function generated by introducing the solution of Eq. (23) into Eq. (15) satisfies the matching condition, Eq. (16), (at least) in the sphere up to the next muffin-tin potential (e.g., the sphere centered at **0** and having the radius $R-\mu^1$ in Fig. 2). Hence, the matching condition, Eq. (16), in this region is already contained in Eq. (23) [i.e., it appears as a consequence of Eq. (23)] and, therefore, it is no longer necessary to be taken into account explicitly as a separate equation.

Consider now a point κ with $R-\mu^1\le\kappa\le R$, e.g., the point F in Fig. 2. In this case, care should be taken in handling the translational properties of the Neumann function, Eq. (17). Thus, by again multiplying Eq. (23) with $j_L(E,\kappa)$ and $j_L(E,\kappa-\mathbf{R})$ respectively, and by using Eqs. (2) and (19), we obtain

$$\sum_{L,L'}j_L(E,\kappa)\left[\mathcal{C}^0_{LL'}(E)A^0_{L'}-\frac{\pi E^{1/2}}{2}\int_{\kappa\ge|\mathbf{R}+\rho|}n^*_L(E,\mathbf{R}+\rho)\mathcal{V}^1(\rho)\Phi^1_{L'}(E,\rho)A^1_{L'}d\rho\right] - \sum_L\int_{\kappa\le|\mathbf{R}+\rho|}G(E,\kappa-\mathbf{R}-\rho)\mathcal{V}^1(\rho)\Phi^1_L(E,\rho)A^1_L d\rho=0 \tag{28a}$$

and

$$\sum_{L,L'}[n_L(E,\kappa)\mathcal{S}^0_{LL'}(E)A^0_{L'}-j_L(E,\kappa-\mathbf{R})C^1_{LL'}(E,|\kappa-\mathbf{R}|)A^1_{L'}] + \sum_L\int_{\rho\ge|\kappa-\mathbf{R}|}G(E,\kappa-\mathbf{R}-\rho)\mathcal{V}^1(\rho)\Phi^1_L(E,\rho)A^1_L d\rho=0\ . \tag{28b}$$

Further, since we have (by direct calculation)

$$\left[\int_{\rho\ge|\kappa-\mathbf{R}|}-\int_{\kappa\le|\mathbf{R}+\rho|}\right]G(E,\kappa-\mathbf{R}-\rho)\mathcal{V}^1(\rho)\Phi^1_L(E,\rho)A^1_L d\rho = \left[\int_{\kappa\ge|\mathbf{R}+\rho|}-\int_{\rho\le|\kappa-\mathbf{R}|}\right]G(E,\kappa-\mathbf{R}-\rho)\mathcal{V}^1(\rho)\Phi^1_L(E,\rho)A^1_L d\rho\ , \tag{29}$$

we obtain, by adding the two equations in Eq. (28),

$$\sum_{L,L'}[j_L(E,\kappa)\Gamma^0_{LL'}(E,\kappa)+n_L(E,\kappa)\Sigma^0_{LL'}(E,\kappa)] = \sum_{L,L'}[j_L(E,\kappa-\mathbf{R})C^1_{LL'}(E,|\kappa-\mathbf{R}|)A^1_{L'}+n_L(E,\kappa-\mathbf{R})S^1_{LL'}(E,|\kappa-\mathbf{R}|)A^1_{L'}]\ , \tag{30}$$

where use was again made of Eqs. (2) and (25) and we introduced

$$\begin{aligned}\Gamma^0_{LL'}(E,\kappa)&=\mathcal{C}^0_{LL'}(E)A^0_{L'}-\frac{\pi E^{1/2}}{2}\int_{\kappa\ge|\mathbf{R}+\rho|}n^*_L(E,\mathbf{R}+\rho)\mathcal{V}^1(\rho)\Phi^1_{L'}(E,\rho)A^1_{L'}d\rho\ ,\\ \Sigma^0_{LL'}(E,\kappa)&=\mathcal{S}^0_{LL'}(E)A^0_{L'}+\frac{\pi E^{1/2}}{2}\int_{\kappa\ge|\mathbf{R}+\rho|}j^*_L(E,\mathbf{R}+\rho)\mathcal{V}^1(\rho)\Phi^1_{L'}(E,\rho)A^1_{L'}d\rho\ .\end{aligned} \tag{31}$$

As we can see [by recalling Eqs. (24) and (25)], the matching condition, Eq. (16), for those points κ which intersect the next muffin-tin sphere, e.g., the point F in Fig. 2, does not follow from Eq. (23).[15] Instead, Eq. (16) for these points represents a condition which is independent of Eq. (23) and, therefore, it must be maintained as such.

By means of essentially the same algebra we derive similar results for the system of Eqs. (22) and (20). Hence, we finally conclude that the system obtained by taking Eq. (22) together with the boundary conditions,

$$\sum_L\Phi^{\mathbf{R}}_L(E,\kappa+\mathbf{R})A^{\mathbf{R}}_L=\sum_L\Phi^{\mathbf{R}'}_L(E,\kappa+\mathbf{R}-\mathbf{R}')A^{\mathbf{R}'}_L\ , \tag{32}$$

for adjacent $\mathbf{R}$ and $\mathbf{R}'$ and those κ with $|\mathbf{R}-\mathbf{R}'|-\mu^{\mathbf{R}}\le\kappa\le|\mathbf{R}-\mathbf{R}'|$, is equivalent to the system of Eqs. (20) and (21) and hence to Eq. (9) which, in turn, is

equivalent to Eq. (1).[16] As we can see, the system of equations defined by Eq. (22) alone[17] is not sufficient for finding the A coefficients of Eq. (15): we have to add the boundary conditions, Eq. (32).

In other words, the A coefficients of Eq. (15) satisfy the system of equations

$$\sum_{\mathbf{R}'}^{N}\sum_{L'}\left[\mathcal{C}^{\mathbf{R}}_{LL'}(E_n)\delta_{\mathbf{R}\mathbf{R}'}-\sum_{L''}N_{LL''}(E_n,\mathbf{R}-\mathbf{R}')\mathcal{S}^{\mathbf{R}'}_{L''L'}(E_n)\right]A^{\mathbf{R}'}_{L'}=0\ , \quad (33)$$

[with $N_{LL''}(E,\mathbf{0})\equiv 0$] which surely represents a necessary condition [from Eqs. (4), (15) and (17)] for these coefficients. If it were also sufficient, then Eq. (22) would be equivalent [by means of Eq. (15)] to Eq. (1). However, Eq. (33) is not sufficient [for, as shown in the example above, it does not generate Eq. (16) which is required by Eqs. (1) and (15)]; therefore Eq. (22) is not equivalent to Eq. (1).

By contrast, multiple-scattering theory[2–7] simply disregards the matching conditions, Eq. (16) and considers Eq. (33) not only as a necessary but also as a sufficient condition for the calculation of the A coefficients. In other words, multiple-scattering theory considers the $A^{\mathbf{R}}_{L}(E_n)$ in Eq. (16) to satisfy only Eq. (33), which is seen, from the example above, to clearly represent a necessary condition but *not* a sufficient one.

IV. AN APPLICATION: MUFFIN-TIN PERIODIC POTENTIAL

As an application of these results, we discuss briefly the case of a periodic potential,

$$V(\mathbf{r}+\mathbf{R})=V(\mathbf{r})\ , \quad (34)$$

of the muffin-tin type,

$$V(\boldsymbol{\rho}+\mathbf{R})=\begin{cases}\mathcal{V}(\boldsymbol{\rho}) & \text{if } \rho\le\mu\\ 0 & \text{otherwise}\ .\end{cases} \quad (35)$$

Since the corresponding eigenvalue equation[18]

$$\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\int_{\Omega}\mathcal{G}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')\mathcal{V}(\boldsymbol{\rho}')\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho}')d\boldsymbol{\rho}'\ , \quad (36)$$

where

$$\mathcal{G}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')=\sum_{\mathbf{R}}e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}G(E,\boldsymbol{\rho},\boldsymbol{\rho}'+\mathbf{R})\ , \quad (37)$$

can be obtained from Eqs. (1), (11) and (12) by dropping the $\mathbf{R}$ dependence of the cell potential, taking $N=\infty$ and introducing Bloch periodic boundary conditions,[19]

$$\begin{aligned}\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho}+\mathbf{R})&=e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho})\ ,\\ \nabla\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho}+\mathbf{R})&=e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}\nabla\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho})\ ,\end{aligned} \quad (38)$$

it follows that the case of the muffin-tin periodic potential can be obtained from the previous results by simply taking the limit $N=\infty$ and introducing the (boundary) conditions,

$$A^{\mathbf{R}}_{L}(\boldsymbol{\kappa},E_n)=e^{i\boldsymbol{\kappa}\cdot(\mathbf{R}-\mathbf{R}')}A^{\mathbf{R}'}_{L}(\boldsymbol{\kappa},E_n)\ , \quad (39)$$

that is, by imposing a supplementary relation (i.e., Bloch periodicity) among the A coefficients of different cells. In doing so, we find that the solution of Eq. (36) admits a multipole expansion

$$\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho}+\mathbf{R})=e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}\sum_{L}\Phi_L(E_n,\boldsymbol{\rho})A_L(\boldsymbol{\kappa},E_n)\ , \quad (40)$$

in the sphere up to the next neighbor where the $A_L(\boldsymbol{\kappa},E_n)$ are obtained from the corresponding equations derived from Eqs. (22) and (32). The system of Eq. (22), which contains N equations corresponding to N scattering centers, reduces in this case [from Eq. (39)] to only one equation represented (up to an arbitrary phase) by the well-known KKR equation

$$\sum_{L'}\left[c_{LL'}(E)-\sum_{L''}N_{LL''}(\boldsymbol{\kappa},E)s_{L''L'}(E)\right]A_{L'}=0\ , \quad (41)$$

where $N_{LL'}(\boldsymbol{\kappa},E)$ stand for the structure constant

$$N_{LL'}(\boldsymbol{\kappa},E)=\sum_{\mathbf{R}\ (\neq 0)}e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}N_{LL'}(E,\mathbf{R})\ . \quad (42)$$

The matching condition, Eq. (32), now becomes

$$\sum_{L}[\Phi_L(E,\boldsymbol{\rho})-e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}\Phi_L(E,\boldsymbol{\rho}+\mathbf{R})]A_L=0\ , \quad (43)$$

for $\min R-\mu\le|\boldsymbol{\rho}+\mathbf{R}|\le\min R$ and expresses, essentially, the Bloch periodicity requirement upon the solution of Eq. (36) described in a multipole expansion representation.[20] In view of the discussion in Sec. III, the KKR equation of Eq. (41) alone is thus seen not to be equivalent to Eq. (36) but the A coefficients of Eq. (40) are given by the solution of *both* Eqs. (41) and (43).

V. CONCLUSIONS

In conclusion, we have considered the (algebraic) homogeneous system of equations for the coefficients of the multipole expansion of the eigenfunction for a finite-range potential and gradually transformed it so as to explicitly take into account the structure of the potential as a finite or infinite collection of nonoverlapping, muffin-tin–type potentials. Essentially, we have found that the separation between structure and potential (considered an exact result within multiple-scattering theory[2–7] and recently[4–6] claimed to have been generalized for the non-muffin-tin periodic potential) represents, in fact, only an approximation which disregards the matching condition imposed by the representation of the eigenfunction as a multipole expansion.

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[8]Motivated mainly by computational advantages, there has been a constant effort to generalize the separation between structure and potential to the case of arbitrary, non-muffin-tin–type scatterers. Several recent papers (Refs. 4–6) claim to have proven this separation as an exact result for the case of arbitrary, non-muffin-tin single scatterers, but this was demonstrated (both computationally (Refs. 3 and 7) and analytically[12]) not to be the case.

[9]F. Calogero, *Variable Phase Approach to Potential Scattering* (Academic, New York, 1967), and references therein.

[10]Here, we analyze only the positive eigenvalues. The negative eigenvalues can be obtained [see, e.g., B. Simon, *Trace Ideals and their Applications* (Cambridge University Press, London, 1979)] by formally replacing $\cos E^{1/2} \rightarrow e^{-(-E)^{1/2}}$.

[11]Equations (3) to (9) hold if the U potential in Eq. (1) is spherically symmetric at the origin and has, at most, a second-order pole at the origin. Similarly, if the potential $\mathcal{V}^{\mathbf{R}}(\mathbf{r})$ is regular enough, then the solution $\Phi_L^0(E,\boldsymbol{\rho})$ of Eq. (13) admits a multipole expansion in the sphere up to the next neighbor. The case of more singular potentials, e.g., δ-function potentials, raises delicate questions concerning the self-adjointness of the Hamiltonian, cf., e.g., S. Albeverio, R. Hoegh-Krohn, and M. Mebkhout, J. Math. Phys. **25**, 1327 (1984), and references therein.

[12]E. Badralexe and A. J. Freeman, Phys. Rev. B **36**, 1378 (1987) and Phys. Rev. B **37**, 1067 (1988).

[13]The function $\Psi(E_n,\mathbf{r})$ as a solution of Eq. (1) at an arbitrary point $\mathbf{r}$ can be obtained by integrating the Schrödinger equation from any (adjacent) center $\mathbf{R}$ and with boundary conditions

$$\Psi(E_n,\mathbf{R}+\boldsymbol{\rho}) \rightarrow \sum_L j_L(E_n,\boldsymbol{\rho}) A_L^{\mathbf{R}}(E_n) \quad \text{as } r \rightarrow 0$$

[from Eqs. (13) and (15)]. Obviously, the result of the integration should not depend on the starting point.

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[15]More precisely, the wave function obtained by introducing the solution of Eq. (22) into Eq. (15) cannot represent the solution of Eq. (1). Actually this wave function satisfies Eq. (16) but only for those $\boldsymbol{\rho}$ with $\mu^{\mathbf{R}} \leq \rho \leq |\mathbf{R}-\mathbf{R}'| - \mu^{\mathbf{R}'}$, e.g., the point C in Fig. 2, unlike the solution of Eq. (1) which satisfies Eq. (16) for any $\boldsymbol{\rho}$.

[16]By using the matching condition, Eq. (16), in the form of Eq. (32), one can show that the system of Eq. (22) and (31) is equivalent to Eq. (1) not only for potentials $\mathcal{V}^{\mathbf{R}}$ in Eq. (11) which are regular everywhere but also for those which have a second-order pole at $\rho=0$ [although Eq. (9) does not exist in this case].

[17]This equation is very appealing: it contains a geometric factor—the matrix $\mathbf{N}(\mathbf{R})$—describing the relative positions of the scattering centers and (only) the single muffin-tin potentials $\mathcal{V}^{\mathbf{R}}$ and hence avoids the integration of Eq. (7) over the whole potential U, Eq. (11). [Besides, if the $\mathcal{V}^{\mathbf{R}}$ are singular at $\rho=0$ then Eq. (7) cannot be solved by using the variable phase method.] If, moreover, the potentials $\mathcal{V}^{\mathbf{R}}$ are identical then the potential contribution in Eq. (22) appears (only) by means of the corresponding T matrix, i.e., by means of the matrix $\mathbf{s}(E)\cdot\mathbf{c}^{-1}(E)$ of the variable-phase method.

[18]The multipole expansion solution of the eigenvalue equation (and the corresponding inhomogeneous equation) with a general periodic potential and a soluble example were discussed by us in detail in Ref. 12.

[19]In fact, the limit $N=\infty$ in Eq. (1) with potential defined by Eqs. (11) and (34) is justified by the simultaneous introduction of the Bloch periodic boundary conditions. In other words, the eigenvalue equation defined by Eq. (1) with a potential which vanishes (fast enough) at infinity has solutions in the space of square-integrable functions; if the potential is periodic, then the corresponding equation no longer has solutions in the space of square-integrable functions but in the space of Bloch periodic functions.

[20]This condition selects those E and A_L for which the superposition $\sum_L \Phi_L(E,\boldsymbol{\rho}) A_L$ is Bloch periodic but not necessarily a solution of Eq. (36). Equation (41) further selects those E and A for which this superposition (further) becomes, in addition, a solution of Eq. (36). The fact that Eq. (41) alone, i.e., the KKR equation, is not equivalent to the eigenvalue equation, Eq. (36), is implicitly contained in the study of the general periodic potential (Refs. 12 and 18) and was explicitly illustrated in E. Badralexe and A. J. Freeman (unpublished) by using a simple example.