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Generalised KKR theory for non-muffin-tin potentials

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Abstract. We show that the secular equation in KKR (Korringa, Kohn and Rostoker) theory retains its separable structure also in the case of non-muffin-tin potentials. This generalisation has been extensively discussed recently. During this discussion, in which the possible necessity of so-called near field corrections played an important role, it became more and more clear that attention should be concentrated on the basis functions used to represent the crystal wavefunction locally. We discuss the construction of reliable basis functions, and show that several alternatives can be indicated, which are all theoretically sound. These different possibilities have quite different implications as far as their numerical evaluation is concerned, and we show that the generalisation of the construction, which is already in use in 'classical' KKR theory, deserves preference. In the literature, it has been claimed that it is absolutely necessary to take into account the part of the crystal potential between the boundary of the Wigner-Seitz cell and its circumscribing sphere. The present derivations make it clear that basis functions, constructed from only the part of the crystal potential inside a Wigner-Seitz cell, may be satisfactory as well as those constructed from local potentials with larger support.

1. Introduction

In a preceding paper (Molenaar 1988), we discussed the so-called near field (NF) error, which is supposed to be frequently made in generalising the KKR theory of Korringa (1947) and Kohn and Rostoker (1954) for crystal potentials beyond the muffin tin (MT) approximation. This paper introduced a new element in the NF error discussion in that it contained a detailed off-shell analysis of multiple scattering (MS) theory for crystals. One of the conclusions was that the well known KKR equations are valid for both MT and non-MT potentials. This would imply that the NF error, which Ziesche (1974) claimed to be present in the work of Williams and Van Morgan (1972, 1974), does not exist. In the last decade, this issue has often been discussed, e.g. by Van Morgan (1977), Faulkner (1979, 1985, 1986), Gonis (1986), Zeller (1987), and Brown and Ciftan (1983, 1984, 1985, 1986a, 1986b). Recent contributions are by Badraxe and Freeman (1987), Brown (1988a, 1988b), Gonis *et al* (1988) and Zeller (1988), which appeared after the preceding paper had been written. The approach and conclusions by Badraxe and Freeman differ much from the present contribution and has been commented by other authors (van Ek and Lodder 1988, Brown 1988b). We shall therefore pay no attention to it in the present paper. The approach of Gonis and co-workers is quite different from the present one, but their general conclusions agree with ours. They do not discuss the issue of the basis functions, used to represent the crystal wavefunction (CWF). The work of Zeller includes

the analytical and numerical analysis of NF corrections for the case of an empty-lattice. He concludes that they vanish up to third order. This fully agrees with our work, in which they are shown to vanish up to all orders for general potentials. The contributions by Brown and Ciftan have been laid down in a series of papers. Because these papers form a consistent entirety, we shall refer to them by Brown and Ciftan, without specification of a particular article. An extensive and rather complete review of their ideas is given by Brown (1988c). The results of their on-shell approach and the present off-shell approach agree much. They both lead to the conclusion, that the secular equation in KKR theory remains its separability between lattice and potential factors also in case of non-MT potentials. However, Brown and Ciftan claim, that the greater part of the literature, including the work of the present author, contains another subtle error, which has to do with the basis used to represent the CWF locally. So, the discussion seems to come to an end as far as the separability is concerned but continues at another, equally essential issue.

The main purpose of this paper is to present a detailed discussion of the appropriate choice of basis functions. We show that, from a theoretical point of view, a multitude of satisfactory bases exists, which includes the ones used by Williams and Van Morgan (1974), Brown and Ciftan and the present author. However, if it comes to the question, how these basis functions could be calculated in practice, we show that the alternatives are certainly not of equal value.

In § 2 we deal with general properties of the CWF and pay special attention to the conditions under which a basis allows for an on-shell, local representation of the CWF. The construction of appropriate basis functions is the subject of § 3.

In this construction, matrices C^i and S^i appear, the calculation of which is a central point in the NF error discussion. We point out that these matrices have to be calculated from a (first order and linear) boundary value problem, rather than from an initial value problem, as stated elsewhere in the literature. The basis functions are uniquely defined except for the choice of a matrix \bar{C}^i . The consequences of three different choices for this matrix are discussed in § 4. Section 5 contains a concise derivation of the secular equation for non-MT potentials, given an appropriate basis. The conclusions are listed in § 6.

Throughout this paper, atomic units are used with $\hbar = 2$, $m = 1$, \hbar and m being Planck's constant and the electron mass, respectively.

2. Crystal wavefunction

The crystal wavefunction (CWF) $|\psi_k^{\text{cr}}\rangle$ is the solution of the time-independent Schrödinger equation (TISE)

$$(-\Delta + V^{\text{cr}})|\psi_k^{\text{cr}}\rangle = E|\psi_k^{\text{cr}}\rangle. \quad (1)$$

We use the notation $k \equiv (n, \mathbf{k})$ with n the band index and \mathbf{k} crystal momentum. The crystal potential V^{cr} has lattice symmetry and we write

$$V^{\text{cr}} = \sum_i V^i. \quad (2)$$

V^i is equal to V^{cr} within the i th Wigner-Seitz (ws) cell Ω^i and vanishes outside it. From translation symmetry, we have

$$V^i(\mathbf{r} - \mathbf{R}_i) = V^j(\mathbf{r} - \mathbf{R}_j) \quad (3)$$

with \mathbf{R}_i and \mathbf{R}_j lattice positions. The dependence of E on the quantum numbers k is the

subject of bandstructure calculations, for which we shall derive a secular equation in § 6. This dependence is also referred to as the E - k or dispersion relation and denoted as

$$E = E_n(\mathbf{k}). \quad (4)$$

From the translation symmetry of V^{cr} it follows, that translation over a lattice vector yields a known phase factor for the CWF. The Bloch theorem

$$\langle \mathbf{r} - \mathbf{R}_i | \psi_k^{\text{cr}} \rangle = \exp(i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)) \langle \mathbf{r} - \mathbf{R}_j | \psi_k^{\text{cr}} \rangle \quad (5)$$

assures, that knowledge of the CWF inside one ws cell implies the knowledge of the CWF everywhere. The CWF can be normalised in the same sense as plane waves via the delta function. In practice, it suffices to normalise and interpret the inner product $\langle \psi_k^{\text{cr}} | \psi_k^{\text{cr}} \rangle$ as a probability density function only within some ws cell, say Ω^i . Potentials V^i , which allow for such a normalisation, are called regular at \mathbf{R}_i .

An essential feature of multiple scattering (MS) theory is the expansion of the CWF within the different ws cells Ω^i in terms of sets of basis functions, centred around the respective lattice sites \mathbf{R}_i . It then remains to calculate the expansion coefficients. From (2), we see, that within Ω^i (1) reduces to

$$(-\Delta + V^i) | \psi_k^{\text{cr}} \rangle = E | \psi_k^{\text{cr}} \rangle. \quad (6)$$

Let us denote the basis functions, meant to expand the CWF within Ω^i , by $|E, L, i, +\rangle$. For general V^i , it is not self-evident to label these functions by the quantum numbers $(E, L \equiv (l, m))$ of the energy-angular momentum representation. However, for spherically symmetric V^i , L is a convenient quantum number, and one is therefore used to do it this way. We assume the basis functions to satisfy in \mathbb{R}^3 an equation analogous to (6):

$$(-\Delta + V^i) |E, L, i, +\rangle = E |E, L, i, +\rangle. \quad (7)$$

We further demand, that $|E, L, i, +\rangle \in L_2(\mathbb{R}^3)$, which is consistent with the regularity of V^i at \mathbf{R}_i and with its bounded support. In § 3, we shall deal with the construction of the basis functions in detail. Here, it suffices to remark, that $(-\Delta + V^i)$ is a Hermitian operator, so that the eigenfunctions can be chosen to form a complete, orthonormal basis in $L_2(\mathbb{R}^3)$. We emphasise, that the potential V^i in (7) has Ω^i as its support and not the circumscribing sphere of Ω^i . Brown and Ciftan state that this would introduce the so-called near-field error. The analysis in this and the following section shows, that a basis defined by (7) is certainly appropriate to represent the CWF within Ω^i .

For an expansion of $|\psi_k^{\text{cr}}\rangle$ at energy $E = E_n(\mathbf{k})$, only basis functions at this particular energy are needed. Although this result is one of the starting points of KKR theory, one seldom realises that any other expansion necessarily contains off-shell components. The essential point is, that the basis functions satisfy within Ω^i the same differential equation as the CWF does. Only then, we may write

$$\langle \mathbf{r} | \psi_k^{\text{cr}} \rangle = \sum_L \langle \mathbf{r} | E, L, i, + \rangle d_{EL,k}^i \quad \text{if } \mathbf{r} \in \Omega^i. \quad (8)$$

3. The construction of basis functions

In this section, we shall discuss the construction of the basis functions. The homogeneous part of equation (7)

$$-\Delta|E, L, i\rangle = E|E, L, i\rangle \quad (9)$$

is the well-known TISE for a free particle. The solutions are given by

$$\langle \mathbf{r} + \mathbf{R}_i | E, L, i \rangle = \frac{E^{1/4}}{\pi^{1/2}} j_l(\sqrt{E}|\mathbf{r}|) Y_L(\hat{r}) \equiv \frac{E^{1/4}}{\pi^{1/2}} j_L(E, \mathbf{r}) \quad (10)$$

where the normalisation is such, that

$$\langle E, L, i | E', L', i \rangle = \delta(E - E') \delta_{L,L'}. \quad (11)$$

The j_l and Y_L are the spherical Bessel function and the (real) spherical harmonic, respectively. These free particle solutions form an orthonormal basis in $L_2(\mathbb{R}^3)$, so that we may write

$$\int_0^\infty dE \sum_L |E, L, i\rangle \langle E, L, i| = \mathbf{1} \quad (12)$$

with $\mathbf{1}$ the unity operator. We remark, that the order of summation and integration may be interchanged in this projection operator in view of the convergence properties of this kind of expansions. To a particular solution of the inhomogeneous equation (7) a linear combination of solutions of the homogeneous equation (9) may be added. This property is expressed by the Lipmann–Schwinger (LS) equation

$$|E, L, i, +\rangle = \sum_{L'} \bar{C}_{LL'}^i(E) |E, L', i\rangle + G(E)V^i |E, L, i, +\rangle. \quad (13)$$

The free space Green's operator $G(E)$ is defined by

$$G(E) = (E + i\varepsilon + \Delta)^{-1} \equiv (E^+ + \Delta)^{-1} \quad (14)$$

with ε infinitesimally small and positive.

If we take the rows of $\bar{C}_{LL'}^i(E)$ in (13) linearly independent, we make sure, that the functions $|E, L, i, +\rangle$ are also linearly independent in $L_2(\mathbb{R}^3)$. Under the condition

$$\det(\bar{C}_{LL'}^i(E)) \neq 0 \quad (15)$$

the functions $|E, L, i, +\rangle$ form a complete basis in the subspace of $L_2(\mathbb{R}^3)$ spanned by the eigenfunctions of the operator $(-\Delta + V^i)$ at eigenvalue E . Although the $|E, L, i, +\rangle$ are orthogonal with respect to energy, as being eigenfunctions of a Hermitian operator, they are in advance not orthogonal with respect to angular momentum indices. By applying a Gram-Schmidt procedure, they could be orthogonalised, but we do not need this property in the following.

Condition (15) leaves us much freedom in the choice of \bar{C}^i . It is important to realise, that every non-singular matrix \bar{C}^i in principle yields a set of basis functions, which is formally appropriate to represent the CWF within Ω^i . However, the different alternatives have quite different implications, as discussed in § 4.

Let us evaluate the particular solution $G V^i |E, L, i, +\rangle$ of equation (7) more in detail. We therefore need the matrix elements of G with respect to the free space basis functions $|E, L, i\rangle$. They are given by

$$\langle E', L, i | G(E) | E'', L', i \rangle = (E^+ - E')^{-1} \delta(E' - E'') \delta_{LL'}. \quad (16)$$

With the use of the projection operator in (12), we obtain the relation

$$\langle \mathbf{r} + \mathbf{R}_i | G(E) V^i | E, L, i, + \rangle = \int_0^\infty dE' \sum_{L'} \langle \mathbf{r} + \mathbf{R}_i | E', L', i \rangle \frac{1}{(E^+ - E')} t_{E'L',EL}^i \quad (17)$$

with the t -matrix t^i , corresponding to the potential V^i , defined by

$$\begin{aligned} t_{EL,E'L'}^i &= \langle E, L, i | V^i | E', L', i, + \rangle \\ &= \frac{E^{1/4}}{\pi^{1/2}} \int_{\Omega^i} d\mathbf{r}' j_L(E, \mathbf{r}') V^i(\mathbf{r}') \langle \mathbf{r}' | E', L', i, + \rangle. \end{aligned} \quad (18)$$

In the last line of this equation, we used the fact that for each i

$$\int_{\mathbb{R}^3} d\mathbf{r} | \mathbf{r} + \mathbf{R}_i \rangle \langle \mathbf{r} + \mathbf{R}_i | = 1 \quad (19)$$

with $| \mathbf{r} \rangle$, $\mathbf{r} \in \mathbb{R}^3$, the eigenfunctions of the position operator. If we substitute expression (18) for the t -matrix into equation (17), the energy integration over E' can be performed analytically by means of the theorem given in the appendix. To that end, we have to split up the integration over Ω^i into a subdomain $\Omega^i(<r)$, which is equal to the open sphere with radius $r \equiv | \mathbf{r} |$ around \mathbf{R}_i and a subdomain $\Omega^i(>r)$, which is the complement of $\Omega^i(<r)$ with respect to Ω^i . In each of these subdomains the theorem in the appendix applies, and we arrive at

$$\langle \mathbf{r} + \mathbf{R}_i | G(E) V^i | E, L, i, + \rangle = \sum_{L'} \left\{ C_{LL'}^i(E, r) j_{L'}(E, r) + S_{LL'}^i(E, r) h_{L'}^+(E, r) \right\} \quad (20)$$

with h^+ the spherical Hankel function of the first kind and the coefficient matrices C^i and S^i given by

$$C_{LL'}^i(E, r) = -i\sqrt{E} \int_{\Omega^i(>r)} d\mathbf{r}' h_{L'}^+(E, \mathbf{r}') V^i(\mathbf{r}') \langle \mathbf{r}' | E, L, i, + \rangle \quad (21a)$$

$$S_{LL'}^i(E, r) = -i\sqrt{E} \int_{\Omega^i(<r)} d\mathbf{r}' j_{L'}(E, \mathbf{r}') V^i(\mathbf{r}') \langle \mathbf{r}' | E, L, i, + \rangle \quad (21b)$$

If we combine expressions (13) and (20), we find

$$\langle \mathbf{r} + \mathbf{R}_i | E, L, i, + \rangle = \sum_{L'} \{ (\bar{C}_{LL'}^i + C_{LL'}^i) j_{L'}(E, r) + S_{LL'}^i h_{L'}^+(E, r) \}. \quad (22)$$

It has for the first time been pointed out by Brown and Ciftan, that a set of coupled,

ordinary differential equations for C^i and S^i can be derived by differentiating equations (21a) and (21b) with respect to the radius r .

$$\frac{d}{dr} C_{LL'}^i(E, r) = \sum_{L''} \{(\bar{C}_{LL''}^i(E) + C_{LL''}^i(E, r))A_{L''L'}^i(E, r) + S_{LL''}^i(E, r)B_{L''L'}^i(E, r)\} \quad (23a)$$

with the matrices A^i and B^i given by

$$A_{LL'}^i(E, r) = i\sqrt{Er^2}j_l(\sqrt{Er})V_{LL'}^i(r)h_l^+(\sqrt{Er}) \quad (24a)$$

$$B_{LL'}^i(E, r) = i\sqrt{Er^2}h_l^+(\sqrt{Er})V_{LL'}^i(r)h_l^+(\sqrt{Er}) \quad (24b)$$

and the matrix $V_{LL'}^i$, as usually, defined by

$$V_{LL'}^i(r) = \int d\hat{r} Y_L(\hat{r}) V^i(r, \hat{r}) Y_{L'}(\hat{r}). \quad (25)$$

Note, that the integration in the rhs of this definition runs over those parts of the surface of a sphere of radius r around \mathbf{R}_i , which lie within Ω^i . This surface of integration may thus consist of several unconnected parts.

For S^i we have an equation analogous to (23a):

$$\frac{d}{dr} S_{LL'}^i(E, r) = -\sum_{L''} \{(\bar{C}_{LL''}^i(E) + C_{LL''}^i(E, r))K_{L''L'}^i(E, r) + S_{LL''}^i(E, r)L_{L''L'}^i(E, r)\} \quad (23b)$$

with K^i and L^i given by

$$K_{LL'}^i(E, r) = i\sqrt{Er^2}j_l(\sqrt{Er})V_{LL'}^i(r)j_{L'}(\sqrt{Er}) \quad (24c)$$

$$L_{LL'}^i(E, r) = A_{L'L}^i(E, r). \quad (24d)$$

Given a potential V^i with support Ω^i , the matrices A^i , B^i , K^i and L^i are easily calculated. For r outside the circumscribing sphere of Ω^i , they vanish. To calculate C^i and S^i numerically, it remains to specify the values of C^i and S^i somewhere in the interval $[0, R_C^i]$, with R_C^i the radius of the circumscribing sphere of Ω^i . It has not yet been pointed out in the literature that, in the first instance, the equations (23a) and (23b) should be considered to establish a boundary value problem with homogeneous boundary conditions

$$C_{LL'}^i(E, r) = 0 \quad r = R_C^i \quad (25a)$$

$$S_{LL'}^i(E, r) = 0 \quad r = 0. \quad (25b)$$

With these conditions the problem is well-posed and could be solved by a variety of standard software. Some care is needed in the neighbourhood of $r = 0$, because there the matrices A and B diverge. These divergences are cancelled in the products in the rhs of (23a) and (23b), but require, from a numerical point of view, subtle treatment. In these considerations, the choice of the matrix \bar{C}^i plays an important role, which we deal with in the following section.

4. The matrix \bar{C}^i

In this section we present three possible choices for the matrix \bar{C}^i and discuss their merits.

4.1.

If we evaluate expression (22) for the single site wavefunction $\langle \mathbf{r} + \mathbf{R}_i | E, L, i, + \rangle$ on or outside the circumscribing sphere with radius R_C^i , we obtain in view of (25a)

$$\langle \mathbf{r} + \mathbf{R}_i | E, L, i, + \rangle = \sum_{L'} \{ \bar{C}_{LL'}^i(E) j_{L'}(E, \mathbf{r}) - iE^{1/4} \pi^{1/2} t_{EL, EL'}^i h_{L'}^+(E, \mathbf{r}) \} \quad r \geq R_C^i. \quad (26)$$

This expression is well-known and commonly used in MS theory in combination with the choice

$$\bar{C}_{LL'}^i(E) = \delta_{LL'}. \quad (27)$$

The usual interpretation of (26) with (27) is to look at the total wavefunction as the sum of an incoming free wave j_L and the corresponding scattered waves h^+ , weighted by the t -matrix. In the MT approximation, one often assumes V^i to be spherically symmetric. In that case, we meet with a diagonal t -matrix and an incoming wave j_L , which gives rise to only one outgoing wave h_L^+ . Condition (27) may be called the 'classical' choice for \bar{C}^i , because it is commonly used in KKR theory for MT potentials.

4.2.

It is proposed by Brown and Ciftan to choose

$$\bar{C}_{LL'}^i(E) + C_{LL'}^i(E, 0) = \delta_{LL'}. \quad (28)$$

This nice idea allows for a different view upon equations (23a) and (23b). It is clear that (23a) for C^i also holds for $\bar{C}^i + C^i$. With condition (28), one has initial conditions for the quantities $\bar{C}^i + C^i$ and S^i at the origin, namely (28) together with (25b). This implies that the differential equations could be solved as an initial value problem rather than as a boundary value problem. This approach is appealing, because the former are numerically easier to solve than the latter. It has, however, three disadvantages:

(i) It is hard to integrate equation (23) away from the origin, because now the rhs certainly diverges.

(ii) The proof that choice (28) is consistent with condition (15) fails until now. For the 'empty lattice' with $V^i \equiv 0$ (or constant) this point is trivial, but for less simple V^i the proof is probably hard.

(ii) The resulting wavefunctions and t -matrices, obtained via condition (28), will much differ from the t -matrices usually applied in KKR theory for MT potentials. One should not introduce such a discontinuity, if not absolutely necessary.

4.3.

To overcome the first disadvantage mentioned in § 4.1, one could try to use the condition

$$\bar{C}_{LL'}^i(E) + C_{LL'}^i(E, 0) = 0. \quad (29)$$

Although this choice diminishes the numerical problems, the two other disadvantages are still valid, unless one can prove that conditions (29) and (27) are in fact identical. This is a nice subject for further research, but will not be pointed out in this paper.

5. The secular equation

In § 2 we formally introduced in each ws cell Ω^i a complete set of basis functions $|E, L, i, +\rangle$. The defining equation (7), together with the mentioned boundary conditions, do not uniquely determine this basis. This point has been further discussed in § 3. Here, we assume that some choice is made and a particular basis set is known. We shall derive the secular equation, from which the expansion coefficients of the CWF and the $E - k$ relation can be calculated, and show that this equation has a separated structure, i.e. the information from the lattice structure and the information from the crystal potential are contained in different factors. The present derivation is much more concise than the one given earlier (Molenaar 1988), though the resulting equation is the same.

The CWF $|\psi^{\text{cr}}\rangle$ satisfies the LS equation

$$|\psi_k^{\text{cr}}\rangle = G(E)V^{\text{cr}}|\psi_k^{\text{cr}}\rangle. \quad (30)$$

In view of the partitioning (2), we write this in the form

$$(1 - GV^i)|\psi_k^{\text{cr}}\rangle = \sum_{j \neq i} GV^j|\psi_k^{\text{cr}}\rangle. \quad (31)$$

Note, that partitioning (2) only holds because V^i has Ω^i as its support. The present derivation would break down if one would make use of local potentials with the circumscribing spheres of Ω^i as supports.

Substitution of the on-shell expansion (8) yields the equation

$$\sum_L (1 - GV^i)|E, L, i, +\rangle d_{EL,k}^i = \sum_{j \neq i} \sum_L GV^j|E, L, j, +\rangle d_{EL,k}^j. \quad (32)$$

Note, that in the sequel the expansions of the CWF are always used within the appropriate ws cells. We take the inner product at both sides with $\langle \mathbf{r} |$ and use equation (13). The lhs of equation (32) then reduces to a sum over free particles wavefunctions:

$$\sum_L \sum_{L'} d_{EL,k}^i \bar{C}_{LL'}^i \langle \mathbf{r} | E, L', i \rangle = \sum_{L'} \frac{E^{1/4}}{\pi^{1/2}} d_{EL,k}^i \bar{C}_{L'L'}^i j_{L'}(E, \mathbf{r} - \mathbf{R}_i). \quad (33)$$

If we insert unity operators as given in (12) into the rhs of (32), we obtain the expression

$$\sum_{j \neq i} \sum_L \int_0^\infty dE' \sum_{L'L''} \langle \mathbf{r} | E', L', i \rangle G_{E'L',E'L''}^{ij}(E) t_{E'L'',EL}^j d_{EL,k}^j \quad (34)$$

with the t -matrices t^j given by (18) and the elements of the matrix G^{ij} defined by

$$\begin{aligned} G_{E'L',E'L''}^{ij}(E) &= \langle E', L', i | G(E) | E'', L'', j \rangle \\ &= \frac{1}{(E^+ - E')} \delta(E' - E'') J_{L'L''}^{ij}(E'). \end{aligned} \quad (35)$$

For $i = j$ this expression reduces to the one given in (16). The matrix J^{ij} is defined by

$$J_{L,L'}^{ij}(E) = \langle E, L, i | E, L', j \rangle. \quad (36)$$

Previously (1988) we showed that J^{ij} is explicitly given by

$$J_{L,L'}^{ij}(E) = 4\pi \sum_{L''} i^{l-l'+l''} C_{LL'L''} j_{L''}(E, \mathbf{R}_i - \mathbf{R}_j) \quad (37)$$

with $C_{LL'L''}$ denoting Gaunt coefficients. For later purposes, we introduce a matrix \bar{G} by replacing the Bessel function in (37) by a Hankel function:

$$\bar{G}_{L,L'}^{ij}(E) = 4\pi \sum_{L''} i^{(l-l'+l'')} c_{LL'L''} h^+(E, \mathbf{R}_i - \mathbf{R}_j). \quad (38)$$

For $i = j$ we take this matrix vanishing. The Fourier transform G of \bar{G} with respect to lattice sites is given by

$$G_{L,L'}(E, \mathbf{k}) = \sum_{j(j \neq i)} \bar{G}_{L,L'}^{ij}(E) \exp(i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)) \quad (39)$$

with j running over lattice sites.

The energy integration in (34) can be analytically performed. If we isolate the energy containing terms, we obtain the integral

$$\int_0^\infty dE' (E')^{1/2} \frac{1}{(E^+ - E')} j_{l'}(\sqrt{E'}|\mathbf{r} - \mathbf{R}_i|) j_{l''}(\sqrt{E'}|\mathbf{R}_i - \mathbf{R}_j|) j_{l''}(\sqrt{E'}|\mathbf{r}' - \mathbf{R}_j|) \quad (40)$$

with \mathbf{r}' running over Ω^j . We restrict the range of \mathbf{r} to an open ball around \mathbf{R}_i , with its radius such that

$$|\mathbf{R}_i - \mathbf{R}_j| > |\mathbf{r} - \mathbf{R}_i| + |\mathbf{r}' - \mathbf{R}_j|. \quad (41)$$

For the known lattice structures, this open ball is not empty. Under condition (41), we may apply the theorem in the appendix. Then, we obtain for the integral (40)

$$\pi i \sqrt{E} j_{l'}(\sqrt{E}|\mathbf{r} - \mathbf{R}_i|) h_{l''}^+(\sqrt{E}|\mathbf{R}_i - \mathbf{R}_j|) j_{l''}(\sqrt{E}|\mathbf{r}' - \mathbf{R}_j|).$$

If we substitute this product back into expression (34), this simplifies to

$$\sum_{j \neq i} \sum_{L, L', L''} i \sqrt{E} j_{L'}(E, \mathbf{r} - \mathbf{R}_i) \bar{G}_{L', L'', L''}^{ij} t_{EL'', EL}^j d_{EL, k}^j. \quad (42)$$

A further reduction is obtained from (3). This implies, that all t -matrices t^j are the same, so that the position index may be dropped. Further, we have that the expansion coefficients d^j are related to each other via the Bloch condition (5):

$$d_{EL, k}^j = \exp(i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)) d_{EL, k}^i. \quad (43)$$

So, we may also drop the upper index of d . Substitution into expression (42) yields

$$\sum_{L, L', L''} i \sqrt{E} j_{L'}(E, \mathbf{r} - \mathbf{R}_i) G_{L', L''}(E, \mathbf{k}) t_{EL'', EL} d_{EL, k}. \quad (44)$$

Expressions (44) and (33) both contain a summation over the particle wavefunction. If we equate them and reorder the indices, we find

$$\sum_{L, L'} j_L(E, \mathbf{r} - \mathbf{R}_i) M_{LL'}(E, \mathbf{k}) d_{EL, k} = 0. \quad (45)$$

with M given by

$$M_{LL'}(E, \mathbf{k}) = \sqrt{E} \sum_{L''} \left[\frac{1}{E^{1/4} \pi^{1/2}} (\bar{C}^i)_{LL''}^j \delta_{L'L''} - i G_{LL''}(E, \mathbf{k}) t_{EL'', EL} \right]. \quad (46)$$

By multiplying equation (45) with a particular spherical harmonic and integrating over

angles, we project out the L summation one particular Bessel function. Because Bessel functions are not vanishing in an open neighbourhood of R_i , we may conclude that the secular equation is

$$\sum_{L'} M_{LL'}(E, \mathbf{k}) d_{EL',k} = 0. \quad (47)$$

We remark that the separation of variables, which is present in the free particle wavefunctions (10) and allows for a projection argument, is not essential to arrive at the secular equation. Instead of the spherical Bessel functions, each other expansion in terms of linearly independent functions in an open neighbourhood of R_i would suffice to reduce an equation like (45) to the reduced form (47). The constant factors in (46) have their origin in the normalisation used for the free space wavefunctions in (10). If we choose $\bar{C}_{LL'}^i = \delta_{LL'}$, the matrix M is the usual KKR matrix for MT potentials. It thus appears that relaxing the muffin tin restriction has no influence on the structure of the resulting secular equation. This generalisation has only impact on the way the t -matrix is calculated.

6. Conclusions

Here, we shall list the most important conclusions from the discussions in the preceding sections.

(a) Solutions (13) of equation (7) form, under conditions (15) and regularity conditions at the origin and infinity, a complete set of basis functions in the Hilbert space $L_2(\mathbb{R}^3)$. Within a ws cell, the CWF can thus be represented by these bases.

(b) Representation (8) with (22) of the crystal wavefunction is on-shell, because the CWF and the basis functions used satisfy the same differential equation within the ws cell.

(c) The choice of the matrix \bar{C}^i in (13) defines the basis uniquely. It makes quite a difference, which choice is made, because the numerical evaluation of the expansion matrices C^i and S^i , defined in (21), heavily depends on it. The 'classical' choice (27) implies that C^i and S^i are to be determined from a boundary value problem with boundary conditions (25a, b). This problem is well posed and can be solved by standard techniques, provided that some numerical care is taken at the origin. Choice (28) for \bar{C}^i allows in theory the matrices C^i and S^i to be determined from an initial value problem with initial conditions (28) and (25b). Although this aspect gives it some preference above the 'classical' approach, this idea has serious drawbacks, both theoretically and numerically.

(d) The form of the secular equation (47) for generalised KKR theory shows a separation between structural and potential parts and is in essence the same as the secular equation of KKR theory. The absence of the MT approximation manifests itself only through the t -matrices used. The form of these t -matrices depends on the basis used. However, the band structure equation (47) yields results, which are independent of the used basis functions.

(e) In the defining equation (7) for the basis functions, we take V^i to be equal to the crystal potential within the i th ws cell and vanishing outside it. Brown and Ciftan take V^i equal to the crystal potential inside the circumscribed sphere and claim that neglect of the potential outside the ws cell, but inside its circumscribing sphere would introduce an essential error. We have shown above that this is not the case. This does not mean

that the approach of Brown and Ciftan is wrong. It simply leads to a different basis, which may also be complete in $L_2(\mathbb{R}^3)$. The only essential requirement in choosing the support of V^i is, that V^i coincides with V^{cr} inside the ws cell, because only then an on-shell expansion of the CWF can be obtained.

In general, we may conclude that, after years of discussions, the confusion about the ‘near field’ corrections in generalised KKR theory has cleared up both along the lines of the commonly used on-shell approach and the present off-shell approach. The result is remarkable in that extending KKR theory beyond the MT approximation lets the secular equation and in particular its separable structure nearly unchanged and only modifies the calculation of the t -matrices in a straightforward manner.

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Appendix

Let I be defined by

$$I = \int_0^\infty dk f(k) (E + i\varepsilon - k^2)^{-1} \prod_{i=1}^n j_{l_i}(kr_i) \tag{A1}$$

with j_{l_i} Bessel functions, E a constant and ε infinitesimally positive.

Under the restrictions

$$\sum_{i=1}^n l_i \text{ is even} \tag{A2}$$

$$f(k) \text{ is an even function of } k \tag{A3}$$

$$\sum_{i=1}^{n-1} r_i < r_n \neq 0 \tag{A4}$$

$$\sum_{i=1}^{n-1} l_i + p \geq l_n + 1 \tag{A5}$$

$$n + 2 > t \tag{A6}$$

where p and t are defined by the asymptotic behaviour of f , i.e.

$$f(z) \xrightarrow{z \rightarrow 0} z^p \quad \text{and} \quad f(z) \xrightarrow{z \rightarrow \infty} z^t \tag{A7}$$

it holds, in the limit $\varepsilon \downarrow 0$, that

$$I = -\frac{1}{2}\pi i \frac{f(\sqrt{E})}{\sqrt{E}} h_{l_n}^+(\sqrt{E}r_n) \prod_{i=1}^{n-1} j_{l_i}(\sqrt{E}r_i) \tag{A8}$$

with $h_l^+ = j_l + in_l$ a spherical Hankel function and n_l a spherical Neumann function.

The proof of this theorem is given in appendix B of Molenaar (1988).

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