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Reformulation of the Korringa–Kohn–Rostoker coherent potential approximation for the treatment of space-filling cell potentials and charge-transfer effects

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Abstract. We present a reformulation of the Korringa–Kohn–Rostoker (KKR) coherent-potential approximation (CPA) which affords a number of conceptual and practical advantages over conventional formulations of the theory. In particular, as presented here the method can facilitate application to systems that cannot be described properly by a muffin-tin approximation to the cell potential and require a full potential treatment. Also, the formalism allows the derivation of the KKR CPA self-consistency condition within both a scattering matrix and a Green function approach, leading to uniquely defined species-resolved charge densities and densities of states. As shown in a companion paper, this formulation also allows the treatment of the so-called charge-transfer effects associated with Wigner–Seitz cells in an alloy which contain net amounts of charge.

1. Introduction

It is generally acknowledged that the coherent potential approximation (CPS) [1–5] (CPA) is the most satisfactory single-site theory for the study of the electronic states in substitutionally disordered alloys. The CPA has been formulated both in terms of tight-binding Hamiltonians [3] as well as within a first-principles multiple-scattering formalism [4, 5], in an extension of the method introduced by Korringa [6] and by Kohn and Rostoker [7] (KKR) for the study of ordered translationally invariant materials. In this last form, the method is referred to as KKR CPA. Recent improvements of the computational aspects of implementing the CPA include the development of CPA codes within the first-principles tight-binding method, and the use of screened and short-ranged structure constants [8–11].

The KKR CPA has been used successfully in a number of applications [4, 5], particularly with respect to alloys of transition metals. In all these applications, use was made of cell potentials that were spherically symmetric and non-overlapping, the so-called muffin-tin (MT) potentials. However, the use of MT potentials is hard to justify in many cases of physical interest. For example, MT potentials do not describe properly systems characterized by unidirectional cells, such as those found in covalently bonded semiconducting materials, or systems containing symmetry-breaking defects, such as surfaces and interfaces. The

application of the method of KKR and of KKR CPA to low-symmetry systems requires a generalization of the method to non-MT space-filling potential cells.

Further justification for the implementation of a full-potential CPA formalism can be sought in considering the calculation of elastic constants of disordered alloys, and in the treatment of the so-called charge-transfer effects. In the former case, one must be able to calculate the change in energy resulting from infinitesimal distortions of the lattice under externally imposed strain whose effects are not represented well under a spherical approximation to the potential. In the second case, charge-transfer effects are associated with the fact that, in an alloy, equivolume Wigner–Seitz (WS) cells may contain an increase in or a deficiency of electrons, thus failing to compensate the nuclear charge. In the case of disordered alloys, the calculation of the electrostatic energy of the solid becomes a major concern. If one desires the treatment of such charged cells within a single-site (SS) theory, and there are substantive grounds for developing such treatment, then a reformulation of the CPA is required. Such a reformulation is provided in this paper.

Indeed, recently a great deal of work [12–32] has been directed at the generalization of the KKR method to space-filling cells. Much of this work has established [25–32] that, as far as the band structure of a material is concerned, multiple-scattering theory (MST) assumes identical forms in both the case of MT and the case of space-filling cells. In fact, in all its manifestations, MST retains one of its most advantageous features, namely the separability of the structural aspects from the potential aspects of a scattering assembly. It also retains a second important property, that of leading directly to the single-particle Green function of an ensemble of scattering cells. Finally, at least in the case of systems with cubic symmetry, MST requires the use of only a small basis set of angular-momentum eigenstates, with converged results being obtained for $\ell \leq 4$, where ℓ is an angular-momentum index.

However, in spite of the similarities between applications of MST to MT and space-filling cells, some important differences exist. The size of the basis set used in the calculation may increase substantially in cases in which the symmetry of the cell potential deviates greatly from spherical or from cubic. Also, unlike the case of MT potentials, formally equivalent forms of the equations of MST may exhibit very different numerical behaviours. For example, the variational nature of the eigenvalues of the secular equation of a scattering assembly with respect to the wavefunction, as well as the rate of convergence of expansions in angular-momentum states, especially in the construction of the wavefunction, depend [32] crucially on the particular form chosen.

The reason for these differences in behaviour between the cases of MT and space-filling cells (or even non-spherical MT potentials) is the lack of angular-momentum conservation in the latter. This leads to the need to use non-diagonal matrices to represent the scattering matrices (*t*-matrices) and other quantities, such as the phase functions, of individual cells which in turn leads to the need for converging internal summations over $L = (\ell, m)$ (with m being the azimuthal quantum number). A further difficulty arises with the presence of the inverse of matrix quantities which can only be calculated in an often highly approximate manner. Even if one assumes that these inverses exist in a formal sense, the need to compute them explicitly can present formidable practical problems of convergence in L .

Of the two interrelated difficulties mentioned above, that associated with the inverses of matrices is the more troubling. The first difficulty, the convergence of internal sums arising from the use of non-diagonal matrices, can often be alleviated [32] through the use of surface (and possibly volume) integrations which provide a closed form of the corresponding expansions in L . However, no such alternatives exist for the calculation of inverses. Therefore, in applying MST to space-filling cells, it would be desirable to use a form which does not require the inversion of non-diagonal matrices.

Forms of the secular equation for the band structure of a material, as well as for the Green function, that do not involve matrix inverses can be readily constructed for the case of ordered, translationally invariant systems. However, at first glance these forms seem to be incompatible with the use of the CPA. Such forms involve the explicit use of at least *two* different cell functions (corresponding to the sine and cosine of the phase shifts in the case of spherical potentials), whereas the KKR CPA provides only a *single* self-consistency condition. This condition has been used traditionally to determine an effective scattering matrix (or an effective ratio of the phase functions). Therefore, it is not immediately evident that one can apply the principles of the CPA unless only a single quantity describing cell scattering enters the self-consistency equation.

The first aim of this paper is to derive forms of the KKR CPA which do not involve matrix inversion of phase functions and consequently depend on the separate knowledge of both the sine and the cosine cell functions. We shall show that this feature can be incorporated into a *single* self-consistency condition for the *product* of the phase functions in contrast with the usual formulations of the KKR CPA that require the use of a *t*-matrix and hence the inversion of a phase function. Furthermore, one of the forms suggested here involves symmetric matrices and leads to eigenvalues of the secular equation that are variational with respect to the wavefunction for any specific alloy configuration.

The reformulation of the KKR CPA presented below has another advantage when compared with conventional derivations [4, 5]. Those derivations are based on the scattering *t*-matrix of an assembly rather than the corresponding Green function. That is to say, the self-consistency condition determining the effective cell scattering matrix is expressed in the form $\langle T^{00} \rangle_{ss} = \bar{T}^{00}$, where T^{00} and \bar{T}^{00} denote the site-diagonal elements of the on-the-energy shell scattering matrix for the disordered material and the effective medium, respectively, and $\langle \dots \rangle_{ss}$ denotes an average over the occupation of a SS, i.e. whether the site is occupied by an atom of type A or B in a binary alloy. Within the conventional approach, a derivation entirely in terms of the Green function $\langle G^{00} \rangle_{ss} = \bar{G}^{00}$ does not appear to be possible. This difficulty arises because different alloy species are associated with different wavefunctions, while no wavefunction can be associated with the cells of an effective medium. Thus, within conventional formalisms, it is not possible to obtain the Green function as a single product between these species-dependent cell functions and the effective scattering matrix.

The formalism presented below alleviates this difficulty. It allows for the independent derivation of the Green function of an effective medium which when set equal to the SS average of the species-dependent Green functions leads to the self-consistency condition of the KKR CPA. It can be easily shown that this form is formally equivalent to the more familiar form involving the scattering matrix.

The matrix formulation of the CPA discussed below also allows the application of the CPA formalism to disordered alloys described by charge-neutral cells which may lead to different volumes associated with cells of different alloy species. So-called charge-transfer effects can greatly affect the electrostatic interactions in a substitutionally disordered material, and their treatment has been the subject of much recent work (see following paper). It is shown here that the expression of the KKR CPA into a configurational-space framework is able to accommodate the treatment of such effects within a coherent and self-consistent alloy theory.

The remainder of this paper takes the following form. In section 2, we review certain basic aspects of full-cell MST which are relevant to the formulation of the CPA presented subsequently. The KKR CPA is then derived both within a conventional approach and a

configurational matrix framework in section 3. Finally, section 4 provides a discussion of the formalism and certain guidelines for its usefulness and its application.

2. Review of full-cell multiple-scattering theory

2.1. Cell basis functions

The solutions, $\psi(k, \mathbf{r})$ of the Schrödinger equation (where $k^2 = E$ denotes the energy parameter)

$$[-\nabla^2 + V(\mathbf{r})]\psi(k, \mathbf{r}) = E\psi(k, \mathbf{r}) \quad (2.1)$$

for individual cell potentials $V(\mathbf{r})$, form the building blocks of MST in general, and of its application to disordered alloys in particular. These solutions can be written as a linear combination of basis functions indexed by angular-momentum eigenstates [32]:

$$\psi(k, \mathbf{r}) = \sum_L A_L \psi_L(k, \mathbf{r}) \quad (2.2)$$

where $L = (\ell, m)$ is an angular-momentum index, with ℓ being the orbital and m the azimuthal quantum numbers. The functions $\psi_L(\mathbf{r})$ are given by the expression

$$\psi_L(k, \mathbf{r}) = \sum_{L'} [C_{LL'}(r)J_{L'}(k\mathbf{r}) - S_{LL'}(r)N_{L'}(k\mathbf{r})] \quad (2.3)$$

in terms of the phase functions $C_{LL'}(r)$ and $S_{LL'}(r)$. Here, $J_L(k\mathbf{r}) = j_\ell(r)Y_L(\hat{\mathbf{r}})$ with $j_\ell(r)$ being a spherical Bessel function and $Y_L(\hat{\mathbf{r}})$ a spherical harmonic of order ℓ . Similarly, $N_{L'}(k\mathbf{r}) = n_{\ell'}(r)Y_{L'}(\hat{\mathbf{r}})$, and $H_{L'}^\pm(k\mathbf{r}) = h_{\ell'}^\pm(r)Y_{L'}(\hat{\mathbf{r}})$ with $n_{\ell'}$ and $h_{\ell'}^\pm$ denoting the Neumann and Hankel functions (of either kind). These are the regular solutions J_L and irregular solutions N_L and H_L^\pm of the free-particle $V = 0$ Schrödinger equation. The phase functions are given by the relations

$$C_{LL'}(r) = \bar{C}_{LL'} - k \int_{r'>r} N_L(k\mathbf{r}')V(\mathbf{r}')\psi_{L'}(k, \mathbf{r}') d^3r' \quad (2.4)$$

and

$$S_{LL'}(r) = k \int_{r'<r} J_L(k\mathbf{r}')V(\mathbf{r}')\psi_{L'}(k, \mathbf{r}') d^3r'. \quad (2.5)$$

where in general the coefficients $\bar{C}_{LL'}$ depend on the potential V and different choices for these coefficients lead to various forms of the wavefunction and to various behaviours with respect to convergence of expansions in angular-momentum space. The solutions of the free-particle Schrödinger equation can be used to expand the free-particle Green function in a series whose terms are indexed by L . For example, using the Bessel and Neumann functions (either of the Hankel functions could also be employed in place of the Neumann functions), we have

$$G_0(\mathbf{r}, \mathbf{r}') = -ik \sum_L J_L(k\mathbf{r})N_{L'}(k\mathbf{r}') \quad \text{for } r' > r \quad (2.6)$$

where the conditions on the lengths of the arguments of the regular and irregular solutions are to be noted. Failure to satisfy these conditions in expanding the free-particle propagator can lead to serious divergences of the equations of MST. In what follows, care is taken to guarantee that these conditions are explicitly satisfied, by carrying out summations each of which conforms to them.

Now, we recall [5] that in the case of spherically symmetric potentials the t -matrix has the explicit representation

$$t_\ell(k) = -\frac{1}{k} \exp(i\delta_\ell) \sin \delta_\ell = -\frac{1}{k} [\cot \delta_\ell - i] \quad (2.7)$$

where δ_ℓ is the phase shift for the ℓ th partial wave. Consequently, we identify the quantity,

$$\underline{t}(k) = -\frac{1}{k} [\underline{S}^{-1} \underline{C} - i]^{-1} \quad (2.8)$$

as the t -matrix for a non-spherical, generally shaped potential cell.

Finally, treating \underline{S} as an invertible matrix, we obtain

$$|\psi'\rangle = \underline{m}|J\rangle - ik|H\rangle \quad (2.9)$$

which for potentials with spherical symmetry corresponds to the expression,

$$\psi_\ell(k, \mathbf{r}) = m_\ell j_\ell(k) - ik h_\ell(k). \quad (2.10)$$

2.2. The secular equation

Within the single-particle picture discussed here, the electronic structure of a multicell assembly is determined through the solutions of a secular equation

$$\det \underline{\mathbf{M}} = 0 \quad (2.11)$$

where the matrix $\underline{\mathbf{M}}$ can be written in a number of formally equivalent forms

$$\underline{M}^{nm} = \underline{m}^n \delta_{nm} - \underline{G}(\mathbf{R}_{nm})(1 - \delta_{nm}) \quad (2.12)$$

or

$$\underline{M}^{nm} = \underline{C}^n \delta_{nm} - \underline{G}(\mathbf{R}_{nm}) \underline{S}^m (1 - \delta_{nm}). \quad (2.13)$$

The last matrix product converges in the case in which no intracell vectors, \mathbf{r} , are larger than any intercell vector, $\mathbf{R}_{nm} = \mathbf{R}_m - \mathbf{R}_n$. In this case we can also write

$$\underline{M}^{nm} = \hat{\underline{S}} \underline{C}^n \delta_{nm} - \hat{\underline{S}} [\underline{G}(\mathbf{R}_{nm}) \underline{S}^m] (1 - \delta_{nm}) \quad (2.14)$$

where a hat symbol denotes the transpose of a matrix, and the square brackets indicate an order of operation that guarantees convergence of the internal L products. In the equations above, the structure constants describing free-electron propagation between sites n and m in the lattice are given by the expression

$$G_{LL'}(\mathbf{R}_{nm}) = -ik \sum_{L''} i^{\ell+\ell''-\ell'} C(LL'L'') H_{L''}(\mathbf{R}_{nm}) \quad (2.15)$$

where $C(LL'L'')$ are Gaunt numbers (integrals of three spherical harmonics).

Denoting by $\underline{\tau}$ the inverse of the matrix \underline{M} , and associating a site index with the solution of the Schrödinger equation for the potential in a given cell, we obtain the expression for the Green function

$$G(\mathbf{r}, \mathbf{r}') = \langle \psi^n(\mathbf{r}) | \underline{\tau}^{nm} | \psi^m(\mathbf{r}') \rangle + \langle \psi^m(\mathbf{r}) | F^m(\mathbf{r}') \rangle \delta_{nm} \quad \text{for } r' > r \quad (2.16)$$

where the vectors \mathbf{r} and \mathbf{r}' are confined in cells Ω_n and Ω_m , respectively.

The expression for the Green function in equation (2.16) has a familiar form, consisting of single-scatterer and multiple-scatterer contributions. In the case of crystal lattices and for a choice of cell centres in which the intercell vectors are larger than intracell vectors, equation (2.16) can be readily converted to the form

$$G(\mathbf{r}, \mathbf{r}') = \langle \psi^n(\mathbf{r}) | \underline{\tau}^{nm} | \psi^m(\mathbf{r}') \rangle + \langle Z^m(\mathbf{r}) | \tilde{J}^m(\mathbf{r}') \rangle \delta_{nm} \quad (2.17)$$

where now $\underline{\tau}^{nm}$ is the inverse of the matrix

$$\underline{M}^{nm} = \underline{\hat{S}}^n \underline{C}^n \delta_{nm} - \underline{\hat{S}}^n [\underline{G}(\mathbf{R}_{nm}) \underline{S}^m] (1 - \delta_{nm}). \quad (2.18)$$

Finally, we mention that the Green function can also be written in the form

$$G(\mathbf{r}, \mathbf{r}') = \langle Z^n(\mathbf{r}) | \underline{\tau}^{nm} | Z^m(\mathbf{r}') \rangle + \langle Z^m(\mathbf{r}) | \tilde{J}^m(\mathbf{r}') \rangle \delta_{nm} \quad (2.19)$$

where the matrix $\underline{\tau}^{nm}$ is the inverse of the matrix

$$\underline{M}^{nm} = \underline{m}^n \delta_{nm} - \underline{G}(\mathbf{R}_{nm}) (1 - \delta_{nm}). \quad (2.20)$$

In the last two equations, the functions $|Z^n(\mathbf{r})\rangle$ are those regular solutions of the Schrödinger equation for cell Ω_n which outside the bounding sphere join smoothly to the functions $|J^n(\mathbf{r})\rangle \underline{m}^n - ik|H^n(\mathbf{r})\rangle$, while the functions $|\tilde{J}^n(\mathbf{r})\rangle$ are those irregular solutions that join smoothly to $|J^n(\mathbf{r})\rangle$. In the form of equation (2.19) the Green function has been used extensively in applications of the KKR CPA in connection with MT potentials. We note that this form involves the inverse of the t -matrix, and hence the inverse of the transpose of the sine function (matrix), in the multiple-scattering part of the Green function and may be difficult to evaluate in cases of full-cell potentials. In these equations and subsequently, we follow commonly used notation and denote the on-the-energy shell part of the scattering matrix by $\underline{\tau}$, a quantity referred to as the scattering path operator [4].

Even though equations (2.17) and (2.16) do not involve individual t -matrices, and consequently they tend to obscure somewhat the scattering aspects of an ensemble of cells, they also do *not* require the inversion of any phase functions, a feature which can be of great computational value. As long as the order of operations is kept as indicated by the square brackets in equation (2.13), or surface integrals are used to close internal sums [31], the expression for the Green function is guaranteed to converge. Furthermore, in the case in which the length of intracell vectors does exceed that of intercell vectors, the product $\underline{G}\underline{S}$ occurring in equation (2.18) can be replaced by a Wronskian integral. This replacement assures convergence [32] for both expressions of the Green function, equations (2.16) and (2.17). Finally, in the form of equation (2.17), the Green function involves a t -matrix for an assembly of cells which leads to energy eigenvalues that are variational with respect to changes in the wavefunction [32]. This feature can be of computational value in the calculation of the electronic structure.

3. The Korringa–Kohn–Rostoker coherent-potential approximation

In this section, we present a derivation of the self-consistency condition of the KKR CPA both within a conventional approach, based on the t -matrix for an assembly of scatterers, as well as within a formalism based on the Green function of the system. We consider atoms (cells) of various kinds $\{\alpha\}$, $\alpha = 1, 2, \dots, n$, distributed randomly over the sites of a three-dimensional lattice, with corresponding concentrations c_α . We seek approximation schemes that lead to the determination of the averaged properties of the material, and in particular to the averaged single-particle Green function.

3.1. Conventional derivation

We begin with the so-called equation of motion of the scattering path operator $\underline{\tau}^{nm}$ [30], which is given by the inverse of the matrix \underline{M}^{nm} in equation (2.20):

$$\underline{\tau}^{nm} = \underline{t}^n \delta_{nm} + \underline{t}^n \sum_k \underline{G}(\mathbf{R}_{nk}) \underline{\tau}^{km} \quad (3.1)$$

where $\underline{t}^n = (\underline{m}^n)^{-1}$ is the t -matrix associated with cell Ω_n . This equation follows from a formal expansion of the inverse of \underline{M}^{nm} in equation (2.20). However, whether this expansion converges in a practical sense depends crucially on the topology (geometry) of the distribution of the cells in space. For example, the expansion converges absolutely [26] in the case of MT potentials when the local basis functions are expanded about the geometric centres of the cells, in which the conditions of the expansion of the free-particle propagator are satisfied. In the case of space-filling cells in which the length of intercell vectors exceeds that of intracell vectors, convergence is again guaranteed provided that the internal sums that occur in the products of a structure constant and a cell t -matrix are carried out completely, one at a time. The order in which these sums are performed is immaterial, as long as no two sums are exchanged. In more general cases, paths that guarantee the convergence of the expansion in equation (3.1) can again be found [28], but their detailed description can become rather involved. In any case, our use of equation (3.1) at this point is mostly for illustrative purposes and for making contact with conventional derivations of the KKR CPA. We shall see that the final results can be written in a form that does not include such expansions, and that they can also be derived without the explicit use of the equation of motion. With this in mind, let us proceed on the basis of equation (3.1).

The CPA consists in approximating the true average of a disordered material by an effective medium. This medium is described by an effective cell t -matrix, denoted \bar{t} , which is independent of site index and is chosen so that any additional scattering which is caused by the presence of a ‘real’ atom in the medium, i.e. by the replacement of a site of the medium with a real site, vanishes on the average. This condition can be formulated in terms of the scattering path operator as follows.

In the presence of an effective medium, the equation of motion can be solved through the use of lattice Fourier transforms to yield the expression

$$\bar{t}^{00} = \frac{1}{\Omega_{BZ}} \int_{BZ} \bar{t}(\mathbf{k}) d^3k = \frac{1}{\Omega_{BZ}} \int_{BZ} [\bar{m} - \underline{G}(\mathbf{k})]^{-1} d^3k \quad (3.2)$$

for the site-diagonal element of the scattering path operator associated with the effective medium. Here, Ω_{BZ} denotes the volume of the first Brillouin zone (BZ) of the reciprocal lattice. The last expression in turn leads to the relation

$$\bar{\Delta} = \bar{m} - [\bar{t}^{00}]^{-1} \quad (3.3)$$

which allows the determination of the so-called renormalized interactor $\bar{\Delta}$ of the effective medium, describing the interaction of a ‘site’ (real or effective) with the surrounding material.

Having determined the effective medium through the effective scattering matrices, we can obtain an expression for the Green function associated with a cell of type α embedded in this medium. With the vectors \mathbf{r} and \mathbf{r}' lying in the impurity cell, we obtain

$$G^\alpha(\mathbf{r}, \mathbf{r}') = \langle Z^\alpha(\mathbf{r}) | \underline{t}^\alpha | Z^\alpha(\mathbf{r}') \rangle + \langle Z^\alpha(\mathbf{r}) | \bar{J}^\alpha(\mathbf{r}') \rangle. \quad (3.4)$$

Finally, the average value of the SS Green function is given by the expression

$$\bar{G}(\mathbf{r}, \mathbf{r}') = \sum_\alpha c_\alpha G^\alpha(\mathbf{r}, \mathbf{r}') = \sum_\alpha c_\alpha [\langle Z^\alpha(\mathbf{r}) | \underline{t}^\alpha | Z^\alpha(\mathbf{r}') \rangle + \langle Z^\alpha(\mathbf{r}) | \bar{J}^\alpha(\mathbf{r}') \rangle]. \quad (3.5)$$

The charge density in a cell of type α is given by the usual relation

$$\rho^\alpha(\mathbf{r}) = -\frac{1}{\pi} \int_{\Omega_n} dE G^\alpha(E, \mathbf{r}, \mathbf{r}) \quad (3.6)$$

while the density of states at a given energy is obtained from the relation

$$n^\alpha(E) = -\frac{1}{\pi} \int_{\Omega_n} d^3r G^\alpha(E, \mathbf{r}, \mathbf{r}). \quad (3.7)$$

The previous discussion provides a summary of the ideas and self-consistency conditions characterizing the KKR CPA. Since the KKR CPA has been reviewed extensively in the literature [4,5] we forego a detailed discussion. We highlight only those features which will figure in the following development.

First, we emphasize that the expressions of the KKR CPA can be expressed either in terms of the inverse of the cell t -matrix, or in terms of the t -matrix itself, as the reader can readily verify. Either of these forms involves the inverse of a cell phase function, equation (2.8), a feature which can lead to numerical difficulties in the case of non-spherical cells. Second, the self-consistency conditions are expressed in terms of the scattering path operator, rather than the Green function. Although the Green function can be defined, equations (3.4) and (3.5), it cannot be used to determine the effective medium. The reason for this is the species dependence of the cell functions $|Z^\alpha(\mathbf{r})\rangle$. Because of this dependence, it is not possible to connect the Green function with the scattering path operator through ‘multiplication’ by a single wavefunction, as is the case for pure materials. Finally, it is possible to derive expressions for both the site off-diagonal scattering path operator as well as the Green function [31]. However, owing to the difficulties associated with the species dependence of the cell wavefunctions these derivations involve further apparent approximations. In the following section, we provide a derivation of the KKR CPA in a form which alleviates these difficulties.

3.2. Derivation of the Green function of the Korringa–Kohn–Rostoker coherent-potential approximation

We now turn to a derivation of the KKR CPA which allows the treatment of the Green function and of the scattering path operator on an equal footing. Since we are interested in expressions for the self-consistency condition that do not involve inverses of cell functions, it is convenient to work with equations (2.17) and (2.18). (We mention in passing that the following development can indeed be carried out with respect to the cell t -matrices of an alloy rather than the cell functions used explicitly below.) In order to simplify our notation, we introduce the quantities

$$\underline{q}^n = \hat{\underline{S}}^n \underline{Q}^n \quad (3.8)$$

and

$$\underline{Q}(\mathbf{R}_{nm}) = \hat{\underline{S}}^n [\underline{G}(\mathbf{R}_{nm}) \underline{S}^m] \quad (3.9)$$

so that equation (2.18) can be written in the form

$$\underline{M}^{nm} = \underline{q}^n \delta_{nm} - \underline{Q}(\mathbf{R}_{nm})(1 - \delta_{nm}). \quad (3.10)$$

Now, building on an idea suggested by Blackman, Esterling and Berk (BEB) [33] in their application of the CPA to alloys with off-diagonal disorder described by a tight-binding Hamiltonian, we introduce occupation numbers $p_{n,\alpha}$ which project on the subspace of atoms of type α and have the properties

$$p_{n,\alpha} = \begin{cases} 1 & \text{if site } n \text{ is occupied by an atom of type } \alpha \\ 0 & \text{otherwise} \end{cases} \quad (3.11)$$

and

$$p_{n,\alpha}^2 = p_{n,\alpha}. \quad (3.12)$$

These numbers also satisfy the relations

$$\frac{1}{N} \sum_n p_{n,\alpha} = c_\alpha \quad (3.13)$$

where N is the total number of sites, and

$$\sum_\alpha p_{n,\alpha} = 1. \quad (3.14)$$

Multiplying equation (3.10) on the left and on the right by all possible combinations of these occupation numbers, and collecting the results in a single matrix, we obtain the expression

$$\underline{\mathbf{M}}^{nm} = \underline{\mathbf{q}}^n \delta_{nm} - \underline{\mathbf{Q}}(\mathbf{R}_{nm})(1 - \delta_{nm}) \quad (3.15)$$

where underlined bold symbols denote matrices in both angular momentum and configuration space. Thus, the site-diagonal matrices such as $\underline{\mathbf{q}}^n$ have matrix elements in configuration space (the space spanned by the $\{p_\alpha\}$) of the form

$$\underline{\mathbf{q}}^{n,\alpha\beta} = \underline{q}^\alpha \delta_{\alpha\beta} = \underline{\hat{S}}^\alpha \underline{C}^\alpha \delta_{\alpha\beta} \quad (3.16)$$

while site off-diagonal matrices have elements in configuration space given by the expression

$$\underline{\mathbf{Q}}(\mathbf{R}_{nm})^{\alpha\beta} = \underline{\hat{S}}^\alpha [\underline{G}(\mathbf{R}_{nm}) \underline{S}^\beta]. \quad (3.17)$$

For clarity we quote the explicit values of these expressions for the case of binary alloys, $A_{1-c}B_c$. In this case, each matrix in angular momentum space, either site diagonal or off-diagonal, is augmented into a matrix of dimension twice that of the original matrix. Thus, we have

$$\underline{\mathbf{q}}^n = \begin{cases} \begin{bmatrix} \underline{q}^A & 0 \\ 0 & 0 \end{bmatrix} & \text{if an A atom occupies site } n \\ \begin{bmatrix} 0 & 0 \\ 0 & \underline{q}^B \end{bmatrix} & \text{if a B atom occupies site } n. \end{cases} \quad (3.18)$$

Introducing the numbers $s_n = 1 - p_n$, we can write

$$\underline{\mathbf{q}}^n = \begin{bmatrix} p_n \underline{q}^A & 0 \\ 0 & s_n \underline{q}^B \end{bmatrix}. \quad (3.19)$$

In general, each matrix quantity \underline{Q}^{nm} in direct space is augmented to the two-dimensional form

$$\underline{\mathbf{Q}}^{nm} = \begin{bmatrix} p_n \underline{Q}^{AA} p_m & p_n \underline{Q}^{AB} s_m \\ s_n \underline{Q}^{BA} p_m & s_n \underline{Q}^{BB} s_m \end{bmatrix}. \quad (3.20)$$

At the same time, matrices in reciprocal space, such as $\underline{\tau}(\mathbf{k})$ and $\underline{Q}(\mathbf{k})$ take the form

$$\underline{\tau}(\mathbf{k}) = \begin{bmatrix} \underline{\tau}^{AA}(\mathbf{k}) & \underline{\tau}^{AB}(\mathbf{k}) \\ \underline{\tau}^{BA}(\mathbf{k}) & \underline{\tau}^{BB}(\mathbf{k}) \end{bmatrix} \quad (3.21)$$

and

$$\underline{\mathbf{Q}}(\mathbf{k}) = \begin{bmatrix} \underline{Q}^{AA}(\mathbf{k}) & \underline{Q}^{AB}(\mathbf{k}) \\ \underline{Q}^{BA}(\mathbf{k}) & \underline{Q}^{BB}(\mathbf{k}) \end{bmatrix}. \quad (3.22)$$

We note that these results can be derived in a straightforward fashion from the equation of motion, equation (3.1), a procedure that will be used explicitly in the next section. This can be accomplished through multiplication of that equation on the left and on the right by

all possible combinations of the occupation numbers p_n and s_n and insertion of the sum $p_k + s_k = 1$ between the two factors in the product $\underline{G}(\mathbf{R}_{nk})\underline{\tau}^{km}$. This yields expressions of the form

$$p_n \underline{\tau}^{nm} p_m = p_n \underline{\tau}^n \delta_{nm} + p_n \underline{\tau}^n \sum_k \underline{G}(\mathbf{R}_{nk}) (p_k + s_k) \underline{\tau}^{km} p_m \quad (3.23)$$

and

$$p_n \underline{\tau}^{nm} s_m = p_n \underline{\tau}^n \sum_k \underline{G}(\mathbf{R}_{nk}) (p_k + s_k) \underline{\tau}^{km} s_m \quad (3.24)$$

since $p_n s_n = 0$. There are two more expressions such as these, obtained through multiplication on the left (right) by s_n (p_m) and s_n (s_m). These four expressions can be combined into a single matrix expression as indicated in equation (3.20). This leads to an equation of motion for a matrix scattering path operator which has the same form as equation (3.1) but in terms of 2×2 matrices in configuration space.

Using the projection-operator property of the p_n and s_n , equation (3.12), we see that in the matrix equation of motion the occupation numbers in the site-diagonal matrices \mathbf{q}^n , equation (3.19), suffice to keep track of the alloy configuration, so that these indices need not be associated with the structure constants, or quantities in reciprocal space. Since it will be necessary to consider this step in some detail in the next section, we shall not give a complete derivation at this point. We also introduce the matrix ket wavefunctions

$$|\underline{\psi}^n\rangle = \begin{bmatrix} |\psi^A\rangle & 0 \\ 0 & |\psi^B\rangle \end{bmatrix} \quad (3.25)$$

and the corresponding bra quantities $\langle \underline{\psi}^n |$. Similar definitions can be made of all other cell functions, such as $\langle Z^m |$. Now with the vectors \mathbf{r} and \mathbf{r}' in no cells other than Ω_n and Ω_m , respectively, we can define a matrix Green function for any configuration of the system in the form

$$\mathbf{G}(\mathbf{r}, \mathbf{r}') = \langle \underline{\psi}^n | \underline{\tau}^{nm} | \underline{\psi}^m \rangle + \langle Z^n | \underline{\tilde{J}}^n \rangle \delta_{nm}. \quad (3.26)$$

The physical Green function is obtained as a sum over all the matrix elements of the matrix Green function in configuration space:

$$G(\mathbf{r}, \mathbf{r}') = \sum_{\alpha\beta} \mathbf{G}(\mathbf{r}, \mathbf{r}')^{\alpha\beta} \quad (3.27)$$

where α and β run over all alloy species.

We are now in a position to derive the self-consistency condition of the KKR CPA. Imposing the condition that the SS average of the site-diagonal element of the matrix Green function $\mathbf{G}(\mathbf{r}, \mathbf{r}')$ be equal to the corresponding quantity associated with the effective medium, we obtain the result

$$\langle \mathbf{G}(\mathbf{r}, \mathbf{r}') \rangle = \bar{\mathbf{G}}(\mathbf{r}, \mathbf{r}') \quad (3.28)$$

where $\bar{\mathbf{G}}(\mathbf{r}, \mathbf{r}')$ is given by an expression analogous to that in equation (3.26), but with $\underline{\tilde{\tau}}^{nm}$ replacing $\underline{\tau}^{nm}$.

The self-consistency condition, equation (3.28), can also be expressed in terms of the effective medium scattering path operator

$$\langle \underline{\tau}^{00} \rangle = \underline{\tilde{\tau}}^{00} \quad (3.29)$$

which can be extracted from equation (3.28).

For clarity, we display explicitly the form of the self-consistency condition, equation (3.29), for a binary alloy:

$$\begin{bmatrix} c_A[\underline{q}^A - \underline{\bar{\Delta}}^{AA}]^{-1} & 0 \\ 0 & c_B[\underline{q}^B - \underline{\bar{\Delta}}^{BB}]^{-1} \end{bmatrix} = \begin{bmatrix} \underline{\bar{\tau}}^{AA} & 0 \\ 0 & \underline{\bar{\tau}}^{BB} \end{bmatrix} = \frac{1}{\Omega_{BZ}} \int_{BZ} d^3k \\ \times \left(\begin{bmatrix} \underline{\bar{\tau}}^{AA} & 0 \\ 0 & \underline{\bar{\tau}}^{BB} \end{bmatrix}^{-1} - \begin{bmatrix} \underline{\bar{\Delta}}^{AA} & \underline{\bar{\Delta}}^{AB} \\ \underline{\bar{\Delta}}^{BA} & \underline{\bar{\Delta}}^{BB} \end{bmatrix} - \begin{bmatrix} \underline{Q}^{AA}(\mathbf{k}) & \underline{Q}^{AB}(\mathbf{k}) \\ \underline{Q}^{BA}(\mathbf{k}) & \underline{Q}^{BB}(\mathbf{k}) \end{bmatrix} \right)^{-1}. \quad (3.30)$$

Upon multiplication on the left and on the right by the matrix cell functions, equation (3.25), the last equation leads directly to a self-consistency condition in terms of Green functions. Clearly, in the case of alloys with n components, the self-consistency condition is expressed in terms of n -dimensional matrices.

The KKR CPA self-consistency condition expressed in the form of equation (3.30) has a number of important properties. First, it is a matrix equation with separate conditions on the different species of an alloy. In that sense, it is also somewhat more difficult to handle computationally. At the same time, in most cases, one need not use this matrix equation in actual computations. Having derived the matrix form of the KKR CPA self-consistency condition and shown that it leads to an independent expression for the Green function of an effective medium, one can readily reduce it to the simpler form of the ordinary (scalar) formulation of the CPA. On the other hand, as is shown in the following paper, it may be necessary to employ the matrix formulation of the KKR CPA to treat a number of physical effects, such as the presence of non-neutral WS cells in a disordered alloy.

A second noteworthy feature of equation (3.30) is that it involves the off-diagonal components of the matrix renormalized interactor $\underline{\bar{\Delta}}^{AB}$. The presence of these elements seems to imply that a site can be occupied simultaneously by both an atom of type A and an atom of type B. However, these elements do not appear in any expansion of the scattering path operator in real space, their function being only to guarantee that the species off-diagonal elements of $\underline{\tau}^{00}$ vanish. This is consistent with the form of equation (3.30).

Finally, the site off-diagonal elements of the scattering path operator as well as the Green function can be obtained in the forms

$$\underline{\tau}^{ij} = \frac{1}{\Omega_{BZ}} \int_{BZ} d^3k \underline{\tau}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{R}_{ij}) \quad (3.31)$$

and

$$G(\mathbf{r}, \mathbf{r}') = \langle \underline{\psi}^i | \underline{\tau}^{ij} | \underline{\psi}^j \rangle. \quad (3.32)$$

In particular, the last equation yields expressions for the site off-diagonal Green function when the sites are occupied by atoms of different chemical species. It is a matter of some straightforward algebra to show that, when site i is occupied by an atom of type α , and site j by an atom of type β , we have

$$\underline{\bar{\tau}}^{\alpha\beta} = \underline{D}^\alpha \underline{\bar{\tau}}^{ij} \underline{D}^\beta \quad (3.33)$$

where $\underline{\bar{\tau}}^{ij}$ is the site off-diagonal element of the scattering path operator obtained in the 'scalar' version of the theory. These quantities can be calculated directly according to

$$\underline{\bar{\tau}}^{ij} = \frac{1}{\Omega_{BZ}} \int_{BZ} \underline{\bar{\tau}}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{R}_{ij}) d^3k = \frac{1}{\Omega_{BZ}} \int_{BZ} \exp(i\mathbf{k} \cdot \mathbf{R}_{ij}) [\underline{m} - \underline{G}(\mathbf{k})]^{-1} d^3k \quad (3.34)$$

or they can be obtained as the sum of the elements of the matrix expression in equation (3.31). In any case, once $\underline{\bar{\tau}}^{ij}$ has been calculated, the corresponding Green function can be found from equation (3.32).

4. Conclusions

In this paper, we introduced a reformulation of the KKR CPA that has a number of advantages compared with the form in which the method has been implemented in the past. The generalization to matrices of the various quantities of the formalism and of the self-consistency condition allows one to derive the KKR CPA independently within both a scattering matrix as well as a Green function approach. When combined with results obtained in the case of ordered materials, this shows that the KKR CPA provides a unique prescription for the calculation of species-resolved charge densities and yields densities of states that are in agreement with those obtained by the Lloyd formula [5].

We presented forms of the self-consistency condition that are particularly suitable for application to non-MT space-filling potential cells. The use of such potentials appears to be unavoidable as the demand grows for applications of the CPA to disordered systems with reduced symmetry, and for a more accurate and precise treatment of the elastic properties of substitutionally disordered alloys. In addition, the formalism presented here allows the study of charge-transfer effects, which are not amenable to treatment within the conventional formulation of the CPA. As is shown in the following paper, this is accomplished through the introduction of a configuration space in which the 'distance' between pairs of cells is species dependent. We caution that care should be taken not to interpret the different lattices so defined as connected with real lattice relaxation effects in the alloy, or representing a real alloy configuration. Those effects, which can indeed be very important, must be treated by perturbative means or by a cluster extension of the CPA. In the following paper, we provide a derivation of the generalization of the CPA to treat charge-transfer effects together with a specific application to Al-Li alloys. We also compare the results of calculations based on these ideas with results obtained by different means.

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- [33] Blackman J A, Esterling D M and Berk N F 1971 *Phys. Rev. B* **4** 2412. It should perhaps be pointed out that the configurational matrix approach of BEB, used in the development reported in the body of the paper, bears a superficial resemblance to the so-called augmented space formalism of Mookerjee A 1975 *J. Phys. C: Solid State Phys.* **8** 2943. The two approaches are by no means equivalent. At the single-particle level, they give different results and, when the augmented space approach is applied to systems with short-range order within the context of the KKR method, it has been found to yield non-analytic results such as negative densities of states (Razee S S and Prasad R 1993 *Phys. Rev. B* **48** 1349). A review of the approach of BEB and of the augmented space formalism with many original references can be found in the book by Gonis A 1992 *Green Functions for Ordered and Disordered Systems* (Amsterdam: Elsevier)