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Coherent-potential and average t-matrix approximations for disordered muffin-tin alloys. I. Formalism

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The average density of states $\langle\rho(E)\rangle$ and the component charge density associated with an A (B) atom in the alloy, $\langle\rho_{A(B)}(E)\rangle$, are discussed for the disordered alloy A_xB_{1-x} within the framework of the muffin-tin Hamiltonian. A new version of the average t-matrix (ATA) is developed. The structure in the spectral density function, $\langle\rho(\vec{k},E)\rangle$, in the coherent-potential approximation (or the new ATA) is seen to result from not only the Bloch-type states in the medium of coherent-potential effective atoms t_{CP} (or the average t-atoms $\langle t\rangle$) but also from non-Bloch-type impurity levels arising when a single A or B atom is embedded in an otherwise perfect effective medium. The proposed ATA equations would allow a simple yet reliable treatment of many aspects of the electronic spectrum of disordered transition and noble-metal alloys.

I. INTRODUCTION

It has become clear in recent years that, in order to obtain a realistic description of the electronic structure of disordered metallic alloys, the atomic potentials must be treated within the framework of the muffin-tin model, as is usually done for the corresponding perfect crystals. In particular, the simple one- and two-band tight-binding model Hamiltonians are not adequate for dealing with the detailed experimental information which is now becoming available, pertaining to the electronic spectrum of transition and noble-metal alloys.[1-3]

The application of the multiple-scattering theory techniques to the disordered muffin-tin alloys has proceeded rapidly. In this connection, two of the most commonly used approximation schemes have been the coherent-potential (CPA) and the average t-matrix (ATA) approximations.[1,2] Both belong to the class of the so-called single-site approximations. However, of the two only the CPA treats the disorder self-consistently and is to be preferred. The attractiveness of the ATA derives mostly from its relative simplicity in application to realistic models.[4-7] In spite of the significant progress made with regard to the application of the CPA and the ATA to the muffin-tin alloys, difficulties have persisted with each of these schemes. The CPA formalism is well developed,[8-10] but its practical implementation to the muffin-tin Hamiltonian has not been undertaken until recently,[11-14] owing to the difficult and repeated Brillouin-zone integrations necessary to solve the CPA self-consistency equations. Additional difficulties involving the free-electron poles must also be faced in order to evaluate the component density of states $\langle\rho_{A(B)}(E)\rangle$ [i.e., the electronic charge density associated with an A (or B) atom in the alloy]. With the ATA, on the other hand, the difficulties are formal in nature: Although the currently used ATA expression for the average total density of states $\langle\rho(E)\rangle$ appears to give reasonable results in all cases studied so far, the corresponding expressions for the component densities $\langle\rho_A(E)\rangle$ and $\langle\rho_B(E)\rangle$ yield *negative* results in many cases and are not reliable.[5]

In this series of two papers, we address some of the questions that have arisen in the application of the CPA and ATA to the disordered muffin-tin alloys. The present paper discusses the relevant formal aspects. A new set of ATA equations (designated as ATA2 for convenience) is considered. The comparison of the ATA2 spectrum with the currently used form of the ATA[5-7] (referred to as ATA1) is presented. However, the bulk of the results for the CPA and ATA2 and their comparison is undertaken in the second following paper.[15]

We emphasize that a fully self-consistent calculation of the electronic spectrum of the disordered alloy requires not only the self-consistent treatment of disorder but also that of the atomic potentials. The CPA treats just the disorder self-consistently in the sense of a single-site approximation. The problem of self-consistency of atomic potentials has been handled to date only via semi-empirical models[2,4,7] in which the effect of disorder on atomic potentials is taken into account by adjusting one or another feature of the constituent atomic potentials to force agreement between theory and one particular experiment. Our ability to do accurate calculations of the component charge density $\langle\rho_{A(B)}(E)\rangle$ has important consequences in this regard. This point is discussed further with the example of $\mathrm{Cu}_x\mathrm{Ni}_{1-x}$ in the article that follows.[15]

An outline of the present paper is as follows: Section II considers the exact equations for $\langle\rho(E)\rangle$ and $\langle\rho_{A(B)}(E)\rangle$. The formula for $\langle\rho(E)\rangle$ is well known.[8-10] The expression for $\langle \rho_{A(B)}(E)\rangle$, which is the focus of our discussion, has also been suggested in an earlier paper.[10] However, several delicate features inherent to this definition were not recognized at that time. We clarify the exact meaning of our definition of $\langle \rho_{A(B)}(E)\rangle$ and its relationship to the more conventional definition in which this quantity is defined as the integral of the charge density over a *Wigner-Seitz unit cell* at the center of which an A (or B) atom is placed.[2] In fact, our definition of $\langle \rho_{A(B)}(E)\rangle$ may be more appropriate for considering transfer of charge between the constituent atoms of an alloy, because this definition does not artificially carve out the Wigner-Seitz unit cell as the basic region of space to which the transfer of the electronic charge is restricted. In any event, our conclusion is that even though the two viewpoints of charge transfer are somewhat different, they are likely to yield similar results for physically relevant quantities sensitive to the environment of the A and B atoms in the alloy.

Section III specializes to the CPA. The expressions for $\langle \rho(E)\rangle^{\mathrm{CP}}$ and $\langle \rho_{A(B)}(E)\rangle^{\mathrm{CP}}$ have already been discussed in Ref. 13. While the free-electron singularities cancel exactly in $\langle \rho(E)\rangle^{\mathrm{CP}}$ owing to the translational symmetry of the average alloy, these singularities are present in an essential way in the expression for $\langle \rho_{A(B)}(E)\rangle^{\mathrm{CP}}$. (The techniques used for handling this problem are outlined in Appendix A.) The focus of our discussion in this section concerns the symmetry properties of the CPA equation. First, we show that the CPA equation is symmetric to the interchange $C_{\mathrm{CP}}(E) \rightarrow C^{*}_{\mathrm{CP}}(E)$, where $C_{\mathrm{CP}}(E)$ denotes the matrix of cotangents of CPA phase shifts. The solution with $\mathrm{Im}[C_{\mathrm{CP}}(E)] < 0$ satisfies the unitarity constraint and is physically relevant. Second, we show that for cubic systems, τ_{CP} is diagonal if only s, p, d phase shifts (i.e., $l \leq 2$) are used for pure constituents.[8] While this statement is by no means surprising, an explicit proof is useful and indicates how CPA can be implemented most conveniently for $l > 2$ and for other symmetries.

The ATA formalism is taken up in Sec. IV. This discussion concerns the manner in which the restricted averages of the path operators $\langle T_{nn'}\rangle_{0=A(B)}$ are decoupled in terms of the corresponding path operators $T^{\mathrm{eff}}_{nn'}$ for an ordered crystal of effective atoms $t_{\mathrm{eff}} = \langle t\rangle$. The currently used form of the ATA decoupling[5,10] (referred to as ATA1) and the proposed ATA2 decoupling are discussed. The density of states in the disordered alloy involves contributions from not only the Bloch-type complex bands but also from the impurity levels which arise when an A or B atom is embedded in an otherwise ordered medium of effective atoms. The physical content of the new ATA2 decoupling is that it treats the single impurity contributions better than ATA1. We show that if $\langle \tau\rangle$ is replaced by τ_{CP} in the ATA2 expressions for $\langle \rho(E)\rangle$ and $\langle \rho_{A(B)}(E)\rangle$, the CPA spectrum will result. In this sense, ATA2 can be viewed as the lowest-order approximation to the CPA, and the ATA2 spectrum may be improved systematically by simply replacing $\langle \tau\rangle$ by successively better approximations to τ_{CP}. Finally, using the illustrative example of $\mathrm{Cu}_{0.75}\mathrm{Ni}_{0.25}$, the spectral density and densities of states in ATA1 and ATA2 are compared in order to elucidate some of the important differences between these two approximations.

II. EXACT EQUATIONS

The substitutionally disordered binary alloy A_xB_{1-x} will be discussed within the framework of the one-electron Hamiltonian

$$H = p^2/2m + \sum_{\alpha} v_{\alpha}^{A(B)}(r) . \tag{2.1}$$

Here the crystal potential is assumed to be given as the sum of nonoverlapping spherically symmetric muffin-tin potentials $v_{\alpha}^{A(B)}(r) \equiv v^{A(B)}(|\vec{r} - \vec{R}_{\alpha}|)$ centered on atomic sites $\{\vec{R}_{\alpha}\}$. The A and B atoms are assumed to occupy the sites $\{\vec{R}_{\alpha}\}$ randomly, so that the probability that a given site is occupied by an A (or B) atom is proportional to its concentration x [or $y \equiv (1-x)$].

The electronic density of states $\rho(E)$ (per atom, per spin) is given most conveniently in terms of the Green's function

$$\mathcal{G}(E) \equiv (E - H)^{-1} \tag{2.2}$$

by the relation

$$\rho(E) = -(\pi N)^{-1} \mathrm{Im}\, \mathrm{Tr}[\mathcal{G}(E^{+})] \tag{2.3a}$$

$$= -(\pi N)^{-1} \mathrm{Im} \int d^3r\, \mathcal{G}(\vec{r}, \vec{r}; E^{+}) . \tag{2.3b}$$

Here $E^{+} \equiv E + i0^{+}$ and N is the total number of atoms in the system. By using the coordinate representation explicitly, Eq. (2.3b) expresses $\rho(E)$ as an integral over the charge density, which is proportional to $\mathrm{Im}\mathcal{G}(\vec{r}, \vec{r}; E^{+})$.

An exact expression for the average density of states $\langle \rho(E)\rangle$ can be obtained by using the Lloyd's formula[16] for the density of states of an arbitrary assembly of muffin-tin atoms. This well-known result is[10]

$$\langle \delta\rho(E)\rangle = -\pi^{-1} \mathrm{Im}\, \mathrm{Tr}\Bigg(x\langle T_{00}\rangle_{0=A} \frac{d\tau_A^{-1}}{dE} + y\langle T_{00}\rangle_{0=B} \frac{d\tau_B^{-1}}{dE} - \sum_{n'} \langle T_{0n'}\rangle \frac{dB_{n'0}}{dE}\Bigg) , \tag{2.4}$$

where $\langle \delta\rho(E)\rangle \equiv \langle\rho(E)\rangle - \rho_0(E)$. $\rho_0(E)$ is the free-electron density of states. $T_{nn'}$, $B_{nn'}$, τ_A and τ_B, respectively, denote the usual path operators, structure functions, and the on-the-energy-shell matrix elements of the A and B atom-scattering matrices. The trace in (2.4) refers only to the angular momentum space. The symbol $\langle\ldots\rangle$ denotes the complete random average, whereas $\langle\ldots\rangle_{n=A(B)}$ denotes a one-site restricted average.

We will not discuss formula (2.4) except to note that the integrations over the electronic coordinates $\vec{r}$ of Eq. (2.3b) have been carried out explicitly in obtaining this equation. For this reason, the detailed real-space charge-density information contained in $\mathrm{Im}\langle\mathcal{G}(\vec{r},\vec{r};E^+)\rangle$ can no longer be extracted in any simple manner from Eq. (2.4). This observation is important in the consideration of the component charge density $\langle\tilde{\rho}_{A(B)}(E)\rangle$, which is traditionally defined[2,10] in terms of the restricted average Green's function

$$\langle\tilde{\rho}_{A(B)}(E)\rangle \equiv -\pi^{-1}\mathrm{Im}\int_{(0)} d^3r\langle\mathcal{G}(\vec{r},\vec{r};E^+)\rangle_{0=A(B)}, \quad (2.5)$$

where the subscript (0) indicates that the integral extends only over the 0th Wigner-Seitz cell volume. Equation (2.5) physically defines $\langle\tilde{\rho}_{A(B)}(E)\rangle$ as the average total charge in a unit cell of the alloy containing an A (or B) atom fixed at its origin.

We emphasize that when an A or B atom is held fixed at the origin, the translational symmetry of the average alloy is broken and there is no compelling reason to choose the Wigner-Seitz cell as the basic region of integration. Indeed, the magnitude of the charge transferred between constituent atoms will vary depending upon how the region of integration in definition (2.5) is chosen. It is also noteworthy that since the geometrical shapes of Wigner-Seitz cells in crystals are not so simple, the integration in Eq. (2.5), which extends over the volume of the unit cell, is likely to pose practical problems for realistic systems. It is clear that a definition of component density of states which does not involve an integration over a specific region of $\vec{r}$ space will have certain advantages over the definition (2.5). One such definition suggests itself from the expression (2.4) for $\langle\rho(E)\rangle$.

Using $\langle T_{0n'}\rangle = x\langle T_{0n'}\rangle_{0=A} + (1-x)\langle T_{0n'}\rangle_{0=B}$, Eq. (2.4) may be rewritten as

$$\langle\delta\rho(E)\rangle = -\pi^{-1}\mathrm{Im\,Tr}\left[x\left(\langle T_{00}\rangle_{0=A}\frac{d\tau_A^{-1}}{dE} - \sum_{n'}\langle T_{0n'}\rangle_{0=A}\frac{dB_{n'0}}{dE}\right) + y\left(\langle T_{00}\rangle_{0=B}\frac{d\tau_B^{-1}}{dE} - \sum_{n'}\langle T_{0n'}\rangle_{0=B}\frac{dB_{n'0}}{dE}\right)\right]. \quad (2.6)$$

The form (2.6) naturally suggests the definition

$$\langle\delta\rho_{A(B)}(E)\rangle = -\pi^{-1}\mathrm{Im\,Tr}\left(\langle T_{00}\rangle_{0=A(B)}\frac{d\tau_{A(B)}^{-1}}{dE} - \sum_{n'}\langle T_{0n'}\rangle_{0=A(B)}\frac{dB_{n'0}}{dE}\right) \quad (2.7)$$

for the A (B) component density of states. Here, as in (2.4), $\langle\delta\rho_{A(B)}(E)\rangle \equiv \langle\rho_{A(B)}(E)\rangle - \rho_0(E)$. Note that, in view of Eqs. (2.6) and (2.7),

$$x\langle\rho_A(E)\rangle + y\langle\rho_B(E)\rangle = \langle\rho(E)\rangle\,, \quad (2.8)$$

which represents the constraint of charge neutrality of the average alloy.

In Ref. 10, expression (2.7) was suggested as being equivalent to the definition (2.5) of the A (B) component density of states. However, as noted before, the real-space integrations over the electronic coordinates have already been carried out in Eq. (2.4) for $\langle\rho(E)\rangle$ and, for this reason, this formula can no longer be viewed as an integral of the charge density over a Wigner-Seitz unit cell. In particular, the quantity $\langle\rho_{A(B)}(E)\rangle$ in Eq. (2.7) cannot be equivalent to the expression (2.5) for $\langle\tilde{\rho}_{A(B)}(E)\rangle$, because the latter involves the Wigner-Seitz unit-cell volume in an essential way.[17]

To understand the nature of Eq. (2.7) for the component charge densities, we rewrite Eq. (2.3b) by using the equation

$$\mathcal{G}(E) = G_0(E) + \sum_n G_0(E)\mathcal{T}_n(E)G_0(E) \quad (2.9)$$

to decompose the Green's function in terms of the scattering operators $\mathcal{T}_n$. Thus

$$\delta\rho(E) = -(\pi N)^{-1}\mathrm{Im}\sum_n \int d^3r\langle\vec{r}\,|G_0\mathcal{T}_nG_0|\,\vec{r}\rangle \quad (2.10a)$$

$$\equiv N^{-1}\sum_n \delta\rho_n(E)\,, \quad (2.10b)$$

where (2.10b) defines

$$\delta\rho_n(E) \equiv -\pi^{-1}\mathrm{Im}\int d^3r\langle\vec{r}\,|G_0\mathcal{T}_nG_0|\,\vec{r}\rangle\,. \quad (2.11)$$

In particular, for $n=0$,

$$\delta\rho_0(E) \equiv -\pi^{-1}\mathrm{Im}\int d^3r\langle\vec{r}\,|G_0\mathcal{T}_0G_0|\,\vec{r}\rangle\,. \quad (2.12)$$

By carrying out a restricted average of both sides of (2.12), we obtain

$$\langle\delta\rho_0(E)\rangle_{0=A(B)} = -\pi^{-1}\mathrm{Im}\int d^3r\langle\vec{r}\,|G_0\langle\mathcal{T}_0\rangle_{0=A(B)}G_0|\,\vec{r}\rangle\,. \quad (2.13)$$

Thus far the quantity $\langle \delta\rho_0(E)\rangle_{0=A(B)}$ is merely a definition. However, it is possible to show, by straightforward though somewhat lengthy manipulations, that the right-hand side of Eq. (2.13) reduces to the expression (2.7) for $\langle \delta\rho_{A(B)}(E)\rangle$. Hence Eq. (2.7) is equivalent to the definition

$$\langle \delta\rho_{A(B)}(E)\rangle = \langle \delta\rho_0(E)\rangle_{0=A(B)} \tag{2.14a}$$

$$= -\pi^{-1}\,\mathrm{Im}\int d^3r \langle \vec{r}\,|\, G_0 \langle \mathcal{T}_0\rangle_{0=A(B)} G_0 \,|\, \vec{r}\rangle \,. \tag{2.14b}$$

To discuss the relationship between the definitions (2.5) and (2.14) [or equivalently (2.7)], it is instructive to consider first the case of a perfect crystal, where the two definitions must be identical. Suppressing the subscripts A (B), the total charge density associated with the 0th site based on Eq. (2.5), in view of (2.9), is

$$\delta\bar{\rho}_0 = -\pi^{-1}\,\mathrm{Im}\sum_m \int_{(0)} d^3r \langle \vec{r}\,|\, G_0 \mathcal{T}_m G_0 \,|\, \vec{r}\rangle \tag{2.15a}$$

$$= -\pi^{-1}\,\mathrm{Im}\left(\int_{(0)} d^3r \langle \vec{r}\,|\, G_0 \mathcal{T}_0 G_0 \,|\, \vec{r}\rangle + \sum_{m\neq 0}\int_{(0)} d^3r \langle \vec{r}\,|\, G_0 \mathcal{T}_m G_0 \,|\, \vec{r}\rangle\right). \tag{2.15b}$$

[Since we are considering a perfect crystal, the ensemble averages in Eq. (2.5) have been suppressed in writing (2.15b).] The translational invariance of the operators $\mathcal{T}_m$ in an ordered crystal can be used to manipulate the second term on the right-hand side of (2.15b) to obtain

$$\delta\bar{\rho}_0(E) = -\pi^{-1}\,\mathrm{Im}\left(\int_{(0)} d^3r \langle \vec{r}\,|\, G_0 \mathcal{T}_0 G_0 \,|\, \vec{r}\rangle + \sum_{m\neq 0}\int_{(m)} d^3r \langle \vec{r}\,|\, G_0 \mathcal{T}_0 G_0 \,|\, \vec{r}\rangle\right) \tag{2.16a}$$

$$= -\pi^{-1}\,\mathrm{Im}\int d^3r \langle \vec{r}\,|\, G_0 \mathcal{T}_0 G_0 \,|\, \vec{r}\rangle \,. \tag{2.16b}$$

Equation (2.16b) now involves an integral over all space and is identical to the definition (2.14) [or (2.5)].

For the disordered alloy, since the translational invariance does not hold for restricted averages, the above manipulations do not carry through. Equations (2.5) and (2.14) may, however, be rewritten [in analogy with (2.15b)] as

$$\langle \delta\bar{\rho}_{A(B)}\rangle = -\pi^{-1}\,\mathrm{Im}\left(\int_{(0)} d^3r \langle \vec{r}\,|\, G_0 \langle \mathcal{T}_0\rangle_{0=A(B)} G_0 \,|\, \vec{r}\rangle + \sum_{m\neq 0}\int_{(0)} d^3r \langle \vec{r}\,|\, G_0 \langle \mathcal{T}_m\rangle_{0=A(B)} G_0 \,|\, \vec{r}\rangle\right), \tag{2.17}$$

$$\langle \delta\rho_{A(B)}\rangle = -\pi^{-1}\,\mathrm{Im}\left(\int_{(0)} d^3r \langle \vec{r}\,|\, G_0 \langle \mathcal{T}_0\rangle_{0=A(B)} G_0 \,|\, \vec{r}\rangle + \sum_{m\neq 0}\int_{(m)} d^3r \langle \vec{r}\,|\, G_0 \langle \mathcal{T}_0\rangle_{0=A(B)} G_0 \,|\, \vec{r}\rangle\right). \tag{2.18}$$

In order to compare (2.17) and (2.18), note that each of the $G_0\mathcal{T}_m G_0$ terms in Eq. (2.15b) may be viewed as giving the contribution to the charge density at the 0th site from some sort of a "muffin-tin orbital" located at the mth site. (This association for our present purposes is only meant to be qualitative.) Both Eqs. (2.17) and (2.18) then contain identical contributions from the muffin-tin orbital located at the 0th site (i.e., from $\langle \mathcal{T}_0\rangle_{0=A(B)}$ term). In addition, $\langle \delta\bar{\rho}_{A(B)}\rangle$ involves the "tails" on the 0th site of the muffin-tin orbitals located at $m\neq 0$ sites. By contrast, $\langle \delta\rho_{A(B)}\rangle$ involves tails of the 0th muffin-tin orbital on $m\neq 0$ sites. Hence the differences between the second terms of (2.17) and (2.18) have to do with the details of how the tails of muffin-tin orbitals are averaged. In this sense, the differences between $\langle \delta\bar{\rho}_{A(B)}\rangle$ and $\langle \delta\rho_{A(B)}\rangle$ may be expected to be small, particularly for single-site approximations which are the primary concern of this paper.

Note that when a single impurity is embedded in a free-electron medium, the perturbation in the free-electron density of states is given by

$$\delta\rho_0^{(\mathrm{imp})} = -\pi^{-1}\int d^3r \langle \vec{r}\,|\, G_0 t_0 G_0 \,|\, \vec{r}\rangle \,. \tag{2.19}$$

Comparing Eqs. (2.19) and (2.12), it is immediately seen that $\delta\rho_0$ can be obtained from $\delta\rho_0^{(\mathrm{imp})}$ by the replacement $t_0 \to \mathcal{T}_0$. In this sense, $\delta\rho_0$ is the perturbation of the free-electron medium *associated with the* 0*th site* when the atom in the 0th cell is surrounded by $N-1$ other atoms. If these $N-1$ atoms are removed, then the perturbation is just $\delta\rho_0^{(\mathrm{imp})}$. By their very definitions, both $\delta\rho_0^{(\mathrm{imp})}$ and $\delta\rho_0$ involve integrals over the entire crystal.

It is noteworthy that Eqs. (2.5) and (2.14) imply a somewhat different picture of the transfer of charge between the alloy constituents. Equation (2.5) can be used to monitor changes in charge in a unit cell surrounding an A (B) atom in the alloy as compared to a pure crystal. By contrast for definition (2.14) the reference system with respect to which changes are considered is an $A(B)$ atom embedded in the free-electron medium, and the perturbed charge distribution is integrated over the entire crystal.

To summarize our discussion, we emphasize that both definitions (2.5) and (2.14) of the component density of states are likely to yield similar results for physically relevant quantities such as the transfer of charge between A and B atoms in an alloy. To date $\langle\tilde{\rho}_{A(B)}(E)\rangle$ based on Eq. (2.5) has not been computed for any realistic muffin-tin Hamiltonian. We have, however, evaluated component charge densities based on Eq. (2.14) [or equivalently Eq. (2.7)] in $\mathrm{Cu}_x\mathrm{Ni}_{1-x}$ and $\mathrm{Cu}_x\mathrm{Zn}_{1-x}$ for a range of constituent concentrations and have found the results to be reasonable.[15]

III. COHERENT-POTENTIAL APPROXIMATION (CPA)

The average total and component CPA densities of states on the basis of Eqs. (2.4) and (2.7) have been discussed elsewhere.[13] Here we discuss certain symmetry properties of the muffin-tin CPA equation and of the CPA effective scattering matrix. To our knowledge, a proof of these properties has not appeared in the literature.

The CPA condition for the on-the-energy-shell matrix elements τ_{CP} of the CPA effective scattering matrix can be written as[8-10]

$$\tau_{\mathrm{CP}}^{-1}=x\tau_A^{-1}+y\tau_B^{-1}+(\tau_{\mathrm{CP}}^{-1}-\tau_A^{-1})T_{00}^{\mathrm{CP}}(\tau_{\mathrm{CP}}^{-1}-\tau_B^{-1}), \tag{3.1}$$

where

$$T_{00}^{\mathrm{CP}}=\frac{1}{N}\sum_{\vec{k}}\,[\tau_{\mathrm{CP}}^{-1}-B_{\vec{k}}(E)]^{-1} \tag{3.2}$$

is given as a Brillouin-zone summation.

Equation (3.1) can be rewritten in the form

$$C_{\mathrm{CP}}(E)\equiv i-(\kappa\tau_{\mathrm{CP}})^{-1} \tag{3.3}$$

$$=xC_A(E)+yC_B(E)+\kappa(C_A-C_{\mathrm{CP}})\times\Big(N^{-1}\sum_{\vec{k}}\,(\kappa C_{\mathrm{CP}}+A_{\vec{k}})^{-1}\Big)(C_B-C_{\mathrm{CP}}), \tag{3.4}$$

where $C_{A(B)}$ and C_{CP} are the matrices of the cotangents of A (B) and CP atom phase shifts, respectively. $A_{\vec{k}}(E)$ is the matrix of *real* Korringa-Kohn-Rostoker (KKR) structure functions[18] related to the structure functions $B_{\vec{k}}(E)$ via the matrix equation

$$A_{\vec{k}}(E)=B_{\vec{k}}(E)-i\kappa\,. \tag{3.5}$$

In Eq. (3.4) all quantities other than the unknown $C_{\mathrm{CP}}(E)$ are real. Consequently, if $C_{\mathrm{CP}}(E)$ is a solution of (3.3), then $C_{\mathrm{CP}}^*(E)$ must also be a solution. The physically relevant solution corresponds to $\mathrm{Im}[(C_{\mathrm{CP}}(E))_l]\leq 0$, since it is easily shown to satisfy the unitarity constraint.[11] This implies, for example, that if during the course of solving the CPA equation a solution with $\mathrm{Im}C_l>0$ is encountered, then the physical solution should be obtained by changing the sign of Im C_l and not by some other means of forcing the solution to satisfy the unitarity condition.

To consider the symmetry properties of τ_{CP}, we specialize to the case of a cubic system and to the use of only s, p, and d phase shifts for pure A (B) atoms. (This is a good approximation for many transition and noble metals. In any event, the following discussion is easily generalized to systems with other symmetries and to include a larger number of pure metal phase shifts.) In the angular momentum representation [with $L\equiv(l,m)$], the atomic scattering matrix $t(\vec{x},\vec{x}\,')$ can be written as (suppressing the superscripts CP)

$$t_{LL'}(x,x')\equiv\int d\Omega_{\hat{x}}\int d\Omega_{\hat{x}'}\,Y_L(\hat{x})t(\vec{x},\vec{x}\,')Y_{L'}(\hat{x}') \tag{3.6a}$$

$$=\int d\Omega_{\hat{x}}\int d\Omega_{\hat{x}'}\Big(N_g^{-1}\sum_P Y_L(P\vec{x})Y_{L'}(P\vec{x}\,')\Big)\times t(\vec{x},\vec{x}\,'), \tag{3.6b}$$

where N_g is the total number of elements in the cubic group and $Y_L(\hat{x})$ is the Lth spherical harmonic associated with unit vector $\hat{x}$. In obtaining (3.6b) the invariance of $t(\vec{x},\vec{x}\,')$ under the operations P of the cubic group has been used.

We now invoke the relation valid for *real* spherical harmonics for $l\leq 2$ (see Appendix B):

$$\sum_P Y_L(P\hat{x})Y_{L'}(P\hat{x}')=\delta_{LL'}f^{(L)}(x,x'), \tag{3.7}$$

where $f^{(L)}(x,x')$ is the *same* function for L values belonging to a given representation of the cubic group. In view of (3.7), Eq. (3.6b) shows that $t_{LL'}\propto\delta_{LL'}$, i.e., the corresponding matrix τ is diagonal.[8,11-13]

It is interesting to note that formally the symmetry properties of the CPA amplitudes are built into the CPA equation via the corresponding properties of the matrix T_{00}^{CP} [cf. Eq. (3.1)]. For $l\leq 2$, for example, by using relation (3.7), it is possible to show that T_{00}^{CP} is a diagonal matrix, provided the KKR structure functions are computed by using real spherical harmonics.

IV. AVERAGE t-MATRIX APPROXIMATION (ATA)

In the context of the one- and two-band tight-binding model Hamiltonians, the ATA is defined by replacing the disordered alloy by an effective crystal of $\langle t\rangle\equiv xt_A+(1-x)t_B$ atoms.[1,2] A closed expression for the average density of states on this basis can be obtained,[4,19,20] but it involves the off-the-energy-shell matrix elements of the A and B atom t matrices. Since the exact expression (2.4) for $\langle\rho(E)\rangle$ does not involve any such elements, this is a deficiency of the usual muffin-tin ATA. For this reason, in Ref. 10 alternative expressions for the ATA spectrum were proposed, which were based on Eqs. (2.4) and (2.7). (We will refer to these as ATA1 in this paper.) ATA1 has been applied to a variety of transition- and noble-metal alloys and found to yield reasonable results for $\langle\rho(E)\rangle$ in all cases studied so far.[21] By contrast, the component densities of states based on ATA1 lead to negative results in many cases and are not reliable. Thus the discussion of alloy properties sensitive to the environment of A and B atoms (in particular, the transfer of charge between A and B atoms) has not been possible within the framework of the muffin-tin average t-matrix approximation.[22]

We now discuss an alternative form of the ATA, which overcomes many of the difficulties encountered with ATA1. The relevant equations giving the decouplings of $\langle T_{00}\rangle_{0=A(B)}$ and $\langle T_{0n}\rangle_{0=A(B)}$ are

$$\langle T_{00}\rangle^{\mathrm{AT2}}_{0=A(B)}=[1-T^{\mathrm{AT}}_{00}(\langle\tau\rangle^{-1}-\tau^{-1}_{A(B)})]^{-1}T^{\mathrm{AT}}_{00} \qquad (4.1\mathrm{a})$$

and

$$\langle T_{0n}\rangle^{\mathrm{AT2}}_{0=A}=\frac{1}{x}(\langle\tau\rangle^{-1}-\tau^{-1}_{B})(\tau^{-1}_{A}-\tau^{-1}_{B})^{-1}T^{\mathrm{AT}}_{0n}\,, \qquad (4.1\mathrm{b})$$

with a similar expression for $\langle T_{0n}\rangle^{\mathrm{AT2}}_{0=B}$ and with the interchanges $x\Leftrightarrow y$ and $A\Leftrightarrow B$. T^{AT}_{00} and T^{AT}_{0n} are the path operators for the ATA medium. The use of the decouplings (4.1) in (2.4) and (2.7) immediately yields the ATA2 spectrum

$$\langle\rho(E)\rangle^{\mathrm{AT2}}=\rho_0(E)-(\pi N)^{-1}\mathrm{Im\,Tr}\sum_{\vec{k}}\left[\left(\frac{x}{1-T^{\mathrm{AT}}_{00}(\langle\tau\rangle^{-1}-\tau^{-1}_{A})}\frac{d\tau^{-1}_{A}}{dE}+\frac{y}{1-T^{\mathrm{AT}}_{00}(\langle\tau\rangle^{-1}-\tau^{-1}_{B})}\frac{d\tau^{-1}_{B}}{dE}-\frac{dB_{\vec{k}}}{dE}\right)\left(\frac{1}{\langle\tau\rangle^{-1}-B_{\vec{k}}}\right)\right] \qquad (4.2)$$

$$\equiv\sum_{\vec{k}}\langle\rho(\vec{k},E)\rangle^{\mathrm{AT2}}\,, \qquad (4.3)$$

and

$$\langle\rho_A(E)\rangle^{\mathrm{AT2}}=\rho_0(E)-(\pi N)^{-1}\mathrm{Im\,Tr}\sum_{\vec{k}}\left[\left(\frac{1}{1-T^{\mathrm{AT}}_{00}(\langle\tau\rangle^{-1}-\tau^{-1}_{A})}\frac{d\tau^{-1}_{A}}{dE}-\frac{1}{x}(\langle\tau\rangle^{-1}-\tau^{-1}_{B})(\tau^{-1}_{A}-\tau^{-1}_{B})^{-1}\frac{dB_{\vec{k}}}{dE}\right)\left(\frac{1}{\langle\tau\rangle^{-1}-B_{\vec{k}}}\right)\right] \qquad (4.4)$$

and a similar expression for $\langle\rho_B(E)\rangle^{\mathrm{AT2}}$, with the interchanges $A\Leftrightarrow B$ and $x\Leftrightarrow y$. The quantities $\langle\rho_{A(B)}(E)\rangle^{\mathrm{AT2}}$ satisfy the charge neutrality constraint

$$x\langle\rho_A(E)\rangle^{\mathrm{AT2}}+y\langle\rho_B(E)\rangle^{\mathrm{AT2}}=\langle\rho(E)\rangle^{\mathrm{AT2}}\,. \qquad (4.5)$$

It should be noted that $\langle\rho(E)\rangle^{\mathrm{AT1}}$ [see Eq. (3.24a) of Ref. 10] as well as $\langle\rho(E)\rangle^{\mathrm{AT2}}$ involve one term of the form ($\vec{k}$-independent factors) $\sum_{\vec{k}}(\langle\tau\rangle^{-1}-B_{\vec{k}})^{-1}\propto T^{\mathrm{AT}}_{00}$. For this reason, even though the ATA2 Eqs. (4.2)–(4.4) involve T^{AT}_{00} in the factor multiplying $(d\tau^{-1}_{A(B)}/dE)$ while ATA1 equations do not, the former are no harder to implement than the latter.

The decoupling (4.1a) physically represents an A (B) atom placed in a medium of $\langle t\rangle$ atoms. Equation (4.1b), on the other hand, is not identical to the corresponding single-impurity equation for $\langle T_{0n}\rangle_{0=A(B)}$. The reason for this is that if $\langle T_{0n}\rangle_{0=A(B)}$ were chosen to be of the single-impurity form, then relation (4.5) would be violated. Furthermore, the corresponding spectral function [cf. Eqs. (4.3) and (4.4)] will contain unphysical free-electron poles.

The ATA2 decouplings (4.1) are completely equivalent to the corresponding CPA decouplings.[10] This formal similarity between the ATA2 and CPA implies that if τ_{CP} is inserted in the ATA2 equations (4.2) and (4.4), the CPA spectrum will result. Since $\langle\tau\rangle$ may be looked upon as the lowest-order approximation to the CPA solution, we can view ATA2 to be the lowest-order approximation to the CPA.

We emphasize that the average density of states is not sensitive to how precisely the $\langle T_{0n}\rangle_{0=A(B)}$ term is decoupled. In fact, as Fig. 1 shows, the density of states in $\mathrm{Cu}_{0.75}\mathrm{Ni}_{0.25}$ obtained by using the decoupling (4.1b) for $\langle T_{00}\rangle_{0=A(B)}$ [i.e., by using Eq. (4.2), shown as a dashed line] is hardly distinguishable from the corresponding density of states obtained by using the single-impurity decoupling

$$\langle T_{0n}\rangle_{0=A(B)}=[1-T^{\mathrm{AT}}_{00}(\langle\tau\rangle^{-1}-\tau^{-1}_{A(B)})]^{-1}T^{\mathrm{AT}}_{0n}$$

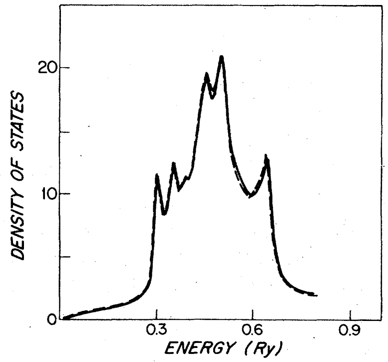

FIG. 1. Density of states $\langle\rho(E)\rangle$ in $\mathrm{Cu}_{0.75}\mathrm{Ni}_{0.25}$. The dashed curve is for the ATA decouplings of Eqs. (4.1) [i.e., by using the corresponding ATA2 density-of-states formula (4.2)]. The solid curve gives the results for the case when instead of forms (4.1) the single-impurity forms are used for both $\langle T_{00}\rangle_{0=A(B)}$ and $\langle T_{0n}\rangle_{0=A(B)}$ (i.e., $\langle T_{00}\rangle_{0=A(B)}$ is given by (4.1a), but $\langle T_{0n}\rangle_{0=A(B)}$ $=[1-T^{\mathrm{AT}}_{00}(\langle\tau\rangle^{-1}-\tau^{-1}_{A(B)})]^{-1}T^{\mathrm{AT}}_{0n}$).

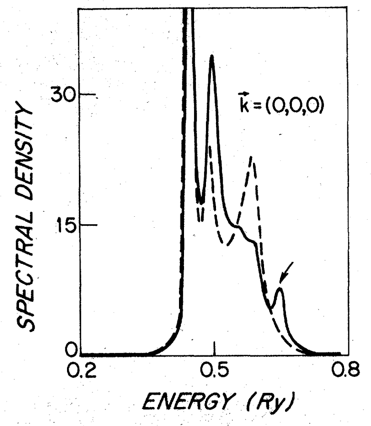

FIG. 2. Bloch spectral density $\langle\rho(\vec{k},E)\rangle$ at the point Γ [i.e., $\vec{k}=(0,0,0)$] in the Brillouin zone for ATA1 (dashed) and ATA2 (solid) in $Cu_{0.75}Ni_{0.25}$. The arrow indicates the peak arising in ATA2 from the solutions of (4.7) for an Ni impurity.

(shown as a solid line). Our experience is that the net contribution to $\langle\rho_{A(B)}(E)\rangle$ is not sensitive to how the term proportional to $(dB_{\vec{k}}/dE)$ in Eqs. (2.4) and (2.7) is approximated. This fact may usefully be borne in mind in treating disordered muffin-tin systems in general.

It is also interesting to compare the spectral density in ATA1 and ATA2. Figure 2 is illustrative in this regard. This figure shows clearly that the spectral function for ATA2 (solid) has more structure than the ATA1 (dashed). Indeed, a reference to Eq. (4.2) shows that peaks in ATA2 arise not only from the complex zeros of

$$\|\langle\tau\rangle^{-1}-B_{\vec{k}}(E)\|=0\,, \qquad (4.6)$$

but also from those of

$$\|1-T_{00}^{\mathrm{AT}}(\langle\tau\rangle^{-1}-\tau_{A(B)}^{-1})\|=0\,. \qquad (4.7)$$

Equations (4.6) and (4.7) are completely analogous to the corresponding CPA equations[13] and have a similar physical interpretation, i.e., (4.6) gives the complex Bloch-type energy bands for an ordered system of ATA scatterers $\langle\tau\rangle$, and (4.7) gives the A (B) impurity levels in an otherwise perfect $\langle\tau\rangle$ medium.[23] In fact, the peak marked by an arrow in Fig. 2 arises from the solutions of (4.7). By contrast, the ATA1 spectrum (dashed) in Fig. 2 has all its peaks associated with the Bloch-type states obtained from (4.6). In this sense, ATA1 essentially misses the structure resulting from the impurity-like levels coming from solutions of (4.7).[24]

Figure 3 compares the densities of states in ATA1 and ATA2 for $Cu_{0.75}Ni_{0.25}$. As indicated earlier, ATA1 yields negative values for impurity spectrum $\langle\rho_{Ni}(E)\rangle$ [dashed in Fig. 3(c)] for a range of energies. By contrast, ATA2 gives positive $\langle\rho(E)\rangle$ as well as $\langle\rho_{Cu(Ni)}(E)\rangle$. Figure 3(a) shows strikingly that the Ni impurity peaks in ATA1 and ATA2 are located at different energies. This is noteworthy since both ATA1 and ATA2 involve the same $\langle t\rangle$ effective scatterers, and they both contain peaks in spectral functions arising from the Bloch-type solutions of Eq. (4.6). The two versions of the ATA differ physically only in that ATA2 contains impurity level contributions from (4.7) while ATA1 does not. In fact, in $Cu_{0.75}Ni_{0.25}$ the impurity level contributions (4.7) dominate, and it is for this reason that the position of Ni virtual bound state in ATA2 and ATA1 turns out to be different.

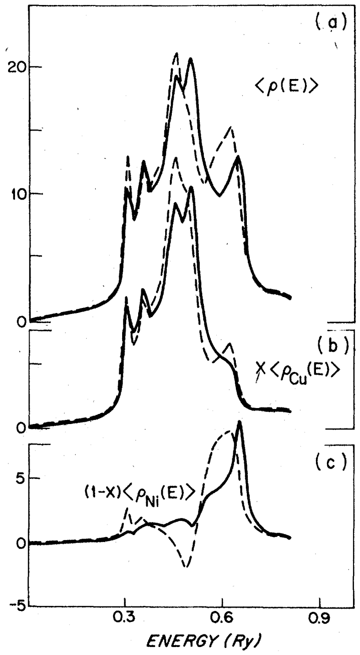

FIG. 3. Comparison of the density of states $\langle\rho(E)\rangle$ and the weighted A and B component densities of states $x\langle\rho_A(E)\rangle$ and $(1-x)\langle\rho_B(E)\rangle$ in $Cu_{0.75}Ni_{0.25}$ in ATA1 (dashed) and ATA2 (solid).

We have applied ATA2 and CPA to Cu_xNi_{1-x} and Cu_xZn_{1-x} over a range of constituent concentrations and found that the two approximations are generally in good agreement. In particular, ATA2 has been found to lead to positive total as well as component densities of states. Details of this comparison are taken up in Ref. 15.

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APPENDIX A: HANDLING OF FREE-ELECTRON POLES IN COMPONENT DENSITIES OF STATES

In the formulae for the component densities of states $\langle\rho_{A(B)}(E)\rangle$ in the CPA [see Eq. (3) of Ref. 13] as well as the ATA, the free-electron poles do not cancel, and therefore the computation of $\langle\rho_{A(B)}(E)\rangle$ involves integrals whose integrands still contain these singularities. We emphasize that this does not mean that these quantities are ill defined, because the prescription for evaluating densities of states is to set $E = E + i\epsilon$ and take the limit $\epsilon \to 0$.

In this appendix we consider the CPA formula[13]

$$\langle\rho_A(E)\rangle^{\mathrm{CP}} = \rho_0(E) - \frac{1}{\pi N}\,\mathrm{Im\,Tr}\sum_{\vec{k}}\left[\left(\frac{1}{1 - T_{00}^{\mathrm{CP}}(\tau_{\mathrm{CP}}^{-1} - \tau_A^{-1})}\frac{d\tau_A^{-1}}{dE} - \frac{dB_{\vec{k}}}{dE}\right)\left(\frac{1}{\tau_{\mathrm{CP}}^{-1} - B_{\vec{k}}}\right)\right] + \frac{1}{\pi N}\,\mathrm{Im\,Tr}\sum_{\vec{k}}\left[\left(\frac{\tau_{\mathrm{CP}}^{-1} - \tau_B^{-1}}{x(\tau_A^{-1} - \tau_B^{-1})} - 1\right)\left(\frac{1}{\tau_{\mathrm{CP}}^{-1} - B_{\vec{k}}}\right)\frac{dB_{\vec{k}}}{dE}\right]. \tag{A1}$$

Note that the term $(\pi N)^{-1}\mathrm{Im\,Tr}[(dB_{\vec{k}}/dE)(\tau_{\mathrm{CP}}^{-1} - B_{\vec{k}})^{-1}]$ in Eq. (A1) can be shown to vary as $-1/[E - (\vec{k} + \vec{K}_n)^2]$ in the vicinity of the free-electron poles[19] at $E = (\vec{k} + \vec{K}_n)^2$. Therefore, these poles will be canceled exactly by the corresponding contributions from the $\rho_0(E)$ term in (A1). (It is for the same reason that the free-electron poles in the total density of states in the CPA and the ATA do not cause any numerical difficulties.) By writing the form (A1), we have isolated the free-electron poles in $\langle\rho_A(E)\rangle^{\mathrm{CP}}$ to the term

$$\rho^{(2)}(E) \equiv \frac{1}{\pi N}\,\mathrm{Im}\sum_{\vec{k}}\sum_{L}\left[\left(\frac{\tau_{\mathrm{CP}}^{-1} - \tau_B^{-1}}{x(\tau_A^{-1} - \tau_B^{-1})} - 1\right)\times\left(\frac{1}{\tau_{\mathrm{CP}}^{-1} - B_{\vec{k}}}\right)\frac{dB_{\vec{k}}}{dE}\right]_{LL} \equiv \sum_{\vec{k}}\sum_{L}\rho_L^{(2)}(\vec{k}, E), \tag{A2}$$

where $\rho_L^{(2)}(\vec{k}, E)$ is the spectral function whose integrals along the special directions enter the computation of $\rho^{(2)}(E)$. We now explicitly add and subtract free-electron poles from $\rho_L^{(2)}(\vec{k}, E)$ by writing

$$\rho_L^{(2)}(\vec{k}, E) = \left(\rho_L^{(2)}(\vec{k}, E) - \sum_n \frac{f_{L,n}}{E - (\vec{k} + \vec{K}_n)^2}\right) + \sum_n \frac{f_{L,n}}{E - (\vec{k} + \vec{K}_n)^2}, \tag{A3}$$

where the constant coefficients $f_{L,n}$ are easily determined by calculating $\rho_L^{(2)}(\vec{k}, E)$ at two $|k|$ values along the special direction of interest in the vicinity of $E = (\vec{k} + \vec{K}_n)^2$ and fitting it to the form

$$\rho_L^{(2)}(\vec{k}, E) \sim f_{L,n}/[E - (\vec{k} + \vec{K}_n)^2] + \beta_{L,n}.$$

The free-electron singularities in (A3) have now been transferred to the term $\sum_n f_{L,n}/[E - (\vec{k} + \vec{K}_n)^2]$. Since $f_{L,n}$ are constants, the contribution from this term can be evaluated analytically.

APPENDIX B: ORTHOGONALITY RELATION FOR CUBIC HARMONICS

In this appendix, we prove that the cubic harmonics satisfy the orthogonality relation

$$\sum_P K_i^{(\mu)}(P\hat{x})K_j^{(\nu)}(P\hat{x}') = (N_P/N_\mu)\delta_{\mu\nu}\delta_{ij}\sum_{l(\mu)} K_l^{(\mu)}(\hat{x})K_l^{(\mu)}(\hat{x}'). \tag{B1}$$

Here $K_i^{(\mu)}(\hat{x})$ denotes the ith cubic harmonic belonging to the μth representation of the cubic group. While the summation on the left-hand side of (B1) extends to all the N_P elements of the group, the one on the right-hand side involves only the N_μ elements of the μth representation.

Since $\{K_i^{(\mu)},\ i = 1, \ldots, N_\mu\}$ form a basis set, a representation for the cubic group can be obtained by simply considering the effect of the group elements on the functions $\{K_i^{(\mu)}\}$. The matrix $D^{(\mu)}(P)$ representing P is then given by

$$K_i^{(\mu)}(P\hat{x}) = \sum_{j(\mu)} D_{ij}^{(\mu)}(P)K_j^{(\mu)}(\hat{x}). \tag{B2}$$

Other representations can be obtained by using other sets of cubic harmonics. The different representations satisfy the relation[25]

$$\sum_P D_{ij}^{(\mu)}(P)D_{kl}^{(\nu)}(P) = (N_P/N_\mu)\delta_{\mu\nu}\delta_{ik}\delta_{jl}. \tag{B3}$$

Using (B2) in (B1) now gives

$$\sum_P K_i^{(\mu)}(P\hat{x})K_j^{(\nu)}(P\hat{x}') = \sum_{l(\mu)}\sum_{k(\nu)}\sum_P D_{il}^{(\mu)}(P)D_{jk}^{(\nu)}(P)K_l^{(\mu)}(\hat{x})K_k^{(\nu)}(\hat{x}'). \tag{B4}$$

The use of relation (B3) on the right-hand side of (B4) immediately yields the relation (B1).

To apply (B1) to the case of spherical harmonics, we note that the 9 *real* spherical harmonics for $l \leqslant 2$ (denoted by Y_1 to Y_9) vary as $\{1, x, y, z, xy, yz, r^2 - 3z^2, zx, (x^2 - y^2)\}$. Each of these functions transforms according to a representation of the cubic group: Y_1 transforms as Γ_1, (Y_2, Y_3, Y_4) as $\Gamma_{15'}$, (Y_5, Y_6, Y_8) as $\Gamma_{25'}$, and (Y_7, Y_9) as Γ_{12}. Since none of these representations is repeated, it is clear that (B1) can be used to obtain the relation for $l \leqslant 2$:

$$\sum_P Y_L(P\hat{x}) Y_{L'}(P\hat{x}') = \delta_{LL'} f^{(L)}(x, x') , \qquad \text{(B5)}$$

where $f^{(L)}(x, x')$ depends only on the representation index Γ_{12}, $\Gamma_{25'}$, $\Gamma_{15'}$, and Γ_1 of the cubic group.

We note in passing that our proof of (B1) uses relation (B3), which implicitly assumes that the representations (μ) and (ν) are orthogonal. It would seem that (Y_7, Y_9) do not form an orthogonal representation. Nevertheless, we have explicitly verified that Eq. (B5) holds for Y_7 and Y_9.

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[17] To our knowledge, formula (2.5) has not actually been used for evaluating $\langle \rho_{A(B)}(E) \rangle$ in the current literature on one- and two-band tight-binding-model Hamiltonians. Equation (2.5) corresponds to the use of Eq. (5.5) of Ref. 2 with definition (5.1) for the projection operators $P_{A(B)}$. But formulae (14.15), which are traditionally used, employ forms (14.11) for $P_{A(B)}$, which clearly do not possess the properties (5.1). It is relatively straightforward to show that expressions (14.15) correspond to the quantity $-(1/\pi)\mathrm{Im}\, \langle 0 | \langle \mathcal{G}(E^+) \rangle_{0=A(B)} | 0 \rangle$, which involves an integral of the restricted average Green's function over the entire crystal and is certainly not equal to $-(1/\pi)\mathrm{Im} \int_{(0)} d^3r \langle \mathcal{G}(\vec{r}, \vec{r}; E^+) \rangle_{0=A(B)}$. Equations (14.15) can be viewed as contributions from the 0th site (not the 0th cell), and in this sense they imply a definition of $\langle \rho_{A(B)}(E) \rangle$ which is similar in spirit to our definition (2.7).

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[22] For the muffin-tin model, approximations to the average alloy spectrum are most conveniently made starting with Eqs. (2.4) and (2.7). But to obtain $\langle \rho(E) \rangle$ and $\langle \rho_{A(B)}(E) \rangle$ within this framework, in addition to specifying t_{eff}, we must provide the decoupling of $\langle T_{00} \rangle_{0=A(B)}$ and $\langle T_{0n} \rangle_{0=A(B)}$ in terms of the quantities $\langle T_{00} \rangle$ and $\langle T_{0n} \rangle$. The spirit of the ATA is then captured by the choice $t_{\mathrm{eff}} = \langle t \rangle$, which does not specify the ATA completely. This difficulty is peculiar to the muffin-tin Hamiltonian, and has been a source of some confusion with regard to the precise meaning of the muffin-tin ATA.

[23] The exact density of states in a disordered alloy will, of course, have contributions from impurity levels associated with clusters of more than one atom. However, within the framework of single-site approximations (such as the CPA and ATA), only single A and B atom clusters are considered.

[24] Strictly speaking, other versions of the ATA can be obtained depending on how $\langle T_{nn'} \rangle_{0=A(B)}$ are decoupled (see footnote 22). On physical grounds, however (within the single-site framework), various possible versions of ATA can be expected to be akin to ATA1 or ATA2, depending upon whether the impurity-like con-

tributions to the spectrum are essentially neglected or are treated reasonably. ATA2 is unique to the extent that it can be viewed as the lowest-order approximation to the CPA.

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