Optical theorem and multiple-scattering theory. Electronic states in substitutional alloys

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When multiple-scattering theory is used to describe the electronic properties of disordered transition-metal systems, decoupling procedures which appear to be physically reasonable can lead to negative densities of states in the vicinity of the resonant d bands. We present a method, based on the application of the optical theorem to the total scattering operator, that allows us to determine a priori which approximation schemes can be relied upon to produce a positive spectrum. The application of this method to substitutionally disordered binary alloys is discussed here. We find that both the average-\( t \)-matrix and coherent-potential approximations will always yield nonnegative densities of states. The application of our technique to approximations based on the Lloyd formula for the density of states is also discussed.

I. INTRODUCTION

A central problem in the theory of disordered systems is the calculation of the average electronic density of states \( \rho(E) \),\(^{1,2} \) While this quantity is, by definition, non-negative, approximate calculations of \( \rho(E) \) in strong-scattering systems often lead to negative results.\(^{3,4} \) For example, in systems involving either noble or transition metals, apparently reasonable approximation schemes are known to yield negative densities of states in the vicinity of the resonant d bands.\(^{5} \)

In this series of two papers we discuss the origin of this unphysical behavior in systems exhibiting compositional and structural disorder. The present paper is concerned with binary substitutional alloys. We develop a procedure that is used to test various approximations to determine whether or not they are guaranteed to yield a non-negative spectrum. We also prove analytically that two of the most widely used schemes, the average-\( t \)-matrix and coherent-potential approximations,\(^7 \) will always give positive densities of states. In a subsequent paper we show that the method developed here can also be applied to the study of liquid and amorphous metals. In the case of these structurally disordered systems, we find that none of the extant approximations are likely to provide a satisfactory description of the electronic spectrum.\(^4,5,6,10-11 \) The main portion of the second paper is then concerned with the derivation of a new system of equations which is (i) explicitly constrained to give positive densities of states and (ii) capable of describing reasonably the structure of the resonant d bands. It should be emphasized that methods developed in these papers do not depend on any assumptions regarding the strength of the atomic scattering operators. This is especially important in the case of calculations based on more realistic one-electron Hamiltonians. [We have in mind here the muffin-tin model as opposed to the single-band tight-binding Hamiltonians used in earlier work on disordered systems.]\(^12 \) In view of the extensive numerical work required in such calculations, it is essential that one establish a priori that the approximations being employed will not lead to patently unphysical behavior in the strong-scattering regime.

In Sec. II of this paper the evaluation of electronic states in disordered systems is discussed within the framework of multiple-scattering theory.\(^1,2 \) This formalism is based on a series expansion of the total scattering operator \( \mathcal{T} \) (for the macroscopic system) in terms of the individual atomic scattering operators. The fact that the exact density of states is non-negative is shown to be related to the inequality

\[
\text{Im}(\langle \mathcal{K} \mid \mathcal{T} \mid \mathcal{K} \rangle) \leq 0. \tag{1.1}
\]

Formally, this constraint on the phase of the diagonal matrix elements of the total scattering operator arises from the optical theorem.\(^13 \) While Eq. (1.1) must be satisfied in each configuration of a disordered system, contributions to \( \text{Im}(\langle \mathcal{K} \mid \mathcal{T} \mid \mathcal{K} \rangle) \) from the individual terms of the multiple-scattering series are not restricted to be of the same sign. We show, however, that the optical theorem allows us to extract from the multiple series a sequence of partial sums, \( S_n \), each of which must give a negative contribution to \( \text{Im}(\langle \mathcal{K} \mid \mathcal{T} \mid \mathcal{K} \rangle) \). The quantities \( S_n \) are then used to develop a procedure by which alternate approximations may be tested. In principle, this procedure can be applied to either structurally or compositionally disordered systems. Specializing to the latter case, we evaluate \( S_1 \) and \( S_2 \) exactly for a random sub-
stitutional binary alloy.

In Sec. III, the procedure described above is applied to four distinct approximation schemes. The leading contributions to the average spectral function are evaluated in the average-\( t \)-matrix and coherent-potential approximations and, in both cases, these contributions are found to have the proper sign. In addition, we prove quite generally that both methods will always yield a positive spectrum. The last two approximations we consider\(^{14,15} \) are based on a reformulation of multiple-scattering theory due to Lloyd.\(^{16} \) In this approach, terms of different order from the multiple-scattering series are combined, and the electronic variables are traced out to give an explicit formula for the density of states in each configuration of the system.\(^{11} \) While this reformulation has certain advantages, it is not always possible to identify a given approximate averaging of Lloyd's equation with a well-defined decoupling of the original multiple-scattering series.\(^{17} \) In the case of the equations proposed by Gyorffy and Stocks,\(^{14} \) we are able to make contact with the original series and can then evaluate the leading contributions to the approximate spectral function. We find that the sign of these terms is not explicitly constrained, which indicates that problems may arise in the strong-scattering limit. Indeed, numerical calculations based on these equations are known to give negative results in the d-band region for the alloy CuNi.\(^{3} \) By contrast, the equations proposed by the present authors\(^{15} \) have been applied to various transition and noble-metal alloys\(^{11,19} \) and have always been found to yield a positive spectrum. These equations, however, cannot be related to a specific decoupling of the multiple-scattering series and we are thus unable to prove that they will never produce unphysical results. Further work in this direction is in progress.

II. GENERAL EQUATIONS

In the muffin-tin model of the substitutional alloy \( A_xB_{1-x} \) the disordered potential \( \xi(\vec{r}) \) is written as a sum of nonoverlapping spherically symmetric contributions,\(^{20} \) \( \xi(\vec{r}) \) is nonvanishing within a muffin-tin sphere of radius \( r_n \) surrounding each of the lattice sites \( \{ \vec{R}_n \} \) and is constant (by convention, zero) in the region between the spheres. The electronic properties of the alloy are then determined by the single-particle Hamiltonian

\[
\xi = -\nabla^2 + \sum_{\alpha} \xi^{A(B)}_\alpha(\vec{r}) = \xi_0 + \xi(\vec{r}).
\]

(2.1)

Within the muffin-tin spheres \( \{1,2,\ldots, n\} \), \( |\vec{r} - \vec{R}_n| < r_n \), the value of \( \xi^{A(B)}(\vec{r}) = \xi^{A(B)}(\vec{r} - \vec{R}_n) \) depends only on whether an \( A \) or \( B \) atom occupies the site \( n \). The arrangement of the \( A \) and \( B \) atoms throughout the periodic lattice is assumed to be random, their relative concentrations are \( x \) and \( y = 1 - x \).

The equilibrium properties of the alloy can be evaluated in terms of the energy \( E \) dependent Green's function

\[
G(E) = \langle (E - \xi)^{-1} \rangle,
\]

(2.2)

where the angular brackets indicate an average over all possible configurations of the \( A \) and \( B \) atoms. For example, the density of states (per atom, per spin) \( \rho(E) \) is obtained by integrating the spectral function\(^{21} \)

\[
A(\vec{k}, E) = -\pi N^{-1} \text{Im}(\langle \hat{k} | G(\vec{k}^{'}) | \hat{k} \rangle)
\]

(2.3)

over all momenta \( \vec{k} \). (Here \( E = E + i0^+ \) and \( N \) is the number of lattice sites.) In multiple scattering theory \( G(E) \) is calculated in terms of the average total scattering operator \( T(E) \):

\[
T = \langle T \rangle = \langle T_1 + T_2 + T_3 + \cdots \rangle,
\]

(2.4)

where

\[
T_1 = \sum_\alpha t_\alpha G_\alpha + \sum_\alpha t_\alpha G_\alpha t_\alpha,
\]

(2.5)

etc., \( G_\alpha = (E - H_\alpha)^{-1} \) is the free electron Green's function and \( t_\alpha = \nu_\alpha (1 - G_\alpha)^{-1} \) is the scattering matrix associated with the ion centered at \( R_\alpha \), \( (t_\alpha \) equals \( t_\alpha^A \) or \( t_\alpha^B \), depending on which species occupies the site \( \alpha \). The relation between \( T \) and \( G \) is

\[
G = G_0 + G_0 T G_0.
\]

(2.6)

In view of Eq. (2.3), it is clear that \( A(\vec{k}, E) \) can be evaluated in terms of just the diagonal matrix element \( \langle \hat{k} | T(E) | \hat{k} \rangle \). Since

\[
\lim_{k^2 \to E} [(E^2 - k^2)^{-1} \langle \hat{k} | T(E^{'}) | \hat{k} \rangle] = -1,
\]

(2.7)

the free-electron contributions to the spectral function cancel when (2.6) is substituted into Eq. (2.3),\(^{23} \) \( A(\vec{k}, E) \) is then given by

\[
A(\vec{k}, E) = -\pi N^{-1} \text{Im}(\langle \hat{k} | T(E^{'}) | \hat{k} \rangle) / (E - k^2)^2
\]

(2.8)

and varies smoothly as \( k^2 - E \).\(^{24} \)

Because the spectral function (2.8) is never negative,\(^{25} \) \( \text{Im}(\langle \hat{k} | T(E^{'}) | \hat{k} \rangle) \) must be less than or equal to zero for all \( \vec{k} \) and \( E \). We emphasize, however, that the contributions to \( \text{Im}(\langle \hat{k} | T(E^{'}) | \hat{k} \rangle) \) from the individual terms of the multiple-scattering series (2.4) are not of uniform sign. To understand how the terms in this series are constrained to give a positive spectrum, we consider the ap-
application of the optical theorem to the total scattering operator $T$. This theorem states that, in each configuration of the alloy, $T$ and its Hermitian conjugate $T^\dagger$ satisfy the relation

$$T - T^\dagger = -2\pi i \, T^\dagger V(E - H_0) T.$$  \hfill (2.9)

Averaging over all possible configurations and taking the appropriate matrix elements, we obtain

$$\text{Im}(\langle \mathbf{k} | T(E^+) | \mathbf{k} \rangle) = -\pi \sum_q \left( \langle \mathbf{q} | T | \mathbf{k} \rangle \right)^2 b(E - q^2) \geq 0$$  \hfill (2.10)

which is, of course, consistent with the fact that the exact spectral function is non-negative.

We are now in a position to rearrange the various contributions from the series (2.4) into a sequence of partial sums, each of which contributes to $A(k, E)$ with the proper sign. To begin, we note that such a sequence is given by

$$S_a = \left( \sum_b t^a_b(E - H_0) t_b + \sum_{b \neq a} [t^a_b(E - H_0) t_b G_{a,b} + t^b_a(E - H_0) t_a G_{b,a}] + \sum_{b \neq a} t^a_b G_{a,b} t^b_a(E - H_0) t_a G_{b,a} \right),$$

\hfill (2.13a)

etc. To understand how the terms in the series (2.4) enter the sequence $\{S_a\}$, we employ the relations $t - t^\dagger = -2\pi i t^\dagger(E - H_0) t$, $G - G^\dagger = -2\pi i b(E - H_0)$ and Eqs. (2.5) and (2.12) to write successive contributions to $\langle T - T^\dagger \rangle$ as

$$\langle T - T^\dagger \rangle = -2\pi i \left( \sum_a t^a_a(E - H_0) t_a \right),$$

\hfill (2.14a)

etc. [Here we have repeatedly used the identity $ab - a^\dagger b^\dagger = (a - a^\dagger) b + a^\dagger (b - b^\dagger)$.] These terms can easily be regrouped into the combinations listed in (2.13). Thus (2.14a) and the middle term on the right-hand side of (2.14b) combined to form (2.13a). Similarly (2.13b) is obtained from (2.14a), (2.14b), and parts of $\langle T_a - T^\dagger_a \rangle$ and $\langle T_1 - T^\dagger_1 \rangle$.

To conclude this section we evaluate the leading contributions to $A(k, E)$ from the sequence $\{S_a\}$. We emphasize that these contributions are guaranteed to have the proper sign only when the averages indicated in (2.11) and (2.13) are carried out exactly. Once the configuration averaging is done approximately, the sign of the resulting contributions to $A(k, E)$ may no longer be fixed. Rather than expressing our results in terms of $t^a$ and $\Delta$, it is more convenient to use the symmetric combinations $\langle t \rangle = x t^a + y t^b$ and $\Delta = t^a - t^b$:

$$t^a = \langle t \rangle + y \Delta, \quad t^b = \langle t \rangle - x \Delta.$$  \hfill (2.15)
Beginning with $S_1$, we have

$$S_1 = \sum_\alpha \left[ x(t^*_\alpha)^* \delta(E - H_0) t^\alpha_\alpha + y(t^\alpha_\alpha)^* \delta(E - H_0) t^*_\alpha \right]$$

$$+ \sum_{\beta \neq \alpha} \left[ \langle t^\alpha_\alpha \rangle^* \delta(E - H_0) \langle t^\alpha_\beta \rangle \right]$$

$$= \sum_\alpha \langle t^\alpha_\alpha \rangle^* \delta(E - H_0) \langle t^\alpha_\alpha \rangle$$

$$+ xy \sum_\alpha \Delta^\dagger_\alpha \delta(E - H_0) \Delta_\alpha . \quad (2.16)$$

Recalling (2.8) and (2.10) the relevant quantity is

$$N^{-1} \langle \bar{E} | S_1 | \bar{E} \rangle = \sum_\alpha \left[ \left| \langle t^\alpha_\alpha \rangle \right|^2 \right] \delta(E - q^2) \geq 0 . \quad (2.17)$$

Here

$$\langle t^\alpha_\alpha \bar{E} \rangle = \langle \bar{E} | \langle t^\alpha_\alpha \rangle \rangle = \langle \bar{E} \Delta_\alpha \rangle ,$$

$$\Delta_\alpha \bar{E} = \langle \bar{E} \Delta_\alpha \rangle = \Delta_\alpha \bar{E}$$

and

$$I(\bar{E} - \bar{E}) = N^{-1} \sum_{\alpha, \beta} e^{-i(t^\beta_\alpha)|t^\beta_\beta|}$$

$$= N^{-1} \sum_{\alpha} e^{-i(t^\beta_\alpha)|t^\beta_\beta|} \geq 0 . \quad (2.18)$$

is the usual crystal form factor. The evaluation of the $S_2$ contribution proceeds similarly but is complicated by the presence of repeated scattering events in the third and fourth terms on the right-hand side of (2.13b) [Physically these fluctuation effects arise when an electron returns to a given site after scattering from one or more intermediate sites.] After some straightforward algebra, we obtain

$$S_2 = \sum_\alpha \langle t^\alpha_\alpha \rangle^* \delta(E - H_0) \langle t^\alpha_\beta \rangle + \sum_{\beta \neq \alpha} \left[ \langle t^\alpha_\alpha \rangle^* \delta(E - H_0) \langle t^\alpha_\beta \rangle G_\alpha(t^\beta_\beta) + \langle t^\alpha_\beta \rangle^* \delta(E - H_0) \langle t^\alpha_\alpha \rangle G_\beta(t^\beta_\beta) \right]$$

$$+ \sum_{\beta \neq \alpha} \left[ \langle t^\alpha_\beta \rangle^* \delta(E - H_0) \langle t^\alpha_\alpha \rangle G_\alpha(t^\beta_\beta) + \langle t^\alpha_\alpha \rangle^* \delta(E - H_0) \langle t^\alpha_\beta \rangle G_\beta(t^\beta_\beta) \right]$$

$$+ xy \left( \sum_\alpha \Delta^\dagger_\alpha \delta(E - H_0) \Delta_\alpha + \sum_{\beta \neq \alpha} \left[ \langle t^\alpha_\alpha \rangle G_\beta(t^\beta_\beta) \delta(E - H_0) \Delta_\beta + \Delta^\dagger_\alpha G_\beta(t^\beta_\beta) \delta(E - H_0) \Delta_\alpha \right] \right)$$

$$+ \Delta^\dagger_\alpha \Delta_\beta \langle t^\alpha_\alpha \rangle G_\beta(t^\beta_\beta) + \Delta_\alpha \Delta^\dagger_\beta \langle t^\alpha_\beta \rangle G_\alpha(t^\beta_\beta) + \Delta^\dagger_\alpha \Delta^\dagger_\beta \langle t^\alpha_\alpha \rangle G_\alpha(t^\beta_\beta)$$

$$+ \Delta_\alpha \Delta^\dagger_\beta \langle t^\alpha_\beta \rangle G_\beta(t^\beta_\beta) . \quad (2.19)$$

The last term in (2.19) can be rewritten as

$$\frac{1}{2} \left( \Delta^\dagger_\alpha \Delta^\dagger_\beta \Delta_\beta G_\alpha(t^\beta_\beta) + \Delta^\dagger_\alpha \Delta_\alpha \Delta^\dagger_\beta G_\beta(t^\beta_\beta) \right) \delta(E - H_0) \delta(E - H_0) \delta(E - H_0) . \quad (2.20)$$

Forming the matrix element $\langle \bar{E} | S_2 | \bar{E} \rangle$, we find three terms, each of which is non-negative

$$N^{-1} \langle \bar{E} | S_2 | \bar{E} \rangle = \sum_\alpha \left[ \left( \langle t^\alpha_\alpha \rangle \rangle^* \delta(E - H_0) \langle t^\alpha_\alpha \rangle \right) \right]$$

$$+ \sum_{\beta \neq \alpha} \left[ \left( \langle t^\alpha_\alpha \rangle \rangle^* \delta(E - H_0) \langle t^\alpha_\beta \rangle \right) \right]$$

$$+ \sum_{\beta \neq \alpha} \left[ \left( \langle t^\alpha_\beta \rangle \rangle^* \delta(E - H_0) \langle t^\alpha_\alpha \rangle \right) \right]$$

$$+ \frac{1}{2} \left( \Delta^\dagger_\alpha \Delta^\dagger_\beta \Delta_\beta \langle t^\alpha_\alpha \rangle \rangle^* \delta(E - H_0) \delta(E - H_0) \delta(E - H_0) \langle \bar{E} \rangle \rangle \geq 0 . \quad (2.20)$$
Here \( G_0(k) = (E' - k^2)^{-1} \) and \( g(\vec{k}) = I(\vec{k}) - 1 \) is the pair distribution function

\[
g(\vec{k}) = N^{-1} \sum_{\vec{x}} e^{i \vec{k} \cdot \vec{r}_g} g_0(\vec{r}_g - \vec{R}_0).
\]

Equation (2.20) is indicative of the higher-order contributions to \( A(\vec{k}, E) \) from the sequence (2.11). In general, \( \langle \vec{k} | S_0 | \vec{k} \rangle \) begins with two terms each of which involves selected parts of \( \text{Im}(|\vec{k}| \langle \tau_n | \vec{R}_0 \rangle) \) through \( \text{Im}(|\vec{k}| \langle \tau_n | \vec{R}_0 \rangle) \), followed by fluctuation terms which are due entirely to repeated scattering events. Thus

\[
N^{-1} \langle \vec{k} | S_0 | \vec{k} \rangle = \sum_q \left( \langle \vec{q}_1, \vec{k} \rangle \right) \langle \vec{q}, \vec{k} \rangle \gamma(\vec{k} - \vec{q})
+ \cdots,
\]

where the dots represent fluctuation terms. From (2.17) and (2.20), we have

\[
Q_1(\vec{q}_1, \vec{k}) = \langle \vec{q}_1, \vec{k} \rangle, \quad D_1(\vec{q}_1, \vec{k}) = \Delta(\vec{q}_1, \vec{k})
\]

and

\[
Q_2(\vec{q}_1, \vec{k}) = Q_1(\vec{q}_1, \vec{k})
+ \sum_{\vec{q}_2} \left( \langle \vec{q}_2, \vec{k} \rangle \right) G_0(k_2) g(\vec{k} - \vec{q}_1) \langle \vec{q}(\vec{q}_2, \vec{k}) \rangle
\]

\[
+ \sum_{\vec{q}_2} \left( \langle \vec{q}_2, \vec{k} \rangle \right) G_0(k_2) g(\vec{k} - \vec{q}_1) \Delta(\vec{q}_2, \vec{k})
\]

or

\[
N^{-1} Q_1(\vec{q}_1, \vec{k}) - \sum_{\vec{q}_2} \left[ \left( \langle \vec{q}_2, \vec{k} \rangle \right) + \sum_{\vec{q}_2} \left( \langle \vec{q}_2, \vec{k} \rangle \right) G_0(k_2) g(\vec{k} - \vec{q}_1) \langle \vec{q}(\vec{q}_2, \vec{k}) \rangle \right] \gamma(\vec{k} - \vec{q})
+ \cdots,
\]

while (3.4a) is identical to the earlier result (2.17), we find that, beginning with \( \langle \vec{k} | S_2 | \vec{k} \rangle \), the ATA does not reproduce the exact contributions to \( A(\vec{k}, E) \) [cf. (2.20) and (3.4b)]. We emphasize that the present analysis indicates only that the ATA spectrum is non-negative; no statement is being made about the relative magnitudes of the ATA and exact spectral functions. [This is hardly

III. ANALYSIS OF APPROXIMATION SCHEMES

A. Average-\( t \)-matrix approximation (ATA)

In the ATA the disordered alloy is replaced by a periodic lattice of complex potentials each of which is so chosen as to reproduce the average scattering of the \( A \) and \( B \) atoms. In terms of the multiple-scattering series, this amounts to the neglect of all correlations except those involving successive sites:

\[
T = \sum_a \langle t_a \rangle + \sum_b \langle t_a \rangle G_0 \sum_b \langle t_b \rangle
\]

Alternatively, the ATA can be generated by the equations

\[
T = \sum_a Q_a,
\]

where

\[
Q_a = \langle t_a \rangle + \langle t_a \rangle G_0 \sum_b \langle t_b \rangle.
\]

The methods developed in Sec. II can easily be used to show that the ATA spectrum is non-negative. Recalling Eqs. (2.14), with the configuration averages now evaluated in the ATA [i.e., as in Eq. (3.1)], and using the identity

\[
(2\pi)^{\frac{1}{2}} \langle t_a \rangle - \langle t_a \rangle = -\langle t_a \rangle \delta(E - H_0 \langle t_a \rangle)
\]

\[
-\alpha \Delta \delta(E - H_0 \Delta),
\]

the leading contributions to the approximate spectral function are proportional to

\[
N^{-1} \langle \vec{k} | S_0 | \vec{k} \rangle - \sum_q \left[ \left( \langle \vec{q}_1, \vec{k} \rangle \right) + \sum_{\vec{q}_2} \left( \langle \vec{q}_2, \vec{k} \rangle \right) G_0(k_2) g(\vec{k} - \vec{q}_1) \langle \vec{q}(\vec{q}_2, \vec{k}) \rangle \right] \gamma(\vec{k} - \vec{q})
+ \cdots
\]

and

\[
N^{-1} \langle \vec{k} | S_2 | \vec{k} \rangle - \sum_q \left[ \left( \langle \vec{q}_1, \vec{k} \rangle + \sum_{\vec{q}_2} \left( \langle \vec{q}_2, \vec{k} \rangle \right) G_0(k_2) g(\vec{k} - \vec{q}_1) \langle \vec{q}(\vec{q}_2, \vec{k}) \rangle \right] \gamma(\vec{k} - \vec{q})
+ \cdots
\]
surprising; the ATA would be of little value if it always either underestimated or overestimated $A(\mathbf{k}, E)$.]

To construct a more general proof, we return to the generating equation (3.2). In a momentum representation we have
\[
\hat{G}(\mathbf{k}, \mathbf{k}') = \exp[-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_m]Q(\mathbf{k}, \mathbf{k}') ,
\]
where
\[
Q(\mathbf{k}, \mathbf{k}') = \langle t(\mathbf{k}, \mathbf{k}') \rangle + \sum_{\mathbf{k}_1} \langle t(\mathbf{k}, \mathbf{k}_1) \rangle G_{\mathbf{k}_1}(\mathbf{k}_1 - \mathbf{k}') Q(\mathbf{k}_1, \mathbf{k}')
\]
\[
= \langle t(\mathbf{k}, \mathbf{k}') \rangle + \sum_{\mathbf{k}_1} \langle t(\mathbf{k}, \mathbf{k}_1) \rangle G_{\mathbf{k}_1}(\mathbf{k}) g(\mathbf{k}_1 - \mathbf{k}') \langle t(\mathbf{k}_1, \mathbf{k}') \rangle
\]
\[
+ \sum_{\mathbf{k}_2} \langle t(\mathbf{k}, \mathbf{k}_1) \rangle G_{\mathbf{k}_1}(\mathbf{k}) g(\mathbf{k}_2 - \mathbf{k}') \langle t(\mathbf{k}_2, \mathbf{k}_1) \rangle G_{\mathbf{k}_1}(\mathbf{k}) g(\mathbf{k}_2 - \mathbf{k}') \langle t(\mathbf{k}_2, \mathbf{k}_1) \rangle + \cdots
\]

[Note that while $\langle t(\mathbf{k}, \mathbf{k}') \rangle = \langle t(\mathbf{k}', \mathbf{k}) \rangle$, $Q(\mathbf{k}, \mathbf{k}')$ and $Q(\mathbf{k}', \mathbf{k})$ are not equal.] In view of Eq. (3.2a), we must show that
\[
\text{Im}Q(\mathbf{k}, \mathbf{k}') = 0 .
\]
Beginning with (3.5a) and using the identities
\[
\text{Im}(abc) = (1 + \text{Im} b)c + a\text{Re}(b)c + a\text{Re}(b)\text{Im}(c)
\]
and (3.3), $\text{Im}Q(\mathbf{k}, \mathbf{k}')$ can be shown to satisfy the linear integral equation
\[
\text{Im}Q(\mathbf{k}, \mathbf{k}') = -\pi \sum \langle t^* (\mathbf{k}, \mathbf{q}) \rangle \delta(E - q^2) g(\mathbf{q} - \mathbf{k}') Q(\mathbf{q}, \mathbf{k}')
\]
\[
+ \Delta^*(\mathbf{q}, \mathbf{k}') \delta(E - q^2) D(\mathbf{q}, \mathbf{k}')
\]
\[
+ \sum_{\mathbf{k}_1} \langle t^* (\mathbf{k}, \mathbf{k}_1) \rangle G_{\mathbf{k}_1}(\mathbf{k}) g(\mathbf{k}_1 - \mathbf{k}') \text{Im}Q(\mathbf{k}_1, \mathbf{k}') ,
\]
\[
\text{Im}Q(\mathbf{k}, \mathbf{k}') = \Delta(\mathbf{q}, \mathbf{k}')
\]
\[
+ \sum_{\mathbf{k}_1} \Delta(\mathbf{q}, \mathbf{k}_1) G_{\mathbf{k}_1}(\mathbf{k}) g(\mathbf{k}_1 - \mathbf{k}') Q(\mathbf{k}_1, \mathbf{k}') .
\]

where $Q(\mathbf{q}, \mathbf{k}')$ is the solution of (3.5) and $D(\mathbf{q}, \mathbf{k}')$ is
\[
D(\mathbf{q}, \mathbf{k}') = \Delta(\mathbf{q}, \mathbf{k}')
\]
\[
+ \sum_{\mathbf{k}_1} \Delta(\mathbf{q}, \mathbf{k}_1) G_{\mathbf{k}_1}(\mathbf{k}) g(\mathbf{k}_1 - \mathbf{k}') Q(\mathbf{k}_1, \mathbf{k}') .
\]

In principle, the solution of Eq. (3.9) can be generated by iteration [cf. (3.5b)]. While the general solution cannot be written in closed form, in the special case $\mathbf{k} = \mathbf{k}'$, we find
\[
\text{Im}Q(\mathbf{k}, \mathbf{k}') = -\pi \sum \langle t^* (\mathbf{q}, \mathbf{k}) \rangle |^2 f(\mathbf{q} - \mathbf{k})
\]
\[
+ xy |D(\mathbf{q}, \mathbf{k})|^2 \delta(E - q^2) \leq 0 ,
\]
and the proposition (3.6) is thus proven.

B. Coherent-potential approximation (CPA)

In this approach the disordered alloy is again represented by a periodic lattice of complex en-

ergy-dependent potentials. If we denote the effective potential centered at the $\alpha$th site by $\sigma_\alpha$, then the equations which define the approximation are usually written as
\[
\langle \bar{T} \rangle = x\bar{T}_A + y\bar{T}_B = 0 ,
\]
where
\[
\bar{T}_i = (\mu_i - \sigma)(1 + G\bar{T}_i) , \quad i = A, B
\]
and $G$ is the Green's function for the effective complex lattice. Unfortunately, Eqs. (3.11) are somewhat inconvenient since they do not readily indicate the manner in which successive terms of the multiple-scattering series (2.4) are being approximated. For the present purposes, an explicit expansion of $T$ in terms of the quantities $\langle \bar{T} \rangle$, $\Delta$, and $G_{\alpha}$ is required. The appropriate reformulation of Eqs. (3.11) has been discussed in Ref. 9 and is reviewed briefly in the Appendix. In the CPA the operator $T$ may again be written as in (3.2a), with $Q_{\alpha}$ being determined by the pair of nonlinear equations
\[
Q_{\alpha} = \langle t_{\alpha} \rangle + \langle t_{\alpha} \rangle G_{\alpha} \sum_{\beta \neq \alpha} Q_{\beta} + xy \Delta_{\alpha} G_{\alpha} \sum_{\beta \neq \alpha} \sigma_\beta G_{\beta} D_{\alpha}
\]
\[
D_{\alpha} = \Delta_{\alpha} + \Delta_{\alpha} G_{\alpha} \sum_{\beta \neq \alpha} Q_{\beta} + [1 + \langle t_{\alpha} \rangle G_{\alpha} + (y - x) \Delta_{\alpha} G_{\alpha}] \sum_{\beta \neq \alpha} \sigma_\beta G_{\beta} D_{\alpha}
\]
where the effective potential $\sigma_\alpha$ is calculated in terms of $Q_{\alpha}$ as
\[
\sigma_\alpha = Q_{\alpha}(1 + G_{\alpha} T)^{-1} .
\]
To check that the leading contributions to the CPA spectral function are non-negative, we compute $\langle \mathbf{E} \mid S_A \mid \mathbf{E} \rangle$ and $\langle \mathbf{E} \mid S_B \mid \mathbf{E} \rangle$. Recalling the discussion following Eqs. (2.14), this requires the evaluation of $\langle T_A \rangle$ through $\langle T_B \rangle$. Iterating Eqs.
The CPA thus reproduces the exact expression (2.17) for \( \langle \mathbf{k} | S_1 | \mathbf{k} \rangle \) and, for \( \langle \mathbf{k} | S_2 | \mathbf{k} \rangle \), gives the first two terms of (2.20) but replaces the last term by
\[
x^3y^3 \sum_{\mathbf{k} \neq \mathbf{a}} \sum_{\mathbf{g} \neq \mathbf{a}} \langle \mathbf{g} | \Delta_\mathbf{a} G_{\mathbf{a}} \Delta_\mathbf{a} | \mathbf{k} \rangle = 2 \delta(E - q^2) \tag{3.14}
\]

Within the CPA, the final expression for \( \operatorname{Im}(\mathbf{k} | T | \mathbf{k}) \) is then
\[
-\pi N^{-1} \operatorname{Im}(\mathbf{k} | T | \mathbf{k}) \sim \sum_{\mathbf{g}} \sum_{\mathbf{a}} |Q(\mathbf{g}, \mathbf{k})|^2 |d(\mathbf{g}, \mathbf{k})|^2 \delta(E - q^2)
\]
\[
+ x y \sum_{\mathbf{k} \neq \mathbf{a}} \sum_{\mathbf{g} \neq \mathbf{a}} \langle \mathbf{g} | \Delta_\mathbf{a} G_{\mathbf{a}} \Delta_\mathbf{a} | \mathbf{k} \rangle = 0 . \tag{3.16}
\]

C. Approximations based on the Lloyd equations

Because the atomic potentials in the muffin-tin model are nonoverlapping, an electron must propagate as a free particle in the interstitial region. It follows that the only property of the potentials that enters an exact calculation of the electronic spectrum (for a given configuration of the alloy) is the set of logarithmic derivatives of the radial wave functions evaluated at the muffin-tin radius \( r_m \), or equivalently, the set of energy-dependent phase shifts \( \delta_{\mathbf{a}}^{(\mathbf{B})}(E) \). The latter quantities are simply related to the energy-shell matrix elements \( t_{\mathbf{a}}^{(\mathbf{B})}(E) \) of the atomic scattering operators \( t_{\mathbf{a}}^{(\mathbf{B})} \). In the angular momentum representation
\[
I_{\mathbf{a}}^{(\mathbf{B})}(k, k') = \delta^{(\mathbf{B})}(E) = -(1/2\pi) \exp(i\delta_{\mathbf{a}}^{(\mathbf{B})}) \sin(b_{\mathbf{a}}^{(\mathbf{B})}) . \tag{3.18}
\]

The relevant equation, first derived by Lloyd, is
\[
\rho(E) = \rho_0(E) - (2/\pi\delta t) \operatorname{Im} \sum_{\mathbf{a}} \sum_{\mathbf{g}} Y_{L}(\mathbf{g}) t_{\mathbf{g}}^{(\mathbf{B})}(E) Y_{L}(\mathbf{k}) . \tag{3.19}
\]

where \( \rho_0(E) \) is the free-electron density of states and the trace operation in (3.19) refers to a combined angular-momentum–lattice representation. The matrix \( B_{\mathbf{g}}^{(\mathbf{B})}(E) \) is translationally invariant and is related to the usual KKR structure functions \( B_{\mathbf{g}}^{(\mathbf{L})}(E) \):
\[
B_{\mathbf{g}}^{(\mathbf{B})}(E) = N^{-1} \sum_{\mathbf{g}} e^{i\mathbf{g} \cdot \mathbf{r}} \rho_0(E) B_{\mathbf{g}}^{(\mathbf{L})}(E) . \tag{3.20}
\]

By contrast, the matrix \( \tau \) is diagonal and random where \( \tau_{\mathbf{a}} \) equals \( \tau_{\mathbf{a}}^T \) or \( \tau_{\mathbf{a}}^L \) depending on whether an A or B atom occupies the site \( \mathbf{a} \).

Various authors have suggested expressions for the electronic density of states based on an approximate averaging of Eqs. (3.19) over all configurations of the alloy. We consider two such ex-
expressions in this subsection. The first was proposed by Gyorffy and Stocks\textsuperscript{14}:

\[
\rho(E) = \rho_0(E) - \frac{2}{N\pi} \text{Im} \sum_{\mathbf{q} \in \mathbb{B}^2} \text{Tr}((\tau)^{-1} - B_0^{-1}) \left[ \frac{d(\tau)^{-1}}{dE} - \frac{dB_0^{-1}}{dE} \right] \\
+ \frac{2}{\pi} \text{Im} \left( \frac{d}{dE} \ln\|(\tau)^{-1} - B_0^{-1}\| + y \frac{d}{dE} \ln\|(\tau)^{-1} - \tau_{\alpha}^{-1}\| \right). \tag{3.22}
\]

The second was derived by the present authors:

\[
\rho(E) = \rho_0(E) - \frac{2}{N\pi} \text{Im} \sum_{\mathbf{q} \in \mathbb{B}^2} \text{Tr} \left\{ (\tau)^{-1} - B_0^{-1} \right\} \left[ \frac{d(\tau)^{-1}}{dE} - \frac{dB_0^{-1}}{dE} \right] \\
+ (1 - \langle \tau \rangle B_0^{-1}) \left[ \frac{x}{dE} \ln\|(\tau)^{-1} - \tau_{\alpha}^{-1}\| + y \frac{d}{dE} \ln\|(\tau)^{-1} - \tau_{\alpha}^{-1}\| \right]. \tag{3.23}
\]

Here \(\langle \tau \rangle = x\tau_A + y\tau_B\) and the matrix operations now refer to just the angular indices.

It should be emphasized that the derivation of the Lloyd equations involves mixing contributions from terms of different order in the multiple-scattering series.\textsuperscript{13} It follows, that once Eq. (3.19) is configuration averaged (approximately) the result will not necessarily correspond to a well-defined decoupling of the original series (2.4). If this is the case, then the procedures developed in Sec. II cannot be used to determine whether the equations at hand are constrained to yield a positive spectrum. To illustrate, Eq. (3.23) has been applied to a variety of disordered transition metal alloys and has always been found to give a positive density of states.\textsuperscript{1,11,10} To our knowledge, however, Eq. (2.23) cannot be derived from any decoupling of the series (2.4) and therefore, a proof that this equation will never yield a negative spectrum falls beyond the scope of the methods developed in this paper. By contrast, Eq. (3.22) is known to give negative results in CuNi alloys. This equation, however, can be obtained directly from the multiple-scattering series and, if the methods developed in Sec. II are applied here, the occurrence of a negative density of states can, in fact, be anticipated. The decoupling of the multiple-scattering series that corresponds to (3.22) is essentially identical to the one used by the present authors to derive the modified quasicrystalline equations for the liquid metal.\textsuperscript{11} We go beyond the ATA by including correlations between the first and last site in each of the higher order terms of the series (2.4). Thus

\[
\langle T_\alpha \rangle = \sum_\alpha \langle t_{\alpha} \rangle, \quad \langle T_\beta \rangle = \sum_{\beta \neq \alpha} \langle t_{\alpha} \rangle G_0(t_{\beta}) G_0(t_{\alpha}), \tag{3.24a}
\]

\[
\langle T_\alpha \rangle = \sum_{\beta \neq \alpha} \langle t_{\alpha} \rangle G_0(t_{\beta}) G_0(t_{\alpha}) + xy \sum_{\beta \neq \alpha} \Delta_\alpha G_0(t_{\beta}) G_0(t_{\alpha}), \tag{3.24b}
\]

\[
\langle T_\alpha \rangle = \sum_{\beta \neq \alpha} \langle t_{\alpha} \rangle G_0(t_{\beta}) G_0(t_{\beta}) G_0(t_{\alpha}) + xy \sum_{\beta \neq \alpha} \Delta_\alpha G_0(t_{\beta}) G_0(t_{\beta}) G_0(t_{\alpha}) \tag{3.24c}
\]

etc. The density of states (per atom) is then

\[
\rho(E) = \rho_0(E) - \frac{2}{N\pi} \text{Im} \text{Tr} \left[ \sum_\alpha G_0(t_{\alpha}) G_0 + \sum_{\beta \neq \alpha} \left( \frac{d}{dE} G_0(t_{\alpha}) \right) G_0(t_{\beta}) + \cdots \right] \\
= \rho_0(E) - \frac{2}{N\pi} \text{Im} \text{Tr} \sum_{\mathbf{q} \in \mathbb{B}^2} \left( \frac{d}{dE} G_0(t_{\alpha}) \right) G_0(t_{\beta}) G_0(t_{\alpha}) + \cdots \\
= \rho_0(E) - \frac{2}{N\pi} \text{Im} \text{Tr} \left[ \sum_{\mathbf{q} \in \mathbb{B}^2} \left( \frac{d}{dE} G_0(t_{\alpha}) \right) G_0(t_{\beta}) G_0(t_{\alpha}) + \cdots \right] \\
= \rho_0(E) - \frac{2}{N\pi} \text{Im} \text{Tr} \sum_{\mathbf{q} \in \mathbb{B}^2} \left[ \langle \tau \rangle^{-1} - B_0^{-1} \right] \left( \frac{d(\tau)^{-1}}{dE} - \frac{dB_0^{-1}}{dE} \right) \\
- \frac{2}{\pi} \text{Im} \text{Tr} \left[ \frac{d}{dE} \left( x \ln(t_{\alpha}) + y \ln(t_{\beta}) - \ln(\tau) \right) \right]. \tag{3.25}
\]
Using the identity
\[
\text{Im Tr} \left[ \frac{d}{dE} \left[ x \ln(\tau_A) + y \ln(\tau_B) - \ln(\tau) \right] \right] = -\text{Im Tr} \left[ x \frac{d}{dE} \ln(\tau)^{-1} - \tau_B^{-1} \right] + y \frac{d}{dE} \ln(\tau)^{-1} - \tau_A^{-1} \right],
\]
Eqs. (3.25) and (3.22) are thus seen to be equivalent. If Eqs. (3.24) are now used to construct the quantity \( N_{\tau}^{(1)}(k, \tau) \), we find
\[
N_{\tau}^{(1)}(k, \tau) = \sum_{\tau} \left[ \langle t(\tilde{q}, \tilde{k}) \rangle + \sum_{t_1} \langle t(\tilde{q}, \tilde{k}_1) \rangle G(t_1, \tau) G(\tilde{k}, \tau) \right] \left[ I(\tilde{q} - \tilde{k}) + xy \left[ \Delta(\tilde{q}, \tilde{k}) + \sum_{t_1} \Delta(\tilde{q}, \tilde{k}_1) G(t_1, \tau) G(\tilde{k} - \tilde{k}_1) \right] \right] \delta(E - q^2)
+ \frac{x^2 y^2}{N} \sum_{\tilde{s}, t_a} \left[ \langle \tilde{q} \mid \delta_a \delta^*_a \delta^*_b \delta_b \rangle \delta(E - H_\tau) G(t_a, \tau) G(\tilde{q}) \right]
+ xy \sum_{\tilde{q}} \left[ \sum_{t_1} \left\{ \Delta^*(\tilde{q}, \tilde{k}_1) G(t_1, \tau) G(\tilde{k} - \tilde{k}_1) \Delta(\tilde{k}_1, \tilde{k}) + \Delta^*(\tilde{q}, \tilde{k}_1) G(t_1, \tau) G(\tilde{q} - \tilde{k}_1) \right\} \right] \delta(q - k).
\]

APPENDIX: PROOF THAT THE CPA SPECTRUM IS NON-NEGATIVE

The average total scattering operator in the alloy \( A \tau B \), can always be written as
\[
T = \sum_{\alpha} \left( xQ^A_{\alpha} + yQ^B_{\alpha} \right) = \sum_{\alpha} Q_{\alpha},
\]
where \( Q^{(A,B)}_{\alpha} \) denotes a restricted average of the series
\[
t_{\alpha} + t_{\alpha} G_{\alpha} \sum_{\beta \neq \alpha} t_{\beta} G_{\beta} \sum_{\gamma \neq \beta} t_{\gamma} G_{\gamma} \sum_{\delta \neq \gamma} t_{\delta} G_{\delta} \cdots
\]
in which the initial site \( \alpha \) is specified to be of type \( A \) (or \( B \)). The effective potential \( \sigma_{\alpha} \) and \( Q_{\alpha} \) are related by the equations
\[
\sigma_{\alpha} = Q_{\alpha} \left( 1 + G_{\alpha} \right)^{-1} = x\sigma^A_{\alpha} + y\sigma^B_{\alpha},
\]
where
\[
\sigma^{(A,B)}_{\alpha} = Q^{(A,B)}_{\alpha} \left( 1 + G_{\alpha} \right)^{-1}.
\]
In Eqs. (4.28) of Ref. 9, Schwartz and Ehrenreich have shown that the CPA may be defined by the pair of equations
\[
\sigma^{(A,B)}_{\alpha} = \nu^{(A,B)}_{\alpha} + \nu^{(A,B)}_{\alpha} G_{\alpha} T^{(A,B)}_{\alpha}
\]
and
\[
T^{(A,B)}_{\alpha} = \left( \nu^{(A,B)}_{\alpha} - \sigma_{\alpha} \right) \left( 1 + G T^{(A,B)}_{\alpha} \right).
\]
Substituting from (A4b) into (A4a) and using Eqs. (A3) we obtain
\[
Q^{(A,B)}_{\alpha} = t_{\alpha}^{(A,B)} + Q^{(A,B)}_{\alpha} G_{\alpha} \sum_{\beta \neq \alpha} \sigma_{\beta} \left( 1 + G_{\alpha} \right),
\]
where
\[
t^{(A,B)}_{\alpha} = \nu^{(A,B)}_{\alpha} \left( 1 + G_{\alpha} \right),
\]
Eqs. (A5), together with (A3) and (A1) generate the coherent-potential expansion of \( Q_{\alpha} \) in terms \( t^A, t^B \), and \( G_{\alpha} \). To put these equations in a more convenient form we introduce the quantities \( F^{(A,B)}_{\alpha} \):
\[
Q^{(A,B)}_{\alpha} = t^{(A,B)}_{\alpha} F^{(A,B)}_{\alpha}.
\]
Equation (A5) then reduces to
\[
F^{(A,B)}_{\alpha} = 1 + G_{\alpha} \sum_{\beta \neq \alpha} \sigma_{\beta} \left( 1 + G_{\alpha} \right) F^{(A,B)}_{\alpha}.
\]
Using
\[
Q_{\alpha} = \langle f_{\alpha} \rangle \left( F_{\alpha} \right) + xy \Delta_{\alpha} \left( F^{A}_{\alpha} - F^{B}_{\alpha} \right)
\]
and
\[
\langle F_{\alpha} \rangle = xF^{A}_{\alpha} + yF^{B}_{\alpha} - \sum_{\beta} \langle Q_{\beta} \rangle,
\]
Eqs. (A5) can be rewritten as
\[ Q_a = \langle t_a \rangle G_0 \sum_{\beta \neq a} Q_{\beta} + x y \Delta_a G_0 \sum_{\beta \neq a} \sigma_\beta G_\beta D_\alpha \] 
(A11a)

\[ D_a = \Delta_a + \Delta_a G_0 \sum_{\beta \neq a} Q_{\beta} \]
\[ + [1 + \langle t_a \rangle G_0 + (y - x) \Delta_a G_0] \sum_{\beta \neq a} \sigma_\beta G_\beta D_\alpha , \] 
(A11b)

which are identical to Eqs. (3.12).

The proof that the CPA spectrum is non-negative now proceeds along lines similar to those used to prove the corresponding result for the ATA. The analysis is considerably more complicated, however, because we must now deal with coupled nonlinear equations. To begin, the operator equations (A11) must be converted to integral equations for \( Q(k, k') \) and \( D(k, k') \). These, in turn, must be used to derive the corresponding equations for \( \text{Im} Q(k, k') \) and \( \text{Im} D(k, k') \). The analysis is most easily described if we adopt a symbolic notation in which all quantities are to be understood as matrices in the momentum representation. For example we introduce the auxiliary quantities \( \alpha \), \( \beta \), and \( \gamma \):

\[ \langle \tilde{k} | \alpha | \tilde{k}' \rangle = xy \langle \tilde{k} | \Delta_g \{ \sigma \} G_0 | \tilde{k}' \rangle \]
\[ = \sum_{k_1} \{ \delta_k k_1 + \langle t(k, \tilde{k}_1) G_0(k_1) + \eta \Delta(k, \tilde{k}_1) G_0(k_1) \} \delta(k_1 - k') \sigma_{\tilde{k}_1, \tilde{k}_2} G_0(\tilde{k}_2) \}, \] 
(A12a)

\[ \langle \tilde{k} | \gamma | \tilde{k}' \rangle = \langle \tilde{k} | (1 - \beta) \gamma \rangle | \tilde{k}' \rangle \]
\[ = \delta_k k + \langle \tilde{k} | \gamma | \tilde{k}_1 \rangle + \sum_{k_1} \langle \tilde{k} | \beta | \tilde{k}_1 \rangle \langle \tilde{k}_1 | \beta | \tilde{k}_2 \rangle + \sum_{k_1, k_2} \langle \tilde{k} | \beta | \tilde{k}_1 \rangle \langle \tilde{k}_1 | \beta | \tilde{k}_2 \rangle \langle \tilde{k}_2 | \beta | \tilde{k}_3 \rangle + \cdots . \] 
(A12c)

Here the symbol \( \{ab\} \) denotes the momentum representation of a convolution of \( a \) and \( b \), i.e., the direct product:

\[ \langle \tilde{k} | \{ab\} | \tilde{k}' \rangle = \langle \tilde{k} | a | \tilde{k}_1 \rangle \langle \tilde{k}_1 | b | \tilde{k}' \rangle . \]

After some straightforward but rather lengthy manipulations, we obtain the following four equations

\[ Q = \tau (1 + G_0 \{gQ\}) , \] 
(A15a)

\[ D = \gamma \Delta (1 + G_0 \{gQ\}) , \] 
(A15b)

where

\[ \tau = t + \sigma \gamma \Delta \] 
(A16)

is, in view of (A15a), to be interpreted as the coherent-potential effective atomic scattering operator

\[ \tau = \sigma + \gamma \Delta \tau . \] 
(A17)

Combining Eqs. (A13d) and (A13c), we find after some rearrangement

\[ \text{Im} Q = -\pi \tau * \delta(E - H_0) \{ IQ \} - A_1 D \]
\[ + \langle t \rangle G_0 \{ g \text{Im} Q \} + \alpha * \text{Im} D , \]
\[ \text{Im} D = -\pi \Delta * \delta(E - H_0) \{ IQ \} - A_2 D \]
\[ + \Delta G_0 \{ g \text{Im} Q \} + \beta * \text{Im} D , \] 
(A18)

where the asterisk denotes complex conjugate (i.e., \( \langle k | a^* | k' \rangle = \langle k | a | k' \rangle ^* \)), \( I \) again denotes the intensity function (2.18), and \( A_1 \) and \( A_2 \) are defined as

\[ A_1 = \pi x y \Delta * (1 + G_0 \{ g \text{Im} \} \} \delta(E - H_0) - \{ g \text{Im} \} G_0 , \] 
(A14a)

\[ A_2 = \pi \{ \beta \{ g \text{Im} \} \} + \langle t \rangle \delta(E - H_0) - \beta \{ g \text{Im} \} G_0 , \] 
(A14b)

Equation (A13a) and (A13b) can be rewritten as

\[ Q = \langle k | t_a | \tilde{k}' \rangle \] 
(A19a)

\[ = xy \Delta (1 - \beta)^* \{ \pi \delta(E - H_0) - G_0 \{ g \text{Im} \} G_0 \} . \] 
(A19b)

[The second of Eqs. (A19) is obtained by substituting from (A14) into (A19a).] Now, suppose that Eq. (A18) is treated formally as a linear integral equation for \( \text{Im} Q(k, k') \); iterating, setting \( k' = k \), and using Eqs. (A15), we find
\[ \text{Im} \mathcal{Q}(\mathbf{k}, \mathbf{q}) = -\pi \sum_{\mathbf{q}} \delta(E - q^2) I(\mathbf{k} - \mathbf{q}) |\mathcal{Q}(\mathbf{k}, \mathbf{q})|^2 \]
\[ = -\sum_{\mathbf{k}_1, \mathbf{k}_2} \left[ \delta^{(k_1, k_2)} + \mathcal{Q}^*(\mathbf{k}_1, \mathbf{k}_2) G_0(h_1) \mathcal{g}(\mathbf{k}_2 - \mathbf{k}_1) A(\mathbf{k}_1, \mathbf{q}) D(\mathbf{q}, \mathbf{k}) \right] \]
\[ + \pi \sum_{\mathbf{q}} \delta(E - q^2) \left[ |\mathcal{Q}(\mathbf{k}, \mathbf{q})|^2 + xy |D(\mathbf{q}, \mathbf{k})|^2 \right] \]
\[ + xy \sum_{\mathbf{k}_1, \mathbf{k}_2} D^*(\mathbf{k}_1, \mathbf{k}_2) G_0^*(h_1) [g(\mathbf{k}_2 - \mathbf{k}_1) \text{Im}(\mathcal{Q}(\mathbf{k}_1, \mathbf{k}_2)) G_0(h_2) D(\mathbf{k}_1, \mathbf{k}_2) \mathcal{Q}(\mathbf{k}, \mathbf{q})]. \] 

(A20a)

The first two terms in (A20) clearly exhibit the proper sign. To prove that the last term also gives a negative contribution, we must consider in detail the equations that govern the behavior of \( \sigma_\alpha \). These are obtained directly from Eqs. (A11) via the identity \( \sigma_\alpha = Q_\alpha (1 + G_0 T)^{-1} \):

\[ \sigma_\alpha = \sigma_\alpha^{(0)} + xy(1 - \sigma_\alpha^{(0)} G_0) \Delta_\alpha G_0 \sum_{\beta \neq \alpha} \sigma_\beta G_\beta P_\alpha \] 
(A21a)

\[ P_\alpha = \Delta_\alpha - \Delta_\alpha G_0 \sigma_\alpha \]

\[ + [1 + \langle t \rangle G_\alpha + (y - x) \Delta G_\alpha] \sum_{\beta \neq \alpha} \delta G_\alpha P_\alpha . \] 
(A21b)

Here

\[ \sigma_\alpha^{(0)} = (1 + \langle t \rangle G_\alpha)^{-1}(t_{\alpha}) \] 
(A22a)

and

\[ P_\alpha = D_\alpha (1 + G_0 T)^{-1} . \] 
(A22b)

Following steps similar to those outlined above (for \( Q_\alpha \) and \( D_\alpha \)), Eqs. (A21) can be used to derive an equation for \( \text{Im} \sigma(\mathbf{k}, \mathbf{k}') \). The result is (again using symbolic notation)

\[ \text{Im} \sigma = -xy P^\dagger (E - H_0) P + xy P^\dagger G_0^\dagger \text{Im} \mathcal{Q} P \] 
(A23)

Now, since \( \sigma(\mathbf{k}, \mathbf{k}') = \sigma(\mathbf{k}', \mathbf{k}) \), \( \text{Im} \sigma(\mathbf{k}, \mathbf{k}') = (2\pi)^{-1} \langle \mathbf{k} | (\sigma - \sigma^*) | \mathbf{k}' \rangle \). Equation (A23) is then equivalent to the operator equation

\[ (2\pi)^{-1}(\sigma_{\alpha} - \sigma^*_{\alpha}) = -xy P^\dagger (E - H_0) P \]

\[ + xy \sum_{\beta \neq \alpha} P^\dagger G_\alpha^\dagger [2i(\sigma_{\beta} - \sigma^*_{\beta})] G_\beta P \] 
(A24)

in the lattice representation. The last term in (A20b) can finally be rewritten as

\[ xy \sum_{\beta \neq \alpha} \langle \mathbf{k} | D^\dagger G_\alpha^\dagger [2i(\sigma_{\beta} - \sigma^*_{\beta})] G_\beta D \mathcal{Q}(\mathbf{k}, \mathbf{q}) | \mathbf{k} \rangle \]

\[ = -x^2 y^2 \sum_{\beta \neq \alpha} \langle \mathbf{k} | D^\dagger G_\alpha^\dagger P_\beta G_\beta P \rangle \delta(E - H_0) P_\beta G_\beta D \mathcal{Q}(\mathbf{k}, \mathbf{q}) | \mathbf{k} \rangle \]

\[ -x^2 y^2 \sum_{\gamma \neq \beta} \langle \mathbf{k} | D^\dagger G_\alpha^\dagger P_\beta G_\beta P \rangle \delta(E - H_0) P_\beta G_\beta P_\gamma G_\gamma D \mathcal{Q}(\mathbf{k}, \mathbf{q}) | \mathbf{k} \rangle + \cdots < 0 \] 
(A25)

and the proof is complete.

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7 See, for example, Sec. 7 of Ref. 2.
12 These two approaches are compared in some detail in Ref. 2.

B. L. Byorffy and M. Stocks, J. Phys. (Paris) 35 (Suppl. No. 5) C4–75 (1974). We emphasize that the equation we are referring to [Eq. (3.22) of this paper] was proposed by Gyorffy and Stocks as an approximate solution of their muffin-tin CPA equations. While this approximate solution is deficient, the results derived in the Appendix of this paper show that the original muffin-tin CPA equations will never yield a negative spectrum.


This point has been the source of some confusion. Indeed, the schemes proposed in both Refs. 14 and 15 were originally described as the average–$t$–matrix approximation. In fact, neither of these approaches is formally equivalent to the original average–$t$–matrix equations [cf. J. L. Beeby, Phys. Rev. A 125, 130 (1966); P. Soven, Phys. Rev. 151, 539 (1966)].


A(k, E) should not be confused with the Bloch spectral density $a(\vec{k}, E)$, which is defined only for $\vec{k}$ in the first Brillouin zone:

$$a(\vec{k}, E) = \sum_n A(\vec{k} + \vec{K}_n, E),$$

where $\vec{K}_n$ denotes a vector in the reciprocal lattice.

For a brief review of multiple-scattering theory see Secs. 6 and 7 of Ref. 2.

P. E. Mijnarends and A. Bansil, Phys. Rev. B 13, 2381 (1976); see Appendix B.

Equation (2.7) implies that, for a given $E$, $(\vec{k} | T | \vec{k})$ has an expansion of the form

$$<\vec{k} | T(E^*) | \vec{k}> = -(E - k^2)^{-1} \alpha(E, \vec{k})(E - k^2)^2 + \ldots,$$

where $\vec{k}$ denotes a unit vector in the direction of $\vec{k}$. Contributions to $\text{Im}[<\vec{k} | T(E^*) | \vec{k}>]$ are of order $(E - k^2)^2$ and the right-hand side of (2.8) is well behaved as $k^2 \rightarrow E$.

See Eq. (3.10) of Ref. 2.

See Sec. 4.2 of Ref. 9.

