PHYSICAL REVIEW B VOLUME 21, NUMBER 8 15 APRIL 1980

Calculating properties with the coherent-potential approximation

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(Received 25 July 1979)

It is demonstrated that the expression that has hitherto been used for calculating the Bloch spectral-density function $A^B(E,\vec{k})$ in the Korringa-Kohn-Rostoker coherent-potential-approximation theory of alloys leads to manifestly unphysical results. No manipulation of the expression can eliminate this behavior. We develop an averaged Green's-function formulation and from it derive a new expression for $A^B(E,\vec{k})$ which does not contain unphysical features. The earlier expression for $A^B(E,\vec{k})$ was suggested as plausible on the basis that it is a spectral decomposition of the Lloyd formula. Expressions for many other properties of alloys have been obtained by manipulations of the Lloyd formula, and it is now clear that all such expressions must be considered suspect. It is shown by numerical and algebraic comparisons that some of the expressions obtained in this way are equivalent to the ones obtained from a Green's function, while others are not. In addition to studying these questions, the averaged Green's-function formulation developed in this paper is shown to furnish an interesting new way to approach many problems in alloy theory. The method is described in such a way that the aspects of the formulation that arise from the single-site approximation can be distinguished from those that depend on a specific choice for the effective scatterer.

I. INTRODUCTION

In the sequence of single-site approximations that have been put forward for the purpose of calculating the electronic states of random substitutional alloys, the true potential for the system is replaced by a model potential that is constructed so that the same effective scatterer appears on each site. For example, in the virtual-crystal approximation (VCA) of Nordheim[1] and Muto[2] the scattering from each site is calculated from a potential function that is the average of the potentials of the two species of atoms that make up the alloy. The t matrix of the effective scatterer is taken to be the average of the two t matrices in Korringa's[3] average t-matrix approximation (ATA), while the definition of the effective scatterer is even more complicated in the coherent-potential approximation (CPA) of Soven.[4]

The papers on these single-site approximations specify the nature of the effective scatterer very precisely, but they are not so precise when outlining the procedures for calculating properties. These theories are designed to lead to an ensemble-averaged Green's function from which all properties of the alloy can be calculated. Such a Green's function has been used in some one-dimensional model calculations[5] and also in calculations done with the one-level tight-binding model.[6,7] It has not been used heretofore in connection with three-dimensional muffin-tin models since alternative formulations[8-10] are considered easier to apply.

The original motivation for the studies described in this paper came from the observation by one of the authors (G.M.S.) that the expression for the Bloch spectral-density function[9] that has been used in all Korringa-Kohn-Rostoker (KKR)-CPA calculations to date leads to numerical results that are manifestly unphysical. A careful study shows that the unphysical features cannot be eliminated by manipulation of the expression, and therefore that it is fundamentally incorrect. This expression was not derived from a Green's function, but rather it was put forward as plausible because it is a spectral decomposition of Lloyd's formula.[11] Expressions for many alloy properties have been obtained by manipulating Lloyd's formula, and the observation of the difficulty with the Bloch spectral density calls into question the applicability of this technique.

The Lloyd formula is often used to calculate the density of states for a system that is made up of a cluster of muffin-tin potentials. It has been shown[12] to be a special case of a theorem by Krein[13] that is used extensively in scattering theory, and it is mathematically sound as long as it is used within proper limits. Neither the Lloyd formula nor Krein's theorem were derived for the kind of complex and energy-dependent model potentials that arise in alloy theory.

If the one-electron Green's function $G(E,\vec{r},\vec{r}\,')$ that describes the propagation of an electron through the solid is known, then the one-electron properties of the solid can be calculated. For example, the density-of-states function $\rho(E)$ is given by

$$\rho(E) = -\frac{1}{\pi}\,\mathrm{Im}\int G(E,\vec{r},\vec{r})\,dv\,, \tag{1.1}$$

while the spectral-density function $A(E,\vec{p})$ is

$$A(E,\vec{p}) = -\frac{1}{\pi N\Omega}\,\mathrm{Im}\int\int e^{i\vec{p}\cdot(\vec{r}-\vec{r}')}G(E,\vec{r},\vec{r}')dv\,dv' , \tag{1.2}$$

with Ω the volume of a unit cell and N the number of unit cells in the crystal. The Bloch spectral-density function $A^B(E,\vec{k})$ is related to $A(E,\vec{p})$. The integrated density-of-states function $N(E)$ defined by

$$N(E) = \int_{-\infty}^{E} \rho(E')dE' , \tag{1.3}$$

is also an interesting property of an alloy.

As mentioned above, the alloy theories considered in this paper which are based on the single-site approximation lead to an approximation $G_c(E,\vec{r},\vec{r}')$ to the ensemble average of the $G(E,\vec{r},\vec{r}')$. The approximation is defined in terms of effective-scattering matrices t^c.

To study the problem of calculating properties of alloys we have developed a formulation for $G_c(E,\vec{r},\vec{r}')$ that goes beyond anything that was previously available. Using this formulation we derive an expression for $A^B(E,\vec{k})$ that is valid for any single-site approximation. When it is used for a CPA calculation, the unphysical features in the earlier results are eliminated. Having demonstrated that the Green's-function formulation resolves the difficulty with $A^B(E,\vec{k})$, we went on to consider other properties.

We find that an expression for $\rho(E)$ and $N(E)$ obtained from the Lloyd formula by Györffy and Stocks[8] gives exactly the same results in CPA calculations as the one obtained here from $G_c(E,\vec{r},\vec{r}')$, although the two expressions look quite different. We prove this equivalence algebraically, but the proof requires the repeated use of the requirement that t^c satisfies the CPA condition. The proof therefore does not hold for other single-site approximations such as the ATA. Also, the proof cannot be carried through for the component densities-of-states formula derived from the Györffy-Stocks expression.[9]

Although the formulas for $G_c(E,\vec{r},\vec{r}')$ were originally developed to study the question of the applicability of the Lloyd-formula techniques, it should be clear that their importance goes beyond this application. They supply a new and useful tool for studying many problems in alloy theory.

The organization of this paper does not follow the historical outline given above. In the following section the formulas for $G_c(E,\vec{r},\vec{r}')$ are derived within the single-site approximation. It becomes clear in this derivation that two cases must be considered. The site-diagonal (SD) case in which $\vec{r}$ and $\vec{r}'$ are in the same unit cell, and the non-site-diagonal (NSD) case in which they are in two different cells. The ensemble-averaged Green's function looks quite different in these two cases. In the derivation of the NSD case a step must be included that goes beyond the literal interpretation of the single-site approximation, but we show in an appendix that it is unambiguously fixed by the single-site philosophy.

In Sec. III expressions for some of the alloy properties that can be calculated from $G_c(E,\vec{r},\vec{r}')$ in the SD case are obtained. The expression for $\rho(E)$ serves as a useful supplement to the Györffy-Stocks formula for CPA calculations, but it should definitely be used for other single-site calculations. In this approach the component densities of states are obtained in the process of calculating $\rho(E)$, and this is the best way to calculate them that is currently available. The SD case is very close to the usual picture of single-site approximations so that, although they are useful, the form of these expressions is not surprising to one who is familiar with the recent theory of alloys.

The spectral-density function of (1.2) and the related Bloch spectral density are examples of properties that require the NSD form of $G_c(E,\vec{r},\vec{r}')$. The form of the expression for $A^B(E,\vec{k})$ derived in Sec. IV is surprising, and it leads to a discussion of the peculiar effects that arise when an NSD property is calculated in the single-site approximation.

In Sec. V the Lloyd formula is written in a site-diagonal form so that it can be compared with the expressions in Sec. III. Extensive algebraic manipulations are needed to prove that the Györffy-Stocks expression for the density of states is equivalent to the one obtained in Sec. III, and the subtlety of the proof illustrates how easy it is to go wrong using the Lloyd formula for alloy problems.

In Sec. VI it is shown that the distinction between SD and NSD properties is camouflaged when the averaging process is carried out on a particular three-dimensional model, the one-level tight-binding model with no off-diagonal randomness. One of the reasons that the need for the considerations in this paper was not perceived before is presumably the great influence of this model in the development of the CPA. The analysis of this model does supply an insight into the behavior of certain functions that appear in the more general case.

Throughout these derivations, results which hold for any single-site approximation are separated from those that rely on a specific choice for t^c. The relevant numerical results are displayed and discussed in Secs. VII and VIII. In Sec. VII component and total density of states calculated with formulas in Sec. III are compared with results for $\rho(E)$ obtained by numerically differentiating the integrated density of states $N(E)$ that is calculated from the Györffy-Stocks formula. This comparison proves numerically that the Lloyd formula can lead to the same $\rho(E)$ as the averaged Green's function, but the details of $\rho(E)$ can be obtained more easily using the latter method. The important property for which the Lloyd formula will continue to be used is $N(E)$. The problems with the earlier calculations of $A^B(E, \vec{k})$ that led to the present analysis are described in Sec. VIII. The Bloch spectral density is calculated using the equations derived in Sec. IV, and it is shown that the unphysical behavior is eliminated. Finally, in Sec. IX conclusions are drawn from this work and speculations are made as to new developments that might arise from it.

II. THE ENSEMBLE-AVERAGED GREEN'S FUNCTION

The first step in deriving the averaged Green's function is to obtain a convenient expression for the Green's function before averaging. It is sufficiently general for the present purposes to consider a potential function

$$V(\vec{r}) = \sum_{i=1}^{N} v_i(\vec{r}_i) , \tag{2.1}$$

that is a sum of potentials centered on a set of N sites whose locations are at the points $\vec{R}_i$. The vectors $\vec{r}_i$ are defined by $\vec{r}_i = \vec{r} - \vec{R}_i$. It will be assumed that each potential is zero outside a bounding sphere of radius S_i:

$$v_i(\vec{r}_i) = 0 , \quad \vec{r}_i > S_i \tag{2.2}$$

and that the bounding spheres do not overlap each other.

The Green's function for a system of scatterers can be written in operator notation as

$$G = G_0 + G_0 T G_0 , \tag{2.3}$$

and the t matrix for the system may be written

$$T = \sum_{i,j=1}^{N} \tau^{ij} . \tag{2.4}$$

The operators τ^{ij} are defined by

$$\begin{aligned} \tau^{ij} &= t^i \delta_{ij} + t^i G_0 \sum_{k \neq i} \tau^{kj} \\ &= t^i \delta_{ij} + \sum_{k \neq j} \tau^{ik} G_0 t^j , \end{aligned} \tag{2.5}$$

where

$$t^i = v_i (1 + G_0 t^i) \tag{2.6}$$

is the t matrix that describes the scattering from the potential on the ith site. The τ^{ij} have been designated scattering-path operators by Györffy[14] who introduced them.

The operator G_0 is the free-electron Green's function which takes the form

$$\begin{aligned} \langle \vec{r} \,|\, G_0 \,|\, \vec{r}' \rangle &= G_0(E, \vec{r}, \vec{r}') \\ &= -i\kappa \sum_L Y_L(\vec{r}) j_l(\kappa r) h_l(\kappa r') Y_L(\vec{r}') , \end{aligned} \tag{2.7}$$

when $r' > r$. In this equation $Y_L(\vec{x})$ is a real spherical harmonic, $j_l(x)$ and $h_l(x)$ are Bessel and Hankel functions, $\kappa = \sqrt{E}$, and L stands for the pair of indices l, m.

The first step in obtaining an expression for $G(E, \vec{r}, \vec{r}')$ when $\vec{r}$ and $\vec{r}'$ are near some site n is to use (2.4) to rewrite (2.3) as

$$G = G^n + G^n T_{nn} G^n , \tag{2.8}$$

where

$$G^n = G_0 + G_0 t^n G_0 \tag{2.9}$$

is the Green's function for an electron moving in the field of the one-potential $v_n(\vec{r}_n)$, and

$$T_{nn} = \sum_{i \neq n} \sum_{j \neq n} \tau^{ij} . \tag{2.10}$$

It is relatively easy to find expressions for the Green's function $G^n(E, \vec{r}_n, \vec{r}_n') = \langle \vec{r}_n \,|\, G^n \,|\, \vec{r}_n' \rangle$ that describes the propagation of an electron in the field of one muffin-tin potential. We will not repeat that derivation, but merely quote the results in forms that are most convenient for the following discussion. The first such expression is

$$G^n(E, \vec{r}_n, \vec{r}_n') = -i\kappa \sum_{LL'} Z_L^n(E, \vec{r}_n) t_{LL'}^n h_{l'}(\kappa r_n') Y_{L'}(\vec{r}_n') , \tag{2.11}$$

which is valid when $r_n' > r_n$ and also $r_n' > S_n$. The second inequality assures that $\vec{r}_n'$ is outside the range of the potential $v_n(\vec{r}_n)$. The function $Z_L^n(E, \vec{r})$ is the solution of the differential equation

$$[-\nabla^2 + v_n(\vec{r}) - E] Z_L^n(E, \vec{r}) = 0 , \tag{2.12}$$

which is regular at the origin and joins smoothly to

$$Z_L^n(E, \vec{r}) = \sum_{L'} Y_{L'}(\vec{r}) j_{l'}(\kappa r) m_{L'L}^n - i\kappa Y_L(\vec{r}) h_l(\kappa r) , \tag{2.13}$$

when $r > S_n$. The matrix $\underline{m}^n$ is the inverse of the t matrix $\underline{t}^n$.

The Heitler-Wigner reaction matrix $\underline{R}$ is related to a t matrix $\underline{T}$ by

$$\underline{R}^{-1} = \underline{T}^{-1} - i\kappa \underline{I} , \tag{2.14}$$

and it can be shown to be a real, symmetric matrix when expressed in terms of real spherical harmonics. This fact can be used in connection with (2.13) to prove the important result that $Z^n_L(E, \vec{r})$ is a real function when it is calculated for a real potential.

An alternative expression for $G^n(E, \vec{r}_n, \vec{r}'_n)$ that is valid for $\vec{r}'_n$ either inside or outside the bounding sphere is

$$G^n(E, \vec{r}_n, \vec{r}'_n) = \sum_{LL'} Z^n_L(E, \vec{r}_n) t^n_{LL'} Z^n_{L'}(E, \vec{r}'_n) - \sum_L Z^n_L(E, \vec{r}_n) J^n_L(E, \vec{r}'_n) , \qquad (2.15)$$

where $J^n_L(E, \vec{r}_n)$ is a real solution of the differential equation in (2.12) which joins smoothly to $Y_L(\vec{r}_n) j_l(\kappa r_n)$ when $r_n > S_n$. This function is not regular at the origin in general.

The function $h_l(\kappa r_n)$ is singular at $\vec{R}_n$ but it is regular at all other points. For that reason it is clear that it can be expanded in spherical Bessel functions when $\vec{r}$ is in the neighborhood of some other site m; that is,

$$-i\kappa h_{l'}(\kappa r_n) Y_{L'}(\vec{r}_n) = \sum_L g^{nm}_{L'L} j_l(\kappa r_m) Y_L(\vec{r}_m) , \qquad (2.16)$$

and the expansion coefficients can be shown to be

$$g^{nm}_{LL'} = -4\pi i \kappa i^{l-l'} \sum_\Lambda i^{-\lambda} C^\Lambda_{LL'} h_\lambda(\kappa R_{nm}) Y_\Lambda(\vec{R}_{nm}) , \qquad (2.17)$$

with $\vec{R}_{nm} = \vec{R}_m - \vec{R}_n$, and $C^\Lambda_{LL'} = \int Y_\Lambda Y_L Y_{L'} d\Omega$.

Inserting (2.15) and (2.11) into the expression for $G(E, \vec{r}, \vec{r}')$ obtained from (2.8) and making use of (2.7) and (2.16) repeatedly leads to the expression

$$G(E, \vec{r}, \vec{r}') = \sum_{LL'} Z^n_L(E, \vec{r}_n) \tau^{nn}_{LL'} Z^n_{L'}(E, \vec{r}'_n) - \sum_L Z^n_L(E, \vec{r}_n) J^n_L(E, \vec{r}'_n) . \qquad (2.18)$$

The general element $\tau^{nm}_{LL'}$ is obtained by first forming the matrix $\underline{M}$ which has elements

$$M^{nm}_{LL'} = m^n_{LL'} \delta_{nm} - g^{nm}_{LL'} . \qquad (2.19)$$

The inverse of $\underline{M}$ must be found and then $\tau^{nm}_{LL'}$ is the n, m, L, L' element of $\underline{M}^{-1}$,

$$\tau^{nm}_{LL'} = (\underline{M}^{-1})^{nm}_{LL'} . \qquad (2.20)$$

Equations such as (2.18) have a long history, going back at least to the work of Beeby.[15] Due to idiosyncrasies in the way they were derived they were originally thought to be valid only when $\vec{r}$ and $\vec{r}'$ are inside the nth bounding sphere. This equation is in fact valid as long as $\vec{r}$ and $\vec{r}'$ do not fall inside any of the bounding spheres other than the nth one, although the l convergence will be bad when r_n and r'_n are large. A particularly convenient aspect of (2.18) is the use of the real functions $Z^n_L(E, \vec{r})$ and $J^n_L(E, \vec{r})$ because it simplifies the operation of finding the imaginary part of the Green's function. In particular, the second sum which is the singular part is seen to be real.

For the special case that the potential function $v_n(\vec{r}_n)$ is spherically symmetric the inverse of the t matrix takes the diagonal form

$$m^n_{LL'} = (-\kappa \cot\eta^n_l + i\kappa) \delta_{LL'} , \qquad (2.21)$$

where the η^n_l are the well-known phase shifts of scattering theory. This simplification is of no help in the following algebra, but it is used in most applications. The major restriction on the potential function is that the various bounding spheres cannot overlap. This restriction could be eliminated using a more complicated formulation that has been described elsewhere,[16] but there seems to be no advantage in that at the present time.

The most convenient form of G to start from when $\vec{r}$ is near site n and $\vec{r}'$ is near m is

$$G = G^{nm} + G^n T_{nm} G^m , \qquad (2.22)$$

where

$$G^{nm} = (G_0 t^n + 1) G_0 (1 + t^m G_0) , \qquad (2.23)$$

and

$$T_{nm} = \sum_{i \neq n} \sum_{j \neq m} \tau^{ij} . \qquad (2.24)$$

Using (2.16), (2.11), and (2.7) it can be shown that

$$\langle \vec{r} | G^{nm} | \vec{r}' \rangle = \sum_{LL'} \sum_{L_1 L_2} Z^n_L(E, \vec{r}_n) t^n_{LL_1} g^{nm}_{L_1 L_2} \times t^m_{L_2 L'} Z^m_{L'}(E, \vec{r}'_m) . \qquad (2.25)$$

The second term in (2.22) can be evaluated just like the second term in (2.8). The resulting expression

$$G(E, \vec{r}, \vec{r}') = \sum_{LL'} Z^n_L(E, \vec{r}_n) \tau^{nm}_{LL'} Z^m_{L'}(E, \vec{r}'_m) \qquad (2.26)$$

is valid as long as $\vec{r}$ is within no bounding sphere other than the nth, and $\vec{r}'$ is in none other than the mth. Again the convergence would be expected to deteriorate if r_n or r'_m became too large.

The expressions for the Green's function in (2.18) and (2.26) are valid for any set of scatterers. Let us now specialize to the case that the site vectors $\vec{R}_n$ form an ordered Bravais lattice. The potential $v_n(\vec{r}_n)$ can take only one of two forms: $v_n(\vec{r}_n) = v_A(\vec{r}_n)$ with probability C_A, $v_n(\vec{r}_n) = v_B(\vec{r}_n)$ with probability C_B. The potential $V(\vec{r})$ then describes a random alloy made up of A and B atoms with concentrations C_A and C_B. The ensemble of such alloys is the set of all structures that can be constructed by arranging M A atoms and $N-M$ B

atoms on the N lattice sites, where $M = C_A N$. There are obviously $N!/(N-M)!M!$ structures in the ensemble.

An expression for the ensemble-averaged Green's function in the single-site approximation can now be derived. We will first consider the site-diagonal (SD) case which means we start from the expression for the Green's function in (2.18).

If $\vec{r}$ and $\vec{r}'$ are both in cell n it is reasonable to first average over the subset of structures in the ensemble that leave the potential in that cell fixed. This yields

$$\langle G(E,\vec{r},\vec{r}')\rangle_n = \sum_{L,L'} Z_L^n(E,\vec{r}_n)\langle \tau_{LL'}^{nn}\rangle_n Z_{L'}^n(E,\vec{r}_n') - \sum_L Z_L^n(E,\vec{r}_n) J_L^n(E,\vec{r}_n') , \qquad (2.27)$$

where $\langle \tau_{LL'}^{nn}\rangle_n$ is the matrix of (2.20) conditionally averaged so that the potential on site n is known to be some particular $v_n(\vec{r}_n)$. The final step in the process consists of averaging over the possible occupants of site n:

$$\langle G(E,\vec{r},\vec{r}')\rangle = \sum_{LL'} [C_A Z_L^A(E,\vec{r}_n)\langle \tau_{LL'}^{nn}\rangle_A Z_{L'}^A(E,\vec{r}_n') + C_B Z_L^B(E,\vec{r}_n)\langle \tau_{LL'}^{nn}\rangle_B Z_{L'}^B(E,\vec{r}_n')] - \sum_L [C_A Z_L^A(E,\vec{r}_n) J_L^A(E,\vec{r}_n') + C_B Z_L^B(E,\vec{r}_n) J_L^B(E,\vec{r}_n')] , \qquad (2.28)$$

where $\langle \tau_{LL'}^{nn}\rangle_A$ or $\langle \tau_{LL'}^{nn}\rangle_B$ are the conditional averages for the case that there is definitely an A or B atom on site n.

This expression for the average SD Green's function is still perfectly general, but it can be greatly simplified by invoking the single-stie approximation. In the single-site approximation, the matrix with elements $\langle \tau_{LL'}^{nn}\rangle_n$ is constructed from the matrix $\underline{M}_n$ which has an effective scattering matrix $\underline{t}^c$ on every site except the nth. The actual scattering matrix $\underline{t}^n$ is put on that site.

In writing the equations for such matrices in the following it is convenient to go over to a notation in which the subscripts L and L' no longer appear explicitly. This is achieved by considering, for example, the element $M_{LL'}^{ij}$ to be the L, L' element of the i, j block $\underline{M}^{ij}$ of the matrix $\underline{M}$.

In this notation the elements of $\underline{M}_n$ are defined by

$$\underline{M}_n^{ij} = \begin{cases} \underline{m}^c \delta_{ij} - \underline{g}^{ij}, & i \neq n \\ \underline{m}^n \delta_{ij} - \underline{g}^{ij}, & i = n , \end{cases} \qquad (2.29)$$

where $\underline{m}^c$ is the inverse of the effective scattering matrix $\underline{t}^c$. The n, n block of $\underline{M}^{-1}$ can be solved for, and it is

$$\langle \underline{\tau}^{nn}\rangle_n = \underline{D}^n \underline{\tau}_c^{00} = \underline{\tau}_c^{00} \underline{\tilde{D}}^n , \qquad (2.30)$$

where

$$\underline{D}^n = [\underline{I} + \underline{\tau}_c^{00}(\underline{m}^n - \underline{m}^c)]^{-1} , \qquad (2.31)$$

and $\underline{\tilde{D}}^n$ is the transpose of $\underline{D}^n$. The matrix $\underline{\tau}_c^{00}$ is the diagonal block of the inverse of $\underline{M}_c$ defined by

$$\underline{M}_c^{ij} = \underline{m}^c \delta_{ij} - \underline{g}^{ij} . \qquad (2.32)$$

It is not necessary to call it $\underline{\tau}_c^{nn}$ because all of the diagonal blocks are the same.

The ensemble-averaged site-diagonal Green's function $G_c(E,\vec{r},\vec{r}')$ can thus be written in the single-site approximation as

$$G_c(E,\vec{r},\vec{r}') = \mathrm{tr}\,\underline{F}^c(\vec{r}_n,\vec{r}_n')\underline{\tau}_c^{00} - \sum_L [C_L^A Z_L^A(E,\vec{r}_n) J_L^A(E,\vec{r}_n') + C_B Z_L^B(E,\vec{r}_n') J_L^B(E,\vec{r}'_n)] , \qquad (2.33)$$

when $\vec{r}$ and $\vec{r}'$ are in cell n. The matrix $\underline{F}^c(\vec{r}_n,\vec{r}_n')$ is

$$\underline{F}^c(\vec{r}_n,\vec{r}_n') = C_A \underline{F}^A(\vec{r}_n,\vec{r}_n')\underline{D}^A + C_B \underline{F}^B(\vec{r}_n,\vec{r}_n')\underline{D}^B , \qquad (2.34)$$

in which the matrices $\underline{F}^A(\vec{r}_n,\vec{r}_n')$ and $\underline{F}^B(\vec{r}_n,\vec{r}_n')$ are obtained by inserting the proper wave functions in the matrix $\underline{F}^n(\vec{r}_n,\vec{r}_n')$ given by

$$F_{LL'}^n(\vec{r}_n,\vec{r}_n') = Z_L^n(E,\vec{r}_n') Z_{L'}^n(E,\vec{r}_n) . \qquad (2.35)$$

The matrices $\underline{D}^A$ and $\underline{D}^B$ are similarly obtained from (2.31). The "tr" in (2.33) means that the trace of the matrix should be taken, and the energy variable E has been suppressed in the matrices.

The ensemble average of the Green's function for the non-site-diagonal (NSD) case can be obtained starting from (2.26). First the average is taken over the subset of the ensemble that leaves the potential in cells n and m fixed:

$$\langle G(E,\vec{r},\vec{r}')\rangle_{n,m} = \mathrm{tr}\,\underline{F}^{nm}(\vec{r}_n,\vec{r}_m')\langle \tau^{nm}\rangle_{nm} . \qquad (2.36)$$

Here, the matrix $\underline{F}^{nm}(\vec{r}_n,\vec{r}_n')$ has elements

$$F_{LL'}^{nm}(\vec{r}_n,\vec{r}_m') = Z_L^m(E,\vec{r}_m') Z_{L'}^n(E,\vec{r}_n) . \qquad (2.37)$$

The matrix $\langle \underline{\tau}^{nm}\rangle_{nm}$ is the restricted average in which the potential on site n is known to be $v_n(\vec{r}_n)$ and the one on m is $v_m(\vec{r}_m)$. The final averaging over the possible occupants of sites n and m leads to

$$\begin{aligned}\langle G(E,\vec{r},\vec{r}\,')\rangle = \operatorname{tr}[&C_A^2\underline{F}^{AA}(\vec{r}_n,\vec{r}\,'_m)\langle\underline{\tau}^{nm}\rangle_{AA}\\ &+C_AC_B\underline{F}^{AB}(\vec{r}_n,\vec{r}\,'_m)\langle\underline{\tau}^{nm}\rangle_{AB}\\ &+C_BC_A\underline{F}^{BA}(\vec{r}_n,\vec{r}\,'_m)\langle\underline{\tau}^{nm}\rangle_{BA}\\ &+C_B^2\underline{F}^{BB}(\vec{r}_n,\vec{r}\,'_m)\langle\underline{\tau}^{nm}\rangle_{BB}]\,,\end{aligned} \tag{2.38}$$

in a notation that should be obvious.

In the single-site approximation, the restricted average matrix $\langle\underline{\tau}^{nm}\rangle_{nm}$ is obtained as an inverse of the matrix $\underline{M}_{nm}$ which is defined by

$$\underline{M}_{nm}^{ij}=\begin{cases}\underline{m}^c\delta_{ij}-\underline{g}^{ij}\,, & i\neq n,\quad i\neq m\\ \underline{m}^n\delta_{ij}-\underline{g}^{ij}\,, & i=n\\ \underline{m}^m\delta_{ij}-\underline{g}^{ij}\,, & i=m\,.\end{cases} \tag{2.39}$$

By carrying out this inversion it can be shown that

$$\begin{aligned}\langle\underline{\tau}^{nm}\rangle_{nm}&=\underline{D}^n\underline{\tau}_c^{nm}[\underline{I}-(\underline{m}^m-\underline{m}^c)\langle\underline{\tau}^{nm}\rangle_{nm}]\\ &=[\underline{I}-\langle\underline{\tau}^{nn}\rangle_{nm}(\underline{m}^n-\underline{m}^c)]\underline{\tau}_c^{nm}\underline{\tilde{D}}^m\,,\end{aligned} \tag{2.40}$$

where $\underline{\tau}_c^{nm}$ is obtained by inverting the matrix $\underline{M}_c$ defined in (2.32).

We now make use of the single-site approximation again to assert that

$$\langle\underline{\tau}^{nn}\rangle_{nm}=\langle\underline{\tau}^{nn}\rangle_n\,. \tag{2.41}$$

This is the approximation that when we are only looking at the site n we can forget that the matrix $\underline{M}_{nm}$ has the true scattering matrix on the site m. Put another way, it is assumed that the matrix $\underline{M}_n$ can be used instead of $\underline{M}_{nm}$ when calculating the conditional average of $\underline{\tau}^{nn}$. This type of approximation goes back to the work of Lax,[17] and it is discussed in more detail in the Appendix. Using it and (2.30) leads to

$$[\underline{I}-\langle\underline{\tau}^{nn}\rangle_{nm}(\underline{m}^n-\underline{m}^c)]=\underline{D}^n\,, \tag{2.42}$$

and hence

$$\langle\underline{\tau}^{nm}\rangle_{nm}=\underline{D}^n\underline{\tau}_c^{nm}\underline{\tilde{D}}^m \tag{2.43}$$

in the single-site approximation.

From (2.38) and (2.43) the ensemble-averaged Green's function for the NSD case may be written in the single-site approximation as

$$G_c(E,\vec{r},\vec{r}\,')=\operatorname{tr}\underline{F}^{cc}(\vec{r}_n,\vec{r}\,'_m)\underline{\tau}_c^{nm}\,, \tag{2.44}$$

where

$$\begin{aligned}\underline{F}^{cc}(\vec{r}_n,\vec{r}\,'_m)=&C_A^2\underline{\tilde{D}}^A\underline{F}^{AA}(\vec{r}_n,\vec{r}\,'_m)\underline{D}^A\\ &+C_AC_B\underline{\tilde{D}}^B\underline{F}^{AB}(\vec{r}_n,\vec{r}\,'_m)\underline{D}^A\\ &+C_AC_B\underline{\tilde{D}}^A\underline{F}^{BA}(\vec{r}_n,\vec{r}\,'_m)\underline{D}^B\\ &+C_B^2\underline{\tilde{D}}^B\underline{F}^{BB}(\vec{r}_n,\vec{r}\,'_m)\underline{D}^B\,.\end{aligned} \tag{2.45}$$

The matrix $\underline{F}^{cc}(\vec{r}_n,\vec{r}\,'_m)$ could be calculated from an equation like (2.37) by associating with each site an effective wave function

$$\begin{aligned}Z_L^C(E,\vec{r}_n)=\sum_{L'}\,&[C_AZ_{L'}^A(E,\vec{r}_n)D_{L'L}^A\\ &+C_BZ_{L'}^B(E,\vec{r}_n)D_{L'L}^B]\,.\end{aligned} \tag{2.46}$$

We are thus led to assert that the way to calculate properties within the single-site approximation is to use the function $G_c(E,\vec{r},\vec{r}\,')$ defined in (2.33) and (2.44) as the one-electron Green's function. From the defining equations it can be seen that $G_c(E,\vec{r},\vec{r}\,')$ describes a periodic system in the sense that

$$G_c(E,\vec{r}+\vec{R}_n,\vec{r}\,'+\vec{R}_n)=G_c(E,\vec{r},\vec{r}\,')\,. \tag{2.47}$$

It is clear that no statement was made in this derivation concerning the way that the effective scattering matrix $\underline{t}^c$ is defined.

At first sight the most remarkable feature of $G_c(E,\vec{r},\vec{r}\,')$ is that the effective wave function for each site is different for the SD and NSD cases. This is different from the result for a truly periodic system which can be obtained by leaving the superscripts off the $Z_L^n(E,\vec{r})$ in (2.18) and (2.26). It has been known for some time that a theory for electronic states in an alloy should be designed to arrive at an effective Green's function but not an effective wave function.[18] The question as to whether $G_c(E,\vec{r},\vec{r}\,')$ will lead to reliable predictions for the properties of alloys can only be answered by using it in calculations that contain as few additional approximations as possible and comparing with the results of experiments.

III. CALCULATING SITE-DIAGONAL PROPERTIES

Because of the periodicity expressed in (2.47) the density of states per cell can be found by integrating the SD form of $G_c(E,\vec{r},\vec{r}\,')$ over the one-unit cell

$$\rho(E)=-\frac{1}{\pi}\operatorname{Im}\int_\Omega G_c(E,\vec{r},\vec{r})dv\,. \tag{3.1}$$

The singular part of (2.33) is real and can be ignored so that

$$\rho(E)=-\frac{1}{\pi}\operatorname{tr}\underline{F}^c\underline{\tau}_c^{00}\,. \tag{3.2}$$

The matrix $\underline{F}^c$ is

$$\underline{F}^c=\int_\Omega\underline{F}^c(\vec{r},\vec{r})dv=C_A\underline{F}^A\underline{D}^A+C_B\underline{F}^B\underline{D}^B\,, \tag{3.3}$$

where the matrices $\underline{F}^A$ and $\underline{F}^B$ have elements of the form

$$F_{LL'}^n=\int_\Omega Z_L^n(\vec{r})Z_{L'}^n(\vec{r})dv\,. \tag{3.4}$$

The next more detailed SD properties are the component densities of states $\rho_A(E)$ and $\rho_B(E)$ that can be associated with a given kind of atom and must satisfy

$$C_A\rho_A(E)+C_B\rho_B(E)=\rho(E)\,. \qquad (3.5)$$

These component densities of states can be identified immediately from (3.3)

$$\rho_n(E)=-\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{tr}\underline{F}^n\underline{D}^n\underline{\tau}_c^{00}\,. \qquad (3.6)$$

Although in the present context this calculation appears both simple and obvious, the component densities of states shown in Sec. VII of this paper are the first ones to be calculated within the CPA for a general muffin-tin system in which we have any confidence.

The charge densities $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$ to be associated with a given atomic species can obviously be obtained from

$$\rho_n(\vec{r})=-\frac{1}{\pi}\int_{-\infty}^{E_F}\mathrm{Im}\,\mathrm{tr}\underline{F}^n(\vec{r},\vec{r})\underline{D}^n\underline{\tau}_c^{00}dE\,,$$

where E_F is the Fermi energy. These quantities must be calculated in order to carry CPA calculations to self-consistency.

Finally, Györffy and his collaborators have shown how theories for soft x-ray emission,[14] electron-phonon interactions,[19] and other properties can be formulated in terms of a density matrix

$$\rho(\vec{r},\vec{r}\,';E)=C_A\,\rho_A(\vec{r},\vec{r}\,';E)+C_B\rho_B(\vec{r},\vec{r}\,';E)\,, \quad (3.7)$$

which is the imaginary part of the SD form of $G_c(E,\vec{r},\vec{r}\,')$. The components of the density matrix are

$$\rho_n(\vec{r},\vec{r}\,';E)=-\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{tr}\underline{F}^n(\vec{r},\vec{r}\,')\underline{D}^n\underline{\tau}_c^{00}\,. \qquad (3.8)$$

The matrix that arises over and over in these formulas is $\underline{\tau}_c^{00}$. It is well known that this matrix can be evaluated by a Bloch-Fourier transform because the matrix $\underline{M}_c$ that is used in evaluating it has the same t matrix $\underline{t}^c$ on each lattice site. Let us define a matrix $\underline{M}_c(\vec{k})$ by

$$\underline{M}_c(\vec{k})=\underline{m}^c-\underline{g}(\vec{k})\,, \qquad (3.9)$$

where

$$\underline{g}(\vec{k})=\sum_{j\neq i}\exp(i\vec{k}\cdot\vec{R}_{ij})\underline{g}^{ij}\,. \qquad (3.10)$$

It can then be shown that in general

$$\underline{\tau}_c^{ij}=\frac{1}{N}\sum_{\vec{k}}\exp(-i\vec{k}\cdot\vec{R}_{ij})\underline{M}_c^{-1}(\vec{k}) \qquad (3.11)$$

or, passing to the limit of an infinitely large crystal,

$$\underline{\tau}_c^{ij}=\frac{\Omega}{(2\pi)^3}\int\exp(-i\vec{k}\cdot\vec{R}_{ij})\underline{M}_c^{-1}(\vec{k})d\vec{k}\,, \qquad (3.12)$$

where the integral is over the central Brillouin zone. The matrix $\underline{\tau}_c^{00}$ that is needed for the calculation of SD properties is obtained from (3.12) by just setting $\vec{R}_{ij}=0$.

The elements defined in (3.10) are formally related to the structure constants of KKR band theory $A_{LL'}(\vec{k})$ by

$$A_{LL'}(\vec{k})=g_{LL'}(\vec{k})-i\kappa\delta_{LL'}\,. \qquad (3.13)$$

Techniques for evaluating these quantities were developed by Ewald,[20] and equations for them are available in the literature. The integrals $F_{LL'}^n$ in (3.4) can be converted into alternative forms which will be discussed in Sec. V. The relevant group theory for simplifying the expressions for the density matrix $\rho_n(\vec{r},\vec{r}\,',E)$ and the charge density $\rho_n(\vec{r})$, is given in the paper by Butler *et al.*[19] for the case of cubic Bravais lattices.

IV. CALCULATING NON-SITE-DIAGONAL PROPERTIES

The most important NSD property in alloy theory is the Bloch spectral density $A^B(E,\vec{k})$. It was introduced by Soven[21] and used by him[6] in connection with the one-level tight-binding model of an alloy. We will see in Sec. VI that it is particularly easy to define for that model.

The Bloch spectral-density function has the property that for a perfect periodic solid it can be expressed as the sum of δ functions

$$A^B(E,\vec{k})=\sum_{\alpha}\delta(E-E_\alpha(\vec{k}))\,, \qquad (4.1)$$

where the $E_\alpha(\vec{k})$ are the energy eigenvalues obtained from a band-theory calculation. For a given $\vec{k}$, $A^B(E,\vec{k})$ is a function of E that is zero except for the energies $E_\alpha(\vec{k})$ where it can be looked upon as having an infinitely sharp peak.

From both intuition and model calculations it is clear that when the system is disordered these peaks will broaden; roughly speaking, the greater the disorder the greater the broadening. This broadening can be related to the lifetime of an electron in a Bloch state and can be measured in experiments such as the de Haas–van Alphen effect where it shows up as a Dingle temperature. It can also be measured in more concentrated alloys using angular-resolved photoemission techniques. The ordinary spectral-density function defined in (1.2) has the same momentum dependence that has been described for $A^B(E,\vec{k})$, but, in addition, it has structure that arises from the Fourier transform of the wave functions.

We now show how to define $A^B(E,\vec{k})$ in terms of a Green's function that is unspecified except that it must satisfy a periodicity condition:

$$G(E,\vec{r}+\vec{R}_n,\vec{r}'+\vec{R}_n)=G(E,\vec{r},\vec{r}')\,. \tag{4.2}$$

This Green's function can be put in the momentum representation by the transformation

$$G(E,\vec{p},\vec{p}')=\frac{1}{N\Omega}\int dv'\int dv\,\exp[i(\vec{p}\cdot\vec{r}-\vec{p}'\cdot\vec{r}')]\times G(E,\vec{r},\vec{r}')\,. \tag{4.3}$$

Specializing this equation to the case that $\vec{p}=\vec{k}+\vec{K}_m$ and $\vec{p}'=\vec{k}'+\vec{K}_m$, where $\vec{k}$ and $\vec{k}'$ are in the central unit cell, and using (4.2) to change the origin in the integrations leads to

$$G(E,\vec{k}+\vec{K}_m,\vec{k}'+\vec{K}_m)=\Delta(\vec{k}-\vec{k}')\frac{1}{\Omega}\int dv'\int dv_0\exp[i(\vec{k}+\vec{K}_m)\cdot(\vec{r}_0-\vec{r}')]\,G(E,\vec{r}_0,\vec{r}')\,, \tag{4.4}$$

where

$$\Delta(\vec{k}-\vec{k}')=\begin{cases}\dfrac{1}{N}\sum\limits_n\exp[i(\vec{k}-\vec{k}')\cdot\vec{R}_n]\\ 1\,, & \vec{k}=\vec{k}'\\ 0\,, & \vec{k}\neq\vec{k}'\,.\end{cases} \tag{4.5}$$

The integration variable $\vec{r}_0$ ranges only over the central unit cell while the range of the $\vec{r}'$ integration is the entire crystal. In the limit that the crystal becomes infinite $\Delta(\vec{k}-\vec{k}')$ will be replaced by a δ function. This is a proof that the Green's function in the momentum representation for any system whose real-space Green's function satisfies (4.2) is diagonal in the Bloch vectors $\vec{k}$ and $\vec{k}'$.

Since

$$\sum_m\exp[i\vec{K}_m\cdot(\vec{r}-\vec{r}')]=\Omega\sum_n\delta(\vec{r}-\vec{r}'+\vec{R}_n)\,, \tag{4.6}$$

it follows that the function

$$\tilde{G}(E,\vec{k},\vec{k}')=\sum_m G(E,\vec{k}+\vec{K}_m,\vec{k}'+\vec{K}_m)\,, \tag{4.7}$$

is given by

$$\tilde{G}(E,\vec{k},\vec{k}')=\Delta(\vec{k}-\vec{k}')\times\sum_n\exp(i\vec{k}\cdot\vec{R}_n)\int dv_0 G(E,\vec{r}_0,\vec{r}_0+\vec{R}_n)\,, \tag{4.8}$$

where the integration variable $\vec{r}_0$ ranges over the central unit cell. We assert that the Bloch spectral-density function is given by

$$A^B(E,\vec{k})=-(1/\pi)\,\mathrm{Im}\tilde{G}(E,\vec{k},\vec{k})\,. \tag{4.9}$$

By writing $G(E,\vec{r},\vec{r}')$ in terms of eigenfunctions it can be shown that $A^B(E,\vec{k})$ is given by (4.1) for an ordered crystal. Experience has shown that the definition of $A^B(E,\vec{k})$ given above satisfies all the criteria for a Bloch spectral-density function.

In either the SD or NSD case the ensemble-averaged Green's function $G_c(E,\vec{r},\vec{r}')$ derived in Sec. II was seen in (2.47) to satisfy the periodicity condition of (4.2). As has just been shown this is the only requirement that a Green's function must satisfy in order that a Bloch spectral-density function be defined. Inserting (2.44) and (2.33) into (4.8) leads to

$$\tilde{G}_c(E,\vec{k},\vec{k})=\mathrm{tr}\underline{F}^{cc}\sum_{n\neq 0}\exp(i\vec{k}\cdot\vec{R}_n)\underline{\tau}_c^{0n}+\mathrm{tr}\underline{F}^c\underline{\tau}_c^{00}-Q(E)\,. \tag{4.10}$$

In this expression $Q(E)$ is the integral over the unit cell of the second term in (2.33) which can be ignored because it is real. The matrix $\underline{F}^{cc}$ is defined by the integral over the unit cell

$$\underline{F}^{cc}=\int\underline{F}^{cc}(\vec{r},\vec{r})dv\,, \tag{4.11}$$

in an obvious analogy with (3.3).

Let us define the matrix $\underline{\tau}_c(E,\vec{k})$ by

$$\underline{\tau}_c(E,\vec{k})=\underline{M}_c^{-1}(\vec{k})\,. \tag{4.12}$$

From (4.5) and (3.11) it follows that

$$\underline{\tau}_c(E,\vec{k})=\sum_j\exp(i\vec{k}\cdot\vec{R}_{ij})\underline{\tau}_c^{ij}\,, \tag{4.13}$$

and clearly

$$\underline{\tau}_c^{00}=\frac{1}{N}\sum_{\vec{k}}\underline{\tau}_c(E,\vec{k})\,. \tag{4.14}$$

With the help of (4.13) it is possible to use (4.10) to obtain the following formula for the Bloch spectral-density function of a disordered alloy

$$A^B(E,\vec{k})=-(1/\pi)\,\mathrm{Im}\,\mathrm{tr}\underline{F}^{cc}\underline{\tau}_c(E,\vec{k})+\Delta(E)\,, \tag{4.15}$$

where

$$\Delta(E)=-(1/\pi)\,\mathrm{Im}\,\mathrm{tr}(\underline{F}^c-\underline{F}^{cc})\underline{\tau}_c^{00}\,. \tag{4.16}$$

The first term in this equation looks a bit like the result of taking the Fourier component of (3.2), but there is actually a considerable difference because the weighting matrix in that equation is $\underline{F}^c$ not $\underline{F}^{cc}$. It will be seen in Sec. VII that for a general muffin-tin model of an alloy the $\Delta(E)$ is extremely important numerically. The first term can undergo large negative excursions when viewed as a function of E for any $\vec{k}$, and it is only the sum of the two terms that behaves properly. It will be seen in Sec. VI that $\underline{F}^{cc}$ and $\Delta(E)$ take on particularly simple forms for the one-level tight-binding model. The behavior of these quantities is easy to see for that simple model. It is also possible to reframe the results in terms of $G_c(E,\vec{k})$ rather than $\underline{\tau}_c(E,\vec{k})$, and the distinction between SD and NSD properties is blurred for that model. It is partly for this reason that (4.15) seems somewhat strange to alloy theorists.

The sum rule in (4.14) can be used to prove the logical requirement

$$\frac{1}{N}\sum_{\vec{k}} A^B(E,\vec{k}) = \rho(E)\,, \tag{4.17}$$

where $\rho(E)$ is the density of states discussed in Sec. III. This comes about because the sum over $\vec{k}$ of the first term in (4.15) cancels the second part of $\Delta(E)$, leaving the first part which is $\rho(E)$.

The existence of the contribution $\Delta(E)$ is clearly a measure of the price that must be paid when a single-site approximation is used to calculate a two-site property such as $A^B(E,\vec{k})$. The way that the two terms in (4.15) contribute to $A^B(E,\vec{k})$ will change depending on which single-site approximation is being used. Perhaps $\Delta(E)$ could be reduced to zero by the proper application of a legitimate two-site theory such as the traveling-cluster approximation (TCA) of Mills.[22]

With all of the apparent strangeness of (4.15) it is interesting that the numerical calculations in Sec. VII show a qualitative agreement with the spectral densities calculated using older formulas. The unphysical behavior is eliminated, but the other parts of the curves are very similar. Presumably, the equations for other NSD properties will have terms analogous to $\Delta(E)$ which correct for the fact that the apparent wave function is different, depending on whether it is associated with the SD or NSD form of $G_c(E,\vec{r},\vec{r}\,')$. This raises again the question as to the usefulness of $G_c(E,\vec{r},\vec{r}\,')$ in the calculation of such properties. As was stated at the end of Sec. II, the only way to answer this question is to calculate the properties and compare with experiment.

Most of the other NSD properties discussed in the literature were treated only within the framework of the one-level tight-binding model. For the reasons already alluded to, this is an overly specialized model. It would be useful to redevelop the discussion of, for example, the electrical conductivity[23] of alloys within the framework developed in this section.

V. COMPARISON WITH EARLIER FORMULAS

A formula for the density of the additional states that are created by a cluster of atomic potentials was obtained by Lloyd[11] as a generalization of Friedel's[24] one-atom formula. It has played a large role in the development of equations for properties in CPA and other single-site approximations.[8,9] It has been assumed that manipulation of this formula leads to the same answers as the ensemble-averaged Green's-function approach for the set of calculations to which it can be applied. The validity of this assumption is examined in this section.

The Lloyd formula is

$$\begin{aligned}\rho(E)-\rho_0(E) &= -\frac{1}{\pi N}\frac{d}{dE}\,\mathrm{Im}\ln\mathrm{Det}\underline{M}\\ &= -\frac{1}{\pi N}\,\mathrm{Im}\,\mathrm{tr}\frac{d}{dE}\ln\underline{M}\,,\end{aligned} \tag{5.1}$$

where the second form is obtained by applying a well-known matrix formula to the first. The function $\rho_0(E)$ is the density of states of a free-electron gas. The matrix $\underline{M}$ was defined in (2.19).

Györffy and Stocks[8] ($\overline{\mathrm{GS}}$) noted that the average density of states for an alloy in the single-site approximation could not be obtained by simply replacing $\underline{M}$ in (5.1) with $\underline{M}_c$ defined in (2.32). They suggested that the density of states for a specific alloy should first be written

$$\begin{aligned}\rho(E)-\rho_0(E) = &-\frac{1}{\pi}\,\mathrm{tr}\,\mathrm{Im}\left(\frac{1}{N}\sum_i \frac{d\underline{\underline{m}}^n}{dE}\,\underline{\tau}^{nn}\right)\\ &+\frac{1}{\pi}\,\mathrm{tr}\,\mathrm{Im}\left(\frac{1}{N}\sum_{m,n}\frac{d\underline{\underline{g}}^{mn}}{dE}\,\underline{\tau}^{nm}\right),\end{aligned} \tag{5.2}$$

and then the averaging process should be carried out in the two steps described in Sec. II. There is no problem in dealing with the first term in (5.2), but there is some question about the way that the second term should be averaged. GS chose to simply replace $\underline{\tau}^{nm}$ by $\underline{\tau}_c^{nm}$, and obtained

$$\begin{aligned}\rho(E)-\rho_0(E)\\ = &-\frac{1}{\pi}\,\mathrm{tr}\,\mathrm{Im}\left(C_A\frac{d\underline{\underline{m}}^A}{dE}\,\langle\underline{\tau}^{00}\rangle_A + C_B\frac{d\underline{\underline{m}}^B}{dE}\,\langle\underline{\tau}^{00}\rangle_B\right)\\ &+\frac{1}{\pi}\,\mathrm{tr}\,\mathrm{Im}\left(\frac{1}{N}\sum_{m,n}\frac{d\underline{\underline{g}}^{mn}}{dE}\,\underline{\tau}_c^{nm}\right).\end{aligned} \tag{5.3}$$

They then manipulated this equation into various other forms by making use of the specific relationships supplied by the CPA.

The fact that the Lloyd formula deals only with the density of states (or integrated density of states) indicates that it can only be compared with the equations for SD properties derived in Sec. III. It is hard to compare the GS derivation with the ones in that section because of the appearance of the off-diagonal terms $\underline{\tau}^{nm}$ in (5.2). The appearance of these off-diagonal terms in the formula is chimerical, and the comparison of the GS assumption with the Green's-function result will be greatly facilitated if (5.2) can be written in a form that is as similar as possible to the general SD formula,

$$\rho(E)=-\frac{1}{\pi}\operatorname{tr}\operatorname{Im}\left(\frac{1}{N}\sum_{n}\underline{F}^{n}\underline{\tau}^{nn}\right), \tag{5.4}$$

which is obtained by integrating (2.18).

Jacobs and Zaman[25] set out to rewrite (5.2) into the form of (5.4). We will rederive the formulas because they unfortunately left out certain crucial terms. The first term in (5.2) is already in the proper form, so we will focus attention on the second one.

The energy derivative of the free-electron Green's function is, in operator notation

$$\frac{dG_0}{dE}=-G_0^2. \tag{5.5}$$

Although we are considering free electrons, space can still be divided up into the same unit cells that will eventually be used for the solid. The Green's function in the position representation is

$$G_0(E,\vec{r},\vec{r}\,')=-i\kappa\sum_{L}Y_L(\vec{r}_n)j_l(\kappa r_n)h_l(\kappa r_n')Y_L(\vec{r}_n\,'), \tag{5.6}$$

where $\vec{r}$ and $\vec{r}\,'$ are both in the nth cell. Using (2.16) it can be seen that

$$G_0(E,\vec{r},\vec{r}\,')=\sum_{LL'}Y_L(\vec{r}_n)j_l(\kappa r_n)\,g_{LL'}^{nm}\,j_{l'}(\kappa r_m')Y_{L'}(\vec{r}_m\,'), \tag{5.7}$$

when $\vec{r}$ is in cell n and $\vec{r}\,'$ is in cell m. The notation and quantities that appear in these equations are all defined in Sec. II. By differentiating (5.7) and comparing with the result obtained when the right-hand side of (5.5) is evaluated in the position representation with the help of (5.6) and (5.7), it is found that

$$\frac{d\underline{g}^{nm}}{dE}=-\sum_{p\neq n}\sum_{p\neq m}\underline{g}^{np}\underline{A}\,\underline{g}^{pm}-\underline{g}^{nm}\underline{B}-\underline{\tilde{B}}\,\underline{g}^{nm}. \tag{5.8}$$

The matrix $\underline{A}$ has elements

$$A_{LL'}=\int j_l(\kappa r)Y_L(\vec{r})Y_{L'}(\vec{r})j_{l'}(\kappa r)\,dv, \tag{5.9}$$

where the integral is over one unit cell. The elements of the matrix $\underline{B}$ arise from the identity

$$\int j_l(\kappa r)Y_L(\vec{r})G_0(E,\vec{r},\vec{r}\,')\,dv=-\dot{j}_l(\kappa r)Y_L(\vec{r})+\sum_{L'}B_{LL'}j_{l'}(\kappa r)Y_{L'}(\vec{r}), \tag{5.10}$$

where

$$\dot{j}_l(\kappa r)=\frac{dj_l}{dE}. \tag{5.11}$$

They can be found by noting that $j_l(\kappa r)Y_L(\vec{r})$ is a solution of the homogeneous Helmholtz equation

$$(\nabla^2+E)j_l(\kappa r)Y_L(\vec{r})=0, \tag{5.12}$$

while $G_0(E,\vec{r},\vec{r}\,')$ is a solution of the inhomogeneous equation

$$(\nabla^2+E)G_0(E,\vec{r},\vec{r}\,')=\delta(\vec{r}-\vec{r}\,'). \tag{5.13}$$

After the standard trick of differentiating (5.12) with respect to energy has been used, these last two equations lead to an equation like (5.10) with

$$\sum_{L'}B_{LL'}j_{l'}(\kappa r)Y_{L'}(\vec{r})=\int\{\dot{j}_l(\kappa r')Y_L(\vec{r}\,')\nabla^2G_0(E,\vec{r}\,',\vec{r})-\nabla^2[\dot{j}_l(\kappa r')Y_L(\vec{r}\,')]\times G_0(E,\vec{r}\,',\vec{r})\}\,dv. \tag{5.14}$$

The application of Green's theorem will transform this volume integral into an integral over the surface of the unit cell which may be evaluated with the help of (5.6) to obtain

$$B_{LL'}=-i\kappa\int\hat{n}\cdot\{\dot{j}_l(\kappa r)Y_L(\vec{r})\nabla[Y_{L'}(\vec{r})h_{l'}(\kappa r)]-\nabla[\dot{j}_l(\kappa r)Y_L(\vec{r})]\,Y_{L'}(\vec{r})h_{l'}(\kappa r)\}\,ds. \tag{5.15}$$

The formula that Jacobs and Zaman obtained was similar to (5.8) except that they approximated the unit cell with a sphere. This allowed them to obtain explicit expression for the nonvanishing elements of $\underline{A}$ and $\underline{B}$, but it is an unnecessary specialization from our point of view.

Inserting (5.8) into (5.2) and using (2.19) leads to an equation that can be further simplified by noting that the products of matrices that appear can be cyclically permuted. The result is that (5.8) can be transformed into

$$\rho(E)=-\frac{1}{\pi}\operatorname{tr}\operatorname{Im}\left(\frac{1}{N}\sum_{n}\underline{\hat{F}}^{n}\underline{\tau}^{nn}\right)+\frac{1}{\pi}\operatorname{tr}\operatorname{Im}\underline{\tilde{B}}+\rho_0(E)+\frac{1}{\pi}\operatorname{tr}\operatorname{Im}\left(\frac{1}{N}\sum_{n}\underline{R}^{n}\right), \tag{5.16}$$

with

$$\underline{\hat{F}}^{n}=\frac{d\underline{m}^{n}}{dE}+\underline{m}^{n}\underline{A}\,\underline{m}^{n}+\underline{m}^{n}\underline{B}+\underline{\bar{B}}\,\underline{m}^{n}+\underline{C}, \tag{5.17}$$

in which

$$\underline{C}=-\sum_{m}\underline{g}^{nm}\underline{A}\,\underline{g}^{mn}, \tag{5.18}$$

and also

$$\underline{R}^{n}=\underline{A}\,\underline{m}^{n}+\underline{B}. \tag{5.19}$$

If $\hat{\underline{F}}^{n}$ equals $\underline{F}^{n}$ and the other terms in (5.16) can be ignored, it follows that this equation for $\rho(E)$ is equivalent to (5.4). We will show that these conditions are met for any solid that can be described by a real potential function like the one in (2.1).

Before comparing $\hat{\underline{F}}^{n}$ with $\underline{F}^{n}$ it is necessary to consider the matrix $\underline{C}$. This matrix was overlooked in the derivation of Jacobs and Zaman. It can be shown with the help of (2.16) that $\underline{C}$ may be rewritten as the integral of a product of Hankel functions and spherical harmonics over all space except for the nth unit cell. Using the trick of differentiating with respect to energy makes it possible to transform this integral into one to which Green's theorem can be applied:

$$C_{LL'}=-\kappa^{2}\int\vec{\mathrm{n}}\cdot\{\dot{h}_{l}(\kappa r)Y_{L}(\vec{\mathrm{r}})\nabla[Y_{L'}(\vec{\mathrm{r}})h_{l'}(\kappa r)] -\nabla[\dot{h}_{l}(\kappa r)Y_{L}(\vec{\mathrm{r}})]\,Y_{L'}(\vec{\mathrm{r}})h_{l'}(\kappa r)\}ds\,, \tag{5.20}$$

where the integration is over the surface of the nth unit cell.

In obtaining (5.20) it is necessary to ignore an integral of exactly the same form over the surface that bounds the entire crystal. This integral is zero only if we add an infinitesimally small imaginary part to the energy. Such mathematical manipulations have proved to be necessary in the past in order to get rid of awkward surface contributions. For example, the reason that we stated in Sec. III that the relation between the $g_{LL'}(\vec{\mathrm{k}})$ and the structure constants $A_{LL'}(\vec{\mathrm{k}})$ expressed in (3.13) is only formal is that the series in (3.10) is not convergent. The primary contribution made by Ewald in Ref. 18 was to show how to deal with such series. He eliminates a contribution from the outer surface of the crystal by essentially the same device that is being used here.

The volume integral in (3.4) can be converted into a surface integral by differentiating (2.12) with respect to energy. The proof that $\underline{F}^{n}=\hat{\underline{F}}^{n}$ for any real potential $V_{n}(\vec{\mathrm{r}})$ then follows from (2.13). Taking the trace of the imaginary part of the matrix in (5.15) and using (2.7) and (1.1) leads to the general result

$$(1/\pi)\,\mathrm{tr}\,\mathrm{Im}\tilde{\underline{B}}=-\rho_{0}(E)\,. \tag{5.21}$$

Thus the second and third terms in (5.16) cancel and may henceforth be ignored.

The integrals in $\underline{R}^{n}$ may be rewritten as the surface integral

$$R^{n}_{LL'}=\int\vec{\mathrm{n}}\cdot\{\dot{j}_{l}(\kappa r)Y_{L}(\vec{\mathrm{r}})\nabla Z^{n}_{L}(E,\vec{\mathrm{r}}) -\nabla[\dot{j}_{l}(\kappa r)Y_{L}(\vec{\mathrm{r}})]\,Z^{n}_{L}(E,\vec{\mathrm{r}})\}ds\,. \tag{5.22}$$

It was pointed out in Sec. II that one of the useful features of the function $Z^{n}_{L}(E,\vec{\mathrm{r}})$ defined in (2.13) is that it is real for a real potential. It follows that for a real potential the last term in (5.16) can be ignored. The same conclusions can clearly be reached by using the matrix $\underline{B}$ in (5.21) and $\tilde{\underline{B}}$ in (5.19) because $\underline{A}$ and $\underline{m}^{n}$ are symmetric.

This completes the proof that for a real potential the density of states can be calculated from either the first term in (5.16) or the Green's-function expression (5.4). For a periodic solid $\underline{\tau}^{nn}$ can be calculated from a Brillouin-zone integral like the one in (3.11). There are much easier ways to calculate the density of states for a periodic solid, but the consistency of these results with earlier ones is reassuring.

Returning to the alloy problem, the averaging process described in Sec. III can be applied to (5.16). With no difficulty this leads to an equation for the density of states and its components that is identical with (3.2) and (3.6). Of course, the more detailed SD properties cannot be found from this equation because such details are already integrated over.

As was pointed out earlier in this section, the averaging procedure is less transparent when dealing with the version of Lloyd's formula that was available to Györffy and Stocks. It is therefore necessary to discover whether or not the density of states calculated with the formula they obtained (5.3) is identical with the ones obtained by averaging (5.16) or the Green's function. This question was examined numerically as will be described in Sec. VII. The answer is yes, they are the same. It turns out that it is necessary to investigate this question algebraically as well because the result is true only if the coherent-potential approximation is used for $\underline{t}^{c}$.

In making the comparison of the GS formula with the Green's-function formula the expression in (5.8) is inserted into (5.3), and the manipulations described before are carried out to obtain

$$\begin{aligned}\rho(E)=&-\frac{1}{\pi}\,\mathrm{tr}\,\mathrm{Im}\left(C_{A}\frac{d\underline{\underline{m}}^{A}}{dE}\,\underline{D}^{A}+C_{B}\frac{d\underline{\underline{m}}^{B}}{dE}\,\underline{D}^{B}\right)\underline{\tau}^{00}_{c}\\&-\frac{1}{\pi}\,\mathrm{tr}\,\mathrm{Im}(\underline{m}^{c}\underline{A}\,\underline{m}^{c}+\underline{m}^{c}\tilde{\underline{B}}+\underline{B}\,\underline{m}^{c}+\underline{C})\underline{\tau}^{00}_{c}\\&+\frac{1}{\pi}\,\mathrm{tr}\,\mathrm{Im}\underline{R}^{c}\,.\end{aligned} \tag{5.23}$$

As before, $\underline{m}^{A}$ and $\underline{m}^{B}$ are the inverses of the scattering matrices for the A and B atoms, $\underline{m}^c$ is the inverse of the effective scattering matrix $\underline{t}^c$, $\underline{D}^A$ and $\underline{D}^B$ are defined in (2.30), and $\underline{\tau}_c^{00}$ is described just below that equation. The matrix $\underline{R}^c$ is obtained by inserting $\underline{m}^c$ in (5.19). One major difference between this result and those obtained previously from (5.16) is that $\underline{R}^c$ is not real and the last term in (5.22) cannot be ignored. There is clearly no connection between (5.23) and the Green's-function result (3.2) in general. Such a connection can be found for a particular choice of $\underline{t}^c$ as will now be shown.

In the notation of this paper the CPA self-consistency equation that must be solved to obtain $\underline{t}^c$ is[4,26,27]

$$C_A\langle\underline{\tau}^{00}\rangle_A + C_B\langle\underline{\tau}^{00}\rangle_B = \underline{\tau}_c^{00} \tag{5.24}$$

or, using (2.30),

$$C_A\underline{D}^A + C_B\underline{D}^B = \underline{I}\,. \tag{5.25}$$

These equations can be manipulated into

$$C_A\underline{m}^A\underline{D}^A + C_B\underline{m}^B\underline{D}^B = \underline{m}^c\,, \tag{5.26}$$

and

$$\begin{aligned}\underline{m}^c &= \underline{m}^A - \langle\underline{\tau}^{00}\rangle_A^{-1} + (\underline{\tau}_c^{00})^{-1}\\ &= \underline{m}^B - \langle\underline{\tau}^{00}\rangle_B^{-1} + (\underline{\tau}_c^{00})^{-1}\,.\end{aligned} \tag{5.27}$$

The first term in (5.23) is seen to be in the same form as the Green's-function result if use is made of the equivalence between $\underline{\hat{F}}^n$ and $\underline{F}^n$ for real potentials. Relations (5.25) and (5.26) can be used to rewrite all the parts of the second term into that form except for the one that is quadratic in $\underline{m}^c$. That part can be transformed by the application of (5.26) and then (5.27) into

$$\begin{aligned}\underline{m}^c\underline{Am}^c\underline{\tau}_c^{00} = {}&(c_A\underline{m}^A\underline{Am}^A\underline{D}^A + C_B\underline{m}^B\underline{Am}^B\underline{D}^B)\underline{\tau}_c^{00}\\ &+ \underline{Am}^c - \underline{A}(C_A\underline{m}^A + C_B\underline{m}^B)\,.\end{aligned} \tag{5.28}$$

The coefficient of $\underline{\tau}_c^{00}$ is just the term that is required for equivalence with the Green's-function result. The last two terms combine with $\underline{R}^c$ to produce

$$\underline{R}^c - \underline{A}\,\underline{m}^c + \underline{A}(C_A\underline{m}^A + C_B\underline{m}^B) = C_A\underline{R}^A + C_B\underline{R}^B\,, \tag{5.29}$$

the weighted mean of $\underline{R}$ matrices for the A and B atoms. Because of the reality of these matrices, they do not contribute to the density of states.

It is thus clear that the GS formula (5.3) can be shown to be equivalent to the one obtained from the ensemble-averaged Green's function (3.2) only with the repeated use of the CPA equations. It may be possible to invoke other equations for $\underline{t}^c$ that would lead to the same equivalence, but it is unlikely. It was, of course, not just luck that led Györffy and Stocks to obtain the correct answer. They ran numerous numerical checks on model systems to verify their assumptions. The results of this section underline the dangers inherent in using the same starting point to derive equations for the ATA or other single-site approximations.[9] It should be pointed out that Jacobs and Zaman did not consider the final terms in (5.1) with the care that we did. This has little effect for a real potential, but those terms become crucial in this application of the formula. Even though the Lloyd formula is correct in principle and can be applied to alloys under special circumstances, the techniques developed in Sec. III appear to be more useful in general. However, the formula for the integrated density of states derived from (5.2) by Györffy and Stocks[8] is very important in practice. Again, it can only be used in connection with a CPA calculation.

VI. ONE-LEVEL TIGHT-BINDING MODEL

Although it is highly specialized and in some ways trivial, the one-level tight-binding model with no off-diagonal randomness has played a large role in the development of the CPA.[6,7,27] The application of the developments in the preceding sections to this model illuminates certain aspects of the averaging process. Insights are obtained into the behavior to be expected of the quantities that appear in the equations. The reason that some of the results of those sections were overlooked before will also become clear. As in the preceding sections, we will endeavor to keep the effects that arise from making a general single-site approximation separate from those that arise from making a particular one.

The Hamiltonian that describes this model may be written

$$H = V + W\,, \tag{6.1}$$

where

$$V = \sum \epsilon^i\,|i\rangle\langle i|\,, \tag{6.2}$$

and

$$W = \sum_{i,j} W^{ij}\,|i\rangle\langle j|\,. \tag{6.3}$$

The site-diagonal energy parameters ϵ^i will, in the alloy, take on one of two possible values, ϵ^A or ϵ^B. The hopping integrals W^{ij} depend only on the separation $\vec{R}_{ij}$ between the sights i and j. It is assumed that $W^{ii} = 0$.

In the earlier discussions of this model the state vectors $|i\rangle$ are not specified in detail except to say that they are associated with the sites i in some sense and satisfy

$$\langle i|j\rangle = \delta_{ij}\,. \tag{6.4}$$

For our purposes we must go a bit further and point out that the usual interpretation of this model is consistent with the requirements that the function

$$U(\vec{r}-\vec{R}_i) = \langle \vec{r}\,|i\rangle \tag{6.5}$$

is real and equal to zero when $\vec{r}$ is outside the ith unit cell. From these conditions and (6.4) it follows that

$$\int U(\vec{r})^2 dv = 1 \tag{6.6}$$

when the integral is over the unit cell. The most important property of $\langle\vec{r}\,|i\rangle$ is that it is independent of whether ϵ^i is ϵ^A or ϵ^B.

Because the same function $U(\vec{r})$ is associated with each site in either the ordered or disordered system, a Bloch state

$$|\vec{k}\rangle = \frac{1}{\sqrt{N}}\sum_i \exp(i\vec{k}\cdot\vec{R}_i)\,|i\rangle \tag{6.7}$$

is useful in dealing with both of these cases. It is easily shown that

$$W\,|\vec{k}\rangle = w(\vec{k})\,|k\rangle\,, \tag{6.8}$$

where

$$w(\vec{k}) = \sum_j \exp(i\vec{k}\cdot\vec{R}_{ij})w^{ij}\,. \tag{6.9}$$

The "free-particle" Green's function in this model describes an electron propagating through the lattice with all the ϵ^i set equal to zero,

$$G_0(E) = \lim_{Z\downarrow E}(Z-W)^{-1}\,. \tag{6.10}$$

Using (6.9) it can be shown that the element $g^{ij} = \langle i\,|G_0|j\rangle$ is given by

$$g^{ij} = \frac{1}{N}\sum_{\vec{k}} \exp(-i\vec{k}\cdot\vec{R}_{ij})G_0(E,\vec{k})\,, \tag{6.11}$$

where

$$G_0(E,\vec{k}) = \lim_{Z\downarrow E}[Z-w(\vec{k})]^{-1}\,. \tag{6.12}$$

The Green's function for an ordered system can also be found readily. For example, the Hamiltonian

$$H_c = \sigma^c\sum_i |i\rangle\langle i\,| + W, \tag{6.13}$$

which describes a system that has the same self-energy σ^c associated with each site, can be used to construct a Green's function

$$G_c = \lim_{Z\downarrow E}(Z-H_c)^{-1}\,. \tag{6.14}$$

The matrix elements of this operator are given by

$$G_c^{ij} = \frac{1}{N}\sum_{\vec{k}} \exp(-i\vec{k}\cdot\vec{R}_{ij})G_c(E,\vec{k})\,, \tag{6.15}$$

where

$$G_c(E,\vec{k}) = \lim_{Z\downarrow E}[Z-w(\vec{k})-\sigma^c]^{-1}\,. \tag{6.16}$$

The Green's function for the alloy

$$G = \lim_{Z\downarrow E}(Z-H)^{-1}\,, \tag{6.17}$$

appears in the position representation as

$$G(E,\vec{r},\vec{r}\,') = U(\vec{r}_n)G^{nm}U(\vec{r}_m')\,, \tag{6.18}$$

when $\vec{r}$ is in cell n and $\vec{r}\,'$ is in cell m. The basic definitions (2.3) through (2.6) can be used to write the matrix element G^{nm} as

$$G^{nm} = g^{nm} + \sum_{p,q} g^{np}\tau^{pq}g^{qm}\,, \tag{6.19}$$

where

$$\tau^{nm} = t^n\delta_{nm} + t^n\sum_{p\neq 0} g^{np}\tau^{pm}\,, \tag{6.20}$$

and

$$t^n = \epsilon^n(1-g^{00}\epsilon^n)^{-1}\,. \tag{6.21}$$

Because of the extreme simplicity of the Hamiltonian in (6.1) manipulations can be carried out that would make no sense for more general models. In particular, it is useful to expand G as

$$G = -V^{-1} - V^{-1}(Z-W)V^{-1} + V^{-1}(Z-W)G(Z-W)V^{-1}\,, \tag{6.22}$$

rather than the more conventional form of (2.3). Solving (2.3) for T and inserting into the above leads to

$$G = -V^{-1} + V^{-1}TV^{-1}\,, \tag{6.23}$$

and hence

$$G^{nm} = -(\epsilon^n)^{-1}\delta_{nm} + (\epsilon^n)^{-1}\tau^{nm}(\epsilon^m)^{-1}\,. \tag{6.24}$$

Inserting (6.24) into (6.18) makes it possible to write $G(E,\vec{r},\vec{r}\,')$ for $\vec{r}$ and $\vec{r}\,'$ in cell n in a form that is analogous to (2.18):

$$G(E,\vec{r},\vec{r}\,') = Z^n(\vec{r}_n)\tau^{nn}Z^n(\vec{r}_n') - Z^n(\vec{r}_n)U(\vec{r}_n')\,, \tag{6.25}$$

where

$$Z^n(\vec{r}_n) = (\epsilon^n)^{-1}U(\vec{r}_n)\,. \tag{6.26}$$

For $\vec{r}$ in cell n and $\vec{r}\,'$ in cell m the equation analogous to (2.26) is

$$G(E,\vec{r},\vec{r}\,') = Z^n(\vec{r}_n)\tau^{nm}Z^m(\vec{r}_m')\,. \tag{6.27}$$

We are now ready to proceed with the averaging and the invoking of the single-site approximation.

Since the function $U(\vec{r}_n)$ does not depend on the kind of atom on the nth site, it is very easy to average the Green's function when it is written as in (6.18). If we do this and then use the single-site approximation in the obvious way, we are led to

$$\langle G(E,\vec{r},\vec{r}\,')\rangle = U(\vec{r}_n) G_c^{nm} U(\vec{r}\,'_m)\,, \tag{6.28}$$

where G_c^{nm} is given by (6.15). This averaging process is the same whether $\vec{r}$ and $\vec{r}\,'$ are in the same cell or not.

Now let us average $G(E,\vec{r},\vec{r}\,')$ as it appears in (6.25) using the same sequence of operations that were used to obtain (2.28). This set of conditional averages leads to

$$\begin{aligned}\langle G(E,\vec{r},\vec{r}\,')\rangle = {} & C_A Z^A(\vec{r}_n)\langle\tau^{nn}\rangle_A Z^A(\vec{r}\,'_n) \\ & + C_B Z^B(\vec{r}_n)\langle\tau^{nn}\rangle_B Z^B(\vec{r}\,'_n) \\ & - C_A Z^A(\vec{r}_n) U(\vec{r}\,'_n) - C_B Z^B(\vec{r}_n) U(\vec{r}\,'_n)\,,\end{aligned} \tag{6.29}$$

where

$$\langle\tau^{nn}\rangle_n = D^n \tau_c^{00}\,, \tag{6.30}$$

with

$$D^n = [1 + \tau_c^{00}(m^n - m^c)]^{-1}\,, \tag{6.31}$$

in which

$$m^n = (\epsilon^n)^{-1} - g^{00}\,, \tag{6.32}$$

and

$$m^c = (\sigma^c)^{-1} - g^{00}\,. \tag{6.33}$$

The integral that leads to τ_c^{00} is somewhat simpler than the one in (3.11) or (3.12). Inverting (6.11) leads to

$$G_0(E,\vec{k}) = \sum \exp(i\vec{k}\cdot\vec{R}_{ij}) g^{ij}\,, \tag{6.34}$$

whereas in the structure constant $g(\vec{k})$ defined in (3.10) the term for which $j=i$ is omitted. Thus

$$\tau_c^{00} = \frac{1}{N}\sum_{\vec{k}} \tau_c(E,\vec{k})\,, \tag{6.35}$$

where

$$\tau_c(E,\vec{k}) = [(\sigma^c)^{-1} - G_0(E,\vec{k})]^{-1}\,. \tag{6.36}$$

By simple substitution, the average in (6.29) leads to

$$\langle G(E,\vec{r},\vec{r}\,')\rangle = U(\vec{r}_n)(C_A G_A^{00} + C_B G_B^{00}) U(\vec{r}\,'_n)\,, \tag{6.37}$$

where the definition

$$G_n^{00} = (\epsilon^n)^{-1}\langle\tau^{nn}\rangle_n(\epsilon^n)^{-1} - (\epsilon^n)^{-1} \tag{6.38}$$

is consistent with (6.24). The right-hand side of (6.38) can be transformed algebraically into another form

$$G_n^{00} = d^n G_c^{00}\,, \tag{6.39}$$

where

$$d^n = [1 - G_c^{00}(\epsilon^n - \sigma^c)]^{-1}\,, \tag{6.40}$$

and G_c^{00} is given in (6.15). This is just the expression that is obtained directly if one sets out to find the Green's function for the system that has ϵ^n on the central site and σ^c on all the others.

Let us now make the important observation that the averaging process that leads to (6.28) and the one that leads to (6.29), and hence (6.37), are intrinsically different. There is no necessity for them to lead to the same answer, and for an arbitrary single-site approximation they will not. Comparing (6.28) and (6.37) shows that they do lead to the same answer if

$$C_A G_A^{00} + C_B G_B^{00} = G_c^{00}\,. \tag{6.41}$$

This is Shiba's form of the CPA equations.[26] We are thus led to the conclusion that the two averaging processes described above lead to the same answer for the SD $\langle G(E,\vec{r},\vec{r}\,')\rangle$ if and only if σ^c is chosen to be the CPA self-energy.

In order that this discussion should clearly apply to the relations derived in the preceding sections, it is useful to go through the operation of showing that the equation in (6.41) is algebraically equivalent to the equation

$$C_A\langle\tau^{00}\rangle_A + C_B\langle\tau^{00}\rangle_B = \tau_c^{00}\,. \tag{6.42}$$

This equation is more like the equation quoted in (5.22) which is used in the muffin-tin case. We do not reproduce this proof here, but the interested reader can carry it out.

It has thus been shown that for the SD case the two different types of averaging processes can lead to the same answer, but there is another type of averaging, namely the averaging of (6.27) for the NSD case. Going through the operations that led to (2.44) yields

$$\langle G(E,\vec{r},\vec{r}\,')\rangle = Z^c(\vec{r}_n)\tau_c^{nm} Z^c(\vec{r}\,'_m)\,, \tag{6.43}$$

where

$$Z^c(\vec{r}_n) = C_A D^A Z^A(\vec{r}_n) + C_B D^B Z^B(\vec{r}_n)\,, \tag{6.44}$$

and

$$\tau_c^{nm} = \frac{1}{N}\sum_{\vec{k}} \exp(-i\vec{k}\cdot\vec{R}_{nm})\tau_c(E,\vec{k})\,. \tag{6.45}$$

It is certainly not manifest that this average is the same as (6.28) or that requiring σ^c to satisfy the CPA condition (6.41) or (6.42) will make it so. However, (6.32) and (6.33), coupled with the CPA condition in the form shown in (5.25) and (5.26), leads to

$$C_A(\epsilon^A)^{-1} D^A + C_B(\epsilon^B)^{-1} D^B = (\sigma^c)^{-1}\,, \tag{6.46}$$

and hence

$$Z^c(\vec{r}_n) = (\sigma^c)^{-1} U(\vec{r}_n) . \qquad (6.47)$$

Inserting this into (6.43) leads to the same result as (6.28) because from (6.24)

$$G_c^{nm} = (\sigma^c)^{-1} \tau_c^{nm} (\sigma^c)^{-1} \qquad (6.48)$$

for n not equal to m. We are thus led to the conclusion that the two averages lead to the same result for NSD properties if and only if σ^c is the CPA self-energy.

It is interesting to calculate the Bloch spectral-density function $A^B(E,\vec{k})$ from the NSD-averaged Green's function in (6.43). The quantities F^{cc} and F^c that go into (4.15) are, in general,

$$F^{cc} = [C_A(\epsilon^A)^{-1} D^A + C_B(\epsilon^B)^{-1} D^B]^2 , \qquad (6.49)$$

and

$$F^c = [C_A(\epsilon^A)^{-1} D^A (\epsilon^A)^{-1} + C_B(\epsilon^B)^{-1} D^B (\epsilon^B)^{-1}] . \qquad (6.50)$$

For the special case that σ^c satisfies the CPA condition it can be shown that

$$F^{cc} = (\sigma^c)^{-2} , \qquad (6.51)$$

and

$$(F^c - F^{cc})\tau_c^{00} = -(\sigma^c)^{-1} . \qquad (6.52)$$

Thus, within the CPA approximation

$$A^B(E,\vec{k}) = -(1/\pi)\,\mathrm{Im}(\sigma^c)^{-2}\tau_c(E,\vec{k}) + \Delta(E) , \qquad (6.53)$$

with

$$\Delta(E) = (1/\pi)\,\mathrm{Im}(\sigma^c)^{-1} . \qquad (6.54)$$

Even in the tight-binding model the self-energy σ^c has a lot of structure in it as a function of E, so it is not surprising that F^{cc} and $\Delta(E)$ have a great deal of structure in the more general muffin-tin case.

Comparing (6.16) and (6.36) leads to

$$G_c(E,\vec{k}) = (\sigma^c)^{-1}\tau_c(E,\vec{k})(\sigma^c)^{-1} - (\sigma^c)^{-1} , \qquad (6.55)$$

so that (6.53) can be written as

$$A^B(E,\vec{k}) = -(1/\pi)\,\mathrm{Im}G_c(E,\vec{k}) . \qquad (6.56)$$

This is the result that should have been expected because we have already seen that the NSD average in (6.43) is identical with the one in (6.28) when the CPA is used.

By applying the techniques of the preceding sections to the simple one-level tight-binding model we have been able to get some insight into the functions introduced in those sections. The other kind of averaging shown in (6.28) can only be done for the special case that the wave functions $Z^A(\vec{r})$ and $Z^B(\vec{r})$ are related by an energy-independent scaling parameter as in (6.26). The failure to distinguish clearly between the averaging process that leads to (6.29) and (6.43) and the one that leads to (6.28) has no doubt led to confusion. Of course, any kind of single-site approximation will lead to the simple expression (6.56) for $A^B(E,\vec{k})$ when the averaging process of (6.28) is used. The averaging process of the preceding sections is the only one that can be used for general models, however.

VII. NUMERICAL ANALYSIS: DENSITIES OF STATES

In this and the following section we will present some numerical results which are based on the formulas derived in the preceding sections. In this section, we will concentrate on SD properties, in particular, the total and component densities of states. A numerical analysis of the Bloch spectral-density formula is presented in the following section.

Total densities of states calculated on the basis of the GS formula and the CPA have already been shown by Stocks *et al.*[28] for copper-nickel alloys. We will therefore use that system for the numerical study of the formulas for the total and component densities of states in this section. The problems associated with the previous, incorrect, formula for the Bloch spectral density are particularly marked for the copper-palladium alloy system, so we will use it in the next section as our primary example for studying that NSD property.

That the GS formula and (3.2) give identical results for the density of states is shown in Fig. 1. Total densities of states are shown for three $\mathrm{Cu}_x\mathrm{Ni}_{1-x}$ alloys having $x = 0.77$, 0.50, and 0.19, calculated using both approaches. The solid line shows the densities of states obtained directly from (3.2) and (3.3). The crosses show the density of states obtained by first calculating the integrated density of states from the GS formula[8]:

$$N(E) - N^0(E) = -\frac{1}{\pi}\,\mathrm{Im}\left[\frac{1}{\Omega_{\mathrm{BZ}}}\int_{\mathrm{BZ}} \ln \mathrm{Det}\underline{M}_c(E,\vec{k})d\vec{k} - C_B \ln \mathrm{Det}\left(\frac{\underline{\underline{m}}^A - \langle \underline{\underline{m}} \rangle}{\underline{m}^A - \underline{m}^c}\right) - C_A \ln \mathrm{Det}\left(\frac{\underline{\underline{m}}^B - \langle \underline{\underline{m}} \rangle}{\underline{m}^B - \underline{m}^c}\right)\right] , \qquad (7.1)$$

at a number of energies and then numerically differentiating $N(E)$ to obtain $\rho(E)$. In (7.1), $\langle m \rangle = C_A \underline{m}^A + C_B \underline{m}^B$.

At almost all values of energy the two methods of obtaining $\rho(E)$ give essentially identical answers. This shows that (7.1) and (3.2) are equivalent and provides a numerical check of the algebra of Sec. V. The numerical tolerance[29] is generally better

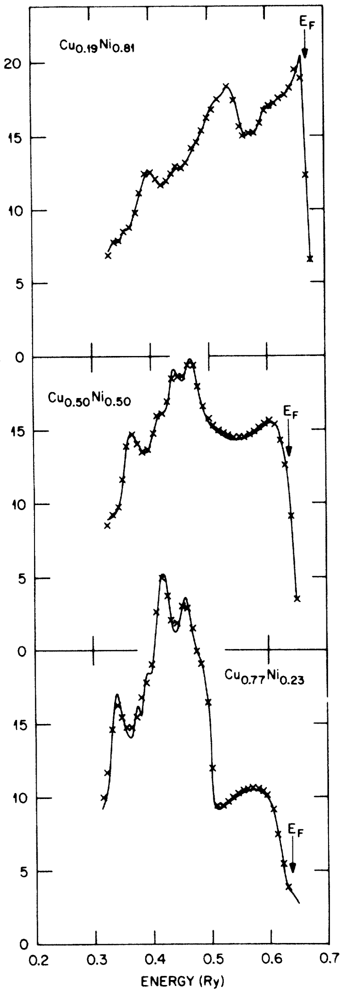

FIG. 1. Densities of states for three Cu_xNi_{1-x} alloys having $x = 0.19$ (upper frame), $x = 0.50$ (middle frame), and $x = 0.77$ (lower frame). The solid lines were calculated according to (3.2), the crosses were calculated using the GS formula (7.1). For each concentration the Fermi energy E_F calculated from the GS formula is marked.

than 0.2%. However, at energies where the density-of-states function is particularly structured, the two methods yield noticeably different values for $\rho(E)$ (with errors as large as 5%). This results from the difficulty in obtaining $\rho(E)$ by numerical differentiation in regions where $\rho(E)$ is changing rapidly. Obviously it is easier to calculate $\rho(E)$ directly from (3.2) in such regions.

The above limitation notwithstanding, it should be stressed that the GS formula is still most useful. It allows us to locate the Fermi energy E_F by solving the CPA equations only for energies in the neighborhood of E_F and the bottom of the conduction band E_B. This is possible because E_F is determined by the requirement $N(E_F) - N(E_B) = C_A z_A + C_B z_B$ where z_A and z_B are the number of conduction electrons associated with the A and B alloying species. In determining E_F we are forced to calculate $N(E_B)$ as well as $N(E_F)$ because, from (7.1), $N(E)$ is obtained from the phase of a complex number which is arbitrary to multiples of 2π.[30]

There is one further complicating factor in calculating the density of states and E_F from (7.1). For systems in which one or more of the A or B phase shifts $\delta_l^{A(B)}$ passes through zero at energies $E_l^{A(B)}$ in the occupied band, $N(E)$ changes discontinuously by $C_{A(B)}(2l+1)$ at those energies. This discontinuity does not correspond to states of the alloy and must be subtracted out. It is the equivalent of the spurious roots which occur in the KKR method for ordered systems and the discontinuous jumps of one state per atom which occur in cluster calculations and which practitioners have long known to ignore. Of course $\rho(E)$ calculated from (3.2) and (3.3) is properly continuous at such energies. The discontinuities in $N(E)$ at the energies $E_l^{A(B)}$ are a minor numerical complication in the evaluation of $N(E)$ and hence $\rho(E)$ from the GS formula, but as we shall show in the next section, the Bloch spectral density based on this formula behaves unphysically in the neighborhood of such energies.

We show in Figs. 2 and 3 the densities of states of Fig. 1 resolved according to atomic species and symmetry type.[31] These components are obtained with the help of (3.6).

Muffin-tin densities of states, which differ only in that the range of integration in (3.4) is restricted to the muffin-tin sphere, have been shown previously[32] and were used to calculate the soft x-ray spectra of Cu-Ni alloys.[33] Since, in the d-band region shown, the densities of states inside the muffin-tin sphere are little different from the total densities of states, we will not comment further on them save to say that using the equations of Sec. III it is no more difficult to calculate the densities of states (total or component and symmetry resolved) inside the full unit cell than it is to calculate the muffin-tin densities of states.

We believe the curves of Figs. 2 and 3 to be the first satisfactory component densities of states to have been shown for the KKR-CPA. Bansil[34] has previously shown component densities of states that he calculated using an expression obtained from a species decomposition of the GS formula.[9] While we have shown in Sec. V that the GS formula for the density of states is equivalent to the Green's-function formula derived in Sec. III, it is not possible to show a similar equivalence between the component densities-of-states formulas of Refs. 9 and 34, and the Green's-function formula (3.6).

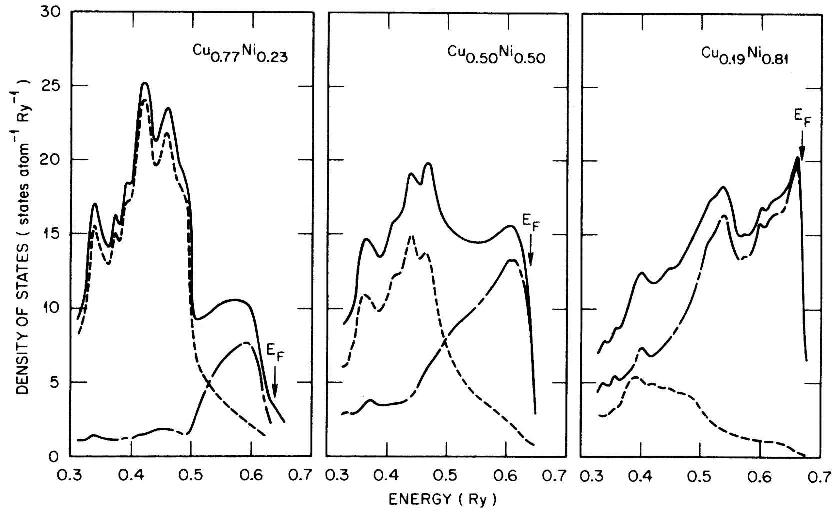

FIG. 2. Species-decomposed densities of states $C_n\rho_n(E)$ for the three Cu_xNi_{1-x} alloys of Fig. 1. The contribution from Cu sites $x\rho_{Cu}(E)$ is given by the dashed line, the contribution from Ni sites $(1-x)\rho_{Ni}(E)$ is given by the dot-dashed line. The total densities of states (solid line) is given by $\rho(E)=x\rho_{Cu}(E)+(1-x)\rho_{Ni}(E)$.

Thus, while the expression obtained from Lloyd's formula may give reasonable results for some systems, we have no confidence in it in general. In any case, (3.6) is much easier to use.

It is interesting to plot the various terms entering (3.5) and (3.6) to find the origin of the structure in $\rho(E)$. For a muffin-tin potential, values of l through $l=2$, and cubic Bravais lattices, the $F_{LL'}^{A(B)}$ are diagonal in L, and thus can be written

$$F_{LL'}^{A}(E)=F_{L}^{A}(E)\delta_{LL'}\,. \qquad (7.2)$$

In Fig. 4 we plot the components of $\underline{F}^{A(B)}(E)$ (Ref. 35) for the Cu and Ni muffin-tin potentials used in the calculation of $\rho(E)$ for the $Cu_{0.5}Ni_{0.5}$ alloy. All components of this quantity are monotonically decreasing functions of energy except for the d components of $\underline{F}^{Cu}(E)$ which have some slight structure in the neighborhood of the d-scattering resonance.

In Fig. 5 we plot the t_{2g} component of $-\mathrm{Im}\underline{\tau}_c(E)$, $-\mathrm{Im}\underline{D}^A(E)\underline{\tau}_c^{00}(E)$ $(\equiv-\mathrm{Im}\underline{\tau}^A)$, and $-\mathrm{Im}\underline{D}^B(E)\underline{\tau}_c^{00}(E)$ $(\equiv-\mathrm{Im}\underline{\tau}^B)$. While $-\mathrm{Im}\tau_{c,t_{2g}}^{00}(E)$ bears a superficial resemblance to $\rho_{t_{2g}}(E)$, it is important to realize that it is in fact related only through the rather complicated equation (3.5). The effect of the matrices $\underline{D}^{A(B)}$ is to partition $\underline{\tau}_c^{00}$ among the constituent species. The remaining factor $\underline{F}^{A(B)}(E)$ adds only a final weak energy dependence to the overall density of states.

In closing this section it should be stressed

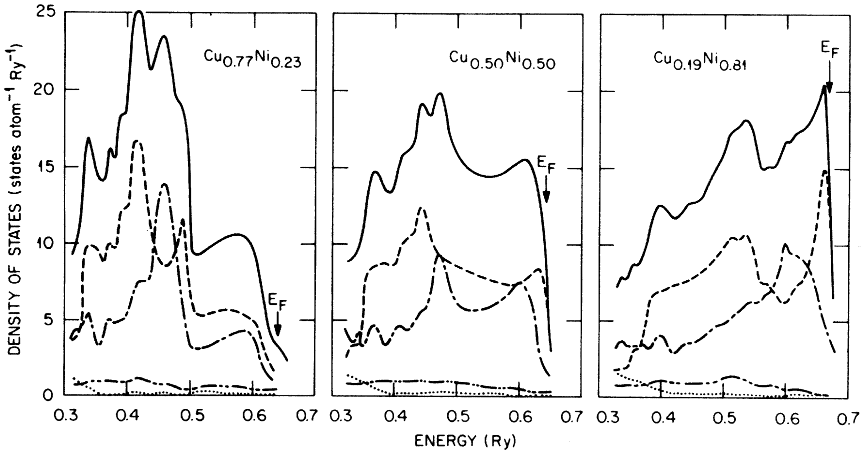

FIG. 3. Symmetry-decomposed densities of states $\rho_\alpha(E)$ for three Cu_xNi_{1-x} alloys of Fig. 1. For $\alpha=a_{1g}$ (dotted line), t_{1u} (dot-dot-dash line), t_{2g} (dashed line), e_g (dot-dash line). The total densities of states (solid line) is given by $\rho(E)=\sum_\alpha\rho_\alpha(E)$.

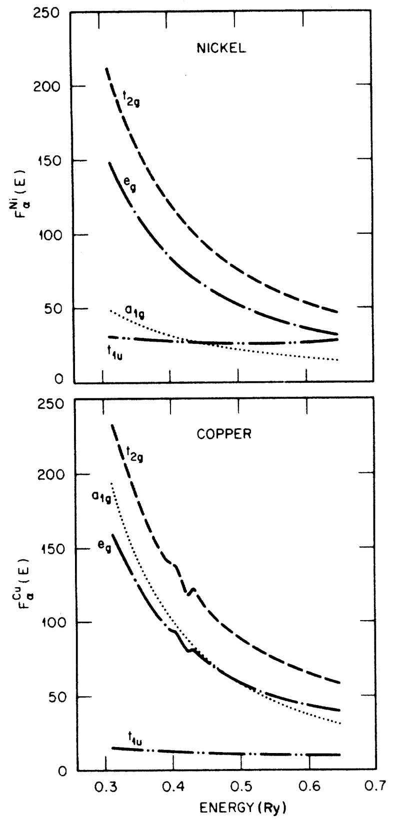

FIG. 4. Symmetrized prefactors $F_\alpha^{Cu}(E)$ and $F_\alpha^{Ni}(E)$ for use in the calculation of densities of states (3.2). The $F_\alpha^{Ni}(E)$ are given in the upper frame, the $F_\alpha^{Cu}(E)$ are given in the lower frame. The symmetry coding is as in Fig. 3. For the t_{1u} component the scale of the ordinate should be multiplied by 10^2.

that, once the CPA equations have been solved, calculation of the densities of states using the equations of Sec. III is very simple. Although we have concentrated here on the density of states it is also clear that calculation of the average charge densities associated with the constituent species is also a trivial matter, opening up the route to the inclusion of charge self-consistency in future KKR-CPA calculations.

VIII. NUMERICAL ANALYSIS: BLOCH SPECTRAL DENSITY

Implicit in the original derivation[8] of the GS formula for the density of states is a spectral decomposition.[9] This spectral decomposition can be called the density of states per $\vec{k}$ point $S_B(E,\vec{k})$, and is given by

$$S_B(E,\vec{k}) = S^0(E,\vec{k}) - \frac{1}{\pi}\,\mathrm{Im\,tr}\left(\frac{d\underline{G}}{dE} - \underline{P}(E)\right)\underline{\tau}_c(E,\vec{k}), \tag{8.1}$$

where

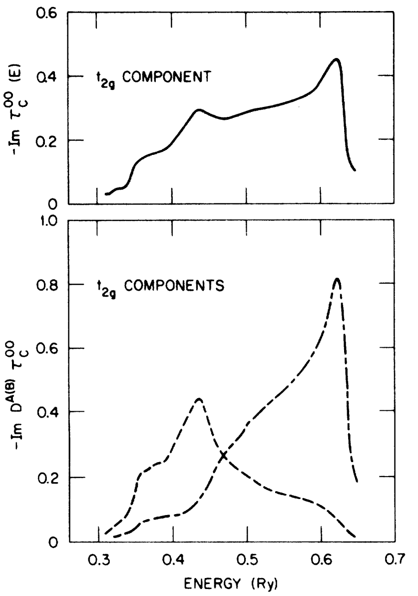

FIG. 5. Upper frame: the t_{2g} component of $-\mathrm{Im\,tr}\underline{\tau}(E)$ for the $Cu_{0.5}Ni_{0.5}$ alloy of Fig. 1. Lower frame: the t_{2g} component of $-\mathrm{Im\,tr}\underline{\tau}^{Cu}(E)$ (dash line) and of $-\mathrm{Im\,tr}\tau^{Ni}(E)$ (dot-dash line) for the $Cu_{0.5}Ni_{0.5}$ alloy.

$$\underline{P}(E) = C_A\underline{D}^A\frac{d\underline{m}^A}{dE} + C_B\underline{D}^B\frac{d\underline{m}^B}{dE}, \tag{8.2}$$

and where $S^0(E,\vec{k})$ is the spectral density for free electrons $[\delta(E-k^2)]$. $S_B(E,\vec{k})$ clearly satisfies the necessary conditions that it integrate to the density of states, i.e.,

$$\rho(E) = \frac{1}{\Omega_{BZ}}\int_{BZ} d\vec{k}\,S_B(E,\vec{k}), \tag{8.3}$$

and in the ordered pure metal it goes over to a delta function at band energies $E_\alpha(\vec{k})$:

$$S_B^{pure}(E,\vec{k}) = \sum_\alpha \delta(E - E_\alpha(\vec{k})). \tag{8.4}$$

As a result, $S_B(E,\vec{k})$ was called a Bloch spectral density even though it was realized that the decomposition embodied in (8.1) is not unique and no formal derivation existed. A great deal of experience with $S_B(E,\vec{k})$ (mostly in Cu_xNi_{1-x} alloys) has shown it to be a physically appealing quantity.[32,36,37] It therefore came as a great surprise to find in Cu_xPd_{1-x} alloys values of E and $\vec{k}$ for which it is negative.

The Bloch spectral density calculated using (8.1) is plotted as a function of energy at the Γ and X points in the fcc Brillouin zone for $Cu_{0.7}Pd_{0.3}$ in Fig. 6. Structure which has a clear physical interpretation in terms of states of the alloy appears, but there is an unphysical structure for energies in the neighborhood of $E=0.35$ Ry. This spurious structure occurs at the same energy for

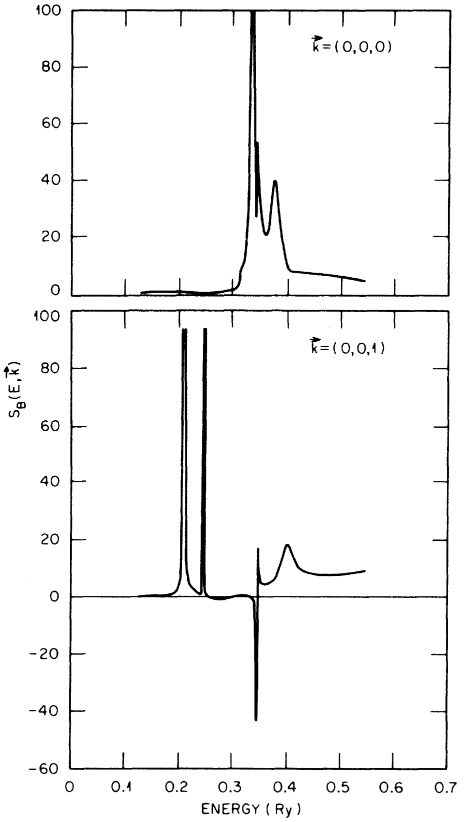

FIG. 6. Bloch spectral density $S_B(E,\vec{k})$ plotted as a function of energy and calculated according to (8.1) for $\mathrm{Cu}_{0.7}\mathrm{Pd}_{0.3}$. The upper frame gives $S_B(E,\vec{k})$ for $\vec{k} = (0,0,0)$, the lower gives $S_B(E,\vec{k})$ for $\vec{k} = (0,0,1)$.

all values of $\vec{k}$ although it is more pronounced away from the Brillouin-zone center.

The origin of this structure is understood. In Fig. 7 we have plotted the $l=0$ component of the term $-\mathrm{Im}\underline{D}^{\mathrm{Cu}}(d\underline{m}^{\mathrm{Cu}}/dE)\underline{\tau}_c(E,\vec{k})$ which appears in (8.1), and also $S_B(\vec{k},E)$ minus this term for $\vec{k} = (0,0,1)$. Obviously the unphysical behavior arises from the term which we have isolated. We have also plotted the Cu s-wave phase shift, from which it can be seen that the unwanted structure occurs as η_0^{Cu} passes through zero.

From the way $(d\underline{m}^{\mathrm{Cu}}/dE)$ enters (8.1) [remember both $\underline{D}^{\mathrm{Cu}}$ and $\underline{\tau}_c(E,\vec{k})$ are complex] we might expect structure in $S_B(E,\vec{k})$ of the kind seen in Figs. 6 and 7 when η_0^{Cu} goes through zero. It is not clear that it has to occur, however. The singular nature of $(d\underline{m}^{\mathrm{Cu}}/dE)$ could conceivably be cancelled by singular behavior in the $l=0$ component of $\underline{m}^c$. Because of the complexity of the KKR-CPA equations which determine $\underline{m}^c$, it is not possible to see analytically if such singular behavior may, in fact, exist. We searched for it numerically and did not find it.

It might be suspected that the well-known difficulties in solving the KKR-CPA equations to great precision raises doubts about the conclusions we have drawn. For this reason we constructed a model which has the necessary complication but which can be solved to arbitrary precision. This model consists of the same $\mathrm{Cu}_{0.7}\mathrm{Pd}_{0.3}$ alloy as was used above, except that we treat only the $l=0$ phase shift in the CPA calculation. All the matrices involved are then one by one. The major contribution to the integral in (3.12) for $\underline{\tau}_c^{00}(\epsilon)$ arises from a region close to a constant energy surface which is essentially spherical. These simplifications greatly facilitate the solution of the equations.

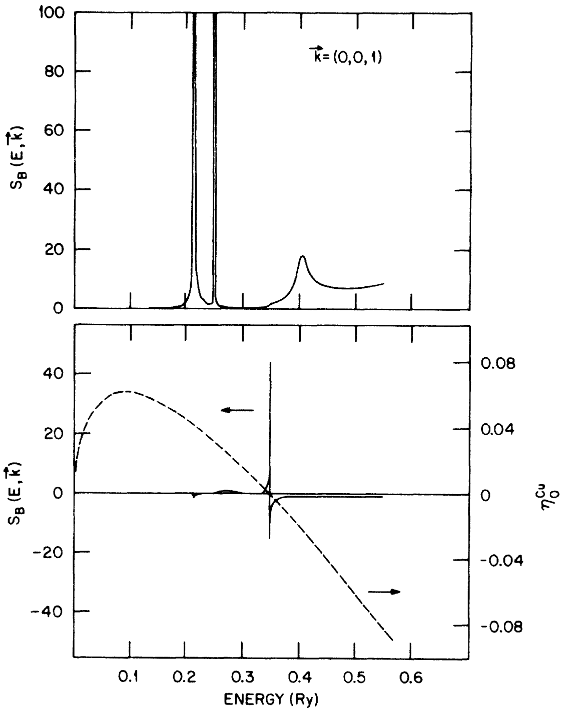

FIG. 7. Upper frame: Bloch spectral density $S_B(E,\vec{k})$ plotted as a function of energy for $\vec{k} = (0,0,1)$ calculated according to (8.1) for $\mathrm{Cu}_{0.7}\mathrm{Pd}_{0.3}$ with the term which gives rise to the singular structure of Fig. 6 suppressed. Lower frame: the singular contribution to $S_B(E,\vec{k})$ (solid line) and the $l=0$ phase shift η_0^{Cu} for a single Cu muffin-tin well (dash line).

In Fig. 8 we have plotted the KKR-CPA scattering amplitude $f_0^c = -\kappa t_0^c$ for this model in the energy range $E = 0.0$ to 0.48 Ry. In the inset we show f_0^c close to the energy at which $\eta_0^{\mathrm{Cu}} = 0$. There is no suggestion of any singular structure in f_0^c. We therefore conclude that the spurious structure in $S_B(E,\vec{k})$ given by (8.1) is real and that the equations are pathological.

In view of the discussion of Secs. III and IV, the origins of the difficulties encountered with (8.1) are clear. While $S_B(E,\vec{k})$ is a spectral decomposi-

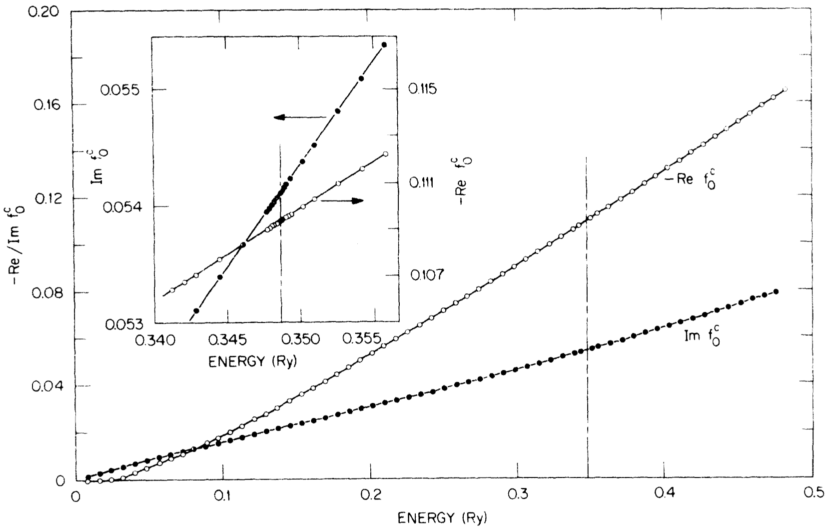

FIG. 8. Real and imaginary parts of the CPA effective scattering amplitude $f_0^c(E)$ for a $Cu_{0.7}Pd_{0.3}$ alloy when only the $l=0$ phase shift is included in the calculation. Inset shows $f_0^c(E)$ in the neighborhood of the energy at which $\delta_0^{Cu}=0$ and $S_B(E,\vec{k})$ is pathological. The white and black dots give the actual calculated points for $\mathrm{Re}f_0^c$ and $\mathrm{Im}f_0^c$, respectively.

tion of $\rho(E)$ it is not a Bloch spectral density. According to (4.8) and (4.9), a proper Bloch spectral density of necessity includes NSD averages which do not occur in the GS equation for $\rho(E)$ since that quantity is purely site diagonal. Thus, there is nothing to be gained by pursuing (8.1) further. We now turn to a discussion of the correct Bloch spectral-density formula for the single-site CPA.

In Fig. 9 we show the Bloch spectral density as a function of energy calculated according to (4.15) for $Cu_{0.7}Pd_{0.3}$ for the Γ point and the X point in the fcc Brillouin zone. The pathological behavior which is present in the older formula is not present in the new. All of the peaks in Fig. 9 can be understood simply. The two large peaks in $A^B(E,\vec{k})$ at Γ are what is left in the alloy of the $\Gamma_{25'}$ and Γ_{12} states of pure Cu. The high-energy shoulder at Γ results from Pd impurity states. At X, the two low-lying states correspond to the X_1 and X_3 states of the pure metals. The high-energy peak is what is left of the X_2 and X_5 states of pure Cu, the states which in pure Cu delineate the top of the d-band complex. Again the high-energy shoulder arises from the Pd "impurities."

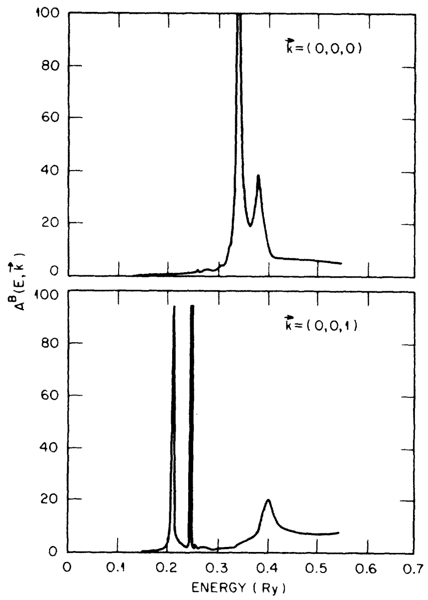

FIG. 9. Bloch spectral density $A^B(E,\vec{k})$ plotted as a function of energy for $Cu_{0.7}Pd_{0.3}$ at the Γ (upper) and X (lower) points and calculated according to (4.15).

Having noted that the unphysical structure seen in Fig. 6 is not present in these calculations, perhaps the next most striking result is that, away from the pathological region, the results based on the correct spectral-density formula are almost identical to those based on the older formula. This similarity between $A^B(E,\vec{k})$ and $S_B(E,\vec{k})$ is not a result peculiar to Cu_xPd_{1-x}. In Fig. 10 we show the Bloch spectral density according to the new equation plotted as a function of energy at five $\vec{k}$ points along the Δ direction in the fcc Brillouin zone for $Cu_{0.77}Ni_{0.23}$. On the scale used in Fig. 10 it is not possible to distinguish between the results of the old and new formulas. The difference between the two is generally less than 0.5%. In view of the fundamentally different nature of the two formulas this similarity is, at first sight, very surprising. It is, at the same time, something of a relief. Bloch spectral densi-

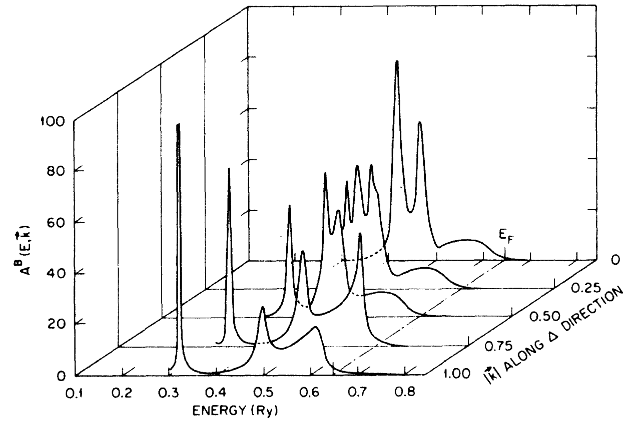

FIG. 10. Bloch spectral density $A^B(E,\vec{k})$ as a function of energy at five $\vec{k}$ points along the Δ direction [$\vec{k}$ = (0, 0, 0), (0, 0, 1/4), (0, 0, 1/2), (0, 0, 3/4), and (0, 0, 1)] for $Cu_{0.77}Ni_{0.23}$ showing the structure from the *d*-band complex. The lowest *sp* band which begins at the Brillouin-zone center and ends at the zone boundary is not shown. The Fermi energy E_F is indicated by the dot-dash line.

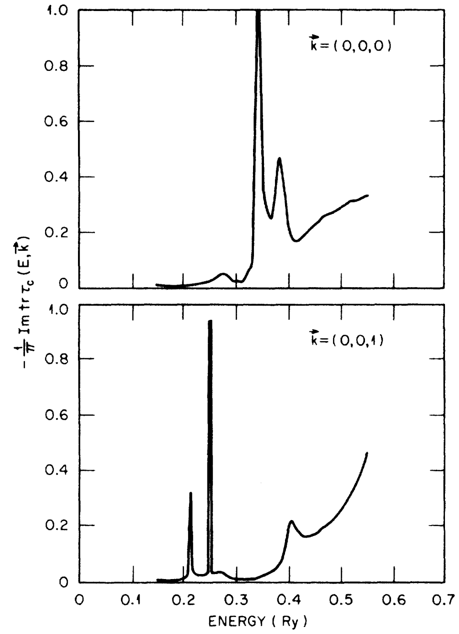

FIG. 11. $-\pi^{-1}\mathrm{Im}\,\mathrm{tr}\underline{\tau}_c(E,\vec{k})$ plotted as a function of energy for $\vec{k}$ = (0, 0, 0) (upper) and $\vec{k}$ = (0, 0, 1) (lower).

ties based on (8.1) have been used as a basis for understanding a number of experimental results, particularly in the Cu_xNi_{1-x} system.[37] On the basis of the checks we have so far performed using the new $A^B(E,\vec{k})$ formula, it appears that conclusions regarding experimental quantities which were made on the basis of the old formula are substantially correct.

The reason for the apparent similarity between the results given by the old and new formula lies in the fact that the major structure comes primarily from $\mathrm{Im}\underline{\tau}_c(E,\vec{k})$. This function is a factor in both formulas. For the case of an ordered system $\mathrm{Im}\underline{\tau}_c(E,\vec{k})$ would be a series of δ functions. Although broadened by disorder, it is still the near δ-function-like behavior of $\mathrm{Im}\underline{\tau}_c(E,\vec{k})$ which dominates in $\mathrm{Im}G(E,\vec{k})$. In Fig. 11 we show $-(1/\pi)\,\mathrm{Im}\,\mathrm{tr}\underline{\tau}_c(E,\vec{k})$ at the Γ and *X* points for $Cu_{0.7}Pd_{0.3}$. This is simply the first term in the formula for $A^B(E,\vec{k})$ with $\underline{F}^{cc}(E)$ set equal to the unit matrix. Clearly all of the major structures in Fig. 9 are present in Fig. 11.

That the major structures in $A^B(E,\vec{k})$ arise primarily from $\underline{\tau}_c(E,\vec{k})$ is not to say that the remaining terms in (4.15) are of no importance. Recall that in the tight-binding model discussed in Sec. VI, $F^{cc}=(\sigma^c)^{-2}$ and $\Delta(E)=(\sigma^c)^{-1}$, both of which are nontrivial functions of the energy. In the muffin-tin model both $\underline{F}^{cc}(E)$ and $\Delta(E)$ are again very highly structured functions of *E* and the way in which the various terms in (4.15) cancel against one another in order to produce the final result is very complicated and system dependent.

In Fig. 12 we show a plot of $A^B(E,\vec{k})$ for $\vec{k}$ = (0, 0, 1) and also the individual terms from (4.15) for the two alloys $Cu_{0.7}Pd_{0.3}$ and $Cu_{0.77}Ni_{0.23}$. The total spectral densities for the two systems are similar, but the way the various terms from (4.15) contribute is very different. In $Cu_{0.77}Ni_{0.23}$ the term $\Delta(E)$ is approximately zero because $\mathrm{Im}\,\mathrm{tr}\underline{F}^{cc}\underline{\tau}_c^{00}(E)\simeq\mathrm{Im}\,\mathrm{tr}\underline{F}^{c}\underline{\tau}_c^{00}(E)$. Thus, as can be seen in Fig. 12, $A^B(E,\vec{k})\simeq-(1/\pi)\,\mathrm{Im}\,\mathrm{tr}\underline{F}^{cc}\underline{\tau}_c(E,\vec{k})$. In $Cu_{0.7}Pd_{0.3}$ however, $\mathrm{Im}\,\mathrm{tr}\underline{F}^{cc}\underline{\tau}_c^{00}(E)$ is generally much larger than $\mathrm{Im}\,\mathrm{tr}\underline{F}^{c}\underline{\tau}_c^{00}(E)$. Furthermore, the two terms are of opposite sign. The resulting $\Delta(E)$ is large and has a great deal of structure, much of which is as sharp as that in $\mathrm{Im}\underline{\tau}_c(E,\vec{k})$. Clearly a great deal of precise cancellation takes place in $A^B(E,\vec{k})$ for this alloy.

IX. DISCUSSION

A very attractive feature of the formulas derived in this paper is that they are no more difficult to deal with numerically than the ones they replace. In fact, they are simpler than some of the earlier ones that lead to incorrect answers. Of course, the calculation of the elements of the effective scattering matrix $\underline{t}^c$ is the only time-consuming part of a CPA calculation. Once these elements have been tabulated for a sufficient set of energies they can be used to calculate any desired properties of the alloy with relatively little additional effort.

There has been a trend toward considering expressions for the density of states and other prop-

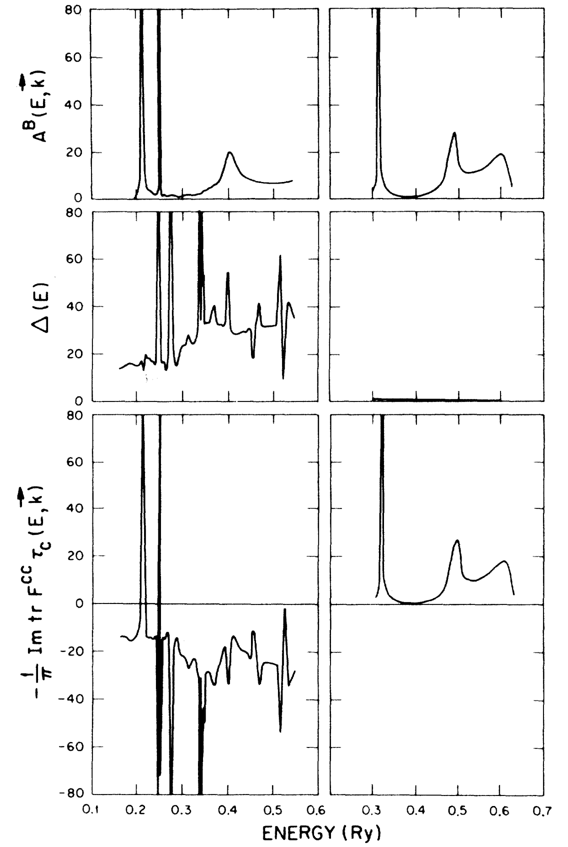

FIG. 12. Various contributions to the Bloch spectral density $A^B(E,\vec{k})$ according to (4.15). Upper curve gives the total $A^B(E,\vec{k})$ for $Cu_{0.7}Pd_{0.3}$ (left) and $Cu_{0.77}Ni_{0.23}$ (right) as a function of energy at $\vec{k}=(0,0,1)$. The middle curve gives the contribution $\Delta(E)$ in (4.16). The lower curve gives the contribution from the first term on the right-hand side of (4.15).

erties based on the Lloyd formula to be equivalent to the ones that would be obtained from averaged Green's functions in theories of other types of disordered systems, particularly amorphous and liquid metals. The experiences in this paper should serve as a warning against the indiscriminate use of this approach.

There are no doubt many expressions for properties that can be derived using the ensemble-averaged Green's function $G_c(E,\vec{r},\vec{r}\,')$ that we have not mentioned in this paper or even considered.

ACKNOWLEDGMENT

This research was sponsored by the Division of Material Sciences, U. S. Department of Energy under Contract No. W-7405-eng-26 with the Union Carbide Corporation.

APPENDIX: COMMENTS ON THE SINGLE-SITE TRUNCATION

The truncation indicated in (2.41) is necessary for the NSD form of the Green's function $G_c(E,\vec{r},\vec{r}\,')$ but not the SD form. It should not be too surprising that the usual rules for applying the single-site approximation do not provide a precise guide for handling all the terms in the NSD case. Attention has been focused in most studies on what we are now calling SD properties, and these are the ones that fit most naturally into the single-site picture.

To see the effect of the truncation more clearly, it is useful to find the inverse of the matrix $\underline{M}_{nm}$ defined in (2.39) without truncation. Using the same procedures as led to (2.40), it can be shown that

$$\langle \underline{\tau}^{mm}\rangle_{nm} = \underline{\tau}_c^{mm}\underline{\tilde{D}}^m - \langle \underline{\tau}^{mn}\rangle_{mn}(\underline{m}^n - \underline{m}^c)\underline{\tau}_c^{nm}\underline{\tilde{D}}^m . \qquad \text{(A1)}$$

Inserting this into the first form in (2.40) and iterating leads to

$$\langle \underline{\tau}^{nm}\rangle = \underline{D}^n\underline{\hat{\tau}}^{nm}\underline{\tilde{D}}^m , \qquad \text{(A2)}$$

where

$$\underline{\hat{\tau}}^{nm} = \underline{\tau}_c^{nm}[1 - (\underline{m}^m - \underline{m}^c)\underline{D}^m\underline{\tau}_c^{mn}(\underline{m}^n - \underline{m}^c)\underline{D}^n\underline{\tau}_c^{nm}]^{-1} . \qquad \text{(A3)}$$

Clearly (2.41) and hence (2.43) corresponds to ignoring the denominator.

When the arguments of Lax[17] were used to arrive at the single-site approximation in the first place, such denominators were ignored when averaging over one of the sites. This is a slightly different situation. The only effect of the denominator would be to introduce structure at the resonant energies for scattering from the pair of atoms treated as a molecule. This is exactly the kind of structure that is ignored in, for example, the density of states in the single-site approximation. It would be inconsistent to include such terms in the NSD case and ignore them in the SD case.

Another study has recently been completed that is relevant to this discussion. The ensemble-averaged Green's function can be obtained from a more abstract approach by expressing it in terms of effective self-energy operators that are associated with each site. Using the cumulant averaging technique these self-energy operators may be written in terms of potential operators v_A and v_B. This technique has most often been used in connection with the one-level tight-binding model, but it has been shown to have a more general validity.[21] The terms that are included in a given approximation to the cumulant average are described by diagrams, and there is broad agreement on what classes of diagrams must be summed in order to obtain a CPA, ATA, or other approximation. Robert Mills[38] has recently evaluated the self-energy for the set of diagrams that corresponds to the CPA. When he specializes to the case of potential operators that in the position representation have the muffin-tin form, his expressions for the ensemble-averaged Green's function are identical to the ones in (2.33) and (2.44). The fact that the results we obtained by a multiple-scattering approach that includes the truncation in (2.41) are reproduced by a diagrammatic derivation lends further weight to the argument that $G_c(E, \vec{r}, \vec{r}')$ is uniquely defined within the single-site approximation.

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[30] Between E_B and E_F the multiples of 2π in the phase of the determinants in (7.1) can be taken care of automatically by first transforming the various matrices into triangular form. The determinant is then given by the product of the diagonal elements and the total phase is given by the sum of the phases of the individual diagonal elements. The phase of each diagonal element turns out to be a monotonic function of the energy and no element has a change of phase greater than 2π between E_B and E_F for any system so far investigated.

[31] For alloys having a cubic crystal structure ($\mathrm{Cu}_x\mathrm{Ni}_{1-x}$ and $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$ are both fcc) the densities of states decompose according to the irreducible representations of the cubic point group. In terms of the real spherical harmonics used in this paper, the a_{1g} representation corresponds to the singlet $l=0$, $m=0$; the t_{1u} to the triplet $l=1$, $m=\pm 1, 0$; the t_{2g} to the triplet $l=2$, $m=-2, \pm 1$; e_g to the doublet $l=2$, $m=0, 2$.

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