

Application of the Coherent Potential Approximation to a System of Muffin-Tin Potentials*

PAUL SOVEN

Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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The coherent potential approximation for the electronic density of states in a disordered substitutional alloy is applied in detail to a system of muffin-tin potentials. All expressions are formulated in terms of the phase shifts of the individual atomic scatterers. A simple example, illustrating a tight-binding system in which the pure constituents have different bandwidths, is discussed.

I. INTRODUCTION

The coherent potential approximation (CPA) has been introduced by several authors^{1,2} as a reasonable approach to the problem of calculating the electronic density of states in a disordered substitutional alloy. It has been studied extensively^{3,4} using an approximation in which the only random element was taken to be a short-ranged potential. Stating this in terms of conventional tight-binding formalism, it has always been assumed that overlap integrals, involving localized functions centered on different lattice sites, were independent of the particular type of atoms on those sites. Thus, both pure-material limits of the binary-alloy problem had identical band shapes, the only difference being the absolute position of the bands in energy.

In this paper we apply the general formalism of the CPA to a system in which all of the potentials are of the muffin-tin variety. The potential is assumed to be spherically symmetric within a sphere surrounding each atom and to be a constant (taken to be zero) between the spheres. No further assumptions are made; consequently the formalism can be used to treat any material for which the assumption on the nature of the potential is reasonable.

In Sec. II of the paper we review the CPA formalism and discuss the rather circuitous route we follow in dealing with the multiple-scattering problem in the rather complex system of potentials. In Sec. III the formulas found in Sec. II are reduced to a form that is more transparent and more amenable to calculation. Some limiting cases are discussed in Sec. IV, and a simple example illustrating the formalism is present in Sec. V.

II. FORMALISM

The alloy is characterized by a particular lattice structure and a random arrangement of potentials \bar{V}_A and \bar{V}_B . Atoms of type A and B are assumed present with concentrations x and $y=1-x$, respectively. The individual potentials are taken to be spherically symmetric within some radius R of their origin, and zero outside of this "muffin-tin" radius. The aim of the calculation is the density of electronic states $\rho(E)$, which

is given by the well-known formula

$$\pi\rho(E) = \text{Im Tr}(\bar{\mathcal{G}}), \quad (1)$$

where $\bar{\mathcal{G}}$ is the Green's function for any particular configuration of the atoms, and the angular brackets $\langle \dots \rangle$ indicate an ensemble average over all configurations.

We do not attempt to apply the CPA directly to the system of potentials \bar{V}_A and \bar{V}_B . Instead, we introduce equivalent (in a sense to be defined shortly) potentials V_A and V_B , which are of a mathematically simpler form. We shall want to compare Green's functions calculated with both pairs of potentials. When doing this we shall say that a Green's function is in the *exterior* region when *both* of its arguments lie outside of every muffin-tin sphere; otherwise it is in the *interior* region.

It is implicit in the work of Beeby,⁵ and is shown explicitly in Appendix A, that in the exterior region the Green's function $\bar{\mathcal{G}}$ is solely determined by the phase shifts of the individual potentials. Consequently, if V_A and V_B are chosen to have the same phase shifts as \bar{V}_A and \bar{V}_B , respectively, then the Green's function \mathcal{G} calculated with them will be identical to $\bar{\mathcal{G}}$ in the exterior region.

On the other hand, the Green's functions differ in the interior region. Let $\bar{\rho}_A(E)$ denote the part of the trace in (1) arising from the integration over the volume within the *sphere* surrounding a particular A atom. Then we have

$$\pi\rho_A(E) = \text{Im} \int \langle \bar{\mathcal{G}}(\mathbf{r}, \mathbf{r}) \rangle_A d\mathbf{r}. \quad (2)$$

$\langle \dots \rangle_A$ denotes a restricted average such that an A atom is definitely at the site under consideration. We also define analogous partial densities $\bar{\rho}_B$, ρ_A , and ρ_B . Note that these densities arise from an integration over the volume inside a muffin-tin sphere; consequently, they are not the complete density of states associated with any particular type of atom.

Let $\gamma_{L,A}$ ⁶ be the exact logarithmic derivative, at energy E and radius R , of the regular solution, for angular momentum L , of the Schrödinger equation involving the potential V_A . Logarithmic derivatives arising from the other potentials are denoted in a corresponding way.⁷ We also need the angular-momentum

decomposition of the Green's function⁸:

$$\mathcal{G}(\mathbf{r}, \mathbf{r}') = \sum_L Y_L(\mathbf{r}) \mathcal{G}_{LL} Y_L(\mathbf{r}'), \quad |\mathbf{r}| = |\mathbf{r}'| = R. \quad (3)$$

It then follows from Anderson's work⁹ that

$$\pi \bar{\rho}_A(E) = -R^2 \text{Im} \sum_L \langle \bar{\mathcal{G}}_{LL} \rangle_A (d\bar{\gamma}_{L,A}/dE). \quad (4)$$

Similar expressions hold for the other partial densities. Since $\mathcal{G} = \bar{\mathcal{G}}$ in the exterior region,¹⁰ we have the relation

$$\langle \bar{\mathcal{G}}_{LL} \rangle_A = \langle \mathcal{G}_{LL} \rangle_A, \quad (5)$$

which leads to the useful expression

$$\pi [\bar{\rho}_A(E) - \rho_A(E)] = -R^2 \text{Im} \sum_L \langle \mathcal{G}_{LL} \rangle_A \times d(\bar{\gamma}_{L,A} - \gamma_{L,A})/dE. \quad (6)$$

There is a similar expression for $\bar{\rho}_B - \rho_B$. Since the difference between $\text{Tr} \langle \bar{\mathcal{G}} \rangle$ and $\text{Tr} \langle \mathcal{G} \rangle$ arises from the difference in the Green's functions in the interior region, we have the following equation relating the two traces:

$$\pi^{-1} \text{Im} \text{Tr} [\langle \bar{\mathcal{G}} \rangle - \langle \mathcal{G} \rangle] = xN(\bar{\rho}_A - \rho_A) + yN(\bar{\rho}_B - \rho_B). \quad (7)$$

N is the total number of atoms. Combining (1), (6), and (7), we find the following exact equation for the density of states:

$$\pi \rho(E) = \text{Im} \text{Tr} \langle \mathcal{G} \rangle - R^2 N \text{Im} \sum_L [x \langle \mathcal{G}_{LL} \rangle_A \times d(\bar{\gamma}_{L,A} - \gamma_{L,A})/dE + y \langle \mathcal{G}_{LL} \rangle_B d(\bar{\gamma}_{L,B} - \gamma_{L,B})/dE]. \quad (8)$$

Equation (8) is useful only if we can find potentials V_A and V_B for which the multiple-scattering problem is simpler to deal with than it is for the actual potentials. We find that choosing the new potentials in the form¹¹

$$V_A(\mathbf{r}, \mathbf{r}') = \sum_L Y_L(\mathbf{r}) [\delta(\mathbf{r}' - R)/R^2] W_{L,A}(E) \times [\delta(\mathbf{r}' - R)/R^2] Y_L(\mathbf{r}') \quad (9)$$

leads to particularly straightforward manipulations. A potential of this form will have the same phase shift as V_A if the amplitudes $W_{L,A}$ satisfy the equation

$$W_{L,A}(E) = R^2 [\bar{\gamma}_{L,A} - \kappa j_l'(\kappa R)/j_l(\kappa R)]. \quad (10)$$

In this expression j_l is the regular spherical Bessel function and $\kappa = E^{1/2}$. $W_{L,B}$ is defined in a similar manner.

We observe that the potential V_A is zero inside the muffin-tin sphere. Consequently, the logarithmic derivatives entering (8) are simply¹²

$$\gamma_{L,A} = \kappa j_l'(\kappa R)/j_l(\kappa R). \quad (11)$$

We may then rewrite Eq. (8) in the form

$$\pi \rho(E) = \text{Im} \text{Tr} \langle \mathcal{G} \rangle - N \text{Im} \sum_L [x \langle \mathcal{G}_{LL} \rangle_A (dW_{L,A}/dE) + y \langle \mathcal{G}_{LL} \rangle_B (dW_{L,B}/dE)]. \quad (12)$$

We now apply the CPA equations to the "alloy" in

which the atomic potentials are V_A and V_B . The basic approach may be summarized as follows.¹⁻⁴ One introduces a "coherent potential" V , presumably similar in some respects to V_A and V_B , but in general a complex, energy-dependent quantity. (In the present situation the actual potentials are themselves energy dependent; the equation presented below impresses an additional energy dependence upon V .) One tries to choose V in such a way so that if we imagine a system having the same lattice structure as the actual alloy but with V placed on every lattice site, then the Green's function G for this system is approximately equal to the ensemble-averaged Green's function for the alloy:

$$\langle \mathcal{G} \rangle = G. \quad (13)$$

It is obviously not possible in practice to find a V for which this will be precisely true. Nonetheless, recent work^{3,4} has shown that the so-called single-site approximation is quite useful. The line of argument employing this approximation goes as follows. Relative to the "medium" in which V is placed on every lattice site, a particular A atom appears as a perturbing potential $V_A - V$. The t matrix describing the scattering produced by this potential, for a particle moving in the medium, satisfies the equation

$$T_A = (V_A - V) + (V_A - V)GT_A, \quad (14)$$

where the G in this equation is that entering into Eq. (13). An analogous quantity T_B may be defined for B atoms. Then a useful equation for calculating V has been shown to be¹

$$xT_A + yT_B = 0, \quad (15)$$

which after suitable operator manipulation may be cast into the form

$$V = U + (V - V_A)G(V - V_B), \quad (16)$$

where the mean potential U is defined by

$$U = xV_A + yV_B. \quad (17)$$

In our evaluation of Eq. (12) for the density of states we will replace $\langle \mathcal{G} \rangle$ by the coherent Green's function G . However, we also need the restricted ensemble averages of \mathcal{G} . Further development of the CPA^{3,4} shows that the equation

$$\langle \mathcal{G} \rangle_A = G^A, \quad (18)$$

where G^A satisfies

$$G^A = G + G(V_A - V)G^A, \quad (19)$$

is consistent with Eq. (13). We will therefore evaluate (12) in the form

$$\pi \rho(E) = \text{Im} \{ \text{Tr} G - N \sum_L [x G_{LL}^A (dW_{L,A}/dE) + y G_{LL}^B (dW_{L,B}/dE)] \}, \quad (20)$$

where the quantities G_{LL}^A and G_{LL}^B are defined as in Eq. (3).

We now solve Eq. (16) for the coherent potential V . It is clear by inspection that with V_A and V_B (and consequently U) in the form (9), V itself may be written

$$V(\mathbf{r}, \mathbf{r}') = \sum_{LL'} Y_L(\mathbf{r}) [\delta(\mathbf{r}-R)/R^2] W_{LL'} Y_{L'}(\mathbf{r}') \times [\delta(\mathbf{r}'-R)/R^2] \quad (21)$$

The double angular momentum subscripts on the "coherent amplitude" $W_{LL'}$ arise from the fact that G , and hence V , need only have the point group symmetry of the lattice. Substitution of (9), and its analog for V_B , (17), and (21) into (16) yields the result

$$V_{LL'} = U_L \delta_{LL'} + \sum_{L''L'''} (W_{LL''} - \delta_{LL''} W_{L,A}) G_{L''L'''} \times (W_{L''L'''} - \delta_{L''L'''} W_{L',B}), \quad (22)$$

where

$$U_L = x W_{L,A} + y W_{L,B}. \quad (23)$$

Defining matrices of the form

$$\mathbf{G} = \{G_{LL'}\}, \quad \mathbf{W} = \{W_{LL'}\}, \quad \mathbf{W}_A = \{\delta_{LL'} W_{L,A}\}$$

allows us to rewrite (22) in the compact form

$$\mathbf{W} = \mathbf{U} + (\mathbf{W} - \mathbf{W}_A) \mathbf{G} (\mathbf{W} - \mathbf{W}_B). \quad (24)$$

It should be observed that the integral equation (16) has been reduced to an algebraic one.

An essential feature of the CPA is its self-consistency aspect. The Green's function entering into Eqs. (16) and (24) is a functional of the potential V . We now develop relatively simple formulas for calculating it.

If P denotes the free-electron Green's function and V_s denotes the potential V when centered on lattice site \mathbf{R}_s , then G satisfies the equation

$$G = P + P \left(\sum_s V_s \right) G. \quad (25)$$

Since the potential in (25) is periodic in the lattice, Fourier transforms can be introduced to simplify the calculations. If we write

$$G(\mathbf{r}, \mathbf{r}') = (1/N) \sum_k G^k(\mathbf{r}, \mathbf{r}'), \quad (26)$$

where the prime indicates summation over the allowed wave vectors in the first Brillouin zone, then the Green's function G^k is related to the Korringa-Kohn-Rostoker^{13,14} (KKR) Green's function P^k through the equation

$$G^k(\mathbf{r}, \mathbf{r}') = P^k(\mathbf{r}, \mathbf{r}') + \int P^k(\mathbf{r}, \mathbf{x}) V(\mathbf{x}, \mathbf{x}') \times G^k(\mathbf{x}', \mathbf{r}') d\mathbf{x} d\mathbf{x}'. \quad (27)$$

Equation (27) is readily solved in the present case. Introducing the notation

$$G^k(L, \mathbf{r}') = \int Y_L(\mathbf{r}) [\delta(\mathbf{r}-R)/R^2] G^k(\mathbf{r}, \mathbf{r}') d\mathbf{r}, \\ G_{LL'}^k = \int G^k(L, \mathbf{r}') Y_{L'}(\mathbf{r}') [\delta(\mathbf{r}'-R)/R^2] d\mathbf{r}' \quad (28)$$

together with analogous quantities involving P^k , we

find that substitution of (21) into (27) yields

$$G^k(\mathbf{r}, \mathbf{r}') = P^k(\mathbf{r}, \mathbf{r}') + \sum_{L,L'} P^k(\mathbf{r}, L) W_{LL'} G^k(L', \mathbf{r}'). \quad (29)$$

Further integrations yield

$$G^k(L, \mathbf{r}') = P^k(L, \mathbf{r}') + \sum_{L'L''} P_{LL'}^k W_{L'L''} G^k(L'', \mathbf{r}'), \quad (30)$$

whence, by matrix inversion,

$$G^k(L, \mathbf{r}') = \sum_{L'} [1 - \mathbf{P}^k \mathbf{W}]^{-1}_{LL'} P^k(L', \mathbf{r}'). \quad (31)$$

Here and below matrices \mathbf{P}^k and \mathbf{G}^k are defined analogously to \mathbf{G} . Equations (29) and (31) may be combined to yield

$$G^k(\mathbf{r}, \mathbf{r}') = P^k(\mathbf{r}, \mathbf{r}') + \sum_{LL'} P^k(\mathbf{r}, L) \times [\mathbf{W}(1 - \mathbf{P}^k \mathbf{W})^{-1}]_{LL'} P^k(L', \mathbf{r}'). \quad (32)$$

While (32) is useful for finding the density of states, the self-consistency equation (24) only involves $G_{LL'}$. Using (30) and (29) we find

$$G_{LL'}^k = \sum_{L''} [(1 - \mathbf{P}^k \mathbf{W})^{-1}]_{LL''} P_{L''L'}^k, \quad (33a)$$

which may be written more compactly as

$$\mathbf{G}^k = (1 - \mathbf{P}^k \mathbf{W})^{-1} \mathbf{P}^k. \quad (33b)$$

Finally, using (26) we have

$$\mathbf{G} = (1/N) \sum_k (1 - \mathbf{P}^k \mathbf{W})^{-1} \mathbf{P}^k. \quad (34)$$

We now develop an expression for the density of states. According to Eq. (20) there are two different types of terms. We consider them in turn. Using Eqs. (28) and (32) the first term in (20) becomes

$$\text{Tr} G = (1/N) \sum_k \int d\mathbf{r} \{ P^k(\mathbf{r}, \mathbf{r}) + \sum_{LL'} P^k(\mathbf{r}, L) \times [\mathbf{W}(1 - \mathbf{P}^k \mathbf{W})^{-1}]_{LL'} P^k(L', \mathbf{r}) \}. \quad (35)$$

An explicit expression for $P^k(\mathbf{r}, \mathbf{r}')$ is¹⁴

$$P^k(\mathbf{r}, \mathbf{r}') = (N/\Omega) \times \sum_n \exp[i(\mathbf{k} + \mathbf{K}_n) \cdot (\mathbf{r} - \mathbf{r}')] / [E - |\mathbf{k} + \mathbf{K}_n|^2], \quad (36)$$

where Ω is the crystal volume and \mathbf{K}_n denotes a reciprocal-lattice vector. Using (36) and (28) it is easy to show that

$$\int P^k(\mathbf{r}, L) P^k(L', \mathbf{r}) d\mathbf{r} = -N (\partial P_{L'L}^k / \partial E), \quad (37)$$

in which case (35) takes the form

$$\text{Tr} G = \sum_k \left(\sum_n [E - |\mathbf{k} + \mathbf{K}_n|^2]^{-1} - \sum_{L,L'} (\partial P_{L'L}^k / \partial E) [\mathbf{W}(1 - \mathbf{P}^k \mathbf{W})^{-1}]_{LL'} \right). \quad (38)$$

We show in Appendix B that the poles of the first term, occurring at the free-electron energies, are can-

celled by corresponding poles in the second term. The first term of (20) then has the simple form¹⁵

$$\text{Im Tr}G = - \text{Im} \sum_{\mathbf{k}} \sum_{LL'} (\partial P_{L'L^{\mathbf{k}}}/\partial E) [\mathbf{W}(1 - \mathbf{P}^{\mathbf{k}}\mathbf{W})^{-1}]_{LL'}. \quad (39)$$

We also need the quantities G_{LL^A} and their analogs for B atoms.

These may be calculated by starting with Eq. (19) and performing manipulations identical to those used in passing from Eq. (29) to Eq. (35). The result is

$$G_{LL^A} = \sum_{L'} [(1 - (\mathbf{W}_A - \mathbf{W})\mathbf{G})^{-1}]_{LL'} G_{L'L}. \quad (40)$$

Our formula for the density of states then becomes

$$\begin{aligned} \pi\rho(E) = & - \text{Im} \sum_{\mathbf{k}} \sum_{L,L'} (\partial P_{L'L^{\mathbf{k}}}/\partial E) \\ & \times [\mathbf{W}(1 - \mathbf{P}^{\mathbf{k}}\mathbf{W})^{-1}]_{LL'} - N \text{Im} \sum_{LL'} G_{L'L} \\ & \times ((x dW_{L,A}/dE) [(1 - (\mathbf{W}_A - \mathbf{W})\mathbf{G})^{-1}]_{LL'} + (A \leftrightarrow B)). \end{aligned} \quad (41)$$

This expression is not quite as complicated as it appears. Considerable simplification will be effected in Sec. III.

III. REDUCTION OF FORMULAS

Our aim in this section is twofold in nature: We want to reduce the results of Sec. II to a form more amenable to calculation while at the same time demonstrating a certain internal consistency to the theory. It is intuitively clear that when all is said and done the density of states in a muffin-tin system can only depend upon the phase shifts of the individual potentials and upon other quantities which describe the structure of the material but do not depend upon the particular choice of muffin-tin radius. As we shall see, the two terms in Eq. (41) do not separately have this property while their sum in fact does.

The algebra leading to the results of this section is straightforward but somewhat long. For this reason we will set down only enough of it to indicate the general way in which the calculation proceeds.

According to Ref. 14, the KKR Green's function, for values of its arguments interior to the muffin-tin sphere, may be expressed in the form

$$\begin{aligned} P^{\mathbf{k}}(\mathbf{r}, \mathbf{r}') = & \kappa \sum_{L,L'} Y_L(r) [\delta_{LL'} j_l(\kappa r_{<}) n_l(\kappa r_{>}) \\ & + i^{l-u} j_l(\kappa r) j_{l'}(\kappa r') B_{LL^{\mathbf{k}}}^k] Y_{L'}(\mathbf{r}'), \end{aligned} \quad (42)$$

where $r_{<}$ is the smaller, and $r_{>}$ the larger, of r and r' . Using the definition of the matrix elements given in (28), it follows that we can write

$$P_{LL^{\mathbf{k}}}^{\mathbf{k}} = \kappa [j_l m \delta_{LL'} + i^{l-u} j_l j_{l'} B_{LL^{\mathbf{k}}}^k]. \quad (43)$$

Here and henceforth all Bessel functions may be assumed to have the argument κR . The potential amplitudes $W_{L,A}$ are defined by Eq. (10). Using the expres-

sion for $\tilde{\gamma}_{L,A}$ given in Schiff,¹⁶

$$\tilde{\gamma}_{L,A} = \kappa (C_{L,A} j_l' - n_l') (C_{L,A} j_l - n_l)^{-1}, \quad (44)$$

where $C_{L,A}$ is the cotangent of the phase shift for the l th partial wave, the following alternative expression for the amplitude is easily derived:

$$W_{L,A} = - [\kappa j_l (j_l C_{L,A} - n_l)]^{-1}. \quad (45)$$

We have mentioned that the coherent potential amplitudes $W_{LL'}$ are nondiagonal in general. Nonetheless, in many cases of practical interest, e.g., cubic materials for which only s , p , and d phase shifts are important, the off-diagonal elements of \mathbf{G} , and hence of \mathbf{W} , vanish because of the symmetry.¹⁷ For simplicity in what follows, we shall assume this to be the case, and simply denote the diagonal elements W_{LL} by W_L .

Under these circumstances, we can express W_L in terms of a complex "phase shift" using an equation similar to (45),

$$W_L = - [\kappa j_l (j_l C_L - n_l)]^{-1}, \quad (46)$$

which should be viewed as the definition of the quantities C_L . Substitution of (43) and (46) into Eq. (32) may be shown to lead to

$$\begin{aligned} G_{LL^{\mathbf{k}}}^{\mathbf{k}} = & \kappa j_l (j_l C_L - n_l) \delta_{LL'} - \kappa i^{l-u} (j_l C_L - n_l) \\ & \times (j_{l'} C_{L'} - n_{l'}) (\mathbf{C} + \mathbf{B}^{\mathbf{k}})^{-1}_{LL'}, \end{aligned} \quad (47)$$

where \mathbf{C} and $\mathbf{B}^{\mathbf{k}}$ are matrices formed from $C_L \delta_{LL'}$ and $B_{LL^{\mathbf{k}}}^{\mathbf{k}}$, respectively. Summation over the Brillouin Zone results in the following expression:

$$G_{LL} = \kappa j_l (j_l C_L - n_l) - \kappa (j_l C_L - n_l)^2 g_L, \quad (48)$$

where

$$g_L = (1/N) \sum_{\mathbf{k}} (\mathbf{C} + \mathbf{B}^{\mathbf{k}})^{-1}_{LL}. \quad (49)$$

We can now find a simple form of Eq. (24). Substitution of (45) and its analog for B atoms, (46) and (48) into (24) yields the system of equations

$$C_L = C_{L,av} + (C_{L,A} - C_L) g_L (C_{L,B} - C_L), \quad (50)$$

in which

$$C_{L,av} = x C_{L,A} + y C_{L,B}. \quad (51)$$

One should note that the various C_L are coupled, because each g_L depends upon all of them.¹⁸

We now consider Eq. (41) for the density of states. Substituting Eqs. (43) and (46) into the first term of (41) yields

$$[\mathbf{W}(1 - \mathbf{P}^{\mathbf{k}}\mathbf{W})^{-1}]_{LL'} = - i^{l-u} (\kappa j_l j_{l'})^{-1} (\mathbf{C} + \mathbf{B}^{\mathbf{k}})^{-1}_{LL'}, \quad (52)$$

where $\mathbf{B}^{\mathbf{k}}$ is the matrix formed from the $B_{LL^{\mathbf{k}}}^{\mathbf{k}}$ of Eq. (43) and \mathbf{C} is the diagonal matrix formed from the complex cotangents C_L . The energy derivative occurring in (41) may be determined using (43):

$$\begin{aligned} (\partial/\partial E) P_{LL^{\mathbf{k}}}^{\mathbf{k}} = & i^{l-u} [\delta_{LL'} (d/dE) (\kappa j_l n_l) \\ & + B_{L'L^{\mathbf{k}}}^{\mathbf{k}} (d/dE) (\kappa j_{l'} j_l) + \kappa j_l j_{l'} (\partial/\partial E) B_{L'L^{\mathbf{k}}}^{\mathbf{k}}]. \end{aligned} \quad (53)$$

Combining (52) and (53), the first term on the right-hand side of (41) takes the form

$$\text{Im} \sum_L \left\{ \sum'_k [(\partial \mathbf{B}^k / \partial E) (\mathbf{C} + \mathbf{B}^k)^{-1}]_{LL} + N g_L (\kappa j i^2)^{-1} [(d/dE) (\kappa j m_i) - C_L (d/dE) (\kappa j i^2)] \right\}, \quad (54)$$

where g_L is defined by Eq. (49).

The second term in (41) may be reduced as follows. Because of our assumption on the high symmetry of the system, all of the matrices appearing there are diagonal. Substitution of (45), (46), and (48) yields the relation

$$\begin{aligned} \text{Im} \{ (x d \mathbf{W}_A / dE) [1 - (\mathbf{W}_A - \mathbf{W}) \mathbf{G}]^{-1} \}_{LL} \\ = y \text{Im} [\kappa j i^2 (C_{L,A} - C_L)]^{-1} \\ \times [\kappa j i^2 (dC_{L,A} / dE) + C_{L,A} (d/dE) (\kappa j i^2) - (d/dE) (\kappa j m_i)] \end{aligned} \quad (55)$$

We note in passing that (55) is an equation relating the imaginary parts of the two expressions; the real parts are not identical. Adding Eq. (55) to the corresponding equation for B atoms, and making use of the defining equation (46), the entire second term of (41) takes the form

$$\begin{aligned} -N \text{Im} \sum_L \{ y (C_{L,A} - C_L)^{-1} (dC_{L,A} / dE) \\ + x (C_{L,B} - C_L)^{-1} (dC_{L,B} / dE) + (\kappa j i^2)^{-1} g_L \\ \times [(d/dE) (\kappa j m_i) - C_L (d/dE) (\kappa j i^2)] \}. \end{aligned} \quad (56)$$

Our expression for the density of states is obtained by adding (54) and (56). All of the terms involving Bessel functions cancel. The result is

$$\begin{aligned} \pi \rho(E) = \text{Im} \sum_L \sum'_k [(\mathbf{C} + \mathbf{B}^k)^{-1} (\partial \mathbf{B}^k / \partial E)]_{LL} \\ + N \text{Im} \sum_L \{ y (C_L - C_{L,A})^{-1} (dC_{L,A} / dE) \\ + x (C_L - C_{L,B})^{-1} (dC_{L,B} / dE) \}. \end{aligned} \quad (57)$$

IV. SPECIAL LIMITS

We first consider the case in which the atoms are identical. Using Eq. (50), it is clear that as $C_{L,B} \rightarrow C_{L,A}$, $C_L \rightarrow C_{L,A}$ as well. The limiting value achieved by the second term of (59) may be determined by using the expression

$$y (C_L - C_{L,A})^{-1} + x (C_L - C_{L,B})^{-1} = g_L, \quad (58)$$

which follows immediately from Eq. (50). In view of the definition (49), the equation for the density of states becomes

$$\begin{aligned} \pi \rho^0(E) = \text{Im} \sum'_k \sum'_L \{ (\mathbf{C}_A + \mathbf{B}^k)^{-1} \\ \times [d \mathbf{C}_A / dE + \partial \mathbf{B}^k / \partial E] \}_{LL}. \end{aligned} \quad (59)$$

Equation (59) represents an exact, if not particularly useful, expression for the density of states of an ordered system of A atoms. It may be shown to reduce to the correct result in the limit of free electrons.

Velický *et al.*³ have shown that, for the tight-binding model they considered, the CPA reduces to the exact Koster-Slater¹⁹ result as the concentration of one of the constituents vanishes. It is of interest to study the same limit for the present formalism.

We consider the limit $y \rightarrow 0$ and deduce a formula for the density of states correct to the first order in y . The quantities g_L and C_L may be expanded as a power series in y ,

$$g_L = \sum_n g_L^{(n)} y^n, \quad (60)$$

and similarly for C_L . If we substitute this expression in Eq. (50), and introduce the notation $\Delta_L = C_{L,B} - C_{L,A}$, then we find the expression

$$\begin{aligned} C_L = C_{L,A} + y \Delta_L (1 + \Delta_L g_L^{(0)})^{-1} \\ + (y \Delta_L)^2 (1 + \Delta_L g_L^{(0)})^{-2} [g_L^{(0)} (1 + \Delta_L g_L^{(0)})^{-1} - g_L^{(1)}], \end{aligned} \quad (61)$$

correct to terms of order y^2 . Using this result the second term in Eq. (57) may be written

$$\begin{aligned} N \text{Im} \sum_L [g_L^{(0)} (dC_{L,A} / dE) + y g_L^{(1)} (dC_{L,A} / dE) \\ + y g_L^{(0)} (1 + \Delta_L g_L^{(0)}) (d\Delta_L / dE)] \end{aligned} \quad (62)$$

correct to first order in y . It is clear that $g_L^{(0)} = g_{L,A}$, the quantity to which g_L reduces when $C_L \rightarrow C_{L,A}$. The term $g_L^{(1)}$ is obtained by expanding (49) in a power series in y . The result is

$$\begin{aligned} g_L^{(1)} = - (1/N) \sum_{L'} \Delta_{L'} (1 + \Delta_{L'} g_{L'}^{(0)}) \\ \times \sum'_k (\mathbf{C}_A + \mathbf{B}^k)^{-1}_{L'L} (\mathbf{C}_A + \mathbf{B}^k)_{LL'}^{-1}. \end{aligned} \quad (63)$$

The first term in (57) may be expanded to yield

$$\begin{aligned} \sum'_k \sum'_L [(\mathbf{C} + \mathbf{B}^k)^{-1} (\partial \mathbf{B}^k / \partial E)]_{LL} \\ - y \sum'_k \sum'_L \Delta_L (1 + \Delta_L g_L^{(0)})^{-1} \\ \times [(\mathbf{C}_A + \mathbf{B})^{-1} (\partial \mathbf{B}^k / \partial E) (\mathbf{C}_A + \mathbf{B})^{-1}]_{LL}. \end{aligned} \quad (64)$$

Combining (62), (63), and (64), the expression for the density of states reduces to

$$\begin{aligned} \rho(E) = \rho^0(E) + (Ny/\pi) \text{Im} \sum_L (1 + \Delta_L g_{L,A})^{-1} \\ \times (d/dE) (\Delta_L g_{L,A}). \end{aligned} \quad (65)$$

The second term in (65) is, except for the factor N , the change in the density of states per B impurity. It is an exact result for the single-impurity problem and may also be derived by more direct techniques.²⁰ Bound states occur when $1 + \Delta_L g_{L,A}$ vanishes outside of the bands of the pure A material. It may be shown that this condition for a bound state is identical to that derived by Beeby²¹ and Johnson.²²

V. ELEMENTARY EXAMPLE

In order to illustrate the formalism, as well as to make contact with earlier work using the CPA, we

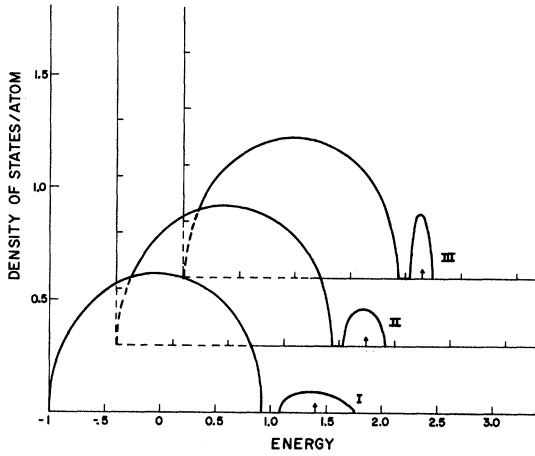


FIG. 1. Density of states for three alloy systems. Pure A has a half-bandwidth of unity, while pure B has a half-bandwidth of 2, 1, and 0.5, for cases I, II, and III, respectively. The arrows indicate the position of the bound state produced by a B impurity in a pure A matrix. The atomic concentration of type B is 0.05. The energy is in dimensionless units.

consider a particularly simple example. We assume that the only nonvanishing phase shifts are the s -wave ones. In addition, we neglect the off-diagonal components of the matrix B^k and consider only the diagonal one corresponding to $l=0$. The KKR Green's functions are singular at the free-electron energies. For negative energies, however, they are rather smooth, slowly varying functions of energy. To construct a tractable problem we assume that the single component of B that we keep has this smooth behavior. In fact, we will assume it to be constant in energy and to depend only upon the wave vector.

The self-consistency equation revolves around the quantity g_L defined in (49). We introduce a distribution function for B^k by the relation²³

$$f(b) = (1/N) \sum_k \delta(b - B^k), \quad (66)$$

in which case g is given by

$$g = \int f(b) (C + b)^{-1} db. \quad (67)$$

It is clear that the integral of $f(b)$ over the domain of b is unity.

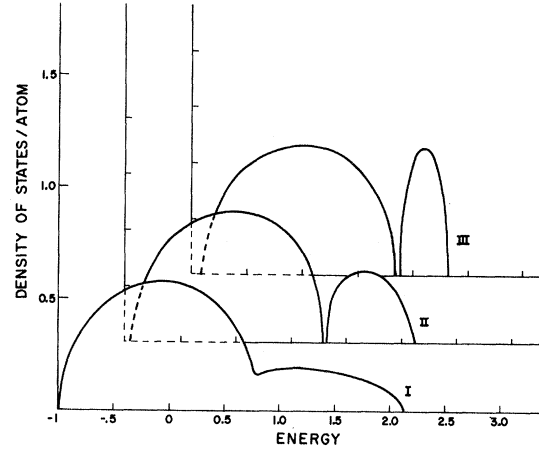
For reasons which will be clear momentarily we take $f(b)$ in the form

$$\begin{aligned} f(b) &= (2/\pi) (1 - b^2)^{1/2}, & |b| < 1 \\ &= 0, & |b| > 1 \end{aligned} \quad (68)$$

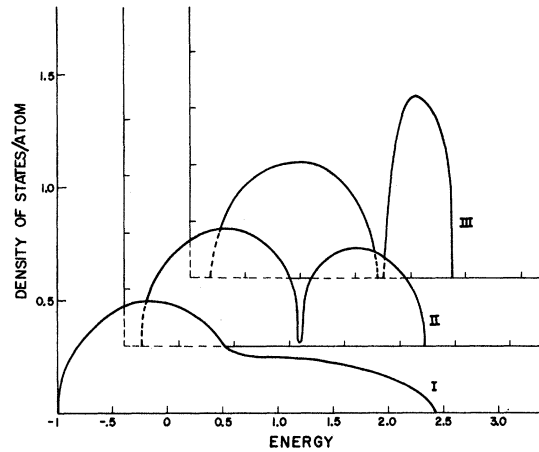
in the appropriate system of units. One then finds

$$g = 2[C - (C^2 - 1)^{1/2}]. \quad (69)$$

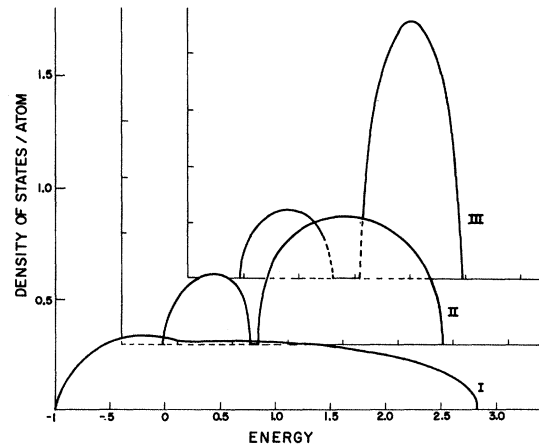
It is known that tight-binding character of energy bands arises from a resonant behavior of one of the phase shifts.²⁴ We accordingly assume that C_A has the



(a)



(b)



(c)

FIG. 2. Density of states for three alloy systems. Pure A has a half-bandwidth of unity, while pure B has a half-bandwidth of 2, 1, and 0.5, for cases I, II, and III, respectively. The atomic concentrations of B are 0.20, 0.40, and 0.80 for (a), (b), and (c), respectively. The energy is in dimensionless units.

form

$$C_A(E) = (E_A - E)/\Gamma_A, \quad (70)$$

with an analogous equation, involving E_B and Γ_B , for C_B . Use of Eq. (59) shows that the state density in a pure A system is given by

$$\rho_A(E) = (2N/\pi)[(\Gamma_A)^2 - (E - E_A)^2]^{1/2}. \quad (71)$$

Equation (71) shows that the model is very similar to that considered by Velicky *et al.*³ in their analysis of the CPA. But whereas in the work of those authors both pure materials had identical bandwidths (the whole effect of alloying arising from a quantity analogous to $E_B - E_A$) in the present case the pure materials can have different bandwidths as well.

Figures 1 and 2 show the density of states, for four different concentrations of constituent B , for three different alloy systems. In all three systems we took $E_A = 0$, $\Gamma_A = 1.0$, and $E_B = 1.0$, but Γ_B was given the values 2.0, 1., and 0.5. The case where $\Gamma_B = 1.0$ is identical to one of those treated in Ref. 3, while the other two show the effect of alloying materials with different bandwidths. The arrows in Fig. 1, which illustrates the results for a rather low concentration of type B , indicates the position of the bound state of an isolated B impurity in otherwise pure A material. The position of the bound state was calculated using Eq. (65). While we have not discussed the question of the localization of states near either type of atom, it is clear that starting from Eq. (4) formulas for the local density of states can be developed. The results of such calculations indicate that the states in the upper part of the split band illustrated in Fig. 1 are largely localized about B atoms. The width of the upper peak is, however, overestimated by the CPA.³ The three parts of Fig. 2 show what happens as the concentration of B atoms is increased. It is clear that the relative widths of the pure material bands is an important parameter. In case I, for example, the diagonal perturbation $E_B - E_A = 1.0$ is, for small concentrations of B , a rather large one compared to the bandwidth of the dominant material. But as more A is added it becomes relatively less important. Hence the transition from the split-band limit of Fig. 1 to the relatively structureless single-band limit of Fig. 2(c). Case II is symmetric in the two constituents, while III illustrates behavior essentially opposite to that of I.

APPENDIX A

We prove in this appendix that if \mathbf{r} and \mathbf{r}' lie outside of the range of every potential of the system (i.e., they are the position vectors of points in the zero potential region) then the value of $\mathcal{G}(\mathbf{r}, \mathbf{r}')$ is determined solely by the phase shifts of the two potentials. Using the language of scattering theory, the previous statement is equivalent to one to the effect that only the on-energy-shell matrix elements of the atomic t matrices are needed to describe propagation in the zero potential region.

The proof is based upon Beeby's work.⁵ Let t_α denote the t matrix corresponding to the potential centered on site \mathbf{R}_α , and let P be the free-electron Green's function. The complete t matrix of the system is given by

$$T = \sum_\alpha t_\alpha + \sum_\alpha \sum_{\beta \neq \alpha} t_\alpha P t_\beta + \dots \quad (A1)$$

and the exact Green's function by

$$\mathcal{G} = P + PTP. \quad (A2)$$

Each atomic t matrix has the form

$$\langle \mathbf{x} | t_\alpha | \mathbf{x}' \rangle = t_\alpha(\mathbf{x} - \mathbf{R}_\alpha, \mathbf{x}' - \mathbf{R}_\alpha), \quad (A3)$$

where

$$t_\alpha(\mathbf{y}, \mathbf{y}') = \sum_L Y_L(\mathbf{y}) t_{l,\alpha}(y, y') Y_L(\mathbf{y}'). \quad (A4)$$

The radial part $t_{l,\alpha}(y, y')$ vanishes if y and/or y' are greater than R .

Consider the series (A1). The second term has the form

$$\langle \mathbf{x} | t_\alpha P t_\beta | \mathbf{x}' \rangle = \int t_\alpha(\mathbf{x} - \mathbf{R}_\alpha, \mathbf{y}) P(\mathbf{y} - \mathbf{y}' + \mathbf{R}_\alpha - \mathbf{R}_\beta) \times t_\beta(\mathbf{y}', \mathbf{x}' - \mathbf{R}_\beta) d\mathbf{y} d\mathbf{y}'. \quad (A5)$$

Using the expansion⁵

$$P(\mathbf{y} - \mathbf{y}' + \mathbf{R}_\alpha - \mathbf{R}_\beta) = \sum_{L, L'} Y_L(\mathbf{y}) j_l(\kappa y) S_{LL'}(\mathbf{R}_\alpha - \mathbf{R}_\beta) \times j_{l'}(\kappa y') Y_{L'}(\mathbf{y}'), \quad (A6)$$

which is valid if $y + y' < |\mathbf{R}_\alpha - \mathbf{R}_\beta|$, together with the decomposition (A4), it is clear that the \mathbf{y} and \mathbf{y}' integrations reduce to terms of the sort

$$\int t_{l\alpha}(|\mathbf{x} - \mathbf{R}_\alpha|, y) j_l(\kappa y) y^2 dy \equiv t_{l,\alpha}(|\mathbf{x} - \mathbf{R}_\alpha|, \kappa), \quad (A7)$$

using Beeby's notation. The quantities $S_{LL'}$ only depend upon the relative position of the sites in question. In the higher-order terms of (A1) one encounters terms of the type (A7) as well as others of the form

$$\int j_l(\kappa y) t_{l\alpha}(y, y') j_{l'}(\kappa y') y^2 dy y'^2 dy' \equiv t_{l\alpha}(\kappa, \kappa). \quad (A8)$$

Thus the second- and higher-order terms of (A1) are composed of expressions of the form

$$Y_L(\mathbf{x} - \mathbf{R}_\alpha) t_{l\alpha}(|\mathbf{x} - \mathbf{R}_\alpha|, \kappa) [\dots] t_{l'\beta}(\kappa, |\mathbf{x}' - \mathbf{R}_\beta|) \times Y_{L'}(\mathbf{x}' - \mathbf{R}_\beta), \quad (A9)$$

where $[\dots]$ represents many factors of $S_{LL'}$ and of terms (A8). The first term in (A1) is simply a sum over α and L of the expressions

$$Y_L(\mathbf{x} - \mathbf{R}_\alpha) t_{l\alpha}(|\mathbf{x} - \mathbf{R}_\alpha|, |\mathbf{x}' - \mathbf{R}_\alpha|) Y_L(\mathbf{x}' - \mathbf{R}_\alpha). \quad (A10)$$

We expand the term PTP in spherical harmonics centered on some particular atomic site. Then using either (A6) or the familiar expression

$$P(\mathbf{x}, \mathbf{y}) = \kappa \sum_L Y_L(\mathbf{x}) [n_l(\kappa x) + i j_l(\kappa x)] j_l(\kappa y) Y_L(\mathbf{y}), \quad (A11)$$

valid if $x > y$, one is led to the conclusion that the t_α

enter the formulas only through expressions of the form (A8). But Beeby has shown that $t_{i\alpha}(\kappa, \kappa)$ depends only upon the phase shifts at the energy $E = \kappa^2$. Consequently the Green's function $\mathcal{G}(\mathbf{r}, \mathbf{r}')$ is uniquely determined by the phase shifts provided that $|\mathbf{r} - \mathbf{R}_\alpha| > R$ and $|\mathbf{r}' - \mathbf{R}_\alpha| > R$ for every \mathbf{R}_α .

APPENDIX B

The point to be proved is that Eq. (38) does not have poles at the free-electron energies $E = |\mathbf{k} + \mathbf{K}_n|^2$. Let $\eta = E - k^2$. Then we must show that, e.g.,

$$\lim_{\eta \rightarrow 0} \eta \sum_{L, L'} (\partial P_{L'L}^k / \partial E) [\mathbf{W}(1 - \mathbf{P}^k \mathbf{W})^{-1}]_{LL'} = 1. \quad (\text{B1})$$

Use of Eq. (36) shows that one can write

$$\mathbf{P}^k = \eta^{-1} \mathbf{A} + \mathbf{F}, \quad (\text{B2})$$

where

$$A_{LL'} = (N/\Omega) (4\pi)^2 i^{l'-l} j_l(kR) Y_L(\mathbf{k}) j_{l'}(kR) Y_{L'}(\mathbf{k}) \quad (\text{B3})$$

and \mathbf{F} is an analytic function of energy near $\eta = 0$. Using (B2) one finds the relation

$$\mathbf{W}(1 - \mathbf{P}^k \mathbf{W})^{-1} = \eta (\eta \mathbf{X} - \mathbf{A})^{-1}, \quad (\text{B4})$$

where

$$\mathbf{X} = \mathbf{W}^{-1} - \mathbf{F}. \quad (\text{B5})$$

Consequently (B1) takes the form

$$\lim_{\eta \rightarrow 0} \sum_{L, L'} [-A_{LL'} + \eta^2 (\partial F_{LL'} / \partial E)] [(\eta \mathbf{X} - \mathbf{A})^{-1}]_{LL'} = 1. \quad (\text{B6})$$

Assume that we are dealing with $N \times N$ matrices. (The result is independent of N , but it is easiest to proceed in this way.) Let $M_{LL'}(\mathbf{Q})$ denote the (L, L') cofactor of some matrix \mathbf{Q} , and $||\mathbf{Q}||$ be the determinant of \mathbf{Q} . The usual formula for the inverse of a matrix tells us that

$$[(\eta \mathbf{X} - \mathbf{A})^{-1}]_{L'L} = M_{LL'}(\eta \mathbf{X} - \mathbf{A}) / ||\eta \mathbf{X} - \mathbf{A}||. \quad (\text{B7})$$

Expand $||\eta \mathbf{X} - \mathbf{A}||$ as a sum of powers of η . Using the rule for differentiating determinants, it follows that the coefficient of η^n ($0 \leq n \leq N$) is the sum of all determinants formed from n columns of the matrix \mathbf{X} and $(N-n)$ columns of the matrix $(-\mathbf{A})$. But (B3) shows that $A_{LL'}$ is a product of a factor depending only upon L times another factor depending only upon L' . Consequently, any such determinant in which two or more columns are taken from $(-\mathbf{A})$ necessarily vanishes. We are therefore led to the expansion

$$||\eta \mathbf{X} - \mathbf{A}|| = -\eta^{N-1} \sum_{LL'} A_{LL'} M_{LL'}(\mathbf{X}) + o(\eta^N), \quad (\text{B8})$$

where the coefficient of η^{N-1} is the sum of all of the above described determinants with only one column coming from $(-\mathbf{A})$.

Since the minor $M_{LL'}(\eta \mathbf{X} - \mathbf{A})$ is an $(N-1)$ st-order determinant of the same form as $||\eta \mathbf{X} - \mathbf{A}||$, the lowest power of η occurring in it must be η^{N-2} . Consequently, the term in $F_{LL'}$ contributes nothing to the limit (36) and may be neglected.

Using (B6)-(B8), the point to be proven becomes

$$\lim_{\eta \rightarrow 0} [-\sum_{L, L'} A_{LL'} M_{LL'}(\eta \mathbf{X} + \mathbf{A})] \times [-\eta^{N-1} \sum_{LL'} A_{LL'} M_{LL'}(\mathbf{X})]^{-1} = 1. \quad (\text{B9})$$

The numerator of (B9) is the sum of all determinants formed by successively replacing one row of the matrix $\eta \mathbf{X} - \mathbf{A}$ by the corresponding row of the matrix $(-\mathbf{A})$. If we let D_L denote the L th such determinant

$$D_L = -\sum_{L'} A_{LL'} M_{LL'}(\eta \mathbf{X} - \mathbf{A}), \quad (\text{B10})$$

then arguments identical to those used in deducing (B8) show that

$$D_L = -\eta^{N-1} \sum_{L'} A_{LL'} M_{LL'}(\mathbf{X}). \quad (\text{B11})$$

Consequently the numerator of (B9) is identical to the denominator, and the limit is indeed unity.

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¹ Paul Soven, Phys. Rev. **156**, 809 (1967).

² Y. Onodera and J. Yoyozawa, J. Phys. Soc. Japan **24**, 1341 (1968).

³ B. Velický, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. **175**, 747 (1968).

⁴ Paul Soven, Phys. Rev. **178**, 1136 (1969).

⁵ J. L. Beeby, Proc. Phys. Soc. (London) **A279**, 82 (1964).

⁶ L denotes both angular momentum quantum numbers.

⁷ While $\gamma_{L,A}$ must equal $\bar{\gamma}_{L,A}$ at energy E , the slopes and higher derivatives need not be identical.

⁸ $Y_L(\mathbf{r})$ is the real spherical harmonic as a function of the angles of the vector \mathbf{r} .

⁹ P. W. Anderson and W. L. McMillan, in *Theory of Magnetism in Transition Metals, Proceedings of the International School of Physics "Enrico Fermi," Course XXXVII*, edited by H. Suhl (Academic, New York 1967), p. 60.

¹⁰ By continuity arguments it is clear that the Green's functions must be identical on, as well as outside of, the muffin-tin spheres.

¹¹ J. C. Slater, Phys. Rev. **145**, 599 (1966); Paul Soven, *ibid.* **151**, 539 (1966).

¹² Since the $\gamma_{L,A}$ in (8) arise from an integration over the volume interior to each atomic sphere, it is clear that they are to be evaluated at radius $R=0$; hence the Bessel functions.

¹³ J. Korringa, Physics **13**, 392 (1947).

¹⁴ W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

¹⁵ In this equation we mean that a principal part of (36) is used to form the energy derivative. Alternatively, the principal part can be taken throughout and W given a small imaginary part.

¹⁶ Leonard I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1955), p. 107.

¹⁷ Of course all diagonal elements for given l need not be identical.

¹⁸ Here and below all equations are formulated in terms of cotangents. For weak scatters a "tangent" formulation is more appropriate and can easily be written down.

¹⁹ G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

²⁰ R. H. Lasseter and Paul Soven (unpublished).

²¹ J. L. Beeby, Proc. Roy. Soc. (London) **A302**, 113 (1967).

²² Keith H. Johnson, J. Chem. Phys. **45**, 3085 (1966).

²³ We omit all angular momentum subscripts in this section. B^k refers to the diagonal component of \mathbf{B}^k corresponding to $l=0$.

²⁴ V. Heine, Phys. Rev. **153**, 673 (1967).