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Theory of the self-energy and its single-site approximations for disordered alloys

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We introduce a projection operator to denote the configuration average for an arbitrarily disordered system. This allows us to derive a formal, exact expression for the self-energy of the average propagator in terms of the disordered part of the Hamiltonian of the system. We use this expression to give a new formulation of the single-site approximations for the equilibrium properties of compositionally disordered alloys. Appropriate choices of the periodic reference medium yield the standard average *t*-matrix (ATA) and coherent potential approximations (CPA). The general expression for the self-energy is shown to satisfy a relation similar to the optical theorem for the *t* matrix. This relation is used to prove directly that the macroscopic density of states is non-negative. This method is used to show easily and generally that both ATA and CPA yield non-negative density of states.

I. INTRODUCTION

The recent progress made in the understanding of the equilibrium electron, phonon, magnon, and exciton properties in disordered alloys rests largely on the introduction of the single-site approximations (SSA), which describe these properties reasonably well throughout the whole range of the concentrations of the constituent atoms.[1-3] The main examples of the SSA are the average t-matrix[4,5] approximation (ATA) and the coherent potential[6,7] approximation (CPA), which differ in the choice of the periodic reference system. These schemes have been formulated in various equivalent ways, such as the decoupling method[1,3] based on the multiple-scattering theory,[8] the corrected cumulant expansion[9,10] and the related diagrammatic method,[1,11] and others.[1,3] Numerous suggestions have been made to extend the SSA in order to describe the effects of pairs and higher-order clusters of the disordered atoms, but they all have proved unsatisfactory.[1] Only recently a promising theory[12,13] has been proposed that deals successfully with this important question.

In contrast to the theory of the equilibrium properties, the theory of the electronic transport properties of a disordered alloy is not as fully developed. For instance, only the analog of the CPA has been formulated so far.[14,15] In fact, this formulation of the theory of transport properties requires *additional ad hoc* decoupling approximations (or, selections of diagrams) over and above the similarly *ad hoc* decoupling schemes used in the theory of the equilibrium properties. Yet, in a disordered alloy the same static arrangement of the constituent atoms determines both the equilibrium electronic properties and the residual (or, low-temperature) transport properties. It is, therefore, highly desirable to develop a theory of the residual transport phenomena in disordered alloys that is based on the same general theoretical framework as the SSA for the equilibrium phenomena.

We have proposed[16] a new formulation of the theory of the SSA for both equilibrium and transport electronic properties along entirely parallel lines. Both schemes ATA and CPA can be obtained by the appropriate choice of the periodic reference Hamiltonian for the alloy.

In this paper we present the details of this new formulation of the SSA for the equilibrium properties and point out some of its advantages. For concreteness we present it in the context of the electronic properties of a disordered alloy.

In the following section, after defining the quantities of interest for the calculation of the macroscopic density of states $\rho(E)$ of a general disordered system, we derive an exact expression for the self-energy of the average propagator in terms of the arbitrarily disordered part of the Hamiltonian of the alloy. In this formulation the introduction of a projection operator to effect the average over any appropriate ensemble representative of the disorder plays a fundamental role. In spite of its formal character, this expression of the self-energy is a convenient and rigorous basis for various approximation schemes, systematic or not.

For the case of a disordered alloy with a potential in the form of a sum of arbitrary atomic potentials disorderly distributed over a lattice, we formulate in Sec. III the SSA as a one-step approximation scheme for the self-energy. Both ATA and CPA are discussed and the equivalence of the intuitive and the self-consistent approaches to the CPA is demonstrated very simply.

The central quantity of interest in the study of the equilibrium and some other properties of disordered systems is the average density of states $\rho(E)$. By definition this is a non-negative quantity, and any approximation to it must preserve this property as a minimum requirement for obvious physical reasons. The question of the sign of $\rho(E)$ under various approximations has been discussed recently,[17,18,12] where it was pointed out that some approximation methods yield negative $\rho(E)$, especially in the case of strong-scattering systems. However, it was shown[17] through rather involved calculations that both the ATA and the CPA for the muffin-tin model of a completely random alloy yield a non-negative density of states.

We demonstrate in Sec. IV that our formulation allows us to prove that the self-energy satisfies an "optical theorem," which shows directly and simply that the density of states $\rho(E)$ is indeed non-negative. This method is then applied in Sec. V and VI to the cases of ATA and CPA, respectively, where it is demonstrated in simple steps that in both approximations schemes $\rho(E) \geq 0$ for arbitrary Hermitian atomic potentials and arbitrary disorder.

II. GENERAL THEORY OF THE SELF-ENERGY

In this section we present a general theory of the average propagator, and in particular its self-energy, that is applicable to a large class of disordered systems. The method used is analogous to the one employed before[19] for the theory of transport in imperfect crystals.

We consider the excitations of a general disordered system that can be described by the Hamiltonian

$$H = H_o + U , \qquad (2.1)$$

where H_o denotes an ordered part of the system and U describes the disordered part that depends on the configuration of the disordered elements of the system. Clearly the separation (2.1) is not unique, since we can rewrite it as

$$H = H_r + V \equiv (H_o + U_0) + (U - U_0) , \qquad (2.2)$$

where U_0 is an arbitrary configuration-independent operator. $H_r \equiv H_o + U_0$ is now the Hamiltonian for an "ordered" reference system and $V \equiv U - U_0$ is the new configuration-dependent part.

For the macroscopic properties of the system we are interested[1] in the average over all possible configurations of the system weighted with their appropriate probabilities, which, for any configuration-dependent quantity Q, we denote by $\langle Q \rangle$. This averaging operation is at the basis of the development of our theory. We thus introduce an operator P to denote the operation of taking the average over the ensemble representative of the disorder of the system, i.e., for any quantity Q we let

$$PQ \equiv \langle Q \rangle . \qquad (2.3)$$

Clearly $P^2 = P$, i.e., P is a projection operator. The fluctuation part of Q is then given by

$$P'Q \equiv (1 - P)Q = Q - \langle Q \rangle . \qquad (2.4)$$

We note that $P'^2 = P'$ and $PP' = P'P = 0$.

The macroscopic equilibrium properties of the system described by the Hamiltonian (2.2) are determined by the density of states with energy E, given by

$$\rho(E) = \mathrm{Tr}\,\langle \delta(E - H) \rangle = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\,\langle G(E^+) \rangle , \qquad (2.5)$$

where Tr denotes the trace over the Hilbert space of the states of H, Im stands for the imaginary part, and $E^+ \equiv E + i\epsilon$ with ϵ a positive infinitesimal. We are thus led to consider the average of the propagator

$$G(z) \equiv (z - H)^{-1} \qquad (2.6)$$

with z a complex number, i.e., $\langle G(z) \rangle$.

In our theory of $\langle G(z) \rangle$, we begin by considering the equation that $G(z)$ satisfies. From its definition (2.6) we have obviously

$$(z - H)G(z) = 1 . \qquad (2.7)$$

We then find from (2.7) an exact equation for $\langle G(z) \rangle$ by the introduction of the projection operator P of (2.3). To accomplish this[19] we write in (2.7)

$$G = PG + P'G = \langle G \rangle + P'G , \qquad (2.8)$$

and then operate on it with P and P' separately. We obtain

$$(z - H_r - PV)\langle G \rangle - PVP'G = 1, \qquad (2.9)$$

$$(z - H_r - P'V)P'G - P'V\langle G \rangle = 0, \qquad (2.10)$$

since $[H_r, P] = [H_r, P'] = PP' = 0$. From (2.10) we obtain $P'G$ in terms of $\langle G \rangle$ and then substitute it into (2.9) to find an exact equation for $\langle G \rangle$, namely,

$$[z - H_r - PV - PV(z - H_r - P'V)^{-1}P'V]\langle G \rangle = 1. \qquad (2.11)$$

Since $\langle G \rangle$ in (2.11) is already averaged, the operator

$$W(z) \equiv P\{V + V(z - H_r - P'V)^{-1}P'V\} \qquad (2.12)$$

with the curly brackets denoting the extent of the operations P and P', is the so-called self-energy operator with respect to the reference Hamiltonian H_r. We thus have

$$[z - H_r - W(z)]\langle G \rangle = 1. \qquad (2.13)$$

Note that in expression (2.12) for $W(z)$ the operator P' that appears in $(z - H_r - P'V)^{-1}$ operates on everything to its right. To make this explicit we may write

$$(z - H_r - P'V)^{-1} = g + gP'Vg + gP'VgP'Vg + \cdots , \tag{2.14}$$

where

$$g(z) \equiv (z - H_r)^{-1} \; . \tag{2.15}$$

Thus, Eq. (2.12) for the self-energy $W(z)$ reads more explicitly

$$W(z) = P\mathcal{T}(z) \tag{2.16a}$$

with

$$\mathcal{T}(z) = V + VgP'V + VgP'VgP'V + \cdots = V(1 - gP'V)^{-1}. \tag{2.16b}$$

This is an exact, formal expression for the self-energy in terms of the general configuration-dependent operator V referred to the arbitrarily chosen periodic Hamiltonian H_r, the propagator for the reference medium $g(z)$, and the general configuration-averaging operator P. It provides, therefore, a convenient and rigorous basis for the formulation of various approximation schemes.

The self-energy $W(z)$ can also be expressed in terms of the t matrix $T(z)$ for the disordered potential V, again referred to the reference Hamiltonian H_r, namely,

$$T(z) \equiv V + VgV + VgVgV + \cdots = V(1 - gV)^{-1}. \tag{2.17}$$

We note that $\mathcal{T}(z)$ is given by the same series in V as $T(z)$, except that $\mathcal{T}(z)$ has the propagator $g(z)P'$ instead of $g(z)$. To obtain $W(z)$ in terms of $T(z)$ from (2.16) and (2.17), we note that we must write $P' = 1 - P$ in (2.16b) and resum. This is most conveniently carried out by expanding the second expression in (2.16b) in powers of PV. We thus have

$$\begin{aligned} \mathcal{T} &= V(1 - gV + gPV)^{-1} \\ &= V[(1 - gV)^{-1} - (1 - gV)^{-1}gPV(1 - gV)^{-1} + \cdots] \\ &= T - TgPT + TgPTgPT - \cdots \\ &= T(1 + g\langle T\rangle)^{-1} \; , \end{aligned} \tag{2.18}$$

as it follows from the definition (2.17) of T and the obvious relation $PQPK = \langle Q\rangle\langle K\rangle$, and

$$W = \langle T\rangle(1 + g\langle T\rangle)^{-1}. \tag{2.19}$$

Finally, from (2.19) we can find $\langle T\rangle$ in terms of W, namely,

$$\langle T\rangle = W(1 - gW)^{-1}\; . \tag{2.20}$$

Thus, the relation between $\langle T\rangle$ and W is identical to the relationship between T and V.

III. SINGLE-SITE APPROXIMATIONS

We now consider for definiteness the case of the electronic properties of a binary, substitutional alloy A_xB_y. As a basic model we take a Bravais lattice with each of the sites $\vec{n}$ occupied by an atom of type A or B with probabilities x and $y \equiv 1 - x$, respectively. In general the various configurations for a given x occur with different probabilities, as, for example, when there is short-range order. If all possible configurations occur with equal probability, then we have, by definition, the special case of a random alloy. In this model the electrons are described by the one-electron Hamiltonian $H = H_0 + U$, where the disordered potential can be written as a sum over the lattice sites $\vec{n}$ of general atomic potentials u_n, i.e.,

$$U = \sum_n u_n \; . \tag{3.1}$$

The atomic potentials u_n assume one to the two possible forms $u^A(\vec{n})$ or $u^B(\vec{n})$ depending on whether atom A or atom B occupies the site $\vec{n}$. Since U_o, the arbitrary potential we can add to H_o to define a reference Hamiltonian H_r, is periodic, it can be written as a sum over lattice sites $\vec{n}$ of the same potential $u_0(\vec{n})$ centered at $\vec{n}$, i.e., $U_0 = \sum_n u_0(\vec{n})$. Thus the disordered potential $V = U - U_0$ with respect to H_r can be written as

$$V = \sum_n v_n \equiv \sum_n [u_n - u_0(\vec{n})] \, , \tag{3.2}$$

i.e., v_n is equal to $v^{A(B)}(\vec{n}) = [u^{A(B)}(\vec{n}) - u_0(\vec{n})]$ when site $\vec{n}$ is occupied by an A (B) atom.

For disordered potentials of the type (3.2) our formulation of the single-site approximation (SSA) for $\langle G\rangle$, which determines the equilibrium properties, proceeds in the following manner. We approximate the quantities that determine $\langle G\rangle$ through its equation (2.13), namely $W(z)$, by keeping the contributions of a single site $\vec{n}$ to its exact expression (2.16) and summing over all $\vec{n}$. We thus find in the SSA,

$$W_{\text{SSA}} = \sum_n P\tau_n , \tag{3.3a}$$

$$\tau_n = v_n(1 - gP'v_n)^{-1} , \tag{3.3b}$$

for the self-energy with respect to the arbitrary periodic reference Hamiltonian H_r. From its definition in (3.3b) it is clear that τ_n differs from the usual t matrix for the potential v_n, namely,

$$t_n \equiv v_n(1 - gv_n)^{-1} \equiv t[g; v_n] \; , \tag{3.4}$$

in that its propagator is gP' instead of g. The relation of τ_n to t_n can thus be found easily by expanding τ_n in powers of Pv_n, in direct analogy to (2.18), and it is

$$\tau_n = t_n(1 + g\langle t_n\rangle)^{-1} . \tag{3.5}$$

Thus, in the general SSA the self-energy with respect to H_r is

$$W_{\mathrm{SSA}} = \sum_n \langle t_n \rangle (1 + g \langle t_n \rangle)^{-1} , \tag{3.6}$$

where g is given by (2.15) and t_n by (3.4). The configuration average $\langle t_n \rangle$ is taken here with any probability distribution appropriate to the disorder of the alloy. In the special case of a random distribution we have

$$\langle t_n \rangle = x t_n^A(\vec{\mathrm{n}}) + y t_n^B(\vec{\mathrm{n}}) , \tag{3.7}$$

with $t^{A(B)}(\vec{\mathrm{n}})$ being the t matrix of the atomic potential $v^{A(B)}(\vec{\mathrm{n}})$.

We recognize that up to now our discussion is valid for an arbitrary reference Hamiltonian $H_r = H_0 + U_0 = H_0 + \sum_n u_0(\vec{\mathrm{n}})$. The precise content of the SSA, however, is determined by the choice of H_r, varying choices yielding different approximations to W and to $\langle G \rangle$. We consider now two ways of choosing the reference medium, that give rise to the ATA and the CPA as specific cases of the SSA. Clearly, it would be preferable to make the choice on the basis of some principle, a point to which we hope to return in another publication.

In the *average t-matrix approximation (ATA)* the reference Hamiltonian H_r is specified[4,5] *a priori* on the basis of physical reasonableness, or mathematical convenience. It is taken to be a Hermitian operator, independent of z. For example, in the case of the muffin-tin model Hamiltonian of the alloy, U_0 is usually taken[3] to be zero and thus $H_r = H_o$ which is just the kinetic energy in that model. The W_{ATA} is given by (3.6) with $g = (z - H_o)^{-1}$ and $v_n = u_n = u^{A(B)}(|\vec{\mathrm{r}} - \vec{\mathrm{n}}|)$, the muffin-tin potentials for the $A(B)$ atom. Another choice[20] is $U_0 = \sum_n u^B(\vec{\mathrm{n}})$ which makes $H_r = H_B$, the Hamiltonian of a perfect B-atom crystal, and $v_n = [u^A(\vec{\mathrm{n}}) - u^B(\vec{\mathrm{n}}) \equiv \phi(\vec{\mathrm{n}})$ on A sites, 0 on B sites]. Then the self-energy (3.6) for a random distribution is

$$\begin{aligned} W_{\mathrm{ATA}} &= \sum_n x t_B[\phi(\vec{\mathrm{n}})]\{1 + x g_B t_B[\phi(\vec{\mathrm{n}})]\}^{-1} \\ &= \frac{x}{1-x} \sum_n t_B[(1-x)\phi(\vec{\mathrm{n}})] , \end{aligned} \tag{3.8}$$

where $t_B[\phi] \equiv \phi(1 - g_B\phi)^{-1}$ is the t matrix of a potential ϕ referred to the Hamiltonian H_B and $g_B = (z - H_B)^{-1}$. The more common usage of ATA, however, specifies H_r to be the so-called "virtual crystal" Hamiltonian $H_r = H_o + \langle U \rangle \equiv H_c$, so that $v_n = u_n - \langle u_n \rangle$. Then the self-energy is

$$\begin{aligned} W_{\mathrm{ATA}} &= \sum_n \langle t_c[v_n] \rangle (1 + g_c \langle t_c[v_n] \rangle)^{-1} \\ &= \frac{xy}{(x-y)^2} \sum_n \{t_c[(y-x)\phi(\vec{\mathrm{n}})] - (y-x)\phi(\vec{\mathrm{n}})\} , \end{aligned} \tag{3.9}$$

where $g_c = (z - H_c)^{-1}$, $t_c[\phi] = \phi(1 - g_c\phi)^{-1}$ and $\phi(\vec{\mathrm{n}}) \equiv u^A(\vec{\mathrm{n}}) - u^B(\vec{\mathrm{n}})$ as in (3.8). This last choice of $H_r = H_c$ has the advantage[21,22] that W_{ATA} is symmetric under the interchange $A \leftrightarrow B$ and $x \leftrightarrow y$, it has the correct behavior for $x \ll 1$ and $y \ll 1$, and thus it serves as a useful interpolation formula over the entire concentration range. It seems that it has not been noticed before that in this choice of H_r, as in the previous case, we can express W_{ATA} in terms of the t matrix of a scaled scattering potential $\phi = u^A - u^B$.

In the *coherent potential approximation* (*CPA*) the final periodic reference medium is not specified *a priori*, but it is selected by a special requirement, which can be motivated in two ways that turn out to be equivalent. First, starting with some periodic medium with Hamiltonian H_r, we seek a "coherent" periodic potential $W_{\mathrm{CPA}} = \sum_n w_n$ such that, if added to H_r, no additional effects, due to the remaining disordered potential $V - W_{\mathrm{CPA}} = \sum_n (v_n - w_n)$, are present in the average propagator $\langle G \rangle$ evaluated in the SSA with respect to the new reference Hamiltonian $H_r + W_{\mathrm{CPA}}$. Thus, this requirement determines $W_{\mathrm{CPA}} = \sum_n w_n$ so that the self-energy with respect to $H_r + W_{\mathrm{CPA}}$ is equal to zero and thus $\langle G \rangle = (z - H_r - W_{\mathrm{CPA}})^{-1}$. This is the intuitive approach to the coherent potential approximation.[6] Since the self-energy in the SSA is given by (3.6), the condition that it vanish gives

$$\langle t[\langle G \rangle ; v_n - w_n] \rangle \equiv \langle (u_n - w_n)[1 - \langle G \rangle (u_n - w_n)]^{-1} \rangle = 0 \tag{3.10}$$

for all $\vec{\mathrm{n}}$ as the defining equation for the coherent potential $W_{\mathrm{CPA}} = \sum_n w_n$. Because of the periodicity of the averaged quantities, condition (3.10) is satisfied for all $\vec{\mathrm{n}}$ if it is satisfied for one. For a random alloy condition (3.10) can be written a little more explicitly as[6]

$$\begin{aligned} w_n &= x v^A(\vec{\mathrm{n}}) + y v^B(\vec{\mathrm{n}}) \\ &\quad - [v^A(\vec{\mathrm{n}}) - w_n] \langle G \rangle [v^B(\vec{\mathrm{n}}) - w_n] . \end{aligned} \tag{3.11}$$

Alternatively, we may adopt a self-consistent point of view[7] and require that, in the evaluation of W_{SSA}, the new reference propagator be $\langle G \rangle$ itself evaluated in the SSA. We now show that this requirement of self-consistency in the evaluation of W_{SSA} is equivalent to the condition (3.10) of the coherent potential requirement. We consider the exact equation (2.12) for the self-energy, and rewrite it, by adding and subtracting W within the parentheses, in the form

$$W = P\{V + V[\langle G \rangle^{-1} - (P'V - W)]^{-1} P'V\} . \tag{3.12}$$

In the SSA with propagator $\langle G \rangle$, i.e., in the CPA, we thus have

$$W_{\mathrm{CPA}} = \sum_n w_n , \tag{3.13}$$

where

$$w_n = P\{v_n + v_n[\langle G\rangle^{-1} - (P'v_n - w_n)]^{-1}P'v_n\}$$
$$= P\{v_n + v_n\langle G\rangle P'v_n + v_n\langle G\rangle(P'v_n - w_n)\langle G\rangle P'v_n + \cdots\}, \tag{3.14}$$

where now $\langle G\rangle = (z - H_r - W_{\rm CPA})^{-1}$. We note that, upon transferring w_n to the right-hand side, this can be written as

$$0 = P\{(v_n - w_n) + (v_n - w_n)\langle G\rangle P'(v_n - w_n) + (v_n - w_n)\langle G\rangle P'(v_n - w_n)\langle G\rangle P'(v_n - w_n) + \cdots\} \tag{3.15}$$

because (i) the w_n of the last factor in each term contributes zero, since $\ldots P'w_n = \ldots P'P\ldots = 0$; (ii) in the intermediate factors we can replace w_n by $(1-P)w_n = P'w_n$, since $Pw_n\langle G\rangle P' = w_n\langle G\rangle PP' = 0$; (iii) the w_n in the first factor contributes zero, since again $Pw_n\langle G\rangle P' = 0$. But Eq. (3.15) is, according to (3.3), simply

$$0 = P\tau[\langle G\rangle; v_n - w_n]$$
$$\equiv P(v_n - w_n)[1 - \langle G\rangle P'(v_n - w_n)]^{-1}. \tag{3.16}$$

However, as in (3.5), we can relate $\tau[\langle G\rangle; v]$ to $t[\langle G\rangle; v]$ and rewrite (3.16) as

$$\langle t[\langle G\rangle; v_n - w_n]\rangle(1 + \langle G\rangle\langle t[\langle G\rangle; v_n - w_n]\rangle)^{-1} = 0. \tag{3.17}$$

Thus Eq. (3.14) for the determination of w_n in this self-consistent approximation is equivalent to Eq. (3.10), i.e., both the coherent potential and the self-consistency requirements are the same. Although most formulations of CPA make use of Eq. (3.10) for the determination of w_n, we shall see in Sec. VI, that the equivalent equation (3.14) is very useful.

It is felt that the CPA yields a better approximation[1] than the ATA. It can easily be shown[7] to have the correct limiting behavior for $x \ll 1$ and $y = 1 - x \ll 1$, and the correct atomic or split-band limit.[23,24]

The single-site approximations for W and $\langle G\rangle$ we have formulated above have been given by a number of other techniques, the most important of which are the decoupling method[1-3] and the corrected cumulant and diagrammatic methods.[1,9-11] It is possible to show that our formalism can yield simply these different formulations. This is particularly important for the case of the diagrammatic methods which are rather involved.

Finally we note that the prescription used above to formulate the SSA is a one-step procedure, that is, it is not a part of a systematic approximation scheme. It is, of course, desirable to have such a systematic scheme so that we can investigate the next approximations to W, and perhaps find the conditions sufficient for the validity of the SSA. The most obvious such scheme is a cluster expansion of W. In this formalism this can be obtained quite simply by noticing first that we can rewrite the exact expression (2.16) for W with $V = \sum_n v_n$ in terms of $\tau_n \equiv v_n(1 - gP'v_n)^{-1}$ of (3.3) as in the well known multiple-scattering expansion,[8,3] namely,

$$W = P\left(\sum_n \tau_n + \sum_n \tau_n g P' \sum_{m\neq n} \tau_m + \cdots\right). \tag{3.18}$$

We can then easily rearrange this sum to yield a cluster expansion for W, for any reference Hamiltonian. The first term of this expansion constitutes the SSA. The next term of the rearranged expansion yields in a straightforward way the pair approximation for any H_r. Thus, the generalization of the general SSA to include pair and higher-order cluster effects can be obtained easily from this formalism, in contrast to earlier attempts[25-29] which proved troublesome. However, such a cluster expansion is not a satisfactory systematic scheme, as it leads[1] to nonanalyticities for $W(z)$. An alternative approach to this important question of a systematic approximation scheme for W with the SSA as the first step has been reported[12,13] recently, and we hope to return to this point on the basis of our formalism.

IV. OPTICAL THEOREM FOR THE SELF-ENERGY

In this section we prove, on the basis of the exact expression (2.16) that there exists an "optical theorem" for $W(z)$, i.e., $W(z)$ satisfies a relation analogous to the optical theorem for $T(z)$ for a Hermitian and energy-independent potential V. This enables us to show directly and simply that the density of states $\rho(E)$ of (2.5) is indeed nonnegative. This method is then used in the following sections to prove that, for both ATA and CPA, $\rho(E) \geqslant 0$ for arbitrary Hermitian atomic potentials v_n and arbitrary disorder.

We note that the series (2.16b) defining $\mathcal{T}(z)$ can be summed formally to yield

$$\mathcal{T}(z) = [1 - Vg(z)P']^{-1}V. \tag{4.1}$$

This can be solved for V in terms of $\mathcal{T}(z)$ to give

$$V = \mathcal{T}(z)[1 + g(z)P'\mathcal{T}(z)]^{-1}. \tag{4.2}$$

Since now V is Hermitian, we have, by taking the Hermitian conjugate of (4.2),

$$V = (1 + \mathcal{T}^\dagger \underleftarrow{P}' g^\dagger)^{-1}\mathcal{T}^\dagger, \tag{4.3}$$

where † denotes the Hermitian adjoint, and $\underleftarrow{P}'$ is the projection operator P' operating on quantities to its left. Note that P and P' are real operations and thus are not affected by the operation of conjugation, so that $\langle\mathcal{T}\rangle^\dagger=\langle\mathcal{T}^\dagger\rangle$. From (4.2) and (4.3) we have

$$\mathcal{T}(1+gP'\mathcal{T})^{-1}=(1+\mathcal{T}^\dagger \underleftarrow{P}' g^\dagger)^{-1}\mathcal{T}^\dagger , \tag{4.4}$$

or by simple rearrangement

$$\mathcal{T}-\mathcal{T}^\dagger=\mathcal{T}^\dagger(g-g^\dagger)\mathcal{T}-\mathcal{T}^\dagger g\langle\mathcal{T}\rangle+\langle\mathcal{T}^\dagger\rangle g^\dagger\mathcal{T} . \tag{4.5}$$

Taking now the configuration average, we find

$$\begin{aligned}\langle\mathcal{T}\rangle-\langle\mathcal{T}^\dagger\rangle&=\langle\mathcal{T}^\dagger(g-g^\dagger)\mathcal{T}\rangle-\langle\mathcal{T}^\dagger\rangle(g-g^\dagger)\langle\mathcal{T}\rangle\\&=\langle(\mathcal{T}-\langle\mathcal{T}\rangle)^\dagger(g-g^\dagger)(\mathcal{T}-\langle\mathcal{T}\rangle)\rangle ,\end{aligned} \tag{4.6}$$

since $Pg=gP$. Defining then $\mathrm{Im}A$ for any operator A by

$$\mathrm{Im}A\equiv(A-A^\dagger)/2i , \tag{4.7}$$

we have for the self-energy $W(z)=\langle\mathcal{T}(z)\rangle$ the general optical theorem

$$\begin{aligned}\mathrm{Im}W(z)&=\mathrm{Im}\langle\mathcal{T}(z)\rangle\\&=\langle[\mathcal{T}(z)-\langle\mathcal{T}(z)\rangle]^\dagger[\mathrm{Im}g(z)][\mathcal{T}(z)-\langle\mathcal{T}(z)\rangle]\rangle .\end{aligned} \tag{4.8}$$

We note that this equation (4.8) is a direct consequence of the relation (4.1) for any $\mathcal{T}(z)$, $g(z)$ and a Hermitian operator V. [This will be of importance below when we consider $W(z)$ in the ATA and CPA for disordered alloys.] Since in (4.8) $g(z)=(z-H_r)^{-1}$, we note that

$$\mathrm{Im}g(z)=-g(z)^\dagger(\mathrm{Im}z)g(z) , \tag{4.9}$$

and we thus conclude from (4.8) that

$$\mathrm{Im}W(z)\leqslant 0 \quad \text{for } \mathrm{Im}z>0 . \tag{4.10}$$

This relation can also be proved[30] from the definition (2.13) of $W(z)$ in terms of $\langle G(z)\rangle$ and the fact that it is an analytic function of z. The method of derivation we have given above on the basis of its explicit expression (2.16), however, is applicable to more general situations and will be used in the following sections.

For $z=E^+\equiv E+i\epsilon$, where ϵ is a positive infinitesimal, we have from (4.8) the particular form of the optical theorem

$$\mathrm{Im}W(E^+)=-\pi\langle[P'\mathcal{T}(E^+)]^\dagger\delta(E-H_r)[P'\mathcal{T}(E^+)]\rangle\leqslant 0 , \tag{4.11}$$

where the square brackets denote the extent of the operation P'. This relation proves in an explicit way that the macroscopic density of states (2.5) is non-negative, since from $\langle G(z)\rangle=[z-H_r-W(z)]^{-1}$ we have

$$\mathrm{Im}\langle G(E^+)\rangle=\langle G(E^+)\rangle^\dagger[-\epsilon+\mathrm{Im}W(E^+)]\langle G(E^+)\rangle\leqslant 0 , \tag{4.12}$$

where the limit $\epsilon\to 0+$ is understood.

Finally, it should be pointed out that if we work with expression (2.18) of $\mathcal{T}(z)$ in terms of $T(z)$, we can derive[31] a relation for $\mathrm{Im}W(z)$ in terms of $W(z)$ and $T(z)$ which also demonstrates the inequality (4.10). However, this relation is quite cumbersome and of no use in the consideration of the ATA and the CPA, which are considered in the next sections.

V. PROOF OF $\rho_{\mathrm{ATA}}(E)\geqslant 0$

For a disordered alloy with $V=\sum_n v_n$, the self-energy in the average ATA is given by (3.3). We note that (3.3b) can also be written as

$$\tau_n(z)=[1-v_n g(z)P']^{-1}v_n . \tag{5.1}$$

On the basis of (5.1) we can then repeat the argument with $\tau_n(z)$ and v_n as in (4.1)–(4.11) with $\mathcal{T}(z)$ and V to find $\mathrm{Im}\langle\tau_n(E^+)\rangle\leqslant 0$ and thus also

$$\mathrm{Im}W_{\mathrm{ATA}}(E^+)=\sum_n \mathrm{Im}\langle\tau_n(E^+)\rangle\leqslant 0 . \tag{5.2}$$

This relation proves, through (2.5) and the analog of (4.12) for

$$\langle G(E^+)\rangle_{\mathrm{ATA}}=[E^+-H_r-W_{\mathrm{ATA}}(E^+)]^{-1} ,$$

that $\rho_{\mathrm{ATA}}(E)\geqslant 0$.

VI. PROOF OF $\rho_{\mathrm{CPA}}(E)\geqslant 0$

For our present purposes it proves convenient to adopt the formulation of the CPA that is based on a requirement for self-consistency, as given in (3.13) and (3.14). We thus have in a more convenient notation

$$W_{\mathrm{CPA}}(Z)=\sum_n\langle\tau_n(z)\rangle , \tag{6.1}$$

where

$$\begin{aligned}\tau_n(z)&=v_n+v_n(\langle G\rangle^{-1}+\langle\tau_n\rangle-P'v_n)^{-1}P'v_n\\&=v_n+v_n(G_n^{-1}-P'v_n)^{-1}P'v_n\\&=v_n+v_nG_nP'v_n+v_nG_nP'v_nG_nP'v_n+\cdots\\&=[1-v_nG_n(z)P']^{-1}v_n\end{aligned} \tag{6.2}$$

with G given by the self-consistent propagator $\langle G\rangle$ in the CPA, i.e., by

$$\langle G(z)\rangle=[z-H_r-W_{\mathrm{CPA}}(z)]^{-1} . \tag{6.3}$$

In (6.2) we have introduced a new propagator $G_n(z)$ such that

$$\begin{aligned}G_n(z)&\equiv[\langle G(z)\rangle^{-1}+\langle\tau_n(z)\rangle]^{-1}\\&=\Big(z-H_r-\sum_{m\neq n}\langle\tau_m(z)\rangle\Big)^{-1} ,\end{aligned} \tag{6.4}$$

as it follows from (6.2) and (6.3).

But expression (6.2) for $\tau_n(z)$ is identical to (4.1) for $\mathcal{T}(z)$ except for the replacement of V and $g(z)$ by v_n and $G_n(z)$, respectively. Proceeding then as in Eqs. (4.1)–(4.8), we find from the analog of (4.8) for $z = E^+$

$$\operatorname{Im}\langle \tau_n(E^+)\rangle = \langle [\tau_n(E^+) - \langle \tau_n(E^+)\rangle]^\dagger \times [\operatorname{Im} G_n(E^+)][\tau_n(E^+) - \langle \tau_n(E^+)\rangle]\rangle \,. \tag{6.5}$$

From expression (6.4) for $G_n(z)$, however, we find

$$\operatorname{Im} G_n(E^+) = G_n(E^+)^\dagger \Big(-\epsilon + \operatorname{Im} \sum_{m\neq n} \langle \tau_m(E^+)\rangle \Big) G_n(E^+) \,. \tag{6.6}$$

Equations (6.5) and (6.6) show at least that the property $\operatorname{Im}\langle \tau_n(E^+)\rangle \leq 0$ is self-consistent; any finite number of iterations, starting with $\operatorname{Im}\langle \tau_m(E^+)\rangle \leq 0$, maintain the nonpositive property of $\operatorname{Im}\langle \tau_n(E^+)\rangle$, as determined through its defining equation (6.2). That is to say, if we use an iteration scheme to solve (6.2) for $\tau_n(E^+)$ starting, say, with the ATA for which $\operatorname{Im}\langle \tau_m(E^+)\rangle \leq 0$, we have from (6.5) that the first iteration for $\operatorname{Im}\langle \tau_n(E^+)\rangle$ is ≤ 0, since on the right-hand side of (6.5) we have then from (6.6) that $\operatorname{Im} G_n(E^+) \leq 0$. Such iteration schemes for the solutions of the CPA equation (6.2) have been considered[32] and their convergence discussed[12,30] for simple models.

For the models of H for which such schemes converge, we have thus shown that

$$\operatorname{Im} W_{\mathrm{CPA}}(E^+) = \sum_n \operatorname{Im}\langle \tau_n(E^+)\rangle \leq 0 \,. \tag{6.7}$$

This in turn proves, through (2.5) and the analog of (4.12) for $\langle G\rangle_{\mathrm{CPA}}$, that $\rho_{\mathrm{CPA}}(E) \geq 0$.

VII. CONCLUSION

The general expression (2.12) for the self-energy W of a disordered system provides a convenient basis for finding approximation schemes for the equilibrium properties of such a system. In particular the quite successful single-site approximations, both ATA and CPA, for an alloy are formulated on the basis of this expression and are seen to yield a number of known results in simple algebraic steps.

This formalism allows us to prove quite simply and generally that both ATA and CPA yield nonnegative density of states. By contrast, we shall show in another publication making use of the optical theorem for $W(E^+)$, that a number of possible extensions of these single-site approximations to include the effects of pairs and higher-order clusters do not yield a density of states with a definite sign. This formalism can be adapted in an entirely parallel way to the discussion of the transport properties of the alloy.[33]

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