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Transport properties of random and nonrandom substitutionally disordered alloys. II. New cluster formulation of the ac conductivity and numerical applications

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A cluster-field theory providing a rigorous foundation for dealing with cluster calculations in ordered and disordered materials is presented. The theory is based on a special matrix (given in the text) which plays the role of intracluster interactions and allows the formulation of a general cluster perturbation theory. The use of this cluster theory is demonstrated by deriving a cluster formula for the ac conductivity of general physical systems with specific attention paid to substitutionally disordered alloys. The formalism is general enough to encompass Hamiltonians of various and diverse kinds, such as those of tight-binding and muffin-tin character, and allows us to obtain previously established results in a straightforward and unified manner. In addition it allows, by utilizing the Ward identity, the rigorous expression of vertex corrections in terms of cluster quantities and makes possible the setting up of controlled approximation schemes for their evaluation. The usefulness of the method is illustrated by means of calculations of the ac conductivity of one-dimensional disordered model systems.

I. INTRODUCTION

In the preceding paper,[1] to be referred to as I, we presented a set of exact numerical results for the ac conductivity of a large class of one-dimensional alloys, characterized by various types of substitutional disorder. In this paper we discuss analytic theories which may be used to calculate the averaged two-particle Green function, and hence the transport properties associated with a disordered material. The formalism is underlined by the coherent potential approximation (CPA),[2–5] which in fact has been applied to the calculation of transport properties[4] of disordered systems. However, it goes much beyond the single-site CPA by extending the CPA to a multisite (cluster) method which allows the calculation of transport properties within feasible, accurate, and controlled levels of approximation. In particular, it provides a consistent method for the calculation of the vertex corrections. In this paper we present a general cluster field theory which allows us unambiguously to visualize and calculate physical properties in terms of cluster quantities. The theory is useful not only in the context of these papers, but is applicable also to any cluster or multicomponent calculation in other fields.

The outstanding success of the CPA in calculating physical properties of substitutionally disordered alloys is well known. However, as was realized almost immediately upon its introduction, the CPA cannot account for the effects of local-environment fluctuations which are known to be very important in determining many physical properties of disordered materials. Various multisite generalizations[6,7] of the CPA were consequently developed to address a variety of problems associated with the calculation of the one-electron properties, essentially the density of states (DOS), in such materials. Of these generalizations very few have proved to be useful and practical—some more so than others—and to possess the desired analytic properties. We will have occasion to make these statements more precise in the course of developing the formalism of this paper. We begin with a brief review of previous efforts in applying the CPA and some of its cluster extensions to the calculation of the transport properties of disordered alloys.

Beginning with the pioneering work of Velický,[4] the CPA has been used to study electronic transport, the ac and dc conductivity in particular, by a number of investigators.[8–14] Velický's formalism and model calculations make it clear that the CPA provides a good overall method for calculating electronic transport away from the mobility edge, whose accuracy is comparable to that obtained in the calculation of the DOS. However, in analogy with the case of DOS calculations, the CPA fails to reproduce the local fine structure in the conductivity spectra. In fact, it can be shown formally, under the random-phase-like approximation of Velický,[4] that the vertex corrections vanish identically within the CPA for a tight-binding (TB) single-band Hamiltonian. These vertex corrections are certainly nonzero and various attempts[8–14] have been made to develop methods for their evaluation. A new approach, based on a cluster generalization of the CPA, the embedded-cluster method (ECM),[6,15] which incorporates the effects of fluctuations from the beginning is presented in this paper.

Velický's single-site theory was later generalized by a number of workers. Chen *et al.*[8] studied the effects of thermal disorder and explained some unusual features of metallic alloys which exhibit negative temperature coefficients of electronic resistivity. Niizeki *et al.*,[14] in a series of papers, formulated a general theory[14] to include the effect of off-diagonal disorder in the additive limit. Blackman[16] used the formalism of Blackman *et al.*[17] for applying the CPA to alloys with general off-diagonal disorder

(ODD) to formulate the calculation of the conductivity in such alloys within the single-site CPA. Schwartz[10] discussed electronic transport within the CPA for a multiband model which bears features characterizing muffin-tin (MT) Hamiltonians. Wysokinsi *et al.*[18] investigated both the thermal and off-diagonal effects on the dc and ac conductivities of binary and ternary alloys. Czycholl *et al.*[12,13] calculated transport quantities by extending the molecular coherent-potential approximation[7] (MCPA) of Tsukada to the calculation of two-particle Green functions.

Most recently, Butler and Stocks[19,20] have succeeded in calculating the dc conductivity of substitutionally disordered $\mathrm{Ag}_c\mathrm{Pd}_{1-c}$ alloys from first principles. Their work is based on the calculation of the electronic structure of substitutional alloys by means of a charge self-consistent version of the CPA in connection with muffin-tin Hamiltonians. The results of these calculations were then used to calculate the low-temperature electrical resistivity and the thermopower of these alloys. Good agreement with experiment was obtained for a wide range of alloy parameters.

In a real alloy, fluctuations in the local environment of a site cause what are known as local-environment effects. These local spatial fluctuations away from the uniform effective medium, which characterizes an ensemble-averaged alloy, are often important in determining the physical properties of a material. The molecular CPA (MCPA) (Ref. 7) was developed to take account of such effects. However, the calculation of the cluster Green function in the MCPA can become computationally very difficult even for moderate-size clusters, such as a near-neighbor cluster in an fcc lattice. In addition, the MCPA requires the introduction of an effective medium with supercell symmetry which violates the translational invariance of the underlying lattice. The embedded-cluster method (ECM),[6,15] on the other hand, although a non-self-consistent theory, is computationally much simpler than the MCPA and avoids the introduction of spurious periodicities. It has been shown to yield analytic cluster Green's functions and non-negative spectral weight functions, and allows the investigation of local-environment effects, such as short-range order[15] (SRO) and compositional modulation,[21] easily and efficiently.

In this paper we formulate a general cluster-field theory and show that most of the work mentioned above can be included within the same unifying framework. We also derive a theory of electronic transport in substitutionally disordered systems based on cluster generalizations of the CPA. This theory is consistent in the sense that the effective-medium self-energy satisfies the fundamental Ward identity. Our cluster theory of electronic transport in substitutionally disordered systems may be viewed as an extension of the single-site CPA transport theory of Velický,[4] just as the ECM is an extension of the original CPA for the calculation of the single-particle equilibrium properties. Within the ECM, the scattering of electrons from a large cluster of atoms embedded in an effective medium is treated exactly; therefore, local-environment effects can be taken into account properly. In contrast to the simple single-site CPA, the ECM yields nonvanishing vertex corrections for transport coefficients.

In Sec. II we first discuss the models we use and review the connection between the first and second quantizations which are relevant to our formalism. We then formulate a cluster-field theory and establish a transformation of operators between these two different quantizations. The cluster theory is then used to derive a cluster formula for the ac conductivity of a general physical system. In Sec. III a cluster approximation scheme for calculating the ac conductivity of disordered systems is presented. As an example, the ac conductivity is formulated within the MCPA for the case of general disordered systems, with explicit formulas given for the calculation of vertex corrections. We then discuss the validity of the Ward identity which ensures the conservation law of macroscopic quantities. The formalism of the embedded-cluster method is then proposed with specific instructions for computational applications. Section IV contains the results of numerical applications of our methods to model one-dimensional substitutionally disordered chains. In Sec. V we give a discussion of our method and summarize possible extensions and further work. Finally, a detailed discussion of the matrix Wick's theorem used in our theory is given in the Appendix.

II. FORMALISM

The field-theoretic approach to many-body problems has found wide application in studies of condensed-matter. This approach has proved particularly successful in connection with systems possessing translational symmetry, such as the uniform electron gas and pure crystals. For such systems the theory can be formulated in terms of essentially scalar quantities. In particular, it involves only the matrix elements of Green functions which are diagonal in a **k**-space representation.

For the study of systems which do not possess translational invariance, however, such as random, substitutionally disordered alloys, it is immediately evident that a real-space representation of the Green function is more appropriate. Strictly speaking, one needs to evaluate exact real-space ensemble averages of various quantities. such as the Green function, over all configurations of a system, which is clearly a computationally impossible task. Consequently, approximate methods have been proposed for carrying out such averages. The most successful and most widely used such method within a single-site context is the coherent-potential approximation[2,3] (CPA). The CPA introduces a self-consistently determined translationally invariant effective medium which allows the use of a **k**-space representation in the evaluation of quantities of physical interest. It is generally accepted that the CPA is the best single-site theory for the study of the one-particle properties of substitutionally disordered systems. Multisite, or cluster, extensions of the original CPA devised in attempts to account for the presence of various physical effects such as off-diagonal disorder and local-environment statistical fluctuations have also been proposed.[5–7]

Realistic applications of the CPA or of its multisite generalizations inevitably involve the use of matrix algebra. Thus many of these methods can be classified in terms of different levels of an underlying, unified cluster theory. This is particularly true of those generalizations of the CPA such as the MCPA (Ref. 7) or the ECM (Refs. 6 and 15), which have proved the most durable of multisite generalizations. Some of these methods, e.g., the MCPA, have been used not only in the calculation of the single-particle properties of disordered materials, but also in the calculation[12,13] of the dynamic, or transport, properties as well. On the other hand, the applications of such methods are usually burdened by a proliferation of indices which are combersome to handle and which tend to obscure the underlying physics. These statements can be amply illustrated by examining the literature associated with the calculation of transport phenomena in substitutionally disordered systems.

The foregoing discussion indicates that it is highly desirable to develop a unified treatment of the transport and other properties of disordered materials which can be applied in a compact, easily retained manner to the calculation of important quantities such as the single-particle and two-particle Green functions. It is the purpose of this paper to introduce such a general treatment of substitutionally disordered systems based on a cluster formulation of canonical field theory. Such a cluster-field theory is possible in the case of substitutionally disordered alloys due to the presence of the underlying translationally invariant lattice. We emphasize that our cluster-field theory is general enough to be applied to any cluster calculations of alloys, characterized by either tight-binding or more realistic Hamiltonians such as those of the muffin-tin type. Furthermore, it is of more general applicability, not limited to the context of these papers. In the remainder of this section we discuss certain popular models used in the discussion of disordered materials and present our cluster-field theory whose versatility and efficiency is demonstrated by deriving a cluster conductivity formula.

A. Models of disordered systems

The equivalence[22] of the first and second quantizations was established soon after the introduction of the latter. In this paper we use the language of canonical field theory, i.e., second quantization, and review the transformations of calculated physical quantities between the above two pictures. Two typical model Hamiltonians, i.e., tight-binding (TB) single-band Hamiltonians and those of a muffin-tin (MT) type, are used throughout this paper to illustrate our cluster formalism. It will become clear that both TB and MT Hamiltonians are only two relatively simple examples in our general theoretical framework.

Within first quantization, a single-particle Hamiltonian is taken to be of the form

$$H=-\frac{\hbar^2}{2m}\nabla^2+\sum_i u(\mathbf{r}-\mathbf{R}_i)\ . \tag{2.1}$$

where the $\mathbf{R}_i$ will be taken as fixed and forming a regular lattice and $u_i=u(\mathbf{r}-\mathbf{R}_i)$ is the potential at $\mathbf{r}$ due to the atom centered at site $\mathbf{R}_i$. For a binary alloy $A_{c_A}B_{c_B}$ $(c_A+c_B=1)$, the potential u_i can assume the value u_A or u_B with respective probabilities c_A or c_B. Multicomponent alloys can be treated within the same formalism.

Within second quantization, a field operator $\psi(\mathbf{r})$ and its conjugate $\psi^\dagger(\mathbf{r})$ can be expanded in terms of eigenfunctions $\Phi_\lambda(\mathbf{r})$ and $\Phi_\lambda^*(\mathbf{r})$ as follows:

$$\psi(\mathbf{r})=\sum_\lambda c_\lambda \Phi_\lambda(\mathbf{r}) \tag{2.2}$$

and

$$\psi^\dagger(\mathbf{r})=\sum_\lambda c_\lambda^\dagger \Phi_\lambda^*(\mathbf{r})\ , \tag{2.3}$$

where $c_\lambda^\dagger$ and c_λ are the creation and annihilation operators of an electron associated with the state λ, and satisfy the canonical anticommutation relations,

$$\begin{aligned}&\{c_\lambda,c_{\lambda'}^\dagger\}=\delta_{\lambda\lambda'}\ ,\\&\{c_\lambda^\dagger,c_{\lambda'}^\dagger\}=\{c_\lambda,c_{\lambda'}\}=0\ .\end{aligned} \tag{2.4}$$

In second quantization, the Hamiltonian can be written in the form

$$\begin{aligned}H&=\int \psi^\dagger(\mathbf{r})H(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}\\&=\sum_\lambda \varepsilon_\lambda c_\lambda^\dagger c_\lambda+\sum_{\substack{\lambda,\lambda'\\(\lambda\neq\lambda')}} W_{\lambda\lambda'}c_\lambda^\dagger c_{\lambda'}\ ,\end{aligned} \tag{2.5}$$

where $H(\mathbf{r})$ is the Hamiltonian defined in Eq. (2.1) and ε_λ and $W_{\lambda\lambda'}$ are defined by the equations

$$\varepsilon_\lambda=\int \Phi_\lambda^*(\mathbf{r})H(\mathbf{r})\Phi_\lambda(\mathbf{r})d\mathbf{r} \tag{2.6}$$

and

$$W_{\lambda\lambda'}=\int \Phi_\lambda^*(\mathbf{r})H(\mathbf{r})\Phi_{\lambda'}(\mathbf{r})d\mathbf{r},\quad \lambda\neq\lambda'\ . \tag{2.7}$$

Any one-particle operator is defined[22] in the same way, e.g., the current operator $\mathbf{J}$ is given by the expression,

$$\begin{aligned}\mathbf{J}&=\int \psi^\dagger(\mathbf{r})\mathbf{J}(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}\\&=\sum_{\lambda,\lambda'} c_\lambda^\dagger \mathbf{J}_{\lambda\lambda'}c_{\lambda'}\ ,\end{aligned} \tag{2.8}$$

with

$$\mathbf{J}_{\lambda\lambda'}=\int \Phi_\lambda^*(\mathbf{r})\mathbf{J}(\mathbf{r})\Phi_{\lambda'}(\mathbf{r})d\mathbf{r}\ . \tag{2.9}$$

In the case of the electron gas one usually chooses plane waves as the basis set, i.e., the indices λ and λ' in the above equations refer to vectors in $\mathbf{k}$ space. The existence of an underlying lattice in a substitutionally disordered alloy provides us with a natural choice of a basis set associated with sites in the lattice. A basis set can be chosen in various models, as either configuration independent or configuration dependent. The latter is more appropriate for dealing with general disordered systems.

Much of the following discussion will be given in terms of a *single-band* model which can serve as a prototype for the discussion of TB as well as MT systems. We will show explicitly how specific choices of the basis functions used in the formalism can lead to well-known expressions associated with Hamiltonians of a TB or of a MT type.

Let us assume then that there exists a single-band basis set $\{\psi_i(\mathbf{r}),\ i=1,2,\ldots,\infty\}$, where $\psi_i(\mathbf{r})$ depends on the configuration of the alloy and in particular on the occupation of site i. The single-band Hamiltonian, obtained by replacing the function $\Phi_\lambda(\mathbf{r})$ in Eqs. (2.6) and (2.7) by the basis functions $\psi_i(\mathbf{r})$, has the form

$$H=\sum_i \varepsilon_i c_i^\dagger c_i+\sum_{\substack{i,j\\(i\neq j)}} W_{ij}c_i^\dagger c_j \; . \tag{2.10}$$

One usually refers to ε_i and W_{ij} as a site energy and hopping integral respectively. Both, in general, can depend on the whole configuration of a disordered material in a rather complicated manner. Different levels of approximations can be made in considering the configurational dependence of these parameters. Thus diagonally as well as off-diagonally disordered models of substitutional alloys can be constructed in the manner discussed in I. Even though Eq. (2.10) has the form of the usual TB Hamiltonian it is not confined to the TB approximation since none of the simplifications commonly involved in TB theories have been made. Thus, for example, W_{ij} includes two-center as well as three-center integrals.

For example, in a TB single-band diagonally disordered model one usually assumes that the matrix elements of the current operator, i.e., $\mathbf{J}_{\lambda\lambda'}$ in Eq. (2.9), do not depend on the configuration of the material. An extra assumption was made in I, namely that the position operator is site diagonal, [cf. Eq. (3.4) in I], which led to $\mathbf{J}_{ij}$ being only a function of hopping integrals, W_{ij}'s. Both of these assumptions must be modified when considering more realistic Hamiltonians such as those of a MT type.

B. Cluster-field theory

In principle, a cluster theory can be formulated either in a real-space or in a momentum-space representation. As already mentioned, a real-space formalism is more appropriate for the discussion of substitutionally disordered alloys. Therefore, we formulate our cluster-field theory in a site representation. This formalism provides us with a natural procedure for calculating transport properties of disordered systems. In this subsection we define our notation, give the basic definitions of cluster quantities, and summarize certain general principles involved in the theory.

In a cluster approach we divide the whole lattice into identical nonoverlapping clusters of atomic sites, thus forming a superlattice. A cluster theory which interplays between Schrödinger wave mechanics and Heisenberg matrix mechanics can then be easily formulated. Within each cluster the intracluster interaction is described by matrix mechanics, i.e., every physical quantity is represented by a matrix, and at the level of the superlattice the intercluster interactions are governed by wave mechanics. This has the advantage that we can define unique cluster operators and regard a cluster as an operational unit without the need to consider explicitly the single-site aspects of the theory.

We first introduce an important and interesting matrix, denoted by $\underline{\Pi}$, which can be used to characterize intracluster interactions. The matrix $\underline{\Pi}$ is the backbone of our cluster theory and is defined by its elements,

$$\underline{\Pi}_{ij}=1,\quad i,j=1,2,\ldots,n\;; \tag{2.11}$$

i.e., $\underline{\Pi}$ is a matrix with all elements equal to 1. The physical meaning of this matrix is that it allows the treatment of every site in a cluster on the same footing. This singular matrix provides us with two simple and surprising relations. The first is

$$\mathrm{Tr}(\underline{\Pi}\,\underline{A})\mathrm{Tr}(\underline{\Pi}\,\underline{B})=\mathrm{Tr}(\underline{\Pi}\,\underline{A}\,\underline{\Pi}\,\underline{B})\;, \tag{2.12}$$

where $\underline{\Pi}$, $\underline{A}$, and $\underline{B}$ are $n\times n$ matrices. Thus, *the operation of taking the trace and of matrix multiplication commute.* This property allows us to perform all calculations in matrix form first and then to obtain physical quantities by taking the trace at the end. Also, for any $n\times n$ diagonal matrices, $\underline{A}$ and $\underline{B}$, we have the second relation,

$$\mathrm{Tr}(\underline{\Pi}\,\underline{A}\,\underline{\Pi}\,\underline{B})=\mathrm{Tr}[(\underline{\Pi}\otimes\underline{\Pi})(\underline{A}\otimes\underline{B})]\;, \tag{2.13}$$

where $\otimes$ denotes a direct product. This relation is useful when we consider nonlocal interactions, as will be discussed later.

In the following discussion we use Greek character superscripts to denote cluster-associated quantities, and use English characters as subscripts to denote the sites in a given cluster. We begin by defining n-dimensional cluster creation and annihilation operator matrices, $(\underline{C}^\alpha)^\dagger$ and $\underline{C}^\alpha$,

$$(\underline{C}^\alpha)^\dagger=\begin{bmatrix} c_1^\dagger & 0 & & \cdots & 0\\ 0 & c_2^\dagger & & & \vdots\\ \vdots & & \ddots & & \\ & & & c_{n-1}^\dagger & 0\\ 0 & \cdots & & 0 & c_n^\dagger \end{bmatrix},\qquad \underline{C}^\alpha=\begin{bmatrix} c_1 & 0 & & \cdots & 0\\ 0 & c_2 & & & \vdots\\ \vdots & & \ddots & & \\ & & & c_{n-1} & 0\\ 0 & \cdots & & 0 & c_n \end{bmatrix}, \tag{2.14}$$

where $c_1,c_2,\ldots,c_n$ and $c_1^\dagger,c_2^\dagger,\ldots,c_n^\dagger$ are the usual annihilation and creation operators associated with the sites in a cluster α of n sites. We also define the cluster wave function and its conjugate as

$$\underline{\psi}^\alpha(\mathbf{r})=\begin{bmatrix} \psi_1(\mathbf{r}) & 0 & & \cdots & 0\\ 0 & \psi_2(\mathbf{r}) & & & \vdots\\ \vdots & & \ddots & & \\ & & & \psi_{n-1}(\mathbf{r}) & 0\\ 0 & \cdots & & 0 & \psi_n(\mathbf{r}) \end{bmatrix},\qquad \underline{\psi}^{\alpha *}(\mathbf{r})=\begin{bmatrix} \psi_1^*(\mathbf{r}) & 0 & & \cdots & 0\\ 0 & \psi_2^*(\mathbf{r}) & & & \vdots\\ \vdots & & \ddots & & \\ & & & \psi_{n-1}^*(\mathbf{r}) & 0\\ 0 & \cdots & & 0 & \psi_n^*(\mathbf{r}) \end{bmatrix}, \tag{2.15}$$

where $\psi_1(\mathbf{r}),\psi_2(\mathbf{r}),\ldots,\psi_n(\mathbf{r})$ are the basis functions associated with the sites in cluster α. With the above definition the field operators, Eqs. (2.2) and (2.3), can be rewritten in the form

$$\psi(\mathbf{r})=\overline{\mathrm{Tr}}(\underline{\Pi}\,\underline{c}\,\underline{\psi}(\mathbf{r})] \ , \tag{2.16}$$

and

$$\psi^\dagger(\mathbf{r})=\overline{\mathrm{Tr}}[\underline{\Pi}\,\underline{c}^\dagger\,\underline{\psi}^*(\mathbf{r})] \ , \tag{2.17}$$

$$\overline{\mathrm{Tr}}A=\sum_{\alpha,\beta}\mathrm{Tr}A_{\alpha\beta} \ , \tag{2.18}$$

where $\overline{\mathrm{Tr}}$ denotes the trace over both matrix and cluster spaces.

Many results can be obtained from these two forms which are the only construction we use in our cluster theory. Any single-particle operator in second quantized form can now be written as

$$\begin{aligned} O^{(1)}&=\int \psi^\dagger(\mathbf{r})O^{(1)}(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}\\ &=\int \overline{\mathrm{Tr}}[\underline{\Pi}\,\underline{c}^\dagger\underline{\psi}^*(\mathbf{r})]O^{(1)}(\mathbf{r})\overline{\mathrm{Tr}}[\underline{\Pi}\,\underline{c}\,\underline{\psi}(\mathbf{r})]d\mathbf{r}\\ &=\overline{\mathrm{Tr}}\left[\underline{\Pi}\,\underline{c}^\dagger\left[\int \underline{\psi}^*(\mathbf{r})O^{(1)}(\mathbf{r})\underline{\Pi}\,\underline{\psi}(\mathbf{r})d\mathbf{r}\right]\underline{c}\right]\\ &=\overline{\mathrm{Tr}}\{\underline{\Pi}\,\underline{O}^{(1)}\} \ , \end{aligned} \tag{2.19}$$

where $O^{(1)}(\mathbf{r})$ is an operator in the first quantized form and we have used the relation Eq. (2.12) to pull out the trace. Note that $O^{(1)}(\mathbf{r})$ is a scalar operator and operates on all elements of a matrix. Equation (2.18) suggests that we can associate any single-site observable $O^{(1)}(\mathbf{r})$ with a matrix $\underline{O}^{(1)}$. For example, the noninteracting single-particle Hamiltonian, Eq. (2.10), can now be rewritten in the cluster basis as

$$H=\overline{\mathrm{Tr}}(\underline{\Pi}\,\underline{H}) \ , \tag{2.20}$$

where

$$\underline{H}=\sum_{\alpha}(\underline{c}^\alpha)^\dagger\underline{\varepsilon}^\alpha\underline{c}^\alpha+\sum_{\substack{\alpha,\beta\\(\alpha\neq\beta)}}(\underline{c}^\alpha)^\dagger\underline{W}^{\alpha\beta}\underline{c}^\beta \ , \tag{2.21}$$

and where $\underline{\varepsilon}^\alpha$ and $\underline{W}^{\alpha\beta}$ are $n\times n$ matrices. The former represents a cluster energy and can be related to single-site quantities,

$$\underline{\varepsilon}^\alpha_{ij}=\begin{cases}\varepsilon_i & \text{if } i=j,\\ W_{ij} & \text{if } i\neq j,\end{cases} \quad i,j\in\alpha \ , \tag{2.22}$$

while the latter is a cluster hopping matrix, with elements $\underline{W}^{\alpha\beta}_{ij}$ denoting the *hopping integral* from site i of cluster α to site j of cluster β.

As a further example, consider a two-particle operator $O^{(2)}$, which in a scalar theory is defined by the expression

$$O^{(2)}=\int\int \psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')O^{(2)}(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r})d\mathbf{r}\,d\mathbf{r}' \ . \tag{2.23a}$$

Within the cluster formalism, $O^{(2)}$ can be written in the form

$$O^{(2)}=\overline{\mathrm{Tr}}(\underline{\Pi}\,\underline{O}^{(2)}) \ . \tag{2.23b}$$

It follows from Eq. (2.13), that a general nonfactorizable operator $O^{(2)}$, e.g., the Coulomb interaction, can be expressed as

$$\underline{O}^{(2)}=\sum_{\alpha,\beta,\gamma,\delta}[(\underline{C}^\alpha)^\dagger\otimes(\underline{C}^\beta)^\dagger]\underline{O}^{\alpha\beta\gamma\delta}(\underline{C}^\gamma\otimes\underline{C}^\delta) \ , \tag{2.23c}$$

where

$$\begin{aligned} O^{\alpha\beta\gamma\delta}=\int\int&[\underline{\psi}^{\alpha*}(\mathbf{r})\otimes\underline{\psi}^{\beta*}(\mathbf{r}')]O^{(2)}(\mathbf{r},\mathbf{r}')\\ &\times[\underline{\psi}^{\gamma}(\mathbf{r}')\otimes\underline{\psi}^{\delta}(\mathbf{r})]d\mathbf{r}\,d\mathbf{r}' \ . \end{aligned} \tag{2.24}$$

Thus a general Hamiltonian, $H=H^{(1)}+H^{(2)}$, can be written in the form

$$\underline{H}=\underline{I}\otimes\underline{H}^{(1)}+\underline{H}^{(2)} \ , \tag{2.25}$$

where a direct-product space must be used in order to include nonlocal potentials. These equations simplify considerably in the case of factorizable two-particle operators such as the current-current correlation function. The advantage of this cluster formulation is that diagrammatic techniques in perturbation theory can be formulated unambiguously. However, Wick's theorem, familiar from scalar perturbation theory, must be modified due to the noncommutative property of both matrices and operators. A more-detailed account on this point is given in the Appendix.

In concluding this section, we examine some general properties of our cluster-field theory. First, we define a cluster anticommutation relation as

$$\{\underline{A},\underline{B}\}_{\underline{\Pi}}=\underline{A}\,\underline{\Pi}\,\underline{B}+(\underline{B}\,\underline{\Pi}\,\underline{A})^T \ , \tag{2.26}$$

where $\underline{A},\underline{B}$ are cluster operators and a superscript T represents the transpose of a matrix. Note that, in general, $(\underline{B}\,\underline{\Pi}\,\underline{A})^T$ is not equal to, $\underline{A}^T\underline{\Pi}\,\underline{B}^T$ because the matrix elements of the cluster operators $\underline{A}$ and $\underline{B}$ may not commute. This can be easily illustrated in terms of the operators defined in Eq. (2.14). It is not difficult to check that the cluster canonical anticommutation relations, corresponding to Eq. (2.4), are still satisfied, i.e.,

$$\begin{aligned} &\{\underline{c}^\alpha,(\underline{c}^\beta)^\dagger\}_{\underline{\Pi}}=\underline{I}\delta_{\alpha\beta} \ ,\\ &\{(\underline{c}^\alpha)^\dagger,(\underline{c}^\beta)^\dagger\}_{\underline{\Pi}}=\{\underline{c}^\alpha,\underline{c}^\beta\}_{\underline{\Pi}}=0 \ . \end{aligned} \tag{2.27}$$

Furthermore, the causal (C) and retarded (R) (as well as the advanced) finite-temperature Green functions can then be defined in a straightforward way,

$$\begin{aligned} &\underline{G}^{\alpha\beta}_C=-i\langle T\{\underline{c}^\alpha(t)\underline{\Pi}[\underline{c}^\beta(0)]^\dagger\}\rangle \ ,\\ &\underline{G}^{\alpha\beta}_R=-i\theta(t)\langle\{\underline{c}^\alpha(t),[\underline{c}^\beta(0)]^\dagger\}_{\underline{\Pi}}\rangle \ , \end{aligned} \tag{2.28}$$

where we use the convention of Ref. 23, i.e., $\langle\cdots\rangle$ denotes both thermal and quantum-mechanical averages.

Two general principles can be drawn from these considerations: (1) The usual Matsubara formalism[23] for scalar Green functions can be extended directly to our cluster-field theory, and (2) perturbation theory, as discussed in the Appendix, can still be performed by generalizing Wick's theorem to a matrix form.

The use of the above principles will now be illustrated in the process of deriving a cluster-conductivity formula.

C. Cluster-conductivity formula

In the linear-response regime the static ac conductivity $\sigma(\omega)$ can be calculated by means of the relation[23]

$$\sigma(\omega)=\frac{i}{\omega}\left[\pi_{\mu\nu}(\omega)+\frac{ne^2}{m_e}\delta_{\mu\nu}\right], \tag{2.29}$$

where ω is the external frequency; n, e, and m_e are the density, charge, and mass of the electrons, respectively; and μ,ν are indices denoting spatial directions. The current-current correlation function $\pi_{\mu\nu}(\omega)$ is given by the expression

$$\pi_{\mu\nu}(\omega)=-i\int_{-\infty}^{\infty}\Theta(t)e^{i\omega t}\langle\{\mathbf{J}_\mu(t),\mathbf{J}_\nu(0)\}\rangle dt\ , \tag{2.30}$$

which can be calculated through the use of the Matsubara formalism.[23] In this formalism one first calculates the complex time response function.

$$\pi_{\mu\nu}(\tau)=-\langle T_\tau[\mathbf{J}_\mu^\dagger(\tau)\mathbf{J}_\nu(0)]\rangle\ , \tag{2.31}$$

where τ is the complex time and T_τ means complex time ordering. The real energy correlation function $\pi_{\mu\nu}(\omega)$ can be obtained by performing the following analytic continuation:

$$i\omega_n \overset{\text{change}}{\longrightarrow} \omega+i\delta \text{ in } \pi_{\mu\nu}(i\omega_n) \tag{2.32}$$

with the complex energy response function $\pi_{\mu\nu}(i\omega_n)$ given in the form

$$\pi_{\mu\nu}(i\omega_n)=\int_0^\beta e^{i\omega_n\tau}\pi_{\mu\nu}(\tau)d\tau\ , \tag{2.33}$$

where β is equal to $\hbar/k_BT$, k_B is Boltzmann's constant, and T is the temperature.

For a general Hamiltonian the complex response function $\pi_{\mu\nu}(\tau)$ can be evaluated in many-body theory by using diagrammatic techniques. However, for a noninteracting single-particle Hamiltonian, Eq. (2.1), there exists a simple form for calculating $\pi_{\mu\nu}(\tau)$. We will derive that compact form by using the cluster theory described previously.

The cluster formalism for the current-current operator can be constructed by using Eq. (2.22),

$$\begin{aligned}\pi_{\mu\nu}(\tau)&=-\int\int\psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')\langle T_\tau[\mathbf{J}_\mu^\dagger(\mathbf{r},\tau)\mathbf{J}_\nu(\mathbf{r}',0)]\rangle\psi(\mathbf{r}')\psi(\mathbf{r})d\mathbf{r}\,d\mathbf{r}'\\&=-\langle T_\tau\int\int\psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')\mathbf{J}_\mu^\dagger(\mathbf{r},\tau)\mathbf{J}_\nu(\mathbf{r}',0)\psi(\mathbf{r}')\psi(\mathbf{r})d\mathbf{r}\,d\mathbf{r}'\rangle\\&=\overline{\mathrm{Tr}}\langle T_\tau(\underline{c\,\Pi\,c}^\dagger\underline{\mathbf{J}}_\mu\underline{c\,\Pi\,c}^\dagger\underline{\mathbf{J}}_\nu)\rangle\\&=\overline{\mathrm{Tr}}[\underline{\mathcal{G}}(-\tau)\underline{\mathbf{J}}_\mu\underline{\mathcal{G}}(\tau)\underline{J}_\nu]\ ,\end{aligned} \tag{2.34}$$

where the definition of the Green function $\underline{\mathcal{G}}$ is evident.[23] In deriving Eq. (2.34), we have used Eqs. (2.16), (2.17), (2.12), and the matrix Wick's theorem given in the Appendix. The calculation of $\pi_{\mu\nu}(\tau)$ can be performed in the usual way by carrying out the corresponding contour integrations.[23] The final form of the correlation function is

$$\pi_{\mu\nu}(\omega)=\frac{1}{V}\overline{\mathrm{Tr}}\left[\int_{-\infty}^{\infty}\frac{d\varepsilon}{2\pi}n_F(\varepsilon)\underline{A}(\varepsilon)\underline{\mathbf{J}}_\mu[\underline{G}^R(\varepsilon+\hbar\omega)+\underline{G}^A(\varepsilon-\hbar\omega)]\mathbf{J}_\nu\right], \tag{2.35}$$

where $n_F(\varepsilon)$ is the Fermi distribution function, $\underline{A}(\varepsilon)$ is the cluster spectral function defined by the expression

$$\underline{A}(\varepsilon)=-\mathrm{Im}[\underline{G}^{R*}(\varepsilon)-\underline{G}^R(\varepsilon)]\ , \tag{2.36}$$

and V is the volume. The real part of the ac conductivity, $\mathrm{Re}\sigma_{\mu\nu}(\omega)$, can be related to $\pi_{\mu\nu}(\omega)$,

$$\mathrm{Re}\sigma_{\mu\nu}(\omega)=-\frac{1}{\omega}\mathrm{Im}\pi_{\mu\nu}(\omega)\ . \tag{2.37}$$

Thus

$$\mathrm{Re}\sigma_{\mu\nu}(\omega)=-\frac{1}{V\omega}\mathrm{Im}\,\overline{\mathrm{Tr}}\left[\int_{-\infty}^{\infty}\frac{d\varepsilon}{2\pi}n_F(\varepsilon)\underline{A}(\varepsilon)\underline{\mathbf{J}}_\mu[\underline{G}^R(\varepsilon+\hbar\omega)+\underline{G}^A(\varepsilon-\hbar\omega)]\mathbf{J}_\nu\right]. \tag{2.38}$$

In the zero-temperature limit and for clusters confined to a single site the above formula reduces to the ac conductivity formula derived by Velicky[4] (the dc conductivity formula can be obtained in the limit $\omega\to 0$),

$$\mathrm{Re}\sigma_{\mu\nu}(\omega)=\frac{1}{\omega V}\mathrm{Im}\,\overline{\mathrm{Tr}}\left[\frac{1}{2\pi}\int_{E-\hbar\omega}^{E}d\varepsilon\,\underline{A}(\varepsilon)\underline{\mathbf{J}}_\mu G^R(\varepsilon+\hbar\omega)\underline{\mathbf{J}}_\nu\right]. \tag{2.39}$$

where E denotes the E Fermi energy.

We conclude this section by emphasizing that the conductivity formulas just derived are of a generic character and can be used both in conjunction with single-band as well as more realistic potentials such as those of the muffin-tin type. In the following section we show that the conductivity formula, Eq. (2.39), reduces to well-known results for the cases of some commonly used model Hamiltonians.

III. CLUSTER EVALUATION OF THE CONDUCTIVITY

We consider a system of noninteracting electrons moving in the presence of a substitutionally random potential. The expression for the real part of the ac conductivity of such a system has been shown to have the form of Eq. (2.38). For the present we confine ourselves to the zero-temperature limit, Eq. (2.39). Our formalism is general enough to illustrate the structure of the theory, and can be easily extended to calculations at finite temperatures. In the zero-temperature limit, Eq. (2.39) can be rewritten in the form

$$\begin{aligned}\mathrm{Re}\sigma_{\mu\nu}(\omega) &= -\frac{1}{\omega V}\mathrm{Im}\left[\overline{\mathrm{Tr}}\left[\frac{1}{2\pi}\int_{E-\hbar\omega}^{E} d\varepsilon\langle \underline{J}_\mu \underline{A}(\varepsilon)\mathbf{J}_\nu \underline{G}^R(\varepsilon+\hbar\omega)\rangle\right]\right]\\ &= \frac{1}{\omega V}\mathrm{Im}\left[\overline{\mathrm{Tr}}\left[\frac{1}{2\pi}\int_{E-\hbar\omega}^{E} d\varepsilon\langle \underline{J}_\mu \mathrm{Im}[\underline{G}^R(\varepsilon)-\underline{G}^A(\varepsilon)]\underline{J}_\nu G^R(\varepsilon+\hbar\omega)\rangle\right]\right]\\ &= \frac{1}{2i\omega V}\mathrm{Im}\left[\overline{\mathrm{Tr}}\left[\frac{1}{2\pi}\int_{E-\hbar\omega}^{E} d\varepsilon\langle \underline{J}_\mu [\underline{G}^R(\varepsilon)-\underline{G}^{R*}(\varepsilon)-\underline{G}^A(\varepsilon)+\underline{G}^{A*}(\varepsilon)]\underline{J}_\nu \underline{G}^R(\epsilon+\hbar\omega)\rangle\right]\right]\ ,\end{aligned} \tag{3.1}$$

where $\langle \cdots \rangle$ denotes a configurational average, and $*$ denotes a complex conjugate. Thus, the main task of evaluating the real part of the ac conductivity is to evaluate the expression (for simplicity, we suppress the space indices)

$$K=\overline{\mathrm{Tr}}\langle \underline{J}\,\underline{G}(\varepsilon)\underline{J}\underline{G}(\varepsilon+\hbar\omega)\rangle\ , \tag{3.2}$$

where $\underline{\mathbf{J}}$, a matrix current operator, can fairly generally be made to include the model used by Blackman, Esterling, and Berk[17] (BEB) to treat ODD as well as MT Hamiltonians used by Butler and Stocks.[19] $\underline{G}$ is a single-particle cluster Green function which depends on the details of the random potential. Note that $\underline{J}$ and $\underline{G}$ are all matrix operators.

The rest of this section is arranged as follows. In Sec. III A we give the random-phase-like decoupling scheme for evaluating Eq. (3.2); in Sec. III B we establish the Ward identity and show that it is satisfied by the random-phase-like decoupling scheme. In Sec. III C we present the concepts and formalism used in the embedded-cluster method.

A. Random-phase-like decoupling scheme

Consider the Hamiltonian of a random system given in Eq. (2.19). The cluster Green function can be written as

$$\underline{G}=\underline{\overline{G}}+\underline{\overline{G}}\,\underline{T}\underline{\overline{G}}\ , \tag{3.3}$$

Where $\underline{\overline{G}}$ is the cluster Green function of an effective medium, and $\underline{T}$, the cluster transition or scattering matrix, can be expressed in the form

$$\underline{T}=\underline{V}(\underline{I}-\underline{\overline{G}}\,\underline{V})^{-1}=(\underline{I}-\underline{V}\,\underline{\overline{G}})^{-1}\underline{V}\ , \tag{3.4}$$

where $\underline{V}$ is the cluster perturbation away from the effective medium.

By using Eqs. (3.2) and (3.3), we arrive at the relations

$$\begin{aligned}K&=\overline{\mathrm{Tr}}\langle \underline{J}(\underline{\overline{G}}+\underline{\overline{G}}\,\underline{T}\,\underline{\overline{G}})\underline{J}(\underline{G}+\underline{G}\,\underline{T}\,\underline{G})\rangle\\ &=\overline{\mathrm{Tr}}(\underline{J}\,\underline{\overline{G}}(\underline{J}+\underline{\Gamma})\underline{\overline{G}})\ ,\end{aligned} \tag{3.5}$$

where we assume that $\langle \underline{T}\rangle=\underline{0}$ and define

$$\underline{\Gamma}=\langle \underline{T}\,\underline{\overline{G}}\,\underline{J}\underline{\overline{G}}\,\underline{T}\rangle\ , \tag{3.6}$$

as the cluster vertex operator.

Within multiple-scattering theory, we can decompose the random potential $\underline{V}$ into the sum of contributions from individual clusters. Therefore the cluster t matrix in turn has the form

$$\begin{aligned}&\underline{T}=\sum_\alpha \underline{Q}^\alpha\ ,\\ &\underline{Q}^\alpha=\underline{T}^\alpha(\underline{I}+\underline{\overline{G}}\sum_{\beta\,(\neq\alpha)}\underline{Q}^\beta)\ ,\end{aligned} \tag{3.7}$$

where

$$\underline{T}^\alpha=\underline{V}^\alpha(\underline{I}+\underline{\overline{G}}\,\underline{T}^\alpha) \tag{3.8}$$

and α is a cluster index. Transposing Eqs. (3.7) and (3.8), one finds

$$\underline{T}=\sum_\alpha \underline{\tilde{Q}}^\alpha\ , \tag{3.9}$$

and

$$\underline{\tilde{Q}}^\alpha=\left[\underline{I}+\sum_{\beta\,(\neq\alpha)}\underline{\tilde{Q}}^\beta\underline{\overline{G}}\right]\underline{T}^\beta\ . \tag{3.10}$$

Introducing the above decompositions of the t matrix into the cluster vertex operator, Eq. (3.6), we have

$$\begin{aligned}\underline{\Gamma}&=\sum_{\alpha,\beta}\langle \underline{Q}^\alpha\underline{\overline{G}}\,\underline{J}\underline{\overline{G}}\,\underline{\tilde{Q}}^\beta\rangle\\ &=\sum_{\alpha,\beta}\left\langle \underline{T}^\alpha\left[\underline{I}+\underline{\overline{G}}\sum_{\delta\,(\neq\alpha)}\underline{Q}^\delta\right]\underline{\overline{G}}\,\underline{J}\,\underline{\overline{G}}\left[\underline{I}+\sum_{\delta\,(\neq\beta)}\underline{\tilde{Q}}^\delta\underline{\overline{G}}\right]\underline{T}^\beta\right\rangle\ .\end{aligned} \tag{3.11}$$

The coherent decoupling consists of neglecting the statistical correlation of the atomic t matrix and the effective wave factors, i.e.,

$$\left\langle \underline{T}^\alpha\left[\underline{I}+\underline{\overline{G}}\sum_{\delta\,(\neq\alpha)}\underline{Q}^\delta\right]\underline{\overline{G}}\,\underline{J}\,\underline{\overline{G}}\left[\underline{I}+\sum_{\delta\,(\neq\beta)}\underline{\tilde{Q}}^\delta\underline{\overline{G}}\right]\underline{T}^\beta\right\rangle=\left\langle \underline{T}^\alpha\left\langle\left[\underline{I}+\underline{\overline{G}}\sum_{\delta\,(\neq\alpha)}\underline{Q}^\delta\right]\underline{\overline{G}}\,\underline{J}\,\underline{\overline{G}}\left[\underline{I}+\sum_{\delta\,(\neq\beta)}\underline{\tilde{Q}}^\delta\underline{G}\right]\right\rangle\underline{T}^\beta\right\rangle\ . \tag{3.12}$$

For $\alpha \neq \beta$, the operators $\underline{T}^{\alpha}$ and $\underline{T}^{\beta}$ are considered statistically independent and are averaged separately. Within appropriately defined approximation schemes, each such average can be made to yield a negligible contribution. Therefore, we may define a quantity $\underline{\Gamma}^{\alpha}$ as

$$\langle \underline{Q}^{\alpha}\underline{\bar{G}}\,\underline{J}\,\underline{\bar{G}}\,\underline{\tilde{Q}}^{\beta}\rangle = \underline{\Gamma}^{\alpha}\delta_{\alpha\beta} \; . \tag{3.13}$$

The physical meaning of the above assumption is that the vertex operator is cluster diagonal, and it can be written in the form

$$\underline{\Gamma} = \sum_{\alpha} \underline{\Gamma}^{\alpha} \; . \tag{3.14}$$

This property allows us to calculate the quantity K, Eq. (3.5), by performing a **k**-space integration over the first Brillouin zone (BZ), i.e.,

$$K = \frac{1}{\Omega_{\mathrm{BZ}}} \int_{\mathrm{BZ}} d\mathbf{k}\, \overline{\mathrm{Tr}}\{\underline{J}^{\alpha}(\mathbf{k})\underline{\bar{G}}^{\alpha}(\mathbf{k})[\underline{J}^{\alpha}(\mathbf{k}) + \underline{\Gamma}^{\alpha}]\underline{G}^{\alpha}(\mathbf{k})\} \; . \tag{3.15}$$

Here Ω_{BZ} is the **k**-space volume of the first Brillouin zone, and $\underline{\bar{G}}^{\alpha}(\mathbf{k})$ and $\underline{J}^{\alpha}(\mathbf{k})$ are the **k**-space cluster Green function and current matrix which are defined as

$$\begin{aligned} \underline{\bar{G}}^{\alpha}(\mathbf{k}) &= \sum_{\beta} \underline{\bar{G}}^{\alpha\beta} e^{i\mathbf{k}\cdot(\mathbf{R}_{\beta}-\mathbf{R}_{\alpha})} \; , \\ \underline{J}^{\alpha}(\mathbf{k}) &= \sum_{\beta} \underline{J}^{\alpha\beta} e^{i\mathbf{k}\cdot(\mathbf{R}_{\beta}-\mathbf{R}_{\alpha})} \; , \end{aligned} \tag{3.16}$$

where $\mathbf{R}_{\alpha}$ and $\mathbf{R}_{\beta}$ are the centers of clusters α and β. For example, in the MCPA, $\underline{G}(\mathbf{k})$ can be written in the form

$$\underline{\bar{G}}(\mathbf{k}) = [\langle \underline{G}^{\alpha}\rangle^{-1} + \underline{\bar{\Delta}}^{\alpha} - W(\mathbf{k})]^{-1} \; , \tag{3.17}$$

where $\langle \underline{G}^{\alpha}\rangle$ and $\underline{\bar{\Delta}}$ have been defined before,[5] and $\underline{W}(\mathbf{k})$ is a **k**-space cluster hopping integral. A similar expression can plausibly be used within the ECM. The decoupling assumption may also be used to simplify the internal average in Eq. (3.13), by considering only the case $\alpha = \beta$:

$$\underline{\Gamma}^{\alpha} = \left\langle \underline{T}^{\alpha}\underline{\bar{G}} \left[\underline{J} + \sum_{\beta(\neq\alpha)} \underline{\Gamma}^{\beta} \right] \underline{\bar{G}}\,\underline{T}^{\alpha} \right\rangle \; . \tag{3.18}$$

When projected on a cluster space, the above equation yields a system of linear equations for the unknown matrix elements of Γ^{α}.

It is useful to rewrite Eq. (3.18) in the form

$$\underline{\Gamma}^{\alpha} = \langle \underline{T}^{\alpha}\underline{\bar{G}}(\underline{J} + \underline{\Gamma} - \underline{\Gamma}^{\alpha})\underline{\bar{G}}\,\underline{T}^{\alpha}\rangle \; , \tag{3.19}$$

which can be solved formally by using the relations

$$\begin{aligned} \underline{\Gamma}^{\alpha} = \Bigg\langle \underline{T}^{\alpha} \Bigg[& \frac{1}{\Omega_{\mathrm{BZ}}} \int_{\mathrm{BZ}} d\mathbf{k}\, \underline{\bar{G}}^{\alpha}(\mathbf{k})[\underline{J}^{\alpha}(\mathbf{k}) + \underline{\Gamma}^{\alpha}]\underline{\bar{G}}^{\alpha}(\mathbf{k}) \\ & - \underline{\bar{G}}\,\underline{\Gamma}^{\alpha}\underline{\bar{G}} \Bigg] \underline{T}^{\alpha} \Bigg\rangle \; . \end{aligned} \tag{3.20}$$

Notice that the matrix $\underline{\Gamma}^{\alpha}$ appears in the middle of the right-hand side of Eq. (3.20) which reflects the fact that the matrix is not column independent. These equations can be solved as follows. Writing out the ij element of Eq. (3.20) explicitly, we have the relation

$$\begin{aligned} \underline{\Gamma}^{\alpha}_{ij} = {} & \left\langle \left(\underline{T}^{\alpha} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} \underline{\bar{G}}(\mathbf{k})\underline{J}(\mathbf{k})\underline{\bar{G}}(\mathbf{k})\underline{T}^{\alpha}\right)_{ij} \right\rangle \\ & + \left\langle \left(\underline{T}^{\alpha} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} [\underline{\bar{G}}(\mathbf{k})]_{ik} \underline{\Gamma}^{\alpha}_{kl} [\underline{\bar{G}}(\mathbf{k})\underline{T}^{\alpha}]_{lj} \right\rangle \\ & - \langle \underline{T}^{\alpha}\underline{\bar{G}})_{ik} \underline{\Gamma}^{\alpha}_{kl} (\underline{\bar{G}}\,\underline{T}^{\alpha})_{lj} \rangle \; . \end{aligned} \tag{3.21}$$

Introducing a symbol $\delta^{kl}_{ij} = \delta_{ik}\delta_{lj}$, we can write this equation in the form

$$\begin{aligned} & \sum_{k,l} \left[\delta^{kl}_{ij} - \left\langle \left[\underline{T}^{\alpha} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} [\underline{\bar{G}}(\mathbf{k})] \right]_{ik} [\underline{\bar{G}}(\mathbf{k})\underline{T}^{\alpha}]_{lj} \right\rangle + \langle (\underline{T}^{\alpha}\underline{\bar{G}})_{ik} (\underline{\bar{G}}\,\underline{T}^{\alpha})_{lj} \rangle \right] \underline{\Gamma}^{\alpha}_{kl} \\ & \qquad = \sum_{k,l} \left[\delta^{kl}_{ij} \left\langle \left[\underline{T}^{\alpha} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} \underline{\bar{G}}(\mathbf{k})\underline{J}(\mathbf{k})\underline{\bar{G}}(\mathbf{k})\underline{T}^{\alpha} \right]_{kl} \right\rangle \right] \; . \end{aligned} \tag{3.22}$$

The system of these linear equations is now formally in a canonical form, which can be solved by a standard routine, through appropriate redefinitions of the various matrix quantities. For example, Eq. (3.22) can be rewritten in the matrix form

$$\left[\underline{I}\otimes\underline{I} - \left\langle \left[T^{\alpha} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} \underline{\bar{G}}(\mathbf{k}) \right] \otimes (\underline{\bar{G}}(\mathbf{k})\underline{T}^{\alpha}) \right\rangle + \langle (\underline{T}^{\alpha}\underline{\bar{G}}) \otimes (\underline{\bar{G}}\underline{T}^{\alpha}) \rangle \right] \underline{\Gamma}^{\mathrm{col}} = \left[\underline{T}^{\alpha} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} \underline{\bar{G}}(\mathbf{k})\underline{J}(\underline{\mathbf{k}})\underline{\bar{G}}(\mathbf{k})\underline{T}^{\alpha} \right]^{\mathrm{col}} , \tag{3.23}$$

where $\otimes$ denotes direct matrix product and the superscript "col" for column denotes the following quantity:

$$\underline{\Gamma}^{\mathrm{col}} = (\Gamma_{11}, \Gamma_{12}, \ldots, \Gamma_{1N}, \Gamma_{21}, \Gamma_{22}, \ldots, \Gamma_{2N}, \ldots, \Gamma_{N1}, \Gamma_{N2}, \ldots, \Gamma_{NN})^{T} \; . \tag{3.24}$$

To conclude this subsection, we summarize the procedure for calculating the zero-temperature ac conductivity of a disordered system. The steps to calculate K, Eq. (3.2) or (3.15), are as follows: (i) determine the Green function $\overline{\underline{G}}$ by using some approximate scheme such as the CPA or the MCPA; (ii) calculate $\overline{\underline{G}}(\mathbf{k})$ by using Eq. (3.17), and then evaluate the cluster current operator, $\underline{J}$; (iii) perform the configurational average over the cluster t matrix in Eq. (3.24), and solve the simultaneous linear equations for the matrix elements of Γ^{α}; and (iv) perform the integration in Eq. (3.15) over the first Brillouin zone. From a knowledge of K the ac conductivity, Eq. (3.2), then follows.

B. Ward identity

As discussed in the preceding section, the evaluation of the average of the product of two one-particle Green functions requires an evaluation of a vertex function. The Ward identity is an exact relationship between vertex functions and single-particle self-energies. Leath[24] analyzed diagrammatically the connection between the CPA self-energy and the vertex correction given by Velický.[4] He showed that the particularly simple form of macroscopic conservation laws developed by Baym[25] is very instructive and can indeed be used to derive the vertex corrections from the self-energy in the single-site CPA. In this section we first give the definition for the irreducible vertex function and establish the Ward identity (in operator form) under the condition that the average of the t matrix vanishes, i.e., $\langle T\rangle=0$. We then show that the decoupling schemes together with the assumption Eq. (3.13) satisfies the Ward identity in the cluster approximation.

For the sake of clarity, we group all the relevant equations here. The starting point is the operator equation

$$G=\bar{G}+\bar{G}T\bar{G}\ , \tag{3.25}$$

where the T operator is given by the form

$$T=(V-\Sigma)[1-\bar{G}(V-\Sigma)]^{-1}\ . \tag{3.26}$$

As in the preceding section, V is the random potential and Σ is the exact self-energy operator which is determined by the condition

$$\langle T\rangle=0\ . \tag{3.27}$$

Thus, Eq. (3.27) implies that the disorder averaged Green function $\langle G\rangle$ is equal to the Green function of the effective medium, i.e.,

$$\langle G\rangle=\bar{G}\ . \tag{3.28}$$

Following the work of Leath[24] and Velický,[4] we have the forms

$$\langle G\otimes G\rangle=\bar{G}\otimes\bar{G}+\bar{G}\otimes\bar{G}\Lambda\langle G\otimes G\rangle \tag{3.29}$$

and

$$\langle G\otimes G\rangle=\bar{G}\otimes\bar{G}+\bar{G}\Gamma\bar{G}\ , \tag{3.30}$$

where

$$\Gamma=\langle T\bar{G}\otimes\bar{G}T\rangle \tag{3.31}$$

is the full vertex function and Λ is the irreducible vertex function. Both Γ and Λ are two-particle operators, i.e., four-point functions in a space-time representation, and are connected by the equation

$$\Gamma=\bar{G}\Lambda\bar{G}+\bar{G}\Lambda\bar{G}\Gamma\ , \tag{3.32}$$

where the proper identification of contractions among operators is understood. Note that we use the notation of direct product to signify that there is no correlation of the indices of the separate operators.

We will now show that Eq. (3.32) can be used to establish the Ward identity, i.e.,

$$\Lambda=(\delta\Sigma)/(\delta\bar{G})\ , \tag{3.33}$$

where δ denotes a functional variation. We first rewrite Eq. (3.26) in the form

$$T^{-1}=(V-\Sigma)^{-1}-\bar{G} \tag{3.34}$$

or

$$T=(V-\Sigma)+(V-\Sigma)\bar{G}T\ . \tag{3.35}$$

Starting with

$$TT^{-1}=1\ , \tag{3.36}$$

we have

$$\delta T=-T(\delta T^{-1})T\ . \tag{3.37}$$

Using Eqs. (3.34) and (3.35), we have

$$\begin{aligned}\delta T&=-T[\delta(V-\Sigma)^{-1}-\delta\bar{G}]T\\&=T(\delta\bar{G})T-(1+T\bar{G})(\delta\Sigma)(1+\bar{G}T)\ ,\end{aligned} \tag{3.38}$$

while Eq. (3.27) leads to the result

$$\delta\langle T\rangle=\langle\delta T\rangle=0\ . \tag{3.39}$$

We then have the equation

$$\delta\Sigma=\langle T\delta\bar{G}T\rangle-\langle T\bar{G}(\delta\Sigma)\bar{G}T\rangle\ , \tag{3.40}$$

i.e.,

$$\delta\Sigma/\delta\bar{G}=\langle T\otimes T\rangle-\langle T\bar{G}(\delta\Sigma/\delta\bar{G})\bar{G}T\rangle\ . \tag{3.41}$$

Thus we have

$$\delta\Sigma/\delta\bar{G}=(1+\langle T\bar{G}\otimes\bar{G}T\rangle)^{-1}\langle T\otimes T\rangle\ . \tag{3.42}$$

On the other hand, from Eqs. (3.31) and (3.32) we obtain

$$\langle T\bar{G}\otimes\bar{G}T\rangle=\bar{G}\Lambda\bar{G}+\bar{G}\Lambda\bar{G}\langle T\bar{G}\otimes\bar{G}T\rangle\ , \tag{3.43}$$

from which it follows that

$$\bar{G}\Lambda\bar{G}=(1+\langle T\bar{G}\otimes\bar{G}T\rangle)^{-1}\langle T\bar{G}\otimes\bar{G}T\rangle\ . \tag{3.44}$$

By comparing Eqs. (3.42) and (3.44) and properly identifying the various (implicit) indices, we have

$$\Lambda=(\delta\Sigma)/(\delta\bar{G})\ , \tag{3.33}$$

which is the Ward identity. Therefore, the self-energy and irreducible vertex function determined by the exact condition, Eq. (3.27), satisfy the Ward identity. The macroscopic conservation laws are all preserved.

As is well known, the exact condition [Eq. (3.27)] cannot be achieved in practical calculations, requiring the use of various approximation schemes at different levels. We will consider a general cluster approximation by assuming that the self-energy is cluster diagonal, i.e.,

$$\Sigma = \sum_{\alpha} \Sigma^{\alpha} \, , \tag{3.45}$$

where Σ^{α} is a functional of the cluster Green function $\underline{G}^{\alpha\alpha}$. The Ward identity then takes the form

$$\underline{\Lambda}^{\alpha} = \delta \underline{\Sigma}^{\alpha} / \delta \underline{\bar{G}}^{\,\alpha\alpha} \, . \tag{3.46}$$

The steps leading to Eq. (3.41) can be duplicated within our cluster theory and give the equation

$$\underline{\Lambda}^{\alpha} = (\underline{I} + \langle \underline{T}^{\alpha} \underline{\bar{G}} \otimes \underline{\bar{G}} \, \underline{T}^{\alpha} \rangle)^{-1} \langle \underline{T}^{\alpha} \otimes \underline{T}^{\alpha} \rangle \, , \tag{3.47}$$

with the analogous iterative equation

$$\underline{\Gamma}^{\alpha} = \underline{\bar{G}} \, \underline{\Lambda}^{\alpha} \underline{\bar{G}} + \sum_{\beta} \underline{\bar{G}} \, \underline{\Lambda}^{\alpha} \underline{\bar{G}} \, \underline{\Gamma}^{\alpha} \underline{\bar{G}} \, \underline{\Gamma}^{\beta} \, . \tag{3.48}$$

We have

$$(\underline{I} + \langle \underline{T}^{\alpha} \underline{\bar{G}} \otimes \underline{\bar{G}} \, \underline{T}^{\alpha} \rangle) \underline{\Gamma}^{\alpha} = \langle \underline{T}^{\alpha} \underline{\bar{G}} \otimes \underline{\bar{G}} \, \underline{T}^{\alpha} \rangle + \sum_{\beta} \langle \underline{T}^{\alpha} \underline{\bar{G}} \, \Gamma^{\beta} \underline{\bar{G}} \, T^{\alpha} \rangle \, , \tag{3.49}$$

i.e.,

$$\underline{\Gamma}^{\alpha} = \langle \underline{T}^{\alpha} \underline{\bar{G}} \otimes \underline{\bar{G}} \, \underline{T}^{\alpha} \rangle + \sum_{\beta \neq \alpha} \langle \underline{T}^{\alpha} \underline{\bar{G}} \, \Gamma^{\beta} \underline{\bar{G}} \, \underline{T}^{\alpha} \rangle \, . \tag{3.50}$$

For clarity, a number of indices such as site and angular momentum symbols have been suppressed. Equation (3.50) is exactly the formula Eq. (3.18) obtained in the preceding subsection by using a random-phase-like approximation, except that here we have removed the current operator. A single-site version of the above result is then an alternative proof for the Ward identity given by Velický.[4]

We have proved that the Ward identity is exactly satisfied if we determine the effective medium by requiring that the average t matrix vanishes, which indicates that the disorder average is consistent with macroscopic conservation laws. The cluster Ward identity was then used to derive the equation for determining the full vertex function which leads to the result obtained in the preceding subsection. Thus the random-phase-like decoupling scheme and the assumption,

$$\langle \underline{Q}^{\alpha} \underline{\bar{G}} \, \underline{J} \, \underline{\bar{G}} \underline{\tilde{Q}}^{\,\beta} \rangle = \underline{\Gamma}^{\alpha} \delta_{\alpha\beta} \, , \tag{3.13}$$

used in the preceding subsection are consistent and fully justified.

C. The conductivity in the embedded-cluster method

In the ECM one calculates exactly the Green function for a cluster of atoms embedded in an effective medium which is determined in some optimal way. In substitutionally disordered alloys numerical investigations have indicated that an appropriate embedding medium is that determined within the CPA. Then the TB Green function for a cluster C of atoms embedded in the medium is written in the form

$$\underline{G}_{CC} = (E\underline{I} - \underline{H}_{C} - \underline{\Delta}_{C})^{-1} \, . \tag{3.51}$$

For single-band systems, all quantities except the energy E are $n \times n$ matrices for n-site clusters. Here, H_C is the intracluster part of the disordered Hamiltonian, while the cluster renormalized interactor $\underline{\Delta}_C$ describes the interaction of the cluster with the surrounding medium and in the absence of off-diagonal disorder is independent of the particular atomic configuration represented by $\underline{H}_C$. Thus, $\underline{\Delta}_C$ can be found easily by noting that $\underline{\bar{G}}_{CC}$, the cluster-diagonal Green function for the effective medium, can be evaluated in two different forms

$$[\underline{\bar{G}}_{CC}]_{ij} = [(E\underline{I} - \underline{\bar{H}}_{C} - \underline{\Delta}_{C})^{-1}]_{ij} \tag{3.52}$$

and also

$$\begin{aligned} [\underline{\bar{G}}_{CC}]_{ij} &= \underline{\bar{G}}_{ij} \\ &= \frac{1}{\Omega_{\mathrm{BZ}}} \int_{\mathrm{BZ}} \underline{\bar{G}}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}_{ij}} d\mathbf{k} \, , \end{aligned} \tag{3.53}$$

where $\underline{\bar{H}}_C$ is the intracluster Hamiltonian for the effective medium, $\underline{\bar{G}}(\mathbf{k})$ is the effective-medium Green function in the $\mathbf{k}$ representation, and $\mathbf{R}_{ij}$ is the vector from site j to site i. From Eqs. (3.51) and (3.52) we obtain,

$$\underline{\Delta}_{C} = E\underline{I} - \underline{\bar{H}}_{C} - (\underline{\bar{G}}_{CC})^{-1} \, , \tag{3.54}$$

so that

$$\underline{G}_{CC} = (\underline{\bar{H}}_{C} - \underline{H}_{C} + \underline{\bar{G}}_{CC}^{-1})^{-1} \, . \tag{3.55}$$

Once $\underline{G}_{CC}$ has been determined, the corresponding local DOS associated with any site in the cluster and for any cluster configuration is obtained in the usual way,

$$n_i(E) = -\frac{1}{\pi} \mathrm{Im}[\underline{G}_{CC}(E)]_{ii} \, , \tag{3.56}$$

where i denotes the site of interest. Averaged results can be obtained by performing an ensemble average over all cluster configurations.

The above program can also be carried out in the calculation of the average of the product of Green functions, e.g., $\langle \underline{J} \, \underline{G} \, \underline{J} \, \underline{G} \rangle$. The standard approximation, i.e., cumulant expansion, is to replace averages of products by products of averages and attempt an independent calculation of the vertex corrections, e.g., $\langle \underline{J} \, \underline{G} \, \underline{J} \, \underline{G} \rangle - \langle \underline{G} \rangle \underline{J} \langle \underline{G} \rangle \underline{J}$.

We have shown that for a finite cluster the conductivity can be calculated in terms of $\mathrm{Tr}\langle JGJG \rangle$, where the trace is over the cluster basis. For a specific configuration, a central-site approximation to the exact result, Eqs. (3.15) and (3.23), can be made, i.e.,

$$\frac{1}{n} \mathrm{Tr} \langle \underline{J} \, \underline{G} \, \underline{J} \, \underline{G} \rangle \sim \langle \underline{J} \, \underline{G} \, \underline{J} \, \underline{G} \rangle_{00} \, , \tag{3.57}$$

where 0 denotes the central site of the cluster. Results can then be obtained by averaging over all cluster configurations.

IV. NUMERICAL RESULTS

A. General comments

Soon after Velický[4] carried out a consistent description of transport processes in diagonally disordered concentrated alloys based on the CPA, several authors discussed the case of more general single-band model Hamiltonians that include the model used by Blackman *et al.*[17] A remarkable property of the model Hamiltonians investigated is that, in the dilute limit, only the s-like partial waves of the scattering due to an isolated impurity have nonzero scattering amplitudes and, hence, the total scattering amplitude is isotropic. Consequently, the vertex corrections vanish in a single-site theory, in spite of the presence of off-diagonal disorder. Niizeki *et al.*[14] investigated a different extension of the CPA from that due to Blackman *et al.*[17] They considered that the off-diagonal elements of the single-band Hamiltonian with additive randomness, Eq. (2.10), are generally random variables and are not correlated with the randomness of the site energies. Such a Hamiltonian may yield, in the dilute limit, impurity potentials giving anisotropic scattering amplitudes, and hence may give rise to nonzero vertex corrections in the single-site CPA.

The most general case of ODD which has been treated properly within the CPA is that considered by Blackman, Esterling, and Berk[17] (BEB). They investigated the model in which the hopping integrals assume values $W_{ij}^{\alpha\beta}$ depending on the species of atoms α,β occupying sites i and j. These authors used a locator technique which provides a particularly suitable formalism for setting up this generalized problem. With the aid of a simple matrix device, they derived expressions for the single-particle propagators that behave correctly in the dilute limits, and interpolate properly between various limits. Blackman[16] has shown how the formalism of BEB can be used in the calculation of the transport properties of substitutionally disordered alloys in the presence of general ODD.

The matrix formulation of the conductivity presented in the preceding section is general enough to encompass TB alloys with both diagonal and off-diagonal disorder. It can also be used with Hamiltonians described by more general potential functions such as those of a MT type. In this latter case, the formalism allows one to obtain in a concise and economical manner results identical to those obtained earlier by Butler[26] for the case of the CPA, as will be shown in detail in a future publication.[27] In addition, it allows a straightforward generalization of Butler's single-site CPA approach to clusters of sites and the straightforward evaluation of local environment effects, i.e., cluster vertex corrections.

B. The ac conductivity within the single-site CPA

1. *Diagonally disordered systems*

It can readily be shown[4] that in the case of single-band TB systems, even in the presence of ODD,[16] vertex corrections vanish identically within the CPA. In this case, the real part of the ac conductivity, Eq. (2.38), takes the form

$$\mathrm{Re}\sigma(\omega)=\frac{\hbar}{2\pi^3 e^2}\frac{1}{\omega}\int_{\mu-\hbar\omega}^{\mu}dE\int_{\mathrm{BZ}}dk[J(k)\mathrm{Im}\overline{G}(k;E+\hbar\omega)\times J(k)\mathrm{Im}\overline{G}(k;E)]\ , \tag{4.1}$$

where $J(\mathbf{k})$ and $\overline{G}(\mathbf{k};E)$ denote the Fourier transforms of the current operator and the CPA Green function, respectively. This is precisely the equation for the real part of the conductivity derived by Velický and Levin.[28] It can be shown rather easily, under the random-phase-like approximation of Sec. III A, that Eq. (4.1) provides a complete description of the conductivity within the CPA for single-band TB systems.

We checked the validity of Eq. (4.1) by using it to calculate the ac conductivity of one-dimensional substitutionally disordered alloys with only diagonal disorder and only nearest-neighbor hopping, $W=1.0$. In Fig. 1 the results of the CPA calculations (solid lines) are compared with exact conductivity spectra (histograms), obtained by the methods presented in paper I. The top row of Fig. 1 depicts the results for weakly scattering alloys, $\varepsilon_A=-\varepsilon_B=1.0$, while the bottom row corresponds to strongly scattering alloys, $\epsilon_A=-\varepsilon_B=2.0$. Conductivity calculations were carried out for two values of the Fermi energy in units of the bandwidth, $\mu=0.2$ for the left column of Fig. 1 [(a) and (c)] and $\mu=0.5$ for the right column [(b) and (d)].

As is seen in the top row of Fig. 1, the ac conductivity of weakly scattering alloys resembles that of pure systems,

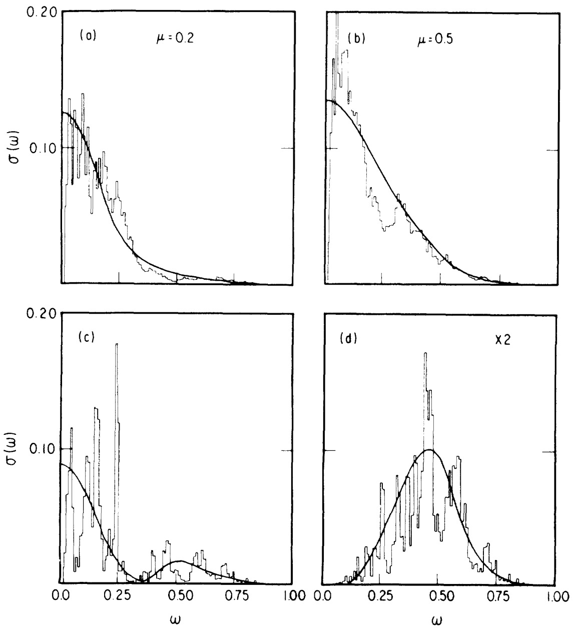

FIG. 1. Comparison of the ac conductivities between the exact results (histograms) and CPA results (curves) for two cases of alloys $A_{0.5}B_{0.5}$: Case I, weak scattering with $\varepsilon_A=\varepsilon_B=1.0$, $W=1.0$, (a) the Fermi energy $\mu=0.2$, (b) $\mu=0.5$; case II, strong scattering with $\varepsilon_A=\varepsilon_B=2.0$, $W=1.0$, (c) $\mu=0.2$, (d) $\mu=0.5$.

i.e., it is strongly peaked at $\omega \sim 0$, and the exact ac conductivity results vanish at $\omega = 0$ in agreement with the requirement that the dc conductivity of one-dimensional disordered systems be strictly zero. On the other hand, the CPA yields a nonvanishing result for the ac conductivity as can be expected from the translational invariance of the CPA effective medium. We note that for weakly scattering alloys, the ac conductivity calculated in the CPA behaves approximately according to the Drude formula,

$$\sigma(\omega) = \sigma(0)/[1 + \omega^2 \tau^2(\omega)] , \tag{4.2}$$

where $\sigma(0)$ denotes the static conductivity of the system and $\tau(\omega)$ the relaxation time. Taranko *et al.*[29] and Wysokinski *et al.*[30] have presented examples in which the definition of the relaxation time given by Eq. (4.2) appears to be senseless. These examples illustrate that the relaxation-time approximation, i.e., the Drude formula, is not adequate for the discussion of transport in strong scattering alloys. An examination of the exact computer-simulation results in Fig. 1, and the results presented in paper I, confirms these conclusions, indicating strongly that Eq. (4.2) is inappropriate for most of the cases that we investigated. On the other hand, the CPA results are seen to provide a not too inaccurate representation of the exact result of *weakly* scattering alloys.

The overall picture changes drastically, however, with increasing scattering strength. As is seen in the bottom row of Fig. 1, the ac conductivity of strongly scattering alloys peaks away from $\omega \sim 0$ and the structure in the exact results increases over that corresponding to the weakly scattering case. It is clear that the Drude formula, Eq. (4.2), is no longer valid. Furthermore, the accuracy of the CPA decreases with increasing scattering strength, as it is known to do in calculations of the DOS. The high peaks and valleys in the exact ac conductivity histograms of strongly scattering alloys are mainly due to the correlations in local statistical fluctuations and cannot be taken into account in a single-site theory like the CPA. As we will see later, a multisite approach to the conductivity is necessary for a proper representation of local environment effects.

As a general complex quantity, the conductivity $\sigma(\omega)$ satisfies the well-known Kramers-Kroning relations. In addition, the real part of $\sigma(\omega)$ satisfies the sum rule,

$$\int_0^\infty \mathrm{Re}\sigma(\omega) d\omega = \frac{\hbar}{2ma} n_1 , \tag{4.3}$$

where n_1 can be identified as the number of effective charge carriers. In Table I we compare the sum rule evaluated in the CPA with that evaluated in terms of the exact ac conductivity. The CPA results are within 10% of the exact ones, with the CPA overestimating the conductivity in most, but not all, cases.

2. *Systems with off-diagonal disorder*

Our investigation within the framework of the CPA of the conductivity of alloys with ODD relies on the formalism of BEB (Ref. 17) as extended to transport quantities by Blackman.[16] Blackman showed that the formalism of BEB provides the proper vehicle for the calculation of the Kubo formula within the CPA for alloys with ODD. He also showed that for single-band TB systems the vertex corrections vanish as they do in applications of the CPA to diagonally disordered alloys. The formalism of BEB provides the most general treatment of s-wave scattering in substitutionally disordered alloys and exhibits[16] the proper behavior in all relevant limits of various physical parameters. In particular, it satisfies[31] the Ward identities and yields exact results in the limits of zero concentration or weak-scattering strength.

For alloys with ODD, the real part of the ac conductivity is given by a simple generalization of the scalar Eq. (4.1) to a matrix equation,

$$\mathrm{Re}\sigma(\omega) = \frac{1}{\pi^3 \hbar} \frac{1}{\omega} \int_{\mu - \hbar\omega}^{\mu} dE \int_{\mathrm{BZ}} dk \, \mathrm{Tr}[\underline{W}(k) \mathrm{Im} \underline{\bar{G}}^{R}(k; E + \hbar\omega) \underline{W}(k) \mathrm{Im} \underline{\bar{G}}^{R}(k; E)] . \tag{4.4}$$

Here the $\mathbf{k}$-space hopping matrix $\underline{W}(\mathbf{k})$ is defined by the equation

$$\underline{W}(\mathbf{k}) = \sum_i \underline{W}_{0i} e^{i\mathbf{k}\cdot\mathbf{R}_{0i}} , \tag{4.5}$$

where

$$W_{ij} = \begin{bmatrix} W_{ij}^{AA} & W_{ij}^{AB} \\ W_{ij}^{AB} & W_{ij}^{BB} \end{bmatrix} . \tag{4.6}$$

The transfer integrals $W_{ij}^{\alpha\beta}$, $\alpha,\beta = A$ or B, describe the occupation-dependent hopping between sites i and j. The matrix $\underline{\bar{G}}(k;E)$ is defined in an analogous fashion.

TABLE I. Comparisons of the ac conductivity sum rule: μ, Fermi energy; "exact" stands for the exact results; "CPA" for CPA results. The bandwidth is normalized to one. The parameters used are for case I, weak scattering with $\varepsilon_A = -\varepsilon_B = 1.0$, $W = 1.0$; and for case II, strong scattering with $\varepsilon_A = -\varepsilon_B = 2.0$, $W = 1.0$.

		$\mu=0.2$	$\mu=0.5$
Case I	exact	2.55×10^{-2}	3.81×10^{-2}
	CPA	2.59×10^{-2}	4.05×10^{-2}
Case II	exact	1.92×10^{-2}	1.44×10^{-2}
	CPA	1.80×10^{-2}	1.62×10^{-2}

The results of ac conductivity calculations for one-dimensional alloys based on Eq. (4.4) (solid curves) are compared with exact numerical simulations (histograms) in Fig. 2. In all cases, the hopping integrals were restricted to nearest neighbors and were assigned the values, $W^{AA}=0.5$, $W^{AB}=W^{BA}=1.0$, and $W^{BB}=2.5$. The top row of Fig. 2 [(a) and (b)] corresponds to alloys with only ODD, $\varepsilon_A=\varepsilon_B=0.0$. The bottom row [(c) and (d)] depicts corresponding results for alloys with both diagonal and off-diagonal disorder, $\varepsilon_A=-\varepsilon_B=2.0$. The columns in Fig. 2 are labeled by the values of the Fermi energy, μ, in units of the bandwidth.

It is clear from the exact results (histograms) shown in Fig. 2 that the introduction of ODD can introduce new and complicating features into the ac conductivity as compared with that of diagonally disordered alloys. Note the tendency, in all figures, of the conductivity to peak away from zero frequency even in the case of vanishing diagonal disorder (top row in Fig. 2). In this case, the CPA yields less-accurate results, with the discrepancy between exact and calculated dc conductivities at $\omega=0$ being particularly prominent. Further, note the presence in the exact results of prominent peaks far away from zero frequency in some cases, e.g., at $\omega\sim0.6$ in panel (b). The emergence of such peaks can be understood on the basis of the DOS spectra (histogram) of these alloys which are depicted in Fig. 3 along with the corresponding CPA results (solid curve). As it is seen here, the DOS is dense near the center of the band and becomes quite dilute near the edges in the region in which it consists almost exclusively of B-hopping contributions. The conductivity peak at $\omega\sim0.6$ [Fig. 2(b)] arises from density-density correlations in this region which is very poorly described by CPA results.

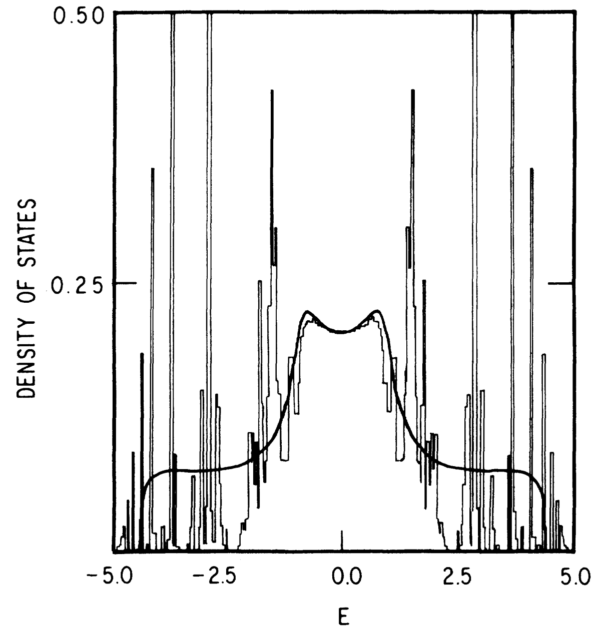

FIG. 3. Comparisons of the densities of states between the exact result and the CPA result for the same model parameters used in Figs. 2(a) and 2(b).

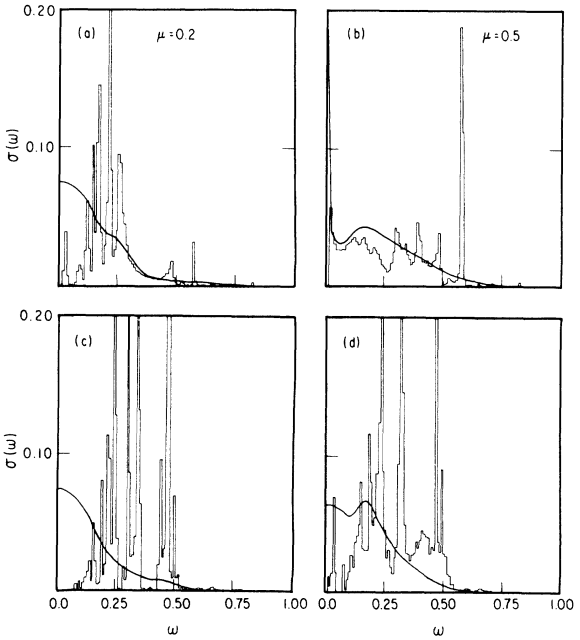

FIG. 2. Conductivity results of the type depicted in Fig. 1, but for alloys with off-diagonal disorder. The hopping integrals, $W_{AA}=0.5$, $W_{AB}=1.0$, and $W_{BB}=2.5$, are the same for all figures except the site energies are different: for (a) and (b) $\varepsilon_A=-\varepsilon_B=0.0$; for (c) and (d) $\varepsilon_A=-\varepsilon_B=2.0$.

The ability of the CPA to represent the ac conductivity of off-diagonally, substitutionally disordered alloys decreases with increasing diagonal disorder, as is clearly seen in the bottom row of Fig. 2. The failure of the CPA at low frequencies is particularly noticeable. On the other hand, as expected, integrated quantities such as the sum rule, Eq. (4.3), are given to within 10% by the CPA even in the case of generally disordered alloys.

C. Cluster calculations

As discussed earlier, the extension of the CPA to the calculation of transport properties was implemented immediately after the introduction of the CPA. The dc conductivity, ac conductivity, and Hall coefficients were calculated by many investigators[28,32] for simple model systems. However, the accuracy of the methods was unknown due to the lack of reliable computer experiments, thus prohibiting its further development. In the preceding section we concluded that single-site theories fail to produce the peaks and dips in the exact conductivity spectra. The results are even worse in some cases with strong off-diagonal disorder. The CPA provides a good first approximation to the calculation of the average of the product of the Green functions in substitutionally disordered systems but its accuracy decreases with increasing disorder, scattering strength, or increasing short-range order (SRO), i.e., nonrandomness, in a material. This limitation results from the fact that the CPA neglects statistical correlations among different sites. In order to account for the effects of local statistical fluctuations, it is necessary to extend the CPA to a multisite or cluster theory. Several such theories[5–7,15] have been proposed, including self-consistent and non-self-consistent approaches. Although well-founded self-consistent theories exist, their numerical implementation becomes difficult even for moderate size clusters in simple, single-band disordered systems. A great deal of work is still required to establish their computational feasibility.

Among non-self-consistent theories, the ECM (Refs. 5—7 and 15) has proved to be very successful in calculating the one-particle Green function associated with a cluster of atoms in substitutionally disordered alloys. Based on the same idea, we calculated the ac conductivity associated with the central site of such clusters, as indicated by Eq. (3.57). This generalization of the ECM provides us with an accurate description of the ac conductivity spectra. To test the effect of the embedding medium, we also carried out a simple molecular cluster calculation which replaces the effective medium by vacuum. We first discuss the molecular-cluster calculations and then present our results obtained by using the ECM for systems with diagonal disorder and short-range order.

1. Molecular-cluster calculations

The difficulty of interpreting the ac conductivity spectra of an infinite crystal by molecular-cluster calculations lies in the discreteness of the DOS which generates δ-function peaks in ac-conductivity spectra. Two procedures can be employed to transform the discrete spectra into continuous ones by broadening these peaks. The first procedure was used in our computer simulations in paper I. The number of energy levels inside a frequency interval, $\Delta\omega$ in Eq. (3.6) of paper I, should be large enough to make the procedure statistically meaningful. Clusters with computationally feasible sizes normally do not satisfy this condition. Thus, we use the second procedure by assigning a small imaginary number η in the energy to broaden the δ-function peaks appearing in the DOS spectra into Lorentzian shapes. The general requirements, $\hbar\omega \gg \eta \gg \hbar\Delta\omega$, are easily fulfilled with the values $\eta = 0.1$ and $\Delta\omega = \frac{1}{120}$

We consider a binary disordered alloy $A_{0.5}B_{0.5}$ with the cluster Hamiltonian,

$$\underline{H} = \underline{c}^{\dagger}\underline{\varepsilon}\,\underline{c}\ , \tag{4.7}$$

where $c^{\dagger}(c)$ is the cluster creation (annihilation) operator and ε is the cluster energy defined earlier. Thus, the system is represented by a single cluster. A straightforward application of our cluster-field theory results in the following formula:

$$\mathrm{Re}\sigma(\omega) = \frac{\hbar}{\pi^2 N a^2 e^2}\frac{1}{\omega}\int_{\mu-\hbar\omega}^{\mu} dE\,\mathrm{Tr}[\langle \underline{J}\,\mathrm{Im}\underline{G}^R(E+\hbar\omega) \times \underline{J}\,\mathrm{Im}\underline{G}^R(E)\rangle]\ . \tag{4.8}$$

All the quantities are the same as previously defined except that the cluster current matrix and Green function have strictly intracluster matrix elements. To calculate Eq. (4.8), it is sufficient to calculate $\mathrm{Tr}\langle \underline{J}\,\underline{G}\,\underline{J}\,\underline{G}\rangle$. One plausible approximation is to replace $(1/N)\mathrm{Tr}(\langle \underline{J}\,\underline{G}\,\underline{J}\,\underline{G}\rangle)$ by $(\underline{J}\,\underline{G}\,\underline{J}\,\underline{G})_{00}$, which represents the local quantity associated with the central site. Thus the steps in calculating the ac conductivity of a molecular cluster reduce to (1) calculating $(\underline{J}\,\underline{G}\,\underline{J}\,\underline{G})_{00}$ for every cluster configuration, (2) averaging the results over all configurations, (3) evaluating the conductivity by using $\langle \underline{J}\,\underline{G}\,\underline{J}\,\underline{G}\rangle_{00}$ and Eq. (4.8). Results of such calculations are depicted in Fig. 4. Figure 4(a), depicts the case with Fermi energy $\mu = 0.2$, and Fig. 4(b) that with $\mu = 0.5$. The other parameters are $\varepsilon_A = -\varepsilon_B = 2.0$ and $W = 1.0$. Again, the histograms are the exact results and the curves represent the results obtained in the molecular-cluster calculation. It is seen, at least qualitatively, that the method reproduces most of the peaks of the exact simulation results. However, the strong dependence of the results on the small imaginary energy part makes quantitative comparisons unreliable. In general, the peaks are sharper than those of the exact ones and their value are too small at low frequencies. However, this partial qualitative success suggests that local environment effects are important in picking out the fine structure in the conductivity spectra. The generalized ECM, presented in the following subsections, takes local

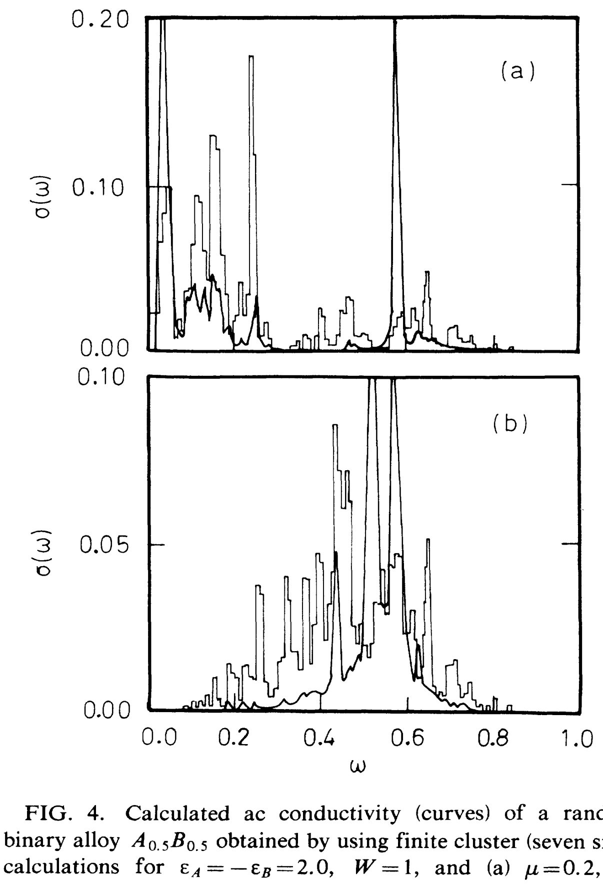

FIG. 4. Calculated ac conductivity (curves) of a random binary alloy $A_{0.5}B_{0.5}$ obtained by using finite cluster (seven sites) calculations for $\varepsilon_A = -\varepsilon_B = 2.0$, $W = 1$, and (a) $\mu = 0.2$, (b) $\mu = 0.5$. Histograms are the exact simulation results.

environment effects into account, as does the molecular-cluster calculation, but avoids the uncertainty resulting from the small imaginary energy part by introducing an effective medium with complex self-energy, e.g., the CPA medium.

2. *Embedded-cluster calculations*

The basic principles involved in applying the ECM to the calculation of transport properties have been given in Sec. III B. We emphasize that the method allows the exact incorporation of vertex corrections which are otherwise difficult to compute in self-consistent theories. In our calculations we considered clusters of moderate size, three to nine atoms, embedded in a CPA effective medium. The proper treatment of such a cluster requires the performance of **k**-space integrals, a procedure which is necessary in realistic three-dimensional calculations. However, in connection with one-dimensional-model systems, such as the ones used in our calculations, an alternative, simpler procedure becomes possible. Because G_{ij} decays rapidly with increasing distance $|\mathbf{R}_{ij}|$, it suffices to consider a finite cluster of CPA effective sites surrounding the embedded cluster. This procedure is certainly not exact but can be expected to approach the exact limit with increasing medium cluster size. The effects of the truncation of the surrounding CPA medium manifested themselves in terms of slightly negative ac conductivity spectra ($\sim 0.1\%$ of maximum values) in some frequency regions in which the exact simulation results vanish or are nearly zero. Increasing the size of the surrounding CPA cluster decreases the size of the negative calculated results, but complete elimination was not achieved within our finite truncation schemes. The following figures present the results of calculations carried out using CPA medium clusters with 50 sites, containing the clusters of real atoms in their center. For an alloy, the ac conductivity takes the form

$$\mathrm{Re}\sigma(\omega)=\frac{\hbar}{\pi^2 N a^2 e^2}\frac{1}{\omega}\int_{\mu-\hbar\omega}^{\mu} dE \sum_{j,k=-N}^{N}\left[\langle \underline{J}_{0i}\,\mathrm{Im}\underline{G}_{ij}^{R}(E+\hbar\omega)\underline{J}_{jk}\,\mathrm{Im}\underline{G}_{k0}^{R}(E)\rangle\right] , \tag{4.9}$$

where N is half the size of the CPA medium cluster. Thus, the procedure to calculate the ac conductivity in the ECM consists of the following: (1) Choosing the size of a cluster to be embedded in the CPA medium; (2) calculating the matrix element $(\underline{J}\,\underline{G}\,\underline{J}\,\underline{G})_{00}$ for every configuration; (3) performing the average over all configurations; and (4) carrying out the energy integration over the allowed transitions. The averaging process depends on the type of disorder considered, since the weight of a given configuration varies with the disorder type.

We first concentrate on the strong scattering case with $\varepsilon_A=-\varepsilon_B=2.0$ and $W=1.0$. The results for two different Fermi energies are presented in Figs. 5 and 6. As usual, all exact simulation results are plotted in histograms and the calculated results are given by smooth curves. In Fig. 5 we show the results for the Fermi energy $\mu=0.2$.

Figure 5(a) shows the result (smooth curve) obtained by using a cluster with three-sites. The curve is still close to the CPA results, but is seen to begin developing a certain amount of structure. Increasing the cluster size to seven sites, Fig. 5(b) suffices to pick out almost all of the sharp peaks and valleys in the exact spectra. Analogous results are seen in Fig. 6 for the case of $\mu=0.5$. Increasing the cluster size yields successively more-accurate results, including properly the effects of local statistical fluctuations and the associated vertex corrections.

Our results indicate that for strong-scattering alloys, even a moderate size cluster (approximately seven sites) suffices in capturing the fine structure of the simulated ac conductivity spectra. When the scattering strength decreases, i.e., in the weak-scattering limit, even single-site

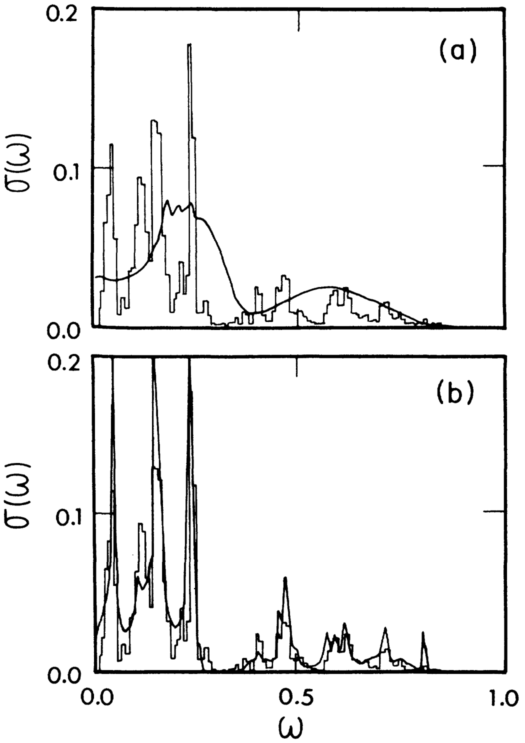

FIG. 5. Results of the type depicted in Fig. 4 except those obtained by using the ECM; (a) three-site calculation; (b) seven-site calculation. Both figures with Fermi energy $\mu=0.2$.

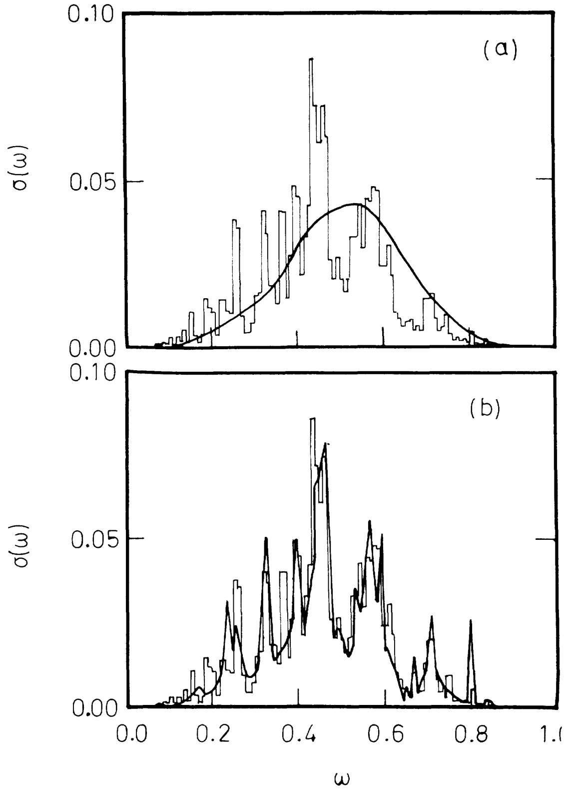

FIG. 6. Results of the type depicted in Fig. 5, but for $\mu=0.5$.

theories can give accurate results, e.g., top row of Fig. 1. Now the peaks and dips can be regarded as perturbations away from a uniform medium and are well described (in an average way) by the CPA. Thus, in this case, even a relatively small cluster (approximately three sites) can be expected to yield accurate results.

3. *Alloys with short-range order*

As discussed in paper I, perfect substitutional disorder is seldom achieved: often correlations between atoms on neighboring lattice sites cannot be ignored. In a binary alloy, for example, it may be energetically preferable to surround an A atom by a B atom than by atoms of the same type. The resulting system exhibits what is known as short-range order (SRO) effects, which are known[1] to influence the DOS and the conductivity spectra. Such effects cannot be taken into account at all within single-site theories such as the CPA but can be described to any desirable degree of accuracy within a cluster theory. The ECM provides a method for calculating the cluster average of the site-diagonal element of the Green function products at the central site of the cluster, denoted by 0, given by the expression

$$\langle (\underline{J}\,\underline{G}\,\underline{J}\,\underline{G})\rangle_{00}=\sum_{K} P_K(\underline{J}\,\underline{G}\,\underline{J}\,\underline{G})_{00}^{K}\,, \tag{4.10}$$

where K denotes a cluster configuration and P_K is the probability of the occurrence of configuration K. Clearly, any degree of SRO can be included in the average through the quantities P_K. Figure 7 depicts the results of nine-site ECM calculations in binary strong scattering alloys with different degrees of SRO. Here SRO effects are considered from the almost complete clustering case ($\alpha=0.9$) to the almost complete ordering case ($\alpha=-0.9$) in four steps, $\alpha=0.9$, 0.5, -0.5, -0.9. As is seen here, the agreement of the ECM results with their exact counterparts is quite good. For the strong clustering case, Fig. 7(d), the ECM results are relatively inaccurate due to the limitation of cluster calculations in dealing with pure systems. However, even in this case, the ECM gives a good description of the ac conductivity spectra.

V. DISCUSSION AND CONCLUSIONS

In this paper we have presented a cluster-field theory which allows the unified treatment of a number of problems associated with substitutionally disordered materials. The formalism developed in this paper is applicable to disordered, as well as ordered, materials describably by either tight-binding or muffin-tin Hamiltonians, and can be used to calculate expectation values of one-body and of many-body operators. The usefulness of this approach was illustrated through the derivation of a cluster-conductivity formula for disordered materials, and numerical calculations based on that formula.

More generally, the formalism of Sec. II and the Appendix provides a rigorous foundation for dealing with physical problems in terms of appropriately chosen cluster quantities. In the proper limits it reduces to well-developed and well-understood methods for the study of disordered materials, such as the CPA for alloys with diagonal and off-diagonal disorder, the molecular CPA, and the embedded-cluster method, and allows the calculations of the single-particle and two-particle propagators within

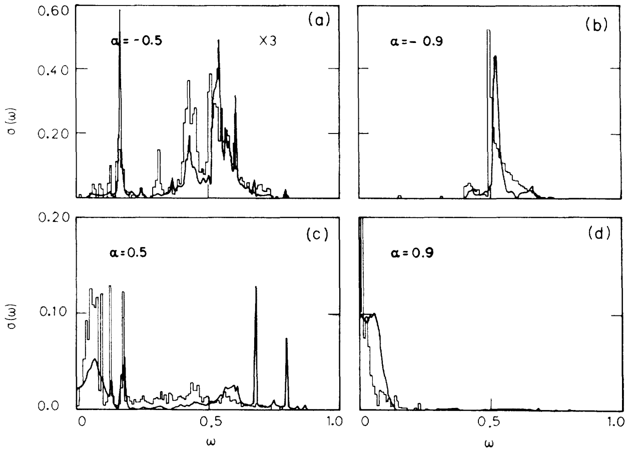

FIG. 7. Calculated ac conductivity (curves) of a binary alloy with short-range order obtained by using the ECM for $\mu=0.4$; (a) $\alpha=-0.5$, (b) $\alpha=-0.9$, (c) $\alpha=0.5$, (d) $\alpha=0.9$. Histograms are the exact simulation results.

any of these methods. Our cluster approach leads to computationally feasible algorithms, matching the art of modern vectorized computers which make the manipulation of large matrices practicable.

The approximation scheme presented in Sec. III for calculating the conductivities of substantially disordered systems is model independent. After determining the single-particle cluster Green function in a cluster space we can calculate the conductivity by using the approximation scheme. The approximation is analytic, in the sense that the Ward identity is fulfilled.

We explored the strengths and weaknesses of various analytic theories in calculating the ac conductivity of substitutionally disordered alloys by means of numerical calculations. The availability of computer-simulation results allowed us to make quantitative calibrations for approximate theories, such as the CPA and the formalism of BEB, and their cluster generalizations.

In the weak-scattering limit the mean free path of an electron is much larger than the interatomic spacing, and single-site theories are expected to give good descriptions for the ac conductivity in this case. We confirmed the above statement and indicated its failure when the scattering strength and disorder increase. The Kubo-Greenwood formula is general for a quantum system and capable of dealing with quantum interference effects, i.e., when the electron mean free path is comparable to the lattice spacing. The proper inclusion of site-site correlations in cluster theories indicates that short-range effects are responsible for the fine structures of the conductivity spectra. At the same time, some important questions are left out in the simple model used in our calculations, such as, for example, the calculations of the ac conductivity for realistic systems and the localization problem associated with disordered materials. It is to be noted that CPA-based calculations for three-dimensional systems can yield quite accurate results as is exemplified by the recent calculation of the residual resistivity by Butler *et al.*[33] The calculations of the ac conductivity for real materials along with the **k**-space evaluation of the vertex corrections in realistic systems are currently in progress and results will be presented in future publications.

ACKNOWLEDGMENTS

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APPENDIX: CLUSTER PERTURBATION THEORY

In the body of this text we limited ourselves to the single-particle Hamiltonian, i.e., Eq. (3.1), without considering nonlocal or many-body effects. However, nonlocal potentials or many-body interactions are present in realistic systems. For the sake of completeness, we present in this Appendix a rigorous perturbation theory based on our cluster-field theory; in particular, we give a detailed discussion of the generalized Wick's theorem, i.e., matrix Wick's theorem.

Before giving the formal exposition of the cluster perturbation theory, we define a "*cluster*" unit matrix and a "*cluster*" exponential function. They are introduced in order to facilitate our matrix formulation. At this point it is important to remind the reader of the two main ingredients in our cluster theory: (1) the existence of a special matrix $\underline{\Pi}$ which allows us to consider all the physical problems exclusively in terms of cluster quantities, and (2) the connection between the cluster and the single-site picture is made possible through the $\underline{\Pi}$ matrix. In an n-site cluster theory, a cluster unit matrix $\underline{E}$ is defined by the expression

$$\underline{E}=\frac{1}{n}\underline{I}\ , \tag{A1}$$

where $\underline{I}$ is the usual $n\times n$ unit matrix, i.e., $I_{ij}=\delta_{ij}$. The *cluster* exponential function $\underline{e}$ is then defined in the form

$$\underline{e}^{\underline{A}}=\underline{E}+\sum_{k=1}^{\infty}\frac{1}{k!}\underline{A}(\underline{\Pi}\,\underline{A})^{k-1}\ , \tag{A2}$$

where $\underline{A}$ is an arbitrary $n\times n$ matrix and $\underline{\Pi}$ is the matrix introduced in Sec. II. The above definitions were motivated so as to fulfill the following properties:

$$\mathrm{Tr}(\underline{\Pi}\,\underline{E})=1\ , \tag{A3}$$

$$e^{\mathrm{tr}(\underline{\Pi}\,\underline{A})}=\mathrm{Tr}(\underline{\Pi}\,\underline{e}^{\underline{A}})\ . \tag{A4}$$

The first relation, Eq. (A3), implies that the appearance of $\underline{\Pi}\,\underline{E}$ in the cluster theory can be removed, e.g., $\mathrm{Tr}(\underline{\Pi}\,\underline{A}\,\underline{\Pi}\,\underline{E})=\mathrm{Tr}(\underline{\Pi}\,\underline{A})$. Mathematically, $\underline{E}$ can be extended to represent the set $\{\underline{E},\ \underline{E}\,\underline{\Pi}\,\underline{E},\ \underline{E}\,\underline{\Pi}\,\underline{E}\,\underline{\Pi}\,\underline{E},\dots\}$. The second relation, Eq. (A4), will be used extensively when we derive the cluster perturbation theory.

In Sec. III B we defined by "*single-cluster*" Green function and discussed its relation to observable properties. That analysis in no way solves the fundamental many-body problem and we must still calculate G for nontrivial physical systems, e.g., systems with nonlocal or many-body interactions. As a general method of attack, we shall show how to evaluate the Green functions within perturbation theory. This procedure is most easily carried out in the interaction picture, where the various terms entering the perturbation expansion can be enumerated with a matrix Wick's theorem. For the sake of clarity, we formulate the perturbation theory at zero temperature; the finite-temperature Matsubara formalism, which has been used in Sec. III C to derive a general finite-temperature ac conductivity formula, can be formulated analogously.

The Hamiltonian of a physical system can usually be written in the form

$$\underline{H}=\underline{H}_0+\underline{V}\ , \tag{A5}$$

where $\underline{H}_0$ is a cluster Hamiltonian which may be solved exactly and the perturbation part $\underline{V}$ can be reduced, fairly generally, to the form

$$\underline{V}=\sum_{\alpha,\beta}(\underline{c}^{\alpha})^{\dagger}\underline{V}^{\alpha\beta}\underline{c}^{B} . \tag{A6}$$

In the interaction representation, cluster operators and wave functions are denoted by a caret. A cluster operator has a time-dependent characteristic, i.e.,

$$\hat{\underline{O}}(t)=\underline{e}^{i\underline{H}_0t}\underline{\Pi}\,\underline{O}\,\underline{\Pi}\,\underline{e}^{-i\underline{H}_0t} , \tag{A7}$$

where $\underline{e}$ is the *cluster* exponential function defined above and $\underline{O}$ is an operator in the Schrödinger picture. The above definition is motivated by the following relation:

$$\begin{aligned}\hat{O}(t)&=e^{iH_0t}\hat{O}e^{-iH_0t}\\&=e^{i\mathrm{Tr}(\underline{\Pi}\,\underline{H}_0)t}\mathrm{Tr}(\underline{\Pi}\,\hat{\underline{O}})e^{-i\mathrm{Tr}(\underline{\Pi}\,\underline{H}_0)t}\\&=\mathrm{Tr}(\underline{\Pi}e^{i\underline{H}_0t})\mathrm{Tr}(\underline{\Pi}\,\hat{\underline{O}})\mathrm{Tr}(\underline{\Pi}e^{-i\underline{H}_0t})\\&=\mathrm{Tr}[\underline{\Pi}\,\hat{\underline{O}}(t)] ,\end{aligned} \tag{A8}$$

where we have associated each scalar operator $\hat{O}(t)$ with a cluster operator $\hat{\underline{O}}(t)$. As a general rule, the $\underline{\Pi}$ matrix is present between any consecutive operators and plays the role of cluster interactions.

The time evolution operator $U(t)$ is now changed to the cluster form, $\underline{U}(t)$,

$$\underline{U}(t)=\underline{e}^{i\underline{H}_0t}\underline{\Pi}\,\underline{e}^{-i\underline{H}_0t} , \tag{A9}$$

which has the standard connection with $U(t)$, $U(t)=\mathrm{Tr}[\Pi\underline{U}(\underline{t})]$. Note that $\underline{U}(0)=\underline{E}$. It follows that $\underline{U}(t)$ satisfies the following equation:

$$\frac{\partial}{\partial t}\underline{U}(t)=-i\hat{\underline{V}}(t)\underline{\Pi}\,\underline{U}(t_1) . \tag{A10}$$

Integrating both sides of the equation with respect to time, we have

$$\underline{U}(t)=\underline{U}(0)-i\int_0^t dt_1\,\hat{\underline{V}}(t)\underline{\Pi}\,\underline{U}(t_1) . \tag{A11}$$

If this equation is repeated iteratively, we obtain

$$\begin{aligned}\underline{U}(t)&=\underline{E}-i\int_0^t dt_1\,\hat{\underline{V}}(t_1)+(-i)^2\int_0^t dt_1\int_0^{t_1}dt_2\,\hat{\underline{V}}(t_1)\underline{\Pi}\,\hat{\underline{V}}(t_2)+\cdots\\&=\underline{E}+\sum_{k=1}^{\infty}(-1)^k\int_0^t dt_1\cdots\int_0^{t_{k-1}}dt_k\,\hat{\underline{V}}(t_1)\underline{\Pi}\,\hat{\underline{V}}(t_2)\cdots\underline{\Pi}\,\hat{\underline{V}}(t_k) .\end{aligned} \tag{A12}$$

By introducing the time-ordering operator T, Eq. (A12) can be abbreviated in the form

$$\underline{U}(t)\equiv T\{\underline{e}^{-i\int_0^t dt_1\,\hat{\underline{V}}(t_1)}\} . \tag{A13}$$

In order to carry out the cluster perturbation theory, a cluster S matrix is conveniently introduced by the following definition:

$$\underline{S}(t,t')=\underline{U}(t)\underline{\Pi}\,\underline{U}^{\dagger}(t') , \tag{A14}$$

which characterizes the time evolution of the wave functions $\hat{\underline{\Psi}}(t')$ into $\hat{\underline{\Psi}}(t)$, i.e.,

$$\hat{\underline{\Psi}}(t)=\underline{S}(t,t')\underline{\Pi}\hat{\underline{\Psi}}(t') . \tag{A15}$$

The cluster S matrix has the following properties:

$$\underline{S}(t,t)=\underline{E} , \tag{A16}$$

$$\underline{S}^{\dagger}(t,t')=\underline{U}(t')\underline{\Pi}\,\underline{U}^{\dagger}(t)=\underline{S}(t',t) , \tag{A17}$$

$$\underline{S}(t,t')\underline{\Pi}\,\underline{S}(t',t'')=\underline{S}(t,t'') , \tag{A18}$$

and can be abbreviated in the form

$$\underline{S}(t,t')=T\{\underline{e}^{-i\int_t^{t'}dt_1\,\hat{\underline{V}}(t_1)}\} . \tag{A19}$$

The cluster creation (or annihilation) operators in the Schrödinger and interaction pictures are connected by the relation

$$\underline{c}^{\alpha}(t)=\underline{S}(0,t)\underline{\Pi}\,\hat{\underline{c}}^{\alpha}(t)\underline{\Pi}\,\underline{S}(t,0) . \tag{A20}$$

Let us denote by $|\ \rangle$ ($|\ \rangle_0$) the ground-state of $\underline{H}$ ($\underline{H}_0$). We then have the relation (i.e., Gell-Mann—Low theorem)

$$|\ \rangle=\underline{S}(0,-\infty)|\ \rangle_0 . \tag{A21}$$

At this stage we can express the cluster Green function in terms of the unperturbed cluster Green function and obtain the form

$$\begin{aligned}\underline{G}^{\alpha\beta}(t,t')&=-i\langle T\{\underline{c}^{\alpha}(t)\underline{\Pi}[\underline{c}^{\beta}(t')]^{\dagger}\}\rangle\\&=-i\Theta(t-t')\,{}_0\langle\ |\underline{S}(-\infty,t)\underline{\Pi}\,\hat{\underline{c}}^{\alpha}(t)\underline{\Pi}\,\underline{S}(t,t')\underline{\Pi}\,\hat{\underline{c}}^{\beta}(t')\underline{\Pi}\,\underline{S}(t',-\infty)|\ \rangle_0\\&\quad+i\Theta(t'-t)\,{}_0\langle\ |\underline{S}(-\infty,t')\underline{\Pi}\,\hat{\underline{c}}^{\beta}(t')\underline{\Pi}\,\underline{S}(t',t)\underline{\Pi}\,\hat{\underline{c}}^{\alpha}(t)\underline{\Pi}\,\underline{S}(t,-\infty)|\ \rangle_0 .\end{aligned} \tag{A22}$$

Multiplying both sides of the above equation by ${}_0\langle\ |\underline{S}(\infty,-\infty)|\ \rangle_0\underline{\Pi}$, we have

$$\begin{aligned}{}_0\langle\ |S(\infty,-\infty)|\ \rangle_0\underline{\Pi}\,\underline{G}^{\alpha\beta}(t,t')=&-i\Theta(t-t')\,{}_0\langle\ |\underline{S}(\infty,t)\underline{\Pi}\,\hat{\underline{c}}^{\alpha}(t)\underline{\Pi}\,\underline{S}(t,t')\underline{\Pi}\,\hat{\underline{c}}^{\beta}(t')\underline{\Pi}\,\underline{S}(t',-\infty)|\ \rangle_0\\&+i\Theta(t'-t)\,{}_0\langle\ |\underline{S}(\infty,t')\underline{\Pi}\,\hat{\underline{c}}^{\beta}(t')\underline{\Pi}\,\underline{S}(t',t)\underline{\Pi}\,\hat{\underline{c}}^{\alpha}(t)\underline{\Pi}\,\underline{S}(t,-\infty)|\ \rangle_0 .\end{aligned} \tag{A23}$$

Following the usual abbreviation, we write the above equation in shorthand form,

$$ {}_0\langle\ |\underline{S}(\infty,-\infty)|\ \rangle_0 \underline{\Pi}\, \underline{G}^{\alpha\beta}(t,t') = -i\, {}_0\langle\ |T\{\underline{\hat{c}}^{\alpha}(t)\underline{\Pi}\,\underline{\hat{c}}^{\beta}(t')\underline{S}(\infty,-\infty)\}|\ \rangle_0 \,, \tag{A24} $$

where the time-ordering operator T arranges the various pieces in their rightful place. Notice that the matrix factor ${}_0\langle\ |\underline{S}(\infty,-\infty)|\ \rangle_0$ cancels vacuum polarization diagrams.

The remaining task is to construct rules for evaluating time-ordered brackets like

$$ T\{\underline{\Pi}(\underline{\hat{c}}^{\alpha})^{\dagger}(t)\underline{\hat{J}}^{\alpha\beta}\underline{\hat{c}}^{\beta}(t)\underline{\Pi}\,[\underline{\hat{c}}^{\gamma}(t')]^{\dagger}J^{\gamma\delta}\underline{\hat{c}}^{\delta}(t')\} \,, \tag{A25} $$

which can, in general, be accomplished in terms of Wick's theorem. A generalized Wick's theorem is needed in our cluster theory because all the operators are written in matrix form. We now give the basic ingredients of such a generalized Wick's theorem by presenting the following two general rules.

(1) The matrix Wick's theorem is a restricted version of the usual single-site Wick's theorem because in general both noncommuting matrices and operators are present. Some related examples of the definitions of time-ordered products are

$$ T\{\underline{c}^{\alpha}(t)\underline{\Pi}[\underline{c}^{\beta}(t')]^{\dagger}\} = \begin{cases} \underline{c}^{\alpha}(t)\underline{\Pi}[\underline{c}^{\beta}(t')]^{\dagger}, & t>t' \\ -\{[\underline{c}^{\beta}(t')]^{\dagger}\underline{\Pi}\,\underline{c}^{\alpha}(t)\}^{T}, & t<t \end{cases} \tag{A26} $$

and

$$ T\{\underline{\Pi}[\underline{c}^{\alpha}(t)]^{\dagger}\underline{J}^{\alpha\beta}\underline{c}^{\beta}(t)\underline{\Pi}[\underline{c}^{\gamma}(t')]^{\dagger}\underline{J}^{\gamma\delta}\underline{c}^{\delta}(t)\} = \begin{cases} \underline{\Pi}\,\underline{c}^{\alpha}(t)\underline{J}^{\alpha\beta}\underline{c}^{\beta}(t)\underline{\Pi}\,\underline{c}^{\gamma}(t')\underline{J}^{\gamma\delta}\underline{c}^{\delta}(t'), & t>t' \\ \underline{\Pi}[\underline{c}^{\gamma}(t')]^{\dagger}\underline{J}^{\gamma\delta}\underline{c}^{\delta}(t')\underline{\Pi}[\underline{c}^{\alpha}(t)]^{\dagger}\underline{J}^{\alpha\beta}\underline{c}^{\beta}(t), & t<t' \,. \end{cases} \tag{A27} $$

The normal-ordered product needs to be changed accordingly.

(2) For a given time-ordered product, e.g.,

$$ \mathrm{Tr}\, {}_0\langle\ |T\{\underline{\Pi}[\underline{c}^{\alpha}(t)]^{\dagger}\underline{J}^{\alpha\beta}\underline{c}^{\beta}(t)\underline{\Pi}[\underline{c}^{\gamma}(t')]^{\dagger}\underline{J}^{\gamma\delta}\underline{c}^{\delta}(t')\}|\ \rangle_0 \,, \tag{A28} $$

only the completely contracted terms need to be evaluated. This results from the general property of the usual Wick's theorem that the expectation value of each incompletely contracted term vanishes. Therefore the terms left in the above example are

$$ \mathrm{Tr}({}_0\langle\ |T\{\underline{\Pi}[\underline{c}^{\alpha}(t)]^{\dagger}\underline{J}^{\alpha\beta}\underline{c}^{\beta}(t)\underline{\Pi}[\underline{c}^{\gamma}(t')]^{\dagger}\underline{J}^{\gamma\delta}\underline{c}^{\delta}(t')\}|\ \rangle_0) \tag{A29} $$

and

$$ \mathrm{Tr}({}_0\langle\ |T\{\underline{c}^{\delta}(t')\underline{\Pi}[\underline{c}^{\alpha}(t)]^{\dagger}\underline{J}^{\alpha\beta}\underline{c}^{\beta}(t)\underline{\Pi} \times[\underline{c}^{\gamma}(t')]^{\dagger}\underline{J}^{\gamma\delta}(t')\}|\ \rangle_0) \,. \tag{A30} $$

The first term represents a disconnected diagram and the second term has the form $\mathrm{Tr}(\underline{G}\,\underline{J}\,\underline{G}\,\underline{J})$. More complicated time-ordered products can be contracted analogously.

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