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Multishell method: Exact treatment of a cluster in an effective medium*

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A method is presented for the exact determination of the Green's function of a cluster embedded in a given effective medium. This method, the multishell method, is applicable even to systems with off-diagonal disorder, extended-range hopping, multiple bands and/or hybridization, and is computationally practicable for any system described by a tight-binding or interpolation-scheme Hamiltonian. It allows one to examine the effects of local environment on the densities of states and site spectral weight functions of disordered systems. For any given analytic effective medium characterized by a non-negative density of states the method yields analytic cluster Green's functions and non-negative site spectral weight functions. Previous methods used for the calculation of the Green's function of a cluster embedded in a given effective medium have not been exact. The results of numerical calculations for model systems show that even the best of these previous methods can lead to substantial errors, at least for small clusters in two- and three-dimensional lattices. These results also show that fluctuations in local environment have large effects on site spectral weight functions, even in cases in which the single-site coherent-potential approximation yields an accurate overall density of states.

I. INTRODUCTION

Since the introduction of the single-site coherent-potential approximation[1-3] (SSCPA), disordered systems have become the subject of intense study. Although the SSCPA is the best single-site approximation for the study of disordered materials, it shares certain limitations common to all single-site theories. Within any single-site theory only the effects of fluctuations confined to a single site can possibly be taken into account. Fluctuations in the local environment of a site, which are responsible for band tailing and for sharp structure in the density of states, and which can strongly affect the formation of magnetic moments are neglected. Furthermore, any single-site theory can yield only $\vec{k}$-independent momentum-state lifetimes and is incapable of treating correctly transport properties[4] and the localization of states[5-10] in disordered alloys. Finally, the effects of short-range order (SRO) and charge transfer cannot be taken properly into account within a single-site theory. In principle, all of these limitations of the SSCPA could be overcome within the framework of a many-site or cluster theory.

The limitations associated with the single-site nature of the SSCPA can be overcome, at least in principle, by generalizing the SSCPA to a many-site or cluster approximation. In the ten years since the introduction of the SSCPA much effort has been expended toward the development of cluster approximations[11-22] in attempts to take proper account of many-site correlations in disordered systems. Such correlations are known to play an important role in the determination of some physical quantities, even for systems for which the SSCPA yields a rather good representation of the density of states. In particular, many experimental studies of disordered magnetic alloys,[23] especially neutron scattering studies,[23,24] require for their interpretation[25-29] the consideration of the effects of local environment on the formation of magnetic moments. Cluster theories allow the study of such local-environment effects in a natural way.

II. MULTISHELL METHOD

A. General discussion

All cluster approximations for disordered materials can be interpreted in the language of mean-field theory in terms of a cluster of real atoms embedded in an effective medium. There are two problems associated with the development of any cluster theory of disordered systems. The first and more difficult problem is that of determining an optimal choice of effective medium. This problem has not yet been solved; in particular, no method has been proposed which yields a translationally invariant analytic effective medium which becomes exact in the limit of large cluster sizes. The second and easier problem is that of finding a computationally practical technique for the accurate evaluation of the Green's function for a cluster of real atoms embedded in a given effective medium. In this paper only the second problem is considered. The multishell method (MSM) presented here is a computationally practicable method for the exact determination of the Green's function of a cluster of atoms embedded in an effective medium and described by a tight-binding or interpolation-scheme Hamiltonian. It is applicable even for the case of two- and three-dimensional lattices and is applicable to the study of electrons, phonons, magnons, or excitons in disordered systems even for interlocking lattices or systems characterized by off-diagonal disorder (ODD), extended-range hopping, multiple and/or degenerate bands, hybridization, SRO, and charge transfer. For a given analytic effective medium the MSM yields analytic cluster Green's functions, as is shown in Appendix A. The usefulness of the MSM of course depends upon one's choice of effective medium. However, for any given analytic effective medium the MSM yields values for alloy densities of states and site spectral weight functions which approach the exact values for large cluster sizes. For small clusters the MSM at least allows one to treat exactly the model problem of a cluster embedded in an effective medium. For two- and three-dimensional lattices the MSM is the only method which does so; for the particular case of a linear chain or Cayley tree the MSM is equivalent to the continued-fraction method[11,12] (CFM) in the absence of ODD.

As in all previous work on this problem, in this paper the Green's-function formalism is used. It is assumed that the entire Hamiltonian, $H^{(C)}$, for a system consisting of a cluster C of real atoms embedded in an effective medium is known. It is convenient to express $H^{(C)}$ as the sum of three parts: (i) the Hamiltonian H_C for an isolated cluster, (ii) the Hamiltonian $\tilde{H}^{(C)}$ which couples the cluster to the surrounding effective medium, and (iii) the Hamiltonian $\bar{H}^{(C)}$ for the effective medium with the cluster removed.

Several methods for the determination of the Green's function $G^{(C)}$ for this system have been proposed previously. The method of Aoi,[13] which consists of evaluating selected contributions to the t matrix of a cluster embedded in a SSCPA effective medium, treats none of the three parts of $H^{(C)}$ exactly. As found by Aoi, the approximations made in his technique result in site spectral weight functions which can become negative near band edges.

The CFM treats H_C and $\tilde{H}^{(C)}$ exactly, but treats $\bar{H}^{(C)}$ within an approximation which is exact only for the case of a Cayley-tree lattice, in particular, a linear chain. It is easily applicable to Cayley-tree clusters of extended range and, with some difficulty, can be applied to the case of more general clusters of extended range embedded in a Cayley-tree lattice and to the case of extended-range hopping integrals. The CFM possesses one great advantage over all other methods of treating a cluster embedded in an effective medium: within the CFM it is not necessary to calculate explicitly the matrix elements $\bar{G}_{ij}$ of the effective-medium Green's function. In all other methods, including the method proposed in this paper, one must calculate two or more such matrix elements, except for a Cayley-tree lattice. This is the most time-consuming computational procedure in the determination of $G^{(C)}$. On the other hand, a continued-fraction expansion can be terminated exactly only for a cluster embedded in a Cayley-tree lattice, so that the CFM cannot properly be used in conjunction with a self-consistent cluster theory for other than Cayley-tree lattices. Even in conjunction with non-self-consistent cluster theories, for small cluster sizes the approximate termination of the CFM expansion is a significant source of error for realistic two- and three-dimensional lattices.

The methods of Brouers *et al.*,[14-16] like the CFM, treat H_C and $\tilde{H}^{(C)}$ exactly, but treat $\bar{H}^{(C)}$ within an approximation which is exact only for the case of a Cayley-tree lattice. The initial method of Brouers *et al.*[14] was formulated in exact analogy with the well-known Bethe-Peierls approximation (BPA) for local spin ordering. For a cluster embedded in a realistic two- or three-dimensional lattice, the BPA yields a significantly more accurate treatment of $\bar{H}^{(C)}$ than does the CFM, as is evident from the replacement of the approximate, artificial square-root form for $\bar{G}_{00}$ found within the CFM by the exact $\bar{G}_{00}$ in the BPA formalism. Within the BPA one takes account of all paths through the effective medium which start and end on the same cluster site, neglecting paths which start and end at different sites. Thus, for a given atom in an alloy, $A_{1-c}B_c$, with a given lattice structure, within the BPA $G^{(C)}_{00}$ depends only on the number of nearest-neighbor atoms of type A, not on the particular configuration of those atoms. More recently, Brouers *et al.*[15,16] have significantly improved the original BPA method, allowing for the approximate treatment of paths through the crystal which connect different cluster sites.

Finally, Miwa[17] has developed a set of exact equations for $G^{(C)}$ for the simple case of a cluster containing a central atom and its six nearest neighbors in a simple cubic lattice with only nearest-neighbor hopping. However, as is pointed out by Miwa, his technique cannot be generalized to apply to systems characterized by extended hopping integrals or off-diagonal disorder. Furthermore, his technique is difficult to apply in the case of interlocking lattices, such as the fcc and hcp lattices, and for larger clusters.

In order to simplify numerical computations, Miwa[17] introduces a series of approximations to his exact equations. As has been shown by Brouers and Ducastelle,[16] the first set of approximations yields results equivalent to those obtained earlier by Brouers *et al.*[15] The resultant theory is referred to in the remainder of this paper as the Brouers-Miwa approximation (BMA). The further set of approximations considered by Miwa yields results equivalent to the original BPA of Brouers *et al.*[14] In Secs. II B and II C the mathematical formalism of the MSM is presented. For simplicity the formalism is given only for the case of binary substitutional, single-band alloys. In Sec. III the exact computational procedure of the MSM is presented, the relative computational difficulty of the different steps of the procedure is discussed and the overall computational feasibility of the method is compared with that of the approximate method of Brouers *et al.*[15,16] and Miwa.[17] In Sec. IV the formalism is extended to systems with ODD. In Sec. V the results of exact MSM sample calculations for a variety of two- and three-dimensional lattices are shown and are compared to some results obtained within the BMA. In Sec. VI conclusions and further discussion are given.

B. Mathematical preliminaries

The usual single-band tight-binding model Hamiltonian assumes the form

$$H=\sum_i \epsilon_i a_i^\dagger a_i+\sum_{i,j} W_{ij}a_i^\dagger a_j \tag{2.1}$$

in a site or Wannier representation. The $a_i^\dagger$ (a_i) create (destroy) an electron on site i. Here, this Hamiltonian is used to describe a disordered binary alloy $A_{1-c}B_c$ with atoms of types A and B distributed in some manner over the N sites of a lattice. The site-diagonal energies ϵ_i in general depend both on the chemical occupation of site i and on its local environment. The variation of ϵ_i from site to site is known as diagonal disorder. The transfer terms W_{ij} describe electron hopping between sites i and j. In general, the W_{ij} also depend on both the occupation and the local environment of the sites i and j. Any dependence of the W_{ij} on the chemical configuration of an alloy is known as off-diagonal disorder.

The single-particle properties of the alloy are given by the ensemble average $\langle G\rangle$ of the single-particle Green's-function operator

$$G(z)=(z-H)^{-1}, \tag{2.2}$$

where $\hbar$ is set equal to 1.

In practice, the Green's-function operator G can be evaluated only approximately. In a cluster approximation one replaces the real alloy outside some cluster by an effective medium characterized by a self-energy Σ. The Hamiltonian for a system consisting of a cluster of atoms C embedded in a translationally invariant effective medium is given by the expression,

$$H^{(C)}=\sum_{i\in C}\left(\epsilon_i a_i^\dagger a_i+\sum_{j\in C}W_{ij}a_i^\dagger a_j+\sum_{j\notin C}\tilde{W}_{ij}a_i^\dagger a_j\right)+\sum_{i\notin C}\left(\sigma_0 a_i^\dagger a_i+\sum_{j\notin C}\overline{W}_{ij}a_i^\dagger a_j+\sum_{j\in C}\tilde{W}_{ij}a_i^\dagger a_j\right). \tag{2.3}$$

Here, the notations $i\in C$ and $i\notin C$ denote sites i which are or are not, respectively, within the cluster C, and σ_0 denotes a site-diagonal matrix element of Σ. The transfer integrals, which in the absence of ODD are given by the equation

$$\overline{W}_{ij}=(W+\Sigma)_{ij}, \tag{2.4}$$

connect sites i and j both of which are in the effective medium, and the $\tilde{W}_{ij}$ connect sites i and j one of which is a cluster site. In this section all transfer integrals are assumed to be scalar quantities; matrix transfer integrals are considered in Sec. IV. For the purposes of this paper it is assumed that the quantities ϵ_i, σ_0, W_{ij}, $\tilde{W}_{ij}$ and $\overline{W}_{ij}$ all are known. The form (2.3) shows clearly the separation of $H^{(C)}$ into the three parts, H_C, $\tilde{H}^{(C)}$, and $\overline{H}^{(C)}$, defined in the Introduction. The Green's-function operator for the Hamiltonian $H^{(C)}$ of (2.3) is defined by the expression

$$G^{(C)}=(z-H^{(C)})^{-1}. \tag{2.5}$$

The explicit dependence of any Green's function on the complex energy z is suppressed here and subsequently. Also, throughout the remainder of this paper the superscript C is dropped in writing the elements of $G^{(C)}$.

C. Formalism

The starting point for the evaluation of the matrix elements G_{ij} is the equation of motion

$$G_{ij}=g_i\left(\delta_{ij}+\sum_k W'_{ik}G_{kj}\right), \tag{2.6}$$

where

$$g_i=\begin{cases}(z-\epsilon_i)^{-1} & \text{for } i\in C\\ \bar{g}\equiv(z-\sigma_0)^{-1} & \text{for } i\notin C\end{cases}, \tag{2.7}$$

is the bare locator for the site i. The transfer terms W'_{ik} are defined by the conditions,

$$W'_{ik}=\begin{cases}W_{ik} & \text{if } i\in C \text{ and } k\in C,\\ \tilde{W}_{ik} & \text{if } i\in C,\ k\notin C,\ \underline{\text{or}}\ k\in C,\ i\notin C,\\ \overline{W}_{ik} & \text{if } i\notin C \text{ and } k\notin C.\end{cases} \tag{2.8}$$

It is convenient to separate the sum over sites k

in (2.6) into a sum over cluster sites and a separate sum over effective-medium sites. For the matrix elements one wishes to calculate, those for which i and j are in the cluster C, Eq. (2.6) assumes the form

$$G_{ij}=g_i\left(\delta_{ij}+\sum_{k\in C} W_{ik}G_{kj}+\sum_{k\notin C}\tilde{W}_{ik}G_{kj}\right). \tag{2.9}$$

The last term on the right can then formally be treated as a perturbation, giving the result

$$\sum_{k\notin C}\tilde{W}_{ik}G_{kj}=\sum_{k\in C}\Delta_{ik}^{(C)}G_{kj}, \tag{2.10}$$

where $\Delta_{ik}^{(C)}$ is given by the series expansion

$$\Delta_{ik}^{(C)}=\sum_{\substack{l\notin C\\ m\notin C}}\tilde{W}_{il}g_l\left[\delta_{lm}+\sum_{n\notin C}\overline{W}_{ln}g_n\left(\delta_{nm}+\sum_{r\notin C}\overline{W}_{nr}g_r(\delta_{rm}+\cdots)\right)\right]\tilde{W}_{mk}=\sum_{l,m\notin C}\tilde{W}_{il}\overline{\Gamma}_{lm}^{(C)}\tilde{W}_{mk}. \tag{2.11}$$

It is clear from this expansion that $\overline{\Gamma}^{(C)}$ is the Green's function for the effective medium with the cluster C replaced by vacuum. It is also clear that $\Delta_{ik}^{(C)}$ arises from the hopping of electrons from site i to site k, touching at least one site l outside the cluster, but not touching any site in the cluster along the way. Substituting Eq. (2.10) into (2.9) one finds the result

$$(g_i^{-1}-\Delta_{ii}^{(C)})G_{ij}-\sum_{\substack{k\in C\\ k\neq i}}(W_{ik}+\Delta_{ik}^{(C)})G_{kj}=\delta_{ij}, \tag{2.12}$$

or in matrix form,

$$G_C=(g_C^{-1}-W_C-\Delta_C^{(C)})^{-1}, \tag{2.13}$$

where G_C, g_C, W_C and $\Delta_C^{(C)}$ are matrices in the space of the cluster C having matrix elements G_{ij}, $g_{ij}=g_i\delta_{ij}$, W_{ij}, and $\Delta_{ij}^{(C)}$, respectively. Given the Hamiltonian $H^{(C)}$, Eq. (2.13) specifies G_C in terms of the renormalized cluster interactor, $\Delta_C^{(C)}$. Thus, it remains only to determine the $\Delta_{ii}^{(C)}$ and $\Delta_{ik}^{(C)}$, which are self-energy corrections to g_i^{-1} and W_{ik}, respectively.

Although the series expansion (2.11) can be evaluated directly only for a Cayley-tree lattice, we have devised a simple method which permits the exact determination of the $\Delta_{ik}^{(C)}$ for any lattice. The first step in the determination of the $\Delta_{ik}^{(C)}$ is the introduction of the interactors,

$$\overline{\Delta}_{ik}^{(C')}=\sum_{l,m\notin C'}\overline{W}_{il}\overline{\Gamma}_{lm}^{(C')}\overline{W}_{mk}, \tag{2.14}$$

for the effective medium. Here, C' is a cluster which contains the cluster C but is not necessarily the same as C. By a derivation exactly analogous to that of Eq. (2.12), it is easily seen that the $\overline{\Delta}_{ik}^{(C')}$ satisfy the equations

$$(\overline{g}^{-1}-\overline{\Delta}_{ii}^{(C')})\overline{G}_{ij}-\sum_{\substack{k\in C'\\ k\neq i}}(\overline{W}_{ik}+\overline{\Delta}_{ik}^{(C')})\overline{G}_{kj}=\delta_{ij}, \tag{2.15}$$

for all sites i and j in the cluster C'. This set of simultaneous linear equations determines the $\overline{\Delta}_{ik}^{(C')}$ as functions of the effective-medium Green's function $\overline{G}$ for any cluster C'. Equations (2.15) can be written more concisely in the matrix form,

$$\overline{\Delta}_{C'}^{(C')}=\overline{g}^{-1}-\overline{W}_{C'}-\overline{G}_{C'}^{-1}; \tag{2.16}$$

which is analogous to Eq. (2.13).

The next step is the determination of the $\Delta_{ik}^{(C)}$ in terms of the $\overline{\Delta}_{ik}^{(C')}$. In general the $\Delta_{ik}^{(C)}$ are given in terms of $\overline{\Delta}^{(C)}$ by the matrix equation

$$\Delta_C^{(C)}=(\tilde{W}\overline{W}^{-1}\overline{\Delta}^{(C)}\,\overline{W}^{-1}\tilde{W})_C, \tag{2.17}$$

where $\tilde{W}$ is the transfer matrix for a homogeneous material and has matrix elements $\tilde{W}_{ij}$ for all i and j, which have the same dependence on $\vec{R}_{ij}=\vec{R}_i-\vec{R}_j$ as do the matrix elements $\tilde{W}_{ij}$ defined immediately after Eq. (2.4). If $\tilde{W}$ is chosen proportional to $\overline{W}$ [$\tilde{W}=\alpha(\omega)\overline{W}$ with α a scalar], then Eq. (2.17) reduces to the simple form

$$\Delta_C^{(C)}=\alpha^2\overline{\Delta}_C^{(C)}, \tag{2.18}$$

which clearly defines the $\Delta_{ik}^{(C)}$. The clusters C' and C are identical in this, the most usual case. The choice $\tilde{W}=\overline{W}$ is obviously appropriate for the case of a site-diagonal self-energy in the absence of ODD, in which case $\overline{W}=W$. For this choice one finds the equality

$$\Delta_C^{(C)}=\overline{\Delta}_C^{(C)}. \tag{2.19}$$

Even if Σ is not chosen to be site diagonal, for the case of only nearest-neighbor hopping, only nearest-neighbor off-diagonal self-energy terms, and only diagonal disorder, the choice $\tilde{W}=\alpha\overline{W}$ is appropriate, in which case Eq. (2.18) holds.

In the case in which the matrices $\tilde{W}$ and $\overline{W}$ are not proportional to one another, Eq. (2.17) does not suffice to determine $\Delta_C^{(C)}$. In that case it relates $\Delta_C^{(C)}$ to the entire matrix $\overline{\Delta}^{(C)}$, not just to its projection, $\overline{\Delta}_C^{(C)}$, onto the space of the cluster C. Thus, in that case one must determine the relationship between $\Delta_C^{(C)}$ and $\Delta_{C}^{(C')}$ for an appropriately chosen larger cluster C'. Consider the cluster $C'=C+\tilde{C}$ which contains all sites i in the cluster C and all sites k outside C which are connected

by matrix elements $\tilde{W}_{ik} \neq \overline{W}_{ik}$ to any site i in C.
By definition, for this cluster one finds the equality

$$\Delta^{(C')} = \overline{W}\,\overline{\Gamma}^{(C')}\overline{W} = \overline{\Delta}^{(C')} . \tag{2.20}$$

Then, $\Delta^{(C)}$ is easily found in terms of $\Delta^{(C')}$ for any cluster C' which contains C. By exact analogy with the derivation of Eq. (2.13) one finds the matrix equation

$$\begin{aligned} G_{C'} &= (g_{C'}^{-1} - W'_{C'} - \Delta_{C'}^{(C')})^{-1} \\ &= \begin{bmatrix} g_C^{-1} - W_C - \Delta_C^{(C')} & -\tilde{W}_{C\tilde{C}} - \Delta_{C\tilde{C}}^{(C')} \\ -\tilde{W}_{\tilde{C}C} - \Delta_{\tilde{C}C}^{(C')} & \bar{g}_{\tilde{C}}^{-1} - \overline{W}_{\tilde{C}} - \Delta_{\tilde{C}}^{(C')} \end{bmatrix}^{-1} , \end{aligned} \tag{2.21}$$

where the supscripts $C\tilde{C}$ and $\tilde{C}C$ denote off-diagonal block matrices connecting the spaces of the clusters C and $\tilde{C} = C' - C$. Projecting Eq. (2.21) onto the space of the cluster C after inverting, one finds the result

$$\begin{aligned} G_C = [\,& g_C^{-1} - W_C - \Delta_C^{(C')} - (\tilde{W} + \Delta^{(C')})_{C\tilde{C}} \\ & \times (\bar{g}_{\tilde{C}}^{-1} - \overline{W}_{\tilde{C}} - \Delta_{\tilde{C}}^{(C')})^{-1}(\tilde{W} + \Delta^{(C')})_{\tilde{C}C}]^{-1} , \end{aligned} \tag{2.22}$$

which determines the desired matrix elements G_{ij} in terms of $\Delta_{C'}^{(C')}$ for the choice $C' = C + \tilde{C}$ defined above. The only assumption made in deriving this result is that of a translationally invariant effective medium characterized by scalar transfer integrals $\overline{W}_{ij}$. In a more proper treatment[30] of ODD it is convenient to define an effective medium characterized by 2×2 matrix transfer integrals, even within the single-site approximation. The multishell method is extended to include such effective-medium matrix transfer terms in Sec. IV.

The above formalism provides a completely general method for the exact evaluation of the Green's-function matrix elements G_{ij} for all sites i and j in a cluster C of real atoms embedded in an effective medium. In Sec. III the computational aspects of the determination of the G_{ij} are considered.

One can obtain the approximate equations of Brouers *et al.*[15,16] and Miwa[17] by replacing each of the $\Delta_{ij}^{(C)}$, for $i \neq j$, in the exact Eq. (2.11) by the average value

$$D^{(C)} = \sum_{i,j} (1 - \delta_{ij})\Delta_{ij}^{(C)} \Big/ \sum_{i,j} (1 - \delta_{ij}) . \tag{2.23}$$

III. COMPUTATION OF THE G_{ij}

The multishell method is most readily applicable to the case of a cluster consisting of a site 0 and its first n coordination shells. In particular, this choice of an n-shell cluster facilitates the determination of the effective-medium matrix elements $\overline{G}_{kl}$ required for the solution of Eq. (2.15). One must determine these matrix elements for all sites k and l in the cluster C', with $C' = C$ or $C' = C + \tilde{C}$. Any such matrix element can be calculated in the momentum representation. In that representation $\overline{G}$ is diagonal with matrix elements,

$$\overline{G}(\vec{k}) = (z - \sigma_0 - \overline{W}_{\vec{k}})^{-1} , \tag{3.1}$$

where

$$\overline{W}_{\vec{k}} = \sum_j \overline{W}_{0j}\, e^{i\vec{k}\cdot(\vec{R}_0 - \vec{R}_j)} \tag{3.2}$$

is the Fourier transform of the $\overline{W}_{ij}$. Then, the required matrix elements $\overline{G}_{kl}$ are obtained from the equations

$$\overline{G}_{kl} = N^{-1} \sum_{\vec{k}} \overline{G}(\vec{k}) e^{i\vec{k}\cdot(\vec{R}_k - \vec{R}_l)} , \tag{3.3}$$

where the sum is taken over all $\vec{k}$ vectors in the first Brillouin zone. The accurate evaluation of the sum (or integral) in Eq. (3.3) is rather time consuming. Furthermore, for an n-shell cluster C' in a d-dimensional lattice, there are approximately $(d+1)n+1$ such distinct matrix elements to be determined. However, there exist simple exact relations between the different $\overline{G}_{kl}$ which greatly reduce the number of matrix elements to be calculated using Eq. (3.3). These relations have been noted previously only for the case of the Cayley-tree lattice. In order to find these relations, one first determines for any given lattice and cluster C' those sites i such that $\Delta_{ii}^{(C')}$ can be shown from topological considerations to be zero. Those sites are easily found using the definition (2.11) and Eq. (2.12). For those sites Eq. (2.12) assumes the form

$$\bar{g}^{-1}\overline{G}_{ij} - \sum_k \overline{W}_{ik}\overline{G}_{kj} = \delta_{ij} , \tag{3.4}$$

where the sum over k goes over all sites. These Eqs. (3.4) constitute the desired simple relations between the different $\overline{G}_{kl}$; no further such relations exist except for the case of the Cayley tree. The number of these relations is maximized by choosing the cluster to contain all shells within l hops of the central atom. For example, for a simple cubic or fcc lattice, the relations (3.4) are of maximum benefit for a cluster having $n = l^2$ shells. In a d-dimensional lattice with only nearest-neighbor hopping, for such an optimally chosen cluster, there only remain to be evaluated using (3.3) approximately $l+1$ independent matrix elements for $d = 2$ and $4l - 1$ for $d = 3$. The number of such matrix elements increases gradually with increasing hopping range until the hopping range exceeds the cluster radius, at which point every distinct $\overline{G}_{kl}$ within the cluster must be calculated directly from Eq. (3.3). Explicit relations among the $\overline{G}_{kl}$ for a near-neighbor cluster in a variety of two- and three-dimensional lattices with nearest-neighbor hopping are given in Appendix B; the corresponding relations for larger clusters are easily found.

Having determined the required matrix elements $\overline{G}_{kl}$, the next step in the computation of the G_{ij} is the determination of the cluster interactors $\overline{\Delta}_{ik}^{(C')}$ and $\Delta_{ik}^{(C)}$. One uses the lattice symmetry of the cluster C' to select the n'_Δ distinct nonzero interactors $\overline{\Delta}_{ik}^{(C')}$, and determines those interactors by inverting an appropriate subset of the Eqs. (2.15). The corresponding $\Delta_{ik}^{(C)}$ are then given trivially by one of Eqs. (2.18)–(2.20). This technique is illustrated in Appendix B, where it is used to derive explicit expressions for the $\Delta_{ik}^{(C)}$ for the case $\tilde{W} = \overline{W}$ for a near-neighbor cluster in a square lattice.

To determine the G_{ij} for any given configuration of atoms in the cluster C it remains only to perform the appropriate matrix inversion indicated by either Eq. (2.13) or (2.22) in the space of the cluster C. For very large clusters it is necessary to perform this matrix inversion numerically for each inequivalent configuration of the cluster C in order to find the exact configurationally averaged Green's functions $\langle G_{ij}\rangle_C$. The effective computational limit on the size of the cluster which can be treated using the multishell method arises from the necessity to perform this matrix inversion many times. Thus, for very large clusters it is necessary in practice to approximate the procedure of configurational averaging. However, for near-neighbor clusters in all lattices and for larger clusters in simple lattices, the required matrix inversions can be performed analytically. For such clusters the computer time required for the solution of Eqs. (2.12) or (2.22) and for configurational averaging is significantly less than that required for the evaluation of the effective-medium Green's functions $\overline{G}_{kl}$.

Finally, one must determine the cluster configurationally averaged Green's function

$$\langle G_{ij}\rangle_C = \sum_J P_J G_{ij}^{(J)} . \tag{3.5}$$

Here, P_J is the probability of occurrence of a given atomic configuration J of the cluster C, and $G_{ij}^{(J)}$ is the value assumed by the Green's-function matrix element for that configuration. In the absence of SRO, the P_J are given by simple binomial distributions. Further, although there exist no simple algebraic expressions for the P_J in the presence of SRO, even in that case there exist computationally simple schemes[25,31] for the self-consistent determination of the P_J as functions of the Warren short-range-order parameters α_l. Thus, the evaluation of Eq. (3.5) presents no computational difficulty, even in the presence of SRO.

IV. MULTISHELL METHOD WITH OFF-DIAGONAL DISORDER

In this section the multishell formalism is generalized to include more properly the effects of ODD. Our discussion follows the method introduced by Blackman, Esterling, and Berk[30] (BEB) for the treatment of ODD. However, in contrast to the single-site BEB theory, the energies ϵ_i and the transfer terms W_{ij} for sites i and j in the cluster C are allowed to depend on the entire configuration of the cluster and on the positions of the sites i and j within the cluster, not only on the chemical occupation of the sites i and j. Thus, in particular, charge-transfer effects can be included within this formalism.

The appropriate matrix bare locators, Green's functions, and transfer integrals are defined for sites i and j in the cluster by the equations,

$$\underline{g}_i = \begin{pmatrix} x_i & 0 \\ 0 & y_i \end{pmatrix} g_i , \tag{4.1}$$

$$G_{ij} = \begin{pmatrix} x_i G_{ij} x_j & x_i G_{ij} y_j \\ y_i G_{ij} x_j & y_i G_{ij} y_j \end{pmatrix} , \tag{4.2}$$

and

$$W_{ij} = \begin{pmatrix} W_{ij} & W_{ij} \\ W_{ij} & W_{ij} \end{pmatrix} , \tag{4.3}$$

where $x_i = 1 - y_i$ is a projection operator which is equal to one if the site i is occupied by an atom of type A, and is zero otherwise.

For a system consisting of a cluster C of real atoms embedded in a translationally invariant matrix effective medium, such as that of BEB, the equation of motion of the Green's function assumes the form,[30,32,33]

$$G_{ij} = g_i \left(\delta_{ij} + \sum_k W'_{ik} G_{kj} \right) . \tag{4.4}$$

which is formally identical to the scalar Eq. (2.6). For effective-medium sites, the bare locator g_i is defined by the equation,

$$g_i = \overline{g} \equiv \left[\begin{pmatrix} z & 0 \\ 0 & z \end{pmatrix} - \begin{pmatrix} \sigma_0^1 & \sigma_0^3 \\ \sigma_0^3 & \sigma_0^2 \end{pmatrix} \right]^{-1} , \tag{4.5}$$

which defines the matrix site-diagonal part σ_0 of the self-energy, which is assumed to be known. For sites i and j in the cluster, W'_{ij} is equal to W_{ij}; for sites i and j not both in the cluster, the W'_{ij} are defined by the equation

$$W'_{ij} = \begin{cases} \tilde{W}_{ij} \equiv \begin{pmatrix} \tilde{W}_{ij} & \tilde{W}_{ij} \\ \tilde{W}_{ij} & \tilde{W}_{ij} \end{pmatrix} & \text{if } i \in C,\ j \notin C, \\ & \underline{\text{or}}\ j \in C,\ i \notin C, \\ \overline{W}_{ij} \equiv \begin{pmatrix} \overline{\alpha}_{ij} & \overline{\zeta}_{ij} \\ \overline{\zeta}_{ij} & \overline{\beta}_{ij} \end{pmatrix} & \text{if } i \notin C \text{ and } j \notin C . \end{cases} \tag{4.6}$$

Following a derivation exactly analogous to that of Eq. (2.12) from Eq. (2.8), one finds the result,

$$(1-g_i\Delta_{ii}^{(C)})G_{ij} - g_i\sum_{\substack{k\in C\\ k\neq i}}(W_{ik}+\Delta_{ik}^{(C)})G_{kj}=g_i\delta_{ij}\ , \qquad (4.7)$$

which assumes the concise matrix form,

$$\underline{G}_C=[\underline{1}-\underline{g}_C(\underline{W}_C+\underline{\Delta}_C^{(C)})]^{-1}\underline{g}_C\ . \qquad (4.8)$$

All quantities appearing here are supermatrices of 2×2 matrices, as denoted by the underlines. The cluster interactors $\Delta_{ij}^{(C)}$ are 2×2 matrices given by expressions formally identical to Eq. (2.11), but with every scalar quantity replaced by the corresponding 2×2 matrix. The development following Eq. (2.13) can be transcribed word for word in the case of ODD. In the most general case, $\underline{\tilde{W}} \neq \alpha(\omega)\underline{\overline{W}}$, one finds the expression

$$\begin{aligned}\underline{G}_C=\{\underline{1}-\underline{g}_C[&\underline{W}_C+\underline{\Delta}_C^{(C')}+(\underline{\tilde{W}}+\underline{\Delta}^{(C')})_{C\bar{C}}\\ &\times(\underline{\bar{g}}_{\bar{C}}^{-1}-\underline{\overline{W}}_{\bar{C}}-\underline{\Delta}_{\bar{C}}^{(C')})^{-1}\\ &\times(\underline{\tilde{W}}+\underline{\Delta}^{(C')})_{\bar{C}C}]\}^{-1}\underline{g}_C\ ,\end{aligned} \qquad (4.9)$$

for the cluster Green's function. Here the cluster interactor $\underline{\Delta}_C^{(C')}$ can be evaluated using the appropriate generalization of Eqs. (2.14)–(2.20).

One could avoid the introduction of the 2×2 matrices used in this section by choosing a scalar effective medium such as the physical effective medium of BEB or some other, more approximate, scalar effective medium. However, the long-range character of the transfer integrals in the BEB physical effective medium suggests that the use of a scalar effective medium for a system characterized by strong ODD would in general require the treatment of very large clusters C' in order to treat the off-diagonal disorder adequately. Thus, the matrix formalism given in this section would appear preferable to the scalar formalism of Sec. II for the treatment of off-diagonal disorder, at least from a computational point of view.

V. NUMERICAL RESULTS

For the case of a linear chain with only nearest-neighbor hopping the problem of a cluster of atoms embedded in an effective medium is treated exactly within the CFM, the BPA, the BMA, and the calculations of Tsukada,[34] Takahashi, and Shimizu,[35] Butler,[36] and many others as well as within the MSM. An examination of the results of numerical calculations of different authors shows that the results obtained depend strongly on the choice of effective medium. In particular, it is essential to choose an analytic effective medium in order to obtain good results. The reader is referred to Refs. 12 and 34–36 for a comparison of typical results obtained for clusters embedded in an analytic effective medium with exact results for disordered alloys. Our calculations show that for clusters of five or more atoms on a linear chain the choice of a SSCPA effective medium yields results essentially identical to those obtained using an effective medium determined within the self-consistent boundary-site approximation[36] (SCBSA) or molecular coherent-potential approximation[34] (MCPA).

We have also performed numerical calculations for a variety of two- and three-dimensional lattices for a single-shell cluster of real atoms embedded in a SSCPA effective medium for binary alloys $A_{1-C}B_C$. Alloy densities of states and site spectral weight functions were calculated. Calculations were performed for the square, hexagonal, simple cubic, and face-centered-cubic lattices. These calculations were designed both to test the validity of the BMA—the most accurate previously used method for treating a cluster embedded in an effective medium—and to show the large effect upon site spectral weight functions of even small fluctuations in local environment. In particular, the results of these calculations show that even for a fixed chemical composition of the nearest-neighbor shell of a given central atom, a rearrangement of the positions of atoms in this shell can cause large changes in the site spectral weight function of the central atom. Such a change is referred to as an isomer effect; different arrangements of a fixed set of atoms in the nearest-neighbor shell of a given atom are referred to as isomers.

It is planned to test the convergence of our results for larger cluster sizes; unfortunately exact results are not now available for interesting realistic three-dimensional lattices such as the fcc lattice. However, in some cases the SSCPA and the MSM for a single-shell cluster in a SSCPA effective medium were found to yield almost identical densities of states. In those cases the densities of states obtained should be very accurate; since fluctuations in the first shell produce on the average almost no effect in those cases, fluctuations in more distant shells also should produce almost no average effect.

In these calculations a tight-binding model Hamiltonian of the form (2.3) with only nearest-neighbor hopping was used. Each energy ϵ_i was assumed to depend only on the chemical occupation of the site i and to take on either the value ϵ_A or the value ϵ_B, depending on the occupation of the site i. The nearest-neighbor transfer integrals, W_{ij}, $\tilde{W}_{ij}$, and $\overline{W}_{ij}$ all were assumed to be equal to the constant value W, independent of the

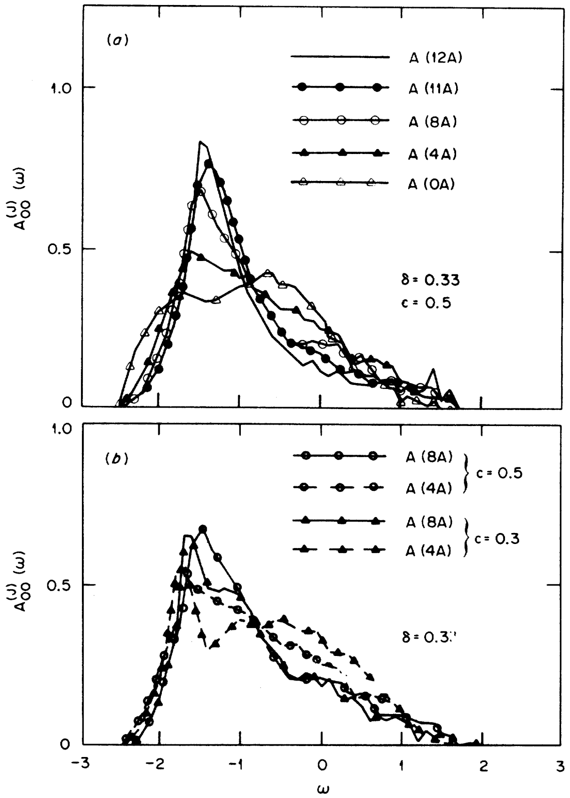

FIG. 1. Exact spectral weight functions $A_{00}^{(J)}(\omega)$ for atoms of type A in a fcc lattice, surrounded by nearest-neighbor configurations J having different numbers n_A of nearest-neighbor atoms of type A, for nearest-neighbor clusters embedded in a SSCPA medium. The scattering strength δ is defined in the text; c is the concentration of atoms of type B.

occupation of the sites i and j and independent of the concentration c.

Site spectral weight functions $A_{00}^{(J)}(\omega)$ were calculated for specific cluster configurations J using the definition

$$A_{00}^{(J)}(\omega) = -\pi^{-1}\mathrm{Im}G_{00}^{(J)}(\omega)\,. \tag{5.1}$$

Densities of states $\rho(\omega)$ were calculated from the defintion

$$\rho(\omega) = \sum_J P_J A_{00}^{(J)}(\omega)\,, \tag{5.2}$$

which is used universally in cluster theories for disordered alloys.

In one-dimensional lattices with only nearest-neighbor hopping the matrix elements $\overline{G}_{ij}$ of the effective-medium Green's function can be evaluated analytically. However, in higher-dimensional systems no such analytic expressions for the Green's function exist, except for the case of the Cayley tree. In performing the preliminary model calculations reported here the method of Gaussian quadratures was used in integrating Eq. (3.3). The accuracy of the integrations was tested both by varying the fineness of the integration net and by checking against exact results for analytically integrable functions. Values of $\rho(\omega)$ and $A_{00}^{(J)}(\omega)$ were calculated on a net of points with $\delta\omega = 0.1$ for a bandwidth of order $2w = 5$. The calculated densities of states and spectral weight functions were found to satisfy the relevant sum rules

$$\int_{-\infty}^{\infty} \rho(\omega)d\omega = 1 \tag{5.3}$$

and

$$\int_{-\infty}^{\infty} A_{00}^{(J)}(\omega)d\omega = 1\,, \tag{5.4}$$

to within better than 1% in all cases. Any deviations from exact satisfaction of the sum rules were within the uncertainties allowed by the coarseness of the integration net over ω.

We performed calculations within the BMA as well as within the exact MSM in order to study the accuracy of the BMA. Although the BMA has been stated explicitly in the literature only for the case of a simple cubic lattice, the MSM formalism makes clear how the BMA can be generalized, as was shown at the end of Sec. II. We call this somewhat generalized approximation the BMA, since it is in the spirit of the original BMA and is exactly equivalent to it for those cases in which the BMA is defined. However, in contrast to the original BMA numerical calculations, in our calculations the exact Green's functions $\overline{G}_{ij}$ are used in calculating the renormalized interactors $\Delta_{ij}^{(C)}$ which occur in Eq. (2.23).

We report here only a few illustrative results from our calculations. In discussing these results, each alloy is characterized by the concentration c of B-type atoms and the scattering strength

$$\delta \equiv (\epsilon_A - \epsilon_B)/w\,, \tag{5.5}$$

with ϵ_A always greater than ϵ_B. The dependence of the spectral weight function $A_{00}^{(J)}(\omega)$ upon concentration c and upon n_A, the number of nearest-neighbor atoms of type A, is illustrated in Fig. 1 for the case of weak scattering ($\delta = 0.33$) in a fcc lattice. The curves shown are averages over curves calculated for all possible isomers. The dependence of $A_{00}^{(J)}(\omega)$ upon nearest-neighbor concentration, $c_{\mathrm{nn}} = 1 - \frac{1}{12}n_A$ for a fcc lattice, is seen to be about as strong as its dependence on c for fixed n_A, with statistically important fluctuations in n_A producing effects of the same order as those produced by a change of 0.2 in alloy concentration for fixed n_A. This result was found to be true in general for all lattices and all scattering strengths (0.33

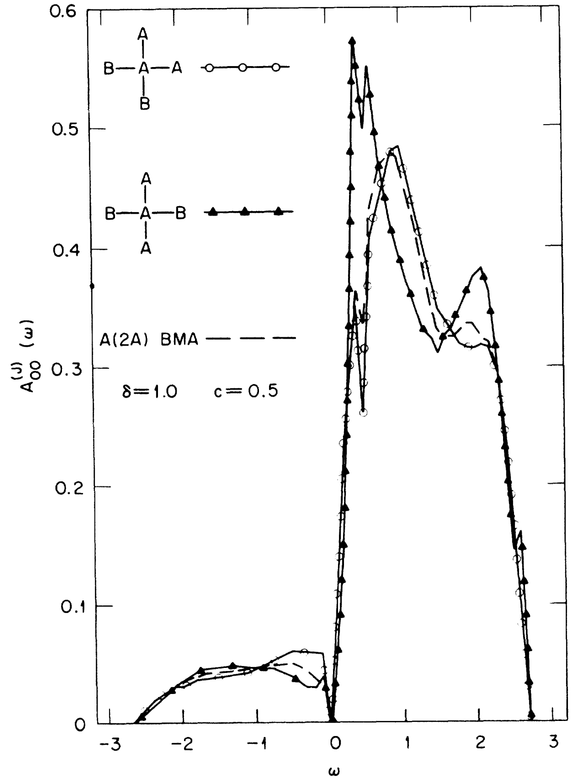

FIG. 2. Exact and BMA spectral weight functions for atoms of type A in a square lattice, surrounded by each of the two distinct nearest-neighbor isomers with $n_A = 2$ and within a SSCPA embedding medium.

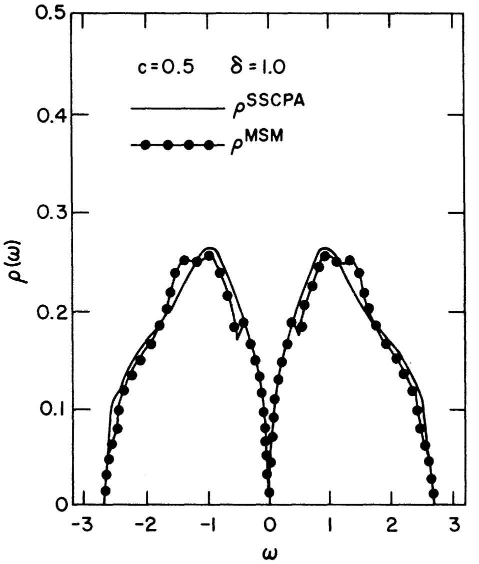

FIG. 3. Density of states curves $\rho(\omega)$ vs ω for a square lattice calculated using (i) the SSCPA and (ii) the MSM for a nearest-neighbor cluster embedded in a SSCPA effective medium.

$\leq o \leq 1)$ studied.

More subtle isomer effects are shown in the following figures. Such effects were found for all lattices and all scattering strengths studied. They were found to become larger with increasing scattering strength and to be larger for the interlocking hexagonal and fcc lattices than for the noninterlocking square and simple cubic lattices. We show such effects for the two-dimensional square and hexagonal lattices rather than for the three-dimensional simple cubic and fcc lattices because the isomers are fewer in number and easier to visualize for two-dimensional lattices.

In Fig. 2 the isomer effect is shown for an atom of type A surrounded by two atoms of type A and two of type B in a square lattice with $c = 0.5$ and $\delta = 1.0$. For this scattering strength, which is just sufficient for band splitting, even a small change in local environment produces a significant change in site spectral weight functions $A_{00}^{(J)}(\omega)$, as is shown by the two solid curves. However, the MSM density of states calculated for this case differs only slightly from the density of states of the embedding SSCPA effective medium, as is shown in Fig. 3. Thus, fluctuations in local environment are seen not to affect $\rho(\omega)$ significantly.

Note that the BMA fails to differentiate between the site spectral weight functions for the two iso-

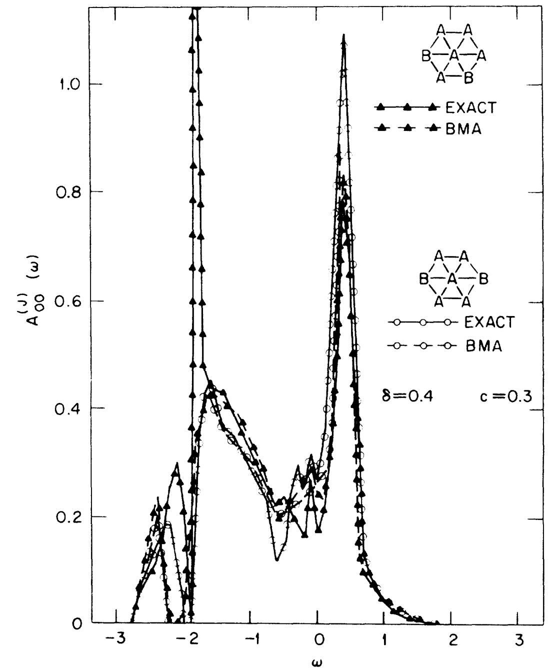

FIG. 4. Exact and BMA spectral weight functions for atoms of type A in a hexagonal lattice for two different isomers with $n_A = 4$ and within a SSCPA embedding medium.

mers depicted in Fig. 2. As is shown by the dashed curve, the BMA yields a site spectral weight function for both isomers which is almost identical to the exact spectral weight function for the top isomer shown but quite distinct from that for the bottom isomer. Thus, the BMA does not even average properly over the results of the two isomers; this leads to errors in $\rho(\omega)$ as well as in site spectral weight functions within the BMA. However, in general the BMA introduces only relatively small errors in $\rho(\omega)$ as compared to the errors which it introduces in some site spectral weight functions.

In Fig. 4 a much larger isomer effect typical of those found in interlocking lattices is shown. The isomer effect is shown for two of the isomers of an atom of type A surrounded by four atoms of type A and two of type B in a hexagonal lattice with $c = 0.3$ for the comparatively weak scattering case, $\delta = 0.4$. For these two isomers the BMA does yield slightly different site spectral weight functions. However, the BMA shows the same qualitative weakness in this case as in the case shown in Fig. 2. The two BMA spectral weight functions are very similar to one another, and both are very similar to the exact site spectral weight function for the bottom isomer depicted and quite different from that for the top isomers.

VI. DISCUSSION AND CONCLUSION

We have presented here a method for the exact calculation of the Green's function of a cluster embedded in an effective medium which is assumed to be known. This method, the multishell method, is useful for treating the effects of local-environment fluctuations on electronic densities of states and site spectral weight functions in disordered systems described by a tight-binding or interpolation-scheme Hamiltonian. Such a Hamiltonian can be used to describe phonon, magnon, and exciton systems as well as the electron states in some real alloys, such as paramagnetic Ni-Cu alloys. As is shown in Appendix A, the MSM yields Green's functions and site spectral weight functions having the proper analytic structure, provided that one chooses an analytic effective medium, such as a virtual crystal, SSCPA, SCBSA,[36] MCPA,[37] or BEB[38] effective medium. The effects of SRO and ODD have been incorporated into the theory. Additional features of real materials such as multiple and/or degenerate bands and hybridization can also be incorporated into the theory in a straightforward way. Attempts are being made to generalize the MSM for use with more realistic electronic Hamiltonians, such as muffin-tin Hamiltonians.

Our numerical results show that the effects on the central-site spectral weight function, $A_{00}^{(J)}(\omega)$, of fluctuations in the chemical occupation of the first shell are very important. We intend also to use the MSM to investigate the importance of such fluctuations in shells beyond the first shell. Although the effects of fluctuations in coordination shells beyond the first must be of some importance, such effects die out rapidly with increasing shell number n for realistic two- and three-dimensional systems. For such systems we anticipate that MSM calculations for small clusters in an appropriately chosen medium will suffice for the determination of almost all physical observables in disordered systems. Our calculations show that for realistic scattering strengths even the effect of fluctuations in the first shell on the configurational average of the site spectral weight functions is small.

Of the other techniques for the calculation of $G^{(C)}$ for a cluster embedded in a given medium, the BMA is the most accurate in the general case. Our calculations for several different lattice structures show that the use of the BMA can yield quite satisfactory densities of states for realistic scattering strengths, but can lead to significant errors in the calculation of the central-site spectral weight functions. In particular, the BMA was found to yield satisfactory spectral weight functions for the simple cubic lattice, but not for interlocking lattices such as the hexagonal and fcc lattices, or even for the square lattice. It is expected that extended-range hopping should have effects similar to increased interconnectedness of the lattice and thus may decrease the accuracy of the BMA even further. Although the MSM requires slightly more computer time than the BMA, our results suggest that the small additional computational difficulty of the MSM is well justified. The relations derived here between different effective-medium Green's-function elements reduce the computer time required in either theory.

For small clusters the CFM treats the problem of a cluster embedded in an effective medium with even less accuracy than the BMA, except for Cayley-tree lattices, for which both are exact. However, the CFM is considerably simpler computationally, so that within the CFM one can consider larger clusters. Also, for very large clusters the importance of the choice and treatment of the effective medium is greatly reduced, so that for such clusters the CFM becomes, in principle, a good technique for the alloy problem. On the other hand, the application of the CFM to large clusters is limited by the very large number of configurations which must be considered separately in calculating any experimentally observable quantity, as in the application of the MSM or any other method. For large clusters for which one must generate configurations statistically, the computational times required for CFM and MSM calculations become similar, and the accuracies of the two methods become comparable. Thus, for treating large clusters it is not clear which method is preferable. However, for realistic three-dimensional systems it appears that one may need to consider only relatively small clusters. For such clusters the MSM is clearly the best method.

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APPENDIX A

It is shown in this appendix that the MSM yields analytic cluster Green's functions and non-negative densities of states and spectral weight functions provided that one chooses an effective medium characterized by a cluster-diagonal analytic self-energy Σ, the eigenvalues of which have nonpositive imaginary parts throughout the upper half of the complex z plane. In particular, the MSM always yields analytic cluster Green's functions and non-negative densities of states and spectral weight functions when used with an effective medium determined within the virtual-crystal approximation, the average Green's-function approximation of Zaman and Jacobs,[12] the SSCPA,[37] the MCPA,[37] the t-matrix self-consistent central-site approximation,[37] the SCBSA[36] for the case of a linear chain with only nearest-neighbor hopping, or the BEB[38] approximation. Explicitly, it is shown that for such a choice of effective medium any cluster Green's function G_C is the inverse of an analytic matrix the eigenvalues of which have positive imaginary parts throughout the upper halfplane.

The cluster Green's function for a cluster of atoms embedded in an effective medium is given by the equation

$$G_C = (z - H_C - \overline{\Delta}_C)^{-1}, \tag{A1}$$

where the matrix renormalized interactor Δ_C is given by the equation

$$\overline{\Delta}_C = \overline{g}_C^{-1} - \overline{W}_C - \overline{G}_C^{-1}. \tag{A2}$$

Here, the cluster matrices $\overline{g}_C$ and $\overline{W}_C$ have matrix elements $\overline{g}_{ij} = (z - \Sigma_{ij})^{-1}\delta_{ij}$ and $\overline{W}_{ij}$, respectively. The effective-medium cluster Green's function $\overline{G}_C$ can be found from its momentum representation,

$$\overline{G}_C = \sum_{\vec{k}} \overline{G}_C(\vec{k}) = \sum_{\vec{k}} (\overline{g}_C^{-1} - \overline{W}_C - W_{\vec{k}})^{-1}, \tag{A3}$$

where $W_{\vec{k}}$ is the Fourier transform of the intercluster transfer matrices $W_{CC'}$, which have matrix elements W_{ij} only for $i \in C$ and $j \in C'$. Equations (A1) and (A2) correspond to Eqs. (2.13) and (2.16) in the text. Equation (A2) establishes the analyticity of $\overline{\Delta}_C$ because from Eq. (A3) the eigenvalues of $\overline{G}_C$ have negative imaginary parts.

It remains only to show that the eigenvalues of $\overline{\Delta}_C$ have nonpositive imaginary parts. From Eq. (A2) one obtains for the imaginary part of $\overline{\Delta}_C$ the expression

$$\begin{aligned}(\overline{\Delta}_C)_2 &= z_2 - (\Sigma_C)_2 - \mathrm{Im}\{\overline{G}_C^{-1}\} \\ &= z_2 - (\Sigma_C)_2 + \overline{G}_C^{-1}\ \mathrm{Im}\{P_C \overline{G} P_C\}(\overline{G}_C^{\dagger})^{-1},\end{aligned} \tag{A4}$$

where P_C is a projection operator onto the space of cluster C and where

$$\overline{G} = (z - \Sigma - W)^{-1} \tag{A5}$$

is the effective-medium Green's function. Using Eq. (A5) in (A4), one obtains the result

$$\begin{aligned}(\overline{\Delta}_C)_2 = -\overline{G}_C^{-1} P_C \Big(\sum_{C' \neq C} \overline{G} P_{C'} (z_2 - \Sigma_2) P_{C'} \overline{G}^{\dagger} \Big) \\ \times P_C (\overline{G}_C^{\dagger})^{-1}.\end{aligned} \tag{A6}$$

From this result it is clear that the imaginary parts of the eigenvalues of $\overline{\Delta}_C$ are nonpositive. Thus, from Eq. (A1) G_C must be analytic and must yield non-negative densities of states and spectral weight functions.

APPENDIX B

Here, we give the explicit relations among the effective-medium cluster Green's functions $\overline{G}_{ij}$ for the case of a nearest-neighbor cluster in several two- and three-dimensional lattices with only nearest-neighbor hopping. The method used yields two relations among the $\overline{G}_{ij}$ for each lattice. Also, for the square lattice an explicit expression for the cluster interactor $\Delta_C^{(c)}$ is given for the usual case $\tilde{W} = \overline{W} = W$. For a translationally invariant effective medium, the matrix elements $\overline{G}_{ij}$ depend only on the vector distance between sites i and j; for a site j in the nth coordination shell about site i, $\overline{G}_{ij}$ is denoted by $\overline{G}_n$, as is shown schematically in Fig. 5 for a nearest-neighbor cluster in a square lattice.

For a cluster C consisting of the central site 0 and its four nearest-neighbor sites 1–4 in a square lattice, Eq. (3.4) yields the following two relations among the effective-medium Green's functions, $\overline{G}_0$, $\overline{G}_1$, $\overline{G}_2$ and $\overline{G}_3$, required for the determination of $\Delta_C^{(c)}$:

$$(z-\sigma_0)\overline{G}_0 - 4\overline{W}\overline{G}_1 = 1 \tag{B1}$$

and

$$(z-\sigma_0)\overline{G}_1 - \overline{W}(\overline{G}_0+\overline{G}_3+2\overline{G}_2) = 0\,. \tag{B2}$$

The cluster interactors then are obtained from Eq. (2.16), which in this case assumes the specific form

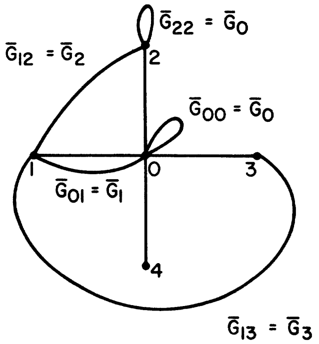

FIG. 5. Nearest-neighbor cluster in a square lattice and typical intracluster effective-medium Green's functions $\overline{G}_n$ for $n=0,1,2,3$.

$$\begin{vmatrix} \Delta_{00} & \Delta_{01} & \Delta_{02} & \Delta_{03} & \Delta_{04} \\ \Delta_{10} & \Delta_{11} & \Delta_{12} & \Delta_{13} & \Delta_{14} \\ \Delta_{20} & \Delta_{21} & \Delta_{22} & \Delta_{23} & \Delta_{24} \\ \Delta_{30} & \Delta_{31} & \Delta_{32} & \Delta_{33} & \Delta_{34} \\ \Delta_{40} & \Delta_{41} & \Delta_{42} & \Delta_{43} & \Delta_{44} \end{vmatrix} = \begin{vmatrix} z-\sigma_0 & -\overline{W} & -\overline{W} & -\overline{W} & -\overline{W} \\ -\overline{W} & z-\sigma_0 & 0 & 0 & 0 \\ -\overline{W} & 0 & z-\sigma_0 & 0 & 0 \\ -\overline{W} & 0 & 0 & z-\sigma_0 & 0 \\ -\overline{W} & 0 & 0 & 0 & z-\sigma_0 \end{vmatrix} - \begin{vmatrix} \overline{G}_0 & \overline{G}_1 & \overline{G}_1 & \overline{G}_1 & \overline{G}_1 \\ \overline{G}_1 & \overline{G}_0 & \overline{G}_2 & \overline{G}_3 & \overline{G}_2 \\ \overline{G}_1 & \overline{G}_2 & \overline{G}_0 & \overline{G}_2 & \overline{G}_3 \\ \overline{G}_1 & \overline{G}_3 & \overline{G}_2 & \overline{G}_0 & \overline{G}_2 \\ \overline{G}_1 & \overline{G}_2 & \overline{G}_3 & \overline{G}_2 & \overline{G}_0 \end{vmatrix}^{-1} . \tag{B3}$$

For this simple case with only nearest-neighbor hopping, Δ_{0j} and Δ_{j0} are equal to zero for all j, and Δ_{ij} depends only on the distance R_{ij} for i and j both different from zero.

For the hexagonal lattice Eq. (3.4) yields the two conditions

$$(z-\sigma_0)\overline{G}_0 - 6\overline{W}\,\overline{G}_1 = 1 \tag{B4}$$

and

$$[(z-\sigma_0) - 2\overline{W}]\overline{G}_1 - \overline{W}(\overline{G}_0+\overline{G}_3+2\overline{G}_2) = 0\,. \tag{B5}$$

For the simple cubic lattice, Eq. (3.4) yields the two relations

$$(z-\sigma_0)\overline{G}_0 - 6\overline{W}\overline{G}_1 = 1 \tag{B6}$$

and

$$(z-\sigma_0)\overline{G}_1 - \overline{W}(\overline{G}_0+\overline{G}_3+4\overline{G}_2) = 0\,. \tag{B7}$$

For the face-centered-cubic lattice, Eq. (3.4) yields the two relations

$$(z-\sigma_0)\overline{G}_0 - 12\overline{W}\overline{G}_1 = 1 \tag{B8}$$

and

$$[(z-\sigma_0) - 4\overline{W}]\overline{G}_1 - \overline{W}\,(\overline{G}_0+\overline{G}_4+2\overline{G}_2+4\overline{G}_3) = 0\,. \tag{B9}$$

As the discussion in Sec. IV makes clear, all of the above relations can be generalized to the case of alloys exhibiting ODD. All that is necessary to do so is to interpret the scalar quantities which appear in Eqs. (B1)–(B9) as 2×2 matrices. The generation of further relations for larger clusters is equally straightforward.

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