PHYSICAL REVIEW B VOLUME 36, NUMBER 9 15 SEPTEMBER 1987-II

Configurational energies and effective cluster interactions in substitutionally disordered binary alloys

A. Gonis,* X. -G. Zhang, and A. J. Freeman
Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201

P. Turchi
Department of Chemistry and Materials Science (L-280), Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

G. M. Stocks and D. M. Nicholson
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6024

(Received 17 April 1987)

The determination of configurational energies in terms of effective cluster interactions in substitutionally disordered alloys from a knowledge of the alloy electronic structure is examined within the methods of concentration waves (CW) and the generalized perturbation method (GPM), and for the first time within the embedded-cluster method (ECM). It is shown that the ECM provides the exact summation to all orders of the effective cluster interaction expansions obtained in the partially renormalized GPM. The connection between the various methods (CW, GPM, and ECM) is discussed and illustrated by means of numerical calculations for model one-dimensional tight-binding (TB) systems and for TB Hamiltonians chosen to describe Pd-V alloys. These calculations, and the formal considerations presented in the body of the paper, show the complete equivalence of converged GPM summations within specific clusters and the ECM. In addition, it is shown that an exact expansion of the configurational energy can be obtained in terms of fully renormalized effective cluster interactions. In principle, these effective cluster interactions can be used in conjunction with statistical models to determine stable ordered structures at low temperatures and alloy phase diagrams.

I. INTRODUCTION

The study of phase formation and stability of substitutional or interstitial solid solutions can be undertaken most efficiently on the knowledge of accurate approximations to the configurational energy (and entropy) and on the use of appropriate statistical models. Such models are most often formulated in terms of effective multisite interactions, e.g., pair, triplet, etc., which can be used to represent the configurational energy of the system under study. These interactions can either be inferred experimentally, determined within phenomenological theories, or obtained as the result of fitting procedures in specific statistical models. Such determinations have been employed in most applications in the past. However, during the last few years a first-principles calculation of these interactions on the basis of the electronic structure of substitutionally disordered alloys has become possible. This paper, as a contribution in this direction, addresses specifically the calculation of ordering energies in terms of uniquely defined, concentration-dependent effective cluster interactions in substitutional alloys. These cluster interactions can be used in conjunction with statistical models in the study of various alloy properties, e.g., stable ordered structures at low temperature and the construction of alloy phase diagrams.

Our discussion will be presented for the case of binary solid solutions, although some of our results will have implications in the more general case of multicomponent alloys. In this discussion we attempt to bring together and present in a unifying light three distinct and apparently diverse methods for the study of alloy ordering: the methods of concentration waves[1-3] (CW) and the generalized perturbation method[4-10] (GPM), both proposed and used previously in the study of alloy phase stability, and for the first time the embedded-cluster method[11-14] (ECM), which has been applied to the study of short-range-order (SRO) effects on the density of states (DOS) of disordered systems. As is indicated in the body of the paper, the feature unifying these methods is that they can all be obtained by means of related expansions of the free energy of a disordered material.

The determination of stable structures and the construction of alloy phase diagrams has until recently relied almost exclusively on experimental and computational methods based on phenomenological models for calculating internal energies, configurational entropies, and heats of mixing. In these methods, effective cluster interactions play a significant role. This approach has led to the development[15] of computer codes capable of producing accurate phase diagrams of complex materials. Because of this success and for the sake of good scientific progress, it is now important to obtain a microscopic understanding of materials properties. Such an understanding should encompass fundamental, microscopic concepts such as disorder energies and effective cluster interactions, and should lead to the construction of alloy phase diagrams with *ab initio*, parametrization-free quantum-mechanical methods. It would then hold the promise of providing a predictive capability of materials properties leading to the design of materials with novel properties compatible with specific engineering applications. In this paper, and in a future publication [hereafter to be referred to as paper II (Ref. 16)], we set forth and attempt to unify recently developed methods[3-15] based on the electronic structure of disordered alloys, which are sufficiently powerful to allow a microscopic study of alloy phase formation and stability. Thus, these methods are a step in the direction of unifying theoretical metallurgy and the basic physics of condensed matter.

In order to illustrate the connection between electronic structure calculations and the phenomenological theory of ordering, we consider the concept of concentration waves. It is well known[1] that the process of "ordering and segregation in binary alloys may be interpreted as the loss of stability of a disordered solution with respect to static concentration waves." On the other hand, these phenomena can also be interpreted in terms of pairwise effective interactions in disordered binary alloys. Thus, given a knowledge of the concentration wave vector (or the pairwise effective interactions), one can readily predict the most stable ordered structure of a system (compatible with kinetic effects) at low temperatures. Until recently, this knowledge could only be derived from experimental studies such as x-ray, electron, and neutron diffraction. During the last few years, however, electronic structure calculations have progressed[3-14] to the point of allowing the direct, first-principles calculation of concentration waves and of alloy phase diagrams.[17] It is ability of this kind which links metallurgy with the science of the solid state.

This link may be amplified further. The theoretical determination of phase structure and stability in binary (and multicomponent) alloys leads[8] to a number of fundamental questions: "What is the nature and relative stability of competing ordered structures? Can the onset of order be described in terms of a small number of parameters with transparent physical meaning, and what is the role played by these parameters in the determination of ordered structures? And, finally, is it possible to calculate these parameters from first principles by means of a microscopic theory?" Apart from computer simulations,[15] the calculation of phase diagrams of binary alloys has been attempted within various schemes such as the cluster variation method[18-23] (CVM), and real-space renormalization-group[24] and Monte Carlo techniques.[25-27] All these studies rely on the knowledge, primarily experimental or as adjustable parameters, of phenomenological multiatom effective interactions. They have shown that these rather small (of the order of mRy) parameters can be qualitatively important, being able to modify the nature of the ground state and of phase transitions, and ultimately of the phase diagram. Cluster interactions have been used[28,29] in attempts to explain asymmetries of various phase diagrams of binary alloys about $c=0.5$ (c denotes concentration of solute or impurity atoms), and the relative stability of two ordered phases characterized by the same two-body interactions. Thus, it is necessary to obtain a rigorous justification for the use of these parameters and to clarify their nature. In addition, we must be able to decide *a priori* questions regarding the possible volume, temperature, and concentration dependence of these interactions. Finally, we must have a reliable guide for the choice of the cluster size, nature etc.—on the basis of which these parameters are to be calculated. In this paper and in paper II, it is shown that the generalized perturbation method[4-10] and the embedded-cluster method[11-14] provide well-defined, controlled, and computationally feasible approximation schemes for the calculation of unique multiatom effective interactions in substitutionally disordered binary alloys. These schemes are based on fully self-consistent methods for the calculation of the electronic structure of alloys and can be related in a straightforward way to appropriate statistical models.

The formal framework of the methods discussed here is provided by the coherent-potential approximation[30-35] (CPA) and a certain number of its extensions.[4-14] As is well known, the CPA constitutes the most satisfactory single-site theory for the study of substitutionally disordered alloys. The CPA is a mean-field theory, based on the assumption that the concentration of each species is uniform throughout the alloy. In order to examine ordering and segregation tendencies in alloys one must consider the effects of concentration fluctuations, δc_i^α, associated with site i and species α in the alloy. The forms chosen for δc_i^α have led to two formally distinct but numerically quite similar (at least for metallic alloys) methods for the study of ordering effects. The choice $\delta c_i^\alpha = c_i^\alpha - c^\alpha$, where c_i^α is the concentration of species α at site i and c^α is the average concentration of the species, is best suited for the study of stability with respect to infinitesimal fluctuations (second-order phase transitions). It leads to the consideration of phase stability in terms of static concentration waves.[1,3,4] It also leads naturally to a definition of long-range-order (LRO) parameters, pair correlation functions, and can be shown[1] to be consistent with phenomenological ordering theories of the Landau form.[36] A Fourier transformation can be used to calculate effective pair interactions and to study those SRO effects arising from the presence of LRO. On the other hand, the choice $\delta c_i^\alpha = P_i^\alpha - c^\alpha$, where $P_i^\alpha = 1$ (0) if site i is occupied (not occupied) by an atom of type α, underlies the development of the GPM and is best suited for the study of finite fluctuations, SRO effects, and the calculation of multisite (cluster) interactions. Thus, these two different modes of expanding the ordering energy in terms of concentration fluctuations are complementary and, at least for binary alloys of transition metals, have been found[17] to yield very similar numerical results.

In contrast to the method of concentration waves, which is consistent with linear-response theory and the mean-field nature of the CPA, the GPM and the ECM are perturbationlike methods which break away from the self-consistency underlying the CPA. This at first glance undesirable feature is compensated by the ability to calculate nonlinear effects caused by finite statistical fluctuations. Thus, these methods lead to rapidly convergent expansions of the configurational energy and allow the use of proper statistical models for the calculation of the entropy, e.g., CVM and Monte Carlo simulations. These methods also hold decisive advantages over other attempts, such as those based[37] on pseudopotential theory, in calculating impurity-impurity interactions. Furthermore, they allow the calculation of multisite effective interactions which in many cases are necessary in order to obtain rapidly convergent and accurate expansions of the ordering energy. In principle, the GPM and the ECM allow the determination of temperature- and concentration-dependent cluster interactions and result in predictions of most stable structures which are, in general, consistent with phenomenological structural maps.[38] In this paper it is shown, for the first time, that a certain class of diagrams in the GPM expansion can be summed uniquely in terms of renormalized cluster interactions obtained in the ECM [see Eq. (5.9)]. Further correction terms, essentially vertex corrections improving the calculation of the configurational energy, must be calculated in a perturbative "GPM-like" expansion leading to fully renormalized expressions for the disorder energy and the cluster interactions.

At this point, it may be instructive to consider briefly some of the essential properties that a fully satisfactory theory of alloy phase stability based on electronic structure should be required to possess. (i) It should allow the determination of *unique* pairwise and higher-order effective interactions as functions of external intensive parameters such as temperature, concentration, and pressure. (ii) It should allow the *prediction* of the structure of an ordered phase, obviating the need for separate calculations for structures assumed to be known beforehand. (iii) In addition to phase stability, it should allow the treatment of other physical effects in disordered materials, e.g., the influence of statistical fluctuations on the transport properties, within essentially the same formalism. (iv) It should become exact in the appropriate limits of the various physical parameters, i.e., $c \rightarrow 0$ or $c \rightarrow 1$, large cluster sizes, etc. (v) It should provide computationally practicable methods of calculation. Of all methods[36–39] proposed thus far for the study of disorder, the Green-function formalism based on the CPA and related extensions seems to hold the greatest promise for fulfiling these requirements.

For the sake of clarity of presentation, we introduce this formalism in terms of tight-binding (TB) Hamiltonians. More realistic potentials and the associated rigorously first-principles methods are considered in paper II. Thus, our discussion will be based on the usual tight-binding Hamiltonian describing a physical system,

$$H = \sum_{i,u,v} |ui\rangle \varepsilon_i^{uv} \langle v,i| + \frac{1}{2} \sum_{\substack{i,j \\ u,v \\ (i \neq j)}} |u,i\rangle W_{ij}^{uv} \langle v,j| \; , \tag{1.1}$$

where the state vectors $|u,i\rangle$ correspond to orbitals u associated with site i, the ε_i^{uv} $[\equiv(\underline{\varepsilon}_i)_{uv}]$ are the site-diagonal energies for orbitals u and v, and the W_{ij}^{uv} $[\equiv(\underline{W}_{ij})_{uv}]$ are intersite transfer integrals (hopping terms) describing electron propagation from orbital v on site j to orbital u on site i. In a random binary alloy, A_cB_{1-c}, both the site-diagonal and the site–off-diagonal terms can be functions of configuration, corresponding to the presence of diagonal and off-diagonal disorder in the alloy. Following common practice, we neglect environmental effects other than those confined to single sites in question and consider the site-diagonal variables $\underline{\varepsilon}_i$ is taking the "values" $\underline{\varepsilon}_i^A$ or $\underline{\varepsilon}_i^B$ depending on whether site i is occupied by an atom of type A or of type B, respectively (diagonal disorder). In terms of the occupation numbers P_i^α we can write

$$\varepsilon_i = \sum_\alpha P_i^\alpha \varepsilon_i^\alpha, \quad \alpha = A \text{ or } B \; . \tag{1.2}$$

In the presence of off-diagonal disorder (ODD), we have similarly

$$\underline{W}_{ij} = \sum_{\alpha,\beta} P_i^\alpha W_{ij}^{\alpha\beta} P_j^\beta, \quad \alpha,\beta = A \text{ or } B \; . \tag{1.3}$$

Thus, $\underline{W}_{ij}$ can assume the "values" $\underline{W}_{ij}^{AA}$, $\underline{W}_{ij}^{AB} = \underline{W}_{ij}^{BA}$ or $\underline{W}_{ij}^{BB}$ depending on the occupation of sites i and j.

Having introduced a rather general, multiband Hamiltonian in Eq. (1.1) containing ODD, we restrict our discussion primarily to the case of a single-band (one-orbital) system containing only diagonal disorder. This greatly simplifies the presentation while leaving the essential points of the formalism intact. Where it is convenient to do so, we will quote the relevant expressions in terms of multiband systems and will also indicate how the generalization to alloys with ODD is to be effected.

The remainder of the paper takes the following form. The concept of concentration waves is reviewed briefly in Sec. II, while Secs. III and IV, respectively, are devoted to a somewhat more-detailed exposition of the GPM and the ECM. A formally exact expansion of the configurational energy is given in Sec. V. Section VI contains the results of numerical calculations of effective cluster interactions for model and more-realistic TB Hamiltonians. A short discussion and some comments are then provided in Sec. VII. Finally, specific examples of some GPM expansions for renormalized cluster interactions are given in an Appendix.

II. THE METHOD OF CONCENTRATION WAVES

The method of concentration waves in the study of the tendencies toward ordering or phase separation in binary alloys was originally proposed by Khachaturyan[1,2,40–44] and co-workers. This method goes significantly beyond previous formalisms[45–47] for studying phase transformations in solid solutions, alleviating various shortcomings of such theories and extending them in nontrivial ways. Perhaps the most outstanding accomplishment of the CW approach to ordering phenomena is the ability to *predict* the structure of the ordered phase. Such predictions are based on the knowledge, heretofore obtainable from experimental studies (e.g., x-ray, electron, and neutron diffraction), of a characteristic function $S^{(2)}(\mathbf{k})$. This function is essentially the lattice Fourier transform of the pair correlation function

$$S_{ij}^{(2)}=\langle P_iP_j\rangle-\langle P_i\rangle\langle P_j\rangle \ , \tag{2.1}$$

where P_i is an occupation number which is equal to 1 (0) when site i is (is not) occupied by a solute atom, and the symbol $\langle \cdots \rangle$ denotes configurational average. It can be shown[48] that the CW method is asymptotically correct in the limiting cases of high and low temperature, its validity extending outside a region surrounding the critical point for a second-order phase transition. The size of this region shrinks with increasing radius of interatomic interactions.

The method[4-10] to be summarized in this section allows the calculation of $S^{(2)}(\mathbf{k})$ from a knowledge of the electronic structure of an alloy, thus obviating the need of obtaining correlation functions experimentally. Although in principle the method of CW is exact within the context of linear-response theory, its implementation requires the use of a mean-field approach to ordering. Thus the method cannot yield critical exponents, nor can it account for the nonlinear effects of local statistical fluctuations. On the other hand, since it allows the treatment of pairwise interactions of infinite range, it may be expected to yield a not too inaccurate estimate of the transition temperature. At the same time pairwise interactions, even taken to be concentration and temperature dependent, may not be sufficient for the calculation of accurate alloy phase diagrams. The incorporation of nonlinear effects and of multisite effective interactions can be accomplished within the cluster expansion schemes discussed in the following two sections.

In order to study the effects of infinitesimal concentration fluctuations throughout the system it is convenient to introduce[49] a generalized version of the CPA. In the inhomogeneous CPA it is assumed that each site in the alloy is characterized by a concentration c_i^α, scattering matrix t_i^α, and self-energy σ_i. The site-dependent self-energy is determined through the condition

$$\langle t_i\rangle\equiv\sum_\alpha c_i^\alpha t_i^\alpha=0 \ , \tag{2.2}$$

where $\langle t_i\rangle$ denotes the single-site average of the scattering matrix,

$$\begin{aligned} t_i^\alpha&=\frac{(\varepsilon_i^\alpha-\sigma_i)}{1-(\varepsilon_i^\alpha-\sigma_i)\overline{G}_{ii}}\\ &=\frac{\delta_i^\alpha}{1-\delta_i^\alpha\overline{G}_{ii}} \end{aligned} \tag{2.3}$$

with $\overline{G}_{ii}$ being the ith site-diagonal matrix element of the CPA effective medium and δ_i^α being defined implicitly by this equation. If environmental effects can be considered as being small in some sense, the thermodynamic function (the Helmholtz free energy) of the alloy can be expanded in powers of $\delta c_i^\alpha=c_i^\alpha-c^\alpha$ or, equivalently for a binary alloy in powers of $\delta c_i=c_i-c$,

$$\begin{aligned}\Omega=\Omega_0+\sum_i S_i^{(1)}\delta c_i+\tfrac{1}{2}\sum_{i,j}S_{ij}^{(2)}\delta c_i\,\delta c_j\\ +\tfrac{1}{3}\sum_{i,j,k}S_{ijk}^{(3)}\delta c_i\,\delta c_j\,\delta c_k+\cdots \ ,\end{aligned} \tag{2.4}$$

where

$$S_{i_1i_2\cdots i_n}^{(n)}=\left[\frac{\delta^{(n)}\Omega}{\delta c_{i_1}\,\delta c_{i_2}\cdots\delta c_{i_n}}\right]_{c_i\equiv c} \tag{2.5}$$

is the expansion coefficient (correlation function) calculated for all $c_i=c$, and Ω_0 is the concentration-dependent but configuration-independent contribution of the homogeneous CPA medium. The summation indices $i,j,k,\ldots$ in Eq. (2.4) run over all sites in the material.

Since in the homogeneous medium all sites are equivalent, and by definition

$$\sum_j \delta c_j=0 \ , \tag{2.6}$$

the term linear in δ_c vanishes identically so that for infinitesimal fluctuations we can write

$$\Delta\Omega=\Omega-\Omega_0=\tfrac{1}{2}\sum_{i,j}S_{ij}^{(2)}\delta c_i\,\delta c_j \ . \tag{2.7}$$

We now introduce the lattice Fourier transforms,

$$\delta c_{\mathbf{k}}=\frac{1}{N}\sum_n \delta c_n\, e^{i\mathbf{k}\cdot\mathbf{R}_n} \tag{2.8}$$

and

$$\begin{aligned}X(\mathbf{k})&=\frac{1}{N}\sum_{\substack{n,m\\(n\neq m)}}(\overline{G}_{nm})^2e^{i\mathbf{k}\cdot\mathbf{R}_{nm}}\\ &=\sum_{\mathbf{q}}\overline{G}(\mathbf{k}+\mathbf{q})\overline{G}(\mathbf{q})-(\overline{G}_{00})^2 \ ,\end{aligned} \tag{2.9}$$

where all k-space summations (integrations) extend over the first Brillouin zone (BZ) of the reciprocal lattice, and $\overline{G}$ denotes the Green function of the homogeneous CPA medium. Using these quantities and a certain amount of CPA algebraic manipulation consistent with Eq. (2.2), we can write Eq. (2.7) in the form

$$\begin{aligned}\Delta\Omega=-\frac{2}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_F}dE\,\Bigg[\sum_{\mathbf{k}}X(\mathbf{k})\left[\sum_{\alpha,\beta}t^\alpha t^\beta\delta c_{\mathbf{k}}^\alpha\delta c_{-\mathbf{k}}^\beta\right]\\ \times[1-\langle t^2\rangle X(\mathbf{k})]^{-1}\Bigg] \ ,\end{aligned} \tag{2.10}$$

where the implicit dependence of the various quantities on the energy is to be understood. Equation (2.10) is true for general multicomponent alloys, yielding the two-particle correlation function between species α and β on sites $i\neq j$ as a direct Fourier transform,

$$S_{ij}^{\alpha\beta}=\frac{2}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_F}\left[\sum_{\mathbf{k}}S^{\alpha\beta}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{R}_{ij}}\right]dE \ , \tag{2.11}$$

where

$$S^{\alpha\beta}(\mathbf{k})=t^\alpha t^\beta X(\mathbf{k})[1-\langle t^2\rangle X(\mathbf{k})]^{-1}-S_{00} \ , \tag{2.12}$$

and the site-diagonal term S_{00} is subtracted in order to eliminate the nonphysical terms $S_{ii}^{(2)}$. In the case of binary alloys the CPA self-consistency condition is equivalent to the relations

$$t^{A}=(1-c)\delta t, \quad t^{B}=-c\,\delta t, \quad \text{and } \langle t^{2}\rangle=-t^{A}t^{B} , \tag{2.13}$$

where $\delta t = t^{A}-t^{B}$. Thus, the effective pair correlation function[1]

$$S^{(2)}=S^{AA}+S^{BB}-S^{AB}-S^{BA} \tag{2.14}$$

can be written in the form

$$S^{(2)}(\mathbf{k})=(\delta t)^{2}X(\mathbf{k})[1-c(1-c)(\delta t)^{2}X(\mathbf{k})]^{-1} . \tag{2.15}$$

If the term $c(1-c)(\delta t)^{2}X(\mathbf{k})$, the so-called vertex correction, can be neglected as being small, we obtain

$$S_{ij}^{(2)}=-\frac{2}{\pi}\,\text{Im}\int_{-\infty}^{E_F}(\delta t)^{2}(\bar{G}_{ij}\bar{G}_{ji})dE \tag{2.16}$$

for the pair correlation function (or effective pair interaction) between sites i and j. In the more general case in which vertex corrections must be taken into account the pair correlation function can be written as

$$S_{ij}^{(2)}=-\frac{2}{\pi}\,\text{Im}\int_{-\infty}^{E_F}(\delta t)^{2}\left[(\bar{G}_{ij})^{2}+\sum_{k\,(\neq i,j)}\langle t^{2}\rangle(\bar{G}_{ik})^{2}(\bar{G}_{kj})^{2}+\cdots\right]dE . \tag{2.17}$$

This real-space expansion shows explicitly that $S_{ij}^{(2)}$ contains the response of all medium sites (summation over k). In the following sections we will have occasion to compare these linear-response expressions, Eqs. (2.11) and (2.17), with those obtained in terms of nonlinear methods (cluster expansions). Let us also note that Eq. (2.11), which allows the calculation of effective correlation functions between any two species in multicomponent alloys, can be used to calculate long-range-order parameters and phase stability in such alloys in the manner considered by Badalyan *et al.*[2]

The $T=0$ K formalism just presented can be readily extended to finite temperatures and generalized to incorporate alloys with ODD and with multiple, possibly degenerate bands. These generalizations require only the rather straightforward extension of the relevant scalar quantities of this section to appropriately chosen matrices.

In a binary alloy, the correlation function $S_{ij}^{(2)}$, Eq. (2.17), is directly proportional[1] to the corresponding LRO parameters, η_{ij}. The Fourier transform $S^{(2)}(\mathbf{k})$ suffices to determine the structure of the ordered state. At the same time, as was mentioned previously, it may be necessary to go beyond the bounds of linear-response theory and pairwise interactions. Methods for accomplishing this are presented in the following sections.

III. EFFECTIVE CLUSTER INTERACTIONS: THE GENERALIZED PERTURBATION METHOD

In order to account properly for the effects of *finite* statistical fluctuations it is necessary to go beyond mean-field, linear-response theories. This can be accomplished by considering the energies associated with distinct alloy configurations.

A. The configurational energy

In general, a specific alloy configuration can be characterized by the set of occupation numbers $\{P_i^{\alpha}\}$. Considering each configuration as consisting of finite fluctuations away from the CPA medium, the band contribution to the free energy, and the only contribution considered in this paper, can be written[8,9] as the sum of two parts,

$$\Omega(\{P_i^{\alpha}\})=\Omega_0(c)+\Omega'(\{P_i^{\alpha}\}) , \tag{3.1}$$

where $\Omega_0(c)$ is the configuration-independent contribution of the CPA medium which depends on the concentration, and Ω' $(\{P_i^{\alpha}\})$ is the concentration *and* configuration-dependent part. The quantity $\Omega_0(c)$ is discussed in more detail in the following sections. The last term in Eq. (3.1), Ω', can be written[9] as the generalized perturbation expansion

$$\begin{aligned}\Omega'(\{P_i^{\alpha}\})&=\frac{2}{\pi N}\text{Im}\left[\int_{-\infty}^{E_F}\text{Tr}\ln(1-T\bar{G}')dE\right]\\&=-\frac{2}{\pi N}\text{Im}\left[\sum_{n=2}^{\infty}\frac{1}{n}\int_{\infty}^{E_F}\text{Tr}(T\bar{G}')^{n}dE\right] ,\end{aligned} \tag{3.2}$$

where Tr denotes the trace. The scattering matrix operator T is site diagonal and has the form

$$\begin{aligned}T&=\sum_{\substack{i,j\\u,v}}P_i^{\alpha}t_i^{\alpha,uv}\,|u,i\rangle\langle v,i| , \quad \alpha=A \text{ or } B\\&=\sum_{i,u,v}\delta c_i\,\delta t^{uv}\,|u,i\rangle\langle v,i| , \quad \delta c_i=P_i^{A}-c ,\end{aligned} \tag{3.3}$$

where the second line follows upon use of Eq. (2.13). Here $t_i^{\alpha,uv}$ is the scattering matrix for orbitals u,v characterizing an atom of type α at site i embedded in the CPA medium. It is given explicitly be means of Eq. (2.3) with the various scalar quantities in that equation being interpreted as matrices in orbital space, and $\delta t = t^{A}-t^{B}$. The quantity $\bar{G}'$ is the strictly off-diagonal part of the homogeneous CPA Green function, the trace is taken over site and orbital space, and the factor of 2 accounts for spin degeneracy. As usual, N denotes the number of sites. Again, for ease of presentation we suppress explicit matrix notation and express most of the ensuing formalism in terms of essentially scalar quantities. The generalization of the results to more general multiband systems is straightforward.

Upon using the first line of Eq. (3.3) in Eq. (3.2) one obtains a cluster expansion of the configurational free energy in terms of the occupation numbers P_i^α,

$$\begin{aligned}\Omega'(\{P_i^\alpha\}) &= \sum_{n=2}^{\infty} \Omega'^{(n)}(\{P_i^\alpha\}) \\ &= \tfrac{1}{2}\sum_{i,j}{}' \sum_{\alpha,\beta} v_{ij}^{\alpha\beta} P_i^\alpha P_j^\beta + \tfrac{1}{3}\sum_{i,j,k}\sum_{\alpha,\beta,\gamma} v_{ijk}^{\alpha\beta\gamma} P_i^\alpha P_j^\beta P_k^\gamma + \tfrac{1}{4}\sum_{i,j,k,l}\sum_{\alpha,\beta,\gamma,\delta} v_{ijkl}^{\alpha\beta\gamma\delta} P_i^\alpha P_j^\beta P_k^\gamma P_l^\delta + \cdots ,\end{aligned} \tag{3.4}$$

where the prime indicates the restriction that no two consecutive indices can refer to the same site. The cluster interactions $v_{ijk}^{\alpha\beta\gamma}\cdots$ are given by the expressions

$$v_{i_0 i_1 \cdots i_{n-1}}^{\alpha\beta\cdots\gamma} = -\frac{2}{\pi}\mathrm{Im}\,\mathrm{Tr}\left[\int_{-\infty}^{E_F} (t_{i_0}^{\alpha}\bar{G}_{i_0 i_1} t_{i_1}^{\beta}\bar{G}_{i_1 i_2} \cdots t_{i_{n-1}}^{\gamma}\bar{G}_{i_{n-1} i_0})\,dE\right] , \tag{3.5}$$

and are clearly configuration dependent. Here, the trace is being taken over the orbital indexes and the term $n=1$ vanishes because in Eq. (3.2) $\mathrm{Tr}(T\bar{G}')=0$.

Equation (3.4) is exact and represents the configurational energy of an alloy. As it stands, however, Eq. (3.4) is rather awkward for computational purposes. In the case of binary alloys a completely equivalent but much more useful expression in terms of *configuration-independent cluster interactions* and of finite fluctuations about the average occupation of a site can be obtained. Using Eqs. (2.13), or equivalently the second line of Eq. (3.3), we obtain[8,9] the following form for the ordering energy:

$$\Omega'(\{P_i^\alpha\}) = \sum_{n=2}^{\infty}\Omega'^{(n)}(\{P_i^\alpha\}) = \tfrac{1}{2}\sum_{i,j}{}' v_{ij}^{(2)}\,\delta c_i\,\delta c_j + \tfrac{1}{3}\sum_{i,j,k}{}' v_{ij_k}^{(3)}\,\delta c_i\,\delta c_j\,\delta c_k + \tfrac{1}{4}\sum_{i,j,k,l}{}' v_{ij_{kl}}^{(4)}\,\delta c_i\,\delta c_j\,\delta c_k\,\delta c_l + \cdots , \tag{3.6}$$

where $\delta c_i = P_i - c$ is the concentration fluctuation at site i, and $P_i \equiv P_i^A$. The cluster interactons (CI) of nth order, $v_{i_0 i_1 \cdots i_{n-1}}^{(n)}$, are given by the expressions

$$v_{i_0 i_1 \cdots i_{n-1}}^{(n)} = -\frac{2}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\left[\int_{-\infty}^{E_F} (\delta t\,\bar{G}_{i_0 i_1}\,\delta t\,\bar{G}_{i_1 i_2}\cdots\delta t\,\bar{G}_{i_{n-1} i_0})\,dE\right] , \tag{3.7}$$

which should be compared to Eq. (3.5).

It is to be noted that Eq. (3.6) is formally identical to Eq. (2.4) of linear-response theory, but that the coefficients $S^{(n)}$ and $v^{(n)}$ are different, being defined, respectively, by Eqs. (2.5) and (3.7). In particular, the correlation functions $S^{(n)}$ are consistent with a CPA-linear-response theory, whereas the $v^{(n)}$ contain vertex connections, i.e., the nonlinear effects of statistical fluctuations. On the other hand, in spite of this formal difference, the results of calculations presented in Sec. V indicate that S and v can be quite similar numerically.

As a simple illustration of Eq. (3.6), we exhibit the second- and fourth-order contributions

$$\Omega'^{(2)}(\{P_i^\alpha\}) = \tfrac{1}{2}\sum_{i,j}{}' v_{ij}^{(2)}[P_iP_j - c(P_i+P_j) + c^2] \tag{3.8}$$

and

$$\begin{aligned}\Omega'^{(4)}(\{P_i^\alpha\}) = \tfrac{1}{4}\sum_{i,j,k,l}{}' v_{ijkl}^{(4)}[&P_iP_jP_kP_l - c(P_iP_jP_k + P_jP_kP_l + P_kP_lP_i + P_lP_iP_j) \\ &+ c^2(P_iP_j + P_iP_k + P_iP_l + P_jP_l + P_jP_k + P_kP_l) - c^3(P_i+P_j+P_k+P_l) + c^4] .\end{aligned} \tag{3.9}$$

Before proceeding with the discussion of methods for evaluating $\Omega'(\{P_i^\alpha\})$ in Eq. (3.6), it may be useful to point out some of its main characteristics. As it stands, Eq. (3.6) is exact and includes the presence of fluctuations on all sites of the material. Consider for example the contributions proportional to $v_{ijkl}^{(4)}$. These are of three kinds associated with the possible allowed coincidences of the sites i,j,k,l,

$$i=k,\quad j=l,\quad i\neq j\ ; \tag{3.10a}$$

$$i=k,\quad j\neq l,\quad i\neq j,\quad k\neq l\quad \text{(and permutations)}\ ; \tag{3.10b}$$

$$i\neq j\neq k\neq l\quad \text{(all sites distinct)}\ . \tag{3.10c}$$

The corresponding contributions to the configurational part of the energy then take the form

$$v_{ij}^{(4)}(\delta c_i)^2(\delta c_j)^2 = v_{ij}^{(4)}[(1-2c)^2\,\delta c_i\,\delta c_j + 2c(1-c)\delta c_i + c^2(1-c)^2]\ , \tag{3.11a}$$

$$v_{ijl}^{(4)}(\delta c_i)^2\,\delta c_j\,\delta c_l = v_{ijl}^{(4)}[(1-2c)\delta c_i\,\delta c_j\,\delta c_l + c(1-c)\delta c_j\,\delta c_l]\ , \tag{3.11b}$$

and

$$v_{ijkl}^{(4)}\,\delta c_i\,\delta c_j\,\delta c_k\,\delta c_l\ , \tag{3.11c}$$

where Eqs. (3.11a) and (3.11b) follow from the identity $(\delta c)^2=(1-2c)\delta c+c(1-c)$. The term in δc_i in Eq. (3.11a) is justified because of the equivalence of sites i and j in the summations in Eq. (3.6). Thus, the terms proportional to $v^{(4)}$ contribute to the four-, three-, and two-body renormalized effective cluster interactions (RECI) terms, defined more precisely below, with the two-site contribution being of two different kinds, coming from Eqs. (3.11a) and (3.11b). Clearly, similar considerations hold for the other terms in Eq. (3.6).

The preceding discussion points to a particularly useful scheme for the evaluation of Eq. (3.6). In this scheme *we regroup Eq. (3.6) in terms of irreducible contributions associated with clusters C of distinct sites and sum over all such clusters.* These summations can be expressed in terms of *renormalized effective cluster interactions* V_C. As will be shown in detail in the following section, such RECI arise naturally in the expansion of the total configurational energy and allow us to write

$$\Omega'(\{P_i\}) = V_0 + \sum_i V_i\,\delta c_i + \tfrac{1}{2}\sum_{i,j}{}'' V_{ij}\,\delta c_i\,\delta c_j + \tfrac{1}{3}\sum_{i,j,k}{}'' V_{ijk}\,\delta c_i\,\delta c_j\,\delta c_k + \cdots\ , \tag{3.12}$$

where the double primes indicate summations over *distinct* sets of sites. For example, the effective pair interaction V_{ij} is given by the expression

$$V_{ij} = v_{ij}^{(2)} + \tfrac{1}{2}(1-2c)^2 v_{ij}^{(4)} + c(1-c)\sum_l v_{ijl}^{(4)} + \cdots\ . \tag{3.13}$$

In evaluating the RECI, V_C, it is a convenient starting point and usually a good approximation to retain only the terms confined to the cluster C. For example, in Eq. (3.13) we consider the terms involving only the specific sites i and j. As will be shown in the following sections, this selective summation can be obtained by considering sites i and j, or in general a cluster C, embedded in the CPA medium. For the case of V_{ij} we find

$$V_{ij} = \overline{\Omega}{}'_{ij}(AA) + \overline{\Omega}{}'_{ij}(BB) - \overline{\Omega}{}'_{ij}(AB) - \overline{\Omega}{}'_{ij}(BA)\ , \tag{3.14}$$

where $\overline{\Omega}{}'_{ij}(\alpha\beta)$ indicates that all sites other than i and j are medium (CPA) sites. Note that in this approximation the terms V_0 and V_i in Eq. (3.12) are equal to zero. For some systems it may be necessary to consider the contributions, such as the third terms in the expansion Eq. (3.13), associated with fluctuations outside the cluster. When such terms are included we shall refer to the interactions V_C as being *fully* renormalized (FRECI).

Renormalized effective interactions associated with n sites can be obtained similarly by collecting together the terms of various orders, $v_{\{j\}}^{(n)}$, associated with a given set of distinct sites $\{j\}$. Although the direct summing of the various orders becomes increasingly cumbersome when $\{j\}$ contains more than three or four sites, expressions for the sums can be obtained within the ECM [see Eq. (4.4) below]. As is shown in the following section, these renormalized interactions allow us to cast the ordering energy in a particularly elegant and useful form.

B. The disorder energy

It is often necessary to have a measure of the energy of the completely disordered state. Since at high temperature $\delta c \rightarrow 0$, the disorder energy is given the expression,

$$\begin{aligned} E_{\rm dis} &= \Omega_0(c) + V_0 \\ &= -\frac{2}{\pi N}\,{\rm Im\,Tr}\left[\int_{-\infty}^{E_F}[\ln\overline{G} + \ln(1-G^d\delta)]dE\right] + V_0\ , \end{aligned} \tag{3.15}$$

where $\Omega_0(c)$, the first two terms in the last expression, is the contribution of the CPA medium, and V_0 is the contribution of the renormalized terms indicated in Eq. (3.12). Here, $\delta=\sum_{n,\alpha}|n\rangle P_n^\alpha \delta_n^\alpha\langle n|$ and the term in δ will make no contribution in the case of lattices with monatomic bases. We note that V_0 is the sum of all terms independent of δc and can be found readily to any desired accuracy by the process indicated in Eq. (3.11a). It can easily be verified that the lowest-order contribution to V_0 comes from $v_{ij}^{(4)}$ and is given by the last term within square brackets in Eq. (3.11a). This term is evaluated explicitly in Sec. V.

As mentioned in Sec. III A, the term V_0 vanishes if only terms confined to a cluster C embedded in a CPA medium are taken into account, but makes a finite contribution if fully renormalized interactions are considered. In this sense, V_0 affords a means of "going beyond" the CPA in evaluating the energy of the disordered state.

The formal similarity between the concentration wave (CW) expression, Eq. (2.4), and the GPM expansion, Eq. (3.6), has already been noted. It is interesting to realize that to first order in $(\delta t)^2$ these two different expressions give identical results. This similarity deteriorates with the inclusion of higher-order terms in both expressions so that, in general, $S_{ij}^{(2)} \neq V_{ij}$. Which of the two descriptions is more appropriate clearly depends on the situation under consideration. In general, CW's appear as a natural means for studying the effects of "small" but long-range interactions, while effective cluster interactions are more appropriate for examining short-range but large (finite) fluctuations.

The renormalized effective cluster interactions can be viewed as the generalization to higher-order clusters of the commonly used effective pair interactions of the well-known Ising model. For a fixed lattice structure, these effective cluster interactions are functions of the distances between cluster sites, the concentration c of solute atoms, the Fermi energy and of the magnitudes of the diagonal and off-diagonal disorder in the alloy. These interactions, whose expressions are given in the following section, allow a unique and rapidly convergent expansion of the ordering energy (configurational energy). In fact, even the individual orders, $v_{ij\cdots k}^{(n)}$, converge rapidly with increasing order n. Thus, the expansion in Eq. (3.6) constitutes a proper perturbation expansion[8,9,49] in terms of the "small" parameter $|\delta t\,\bar{G}_{ij}|$.

In the formalism presented in this section, only the "single-particle" part of the energy is taken into account. Consideration of the electron-electron interaction (double-counting terms) and of exchange and correlation effects can be expected in most cases to introduce quantitative changes while leaving the qualitative trends in a calculation nearly intact. In any case a fully charged self-consistent approach within a TB formalism is hampered by the introduction of phenomenological parametrizations for the descriptions of various physical effects, e.g., hybridization, charge transfer, etc. Such effects can be taken into account in a much more elegant way within the framework of II.

The discussion of this section can be made applicable to alloys characterized by both diagonal and off-diagonal disorder, and can be extended to finite temperatures. The rigorous application of the CPA to alloys with general ODD has been given by Blackman, Esterling, and Berk[50] (BEB), while the geometric limit of ODD has been treated by Shiba.[51] The application of the GPM to the latter case has been reported by Bieber and Gautier.[52] The extension to alloys with general ODD can be made through the introduction of matrices in configuration space, as suggested originally by BEB,[50] and amplified in later work.[53] Finally, a finite-temperature formalism can be obtained, at least in an approximate fashion, through the introduction of the Fermi distribution function in the integrals over the energy discussed above. More accurate formulations in terms of Matsubara frequency sums can also be constructed.

IV. EFFECTIVE CLUSTER INTERACTIONS: THE EMBEDDED-CLUSTER METHOD

In this section it is shown that the formalism of the embedded-cluster method[11-14] allows the summation of the GPM expansions and the determination of renormalized cluster interactions. The latter can be used to obtain particularly useful expressions for the ordering energy.

A. Summations of the GPM expansions

Because of the significance of the role played by pair interactions in the discussion of ordering phenomena, we shall consider the case of pairs separately.

1. Pair interactions

The expression for the renormalized effective pair interactions in an alloy, Eq. (3.14), has a simple physical interpretation: It includes all possible scatterings off a pair of atoms embedded in a CPA effective medium. Thus, it is not surprising that Eq. (3.14) can be expressed in terms of the full scattering matrix associated with a pair of impurity sites. Indeed, straightforward expansions and comparisons show that the summation of all terms in Eq. (3.2) involving two specific sites in a given configuration take the form

$$\Omega'(P_i^\alpha P_j^\beta)=\frac{2}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\left[\int_{-\infty}^{E_F}\ln Q^{\alpha\beta}\,dE\right], \tag{4.1}$$

representing the summation to *all* orders in the corresponding GPM expansion. Here, the matrix quantity

$$(Q^{\alpha\beta})_{ij}=\delta_{ij}-t_i\bar{G}_{ij}(1-\delta_{ij}),\quad t_i\equiv t_i^\alpha \tag{4.2}$$

is simply related to the full scattering matrix $T^{\alpha\beta}$ for the two sites

$$T^{\alpha\beta}=\delta D(Q^{\alpha\beta})^{-1}, \tag{4.3}$$

where δ and D^{-1} are site-diagonal matrices with elements $\delta_i^\alpha=\varepsilon_i^\alpha-\sigma_i$ and $(D^{-1})_{ii}^\alpha=(1-\delta_i^\alpha\bar{G}_{ii})$, respectively (in the homogeneous CPA $\sigma_i\equiv\sigma_0$ and $\bar{G}_{ii}\equiv\bar{G}_{00}$). Direct comparison also shows that the renormalized effective pair interaction, Eq. (3.14), is simply the quantity

$$\begin{aligned}V_{ij}&=-\frac{2}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\left[\int_{-\infty}^{E_F}\ln[(Q^{AA}Q^{BB})(Q^{AB}Q^{BA})^{-1}]dE\right]\\&=\sum_{n=1}\frac{1}{n}[(1-c)^n-(-c)^n]^2v_{ij}^{(n)}.\end{aligned} \tag{4.4}$$

The last summation is the direct result of considering those terms in Eq. (3.13) which involve only sites i and j.

2. Multisite interactions

Configuration-dependent multisite (cluster) interactions and effective cluster interactions can be expressed in terms of the appropriate scattering matrices, or the associated quantities, Q (explicit matrix notation suppressed). The corresponding expressions are easily obtained in the ECM.

At $T=0$ K the free energy (thermodynamic potential) is given by the expression,

$$\Omega=\tilde{E}-\mu N\quad(\mu=E_F), \tag{4.5}$$

where $\tilde{E}$ in this treatment is the band contribution to the internal energy,

$$\tilde{E}=\int_{-\infty}^{E_F}E'n(E')dE', \tag{4.6}$$

and $N\equiv N(E_F)$ is the integrated density of states at the Fermi energy,

$$N(E_F)=\int_{-\infty}^{E_F}n(E')dE'. \tag{4.7}$$

It follows that the free energy associated with a particular alloy configuration can be written in the form

$$\Omega=-\int_{-\infty}^{E_F} N(E')dE'=\frac{2}{\pi}\text{Im}\left[\int_{-\infty}^{E_F}\text{Tr}\ln G(E')dE'\right], \tag{4.8}$$

where $G(E)$ denotes the Green function for the given configuration. In the ECM, the true disordered alloy is approximated by a cluster of atoms embedded in the single-site homogeneous CPA effective medium. The Green function for such a cluster takes the form

$$G(E)=\overline{G}(D^{-1}Q^{-1}), \tag{4.9}$$

where $\overline{G}$ is the cluster-diagonal part of the CPA medium Green function and the matrices D^{-1} and Q are defined by means of Eq. (4.2). Upon using Eq. (4.9) in Eq. (4.8), we obtain

$$\Omega=\frac{2}{\pi N_c}\text{Im}\left[\int_{-\infty}^{E_F}\text{Tr}(\ln\overline{G}-\ln D-\ln Q)dE\right], \tag{4.10}$$

where N_c denotes the number of sites in cluster C. The term involving $\overline{G}$ gives the concentration-dependent contribution of the CPA medium and is independent of configuration. The single-site terms D depend only on the number of atoms of the different species present in the cluster but are independent of the arrangement of those atoms. (These terms vanish identically in all contributions entering the definition of *effective* cluster interactions). As it stands, Eq. (4.10) yields an expression for the ordering energy in terms of configuration-dependent cluster interactions which in the CPA limit agree completely with expressions derived previously, Eq. (3.12). In this limit, only renormalized interactions associated with cluster sites are considered and the disorder energy is given by the first two terms on the right-hand side of Eq. (4.10).

B. Effective cluster interactions in the ECM

The configuration-dependent quantities defined in Eq. (4.10),

$$\begin{aligned}\Omega'(\{P_i^\alpha\})&=-\frac{2}{\pi}\text{Im}\left[\int_{-\infty}^{E_F}\text{Tr}\ln Q\,dE\right],\\&=-\frac{2}{\pi}\text{Im}\left[\int_{-\infty}^{E_F}\ln\det Q\,dE\right],\end{aligned} \tag{4.11}$$

can be combined to yield renormalized effective cluster interactions in binary alloys. Term-by-term comparison with the corresponding GPM expansions allows us to prescribe a simple, computationally feasible method for the construction of the RECI in the CPA limit.

In a binary alloy, A_cB_{1-c}, the interchange energy for the two species is given by the expression,

$$V_i^{(1)}=-\int_{-\infty}^{E_F}(N_i^A-N_i^B)dE=V_i^{(1)}, \tag{4.12}$$

which consistently with Eq. (4.8) defines a "single-body" interaction resulting from the interchange of a B atom with an A atom at site i in the alloy, all other sites confined to being medium sites. Effective pair interactions can be obtained as the difference in the single-body interactions at i, when site j ($\neq i$) is taken to be occupied by an A or a B atom. Consistent with the definition of the integrated densities of states for different configurations, we have

$$\begin{aligned}V_{ij}^{(2)}&\equiv(V_i^{(1)})_j^A-(V_i^{(1)})_j^B\\&=-\int_{-\infty}^{E_F}\{[N_{ij}^{AA}(E)-N_{ij}^{BA}(E)]\\&\qquad-[N_{ij}^{AB}(E)-N_{ij}^{BB}(E)]\}dE,\end{aligned} \tag{4.13}$$

which according to Eqs. (4.10) and (4.11) can be written in the form of Eq. (4.4). This process can be continued; we find that n-site effective cluster interactions or n-body irreducible contributions to the energy at $T=0$ K are given by

$$\begin{aligned}V_{i_0i_1\cdots i_{n-1}}^{(n)}&=(V_{i_0i_1\cdots i_{n-2}}^{(n-1)})_{n-1}^A-(V_{i_0i_1\cdots i_{n-2}}^{(n-1)})_{n-1}^B\\&=-\frac{2}{\pi}\text{Im}\left[\int_{-\infty}^{E_F}\text{Tr}\ln\left[\prod_J Q^{J\,(\text{even})}\right]\left[\prod_J Q^{J\,(\text{odd})}\right]^{-1}dE\right],\end{aligned} \tag{4.14}$$

where J(even) and J(odd) denote cluster configurations with even and odd numbers of minority (B) atoms, respectively.

It is a simple exercise to show that for the case of pair interactions Eq. (4.14) yields the expansion in Eq. (4.4). In general, Eq. (4.14) represents the summation of *all* contributions to the RECI, i.e., it is the sum to all orders in δc of the corresponding GPM series, Eq. (3.6), in the CPA limit.

The renormalized effective cluster interactions defined by Eq. (4.14) represent truly irreducible contributions to the configurational energy of an alloy. Thus, the RECI associated with n-site clusters contain *no* terms contributing to m-site RECI, for $m<n$. This is because any such term occurs an equal number of times with a positive and a negative sign, being contributed by the numerator and denominator, respectively, in Eq. (4.14). In order to obtain accurate representations of the ordering energy in binary alloys, it is often necessary to consider *fully* renormalized effective cluster interactions (FRECI), which include summations of paths linking the primary cluster to sites in the surrounding medium. A

somewhat more general approach to the calculation of alloy energies based on the ECM that clarifies many of these concepts is presented in the next section

V. A FORMALLY EXACT EXPANSION OF CONFIGURATIONAL ENERGIES

An exact expression for the configurational energy of a disordered material directly in terms of fully renormalized cluster interactions can be obtained along the following lines. The thermodynamic potential (energy at $T=0$ K) corresponding to a given configuration J of a m-component alloy has the form

$$\Omega(\{P_i^\alpha\}) = \sum_J E^J \mathcal{P}^J = \sum_J E^{\alpha_1^J \alpha_2^J \cdots \alpha_N^J} \prod_{i=1}^{N} \mathcal{P}[\alpha_i^J] , \tag{5.1}$$

where $\mathcal{P}$ equals 1 (0) according to whether the alloy is (is not) in configuration J, α_i^J denotes the type of atom occupying site i, $\mathcal{P}[\alpha_i^J]$ is an occupation number for the species on site i, and N is the number of sites in the alloy. In the case of a binary alloy, A_cB_{1-c}, the use of the relations

$$P_i = P_i^A, \quad P_i^B = 1 - P_i \tag{5.2a}$$

and

$$\delta c_i = P_i - c, \quad P_i = c + \delta_i, \quad 1 - P_i = (1-c) - \delta c_i \tag{5.2b}$$

in Eq. (5.1) allows us to express the configurational energy in the form

$$\Omega(\{P_i\}) = E^{(0)} + \sum_{i=1}^{N} E_i^{(1)} \delta c_i + \tfrac{1}{2} \sum_{i,j}{}'' E_{ij}^{(2)} \delta c_i \, \delta c_j + \tfrac{1}{3} \sum_{i,j,k}{}'' E_{ijk}^{(3)} \delta c_i \, \delta c_j \, \delta c_k + \cdots . \tag{5.3}$$

The coefficients $E_{i_1 i_2 \cdots i_n}^{(n)}$ which occur in this expansion are interchange energies associated with clusters C_n of n sites, and as the following definitions show explicitly they are exact. First, we define an n-site interchange energy for a given configuration J_{C_n} outside cluster C_n,

$$E_{i_1 i_2 \cdots i_n}^{(n)}(J_{C_n}) = \prod_{j=1}^{n} (1 - Q_{ij}^{AB}) E_{i_1 i_2 \cdots i_n}^{AA \cdots A}(J_{C_n}) , \tag{5.4}$$

where Q_{ij}^{AB} changes an A atom to a B atom on site i_j and $E_{i_1 i_2 \cdots i_n}^{AA \cdots A}(J_{C_n})$ denotes the configurational energy associated with A atoms on sites $i_1, i_2, \ldots, i_n$. Now, the expansion coefficients in Eq. (5.3) (the fully renormalized effective interactions) are given as the averages of $E_{i_1 i_2 \cdots i_n}^{(n)}(J_{C_n})$ over all configurations J_{C_n} of the material *surrounding* cluster C_n,

$$E_{i_1 i_2 \cdots i_n}^{(n)} = \langle E_{i_1 i_2 \cdots i_n}^{(n)}(J_{C_n}) \rangle = \sum_{J_{C_n}} P_{J_{C_n}} E_{i_1 i_2 \cdots i_n}^{(n)}(J_{C_n}) , \tag{5.5}$$

where $P_{J_{C_n}}$ is the probability of occurrence of J_{C_n}. For example,

$$E^{(0)} = \langle E \rangle = \sum_J P_J E^J , \tag{5.6a}$$

$$E^{(1)} = \langle E_i^{(1)}(J_i) \rangle = \sum_{J_i} P_{J_i} (E_i^A(J_i) - E_i^B(J_i)) , \tag{5.6b}$$

$$E_{ij}^{(2)} = \langle E_{ij}^{(2)}(J_{ij}) \rangle = \sum_{J_{ij}} P_{J_{ij}} (E_{ij}^{AA}(J_{ij}) - E_{ij}^{AB}(J_{ij}) - E_{ij}^{BA}(J_{ij}) + E_{ij}^{BB}(J_{ij})) , \tag{5.6c}$$

and so on.

It is seen that Eq. (5.3), involving effective cluster interchange energies, is formally exact and thus avoids the need of resuming a series such as that of the GPM. Furthermore, since this expansion is independent of the choice of a reference medium, it affords one considerable freedom in selecting a medium that yields an optimal rate of convergence. [We emphasize that Eqs. (5.5) and (5.6) are identities and hold for *any* configurationally-dependent quantity such as the total energy of an alloy. However, as we specified previously only the band contribution to the energy is considered in this paper.] In order to evaluate Eq. (5.3) we note that the (band) configurational energy E^J can be written in the form

$$E^J = \frac{2}{\pi N} \operatorname{Im} \operatorname{Tr} \int_{-\infty}^{E_F} \ln[\bar{G}(D^J)^{-1}(Q^J)^{-1}] dE = \frac{2}{\pi N} \operatorname{Im} \operatorname{Tr} \int_{-\infty}^{E_F} (\ln\bar{G} - \ln D^J - \ln Q^J) dE , \tag{5.7}$$

where Eqs. (4.8)–(4.10) have been used and $\bar{G}$ denotes the Green function of a uniform reference medium which is as yet unspecified. From Eq. (4.2) we obtain the still exact expansion,

$$\operatorname{Tr} \ln Q^J = \operatorname{Tr} \ln(1 - T\bar{G}') = \operatorname{Tr}(T\bar{G}' + \tfrac{1}{2} T\bar{G}' T\bar{G}' + \tfrac{1}{3} T\bar{G}' T\bar{G}' T\bar{G}' + \cdots) = \tfrac{1}{2} \sum_{i,j}{}' t_i \bar{G}_{ij} t_j \bar{G}_{ji} + \tfrac{1}{3} \sum_{i,j,k}{}' t_i \bar{G}_{ij} t_j \bar{G}_{jk} t_k \bar{G}_{ik} + \tfrac{1}{4} \sum_{i,j,k,l}{}' t_i \bar{G}_{ij} t_j \bar{G}_{jk} t_k \bar{G}_{kl} t_l \bar{G}_{li} + \cdots . \tag{5.8}$$

It is clear that the evaluation of Eq. (5.3) or (5.8) can only be carried out within an approximation. Because of the self-consistency condition, Eq. (2.2), the Green function obtained in the CPA is exact to order t^4, hence the CPA provides a particularly well-suited medium for the summations in Eq. (5.3). At the first level of this approximation, all sites outside a given cluster C_n are taken as being occupied by effective-medium (CPA) "atoms." In other words, the true configurational averages of $E_{i_1 i_2 \cdots i_n}^{(n)}(J_{C_n})$ are replaced with the values assumed by the interchange energies of an n-site cluster embedded in a CPA medium. Calling this the CPA approximation for the configurational energy, we now write

$$E^{J}_{\mathrm{CPA}}=E_{\mathrm{CPA}}+\sum_{i} V_i^{(1)}\delta c_i+\tfrac{1}{2}\sum_{i,j}{}'' V_{ij}^{(2)}\delta c_i\,\delta c_j+\tfrac{1}{3}\sum_{i,j,k}{}'' V_{ijk}^{(3)}\delta c_i\,\delta c_j\,\delta c_k+\cdots\ , \tag{5.9}$$

where E_{CPA} is the contribution of the CPA medium, i.e., it is the term arising from $\overline{G}$, and the various $V^{(n)}_{i_1 i_2\cdots i_n}$ are RECI defined in Eq. (4.14). *This equation is the central result of this paper.* It shows that in the CPA approximation the configurational energy of an alloy can be calculated within the ECM as a sum of irreducible, renormalized cluster interactions associated with clusters of atoms embedded in a CPA effective medium. In the case of monatomic lattices the one-body contribution vanishes identically since $\sum \delta c_i\equiv 0$.

As mentioned earlier, the CPA can be expected to yield quite accurate results for most systems of physical interest. At the same time, Eq. (5.8) allows one to calculate the corrections to the various parts, $V^{(n)}$, in a straightforward way, and in this sense, contributions of fluctuations beyond those consistent with the CPA can be taken into account. As is probably evident by now, these contributions to $V^{(n)}$ arise from fluctuations outside the cluster C_n and their inclusion leads to fully renormalized effective cluster interactions [see Eqs. (3.13) and following discussion]. We illustrate these comments by evaluating explicitly the lowest-order contribution to the disorder energy, E_{CPA}, and to $V_i^{(1)}$ and $V_{ij}^{(2)}$. Upon using the CPA condition in conjunction with Eq. (5.8), we obtain the lowest-order correction to the term V_0:

$$V_0=\frac{2}{\pi N}\mathrm{Im}\left[\tfrac{1}{4}c^2(1-c)^2\int_{-\infty}^{E_F}(\delta t)^4\sum_{i,j}(\overline{G}'_{ij}\overline{G}'_{ji})^2dE\right]+\cdots\ , \tag{5.10}$$

giving the alloy disorder energy according to Eq. (3.15). [Note that this correction arises from the last term in Eq. (3.11a).]

Similarly, we obtain the FRECI

$$\widetilde{V}_i^{(1)}=V_i^{(1)}+\frac{1}{2\pi}\mathrm{Im}\left[(2c-1)c(1-c)\int_{-\infty}^{E_F}(\delta t)^4\sum_{j}(\overline{G}'_{ij}\overline{G}'_{ji})^2dE\right]+\cdots\ . \tag{5.11}$$

and

$$\widetilde{V}_{ij}^{(2)}=V_{ij}^{(2)}+\frac{1}{\pi}\mathrm{Im}\left[c(1-c)\int_{-\infty}^{E_F}(\delta t)^4\sum_{k}(\overline{G}'_{ik}\overline{G}'_{kj})^2dE\right]+\cdots\ . \tag{5.12}$$

Expressions for corrections to higher-order FRECI can be obtained along similar lines. We emphasize again that the quantities $\widetilde{V}^{(n)}$ are approximations to the exact quantities $E^{(n)}$ in Eq. (5.3) whose accuracy can be expected to increase rapidly as more of the fluctuations of the medium are taken into account (higher-order corrections are included). At the same time, given the accuracy of the CPA medium, it may not be necessary to include more than the lowest-order contributions, and those even rarely.

VI. NUMERICAL RESULTS

We have used the formalism of the preceding sections to carry out numerical calculations of cluster interactions with respect to one-dimensional single-band TB alloys, and with respect to a more-realistic, multiband TB Hamiltonian with parameters chosen to describe the alloy $\mathrm{Pd}_{0.75}\mathrm{V}_{0.25}$.

A. One-dimensional calculations

Figure 1 depicts the renormalized effective nearest-neighbor pair interaction, Eq. (4.4), as a function of the Fermi energy for the case of a one-dimensional TB alloy, calculated within the GPM, the ECM (both shown as the solid curve), and the formalism of CW (dotted curve). In this case the GPM and the ECM yield practically indistinguishable results which differ only slightly from those obtained in the CW method. Thus, for this alloy, $V_{ij}\cong v_{ij}^{(2)}\cong S_{ij}^{(2)}$ and the general expansion, Eq. (4.14), converges essentially after the first term.

Effective cluster interactons for three-site clusters calculated in the ECM (solid curve) and the GPM are shown in Fig. 2. In this case the lowest-order GPM term, which is proportional to $(\delta t)^3$, is only slightly different from the ECM result, and converges rapidly to it upon inclusion of the next two terms in the expansion. Such strong convergence is quite similar to that found in the case of more-realistic three-dimensional calculations discussed in Sec. VI B.

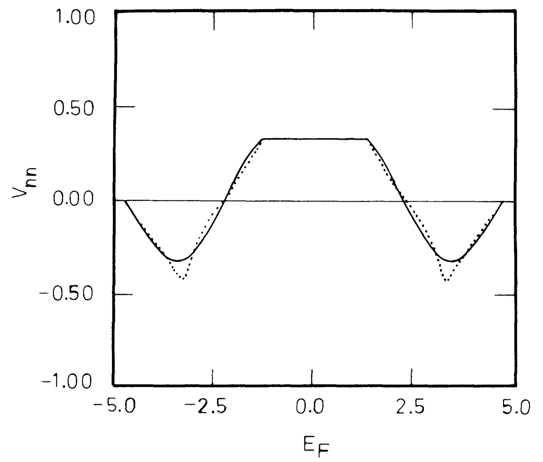

FIG. 1. GPM and ECM nearest-neighbor effective pair interactions (solid curve) and CW correlation function (dotted curve) for a one-dimensional-model TB alloy. Here, $\varepsilon_A = -\varepsilon_B = 3.0$, and $W = 1.0$, in arbitrary units. In all figures cluster interactions are plotted as a function of the Fermi energy E_F.

B. Three-dimensional calculations

Figures 3–10 contain results obtained for the case of fcc, paramagnetic transition metal alloys described by a TB *d*-band Hamiltonian. The TB parameters chosen in these calculations, the site-diagonal terms ε_i^{uv}, and the nearest-neighbor hopping integrals W^{uv}, reproduce quite satisfactorily the density-of-states curves for $\mathrm{Pd}_{0.75}\mathrm{V}_{0.25}$ obtained on the basis of fully self-consistent Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA) calculations with muffin-tin potentials (see II). Here, we have set $\varepsilon_{\mathrm{Pd}}^{d} = 0.0$, $\varepsilon_{\mathrm{V}}^{d} = 3.12$, $W^{dd\sigma} = -1.385$, $W^{dd\pi} = |W^{dd\sigma}|\, 2.0$, $W^{dd\delta} = 0.0$. These parameters lead to a common bandwidth for the fcc pure metals of $\overline{W} = 11.04$ in canonical units. For a typical bandwidth of 5 eV the canonical energy unit taking into account orbital and spin degeneracy is roughly equal to 4.5 eV.

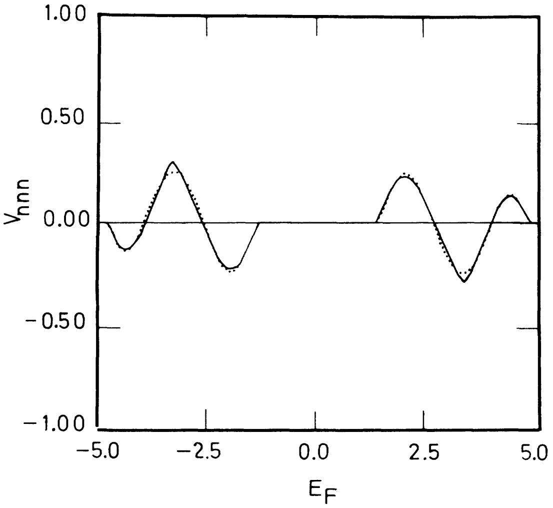

FIG. 2. ECM renormalized three-site interaction (solid curve) and the lowest-order term in the GPM expansion (dotted curve) for the same model one-dimensional alloy described in Fig. 1.

The evaluation of the various Green functions entering the calculation, i.e., $\overline{G}_{ii}$ and $\overline{G}_{ij}$, were carried out using the recursion method[54–56] with ten levels of a continued fraction. Figure 3 shows the species resolved and total CPA DOS (upper panel), along with ECM configurational DOS's (lower panel) for pairs of atoms at nearest-neighbor sites embedded in the CPA medium. The total integrated DOS in the CPA (dotted curve) is also shown, normalized to 1.0. Similarly, Fig. 4 depicts the configurational DOS's for three sites forming an equilateral triangle. The upper panel shows the DOS's associated with a Pd atom for various configurations of the remaining two sites along with the CPA integrated DOS. Analogous results for a V atom are shown in the

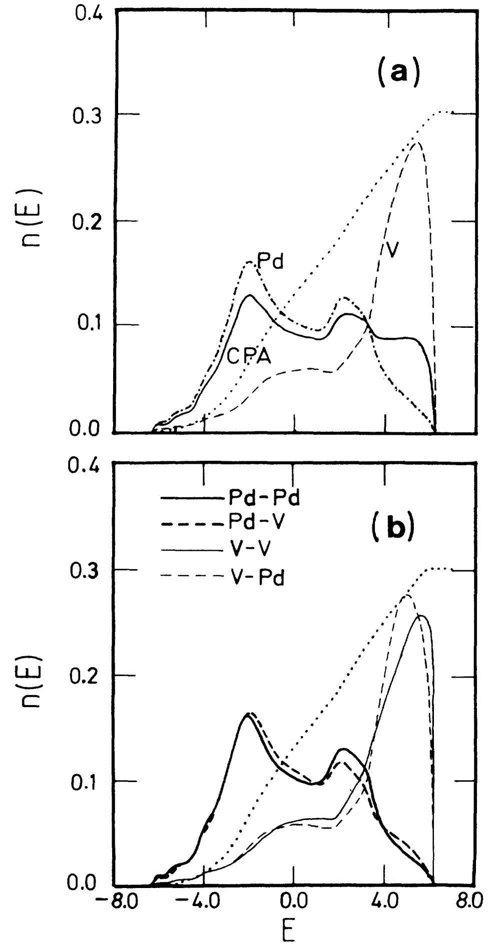

FIG. 3. (a) Total CPA and species resolved DOS for $\mathrm{Pd}_{0.75}\mathrm{V}_{0.75}$ alloys, corresponding to the parameters specified in the text. (b) Configurational DOS for nearest-neighbor pairs evaluated in the ECM for $\mathrm{Pd}_{0.75}\mathrm{V}_{0.25}$ alloys. The integrated DOS (dotted curve) is also shown. Here, and in all subsequent figures, the DOS's are normalized to 1.0.

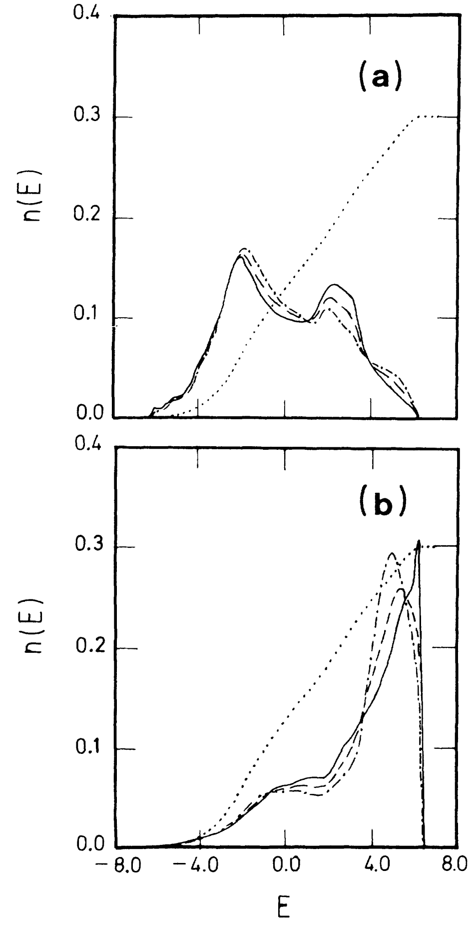

FIG. 4. Configurational DOS for nearest-neighbor triangular clusters evaluated in the ECM for the alloy specified in Fig. 3: (a) Pd DOS for three Pd atoms (solid curve), two Pd and one V atom (dashed curve), and Pd with two V atoms (dashed-dotted curve); (b) results analogous to those of (a) but with the roles of Pd and V atoms interchanged.

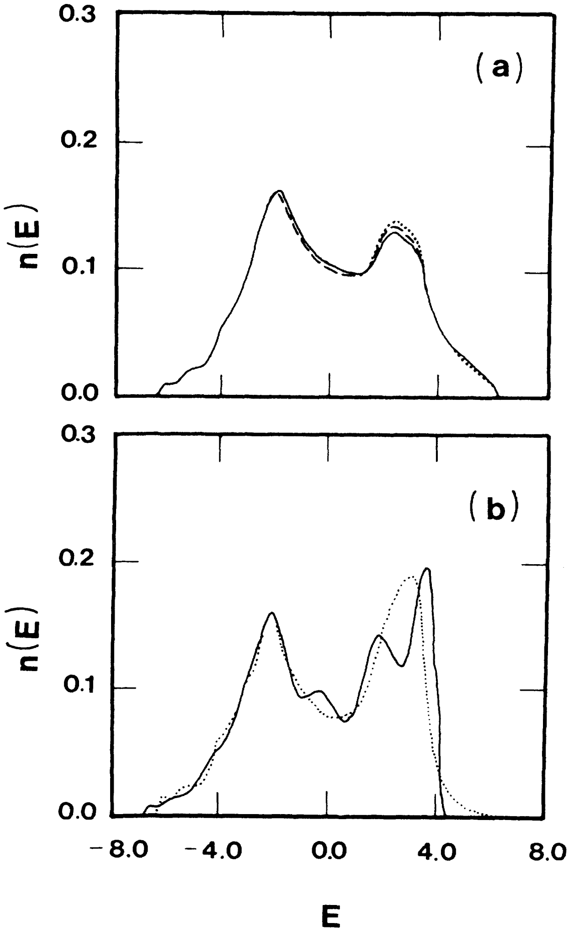

FIG. 5. ECM densities of states for clusters of Pd atoms in the $Pd_{0.75}V_{0.75}$ alloy: (a) two nearest-neighbor Pd atom DOS (solid curve), equilateral nearest-neighbor triangle DOS (dashed curve), and nearest-neighbor tetrahedron DOS (dashed-dotted curve). (b) DOS for pure Pd (solid curve) and that for a Pd atom surrounded by 12 nearest-neighbor Pd atoms (dotted curve). Note the similarity of the dotted curve to the DOS for pure Pd shown in (b).

lower panel. The effects of local environment, SRO effects, are clearly illustrated in Fig. 5, which depicts the DOS on a Pd site "surrounded" by ever increasing numbers of Pd atoms. Note that the DOS for a Pd atom surrounded by 12 Pd near neighbors resembles quite closely that of pure Pd. Thus, the center of a nearest-neighbor cluster is still influenced by the medium surrounding the cluster, but this influence can be expected to diminish with increasing cluster size. These figures indicate that different cluster configurations do indeed yield quantitatively different DOS's which, however, are qualitatively quite similar and numerically very close to one another. Consequently, one may expect the corresponding effective interactions to be small, as they depend on combinations of integrals of the integrated DOS for the various configurations.

Cluster interactions $v_{ij}^{(n)}$ and renormalized effective pair interactions V_{ij} calculated, respectively, in the GPM and ECM for nearest-neighbor sites are shown in Fig. 6. The thick solid curve depicts the RECI for a pair calculated in the ECM, while the other curves exhibit various contributions of the GPM expansion, Eq. (3.14). Thus, the terms $v_{ij}^{(2)}$, $v_{ij}^{(4)}$, $v_{ij}^{(6)}$, and $v_{ij}^{(8)}$, which are expressed in terms of the corresponding powers of δt, i.e., $v^{(n)} \sim (\delta t)^n$, are shown by the thin solid, dash-dotted, dashed, and dotted curves, respectively. Several important characteristic features of ECI can be distinguished in Fig. 6.

First, it is seen that the various terms $v_{ij}^{(n)}$, $n > 2$, are several factors smaller than the leading term $v_{ij}^{(2)}$, which in turn is extremely similar to the renormalized ECM result (thick solid curve). These higher-order terms enter the summation, Eq. (3.14), for the effective pair interactions multiplied by numerically small, concentration-dependent factors and their overall significance in the final summation decreases rapidly with increasing order n. Thus, the lowest-order term gives an extremely accurate representation of the sum and indicates that the

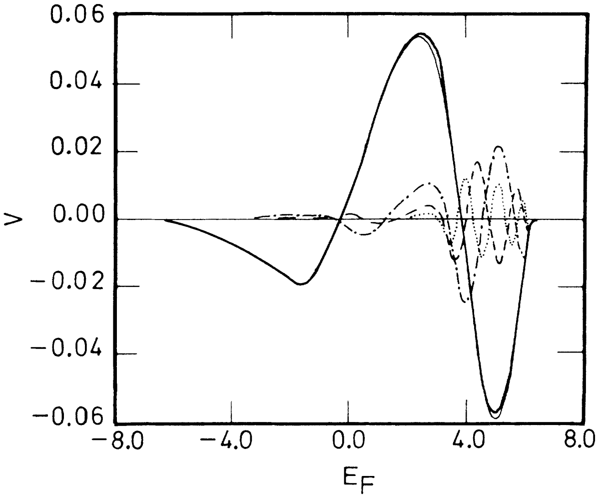

FIG. 6. Effective pair interactions, for the $Pd_{0.75}V_{0.25}$ alloy calculated in the GPM and ECM. The GPM contributions associated with $(\delta t)^n$ for $n=2$, 4, 6, and 8 are shown by the thin solid, dashed-dotted, dashed, and dotted curves, respectively. The renormalized ECM effective pair interaction is shown by the thick solid line.

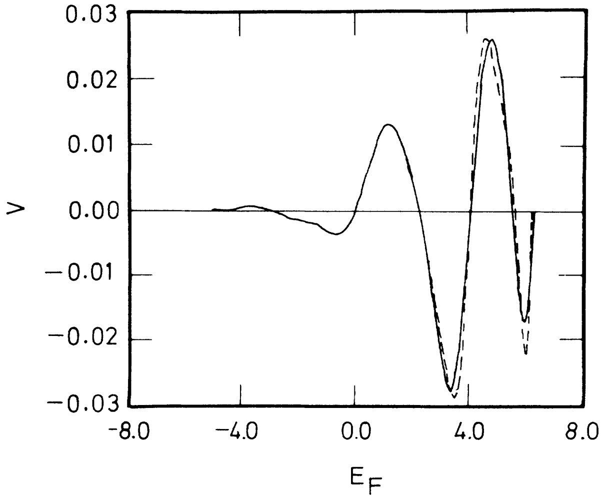

FIG. 8. Cluster interactions for three sites aligned along the (110) direction in the fcc $Pd_{0.75}V_{0.25}$ alloy. The dashed curve represents the summation of the GPM expansion to sixth order, while the solid curve shows the renormalized ECM effective interaction.

GPM is a valid, rapidly convergent perturbation expansion based on the "small" expansion parameter $|\bar{G}_{ij}\delta t|$. Second, the effective pair interactions, as well as the individual GPM terms, for near-neighbor and more-distant pairs (see following figures), exhibit considerable structure as a function of the Fermi energy. This structure can be expected on the basis of a moment analysis[8,9] which yields the number of zeros of these functions. Because of this structure, phase stability depends greatly on the value of the Fermi energy, with the most stable structure often being determined by the predominant pair interactions at a particular value of E_F.

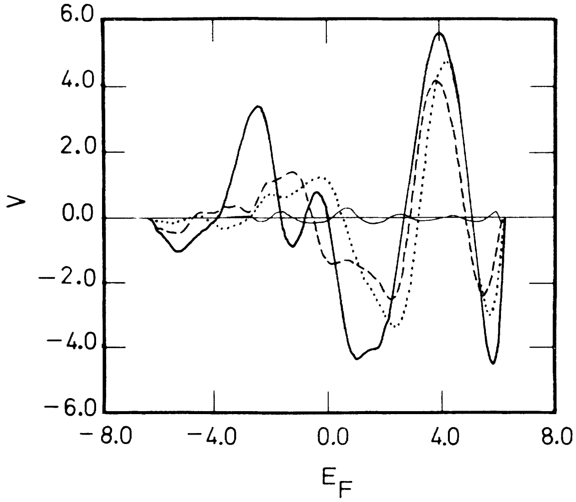

FIG. 7. Renormalized effective pair interactions in the $Pd_{0.75}V_{0.25}$ alloy nearest neighbors (thick solid curve), third nearest neighbors (dotted curve), and fourth nearest neighbors (dashed curve) calculated in the ECM. These curves are practically indistinguishable from those obtained to second order in the GPM expansion. The vanishingly small fourth-order GPM contribution to second nearest-neighbor interaction is shown by the thin solid curve.

The last point is amply illustrated by the result depicted in Fig. 7, which shows effective pair interactions for second (thick solid curve), third (dashed curve), and fourth (dotted curve) neighbor pairs calculated in the ECM. These results are indistinguishable from those corresponding to the lowest-order GPM expansion as indicated by the vanishingly small contribution $v_{ij}^{(4)}$ (thin solid curve) to the second-nearest-neighbor pair interaction. It is to be pointed out that these interactions are an order of magnitude smaller than those for nearest-neighbor pairs. However, because of the variation with E_F these interactions can be quite important in determining the ordering properties of a binary alloy; they are, for example, the sole determining factor of phase stability for values of E_F at which the nearest-neighbor effective pair interactions go through zero.

Effective cluster interactions for three-site clusters arranged linearly and in the form of an equilateral triangle of nearest-neighbor distances are shown in Figs. 8 and 9, respectively. It is seen in these figures that the linear arrangement yields effective interactions of the same order of magnitude as the nearest-neighbor pair, and about an order of magnitude larger than that of the equilateral triangle. Again, the GPM expansion converges rapidly toward the renormalized ECM result as is easily inferred from a comparison of the solid (ECM) and dashed (summation to sixth order in GPM) curves in Fig. 8. Some of the lowest-order contributions to the GPM curves are shown explicitly in the Appendix. The structure of the

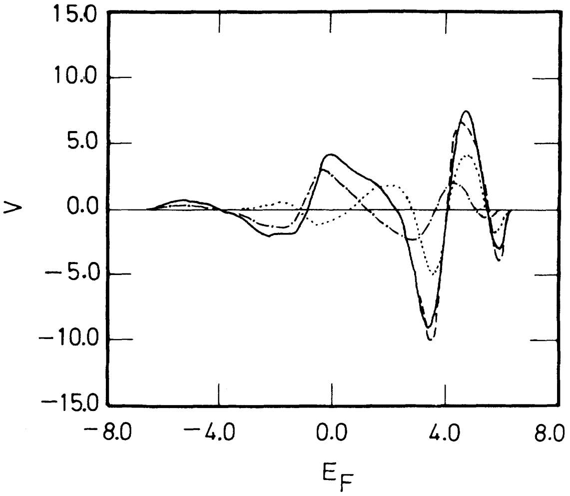

FIG. 9. Cluster interactions for three sites forming an equilateral nearest-neighbor triangle in fcc alloy $Pd_{0.75}V_{0.25}$. The solid curve depicts the renormalized effective interaction calculated in the ECM, and is to be compared to the summation of the lowest order in the GPM expansion (dashed curve). The contributions of two of those orders, corresponding to $(\delta t)^3$ and $(\delta t)^4$ are shown by the dashed-dotted and the dotted curves, respectively.

curves in these figures can also be anticipated on the strength of a moment analysis, with the implication toward phase stability being similar to that with respect to pair interactions. Finally, Fig. 10 shows renormalized (ECM) effective interactions for a tetrahedral arrangement of sites. The magnitude of these interactions are small, being comparable to those of the triangle, Fig. 9, while the structure, e.g., number of zeros, increases as expected with increasing number of sites.

Effective cluster interactions, such as the ones exhibited in this section, can be used in the study of phase stability and in the construction of coherent alloy phase diagrams for binary alloys. Such applications are currently under consideration and results will be presented in future publications.

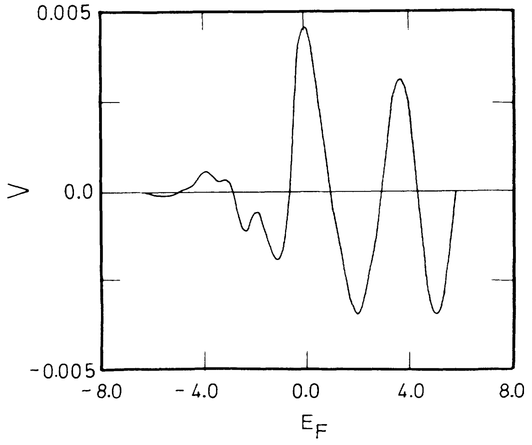

FIG. 10. Renormalized cluster interactions for a tetrahedral cluster of sites in the $Pd_{0.75}V_{0.25}$ alloy calculated in the ECM.

VII. SUMMARY AND CONCLUSIONS

The most important result of this paper is summarized in Eqs. (5.9)–(5.12), which give an expansion of the configurational energy in terms of irreducible, fully renormalized effective cluster interactions. These interactions can be expected to become smaller with increasing cluster size, resulting in a rapidly convergent expansion in Eq. (5.9).

It may be helpful to reiterate and summarize the various different types of interactions which have figured in different stages of our discussion. The basic units of an expansion of the energy are the cluster interactions which occur in Eq. (3.4). These are configuration-dependent quantities and are meaningful in connection with multicomponent alloys. In the case of binary alloys, use of the CPA allows one to cast this expansion into different forms. By combining together terms of the same order, we obtain the GPM expansion in terms of effective cluster interactions (ECI). These are the terms $v_{ij\cdots k}^{(n)}$ defined in Eq. (3.7). The summation to all orders n of these ECI yields the renormalized effective cluster interactions (RECI) obtained in the ECM by means of Eq. (4.14). These are precisely the interactions entering Eq. (5.9). Finally, fully renormalized effective cluster interactions (FRECI) are defined by means of Eqs. (5.10)–(5.12) and their obvious extensions to higher order. These latter quantities yield a rapidly converging expansion for the configurational energy. This expansion is numerically identical to that obtained in the complete summation of the fully renormalized GPM expansion. Note, in particular, that the correction terms in Eqs. (5.10)–(5.12) are "GPM-like," i.e., they are given in terms of powers of $\delta t\overline{G}'$ and of c, and are associated with specific sets of sites and paths connecting these sites.

We have summarized, and compared formally and by means of calculations, three different methods which can be used in the study of alloy phase formation and stability. The method of concentration waves was briefly examined and compared to that of the GPM and of the ECM. At least for the case of the model systems used in this comparison these three methods were found to yield very similar results for the effective pair interactions. The CW formalism allows the study of long-range-order effects and the prediction of coherent ordered structures. Compared to the GPM and the ECM it has the advantage of being consistent with the mean-field condition of the CPA and the theory of linear response to infinitesimal fluctuations.

This condition is violated in the GPM and the ECM which treat finite fluctuations away from the CPA medium. Compared to the CW approach, these methods allow a more rigorous treatment of short-range order and of nonlinear effects, but at the expense of inconsistency with the underlying mean-field nature of the CPA. Thus, the CW method on the one hand, and those of the

GPM and ECM on the other, appear to be complementary, i.e, applicable to different limiting regions of the relevant physical parameters.

The connection between the GPM and the ECM in terms of effective cluster interactions was clarified in Secs. III and IV. As was shown in Sec. IV, the ECM provides the complete summation to all orders of the effective interactions associated with specific clusters. These summations naturally lead to renormalized and fully renormalized effective cluster interactions and to rapidly convergent expansions of the configurational energy.

Most of the results obtained in this paper are applicable only to binary alloys and are explicitly based on the use of the CPA. Of course, configuration-dependent cluster interactions in multicomponent alloys can always be defined for specific clusters by means of Eq. (3.5). These could be used within appropriate models[2] in the study of phase stability of disordered multicomponent systems. However, the rather attractive description in terms of configuration-independent effective cluster interactions does not seem to be applicable to such alloys.

The use of the CPA is quite crucial to the formalism presented here. It allows the use of Eq. (2.13) on which many formal manipulations are based. Thus, even though a charge self-consistent cluster theory could, in principle, be constructed within the ECM, such a theory would not be consistent with many of the rigorous expressions derived in Sec. III and IV. A charge self-consistent ECM calculation should be approached with care.

Although the discussion in this paper was given primarily in terms of a rather simplified, single-band TB Hamiltonian with only diagonal disorder, several generalizations are evidently possible with only minimum effort. Multiband systems even in the presence of ODD can be treated within essentially the same formalism as single-band alloys, but with some increase in computational labor. More importantly, the methods presented in this paper are also applicable to alloys describable by more-realistic Hamiltonians such as those of muffin-tin type. Finally, these methods can also be applied[57] to the study of phase stability of reduced symmetry systems such as surfaces and interfaces in realistic systems, using corresponding expressions[58,59] for the medium Green functions.

The cluster interactions discussed in this paper hold the promise of allowing a true first-principles study of alloy phase stability and the construction of alloy phase diagrams. Applications along these lines are currently under way.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, under Contract No. DE-FG02-84ER45 with Northwestern University, No. W-7405-eng-48 with the Lawrence Livermore National Laboratory (University of California), and No. DE-AC05-84OR21400 with Martin Marietta Energy Systems.

APPENDIX

Equation (4.4) represents the summation of all terms in the GPM expansion, Eq. (3.76), which involves only two sites. As a further example of the GPM expansion, we present expressions for the terms up to sixth order in the GPM series associated with three sites. We consider explicitly the cases in which the three sites form a linear chain along the [110] direction, and an equilateral triangle of nearest neighbors in an fcc lattice.

For simplicity and ease of presentation we replace the subscripts which enter the expression $v^{(n)}_{ijk\cdots l}$ by an explicit set of n straight lines connecting the sites in a given order. Thus, these straight lines represent the propagator paths in Eq. (3.7). For example, the term $\bar{G}_{ij}\bar{G}_{ji}$ which enters the definition of $v^{(2)}_{ij}$ is represented by two short lines so that we can write $v^{(2)}_{ij}=v^{(2)}_{=}$. Similarly, the term $\bar{G}_{ik}\bar{G}_{ki}\bar{G}_{ij}\bar{G}_{ji}$ for i, j, and k along a straight line is represented by two long lines and two short lines so that this particular path will contribute to $v^{(4)}_{ijk}$ in the form $v^{(4)}_{\substack{=\\=}}$.

1. The linear arrangement of three sites

The GPM expansion for three sites arranged on a line along the (110) direction in an fcc lattice carried to sixth order has the form

$$V_{ijk}\cong 2v^{(3)}_{=\,=}+2(1-2c)v^{(4)}_{\substack{\equiv\\=}}+(1-2c)v^{(4)}_{=}\,=+2(1-2c)^2v^{(5)}_{\substack{=\\\equiv}}+4(1-2c)^2v^{(5)}_{\equiv\,-}+4(1-2c)^3v^{(6)}_{\equiv\,\equiv}$$

$$+2(1-2c)(1-3c+3c^2)(v^{(6)}_{\equiv\,=}+v^{(6)}_{\substack{\equiv\\\equiv}}+v^{(6)}_{\substack{=\\\equiv}})+\cdots . \tag{A1}$$

2. An equilateral triangle

For the case of three sites arranged in the form of an equilateral triangle we obtain

$$V_{ijk}=2v^{(3)}_{\triangle}+3(1-2c)v^{(4)}_{/\!/\,=}+6(1-2c)^2v^{(5)}_{/\!/\!\triangle}+4(1-2c)^3v^{(6)}_{\triangle\!\!\triangle}+6(1-2c)(1-3c+3c^2)v^{(6)}_{/\!/\!/\!/\,=}+\cdots . \tag{A2}$$

We note that the complete summations of the series (A1) and (A2) is given by the ECM expression, Eq. (4.14), applied to the appropriate set of sites. The partially summed expressions (A1) and (A2) were used to calculate the GPM renormalized interactions depicted in Figs. 8 and 9, respectively.

*Present address: Division of Chemistry and Materials Science (L-280), Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550.

[1] A. G. Khachaturyan, *Theory of Structural Transformations in Solids* (Wiley, New York, 1983).

[2] D. A. Badalyan, A. G. Khachaturyan, and A. I. Kitaigorodskii, Sov. Phys.—Crystallog. **14**, 333 (1969).

[3] B. L. Györffy and G. M. Stocks, Phys. Rev. Lett. **50**, 374 (1983).

[4] F. Ducastelle and F. Gautier, J. Phys. F **6**, 2039 (1976).

[5] G. Treglia, F.Ducastelle, and F. Gautier, J. Phys. F **8**, 1437 (1978).

[6] F. Ducastelle and G. Treglia, J. Phys. F **10**, 2137 (1980).

[7] A. Bieber, F. Ducastelle, F. Gautier, G. Treglia, and P. Turchi, Solid State Commun. **45**, 585 (1983).

[8] A. Bieber and F. Gautier, J. Phys. Soc. Jpn. **53**, 2061 (1984).

[9] A. Bieber and F. Gautier, Z. Phys. B **57**, 335 (1984).

[10] P. Turchi, Ph.D. thesis, Universite Pierre et Marie Curie, Paris, France, 1984 (unpublished).

[11] A. Gonis and J. W. Garland, Phys. Rev. B **16**, 2424 (1977).

[12] C. W. Myles and J. B. Dow, Phys. Rev. Lett. **42**, 254 (1979); Phys. Rev. B **19**, 4939 (1979).

[13] A. Gonis, W. H. Butler, and G. M. Stocks, Phys. Rev. Lett. **50**, 1482 (1982).

[14] A. Gonis, G. M. Stocks, W. H. Butler, and H. Winter, Phys. Rev. B **29**, 555 (1984).

[15] A comprehensive overview of the current status of the art can be obtained through the publications of the calculated phase diagram (CALPHAD) group.

[16] A. Gonis, X.-G. Zhang, A. J. Freeman, P. Turchi, G. M. Stocks, and D. M. Nicholson (unpublished).

[17] D. M. Nicholson, G. M. Stocks, F. J. Pinski, A. Gonis, B. L. Gyorffy, and D. D. Johnson (unpublished).

[18] R. Kikuchi, Phys. Rev. **81**, 988 (1951).

[19] D. de Fontaine, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 34.

[20] R. Kikuchi, J. M. Sanchez, D. de Fontaine, and H. Yamanchi, Acta Metall. **28**, 651 (1980).

[21] J. M. Sanchez and D. de Fontaine, Phys. Rev. B **21**, 216 (1980).

[22] J. M. Sanchez and D. de Fontaine, Phys. Rev. B **25**, 1759 (1980).

[23] J. M. Sanchez, D. de Fontaine, and W. Teitler, Phys. Rev. B **26**, 1465 (1982).

[24] G. D. Mahan and F. H. Claro, Phys. Rev. B **16**, 1168 (1977).

[25] M. K. Phani, J. L. Lebowitz, and M. H. Kalos, Phys. Rev. B **21**, 4027 (1980).

[26] K. Binder, Phys. Rev. Lett. **45**, 811 (1980).

[27] K. Binder, J. L. Lebowitz, M. H. Phani, and M. H. Kalos, Acta Metall. **29**, 1655 (1981).

[28] J. W. Cahn and R. Kikuch, Acta Metall. **27**, 1329 (1979).

[29] P. C. Clapp, Acta Metall. **22**, 573 (1974).

[30] P. Soven, Phys. Rev. **156**, 809 (1967).

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

[32] R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. **46**, 465 (1974).

[33] B. L. Györffy and G. M. Stocks, in *Electrons in Disordered Metals and Metallic Surfaces,* edited by P. Phariseau, B. L. Gyorffy, and L. Sheire (Plenum, New York, 1978), p. 89 and references therein.

[34] J. S. Faulkner and G. M. Stocks, Phys. Rev. B **21**, 3222 (1980).

[35] J. S. Faulkner, in *Progress in Materials Science,* edited by J. W. Christian, P. Haasen, and T. B. Massalski (Pergamon, New York, 1982), Vol. 27, Nos. 1 and 2 and references therein.

[36] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958).

[37] V. Heine and D. Weaire, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 24, p. 249.

[38] D. G. Pettifor, J. Less-Common Met. **114**, 7 (1985); J. Phys. C **19**, 285 (1986).

[39] J. W. Connolly and A. R. Williams, Phys. Rev. B **27**, 5169 (1983).

[40] A. G. Khachaturyan, Phys. Met. Metallog. **13**, 493 (1962).

[41] A. G. Khachaturyan, Fiz. Tverd. Tela (Leningrad) **5**, 26 (1963) [Sov. Phys.—Solid State **5**, 16 (1963)].

[42] A. G. Khachaturyan, Fiz. Tverd. Tela (Leningrad) **5**, 750 (1963) [Sov. Phys.—Solid State **5**, 548 (1963)].

[43] A. G. Khachaturyan, Phys. Status Solidi B **60**, 9 (1973).

[44] A. G. Khachaturyan, in *Order Disorder Transformations,* edited by H. Warlimont (Springer-Verlag, New York, 1974, p. 114.

[45] W. L. Bragg and E. J. Williams, Proc. R. Soc. London, Ser. A **145**, 699 (1934); **152**, 231 (1935).

[46] H. A. Bethe, Proc. R. Soc. London, Ser. A **150**, 552 (1935).

[47] R. Peierls, Proc. R. Soc. London, Ser. A **154**, 207 (1936).

[48] R. A. Suris, Fiz. Tverd. Tela **4**, 1154 (1962).

[49] F. Gautier, F. Ducastelle, and J. Giner, Philos. Mag. **31**, 1373 (1975).

[50] J. A. Blackman, D. M. Esterling, and N. F. Berk, Phys. Rev. B **4**, 2412 (1971).

[51] H. Shiba, Prog. Theor. Phys. **46**, 77 (1971).

[52] A. Bieber and F. Gautier, Physica **107B**, 71 (1981).

[53] A. Gonis and J. W. Garland, Phys. Rev. B **16**, 1495 (1977).

[54] R. Haydock, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35, p. 215.

[55] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C **5**, 2845 (1972); **8**, 2591 (1975).

[56] G. Treglia and A. Bieber, J. Phys. (Paris) **45**, 283 (1984).

[57] R. H. Brown and A. E. Carlsson (unpublished).

[58] A. Gonis (unpublished).

[59] A. Gonis and X. G. Zhang (unpublished).