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Pair Effects in Substitutional Alloys. II. Multiple-Scattering Formulation*

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A single-band model Hamiltonian is used to study the effects of clustering on the electronic properties of disordered binary alloys. Alternate methods are used to calculate corrections to the coherent potential (CP) approximation due to two-atom clusters. The distinction between these methods is essentially one of self-consistency vs non-self-consistency. The non-self-consistent calculation isolates those terms in the multiple-scattering series that correspond to two-atom molecules embedded in the CP medium. These terms can be summed exactly, and the resulting expression for the electron propagator indicates that under certain conditions discrete states may exist outside the CP band edges. In the dilute split-band limit, for example, nearest-neighbor clusters are found to produce satellite levels on either side of the impurity subband. The second approach, which is identical to the method proposed by Cyrot-Lackmann and Ducastelle, is based on a reformulation of the multiple-scattering equations in terms of two-site scattering operators. The relationship between these results and the self-consistent pair equations derived by Schwartz and Siggia is discussed in detail. The latter equations have been shown to describe both the broadening of the satellite levels and the shifting of the CP-band edges.

I. INTRODUCTION

This paper is concerned with the effects of two-atom clusters in disordered binary alloys. Recently, the electronic structure of such systems has been discussed within the framework of self-consistent multiple-scattering theory.[1-7] In this approach the random scatterers are viewed as being embedded in an effective medium whose choice is open. This choice is made self-consistently by requiring that there be no scattering of an electron by the disordered potential of the alloy. Formally, this condition is equivalent to setting the average of the total-scattering operator T to zero. In practice, however, it is impossible to satisfy this self-consistency condition exactly. As a first approximation it may be replaced by the simpler requirement $\langle t_n \rangle = 0$ (i.e., that the average scattering by a single site should vanish). The effective medium determined by this choice is usually referred to as the coherent potential (CP) medium. On the basis of a comparison with exact results concerning the localization and the leading moments of the electronic density of states, several authors[2,3] have concluded that the coherent potential approximation (CPA) provides the best possible single-site description of the alloy. Within the appropriate limits the CPA exhibits dilute-alloy, virtual-crystal, and well-separated-impurity-band behavior.

In a previous paper, Schwartz and Siggia[8] (SS) have reexamined the formal basis of the CPA. Employing functional derivative techniques, these authors derived an exact expansion for the electron self-energy $\Sigma(z)$. Their analysis revealed that in addition to the concentration x and the impurity potential δ, the moments of $\Sigma(z)$ also depend on the geometrical parameter Z^{-1}, where Z is the number of nearest neighbors. In addition to being exact to first order in x and third order in δ, the CPA retains just those contributions of higher order in x and δ that are independent of Z^{-1}. Having established that the parameter Z^{-1} provides a criterion for distinguishing between different methods, all of which are exact to the same order in x and δ, SS were then able to extend the CPA to higher orders in x, δ, and Z^{-1}. At the next level, their results provide the best possible treatment of pair clusters, just as the CPA is the best treatment of one-atom (i.e., single-site) clusters. The most obvious consequence of these two-atom clusters is the appearance of satellite levels on either side of the impurity subband.

In the present paper we return to the original multiple-scattering formulation of the alloy problem. The results obtained by SS are rederived and given a simple physical interpretation.[9] Two methods in terms of which the effects of clustering may be taken into account are developed and compared. In the first approach we essentially consider two-atom molecules embedded in the CP effective medium. Under certain conditions, discrete states are found to exist outside the edges of the CP impurity subband. These discrete levels are simply the bonding and antibonding states of a two-atom system, and may be viewed as a primitive form of the satellite states discussed by SS. It should be emphasized that this calculation is not self-consistent in the sense that the effective medium is specified at the outset. By contrast, the second method does treat the effects of clustering self-consistently. Leaving the medium unspecified, we return to the basic equations of multiple-scattering theory. These equations are reformulated in terms of the quantity $t^{(2)}(n, m)$; the scattering operator for a pair of atoms at the sites n and m. $t^{(2)}(n, m)$ may be written as the sum of two contributions $t_n^{(2)}(m)$ and $t_m^{(2)}(n)$, associated, respectively, with the cases in which the electron scatters first from n or m. In terms of the single-site operators t_n and t_m, and the electron propagator G, $t_m^{(2)}(n)$ is given by

$$t_m^{(2)}(n) = t_m + t_m G t_n (1 - G t_m G t_n)^{-1} (1 + G t_m) .$$

The first term on the right-hand side is the single-site part of $t_m^{(2)}(n)$, while the second term describes all possible repeated scattering between m and n. The self-consistency condition for pairs is then equivalent to the following physical statement: If an electron is incident on the site n then, on the average, scattering by that site, plus the scattering by all pairs involving the site n, must vanish. Formally, the requirement is

$$0 = \langle t_n \rangle + \langle t_n G \sum_{m \neq n} t_m^{(2)}(n) \rangle . \qquad (1.1)$$

This result is equivalent to the pair equations recently proposed by Cyrot-Lackmann and Ducastelle.[10,11] Equations (1.1) are exact to second order in x and asymptotically (as $E \to \infty$) to third order in Z^{-1}. They are, however, unnecessarily complicated in the sense that they contain many contributions that are higher order in *both* x and Z^{-1}. Transforming this result into a system of equations for the electron self-energy and retaining all contributions of order x^2 and in addition those higher-order terms through $O(Z^{-3})$, we are able to rederive the pair equations obtained by Schwartz and Siggia.

In summary, we have found that a non-self-consistent theory of two-atom clusters leads to discrete states outside the edges of the CP minority band while a self-consistent treatment of these same effects predicts a broadening of the satellite levels and a shifting of the minority band edges. There is a direct parallel between these results and the relation of the Slater-Koster and dilute CP theories. The non-self-consistent Slater-Koster theory predicts that strong impurities lead to discrete states, in contrast to the CPA which gives a broadened impurity band for arbitrarily small concentrations.

II. TWO-SITE CLUSTERS, NON-SELF-CONSISTENT APPROACH

Consider the alloy to be described in a tight-binding representation. A single orbital $|n\rangle$ is associated with each site n. If only nearest-neighbor hopping is allowed, the one-electron Hamiltonian may be written as

$$H = \sum_n |n\rangle \epsilon_n \langle n| + \sum_{m \neq n} |n\rangle h \langle m| \equiv D + W . \qquad (2.1)$$

The diagonal elements ϵ_n are random atomic levels which assume one of two possible values δ, 0 depending on whether an atom of type A or B occupies the site n. The respective concentrations are x and $y \equiv 1 - x$, both varying between 0 and 1. The off-diagonal elements are hopping integrals whose value is normalized to $h = Z^{-1}$, where Z is the number of nearest neighbors. W therefore describes a perfect crystal with unit bandwidth and may be interpreted as the Hamiltonian for the pure system in which $\delta = 0$. Specializing to a simple cubic crystal, the matrix elements of W in a Bloch representation are given by

$$\langle k | W | k' \rangle = \delta_{kk'} s(k) , \qquad (2.2)$$

where

$$s(k) = -\tfrac{1}{3}(\cos k_x a + \cos k_y a + \cos k_z a) , \qquad (2.3)$$

and a is the lattice constant. In view of Eqs. (2.1) and (2.2) we see that the model is completely specified by the three parameters x, δ, and Z^{-1}.

The single-particle properties of the Hamiltonian may be derived from the ensemble average Green's function $\langle G(z) \rangle$ or, alternatively, from the electron self-energy $\Sigma(z)$. These quantities are functions of the complex energy z and are defined by the relations

$$\langle G(z) \rangle \equiv \langle (z - H)^{-1} \rangle \equiv [z - W - \Sigma(z)]^{-1} . \qquad (2.4)$$

Because the average alloy is characterized by the effective medium described by $\Sigma(z)$, it is often convenient to rewrite the Hamiltonian as

$$H = W + U(z) + [D - U(z)] = \tilde{H} + [D - U(z)] . \qquad (2.5)$$

Here $\tilde{H}$ is some suitably chosen reference Hamiltonian, $U(z)$ a starting approximation to $\Sigma(z)$, and the term $[D - U(z)]$ describes scattering relative to $\tilde{H}$.

Instead of the propagator $\langle G(z) \rangle$, the problem may be formulated in terms of the average total-scattering operator $\langle T \rangle$. For a given configuration of the alloy, T is a functional of $U(z)$ and is defined by the equation

$$G = \tilde{G} + \tilde{G} T \tilde{G} , \qquad (2.6)$$

where $\tilde{G}(z) \equiv (z - \tilde{H})^{-1}$ is the reference propagator. The introduction of the operator T is useful if the disordered potential $[D - U(z)]$ can be decomposed into a sum of contributors v_n from each site. The usual equations of multiple-scattering[1-3] theory may then be used to express $\langle T \rangle$ in terms of

$$t_n = (1 - v_n \tilde{G})^{-1} v_n , \qquad (2.7)$$

the atomic-scattering matrix for the site n. The result is

$$\langle T\rangle = \textstyle\sum_n \langle T_n\rangle \,, \tag{2.8a}$$

where

$$\langle T_n\rangle = \langle t_n\rangle \Big(1 + \tilde{G} \sum_{m\neq n} \langle T_m\rangle\Big) + \Big\langle (t_n - \langle t_n\rangle)\tilde{G} \sum_{m\neq n} (T_m - \langle T_m\rangle)\Big\rangle \tag{2.8b}$$

$$= \Big\langle t_n + t_n\tilde{G} \sum_{m\neq n} t_m + t_n\tilde{G} \sum_{m\neq n} t_m \tilde{G} \sum_{p\neq m} t_p + \cdots \Big\rangle \,. \tag{2.8c}$$

Equations (2.6)–(2.8) are exact and in principle provide a complete description of the electronic properties of the alloy. If, as a first approximation, all fluctuations in the effective scattering are neglected, we obtain the usual single-site approximation

$$\langle T_n\rangle = \langle t_n\rangle \Big(1 + \tilde{G} \sum_{m\neq n} \langle T_m\rangle\Big) \,. \tag{2.9}$$

The formal basis of this approximation will be examined in detail in Sec. III.

In the self-consistent approach to multiple-scattering theory, the effective Hamiltonian $\tilde{H}$ is regarded as an unknown of the problem whose value is fixed by the requirement $\langle T_n\rangle = 0$. Within the single-site approximation (2.9), this exact condition reduces to the simpler equation

$$\langle t_n\rangle = 0 \tag{2.10}$$

and is usually referred to as the coherent potential approximation (CPA). Although this approach is known to provide a reasonable description of the electronic properties, it is nevertheless true that the CPA gives only an approximate treatment of the higher-order terms in the multiple-scattering expansion (2.8c). In particular, all the terms on the right-hand side of (2.8c), except the first two, will involve multiple-scattering events in which the electron scatters repeatedly from each of a cluster of atoms. In general, the average contribution from these clustering events will be nonvanishing despite the fact that $\langle t_n\rangle$ equals zero. In other words, the coherent potential requirement $\langle t_n\rangle = 0$ provides only an approximate realization of the exact self-consistency requirement $\langle T_n\rangle = 0$. In the remainder of this section we describe an elementary calculation that illustrates the new qualitative features associated with the simplest clusters, those involving only two atoms.

To begin, we consider the third term in (2.8c). Although the summations are restricted so that successive sites cannot be equal, it is still possible for n and p to coincide. When all three sites are distinct, the averaging may legitimately be expressed as a product of three factors of $\langle t\rangle$. If, however, n and p are equal then the averaging must be carried out more carefully. After some rearrangement, the third-order contribution to $\langle T_n\rangle$ (to be denoted as $\langle T_n^{(3)}\rangle$) can be written as

$$\langle T_n^{(3)}\rangle = \langle t_n\rangle \tilde{G} \sum_{m\neq n} \langle t_m\rangle \tilde{G} \sum_{p\neq m} \langle t_p\rangle + xy\Delta_n \tilde{G} \sum_{m\neq n} \langle t_n\rangle \tilde{G} \Delta_n \,, \tag{2.11}$$

where

$$\Delta_n = t_n^A - t_n^B \,. \tag{2.12}$$

In deriving this result, we have employed the identities

$$t_n^A = \langle t_n\rangle + y\Delta_n \,, \tag{2.13a}$$

$$t_n^B = \langle t_n\rangle - x\Delta_n \,. \tag{2.13b}$$

The first term on the right-hand side of (2.11) is just the result of the usual average t-matrix approximation,[12–15] while the second term provides an additional contribution arising from the repeated scattering event. Within the CPA, however, $\langle t_n\rangle = 0$ (all n), *both* terms in (2.11) vanish, and there is no correction, i.e., $\langle T_n^{(3)}\rangle = 0$.

This kind of analysis can be carried out on all the succeeding terms of (2.8c). Each term can be separated into distinct multiple-scattering events, averaged exactly, and finally expressed in terms of $\langle t\rangle$ and Δ via Eqs. (2.13). In a given event, suppose that at least one site is not involved in any repeated scattering, i.e., appears only once. The average contribution from this event will contain a factor of $\langle t_p\rangle$ [as in the second term of (2.11)] and automatically vanishes within the CPA. On the other hand, if every atom scatters the electron more than once, then the average contribution from this event will not vanish, and we obtain a finite correction to the CPA. For example, beginning in fourth order, there is always a correction associated with repeated scattering within a cluster of just two atoms. The first of these pair corrections is given by

$$\langle T_n^{(4)}\rangle = x^2y^2\Delta_n\tilde{G} \sum_{m\neq n} \Delta_m\tilde{G}\Delta_n\tilde{G}\Delta_m \,,$$

and as might have been expected is of second order in the impurity concentration x. Indeed, it is not difficult to show that the contribution from each of these pair events is $O(x^2)$ and, what is more important, that these are the only corrections of order x^2. The relevant physical events are shown schematically in Fig. 1, and the indicated summation can be carried out exactly. The resulting expression for $\langle T_n\rangle$ is given by

$$\langle T_n\rangle = |n\rangle\langle\tau^{(2)}\rangle\langle n| + \sum_{m(\neq n)} |n\rangle\langle\tau_{nm}^{(2)}\rangle\langle m| \,, \tag{2.14a}$$

where

$$\langle\tau_{nm}^{(2)}\rangle = x^2y^2\Delta^4\tilde{G}_{nm}\tilde{\Gamma}_{nm}\left(\frac{y^2}{1-y^2\Delta^2\tilde{\Gamma}_{nm}} + \frac{2xy}{1+xy\Delta^2\tilde{\Gamma}_{nm}}\right.$$

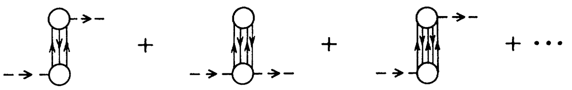

FIG. 1. Physical events contributing to pair corrections to the CPA.

$$+\frac{x^2}{1-x^2\Delta^2\tilde{\Gamma}_{nm}}\Bigg) \qquad (2.14b)$$

$$=x^2y^2\Delta^4\tilde{G}_{nm}\tilde{\Gamma}_{nm}(1-xy\Delta^2\tilde{\Gamma}_{nm})A_{nm}^{-1}, \qquad (2.14c)$$

$$\langle\tau^{(2)}\rangle=x^2y^2\Delta^5\sum_{m\neq n}\Bigg(\frac{y^3\tilde{\Gamma}_{nm}^2}{1-y^2\Delta^2\tilde{\Gamma}_{nm}}+\frac{xy(y-x)\tilde{\Gamma}_{nm}^2}{1+xy\Delta^2\tilde{\Gamma}_{nm}}$$

$$-\frac{x^3\tilde{\Gamma}_{nm}^2}{1-x^2\Delta^2\tilde{\Gamma}_{nm}}\Bigg) \qquad (2.14d)$$

$$=x^2y^2(y-x)\Delta^5\sum_{m\neq n}\tilde{\Gamma}_{nm}A_{nm}^{-1}, \qquad (2.14e)$$

and

$$\tilde{\Gamma}_{nm}\equiv\tilde{G}_{nm}\tilde{G}_{mn}\equiv\langle n|\tilde{G}|m\rangle\langle m|\tilde{G}|n\rangle, \qquad (2.15a)$$

$$\Delta=\langle n|\Delta_n|n\rangle, \qquad (2.15b)$$

$$A_{nm}=1-\Delta^2\tilde{\Gamma}_{nm}[(y-x)^2+xy](1+xy\Delta^2\tilde{\Gamma}_{nm})$$

$$+x^3y^3\Delta^6\tilde{\Gamma}_{nm}^3. \qquad (2.15c)$$

The expression for $\langle T_n\rangle$ given by (2.14) is exact to $O(x^2)$. It should be emphasized, however, that this calculation is not completely satisfactory since it provides only a non-self-consistent description of pair clusters embedded in a CPA medium. We have summed selected parts of a perturbation series each term of which is expressed in terms of the CP Green's function and self-energy. Indeed, it is clear from the particular algebraic structure of this result that the analytic properties of the new Green's function [obtained by combining Eqs. (2.14), (2.8a), and (2.6)] are essentially identical to those of the unperturbed CP Green's function $\tilde{G}$. Accordingly, the continuous contribution to the new density of states will be nonvanishing only within the limits of the CP band edges. By contrast, it is not difficult to illustrate that the present results do predict the existence of discrete states. To see this, we must demonstrate that the zeros of the denominators in (2.14) fall outside the CP band edges. Because $\tilde{G}(z)$ is Hermitian in this energy range, $\Delta^2\tilde{\Gamma}_{nm}$ is real and positive, and only the first and last terms in (2.14b) and (2.14d) need be considered. A typical denominator in (2.14), say $(1-y^2\Delta^2\tilde{\Gamma}_{nm})$ is most likely to vanish if y and δ are large while $|\vec{R}_n-\vec{R}_m|$ is as small as possible. We shall, therefore, restrict our attention to the dilute split-band limit and the case in which n and m are nearest neighbors.

For numerical results, we specialize to the cosine band model of Eqs. (2.1) and (2.3). Solutions of the CP equation (2.10) will be presented and the resulting Green's function used to study the singularities of Eq. (2.14). Figures 2 and 3 show the values of the density of states and the denominator $1-y^2\Delta^2\tilde{\Gamma}_{100}$ for $x=0.05$ and three values of δ. The density of states is seen to exhibit the development of the band shape for increasing δ from a single band distorted at its upper edge, through a stage in which the band splits, and finally to a stage in which the two subbands are essentially independent. The simplest case is $\delta=0.75$ in which the band is not yet split although a minority subband is beginning to emerge. The denominator in Fig. 3(a) exhibits structure only in the neighborhood of this incipient minority band. Here the real part dips sharply towards zero twice, but the criterion for a discrete state, namely, $1-y^2\Delta^2\tilde{\Gamma}_{100}=0$

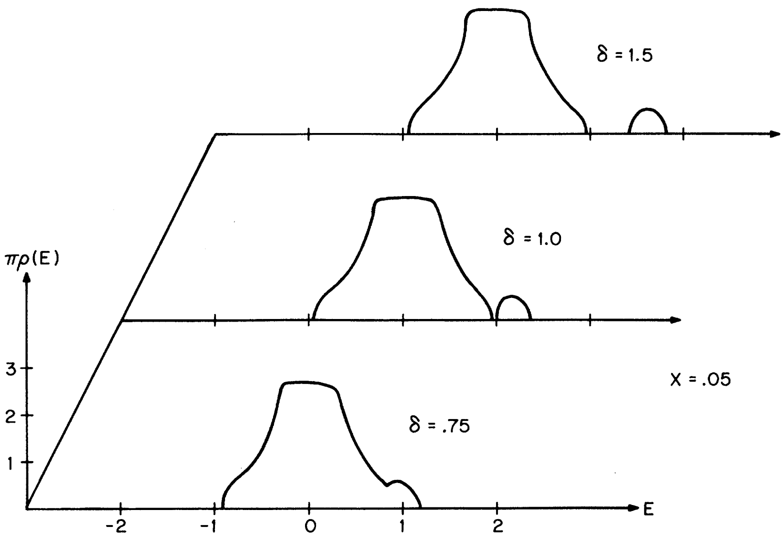

FIG. 2. Electronic density of states obtained from the CPA.

is never satisfied. Increasing δ to 1.0 splits off a subband, and we see from Fig. 3(b) that there are discrete states above and below the impurity band. $\mathrm{Re}(1-y^2\Delta^2\tilde{\Gamma}_{100})$ vanishes four times in this energy range. The middle two roots, however, do not correspond to discrete states as they occur at energies for which $\mathrm{Im}(1-y^2\Delta^2\tilde{\Gamma}_{100})$ is quite large. For the largest value of δ considered, namely, $\delta=1.5$, the constituent subbands are well separated. The situation is qualitatively similar to that of the case $\delta=1.0$. Figure 3(c) shows that once again there are "satellite" levels on either side of the impurity subband.

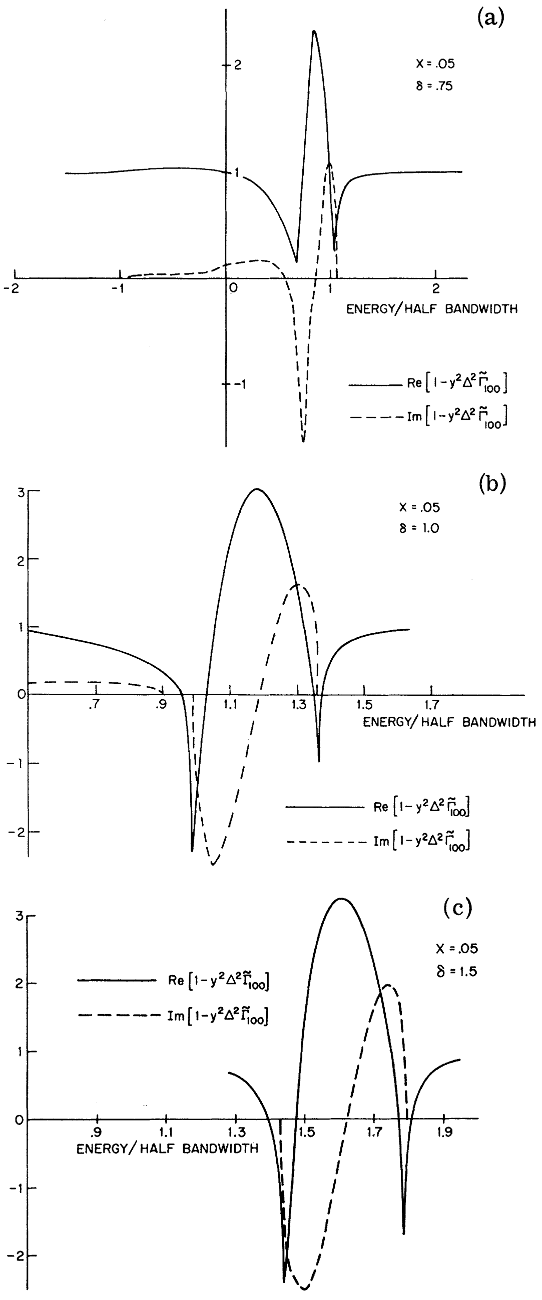

FIG. 3. Behavior of the denominator $1-y^2\Delta^2\tilde{\Gamma}_{100}$ as a function of E. Note that the sharp structure always occurs at the edges of the minority subband.

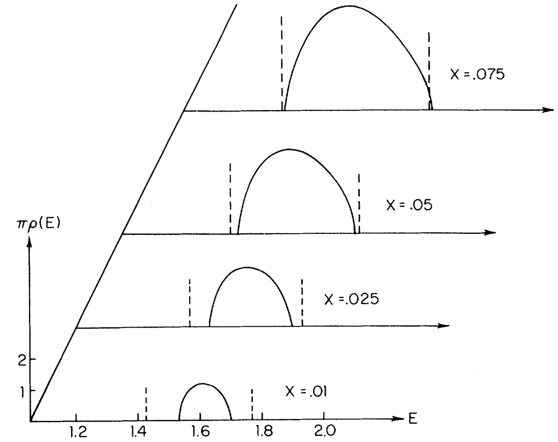

FIG. 4. Concentration dependence of the bonding and antibonding satellite levels. The value of δ is 1.5. The upper level in the case $x=0.075$ lies just inside the band edge and therefore corresponds to a resonant level rather than a true discrete state.

It is also of interest to study the behavior of the satellite levels as a function of increasing concentration. This is done in Fig. 4. Here the solid lines are the CP minority band densities of states and the vertical dashed lines indicate the positions of the roots of $(1-y^2\Delta^2\tilde{\Gamma}_{100})$. As the concentration of impurities is raised, and the likelihood of hopping between them increased, the minority band broadens and eventually merges with the satellite states. Accordingly, in the case $x=0.075$, the right-hand dashed line represents a root of $\mathrm{Re}(1-y^2\Delta^2\tilde{\Gamma}_{100})$ and describes a resonant state degenerate with the continuum rather than a truly discrete level.

Added insight into the structure of Eqs. (2.14) is gained if we consider the calculation of the scattering operator $t^{(2)}(n,m)$ for a two-atom molecule embedded in the CP medium. Beginning with the obvious generalization of Eq. (2.7), $t^{(2)}(n,m)$ is easily expressed in terms of the single-site scattering operators t_n and t_m:

$$t^{(2)}(n,m)=[1-(v_n+v_m)\tilde{G}]^{-1}(v_n+v_m)$$

$$=t_n(1-\tilde{G}t_m\tilde{G}t_n)^{-1}(1+\tilde{G}t_m)+t_m(1-\tilde{G}t_n\tilde{G}t_m)^{-1}(1+\tilde{G}t_n) \qquad (2.16a)$$

$$\equiv t_n^{(2)}(m)+t_m^{(2)}(n)\,. \qquad (2.16b)$$

These equations have a simple physical interpretation. $t_n^{(2)}(m)$, the first term on the right-hand side, describes an electron scattering first from n, then undergoing any number of repeated scatterings between n and m, and finally emerging from either n or m. Similarly, $t_m^{(2)}(n)$ describes the corresponding process beginning at the site m. To make contact with our previous results, the right-hand side of Eqs. (2.16) must be averaged over the possible configurations of the sites n and m. For example, consider the off-diagonal element

$$\langle t_n(1-\tilde{G}t_mGt_n)^{-1}Gt_m\rangle = |n\rangle x^2y^2\Delta^2\tilde{G}_{nm}\left(\frac{1}{1-y^2\Delta^2\tilde{\Gamma}_{nm}}-\frac{2}{1+xy\Delta^2\tilde{\Gamma}_{nm}}+\frac{1}{1-x^2\Delta^2\tilde{\Gamma}_{nm}}\right)\langle m|$$

$$= |n\rangle x^2y^2\Delta^4\Gamma_{nm}\tilde{G}_{nm}\left(\frac{y^2}{1-y^2\Delta^2\tilde{\Gamma}_{nm}}+\frac{2xy}{1+xy\Delta^2\tilde{\Gamma}_{nm}}+\frac{x^2}{1-x^2\Delta^2\tilde{\Gamma}_{nm}}\right)\langle m| \cdot \tag{2.17a}$$

Here the identities $t_n^A=\langle t_n\rangle+y\Delta_n\rightarrow y\Delta_n$ and $t_n^B=\langle t_n\rangle-x\Delta\rightarrow -x\Delta$ have been used. Similarly, averaging the diagonal elements in (2.16) yields

$$\langle t_n(1-\tilde{G}t_m\tilde{G}t_n)^{-1}\rangle = |n\rangle x^2y^2\Delta^5\tilde{\Gamma}_{nm}\left(\frac{y^3}{1-y^2\Delta^2\tilde{\Gamma}_{nm}}+\frac{xy(y-x)}{1+xy\Delta^2\tilde{\Gamma}_{nm}}-\frac{x^3}{1-x^2\Delta^2\tilde{\Gamma}_{nm}}\right)\langle n|\,. \tag{2.17b}$$

Comparing Eqs. (2.14) and (2.17), we see that the form of the total-scattering operator implied by the former equations is simply

$$\langle T\rangle=\sum_n\langle T_n\rangle=\tfrac{1}{2}\sum_{n\neq m}\langle t^{(2)}(n,\,m)\rangle\,, \tag{2.18}$$

and our results do indeed represent the effects of all possible pair clusters embedded in the CPA medium. Accordingly, the discrete states discussed in connection with Figs. 3 and 4 may be viewed as molecular bonding and antibonding levels of these two-atom systems.

III. SELF-CONSISTENT TREATMENT OF PAIR CLUSTERS

In Sec. II pair corrections to the CPA were evaluated by summing selected terms in the perturbation series for the average total-scattering operator. A satisfactory treatment of the problem, however, should involve the self-consistent calculation of a new effective medium. Within a multiple-scattering framework, the exact condition $\langle T_n\rangle=0$ must be combined with an approximate expression for $\langle T_n\rangle$ that includes pair clusters on an equal footing with the single-site effects described by the CPA. This is done most easily if the equations of motion are reformulated in terms of the pair-scattering operators $t^{(2)}(n,\,m)$.

Equation (2.7) expresses the total-scattering operator T in terms of the single-site operators t_n. This relation may be rewritten as a pair of equations for the quantities T_n and T_m,

$$T_n=t_n+t_n\tilde{G}T_m+t_n\tilde{G}\sum_{p\neq n,m}T_p\,,$$

$$T_m=t_m+t_m\tilde{G}T_n+t_m\tilde{G}\sum_{p\neq n,m}T_p\,.$$

Recalling the definition (2.16), the solution of these equations is

$$T_n=t_n+t_n\tilde{G}\sum_{m\neq n}t_m^{(2)}(n)+t_n\tilde{G}\sum_{m\neq n}t_m^{(2)}(n)\tilde{G}\sum_{p\neq n,m}T_p\,. \tag{3.1}$$

This result is valid for any configuration of the alloy and for any choice of reference Hamiltonian U in Eq. (2.5). The first two terms in Eq. (3.1) are associated with scattering by single sites and pairs, while the final term describes events involving at least three distinct sites. In performing the ensemble average, these higher-order terms may be decoupled from the one- and two-atom contributions. The alloy is then described by the closed system of equations

$$\langle T_n\rangle=\langle t_n\rangle+\langle t_n\tilde{G}\sum_{m\neq n}t_m^{(2)}(n)\rangle(1+\tilde{G}\sum_{p\neq n,m}\langle T_p\rangle)\,. \tag{3.2}$$

The general self-consistency requirement $\langle T_n\rangle=0$ (all n) now leads to the requirement

$$0=\langle t_n\rangle+\langle t_n\tilde{G}\sum_{m\neq n}t_m^{(2)}(n)\rangle\,. \tag{3.3}$$

Equation (3.3) is the desired generalization of the CP condition $\langle t_n\rangle=0$. This result is essentially identical to the pair equations recently discussed by Cyrot-Lackmann and Ducastelle.[10] The remainder of this section is devoted to establishing the relationship between these equations and the results obtained by Schwartz and Siggia.

The analysis carried out by Schwartz and Siggia (SS) was based on a detailed examination of the moments of the CP self-energy:

$$\mu_p=\int_{-\infty}^{\infty}E^p\,\mathrm{Im}\Sigma(E^+)\,dE\,. \tag{3.4}$$

The essential point is that in addition to being exact to first order in x and third order in δ, the CP moments μ_p also contain all contributions of higher order in x and δ that are independent of the reciprocal coordination number Z^{-1}. A proper generalization of the CPA must of course continue this systematic treatment of the parameter Z^{-1}. Indeed, it will be seen that the equations derived above include all contributions to the moments of $\Sigma(z)$ that are of order x^2 and δ^5 and, in addition, those higher-order terms through $O(Z^{-3})$. It is also true, however, that these pair equations retain many additional terms that are of higher order in *both* x and Z^{-1}. If such terms are eliminated at the outset, the final expression for $\Sigma(z)$ will be greatly simplified. Following this course, the self-consistent equation (3.3) will be shown to reduce to the pair equations derived by SS.

To begin, we emphasize that the self-consistency condition (3.3) must be viewed as a system of coupled equations, one for each matrix element of the operators involved. The essential new features of this result are most easily isolated if the second term on the right-hand side is evaluated within the CPA. As in the derivation of Eqs. (2.17), the averaged two-site scattering operators are then expressed in terms of $\tilde{G}_{nm}$ and Δ. Dividing (3.3) into its diagonal and off-diagonal components, we obtain

$$0=\langle n|\langle t_n\rangle|n\rangle+x^2y^2(y-x)\Delta^5\sum_{m\neq n}\tilde{\Gamma}^2_{nm}/A_{nm}\,, \tag{3.5a}$$

$$0=\langle n|\langle t_n\rangle|m\rangle+x^2y^2\Delta^4\tilde{G}_{nm}\tilde{\Gamma}_{nm}(1-xy\,\Delta^2\tilde{\Gamma}_{mn})/A_{nm}\,, \tag{3.5b}$$

where the denominator A_{nm} is defined by (2.15c). The second terms in each of Eqs. (3.5) permit us to estimate the pair corrections to the CPA. In fact, it will be seen that these terms include all the relevant pair effects. In both cases the corrections are of second order in the concentration x and involve at least three powers of the off-diagonal matrix elements of $\tilde{G}$. As noted by SS, the asymptotic behavior (as $z\rightarrow\infty$) of $\tilde{G}_{nm}$ introduces the dependence of the moments of $\Sigma(z)$ on the parameter Z^{-1}:

$$G_{nm}(z)\rightarrow(z^2Z)^{-1}\quad(n,\ m\ \text{nearest neighbors}).$$

Because every atom is surrounded by Z nearest neighbors, the leading contributions from the pair terms in each of Eqs. (3.5) are of order $x^2\delta^2/Z^3$ and $x^2\delta^4/Z^2$, respectively. The denominators A_{nm} then provide all remaining contributions of order x^2.

The form of Eqs. (3.5) forces us to adopt an effective medium (i.e., self-energy) that contains both diagonal and off-diagonal matrix elements:

$$\Sigma(z)=\textstyle\sum_n\sigma_n\,, \tag{3.6a}$$

where

$$\sigma_n=|n\rangle\sigma(z)\langle n|+\sum_{m\neq n}|n\rangle\sigma_{nm}(z)\langle m|\,. \tag{3.6b}$$

To write explicit equations for the self-energy, $\langle t_n\rangle$ and Δ in Eqs. (3.5) must be eliminated in favor of $\sigma(z)$ and $\sigma_{nm}(z)$. Returning to the basic equation (2.7), the operator t^A_n is seen to satisfy the relation

$$t^A_n=(|n\rangle\epsilon^A\langle n|-\sigma_n)+(|n\rangle\epsilon^A\langle n|-\sigma_n)\tilde{G}t^A_n\,. \tag{3.7}$$

When (3.6) is substituted into (3.7), the latter equations can be solved exactly for the matrix elements of $t^A_n\equiv|n\rangle t^A\langle n|+\sum_{m\neq n}|n\rangle t^A_{nm}\langle m|$,

$$t^A=(\epsilon^A-\sigma)[1-(\epsilon^A-\sigma)\tilde{F}+\sum_{n'\neq n}\sigma_{nn'}\tilde{G}_{n'n}]^{-1}\,, \tag{3.8a}$$

$$t^A_{nm}=-\sigma_{nm}[1-(\epsilon^A-\sigma)\tilde{F}+\sum_{n'\neq n}\sigma_{nn'}\tilde{G}_{n'n}]^{-1}\,, \tag{3.8b}$$

where $\tilde{F}\equiv\langle n|\tilde{G}|n\rangle$ is independent of n. The off-diagonal elements of t^A_n (and hence those of $\langle t_n\rangle$) are directly proportional to σ_{nm}. Equations (3.5) then imply that σ_{nm} is $O(x^2/Z^2)$. To the order in which we are working [i.e., retaining only those contributions to Σ that are $O(x^2)$ *or* $O(Z^{-3})$], we can therefore neglect the part of the denominators in (3.8) that explicitly involve σ_{nm}. Combining these simplified equations with the corresponding results for t^B_n, we obtain

$$\langle n|\langle t_n\rangle|n\rangle=xt^A+yt^B=\frac{x\delta-\sigma+\sigma\tilde{F}(\delta-\sigma)}{[1-(\delta-\sigma)\tilde{F}](1+\sigma\tilde{F})}\,, \tag{3.9a}$$

$$\langle n|\langle t_n\rangle|m\rangle=xt^A_{nm}+yt^B_{nm}=\frac{-\sigma_{nm}[1-(y\delta-\sigma)\tilde{F}]}{[1-(\delta-\sigma)\tilde{F}](1+\sigma\tilde{F})}\,. \tag{3.9b}$$

Using the CP equation

$$\sigma=x\delta/[1-(\delta-\sigma)\tilde{F}]\,,$$

the denominators in Eqs. (3.9) may be approximated as

$$\begin{aligned}[1-(\delta-\sigma)\tilde{F}](1+\sigma\tilde{F})&=1-(\delta-\sigma)\tilde{F}+\tilde{F}[1-(\delta-\sigma)\tilde{F}]\\&\simeq1-(\delta-\sigma)\tilde{F}+x\delta\tilde{F}\\&=1-(y\delta-\sigma)\tilde{F}\,.\end{aligned} \tag{3.10}$$

Similarly, the quantity Δ is easily expressed in terms of σ and $\tilde{F}$:

$$\Delta=\langle n|\Delta_n|n\rangle=\delta/[1-(y\delta-\sigma)\tilde{F}]\,. \tag{3.11}$$

In deriving Eqs. (3.9)–(3.11), we have neglected part of the implicit dependence of the scattering operators on the self-energy. We are also justified in making further simplifications in the explicit dependence of Eqs. (3.5). For example, if we approximate

$$A_{nm} \simeq 1-(y-x)^2\Delta^2\tilde{\Gamma}_{nm}\,, \tag{3.12}$$

and in addition neglect the second term in the parentheses of Eq. (3.5b), our equations are still exact through $O(x^2)$ and $O(Z^{-3})$. Combining Eqs. (3.9)–(3.12) with Eqs. (3.5), the final equations for the self-energy may be written as

$$\sigma = \frac{x\delta(1+\sigma\tilde{F})}{1-(y\delta-\sigma)\tilde{\tilde{F}}} + x^2y^2(y-x)\Delta^5 \sum_{m\neq n} \frac{\tilde{\Gamma}^2_{nm}}{1-(y-x)^2\Delta^2\tilde{\tilde{\Gamma}}_{nm}}, \tag{3.13a}$$

$$\sigma_{nm} = \frac{x^2y^2\Delta^4\tilde{G}_{nm}\tilde{\Gamma}_{nm}}{1-(y-x)^2\Delta^2\tilde{\Gamma}_{nm}}\,. \tag{3.13b}$$

These results are identical to the pair equations obtained by SS [their Eqs. (3.13)]. Equations (3.13) must be solved simultaneously and self-consistently for the matrix elements $\sigma(z)$ and $\sigma_{nm}(z)$. Numerical calculations were presented by SS, and it was shown that these equations lead to both a broadening of the satellite levels and a shifting of the minority band edges.

To conclude, let us review the different approximations that have been used to derive Eqs. (3.13) from the original self-consistency condition (3.3). First, the second term in (3.3) was evaluated in the CPA, i.e., assuming that $\langle t\rangle = 0$ and that the operators $\langle t\rangle$ and Δ were site diagonal. In addition, the implicit dependence of the scattering matrices t_n^A and t_n^B on the self-energy was evaluated approximately and further simplifications were made in the form of Eqs. (3.5). The essential point is that all of these approximations involve the neglect of terms that are of higher order in *both* x and Z^{-1}. In Eqs. (3.13) the quantity Δ introduces terms that are of higher order in x but are independent of Z^{-1}. Similarly, the contribution from the denominators of (3.13) are of higher order in Z^{-1} but are all of order x^2. The final equations for $\Sigma(z)$ are then uniformly correct to order x^2 and in addition are asymptotically correct to $O(Z^{-3})$.

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