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Equivalence of Expanding in Localized or Bloch States in Disordered Alloys*

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Calculations are made of the configuration-averaged density of states and the electrical conductivity of a binary disordered alloy by two quite distinct techniques, namely, by beginning with the Bloch states of a perfect crystal and making a cluster expansion in the scattering off imperfections, and by beginning with localized atomic states and making a cluster expansion in the interatomic hopping matrix elements. The two techniques are shown to give the same results when all irreducible single-site diagrams are included in the self-consistent field approximation and multiple-occupancy corrections are made self-consistently; it is conjectured that this equivalence holds at each level of the cluster expansion. In the process, the connection between the recent calculation of transport properties by Velický in the coherent potential approximation, the diagrammatic technique of Edwards, and the diagramatic technique of Matsubara and Toyozawa is established.

I. INTRODUCTION

It has recently become clear that formally, at least, the general problems of determining the nature of electron, phonon, magnon, and exciton states in disordered alloys are the same. Perhaps the most widely used approaches to the problem have been to calculate the Green's functions averaged over an ensemble of all configurations of the atoms by perturbation-expansion techniques. The usual technique, which was introduced by Edwards,[1] is to begin with the states of a perfect crystal and make a cluster expansion in the scattering due to the imperfections, which can with sufficient scattering lead to states localized about the imperfections. Another technique, first used for the configurationally averaged crystal by Matsubara and Toyozawa,[2] is to begin with localized states, whose energies vary from site to site and make a cluster expansion in the hopping matrix elements between localized states which, with sufficient hopping, can

lead to delocalized or band states. The first method, expansion about the Bloch states, has recently been extended in various equivalent ways to a self-consistent treatment (which has been shown to be reasonably accurate in certain cases for the general behavior of the density of states throughout the entire concentration range[3]) by Soven[4] and Yonezawa[5] for electrons, Taylor,[3] Leath,[6] and Aiyer *et al.*[7] for phonons, and Onodera and Toyozawa[8] for excitons. The second method has been studied more recently by Matsubara and Kaneyoshi.[9] The primary purpose of the present work is to demonstrate that for single site, self-consistent scatterings, the two quite different expansions give just the same results for the density of states and the transport coefficients, providing multiple-occupancy corrections are included self-consistently.[6,7] It is also shown that the diagrams of Edwards,[1] Langer,[10] and Verboven,[11] when properly corrected for multiple occupancy, give the so-called *coherent potential approximation* for the electrical conductivity[12] and that this conductivity satisfies a Ward identity which can be used quite simply to obtain the vertex corrections. In particular, the recent speculation by Ziman[13] concerning the advantage of expanding in localized states appears to be wrong.

Since the question of localized versus band states has been most frequently raised and discussed in reference to the electronic problem in semiconductors and in order to make the problem specific, the notation of the electronic problem will be used.

We consider a disordered binary alloy made by randomly placing concentrations (fractions) c of atoms of type B, and $(1-c)$ of atoms of type A on a regular lattice. We work in the tight-binding formalism and assume the simple model used by Anderson,[14] Soven,[4] and Matsubara and Toyozawa.[2] (It seems that the results presented here would also hold for more realistic models.) In this model one assumes that there is only one eigenvalue in the energy range of interest, that the atomic wave functions for A and B atoms are essentially identical, and that the matrix elements of the alloy Hamiltonian between orbitals centered on different lattice sites is independent of the types of atoms occupying those sites. The diagonal matrix elements of the Hamiltonian (the atomic eigenvalues) vary from site to site, taking on the values ϵ_A and ϵ_B. The model alloy Hamiltonian is thus of the form

$$H=\sum_n \epsilon_n a_n^+ a_n+\sum_n \sum_m W(n-m)a_n^+ a_m \quad , \tag{1}$$

where $W(n-m)$ is translationally invariant, ϵ_n takes on the values ϵ_A and ϵ_B on A and B sites, respectively, and $a_n^+(a_n)$ is a creation (annihilation) operator for an electron in the atomic state at site n and is assumed independent of the atom type at n and the concentration c.

The proof for the density of states and the transport coefficients is most directly established via the one- and two-particle Green's functions. The one-particle retarded Green's function $G(n,m)$ satisfies the operator equation

$$(\epsilon+is-H)G=1 \tag{2}$$

for a particular configuration of atoms. The two-particle Green's function, for a particular configuration of atoms, is just the direct product of one-particle Green's functions

$$G^{(2)}=G\cdot G \tag{3a}$$

or

$$G^{(2)}(l,m;n,p)=G(l,n)G(m,p) \quad , \tag{3b}$$

where $G(l,n)$ is given by Eq. (2), since we include only electron-impurity interactions here.

The density of states $\rho(E)$ and the transport coefficients are simply related to the Green's functions according to the standard formulas

$$\rho(E)=-\operatorname{Im}\operatorname{Tr}\{G\}/\pi \quad , \tag{4}$$

where Im is the imaginary part, and Tr denotes the trace over any complete set, and

$$\chi_{C_2C_1}(z)=-i\int_0^\infty dt\, e^{izt}\operatorname{Tr}[e^{iHt}C_2e^{-iHt},C_1]f(H) \quad , \tag{5}$$

where $f(H)$ is the density matrix, C_1 and C_2 are typically electric or energy current operators. This formula is simply related to $G^{(2)}=G\cdot G$.[15]

In practice it is impossible to calculate the Green's function of Eq. (2) for any particular configuration of impurities in a realistic alloy. However, one can approximately calculate the Green's function averaged over an ensemble of all distributions of the atoms on the lattice sites. This will be valid if the energy shifts produced in the states at a particular site by the presence or distribution of impurities at a distance l, which is much smaller than the sample size L, are smaller than the resolution width of the experiment measuring the property. A theorem relevant to this has been proven by Matsuda,[16] who showed that, for a one-dimensional chain with only nearest-neighbor interactions, $G(E+i\Gamma;n,m)$ dies out at least exponentially with $(n-m)$ at a rate proportional to Γ, which was sufficiently large for reasonable experimental resolution widths Γ that the above criterion was easily satisfied for the phonon density of states. Hopefully similar theorems exist in two and three dimensions.

There are two special cases when the Hamiltonian of Eq. (1) yields a trivially soluble problem for the configuration averaged $\langle G\rangle$. The first is when ϵ_n takes on the same value, say, ϵ_A, on each site; this represents a perfect crystal of A atoms with a Green's function

$$P = (\epsilon - \epsilon_A - W)^{-1} \quad , \tag{6}$$

which is diagonal in the Bloch representation

$$P(\vec{k}, \vec{k}') = \delta_{\vec{k},\vec{k}'} \frac{1}{\epsilon - \epsilon(\vec{k})} \quad , \tag{7}$$

where $\epsilon(\vec{k})$ is the perfect-crystal energy in the band of interest. Thus, one can develop a perturbation expansion [of validity at least for small $(\epsilon_A - \epsilon_B)$] by separating the alloy Hamiltonian into a perfect crystal H_0 and a scattering part V:

$$H = [\epsilon_A \textstyle\sum_n a_n^+ a_n + \sum_n \sum_m W(n-m) a_n^+ a_m]$$

$$+ \textstyle\sum_n (\epsilon_n - \epsilon_A) a_n^+ a_n = (H_0) + V \tag{8}$$

and treating the diagonal scattering term V as the perturbation.

The second soluble case is when $W = 0$ and G becomes diagonal in the atomic or Wannier representation, taking on the values $(\epsilon - \epsilon_A)^{-1}$ and $(\epsilon - \epsilon_B)^{-1}$, which gives

$$\langle g(n, m) \rangle = \left\langle \frac{\delta_{nm}}{\epsilon - \epsilon_n} \right\rangle = \delta_{nm} \frac{1-c}{\epsilon - \epsilon_A} + \frac{c}{\epsilon - \epsilon_B} \quad . \tag{9}$$

Thus, if the alloy Hamiltonian is separated into a local part h and a hopping part W,

$$H = (\textstyle\sum_n \epsilon_n a_n^+ a_n) + \sum_n \sum_m W(n-m) a_n^+ a_m = (h) + W \ , \tag{10}$$

one can develop a useful perturbation expansion (at least for small W) by treating the hopping Hamiltonian W as the perturbation. Sections II–VI are devoted to a discussion of the proper way to make each expansion and to show a self-consistent partial summation that gives the same Green's function for each expansion.

Sections II and III are devoted to explaining the expansion of the one- and two-particle Green's functions, respectively, in terms of band states with a discussion of the connection between the diagram techniques and the multiple-scattering or coherent-potential approximations. Sections IV and V are devoted likewise to the localized-state expansion with the derivation of the equality of the Green's functions calculated by each method when the self-consistent single-site terms are included. Section VI contains a very brief discussion of the failure of these calculations to describe the transition that takes place in the transport properties near the critical percolation concentration.

II. BAND-STATE EXPANSION – ONE-PARTICLE GREEN'S FUNCTION

We now study the scattering by substitutional imperfections in an otherwise perfect crystal. The crystal we choose as the reference or unperturbed crystal will not affect the results as long as a properly corrected self-consistent approximation is made.[17] One can easily show, when expanding in terms of the tight-binding wave functions of energy ϵ_γ of a reference perfect crystal that the states calculated by including single-site scattering self-consistently is independent of ϵ_γ. For example, various authors have used the A- or B-atom crystal,[5-7] the virtual crystal,[8] or a self-consistently determined perfect crystal[3,4] as the reference crystal and gotten the same results. Thus, for simplicity, we shall use the separation of the Hamiltonian in Eq. (8) and call the A-atom lattice the host and consider the scattering by B atoms.

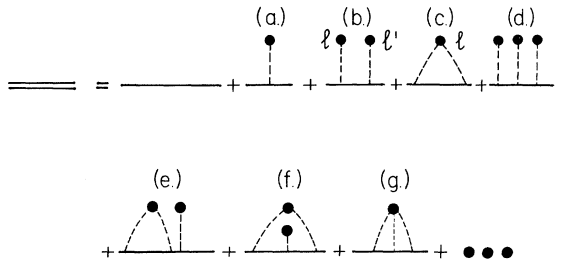

FIG. 1. Some diagrams appearing in the expansion (12) of the Green's function in Bloch States with scattering by defects.

We easily obtain the equation of motion for G in the alloy by putting Eqs. (8) and (6) into (2) to obtain

$$G = P + PVG \quad , \tag{11}$$

where $V_l = \epsilon_B - \epsilon_A$ on B-atom sites and zero otherwise. Iterating and configurationally averaging we formally obtain, in Wannier representation,

$$\langle G(n, m) \rangle = P(n, m) + \sum_l P(n, l) \langle V_l \rangle P(l, m)$$

$$+ \sum_{l, l'} P(n, l) \langle V_l P(l, l') V_{l'} \rangle P(l', m) + \cdots , \tag{12}$$

where $\langle \cdots \rangle$ represents the configuration average. The propagators $P(n, l)$ of the perfect crystal are independent of the average, and hence only serve to connect scatterings V_l by the B atoms. Thus, we only must consider averages of the form $\langle V_l V_{l'} \cdots \rangle$ which, for a random distribution of atoms, factor into products of averages $\langle V_l^n \rangle$ representing all the scattering by each site. Therefore, we can construct initial diagram rules[1,10] for representing the various terms in the expansion. Typical diagrams are shown in Fig. 1, where the horizontal solid propagator line represents $P(n, m)$ and connects the scattering V_n (dashed lines) which, if there is repeated scattering by a single site, are drawn together at an interaction site (solid circle) which is given weight c, the probability of finding a B atom at that site. We can define an irreducible part as a diagram that can not be cut into disconnected parts by breaking a single propagator line, so that the sum of all ir-

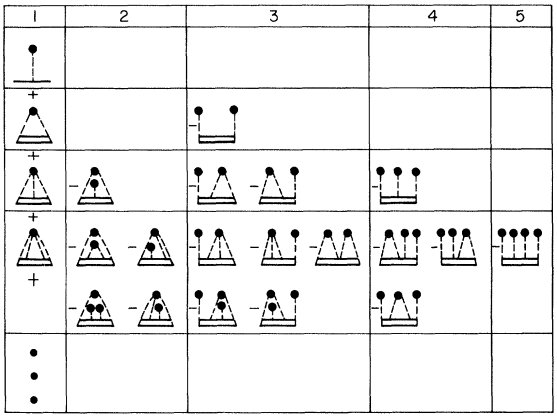

FIG. 2. Irreducible diagrams involving only a single site are shown in column 1 and sum to the value given by Eq. (14), or (46) for the Bloch-state or localized-state expansions, respectively. The nth column contains multiple-occupancy corrections with $(n-1)$ irreducible parts. The sum of all columns gives Σ as in Eq. (17), or σ as in Eq. (50) for the Bloch- or localized-state expansion, respectively.

reducible parts Σ, the self-energy, is related to $\langle G\rangle$ by the Dyson equation

$$\langle G\rangle = P + P\Sigma\langle G\rangle \ . \tag{13}$$

A cluster expansion then results if one first includes all irreducible scattering by single sites, then by pairs of sites, clusters of three sites, etc. The simplest class with anything similar to the correct analytic properties for Σ, the self-consistent single-site scattering, is discussed here. These terms correspond to the diagrams shown in the first column of Fig. 2, where the double solid line represents the full propagator $\langle G\rangle$ inserted self-consistently. This simple class of diagrams is local or diagonal in Wannier representation since all scatterings are by the same site. The sum of these diagrams (the first column of Fig. 2) gives

$$\Sigma_{\text{bare}} = cV/(1 - VG_0) \ , \tag{14}$$

where

$$V = \epsilon_B - \epsilon_A, \quad G_0 = \langle G(n,n)\rangle \ .$$

We have, however, omitted important multiple-occupancy corrections since in treating products like $\langle V_l V_{l'}\rangle = c^2V^2$ in Fig. 1(b) we should have made certain that the sites do not coincide, or $l = l'$. This can, however, be handled by substracting $c^2V^2G_0$ from Fig. 1(c). The self-consistent procedure developed previously [2,7] is used here to make these corrections. We substract from each diagram all diagrams which can be obtained by breaking the scattering lines away from the interaction site and *that yield diagrams already included explicitly*. These correction diagrams are shown in the higher columns of Fig. 2 where the nth column contains those corrections with $(n-1)$ irreducible parts. The corrected self-energy, obtained by summing all the columns, is given by the relation[6]

$$\Sigma[G_0] = \frac{cV}{1 - VG_0} - \left(\frac{\Sigma[\Gamma_0]}{1 - \Sigma[\Gamma_0]G_0} - \Sigma[G_0]\right) \ , \tag{15}$$

where Σ is treated as a functional of its internal propagator, and $\Gamma_0 = G_0/(1 - \Sigma[\Gamma_0]G_0)$ accounts for all the insertions in the internal propagators. The solution of this equation is

$$\Sigma[\Gamma_0] = cV/[1 - (1-c)VG_0] \ , \tag{16}$$

or

$$\Sigma = \Sigma[G_0] = cV/[1 - (1-c)VG_0/(1 + \Sigma G_0)] \ , \tag{17a}$$

which can also be written in the form

$$\sum = cV/[1 - (V - \Sigma)G_0] \ . \tag{17b}$$

This gives the result obtained in the so-called coherent-potential approximation in multiple-scattering theory by Soven[4] and Taylor.[3] In particular, this formula is equivalent to Eq. (13) of Ref. 4, that is easily obtained by replacing Σ by $\Sigma - \epsilon_A$ everwhere in Eq. (17a), which just shifts the unperturbed energy by the proper amount.

A very physical way of rewriting Eq. (17), that was pointed out in Aiyer *et al.*,[7] is

$$\Sigma = cV/(1 - VG_0^A) \ , \tag{18}$$

where G_0^A is the Green's function evaluated on A-atom sites and gives $(1-c)$ times the density of states on A-atom sites. Thus, it is $G^A(n,n)$, a Green's function containing no scatterings by site n, which must be substituted self-consistently rather than the full Green's function G_0 which would contain uncorrected multiple scattering by site n.

III. BAND-STATE EXPANSION – TWO-PARTICLE GREEN'S FUNCTION

The configurationally averaged two-particle Green's function is given by the relation[1,12,15]

$$G^{(2)}(l,m;np) = G(l,n)G(m,p) \ , \tag{19}$$

which, via the iteration of Eq. (11), can be expanded in the form

$$\langle G^{(2)}\rangle = P\cdot P + P\langle V\rangle P\cdot P + P\cdot P\langle V\rangle P + P\langle VP\cdot PV\rangle P + \cdots \ . \tag{20}$$

The same diagram rules as in Sec. II lead to diagrams of the type shown in Fig. 3, but with two propagator lines. Self-energy corrections to each line appear as for the one-particle Green's function and also irreducible vertex parts (which can not be cut into two diagrams by breaking each propagator

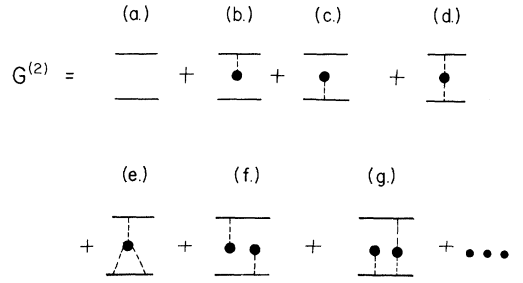

FIG. 3. Some diagrams appearing in the expansion (20) of the two-particle Green's function $\langle GG\rangle$ in terms of the scattering by defects.

line once) appear as in Figs. 3(d) and 3(e). The sum of all irreducible vertex parts, the four-point vertex function Λ, is related to $G^{(2)}$ by a Bethe-Salpeter equation

$$\langle G^{(2)}\rangle = \langle G\rangle\cdot\langle G\rangle + [\langle G\rangle\cdot\langle G\rangle]\Lambda\langle G^{(2)}\rangle \quad , \tag{21}$$

which in the Wannier representation is

$$\langle G^{(2)}(lm, np)\rangle = \langle G(l,m)\rangle\langle G(n,p)\rangle + \sum_{r,s,t,u}\langle G(l,r)\rangle \times\langle G(m,s)\rangle\Lambda(rs,tu)\langle G^{(2)}(tu,np)\rangle \quad . \tag{22}$$

The class of diagrams in Λ that is consistent with the single-site self-energy diagrams discussed above is the irreducible scattering of both particles by the same impurity as shown in the first column of Fig. 4.

The first column sums to the bare single-site vertex part without multiple-occupancy corrections (except those already included in the self-energy Σ) which is completely diagonal in Wannier representation with the diagonal element $\Lambda_{\text{bare}}(nn,nn)$ given by

$$\Lambda_{\text{bare}} = cV^2/(1-VG_0)^2 \quad , \tag{23}$$

which is essentially the formula one would obtain by the simple diagram rules of Edwards,[1] Langer,[10] or Verboven.[11] The multiple-occupancy corrections, however, must be made and are obtained quite easily according to the above rules by subtracting those diagrams which are obtained by breaking apart the vertices in all consistent ways, as shown in Fig. 4 where the nth column ($n \geq 2$) corresponds to those corrections with $(n-2)$ irreducible vertex parts. For example, column 2 contains those corrections with no vertex parts and sums to λ_2, given by

$$\lambda_2 = -\{\Sigma(\Gamma_0)/[1-\Sigma(\Gamma_0)G_0]\}^2 \quad , \tag{24}$$

where $\Gamma_0 = G_0/[1-\Sigma(\Gamma_0)G_0]$ as before and $\Sigma(\Gamma)$ is treated as a functional of its internal propagator.

The third column λ_3 is

$$\lambda_3 = -\{\Lambda(\Gamma_0)/[1-\Sigma(\Gamma_0)G_0]^4 - \Lambda(G_0)\} \tag{25}$$

since there can be any number of self-energy parts on the four external corners and there must be at least one self-energy part internal to vertex part Λ if there are no external self-energy parts in the correction. The sum of all columns gives the fully corrected vertex function

$$\Lambda(G_0) = \sum_{i=1}^{\infty}\lambda_i \quad ,$$

$$\Lambda(G_0) = \frac{cV^2}{(1-VG_0)^2} - \left(\frac{\Sigma(\Gamma_0)}{1-\Sigma(\Gamma_0)G_0}\right)^2 - \left(\frac{\Lambda(\Gamma_0)/[1-\Sigma(\Gamma_0)G_0]^4}{1-\Lambda(\Gamma_0)\Gamma_0^2} - \Lambda(G_0)\right) \quad , \tag{26}$$

which, by expressing G_0 in terms of Γ_0 and using Eq. (17b), can be written

$$\frac{\Lambda(\Gamma_0)}{1-\Lambda(\Gamma_0)\Gamma_0^2} = \frac{(1-c)}{c}\left(\frac{\Sigma(\Gamma_0)}{1+\Sigma(\Gamma_0)\Gamma_0}\right)^2 \quad . \tag{27}$$

The changing of variables $\Gamma_0 \to G_0$ to find the vertex function of interest $\Lambda(G_0)$ is now trivial,

$$\frac{\Lambda(G_0)}{1-\Lambda(G_0)G_0^2} = \frac{(1-c)}{c}\left(\frac{\Sigma}{1+\Sigma G_0}\right)^2 = \frac{\Sigma(V-\Sigma)}{(1+\Sigma G_0)[1-(V-\Sigma)G_0]} \quad , \tag{28}$$

where the last equality follows from the relation

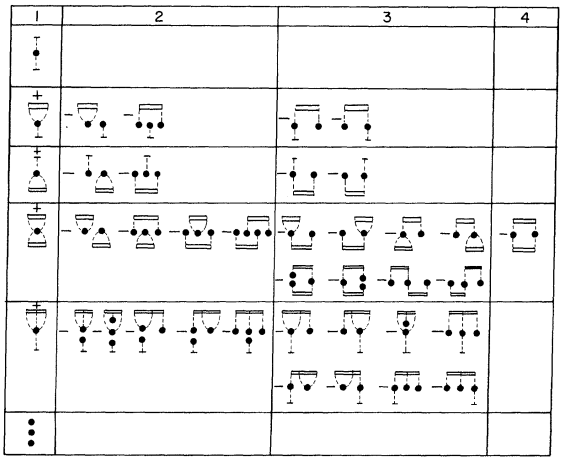

FIG. 4. Irreducible vertex diagrams containing scattering by a single site (column 1) which sums to the value given by Eq. (23) for the Bloch-state expansion. The nth column contains multiple-occupancy corrections with $(n-2)$ irreducible vertex parts. The sum of all columns gives the irreducible vertex function Λ in Eq. (29) for the Bloch-state expansion and γ in Eq. (61) for the localized-state expansion.

$(1-c)V/(1+\Sigma G_0)=(V-\Sigma)$ which is obvious from Eqs. (17). The solution of this equation can be simply written

$$\Lambda=\frac{[(1-c)/c][\Sigma/(1+\Sigma G_0)]^2}{1+[(1-c)/c][\Sigma G_0/(1+\Sigma G_0)]^2}$$

$$=\frac{\Sigma(V-\Sigma)}{1-(V-2\Sigma)G_0}\ , \tag{29}$$

after a little algebra. The meaning of Eq. (28) is not as simple as before for Σ; essentially this equation says that not only must one not rescatter by the same site in the internal propagators on each line separately, but also one must also handle coincidences of the internal scatterings from each line with the other properly.

Although Eq. (29) appears somewhat different, it is essentially the same result as that obtained by Velický who worked in the coherent-potential approximation.[12] In this technique, developed by Soven,[4] one sums the single-site diagrams for the particular choice of unperturbed energy Σ, called the coherent potential here rather than the self-energy, such that the average single-site t matrix $\langle t_n\rangle$ is zero, which in our notation gives

$$\langle t_n\rangle=-\frac{(1-c)\Sigma}{1+\Sigma G_0}+\frac{c(V-\Sigma)}{1-(V-\Sigma)G_0}=0\ , \tag{30}$$

which immediately gives Eq. (17b) above. In generalizing the technique to the conductivity or the two-particel Green's function, Velický concluded, properly, that the consistent treatment was pairwise random-phase decoupling of the t_n matrices so that the two-electron t matrix $\Lambda/(1-\Lambda G_0^2)$ was $\langle t_n^2\rangle$. That is, he calculated

$$\langle t_n^2\rangle=\frac{(1-c)\Sigma^2}{(1+\Sigma G_0)^2}+\frac{c(V-\Sigma)^2}{[1-(V-\Sigma)G_0]^2}$$

$$=\frac{(1-c)}{c}\,\frac{\Sigma^2}{(1+\Sigma G_0)^2}\ , \tag{31}$$

where Eq. (30) was used to obtain last equality. This result is identical to Eq. (28) so the two calculations coincide and the coherent-potential approximation agrees with the diagrammatic technique after proper multiple-occupancy corrections even for the conductivity.

Also the vertex corrections above satisfy a Ward identity (as shown in Ref. 11), and hence the resulting transport coefficients maintain the macroscopic conservation laws. The particularly simple form of these conservation laws developed by Baym[18] is also instructive and can indeed be used to derive the vertex corrections from the self-energy. Baym's form of the Ward identity in this notation becomes

$$\Lambda(l,m;np)=\frac{\delta\Sigma(l,n)}{\delta G(m,p)}=\frac{\delta\Sigma(m,p)}{\delta G(l,n)}\ . \tag{32}$$

In this case of only single-site contributions Λ is completely diagonal with only the term

$$\Lambda=\delta\Sigma/\delta G_0 \tag{33}$$

for $l=m=n=p$, so the second equality in (32) is trivially satisfied. This will not be the case when Σ becomes nonlocal by the inclusion of other diagrams and in that case one must also be sure that Σ can be obtained from a certain sum of free-energy diagrams as described by Baym.[18] (In our case, that class of diagrams is simply the wagon-wheel diagrams in Fig. 5 times the appropriate $1/n$ combinatorial factor.) It is easy to verify that

$$\delta\Sigma/\delta G_0=\frac{\delta\{cV/[1-(V-\Sigma)G_0\}}{\delta G_0}$$

$$=\frac{\Sigma(V-\Sigma)}{1-(V-\Sigma)G_0+\Sigma G_0}\ , \tag{34}$$

which agrees with (29). One can see this result immediately, since the diagrams of Fig. 4 (including the multiple-occupancy corrections) can be gotten by removing one internal G_0 from the Σ diagrams of Fig. 2 in all possible ways, which is just the effect of the operation $\delta\Sigma/\delta G_0$. In fact, this procedure is so simple that it is a useful tool for deriving the consistent Λ for any class of diagrams.

Finally, we note that Velicky[12] has pointed out that the contribution of the vertex corrections to the $k=0$ conductivity vanishes by crystal inversion symmetry for this simple class of diagrams with a local Λ. This result holds for the two-particle correlation functions in Eq. (5) when either C_1 or C_2 is odd under inversion and Λ is correspondingly diagonal. It will not hold for scattering by clusters of atoms or in cases such as the $k\neq 0$ response $\sigma(k,\omega)$.

IV. LOCALIZED-STATE EXPANSION – ONE-PARTICLE GREEN'S FUNCTION

The expansion in localized states for configuration-averaged alloy properties, introduced by Matsubara and Toyozawa[2] (MT) and extended by Matsubara and Kaneyoshi[9] is discussed here and modified to include self-consistent multiple-occupancy corrections. A brief clearly written outline of the MT technique is

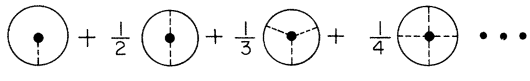

FIG. 5. Wagon-wheel free-energy diagrams multiplied by the combinatorial factors $1/n$. This class of diagrams Φ is related to the single-site self-energy Σ by $\Sigma=\delta\Phi/\delta G_0$ as in the discussion of Baym (Ref. 18).

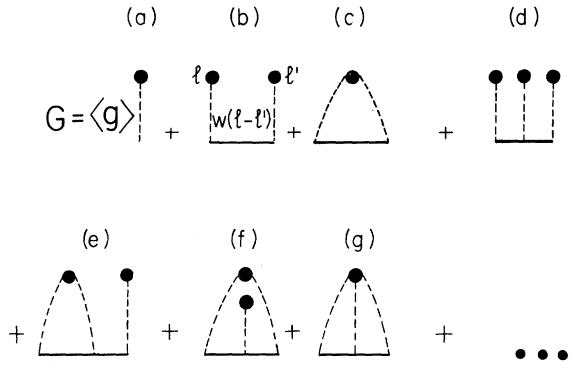

FIG. 6. Some diagrams appearing in the localized-state expansion (37) of the Green's function in terms of the hopping from site to site.

given by Ziman.[13]

The technique seems obviously inspired by the earlier expansion due to Anderson[14] who did not configurationally ensemble average, but rather studied the probability distribution within the ensemble. The Anderson expansion for a particular alloy in our notation is generated by

$$G = g + gWG \quad , \tag{35}$$

where, in the Wannier representation,

$$g(n, m) = \left(\frac{1}{\epsilon - \epsilon_n}\right)\delta_{n,m} = g_n \delta_{n,m} \quad , \tag{36}$$

which is the Green's function for localized states, with no hopping, and takes on the values $(\epsilon - \epsilon_A)^{-1}$ and $(\epsilon - \epsilon_B)^{-1}$ on A- and B-atom sites, respectively, and where $W(n-m)$ represents the hopping as defined in Eq. (1). We now iterate and configurationally average this equation of motion as before to obtain

$$\langle G(n, m)\rangle = \langle g_n\rangle\delta_{nm} + \langle g_n W(n-m) g_m\rangle + \langle \textstyle\sum_l g_n W(n-l) g_l W(l-m) g_m\rangle + \cdots \quad , \tag{37}$$

where in our model only g_n depends upon the configurations of the species. We can represent the terms in Eq. (37) by topologically the same diagrams as in Sec. II but with no external lines, as shown, for example, in Fig. 6. The transportation from site to site, the solid line, is no longer provided by the propagator g which is local but is provided by the interaction $W(n-m)$ which in this role we shall call the *interactor* as suggested by Ziman.[13] An upright dashed line corresponds here to the localized-site Green's function or resolvent g. Upon averaging, the rules become only slightly more complicated than before; a cluster of r resolvent g lines at the same site [for example, Figs. 6(c) and 6(g)] have the value $\langle (g_n)^r\rangle$. For example, the diagram in Figs. 6(a) and 6(f) have the values

$$\langle g_n\rangle = (1-c)/(\epsilon - \epsilon_A) + c/(\epsilon - \epsilon_B) \, , \tag{38}$$

and

$$\sum_m \langle g_n^2\rangle\langle g_m\rangle W^2(n-m) = \left(\frac{(1-c)}{(\epsilon-\epsilon_A)^2} + \frac{c}{(\epsilon-\epsilon_B)^2}\right)\left(\frac{1-c}{(\epsilon-\epsilon_A)} + \frac{c}{(\epsilon-\epsilon_B)}\right) \times \sum_m W^2(n-m), \tag{39}$$

respectively. Actually no diagrams like Fig. 6(c), with a diagonal interactor appear, since $W(n-m) = 0$ as there is no hopping to the same site but we can include them formally to make the calculation parallel to that in Sec. II even if their contribution is zero. The reader should note that, even for a perfect A-atom crystal, the series must be summed but in this case Eq. (37) is simply the geometric series

$$G = \frac{1}{\epsilon - \epsilon_A} + \frac{1}{(\epsilon-\epsilon_A)^2} W + \frac{1}{(\epsilon-\epsilon_A)^3} W^2 + \cdots \, , \tag{40}$$

which can be immediately summed to the standard result

$$G = (\epsilon - \epsilon_A - W)^{-1} \quad . \tag{41}$$

We can clearly define an irreducible part as we did before; the sum of all irreducible parts σ we shall call the *self-resolvent* (by analogy with the self-energy), since it represents the renormalization of the localized-state resolvent operator g. The pseudo-Dyson equation satisfied by σ is

$$\langle G\rangle = \sigma + \sigma W\langle G\rangle \quad , \tag{42}$$

so that

$$\langle G\rangle = \sigma/(1-\sigma W) = (\sigma^{-1} - W)^{-1} \quad . \tag{43}$$

The relationship between the true self-resolvent σ and the true self-energy Σ according to Eqs. (13) and (43) is

$$\sigma^{-1} = \epsilon - \epsilon_A - \Sigma \quad , \tag{44}$$

so that if Σ is local so also will be σ.

The single-site self-resolvent will then be just the same diagrams shown in the first column of Fig. 2 with the same multiple-occupancy corrections shown in the higher columns. The double internal interactor line here represents U, the fully renormalized interactor

$$U = W + W\langle G\rangle W \quad . \tag{45}$$

Then, we find for the first column of Fig. 2,

$$\sigma_{\text{bare}} = \left\langle \frac{g_n}{1 - U_0 g_n}\right\rangle = \frac{(1-c)g_A}{1 - U_0 g_A} + \frac{c g_B}{1 - U_0 g_B} \quad , \tag{46}$$

where $g_A = (\epsilon - \epsilon_A)^{-1}$ which is analogous to Eq. (14).

The sum of all columns gives, in analogy to Eq. (15), the fully corrected σ,

$$\sigma = \sigma(U_0) = \left\langle \frac{g_n}{1 - U_0 g_n} \right\rangle - \left(\frac{\sigma(\phi_0)}{1 - \sigma(\phi_0)U_0} - \sigma(U_0) \right) , \tag{47}$$

where $\phi_0 = U_0/[1 - \sigma(\phi_0)U_0]$. The solution of this equation is

$$\sigma = \left\langle \frac{g_n}{1 - U_0 g_n} \right\rangle \Big/ \left(1 + \phi_0' \left\langle \frac{g_n}{1 - \phi_0' g_n} \right\rangle \right) \tag{48}$$

or

$$\sigma = \left(\frac{(1-c)g_A}{1 - \phi_0' g_A} + \frac{c g_B}{1 - \phi_0' g_B} \right) \Big/ \left[1 + \phi_0' \left(\frac{(1-c)g_A}{1 - \phi_0' g_A} + \frac{c g_B}{1 - \phi_0' g_B} \right) \right]$$

$$= \frac{(1-c)g_A + c g_B - \phi_0' g_A g_B}{1 - [c g_A + (1-c) g_B]\phi_0'} , \tag{49}$$

where $\phi_0' = U_0/(1 + \sigma U_0)$. If we now eliminate ϕ_0' in terms of U_0, we obtain

$$\sigma = \frac{[(1-c)g_A + c g_B](1 + \sigma U_0) - U_0 g_A g_B}{(1 + \sigma U_0) - [c g_A + (1-c) g_B] U_0} , \tag{50}$$

which is analogous to Eq. (17) (it would be exactly parallel if g_A were zero). In order to see whether this equation gives the same Green's function as in Sec. II we must eliminate g_A, g_B, σ, and U_0 in terms of V, Σ, and G_0. First we pull the term containing σ in the numerator on the right-hand side of (50) over to the left-hand side, then divide by the coefficient of σ on the left, and substitute $g_{A,B} = (\epsilon - \epsilon_{A,B})^{-1}$ to obtain

$$\sigma = \frac{\epsilon - c\epsilon_A - (1-c)\epsilon_B - U_0}{(\epsilon - \epsilon_A)(\epsilon - \epsilon_B)(1 + \sigma U_0) - (2\epsilon - \epsilon_A - \epsilon_B)U_0} . \tag{51}$$

Then, according to Eqs. (42) and (45), we can make the substitution

$$U = \sigma^{-1} \langle G \rangle \sigma^{-1} - \sigma^{-1} , \tag{52a}$$

$$U_0 = \sigma^{-2} G_0 - \sigma^{-1} , \tag{52b}$$

since σ is diagonal here. Then, to find the effective Σ which corresponds to σ (i.e., gives the same $\langle G \rangle$) we substitute for σ from Eq. (44), treating (44) as the definition of Σ. After these two substitutions into (51), some algebra, and the identification $V = \epsilon_B - \epsilon_A$, we find enormous cancellations with the result

$$\Sigma = cV/[1 - (V - \Sigma)G_0] , \tag{53}$$

which is Eq. (17b) so that indeed the effective Σ calculated via the single-site localized-state expansion agrees with that from the band-state expansion and the lowest-order theorem is established. We do not know whether such a theorem holds for pair scattering or for higher clusters but it seems likely. Clearly the multiple-occupancy corrections and the self-consistency were essential in establishing this equivalence.

In Sec. V we briefly outline the calcuation of the two-particle Green's function by the localized-state expansion and show that this equivalence holds also there.

V. LOCALIZED-STATE EXPANSION – TWO-PARTICLE GREEN'S FUNCTION

The proof of the equivalence of the two approaches for the two-particle Green's function can be established quite easily and quite generally whenever the equivalence [Eq. (44)] holds for the one-particle Green's function.

We first establish the condition required for equivalence of the two approaches by defining the vertex function. Typical two-particle diagrams are shown in Fig. 7 where diagrams 7(b) and 7(c) contain irreducible vertex parts. The sum of all irreducible vertex parts we shall call γ, the vertex function which is related to the full two-particle averaged Green's function by a pseudo-Bethe-Salpeter equation

$$(W \cdot W)\langle G^{(2)} \rangle (W \cdot W) = (W \langle G \rangle W \cdot W \langle G \rangle W) + (U \cdot U)\gamma(U \cdot U)[I - \gamma(U \cdot U)]^{-1} , \tag{54}$$

where $\langle G^{(2)} \rangle$ has been multiplied on each side by $(W \cdot W)$ to add external interactor lines in each diagram, and where U is the fully renormalized interactor defined by Eq. (45). If this $\langle G^{(2)} \rangle$ is to be the same as that calculated by the iteration of Eq. (21), then we must have the formula

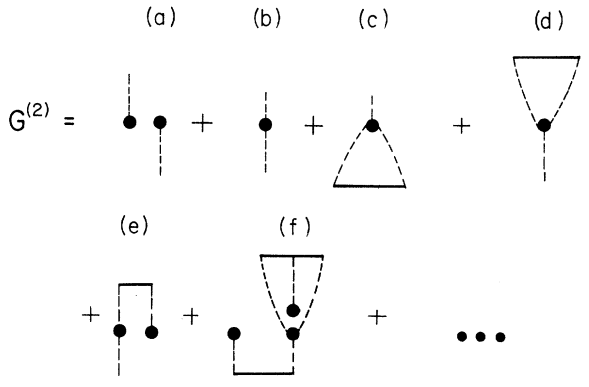

FIG. 7. Some diagrams appearing in the localized-state expansion of the two-particle Green's function $\langle GG \rangle$ in terms of the hopping from site to site.

$$(W\langle G\rangle W\cdot W\langle G\rangle W)+(U\cdot U)\gamma(U\cdot U)[I-\gamma(U\cdot U)]^{-1}$$
$$=(W\langle G\rangle W\cdot W\langle G\rangle W)[I-\Lambda(\langle G\rangle\cdot\langle G\rangle)]^{-1} \quad (55)$$

relating the two vertex functions. Using Eqs. (42) and (45), we obtain

$$U=W\langle G\rangle\sigma^{-1} \quad , \quad (56)$$

which can be used to eliminate the $(U\cdot U)$ factors in the numerator of (55) and reduce it to the identity

$$\frac{(\sigma^{-1}\cdot\sigma^{-1})\gamma(\sigma^{-1}\cdot\sigma^{-1})}{I-\gamma(U\cdot U)}=\frac{\Lambda}{I-\Lambda(\langle G\rangle\cdot\langle G\rangle)} \quad . \quad (57)$$

Upon substituting $U=\sigma^{-1}\langle G\rangle\sigma^{-1}-\sigma^{-1}$ and solving for $(\sigma\cdot\sigma)\Lambda$, we find

$$(\sigma\cdot\sigma)\Lambda=-\gamma[(\sigma^{-1}\sigma^{-1})-\sigma^{-1}\cdot(\sigma^{-1}\langle G\rangle\sigma^{-1})$$
$$-(\sigma^{-1}\langle G\rangle\sigma^{-1})\cdot\sigma^{-1}]^{-1}\gamma(\sigma^{-1}\cdot\sigma^{-1}) \quad . \quad (58)$$

But we can eliminate Λ since, by Eqs. (32) and (44), we know that

$$\Lambda=\delta\Sigma/\delta\langle G\rangle=-\delta(\sigma^{-1})/\delta\langle G\rangle=(\sigma^{-1}\cdot\sigma^{-1})\delta\sigma/\delta\langle G\rangle \quad ,$$
$$=\{I-\gamma[(\sigma^{-1}\cdot\sigma^{-1})-\sigma^{-1}\cdot(\sigma^{-1}\langle G\rangle\sigma^{-1}) \quad (59)$$
$$-(\sigma^{-1}\langle G\rangle\sigma^{-1})\cdot\sigma^{-1}]\}^{-1}$$

or

$$(\sigma\cdot\sigma)\Lambda=\delta\sigma/\delta\langle G\rangle \quad ,$$

and Eq. (58) becomes

$$\delta\sigma/\delta\langle G\rangle=\gamma\{(\sigma^{-1}\cdot\sigma^{-1})+\delta\sigma/\delta\langle G\rangle[(\sigma^{-1}\cdot\sigma^{-1})$$
$$-\sigma^{-1}\cdot(\sigma^{-1}\langle G\rangle\sigma^{-1})-(\sigma^{-1}\langle G\rangle\sigma^{-1})\cdot\sigma^{-1}]\} \quad , \quad (60a)$$

which reduces to

$$\delta\sigma/\delta\langle G\rangle=\gamma[\delta(\sigma^{-1}\langle G\rangle\sigma^{-1}-\sigma^{-1})/\delta\langle G\rangle]=\gamma\delta U/\delta\langle G\rangle \quad . \quad (60b)$$

Thus we find

$$\gamma(lm;np)=\delta\sigma(l,n)/\delta\langle U(m,p)\rangle \quad (61)$$

if the two calculations agree. But, this is just the derivative of the self-resolvent with respect to its internal interactor which clearly yields topologically just the same diagrams as those for $\Lambda=\delta\Sigma/\delta\langle G\rangle$, which in the single-site case are just those shown in Fig. 4.

This result could have been obtained slightly more elegantly by going back to Baym's paper[18] and noting that $\Lambda=\delta\Sigma/\delta\langle G\rangle$ followed from the argument that $G^{(2)}$ must be $\delta\langle G\rangle/\delta V$, where V is some external potential. That same argument here, coupled with the pseudo-Bethe-Salpeter equation (54), gives Eq. (61) rather easily.

In summary, we have shown here that if the Ward identity is satisfied and if the same diagrams are included self-consistently in σ and γ as in Σ and Λ then the two techniques give the same two-particle Green's function. It is, perhaps, worth pointing out that, in the single-site irreducible scattering, both Λ and γ are completely diagonal on all four indices and Eq. (57) relating them becomes the scalar equation

$$\sigma^{-4}\gamma/(1-\gamma U_0^2)=\Lambda/(1-\Lambda G_0^2) \quad . \quad (62)$$

VI. DISCUSSION

We have explicitly demonstrated that the two techniques of expanding in localized and Bloch states agree for the case of spin-independent single-site scatterings, the first term in the cluster expansion. We conjecture, however, that the theorem holds for any order in the cluster expansion providing the calculation is made with a self-consistent field and multiple-occupancy corrections are made self-consistently. Clearly both the self-consistent-field and the multiple-occupancy corrections were essential to obtaining the present result.

Basically the calculation in Secs. IV and V differs from that of Matsubara and Kaneyoshi[9] in that the cluster expansion developed here was not the usual one with the full cumulants or semi-invariants but one with self-consistently evaluated partial cumulants as discussed in Ref. 7. This self-consistent technique was developed originally for the band-state expansion to remove spurious and serious divergences that resulted from the overcorrections implicit in the cumulant technique. A detailed discussion of these divergences is given by Leath and Goodman.[19] In the localized-state expansion, similar divergences must occur since the series is formally the same, thus the same technique was used here.

The formulas developed here are clearly valid in both the virtual crystal (weak impurity scattering) and the atomic (weak hopping) limits and thus form interpolation formulas between the two extremes. This feature has been pointed out by Onodera and Toyozawa,[8] Velický *et al.*,[20] and more recently by Ziman.[13] Also, these equations form interpolation formulas over the entire range of concentrations of the atomic species.[3,4]

It is also probably worth pointing out that not only Ziman's speculations concerning the advantage of expanding in localized states is apparently wrong, but also his reason is wrong because a crucial error was made in his calculation of the "medium-propagator approximation." This error has to do with multiple-occupancy corrections which are not taken into account properly by his Eq. (39). The correct result, as one can easily see from Eq. (17a) above, is obtained by replacing G^m by $G^m/(1+\bar{v}'G^m)$, in his Eq. (39). This would make his Eq. (50) become

$$\bar{v}'(E)=\frac{\frac{1}{4}W^2G^m(E)}{4c(1-c)-(1-2c)WG^m(E)+4c(1-c)\bar{v}'(E)G^m(E)}. \tag{63}$$

The extra term $4c(1-c)\bar{v}'(E)G^m(E)$ is crucial and gives a splitting of the energy bands in a 50-50 alloy whenever $W>\frac{1}{2}B$, in Ziman's notation. This result also is easily obtained via the coherent-potential approximation from Ziman's Eq. (39) by replacing w_l by $(w_l-\bar{v}')$ and setting $\bar{t}'=0$. Thus, the correct conclusion from this calculation should be that, compared to the Anderson localization criterion as discussed by Ziman, the medium propagator method produces split bands too easily (rather than not at all) since it does not exhibit impurity band tails. Perhaps this feature can be corrected by considering other classes of diagrams. Clearly, the single-site scattering (or the coherent-potential approximation) is a kind of molecular field theory which might not be expected to predict details near the transition from localized to band states properly.

It is also possible that the source of the difficulty is in calculating the configuration-averaged Green's function itself. Clearly, experiments are done on a single sample, not an ensemble of crystals. If, however, the Green's function dies out fast enough with distance, the energy levels in one part of the sample might not be sensitive to the configuration of impurities at a distance so that a single sample would become effectively a loosely coupled ensemble of samples and the ensemble average would be justified. The answer depends upon how fast is fast enough for the decay of the Green's function. The ensemble average can be viewed as a coarse-grain average of the Green's function or density of states which gives a small width to each state (at least this interpretation has been shown to be valid for one-dimensionsl system by Matsuda[16]). For measurements of the density of states, or for typical computer histograms in the literature, there is an experimental resolution width which, if larger than the coarse-graining width (it is for the case considered by Matsuda), makes these techniques insensitive to whether the states are localized (but very close together in energy) or whether they have merged to form a conducting band. In these cases the configuration-averaged Green's function is a quite useful concept as borne out, for example, in the phonon density-of-state calculations of Taylor for three-dimensional systems.

Near the critical percolation concentration, however, conductivity measurements are quite sensitive to whether, e.g., electrical shorts have developed through the system and hence to the details of whether the states are localized or overlapping. If one wants to learn more precisely about the nature of the transport transition, it would seem that one might have to abandon the average value of the terms in the series and look in detail at the distribution of values of the terms as Anderson has suggested.[14] Since the present theorem as presented here relied on the configuration average, it would be of interest to see if such a theorem exists in general for the terms in the series.

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