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Abstract. By means of a new family of Ward identities, we obtain expressions for two-particle Green functions for electrons in random alloys with off-diagonal disorder, including the case of short-range order. The Ward identities are expressed in a formalism in which the configuration averages are only partially carried out, and the disorder field is represented by conditional probabilities of all orders. In the test case of a cubic, tight-binding nearest-neighbour binary alloy, and by numerical differentiation of the one-particle CPA-type Green function, we find that the approximation in which the vertex corrections are neglected is considerably in error.

1. Introduction

As is well known, there are many interesting properties of a solid which cannot be calculated solely from the knowledge of its one-particle Green function. This is the case, for instance, for the DC electrical conductivity of an alloy (Langer 1960), even if one neglects the effects of other complications such as those arising from the randomness of the current operator (Niizeki 1977, Mookerjee *et al* 1985).

Proceeding from the Kubo formula, it is seen that the electrical conductivity is given by a number of terms, some of which can be calculated from the one-particle Green function by means of Ward–Velický identities (Ward 1950, Velický 1969). The remnant terms cannot be obtained in this way, and one has to resort to the methods of perturbation theory—by setting up and approximately solving, for instance, an equation of the Bethe–Salpeter type (Langer 1961, Glasser 1963). Unfortunately it turns out, at least in the case of the impurity resistance in metals, that the former class of terms do not contribute in leading order. Thus, the terms that are easy to calculate turn out to be practically irrelevant in this case (Langer 1960).

Another interesting problem whose solution requires at least the knowledge of the average two-particle Green function is that of the localization of electronic states in solids as a function of dimensionality and degree of disorder. For instance, Chitanvis and Leath (1982, 1983) investigated the conjecture that two is the critical dimension for localization produced even by weak disorder. For this purpose, these authors calculated the vertex function using the coherent potential approximation, a Bethe–Saltpeter equation summing all the maximally crossed diagrams, and a generalization of the travelling-cluster approximation. Furthermore, they used the satisfaction of the Ward–Velický identities as a test of validity in these approximate schemes .

These useful Ward–Velický identities can be simply proven. As is well known, the one-particle Green function $G(\mathcal{E})$ is given by

$$G(\mathcal{E}) = \frac{1}{\mathcal{E} - H} \tag{1}$$

where $\mathcal{E}$ is a complex energy parameter and H is the Hamiltonian of the system. Thus, if $\langle \cdots \rangle$ denotes the configuration average, one readily finds that

$$\langle G(\mathcal{E}_1) \rangle - \langle G(\mathcal{E}_2) \rangle = -(\mathcal{E}_1 - \mathcal{E}_2)\langle G(\mathcal{E}_1)G(\mathcal{E}_2) \rangle \tag{2}$$

and in particular,

$$-\frac{\partial \langle G(\mathcal{E}) \rangle}{\partial \mathcal{E}} = \langle G(\mathcal{E})^2 \rangle. \tag{3}$$

In this paper we introduce another class of Ward identities in which the many-particle Green functions are calculated in terms of derivatives with respect to the perturbation instead of the complex energy. Thus, this approach is similar to that of Baym (Baym and Kadanoff 1961, Baym 1962). Another difference with the usual procedure is that these new identities are expressible only in terms of partially averaged quantities with the full configuration average to be performed at the end of the calculation. In the rest of this paper we employ these identities in two different ways. First, we derive a number of formulae of the Bethe–Salpeter type for the two-particle Green function of an electron in a random alloy with off-diagonal disorder, including the case of short-range order. In principle these forms are, of course, equivalent. But they need not be equally useful in a given perturbative computation and thus it is convenient to have a method which systematically generates all of them. On the other hand, in a calculation of a model tight-binding binary alloy, we use these Ward identities directly as a means of generating the two-particle Green function by numerical differentiation of the one-particle Green function. One can then compare these exact values with those obtained in the (frequently made) approximation in which the vertex corrections are neglected.

2. The one-particle Green function

In this paper we use a simple model, closely related to the tight-binding approximation as applied to the description of a random substitutional alloy with chemical species A, B, C, ..., etc. This model has the advantage of being completely tractable, of having been widely used in a number of theoretical discussions, and of not being wholly unrealistic. The model consists of a crystal in which the electrons can be described by a single Wannier orbital associated with each site. The diagonal part $\mathcal{E}_n$ equals $\mathcal{E}_A$, $\mathcal{E}_B$, $\mathcal{E}_C$, ..., etc, while the off-diagonal part consists of matrix elements $W_{n,m}$, having values $W_{n,m}^{A,A}$, $W_{n,m}^{A,B} = W_{n,m}^{B,A}$, ..., etc, depending on the distance between the sites with indices n and m, and on the nature of the atomic species occupying each position. We do not assume that this interaction is of the nearest-neighbour type. Explicitly, the Hamiltonian is

$$H = \sum_n |n\rangle \mathcal{E}_n \langle n| + \sum_{n \neq m} |n\rangle W_{n,m} \langle m|. \tag{4}$$

If we denote by $g_{n,m}(\mathcal{E}) = g_n(\mathcal{E})\delta_{n,m}$ the Green function for a localized state with no hopping, depending on the energy $\mathcal{E}$ and on the type of atom situated at n, we have for the Green function $G_{n,m}(\mathcal{E})$ for a given alloy

$$G_{n,m} = g_n\delta_{n,m} + g_n W_{n,m} g_m + \sum_l g_n W_{n,l} g_l W_{l,m} g_m$$

$$+ \sum_{l,l'} g_n W_{n,l} g_l W_{l,l'} g_{l'} W_{l',m} g_m + \cdots . \tag{5}$$

Of course in practice one does not know which atomic species occupies each site, but only certain statistical properties of the alloy, such as the concentrations c_α of the species ($\alpha = A, B \ldots$), the range of the order etc. Correspondingly, we calculate quantities which are averages computed over assemblies of such alloys, characterized by a suitable number of statistical parameters.

For convenience, we perform this average in two stages. If we first represent any given alloy by a function s which assigns to each site n an atom of species $s(n)$, and denote by $P[s]$ the probability with which the alloy appears in the assembly, we can define the average Green function $G_{n,m}^{\alpha,\beta} = \langle G_{n,m}\rangle_{\alpha,\beta}$ by

$$G_{n,m}^{\alpha,\beta} = \frac{1}{c_\alpha}\sum_s G_{n,m}[s]\delta_{s(n),\alpha}\delta_{s(m),\beta}P[s]. \tag{6}$$

From (5) we have that (Rössler and Lazo 1981)

$$G_{n,m}^{\alpha,\beta} = g_\alpha\delta_{n,m}^{\alpha,\beta} + g_\alpha W_{n,m}^{\alpha,\beta} g_\beta P_{n,m}^{\alpha,\beta} + \sum_{l,\gamma} g_\alpha W_{n,l}^{\alpha,\gamma} g_\gamma W_{l,m}^{\gamma,\beta} g_\beta P_{n,l,m}^{\alpha,\gamma,\beta}$$

$$+ \sum_{l,l',\gamma,\gamma'} g_\alpha W_{n,l}^{\alpha,\gamma} g_\gamma W_{l,l'}^{\gamma,\gamma'} g_{\gamma'} W_{l',m}^{\gamma',\beta} g_\beta P_{n,l,l',m}^{\alpha,\gamma,\gamma',\beta} + \cdots \tag{7}$$

where $P_{n,m}^{\alpha,\beta}$, $P_{n,m,l}^{\alpha,\beta,\gamma}$, ... , etc. are the *conditional probabilities*

$$P_{n,m}^{\alpha,\beta} = \frac{1}{c_\alpha}\sum_s \delta_{s(n),\alpha}\delta_{s(m),\beta}P[s] \tag{8}$$

$$P_{n,m,l}^{\alpha,\beta,\gamma} = \frac{1}{c_\alpha}\sum_s \delta_{s(n),\alpha}\delta_{s(m),\beta}\delta_{s(l),\gamma}P[s] \tag{9}$$

and so on. Here the symbol $\delta_{s(n),A}$ is equal to one if the site n is occupied by an atom of species A, and is zero otherwise. Also

$$\delta_{a,b}^{\alpha,\beta} \equiv \delta_{\alpha,\beta}\delta_{a,b}.$$

We note that the statistical parameters which characterize the assembly in this schema are these conditional probabilities and the concentrations

$$c_\alpha = \sum_s \delta_{s(n),\alpha}P[s].$$

Most of the calculations in the present theory are performed on these partially averaged quantities. It seems also that the interesting results can only be expressed in terms of variables of this type. This is certainly the case of the Ward-type identities which connect one- to two-particle Green functions. This situation is reminiscent of what happens in the so-called augmented-space formalism (Mookerjee 1973a,b, 1975, Kaplan and Gray 1976, 1977, 1978, Diehl and Leath 1979a,b, Diehl, Leath and Kaplan 1979, Kaplan *et al* 1980, Chitanvis and Leath 1983) except that the variables describing the chemical species at each site, and thus the disorder field, appear here in a natural manner. We note that Gray and Kaplan included the case of short-range order in the augmented-space formalism and described the disorder field precisely in this way.

However, these quantities have to be fully averaged before they are compared with experiment. We have, for instance that the *fully averaged* Green function is

$$\bar{G}_{n,m} \equiv \sum_{\alpha,\beta} c_\alpha G^{\alpha,\beta}_{n,m} = \sum_s G_{n,m} P[s] \tag{10}$$

as is easily checked.

The form of the propagator (7) is particularly convenient for perturbation theory. We can represent the terms appearing in this expansion by essentially the same diagrams as those employed by Leath (1970). If we denote by σ the sum of all irreducible diagrams, we find that the Green function (7) satisfies the *pseudo-Dyson* equation

$$G^{\alpha,\beta}_{a,b} = \sigma^{\alpha,\beta}_{a,b} + \sum_{c,c',\gamma,\gamma'} \sigma^{\alpha,\gamma'}_{a,c} W^{\gamma,\gamma'}_{c,c'} G^{\gamma',\beta}_{c',b}.$$

In order to proceed further, one has to specify the form of the conditional probabilities appearing in (7). The simplest schema consists in assuming a uniform distribution of the atom composing the alloy. This problem has been solved by Leath (1968, 1970) in a particularly elegant form. (We note however that Leath did not treat, as we do here, the case of off-diagonal disorder.) In the framework of the present paper, Leath's procedure can be described as follows: one defines first the dressed interaction

$$\bar{W}^{\alpha,\beta}_{a,b} = \sum_{\gamma,c} v^{\alpha,\gamma}_{a,c} W^{\gamma,\beta}_{c,b} \tag{12}$$

with

$$v^{\alpha,\beta}_{a,b} = \delta^{\alpha,\beta}_{a,b} + \sum_{\gamma,c} W^{\alpha,\gamma}_{a,c} G^{\gamma,\beta}_{c,b}. \tag{13}$$

Of particular importance in this treatment is the dressed interaction of each site with itself. This quantity (which obviously does not depend on the particular site envisaged) will be denoted by $\bar{W}^{\alpha,\beta}_0$. Leath has shown that, within the limits of the coherent-potential approximation (CPA), the self-resolvent σ is a functional of $\bar{W}$, diagonal in the site representation. Thus, all quantities are matrices in the space of the chemical species (2×2 matrices for a binary alloy, 3×3 for a ternary alloy etc.).

It is particularly convenient to employ matrix notation in this space. Thus, Leath's result can be written

$$\sigma(\bar{W}) = [1 + \sigma_0(X)X]^{-1}\sigma_0(X) \tag{14}$$

where

$$\sigma_0^{\alpha,\beta}(X) = \frac{g_\alpha \delta_{\alpha,\beta}}{1 - g_\alpha X_0^{\alpha,\alpha}} \tag{15}$$

and

$$X(\bar{W}) = [1 + \bar{W}_0\sigma(\bar{W})]^{-1}\bar{W}_0. \tag{16}$$

An interesting generalization of this theory, also capable of describing the effects of short-range order, was developed by Rössler and Lazo (1981). By means of a generalized superposition approximation, which however gives a correct account of the effects of self-correlation, they were able to write all conditional probabilities as certain functions of the atomic concentrations and the spatial correlations, or Cowley parameters (Cowley 1950).

We shall proceed here by a different method to that used by Rössler and Lazo. We note that the perturbative series (7) can be summed in this case by a straightforward extension of Leath's formalism. First of all (in the notation of the present paper), the pseudo-Dyson equation (11) is written as

$$G_{a,b}^{\alpha,\beta} = \sigma_{a,b}^{\alpha,\beta} + \sum_{c,c',\gamma,\gamma'} \sigma_{a,c}^{\alpha,\gamma'} U_{c,c'}^{\gamma,\gamma'} G_{c',b}^{\gamma',\beta} \tag{17}$$

where the weighted interaction U is defined by

$$U_{a,b}^{\alpha,\beta} \equiv W_{a,b} p_{a,b}^{\alpha,\beta} \tag{18}$$

(no sum over repeated indices is implied) and where $p_{a,b}^{\alpha,\beta}$ is the conditional probability that, given that an atom of species α occupies the site a, another atom of species β occupies (a different) site b. In the case of a binary alloy with concentrations c_A and c_B and Cowley parameter $\gamma_{n,m}$, for instance, one has that

$$
\begin{aligned}
p_{n,m}^{A,A} &= c_A + \gamma_{n,m} c_B & p_{n,m}^{B,B} &= c_B + \gamma_{n,m} c_A \\
p_{n,m}^{A,B} &= c_B(1 - \gamma_{n,m}) & p_{n,m}^{B,A} &= c_A(1 - \gamma_{n,m}).
\end{aligned} \tag{19}
$$

These interactions are renormalized according to

$$\bar{W}_{a,b}^{\alpha,\beta} \equiv \sum_{\gamma,c} V_{a,c}^{\alpha,\gamma} W_{c,b}^{\gamma,\beta} \tag{20}$$

$$\bar{U}_{a,b}^{\alpha,\beta} \equiv \sum_{\gamma,c} V_{a,c}^{\alpha,\gamma} U_{c,b}^{\gamma,\beta} \tag{21}$$

with

$$V_{a,b}^{\alpha,\beta} = \delta_{a,b}^{\alpha,\beta} + \sum_{\gamma,c} U_{a,c}^{\alpha,\gamma} G_{c,b}^{\gamma,\beta} \tag{22}$$

instead of (13). We find here also that (in a straightforward generalization of CPA), σ is diagonal in the site indices and a functional of $\bar{W}_0$ and $\bar{U}_0$ given by

$$\sigma(\bar{W},\bar{U}) = [1 + \sigma_0(X)Y]^{-1}\sigma_0(Y) \tag{23}$$

with

$$X(\bar{W},\bar{U}) = [1 - Y\sigma(\bar{W},\bar{U})]\bar{W}_0 \tag{24}$$

$$Y(\bar{W},\bar{U}) = \bar{U}_0[1 + \sigma(\bar{W},\bar{U})\bar{U}_0]^{-1} \tag{25}$$

and where σ_0 is still given by (15).

3. The two-particle Green function

It is well known that, if one wants to calculate particle densities or particle currents for instance, it is not enough to know the one-particle propagator (5). Rather, one requires the two-particle Green function

$$
\begin{aligned}
G_{a,b,m,n}^{\alpha,\beta,\mu,\nu} &\equiv \langle G_{a,b} G_{m,n}\rangle_{\alpha,\beta,\mu,\nu} \\
&= g_\alpha g_\mu \delta_{a,b}^{\alpha,\beta} \delta_{m,n}^{\mu,\nu} P_{a,m}^{\alpha,\mu} + g_\alpha W_{a,b}^{\alpha,\beta} g_\beta g_\mu \delta_{m,n}^{\mu,\nu} P_{a,b,m}^{\alpha,\beta,\mu} \\
&\quad + g_\alpha \delta_{a,b}^{\alpha,\beta} g_\mu W_{m,n}^{\mu,\nu} g_\nu P_{a,m,n}^{\alpha,\mu,\nu} \\
&\quad + \sum_{\gamma,c} g_\alpha W_{a,c}^{\alpha,\gamma} g_\gamma W_{c,b}^{\gamma,\beta} g_\beta g_\mu \delta_{m,n}^{\mu,\nu} P_{a,c,b,m}^{\alpha,\gamma,\beta,\mu} \\
&\quad + g_\alpha W_{a,b}^{\alpha,\beta} g_\beta g_\mu W_{m,n}^{\mu,\nu} g_\nu P_{a,b,m,n}^{\alpha,\beta,\mu,\nu} \\
&\quad + \sum_{\lambda,l} g_\alpha \delta_{a,b}^{\alpha,\beta} g_\mu W_{m,l}^{\mu,\lambda} g_\lambda W_{l,n}^{\lambda,\nu} g_\nu P_{a,m,l,n}^{\alpha,\mu,\lambda,\nu} + \cdots
\end{aligned}
\tag{26}
$$

by the same arguments used to obtain (7).

It is possible to sum this perturbative series using the usual methods of diagrammatic analysis. But, as noted by Leath (1970), it is simpler to proceed as follows. We begin with the remarkable identity

$$G_{a,b,n,m}^{\alpha,\beta,\mu,\nu}(\mathcal{E}) = \frac{\partial G_{a,n}^{\alpha,\nu}(\mathcal{E})}{\partial W_{b,m}^{\beta,\mu}}. \tag{27}$$

This equation, although expected on general grounds (Baym 1962), can be established in the present case by direct term-by-term differentiation of equation (7). Unfortunately (as is also easily checked out), this procedure does not generalize to the calculation of the n-particle Green function for $n > 2$.

We note, further, a number of theoretical relationships which are consequences of (27)—we analyse only the case in which short-range order is possible, (Rössler and Lazo 1981), as the complete random alloy (Leath 1968, 1970) can be deduced from it as a special case. By differentiating the two sides of (17), one has that

$$G_{a,b,n,m}^{\alpha,\beta,\mu,\nu}(\mathcal{E}) = G_{a,b}^{\alpha,\beta}(\mathcal{E})p_{b,m}^{\beta,\mu} G_{m,n}^{\mu,\nu}(\mathcal{E}) + \sum_{\gamma,\gamma',c,c'} V_{a,c}^{T\alpha,\gamma}(\mathcal{E}) S_{c,b,m,c'}^{\gamma,\beta,\mu,\gamma'}(\mathcal{E}) V_{c',n}^{\gamma',\nu}(\mathcal{E}) \tag{28}$$

where V is given by (22), V^T is defined by

$$V^{T\alpha,\beta}_{a,b} = \delta^{\alpha,\beta}_{a,b} + \sum_{\gamma,c} G^{\alpha,\gamma}_{a,c} U^{\gamma,\beta}_{c,b} \tag{29}$$

and

$$S^{\alpha,\beta,\mu,\nu}_{a,b,m,n} = \frac{\partial \sigma^{\alpha,\nu}_{a,n}}{\partial W^{\beta,\mu}_{b,m}}. \tag{30}$$

As a consequence of (23) and (30), we find that S is a function of the renormalized interactions $\bar{W}$ and $\bar{U}$ (defined in (20) and (21)) and their derivatives with respect to the bare interaction $\bar{W}_2 \equiv \partial \bar{W}/\partial W$ and $\bar{U}_2 \equiv \partial \bar{U}/\partial W$. Thus

$$\begin{aligned} S(\bar{W},\bar{W}_2,\bar{U},\bar{U}_2) &= \sigma(\bar{W},\bar{U})\bar{U}_2\sigma(\bar{W},\bar{U}) \\ &\quad + [1 - \sigma(\bar{W},\bar{U})Y]^{-1}s_0(X,X_2)[1 - Y\sigma(\bar{W},\bar{U})]^{-1} \end{aligned} \tag{31}$$

$$s^{\alpha,\beta,\mu,\nu}_{0a,b,m,n}(\bar{W},\bar{W}_2) = \delta^{\alpha,\nu}_{a,n}g^2_\alpha(1 - g_\alpha \bar{W}^{\alpha,\alpha}_0)^{-2}\bar{W}_2{}^{\alpha,\beta,\mu,\nu}_{a,b,m,n} \tag{32}$$

$$\bar{W}_2 = [1 - Y\sigma(\bar{W},\bar{U})]^{-1}\{X_2 + [Y_2\sigma(\bar{W},\bar{U}) + YS(\bar{W},\bar{W}_2,\bar{U},\bar{U}_2)]\bar{W}\} \tag{33}$$

$$\bar{U}_2 = [1 - Y\sigma(\bar{W},\bar{U})]^{-1}\{Y_2 + [Y_2\sigma(\bar{W},\bar{U}) + YS(\bar{W},\bar{W}_2,\bar{U},\bar{U}_2)]\bar{U}\} \tag{34}$$

and

$$X = [1 - Y\sigma(\bar{W},\bar{U})]\bar{W}_2 - [Y_2\sigma(\bar{W},\bar{U}) + YS(\bar{W},\bar{W}_2,\bar{U},\bar{U}_2)]\bar{W} \tag{35}$$

$$Y = [1 - Y\sigma(\bar{W},\bar{U})]\bar{U}_2 - [Y_2\sigma(\bar{W},\bar{U}) + YS(\bar{W},\bar{W}_2,\bar{U},\bar{U}_2)]\bar{U}. \tag{36}$$

Again, this highly non-linear set of equations determine the function S and thus, the two-particle Green function $G^{\alpha,\beta,\mu,\nu}_{a,b,n,m}$, by (28). Needless to say, all quantities appearing in equations (30)–(35) should be evaluated at the same energy $\mathcal{E}$.

There is an alternative formulation. By differentiating again both sides of (17) with respect to W, or by rearranging equation (28), one finds that

$$G^{\alpha,\beta,\mu,\nu}_{a,b,n,m}(\mathcal{E}) = G^{\alpha,\beta}_{a,b}(\mathcal{E})p^{\beta,\mu}_{b,m}G^{\mu,\nu}_{m,n}(\mathcal{E}) + \sum_{\gamma,\lambda,c,l} G^{\alpha,\gamma}_{a,c}(\mathcal{E})K^{\gamma,\beta,\mu,\lambda}_{c,b,m,l}(\mathcal{E})G^{\lambda,\nu}_{l,n}(\mathcal{E}) \tag{37}$$

where

$$K^{\alpha,\beta,\mu,\nu}_{a,b,m,n}(\mathcal{E}) = -\frac{\partial [\sigma^{-1}]^{\alpha,\nu}_{a,n}}{\partial W^{\beta,\mu}_{b,m}}. \tag{38}$$

Proceeding from equation (31), one can find an explicit formula for the vertex correction K. In a third formulation, we can take as our starting point the pseudo Bethe–Salpeter equation

$$\begin{aligned} G^{\alpha,\beta,\mu,\nu}_{a,b,n,m}(\mathcal{E}) &= G^{\alpha,\beta}_{a,b}(\mathcal{E})p^{\beta,\mu}_{b,m}G^{\mu,\nu}_{m,n}(\mathcal{E}) \\ &\quad + \sum_{\gamma,\lambda,\sigma,\tau,c,l,s,t} G^{\alpha,\gamma}_{a,c}(\mathcal{E})\Lambda^{\gamma,\sigma,\tau,\lambda}_{c,s,t,l}(\mathcal{E})G^{\sigma,\beta,\mu,\tau}_{s,b,m,t}(\mathcal{E})G^{\lambda,\nu}_{l,n}(\mathcal{E}) \end{aligned} \tag{39}$$

(differing somewhat in structure with the corresponding expression of Leath (1970), equation (54)). Here

$$\Lambda_{a,b,m,n}^{\alpha,\beta,\mu,\nu}(\mathcal{E}) = -\frac{\partial[\sigma^{-1}(\mathcal{E})]_{a,n}^{\alpha,\nu}}{\partial G_{b,m}^{\beta,\mu}(\mathcal{E})}. \tag{40}$$

which is perhaps more closely related to Baym's version of the Ward identities than our starting formula (27).

In practice, one can dispense with solving the complicate set (30)–(36) or their analogous equations (37) and (39). One can instead solve the much simpler set (23)–(25) and then obtain the two-particle Green function by numerical differentiation according to equation (27).

4. The vertex corrections

The non-linear set of equations (15) and (23)–(25) was numerically solved for a number of values of the hopping matrix elements and the Cowley parameter, in the special case of a hypothetical tight-binding cubic binary alloy. (The tight-binding case implies, of course, a profound simplification of the calculations as shown by Rössler and Lazo 1981). By means of an eight-point differentiation formula (Abramowitz and Stegun 1965), and according to equation (27), the two-particle Green function was directly computed from the corresponding one-particle function.

It is interesting to compare these results with those obtained when the vertex corrections are neglected, that is (by equation (28))

$$G_{a,b,n,m}^{\alpha,\beta,\mu,\nu} \simeq G_{a,b}^{\alpha,\beta} P_{b,m}^{\beta,\mu} G_{m,n}^{\mu,\nu}$$

a simplification which is often made without apology. We note that, in any case, a number of resemblances between the exact and the approximate Green function are bound to appear. First, its support i.e. the interval in energy in which the function is different from zero, would have to be accurately described by the approximation. Furthermore, both the exact and the approximate functions have to reflect the natural symmetries of the problem. Lastly, the number—and to some extent, the nature—of the van Hove singularities of the exact and the approximate spectra would have to appear in close correspondence. Also, these resemblances are more visible in a model calculation (such as the present one) than in a more realistic theory, because the additional detail which differentiates the exact from the approximate spectra is absent here.

Real and imaginary values of the exact and approximate two-particle Green functions are compared in figures 1 and 2, respectively, for a typical case (a 50–50 binary alloy with $W_{AB} = 0.5$ and $\gamma = -0.2$). Similar results are found for other concentrations and values of the hopping matrix elements. It is seen that—even if the expected similarities between the Green functions containing and neglecting the vertex corrections are readily apparent—these two are, in fact, nearly as different as they could be. First, the approximation and the exact functions seem to be mirror images of each other about the energy axis. Besides (although this may not be immediately clear from the figures, because the curves are not drawn to the same scale), the values of the approximate two-particle Green function are smaller in absolute value than the exact one by a factor of about 10.
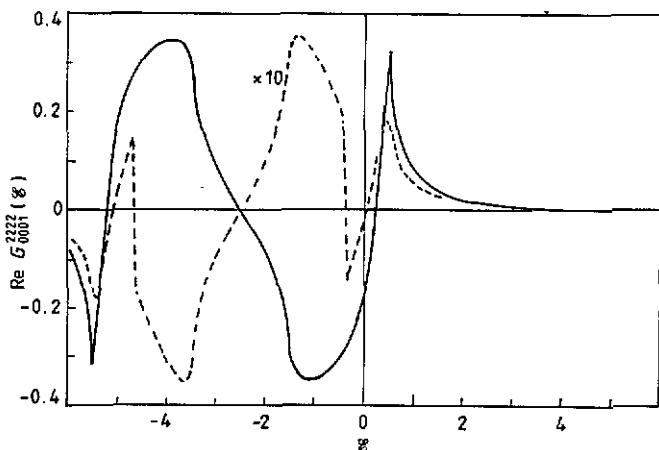
Figure 1. Values of the real part of the two-particle Green function (full curve) in a 50–50 binary alloy with the diagonal part of $W = 0.5$ and $\gamma = -0.2$, compared with $10\times$ the approximation which neglects the vertex correction for the same case (dashed curve).

Figure 2. Values of the imaginary part of the two-particle Green function (full curve) in a 50–50 binary alloy with the diagonal part of $W = 0.5$ and $\gamma = -0.2$, compared with $10\times$ the approximation which neglects the vertex correction for the same case (dashed curve).
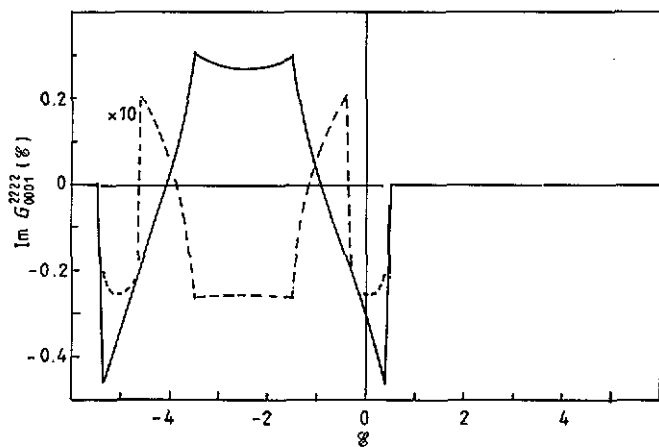
5. The two-point Green function

As is well known (Langer 1960, 1961, Glasser 1963), the Green function required for a rigorous calculation of the electrical conductivity of the random alloy is

$$\mathcal{G}^{\alpha,\beta,\mu,\nu}_{a,b,m,n}(\mathcal{E},\mathcal{E}') \equiv \langle G^{\alpha\beta}_{ab}(\mathcal{E}) G^{\mu\nu}_{mn}(\mathcal{E}') \rangle. \tag{41}$$

In the rest of this section we shall generalize the technique found previously in order to compute this two-particle, two-energy Green function too by means of a Ward-like

identity. In terms of the conditional probabilities of all orders one has, as in (26),

$$
\begin{aligned}
\mathcal{G}_{a,b,n,m}^{\alpha,\beta,\mu,\nu}(\mathcal{E},\mathcal{E}') &= g_\alpha(\mathcal{E})g_\mu(\mathcal{E}')\delta_{a,b}^{\alpha,\beta}\delta_{m,n}^{\mu,\nu}P_{a,m}^{\alpha,\mu} \\
&\quad + g_\alpha(\mathcal{E})W_{a,b}^{\alpha,\beta}g_\beta(\mathcal{E})g_\mu(\mathcal{E}')\delta_{m,n}^{\mu,\nu}P_{a,b,m}^{\alpha,\beta,\mu} \\
&\quad + g_\alpha(\mathcal{E})\delta_{a,b}^{\alpha,\beta}g_\mu(\mathcal{E}')W_{m,n}^{\mu,\nu}g_\nu(\mathcal{E}')P_{a,m,n}^{\alpha,\mu,\nu} \\
&\quad + \sum_{\gamma,c} g_\alpha(\mathcal{E})W_{a,c}^{\alpha;\gamma}g_\gamma(\mathcal{E})W_{c,b}^{\gamma;\beta}g_\beta(\mathcal{E})g_\mu(\mathcal{E}')P_{a,c,b,m}^{\alpha,\gamma,\beta,\mu} \\
&\quad + g_\alpha(\mathcal{E})W_{a,b}^{\alpha;\beta}g_\beta(\mathcal{E})g_\mu(\mathcal{E}')W_{m,n}^{\mu,\nu}g_\nu(\mathcal{E}')P_{a,b,m,n}^{\alpha,\beta,\mu,\nu} \\
&\quad + \sum_{\lambda,l} g_\alpha(\mathcal{E})\delta_{a,b}^{\alpha,\beta}g_\mu(\mathcal{E}')W_{m,l}g_\lambda(\mathcal{E}')W_{l,n}^{\lambda,\nu}g_\nu P_{a,m,l,n}^{\alpha,\mu,\lambda,\nu} + \cdots .
\end{aligned}
\tag{42}
$$

Obviously, the calculation of this quantity by means of perturbation-theoretical methods does not appear to be easy. One can, alternatively, proceed as follows. Let us first introduce generalized hopping matrix elements $W_{a,b}^{\alpha;\beta}(\mathcal{E},\mathcal{E}')$, which are non-local in energy. Next, let us *define* a new function $H_{a,b}^{\alpha,\beta}(\mathcal{E},\mathcal{E}')$ analogous to equation (26)

$$
\begin{aligned}
H_{a,b}^{\alpha,\beta}(\mathcal{E},\mathcal{E}') &= g_\alpha(\mathcal{E})\delta(\mathcal{E}-\mathcal{E}')\delta_{a,b}^{\alpha,\beta} + g_\alpha(\mathcal{E})W_{a,b}^{\alpha,\beta}(\mathcal{E},\mathcal{E}')g_\beta(\mathcal{E}')P_{a,b}^{\alpha,\beta} \\
&\quad + \sum_{c,\gamma} \int_{-\infty}^{\infty} d\mathcal{E}''\, g_\alpha(\mathcal{E})W_{a,c}^{\alpha;\gamma}(\mathcal{E},\mathcal{E}'')g_\gamma(\mathcal{E}'')W_{c,b}^{\gamma;\beta}(\mathcal{E}'',\mathcal{E}')g_\beta(\mathcal{E}')P_{a,c,b}^{\alpha,\gamma,\beta} \\
&\quad + \sum_{c,c',\gamma,\gamma'} \int_{-\infty}^{\infty} d\mathcal{E}'' \int_{-\infty}^{\infty} d\mathcal{E}'''\, g_\alpha(\mathcal{E})W_{a,c}^{\alpha;\gamma}(\mathcal{E},\mathcal{E}'')g_\gamma(\mathcal{E}'')W_{c,c'}^{\gamma;\gamma'}(\mathcal{E}'',\mathcal{E}''') \\
&\quad \times g_{\gamma'}(\mathcal{E}''')W_{c',b}^{\gamma';\beta}(\mathcal{E}''',\mathcal{E}')g_\beta(\mathcal{E}')P_{a,c,c',b}^{\alpha,\gamma,\gamma',\beta} + \cdots .
\end{aligned}
\tag{43}
$$

At the end of this section we shall discuss how this function can be computed in practice. In the meantime, let us note first that if we take

$$
W_{a,b}^{\alpha;\beta}(\mathcal{E},\mathcal{E}') = \delta(\mathcal{E}-\mathcal{E}')W_{a,b}^{\alpha,\beta}
\tag{44}
$$

where $W_{a,b}^{\alpha,\beta}$ is an ordinary matrix element local in the energy variable, we obviously have that

$$
H_{a,b}^{\alpha,\beta}(\mathcal{E},\mathcal{E}') = \delta(\mathcal{E}-\mathcal{E}')G_{a,b}^{\alpha,\beta}(\mathcal{E})
\tag{45}
$$

where $G_{a,b}^{\alpha,\beta}(\mathcal{E})$ is the ordinary Green function. Further, if we now *define* a new two-particle function $H_{a,b,n,m}^{\alpha,\beta,\mu,\nu}(\mathcal{E},\mathcal{E}';\mathcal{E}_1,\mathcal{E}_2)$ by

$$
H_{a,b,n,m}^{\alpha,\beta,\mu,\nu}(\mathcal{E},\mathcal{E}';\mathcal{E}_1,\mathcal{E}_2) \equiv \frac{\delta H_{a,n}^{\alpha,\nu}(\mathcal{E},\mathcal{E}')}{\delta W_{b,m}^{\beta,\mu}(\mathcal{E}_1,\mathcal{E}_2)}
\tag{46}
$$

and calculate it at the particular value given by (44), we find that it reduces to the required quantity (42)

$$
H_{a,b,n,m}^{\alpha,\beta,\mu,\nu}(\mathcal{E},\mathcal{E}';\mathcal{E}_1,\mathcal{E}_2) = \delta(\mathcal{E}-\mathcal{E}_1)\delta(\mathcal{E}'-\mathcal{E}_2)\mathcal{G}_{a,b,m,n}^{\alpha,\beta,\mu,\nu}(\mathcal{E},\mathcal{E}').
\tag{47}
$$

Thus, this procedure is similar to the method of ordered variation, well known in the theory of the electrical resistivity in liquid metals (Popielawski 1979, Roth and Singh 1982).

Let us specialize now to the case of an allow with short-range order. We find, in direct analogy with (17), that $H_{a,n}^{\alpha,\nu}$ satisfies a pseudo-Dyson equation

$$
H_{a,n}^{\alpha,\nu}(\mathcal{E},\mathcal{E}') = S_{a,n}^{\alpha,\nu}(\mathcal{E},\mathcal{E}')
$$
$$
+ \sum_{c,c',\gamma,\gamma'} \int_{-\infty}^{\infty} \mathrm{d}\mathcal{E}'' \int_{-\infty}^{\infty} \mathrm{d}\mathcal{E}''' \, S_{a,c}^{\alpha,\gamma}(\mathcal{E},\mathcal{E}'') U_{c,c'}^{\gamma,\gamma'}(\mathcal{E}'',\mathcal{E}''') H_{c',n}^{\gamma',\nu}(\mathcal{E}''',\mathcal{E}')
$$

(48)

where U is, as before, the energy-dependent interaction W weighted by the binary conditional probability p,

$$
U_{a,b}^{\alpha,\beta}(\mathcal{E},\mathcal{E}') \equiv W_{a,b}^{\alpha,\beta}(\mathcal{E},\mathcal{E}') p_{a,b}^{\alpha,\beta}
$$

(49)

and S, which also plays here the role of a pseudo-Dyson function, is the sum of all irreducible diagrams (Leath 1970). We note that this quantity is a unique functional of the renormalized interactions $\bar{W}$ and $\bar{U}$

$$
\bar{W}_{a,b}^{\alpha,\beta}(\mathcal{E},\mathcal{E}') = \sum_{c,\gamma} \int_{-\infty}^{\infty} \mathrm{d}\mathcal{E}'' \, V_{a,c}^{\alpha,\gamma}(\mathcal{E},\mathcal{E}'') W_{c,b}^{\gamma,\beta}(\mathcal{E}'',\mathcal{E}')
$$

(50)

$$
\bar{U}_{a,b}^{\alpha,\beta}(\mathcal{E},\mathcal{E}') = \sum_{c,\gamma} \int_{-\infty}^{\infty} \mathrm{d}\mathcal{E}'' \, V_{a,c}^{\alpha,\gamma}(\mathcal{E},\mathcal{E}'') U_{c,b}^{\gamma,\beta}(\mathcal{E}'',\mathcal{E}')
$$

(51)

where the renormalizing function V is given in terms of H by

$$
V_{a,b}^{\alpha,\beta}(\mathcal{E},\mathcal{E}') = \delta(\mathcal{E}-\mathcal{E}')\delta_{a,b}^{\alpha,\beta} + \sum_{c,\gamma} \int_{-\infty}^{\infty} \mathrm{d}\mathcal{E}'' \, U_{a,c}^{\alpha,\gamma}(\mathcal{E},\mathcal{E}'') H_{c,b}^{\gamma,\beta}(\mathcal{E}'',\mathcal{E}')
$$

(52)

(cf. equations (20–22)). Clearly, in the limit given by equation (44), all these quantities turn out to be diagonal in the energy variables and the equations of this section reduce to the corresponding relations of section 3.

Proceeding in this way, we can deduce the analogy of the non-linear system (23)–(25) determining the function S and thus, by (48), the Green function H. We find that the numerical work needed to solve these equations is not essentially more difficult than that required for the solution of the simplest case of equations (23)–(25). For instance, in the test case treated here, we have found that the main changes arise in transforming a Newton–Raphson method operating with 2×2 matrices to another which has to work with 4×4 matrices. Thus, the procedure deduced here for obtaining the two-point Green functions—and hence, the transport coefficients of a random alloy with short-range order—appears to be perfectly feasible.

6. Summary and discussion

In this paper we have studied the problem of calculating the two-particle Green function for an electron in a random alloy from a knowledge of its one-particle

function. This was done in a formalism in which the configuration averages are only partially carried off, and the disorder field is prescribed by means of conditional probabilities of all orders (Rössler and Lazo 1981). In this formalism, the one- and two-particle Green functions are connected by means of a new class of Ward identities, different from the well known Ward–Velický formulae (Ward 1950, Velický 1969).

In order to illustrate the uses of these identities, we have performed here two further calculations: first, we have obtained a number of different equations of the Bethe–Salpeter type for the two-particle Green function and have also found pre-scriptions for calculating their kernels by combining the Ward identities with existing CPA-type expressions for the one-particle Green function, with or without short-range order. On the other hand, we have shown that the problem of solving these com-plicated equations can be obviated by calculating the vertex corrections by direct numerical differentiation of the one-particle Green function.

It may be that the Bethe–Salpeter equations found here have more interest in principle than in practice, because their kernels are found to be defined by com-plicated sets of non-linear matrix equations. (These sets, however, appear to be soluble in each case by means of numerical methods.) Furthermore, it is probably inconsistent to take as a starting point for calculations of two-particle Green func-tions, one-particle functions obtained from a single-site CPA. Probably, the correct procedure would be to use at least a 2-CPA—at the risk however, of losing analyticity. On the other hand, although these Bethe–Salpeter-type equations are equivalent in principle, they may not be equivalent from the point of view of perturbation theory, and thus it is probable that a method capable of systematically generating all of them can be advantageous in practice.

We note that the results obtained in this paper apply equally to the problem of phonons, excitons, magnons or electrons propagating in disordered systems. Also, they seem to be readily generalizable to a more realistic model than the Velický (1969) tight-binding case we use here. Furthermore, as even the generalization of the 1-CPA we use here is such that the vertex corrections involving the velocity operator do not vanish identically, the methods of this paper may be useful in throwing new light on the problem of the electronic localization in two-dimensional systems (Chitanvis and Leath 1982, 1983).

Of course, the test of usefulness of these procedures lies in their capability to accurately calculate interesting properties of disordered materials. We expect to publish soon certain new results on the electrical resistivities of random alloys with short-range order.

Acknowledgments

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