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New Approximation in the Electronic Theory of Disordered Alloys*

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A multiple-scattering theory of binary disordered alloys is presented using a single-site approximation in a form different from that of the coherent-potential theory. A reference Hamiltonian and its propagator are defined by the requirement that there be no forward scattering in this reference frame. The reference Hamiltonian is periodic with the periodicity of the lattice. The resultant solutions are self-consistent and have the advantage of permitting one to directly calculate the various matrix elements, both diagonal and nondiagonal, of the alloy propagator. The formalism is not limited to a single-band model Hamiltonian nor to localized perturbations, but has wide applicability. The limitations of the approximations and idealizations made in this theory are discussed, especially the neglect of a self-consistent treatment of the potential perturbations.

I. INTRODUCTION

Much recent work on the theory of disordered systems has employed the multiple-scattering description.[1-11] In this approach, the propagation of an electron or lattice wave in a disordered system is regarded as a succession of elementary scatterings on the random atomic scatterers, which are then averaged over all configurations of atoms. The coherent-potential (CP) theory has been shown[1] to be the best of the ones presently available employing the single-site approximation, where correlations between clusters of scatterers are neglected. The CP theory determines in a self-consistent fashion the Hamiltonian with a periodic potential (permitted to be complex) which "best" approximates that of the actual alloy. The criterion used to determine this Hamiltonian is to first replace one site of the periodic potential by an atom of the alloy and then average the scattering from this site by distributing on it the various atoms in the alloy. Setting this average scattering to zero determines the Hamiltonian. In an outstanding paper, Velický, Kirkpatrick, and Ehrenreich[1] give a discussion of the CP theory and clearly specify the approximations that enter into it. They and other authors[3,5,8] applied this theory to a binary disordered alloy where the potential introduced by each atom is localized to just its own lattice site. Takeno[2] developed the theory for the case of a potential which extends over more than one lattice site.

In this paper a self-consistent theory with a different single-site approximation is presented. The criterion for choosing the reference Hamiltonian in this theory is that the total forward scattering be zero. This is to be distinguished from the CP theory which requires that the total *averaged* scattering from *each* site be zero, both forward and nonforward.

In Sec. II we consider multiple-scattering theory and define our form of the single-site approximation. The importance of finding a reference Hamiltonian which sets the total forward scattering to zero is indicated in this section. In Sec. III a more detailed discussion of the properties of the theory and its comparison with other approaches are given.

II. SINGLE-SITE APPROXIMATION

The problem we will consider is an independent-particle model of a disordered solid solution binary alloy composed of N_1 type-one atoms and N_2 type-two atoms. The Hamiltonian for the alloy we assume can be written in the form

$$H = H_0 + V , \qquad V = \sum_m' V_m , \tag{1}$$

where H_0 is a periodic Hamiltonian of a pure solid composed of type-one atoms, and V_m is the potential perturbation contributed by a type-two atom replacing a type-one atom at the site m. The prime over the summation sign is to signify that the sum is not over all lattice sites, but just those with type-two atoms. By assuming a solid solution, we guarantee that m will always be on a lattice site and we make the further assumption that no distortions are introduced by alloying, i.e., no volume change on alloying. In the actual case, V_m has to be solved self-consistently[12] as its value depends on the distribution of the electrons in its vicinity in the alloy. It would in general vary from site to site, depending on its surroundings. However, in order to make the problem more tractable, we assume that V_m is known, independent of the solution of the problem, and is the same around each site independent of its surroundings, but its range is not necessarily restricted to just one lattice site.

Our goal is to determine the Green's function G of the Hamiltonian in (1),

$$G=(E-H)^{-1} \; . \tag{2}$$

To do this we first determine G_A, defined by

$$G_A=(E-H_A)^{-1} \; , \tag{3}$$

where

$$H_A=H_0+A \tag{4}$$

and

$$A=\sum_{n,n',\vec{k}} |n\vec{k}\rangle A_{n,n'}(\vec{k})\langle n'\vec{k}| \; , \tag{5}$$

a diagonal operator in the wave vectors of the Bloch states $|nk\rangle$ which are solutions of H_0. The Bloch states have the property that

$$H_0|n\vec{k}\rangle=E_n(\vec{k})|n\vec{k}\rangle \; . \tag{6}$$

Here $\vec{k}$ represents the crystal wave vector of the Bloch state and n represents the band index. Note that A couples to different bands, but not to different $\vec{k}$, and thus G_A is diagonal $\vec{k}$ but is coupled between bands. In terms of G_A, we can write the equality

$$G=G_A+G_A(V-A)G \; . \tag{7}$$

We next introduce the T operator by the equation

$$(V-A)G=TG_A \; . \tag{8}$$

Inserting (8) into (7), we obtain

$$G=G_A+G_A TG_A \; . \tag{9}$$

If we define G_A by requiring that the forward scattering of T be zero,

$$\langle n'\vec{k}|T|n\vec{k}\rangle=0 \; , \tag{10}$$

then G_A has the same diagonal elements as G. The density of states of the alloy depends solely on the diagonal elements of G, and thus G_A can be used to calculate this density of states. In what follows, we assume that G_A is defined by condition (10).

We can obtain an equation for T by replacing G in (8) by the expression in (9):

$$T=(V-A)(1+G_A T) \; . \tag{11}$$

Let us assume that T can be written as a sum of contributions from the same lattice sites that contribute to V. Thus we can write

$$T={\sum_m}' Q_m \; . \tag{12}$$

We also can write

$$V-A={\sum_m}'(V_m-A/N_2) \; , \tag{13}$$

where N_2 is the total number of scattering atoms of type two. It is important to note the difference from the coherent-potential approximation (CPA) implied by (13). In the CPA, the operator A is assumed to be periodic and to contribute to the scattering from each site, both ones with impurities and with host atoms. In our case, we associate A with only the impurity sites. This is not to imply that A is localized on only the impurity sites. Quite the contrary, A covers the volume of the alloy and this is essential to its property of contributing to the scattering only in the forward direction. In the bookkeeping used here, A is associated with only the impurities and each impurity contributes A/N_2 to the total A. It must be remembered that we are not assuming, as done in the CPA, that the impurity potential is localized at each site. Not only A/N_2, but V_m, extends over more than the site m. In contrast to the CPA, the formalism presented here is not limited to the special case where the perturbations are localized around each site.

Substituting (12) and (13) into (11), we find that

$$Q_l=T_l\left(1+G_A\sum_{m\neq l}{}' Q_m\right) \; , \tag{14}$$

where T_l is the single-impurity t matrix defined by

$$T_l=[1-(V_l-A/N_2)G_A]^{-1}(V_l-A/N_2) \; . \tag{15}$$

In the limit that the volume Ω of the alloy becomes very large and $N_2/(N_1+N_2)=c$ stays constant, N_2 also becomes very large and A/N_2, which is proportional to Ω^{-1}, can be treated as a perturbation. As shown in Appendix A, to first order in Ω^{-1}, T_l can be written as

$$T_l=t_{lA}-A/N_2 \; , \tag{15$'$}$$

where $t_{lA}=[1-V_l G_A]^{-1}V_l$. In (15$'$) we neglect terms of the form AV_l/N_2 and $(A/N_2)^2$ and higher order since these are at least of order Ω^{-1} compared to retained terms. We illustrate this for the neglected term AV_l/N_2 by comparing it with the retained term V_l. In order to neglect AV_l/N_2 compared to V_l, we must show that *all* matrix elements of the former are of the order Ω^{-1} compared to the corresponding elements of the latter. Use the Bloch state representation and consider the matrix element

$$\langle k|AV_l/N_2|k'\rangle=A(k)/N_2\,\langle k|V_l|k'\rangle \; .$$

We see immediately that this matrix element is $A(k)/N_2$ times the corresponding element of V_l. But $A(k)/N_2$ is of the order of Ω^{-1}, going to zero as $\Omega\rightarrow\infty$. Physically, as we show later, $A(k)/N_2$ is the change in the energy of the state $|k\rangle$ produced by the addition of one impurity. We know that such a change is proportional to the increase in the number of impurities *per unit volume*. The addition of one impurity changes the number per unit volume by Ω^{-1}. Thus, AV_l/N_2 is of the order of Ω^{-1} times V_l and therefore is negligible when $\Omega\rightarrow\infty$.

The requirement (10) can be written in terms of the Q_m by use of (12) as

$$\sum_m{}' \langle n'\vec{k}|\,Q_m\,|n\vec{k}\rangle = 0 \ . \tag{16}$$

Consider each site m in the sum separately. Its matrix element in (16) will depend only on its surroundings and not where the origin for the coordinate is chosen. As we change from one site to another in the alloy, its surroundings will vary in a random fashion because of our assumption of a random alloy. The sum in (16) divided by N_2, the total number of impurity sites, is equivalent to finding the Q_m from a *fixed* site by averaging over all possible distributions of the various *surrounding* atoms. We can therefore rewrite (16) as

$$(\langle n'\vec{k}|\,Q_m\,|n\vec{k}\rangle\,)_{\mathrm{av}} = 0 \ , \tag{17}$$

where the indicated average is one where an atom is fixed at the mth site and an average is taken over all possible distributions of the *surrounding* atoms. We iterate Eq. (14) once to obtain

$$Q_p = T_p + T_p G_A \sum_{m\neq p}{}' T_m + T_p G_A \sum_{m\neq p}{}' T_m G_A \sum_{l\neq m}{}' Q_l \ . \tag{18}$$

Using (18), condition (17) becomes

$$0 = \langle n'\vec{k}|\,T_m\,|n\vec{k}\rangle + \sum_{n'',n''',\vec{k}'}{}' \langle n'\vec{k}|\,T_m\,|n''\vec{k}'\rangle\langle n''\vec{k}'|\,G_A\,|n'''\vec{k}'\rangle \Big(\sum_{l\neq m}{}' \langle n'''\vec{k}'|\,T_l\,|n\vec{k}\rangle\Big)_{\mathrm{av}}$$

$$+ \sum_{\substack{n'',n''',n^{\mathrm{IV}},\\ n^{\mathrm{V}},\vec{k}',\vec{k}''}}{}' \langle n'\vec{k}|\,T_m\,|n''\vec{k}'\rangle\langle n''\vec{k}'|\,G_A\,|n'''\vec{k}'\rangle \Big(\sum_{l\neq m}{}' \langle n'''\vec{k}'|\,T_l\,|n^{\mathrm{IV}}\vec{k}''\rangle\langle n^{\mathrm{IV}}\vec{k}''|\,G_A\,|n^{\mathrm{V}}\vec{k}''\rangle \sum_{p\neq l}{}' \langle n^{\mathrm{V}}\vec{k}''|\,Q_p\,|n\vec{k}\rangle\Big)_{\mathrm{av}} \ . \tag{19}$$

The average need not be taken over the T_m matrix elements since we are assuming that V_m at each site is the same, independent of its surroundings. We can express

$$\langle n\vec{k}|\,T_m\,|n'\vec{k}'\rangle = \langle n\vec{k}|\,t\,|n'\vec{k}'\rangle\, e^{i(\vec{k}'-\vec{k})\cdot\vec{R}_m} \ ,$$

$$\langle n''\vec{k}'|\,Q_l\,|n\vec{k}\rangle = \langle n''\vec{k}'|\,q_l\,|n\vec{k}\rangle\, e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_l} \ , \tag{20}$$

where $\langle n\vec{k}|t|n'\vec{k}'\rangle$ and $\langle n''\vec{k}'|q_l|n\vec{k}\rangle$ are the matrix elements evaluated by using the site of interest as the origin of the wave functions. The sites l and m are located at $\vec{R}_l$ and $\vec{R}_m$, respectively. We assume that t is independent of the site since V_m is assumed to be the same around each site. However, we expect that q_l will depend on l since this should depend on, say, the distance between the lth and mth site. The approximation that we make is to neglect this site dependence of q_l and assume that it is equal to its average value which we denote by q. With this approximation, the required averaging over sites only affects the exponentials of Eq. (20). The required averages as derived in Appendix B are

$$\Big(\sum_{l\neq m}{}' e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_l}\Big)_{\mathrm{av}} = -c\,e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_m} \ , \qquad \vec{k}\neq\vec{k}' \tag{21}$$

$$\Big(\sum_{l\neq m}{}' e^{i(\vec{k}'-\vec{k}'')\cdot\vec{R}_l} \sum_{p\neq l}{}' e^{i(\vec{k}''-\vec{k})\cdot\vec{R}_p}\Big)_{\mathrm{av}} = (2c^2-c)\,e^{i(\vec{k}'-\vec{k})\cdot\vec{R}_m} \ ,$$

$$\vec{k}\neq\vec{k}',\ \vec{k}''\neq\vec{k},\ \vec{k}''\neq\vec{k}' \tag{21'}$$

where $c = N_2/N$, the fractional amount of the type-two scattering atoms. In obtaining (21) and (21′), we require that $\vec{k}'\neq\vec{k}$, $\vec{k}'\neq\vec{k}''$, and $\vec{k}''\neq\vec{k}$. That $\vec{k}''\neq\vec{k}$ in (21′) is assured by condition (17). The terms we miss, namely, those with $\vec{k}'=\vec{k}$ and $\vec{k}'=\vec{k}''$ are, as shown in Appendix C, of order t^4. The single-site approximation already has errors[1,3] of the order of t^4, so that we introduce no additional errors by neglecting them. The assumption is also made that the atoms are completely random in their distribution. Combining (21) with (19) and (20), we obtain the relation

$$\langle n'\vec{k}|\,t[1 - c\,G_A t + (2c^2-c)\,G_A t G_A q]\,|n\vec{k}\rangle = 0 \ . \tag{22}$$

We can calculate a general matrix element of Q_m in (18) using the same approximation as led to (22), but now this introduces errors of order t^3, and we obtain

$$\langle n'\vec{k}'|\,q\,|n\vec{k}\rangle = \langle n'\vec{k}'|\,t[1 - c\,G_A t + (2c^2-c)\,G_A t G_A q]\,|n\vec{k}\rangle \tag{23}$$

or

$$q = t[1 - c\,G_A t + (2c^2-c)\,G_A t G_A q] \ . \tag{23'}$$

From Eq. (23′) we can solve for q to find that

$$q = [1-(2c^2-c)(tG_A)^2]^{-1}(1-c\,tG_A)\,t \ . \tag{24}$$

Using the fact that from (15′)

$$t = t_A - A/N_2 \ , \tag{25}$$

where $t_A = (1-vG_A)^{-1}v$, and v is V_n evaluated at the site at the origin, we find for q in (24) that

$$q = t_{AC} - A/N_2 \ , \tag{26}$$

where

$$t_{AC} = [(1-vG_A)^2 + (c-2c^2)(vG_A)^2]^{-1}[1-(1+c)vG_A]v \ ,$$

and we have again neglected terms of order Ω^{-2}. Condition (17) can now be written as

$$\langle n'\vec{\mathrm{k}}|\,Q_m\,|n\vec{\mathrm{k}}\rangle = \langle n'\vec{\mathrm{k}}|\,q\,|n\vec{\mathrm{k}}\rangle = 0 \ . \tag{27}$$

Using (26), Eq. (27) becomes

$$\langle n'\vec{\mathrm{k}}|A\,|n\vec{\mathrm{k}}\rangle \equiv A_{n'n}(\vec{\mathrm{k}}) = N_2\,\langle n'\vec{\mathrm{k}}|\,t_{AC}\,|n\vec{\mathrm{k}}\rangle \ . \tag{28}$$

Equation (28) is the self-consistent relation which determines A and is the central result of this paper. The self-consistency enters because A not only enters into the left-hand side of (28), but also into t_{AC} through G_A.

III. DISCUSSION

We discuss how the approximation made here compares with that made in the CP theory. In the CP theory the average T matrix from *each* site is set equal to zero,[1] while in the approach used here, the total forward scattering is set equal to zero; the average T matrix from each site is not equal to zero. However, the average of the total T matrix of Eq. (12) is zero. The single-site approximations made in the averaging in both the CP theory and the one presented here are essentially the same.

From the criterion used in this paper we are able, just as in the CP theory, to obtain the values of the diagonal elements of G. In fact, the G_A defined by the criterion (10) has the same diagonal elements as G, as can be verified by taking the diagonal elements of Eq. (9) and obtaining

$$\langle n\vec{\mathrm{k}}|\,G\,|n'\vec{\mathrm{k}}\rangle = \langle n\vec{\mathrm{k}}|\,G_A\,|n'\vec{\mathrm{k}}\rangle = \langle n\vec{\mathrm{k}}|\,(E - H_0 - A)^{-1}\,|H'\vec{\mathrm{k}}\rangle \ . \tag{29}$$

The right-hand side of (29) can be calculated in terms of the $E_{n''}(\vec{\mathrm{k}})$ and $A_{n''n'''}(\vec{\mathrm{k}})$ defined by Eq. (6) and by Eqs. (5) and (28), respectively. If interband elements can be neglected we note that $A_{nn}(\vec{\mathrm{k}})$ is the self-energy or energy shift of the state $|n\vec{\mathrm{k}}\rangle$ in the alloy.

The accuracy of (29) depends on how accurately (10) is satisfied. The approximations made following Eq. (21) indicated that (10) and thus (29) are correct to order t^3 or V^3. This accuracy is the same as that of the CP theory.[3] The error made in the theory presented here may be smaller than that of the CP theory because the distance between scatterers is greater than in the case of the CP theory. In the CP theory, every site scatters while in the theory presented here only the type-two atoms scatter. The neglected interaction between scattering sites may be smaller, therefore, in the theory presented here. However, this conclusion is only tentative since a compensating characteristic of the CP theory may be that the average scattering from each site is zero, while this is not true for the theory presented here.

The main advantages of the approach presented here are that it applies to more general perturbations than the CPA and it gives directly the off-diagonal elements of G. The CP theory, through its averaging process, loses the information of the off-diagonal elements of G, and it is a much more involved process to obtain it again.[13] From Eqs. (9), (12), (20), and (26), we can write

$$G = G_A + G_A {\sum_m}' (t_{ACm} - A/N_2)\, G_A \tag{30}$$

and

$$\langle n\vec{\mathrm{k}}|\,G\,|n'\vec{\mathrm{k}}'\rangle = \langle n\vec{\mathrm{k}}|\,G_A\, t_{AC}\, G_A\,|n'\vec{\mathrm{k}}'\rangle {\sum_m}' e^{i(\vec{\mathrm{k}}' - \vec{\mathrm{k}})\cdot\vec{\mathrm{R}}_m}, \qquad \vec{\mathrm{k}}' \neq \vec{\mathrm{k}} \ . \tag{31}$$

Here t_{ACm} is the operator t_{AC} centered about the site at $\vec{\mathrm{R}}_m$. Note that averaging over all sites in (31) will make the off-diagonal elements zero, as should be the case.

For small c, using Eq. (28), we find that $A_{nn}(\vec{\mathrm{k}})$ becomes, to first order in c,

$$A_{nn}(\vec{\mathrm{k}}) \rightarrow N_2\,\langle n\vec{\mathrm{k}}|\,t_0\,|n\vec{\mathrm{k}}\rangle \ , \tag{32}$$

where

$$\begin{aligned} t_0 &= (1 - vG_0)^{-1}\,v \ , \\ G_0 &= (E - H_0)^{-1} \ . \end{aligned} \tag{33}$$

We note that t_0 is the t matrix for a single scatterer in the pure matrix with the Hamiltonian H_0. This result agrees with that of previous ones.[2,14]

A knowledge of the matrix elements of G given in Eqs. (29) and (31) permits one to calculate all of the desired properties of the alloy. It is planned that this be done in a subsequent publication using specific models. It should be pointed out, though, that the usual divergent problems that occur in calculating some properties of alloys such as the conductivity at zero frequency[9,10] are automatically eliminated by the approach presented here. Choosing G_A such that the forward scattering of T is zero eliminates these divergent problems just as in the CPA. The forward scattering if not zero presents such a problem because then the contributions from the various scatterers always add in phase. No matter how small the forward scattering may be, it will eventually become large and divergent in perturbation theory as one moves sufficiently far through the solid to sense the contributions from enough scatterers. Thus, if forward scattering is present, one must go to all orders in perturbation theory to eliminate this divergence. It was reasoning of this sort that first motivated the use of condition (10).

We end with a statement on the limitations of the treatment of the alloy problem as employed here and elsewhere. It is usually assumed that the potential perturbation at a given site is a known in the problem. Unfortunately, the actual situation is not so simple.[12] The potential perturbation depends on the distribution of the alloy electrons in its vicinity, and, of course, this is not known till the alloy problem is solved. Clearly a self-consistent solution of the potential is required. This self-consistency should be distinguished from the one discussed in this paper in relation to Eq. (28). In the actual problem, both self-consistencies must be applied to obtain the final answer. The self-consistent treatment of the potential leads to the result that, in concentrated alloys, a nonanalytic dependence on c becomes important for alloys where the two constituents have a differing valence number.[15] Such a result is completely missed if the potential perturbation is not treated self-consistently.

The single-site approximation neglects correlations between neighboring scatterers and treats the scattering from each site as being the same independent of its surroundings. There have been attempts to include some of the effects of correlations between neighboring scatterers, but it should be pointed out that such calculations are meaningless unless the potential is also treated self-consistently. The correlation between neighbors modifies the scattering because it modifies the electron distribution around the scatterer.[12,16] To treat the potential perturbation as fixed and the same about each site, and yet to permit the electron distribution around a scatterer to vary because of correlations, is not consistent. The contribution of the potential variation due to this correlation is as important as the correlated scattering terms and it is meaningless to do one without the other. Correlations between neighboring scatterers are negligible when the number of scatterers are dilute or when they are a weak perturbation so that nonlinear effects are small. We thus expect the single-site approximation to be best under these circumstances.

APPENDIX A

In this appendix we estimate the size of matrix elements and show explicitly that the neglected terms in going from (15) to (15′) are of the order of Ω^{-1} compared to retained terms. Consider (15) and make the substitution for V_l of

$$V_l = t_l\,(1 + G_A t_l)^{-1} \ , \tag{A1}$$

which follows from the definition of t_l given just after (15′). We then obtain for (15)

$$T_l = [1 + aG\,(1 + tG)]^{-1}(1 + tG)\,[(1 + tG)^{-1}t - a], \tag{A2}$$

where $a = A/N_2$ and we have dropped the subscripts for simplicity.

Expanding (A2) to the first order in a, we obtain

$$T_l = t - a - aGt - tGa - a(Gt)^2 + \cdots \ . \tag{A3}$$

We neglect all terms of order a^2 and higher because a is the order of Ω^{-1} as shown in (A6). What is not so obvious is that the last three terms in (A3) are also negligible because they are of order Ω^{-1} times the first two terms. We show that this is so.

We first estimate the magnitude of the terms t and a. In this discussion we neglect interband terms (by dropping the n label) since they will not affect the order-of-magnitude estimates:

$$\langle \vec{k}' | t_l | \vec{k} \rangle = t_{k'k} = N^{-1} \sum_{m,m'} e^{i\vec{k}\cdot\vec{R}_m}\, e^{i\vec{k}'\cdot\vec{R}_{m'}} \langle m' | t_l | m \rangle \ , \tag{A4}$$

where $|m\rangle$ is the Wannier-like state localized at site R_m and N is the total number of atoms in the alloy. Since t_l is localized about a site (for example the m_0 site), we can estimate the magnitude as

$$t_{kk'} = t_0/N \ , \tag{A5}$$

where $t_0 = \langle m_0 | t | m_0 \rangle$. From Eq. (28) we see that the magnitude of a is also

$$a(k) = A(k)/N_2 = \langle \vec{k} | A/N_2 | \vec{k} \rangle \approx t_0/N \ . \tag{A6}$$

Now consider the term in (A3)

$$\langle \vec{k}' | tGa | \vec{k} \rangle = t_{k'k} G_{kk} a(k) \ . \tag{A7}$$

The magnitude of G_{kk} is

$$G_{kk} \approx \Delta^{-1} \ , \tag{A8}$$

where Δ is an energy of the order of the bandwidth.

The magnitude of (A7) is then

$$\langle \vec{k}' | t_l\, Ga | \vec{k} \rangle \approx t_0^2 \Delta^{-1} N^{-2} \ . \tag{A9}$$

Clearly the term aGt in (A3) also has the same magnitude of (A9).

It remains to estimate the last term in (A3),

$$\langle \vec{k}' | a(Gt)^2 | \vec{k} \rangle = a(k')\, \langle \vec{k}' | (Gt)^2 | \vec{k} \rangle \ . \tag{A10}$$

Now

$$\begin{aligned} \langle \vec{k}' | (Gt)^2 | \vec{k} \rangle &= \sum_{k''} \langle \vec{k}' | Gt | \vec{k}'' \rangle \langle \vec{k}'' | Gt | \vec{k} \rangle \\ &= \sum_{k''} G_{k'k'} t_{k'k''} G_{k''k''} t_{k''k} \approx \sum_{k''} \left(\frac{t_0}{\Delta N} \right)^2 \ . \end{aligned} \tag{A11}$$

In the last step of (A11) we used (A5) and (A8). Since there are N different values of $\vec{k}''$ (A11) becomes

$$\langle \vec{k}' | (Gt)^2 | \vec{k} \rangle \approx N^{-1} (t_0/\Delta)^2 \ . \tag{A12}$$

Substituting this back into (A10) and using (A6) we find

$$\langle \vec{k}'|a(Gt)^2|\vec{k}\rangle \approx (N\Delta)^{-2} t_0^3 \ . \tag{A13}$$

From (A5) and (A6) we note that the first two terms of (A3) are of the same order of magnitude in N or Ω. By comparing (A5) and (A6) with (A9) and (A13) we see that the last three terms of (A3) are of the order of N^{-1} or Ω^{-1} times the first two terms. We use the fact that $t_0/\Delta \approx 1$. As Ω and $N \to \infty$, only the first two terms of (A3) need be retained.

APPENDIX B

In deriving (22) we were required to evaluate the averages of (21), namely,

$$\Big(\sum_{l\neq m}{}' e^{i(\vec{k}-\vec{k}')\cdot \vec{R}_l} \Big)_{\text{av}} \tag{B1}$$

and

$$\Big(\sum_{l\neq m}{}' e^{i(\vec{k}'-\vec{k}'')\cdot \vec{R}_l} \sum_{p\neq l}{}' e^{i(\vec{k}''-\vec{k})\cdot \vec{R}_p} \Big)_{\text{av}} \ . \tag{B2}$$

In both sums a perturbing type-two atom is on the mth site. The indicated averaging is over an ensemble of alloys assuming a completely random distribution of type-one and type-two atoms. The sums in (B1) and (B2) are over only those sites which have a type-two atom, as indicated by the prime on the summation sign.

First consider (B1). The probability in averaging over ensembles that a site l has a type-two atom is $c = N_2/N$. Thus the average over ensembles in (B1) becomes

$$\Big(\sum_{l\neq m}{}' e^{i(\vec{k}-\vec{k}')\cdot \vec{R}_l} \Big)_{\text{av}} = c \sum_{l\neq m} e^{i(\vec{k}-\vec{k}')\cdot \vec{R}_l} \ . \tag{B3}$$

The sum on the right-hand side of (B3) is over all sites except m, as denoted by the fact that it does not have a prime on the summation sign. Using the fact that, summing over all sites,

$$\sum_{l} e^{i(\vec{k}-\vec{k}')\cdot \vec{R}_l} = 0 \ , \qquad k \neq k' \tag{B4}$$

we have that

$$\sum_{l\neq m} e^{i(\vec{k}-\vec{k}')\cdot \vec{R}_l} = - e^{i(\vec{k}-\vec{k}')\cdot \vec{R}_m} \ , \quad k\neq k' \tag{B5}$$

and we can substitute (B5) in (B3) to obtain

$$\Big(\sum_{l\neq m}{}' e^{i(\vec{k}-\vec{k}')\cdot \vec{R}_l} \Big)_{\text{av}} = - c\, e^{i(\vec{k}-\vec{k}')\cdot \vec{R}_m} \ , \quad k \neq k' \ . \tag{B6}$$

The evaluation of the sum in (B2) is as follows. Consider the lth term in (B2),

$$\Big(e^{i(\vec{k}'-\vec{k}'')\cdot \vec{R}_l} \sum_{p\neq l}{}' e^{i(\vec{k}''-\vec{k})\cdot \vec{R}_p} \Big)_{\text{av}} \ . \tag{B7}$$

In evaluating (B7) we must remember that a type-two atom is definitely on both the mth and lth site. The average over ensembles leads to a probability c that all other sites (not equal to m or l) have a type-two atom,

$$\Big(\sum_{p\neq l}{}' e^{i(\vec{k}''-\vec{k})\cdot \vec{R}_p} \Big)_{\text{av}} = \sum_{p\neq l,m} c\, e^{i(\vec{k}''-\vec{k})\cdot \vec{R}_p} + e^{i(\vec{k}''-\vec{k})\cdot \vec{R}_m} \ . \tag{B8}$$

Using (B4), we find that

$$\sum_{p\neq l,m} e^{i(\vec{k}''-\vec{k})\cdot \vec{R}_p} = - e^{i(\vec{k}''-\vec{k})\cdot \vec{R}_l} - e^{i(\vec{k}''-\vec{k})\cdot \vec{R}_m} \ , \quad \vec{k}'' \neq \vec{k} \ . \tag{B9}$$

Substituting (B9) into (B8), we find

$$e^{i(\vec{k}'-\vec{k}'')\cdot \vec{R}_l} \Big(\sum_{p\neq l}{}' e^{i(\vec{k}''-\vec{k})\cdot \vec{R}_p} \Big)_{\text{av}} = - c\, e^{i(\vec{k}'-\vec{k})\cdot \vec{R}_l} + (1-c)\, e^{i(\vec{k}''-\vec{k})\cdot (\vec{R}_m - \vec{R}_l)} \ , \quad \vec{k}'' \neq \vec{k} \ . \tag{B10}$$

Summing (B10) over $l \neq m$ and averaging over ensembles using (B6), we obtain

$$\Big(\sum_{l\neq m}{}' e^{i(\vec{k}'-\vec{k})\cdot \vec{R}_l} \sum_{p\neq}{}' e^{i(\vec{k}''-\vec{k})\cdot \vec{R}_p} \Big)_{\text{av}} = (2c^2 - c)\, e^{i(\vec{k}'-\vec{k})\cdot \vec{R}_m} \ , \quad \vec{k} \neq \vec{k}', \ \vec{k}'' \neq \vec{k}, \ \vec{k}'' \neq \vec{k}' \ . \tag{B11}$$

APPENDIX C

In deriving (22) from (19), we had to assume that $\vec{k} \neq \vec{k}'$ in (21), and $\vec{k} \neq \vec{k}'$, $\vec{k}' \neq \vec{k}''$ in (21′). In this appendix, we estimate the errors introduced by this neglect.

By assuming $\vec{k}' \neq \vec{k}$ in (21′), we have neglected the following terms in (19):

$$\sum_{\substack{n'', n''', n^{\text{IV}} \\ n^{\text{V}}, k''}} \langle n'\vec{k}|T|n''\vec{k}\rangle \langle n''\vec{k}|G_A|n'''\vec{k}\rangle \langle n'''\vec{k}|t|n^{\text{IV}}\vec{k}''\rangle \langle n^{\text{IV}}\vec{k}''|G_A|n^{\text{V}}\vec{k}''\rangle \langle n^{\text{V}}\vec{k}''|q|n\vec{k}\rangle \times \Big(\sum_{l\neq m}{}' e^{i(\vec{k}''-\vec{k})\cdot \vec{R}_l} \sum_{p\neq l}{}' e^{i(\vec{k}-\vec{k}'')\cdot \vec{R}_p} \Big)_{\text{av}} \ . \tag{C1}$$

Note that we distinguish between T and t in the first matrix element. As indicated by (15′), T and t differ only in their diagonal elements. Whereas the diagonal element of t has the magnitude estimated by (A5), the diagonal element of T has a magnitude which is different. Its magnitude is estimated near the end of this appendix.

The term in (C1) being averaged over ensembles can be summed similarly to the method employed in Appendix B. A type-two atom is definitely at the site m. Choose a particular term $l \neq m$ so that we definitely have a type-two atom also at the lth site. Then

$$\Big(e^{i(\vec{k}''-\vec{k})\cdot\vec{R}_l} {\sum_{p\neq l}}' e^{i(\vec{k}-\vec{k}'')\cdot\vec{R}_p} \Big)_{\text{av}} = e^{i(\vec{k}''-\vec{k})\cdot\vec{R}_l} \Big(e^{i(\vec{k}-\vec{k}'')\cdot\vec{R}_m} + \sum_{p\neq l,m} c\, e^{i(\vec{k}-\vec{k}'')\cdot\vec{R}_p} \Big)$$

$$= (1-c)\, e^{i(\vec{k}''-\vec{k})\cdot(\vec{R}_l-\vec{R}_m)} - c \,, \quad \vec{k} \neq \vec{k}'' \,. \tag{C2}$$

We note that when $\vec{k}=\vec{k}''$ the contribution of the term is zero because of (17). Completing the average of ensembles in (C1) over $l \neq m$, we obtain

$$\Big({\sum_{l\neq m}}' e^{i(\vec{k}''-\vec{k})\cdot\vec{R}_l} {\sum_{p\neq l}}' e^{i(\vec{k}-\vec{k}'')\cdot\vec{R}_p} \Big)_{\text{av}} = -N_2 c \,, \quad \vec{k} \neq \vec{k}'' \,. \tag{C3}$$

Inserting (C3) into (C1), we obtain for the neglected terms ($\vec{k}' \neq \vec{k}$),

$$-N_2 c \sum_{n'',n'''} \langle n'\vec{k}|T|n''\vec{k}\rangle \langle n''\vec{k}|G_A|n'''\vec{k}\rangle \times \langle n'''\vec{k}|t G_A q|n\vec{k}\rangle \,. \tag{C4}$$

In the above calculation, we keep in mind that our volume Ω will go to infinity in such a manner that the ratio N_2/Ω is a constant. Thus we neglected 1 or 2 compared with N_2.

Repeating a similar calculation as above, we find that we have neglected terms of the following form by assuming that $\vec{k}' \neq \vec{k}''$ in (21′):

$$N_2(1-c) \sum_{k',n'',n'''} \langle n\vec{k}|t G_A|n''\vec{k}'\rangle \langle n''\vec{k}'|T|n'''\vec{k}'\rangle \times \langle n'''\vec{k}'|G_A q|n\vec{k}\rangle \,. \tag{C5}$$

Again by similar arguments we find that we have neglected the following terms by assuming $\vec{k} \neq \vec{k}'$ in (21):

$$N_2 \sum_{n'',n'''} \langle n'\vec{k}|T|n''\vec{k}\rangle \langle n''\vec{k}|G_A|n'''\vec{k}\rangle \langle n'''\vec{k}|T|n\vec{k}\rangle \,. \tag{C6}$$

We next compare the neglected terms (C4)–(C6) with a typical nonneglected term in (22), say,

$$\langle n'\vec{k}|t|n\vec{k}\rangle \,. \tag{C7}$$

Using the estimate of the size of the matrix elements given in Appendix A, we find that all terms are of the order Ω^{-1} and thus we cannot differentiate on that basis.

Next we estimate the size of the neglected terms by the order of t. Consider (C4). The last term is of order t^2 while $\langle n'\vec{k}|T|n''\vec{k}\rangle$ is of order t^2 by (19). Thus (C4) is of order t^4. By a similar fashion, we see that both (C5) and (C6) are also of order t^4. Thus, the error we make in our approximation is of order t^4, similar to that of the CPA or any other single-site approximation.

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