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Exact properties of the self-energy of mixed crystals

J. Monecke
Institute of Theoretical Physics, Freiberg University of Mining and Technology, Bernhard-von-Cotta-Strasse 4,
D-09596 Freiberg, Germany

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Despite many attempts there exist few exact results in the physics of disordered media. One outstanding example in classical physics is the Bergman spectral representation for the effective dielectric constant of a macroscopically heterogeneous material. We show that the idea of Bergman to analyze analytic properties in a complex material constant (here in a complex potential) plane can be applied to quantum-mechanical problems, too, and prove for a standard one-band tight-binding Hamiltonian of a mixed crystal that the self-energy has a spectral representation which is a simple generalization of Bergman's original one. The first moments of the corresponding spectral function are calculated and an expression for the self-energy of mixed crystals is rederived which avoids the shortcoming of the coherent potential approximation result, that does not reproduce the small and the large concentration limits near the energies of bound states of single impurities. [S0163-1829(97)00211-7]

I. INTRODUCTION

The problem of the determination of the energy eigenvalue spectrum of a mixed crystal is of outstanding theoretical and technological interest, and has a long history (see, e.g., Ref. 1). One of the first results was the conjecture of Saxon and Hutner,[2] obtained on the basis of the treatment of two impurities in a one-dimensional Kronig-Penney model, that a common energy gap of two pure crystals (of the same structure and lattice constant) survives in a mixed-crystal buildup from these two constituents. The conjecture was proved by Luttinger[3] and arguments have been given[4–6] that it is also correct in the three-dimensional case, at least for special simple impurity potentials. Most works concentrated on a slight generalization of this simple model, and considered a one-band tight-binding model with impurities described by short-range δ-like potentials in Wannier space. Well-known results are the average t matrix and the coherent-potential approximations (see, e.g., Ref. 1), the latter generally being considered as the best possible single-site approximation.

Long-range and, hence, overlapping impurity potentials have been considered in detail by Klauder.[7] However, for such potentials no possibility has been found to exclude so-called multiple occupancies.[1] The best of Klauder's approximations, his Vth one, hence can be used only in the case of small impurity concentration.

It was recognized early,[8] that all single-site approximations violate the Saxon-Hutner conjecture, and that they do not result in band tails which are due to impurity clusters, such as have been studied intensively, e.g., by Lifshitz[9] and Halperin and Lax.[10] Band tails are important for the study of electron localization[11] due to disorder: a small density of states deep in the tail corresponds to a small number of large impurity clusters far away from each other in the mean and, hence, favors localization. Later most works on mixed crystals concentrated on localization effects, not considering configuration averages of one-particle Green functions (see, e.g., Ref. 12).

It is interesting to note that most scientists engaged in the theory of mixed crystals ignored the substantial knowledge of related classical problems, and theories of effective material constants of macroscopically heterogeneous media, going back to the famous work of Rayleigh.[13] The average t matrix and the coherent-potential approximations, e.g., are fully equivalent to the Maxwell-Garnett[14] (or Bruggeman[15]) approximations to the dielectric function of a composite derived in 1904 (1935) (see, e.g., Sec. VI).

A fundamental progress in the physics of heterogeneous materials was achieved by Bergman,[16] who proved the existence of a spectral representation for the dielectric function, analyzing analytic properties in a complex material constant plane. This spectral representation was proved to be one of the most powerful theoretical tools treating macroscopic heterogeneous media, and is one of very few exact results in the physics of disordered media (see, e.g., Ref. 17). It is the aim of the present paper to apply the idea of Bergman to the quantum-mechanical problem of the determination of the self-energy of a mixed crystal model, and to derive an analogous spectral representation (in the complex potential plane in this case).

In Sec. II of the present paper the model Hamiltonian and some standard definitions will be given in order to fix the notations. In Sec. III an averaging procedure is defined which involves only one given sample but is identical with the usual configuration averaging for so-called self-averaging samples. In Sec. IV spectral representations for the averaged T matrix and the self-energy are derived. In Sec. V the first moments of the corresponding spectral functions, as well as exact bounds for the position of poles and branch cuts in the complex potential plane (assuming the validity of the Saxon-Hutner conjecture for the model treated), are shown. In Sec. VI different known approximations to the self-energy are discussed in terms of these results. In particular, it is shown that the coherent-potential approximation does not reproduce the correct second moment, and it is discussed in detail why this approximation is not valid in the limits of small and large impurity concentrations at energies near those of bound states of single impurities. In Sec. VII a simple expression for the self-energy is rederived, which has been shown[18] to avoid these shortcomings. Conclusions are presented in Sec. VIII.

II. MODEL HAMILTONIAN AND STANDARD DEFINITIONS

In this paper we restrict ourselves to the standard one-band tight-binding model[1,19] of a mixed crystal given by the Hamiltonian

$$H=\sum_{l,l'} t_{ll'}b_{l'}^{+}b_{l}^{-}+V_A\sum_{l\epsilon A} b_{l}^{+}b_{l}^{-}+V_B\sum_{l\epsilon B} b_{l}^{+}b_{l}^{-}. \tag{1}$$

This model describes two kinds of atoms, A and B, with different δ-like potentials V_A and V_B in Wannier space, distributed at random on sites l. Their concentration will be written as $c_A=1-c, c_B=c$. The hopping matrix elements $t_{ll'}$ are supposed to depend only on the distances between the sites l and l', and not on the kind of atoms occupying them. In the following we use the equivalent expression

$$\begin{aligned}H&=\sum_{l,l'} t_{ll'}b_{l'}^{+}b_{l}^{-}+V_A\sum_{l} b_{l}^{+}b_{l}^{-}+\sum_{l} V_l b_{l}^{+}b_{l}^{-}\\&=H_0+\sum_{l} V_l b_{l}^{+}b_{l}^{-},\end{aligned} \tag{2}$$

with

$$V_l=(V_B-V_A)\delta_{l\epsilon B}=V\delta_{l\epsilon B}.$$

The Hamiltonian H_0 describes an ordered lattice of A atoms which will be referred to as the unperturbed system. The following formal solution of the eigenvalue problem given by Eq. (2) is the standard one, and is repeated here only in order to fix the notations.

The eigenfunctions of Eq. (2) can be obtained from the complete orthonormal set of functions $\varphi(r-r_l)\mathrel{\hat{=}}\varphi_l=b_l^{+}|0\rangle=|l\rangle$ as

$$\Psi(r)=\sum_{l} a_l(k)\varphi(r-r_l), \tag{3}$$

with

$$a_l(k)=a_l^0(k)+\sum_{l'} G^0_{ll'}V_{l'}a_{l'}(k), \tag{4}$$

where

$$a_l^0(k)=\frac{1}{\sqrt{N}}e^{ikr_l} \tag{5}$$

gives the eigenfunctions of the (periodically continued) unperturbed system. $\Psi(r)$ as given by Eqs. (3) and (4) is not normalized, in general. $G^0_{ll'}$ is the unperturbed Green function defined by

$$G^0_{ll'}=\langle l'|\frac{1}{E-H_0}|l\rangle, \tag{6}$$

and obeys the equation

$$\sum_{l'}[(E-V_A)\delta_{ll'}-t_{ll'}]G^0_{l'l''}=\delta_{ll''}. \tag{7}$$

$a_l(k)$ can be obtained likewise from the equations

$$a_l(k)=a_l^0(k)+\sum_{l'} G_{ll'}V_{l'}a^0_{l'}(k) \tag{8}$$

or

$$a_l(k)=a_l^0(k)+\sum_{l',l''} G^0_{ll'}T_{l'l''}a^0_{l''}(k) \tag{9}$$

introducing the Green function

$$G_{ll'}=\langle l'|\frac{1}{E-H}|l\rangle \tag{10}$$

with

$$\sum_{l'}[(E-V_A-V_l)\delta_{ll'}-t_{ll'}]G_{l'l''}=\delta_{ll''}, \tag{11}$$

which can be expressed in terms of $G^0_{ll'}$ as

$$G_{ll'}=G^0_{ll'}+\sum_{l''} G^0_{ll''}V_{l''}G_{l''l'} \tag{12}$$

and the T matrix defined by

$$T_{ll'}=V_l\delta_{ll'}+\sum_{l''} V_l G^0_{ll''}T_{l''l'}. \tag{13}$$

After the Fourier transformation

$$a_q(k)=\frac{1}{\sqrt{N}}\sum_{l} a_l(k)e^{-iqr_l} \tag{14}$$

we obtain, from Eqs. (4) with (5) and from Eqs. (12) and (13),

$$a_q(k)=\delta_{qk}+G^0(q,E)\sum_{p} V(q-p)a_p(k), \tag{15}$$

$$\begin{aligned}G(q,p,E)=&\,G^0(q,E)\delta_{qp}+G^0(q,E)\\&\times\sum_{p'} V(q-p')G(p',p,E),\end{aligned} \tag{16}$$

and

$$T(q,p,E)=V(q-p)+\sum_{p'} V(q-p')G^0(p',E)T(p',p,E), \tag{17}$$

with

$$G^0(q,E)=\frac{1}{E-\epsilon(q)-V_A}, \tag{18}$$

$$\epsilon(q)=\frac{1}{N}\sum_{l,l'} t_{ll'}e^{-iq(r_l-r_{l'})}. \tag{19}$$

The exact eigenvalues of the Hamiltonian (2) are given by the poles and branch cuts either of $G(q,p,E)$ or of $T(q,p,E)$, and can be obtained, in principle, solving one of the integral equations (16) or (17).

III. DEFINITION OF AVERAGE QUANTITIES FOR ONE GIVEN SAMPLE

We now try to replace the Hamiltonian (2) of the given mixed crystal by a Hamiltonian with identical (additional to V_A) on all lattice sites potentials M (called the self-energy) in such a way, that the second Hamiltonian reproduces the exact eigenvalues of Eq. (2). This is possible only, of course, if the self-energy M itself depends on the energy E.

In contrast to standard treatments,[20] the definition of M given below does not involve an ensemble averaging over many samples of mixed crystals. Let $\Psi(r)$ be an eigenstate of Eq. (2), and let

$$u_k(r)=e^{-ikr}\Psi(r) \tag{20}$$

and

$$\overline{u_k}(r)=\frac{1}{N}\sum_i u_k(r+r_i)=\overline{u_k}(r+r_l), \tag{21}$$

where k is a real vector within the first Brillouin zone of the unperturbed lattice. Then

$$\overline{\Psi}_k(r)=e^{ikr}\overline{u_k}(r) \tag{22}$$

defines a set of averaged wave-functions which are of Bloch-type.

Expanding $\overline{\Psi}_k(r)$ as

$$\overline{\Psi}_k(r)=\sum_l \overline{a_l}(k)\varphi(r-r_l), \tag{23}$$

we obtain

$$\overline{a_l}(k)=\frac{1}{N}\sum_i a_{l+i}(k)e^{-ikr_i}, \tag{24}$$

which are given from Eq. (4) by

$$\overline{a_l}(k)=a_l^0(k)+\sum_{l'} G_{ll'}^0\frac{1}{N}\sum_i V_{l'+i}a_{l'+i}(k)e^{-ikr_i}. \tag{25}$$

$\overline{a_l}(k)$ and $\overline{\Psi}_k(r)$ have the properties

$$\text{(i)}\quad \overline{a_{l+i}}(k)=\overline{a_l}(k)e^{ikr_i},$$

$$\text{(ii)}\quad \overline{\Psi}_k(r+r_i)=e^{ikr_i}\overline{\Psi}_k(r),$$

$$\text{(iii)}\quad \overline{\Psi}_k(r)=\frac{1}{N}\sum_i e^{-ikr_i}\Psi(r+r_i). \tag{26}$$

The definition of the self-energy as

$$M(k,E)\overline{a_l}(k)=\frac{1}{N}\sum_i V_{l+i}a_{l+i}(k)e^{-ikr_i} \tag{27}$$

results in

$$\overline{a_l}(k)=a_l^0(k)+M(k,E)\sum_{l'} G_{ll'}^0\overline{a_{l'}}(k). \tag{28}$$

In the case of $k=0$, definition (27) together with Eq. (24) is the strict analog of the definition of the effective dielectric constant of a composite material[16]

$$\varepsilon\frac{1}{V}\int \vec{E}(\vec{r})dV=\frac{1}{V}\int \varepsilon(\vec{r})\vec{E}(\vec{r})dV.$$

We now define an averaged Green function and an averaged T matrix by

$$\overline{G_{ll'}}=\frac{1}{N}\sum_i G_{l+i,l'+i}=\overline{G(l-l')} \tag{29}$$

and

$$\overline{T_{ll'}}=\frac{1}{N}\sum_i T_{l+i,l'+i}=\overline{T(l-l')}. \tag{30}$$

After Fourier transformation, we obtain

$$\overline{a_q}(k)=a_k(k)\delta_{qk}=a_k\delta_{qk}, \tag{31}$$

$$a_k=\frac{1}{1-M(k,E)G^0(k,E)}, \tag{32}$$

$$\overline{G(q,p,E)}=G(q,q,E)\delta_{qp}=G(q,E)\delta_{qp}, \tag{33}$$

$$G(k,E)=\frac{G^0(k,E)}{1-M(k,E)G^0(k,E)}, \tag{34}$$

$$\overline{T(q,p,E)}=T(q,q,E)\delta_{qp}=T(q,E)\delta_{qp}, \tag{35}$$

$$M(k,E)[1+G^0(k,E)T(k,E)]=T(k,E), \tag{36}$$

and

$$T(k,E)=\frac{1}{\sqrt{N}}\sum_l V_la_l(k)e^{-ikr_l}. \tag{37}$$

Equations (28), (33), and (34) are identical with the corresponding ones of a crystal with only one kind of atom V_A+M on all sites, which proves that definition (27) replaces the mixed crystal by a one-atomic one. Because the poles of $\overline{G_{ll'}}$ by definition (29) are identical to those of $G_{ll'}$, the so-defined one-atomic crystal has the same eigenvalue spectrum as the original mixed one.

IV. SPECTRAL REPRESENTATION OF THE AVERAGED *T* MATRIX AND THE SELF-ENERGY

Following Bergman and Stroud,[17] we define a scalar product between arbitrary quantities α_l and β_l given on the B sites as

$$(\alpha,\beta)=\frac{1}{N}\sum_{l\epsilon B}\alpha_l^*\beta_l=\frac{1}{N}\sum_l \alpha_l^{ast}\delta_{l\epsilon B}\beta_l. \tag{38}$$

Defining further a_{l0} with $l\epsilon B$ as

$$a_{l0}=a_le^{-ikr_l} \tag{39}$$

we can write Eq. (37) as

$$T(k,E)=V(1,a_0)\sqrt{N}.$$

Within this scalar product, a_0 obeys the operator equation [from Eq. (4)]

$$a_0=\frac{1}{\sqrt{N}}+V\Gamma a_0, \tag{40}$$

with Γ given by

$$\Gamma_{ll'}=e^{-ikr_{l'}}G^0_{ll'}e^{ikr_l}\delta_{l\epsilon B}\delta_{l'\epsilon B}. \tag{41}$$

It is easily seen that Γ is a self-adjoint operator for all energies outside the unperturbed band of the A crystal, where $\mathrm{Im}G^0_{ll'}(E)=0$. Equation (40) has the formal solution

$$a_0=\frac{1/\sqrt{N}}{1-V\Gamma}, \tag{42}$$

and we obtain

$$T(k,E)=\left(1,\frac{1}{s-\Gamma}1\right), \tag{43}$$

with $s=1/V$.

With the complete orthonormal set of eigenfunctions φ^i_l of $\Gamma_{ll'}$ (for E outside the unperturbed band)

$$\sum_{l'}\Gamma_{ll'}\varphi^i_{l'}=s_i\varphi^i_l, \tag{44}$$

we obtain

$$T(k,E)=\sum_i(1,\varphi_i)\left(\varphi_i,\frac{1}{s-\Gamma}1\right)=\sum_i\frac{|(1,\varphi_i)|^2}{s-s_i}=\sum_i\frac{f_i}{s-s_i} \tag{45}$$

with k- and E-dependent s_i's, which are real outside the unperturbed band. The residua f_i depend on k and E, too.

The s_i-values may be continuous, in general, and we have to write finally the spectral representation as

$$T(k,E)=\int ds'\frac{f(s')}{s-s'}, \tag{46}$$

with

$$s=\frac{1}{V}=\frac{1}{V_B-V_A}.$$

Therefore, for energies outside the unperturbed band the averaged T matrix as a function defined in the complex s plane is analytic beside single poles and branch cuts on the real axis. From Eq. (36) we obtain

$$M(k,E)=\frac{\int ds'\frac{f(s')}{s-s'}}{1+G^0(k,E)\int ds'\frac{f(s')}{s-s'}} \tag{47}$$

as a spectral representation of the self-energy of one given sample.

Poles of the T matrix in the energy plane correspond to poles in the $s=1/V$ plane via $s_i=s_i(k,E)$. At poles of T, Eq. (47) results in

$$M(k,E)G^0(k,E)=1 \tag{48}$$

or

$$\frac{1}{N}\sum_k\frac{M(k,E)}{E-V_A-\varepsilon(k)}=1, \tag{49}$$

in strict analogy to the Koster-Slater equation[19]

$$\frac{1}{N}\cdot\sum_k\frac{V}{E-V_A-\varepsilon(k)}=1 \tag{50}$$

for the case of one impurity with δ-like potential V.

The spectral representations (46) and (47) are obtained for E outside the unperturbed band of the A crystal. Both $T(k,E)$ and $M(k,E)$ for E inside this band have to be obtained by analytic continuation to $E+i\varepsilon$ [$T(k,E)$ and $M(k,E)$ are analytic functions in the complex E-plane besides of poles and banch cuts on the real axis].

Equation (47) corresponds to Bergman's spectral representation of the dielectric constant of heterogeneous media. However, in the electrostatic problem the nominator corresponding to that of Eq. (47) is identical to one because the wave number k is zero in the static case and $G^0(k=0,E)=0$ due to the boundary conditions chosen on the surfaces of a finite sample. As in the case of Bergman's spectral representation of the dielectric constant, the spectral respresentations Eqs. (46) and (47) represent exact separations between structure and material-dependent properties of mixed crystals: f_i,s_i [or $f(s)$] depend only on the special structure of the mixed crystal (i.e., on the knowledge of which sites l are occupied by the perturbing potential), whereas the magnitude $V=V_B-V_A$ of the perturbing potential enters only the quantity s. Different from the case for the dielectric constant, f_i,s_i [or $f(s)$] depend, however, on the choice of the unperturbed system as discussed in Secs. V and VII.

$T(k,E)$ as given by Eq. (45) is a rational function. $M(k,E)$ as given by Eq. (47) then is rational, too, and consequently has a similar spectral representation

$$M(k,E)=\sum_i\frac{g_i}{s-\tilde{s}_i},\quad \text{resp.}\quad =\int\frac{g(s')ds'}{s-s'}. \tag{51}$$

In the electrostatic case treated by Bergman,[16] the poles of the spectral representation correspond to electrostatic resonances, corresponding to energy eigenvalues in the quantum-mechanical case. Hence the spectral representation for the T matrix (46) and the spectral representation for the self-energy (47) are analogs to Bergman's result. The poles, or the branch cuts of Eq. (51), are connected to but not identical with the spectrum of the energy eigenvalues.

V. EXACT PROPERTIES OF THE SPECTRAL FUNCTIONS $f(s)$ AND $g(s)$

The knowledge of analytical properties of $T(k,E)$ and $M(k,E)$ in the complex $1/V$-plane is interesting, and would, e.g., allow a test of approximate results, but it could not be used in order to obtain quantitative approximations if no additional exact results for the spectral function $f(s)$ and $g(s)$ in (46) and (51) would be known. From $f_i=|(1,\varphi_i)|^2$, we first obtain

$$\text{(i)}\quad 0\leqslant f_i\leqslant 1 \quad\text{or}\quad 0\leqslant f(s)\leqslant 1. \tag{52}$$

From Eq. (46), for large s (small $V=V_B-V_A$), we obtain

$$T(k,E)=\frac{1}{s}\int ds'\left[1+\frac{s'}{s}+\cdots\right]f(s'). \tag{53}$$

The terms of this series expansion can be calculated exactly up to the first order in V, and up to all orders in the special case of a homogeneous isotropic distribution of the B sites in an infinite crystal (such a distribution is self-averaging and yields the same results as an ensemble average). So it is possible to obtain the first moment $\mu_0=\Sigma_i f_i$ [or $=\int f(s)ds$], and the next ones $\mu_n=\Sigma_i s_i^n f_i$ [or $=\int s^n f(s)ds$] for this special distribution, exactly: From Eq. (37), with Eqs. (8) and (5),

$$a_l=\frac{1}{\sqrt{N}}\left[e^{ikr_l}+\sum_{l'} G^0_{ll'}V_{l'}e^{ikr_{l'}}+\cdots\right], \tag{54}$$

we obtain

$$\begin{aligned}T(k,E)&=\frac{1}{N}\sum_l V_l+\frac{1}{N}\sum_{l,l'} V_lG^0_{ll'}V_{l'}e^{-ik(r_l-r_{l'})}+\cdots\\&=cV+\frac{1}{N}\sum_l V_lV_lG^0(E)\\&\quad+\frac{1}{N}\sum_{l\neq l'} V_lG^0_{ll'}V_{l'}e^{-ik(r_l-r_{l'})}+\cdots\\&=cV+cV^2G^0(E)+\frac{1}{N}\sum_{l\neq l'} V_lG^0_{ll'}V_{l'}e^{-ik(r_l-r_{l'})}\\&\quad+\cdots,\end{aligned} \tag{55}$$

with

$$G^0(E)=G^0_{ll}(E)=\frac{1}{N}\sum_k G^0(k,E).$$

Comparing Eqs. (53) and (55), we obtain

$$\text{(ii)}\quad \mu_0=\sum_i f_i=c \quad\text{or}\quad \mu_0=\int f(s)ds=c. \tag{56}$$

$G^0_{ll'}e^{-ik(r_l-r_{l'})}$ in the last line of Eq. (55) depends only on the distances between l and l'. The double summation has to be carried out only over B sites ($V_l=0$ otherwise). In the case of an infinite sample with a homogeneous distribution of the B sites, the double sum over these sites is simply equal to (a weighted) double sum over all sites, all distances $l-l'$ with $l,l'\epsilon B$ occur with the same probability as $l-l'$ without the restriction to the B sublattice,

$$\sum_{l\neq l',l,l'\epsilon B}=c^2\sum_{l\neq l'} \quad\text{for } N\to\infty. \tag{57}$$

Therefore, we can write

$$\begin{aligned}\frac{1}{N}\sum_{l\neq l'} V_lG_{ll'}V_{l'}e^{ik(r_l-r_{l'})}&=c^2V^2\frac{1}{N}\sum_{l\neq l'} G_{ll'}e^{-ik(r_l-r_{l'})}\\&=c^2V^2[G^0(k,E)-G^0(E)],\end{aligned}$$

and obtain

$$T(k,E)=cV+c(1-c)V^2G^0(E)+c^2V^2G^0(k,E). \tag{58}$$

Comparing Eqs. (58) with Eqs. (53) and (56), we obtain

$$\text{(iii)}\quad \mu_1=\sum_i s_if_i=c(1-c)G^0(E)+c^2G^0(k,E)$$

or (59)

$$\mu_1=\int sf(s)ds=c(1-c)G^0(E)+c^2G^0(k,E)$$

for isotropic and homogeneous distributions.

In the famous work of Yonezawa and Matsubara,[20] sums of the kind $\Sigma_{l_1\epsilon B}\Sigma_{l_2\epsilon B}\cdots\Sigma_{l_n\epsilon B}e^{-i\Sigma_jp_jr_j}$ have been calculated for all n in the case of isotropic and homogeneous distributions of the B sites. Using these results all moments μ_n can be calculated exactly. We obtain, e.g.,

$$\begin{aligned}\text{(iv)}\quad \mu_2=&\,c^3[G^0(k,E)]^2+(c-3c^2+2c^3)[G^0(E)]^2\\&+2c(c-c^2)G^0(k,E)G^0(E)\\&+c(c-c^2)\frac{1}{N}\sum_q [G^0(q,E)]^2.\end{aligned} \tag{60}$$

The resulting series (53) cannot be summed up, however, and exact expressions for $T(k,E)$ and $M(k,E)$ cannot be obtained.

For $c\to 0$ this summation can be performed and reproduces the result of Koster and Slater,[19]

$$\begin{aligned}T(k,E)&=c\cdot V+cV^2G^0(E)+cV^3[G^0(E)]^2+\cdots\\&=\frac{cV}{1-VG^0(E)},\end{aligned} \tag{61}$$

corresponding to $T=1/N\Sigma_{i\epsilon B}t_i=ct$, where t is the t matrix of one impurity. As opposed to the Bergman spectral representation of the dielectric function, all moments μ_i for $i\geqslant 1$ depend via $G^0(E)$ and $G^0(k,E)$ on the choice of the unperturbed system (potential V_A).

Defining the moments of the self-energy in analogy to those of the T matrix as $\nu_n=\int s^ng(s)ds$, from Eqs. (47), (56), (59) and (60) we obtain

$$\text{(i)}\quad \nu_0=c,$$

$$\text{(ii)}\quad \nu_1=c(1-c)G^0(E),$$

$$\begin{aligned}\text{(iii)}\quad \nu_2=&\,(c-3c^2+2c^3)[G^0(E)]^2\\&+c^2(1-c)\frac{1}{N}\sum_q [G^0(q,E)]^2.\end{aligned} \tag{62}$$

Further, at least in the case of δ-like potentials, the poles $s=s_i$, or the branch cuts of the averaged T matrix, are restricted for a given energy E outside the unperturbed band to special sections of the real axis:

Equation (44) has solutions for energies outside the unperturbed band (for a given V) only where the homogeneous counterpart

$$a_l(k)=\sum_{l'} G^0_{ll'}V_{l'}a_{l'}(k) \tag{63}$$

to the inhomogeneous equation (4) has solutions, i.e., at energy eigenvalues. This statement is equivalent to the fact that the T matrix can have poles (or branch cuts) for a given V only at eigenenergies. On the other hand, we know from the Saxon-Hutner conjecture[2] (for a discussion see Ref. 1) that the energy eigenvalues of a mixed crystal with δ-like potentials are restricted to the energy regions where both end members (the A and B crystals) have eigenvalues.

Hence, for a given E above the unperturbed energy band, $E>E_0=V_A+(W/2)$, W being the width of the unperturbed energy band (for simplicity assumed here to be symmetric), the possible potential values V corresponding to poles or branch cuts are restricted by $V_{\min}=E-E_0\leqslant V\leqslant V_{\max}=E-E_u$, with $E_u=V_A-(W/2)$, and for $E>E_0$ we obtain

$$s_{\max}=\frac{1}{E-E_0}\geqslant s_i\geqslant s_{\min}=\frac{1}{E-E_u} \tag{64}$$

as restrictions for possible poles and branch cuts on the real axis. For $E<E_u=V_A-(W/2)$ we obtain

$$s_{\max}=\frac{1}{E-E_u}\geqslant s_i\geqslant s_{\min}=\frac{1}{E-E_0} \tag{65}$$

in the same manner.

VI. SPECTRAL MOMENTS OF SINGLE-SITE THEORIES

Most self-energies of so-called single-site approximations (see, e.g., Ref. 1) are given by

$$\Sigma=M+V_A=\overline{V}+\frac{\langle t\rangle}{1+\langle t\rangle G^0_{\overline{V}}(E)}, \tag{66}$$

with

$$G^0_{\overline{V}}(E)=\frac{1}{N}\sum_k \frac{1}{E-\varepsilon(k)-\overline{V}}, \tag{67}$$

and the averaged single-site t matrix

$$\langle t\rangle=\frac{(1-c)(V_A-\overline{V})}{1-(V_A-\overline{V})G^0_{\overline{V}}(E)}+\frac{c(V_B-\overline{V})}{1-(V_B-\overline{V})G^0_{\overline{V}}(E)}. \tag{68}$$

Equation (66) together with Eq. (68) results in

$$\frac{\Sigma-\overline{V}}{1-\left(\Sigma-\overline{V}\right)G^0_{\overline{V}}(E)}=(1-c)\frac{(V_A-\overline{V})}{1-(V_A-\overline{V})G^0_{\overline{V}}(E)}+c\frac{(V_B-\overline{V})}{1-(V_B-\overline{V})G^0_{\overline{V}}(E)}. \tag{69}$$

Different self-energy expressions differ by the choice of the potential $\overline{V}$ which is chosen as

(i) $\overline{V}=V_A$: average t-matrix approximation A, (70)

(ii) $\overline{V}=V_B$: average t-matrix approximation B, (71)

(iii) $\overline{V}=(1-c)V_A+cV_B$: symmetrized average t-matrix approximation, (72)

(iv) $\overline{V}=\Sigma=M+V_A$: coherent-potential approximation. (73)

$\overline{V}=\infty$ results in the virtual-crystal approximation $\Sigma=(1-c)V_A+cV_B$. The only exception is the Klauder-V (Ref. 7) self-energy, an approximation to the coherent-potential expression given by

$$M=\frac{c(V_B-V_A)}{1-(V_B-V_A)G^0_{M+V_A}(E)}. \tag{74}$$

This can be considered a small-c expansion $M\sim 0$ of the coherent-potential approximation, obtained from Eqs. (69) and (72) to be given by

$$M=\frac{c(V_B-V_A)}{1-(V_B-V_A-M)G^0_{M+V_A}(E)}, \tag{75}$$

maintaining, however, the self-consistency in the Green function $G^0_{M+V_A}(E)$. Replacing this function in Eq. (74) by $G^0_{V_A}(E)$, the Koster-Slater result $M=\langle t\rangle$ with $\langle t\rangle=ct$ and

$$t=\frac{V}{1-VG^0_{V_A}(E)} \tag{76}$$

[see Eq. (61)] is obtained.

The different single-site expressions for the self-energies are the strict analogs to different expressions for the dielectric constant of heterogeneous media. Introducing like $\overline{V}$ a mean dielectric constant $\overline{\varepsilon}$ in the case of a medium consisting of two materials with different ε_A and ε_B, most known expressions for the effective dielectric constant ε are given by

$$\frac{\varepsilon-\overline{\varepsilon}}{2\overline{\varepsilon}+\varepsilon}=(1-c)\frac{\varepsilon_A-\overline{\varepsilon}}{2\overline{\varepsilon}+\varepsilon_A}+c\frac{\varepsilon_B-\overline{\varepsilon}}{2\overline{\varepsilon}+\varepsilon_B}. \tag{77}$$

Choosing for $\overline{\varepsilon}$ either ε_A or ε_B we obtain the two different Maxwell-Garnett[14] expressions in analogy to the average t matrix approximations A and B.

$\overline{\varepsilon}=(1-c)\varepsilon_A+c\varepsilon_B$ gives the result obtained in Refs. 21 and 22 by other methods. The self-consistent choice $\overline{\varepsilon}=\varepsilon$

results in the Bruggeman expression,[15] and the small-c expansion leading to the Koster-Slater self-energy (61) here results in the expression given by Landau[23] and Böttcher.[24] Choosing $\bar{\varepsilon}=\infty$, we obtain one of the Wiener expressions[25] $\varepsilon=(1-c)\varepsilon_1+c\varepsilon_2$, the analog of the virtual-crystal approximation.

Expanding expressions (73)–(72) in powers of $V=V_B-V_A$ (or $\bar{V}$), in the first three cases we obtain

$$\text{(i)}\quad M=cV+c(1-c)V^2G^0_{V_A}(E), \tag{78}$$

$$\text{(ii)}\quad M=cV+c(1-c)V^2G^0_{V_B}(E), \tag{79}$$

$$\text{(iii)}\quad M=cV+c(1-c)V^2G^0_{\bar{V}}(E)\quad \text{with } \bar{V}=(1-c)V_A+cV_B. \tag{80}$$

If $G^0(E)$ would be an analytic function of E, the differences $G^0_{V_B}(E)-G^0_{V_A}(E)$ [or $G^0_{\bar{V}}(E)-G^0_{V_A}(E)$] for small V would be proportional to V. Therefore, all three expressions would yield the first two moments of $M(k,E)$, as given by Eq. (62).

In the case of the coherent-potential approximation, we obtain

$$\text{(iv)}\quad M=cV+cV[V-M]G^0_{V_A+M}(E). \tag{81}$$

The coherent-potential approximation would result in the correct second moment only if for small V $M(k,E)$ would be given by $M(k,E)=cV$ [and if $G^0(E)$ would be analytic], which is not the case for energies in the vicinity of those of bound states of one impurity [given by $1=VG^0(E)$] due to a peak in Im$M(k,E)$.[8,18]

In the case of the Klauder-V approximation, we obtain

$$\text{(v)}\quad M=cV+cV^2G^0(E-V_A-M), \tag{82}$$

which results in a wrong second moment, too. The fact that $G^0(E)$ is not analytic will be considered in Sec. VII.

It is generally believed that the coherent-potential approximation as the result of a self-consistent theory is the best possible single-site approximation. Connected with the fact that it does not reproduce the second moment at special energies, it shows still another even more important shortcoming: for energies near those of bound states of single impurities, the coherent-potential approximation does not reproduce the correct small and large concentration limits. This is due to the fact that a linearized (in a small parameter, c in our case) solution of a nonlinear equation differs from the exact solution of the corresponding linearized equation, in general. The operations ''linearization'' and ''solution'' do not commute. Let us consider the easiest possible example: The nonlinear in c equation $(x-a_1-c)(x-a_2-c)=0$ has the solutions $x_1=a_1+c$ and $x_2=a_2+c$. The linearized equation $x^2-x(a_1+a_2+2c)+a_1a_2+c(a_1+a_2)=0$ has the solutions

$$x'_{1/2}=\frac{a_1+a_2+2c}{2}\pm\left(\frac{(a_1+a_2+2c)^2}{4}-a_1a_2-c(a_1+a_2)\right)^{1/2}, \tag{83}$$

which coincide for small c with x_1 and x_2 as long as $a_1\neq a_2$. If, however, $a_1=a_2=a$, this means if we have degenerate solutions for $c=0$, we obtain $x'_1=a+2c$ and $x'_2=a$, which are not correct in the small-c limit.

The result of the coherent-potential approximation is given by

$$\Sigma=M+V_A=V_A+\frac{c(V_B-V_A)}{1-(V_B-\Sigma)G^0(E-\Sigma)}. \tag{84}$$

Choosing, e.g., $V_A=-D/2, V_B=D/2$, and the Hubbard[26] Green function (bandwidth $W=2$)

$$ReG^0(E)=2[E-\text{sgn}(E)\sqrt{E^2-1}], \tag{85}$$

we obtain a third-order equation for Σ.[8,18] The three solutions for $c=0$ are given by

$$\Sigma=\left(-\frac{D}{2},-\frac{D}{2},\frac{1+D^2-DE}{2(D-2E)}\right). \tag{86}$$

The degeneracy of the first two solutions is due to the fact that we have had to square $G^0(E)$ in order to obtain the third-order equation for Σ, and is of no relevance. But the energy of a single impurity of strength $V_B=D/2$ is given by $1=DG^0[E+(D/2)]$ which results in $E=(D/2)+(1/4D)$. At this energy the third solution for $c=0$ becomes degenerate with the first two. Hence, the solution of the coherent potential equation would be correct linearly in c only if Eq. (84) itself would be correct up to c^2. This, however, is not the case because some of the graphs $\sim c^2, \sim c^3$, etc. are neglected in single-site theories (see, e.g., Refs. 1 and 20). The same is true in the case of the Klauder-V approximation. Exchanging V_A with V_B the same arguments can be repeated for the case of small $1-c$. The physical consequence of this shortcoming is that the densities of states of both the coherent potential and the Klauder-V approximations near the energies of bound states of single impurities do not become δ like for small c (or small 1-c) and that the widths of the impurity bands are too large, as discussed in Refs. 18 and 27.

VII. AN IMPROVED EXPRESSION FOR THE SELF-ENERGY OF MIXED CRYSTALS

The three different average t-matrix approximations cited in Sec. VI result in correct second spectral moments if $G^0(E)$ is an analytic function of energy. However, they do not fulfill the Saxon-Hutner conjecture: $G^0_{\bar{V}}(E)$ and, hence, $M(k,E)$ have nonvanishing imaginary parts only for

$$-\frac{W}{2}+\bar{V}\leqslant E\leqslant\frac{W}{2}+\bar{V}, \tag{87}$$

where W is the unperturbed bandwidths (assumed to be symmetric), and not in the entire regions

$$-\frac{W}{2}+V_A\leqslant E\leqslant\frac{W}{2}+V_A \quad \text{and} \quad -\frac{W}{2}+V_B\leqslant E\leqslant\frac{W}{2}+V_B, \tag{88}$$

where possible large clusters of only A (B) atoms obviously contribute to the density of states with small but finite probability.

Until now we treated the crystal in which all lattice sites are occupied by A atoms (potentials V_A) as the unperturbed one. As a result the second moment of the self-energy in Eq. (62) depends on $G^0(E)=G^0_{V_A}(E)$. Repeating the whole analysis, choosing the B crystal with all lattice sites ocupied by B-atoms as the unperturbed one, the second moment of the self-energy would be different from that given by Eq. (62):

$$\widetilde{\nu}_1=c(1-c)G^0_{V_B}(E)\neq\nu_1=c(1-c)G^0_{V_A}(E). \tag{89}$$

As opposed to Bergman's spectral representation of the dielectric constant, the second moments of the T matrix and of the self-energy depend not only on the concentration but on the choice of the unperturbed system (A or B crystal), too. Because $G^0(E)$ is not an analytic function of E the difference $G^0_{V_B}-G^0_{V_A}$ cannot be expanded in a power series in $V=V_B-V_A$ and, hence, the difference between the two second moments cannot be compensated for by higher-order ones. The same is true for the third moment and all higher moments. Because an exact expression for the self-energy has to be independent of the special choice of the unperturbed system we have to conclude, that series expansions in powers of $V=V_B-V_A$ like Eq. (53) cannot converge. In difference to the case of the classical dielectric constant it is not possible to construct an approximate theory which is correct in the limit of small $V_B-V_A=V$ for all c (reproducing a unique second moments of the T matrix or the self-energy). The physical reason behind this difficulty is that each higher moment contains one higher degree in the concentration c. For its exact calculation at least one more impurity has to be taken into account. However, adding one more impurity to a given impurity configuration gives rise to the formation of additional (molecular) energy eigenstates, which obviously results in a nonanalytic behavior.

However, the T matrix and the self-energy Σ are exactly known for arbitrary $V=V_B-V_A$ in the limits $c\to 0$ and $c\to 1$. This allows us to construct an interpolation formula for the self-energy, which is correct for all V in the limits $c\to 0$ and $c\to 1$: With $\Sigma=V_A+M$ and $M=T/[1+G^0(k,E)T]$, from Eq. (61) we obtain

$$\Sigma=V_A+\frac{c(V_B-V_A)}{1-(V_B-V_A)G^0_{V_A}(E)}. \tag{90}$$

Choosing the unperturbed system to be a B crystal (all lattice sites occupied by B atoms), we likewise obtain

$$\Sigma=V_B-\frac{(1-c)(V_B-V_A)}{1+(V_B-V_A)G^0_{V_B}(E)}, \tag{91}$$

which is correct in the limit of $c\to 1$. Therefore, the limiting values $\Sigma|_{c=0}$, $(d\Sigma/dc)|_{c=0}$, $\Sigma|_{c=1}$, and $(d\Sigma/dc)|_{c=1}$ are exactly known for all $V=V_B-V_A$.

The second (and higher) derivatives of Σ in both limits $c\to 0$ and $c\to 1$ could, in principle, be obtained from the exact knowledge of all higher moments μ_i (ν_i) for $i\geqslant 2$ in the case of isotropic and homogeneous impurity distributions V_B (V_A) in the A (B) crystal, calculated from the results of Yonezawa and Matsubara.[20] These calculations would correspond to the solution of the eigenvalue problem for two (and more) impurities at arbitrary distances, which is possible within the choosen simple model of δ-like potentials. However, the necessary summation of the infinite series [leading to Eq. (61) in first order in c] cannot be performed in the second order and in higher orders in c [or in $(1-c)$ in the case of a B crystal].

Due to the lack of knowledge about $(d^2\Sigma/dc^2)|_{c=0}$, $(d^2\Sigma/dc^2)|_{c=1}$, and the higher derivatives, there is only the possibility to obtain an approximate $\Sigma(c)$, using a Padé-interpolation formula

$$\Sigma(c)=\frac{\alpha'+\beta'c+\gamma'c^2}{1+\delta c}=\alpha+\beta c+\frac{\gamma}{1+\delta c}, \tag{92}$$

where α,β,γ and δ are chosen in such a way that $\Sigma|_{c=0}$, $(d\Sigma/dc)|_{c=0}$, $\Sigma|_{c=1}$ and $(d\Sigma/dc)|_{c=1}$ are reproduced exactly. The result is given by

$$\alpha=\Sigma|_{c=0}-\gamma,\quad \beta=\gamma\delta+\left.\frac{d\Sigma}{dc}\right|_{c=0},$$

$$\gamma=\frac{1+\delta}{\delta^2}\left[\Sigma|_{c=1}-\Sigma|_{c=0}-\left.\frac{d\Sigma}{dc}\right|_{c=0}\right], \tag{93}$$

$$\delta=\frac{\left.\frac{d\Sigma}{dc}\right|_{c=0}-\left.\frac{d\Sigma}{dc}\right|_{c=1}}{\Sigma|_{c=1}-\Sigma|_{c=0}-\left.\frac{d\Sigma}{dc}\right|_{c=1}}-2.$$

This is identical with what was obtained in Ref. 18, where it was shown that Eq. (92) with Eq. (93) fullfills the Saxon-Hutner conjecture and has correct analytic properties as a function of complex E.

As an interpolation between two single-site theories, Eq. (92) with Eq. (93) does not correctly describe molecular eigenstates due to impurity molecules (see, e.g., Ref. 28) and, hence, cannot result in a correct description of band tails. The general behavior of the density of states, however, was proved[18] to be quite satisfactory: as opposed to the coherent-potential approximation a reasonable band tailing is obtained and in the limits $c\to 0$ and $c\to 1$ the density of states shows the expected peak structure at energies near those of bound states of single impurities.

VIII. CONCLUSIONS

We have proved that the self-energy of the standard model of a mixed crystal has a spectral representation in the complex $s=1/(V_B-V_A)$ plane which is a simple generalization of that obtained by Bergman for the dielectric constant of a classical heterogeneous material. The first three moments of the corresponding spectral function have been calculated, and exact bounds for the positions of poles and branch cuts of the averaged T matrix in the s plane have been obtained. The results are used to test the quality of approximate expressions for the self-energy. In particular, it was proved that the coherent potential and the Klauder-V approximations fail to reproduce the second moment.

As opposed to the Bergman spectral representation of the dielectric function, the moments of the spectral function depend on the choice of the unperturbed system in a nonanalytic way. This fact prevents the construction of a self-energy which is correct for all concentrations in the limit of small perturbing potentials. However, it is possible to obtain an expression for the self-energy which, for arbitrary perturbing potentials, reproduces the exactly known limits $c \rightarrow 0$ and $c \rightarrow 1$ and interpolates between them in a reasonable way. The basic assumption used is that all potentials are short ranged and do not overlap. In this sense the whole analysis has model character only. This, however, is a general unsolved problem in all disorder theories: as far as we know, as of now there exists no technique to exclude possible multiple occupancies in theories with overlapping potentials.

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