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Comments and Addenda

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Low-concentration limit of the frequency-dependent electrical conductivity for disordered binary alloys

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The frequency-dependent electrical conductivity for binary disordered alloys with diagonal disorder is calculated exactly in the single-impurity limit. To evaluate the expression numerically at finite impurity concentrations, an approximation valid for frequencies larger than a number Γ proportional to the concentration is introduced. At sufficiently low concentrations ($y < 10^{-4}$), Velicky's coherent-potential approximation to the conductivity agrees numerically with this expression. Inadequacies of the exact result in the $\omega \rightarrow 0$ limit are due to terms of $O(y^2)$ neglected in the equation-of-motion method for the single-impurity model problem.

In the study of electronic properties of disordered alloys, the coherent-potential approximation (CPA)[1] can be regarded as a scheme which interpolates between prescribed limits corresponding to weak or strong scattering and also to the entire range of impurity concentrations. This point of view was originally suggested by Onodera and Toyozawa[2] and was subsequently emphasized by Velicky, Kirkpatrick, and Ehrenreich,[3] who gave a detailed comparison of CPA results for the single-particle Green's function to the exact results for the small-bandwidth limit, the low-concentration limit, and the weak-scattering (Boltzmann) limit. Velicky was able to show[4] that a coherent-potential approximation for the transport coefficients collects all terms of lowest order in the impurity concentration and all terms up to third order in the impurity scattering strength. Thus Velicky established CPA as an interpolation scheme for the transport coefficients valid for all concentrations and all scattering strengths. A detailed comparison of Velicky's CPA to the known exact limits of the frequency-dependent conductivity is given in Ref. 5.

Of particular interest is the behavior of the CPA conductivity in the low-concentration limit. It has been noted[6,7] that Velicky's method is inherently incapable of predicting the existence of localized states or of a mobility edge in three dimensions. This failure is usually ascribed to the mean-field-like nature of the CPA, which overestimates the width of the impurity band in the split-band regime for low concentrations. Since we expect physically that widely separated (in low concentration) impurities with large scattering potentials will produce localized states near the impurity sites, the failure of CPA to predict this behavior at low concentrations is disturbing. It would be more satisfying to have an expression valid at low concentrations which did not suffer from this inadequacy. One step toward such an expression is taken in the present work.

Prior to CPA, work on the low-concentration conductivity was done by Langer[8] at $\omega = 0$ and by Lonke and Ron[9] at high frequencies. See Ref. 5 for a discussion.

Exact calculations of simplified models have played an important role in the theory of disordered alloys. The Koster-Slater single-impurity problem[10] for the single-particle Green's function is a well-known example. In fact the single-impurity calculation forms the foundation for the coherent-potential approximation. Another exact calculation[11] has proven useful as a touchstone for comparison of approximations for the Green's functions of the alloy problem with off-diagonal disorder. Since exact results (however restricted in scope) have proven useful in constructing physically interesting interpolation schemes in the past, we will present the following derivation of an exact expression for the frequency-dependent conductivity in the single-impurity limit.

The single-impurity limit is often treated in connection with studies of alloy density of states. We assume a finite crystal of N sites occupied by A-type atoms with $\epsilon_A = 0$. Then we replace the atom at the origin by a B-type impurity with $\epsilon_B = \delta$ so the second-quantized Hamiltonian in terms of Wannier states is

$$H = \sum t_{ij} c_i^\dagger c_j + \delta c_0^\dagger c_0 \,. \tag{1}$$

In Eq. (1) $c_i^\dagger$ (c_i) creates (annihilates) a Wannier state at the ith site. In terms of Bloch states, it is

$$H = \sum_k \epsilon_k n_k + \frac{\delta}{N} \sum_{kq} c_k^\dagger c_{k+q} \,. \tag{2}$$

We assume a single band so the band index is suppressed. We will study Zubarev-type[12] retarded thermal Green's functions, which will be indicated by the standard double-bracket notation. Single brackets will indicate a thermal average.

The single-particle Green's function

$$G_{kk'}(E) = \langle\langle c_k ; c_{k'}^\dagger \rangle\rangle_E \tag{3}$$

has an exact solution in this model given by

$$G_{kk'}(E) = \frac{\delta_{kk'}}{E - \epsilon_k} + \frac{1}{E - \epsilon_k} \frac{\delta/N}{1 - \delta F_0(E)} \frac{1}{E - \epsilon_{k'}} \,, \tag{4}$$

where $\delta_{kk'}$ is the Kronecker delta and

$$F_0(E) = N^{-1} \sum_k (E - \epsilon_k)^{-1} \,.$$

By multiplying the single-scattering t matrix

$$t(E) = \delta / [1 - \delta F_0(E)] \tag{5}$$

by y (finite concentration of B impurities) instead of N^{-1} in (4), we obtain the physically interesting case of yN independent B impurities in a host A crystal. As long as the average spacing ($\sim y^{-1/3}$) between impurities is large compared with the wavelength of an electron near the Fermi energy, we expect corrections of higher order in y to be negligible.

To first order in y, we obtain the configuration-averaged Green's function

$$\langle G_{kk'}(E) \rangle_c = \frac{\delta_{kk'}}{E - \epsilon_k - \Sigma(E)} \,, \tag{6}$$

where

$$\Sigma(E) = y\delta / [1 - \delta F_0(E)] \tag{7}$$

and $\langle\ \rangle_c$ is the average over configurations.

In the same spirit it is possible to find a solution for $\sigma(\omega)$ in this limiting case. It is convenient to write $\sigma(\omega)$ in the form

$$\sigma_{\mu\nu}(\omega) = -\Omega^{-1} \langle\langle J_\mu ; P_\nu \rangle\rangle_\omega = -\frac{2e}{\Omega} \sum_k v_k^\mu D_{kk}^\nu(\omega) \,, \tag{8}$$

where Ω is the crystal volume,

$$\vec{\mathrm{P}} = e \sum \vec{\mathrm{R}}_i n_i \,, \quad \vec{\mathrm{J}} = -i [\vec{\mathrm{P}}, H] \,, \quad v_k^\mu = \frac{\partial \epsilon_k}{\partial k_\mu} \,,$$

and

$$D_{kk'}^\nu = \langle\langle c_k^\dagger c_{k'} ; P_\nu \rangle\rangle_\omega \,.$$

We drop the explicit ν dependence in the future.

From the equation-of-motion method,[12] we find D satisfies

$$\omega D_{kk'}(\omega) = ie \left(\frac{\partial}{\partial k} + \frac{\partial}{\partial k'} \right) \langle c_k^\dagger c_{k'} \rangle - ie\, Y_{kk'}(\omega) \,, \tag{9}$$

where

$$e Y_{kk'}(\omega) \equiv \langle\langle c_k^\dagger c_{k'} ; J \rangle\rangle \,.$$

Then Y satisfies

$$(\omega^+ + \epsilon_k - \epsilon_{k'}) Y_{kk'}(\omega) = (v_{k'} - v_k) \langle c_k^\dagger c_{k'} \rangle + (\delta/N) [R_k(\omega) - S_{k'}(\omega)] \,, \tag{10}$$

where

$$R_k(\omega) \equiv \sum_{k'} Y_{kk'}(\omega) \,, \quad S_k(\omega) \equiv \sum_{k'} Y_{k'k}(\omega) \,.$$

It is possible to eliminate Y from (10) and obtain the coupled set of singular integral equations for R_k and S_k

$$\begin{aligned} &[1 - \delta F_0(\epsilon_k + \omega^+)] R_k(\omega) + \frac{\delta}{N} \sum_{k'} \frac{S_{k'}(\omega)}{\epsilon_k + \omega^+ - \epsilon_{k'}} = Q_k^R(\omega) \,, \\ &[1 - \delta F_0(\epsilon_k - \omega^+)] S_k(\omega) + \frac{\delta}{N} \sum_{k'} \frac{R_{k'}(\omega)}{\epsilon_k - \omega^+ - \epsilon_{k'}} = Q_k^S(\omega) \,, \end{aligned} \tag{11}$$

where

$$\begin{aligned} Q_k^R(\omega) &= -v_k \sum_{k' \neq k} \frac{\langle c_k^\dagger c_{k'} \rangle}{\epsilon_k + \omega^+ - \epsilon_{k'}} \,, \\ Q_k^S(\omega) &= -v_k \sum_{k' \neq k} \frac{\langle c_{k'}^\dagger c_{k'} \rangle}{\epsilon_k - \omega^+ - \epsilon_{k'}} \,. \end{aligned} \tag{12}$$

The expressions in (12) have been simplified by using time-reversal invariance, the fact that $\langle c_k^\dagger c_{k'} \rangle$ depends on k, k' only through ϵ_k, $\epsilon_{k'}$, and by neglecting a term of $O(1/N)$. Since the term neglected is also proportional to v_k and contributes to $\sigma(\omega)$ only to $O(1/N^2)$, it is neglected in (12) for convenience and does not alter the arguments. The expectation values are calculated according to[12]

$$\langle c_k^\dagger c_{k'}\rangle = \int_{-\infty}^{\infty}\frac{dE}{2\pi i}\, f(E)\,[G_{kk'}(E^-) - G_{kk'}(E^+)]\,,$$

where G is given by (4) and f is the Fermi function.

The equations (11) with inhomogeneous parts given by (12) form a coupled set of singular integral equations.[13] We will not discuss the general theory of such equations here. Suffice it to say it is possible to show the equations have a unique solution which is completely determined by the Q's. This conclusion may be reached using arguments similar to those of Bloomfield and Hamann[14] (in a different context) to show the so-called "index" of the equations is zero, implying a unique solution. We would also suspect the solution is unique from physical arguments.

Since the solution is unique, finding a particular solution will suffice to solve the problem. The Q_k's are proportional to v_k. Therefore, suppose

$$R_k(\omega)\equiv iev_k r(\epsilon_k,\omega)\,,\quad S_k(\omega)\equiv iev_k s(\epsilon_k,\omega)\,. \qquad (13)$$

Substituting this ansatz into (11), we find the troublesome k-state sums containing R_k and S_k vanish identically from time-reversal symmetry. We also see that (13) is a consistent solution of the equations. The functions r and s are easily found to be functions only of ϵ_k and ω^+ as anticipated. Thus R and S are given by the elementary forms

$$\begin{aligned} R_k(\omega) &= [1-\delta F_0(\epsilon_k+\omega^+)]^{-1}\,Q_k^R(\omega)\,,\\ S_k(\omega) &= [1-\delta F_0(\epsilon_k-\omega^+)]^{-1}\,Q_k^S(\omega)\,. \end{aligned} \qquad (14)$$

Equation (14) is the unique solution of the coupled integral equations (11). The only approximation made between (8) and (14) is discussed after Eq. (12) and is of no significance since our equations are only valid to $O(1/N)$.

To obtain the exact solution for the conductivity we first combine Eqs. (8)–(10) to express σ in terms of R and S. We find

$$\sigma_{\mu\nu}(\omega) = -\frac{2ie^2}{\omega\Omega}\sum_k v_k^\mu\left(\frac{\partial}{\partial k_\nu}\langle n_k\rangle - \frac{\delta}{N\omega}\,[R_k^\nu(\omega)-S_k^\nu(\omega)]\right). \qquad (15)$$

Substituting (14) into (15) gives the final result.

Although (15) is an exact result, it is not especially useful in its present form. Equations (4) and (15) are both exact solutions for the single-impurity model being studied. It is well-known that the canonical form for the configuration-averaged Green's function is given by (6), which immediately suggests the approximation (2) for the self-energy at low impurity concentrations. It has been shown elsewhere[5] that the canonical form for the configuration-averaged conductivity is given by

$$\sigma(\omega) = \frac{2ie^2}{\Omega}\frac{N}{m^*}\,[\omega^+ - \Delta(\omega)]^{-1}\,, \qquad (16)$$

where

$$\frac{N}{m^*} = \frac{1}{3}\sum_k v_k^2\left(-\frac{\partial}{\partial\epsilon_k}\langle n_k\rangle\right).$$

Treating the impurity contribution in (15) as the first term of a geometric series and summing, we find the approximate expression for $\Delta(\omega)$ at low concentrations is

$$\Delta(\omega) \cong \frac{y\delta m^*}{3N}\sum_k v_k[R_k(\omega)-S_k(\omega)]\,. \qquad (17)$$

Equation (17) is valid assuming $\omega \gg \Gamma \sim O(y)$, where Γ is some relevant inverse relaxation time.

Numerical studies of (17) have been done.[5] It is found for truly small concentrations ($y<10^{-4}$) that CPA agrees with (17) when $\omega > O(y)$. Details of this numerical work will appear elsewhere. As $\omega \to 0$, we find analytically that (17) does not reproduce the correct expression for the low-concentration dc conductivity.[8] This failure at $\omega=0$ is inherent in the single-impurity model and is not merely an artifact of the approximation made in (17). [The validity of this statement is easily checked by evaluating (15) at $\omega=0$. Even though (15) is exact, it is singular at $\omega=0$. We expect σ to be large—$O(N)$ or $O(y^{-1})$—at $\omega=0$ but not singular.] The reason for the failure of our derivation at $\omega=0$ is subtle but can be clarified by studying the higher-order (in y) contributions to the conductivity in the equation-of-motion method.[5] It is well known that the order in which ω and y approach zero is crucial. Interchanging the order of the two limits need not lead to the same result if the series obtained from the equation of motion is not absolutely convergent for all values of ω. (In fact the series clearly diverges as $\omega \to 0$ for fixed y.) Therefore, a careful analysis is required to obtain meaningful physical results. It turns out to be necessary to include certain terms of $O(y^2)$ to reproduce the correct $\omega=0$ behavior. On the other hand, since y is a very small number in the present work, (17) gives a good approximation even for moderately small ω's. $\sigma(0)$ may be correctly determined numerically by extrapolating the curve of $\sigma(\omega)$ at moderately small ω to $\omega=0$. This approach has been shown to be successful in Ref. 5.

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