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One-body models for transport properties of valence fluctuators: Exact results

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We consider various transport processes for (a) the resonant level lattice and (b) the dilute resonant level scattering of conduction electrons. These models, of possible relevance to valence fluctuators, consist of narrow resonant levels hybridizing with a broad conduction-band continuum. For case (a), hybridization results in strongly-energy-dependent effective masses in the vicinity of the resonance energy. However, these mass effects do not appear in the plasma frequency or the dc resistivity. Indeed, for normal conduction-electron impurity scattering, the weak-coupling memory function method, the exact Boltzmann-equation solution, and the exact Green's-function solution (in the dilute limit) are shown to be in essential agreement. For normal electron-phonon scattering we show that the weak-coupling memory function approach treated correctly to second order in the electron-phonon coupling yields the Bloch-Grüneisen law despite the presence of large, energy-dependent effective masses. Moreover, application of nonconserving approximations which have previously yielded appealing fits to the resistivity of valence fluctuating $CePd_3$ cannot account for the striking absorptivity of that material. Finally, we show for case (b) that the weak-coupling memory function approach yields resistivities in qualitative disagreement with the exact Boltzmann equation, although the zero-temperature ac conductivity agrees quite well in the dilute limit. We conclude that the weak-coupling memory function approach is ill suited for calculating transport properties in the presence of resonant scattering.

I. INTRODUCTION

This paper is a contribution to that part of the scientific literature concerned with the use of approximate methods to study Hamiltonians whose "exact" solution is known. Only a small part of the work done in this area is published in line with the dictum: Who publishes negative results? We do so in this case because the model appears to be one of growing physical interest in the rare-earth and actinide compound literature. The model is an extension of the resonant level model[1] (one f-like atom interacting with a structureless conduction band) to a lattice of such f-like atoms. Since the resulting Hamiltonian is quadratic, all properties can be calculated exactly, including the dc and ac conductivities associated with the scattering by a dilute concentration of impurities. We also treat electron-phonon scattering in the standard second-order approximation.[2]

In Fig. 1 we illustrate the extraordinary conductivities observed in a typical compound, $CePd_3$. Note in Fig. 1 the maximum in the dc resistivity at ~100 K and the overall large value of the resistivity, being an order of magnitude larger than most metals at room temperature.[3] Figure 1 shows the absorptivity $A(\sim\sqrt{\omega/\sigma})$; the large bump in $A(\omega)$ compared to a Drude result (dotted line) suggests a large bump in the scattering rate with frequency.[4] Prudence requires that single-particle mechanisms be examined before investigating many-body possibilities.

The points of this paper are simple. (1) The single-particle model in this paper cannot explain the data. (2) Any published suggestions to the contrary result from the failure to use a current operator consistent with the conservation of charge,[5,6] and/or an improper treatment of effective-mass factors which explicitly cancel in the dc resistivity.[5–8]

The plan of this paper is as follows. In Sec. II the con-

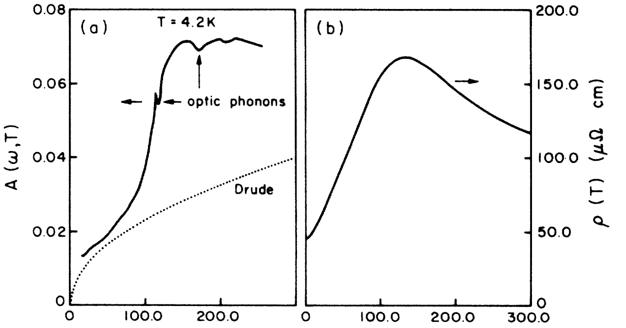

FIG. 1. Resistivity and absorptivity of $CePd_3$. (a) The far-infrared absorptivity at low temperature has a sharp onset near 15 meV (120 cm^{-1} or 180 K) which rises well above the expected Drude value. (b) The resistivity has a pronounced and large maximum of ≈160 $\mu\Omega$ cm at ~120 K.

tinuity equation is used to derive the current operator which in turn is used, via the f-sum rule, to deduce that the plasma frequency is unaffected by the presence of the f-like atoms in the model. Approximate expressions for the current operator and approximate calculation schemes for the plasma frequency give large temperature-dependent deviations from this result; these deviations will be a source of some of the problems associated with the memory function treatment commented on in Sec. V.

The next sections (III and IV) are devoted to a calculation of the dc resistivity using the Boltzmann equation. (The same result is derived in Appendix C with a Green's-function approach.) The result common to both is that potentially large effective masses associated with the hybridized bands do not appear in the final result, and hence the dc resistivity due to impurities is essentially temperature independent.

In Sec. IV the memory function approach is used to calculate the dc resistivity and ac conductivity due to both impurity and electron-phonon scattering. None of the sensational experimental properties can be found in the calculated ones.

Finally, in Sec. V we consider a resonant scattering mechanism (a resonant level impurity) and show that the weak-coupling memory function formalism is unable to qualitatively mimic the exact result, which has been noted previously for the magnetic susceptibility of that model.[9]

II. HAMILTONIAN, ELECTRICAL CURRENT, AND f-SUM RULE

In this section we describe our model Hamiltonian and the types of scattering terms we shall consider. In addition, we derive the current operator and use it to obtain an explicit formula for the plasma frequency via the f-sum rule. A major result is that the plasma frequency is unaffected by conduction-electron—resonant-electron hybridization, a result which holds for all temperatures.

The periodic resonant level model describes a system of conduction electrons interacting with localized $4f$ electrons (with energy ϵ_r) and impurities or longitudinal acoustic phonons

$$H=H_e+H_1 \,, \tag{2.1}$$

$$\begin{aligned} H_e=&\sum_{\mathbf{k},\sigma}\epsilon_k d^\dagger_{\mathbf{k}\sigma}d_{\mathbf{k}\sigma}+\sum_{i,\sigma}\epsilon_r f^\dagger_{i\sigma}f_{i\sigma}\\ &+\frac{V}{\sqrt{N}}\sum_{i,\mathbf{k},\sigma}(e^{i\mathbf{k}\cdot\mathbf{R}_i}d^\dagger_{\mathbf{k}\sigma}f_{i\sigma}+\text{H.c.})\,. \end{aligned} \tag{2.2}$$

Thus Hamiltonian H_e is diagonalized in Appendix A. We consider these forms for H_1

$$H_1^{\text{imp}}=\frac{G}{N}\sum_{\mathbf{k},\mathbf{k}',\sigma}d^\dagger_{\mathbf{k}\sigma}d_{\mathbf{k}'\sigma} \tag{2.3}$$

or

$$H_1^{\text{ph}}=H_{\text{ph}}+H_{e\text{-ph}} \,, \tag{2.4}$$

where

$$H_{\text{ph}}=\sum_{\mathbf{q}}\omega_q b^\dagger_{\mathbf{q}}b_{\mathbf{q}} \,, \tag{2.5}$$

$$H_{e\text{-ph}}=\sum_{\mathbf{k},\mathbf{k}',\sigma}[g(\mathbf{k}-\mathbf{k}')d^\dagger_{\mathbf{k}\sigma}d_{\mathbf{k}'\sigma}\phi_{\mathbf{k}-\mathbf{k}'}+\text{H.c.}]\,. \tag{2.6}$$

In (2.2) the operators $d^\dagger_{k\sigma}$ ($f^\dagger_{i\sigma}$) create a $5d/6s$ conduction electron of wave number $\mathbf{k}$, spin σ, and energy ϵ_k (a $4f$ localized electron at site $\mathbf{R}_i$, and spin σ) whereas the $b^\dagger_{\mathbf{q}}$ create a phonon with wave number q and energy ω_q, and $\phi_{\mathbf{q}}=(b_{\mathbf{q}}+b^\dagger_{-\mathbf{q}})$. We neglect any k dependence of the hybridization coefficient V between the conduction and $4f$ electrons. N is the number of sites. G denotes the strength of the scattering potential of the impurities. The electron-phonon interaction is taken only between the conduction electrons and longitudinal acoustic phonons. The coupling constant is given by

$$g(q)=(2NM_i\omega_q)^{-1/2}C(q)$$

($q=|\mathbf{q}|$), where M_i is the ionic mass and $C(q)$ is a slowly varying function of q.[10] Also, we work within a volume Ω and use constants $\hbar=k_B=1$.

In order to calculate transport properties of the system described by Hamiltonian (2.1) we need to know the appropriate current operator. In this respect we follow the standard prescription of using the particle density

$$\rho(\mathbf{q})=\sum_{\mathbf{k},\sigma}(d^\dagger_{\mathbf{k}+\mathbf{q},\sigma}d_{\mathbf{k}\sigma}+f^\dagger_{\mathbf{k}+\mathbf{q},\sigma}f_{\mathbf{k}\sigma})+O(q^2) \tag{2.7}$$

in conjunction with the continuity equation:

$$i\mathbf{q}\cdot\mathbf{j}(\mathbf{q})=ie[H_e,\rho(\mathbf{q})] \tag{2.8}$$

to obtain the longitudinal part of the electric current as ($\hat{\mathbf{q}}=\mathbf{q}/q$)

$$j_{dd}=\lim_{q\to 0}\left[\frac{1}{|q|}\mathbf{q}\cdot\mathbf{j}(\bar{q})\right]=e\sum_{\mathbf{k},\sigma}\left[\frac{\partial\epsilon_k}{\partial\mathbf{k}}\right]\cdot\hat{\mathbf{q}}d^\dagger_{\mathbf{k}\sigma}d_{\mathbf{k}\sigma}\,. \tag{2.9}$$

Had we considered V as k dependent we would have obtained an additional contribution to the longitudinal current of the form

$$\sum_{\mathbf{k},\sigma}\left[\frac{\partial V_{\mathbf{k}}}{\partial\mathbf{k}}\right]\cdot\hat{\mathbf{q}}(d^\dagger_{\mathbf{k}\sigma}f_{\mathbf{k}\sigma}+f^\dagger_{\mathbf{k}\sigma}d_{\mathbf{k}\sigma})$$

(see Ref. 11). Nonetheless, in Ref. 5 it is argued that the true current j_{dd} underestimates the effects of correlations and another current is used, given by

$$\mathbf{j}_{\alpha\alpha}=e\sum_{\mathbf{k},\alpha}\left[\frac{\partial E_{\mathbf{k}\alpha}}{\partial\mathbf{k}}\right]\alpha^\dagger_{\mathbf{k}\sigma}\alpha_{\mathbf{k}\sigma} \tag{2.10}$$

to calculate the resistivity as a function of the temperature T, $\rho_{\alpha\alpha}(T)$, which is similar to the experimental resistivity of CePd_3. In Sec. IV of this paper we show that even if one agreed to work with the current $j_{\alpha\alpha}$ (which falsely introduces mass effects not contained in the true current j_{dd}) and used the same parameters that fit the resistivity, the resulting ac conductivity differs considerably from the experimental one.

In summary, the appropriate current derived from Eq. (2.1) is j_{dd}; one cannot mimic the effects of correlation by truncating j_{dd} and introducing mass effects which enhance the resistivity. [In Sec. IV we shall calculate the resistivity $\rho_{dd}(T)$ using the true current j_{dd}.]

Now we show that ω_p^2, the plasma frequency in the presence of hybridization, is equal to ω_{0p}^2, that in the absence of hybridization, at all temperatures.

From the f-sum rule,[12,13] we have

$$\omega_p^2 = \lim_{q\to 0} \left[\frac{4\pi e^2}{\Omega q^2} \langle [[\rho(\mathbf{q}), H_e], \rho^\dagger(\mathbf{q})] \rangle \right] . \tag{2.11}$$

Because the f electrons are dispersionless, using (2.2), (2.7), and (2.8) we can immediately write

$$\omega_p^2 = \frac{4\pi e^2}{\Omega m} \sum_{\mathbf{k}} \langle d_{\mathbf{k}}^\dagger d_{\mathbf{k}} \rangle . \tag{2.12}$$

From the diagonalization of (2.2) (Appendix A) we know that in terms of the new (α and β) bands

$$\langle d_{\mathbf{k}}^\dagger d_{\mathbf{k}} \rangle = u_{\mathbf{k}}^2 \langle \alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} \rangle + v_{\mathbf{k}}^2 \langle \beta_{\mathbf{k}}^\dagger \beta_{\mathbf{k}} \rangle , \tag{2.13}$$

where u_k and v_k are the coefficients of the canonical transformation relating the d's and f's to the α's and β's (see Appendix A). Since the density of states of the α (β) bands are $N(0)u_{K}^{-2}$ $[N(0)v_{K}^{-2}]$ with $N(0)$ the bare density of states, we finally obtain (f is the Fermi function)

$$\omega_p^2 = \frac{4\pi n e^2}{m} \left[\int dE_\alpha N(0) f(E_\alpha) + (\alpha \to \beta) \right] . \tag{2.14}$$

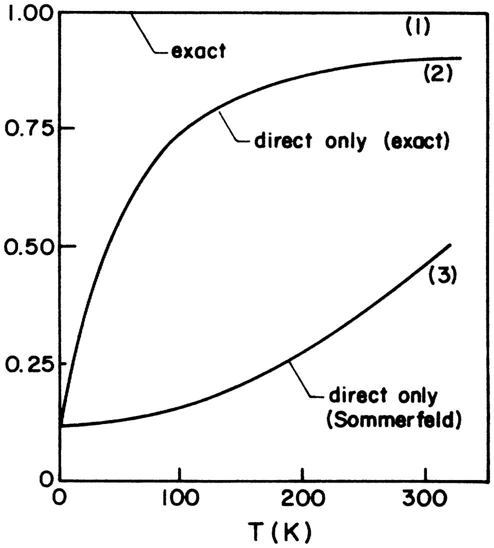

FIG. 2. Temperature dependence of the plasma frequency. Applying the f-sum rule [Eq. (2.7)] to a model for valence fluctuators in which an undispersed f-band hybridizes with a broad conduction band [the f-d hybridization model of Eq. (2.1)], we have computed the temperature dependence of the electronic plasma frequency. We measure ω_p^2 in units of ω_{0p}^2, the plasma frequency in the absence of hybridization. The most striking results are obtained by treating direct contributions using the Sommerfeld approximation and neglecting indirect terms. This was the approach used in Ref. 5; for their parameter choices [$V = 40$ K is the hybridization potential, $\epsilon_r(T) = (15 + 2.5 \times 10^{-4} T^2)$ K is the $4f$ level position] the lowest curve results. Correct treatment of direct terms with neglect of interband f terms results in the middle curve, which shows the Sommerfeld approximation to be inadequate for all but the lowest temperatures. Finally, the correct result is obtained by including interband terms and treating direct terms exactly. This results in the uppermost curve, which is temperature independent and indistinguishable from the zero hybridization result. Note that at $T = 0$, some 90% of the total ω_p^2 value comes from interband contributions.

The quantity within large parentheses is just the band filling [apart from corrections of order $(V/W)^2$], which is unchanged by hybridization. Thus

$$\omega_p^2 = \omega_{0p}^2 [1 + O((V/W)^2)] . \tag{2.15}$$

In contrast, the corresponding formula for ω_p^2 used in Ref. 5 is

$$\omega_p^2 = \omega_{0p}^2 / \{1 + [V/\epsilon_r(T)]^2\} , \tag{2.16}$$

where $\epsilon_r(T)$ is the (strongly-) temperature-dependent f-level energy. The origin of (2.16) can be readily seen in three steps. (i) One can split (2.11) (somewhat artificially) into terms apparently arising from direct and interband contributions:

$$\omega_p^2 = \lim_{q\to 0} \left[\frac{8\pi e^2}{3\Omega q^2} (I_{\text{direct}} + I_{\text{interband}}) \right] \tag{2.17}$$

with

$$I_{\text{direct}} = \left[\frac{k_F}{m} \right]^2 \sum_{\mathbf{k}} \left[u_k^4 \left[\frac{-\partial f_k^\alpha}{\partial E_{k\alpha}} \right] + v_k^4 \left[\frac{-\partial f_k^\beta}{\partial E_{k\beta}} \right] \right] , \tag{2.18}$$

$$I_{\text{interband}} = 2 \left[\frac{k_F}{m} \right]^2 \sum_{\mathbf{k}} u_k^2 v_k^2 \frac{f_k^\alpha - f_k^\beta}{E_{k\beta} - E_{k\alpha}} . \tag{2.19}$$

(ii) For a normal metal, Eq. (2.19) is negligible as higher bands are separated from the Fermi level by energies $\sim\omega$. (iii) in a normal metal one can apply the Sommerfeld expansion[14] to (2.18) with minimal error. Equation (2.18) with these latter two approximations gives (2.16).

To demonstrate how badly (2.16) serves, we have plotted in Fig. 2 the correct (constant) result along with the result of (2.16) for the parameters of Ref. 5 and the exact evaluation of (2.18) (not a Sommerfeld expansion). Two things are apparent: (1) the Sommerfeld approximation is a poor approximation for (2.18), primarily because the integral varies rapidly over a small energy scale, and (2) it is also a poor approximation to ignore interband contributions which make up some 90% of the zero-temperature result for the given parameters.

We conclude that (2.16), obtained from what seems to be reasonable assumptions, is in fact inconsistent with the f-sum rule and gives rise to spurious temperature dependence in the plasma frequency.

III. BOLTZMANN-EQUATION TREATMENT FOR THE IMPURITY PROBLEM

In this section we solve the transport problem for the dilute impurity potential (2.3) within the Boltzmann-equation framework[15] to demonstrate the explicit cancellation of the mass factors u^2 and v^2 (and hence a dull resistivity).

To this end, we note that the semiclassical impurity problem can be solved exactly to leading order in the concentration within the relaxation time approximation. We first obtain the quantum-mechanical relaxation times by solving the T matrix equations for elastic scattering. These are derived in Appendix B. Because of elasticity, only the diagonal rates matter, and these are

$$\tau_{\alpha\alpha}^{-1}=\frac{2\pi c(G^2/2W)u_k^2}{[1+GL(E_{k\alpha})/2W]^2+(\pi G/2W)^2}\,, \tag{3.1}$$

and

$$\tau_{\beta\beta}^{-1}=\frac{2\pi c(G^2/2W)v_k^2}{[1+GL(E_{k\beta})/2W]^2+(\pi G/2W)^2}\,, \tag{3.2}$$

where c is the impurity concentration, and $L(\omega)=\ln|\omega-E_\alpha^+|-\ln|\omega-E_\beta^-|$. E_β^- (E_α^+) is the band minimum (maximum) for the β (α) band (see Appendix A).

In equilibrium, the linearized Boltzmann equations read

$$e\boldsymbol{\epsilon}\cdot\mathbf{V}_{\alpha k}\left[\frac{-\partial f_0^\alpha}{\partial E_{kd}}\right]=\frac{\mathbf{C}_{k\alpha}\cdot\mathbf{V}_{k\alpha}}{\tau_{\alpha\alpha}(\mathbf{k})}\left[\frac{-\partial f_0^\alpha}{\partial E_{k\alpha}}\right]\,, \tag{3.3}$$

where the **C**'s are to be solved for, $\boldsymbol{\epsilon}$ is the thermoelectric field, and, e.g., $\mathbf{V}_{\alpha\mathbf{k}}$ is the electronic velocity for the α band. The equation for the β band comes by changing α to β in (3.3).

We next need the semiclassical current; solving (3.3) for **C**, multiplying by $ne\mathbf{V}$, and averaging yields

$$\mathbf{j}=\frac{e^2}{3\Omega}\int dk\frac{k^2}{\pi^2}\left[V_{\alpha k}^2\tau_{\alpha\alpha}(k)\left[\frac{-\partial f(E_{k\alpha})}{\partial E_{k\alpha}}\right]+(\alpha\leftrightarrow\beta)\right]\boldsymbol{\epsilon}\,, \tag{3.4}$$

from which the conductivity is read off as (V_{F0} is the unperturbed Fermi velocity)

$$\sigma=\frac{\omega_{0p}^2}{4\pi}\left[\int_{-W}^{E_\alpha^+}dE\left[\frac{N_\alpha(E)}{N(0)}\right]\left[\frac{V_\alpha(E)}{V_{F0}}\right]^2\times\tau_{\alpha\alpha}(E)\left[\frac{-\partial f}{\partial E}\right]+(\alpha\leftrightarrow\beta)\right]\,. \tag{3.5}$$

However, in view of the results of diagonalizing (3.2) (see Appendix A)

$$[N_\alpha(\epsilon)/N(0)]V_\alpha^2/V_{F0}^2=u^2(\epsilon)\,,$$
$$[N_\beta(\epsilon)/N(0)]V_\beta^2/V_{F0}^2=v^2(\epsilon)\,,$$

and thus the mass factors cancel,[16] leaving

$$\sigma=\frac{ne^2\tau_0}{m}\left[\int_{-W}^{E_\alpha^+}dE+\int_{E_\beta^-}^{W}dE\right]\left[\frac{-\partial f}{\partial E}\right]t(E)\,, \tag{3.6}$$

where $t(E)$ is defined by

$$\tau_{\alpha\alpha}(k)u_{\mathbf{k}}^2=\tau_0 t(E_{\alpha\mathbf{k}})\,, \tag{3.7}$$

$\tau_0=\pi cG^2/W$ being the Born result for zero hybridization.

The result of computing $\rho(T)$ from (3.5) is displayed in Fig. 3. We note that apart from a very small bump due to the frequency dependence of $t(E)$, the result is indistinguishable from the constant value obtained by summing the Born series for τ^{-1} to all orders.

We remark that a Green's-function calculation, which includes all possible interband effects, reduces to Eq. (3.5) in the limit of zero frequency and to leading order in the concentration c; namely, to order 1 where

$$\sigma(T)=\frac{1}{c}\sigma^{(-1)}+\sigma_{(0)}+c\sigma^{(1)}+\cdots\,.$$

Details of this derivation are presented in Appendix C.

We conclude that for this exact treatment of impurity scattering in a model with hybridized bands, no striking temperature dependence of the resistivity emerges despite a striking energy dependence in the effective mass. The reason is the cancellation of mass factors in the dc conductivity.

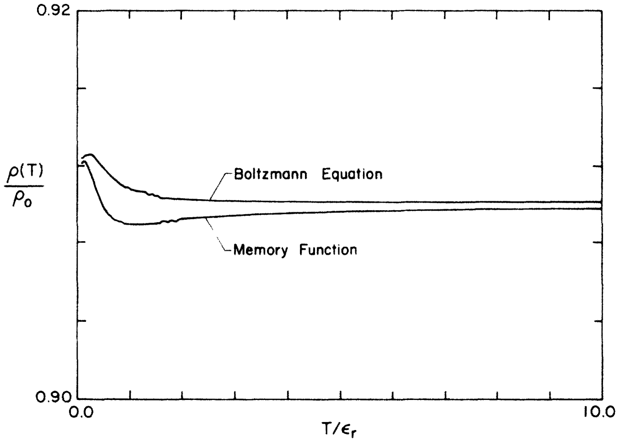

FIG. 3. Resistivity due to impurity scattering for the hybridized band model. The solid curve is the Boltzmann-Kubo result for the resistivity. The resistivity is measured in units of the Born-approximation result $\rho_0=(4\pi^2/\omega_p^2)|G|^2c/W$ with G the impurity potential, c the concentration, W the conduction bandwidth. The temperature is measured in units of the zero-temperature f-band position with respect to the Fermi level. The dashed curve is the result of the weak-coupling memory function approximation (Ref. 17). The two results are forced to agree at $T=0$ by the sharpness of the Fermi surface. However, for finite T they differ by $\lesssim 0.2\%$ throughout the displayed temperature range.

IV. MEMORY FUNCTION RESULTS

In this section we show how correct calculation of the conductivity within the d-f hybridization model will give rise to normal metallic behavior for normal impurity scattering and the ordinary electron-phonon coupling.

A. Formalism

The primary definitions and analyticity properties of the memory function formalism are summarized in Table I; for more details the reader is urged to see Refs. 17 and 18. The results listed in Table I are not new and are included solely for completeness and clarity.

In order to calculate the memory function and hence the conductivity, we follow Ref. 17 where it is assumed

TABLE I. Memory function relations.

Definitions ($\eta \to 0^+$)	
$M(z)=\dfrac{z\chi(z)}{\chi(0+i\eta)-\chi(z)}$,	$\sigma(z)=\dfrac{ie^2\chi(0+i\eta)}{z+M(z)}$
$\chi(z)=\dfrac{-i}{3\Omega}\int_0^\infty dz\, e^{izt}\langle[j_d(t),j_d(0)]\rangle$	
Functional relations	
$M^*(z)=M(z^*)$	$\chi^*(z)=\chi(z^*)$
$M(z)=-M(-z)$	$\chi(z)=\chi(-z)$
$M(z)\sim 1/z$, as $z\to\infty$	$\chi(z)\sim 1/z^2$, as $z\to\infty$

that its behavior is regular in the concentrations c of impurities and the electron-phonon coupling g and write

$$z\chi(z)=\chi_0 M(z)+O(c^2,g^3)\ . \qquad (4.1)$$

Using the definition of the current-current correlation function

$$\chi(z)=-\langle\langle j_{dd},j_{dd}\rangle\rangle_z\ , \qquad (4.2)$$

where $\langle\langle\ \rangle\rangle_z$ is Zubarev notation[19] for correlation functions,

$$\langle\langle A,B\rangle\rangle_z=-\frac{i}{\Omega}\int_0^\infty e^{izt}\langle[A(t),B(0)]\rangle dt \qquad (4.3)$$

with the equation of motion

$$z\langle\langle A;B\rangle\rangle_z=\langle[A,B]\rangle+\langle\langle[A,H];B\rangle\rangle_z \qquad (4.4)$$

($\langle\ \rangle$ and [ ] denote thermal averaging at temperature T and commutator brackets, respectively), one obtains

$$M(z)\approx\frac{z\chi(z)}{\chi_0}=\frac{1}{z\chi_0}[\phi(z)-\phi(0)]\ , \qquad (4.5)$$

where

$$\phi(z)=\langle\langle[j_{dd},H_1];[j_{dd},H_1]\rangle\rangle_z\ . \qquad (4.6)$$

B. dc resistivity

The dc resistivity is now obtained through the use of the formula for $\sigma(z)$ in Table I after taking $z=\omega+i0$ and letting ω approach zero:

$$\rho_{dd}(T)=\lim_{\omega\to 0}\frac{M''(\omega)}{e^2\chi_0}=\lim_{\omega\to 0}\left[\frac{1}{e^2\chi_0^2}\frac{\phi''(\omega)}{\omega}\right]\ . \qquad (4.7)$$

Equation (4.7) is the basic formula used in Ref. 5 to calculate the dc resistivity and follows directly from the formalism of Ref. 17. The basic assumption that is needed in the derivation of (4.7) is the regular dependence of $M(z)$ upon the concentration of impurities or the electron-phonon coupling which made the expansion (4.1) valid (this is not true in general).

In order to calculate $\rho_{dd}(T)$ for impurity or electron-phonon scattering we need to calculate (the imaginary part of) the function $\phi(z)$ and use the correct value for the quantity χ_0 (see Sec. II) which satisfies the f-sum rule (since $\omega_p^2=4\pi e^2\chi_0$).

The calculation of $\phi(z)$ for impurity scattering, using the Hamiltonian (2.3) along with the (3.2) term, yields the resistivity

$$\rho^I_{dd}(T)=\rho^I_0/(\omega_p^2/\omega_{0p}^2)^2\ . \qquad (4.8)$$

The impurity resistivity is simply inversely proportional to the square of the number of carriers (or the fourth power of the plasma frequency which has been calculated in Sec. II). The coefficient ρ^I_0 is the analog to Eq. (3.5), where instead of averaging $t(E)$, one averages $t^{-1}(E)$; namely

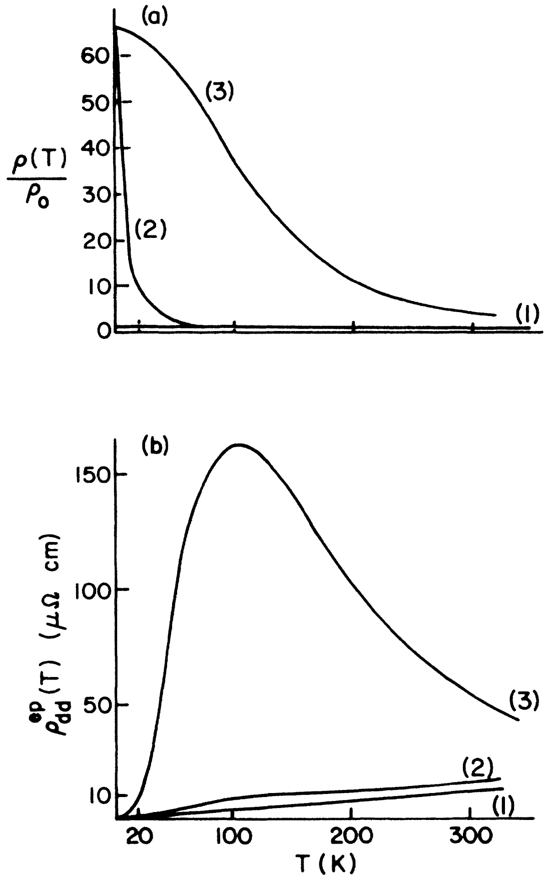

FIG. 4. dc resistivities calculated within the weak-coupling memory function formalism. For (a) and (b) the underlying band model is the resonant-level lattice of Eq. (2.2), with V and $\epsilon_r(T)$ chosen as per Fig. 2. The numbers on the curves refer, as per Fig. 2, to exact calculation of ω_p^2 (curve 1), exact treatment of direct contributions with neglect of interband terms (curve 2), and the Sommerfeld expansion treatment of direct terms with neglect of interband contributions (curve 3). In (a) only impurity scattering [Eq. (2.3)] is kept and treated within the Born approximation, with all resistivities measured in units of ρ_0, the Born result. All the spectacular temperature dependence visible in curves 2 and 3 is removed when the plasma frequency is computed with inclusion of innerband terms. In (b) electron-phonon scattering is kept [Eq. (2.6)], and the normal ($V=0$) resistivity at Θ and ρ_Θ, is chosen to be 6 $\mu\Omega$ cm. The spectacular maximum in curve 3, reminiscent of the resistivity of CePd$_3$ displayed in Fig. 1, is removed when the plasma frequency is properly computed, and the correct result (curve 1) is indistinguishable from the $V=0$ Bloch-Grüneisen law.

$$\rho_0^I=\rho_0\int dE\left[-\frac{\partial f}{\partial E}\right]\frac{1}{t(E)}\ ,$$

with ρ_0 the Born-approximation result.

Figure 4(a) shows the behavior of $\rho_{dd}^I(T)$ using three different schemes in the calculation of ω_p^2/ω_{0p}^2 and treating ρ_0^I only in the Born approximation. It is important to note that spectacular effects show up when one makes the approximation (2.16) used in Ref. 5. The correct result given by curve (1) [where one uses (2.15)] is indistinguishable from the zero hybridization impurity resistivity.

For electron-phonon scattering we obtain similar results. We can calculate the resistivity $\rho_{dd}^{e\text{-ph}}(T)$ through the use of Hamiltonian (2.1) with the term (2.4). As per Ref. 5, we obtain

$$\rho_{dd}^{e\text{-ph}}(T)=\left[\frac{\omega_{0p}}{\omega_p}\right]^2\rho_0\left[\frac{T}{\Theta}\right]^5\int_0^{\Theta/T}dz\frac{z}{e^z-1}\left[\int_{E_\alpha^-/T}^{E_\alpha^+/T}+\int_{E_\beta^-/T-z}^{E_\alpha^+/T}+\int_{E_\beta^-/T}^{E_\beta^+/T}\right]du\,F(u,z)\ , \tag{4.9}$$

where Θ is the Debye temperature. The function $F(u,z)$ is given by

$$F(u,z)=\frac{1}{1+e^{-(u+z)}}\frac{1}{(e^u+1)}\ , \tag{4.10}$$

and the resistivity prefactor ρ_0 (see Ref. 5) is chosen such that the numerical value of $\rho_{dd}^{e\text{-ph}}(T)$ agrees with typical metallic resistivities in the absence of hybridization. A good value for ρ_0 is 100 $\mu\Omega$ cm, which corresponds to a normal resistivity at Θ (ρ_Θ) of 6 $\mu\Omega$ cm.

Figure 4(b) shows how the different ways of calculating the plasma frequency (see Sec. II) dramatically affect $\rho_{dd}^{e\text{-ph}}(T)$. The most spectacular effect showing up in $\rho_{dd}^{e\text{-ph}}(T)$ is once again the approximation of ω_p^2/ω_{0p}^2 used in Ref. 5 (curve 3). The correct resistivity (curve 1) $\rho_{dd}^{e\text{-ph}}(T)$ is indistinguishable from the typical metallic curve ($V=0$ case).

C. ac conductivity

The use of $j_{\alpha\alpha}$ introduces frequency-dependent mass effects in the resistivity. However, we show below that even if one agreed to use $j_{\alpha\alpha}$ on the basis of the rough agreement between $\rho_{\alpha\alpha}(T)$ and the experiment, one would still be unable to explain the ac conductivity data.[4] The ac absorptivity of CePd$_3$ has been measured[4] in the far infrared. The absorptivity is related to the dielectric constant via

$$A(\omega)\simeq4\,\mathrm{Re}\left[\frac{1}{\epsilon(\omega)}\right]^{1/2}\ , \tag{4.11}$$

where

$$\epsilon(\omega)=1+\frac{4\pi i\sigma(\omega)}{\omega}\ . \tag{4.12}$$

The real and imaginary parts of σ are given in terms of the real and imaginary parts of the memory function $M'_{\alpha\alpha}(\omega)$ and $M''_{\alpha\alpha}(\omega)$, respectively.

Following the procedures outlined above we calculate the imaginary part of the memory function at $T=0$ K. We find (using the notation of Ref. 5)

$$M''_{\alpha\alpha}(\omega)=A_0\int_0^{\min\{\omega,\Theta\}}dx\,x^2[g(x,\omega)+g(x,-\omega)]\ , \tag{4.13}$$

where A_0 (on the order of $1/\Theta^2$) is chosen so that the absorptivity, in the absence of hybridization, agrees with typical metallic values, and

$$g(x,\omega)=\left[1-\frac{x}{\omega}\right]\left[\frac{x}{\Theta}\xi(x,\omega)-\frac{k_F}{q_D}[1-\xi(x,\omega)]^2\right] \tag{4.14}$$

with

$$\xi(x,\omega)=[1+(V/\epsilon_r^0)^2]\Bigg/\left[1+\left[\frac{V}{\epsilon_r^0-x+\omega}\right]^2\right]\ . \tag{4.15}$$

The real part $M'_{\alpha\alpha}(\omega)$ is calculated through a Hilbert transform of $M''_{\alpha\alpha}(\omega)$. Figure 5(a) shows the variation of

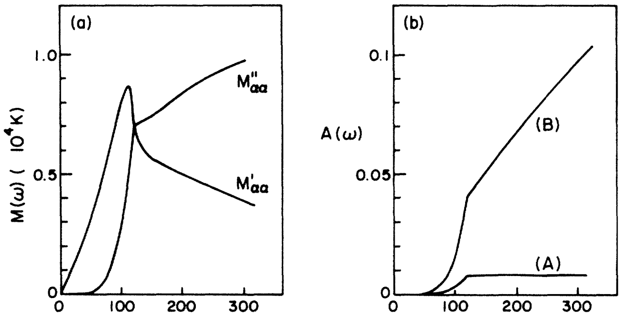

FIG. 5. (a) Real and imaginary parts of the memory function $M'_{\alpha\alpha}(\omega)$ and $M''_{\alpha\alpha}(\omega)$, respectively, as functions of frequency ω at zero temperature. The hybridization parameter is $V=120$ K, the same value used in Ref. 5 to fit the dc resistivity $\rho_{\alpha\alpha}(T)$. The other parameters are the Debye frequency $\Theta=169$ K, $k_F/q_D=1$, and $\epsilon_r^0=37.5$ K (all from Ref. 5). The plasma frequency and the prefactor of the imaginary part are chosen in order to yield the correct order of magnitude of the absorption in the absence of hybridization (see text); they are given by $\omega=10^{15}$ Hz, $A_0=10^{-5}$ K^{-2}, respectively. The vertical scale is to be multiplied by 10^4 K. (b) Variation of the absorption with frequency at zero temperature. Curve A corresponds to zero hybridization $V=0$, whereas curve B is calculated for $V=120$ K. The rest of the parameters are the same as those used in (a). Note the break in the slope at a frequency of 110 cm^{-1} which corresponds to the Debye frequency. For clarity we have multiplied the vertical scale corresponding to curve A by 10 in order to show it on the same vertical scale.

$M'_{aa}(\omega)$ and $M''_{aa}(\omega)$ in the infrared at $T=0$ K, whereas Fig. 5(b) shows the absorptivity at $T=0$ K in the far infrared for $V=0$ and 120 K (which is the same value for the dc resistivity of Ref. 5). The absorptivity of Fig. 5(b) does not correspond at all to the experimental result.[4] We conclude that the anomalous dc resistivity and anomalous far-infrared absorptivity of CePd$_3$ cannot be explained by the model of Ref. 5. One cannot by any means introduce artificial mass effects or induce an artificial change in the number of carriers (without violating the sum rules) in order to explain these anomalies.

V. FAILURE OF THE WEAK-COUPLING MEMORY FUNCTION FORMALISM FOR RESONANT SCATTERING

In the preceding sections we have seen that when treated with care, the weak-coupling memory function formalism[17] can yield conductivities in good agreement with Boltzmann-equation and Green's-function results. This held specifically for normal impurity and electron-phonon scattering, even in the presence of a lattice of resonant levels.

In this section we include resonant scattering and show that the weak-coupling approach[17] breaks down. This is most easily seen by considering a metal with a dilute concentration of s-wave resonant-level scatterers.

To lowest order in the concentration, impurity averaging yields the following expression for the conduction-electron self-energy:[20,21]

$$\Sigma(\omega)=\frac{s\Gamma/2}{\omega-\epsilon_r+i\Gamma}\ , \tag{5.1}$$

where $S=(8W/3\pi)c$, c being the concentration of scatterers, Γ is the resonance width, and ϵ_r is the resonance energy with respect to the Fermi level.

The Boltzmann equation and Kubo formula yield exactly the same result for the dc resistivity $\rho(T)$. First, the Kubo-formula result for the conductivity is given by[21]

$$\sigma(\omega,T)=\frac{i\omega_p^2}{4\pi\omega}\int_{-\infty}^{\infty}d\epsilon\frac{[f(\epsilon-\omega)-f(\epsilon)]/\omega}{\omega+\Sigma^*(\epsilon-\omega)-\Sigma(\epsilon)}\ . \tag{5.2}$$

The resulting dc resistivity[20] is given by

$$\rho(T)=\frac{4\pi}{\omega_p^2}\frac{s\Gamma^2}{\Gamma^2+\epsilon_r^2+\frac{1}{3}\pi^2(k_BT)^2}\ , \tag{5.3}$$

where ψ' is the trigamma function.[22] According to the weak-coupling memory function prescription,[17] $M(\omega)$ is given by

$$M(\omega)\approx\int d\epsilon\left[\frac{f(\epsilon-\omega)-f(\epsilon)}{\omega}\right]\times\left[\frac{s\Gamma/2}{\epsilon-\omega-\epsilon_r-i\Gamma}-\frac{s\Gamma/2}{\epsilon_r-\epsilon+i\Gamma}\right]\ . \tag{5.4}$$

Inserting (5.4) into the relation (4.5) and taking the zero-frequency limit gives the memory function result for the resistivity, denoted by $\rho_M(T)$,

$$\rho_M(T)=\frac{4\pi}{\omega_p^2}\frac{s\Gamma}{2\pi T}\mathrm{Re}\psi'(\tfrac{1}{2}+\Gamma/2\pi T+i\epsilon_r/2\pi T)\ . \tag{5.5}$$

[We note that including the density-of-states corrections as per Ref. 17 modifies the result of (5.5) to

$$\rho_M(T)=\frac{4\pi}{\omega_p^2}\left[(1+\epsilon_r/W)\frac{s\Gamma}{2\pi T}\times\mathrm{Re}\psi'(\tfrac{1}{2}+\Gamma/2\pi T+i\epsilon_r/2\pi T)+\frac{\Gamma}{W}\frac{s\Gamma}{2\pi T}\mathrm{Im}\psi'(\tfrac{1}{2}+\Gamma/2\pi T+i\epsilon_r/2\pi T)\right]\ , \tag{5.6}$$

which hardly constitutes a major correction to (5.5).]

These results are illustrated in Fig. 6. It should be

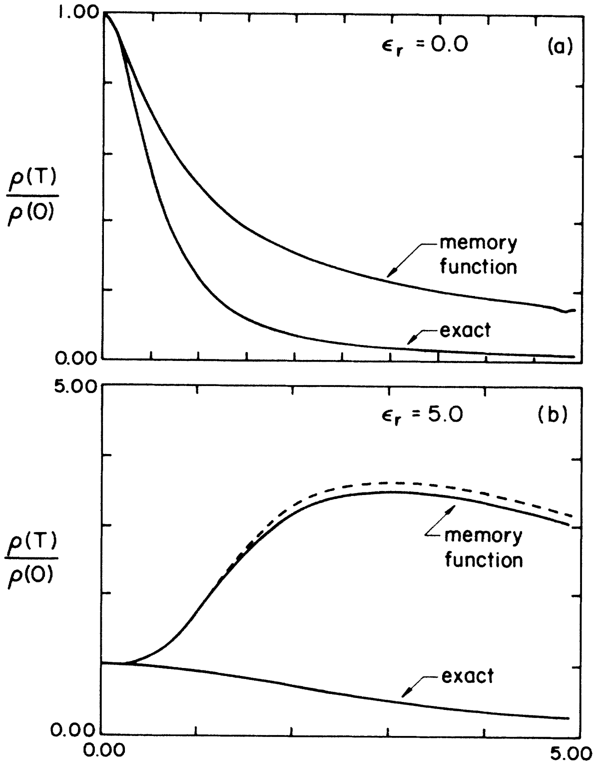

FIG. 6. Resonant-level-model resistivity. The resistivity is measured in units of the zero temperature result for dilute resonant level scattering. Temperature is measured in units of the resonance width Γ. For $\epsilon_r=0$ [part (a)] the Boltzmann-Kubo curve decreases monotonically falling off as $1/T^2$ for high T. The memory function result for $\epsilon_r=0$ (as per Ref. 17) agrees at $T=0$ with the dashed curve, but decays like $1/T$ for high T. The departure from the Boltzmann-Kubo result is more striking for $\epsilon_r=5\Gamma$ [part (b)]. The Boltzmann-Kubo result is qualitatively identical to that of (a). In contrast, the memory function result has a pronounced maximum at $T=3\Gamma$. Note that changing the Fermi energy from $10^6\Gamma$ to 100Γ (dashed curve) has negligible effect on ρ. The zero-temperature resistivity within this model is given by $(4\pi/\omega_{0p}^2)s\Gamma^2/(\Gamma^2+\epsilon_r^2)$, with $s=8Wc/3\pi$, c being the impurity concentration.

pointed out that (5.3), which is the exact expression to leading order in the concentration, decreases monotonically, and behaves as $1/T^2$ for high temperatures. However, $\rho_M(T)$ has a maximum for $\epsilon_r \neq 0$ and decays like $1/T$ for high temperatures. Hence, the weak-coupling memory function result is in strong qualitative disagreement with the known exact results for the dc resistivity of conduction electrons in the presence of resonant scatterers.

There is one regime, however, where the weak-coupling memory function formalism agrees with the Green's-function result. Comparing the zero-temperature conductivities from the two different methods, we find that

$$\rho_M(0) = \rho(0) = \frac{4\pi}{\omega_p^2} \frac{s\Gamma^2}{\Gamma^2 + \epsilon_r^2} , \tag{5.7}$$

which is due to the sharpness of the Fermi surface $[(-\partial f/\partial\epsilon) \simeq \delta(\epsilon),\ T \to 0]$. (This apparently has been noticed before; see p. 505 of Ref. 23.) Since the weak-coupling result agrees by construction with the Green's-function result at high frequencies, then for sufficiently small s, the zero-temperature conductivities should be in substantial agreement. This is indeed the case as seen in Fig. 7, where we have plotted the memory function result (crosses)

$$\sigma_M(\omega, T=0) = \frac{i\omega_p^2}{4\pi \left[\omega + \dfrac{s\Gamma}{2\omega} \ln \left[\dfrac{\epsilon^2 + \Gamma^2}{\epsilon_r^2 + \Gamma^2 - \omega^2 - 2i\Gamma\omega} \right] \right]} \tag{5.8}$$

and the Green's-function result (5.2) for various parameter choices.

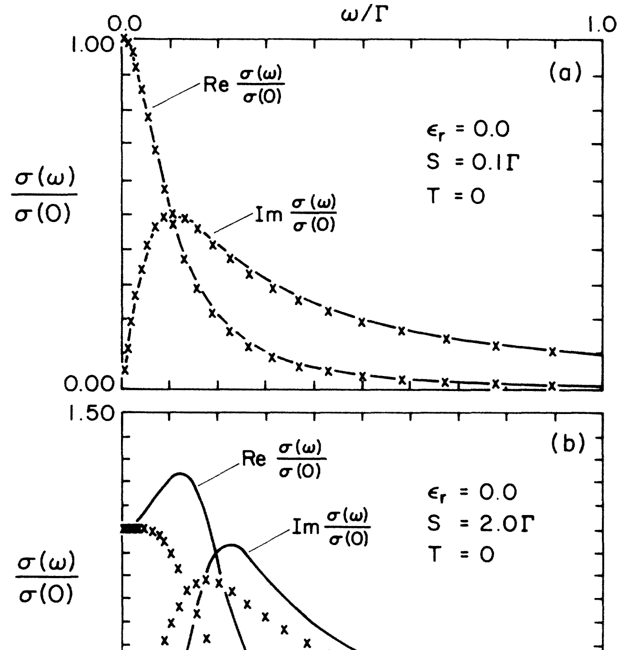

FIG. 7. ac conductivity for the resonant-level model at zero temperature. The real and imaginary parts of the ac conductivity have been computed via the Kubo formula (solid line) and via the weak-coupling memory function (crosses) formalism of Ref. 17. In (a) the solid curve shows the Kubo result for Reσ for a resonance position $\epsilon_r = 0.0\Gamma$ and strength $s = 0.1\Gamma$, so that one might indeed hope to be within the weak-coupling regime. In this case the memory function result (crosses) agrees quite well with the Kubo result. The same can be said of the imaginary part of conductivity. However, if we change s to 2.0Γ we leave the weak-coupling regime and agreement between the two methods ceases, as seen in Fig. 7(b), where the same notation is used as in (a). Note that conductivities are measured in units of $\sigma(0) = (\omega_p^2/4\pi)[(\Gamma^2+\epsilon_r^2)/s\Gamma^2]$.

We conclude that the weak-coupling memory function formalism is ill suited for calculating the dc properties of a metal in the presence of resonant scattering. However, the weak-coupling approach can yield simple and accurate answers for the zero-temperature ac properties if resonant scattering is present, provided that the overall scattering strength is not too strong.

ACKNOWLEDGMENTS

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APPENDIX A: DIAGONALIZATION OF THE ELECTRONIC HAMILTONIAN

The electronic Hamiltonian (2.1b) can be diagonalized by the following transformation:

$$\begin{bmatrix} d_{\mathbf{k}\sigma} \\ f_{\mathbf{k}\sigma} \end{bmatrix} = \begin{bmatrix} u_{\mathbf{k}} & v_{\mathbf{k}} \\ -v_{\mathbf{k}} & u_{\mathbf{k}} \end{bmatrix} \begin{bmatrix} \alpha_{\mathbf{k}\sigma} \\ \beta_{\mathbf{k}\sigma} \end{bmatrix} = \hat{S}_{\mathbf{k}}^{-1} \begin{bmatrix} \alpha_{\mathbf{k}\sigma} \\ \beta_{\mathbf{k}\sigma} \end{bmatrix} \tag{A1}$$

with the result

$$H_e = \sum_{\mathbf{k},\sigma} (E_{\mathbf{k}\alpha} \alpha_{\mathbf{k}\sigma}^{\dagger} \alpha_{k\sigma} + E_{\mathbf{k}\beta} \beta_{\mathbf{k}\sigma}^{\dagger} \beta_{\mathbf{k}\sigma}) , \tag{A2}$$

$$\left. \begin{matrix} E_{\mathbf{k}\alpha} \\ E_{\mathbf{k}\beta} \end{matrix} \right\} = \tfrac{1}{2} \{ \epsilon_{\mathbf{k}} + \epsilon_r \mp [4V^2 + (\epsilon_{\mathbf{k}} - \epsilon_r)^2]^{1/2} \} . \tag{A3}$$

We consider the d electrons to have a tight-binding band ϵ_k with a constant density of states $\frac{1}{2}W(-W \le \epsilon_{\mathbf{k}} \le W)$. The coefficients of the canonical transformation are

$$\left. \begin{matrix} u_{\mathbf{k}}^2 \\ v_{\mathbf{k}}^2 \end{matrix} \right\} = \frac{1}{2} \left[1 \mp \frac{\epsilon_{\mathbf{k}} - \epsilon_r}{[4V^2 + (\epsilon_{\mathbf{k}} - \epsilon_r)^2]^{1/2}} \right] \tag{A4}$$

or equivalently

$$u_{\mathbf{k}}^2 = \left[1 + \left[\frac{V}{\epsilon_r - E_{\mathbf{k}\alpha}} \right]^2 \right]^{-1} , \tag{A5a}$$

$$v_{\mathbf{k}}^2 = \left[1 + \left[\frac{V}{\epsilon_r - E_{\mathbf{k}\beta}} \right]^2 \right]^{-1} . \tag{A5b}$$

Use of (A4) and (A5) results in the following identities which have been used in the derivation of various formulas in this paper:

$$u_{\mathbf{k}}^2+v_{\mathbf{k}}^2=1\ , \tag{A6}$$

$$(E_{\mathbf{k}\alpha}-\epsilon_r)(\epsilon_r-E_{\mathbf{k}\beta})=V^2\ , \tag{A7}$$

$$u_{\mathbf{k}}^2v_{\mathbf{k}}^2=\frac{V^2}{(E_{\mathbf{k}\alpha}-E_{\mathbf{k}\beta})^2}\ . \tag{A8}$$

Also, the densities of states $N_\alpha(E_{\mathbf{k}\alpha})$ and $N_\beta(E_{\mathbf{k}\beta})$ are given, respectively, by $N(0)/u_{\mathbf{k}}^2$ and $N(0)/v_{\mathbf{k}}^2$, with $N(0)$ the normal density of states at the Fermi level.

Finally, to a good approximation, the band edges are denoted by (with ± signifying the upper or lower edge)

$$E_\alpha^\pm\approx\begin{cases}-W-V^2/W & \text{for } -,\\ \epsilon_r-V^2/W & \text{for } +\ ,\end{cases} \tag{A9}$$

$$E_\beta^\pm\approx\begin{cases}W+V^2/W & \text{for } +,\\ \epsilon_r+V^2/W & \text{for } -\ .\end{cases} \tag{A10}$$

We note that these results are well known in the literature and are reproduced here for completeness and clarity.

APPENDIX B: DEVIATION OF THE T MATRIX FOR H_1^{imp}

We generalize H_1^{imp} [Eq. (2.3)] to include d-f and f-f scattering[2,24]

$$H_1^{\text{imp}}=\frac{1}{N}\sum_{\mathbf{R},\mathbf{k},\mathbf{k}'}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}}(d_{\mathbf{k}}^\dagger f_{\mathbf{k}}^\dagger)\begin{bmatrix}U_{dd} & U_{df}\\ U_{df} & U_{ff}\end{bmatrix}\begin{bmatrix}d_{\mathbf{k}'}\\ f_{\mathbf{k}'}\end{bmatrix} \tag{B1}$$

$$=\frac{1}{N}\sum_{\mathbf{R},\mathbf{k},\mathbf{k}'}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}}(\alpha_{\mathbf{k}}^\dagger\beta_{\mathbf{k}}^\dagger)\hat{S}_{\mathbf{k}}\hat{U}\hat{S}_{\mathbf{k}'}^{-1}\begin{bmatrix}\alpha_{\mathbf{k}'}\\ \beta_{\mathbf{k}'}\end{bmatrix} \tag{B2}$$

with $\hat{U}$ the 2×2 matrix of (B1) and $\hat{S}_k$ defined in (A1). We denote the product $\hat{S}_k\hat{U}\hat{S}_{k'}^{-1}$ as $(\hat{H}_1)_{kk'}$.

The Born series is thus

$$\hat{T}_{kk'}(z)=\hat{H}_{1kk'}+\sum_{k''}\hat{H}_{1kk''}\hat{G}_{0k''}(z)\hat{H}_{1k''k'}+\cdots \tag{B3}$$

with

$$G_{0\mathbf{k}}(z)=\begin{bmatrix}(z-E_{\mathbf{k}\alpha})^{-1} & 0\\ 0 & (z-E_{\mathbf{k}\beta})^{-1}\end{bmatrix}\ . \tag{B4}$$

Using (B1) and (B2) we can immediately sum (B3) to obtain

$$\hat{T}_{kk'}(z)=\hat{S}_k\left[1-\sum_{k''}\hat{U}\hat{S}_{k''}^{-1}\hat{G}_{0k''}(z)\hat{S}_{k''}\right]^{-1}\hat{U}\hat{S}_{k'}^{-1}\ . \tag{B5}$$

Obviously, for fully general $\hat{U}$, $\hat{T}_{kk'}$ has a rather complicated structure. We note two limiting cases.

(i) The "least-resonant" case ($U_{dd}=G$; $U_{df}=U_{ff}=0$). This gives

$$\hat{T}_{kk'}(z)=\frac{G/N}{1-G[A_{u\alpha}(z)+A_{v\beta}(z)]}\begin{bmatrix}u_ku_{k'} & u_kv_{k'}\\ u_{k'}v_k & v_kv_{k'}\end{bmatrix} \tag{B6}$$

with, e.g.,

$$A_{u\gamma}(z)=\frac{1}{N}\sum_{\mathbf{k}}\frac{u_k^2}{z-E_{k\gamma}},\quad \gamma=\alpha,\beta\ . \tag{B7}$$

Use of the optical theorem

$$\hat{\tau}^{-1}(\mathbf{k},\omega)=-2\,\mathrm{Im}\hat{T}_{kk}(\omega+i\eta),\quad \eta\to0^+ \tag{B8}$$

gives the diagonal rates quoted in Sec. III.

(ii) The "most-resonant" case ($U_{dd}=0=U_{df}$; $U_{ff}\neq0$). This gives

$$\hat{T}_{kk'}(z)=\frac{U_{ff}/N}{1-U_{ff}[A_{u\beta}(z)+A_{v\alpha}(z)]}\begin{bmatrix}v_kv_{k'} & u_{k'}v_k\\ u_ku_{k'} & u_ku_{k'}\end{bmatrix} \tag{B9}$$

and hence the diagonal rate [$\Gamma=\pi N(0)V^2$]

$$\tau_{\alpha\alpha}^{-1}(E_{k\alpha})=\frac{2c}{\pi N_0}\frac{u_k^2(U_{ff}\Gamma)^2}{[(E_{k\alpha}-\epsilon_r)(E_{k\alpha}-\epsilon_r-U_{ff})-(U_{ff}\Gamma/\pi)L(E_{k\alpha})]^2+(U_{ff}\Gamma)^2}\ . \tag{B10}$$

$\tau_{\beta\beta}^{-1}$ has the same form with u_k^2 being replaced by v_k^2. [$L(E)$ is defined as per (3.2).]

We note the presence of the mass factor u_k^2, just as in the least-resonant case. This is sufficient to give rise to the same cancellation of mass factors in $\rho(T)$, leaving behind only the average of $\sin^{-2}\delta(\epsilon)$, with

$$\delta(\epsilon)=\tan^{-1}\left[\frac{U_{ff}\Gamma}{(\epsilon-\epsilon_r)(\epsilon-\epsilon_r-U_{ff})-(U_{ff}\Gamma/\pi)L(\epsilon)}\right]\ . \tag{B11}$$

The unitarity limit is thus explicitly maintained, as $\sin^2\delta(\epsilon)$ will at most go to 1 near ϵ_r.

In contrast, if we had used the Born approximation,[25,26] then

$$\tau_{\alpha\alpha}^{-1}(E_{k\alpha})=\frac{2c}{\pi N_0}\frac{(U_{ff}\Gamma)^2}{[(E_{k\alpha}-\epsilon_r)^2+V^2](E_{k\alpha}-\epsilon_r)^2}\ , \tag{B12}$$

which tends to $(2c/\pi N_0)(\pi U_{ff}/2V)^2$ at E_α^+. For $V\to0$, this could be large. In contrast, $\tau_{\alpha\alpha}^{-1}(E_\alpha^+)$ of (B11) goes to zero for $V\to0$. Moreover, the explicit cancellation of mass factors will not take place if (B13) is put into Eq. (3.4); rather, the factor of $(E_{k\alpha}-\epsilon_r)^2$ will suppress $\sigma(T)$ and falsely give an enhancement to $\rho(T)$.

We conclude that the use of the Born approximation is invalid in this case of strong scattering.

APPENDIX C

Using the diagrammatic approach, we shall derive Eq. (3.5). We shall utilize the Kubo formula and finite-temperature Green's-function formalism. The essence of the derivation is that the leading term (of order of the inverse concentration) in the dc conductivity arises from direct (intraband) processes. Interband contributions, which are beyond the scope of the semiclassical theory of Sec. III, give dc contributions of order unity.

Our derivation closely follows that of Murata.[21] From linear response theory

$$\sigma(i\omega)=\frac{ie^2}{i\omega}[\chi(0)-\chi(i\omega)]\ , \qquad \text{(C1)}$$

where $i\omega=2\pi ni/\beta$, n being an integer, will be analytically continued to $\omega+i\eta$, $\eta\to 0$ and ω real.

For $\chi(i\omega)$ we use the interaction representation formula[24]

$$\chi(i\omega)=\frac{1}{\Omega}\int_0^\beta d\tau\, e^{i\omega\tau}\langle T_\tau S(\beta)\mathbf{j}_I(\tau)\cdot\mathbf{j}(0)\rangle \qquad \text{(C2)}$$

with

$$\mathbf{j}_I(\tau)=e^{\tau H}\mathbf{j}e^{-\tau H}\ . \qquad \text{(C3)}$$

The current $\mathbf{j}=\sum_{\mathbf{k},\sigma}\mathbf{v}_\mathbf{k}d^\dagger_{\mathbf{k}\sigma}d_{\mathbf{k}\sigma}$ is that of Eq. (2.9).

Expanding the S matrix to lowest order yields the "bubble diagram,"[24]

$$\chi(i\omega)=\frac{1}{m^2\Omega}\sum_{\substack{\mathbf{k},\sigma,\\ \mathbf{k}',\sigma'}}\mathbf{k}\cdot\mathbf{k}'\int_0^\beta d\tau\, e^{i\omega\tau} \times\langle T_\tau d^\dagger_{\mathbf{k}\sigma}(\tau)d_{\mathbf{k}\sigma}(\tau)d^\dagger_{\mathbf{k}'\sigma}d_{\mathbf{k}'\sigma'}\rangle\ . \qquad \text{(C4)}$$

We now want to express d operators in terms of α and β operators, and thus use the Green's functions appropriate to the true bands. We take the lowest-order result of impurity averaging,

$$\hat{\Sigma}_r(\mathbf{k},\omega)=N_i\hat{T}_{kk}(\omega+i\eta),\quad \eta\to 0 \qquad \text{(C5)}$$

where $\hat{\Sigma}_r$ is the retarded self-energy, N_i is the number of impurities, and $\hat{T}$ is given by Eq. (B7).

This gives the Green's function

$$\hat{G}(k,\omega)=\frac{\begin{bmatrix}\omega-E_{\beta k}-\Sigma_{\beta\beta}(\mathbf{k},\omega) & \Sigma_{\alpha\beta}(\mathbf{k},\omega)\\ \Sigma_{\alpha\beta}(\mathbf{k},\omega) & \omega-E_{\alpha k}-\Sigma_{\alpha\alpha}(\mathbf{k},\omega)\end{bmatrix}}{[\omega-E_{\beta\mathbf{k}}-\Sigma_{\beta\beta}(\mathbf{k},\omega)][\omega-E_{\alpha\mathbf{k}}-\Sigma_{\alpha\alpha}(\mathbf{k},\omega)]-[\Sigma_{\alpha\beta}(\mathbf{k}\omega)]^2}\ . \qquad \text{(C6)}$$

Transformation to the $\alpha\beta$ basis gives

$$\chi(i\omega)=\frac{2}{3m^2\Omega\beta}\sum_{\mathbf{k},l}k^2[I_{\text{direct}}(\mathbf{k},l)+I_{\text{interband}}(\mathbf{k},l)]\ , \qquad \text{(C7)}$$

where l is an integer, $\omega_l=(2l+1)\pi i/\beta$, and

$$I_{\text{direct}}(\mathbf{k},l)=u_k^4G_{\alpha\alpha}(\mathbf{k},i\omega+i\omega_l)G_{\alpha\alpha}(\mathbf{k},i\omega_l) +v_k^4(\alpha\to\beta)\ . \qquad \text{(C8)}$$

We shall return to $I_{\text{interband}}$ later.

Define the spectral function $\hat{A}$ as $\hat{A}=-\operatorname{Im}\hat{G}$ retarded. Doing the l sum on I_{direct} gives

$$\chi_{\text{direct}}=\frac{2}{3m^2}\int dk\frac{k^4}{2\pi^2}\int d\zeta\int d\zeta'\frac{1}{\pi^2}\frac{f(\zeta)-f(\zeta')}{\zeta-\zeta'-i\omega}S_{\text{direct}} \qquad \text{(C9)}$$

with

$$S_{\text{direct}}=u_k^4A_{\alpha\alpha}(\mathbf{k},\zeta)A_{\alpha\alpha}(\mathbf{k},\zeta')+v_k^4(\alpha\to\beta)\ . \qquad \text{(C10)}$$

The conduction-band density of states has a high-energy cutoff; thus, to order $1/W$ we can replace $N(\epsilon)k^2/2m$ by $N(0)W=3n_e/2$, the latter holding in a match to the free-electron limit, n_e being the conduction-electron density.

We now combine the direct terms. The effective mass is defined as

$$\frac{m}{m^*(E)}=\frac{(E-\epsilon_r)^2+V^2}{(E-\epsilon_r)^2}\ , \qquad \text{(C11)}$$

and we can write

$$\chi_{\text{direct}}=\frac{n_e}{m}P\int dE\int d\zeta\int d\zeta'\frac{1}{\pi^2}\frac{f(\zeta)-f(\zeta')}{\zeta-\zeta'-i\omega}\frac{m}{m^*(E)} \times A(E,\zeta)A(E,\zeta')\ , \qquad \text{(C12)}$$

where

$$A(E,\zeta)=\begin{cases}A_{\alpha\alpha}(E,\zeta), & E_\alpha^-\le E\le E_\alpha^+\\ A_{\beta\beta}(E,\zeta), & E_\beta^-\le E\le E_\beta^+\end{cases} \qquad \text{(C13)}$$

and P is a mnemonic for integrating E_α from E_α^- to E_α^+ and E_β^- to E_β^+.

We note that the E integral may be extended into the gap with error V^2/W at worst, and the upper and lower bounds may be extended to $\pm\infty$ with the error of order $1/W$. The advantage to these extensions is that the E integral can be evaluated with contour techniques.

Before we do this, we need to get $A(E,\zeta)$ into a more workable form. The problem is that, e.g., in $A_{\alpha\alpha}$ there are poles near both $E_{k\alpha}$ and $E_{k\beta}$. However, the pole near $E_{k\beta}$ (call it $\pm\zeta_{\beta k}$) to second order in c can easily be found. Define $S(\zeta)$ by $\sum_{\alpha\alpha}(k,\zeta)=u^2S_k(\zeta)$, then

$$\zeta_{\beta k}=E_{k\beta}+v_{k\beta}^2S(E_{k\beta})\left[1+v_k^2\frac{\partial S}{\partial k}\bigg|_{E_{k\beta}}+\frac{u_k^2S(E_{k\beta})}{E_{k\beta}-E_{k\alpha}}\right]\ . \qquad \text{(C14)}$$

This gives the residue of $G_{\alpha\alpha}$ at $\zeta_{\beta k}$ as

$$\frac{v_kS(E_{k\beta})}{(E_{k\beta}-E_{k\alpha})^2}\left[v_k^2\frac{\partial S}{\partial\zeta}\bigg|_{E_{k\beta}}(E_{k\beta}-E_{k\alpha})+u_k^2S(E_{k\beta})\right]\ . \qquad \text{(C15)}$$

Since $E_{k\beta}-E_{k\alpha}>2V$, this is always of order c^2. Hence, to leading order in c in the dilute limit, $G_{\alpha\alpha}$ is well approximated by

$$G_{\alpha\alpha}(\mathbf{k},\zeta)=[\zeta-E_{k\alpha}-u_k^2S(\zeta)]^{-1} = \left[\zeta-E_{k\alpha}-\frac{mS(\zeta)}{m^*(E_{k\alpha})}\right]^{-1} , \tag{C16}$$

which leads us to define a self-energy for $A(E,\zeta)$,

$$\Sigma(E,\zeta)=\frac{m}{m^*(E)}S(\zeta) . \tag{C17}$$

We now do the E integral, which is

$$-\tfrac{1}{4}\int dE\frac{m}{m^*(E)}\left[\frac{1}{\zeta-E-\Sigma^*(E,\zeta)}-\frac{1}{\zeta-E-\Sigma(E,\zeta)}\right][1+(\zeta\to\zeta')] . \tag{C18}$$

Only the terms $[\zeta-E-\Sigma^*(E,\zeta)]^{-1}[\zeta'-E-\Sigma(E,\zeta')]^{-1}$ + c.c. contribute; we close the contour for the first term in the upper-half plane, and that for the second term in the lower-half plane. The poles of m/m^* are irrelevant as those factors of m/m^* in the denominator cancel the singularity in the numerator. The integral can thus be written as

$$\pi\,\mathrm{Im}\left[\frac{m/m^*(\bar{E})}{\zeta'-\zeta+\Sigma(\bar{E},\zeta)-\Sigma^*(\bar{E},\zeta')}\right] , \tag{C19}$$

where $\bar{E}$ is given implicitly by

$$\bar{E}=\zeta-\Sigma(\bar{E},\zeta)=\zeta-\Sigma(\zeta,\zeta)+O(c^2) . \tag{C20}$$

This latter result is really the essence of the quasiparticle approximation which is tacit in semiclassical theory.

We thus arrive at the spectral representation

$$\chi_{\mathrm{direct}}(z)=\frac{-n_e}{m}\int\frac{d\zeta'}{\pi}\frac{1}{z-\zeta'}\mathrm{Im}\int d\zeta\frac{[f(\zeta-\zeta')-f(\zeta)][m/m^*(\bar{E}(\zeta))]}{\zeta'+\Sigma^*(\bar{E}(\zeta),\zeta-\zeta')-\Sigma(\bar{E}(\zeta),\zeta)} , \tag{C21}$$

which leads to the unambiguous identification

$$\mathrm{Im}\chi_{\mathrm{direct}}(\omega\to0) =\frac{n_e\omega}{m}\mathrm{P}\int d\zeta\left[\frac{-\partial f}{\partial\zeta}\right]\frac{1}{2\,\mathrm{Im}S(\zeta)}+O(1) , \tag{C22}$$

where we used $m/m^*(\bar{E})=m/m^*(\zeta)+O(c)$. Noting that $\tau_0t(\zeta)$ in Eq. (3.5) is the same as $2\,\mathrm{Im}S(\zeta)$, we have established that to order $1/c$,

$$\mathrm{Im}\sigma_{\mathrm{direct}}(\omega\to0)=\frac{\omega_p^2}{4\pi\omega}\mathrm{Im}\chi_{\mathrm{direct}}(\omega\to0)$$

agrees with the Boltzmann result.

The spectral representation (C21) unambiguously defines $\mathrm{Im}\chi_{\mathrm{direct}}$; it defines χ_{direct} apart from a constant. Let us define

$$\delta m/m^*(E)=V^2/[(E-\epsilon_r)^2+V^2] .$$

We note that for $\omega\to\infty$

$$\frac{n}{m}\int d\zeta\frac{f(\zeta-\omega)-f(\zeta)}{\omega+\Sigma^*(\bar{E},\zeta-\omega)-\Sigma(\bar{E},\zeta)}\frac{m}{m^*(\bar{E}(\zeta))} \approx\frac{n_e}{m}\int d\zeta\frac{f(\zeta-\omega)-f(\zeta)}{\omega}\left[1-\frac{\delta m}{m^*(\zeta)}\right] . \tag{C23}$$

The second term on the right goes like $1/\omega$ for $\omega\to\infty$; the first term is χ. From this we see that $\chi_0-\chi_{\mathrm{direct}}$ has the form

$$\chi_0-\chi_{\mathrm{direct}}(\omega) =\frac{n_e}{m}\int d\zeta\frac{f(\zeta-\omega)-f(\zeta)}{\omega+\Sigma^*(\bar{E},\zeta-\omega)-\Sigma(\bar{E},\zeta)}\frac{m}{m^*(E)} \tag{C24}$$

valid for both $\omega\to0$ and $\omega\to\infty$.

Finally, we focus on the interband terms. The largest contribution comes from the term involving the product

$$G_{\alpha\beta}(\mathbf{k},i\omega+i\omega_l)[G_{\alpha\alpha}(\mathbf{k},i\omega_l)+G_{\beta\beta}(\mathbf{k},i\omega_l)] .$$

In the same approximation as (C16), one can set $G_{\alpha\beta}=\Sigma_{\alpha\beta}G_{\alpha\alpha}G_{\beta\beta}$. Carrying through the same kind of analysis which led to Eq. (C21), one obtains a term in $\mathrm{Im}\chi(\omega\to0)$ of the form

$$\mathrm{Im}\int d\zeta\frac{[f(\zeta-\omega)-f(\zeta)]S(\zeta)[m/m^*(\zeta)][\delta m/m^*(\zeta)]^4}{[\omega+\Sigma^*(\zeta,\zeta-\omega)-\Sigma(\zeta,\zeta)]\left[\omega+\dfrac{(\zeta-\epsilon_r)^2+V^2}{(\zeta-\epsilon_r)}+\dfrac{\delta m}{m^*(\zeta)}S^*(\zeta-\omega)-\dfrac{m}{m^*(\zeta)}S(\zeta)\right]} .$$

As $\omega\to0$, there is a leading c^0 term coming from this; this establishes the claim about interband terms. Any other combination $(G_{\alpha\beta}G_{\alpha\beta},G_{\alpha\alpha}G_{\beta\beta})$ gives at most terms of order c.

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