Reconstructing the Thermodynamic Properties out of Scattering Cross Sections

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Using Green's functions of electrons scattered at an impurity site, I derive expressions for the energy δU solely in terms of the electronic scattering cross section. My formulas can correlate the excess specific heat of dilute alloys with their resistivity. Formulas are derived for nontrivial scattering mechanisms illustrated by three well-known models, all capable of exhibiting the anomalous scattering known as the Kondo effect.

There is a widespread belief that all the information concerning transport and thermodynamic properties of a many-body system is contained within a single, appropriately chosen, Green's function. Here I am able to substantiate this in special cases of electrons scattered by an impurity center, as in a dilute metallic alloy. The scattering may be due to a simple potential difference at the site of the impurity, or to spin-dependent scattering as in the *s*-*d* exchange model,[1] or to a combination of one- and two-body forces as in Anderson's[2] and Wolff's[3] models. Any of these may be used to study the Kondo effect,[4] which consists principally of a logarithmic anomalous scattering cross section. My main result consists of an integral transform, rigorously expressing one physical observable, the internal energy, using another physical observable, the electronic scattering cross section, which is assumed to be known.

Let us suppose the Hamiltonian to be of the form

$$\mathcal{H}=\sum_{k,\sigma}\epsilon_k c_{k\sigma}{}^{\dagger}c_{k\sigma}+\sum_{\sigma,\sigma'}M_{\sigma,\sigma'}\Phi_\sigma{}^{\dagger}\Phi_{\sigma'}. \tag{1}$$

A most general form of the 2×2 matrix $M_{\sigma,\sigma'}$ is $V\delta_{\sigma,\sigma'}+J_xS_x\sigma_x+J_yS_y\sigma_y+J_zS_z\sigma_z$, where V represents potential scattering, the S_i are components of the impurity spin (which do not commute with one another) and the σ_i are the Pauli spin matrices. We treat the case of two-body forces separately.

The wave operators at the site of the impurity are the Wannier operators:

$$\Phi_\sigma=N^{-1/2}\sum_k c_{k\sigma}. \tag{2}$$

The electronic scattering time $\tau_\sigma(\omega)$ per unit concentration of the dilute impurity species is obtainable from the anticommutator retarded one-particle Green's function[5]:

$$\langle\langle c_{k\sigma}|c_{k'\sigma}{}^{\dagger}\rangle\rangle=\frac{\delta_{k,k'}/2\pi}{\omega-\epsilon_k}+\frac{1}{2\pi N}\,\frac{1}{\omega-\epsilon_k}\,\frac{1}{\omega-\epsilon_{k'}}\,G_\sigma(\omega), \tag{3}$$

in which $G_\sigma(\omega)$, the t matrix, is a quantity $O(1)$ defined as

$$G_\sigma(\omega)=-i\int_0^\infty dt e^{i\omega t}\langle\{\sum_{\sigma'}M_{\sigma,\sigma'}(t\ )\Phi_{\sigma'}(t),\sum_{\sigma''}M_{\sigma,\sigma''}{}^{\dagger}\Phi_{\sigma''}{}^{\dagger}\}\rangle_{\mathrm{TA}}, \tag{4}$$

where $\langle\rangle_{\mathrm{TA}}$ indicates thermal average. The scattering time, an intrinsically nonnegative quantity, is simply

$$1/\tau_\sigma(\omega)\equiv\pm 2\operatorname*{Im}_{\delta\to 0^+}G_\sigma(\omega\mp i\delta). \tag{5}$$

Generally, $\tau_\sigma(\omega)$ depends on the temperature β^{-1} as well as the energy ω. As for the internal energy, it is a quantity $O(N)$ given by

$$U\equiv\langle\mathcal{H}\rangle_{\mathrm{TA}}=2\int_{-\infty}^{\infty}d\omega f(\beta\omega)\omega\operatorname*{Im}_{\delta\to 0^+}\sum_{k,\sigma}\langle\langle c_{k\sigma}|c_{k\sigma}{}^{\dagger}\rangle\rangle_{\omega-i\delta}, \tag{6}$$

with f being the Fermi function. In order to determine δU, the internal energy of the impurity, which is the physically meaningful quantity $O(1)$, it is required to subtract the unperturbed internal energy U_0. While this may seem to be a straightforward matter of substituting (3) into (6) and subtracting a similar expression with $M=0$, this approach unfortunately leads to singular denominators of the type $(\omega-\epsilon_k)^2$, and attempts to remove the divergences are fraught with ambiguity.

The following procedure yields unambiguous results in the thermodynamic limit $N\to\infty$. Because one is only required to use the Green's functions with $k=k'$ in Eq. (6), one rewrites them in a more perspicuous form:

$$\langle\langle c_{k\sigma}|c_{k\sigma}{}^{\dagger}\rangle\rangle_{\omega-i\delta}=\frac{1/2\pi}{\omega-\epsilon_k-N^{-1}G_\sigma(\epsilon_k-i\delta)-i\delta}+O(N^{-2}). \tag{7}$$

This form at once demonstrates the interlacing of the new and old eigenvalues, and satisfies the important spectral sum rule:

$$2\operatorname{Im}\int_{-\infty}^{\infty}d\omega\langle\langle c_{k\sigma}|c_{k\sigma}{}^{\dagger}\rangle\rangle_{\omega-i\delta}=1, \tag{8}$$

which in the Green's-function formalism is tantamount to the usual requirement of wave-function normalization. The analytic properties of G require it to satisfy the dispersion relations

$$R_\sigma(\omega)=\frac{\mathrm{P}}{2\pi}\int_{-\infty}^{\omega}d\omega'\,\frac{1}{\tau_\sigma(\omega')}\,\frac{1}{\omega-\omega'},\quad \frac{1}{2\tau_\sigma(\omega)}=\frac{\mathrm{P}}{\pi}\int_{-\infty}^{\infty}d\omega'\,\frac{R_\sigma(\omega')}{\omega-\omega'}, \tag{9}$$

where P indicates that one uses the principal part of the integral. Note that the imaginary part of (7) is a δ function, *independent of both the imaginary quantities* in the denominator, in the limits $\delta\to 0$ and $N\to\infty$. Thus

$$\delta U=N^{-1}\sum_{k\sigma}R(\epsilon_k)\,\partial[f(\beta\epsilon_k)\epsilon_k]/\partial\epsilon_k. \tag{10}$$

Replacing the sum by an integral over the normalized density of states $\rho(\epsilon)$ and R by its value (9), we obtain a new result, a formula in which the model parameters $M_{\sigma\sigma'}$ *do not appear explicitly:*

$$\delta U = \frac{1}{2\pi}\sum_{\sigma}\int\int_{-\infty}^{\infty} d\epsilon\, d\epsilon'\, \rho(\epsilon)\, \frac{1}{\tau_{\sigma}(\epsilon')}\left(\frac{1}{\epsilon - \epsilon'}\right)\frac{\partial}{\partial\epsilon}[\epsilon f(\beta\epsilon)]. \tag{11}$$

To test this, let us consider the first Born approximation to potential scattering (second order in V):

$$[\tau_{\sigma}(\epsilon)]^{-1} = 2\pi V^2 \rho(\epsilon). \tag{12}$$

According to (11) this implies

$$\delta U^{(2)} = 2V^2 \int\int d\epsilon\, d\epsilon'\, \rho(\epsilon)\rho(\epsilon')(\epsilon - \epsilon')^{-1}\partial[\epsilon f(\beta\epsilon)]/\partial\epsilon. \tag{13}$$

This is to be compared with standard thermodynamic perturbation theory. In second order,

$$\delta F_{\mathrm{PT}}^{(2)} = 2V^2 \int\int d\epsilon\, d\epsilon'\, \rho(\epsilon)\rho(\epsilon')(\epsilon - \epsilon')^{-1} f(\beta\epsilon). \tag{14}$$

From this we compute the internal energy:

$$\delta U_{\mathrm{PT}}^{(2)} \equiv (\partial/\partial\beta)(\beta\delta F_{\mathrm{PT}}^{(2)}). \tag{15}$$

Use of the identity $\beta\partial f/\partial\beta = \epsilon\partial f/\partial\epsilon$ renders this identical with (13). Moreover, formula (11) remains valid whether or not the thermodynamic functions are analytic in the coupling constant. For completeness, it will be noted that the perturbation which involves the diagonal operators $c_{k\sigma}^{\dagger}c_{k\sigma}$ and contributes to first order in the energy does not contribute to the scattering, and is therefore not explicitly present in the formula (11). To include it, it is sufficient to add to R_{σ}, as defined in (9), an extra term $\langle M_{\sigma\sigma}\rangle$ before evaluating the expression (10), obtaining

$$\delta U^{(1)} = \frac{1}{N}\sum_{k\sigma}\langle M_{\sigma\sigma}\rangle \frac{\partial}{\partial\epsilon k}[f(\beta\epsilon_k)\epsilon_k] = \sum_{\sigma}\int_{-\infty}^{\infty} d\omega\, \rho(\omega)\langle M_{\sigma\sigma}\rangle\frac{\partial}{\partial\omega}[f(\beta\omega)\omega]. \tag{16}$$

Generally, first-order contributions such as this are structureless and may be ignored in the specific heat.

The case of mixed one- and two-body forces is illustrated by the Wolff model[3,6]:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2 = \sum\nolimits_{k\sigma}\epsilon_k c_{k\sigma}^{\dagger}c_{k\sigma} + \sum\nolimits_{\sigma}V_{1\sigma}\Phi_{\sigma}^{\dagger}\Phi_{\sigma} + V_2\Phi_{\uparrow}^{\dagger}\Phi_{\uparrow}\Phi_{\downarrow}^{\dagger}\Phi_{\downarrow}. \tag{17}$$

The calculation and the final result will be very similar to the s-d model. Once again the Green's function takes the form indicated in Eq. (3), with the t matrix being

$$G_{\sigma}(\omega) = -i\int_0^{\infty} dt\, e^{i\omega t}\langle\{V_{1\sigma}\Phi_{\sigma}(t) + V_2\Phi_{\sigma}(t)\Phi_{-\sigma}^{\dagger}(t)\Phi_{-\sigma}(t), V_{1\sigma}\Phi_{\sigma}^{\dagger} + V_2\Phi_{\sigma}^{\dagger}\Phi_{-\sigma}^{\dagger}\Phi_{-\sigma}\}\rangle_{\mathrm{TA}}. \tag{18}$$

The scattering time $\tau_{\sigma}(\omega)$ is related to the imaginary part of $G_{\sigma}(\omega)$, as in Eq. (5), and the real part of $G_{\sigma}(\omega)$ is then connected to the imaginary by the Kramers-Kronig relation, Eq. (9). It is only the form of the internal energy which must be modified. Use of (6) yields $U + \langle\mathcal{H}_2\rangle_{\mathrm{TA}}$, which is useless. Among several alternative formulations, the following appears to be the simplest:

$$U = 2\int_{-\infty}^{\infty} d\omega\, f(\beta\omega)\, \underset{\delta\to 0}{\mathrm{Im}}\sum_{k\sigma}\tfrac{1}{2}(\omega + \epsilon_k)\langle\langle c_{k\sigma}|c_{k\sigma}^{\dagger}\rangle\rangle_{\omega - i\sigma} + \tfrac{1}{2}\langle\mathcal{H}_1\rangle_{\mathrm{TA}}. \tag{19}$$

The use of (7) once again permits the correct evaluation of the first term. The second term requires $\langle\langle c_{k\sigma}|c_{k'\sigma}^{\dagger}\rangle\rangle$ with $k \neq k'$, for which the original form (3) is adequate. Omitting details, the result is

$$\delta U = (4\pi)^{-1}\sum\nolimits_{\sigma}\int\int_{-\infty}^{\infty} d\epsilon\, d\epsilon'\, \rho(\epsilon)[\tau_{\sigma}(\epsilon')]^{-1}(\epsilon - \epsilon')^{-1}\{f(\beta\epsilon) + 2\epsilon\partial f(\beta\epsilon)/\partial\epsilon + V_{1\sigma}\lambda(\epsilon)[f(\beta\epsilon) - f(\beta\epsilon')]\}, \tag{20}$$

where we introduce an auxiliary function,

$$\lambda(\epsilon) = 2\mathrm{P}\int_{-\infty}^{\infty} d\omega\, \rho(\omega)(\epsilon - \omega)^{-1}. \tag{21}$$

Aside from the model parameter V_1, only a knowledge of the scattering time $\tau_{\sigma}(\omega)$ is required to calculate the internal energy (hence, the specific heat, free energy, etc.) associated with the impurity. It should be re-emphasized that it is the total and *exact* scattering time, including *all* interference effects between the two scattering potentials i.e., the experimental value, that enters into this expression. Had we included spin-nondiagonal one-body terms such as $\Phi_{\uparrow}^{\dagger}\Phi_{\downarrow}$, then spin-nondiagonal Green's functions $\langle\langle c_{k,\sigma} | c_{k',-\sigma}^{\dagger}\rangle\rangle$ would have been needed in the calculation of the internal energy which could *not* have been expressed solely in terms of the physical observable $\tau_\sigma(\omega)$. Thus for the method to work, we can allow either spin-flip terms with no two-body forces, or *vice-versa;* but the combination of the two is anathema. When $V_{1\sigma} \to 0$, Eq. (20) becomes nearly identical to (11).

The results generalize to certain velocity-dependent potentials such as

$$\mathcal{H}_2 = N^{-2} \sum_{k_i \sigma_i} V_2(k_1\sigma_1, \dots, k_4\sigma_4) c_{k_1\sigma_1}{}^{\dagger} c_{k_2\sigma_2}{}^{\dagger} c_{k_3\sigma_3} c_{k_4\sigma_4},$$

in Eq. (17), or $M_{k\sigma,k'\sigma'} c_{k\sigma}{}^{\dagger} c_{k'\sigma'}$ in Eq. (1), provided we use the appropriate generalized t matrix:

$$\langle G_\sigma(\omega)\rangle = \int d_3k[\delta(\omega - \epsilon_k)/\rho(\omega)](-i)\int_0^\infty dt\, e^{i\omega t}\langle\{\Omega_{k\sigma}(t\ ), \Omega_{k\sigma}{}^{\dagger}\}\rangle_{\mathrm{TA}}, \tag{22}$$

where

$$\Omega_{k\sigma} \equiv \sqrt{N}[c_{k\sigma}, \mathcal{H} - \mathcal{H}_0]. \tag{23}$$

The last theory to be examined is due to Anderson,[2,7] who included an extra d orbital at the impurity site. The well-known Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0 + V_1 \textstyle\sum_\sigma (\Phi_\sigma{}^{\dagger} d_\sigma + \mathrm{H.c.}) + \sum_\sigma E_{d\sigma} \Phi_\sigma{}^{\dagger} \Phi_\sigma + V_2 d_\uparrow{}^{\dagger} d_\uparrow d_\downarrow{}^{\dagger} d_\downarrow. \tag{24}$$

Again the Green's function takes the form (3), with the t matrix

$$G_\sigma(\omega) = 2\pi\langle\langle d_\sigma | d_\sigma{}^{\dagger}\rangle\rangle V_1{}^2. \tag{25}$$

It is advantageous to express the internal energy not in terms of $\tau_\sigma(\omega)$ but in terms of $\alpha_\sigma(\omega)$, a new quantity defined by

$$[\tau_\sigma(\omega)]^{-1} = (4\pi V_1{}^2)\,\mathrm{Im}\langle\langle d_\sigma | d_\sigma{}^{\dagger}\rangle\rangle \equiv (4\pi V_1{}^2)\alpha_\sigma(\omega)\rho(\omega). \tag{26}$$

$\alpha_\sigma(\omega)$ will in general be a function of V_1, V_2, and ω, and β. Then,

$$\delta U = V_1{}^2 \int d\epsilon\, \rho(\rho) \int d\epsilon'\, \rho(\epsilon')[\textstyle\sum_\sigma \alpha_\sigma(\epsilon')/(\epsilon - \epsilon')]\{4\partial[\epsilon f(\beta\epsilon)]/\partial\epsilon + [f(\beta\epsilon) - f(\beta\epsilon')]\}$$
$$+ \int d\epsilon\, \rho(\epsilon) f(\beta\epsilon) \textstyle\sum_\sigma (\epsilon + E_{d\sigma})\alpha_\sigma(\epsilon). \tag{27}$$

In the limit $V_1{}^2 \to 0$ the second term dominates, but the first term has a structure reminiscent of Eq. (11). The above is my least "neat" result.

The energy in all cases can also be computed by an alternative method, e.g., integration over a suitably chosen coupling constant, using Feynman's theorem. If chosen with care, this expression should only involve the scattering function (albeit integrated over the coupling constant and differentiated with respect to the temperature). Equating the two formulas then permits a rigorous test of the scaling and renormalization-group hypotheses which are so popular in the study of the Kondo effect nowadays.[8]

Finally, the inverse problem of finding the scattering functions from a knowledge of the thermodynamic ones by inverting Eqs. (11), (20), or (27) has no mathematical solution. Nevertheless these equations could be used in a practical sense to decide, given plausible alternatives, which is the scattering function most compatible with our knowledge of the thermodynamic functions, the latter being at at present known much more accurately than the former. In some cases the energy is known explicitly in the form (10), and the dispersion relations Eq. (9) can be used to calculate the scattering time. I have found this procedure to be possible in the case of the Wolff model[3,6] and shall shortly submit the results for publication.

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