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PARAMAGNETIC IMPURITIES IN METALS AT FINITE TEMPERATURES*

H. SUHL

University of California, San Diego, La Jolla, California

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Abstract

Dispersion theory is combined with the Green's function technique to discuss the scattering of electrons by paramagnetic impurities in normal metals at finite temperatures. The thermodynamic Green's function is derived from an approximate solution of an equation for a modified (non-unitary) scattering matrix. As a check on the consistency of our theory, we generalize it to arbitrary impurity spin S, and show that in the limit $S \to \infty$, it reduces to ordinary potential scattering of electrons with spin parallel or antiparallel to a localized fixed Zeemann field. Some observations are made on the problem of the residual resistance. The effect of additional non-magnetic scattering is briefly considered. Finally, a justification is given for the neglect of multiparticle intermediate states in the dispersion equations.

1. Introduction

IN a previous paper [1], the Chew-Low method was applied to the question first raised by Kondo [2], concerning some anomalous properties of metals with paramagnetic impurities in exchange interaction with the conduction electrons. Kondo found that (a) at zero temperature, the scattering cross section, calculated to third order in the exchange coupling, goes to infinity logarithmically as the electron energy approaches the Fermi energy, and (b) at finite temperature, the residual resistance, calculated in similar order, diverges as log T as the temperature T goes to zero. These conclusions come about as the result of the sharpness of the Fermi level. The exclusion principle, which can be disregarded for ordinary potential scattering comes into play in the sums over intermediate states as soon as the scatterer has internal degrees of freedom (such as are possessed by a paramagnetic impurity).

In reference 1, we used the Chew-Low method to show that Kondo's divergent result (a) changes into a scattering resonance for anti-ferromagnetic exchange coupling (and into non-resonant scattering for the ferromagnetic sign). The Chew-Low method amounts to the summation of an infinite class of perturbation terms, which are hard to sum by standard methods on account of the complexity of the spin dynamics.** In the present paper we discuss the finite temperature case.

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** A method of overcoming these difficulties has been proposed by A.A. Abrikosov (paper given at Many-Body Conference in Novosibirsk in March, 1965).

The Chew-Low method as such can no longer be used, but general dispersion theory can be, with minor modifications. We find that the resistivity in fact goes to zero as $(\log T)^{-2}$ as $T \to 0$. The question whether, nevertheless, a resistance minimum remains when the residual scattering is combined with lattice scattering, remains to be decided by numerical computation. Meanwhile it is shown that the quasiparticle decay rate (a concept which is only approximately meaningful for non-potential scattering) has a resonance only at temperatures below a critical one, given by an equation like that for the transition temperature of a super-conductor. The specter of "complex poles" in the scattering amplitudes arose in reference 1 and is present here also, though only at even lower temperatures. Whether these poles are only a technicality, or whether they signal collapse of the normal state, as suggested by Nagacka [3] we do not examine here.

2. Thermodynamic Green's Function

We define the one-particle thermodynamic Green's function in the usual way [4] by

$$\mathcal{G}\left(r_1,r_2,\tau\right) = -\,\mathrm{Trace}\, e^{-\beta\mathcal{H}} e^{\mathcal{H}\tau}\,\Psi(r_1)\, e^{-\mathcal{H}\tau}\,\Psi^{\dagger}(r_2)\,/\mathrm{Trace}\, e^{-\beta\mathcal{H}}\quad \tau > 0$$

$$= +\,\mathrm{Trace}\, e^{-\beta\mathcal{H}} e^{-\mathcal{H}\tau}\,\Psi^{\dagger}(r_2)\, e^{\mathcal{H}\tau}\,\Psi(r_1)\,/\mathrm{Trace}\, e^{-\beta\mathcal{H}}\quad \tau < 0$$

Here $\Psi(r)$, $\Psi^{\dagger}(r)$ are the annihilation and creation operators of electrons at r, in Schroedinger representation, $\mathcal{H}$ is the complete Hamiltonian, and $\beta = 1/kT$ where T is the temperature, and k Boltzmann's constant. $\mathcal{G}$ may be written as a Fourier series

$$\mathcal{G}\left(r_1\, r_2\, \tau\right) = \frac{1}{\beta} \sum_n e^{-i\omega_n \tau}\, \mathcal{G}\left(r_1\, r_2\, \omega_n\right)$$

where $\omega_n = (2n + 1)\pi/\beta$.

Our first step will be to express $\mathcal{G}(\omega_n)$ in terms of a thermal average of a pseudo-scattering matrix which satisfies relations equivalent to those of reference 1.

Let

$$\mathcal{H} = \mathcal{H}^{\circ} + \mathcal{H}'$$

where $\mathcal{H}^{\circ}$ is the kinetic energy of the conduction electrons, and

$$\mathcal{H}' = \frac{1}{2} J\Omega_o \vec{S} \cdot \Psi^{\dagger}(o)\, \vec{\sigma}\, \Psi(o)$$

with J the exchange integral, Ω_0 an atomic volume, $\vec{S}$ the impurity spin (taken to be one half in this section), and $\vec{\sigma}$ the Pauli matrix vector. Then it is readily verified that

$$\left(\frac{\partial}{\partial\tau} - \frac{1}{2m}\nabla_2^2\right)\left(\frac{\partial}{\partial\tau} - \frac{1}{2m}\nabla_1^2\right)\mathcal{G}\left(r_1 r_2, \tau\right) = \delta(\tau)\delta\left(r_1 - r_2\right) + \frac{1}{2m}\delta(\tau)\nabla_2^2\,\delta\left(r_1 - r_2\right)$$

$$+ \mathcal{M}\left(r_1 r_2, \tau\right) \qquad (1)$$

where

$$\mathcal{M}\left(r_1,r_2,\tau\right) = \delta(\tau)\mathcal{B}\left(r_1r_2\right) - Tr\, e^{-\beta\mathcal{H}}\left[\mathcal{J}^{\dagger}(r_1 0)\,\mathcal{J}(r_2,\tau)\,\eta(\tau) - \mathcal{J}(r_2\tau)\,\mathcal{J}^{\dagger}(r_1 0)\eta(-\tau)\right] \Big/ Tr\, e^{-\beta\mathcal{H}}$$

is the thermally averaged position representative of a modified scattering matrix (analogous to T of reference 1). In these expressions η is the usual step function, $\nabla^2_{1,2}$ are the Laplacians with respect to r_1, r_2.

The "interaction current" $\mathcal{J}(r, \tau)$ is defined by

$$\mathcal{J}^{\dagger}(r,\tau) = e^{\mathcal{H}\tau}\left(\Psi(r),\mathcal{H}^{\prime}\right) e^{-\mathcal{H}\tau}$$

and the "Born" term is the averaged anticommutator

$$\mathcal{B}\left(r_1r_2\right) = Tr\, e^{-\beta\mathcal{H}}\left[\mathcal{J}^{\dagger}\left(r_1\right)\ \Psi^{\dagger}\left(r_2\right)\right]_{+} \Big/ Tr\, e^{-\beta\mathcal{H}}$$

For ease of writing, the spin coordinates have been incorporated in r_1r_2*, i.e. $\mathcal{G}$ is a matrix $\mathcal{G}(r_1\sigma_1,\ r_2\sigma_2,\ \tau)$ in spin-space; and so are $\mathcal{M}$ and $\mathcal{B}$. By changing to Fourier transforms defined by

$$\mathcal{G}\left(r_1\sigma_1,r_2\sigma_2,\tau\right) = \frac{1}{\beta(2\pi)^3}\sum_n e^{-i\omega_n\tau}\int \mathcal{G}\left(k_1\sigma_1,k_2\sigma_2,\omega_n\right) e^{i\left(\vec{k}_1\vec{r}_1-\vec{k}_2\vec{r}_2\right)}\, d\vec{k}_1 d\vec{k}_2$$

equation (1) may be rewritten

$$\left(-i\omega_n+\epsilon_{k_2}\right)\left(-i\omega_n+\epsilon_{k_1}\right)\mathcal{G}\left(k_1k_2\omega_n\right) = \left[i\omega_n-\epsilon_{k_2}\right]\delta\left(k_1-k_2\right) + \mathcal{M}\left(k_1,k_2,i\omega_n\right) \tag{2}$$

where

$$\mathcal{M}\left(k_1,k_2,i\omega_n\right) = \mathcal{B}\left(k_1,k_2\right) - \sum_{pq} e^{-\beta E_p}\left[\frac{\mathcal{J}^{\dagger}{}_{pq}(k_1)\,\mathcal{J}_{qp}(k_2)}{E_p-E_q-i\omega_n} + \frac{\mathcal{J}_{pq}(k_2)\,\mathcal{J}^{\dagger}{}_{qp}(k_1)}{E_q-E_p-i\omega_n}\right] \Big/ Tr\, e^{-\beta\mathcal{H}} \tag{3}$$

$$= \mathcal{B}\left(k_1k_2\right) - \sum_{pq} e^{-\beta E_p}\,\mathcal{J}^{\dagger}{}_{pq}(k_1)\,\mathcal{J}_{qp}(k_2)\,\frac{1+e^{-(E_q-E_p)\beta}}{E_q-E_p-i\omega_n} \Big/ Tr\, e^{-\beta\mathcal{H}} \tag{3a}$$

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* except where r_1r_2 occur as integration variables for Fourier transform purposes.

and where the spin indices have been re-incorporated in the k's. The interaction currents are related to the previous ones by

$$\mathcal{J}^{\dagger}(k\sigma) = \frac{1}{(2\pi)^{3/2}} \int e^{-i\vec{k}\cdot\vec{r}}\, \mathcal{J}^{\dagger}(r\sigma,0)\, d\vec{r} \ .$$

In arriving at (3), we have inserted a complete set of intermediate states between the $\mathcal{J}$'s, and have availed ourselves of the fact that $\mathcal{M}(r_1 r_2 \tau)$ is like a Green's function with $\mathcal{J}$'s replacing Ψ's, and shares the property

$$\mathcal{M}(\tau) = -\mathcal{M}(\tau+\beta), \ -\beta < \tau < 0$$

with the Green's function.

Introducing the free particle Green's function $\mathcal{G}_0$, with

$$\mathcal{G}_0^{-1}(k\omega_n) = (i\omega_n - \epsilon_k)$$

we may solve (2) for $\mathcal{G}$:

$$\mathcal{G}(k_1 k_2 \omega_n) = \mathcal{G}_0(k_1\omega_n)\,\delta(k_1-k_2) - \mathcal{G}_0(k_1\omega_n)\,\mathcal{M}(k_1 k_2 \omega_n)\,\mathcal{G}_0(k_2\omega_n) \tag{4}$$

3. Modified Scattering Matrix

The major task in the determination of $\mathcal{G}$ is therefore the determination of $\mathcal{M}$. We do this first for a single impurity, commenting on the result for finite concentration later on.

The formula 3 for $\mathcal{M}$ is in the form of a trace over a complete set of eigenstates of the full Hamiltonian $\mathcal{H}$. We now assume that the formalism of scattering theory in terms of field operators, as outlined for example in the book by Goldberger and Watson [5] is applicable to the present problem. In this formalism (of admittedly undetermined rigor), two complete sets of in- and out-states of N-particles

$$|\{k\}\,\text{in}\rangle = \prod_{k=k_1}^{k_N} a_i^{\dagger}(k)\,|\text{vac}\rangle \ ; \ |\{k\}\,\text{out}\rangle = \prod_{k=k_1}^{k_N} a_0^{\dagger}(k)\,|\,\text{vac}\,\rangle$$

are taken to be unitarily equivalent *exact* eigenstates of the full Hamiltonian, in spite of their apparent independent-particle character. The unitary transformation connecting them is the $\mathcal{S}$-matrix:

$$|\mathcal{S} = \sum_{\{k\}} |\{k\}\,\text{in}\rangle\langle\{k\}\,\text{out}\,|$$

The definitions of the a_i and a_0 are given by

$$a_{i,0}(k,t) = \int \chi_k^{*}(\vec{r},t)\ \Psi_{i,0}(\vec{r},t)\ d\vec{r} \tag{5}$$

in which the $\Psi_{i,0}$ are solutions of Heisenberg operators evolving according to the non-interacting Hamiltonian

$$i\,\Psi_{i,o}(r,t) = -\frac{1}{2m}\,\nabla^2\,\Psi_{i,o}(r,t) \tag{6}$$

and where χ_k is a wave-packet solution of

$$i\,\chi_k = -\frac{1}{2m}\,\nabla^2\,\chi_k \tag{7}$$

centered around a wave with momentum k. Eventually χ_k is allowed to approach the limit of that central plane wave:

$$\chi_k \longrightarrow \frac{1}{(2\pi)^{3/2}} \times e^{i(kr - \epsilon_k t)}$$

It is easily seen that $a_{i,0}(k)$ defined by equation (5) is time-independent, due to (6) and (7). We also define a time-dependent operator

$$a(kt) = \int \chi_k^*(r,t)\;\Psi(r,t)\,d\vec{r} \tag{8}$$

where Ψ is the Heisenberg field operator satisfying

$$i\dot{\Psi} = (\Psi, \mathcal{H})\ . \tag{9}$$

For ordinary potential scattering in reasonable potentials the limits

$$\operatorname*{Lt}_{t\to\pm\infty} \langle\alpha|\ a(kt)\ |\beta\rangle$$

have been proven to exist, and to equal $\langle\alpha\,|a_0(k)|\,\beta\rangle$ and $\langle\alpha\,|a_i(k)|\,\beta\rangle$, respectively. Here $|\alpha\rangle$ and $|\beta\rangle$ are arbitrary states. This so-called "asymptotic condition" we assume to hold in the present non-potential scattering problem also. It is readily verified, in view of (7) and (9), that

$$\begin{aligned} i\,\dot{a}(k,t) &= \int \chi_k^*(r,t)\;\mathcal{J}^\dagger(\vec{r},it)\,d\vec{r} \\ &= \int \chi_k^*(r,t)\;\; j^\dagger(r,t)\,d\vec{r} \\ &= J^\dagger(k,t), \text{ say.} \end{aligned}$$

Evidently, as χ_k^* is allowed to approach a plane wave, we have $J^\dagger(k,\ t) = j^\dagger(k,\ t)\,e^{i\epsilon_k t}$, where $j(k,\ t) = \mathcal{J}^\dagger(k,\ it)$. Note that, in particular, $\mathcal{J}^\dagger(k,\ 0) = j^\dagger(k,\ 0) = \mathcal{J}(k,\ 0) = j(k)$, say.

Given an N-particle system, we may define an $\mathcal{S}$ matrix for scattering of one additional particle by

$$\mathcal{S}_{pk;p'k'} = \langle p'k'\,\text{out}|p\ k\ \text{in}\rangle = \langle p'\,\text{out}|a_o(k')\,a_i^*(k)|p\ \text{in}\rangle$$

where $|p\ \text{in}\rangle$ is some exact in-state with a certain linear momentum distribution, and impurity spin orientation, and $|p'\ \text{out}\rangle$ some out-state similarly specified, but restricted by energy conservation

$$E_p + \epsilon_k = E_{p'} + \epsilon_{k'}$$

It is evidently possible to establish equations for the j's by the method used in dispersion theory. However, the $\mathcal{S}$ matrix is not what is required here. In most problems solved by dispersion methods p and p' are vacuum states, or at least *effective* vacuum states (as was the case in reference 1). The distinction between $|p \text{ in}\rangle$ and $|p \text{ out}\rangle$ then disappears. In the present problem the $|p\rangle$ states are arbitrarily excited states of the N-electron gas. The $\mathcal{M}$ operator of equation (3) bears a certain resemblance (before thermal averaging) to the T-operator of reference 1, but its matrix elements are taken, not between in- and out-states of the system (as is appropriate to the T matrix), but between identical states. These identical states may be any complete set of eigenstates of $\mathcal{H}$, provided they are equivalent to within a unitary transformation that commutes with $\mathcal{H}$. Therefore, these states may be taken to be in-states. In view of this, it becomes convenient to define a modified matrix

$$\mathcal{L}_{pk;p'k'} = \langle p' \text{ in} | a_0(k') a_i^*(k) | p \text{ in} \rangle$$

and, to evaluate $\mathcal{G}$, we eventually are interested only in the case $p' = p$.

It is easy to show (see appendix 1), that the $\mathcal{L}$ matrix is no longer unitary. This is connected with the fact that while the states $a_i^*(k)|p \text{ in}\rangle$ form an orthogonal set for different k, the states $a_0^*(k)|p \text{ in}\rangle$ do not. However, we shall assume that the states $a_0^*(k)|p \text{ in}\rangle$, even though they form a skew basis, span exactly the same space as do the states $a_i^*(k)|p \text{ in}\rangle$. If satisfied, this assumption ensures the existence of the $\mathcal{L}$ matrix, and its non-unitarity will not trouble us. From now on we abbreviate $|p \text{ in}\rangle$ by $|p\rangle$.

To obtain equations for the matrix elements of j (and thus of $\mathcal{J}$), we proceed in close analogy with the usual derivation of non-relativistic dispersion relations* (see reference 5, for example).

We may write

$$\mathcal{L}_{pk,p'k'} = \langle p' | a_0(k') | p\ k \text{ in} \rangle .$$

With the help of the asymptotic condition, this may be written

$$\mathcal{L}_{pk,p'k'} = \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} \langle p' | a(k',t) | p\ k \text{ in} \rangle \, dt + \langle p' | a_i(k') | p\ k \text{ in} \rangle$$

$$= \delta(p-p')\,\delta(k-k') + \frac{1}{i} \int_{-\infty}^{+\infty} \langle p' | J^{\dagger}(k',t) | p\ k \text{ in} \rangle \, dt$$

$$= \delta(p-p')\,\delta(k-k') + M_{pk,p'k'}$$

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* The Chew-Low method described in reference 1 does not work in the present case, since it is no longer possible to solve the equation preceding (12) in reference 1 unambiguously when the $|\omega\rangle$ state is an arbitrary excited state of the Fermi gas.

where

$$M_{pk,p'k'} = \frac{1}{i}\int_{-\infty}^{+\infty} \langle p'|J^{\dagger}(k',t)|p\ k\ \text{in}\rangle\, dt$$

$$= \frac{1}{i}\ \underset{t_0\to-\infty}{\text{Lt}}\ \int_{-\infty}^{+\infty} \langle p'|J^{\dagger}(k',t)\,a^{\dagger}(kt_0)|p\rangle\, dt$$

$$= \frac{1}{i}\ \underset{t_0\to-\infty}{\text{Lt}}\ \int_{-\infty}^{+\infty} \langle p'|R\left(J^{\dagger}(k',t)\,a^{\dagger}(kt_0)\right)|p\rangle\, dt -$$

$$\frac{1}{i}\ \underset{t_0\to-\infty}{\text{Lt}}\ \int_{-\infty}^{+\infty} \langle p'|a^{\dagger}(kt_0)\ J^{\dagger}(k't)|p\rangle\, dt$$

and where R is the retarded anti-commutator defined by

$$R\left(A(t)\ B(t')\right) = \eta(t-t')\ \left(A(t)\ B(t') + B(t')\ A(t)\right)$$

The last result may be written

$$M_{pk,p'k'} - \tilde{M}^{*}_{pk'p'k} = \frac{1}{i}\ \underset{t_0\to-\infty}{\text{Lt}}\ \int_{-\infty}^{+\infty} \langle p'|R\left(J^{\dagger}(k',t)\ a^{\dagger}(k,t_0)\right)|p\rangle\, dt$$

$$= -\frac{1}{i}\int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} dt'\ \frac{d}{dt'}\langle p'|R\left(J^{\dagger}(k',t)\ a^{\dagger}(k,t')\right)|p\rangle \qquad (10)$$

$$= \frac{1}{i}\int_{-\infty}^{+\infty} \mathscr{B}_{p'k',pk}(t)\ dt - \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} dt'\ \langle p'|R\left(J^{\dagger}(k't)\ J(kt')\right)|p\rangle$$

where

$$\tilde{M}_{pk',p'k} = \frac{1}{i}\ \underset{t_0\to-\infty}{\text{Lt}}\ \int \langle p|J(k't)\ a(kt_0)|p'\rangle\, dt$$

is the matrix for scattering of a hole with wavenumber and spin k from the in-state p' to wavenumber and spin k' and in-state p. (The corresponding $\tilde{\mathscr{L}}$ operator is $\tilde{\mathscr{L}} = 1 - \tilde{\mathscr{M}}$). The leading term in equation (9) is the Born suggested that the plot shown in term, with

$$\mathscr{B}_{p'k',pk}(t) = \langle p'|\left(J^{\dagger}(k',t)\ a^{\dagger}(k',t)\right)_{+}|p\rangle$$

Inserting a complete set of in-states between the two J's in the last integral of (10),

expressing the time-dependent operators in terms of their values at time zero, carrying out the time integrations, and allowing the packets to approach plane waves, we get the following equation, valid on the energy shell $E_p + \epsilon_k = E_{p'} + \epsilon_{k'}$

$$\mathcal{M}(p'k';pk) + \left\{\tilde{\mathcal{M}}(pk',p'k)\right\}^* \tag{11}$$

$$= \mathcal{B}(p'k',pk) - \sum_q \frac{\langle p'|j^\dagger(k')|q\rangle\langle q|j(k)|p\rangle}{E_q - E_p - \epsilon_k - i\delta} + \frac{\langle p'|j(k)|q\rangle\langle q|j^\dagger(k')|p\rangle}{E_{p'} - E_q - \epsilon_k - i\delta}$$

where

$$\mathcal{M}_{pk,p'k'} = -2\pi i\ \delta\left(E_p + \epsilon_k - E_{p'} - \epsilon_{k'}\right)\mathcal{M}\left(p'k';pk\right) ,$$

$$\mathcal{M}(p'k';pk) = \langle p'|j^\dagger(k')|p\ k\ \text{in}\rangle$$

$$\tilde{\mathcal{M}}(pk',p'k) = \langle p|j(k')|p'\bar{k}\ \text{in}\rangle$$

$$\mathcal{B}(p'k',pk) = J\Omega_0\langle p'k'|\vec{S}\cdot\vec{s}|pk\rangle/8\pi^3$$

(the bar denoting a hole); and where the last result following from

$$\mathcal{B}(p'k',pk) = \langle p'|\left(j^\dagger(k')\ a^\dagger(k)\right)_+|p\rangle$$

The occupation numbers $n_k(p)$ giving the number of conducting electrons occupying wave-packet state k in the in-state $|p\rangle$ of the system are good quantum numbers of value zero or one. We may therefore write

$$\left(1 - n_k(p)\right)\mathcal{M}(p'k';pk) + n_k(p')\ \tilde{\mathcal{M}}^*(pk',p'k)$$

in place of $\mathcal{M} + \tilde{\mathcal{M}}^*$. Let us define a function of the complex variable z by

$$\mathcal{F}(p'k',pk,z) = \mathcal{B}(p'k',pk) - \sum_q \frac{\langle p'|j^\dagger(k')|q\rangle\langle q|j(k)|p\rangle}{E_q - E_p - z}$$

$$- \sum_q \frac{\langle p'|j(k)|q\rangle\langle q|j^\dagger(k')|p\rangle}{E_{p'} - E_q - z}$$

In terms of $\mathcal{F}$ we have

$$\mathcal{M}(p'k',pk\,(p) = \operatorname*{Lt}_{z\to\epsilon_k+i\delta}\mathcal{F}(p'k',pk,z)$$

and (12)

$$\tilde{\mathcal{M}}(pk',p'k\epsilon p') = \underset{z\to\epsilon_k+i\delta}{\mathrm{Lt}} \mathcal{F}(pk,p'k';z^*)$$

provided $E_p = E_{p'}$, where $k \notin p$, $(k \epsilon p)$ mean: the electron of wavenumber k not contained (contained) in $|p>$. At absolute zero, equation (12) reduces to the crossing relations of reference 1. For, at absolute zero p, p' are ground states and

$$\begin{aligned}\tilde{\mathcal{M}}(p,k,p'k'\epsilon p') &= \underset{z\to\epsilon_k+i\delta}{\mathrm{Lt}} \mathcal{F}(p,k';p'k;z^*)\\ &= \mathcal{F}(pk';p'k;\epsilon_k - i\delta)\\ &= \mathcal{F}(pk';p'k;-|\epsilon_k| - i\delta)\\ &= \mathcal{M}(p,k'p'k\epsilon p')_{z=-|\epsilon_k|-i\delta}\end{aligned}$$

since $\epsilon_{k'}$ must be negative, and $\epsilon_k = \epsilon_{k'}$ by energy conservation. Aside from a trivial change in notation this is the crossing relation (21) of reference (1), which continues $\mathcal{M}$ from the physical into the unphysical range of energies.

Even though we are not now considering the ground state, we still only need the case $E_p = E_{p'}$ in the construction of $\mathcal{G}$. To find $\mathcal{M}$, we make the same approximation as in reference 1; we admit only those in-states $|p>$ states that differ from $|p>$ only in that they carry an additional particle or hole. Then we have, with $E_{p''} = E_p = E_{p'}$

$$\mathcal{F}(p'k';pk,\epsilon_k+i\delta) = \mathcal{B}(p'k';pk) - \sum_{\epsilon_{k''}p''} \frac{\mathcal{M}(p'k',p''k''\epsilon p'')\mathcal{M}^*(p'k,p''k''\epsilon p'')}{\epsilon_{k''} - \epsilon_k - i\delta}$$

$$- \sum_{\epsilon_{k''}p''} \frac{\tilde{\mathcal{M}}(p'k,p''k''\epsilon p'')\,\tilde{\mathcal{M}}^*(p'k,p''k''\epsilon p'')}{\epsilon_{k''} - \epsilon_k - i\delta}$$

since in the first sum $E_q = E_{p''} + \epsilon_{k''} = E_p + \epsilon_{k''}$, and in the second, $E_q = E_{p'} - \epsilon_{k''} = E_p - \epsilon_{k''}$. In view of equations (12), the last result is an equation for $\mathcal{F}$:

$$\mathcal{F}(p'k',pk,\epsilon_k+i\delta) = \mathcal{B}(p'k';pk) - \Sigma \frac{\mathcal{F}(p'k',p''k'';\epsilon_{k''}+i\delta)\,\mathcal{F}(pk,p''k'';\epsilon_{k''}+i\delta)^* \left(1-n_{k''}(p'')\right)}{\epsilon_{k''} - \epsilon_k - i\delta}$$

$$- \Sigma \frac{\mathcal{F}(p'k'',p''k,\epsilon_{k''}-i\delta)\,\mathcal{F}(pk'',p''k',\epsilon_{k''}-i\delta)^*\, n_{k''}(p'')}{\epsilon_{k''} - \epsilon_k - i\delta} \qquad (13)$$

Before proceeding with its discussion, we note that for ordinary potential scattering from a very short range potential, $\mathcal{B}$ is a constant, and there exists, then, a solution

$$\mathcal{F}(\epsilon_k + i\delta)$$

of equation (12) which does not depend on the state $|p>$ (now non-degenerate) and depends on k only through ϵ_k. The n-factors in the two sums cancel out, corresponding to the well-known

fact that for potential scattering the state of the gas is essentially irrelevant; the Green's function depends on $\mathcal{F}(i\omega_n)$, where $\mathcal{F}(z)$ may as well be calculated for the absolute zero of temperature. In our present problem the two sums obviously do not combine in this simple fashion. A more detailed analysis is therefore needed. Let us write $p = \hat{p}, \tau$, where $\hat{p}$ describes the "orbital" quantum number of $|p>$, and τ the degeneracy index corresponding to the localized spin states. We note that $E_p = E_{\hat{p}}$. Now the sums on the right hand side of equation (12) extend over all p'' such that $E_{\hat{p}''} = E_{\hat{p}} = E_{\hat{p}'}$. They are therefore functions of k', k'' and $E_{\hat{p}}$ only. We have no evidence that the same is true of $\mathcal{B}$. However, the operator of which $\mathcal{B}(p'k', pk)$ is the matrix element is essentially $\vec{S}\cdot\vec{s}$ (see ref. 1) where $\vec{s}$ acts on the spin-part σ of $|\vec{k}>$. Hence we may write

$$\mathcal{B}(p'k',pk) = \mathcal{B}(p'\sigma',p\sigma) \sim \langle p'|\vec{S}|p\rangle \cdot \langle\sigma'|\vec{s}|\sigma\rangle$$

$$= \langle\hat{p}'\tau'|\vec{S}|\hat{p}\,\tau\rangle \cdot \langle\sigma'|\vec{s}|\sigma\rangle$$

For the uncoupled system, $\langle\hat{p}'\tau'|\vec{S}|\hat{p}\,\tau\rangle = \delta_{\hat{p}'\hat{p}}\langle\tau'|\vec{S}|\tau\rangle$, so that there is no $\hat{p}$-dependence. The interesting resonant effects certainly have nothing to do with $\mathcal{B}$. Therefore, we neglect the $\hat{p}$ dependence of $\mathcal{B}$ in the weak coupling limit also. It then follows that $\mathcal{F}$ is a function of τ, τ', σ, σ', ϵ_k and $E_{\hat{p}} = E_{\hat{p}'}$ only. But in that case, the summation over p'' on the right hand side of (12) simply has the effect of replacing $n_{k''}(p'')$ by its microcanonical average $n^{(m)}{}_{k''}(E_{\hat{p}})$ over the energy surface $E_{\hat{p}''} = E_{\hat{p}}$. Next, we may imagine solving (12) by iteration, starting with a zero-order $\mathcal{F}$ equal to $\mathcal{B}$. Having written down the iterative series for $\mathcal{F}$ we carry out the operation

$$\sum e^{-\beta E_{\hat{p}}}\ \mathcal{F}\left(E_{\hat{p}};\tau'\sigma',\tau\sigma,\epsilon_k+i\delta\right).$$

In the iterative series, since we take $\mathcal{B}$ to be independent of $\hat{p}$, this has the effect of replacing each $m_k^{(m)}$ by the Fermi function $f(\beta\epsilon_k)$, since the occupation numbers in different k-states are uncorrelated. (This is not quite correct since we have not yet introduced a chemical potential, so that there remains a constraint on particle number. That constraint is easily removed by taking the grand ensemble average of $\mathcal{F}$.) The averaged iterative series is therefore what we would obtain if we iterated the equation

$$\mathcal{F}(\tau'\sigma',\tau\sigma,\epsilon_k+i\delta) = \mathcal{B}(\tau'\sigma',\tau\sigma) -$$

$$-\sum_{k'}\frac{\mathcal{F}\left(\tau'\sigma',\tau''\sigma'',\epsilon_{k'}+i\delta\right)\left\{\mathcal{F}\left(\tau\sigma,\tau''\sigma''\epsilon_{k'}+i\delta\right)\right\}^*\left(1-f(\beta\epsilon_{k'})\right)}{\epsilon_{k'}-\epsilon_k-i\delta}$$

$$-\sum_{k'}\frac{\mathcal{F}\left(\tau'\sigma'',\tau''\sigma,\epsilon_{k'}-i\delta\right)\left\{\mathcal{F}\left(\tau\sigma'',\tau''\sigma',\epsilon_{k'}-i\delta\right)\right\}^* f(\beta\epsilon_{k'})}{\epsilon_{k'}-\epsilon_k-i\delta} \tag{13a}$$

where

$$\mathcal{F}(\tau'\sigma',\tau\sigma,z) = \sum e^{-\beta E_{\hat{p}}}\mathcal{F} \Big/ \sum e^{-\beta E_{\hat{p}}}. \tag{14}$$

As in ref. 1, we now introduce the scattering amplitudes t_0 and t_1 through

$$\mathcal{F}(z) = \frac{\Omega}{8\pi^3}\left[t_0(z)P_0 + t_1(z)P_1\right]$$

where $P_0 = 1/4 - \vec{s}\cdot\vec{S}$; $P_1 = 3/4 + \vec{s}\cdot\vec{S}$ are singlet and triplet projection operators. The rest of the argument now proceeds precisely as in ref. 1. We obtain the coupled integral equations

$$t_0(z) = -\frac{3}{4}\frac{J}{N} + \int_{-\infty}^{+\infty}\frac{|t_0(x+i\delta)|^2\rho(x)dx}{z-x} - \frac{3}{4}\int_{-\infty}^{+\infty}\frac{|t_0(x+i\delta)-t_1(x+i\delta)|^2 f(\beta x)\rho(x)}{z-x}\,dx$$

$$t_1(z) = \frac{1}{4}\frac{J}{N} + \int_{-\infty}^{+\infty}\frac{|t_1(x+i\delta)|^2\rho(x)dx}{z-x} + \frac{1}{4}\int_{-\infty}^{+\infty}\frac{|t_0(x+i\delta)-t_1(x+i\delta)|^2 f(\beta x)\rho(x)}{z-x}\,dx\,, \tag{15}$$

a result which is not surprising.* The reason for the $\Omega/8\pi^3$-factor in the definition of $\mathcal{F}$ is the δ-function normalization of the states, which means that the unit operators inserted in the products of the two $\mathcal{F}$'s in equation (14) must be taken in the form $\int|p'k''\rangle\langle k''p''|d\mathbf{k}''$, etc., and $d\mathbf{k} = 8\pi^3\rho(x)dx/\Omega$, where ρ is the density of energy states. In equation (15) N denotes Ω/Ω_0, the number of atoms in the crystal. It is clear now that, in equation (4)

$$\mathcal{M}\left(k_1k_2\omega_n\right) = \frac{1}{2}\sum_{\tau=+,-}\mathcal{F}\left(\tau\sigma';\tau\sigma,i\omega_n\right)$$

$$= \frac{1}{2}\left\{\frac{1}{4}t_0(i\omega_n) + \frac{3}{4}t_1(i\omega_n)\right\}\frac{\Omega}{8\pi^3}$$

At the absolute zero it is easy to apply multiple scattering theory to show that the self-energy operator is simply the total forward scattering amplitude for one impurity, multiplied by the (low) concentration.** We have not succeeded in proving the corresponding result at finite temperatures, due to the extra Fermi-factor; however, if it is assumed that the impurities are sufficiently dilute so that the neighborhood of each may be treated as a separate statistical ensemble, the argument for $T = 0$ should apply to finite temperatures also, with the result that

$$\mathcal{G}\left(k_1,k_2,\omega_n\right) = \frac{\delta_{\sigma\sigma'}\,\delta(k_1-k_2)}{i\omega_n - \epsilon_k - \tfrac{1}{2}\xi\left\{\frac{1}{4}t_0(i\omega_n) + \frac{3}{4}t_1(i\omega_n)\right\}}$$

From this, the retarded time-dependent Green's function can be obtained in the usual way by

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* The Fermi level, we recall, has been taken at $x = 0$.

** See Appendix 2.

analytic continuation, i.e., by setting $i\omega_n = z$.

Residual Resistance

A complete solution of the problem of response to an electromagnetic field requires solution of the integral equation for the photon vertex, which will be the subject of a forthcoming publication. For a rough calculation of the low-frequency resistance, we disregard the difference between the reciprocal transport relaxation time and the imaginary part of the self energy operator. Then the conductivity, as limited by the impurities is

$$\sigma = \frac{e^2 n_0}{m} \int_{-\infty}^{+\infty} \tau(\epsilon) \frac{\partial f}{\partial \epsilon} \, d\epsilon \tag{16}$$

where n_0 is the electron concentration, and

$$\frac{1}{\tau(\epsilon)} = -\frac{\xi}{2} \, \mathrm{Im} \left\{ \frac{1}{4} t_0(\epsilon + i\delta) + \frac{3}{4} t_1(\epsilon + i\delta) \right\} \tag{17}$$

It is impossible to make the customary expansion of equation (16) in powers of T, utilizing the sharpness of the Fermi surface, because the derivatives of τ become infinite as $T \to 0$ and $\epsilon \to 0$. Nevertheless, it is clear from (16) that $1/\sigma \to 0$ at $T \to 0$, since at absolute zero, the amplitudes t_0, t_1 go to zero at the Fermi level. We conjecture, however (on the grounds of the inexpansibility of equation (16) that the $[1/\sigma(T)]$ curve has a vertical tangent at $T = 0$. Whether the Kondo resistance minimum actually occurs, is hard to determine without numerical calculation. For reasonably low temperatures, an approximate solution of equations (15) is

$$\frac{1}{t_0(\epsilon)} = -\frac{4N}{3J} + i\pi\rho - \frac{4}{3} \left[-\frac{1}{2} P \int_{-\infty}^{+\infty} \frac{\tanh \frac{\beta x}{2}}{x - \epsilon} \rho \, dx + i\pi\rho \, f(\beta\epsilon) \right]$$

$$\frac{1}{t_1(\epsilon)} = \frac{4N}{J} + i\pi\rho + 4 \left[-\frac{1}{2} P \int_{-\infty}^{+\infty} \frac{\tanh \frac{\beta x}{2}}{x - \epsilon} \rho \, dx + i\pi\rho \, f(\beta\epsilon) \right]$$

where repeated use has been made of the assumption $P \int_{-\infty}^{+\infty} \rho dx/x - \epsilon = 0$. It is easily seen that there are two resonances, symmetrically disposed about $\epsilon = 0$, provided β is greater than a certain β_c given by

$$\frac{1}{J\rho_1} = \int \frac{\tanh \beta_c x/2}{x} \, dx$$

where ρ_1 is the density of states per particle. If the integral is cut off at $\pm \epsilon_f$, it is seen that resonance occurs only if $T \leqslant T_c$ where

$$kT_c \sim \epsilon_f \exp -1/J\rho_1$$

At $T = T_c$ the resonance occurs at the Fermi level, and moves towards $\epsilon = \pm \epsilon_f \exp - 1/J\rho_1$ as

$T \to 0$. From equations (15) and (17), we have

$$\frac{1}{\tau(\epsilon)} = \frac{\xi\pi\rho}{2} \left[\frac{1}{4} |t_0(\epsilon)|^2 + \frac{3}{4} |t_1(\epsilon)|^2 \right]$$

(optical theorem). At temperatures so low that $\partial f/\partial \varepsilon$ still does not encompass the resonance, we have

$$\sigma = \frac{e^2 n_0}{m} \left[\frac{1}{2\xi\pi\rho} \tau(0) + 2(kT)^2 \tau'(0) \int_0^\infty \frac{x\,dx}{1+e^x} + \cdots \right].$$

This expansion converges poorly as $T \to 0$; nevertheless, the leading term indicates that σ goes to infinity like $(\log kT/\epsilon_f)^2$ as $T \to 0$, since

$$\int \frac{\tanh \beta x/2}{x}\, dx \sim \log \frac{\epsilon_f}{kT} + O(1).$$

4. Some Minor Generalizations

a) Classical Limit

It is of some interest to examine the scattering equations for $S > 1/2$. In particular, as S becomes very large, we would expect the scattering equations to approach those for ordinary potential scattering from a highly localized Zeeman field. That is to say, up and down spin electrons will have different scattering amplitudes (one of these showing a tendency to resonance), and the "crossing terms" should be absent from the equations. To see that this does, in fact, take place, as $S \to \infty$, we revert to the simpler zero temperature case of reference 1. The projection operators P_0 and P_1 now refer to the $S - 1/2$ and $S + 1/2$ manifolds. They are

$$P_0 = \frac{1}{2S+1} \left\{ S - 2(\underset{\sim}{S} \cdot \underset{\sim}{s}) \right\}$$

$$P_1 = \frac{1}{2S+1} \left\{ S + 1 + 2(\underset{\sim}{S} \cdot \underset{\sim}{s}) \right\}$$

The scattering matrix is $T = t_0 P_0 + t_1 P_1$, and the matrix product in the crossed channel, $\tilde{T}^\dagger \tilde{T}$, may be evaluated by noting that

$$\tilde{P}_0^2 = (2S+1)^{-2} \left[\left(4S^2 + 2S - 1 \right) \tilde{P}_0 + 2S\, \tilde{P}_1 \right];$$

$$\tilde{P}_1^2 = (2S+1)^{-2} \left[-2(S+1)\tilde{P}_0 + (4S^2 + 6S + 1)\tilde{P}_1 \right]$$

$$\tilde{P}_0 \tilde{P}_1 = -2(2S+1)^{-2} \left[-(S+1)\tilde{P}_0 + S\, \tilde{P}_1 \right]$$

It is then seen that

$$\tilde{T}^{\dagger}\tilde{T} = \left\{ |t_0|^2 - \frac{2(S+1)}{(2S+1)^2} |t_0 - t_1|^2 \right\} \tilde{P}_0$$

$$+ \; |t_1|^2 + \frac{2S}{(2S+1)^2} |t_0 - t_1|^2 \; \tilde{P}_1$$

Also, the Born term, proportional to $s \cdot S$, decomposes according to $\frac{1}{2}(S P_1 - (S+1)P_0)$. The resulting equations are then

$$t_0 = -\frac{S+1}{2}\frac{J}{N} + \int_{-\infty}^{+\infty} \frac{|t_0|^2}{z-x}\,dx - \frac{2(S+1)}{(2S+1)^2} \int_{-\infty}^{0} \frac{|t_0 - t_1|^2}{z-x}\,dx$$

$$t_1 = \frac{S}{2}\frac{J}{N} + \int_{-\infty}^{+\infty} \frac{|t_1|^2}{z-x}\,dx + \frac{2S}{(2S+1)^2} \int_{-\infty}^{0} \frac{|t_0 - t_1|^2}{z-x}\,dx,$$

showing that as $S \to \infty$, the problem reduces to ordinary potential scattering for electrons with spin orientation parallel and antiparallel to the large impurity spin.

b) Additional Spin-Independent Scattering

Added potential scattering V_p modifies the Born term, which assumes the form

$$\left(V_p + J\frac{S}{2}\right) P_1 \quad + \quad \left(V_p - J\frac{S+1}{2}\right) P_o \quad .$$

This case is quite difficult to discuss. However, if $S = 1/2$, and J is small compared with V_p, as should sometimes be the case for transition element impurities, we may examine the equations for t_0 and t_1 by a perturbation method. Taking the case $T = 0$, we write

$$\frac{1}{t_o} = \frac{1}{t} - 3\tau \qquad \frac{1}{t_1} = \frac{1}{t} + \tau$$

where

$$\frac{1}{t} = \frac{1}{V_p} + i\pi$$

is the reciprocal scattering amplitude for potential scattering alone (disregarding the term $P\int \rho\, dx'/x - x'$). If J is small τ may be expected to be small. Substituting $1/t_0$ and $1/t_1$ into the integral equations and expanding the crossing term to second order in τ, we find that τ satisfies

$$\tau = -\frac{J}{4V_p^2} + |t|^2 \int_{-\infty}^{0} \frac{|\tau|^2}{x - z}\, \rho\, dx$$

whose solution is

$$\frac{1}{\tau} = -\frac{4V_p^2}{J} + |t|^2\, \rho \int_{-\infty}^{0} \frac{dx}{z - x}$$

This means that

$$\frac{1}{\tau(\epsilon)} = -\frac{4V_p^2}{J} - |t|^2\, \rho\, \log \frac{\epsilon}{\epsilon_f}$$

as $z \to \varepsilon + i\delta$, and $\varepsilon > 0$. For $J > 0$, τ has a pole and the expansion of the crossing term is not valid near the pole. Presumably the higher power terms would eliminate this pole. Disregarding this difficulty, we find, for $\varepsilon > 0$

$$t_o = t/\left\{1 + 3t\left(\frac{V_p^2}{J} + |t|^2\, \rho\, \log \frac{z}{\epsilon_f}\right)^{-1}\right\} \qquad Rlz > 0$$

$$t_1 = t/\left\{1 - t\left(\frac{V_p^2}{J} + |t|^2\, \rho\, \log \frac{z}{\epsilon_f}\right)^{-1}\right\}$$

If Rlt is approximated by V_p we then get resonances at

$$z_{\text{singlet}} = \epsilon_f \exp -\left(3 + V_p/J\right)/\rho V_p$$

$$z_{\text{triplet}} = \epsilon_f \exp \left(1 - V_p/J\right)/\rho V_p$$

These results suggest that, even when J is negative (ferromagnetic in our notation) a resonance of the singlet amplitude may occur near the Fermi level, if $|J| > V_p/3$. This large $|J|$ may, however, be out of the range of validity of this calculation.

5. Justification of the Neglect of Higher Order Processes

We now present evidence that the processes neglected in the discussion of the T matrix at the absolute zero of temperature do not, in fact, contribute logarithmic singularities, in contrast with those retained. The terms neglected in the equation for the one-particle to one particle scattering matrix element $T_{k'\omega';k\omega}(z)$ had the form (see ref. 1)

$$\sum_m \frac{\langle \omega' | j_{k'}^{\dagger} | m \rangle^- \ {}^-\langle m | j_k | \omega \rangle}{z - E_m}$$

plus a corresponding "crossing" term. Here the $|m\rangle^-$ are exact intermediate scattering states with excitation energy ϵ_m, composed of one electron above the Fermi surface, accompanied by at least one hole-electron pair. It is safe to assume that ${}^-\langle m | j_k | \omega \rangle$ is bounded (in fact, away from a resonance it must be of at least second order in the coupling strength). We show by means of a phase-space argument that the sum in equation (1) does not diverge near $z = 0$, in contrast to the same sum, but with $|m\rangle^-$ denoting intermediate scattering states with only an electron and no pairs.

For an examination of the vicinity of $z = 0$, we may take the numerator outside the summation sign. Then it remains to consider

$$\int \frac{\rho_{sp} \ d\epsilon_{sp}}{z - \epsilon_{sp}}$$

where ϵ_{sp} is the energy of a state with a single electron above the Fermi sea, plus a hole electron pair, and ρ_{sp} is the density of such states. This density is a convolution of three single electrons densities ρ_s. Consider first the electron-hole pair density ρ_p. We have

$$\rho_p = \frac{d}{d\epsilon_p} \int \rho_{s_1} \ \rho_{s_2} \ d\epsilon_{s_1} \ d\epsilon_{s_2}$$

where ϵ_{s_1}, ϵ_{s_2} are single particle energies, and the integration is carried out over the triangular region $\epsilon_{s_1} - \epsilon_{s_2} < \epsilon_p \quad \epsilon_{s_1} < 0, \ \epsilon_{s_2} < 0$. Taking $\rho_{s_1} = \rho_{s_2} = \rho_s = \text{constant}$, we get

$$\rho_p = \rho^2 \ \epsilon_p \ .$$

The density of states of the triple configuration is then seen to be

$$\rho_{sp} = \frac{d}{d\epsilon_{sp}} \int \rho_p \ \rho_s \ d\epsilon_p \ d\epsilon_s$$

the integration extending over $\epsilon_p, \ \epsilon_s > 0$ and $\epsilon_p + \epsilon_s < \epsilon_{sp}$. The result is $\frac{1}{2} \rho^3 \ \epsilon_{sp}^2$. Therefore

$$\int_0^{\infty} \frac{\rho_{sp} \ d\epsilon_{sp}}{z - \epsilon_{sp}}$$

does not diverge logarithmically near $z = 0$. A similar conclusion applies to the crossing term. Processes with more hole electron pairs than one have even smaller intermediate state densities.

As for the non-logarithmic part of the sum

$$\sum \langle \omega' | j k'^{\dagger} | m \rangle^- \ {}^-\langle m | j k | \omega \rangle / z - E_m ,$$

it is seen rather easily that multiparticle intermediate states are unimportant in the weak coupling limit. The reason is that for ordinary potential scattering terms like

$$< \omega \, |jk'^{\dagger}| \text{ particle + pair} >^{-}$$

are rigorously zero. For exchange scattering they are non-zero only to the extent that an unperturbed one-particle in-state acquires an admixture of a particle + pair state when the perturbation is turned on. This admixture is of order J/ε_f. Hence the matrix elements to multiparticle intermediate states are down by a factor J/ε_f from those to one-particle intermediate states. An exception could occur only if the T-matrix element

$$< \text{particle} \, |T| \, \text{particle + pair} >$$

has a resonance.

6. Acknowledgements

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APPENDIX 1:

Non-Unitarity of the $\mathscr{L}$ Matrix

For simplicity we use a discrete representation. It is sufficient to prove the non-unitarity for two particles α, β one of which (β) together with the impurity spin constitutes the target, the other the "$N + 1$"th particle. The $\mathscr{L}$ matrix is defined by

$$\mathscr{L}_{a'a} = <\beta \text{ in} | a_{a' \text{ out}} a^{\dagger}_{a \text{ in}} | \beta \text{ in}>$$

$$\mathcal{C} = \langle \text{vac} | a_{\beta\ \text{in}}\, a_{\alpha'\ \text{out}}\, a^{\dagger}_{\alpha\ \text{out}}\, a^{\dagger}_{\beta\ \text{in}} | \text{vac} \rangle$$

where $|\text{vac}\rangle$ is the bare state of the impurity spin. Consider the true S matrix defined by

$$a^{\dagger}_{\beta\ \text{in}} |\text{vac}\rangle = \sum_{\beta\beta'} S_{\beta\beta'}\, a^{\dagger}_{\beta'\ \text{out}} |\text{vac}\rangle$$

In therms of S, we have for the overlap integral

$$\mathcal{O} = \langle \text{vac} | a_{\beta\ \text{in}}\, a^{\dagger}_{\beta\ \text{in}} | \text{vac} \rangle\, \delta_{\alpha\alpha'} - \langle \text{vac} | a_{\beta\ \text{in}}\, a^{\dagger}_{\alpha\ \text{out}}\, a_{\alpha'\ \text{out}}\, \beta' S_{\beta\beta'}\, a^{\dagger}_{\beta'\ \text{out}} | \text{vac} \rangle$$

$$= \delta_{\alpha\alpha'} - \langle \text{vac} | a_{\beta\ \text{in}}\, a^{\dagger}_{\alpha\ \text{out}} | \text{vac} \rangle\, S_{\beta\alpha'}$$

$$= \delta_{\alpha\alpha'} - S^{\dagger}_{\beta\alpha}\, S_{\beta\alpha'}$$

Hence the states $a_{\text{out}} |\beta\rangle$ are orthonormal only if either or both of ε_{α}, $\varepsilon_{\alpha'}$ are not equal to ε_{β}. In the general case of an additional particle impinging on the N-particle system, the orthogonality requirement would be that the extra incident or outgoing particle should have its energy unequal to the energies of those already present. This was the case in reference 1. A unitary transformation then exists between in and out states of the $(N + 1)$-th particle, and the matrix is then unitary.

APPENDIX 2:

Multiple Scattering

When the concentration of impurities is finite, the Ruderman-Kittel interaction partially resolves the 2^{N_i} fold degeneracy (where N_i is the number of impurities of spin one half) of the states of the system. This resolution is quadratic in the concentration ξ, for small ξ, and we neglect it in an approximation linear in ξ. At the absolute zero of temperature, the procedure for establishing the Green's function (real times) is then simple. We define the ground-state Green's function by

$$G_{kk'}(t) = -\sum_{\omega} \langle \omega | a_k\, e^{-i\mathcal{H}t}\, a^{\dagger}_{k'} | \omega \rangle \Big/ \sum \langle \omega | \omega \rangle, \quad t > 0$$

$$= i \sum_{\omega} \langle \omega | a^{\dagger}_{k'}\, e^{+i\mathcal{H}t}\, a_k\, | \omega \rangle \Big/ \sum \langle \omega | \omega \rangle, \quad t < 0$$

where the summations extend over the 2^{N_i} different degenerate ground states. It is sufficient to consider g for $t > 0$. We have

$$G_{kk'}(t>0) = \frac{1}{2\pi} \sum_{\omega} \int \langle \omega | a_k \frac{1}{z-\mathcal{H}} a_{k'}^{\dagger} | \omega \rangle e^{-izt} \, dz / \sum \langle \omega | \omega \rangle$$

where the contour z encircles the real axis in the *clockwise* direction. Writing $\mathcal{H} = \mathcal{H}^0 + \mathcal{H}'$, $R(z) = 1/z - \mathcal{H}$ and $d(z) = 1/z - \mathcal{H}^0$, we see that

$$R(z) = \frac{1}{d(z)} + \frac{1}{d(z)} \mathcal{H}' R(z)$$

$$= \frac{1}{d} + \frac{1}{d} \mathcal{H}' \frac{1}{d} + \frac{1}{d} \mathcal{H}' \frac{1}{d} \mathcal{H}' \frac{1}{d} + \cdots$$

The T matrix is defined by

$$T(z) = \mathcal{H}' + \mathcal{H}' \frac{1}{d} T(z)$$

$$= \mathcal{H}' + \mathcal{H}' \frac{1}{d} \mathcal{H}' + \mathcal{H}' \frac{1}{d} \mathcal{H}' \frac{1}{d} \mathcal{H}' + \cdots$$

From these two equations it follows that

$$R(z) = \frac{1}{d} + \frac{1}{d} T(z) \frac{1}{d} \quad *$$

Suppose that t^{α} is the scattering operator for a single impurity located at r_{α}. Then we have the exact multiple scattering expansion

$$T = \sum t^{\alpha} + \sum_{\alpha} t^{\alpha} \sum_{\beta \neq \alpha} \frac{1}{d} t^{\beta} + \sum_{\alpha} t^{\alpha} \sum_{\beta \neq \alpha} \frac{1}{d} t^{\beta} \sum_{\gamma \neq \beta} \frac{1}{d} t^{\gamma} \cdots$$

The matrix element for the scattering of a single electron from wavenumber and spin k to wavenumber and spin k', while the target goes from $|\omega\rangle$ to $|\omega'\rangle$ is

$$T_{\omega' k'; \omega k} = \langle \omega'' a_{k'} \, T \, a_k^{\dagger} | \omega \rangle$$

For an impurity at r_{α}, the t-matrix is

$$t^{\alpha}_{\omega' k'; \omega k} = e^{i\vec{r}_{\alpha} \cdot (\vec{k} - \vec{k}')} \, t_{\omega' k'; \omega k}$$

(where the k's in the exponent of course do not include their spin parts). In this expression

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* This equation was first used by Luttinger and Kohn in their discussion of transport theory [6].

the t without superscript refers to scattering off an impurity at the origin. Consider not the average of T over impurity configurations. The average $\Sigma\, t^{\alpha}_{\omega k'\omega k}$ is clearly $N_i t_{\omega k,\omega k}\delta_{k'k}\delta_{\omega'\omega}$. Next

$$\overline{\langle \omega k' | \Sigma\, t^{\alpha} \sum_{\beta=\alpha} \frac{1}{d} t^{\beta} | \omega k\rangle} = N_i(N_i-1) \sum_{\omega'' k''} t_{\omega k\, \omega'' k''} \frac{1}{z-\epsilon_{k''}} t_{\omega'' k''\, \omega k}$$

so long as we restrict ourselves to one particle intermediate states. In this expression we have written $a_k\,|\,\omega\rangle = |\,\omega k\rangle$ etc. and used the fact that $a_k(1/d) = (1/z - \epsilon_k)a_k$. The state $|\omega\rangle$ may be written $|\omega_1\omega_2 \ldots \omega_{N_i}\rangle$, where each ω_n is plus or minus, corresponding to the orientations of the various impurity spins. To lowest order in the concentration we may assign one of the ω_n to each impurity site. Then so far as the ω's are concerned t^{α} has matrix elements of the form

$$\delta_{\omega_1\omega_1'} \cdots \delta_{\omega_{\alpha-1}\omega_{\alpha-1}'}\ \delta_{\omega_{\alpha+1}\omega_{\alpha+1}'} \cdots \langle \omega_\alpha | t^{\alpha} | \omega_\alpha'\rangle \ .$$

The unit operator $\Sigma\, |\omega''\rangle\langle\omega''|$ inserted between the t's in $\langle\omega\,|\,t^{\alpha}\,t^{\beta}\,|\,\omega\rangle$, for $\alpha \neq \beta$ thus gives only one non-zero term, i.e., $\langle\omega\,|\,t^{\alpha}\,|\,\omega\rangle\langle\omega\,|\,t^{\beta}\,|\,\omega\rangle$. Thus we have

$$\overline{\langle \omega k' | \Sigma t^{\alpha} \sum_{\beta\neq\alpha} \frac{1}{d} t^{\beta} | \omega k\rangle} = N_i(N_i-1)\, t_{\omega k,\omega k} \frac{1}{z-\epsilon_k} t_{\omega k,\omega k}$$

Next consider

$$\langle \omega k' | \sum_{\alpha} t^{\alpha} \sum_{\beta\neq\alpha} \frac{1}{d} t^{\beta} \sum_{\gamma\neq\beta} \frac{1}{d} t^{\gamma} | \omega k\rangle$$

For $\alpha \neq \beta \neq \gamma$ this gives $N_i(N_i-1)(N_i-2)\, t_{\omega k,\omega k} \frac{1}{z-\epsilon_k} t_{\omega k,\omega k} \frac{1}{z-\epsilon_k} t_{\omega k,\omega k}$

while for $\alpha = \gamma$ and $\alpha,\ \gamma \neq \beta$ it gives

$$N_i^2 \sum t_{\omega k\, \omega'' k''} \frac{1}{z-\epsilon_{k''}} t_{\omega'' k''\, \omega'' k''} \frac{1}{z-\epsilon_{k''}} t_{\omega'' k''\, \omega k}$$

This term, after summation is of order $\xi^2 J^3/\epsilon_f^2$, whereas the term $\Sigma\, t^{\alpha} \Sigma\, (1/d)\, t^{\beta}$ is of order $\xi^2 J^2/\epsilon_k$, where a typical ϵ_k is itself much smaller than ϵ_f. Continuing the argument in this way we see that in each order of the concentration, the terms with all sites different dominate the others. Redefining t as the previously introduced t, but without the $1/N$-factor, and replacing $N_i(N_i - 1)$ by N_i^2, etc., we obtain a geometric series for the averaged $T_{\omega k,\omega k'}$, which is summed to

$$\sum_{\omega} \left\{ T_{\omega k, \omega k'} \Big/ \langle \omega \mid \omega \rangle \right\} = \frac{\delta_{kk'} \, \tfrac{1}{2} \xi (z - \epsilon_k) \sum_{\omega} t^{(z)}_{\omega k, \omega k}}{(z - \epsilon_k) - \tfrac{1}{2} \xi \sum_{\omega} t^{(z)}_{\omega k, \omega k}}$$

and so, after decomposition into singlet and triplet amplitudes one finds for the resolvent

$$\sum \frac{R_{\omega k, \omega k'}}{\langle \omega \mid \omega \rangle} = \delta_{kk'} \Big/ \left[z - \epsilon_k - \frac{\xi}{2} \left\{ \frac{1}{4} t_o(z) + \frac{3}{4} t_1(z) \right\} \right]$$

A corresponding result follows for $t < 0$ if hole instead of particle scattering is considered.

We have not succeeded in proving an exact multiple scattering expansion and resummation in the finite temperature case. However, if the scatterers are sufficiently dilute so that the environment of each may be considered to be in local equilibrium, there is little doubt that the same procedure must be valid. We had

$$F(z) = \frac{\Omega}{8\pi^3} \left(t_o(z) \, P_o + t_1(z) \, P_1 \right)$$

for the modified scattering matrix from a single impurity at finite temperatures. If we formally repeat the above argument, and recall that the states are normalized to δ-functions we find

$$\mathcal{G}\left(k_1, k_2, \omega_n\right) = \frac{\delta_{\sigma\sigma'} \, \delta(k_1 - k_2)}{i\omega_n - \epsilon_k - \frac{1}{2} \xi \left\{ \frac{1}{4} t_o(i\omega_n) + \frac{3}{4} t_1(i\omega_n) \right\}}$$