

Friedel Sum Rule for Anderson's Model of Localized Impurity States*

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The Friedel sum rule is derived for Anderson's model of localized impurity states in metals. The result is valid even when all many-body correlations are taken into account.

I. INTRODUCTION

RECENTLY, Anderson's model¹ for localized impurity states in metals has been a subject of considerable investigation. Klein and Heeger^{2,3} have used Anderson's Hartree-Fock solution to interpret their data on specific heat and susceptibility. In addition, they have shown that these data combined with measurements of the residual resistivity can be interpreted in a manner consistent with the Friedel sum rule. Even within the Hartree-Fock approximation, however, the Friedel sum rule for Anderson's model has been given only partial justification,^{3,4} and some have expressed doubt as to its validity. Moreover, recent theoretical investigations⁵⁻⁸ suggest that the Hartree-Fock approximation is not even qualitatively correct for certain regions of interest. In the absence of reliable solutions, one would like to have confidence in the validity of as many exact sum rules as possible.

Here we show that the Friedel sum rule is an exact consequence of Anderson's Hamiltonian for the case where there is no local moment. Our proof is similar in many ways to that given by Langer and Ambegaokar⁹ for potential scattering in an interacting Fermi liquid.¹⁰ In particular, our proof makes use of the properties of the exact perturbation expansion⁵ of the Green's func-

tion in terms of the d - d potential U . We do not regard this as a serious drawback, however, since so long as there is no local moment, one expects no instabilities in the perturbation theory.

In Sec. II we derive the Low equation¹¹ for the T matrix, and relate it to the d -electron Green's function. From the unitarity condition we derive an exact inequality that the self-energy must satisfy. In Sec. III, we use a Luttinger-Ward¹² identity to calculate the number of electrons displaced by the impurity. This relation is quite similar to the approximate (Hartree-Fock) formula used by Klein and Heeger,³ and may be useful for the interpretation of experimental results. Finally, we combine this with the results of Sec. II, and thus derive the Friedel sum rule.

II. THE LOW EQUATION

The Anderson Hamiltonian for a single d orbital is

$$H = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\sigma} V_{\mathbf{k}} (c_{\mathbf{k}\sigma}^\dagger c_{d\sigma} + c_{d\sigma}^\dagger c_{\mathbf{k}\sigma}) + \sum_{\sigma} (\epsilon_d n_{d\sigma} + \frac{1}{2} U n_{d\sigma} n_{d-\sigma}). \quad (1)$$

We wish to construct the S -matrix elements¹³ for the elastic scattering of an electron or hole off the localized impurity. If $|\Psi_{\mathbf{k}\sigma}^\pm\rangle$ represent the exact incoming and outgoing states, the S matrix is

$$S_{\mathbf{k}'\sigma'; \mathbf{k}\sigma} = \langle \Psi_{\mathbf{k}'\sigma'}^- | \Psi_{\mathbf{k}\sigma}^+ \rangle. \quad (2)$$

First consider the case of electron scattering, so that the single-particle energies corresponding to \mathbf{k} and \mathbf{k}' are greater than the Fermi energy μ . Then the in and out states are simply

$$|\Psi_{\mathbf{k}\sigma}^\pm\rangle = \frac{\pm i\eta}{E_0 + \epsilon_{\mathbf{k}} - H \pm i\eta} c_{\mathbf{k}\sigma}^\dagger |\Psi_0\rangle, \quad (3)$$

where η is a positive infinitesimal. Here $|\Psi_0\rangle$ is the ground state of the system without the extra electron to be scattered, and satisfies $H|\Psi_0\rangle = E_0|\Psi_0\rangle$. We consider only the case where there is no magnetic moment,

¹¹ Recently, a similar technique has been used by H. Suhl, Phys. Rev. **138**, A515 (1965) in a related problem.

¹² J. M. Luttinger and J. C. Ward, Phys. Rev. **118**, 1417 (1960).

¹³ For a discussion of the scattering theory involved here, see W. Brenig and R. Haag, Fortschr. Physik **7**, 183 (1959) [English transl.: in *Quantum Scattering Theory*, edited by Mark Ross (Indiana University Press, Bloomington, Indiana, 1963)].

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¹ P. W. Anderson, Phys. Rev. **124**, 41 (1961).

² A. P. Klein and A. J. Heeger, Phys. Rev. Letters **15**, 786 (1965).

³ A. P. Klein and A. J. Heeger, Phys. Rev. **144**, 458 (1966).

⁴ E. Daniel and J. Friedel, in *Low Temperature Physics: LT9*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), p. 933.

⁵ J. R. Schrieffer and D. C. Mattis, Phys. Rev. **140**, A1412 (1965).

⁶ B. Kjöllerström, D. J. Scalapino, and J. R. Schrieffer, Bull. Am. Phys. Soc. **11**, 79 (1966).

⁷ B. Kjöllerström, D. J. Scalapino, and J. R. Schrieffer, Phys. Rev. **148**, 665 (1966).

⁸ A. C. Hewson, Phys. Letters **19**, 5 (1965); Phys. Rev. **144**, 420 (1966); A. C. Hewson and M. J. Zuckermann, Phys. Letters **20**, 219 (1966).

⁹ J. S. Langer and V. Ambegaokar, Phys. Rev. **121**, 1090 (1961).

¹⁰ That Anderson's Hamiltonian is formally a special case of the Hamiltonian considered by Langer and Ambegaokar suggests that one method of proof would merely involve the specialization of the results. However, because of the different dependences of the respective scattering potentials and Green's functions on the volumes of the systems (due to the localized nature of the d state in Anderson's model), the two scattering problems are not manifestly equivalent. The direct adaptation of Langer and Ambegaokar's results to the present problem is possible, but tricky. We regard the explicit derivation given here as preferable.

so that $|\Psi_0\rangle$ may be specified unambiguously, and so that spin-flip scattering cannot occur. Henceforth, then, we suppress all spin indices.

The states $|\Psi_{\mathbf{k}}^\pm\rangle$ satisfy $H|\Psi_{\mathbf{k}}^\pm\rangle = (E_0 + \epsilon_{\mathbf{k}})|\Psi_{\mathbf{k}}^\pm\rangle$, and are normalized for an infinite system if $|\Psi_0\rangle$ is. They may be written as

$$|\Psi_{\mathbf{k}}^\pm\rangle = c_{\mathbf{k}}^\dagger |\Psi_0\rangle + \frac{1}{E_0 + \epsilon_{\mathbf{k}} - H \pm i\eta} V_{\mathbf{k}} c_d^\dagger |\Psi_0\rangle, \quad (4)$$

so that

$$|\Psi_{\mathbf{k}}^+\rangle - |\Psi_{\mathbf{k}}^-\rangle = -2\pi i \delta(E_0 + \epsilon_{\mathbf{k}} - H) V_{\mathbf{k}} c_d^\dagger |\Psi_0\rangle. \quad (5)$$

Hence, the T matrix, defined on the energy shell by

$$S_{\mathbf{k}'\mathbf{k}} = \delta_{\mathbf{k}'\mathbf{k}} - 2\pi i \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}) T_{\mathbf{k}'\mathbf{k}}, \quad (6)$$

is given by

$$\begin{aligned} T_{\mathbf{k}'\mathbf{k}} &= V_{\mathbf{k}'} \langle \Psi_{\mathbf{k}'}^- | c_d^\dagger | \Psi_0 \rangle \\ &= V_{\mathbf{k}'} V_{\mathbf{k}} \left\langle \Psi_0 \left| c_d \frac{1}{E_0 + \epsilon_{\mathbf{k}} - H + i\eta} c_d^\dagger \right| \Psi_0 \right\rangle \\ &\quad + V_{\mathbf{k}} \langle \Psi_0 | c_{\mathbf{k}'} c_d^\dagger | \Psi_0 \rangle. \quad (7) \end{aligned}$$

Finally, because the spectrum of H , when acting on an $N-1$ particle state, goes down only to $E_0 - \mu$, we may write

$$\begin{aligned} 0 &= \frac{-i\eta}{E_0 - \epsilon_{\mathbf{k}'} - H - i\eta} c_{\mathbf{k}'} |\Psi_0\rangle \\ &= c_{\mathbf{k}'} |\Psi_0\rangle - \frac{1}{E_0 - \epsilon_{\mathbf{k}'} - H - i\eta} V_{\mathbf{k}'} c_d |\Psi_0\rangle, \quad (8) \end{aligned}$$

so that (7) becomes

$$\begin{aligned} T_{\mathbf{k}'\mathbf{k}} &= V_{\mathbf{k}'} V_{\mathbf{k}} \left\{ \left\langle \Psi_0 \left| c_d \frac{1}{\epsilon_{\mathbf{k}} + i\eta + E_0 - H} c_d^\dagger \right| \Psi_0 \right\rangle \right. \\ &\quad \left. + \left\langle \Psi_0 \left| c_d^\dagger \frac{1}{\epsilon_{\mathbf{k}'} + i\eta - E_0 + H} c_d \right| \Psi_0 \right\rangle \right\}. \quad (9) \end{aligned}$$

A similar result may be derived for hole scattering when $\epsilon_{\mathbf{k}} < \mu$.

The Low Eq. (9) takes on an extremely simple form if we note that the quantity in curly brackets is just the Green's function¹⁴ for the d orbital,

$$G(z) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{A(\omega)}{z - \omega}, \quad (10)$$

where the spectral weight function $A(\omega)$ is defined in the usual way by

$$A(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \Psi_0 | c_d(t) c_d^\dagger(0) + c_d^\dagger(0) c_d(t) | \Psi_0 \rangle. \quad (11)$$

¹⁴ Our definitions and notation for Green's functions and related quantities parallel those of L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin and Company, Inc., New York, 1962).

Thus Eq. (9) becomes (for $\epsilon_{\mathbf{k}} = \epsilon_{\mathbf{k}'}$)

$$T_{\mathbf{k}'\mathbf{k}} = V_{\mathbf{k}'} V_{\mathbf{k}} G(\epsilon_{\mathbf{k}} + i\eta). \quad (12)$$

For subsequent analysis, we define the self-energy $\Sigma(z)$ according to

$$G^{-1}(z) = z - \epsilon_d - \Sigma(z), \quad (13)$$

and its imaginary part

$$\Gamma(\omega) = -2 \operatorname{Im} \Sigma(\omega + i\eta) = 2 \operatorname{Im} \Sigma(\omega - i\eta). \quad (14)$$

According to the optical theorem, the total transition rate for an electron of momentum \mathbf{k} above the Fermi surface to all other energy-conserving final states is

$$\tau^{-1}(\mathbf{k}) = -2 \operatorname{Im} T_{\mathbf{k}\mathbf{k}} = |V_{\mathbf{k}}|^2 A(\epsilon_{\mathbf{k}}). \quad (15)$$

This agrees with a result first derived in another way by Zuckermann,¹⁵ and used by Klein and Heeger.³ On the other hand, the transition rate due to elastic scattering is

$$\begin{aligned} \tau_e^{-1}(\mathbf{k}) &= 2\pi \sum_{\mathbf{k}'} |T_{\mathbf{k}'\mathbf{k}}|^2 \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}) \\ &= |V_{\mathbf{k}}|^2 A(\epsilon_{\mathbf{k}}) [2\pi \sum_{\mathbf{k}'} |V_{\mathbf{k}'}|^2 \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}) / \Gamma(\epsilon_{\mathbf{k}})]. \quad (16) \end{aligned}$$

Since $\tau^{-1} \geq \tau_e^{-1}$ by unitarity, a comparison of (15) and (16) shows that

$$\Gamma(\epsilon_{\mathbf{k}}) \geq 2\pi \sum_{\mathbf{k}'} |V_{\mathbf{k}'}|^2 \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}). \quad (17)$$

In general, the final state can consist of an electron plus any number of electron-hole pairs, so that (17) does not help us much. However, as $\epsilon_{\mathbf{k}}$ approaches the Fermi level, the phase space for all but elastic scattering vanishes, so that we may expect that

$$\Gamma(\mu) = 2\pi \sum_{\mathbf{k}'} |V_{\mathbf{k}'}|^2 \delta(\mu - \epsilon_{\mathbf{k}'}). \quad (18)$$

III. THE FRIEDEL SUM RULE

Here we prove that the sum of the phase shifts is equal to π times the number of electrons displaced by the impurity. In the case of a single d orbital, of course, we expect only one phase shift for each spin direction. We begin by calculating the number of displaced electrons, among which are included not only the d electrons, but also some of the conduction electrons. Thus we need the conduction-electron Green's function $G_{\mathbf{k}}$. It follows immediately from the equations of motion that¹⁶

$$G_{\mathbf{k}}(z) = \frac{1}{z - \epsilon_{\mathbf{k}}} + \frac{|V_{\mathbf{k}}|^2}{(z - \epsilon_{\mathbf{k}})^2} G(z). \quad (19)$$

It will be convenient to divide the self-energy $\Sigma(z)$ (associated with G , not $G_{\mathbf{k}}$) into two parts:

$$\begin{aligned} \Sigma(z) &= \Sigma_{dd}(z) + \Sigma_{sd}(z), \\ \Sigma_{sd}(z) &= \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 / (z - \epsilon_{\mathbf{k}}). \quad (20) \end{aligned}$$

¹⁵ M. J. Zuckermann, Phys. Rev. **140**, A899 (1965).

¹⁶ See Ref. 1. Note that the derivation depends in no way on the use of the Hartree-Fock approximation.

Then the number of displaced electrons (of both spins) may be written simply as [using (19) and the second line of (20)]

$$N = -\frac{2}{\pi} \operatorname{Im} \int_{-\infty}^{\mu+i\eta} dz \left(1 - \frac{\partial \Sigma_{sd}(z)}{\partial z} \right) G(z). \quad (21)$$

To proceed further we must use some specific properties of the self-energy. As pointed out by Schrieffer and Mattis,⁵ the expansion of Σ_{dd} in terms of U and $G(z)$ is formally identical to the expansion of the total self-energy of an electron in an interacting Fermi liquid, except that there are no momentum sums. This means that various identities proved for the Fermi liquid¹² must hold here as well. In particular, we have

$$\operatorname{Im} \Sigma_{dd}(\mu \pm i\eta) = 0, \quad (22)$$

in agreement with (18), and also

$$\operatorname{Im} \int_{-\infty}^{\mu+i\eta} dz \frac{\partial \Sigma_{dd}(z)}{\partial z} G(z) = 0. \quad (23)$$

Combining (23) and (21) gives

$$\begin{aligned} N &= -\frac{2}{\pi} \operatorname{Im} \int_{-\infty}^{\mu+i\eta} dz \frac{\partial}{\partial z} \ln G(z) \\ &= -\frac{2}{\pi} [\operatorname{Im} \ln G(\mu+i\eta) - \pi], \end{aligned} \quad (24)$$

where we have chosen the cut along the positive real axis with $\arg G(\infty+i\eta) = 2\pi$. Notice that (24) is formally identical to the approximate Hartree-Fock expression used by Klein and Heeger. One can in addition use the techniques of Fermi-liquid theory to calculate the specific heat.¹⁷ Unfortunately, the specific heat contains an additional unknown parameter, the wavefunction renormalization constant $[1 - (\partial/\partial\omega)\Sigma_{dd}]_{\omega=\mu}$.

We now go back and compute the phase shifts from Eqs. (6) and (12). Because the T matrix is factorizable when on the energy shell, the S matrix is trivially diagonalizable. $S-1$ has but a single nonzero eigenvalue

$$\exp 2i\delta(\epsilon_k) - 1 = -2\pi i \sum_{k'} |V_{k'}|^2 \delta(\epsilon_k - \epsilon_{k'}) \times G(\epsilon_k + i\eta). \quad (25)$$

The eigenvector (angular function) associated with (25) is just $V_{\mathbf{k}}$ evaluated on the energy shell. Therefore,

we find, using (13), (14), (20), and (22) that

$$\begin{aligned} 2i\delta(\mu) &= \ln[1 - i\Gamma(\mu)G(\mu+i\eta)] \\ &= \ln[G(\mu+i\eta)G^{-1}(\mu-i\eta)]. \end{aligned} \quad (26)$$

¹⁷ See, for example, A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963), pp. 169ff.

We pick the branch of the logarithm as before, so that $0 \leq \delta \leq \pi$. Comparison of (24) and (26) gives

$$\delta(\mu) = (\pi/2)N, \quad (27)$$

which is the desired result.

Next we mention that there is no difficulty in extending the above results to the more realistic case of five d orbitals. Then, there is an s - d mixing potential V_{kn} for each orbital n , and the d Green's function G is a 5×5 matrix. However, it follows from group-theoretical considerations³ that the orbitals may be chosen so that G is diagonal, and so that

$$\sum_{\mathbf{k}} V_{kn} \frac{1}{z - \epsilon_{\mathbf{k}}} V_{kn'} = \delta_{n,n'} \sum_{\mathbf{k}} |V_{kn}|^2 \frac{1}{z - \epsilon_{\mathbf{k}}}. \quad (28)$$

Use of (28) allows one to diagonalize the S matrix as before. There are now 5 phase shifts (for a given energy and spin direction), and (27) is replaced by

$$\sum_{n=1}^5 \delta_n(\mu) = \frac{1}{2}\pi N. \quad (29)$$

Some of the δ_n will of course be degenerate, as required by crystalline symmetry.

We conclude by mentioning that if there is a local moment, our result still holds if the perturbation expansion in U remains valid. In this case Eq. (22) implies by unitarity that spin-flip scattering does not occur. Thus we still have a one-channel problem, and the proof goes through as before. That spin-flip scattering cannot occur can be seen more simply from the following argument. Under local moment conditions, the Hamiltonian (1) contains an effective antiferromagnetic s - d interaction.¹⁸ Hence, the local moment is smaller than the moment of a free electron, so that spin-flip scattering is ruled out by a conservation law.¹⁹ We should point out however, that the existence of a Friedel sum rule at zero temperature could be of little use in practice in the case where there is a local moment. It is well known that an antiferromagnetic s - d coupling causes the scattering cross section to be a rapidly varying function of energy near the Fermi energy.²⁰ Hence, the resistivity at a small but finite temperature will be considerably different from that at zero temperature.

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¹⁸ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **28**, 846 (1962).

¹⁹ Low-order perturbation theory in the s - d mixing potential does predict spin-flip scattering. Such an expansion is therefore incorrect at zero temperature. This invalidity is signalled by the appearance of logarithmically divergent terms.

²⁰ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **32**, 37 (1964); A. A. Abrikosov, *Physics* **2**, 5 (1964); H. Suhl, *Phys. Rev.* **138**, A515 (1965); **141**, 483 (1966); *Physics* **2**, 39 (1965); *Phys. Rev.* **141**, 483 (1966).