Exchange Character of the Anderson Hamiltonian

Joel A. Appelbaum* and K. H. Bennemann

Department of Physics and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois

AND

J. W. Garland†

Department of Physics, University of California, Berkeley, California

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The exchange character of the Anderson model Hamiltonian has been studied. We find that for determining the conduction-electron Green's function, this Hamiltonian can be replaced by an effective Hamiltonian in which the strong d-d exchange term $Un_{d\uparrow}n_{d\downarrow}$ has been treated exactly and the s-d mixing term V_{mix} has been modified so that it exhibits explicitly exchange character. Hence, V_{mix} gives rise to a Kondo-like divergence in the conduction-electron self-energy. Extending the Anderson Hamiltonian by adding an s-d exchange interaction, we find this exchange interaction is left unchanged in going to our effective Hamiltonian.

I N the Anderson model[1] of localized magnetic states, the self-energy of the conduction electrons exhibits singularities similar to those found for conduction electrons interacting with localized spins via an s-d exchange interaction.[2-4] This anomalous behavior of the electron self-energy has been made plausible by the work of Schrieffer and Wolff[2] showing that the s-d mixing term in the Anderson Hamiltonian can be eliminated to first order by means of a canonical transformation and can partly be rewritten to second order as an s-d exchangelike term with an energy-dependent exchange interaction strength. It is the purpose of this paper to examine the structure of the Anderson Hamiltonian from a different point of view which further exhibits the connection between the Anderson and Kondo Hamiltonians.

We begin with the Anderson Hamiltonian

$$H = H_0 + V_{\mathrm{mix}}, \qquad (1)$$

where

$$H_0 \equiv \sum_{k,\sigma} \epsilon_{k\sigma}{}^s n_{k\sigma}{}^s + \sum_{\sigma} E_{d\sigma} n_{d\sigma} + H_u, \qquad (2)$$

$$H_u \equiv U n_{d\uparrow} n_{d\downarrow}, \qquad (3)$$

$$V_{\mathrm{mix}} \equiv \sum_{k,\sigma} V_{kd}(a_{k\sigma}{}^\dagger d_\sigma + d_\sigma{}^\dagger a_{k\sigma}), \qquad (4)$$

and $a_{k\sigma}{}^\dagger$ and $a_{k\sigma}$ are the creation and destruction operators for conduction electrons (s electrons) with momentum k and spin σ, respectively. $d_\sigma{}^\dagger$ and d_σ have similar meanings for the d electrons. $\epsilon_{k\sigma}{}^s$ and $E_{d\sigma}$ are the single-electron energies for s and d electrons, respectively. As has been discussed by a number of authors,[1,5] V_{mix} results from electron scattering due to

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[1] P. W. Anderson, Phys. Rev. 124, 41 (1961).
[2] J. R. Schrieffer and P. A. Wolff, Phys. Rev. 149, 491 (1966).
[3] D. J. Scalapino, Phys. Rev. Letters 16, 937 (1966).
[4] D. R. Hamann Phys. Rev. 154, 596 (1967).
[5] M. Bailyn, Advan. Phys. 15, 179 (1966).

the crystal potential involving transitions between s and d states and also from a Hartree factorization of that part of the Coulomb interaction among s and d electrons which contains one s-electron operator and three d-electron operators or vice versa.

Since we should like to study the properties of the s electrons, we examine the s-electron Green's function which in the interaction representation is given as the time-ordered expectation value

$$G_{k\sigma}{}^s(t-t') = -i\langle T(\bar{a}_{k\sigma}(t)\bar{a}_{k\sigma}{}^\dagger(t')S)\rangle / \langle S\rangle, \qquad (5)$$

with

$$S \equiv T \exp\left(-i \int_{-\infty}^{\infty} V_{\mathrm{mix}}(\tau) d\tau\right), \qquad (6)$$

and

$$\bar{a}_{k\sigma}{}^\dagger(t) = a_{k\sigma}{}^\dagger(t) \equiv a_{k\sigma}{}^\dagger e^{i\epsilon_{k\sigma}{}^s t}, \qquad (7)$$

$$\bar{d}_\sigma{}^\dagger(t) = d_\sigma{}^\dagger(t) e^{iUn_{-\sigma}t} \equiv d_\sigma{}^\dagger e^{iE_{d\sigma}t} e^{iUn_{-\sigma}t}, \qquad (8)$$

which follows from using the transformation formula

$$\bar{O}(t) = e^{iH_0 t} O e^{-iH_0 t} \qquad (9)$$

for going from the Schrödinger to the interaction representation. The Green's function $G_{k\sigma}{}^s$ is now evaluated using H_0 as a zeroth-order Hamiltonian,[6] since it can be treated exactly, and at zero temperature for simplicity. This division of the total Hamiltonian has the advantage that at the very outset exact care is taken of the strong d-d exchange interaction H_U. Notice that H_U has the special property that the eigenvectors which diagonalize $(H_0 - H_U)$ diagonalize also H_0.[6] We assume in the following that U is sufficiently large so that the ground state of H_0 contains only one d electron with spin $\frac{1}{2}$.

The Green's function $G_{k\sigma}{}^s$ is now usually treated by diagramatic techniques, in which the exact $G_{k\sigma}{}^s$ is expanded in terms of

$$\bar{G}_{k\sigma}{}^s(t-t') = -i\langle T(\bar{a}_{k\sigma}(t)\bar{a}_{k\sigma}{}^\dagger(t'))\rangle \qquad (10)$$

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[6] This stems from our assumption that one has a single orbitally nondegenerate d level.

and

$$\bar{G}_\sigma{}^d(t-t')=-i\langle T(\bar{d}_\sigma(t)\bar{d}_\sigma{}^\dagger(t'))\rangle. \qquad (11)$$

This is not possible under the present circumstance, since the application of Wick's theorem is not valid for the operators $\bar{d}_\sigma(t)$ and $\bar{d}_\sigma{}^\dagger(t)$ as becomes clear in the following.

In order to apply Wick's theorem to a product of creation and annihilation operators it is necessary that the unequal-time commutation relations among these operators be c numbers.[7] Now normally $\bar{O}(t)$ differs from O only in having an extra $\exp(-i\epsilon t)$ factor, so that the commutation relation for O and $O^\dagger$ is sufficient to ensure that $[O(t),O^\dagger(t')]$ is a c number. However, in our case, $\bar{d}_\sigma{}^\dagger(t)$ differs from $d_\sigma{}^\dagger$ by the time-dependent operator $e^{i(E_{d\sigma}+U_{n-\sigma})t}$ and hence $[\bar{d}_\sigma(t), \bar{d}_\sigma{}^\dagger(t')]$ is no longer a c number.

In an attempt to circumvent this problem, we notice that $\bar{d}_\sigma{}^\dagger(t)$ and $\bar{d}_\sigma(t)$ are given by

$$\bar{d}_\sigma{}^\dagger(t)=d_\sigma{}^\dagger(t)+f^*(t)d_\sigma{}^\dagger(t)d_{-\sigma}{}^\dagger(t)d_{-\sigma}(t) \qquad (12)$$

and

$$\bar{d}_\sigma(t)=d_\sigma(t)+f(t)d_\sigma(t)d_{-\sigma}{}^\dagger(t)d_{-\sigma}(t), \qquad (13)$$

where

$$f(t)\equiv e^{-iUt}-1. \qquad (14)$$

Rewriting V_{mix}, then, in terms of $a_{k\sigma}(t)$, $a_{k\sigma}{}^\dagger(t)$, $d_\sigma(t)$, and $d_\sigma{}^\dagger(t)$, we obtain

$$V_{\text{mix}}=\sum_{k,\sigma}\{V_{kd}(a_{k\sigma}{}^\dagger(t)d_\sigma(t)+d_\sigma{}^\dagger(t)a_{k\sigma}(t))$$
$$+\tilde{V}_{kd}(t)a_{k\sigma}{}^\dagger(t)d_\sigma(t)d_{-\sigma}{}^\dagger(t)d_{-\sigma}(t)$$
$$+\tilde{V}_{kd}{}^*(t)d_\sigma{}^\dagger(t)a_{k\sigma}(t)d_{-\sigma}{}^\dagger(t)d_{-\sigma}(t)\}, \qquad (15)$$

with

$$\tilde{V}_{kd}(t)\equiv V_{kd}f(t). \qquad (16)$$

Using this expression for V_{mix} in determining S, we can apply Wick's theorem to the operators $d_\sigma(t)$, $d_\sigma{}^\dagger(t)$, and we can then expand $G_{k\sigma}{}^s(t-t')$ in terms of

$$G^0{}_{k\sigma}{}^s(t-t')=-i\langle T(a_{k\sigma}(t)a_{k\sigma}{}^\dagger(t'))\rangle \qquad (17)$$

and

$$G^0{}_\sigma{}^d(t-t')=-i\langle T(d_\sigma(t)d_\sigma{}^\dagger(t'))\rangle. \qquad (18)$$

Now, we notice that from the point of view of calculating $G_{k\sigma}{}^s(t-t')$ our effective Hamiltonian in the Schrödinger representation takes the form

$$H\Rightarrow H_{\text{eff}}=\sum_{k,\sigma}\epsilon_{k\sigma}{}^s n_{k\sigma}{}^s+\sum_\sigma E_{d\sigma}n_{d\sigma}+V_{\text{mix}}(t). \qquad (19)$$

This is an exact result. This effective Hamiltonian no longer contains H_U explicitly. The exchange character of H_U has been transferred entirely to V_{mix}.

In this connection, notice also that if an s-d exchange interaction of the form

$$V_{\text{ex}}=-\sum_{k,k'\atop\sigma,\sigma'} J(k,k')a_{k\sigma}{}^\dagger a_{k'\sigma}d_\sigma{}^\dagger d_{\sigma'}, \qquad (20)$$

or[8–10]

$$V_{\text{ex}}=-J\sum_{k,k'\atop v,v'} a_{kv}{}^\dagger a_{k'v'}\boldsymbol{\sigma}_{vv'}\cdot\mathbf{S}, \qquad (21)$$

which results from replacing the d-electron operators by spin operators, is added to the Anderson Hamiltonian given by Eq. (1), then this exchange interaction between s and d electrons is not altered by the transformation used in deriving the effective Hamiltonian given by Eq. (19). Notice that Eq. (20) represents only that part of the total exchange interaction between s and d electrons which involved two s and two d electrons. Clearly, one should in general also include in V_{ex} exchange interactions involving three s electrons and one d electron and vice versa. For simplicity, we do not discuss these terms.

Figure 1(a) shows an elementary exchange scattering event contained in the effective Hamiltonian given by Eq. (19). For comparison, Fig. 1(b) shows a corresponding scattering event described by V_{ex}.

Notice that Fig. 1(a) demonstrates how a conduction electron spin-flip process results from successive scattering involving $\tilde{V}$ and V.

The exchange character of V_{mix} is now evident, and it is thus clear that the self-energy of the conduction electrons exhibits a Kondo-like singularity. Notice that in the case of V_{ex} singularities first appear in order J^3, and since it requires two V vertices to generate an elementary exchange scattering corresponding to V_{ex}, the Anderson Hamiltonian will exhibit Kondo-like singularities first in order V^6.

The physical meaning of V_{mix} can be further appreciated if we consider the limit in which $U\gg(\epsilon_{k\sigma}{}^s,E_{d\sigma})$. Then we know the system cannot respond to the rapidly oscillating parts of V_{mix} (the terms proportional to e^{iUt} and e^{-iUt}). If we ignore these terms in V_{mix} we obtain

$$\sum_{k,\sigma} V_{kd}(a_{k\sigma}{}^\dagger d_\sigma+d_\sigma{}^\dagger a_{k\sigma})(1-n_{-\sigma}{}^d). \qquad (22)$$
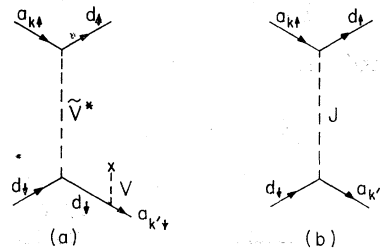

FIG. 1. (a) Scattering graph resulting from V_{mix}.
(b) Scattering graph resulting from V_{ex}.

[7] S. S. Schweber, *Introduction to Relativistic Quantum Field Theory* (Harper and Row, New York, 1962).

[8] T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956).

[9] J. Kondo, Progr. Theoret. Phys. (Kyoto) **27**, 772 (1962).

[10] It is interesting to observe that the fictitious fermions introduced by Abrikosov (Ref. 11), at least for the spin-$\frac{1}{2}$ case, are none other than the real fermions (d electrons) which were replaced in deriving Eq. (21).

[11] A. A. Abrikosov, Physics **2**, 5 (1965).

FIG. 2. Graphical representation of the self-energy for spin ↑ and ↓ s electrons assuming an unperturbed ground state consisting of the s-electron Fermi sea and a d electron with spin ↑.
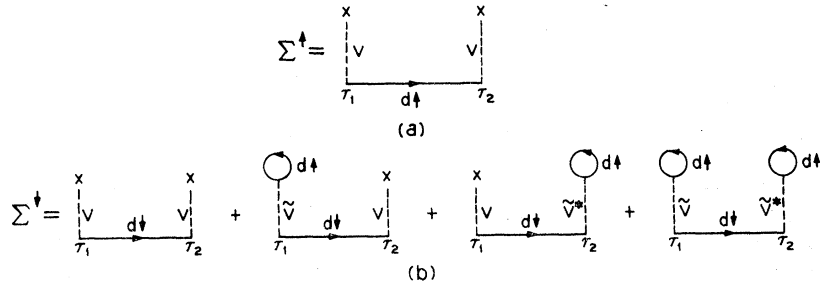
This is identical to the V_{mix} defined by Eq. (4), except for the added operator $(1-n_{-\sigma}{}^d)$. This extra factor prevents V_{mix} from generating a doubly occupied d state and, by doing so, gives exchange character to V_{mix}.

It should be pointed out that while we have demonstrated quite generally the presence of Kondo-like singularities in the electron Green's function for the Anderson model we have not proved, and it may not be true, that the detailed dynamic structure of the Anderson and Kondo Hamiltonians are identical.

With these reservations in mind it is nevertheless interesting to make contact with the work of Schrieffer and Wolff.[2]

The self-energy for the conduction electrons we calculate using $V_{\text{mix}}(t)$ will have contributions to it from both direct as well as exchange scattering contained in $V_{\text{mix}}(t)$. The exchange and direct contribution to the self-energy can be disentangled in the lowest-order self-energy graphs by taking the difference between the self-energy for a spin-up s electron and that for a spin-down s electron (we assume our ground state consists of a d electron with spin up and a Fermi sea of s electrons).

The self energies for spin-up and spin-down s electrons are shown in Fig. 2. We have drawn each graph in Fig. 2 in its time-coordinate form because of the time dependence of V_{mix}. While each graph does not maintain time translational invariance, the sum of the graphs is, of course, time translationally invariant.

The lowest-order self energy due to an effective exchange interaction

$$V_{\text{ex}} = -\sum_{k,k'} J_{\text{eff}}(\mathbf{k},\mathbf{k}')[(a_{k\uparrow}{}^{\dagger}a_{k'\uparrow} - a_{k\downarrow}{}^{\dagger}a_{k'\downarrow})S_z$$
$$+ a_{k\uparrow}{}^{\dagger}a_{k'\downarrow}S^- + a_{k\downarrow}{}^{\dagger}a_{k'\uparrow}S^+], \quad (21)$$

where $S = \frac{1}{2}$, and assuming $S_z = \frac{1}{2}$ (this corresponds to a d-electron state with spin up being occupied), is

$$-\tfrac{1}{2}J_{\text{eff}}(k,k), \quad \text{spin } \uparrow s \text{ electrons}$$
$$\tfrac{1}{2}J_{\text{eff}}(k,k), \quad \text{spin } \downarrow s \text{ electrons}.$$

The difference between the self energies for a spin ↑ and a spin ↓ electron for the effective exchange interaction given above, $-J_{\text{eff}}(k,k)$, is set equal to the difference between the Fourier transform of the self-energies shown in Figs. 2a and 2b. This procedure defines the effective exchange vertex for the Anderson Hamiltonian, which is given below:

$$J_{\text{eff}}(\mathbf{k},\mathbf{k}_j;\omega) = |V_{kd}|^2(G_{\downarrow}{}^{0d}(\omega-U) - G_{\uparrow}{}^{0d}(\omega)), \quad (23)$$

with

$$G_{\downarrow}{}^{0d}(\omega) = (\omega - \epsilon_{d\downarrow} + i\delta)^{-1}, \quad (24)$$
$$G_{\uparrow}{}^{0d}(\omega) = (\omega - \epsilon_{d\uparrow} - i\delta)^{-1}.$$

The derivation of (23) is found in the Appendix. All energies are measured from the Fermi energy $(\hbar=1)$. In particular, for small electron excitation, one gets energies which, for many electronic properties, are most important,

$$J_{\text{eff}}(k,k,0) = -|V_{kd}|^2 \frac{U}{|\epsilon_d|(U-|\epsilon_d|)}, \quad (25)$$

using the fact the $\epsilon_d < 0$. This is essentially the result obtained by Schrieffer and Wolff.[12]

We would like to mention that our discussion can be generalized to finite temperature by using thermal Green's functions. However, our conclusions would be essentially unmodified, although our expression for V_{mix} in the effective Hamiltonian would then become "temperature-dependent."

Finally, note that it is interesting to study more generally the relation between the Anderson and Kondo Hamiltonians by using the two-electron scattering matrix and an electron-electron interaction which is more general than the one used in the Anderson or Kondo Hamiltonian. Then, for example, all results obtained in this paper can be easily rederived from the integral equation for the two-electron scattering matrix.

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[12] Our J_{eff} differs by a factor of two from $S-W$ because of differing definitions for J.

APPENDIX

The self-energies given in Figs. 2a and 2b can be evaluated in the usual way starting from the s-electron Green's function[13]

$$G_{k\sigma}{}^s(t-t') = -i\langle T(a_{k\sigma}(t)a_{k\sigma}{}^\dagger(t')S)\rangle_{\text{cont}}, \qquad (A1)$$

where $\langle \ \rangle_{\text{cont}}$ indicates the fact that we consider only connected diagrams, and by expanding S to second order in V and $\bar{V}$.

When this is done for spin $\uparrow$ s electrons we get

$$G_{k\uparrow}{}^s(t-t') = G_{k\uparrow}{}^{0s}(t-t') + V^2 \int\int G_{k\uparrow}{}^{0s}(t-\tau)$$

$$\times G_{\downarrow}{}^{0d}(\tau-\tau')G_{k\uparrow}{}^{0s}(\tau'-t')d\tau d\tau' \qquad (A2)$$

from which we see that

$$\Sigma^\dagger(\tau-\tau') = V^2 G_{\downarrow}{}^{0d}(\tau-\tau'), \qquad (A3)$$

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[13] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

using

$$G = G^0 + G^0\Sigma G = G^0 + G^0\Sigma G^0 + \cdots, \qquad (A4)$$

where $\Sigma^\dagger$ is the self-energy shown in Fig. 2a.

In a similar way, one obtains for the self-energies in Fig. 2b, reading from left to right,

$$\Sigma_1{}^\downarrow(\tau-\tau') = V^2 G_{\downarrow}{}^{0d}(\tau-\tau'), \qquad (A5)$$

$$\Sigma_2{}^\downarrow(\tau,\tau') = V^2 G_{\downarrow}{}^{0d}(\tau-\tau')f(\tau), \qquad (A6)$$

$$\Sigma_3{}^\downarrow(\tau,\tau') = V^2 G_{\downarrow}{}^{0d}(\tau-\tau')f^*(\tau'), \qquad (A7)$$

$$\Sigma_4{}^\downarrow(\tau,\tau') = V^2 G_{\downarrow}{}^{0d}(\tau-\tau')f(\tau)f^*(\tau'). \qquad (A8)$$

Adding (A5) through (A8), we obtain the total self-energy $\Sigma^\downarrow(\tau-\tau')$:

$$\Sigma^\downarrow(\tau-\tau') = V^2 G_{\downarrow}{}^{0d}(\tau-\tau')e^{iU(\tau'-\tau)}. \qquad (A9)$$

Notice that while Σ_2, Σ_3, and Σ_4 are functions of τ and τ', $\Sigma^\downarrow$ is a function only of $\tau-\tau'$.

Fourier transforming $\Sigma^\dagger$ and $\Sigma^\downarrow$, and taking their difference, one obtains the J_{eff} given in Eq. (23).

Surface Structure of Clean Au (100) and Ag (100) Surfaces*

P. W. Palmberg† and T. N. Rhodin

Department of Engineering Physics, Cornell University, Ithaca, New York

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The proposal that reconstructed phases may exist for the clean (100) surfaces of some fcc metals is considered in terms of results obtained from low-energy electron-diffraction studies of epitaxial single-crystal films of silver and gold grown in ultrahigh vacuum (1×10^{-10} Torr). The purpose of this paper is to show that the experimentally observed (1×5) structure on the Au(100) surface and the (1×1) structure on the Ag (100) surface are characteristic of the clean surface, and to suggest a possible atomic structure for the reconstructed Au(100) surface. The evidence from the epitaxial film studies indicates the occurrence of a thin hexagonal layer of pure gold on the (100) substrate rather than an impurity-stabilized surface layer of hexagonal symmetry, of some unknown substance. It is suggested that the interfacial energy between a thin hexagonal layer and the nonreconstructed substrate may be the determining factor in the occurrence of reconstruction on the (100) surface of fcc metals.

ALTHOUGH it is generally assumed that clean metal surfaces are characterized by a bulk atomic arrangement, some recent experiments on Pt,[1] Pd,[2] Au[2,3] and Ag[3] suggest that reconstructed phases may exist for the clean (100) surface of some metals. There

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[1] S. Hagstrom, H. B. Lyon, and G. A. Somorjai, Phys. Rev. Letters **15**, 491 (1965); see also, H. B. Lyon and G. A. Somorjai, J. Chem. Phys. **46**, 2539 (1967).

[2] H. B. Lyon, A. M. Mattera, and G. A. Somoraji, *Fundamentals of Gas-Surface Interactions*, edited by M. Rogers, H. Saltsburg, and J. N. Smith, Jr. (Academic Press Inc., New York, 1967); See also: A. M. Mattera, R. M. Goodman, and G. A. Somorjai, Surface Science **7**, 26 (1967).

[3] D. G. Fedak and N. A. Gjostein, Phys. Rev. Letters **16**, 171 (1966); Acta Met. **15**, 827 (1967).

has been considerable disagreement on whether these observed superstructures are characteristic of clean metals or whether they are stabilized by impurities. The purpose of this paper is to report on some experiments in which it is believed that contamination does not play a role and to suggest a possible atomic structure for the Au (100) surface.

One of the difficulties encountered in preparing surfaces for low-energy electron diffraction (LEED) studies is diffusion of impurities from the bulk. Even for crystals of highest available purity, bulk contamination represents an almost inexhaustable source of surface impurities unless the samples are extremely thin. One method of forming very thin crystals is to grow epitaxial films on inert substrates.