GROUND STATE OF THE KONDO MANY-BODY SCATTERING PROBLEM*

A. J. Heeger and M. A. Jensen
Department of Physics and Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania
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The logarithmic divergence in the conduction-electron–magnetic-impurity scattering amplitude found by Kondo[1] suggested the possibility of an instability in the system at sufficiently low temperatures. Although Yosida[2] has indeed found a bound state in a one-electron calculation directly analogous to the familiar Cooper pair problem of superconductivity, it is not clear how this is related to the actual many-body problem. By using a particular truncation scheme in the equations of motion for the electron Green's functions, Nagaoka[3] has demonstrated that a many-body calculation can give a bound state. Unfortunately, it is hard to make an a priori justification of his truncation scheme. On the other hand, Abrikosov,[4] using diagramatic perturbation theory, and Suhl,[5] using Chew-Low scattering theory, do not find a bound state although these results appear to be valid only to logarithmic accuracy.[6] In this paper we investigate the ground state of this problem by means of a many-body variational calculation and show that for an antiferromagnetic s-d exchange interaction a bound state does exist.

The question of the interaction of the conduction electrons with a magnetic impurity is related to the basic question of the existence of a localized moment on the magnetic impurity atom. The latter problem has been discussed in detail by Anderson[7] and many others. The antiferromagnetic s-d exchange Hamiltonian can be obtained directly from the Anderson localized impurity model[8] when the intra-atomic Coulomb interaction, U, is large. Thus with this model one is able to build in an inherent symmetry between the electrons localized on the impurity and those in the conduction band. From this point of view a solution of the exchange Hamiltonian is equivalent to a self-consistent solution of the strongly correlated Anderson Hamiltonian. We will therefore assume that U is large (compared with the virtual level width) and take as a starting point maximum correlation for electrons of opposite spin when in an impurity orbital. For simplicity we restrict ourselves to a one-orbital impurity so that the impurity is either spin up or spin down but never doubly occupied.

The Hamiltonian for a single magnetic impurity in an electron gas is

$$H=\sum_{k,\sigma}\epsilon_k C_{k,\sigma}^{+}C_{k,\sigma}+\sum_{\sigma}E_d C_{d,\sigma}^{+}C_{d,\sigma}$$
$$+\frac{1}{2}\sum_{k,q}\frac{|J_{kq}|}{N}[(C_{q\uparrow}^{+}C_{k\uparrow}-C_{q\downarrow}^{+}C_{k\downarrow})S_z+C_{q\uparrow}^{+}C_{k\downarrow}S_{-}+C_{q\downarrow}^{+}C_{k\uparrow}S_{+}], \tag{1}$$

where in terms of the above model

$$S_z=\tfrac{1}{2}(C_{d\uparrow}^{+}C_{d\uparrow}-C_{d\downarrow}^{+}C_{d\downarrow}),\quad S_{+}=C_{d\uparrow}^{+}C_{d\downarrow},\quad S_{-}=C_{d\downarrow}^{+}C_{d\uparrow}. \tag{2}$$

The C and C^{+} operators obey the usual anticommutation relations, and the correlation restricts the states such that

$$C_{d,\sigma}^{+}C_{d,-\sigma}^{+}|\mathrm{vac}\rangle=0. \tag{2}$$

In order to fix the sign of the off-diagonal matrix elements of the interaction we follow the example of the BCS theory of superconductivity[9] and occupy the electron states in pairs. The most general product wave function which does this is

$$|\Psi\rangle=\prod_k\left[U_k+\frac{p_k}{\sqrt{2}}(C_{k\uparrow}^{+}C_{d\downarrow}^{+}-C_{k\downarrow}^{+}C_{d\uparrow}^{+})+f_k C_{k\uparrow}^{+}C_{k\downarrow}^{+}\right]|\mathrm{vac}\rangle. \tag{4}$$

In writing the above we have omitted the possibility of triplet pairing as it will be clear in the following analysis that inclusion of such terms can never lead to a lowering of the energy since the strongly correlated Anderson model demands antiferromagnetic J. The strong correlation [Eq. (3)] removes from the above wave function those states involving products of more than one C_d^+ operator, and we also exclude products involving no impurity operator. The wave function appropriate for our model is

$$|\Psi\rangle = K\sum_k \frac{p_k}{\sqrt{2}}(C_{k\uparrow}^+ C_{d\downarrow}^+ - C_{k\downarrow}^+ C_{d\uparrow}^+) \prod_{q\neq k}(U_q + f_q C_{q\uparrow}^+ C_{q\downarrow}^+)|\text{vac}\rangle, \tag{5}$$

where K is a normalization constant. The normalization condition (as well as the condition that there be a single impurity) is written

$$K^2 \prod_q (1-p_q^2)\sum_k \frac{p_k^2}{1-p_k^2} = 1. \tag{6}$$

We normalize exactly by setting

$$K^2 = 1/\Pi_q(1-p_q^2), \tag{7}$$

$$\textstyle\sum_k [p_k^2/(1-p_k^2)] = 1. \tag{8}$$

The energy of the system, obtained from Eqs. (1) and (5), is then given by

$$E = \sum_k \epsilon_k (p_k^2 + 2f_k^2) + E_d - \frac{3}{4}\sum_{k,q}\frac{|J_{kq}|}{N}(U_k U_q + f_k f_q)p_k p_q \tag{9}$$

subject to the conditions that

$$U_k^2 + p_k^2 + f_k^2 = 1, \tag{10}$$

$$\textstyle\sum_k (p_k^2 + 2f_k^2) = N, \tag{11}$$

and the above normalization condition [Eq. (8)].

We reference all energies relative to the Fermi energy and thereby automatically conserve particles. Minimization of the energy subject to the constraints leads to an integral equation for a "gap" parameter, Δ_k, given by

$$\Delta_k = \frac{3}{4}\sum_{\substack{q<k_F \\ \text{or} \\ q>k_F}} \frac{|J_{kq}|}{N} p_q (1-p_q^2)^{1/2}, \tag{12}$$

where

$$p_q^2 = \frac{1}{2}\left[1 - \frac{|\epsilon_q| + \lambda}{[(|\epsilon_q| + \lambda)^2 + 4\Delta_q^2]^{1/2}}\right] \tag{13}$$

and

$$f_q = (1-p_q^2)^{1/2}, \quad q<k_F, \qquad = 0, \quad q>k_F;$$

$$U_q = 0, \quad q<k_F, \qquad = (1-p_q^2)^{1/2}, \quad q>k_F, \tag{14}$$

with the Lagrange multiplier, λ, determined self-consistently from the normalization condition, Eq. (8). Assuming J_{kq} constant in a square band of width $2D$ centered on the Fermi surface and zero outside (the cutoff, D, physically results from the momentum dependence of the interaction), one finds the following solution for Δ:

$$\Delta = \left(\frac{D}{N(0)}\right)^{1/2} \exp\left[\frac{-2N}{3|J|N(0)}\right], \tag{15}$$

where $N(0)$ is the conduction-electron state density for a single spin. Since $\Delta_k(=\Delta)$ is the pairing energy for an electron in a particular k state, to find the total condensation energy one must evaluate the total energy for the single-impurity problem [Eq. (9)]. The resulting energy is

$$W = -\lambda = -2N(0)\Delta^2 = -D\exp[-4N/3|J|N(0)] \equiv -K_B T_{\text{Kondo}}, \tag{16}$$

which is identical with the binding energy found by Yosida in lowest order. However, there are very important differences. Firstly, in the present theory, the variational calculation leads to symmetric pairing relative to the Fermi surface. As a result of this, the electron-

hole states considered by Yosida in his higher order theory are partially contained in the above ground-state wave function. Those parts of the electron-hole states not included can be added into the ground state via perturbation theory without significant change in the ground-state energy.[10] Secondly, since the finite condensation energy results from a straightforward variational calculation using the full *s-d* exchange Hamiltonian, the result may be considered a proof of the existence of a condensed state for this system in contrast to the results of Suhl[5] and Abrikosov.[4] However, it must be noted that although the Schrieffer-Wolff transformation and the variational calculation presented here are straightforward, Suhl[11] has suggested that a singlet bound state is inconsistent with a finite *s-d* exchange integral unless there are explicitly spin-dependent forces in the problem. In fact, such spin-dependent forces are always present (e.g., the spin-orbit interaction). Furthermore, the consideration of spin-flip scattering from the many-body singlet is itself inconsistent since the k state involved already forms part of the singlet. One must instead construct the appropriate quasiparticle excitations for the problem and study these via scattering theory.

The conduction-electron–impurity singlet pairing function is given by

$$p_K^2 = \frac{K_B T_K}{2N(0)[\,|\epsilon_K| + K_B T_K\,]^2} \qquad (17)$$

which is shown in Fig. 1. It is noteworthy that the pairing is formed from momentum states rather far from the Fermi momentum [$\Delta k \sim (K_B T_K / E_F) k_F$] whereas from a kinetic energy argument alone, one might expect to do better using predominantly k states closer to k_F. This result is physically reasonable if one thinks about the problem of conduction-electron spin correlation in real space rather than momentum space. One clearly wants to introduce in position space local singlet spin correlation and to do this requires correlation in k states over a wide range of k values.

We conclude that in this model the ground state is a many-body singlet (spin compensated) bound state. We expect that above the characteristic temperature, T_K, this state will be broken up; however, as discussed by Schrieffer,[12] such a "phase transition" cannot be sharp since the condensation involves a small number of degrees of freedom and so will be broadened by thermal fluctuations. An extension of the above singlet-state calculation to finite temperature is in progress.

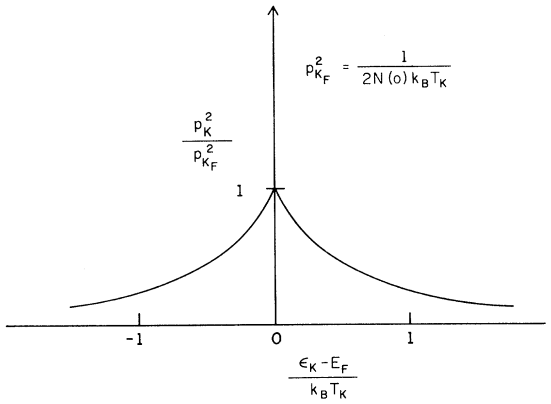

FIG. 1. The conduction-electron–impurity singlet pairing function is shown as a function of momentum [$\epsilon_K = (\hbar^2 k^2/2m) - E_F$]. Note that the pairing occurs over a relatively wide range of k states centered on the Fermi surface in agreement with the localized nature of the problem.

If J were ferromagnetic ($J<0$) we would find a triplet bound state, but since ferromagnetic J is fundamentally outside the Anderson strongly correlated model, such a calculation is inconsistent. One can get a net ferromagnetic interaction by including, for example, direct *s-d* exchange, in addition, in which case a triplet bound state would appear meaningful. Finally, as suggested above, one should be able to obtain these results directly from the Anderson Hamiltonian using techniques similar to those presented here.

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[1]J. Kondo, Progr. Theoret. Phys. (Kyoto) 32, 37 (1964).

[2]K. Yosida, Phys. Rev. 147, 223 (1966).

[3]Y. Nagaoka, Phys. Rev. 138, A112 (1965).

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

[5]H. Suhl, Phys. Rev. 141, 483 (1966); H. Suhl and

D. Wong, to be published.
[6]S. D. Silverstein and C. B. Duke, to be published.
[7]P. W. Anderson, Phys. Rev. 124, 41 (1961).
[8]P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. 6, 124 (1961); J. Kondo, Progr, Theoret. Phys. (Kyoto) 28, 846 (1962); J. R. Schrieffer and P. A. Wolff, Phys. Rev. 149, 491 (1966).
[9]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
[10]A. J. Heeger and M. A. Jensen, to be published.
[11]H. Suhl, Phys. Rev. Letters 17, 1141 (1966).
[12]J. R. Schrieffer, to be published.

SCREENING-ENHANCED SHUBNIKOV–de HAAS OSCILLATIONS IN Sb-DOPED GRAY TIN*

Bruce L. Booth and A. W. Ewald
Northwestern University, Evanston, Illinois
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Utilizing Shubnikov–de Haas measurements, we have determined the Dingle temperature, T_D, as a function of ionized-impurity concentration in Sb-doped gray tin. The results are in good qualitative and quantitative agreement with the predictions of the theory of ionized-impurity scattering in a many-valley semiconductor as developed by Robinson and Rodriguez.[1] The quantitative agreement also confirms a recent theoretical result of Brailsford[2] concerning the relation of T_D to the lifetime of a state at the Fermi level.

The sudden appearance of Shubnikov–de Haas oscillations when the electron concentration in a many-valley semiconductor is increased sufficiently to populate subsidiary minima was first observed by Becker and Fan[3] in Te-doped GaSb. In this material the conduction band is characterized by an absolute minimum at the Brillouin-zone center and subsidiary minima at the L points. The central-valley electrons have a small effective mass while the $\langle 111\rangle$ valleys have a relatively high density of states. Robinson and Rodriguez proposed that the seemingly anomalous concentration dependence of the oscillatory amplitude could be explained in terms of the screening of ionized impurities by the heavy $\langle 111\rangle$ electrons. They showed that as the carrier concentration is increased, the screening length decreases abruptly when the Fermi level reaches the subsidiary minima; the resulting increase in lifetime of the $\vec{k}=0$ electrons causes the oscillation amplitude to increase by orders of magnitude. Unfortunately, a direct quantitative comparison of this theory with the original and subsequent[4] experimental results on GaSb is not possible because the experimentally determined nonthermal broadening temperature T' is inherently different from the calculated T_D. While both measure the effect of Landau-level broadening on the amplitude of de Haas–van Alphen–type oscillations, the broadening involved in T_D is only that due to ionized-impurity scattering, whereas T' may involve, in addition, broadening due to neutral-impurity scattering and also that due to sample inhomogeneity.

Another material suitable for the investigation of screening-enhanced oscillations is gray tin. Its conduction band is very similar to that of GaSb with respect to the band-edge separation and to the ratio of heavy-to-light electron effective masses.[5,6] The absolute effective masses are somewhat smaller in gray tin and the correspondingly lower density of states in the central valley leads to a lower critical concentration. Apart from these similarities and minor differences, gray tin offers two distinct advantages for the investigation of the screening effect. Absence of intervalley scattering in an elemental semiconductor should result in a more pronounced effect and also permits the use of a simplified expression for the lifetime.[1] Secondly, because donor ionization is complete, the results are not complicated by neutral-impurity scattering.

In view of this favorable situation, we have extended the previous Shubnikov–de Haas measurements[6] to Sb-doped specimens in the broad concentration range from 7×10^{15} to 7×10^{18} cm^{-3}. Samples of high homogeneity were prepared by zone leveling suitable alloyed white-tin filaments which were then transformed to the gray phase. Etching revealed single-crystal segments which were selected for measurement. The measurements were made using magnetic field modulation and phase-sensitive detection at twice the modulation frequency. Figure 1 shows the X-Y recorder trace of the oscillations at 1.33°K in a sample containing 2.5