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[6]There are other ways of writing Z in functional average form as Mühlschlegel (Ref. 5) has shown. Independently, D. R. Hamann, this issue [Phys. Rev. Letters 23, 95 (1969)] has employed two random fields to study the Kondo problem.

[7]In polar coordinates, $d^2\xi_\nu = \frac{1}{2}dR_\nu{}^2 d\theta_\nu$.

[8]An alternative scheme for the evaluation of Eq. (2) is to perform a coupling-constant integral over the strength of V_k as Mühlschlegel (Ref. 5) has done. Unfortunately, in the full ferromagnetism problem as opposed to the one-center approximation, this procedure has the serious drawback of requiring one to integrate through the insulator-metal transition.

[9]Large-amplitude localized spin fluctuations have been discussed from other points of view by A. D. Caplin and C. Rizzuto [Phys. Rev. Letters 21, 746 (1968)]; P. Lederer and D. L. Mills [Phys. Rev. Letters 20, 1036 (1968)]; N. Rivier and M. J. Zuckerman [Phys. Rev. Letters 21, 904 (1968)]; and M. Levine and H. Suhl [Phys. Rev. 171, 567 (1968)].

[10]We note that the terms 1 and $-|\Omega_\nu|R/\beta\Gamma$ in Eq. (10) correspond to the adiabatic and transient terms, respectively, in the Nozières–de Dominicis [P. Nozières and C. de Dominicis, Phys. Rev. 178, 1097 (1969)] solution of the x-ray intensity problem as employed in the magnetic impurity problem by P. W. Anderson and G. Yuval [Phys. Rev. Letters 23, 89 (1969) (this issue)] and by Hamann (Ref. 6).

[11]Hamann, Ref. 6.

FLUCTUATION THEORY OF DILUTE MAGNETIC ALLOYS

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A simple explanation of the Kondo effect is shown to follow from a functional integral form of Anderson's dilute-alloy model.

This Letter describes a new approach to the theory of dilute magnetic alloys. The nonperturbational energy lowering associated with the Kondo effect[1] is shown to be a simple consequence of the statistics of fluctuations on the impurity site.

This theory uses a transformation due to Hubbard to replace the two-particle interaction by a Gaussian average over fluctuating one-particle potentials.[2] To apply Hubbard's transformation, Anderson's dilute-alloy Hamiltonian[3] must be written in the form

$$\mathcal{H}_0 = \sum_{k\sigma} \epsilon_{k\sigma} n_{k\sigma} + \sum_\sigma \epsilon_{d\sigma} + V \sum_{k\sigma} [C_{k\sigma}{}^\dagger C_{d\sigma} + C_{d\sigma}{}^\dagger C_{k\sigma}], \tag{1}$$

$$\mathcal{H}_1 = \tfrac{1}{4} U[(n_d)^2 - (S_{dz})^2], \tag{2}$$

where

$$n_d = n_{d\uparrow} + n_{d\downarrow}, \tag{3}$$

$$S_{dz} = n_{d\uparrow} - n_{d\downarrow}. \tag{4}$$

Straightforward application of Hubbard's method gives the partition function Z as the double functional integral

$$Z = Z_0 \int \delta x \, \delta y \langle T_\tau \exp\{-\int_0^\beta d\tau [\pi x^2/\beta + \pi y^2/\beta + \tilde{\mathcal{H}}_1]\}\rangle, \tag{5}$$

where

$$\tilde{\mathcal{H}}_1 = (\pi U/\beta)^{1/2}[x(\tau) S_{dz}(\tau) + i y(\tau) n_d(\tau)]. \tag{6}$$

In (5), $\beta = 1/kT$, the angular brackets denote the thermal average with respect to $\mathcal{H}_0$, Z_0 is the partition function for $\mathcal{H}_0$, and T_τ is the ordering operator with respect to τ.[4] In (6), the operators are in the interaction representation defined by $\mathcal{H}_0$, and the fields x and y are c numbers.

The spin-up and spin-down electrons are only implicitly coupled through the functional integration. For any particular $x(\tau)$ and $y(\tau)$, the quantum-mechanical problems for the two spin systems factor. We must evaluate

$$\exp(C_\sigma) \equiv \langle T_\tau \exp[-\int_0^\beta d\tau\, v_\sigma(\tau) n_{d\sigma}(\tau)]\rangle, \tag{7}$$

where V_σ is easily identified from (6). C_σ can be expanded as a sum of connected closed-loop diagrams,[4] which is given in closed form by

$$C_\sigma = -\int_0^1 d\lambda \int_0^\beta d\tau\, v_\sigma(\tau) G_{d\sigma}(\tau, \tau^\dagger). \tag{8}$$

$G_{d\sigma}$ satisfies the "Dyson" equation

$$G_{d\sigma}(\tau, \tau') = G_{d\sigma}^0(\tau, \tau') + \lambda \int_0^\beta d\tau''\, G_{d\sigma}^0(\tau, \tau'') v_\sigma(\tau'') G_{d\sigma}(\tau'', \tau'). \tag{9}$$

The coupling-constant integration in (8) yields correct counting of the closed loops.

The preceding development is exact. We now argue that rapid fluctuations in n_d and S_{dz}, at rates of the order of the d level width Δ, are not important to the magnetic behavior of the impurity. However S_{dz} should also undergo large low-frequency fluctuations resulting from precession if the system has a local moment. We replace the field $y(\tau)$ coupling the density fluctuations by its mean value, and solve (9) using an approximation for G_d^0 which is only valid for frequencies lower than Δ. This, in effect, decouples the high-frequency fluctuations of the spin-up and spin-down systems.

The approximation used on (9) was developed by Nozières and de Dominicis in their study of the x-ray threshold problem.[5] It consists of replacing $G_{d\sigma}^0$ by the form

$$G_{d\sigma}^0(\tau) \approx -\frac{1}{\pi} \frac{\Delta}{\Delta^2 + \epsilon_{d\sigma}^2} \left[\frac{\mathrm{P}}{\tau} + \frac{\pi \epsilon_{d\sigma}}{\Delta} \delta(\tau) \right], \tag{10}$$

which is correct for $|\tau|\Delta > 1$ and in integrals. P indicates principal value. With this approximation, (9) can be solved by the methods of Muskhelishvili.[6] The solution is

$$G_{d\sigma}(\tau, \tau') = G_{d\sigma}^A(\tau, \tau') + G_{d\sigma}^T(\tau, \tau'). \tag{11}$$

The first term in (11) is identical to (10) with ϵ_d replaced by $\lambda v(\tau)$. This is clearly the part of G_d which adiabatically follows the fluctuating potential. The second term contains the transient effects and is a rather complicated functional of v.

For simplicity, we have chosen $\epsilon_d = -\frac{1}{2}U$. The y field (in the Hartree-Fock approximation) then gives a net $\epsilon_d = 0$ in (10).

Equation (8) requires the equal-time limit of G_d. The adiabatic term in (11), as actually calculated, is undefined in this limit; so we use the exactly calculated $G_d^0(\tau, \tau^\dagger)$ evaluated at $\epsilon_d = \lambda v(\tau)$. It is possible to carry out the λ and τ integrations in (8) explicitly, since at $\tau = \tau'$ the complicated features of the transient term cancel out.

Combining results for the spin-up and spin-down systems yields

$$Z = Z_0 \int_0^\beta \delta x \exp\{-\int_0^\beta d\tau [V(x) + T(x)]\}. \tag{12}$$

In terms of the dimensionless field $\xi = x(\pi U/\Delta^2\beta)^{1/2}$,

$$V = (\Delta^2/U)\xi^2 - (2\Delta/\pi)[\xi \tan^{-1}\xi - \tfrac{1}{2}\ln(1+\xi^2)], \tag{13}$$

$$T = -\frac{\mathrm{P}}{\pi^2} \int_0^\beta \frac{d\tau'}{\tau - \tau'} \xi(\tau) \frac{d\xi(\tau')}{d\tau'} \left[\frac{1}{\xi^2(\tau) - \xi^2(\tau')} \ln \frac{1+\xi^2(\tau)}{1+\xi^2(\tau')} \right]. \tag{14}$$

V comes from the adiabatic part of G_d, and T from the transient part. The V term is exact for τ-independent ξ. The T term reproduces the Nozières–de Dominicis transient response correctly when ξ consists of an on-off step.[5] Equations (12)-(14) contain all the physics of the Anderson model which we believe relevant to its magnetism.

The "potential" term V has a single minimum at $\xi = 0$ for $U < \pi\Delta$, as shown in Fig. 1. For this case,

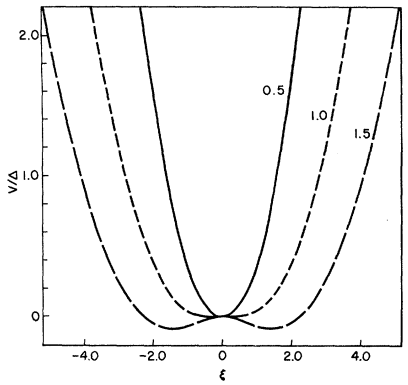

FIG. 1. $V(\xi)/\Delta$ vs ξ for $U/\pi\Delta = 0.5$, 1, and 1.5.

we expand V and T about $\xi = 0$. Using a Fourier-series representation for ξ,

$$\int_0^\beta d\tau T = (\beta/\pi)\sum_n |a_n|^2 |\omega_n|, \tag{15}$$

where a_n are the Fourier coefficients at $\omega_n = 2\pi \times n/\beta$. The sum must be cut off at $|\omega_n| = \Delta$ because of the restriction on (10). The functional integral separates into a product of Gaussian integrals of each Fourier coefficient, and the free energy is

$$\Omega = \Omega_0 + \frac{1}{2\beta}\sum_{|\omega_n|<\Delta} \ln\left[1 - \frac{U}{\pi\Delta} + \frac{|\omega_n| U}{\pi\Delta^2}\right].$$

This is precisely the contribution to Ω from the triplet part of a sum of bubble diagrams if each individual bubble is approximated by the first two terms of its expansion about $\omega = 0$ and this cutoff. The apparent absence of the corresponding ladder sum indicates that the small-ξ expansion is not spherically symmetric term by term.

For $U > \pi\Delta$, $V(\xi)$ has two equivalent minima at $\pm \xi_0$, as shown in Fig. 1. Evaluating the functional integral at one or the other of these corresponds to Anderson's spin-up or spin-down unrestricted Hartree-Fock approximation.[2,3]

For large ξ, we believe that a form like (15) is still a good approximation if a renormalizing factor $(1 + \langle \xi^2 \rangle)^{-1}$ is included. This renormalization occurs because the Nozières–de Dominicis transient effect depends on the change in scattering phase shift, which saturates for large ξ.

A key point for understanding the behavior of the functional integral in the two-minimum case is that the transient term is positive definite. Any individual term in the functional integral is smaller than the Hartree-Fock term $\xi = \xi_0$. There is no dynamical effect favoring "zero-point motion." However, the increase of available volume in function space is sufficiently rapid to overcome the unfavorable energetic effects for a certain class of functions.

Consider the set of functions which switch between $+\xi_0$ and $-\xi_0$ ν times in the interval $(0, \beta)$. Because of the high-frequency cutoff, these functions must take the minimum time $1/\Delta$ to go through the "potential barrier" V_b; so

$$\int_0^\beta d\tau\, V \approx \nu V_b/\Delta. \tag{17}$$

Equation (15) and its renormalized version are clearly proportional to the average frequency of ξ. For most functions in the set, this should be ν/β times a coefficient α of order unity; so

$$\int_0^\beta d\tau\, T \approx \nu\alpha\,\xi_0^2/(1+\xi_0^2). \tag{18}$$

The number of functions in the set is just the number of ways of choosing ν of the $N = \beta\Delta$ distinguishable positions for the zeros of ξ. The partition function is

$$Z = \sum_\nu \binom{N}{\nu} e^{-A\nu}, \tag{19}$$

where A is the sum of the coefficients in (17) and (18).

For large β, the contribution of a particular ν_0 dominates the sum. It is easily found by using Stirling's approximation to be

$$\nu_0 = \beta\Delta e^{-A}. \tag{20}$$

The free energy is

$$\Omega = \Omega_{\mathrm{HF}} - \Delta e^{-A}. \tag{21}$$

For large U, $A \sim U/\Delta$, and the energy lowering we have found can be identified with the Kondo effect.[1,7] It disappears at the Kondo temperature because $\nu_0 \sim 1$.

When the functional integration is restricted to functions which hop between the two minima, our expression for Z is similar to a rearranged form of perturbation theory for the s-d exchange model recently proposed by Anderson and Yuval.[8] Their theory also lacks term-by-term spherical symmetry.

The present results show that the Kondo effect can be regarded as a simple consequence of balancing the virtual energy cost of flipping the net d spin against the fluctuation phase space gained thereby.

Calculation of the low-temperature susceptibility and specific heat requires more detailed knowledge of the dominant ξ functions, and this problem is presently under study.[9]

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MAGNETIC-PHASE DIAGRAM OF MnF_2 FROM ULTRASONIC AND DIFFERENTIAL MAGNETIZATION MEASUREMENTS

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The magnetic-phase diagram, in the H-T plane, of MnF_2 was measured using ultrasonic and differential magnetization techniques. The paramagnetic-antiferromagnetic boundary, for $\vec{H}$ along the c axis, is well represented by $T_N - T = (1.65 \pm 0.15) \times 10^{-10} H^2$ °K/G^2. The triple point is at $T_3 = 65.1 \pm 0.2$°K and $H_3 = 120 \pm 4$ kG. The phase boundaries are discussed in light of existing theories.

In this Letter we report on high-field studies of the magnetic-phase boundaries of the classic uniaxial antiferromagnet MnF_2 using ultrasonic and differential magnetization techniques. The new results include (1) the observation of an attenuation peak for ultrasonic waves at the paramagnetic transition in finite magnetic fields up to the high-field triple point ($T_3 = 65.1 \pm 0.2$°K, $H_3 = 120 \pm 4$ kG) and (2) the determination of the complete boundaries, in the H-T plane, between the paramagnetic and antiferromagnetic phases and between the antiferromagnetic and spin-flop phases. When plotted in a normalized form the paramagnetic-to-antiferromagnetic boundary in MnF_2 is shown to be similar to the measured boundaries in other antiferromagnets containing Mn^{++}. An analysis of the antiferromagnetic to spin-flop boundary shows that the magnetic-field dependence of the susceptibility should affect this phase boundary near the triple point.

MnF_2 has a tetragonal lattice and is antiferromagnetic below the Néel temperature $T_N = 67.4$°K. The anisotropy energy of this material is very small compared with the exchange energy, and it is uniaxial with the c axis (tetragonal axis) as the easy axis for the sublattice magnetizations. For such a material the magnetic-phase diagram in the H-T plane, when the applied magnetic field $\vec{H}$ is along the c axis, should consist of three phases[1]: paramagnetic (P), antiferromagnetic (AF), and spin-flop (SF). In the P phase the magnetizations of the two sublattices point along the c axis, are parallel to each other, and have equal magnitudes. In the AF phase the sublattice magnetizations are along the c axis but are antiparallel to each other. In the SF phase, and when H is small compared with the exchange field H_E, the sublattice magnetizations are roughly antiparallel to each other and are almost perpendicular to the c axis. The AF-SF transition is a first-order transition which is accompanied by an abrupt change in the magnetic moment.[2] Calculations based on the molecular-field approximation show that the P-AF transition is a second-order tran-