Comments and Addenda

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Fluctuation Theory of Dilute Magnetic Alloys

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(Received 1 December 1969)

We comment on a recent letter by D. R. Hamann [Phys. Rev. Letters **23**, 95 (1969)] entitled "Fluctuation Theory of Dilute Magnetic Alloys."

IN a recent letter, Hamann[1] has discussed the Anderson[2] model for a dilute magnetic alloy using a functional integral method.[3,4] Considering a special class of functions corresponding to spin flips at the impurity site, it is argued that as temperature is decreased through the Kondo temperature, a progressive nonanalytic lowering of the free energy occurs. This is to be identified with the Kondo effect.[5] We show here very simply that the energy lowering is independent of temperature, and thus this flipping process, as described by Hamann, cannot be an explanation for the Kondo effect. We first briefly summarize the functional integral method as discussed by Hamann.

The Anderson-model Hamiltonian is

$$H=\sum_{k\sigma}\epsilon_{k\sigma}n_{k\sigma}+\sum_{\sigma}\epsilon_{d\sigma}n_{d\sigma}+V\sum_{k\sigma}(c_{k\sigma}^{+}c_{d\sigma}+c_{d\sigma}c_{k\sigma}^{+})+\tfrac{1}{2}U\sum_{\sigma}n_{d\sigma}n_{d-\sigma}$$
$$=H_0+H_V+H_U\,, \tag{1}$$

where k denotes the conduction-electron states, d the impurity state, and σ is a spin index. Using a transformation due to Stratonovich and to Hubbard,[6] the two-particle interaction $Un_{d\sigma}n_{d-\sigma}$ is replaced by a Gaussian average of random fluctuating one-body potentials. Explicitly,

$$Z=\mathrm{Tr}e^{-\beta H}=\int\int D\{x_\tau\}D\{y_\tau\}\,\mathrm{Tr}\Bigg(T\Bigg\{\exp-\int_0^\beta d\tau\Bigg[\frac{\pi x_\tau^2}{\beta}+\frac{\pi y_\tau^2}{\beta}+H_{0\tau}+H_{V\tau}\left(\frac{\pi U}{\beta}\right)^{1/2}[x_\tau(n_{\alpha\uparrow\tau}-n_{\alpha\downarrow\tau})+y_\tau(n_{\alpha\uparrow\tau}+n_{\alpha\downarrow\tau})]\Bigg]\Bigg\}\Bigg)\,. \tag{2}$$

If only the static term $x_\tau=x$ is considered and y_τ is averaged over, it is found that [see Eq. (13) of

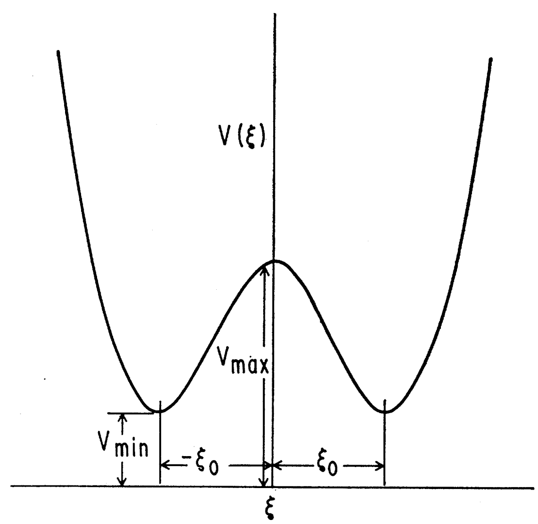

FIG. 1. General form of effective free energy $V(\xi)$ as a function of the static random field ξ for $U/\pi\Delta>1$.

[1] D. R. Hamann, Phys. Rev. Letters **23**, 95 (1969).
[2] P. W. Anderson, Phys. Rev. **124**, 41 (1961).
[3] B. Mühlschlegel, University of Pennsylvania, 1965, lecture notes (unpublished).
[4] S. Q. Wang, W. E. Evenson, and J. R. Schrieffer, Phys. Rev. Letters **23**, 92 (1969).
[5] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).
[6] R. L. Stratonovich, Dokl. Akad. Nauk SSSR **6**, 1097 (1957) [Soviet Phys.—Doklady **2**, 416 (1957)]; J. Hubbard, Phys. Rev. Letters **3**, 77 (1959).

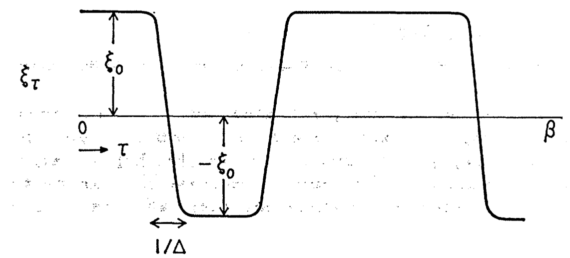

FIG. 2. Typical path for the random field ξ_τ as a function of τ, corresponding to switching between the minima of $V(\xi)$.

Hamann's letter]

$$Z=Z_0\int_{-\infty}^{+\infty} e^{-\beta V(\xi)}\,d\xi\,, \tag{3}$$

where

$$V(\xi)=(\Delta^2/U)\xi^2-(2\Delta/\pi)[\xi\tan^{-1}\xi-\tfrac{1}{2}\ln(1+\xi^2)] \tag{4}$$

and $\xi=[x(\pi U/\beta)^{1/2}]/\Delta$ is a dimensionless random magnetic field, scaled by the width Δ of the d level. The expression (4) is obtained for the symmetric case $\epsilon_d=-\frac{1}{2}U$. For $U/\pi\Delta>1$, the potential energy $V(x)$ has the form of Fig. 1, with a symmetrical double minimum at $\xi=\pm\xi_0$. Evaluating the functional integral at one or the other of the minima corresponds to the magnetic solution obtained in Hartree-Fock approximation by Anderson. Since the "magnetic" field $\pm\xi_0$ is nonzero, the d electron has spin-up or spin-down.

Hamann has argued that a certain class of paths for ξ_τ, in which ξ switches between $\pm\xi_0$ are important in the Kondo regime ($\beta T_K\sim 1$), because of their high degeneracy. These physically correspond to repeat spin flips. (See Fig. 2). The energy lowering due to this class of paths is estimated as follows: To flip the d spin, the energy barrier to be overcome is $(V_{\max}-V_{\min})\simeq U$. The "time" required for any such change is $\sim 1/\Delta$, this being the lifetime of the d state. Thus, the partition function, including spin flips, is seen from (2) to be

$$Z=Z_{\rm HF}\sum_\nu \binom{N}{\nu} e^{-\nu U/\Delta}. \tag{5}$$

Here

$$\binom{N}{\nu}$$

is the number of different ways in which ν flips can occur. $N\cong\beta\Delta$ is the maximum number of spin flips possible in a "time" β. Hamann uses Stirling's approximation to find the dominant fluctuation rate $\nu_0=\beta\Delta e^{-U/\Delta}\simeq\beta T_K$ and evaluates its contribution to free energy to be $-T_K$. This energy lowering disappears around the Kondo temperature, because then the dominant fluctuation rate is small, i.e., $\nu_0\sim 1$.

However, the sum in (5) is just a binomial series, and summing it gives

$$Z=Z_{\rm HF}(1+e^{-U/\Delta})^{\beta\Delta}.$$

Thus, the free energy is

$$F=F_{\rm HF}-T_K\,, \tag{6}$$

where we have assumed $e^{-U/\Delta}\ll 1$. This means that for *all* $\beta\Delta\ll 1$ (the condition of validity of the entire discussion), the Hartree-Fock state is unstable, by an energy T_K, against a state in which such repeated spin-flip transitions occur. The entropy and the specific heat associated with this state are zero. It is probably necessary to consider more carefully the transient temperature-dependent effects of the flipping to decide whether it is responsible for the Kondo phenomenon.

Such a consideration may, for example, show that as suggested by Hamann, there is always a fluctuation rate dominating the contribution to free energy and leading to a Kondo effect.