Thermodynamics of the Kondo problem

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A system of nonlinear integral equations which was formulated previously for the Kondo problem is solved numerically. The temperature dependence of the heat capacity and the magnetic susceptibility is calculated for spin $s = 1/2$, $s = 1$, and $s = 3/2$ in the limit of a weak magnetic field. For $s = 1/2$ a comparison is made with the experiments by Felsh (Ce in LaB_6) and the calculations by Wilson *et al.*

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A magnetic impurity in a nonmagnetic metal exhibits a characteristic behavior with decreasing temperature which has been labeled the "Kondo effect."[1] Progress in calculating the specific characteristics of this complex effect can be credited to Wilson, who succeeded in calculating, in particular, the temperature dependence of the magnetic susceptibility.[2] Sometime later, the same method was used to study the Anderson model[3] and to calculate the heat capacity in the Kondo problem[4] on the basis of an equivalent problem involving a resonant level.[5] The complexity of the Wilson method can be seen from both the length of the papers in Refs. 2 and 3 and the comment by Oliveira and Wilkins[4] that calculations of the heat capacity directly for the Kondo problem require 100 times more computer time than for the resonant-level problem and are therefore impracticable.

It was shown comparatively recently that the Kondo problem does allow an exact solution in the sense that it reduces to a system of nonlinear integral equations.[6–8] These equations have been studied analytically in the limits of high and low temperatures.[8] It has also been shown that the solution of these equations simultaneously yields results for all spins s of the impurity.[9]

We have now developed a method for solving these equations numerically. In the present letter we are reporting results calculated on the temperature dependence of the heat capacity $C(T)$, the magnetic susceptibility $\chi(T)$, and the derivative of the heat capacity with respect to the square of the magnetic field, $C^H(T) \equiv \partial C(T,H)/\partial H^2 (H=0) \equiv 1/2T\partial^2\chi(T)/\partial T^2$. The accuracy of our calculations is such that we can make the first comparison with experimental results.

We write the system of equations derived in Ref. 8 in the form

$$\log[\exp\Phi_1 - 1] = -\exp(-\pi x) + s*\Phi_2(x); \qquad s*f(x) \equiv \frac{1}{2}\int_{-\infty}^{\infty} \frac{f(y)dy}{\mathrm{ch}[\pi(x-y)]}, \quad (1)$$

$$\log[\exp\Phi_k - 1] = s*[\Phi_{k-1}(x) + \Phi_{k+1}(x)]; \quad 1 < k < N.$$

$$\log[(\exp\Phi_N + \mathrm{sh}^2 Na)^{1/2} - \mathrm{ch} Na] = s*\Phi_{N-1}(x),$$

where x varies from $-\infty$ to ∞, and $\alpha = H/2T$.

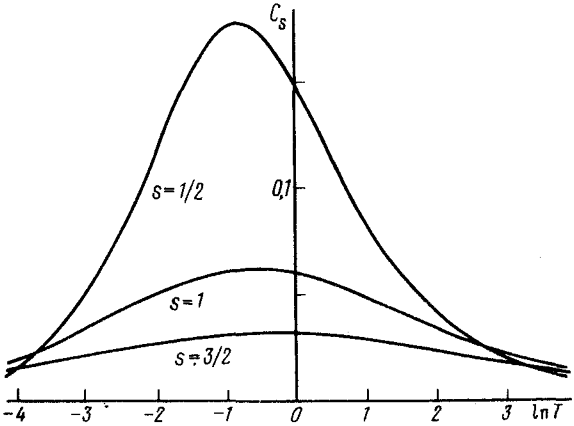

FIG. 1. Temperature dependence of the heat capacity for various spins.

For finite N this system of equations corresponds to the anisotropic *s-d* model, while results for the Kondo problem are obtained in the limit $N\rightarrow\infty$. The function Φ_{2s} determines the free energy for an impurity with a spin s in accordance with the rule[9]

$$F_s(T, H) = -\frac{T}{2}\int_{-\infty}^{\infty}\frac{\Phi_{2s}(x)dx}{\mathrm{ch}(\pi x - \ln T)}. \tag{2}$$

Here and below, the magnetic field H and the temperature T are expressed in a system of units in which $T_K = 1$ (T_K is the Kondo temperature). This scale for T is fixed by the condition that in the limit $T\rightarrow 0$ the susceptibility becomes $\chi_{1/2}(T) = 1/2\pi$ (for the Kondo temperature in the Wilson scale[2] we would then have $T_K^{\infty} = 2\pi\times 0.103$).

We restrict the discussion to weak magnetic fields, $H \ll T$. A linearization of (1) with respect to H^2 through the use of the expansion $\Phi_K = \phi_k + H^2\psi_k$ then leads to a system of equations for ϕ_k which is identical to system (1) with $\alpha = 0$, and it also leads to a system of linear equations for ψ_k. An accuracy sufficient for our purposes (a relative error less than 1%) is achieved with $N = 10$. In this case, 120 iterations were required to find the solution, and the calculations took about 6 h on a Wang 2200-VP minicomputer.

The unknown functions are expressed in terms of ϕ_k and ψ_k in accordance with definition (2); for example,

$$C_s(T) = -\frac{d}{dT}T^2\frac{dF_s}{dT} = \frac{1}{2}\int_{-\infty}^{\infty}\frac{dx}{\mathrm{ch}\pi x}(2t^2 - t - 1)\phi_{2s}(x + \ln T); \quad t \equiv \mathrm{th}\pi x. \tag{3}$$

The functions $C_{1/2}(T)$ and $\chi_{1/2}(T)$ are expanded in powers of T at $T \ll 1$; for example,

$$C_{1/2}(T) = 2T\int_{-\infty}^{\infty}\phi_1(x)\exp(-\pi x)dx - 12T^3\int_{-\infty}^{\infty}\phi_1(x)\exp(-3\pi x)dx. \tag{4}$$

Figure 1 shows the temperature dependence $C_s(T)$ for $s = 1/2$, $s = 1$, and $s = 3/2$. The positions and heights of the maxima of $C_s(T)$ are found to be

$$
\begin{aligned}
s &= 1/2; \quad & T_m &= 0.45; \quad & C_{1/2}(T_m) &= 0.177;\\
s &= 1; \quad & T_m &= 0.53; \quad & C_1(T_m) &= 0.063; \qquad (5)\\
s &= 3/2; \quad & T_m &= 0.56; \quad & C_{3/2}(T_m) &= 0.033.
\end{aligned}
$$

It can be seen in Fig. 1 that at $T \sim 1$ the heat capacity $C_s(T)$ falls off rapidly with increasing s. The curves of $C_s(T)$ intersect in the region $|\ln T| \sim 3$-4, in accordance with the increase in $C_s(T)$ with s at $|\ln T| \gg 1$. The asymptotic behavior $C_{1/2}(T) \simeq 3/4\,\pi^2/\ln^4 T$ (Ref. 8) at $|\ln T| \gg 1$ is apparently applicable only in the very remote region, since even at $\ln T \sim 8$ the heat capacity $C_{1/2}(T)$ is several times smaller than would follow from the asymptotic behavior. An expansion like that in (4) for $H \ll T \ll 1$ yields

$$C_{1/2}(T, H) \simeq \pi/3\, T - 15.4\, T^3 - 0.433 T H^2. \qquad (6)$$

The heat capacity for $s = 1/2$ was calculated previously[4] through the use of the equivalence of the Kondo problem to the problem of a resonant level. From Ref. 4 we have $T_m \simeq 0.67 \cdot 2\pi \cdot 0.103 \simeq 0.43$, which differs from our own results by 4%; the value which we calculate for $C_{1/2}(T_m)$ is ~3% lower than that in Ref. 4.

Figure 2 shows the results for $\chi_s(T)$. At $T \ll 1$ we have

$$\chi_{1/2}(T) = 1/2\pi - 0.433 T^2 = 1/2\pi \left[1 - \frac{T^2}{\theta_0^2}\right]; \qquad \theta_0 \simeq 0.606. \qquad (7)$$

Within the calculation error (~0.5%), our results for $\chi_{1/2}(T)$ agree with those shown in Fig. 17 in Ref. 2. An interpolation of $\chi_{1/2}(T)$ between the points $T = 0.5 T_K^\infty$ and

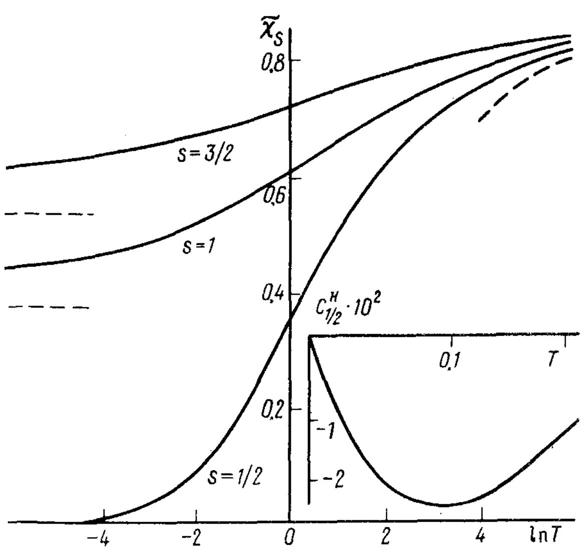

FIG. 2. Temperature dependence of reduced susceptibility $\tilde{\chi}_s(T) \equiv 3T\chi_s(T)/s(s+1)$ ($\tilde{\chi}_s \to 1$ in the limit $T \to \infty$). Dashed curve at right—High-temperature asymptotic behavior[9] $\tilde{\chi}_{1/2}(T)$; dashed lines at left—low-temperature asymptotic behavior, $\tilde{\chi}_s(0) = (s^2 - 1/4)/s(s+1)$; inset—$C^H_{1/2}(T)$ in the range of T where it is negative [$C^H_s(T)$ is always positive for $s > 1/2$].

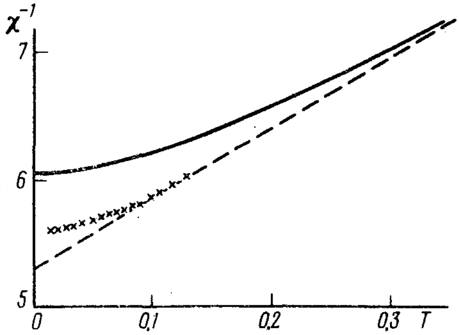

FIG. 3. The dependence $1/\chi(T)$ at low temperatures. Crosses–Experimental results obtained by Felsh[10] for $T < 0.4$ K; dashed line–expression (8).

$T = 4T_K^\infty$ ($T_K^\infty = 2\pi \cdot 0.103 T_K$) yields

$$\chi_{1/2}(T) \approx 0.167(g\mu_B)^2/(T + 0.91T_K) = 0.167(g\mu_B)^2/(T + 1.41T_K^\infty), \tag{8}$$

where we have gone back to the standard units (g and μ_B are the gyromagnetic ratio and the Bohr magneton).

We might note that the interpolation formula (IX.99) in Ref. 2 is written incorrectly: Instead of the number 1.41 [see (8)] there is a 2. This error was repeated in Refs. 3 and 10.

Figure 3 shows the dependence $1/\chi(T)$ for $T \lesssim 0.3$ ($T \lesssim 0.5T_K^\infty$; in this interval, there is a large scatter in the results in Fig. 17 of Ref. 2).

The only experimental results on the Kondo effect which we can compare with the theory are results on the susceptibility; the resistance has not yet been calculated, while the heat capacity has not been measured. Furthermore, it is necessary to restrict the comparison to the spin of ½, since in atoms with $s > ½$ the orbital degeneracy (ignored in the theoretical model) is extremely important. (It is possible that impurities with $s < ½$, which conform to the Kondo model, will be obtained through the interaction of an electron spin with a nuclear spin, as in the case of ytterbium isotopes.[11])

We are thus restricted to a comparison with the experiments by Felsh,[10] who measured the susceptibility of Ce in LaB_6, where the effective spin is $s = ½$ because of the crystal field. For $1/\chi(T)$ Felsh found a linear dependence at 0.3 K $< T <$ 10 K, from which we find, using (8), $T_K = 3.1$ K and $g = 1.6$. The crosses in Fig. 3 show Felsh's data for $T < 0.4$ K, where $1/\chi(T)$ deviates from linearity. At $T < 0.1T_K$ there is a noticeable discrepancy between the calculations and experiments. The same conclusion follows from a comparison with expansion (7), according to which we would have $\theta_0 = 0.606T_K \simeq 1.88$ K, while the experimental results are 1.12 K $< \theta_0 <$ 1.28 K.

In addition to measuring $\chi(T)$ in the limit $H \to 0$, Felsh measured the magnetic moment $M(H)$ at $T \ll T_K$, specifically, at $T \simeq 0.05$ K ($T/T_K \simeq 0.02$). Unfortunately, there are only eight experimental points in Fig. 8 in Ref. 10, but they do show that the $M(H)$ curve as an inflection point at $H \sim 10$ kOe. On the contrary, the expression derived for $M(H)$ in Ref. 9 describes a curve without an inflection point. An estimate of the field $H_K \equiv T_K/g\mu_B$ from the results found above for T_K and g yields $H_K \simeq 28$ kOe. The theoretical $M(H)$ dependence for this H_K runs significantly lower than the experimental points.

It should be concluded that Felsh's experiments agree with the Kondo model in that $\chi(0)$ is finite, and $1/\chi(T)$ is linear in a certain T interval, but quantitatively there is a clear discrepancy. We may hope that the exact solution recently found for the Kondo model will serve as both a stimulus and a criterion for a search for experimental systems that conform to this model.

We note in conclusion that a system of equations for a Heisenberg chain of spins ½, analogous to (1), has been solved previously by Takahashi.[12] Judging from Fig. 1(e) of that paper, where there are no calculation points on three of the four curves for $T \lesssim 0.08$, the approach taken in Ref. 12 is not adequate for going to low temperatures. This difficulty also arose in the early stages of the present study, but we were able to overcome it. The results reported above were obtained through a solution of system (1) over the interval $-4 < x < 4$, which corresponds to the temperature interval $10^{-5} \lesssim T \lesssim 10^5$.

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