COHERENCE EFFECT IN THE TWO-IMPURITY KONDO PROBLEM

M. Lavagna and M. Cyrot

Laboratoire Louis Néel, CNRS, 166X, 38042 Grenoble Cedex, France

(Received 28 March 1985 by E.F. Bertaut)

With the aid of a Brillouin–Wigner expansion, we consider the coherence between two Kondo impurities. By an appropriate summation, we show that the spin–exchange mechanism leads to two different energies (or characteristic temperatures T_K^+ and T_K^-) which are the analogue of the bonding and anti-bonding states of the H_2 molecule. The implication on physical properties (thermal expansion, specific heat) are considered and their temperature variation calculated.

THE MAGNETISM of an impurity depends on the relative importance of its characteristic time scales. A conduction electron feels the well-defined moment of the impurity only if the time $\hbar/T$ taken by the thermal electron wave packet to sweep by the impurity is smaller than the typical flipping time of the impurity spin $\tau_S \sim \hbar/T_K$. This problem can now be resolved either by semi-phenomenological model [1] or by exact calculation.

The question then arises concerning the possibility of a coherence between the spin-flip of two Kondo impurities. This problem has been of interest for years. In the first models [2], an interaction between impurities of a Ruderman–Kittel type was added although it is in principle contained in the starting Hamiltonian. In fact, the exchange interaction leads not only to the individual Kondo effect T_K but also to the Ruderman–Kittel interaction I . The fundamental problem is the comparison of these two energies. If $T_K \gg |I|$, each impurity forms a Kondo singlet. In the inverse limit, i.e. $|I| \gg T_K$, the coupling between impurities locks them either in a ferromagnetic or an anti-ferromagnetic state. In the ferromagnetic case, as temperature is lowered, the problem is initially equivalent to a Kondo effect of spin one. Using a renormalisation technique, Jayaprakash *et al.* [3] have shown that this is then followed by a two-stage Kondo effect which successively works its way through the odd and even channels of the conduction band. The physical significance of this two-steps process and its implications remain however rather unclear. Our aim, by using a completely different approach, which we first develop, is to show that these two characteristic energies are linked to the coherence effect between both impurities. Its effect on the physical properties will be clearly shown.

Jayaprakash *et al.* started with the Kondo model for two impurities. In order to study the coherence

effect, we start from the more general Anderson model which reduces to the previous one via the Schrieffer–Wolff transformation. However, the Anderson model accounts for the physics involved more completely. Our starting Hamiltonian is therefore:

$$H = H_0 + H_v,$$

$$H_0 = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{im} E_d d_{im}^\dagger d_{im} + U \sum_i n_{i\uparrow} n_{i\downarrow},$$

$$H_v = \sum_{ikm\sigma} V_{kd} \exp(ik \cdot R_i) d_{im}^\dagger c_{k\sigma} + h.c. \quad (1)$$

in the usual notation where $c_{k\sigma}^\dagger$ creates a conduction–electron of spin σ , and $d_{im}^\dagger$ creates an f -electron at site i with orbital index m .

Difficulties arise in treating H_v by a perturbation technique since Wick’s theorem does not apply due to the presence of the final term in the expression for H_0 . Using a regularisation procedure as developed by Keiter and Kimball [4], the grand partition function Z (compared to the non-perturbed Z_0) can be written:

$$Z/Z_0 = \sum_i n_i \exp(-\beta E_i), \quad (2)$$

where n_i are the occupation probabilities of the non-perturbed states $|i\rangle$ of energies ϵ_i and where the E_i are determined from the self-consistent Brillouin–Wigner equation:

$$E_i = \epsilon_i + \langle i|V|i\rangle + \langle i|VG_0PV|i\rangle + \dots \quad (3)$$

($G_0 = 1/(E_i - H_0)$ and P is the projection operator on the states orthogonal to $|i\rangle$).

First, we will show how to apply this formalism to the case of a single impurity. For the Kondo limit, one can restrict the Anderson Hamiltonian to the infinite U case which avoids the states of double

d -occupancy. Figure 1 shows the 2nd and 4th-order Brillouin-Wigner corrections ΔE to the non-perturbed state $d^+|F\rangle$ of energy $E_d(|F\rangle)$ is the conduction Fermi sea). If N is the orbital degeneracy, we have:

$$\Delta E = E - E_d = \sum_k \frac{(1-f_k)|V_{kd}|^2}{E - \epsilon_k} + 2N \sum_{kk'} \frac{(1-f_k)f_{k'}|V_{kd}|^2|V_{k'd}|^2}{(E - \epsilon_k)^2(E - E_d - \epsilon_k + \epsilon_{k'})} + \dots \quad (4)$$

We sum up the series as follows:

$$\Delta E = \sum_k \frac{(1-f_k)|V_{kd}|^2}{(E - \epsilon_k) - 2N \sum_{k'} \frac{f_{k'}|V_{k'd}|^2}{\Delta E - \epsilon_k + \epsilon_{k'}}} \quad (5)$$

At zero temperature, for a rectangular density-of-states ρ of width $2D$, we have in the Kondo limit ($E_d \gg \Pi|V|^2\rho$):

$$\Delta E = -(\gamma D/2) \exp(E_d/2NV^2\rho). \quad (6)$$

(γ is the Euler member).

As expected, the energy of the ground state is lowered by T_K . At finite temperature, the denominator of (5) expressed as $E_d + 2NV^2\rho\{\ln D/2\pi T - \psi[0, 5 + i(\Delta E - \epsilon)/2\pi T]\}$ is equal to zero (leading to a divergence of ΔE) at a temperature of order T_K . At last, this method leads to a correct evaluation of the physical properties: in particular, the specific heat given by $-T\partial^2\Delta E/\partial T^2$ varies as $4\pi^2 T/3T_K$.

In a previous work, Ramakrishnan and Sur [5] correctly treated the mixed-valent impurity considering only 2nd-order corrections, but did not succeed in describing the Kondo regime. Here we show that a summation including 4th-order terms is sufficient to describe the Kondo effect. This is not surprising as this term already contains the spin-flip process (cf. Fig. 1: choice of the σ -spin in the intermediate loop) which is the very essence of the Kondo mechanism.

We now consider the case of two impurities a distance R apart. The non-perturbed states of energy $2E_d$ can be classified according to their parity with the spin-exchange:

$$d_{1\uparrow}^+ d_{2\uparrow}^+ |F\rangle; (\sqrt{2})^{-1}(d_{1\uparrow}^+ d_{2\downarrow}^+ + d_{1\downarrow}^+ d_{2\uparrow}^+) |F\rangle;$$

$$d_{1\downarrow}^+ d_{2\downarrow}^+ |F\rangle: \text{triplet},$$

$$(\sqrt{2})^{-1}(d_{1\uparrow}^+ d_{2\downarrow}^+ - d_{1\downarrow}^+ d_{2\uparrow}^+) |F\rangle: \text{singlet}.$$

Figure 2 shows the addition 4th-order diagram. At $T = 0$, ΔE satisfies the following equation:

$$\Delta E = 2V^2 \sum_k \frac{1}{E - E_d - \epsilon_k} + \frac{4NV^4}{E_d^2} \sum_{kk'} \frac{1}{\Delta E - \epsilon_k + \epsilon_{k'}} \quad (7)$$

The second term describes the spin-flip of an isolated impurity, and the third one the spin-exchange between both impurities. This one contributed with a plus or minus sign depending on whether the non-perturbed states are symmetrical (or anti-symmetrical) with the spin-exchange, i.e. triplet (or singlet). By putting $\Delta E = 0$ in the denominators, the two terms give the usual self-energy and exchange coupling of *RKKY*-type [6]. The presence of ΔE , which is characteristic of the Brillouin-Wigner perturbations, makes the self-energy term correspond to the individual Kondo effect (see above). By extension, the motion related to the *RKKY* exchange interaction will be called the "collective Kondo effect"; it is directly related to a swapping mechanism between both spins.

(i) limit $k_F R \ll 1$ ($I \gg T_K$)

In this limit, the summation can be performed in a similar way to the single impurity case. It gives:

$$\Delta E = -\gamma D \exp[E_d/2V^2\rho(N \pm \sin k_F R/k_F R)]. \quad (8)$$

The sign plus and minus are respectively related to the triplet and singlet states.

For $N=1$, we obtain the two characteristic temperatures T_K^+ and T_K^- derived by Jayaprakash *et al.* [3] using scaling techniques. However, the physical meaning of these two temperatures is clearly shown here since they are related to coherence effects in the many-impurity problem. In the limit $1/N \rightarrow 0$, the coherence effects become negligible and the Kondo lattice reduces to a collection of single impurities as expected by Coleman [7] and Rasul *et al.* [8]

(ii) limit $k_F R \gg 1$ ($I \ll T_K$)

The contribution of the last term in (7) can be evaluated *a posteriori* in the effective mass approximation. One finds:

$$\Delta E = -2T_K \mp I(R) \cos\left(2\pi \frac{R}{v_F} \frac{\Delta E}{h}\right), \quad (9)$$

where $I(R)$ is the usual *RKKY* interaction and v_F is the Fermi velocity.

This equation provides a clear interpretation of the relevant time scales. $\tau_R = R/v_F$ is the running time of a conduction-electron from one impurity to the other, and $\tau_S = h/\Delta E$ is the characteristic flipping time. If the ratio of the two times is an integer, the conduction-electron emitted by the first impurity arrives just at the right time when the second impurity is about to spin-flip: the coherence is maximum and $\Delta E = -2T_K \mp I(R)$. Generally, the coefficient of $I(R)$ can take any value

Fig. 1. 2nd and 4th-order Brillouin-Wigner diagrams for the single Anderson (U_∞) impurity. The straight and dotted lines represent respectively the $c^+|F\rangle$ and $d^+|F\rangle$ states.

Fig. 2. Additional 4th-order Brillouin-Wigner diagram for the two Anderson (U_∞) impurities. $\square$ designs the initial states.

between -1 and $+1$ corresponding to all possible stages of the coherence.

Figure 3 shows the schematic variation of T_K^+ and T_K^- with R : both energies tend to T_K at $k_F R \gg 1$ with oscillations resembling the RKKY ones.

There is a direct analogy with the hydrogen molecule treated in an LCAO approximation. Instead of a direct term of electronic transfer, the intersite correlations act by a more complex mechanism of Kondo exchange as described above. Nevertheless, the physics remains the same: starting from two individual Kondo singlet (instead of two atomic levels), there is the formation of bonding and anti-bonding states, respectively related to a triplet i.e. T_K^+ , and a singlet i.e. T_K^- as shown in Fig. 4.

Contrary to the widespread idea which relates the upper characteristic temperature to T_K of a single impurity, and the lower one to a coherence temperature (by analogy with the Stoner and the magnetic order temperatures in itinerant magnetism), it appears here that both characteristic temperatures are born of the coherence, the connection being bonding or anti-bonding according to the parity with the spin-exchange.

The thermodynamical properties can be obtained by a direct generalisation of equation (7) to finite temperature:

$$\Delta E = \sum_k \frac{(1 - f_k) |V_{kd}|^2}{E_d - 2 \sum_{k'} \frac{f_{k'} |V_{k'd}|^2}{\Delta E - \epsilon_k + \epsilon_{k'}} \left(N \pm \cos \mathbf{k} \cdot \mathbf{R} \frac{\sin k'R}{k'R} \right)} \quad (10)$$

For $T \gg T_K^+$, both bonding and anti-bonding states melt together into the single impurity level: the

Fig. 3. Schematic variation of T_K^+ and T_K^- with the distance R .

Fig. 4. Formation of the bonding and anti-bonding states in the two-impurity Kondo problem.

system is completely incoherent and the properties are characteristic of an isolated impurity. The coherence then progressively sets up when decreasing temperature. At very low temperature, only the bonding triplet is occupied and the properties are characteristic of this state ($C_V = 4\pi^2 T / 3T_K^+$). For fairly low temperatures, the problem is reduced to a two-level system whose splitting $\eta = T_K^+ - T_K^-$ is nearly invariant with T . The electronic contribution to the specific heat passes through a maximum at a temperature $T_{\max} \sim \eta/3$ typical of the coherence.

Direct evidence of the two characteristic energies has been given in CeAl_3 by a study [9] of the thermal expansion α . The change in sign of α with temperature leads to the existence of two temperatures whose variations with pressure are inverse to each other as predicted in Figure 3.

In conclusion, we have shown that the coherence effect leads to two characteristic energies which permit us to explain the temperature behaviour of various physical quantities. The problem of the generalisation of this results to the case of many Kondo impurities remains. It is quite probable that the gap in the density-of-states pointed out some years ago by Lacroix and Cyrot [10] for the Kondo lattice separates analogous bonding and anti-bonding states.

Acknowledgements — We are indebted to B. Barbara and J. Flouquet whose physical intuition has been of the greatest interest in the work.

REFERENCES

1. P. Nozières, *J. Physique* **39**, 1117 (1978).
2. K. Matho & M.T. Béal-Monod, *Phys. Rev.* **B5**, 1899 (1972).
3. C. Jayaprakash, H.R. Krishna-Murthy & J.W. Wilkins, *Phys. Rev. Lett.* **47**, 737 (1981).
4. H. Keiter & J.C. Kimball, *Int. J. Magn.* **1**, 233 (1971).
5. T.V. Ramakrishnan & K. Sur, *Phys. Rev.* **B26**, 1798 (1982).
6. See for example, D.C. Mattis, *The Theory of Magnetism*, (Edited by Springer-Verlag), p.231 (1981).
7. P. Coleman, *Phys. Rev.* **B28**, 5255 (1983).
8. J.W. Rasul, N. Read & A.C. Hewson, *J. Phys.* **C16**, L1079 (1983).
9. M. Ribault, A. Benoit, J. Flouquet & J. Palleau, *J. Physique* **40**, 413 (1979).
10. C. Lacroix & M. Cyrot, *Phys. Rev.* **B20**, 1969 (1979).