Magnetic exchange interactions in cerium compounds

César Proetto* and Arturo López

Centro Atómico Bariloche† and Instituto Balseiro,‡ 8400 S.C. de Bariloche, Argentina

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Exchange interactions induced by hybridization of f levels to conduction-electron states in some Ce compounds are considered in detail. The usual treatment in which these interactions are derived through a second-order canonical transformation does not include all contributions. Using a free-electron conduction band, closed expressions are obtained for the range function, which approaches the Ruderman-Kittel-Kasuya-Yosida (RKKY) function asymptotically. For nearest and next-nearest neighbors the interactions are dominated by a new range function which differs from the RKKY function.

The magnetic interactions among Ce ions have been considered in a number of recent papers.[1-5] The effective exchange coupling which is thought to explain[6,7] the complex magnetic orderings of several Ce compounds, such as CeSb and CeBi, arises from the hybridization between localized and conduction-electron states. These interactions which are fourth order in the hybridization matrix element V can give rise to anisotropic alignments.[1,2] They were first considered by Coqblin and Schrieffer,[8] who derived them from an Anderson model Hamiltonian by means of a canonical transformation.[9] This procedure gives a range function of the Ruderman-Kittel-Kasuya-Yosida (RKKY) type.

In this paper we show that this approach does not include all fourth-order contributions to the exchange energy and that the correct expression, which requires a fourth-order canonical transformation,[10] takes into account both conduction-electron spin polarization effects and charge fluctuation contributions. The latter, which are clearly depicted in the perturbation diagrams drawn in Ref. 11, become increasingly important as the localized level approaches the Fermi energy.

As it turns out, the full expression for the range function can be explicitly evaluated using a free-electron-like conduction band. Our results show that the range function approaches the RKKY function asymptotically but that the two functions get out of phase at small distances. This means that any fit to experimental data should take this refined range function into account,[3] especially for nearest neighbors.

The model Hamiltonian we have in mind is a many-site Anderson model and has been used to deal with intermediate-valence systems in Refs. 4 and 5. The situation of the Ce^{3+} ions we are interested in is not fully a mixed-valent situation so that perturbation theory should be applicable. Our explicit expression being strictly fourth order, can be used to check the results of more sophisticated approaches. In fact we

can say that the results of Ref. 4 agree qualitatively with ours, whereas the spin susceptibility obtained in Ref. 5, when considered to order V^4, gives a rather different looking Fourier transform.

The equivalence between the single-site Anderson model and the Kondo Hamiltonian, shown by Schrieffer and Wolff (SW) to order V^2, has led many authors to think that the effective intersite interaction in a many-site model (order V^4) follows from second-order perturbation theory applied to the effective Hamiltonian which is obtained after the canonical transformation. The correct result for the fourth-order intersite exchange as calculated using perturbation theory in Ref. 11 can be obtained within the canonical transformation scheme only after one has performed a fourth-order SW transformation. This procedure[10] leads to a fourth-order effective Hamiltonian containing only even terms in V, of the form $H_{eff} = H^{(0)} + H^{(2)} + H^{(4)} + \cdots$, where the matrix elements of $H^{(2)}$ and $H^{(4)}$ between eigenstates of $H^{(0)}$ are

$$\langle a | H^{(2)} | b \rangle = \frac{1}{2} \sum_c V_{ac} V_{cb} (D_{ac} - D_{cb}) \ ,$$

$$\langle a | H^{(4)} | b \rangle = \frac{1}{8} \sum_{cde} V_{ac} V_{cd} V_{de} V_{eb}$$

$$\times (D_{ac} D_{cd} D_{de} - D_{cd} D_{de} D_{eb} \qquad (1)$$

$$+ 3 D_{ac} D_{de} D_{eb} - 3 D_{ac} D_{cd} D_{eb}) \ ,$$

where $D_{ij} = (E_i - E_j)^{-1}$ and $V_{ab} = \langle a | V | b \rangle$.

The correct procedure to obtain the intersite exchange interactions consists of calculating all fourth-order contributions from H_{eff}, that is

$$E^{(4)} = \sum_d H_{id}^{(2)} H_{df}^{(2)} D_{id} + H_{if}^{(4)} \ , \qquad (2)$$

where $|i\rangle$ and $|f\rangle$ are two degenerate ground states of $H^{(0)}$ differing in the z projection of the angular

momenta of two sites. Inserting (1) into (2) one obtains the conventional fourth-order perturbation theory result,

$$E^{(4)} = \sum_{cde} V_{ic} V_{cd} V_{de} V_{ef} D_{ic} D_{id} D_{ie} \ .$$

When applied to the Ce hybridization Hamiltonian of Ref. 8 this procedure gives a coupling constant between magnetic ions of the form[2] $E^{MM'}(R)$ $= J(R) G(M,M')$ where the only nonvanishing G's are M, $M' = \pm \frac{1}{2}$. The range function is given by

$$J(R) = \frac{1}{N} \sum_q e^{i\vec{q} \cdot \vec{R}} J(q)$$

$$= \frac{V^4}{N} \sum_{\vec{q}} e^{i\vec{q} \cdot \vec{R}} \sum_{\vec{q}} \frac{(1 - f_{\vec{k}})}{(E - \epsilon_{\vec{k}})^2}$$

$$\times \left[\frac{f_{\vec{k}+\vec{q}}}{\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}} + \frac{1 - f_{\vec{k}+\vec{q}}}{\epsilon_{\vec{k}+\vec{q}} - E} \right] \ ,$$

(3)

where $f_{\vec{k}}$ is the zero-temperature Fermi function. The first term in the large parentheses contains contributions from $H^{(2)}$ and from $H^{(4)}$ which involve spin-flip scattering of a conduction electron at some intermediate step and therefore give rise to an exchange interaction between localized ions mediated by the conduction-electron spin polarizability. The approximation of taking the factor $(E - \epsilon_k)^{-2}$ out of the summation makes this term look identical with the result of considering only the first term in (2) in which a similar approximation is applied. The second term in the large parentheses contains contributions that come only from $H^{(4)}$ which, at some intermediate step, have simultaneous promotion of two localized electrons to the conduction band.

If we assume a free-electron-like ϵ_k, $J(q)$ in (3) can be evaluated analytically without any approximation giving

$$J(q) = \frac{\Gamma^2}{4\pi^2 \epsilon_F \rho_0} \frac{1}{q^2 - 4k_0^2}$$

$$\times \left[\frac{2}{k_0} \ln \left| \frac{k_F + k_0}{k_F - k_0} \right| - \frac{q^2 - 4k_F}{q(k_0^2 - k_F^2)} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| \right] \ ,$$

(4)

where ρ_0 is the density of states at the Fermi energy $\epsilon_F = k_F^2/2m$, the resonant level width $\Gamma = \pi \rho_0 V^2$ and $E = k_0^2/2m$. The function $J(q)$ is shown in Fig. 1 of Ref. (10) where it is seen that it differs markedly from the Lindhard function. The expression of $J(q)$ for E below the bottom of the conduction band can be readily obtained from (4) replacing k_0 by ik_0. The range function can be obtained in both cases. For $E > 0$ (above the bottom of the conduction band) it reads
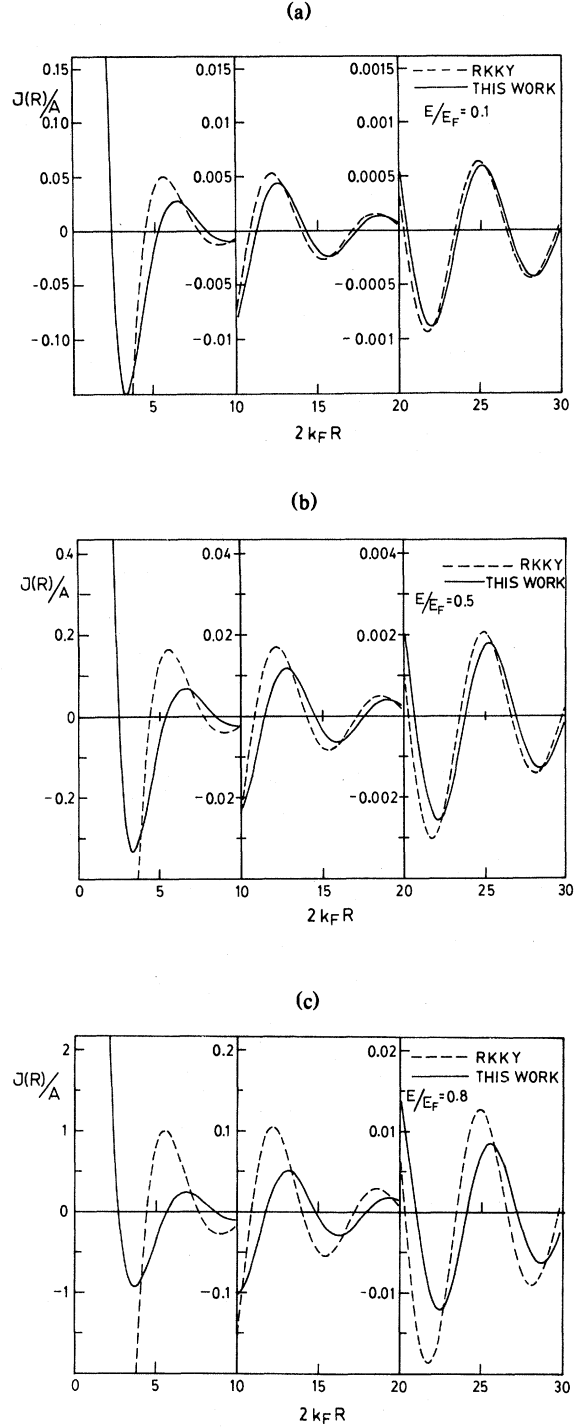

FIG. 1. Range function $J(R)$ and comparison with RKKY function for (a) $E/\epsilon_F = 0.1$, (b) $E/\epsilon_F = 0.5$, and (c) $E/\epsilon_F = 0.8$. Notice the change in scale for each figure. It is seen that the difference between the improved range function and the RKKY behavior increases as E approaches the Fermi energy. The constant $A = \Gamma^2/\rho_0 \epsilon_F^2$.

$$J(R) = \frac{-\Gamma^2}{\rho_0 \epsilon_F^2} \left[\frac{\sin(2k_F R)}{R^2(k_0^2 - k_F^2)} + \frac{\cos(2k_0 R)}{k_0 R} \{ \text{Ci}[2(k_F - k_0)R] - \text{Ci}[2(k_F + k_0)R] \} \right.$$

$$\left. - \frac{\sin(2k_0 R)}{k_0 R} \{ \text{si}[2(k_F - k_0)R] + \text{si}[2(k_F + k_0)R] \} \right] , \tag{5}$$

where si(x) and Ci(x) are the integral sine and cosine functions. The asymptotic behavior of the function in the large parentheses is as

$$\frac{1}{(E - \epsilon_F)^2} \left[\frac{\cos^2 k_F R}{(2k_F R)^3} - \frac{E + 3\epsilon_F}{E - \epsilon_F} \frac{\sin(2k_F R)}{(2k_F R)^4} \right]$$

which shows that the closer the localized level lies to the Fermi energy the further out one has to go in order to recover the RKKY behavior. For small R the dominant term is the first one in the large parentheses in (5),

$$\frac{1}{(E - \epsilon_F)^2} \frac{\sin(2k_F R)}{(2k_F R)^2} ,$$

which becomes more important as E approaches the Fermi energy. This behavior is similar to that obtained in Ref. 4.

Figure 1 gives $J(R)$ for (a) $E/\epsilon_F = 0.1$, (b) $E/\epsilon_F = 0.5$, and (c) $E/\epsilon_F = 0.8$. It is seen that in case (a) there is no appreciable difference between the full-range function and the RKKY approximation. Cases (b) and (c) show how the differences become more marked as E approaches the Fermi energy.

With $\Gamma \cong 200$ K and $\epsilon_F \cong 10^4$ K, we see that case (c), which might be the situation for some Ce compounds, lies well within the range of validity of perturbation theory. It is seen that for distances where one expects the nearest magnetic neighbors to sit, $2k_F R \cong 10$, the refined range function cannot be approximated by the RKKY function.

Application to specific examples is beyond the scope of this paper but we hope that thermodynamic models for the transitions in Ce compounds[1-3] will benefit from refined calculations based on these results. In particular we want to point out that the phase boundaries determined in Ref. 3, as mentioned by the authors, could not be fitted using an RKKY range function for the nearest neighbors.

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‡Comisión Nacional de Energía Atómica and Universidad Nacional de Cuyo.
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