Role of the $d - f$ Coulomb interaction in intermediate valence and Kondo systems: a numerical renormalization group study

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Using numerical renormalization group method the temperature dependences of the magnetic susceptibility $\chi(T)$ and specific heat $C(T)$ are obtained in the single-impurity Anderson model with inclusion of the $d - f$ Coulomb interaction. It is shown that the exciton effects owing to this interaction can change considerably the dependence $C(T)$ in comparison with the standard Anderson model at not too low temperatures, whereas the dependence $\chi(T)$ remains universal. The renormalization of the effective hybridization parameter and $f$-level position, which is connected with the $d - f$ interaction, is calculated, a satisfactory agreement with the Hartee-Fock approximation being derived.

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There is an interesting class of the $4f$-electron compounds demonstrating intermediate valence (IV) of rare earth elements (usually between 2+ and 3+) in a number of properties, e.g., in the lattice constants (which are intermediate between those for isovalent compounds with di- and trivalent ions), core-level spectra (which are mixtures of the spectra for di- and trivalent ions with comparable weights), and many others [1,2,3,4]. Heavy fermion (HF) compounds [5] form another important class of the $f$-electron systems with anomalous properties. For the HF metals it is commonly accepted now they are frequently considered also as the Kondo lattices, which means that the small energy scale in the electron properties is the Kondo temperature $T_K$, i.e. the width of the Kondo resonance owing to spin-dependent scattering of conduction electrons by $f$-electron centers [4]. As for the IV compounds, they are frequently considered also as the Kondo lattices, but just with higher $T_K$ (see, e.g., Ref.4).

Actually, such a consideration is not quite accurate since, besides the spin (“Kondo”) fluctuations, valence or charge fluctuations should be also treated in such systems. They are determined in part by the Coulomb repulsion $G$ between conduction and localized electrons (the Falicov-Kimball interaction [6]). Taking into account the $d - f$ interaction together with the hybridization processes it is possible to describe the IV state as a kind of exciton condensation [3,4]. Recently, the method of first-principle calculations of the parameter $G$ has been proposed, and it was demonstrated that an account of this interaction is necessary to describe properly the equation of state for IV phase of Yb under pressure [14].

At present, the usual Kondo effect is theoretically studied thoroughly within the $s - d$ exchange (Kondo) and Anderson models. Moreover, in the one-impurity situation the exact numerical (renormalization group) [11,12] and analytical Bethe-ansatz [13,14] solution of this problem is obtained. Universal curves describing the behavior of thermodynamic properties were obtained for the Kondo [11,12] and intermediate valence [12] regimes, which permit a detailed comparison with experimental data on anomalous $f$-systems. At the same time, in the presence of both the $s - d$ exchange and Coulomb interaction such a detailed information is absent.

Formally, the charge fluctuations can be also described in terms of a pseudo-Kondo effect, the states with (without) $f$-hole being considered as pseudospin-up (down) states, respectively [13,16]. It is the degeneracy of quantum states for a scattering center which is important for the formation of the Kondo resonance [17]. In the IV case the divalent and trivalent states are degenerate by definition, thus this analogy is not surprising. Therefore it is natural to consider the Kondo phenomenon for the IV compounds taking into account both spin and charge fluctuations, or, equivalently, both the “Kondo” and exciton (“Falicov-Kimball”) effects. Since there is no clear demarcation between the IV and Kondo systems, it can be supposed that the exciton effects are relevant also for the latter case. Recent analysis of the interplay of the true Kondo and pseudo-Kondo (exciton) effects by the “poor-man scaling” approach [19,20] has demonstrated an essential modification of the low-energy (infrared) behavior in comparison with pure cases of the Anderson model and Falicov-Kimball (“resonant level”) models. However, this approach can give only a qualitative insight in the properties of the system. Here we investigate the effects of this interplay by applying numerical renormalization group (NRG) approach [11,12].

We proceed with the Hamiltonian of the asymmetric Anderson model with inclusion of the Falicov-Kimball interaction (on-site $d - f$ Coulomb repulsion $G$),

$$
\mathcal{H} = \sum_{k\sigma} t_{k\sigma} c_{k\sigma}^\dagger c_{k\sigma} + \sum_{\sigma} \left[ E_f f_{\sigma}^\dagger f_{\sigma} + V \left( c_{\sigma}^\dagger f_{\sigma} + f_{\sigma}^\dagger c_{\sigma} \right) \right] + G \sum_{\sigma} f_{\sigma}^\dagger f_{\sigma} c_{\sigma}^\dagger c_{\sigma},
$$

where the on-site $f - f$ Coulomb interaction $U$ is put to
infinity, so that the doubly occupied states are forbidden; \( f_{\uparrow}^\dagger f_{\downarrow} = |\sigma\rangle \langle \sigma| \) are the Hubbard operator \(|\sigma\rangle \langle \sigma|\) and \(|\sigma\rangle\) are single-occupied and empty site states); we neglect for simplicity \( k \)-dependence of the hybridization matrix element \( V \).

We use the standard NRG method for the Anderson model \[12\] with some important modifications. At each NRG step one obtains a finite-resolution spectrum which is truncated owing to neglect of high-energy states \[11\]. Thus we have a sequence of truncated energy spectra, the level resolution decreasing with increasing iteration step. An automatic choose of an optimal temperature for each NRG step is a main distinctive feature of our calculations. Indeed, we cannot perform calculations of thermodynamic averages at too low temperatures since the discreteness of energy level leads to an uncontrollable error. On the other hand, at sufficiently high temperatures the high-energy states neglected can give an appreciable contribution to the partition function, which is proportional to the factor of \( \exp (-E/k_B T) \). Therefore we estimate the contribution of the upper states and increase the temperature to make their contribution to be equal to the error chosen.

We have used a rectangular conduction electron density of states with the half-bandwidth of \( D = 1 \). The magnetic susceptibility, specific heat, and impurity level occupation number \( n_f \) (valence) were calculated. Computational results are shown in the figures. Figs. \[1\] and \[2\] demonstrate a crossover from a two-maximum to one-maximum temperature behavior of specific heat. It should be noted that such a crossover takes place also in the standard Anderson model with changing \( E_f \) \[21\].

**TABLE I:** The dependences of the Kondo temperature \( T_K \) and impurity occupation number \( n_f \) on \( G \) for \( V = 0.1 \); the Hartree-Fock values \( V^{HF} \) and \( E^{HF} \) are defined by Eq. \[2\]. The quantities \( E_f^{(G=0)} \) and \( V^{(G=0)} \) are discussed in the text.

| \( E_f \) | \( G \) | \( k_BT_K \) | \( n_f \) | \( E^{(G=0)} \) | \( E^{HF} \) | \( V^{(G=0)} \) | \( V^{HF} \) |
|---|---|---|---|---|---|---|---|
| -0.06 | 0 | 7.439 \times 10^{-5} | 0.875 | -0.06 | -0.06 | 0.1 | 0.1 |
| -0.06 | 0.01 | 2.290 \times 10^{-4} | 0.825 | -0.049 | -0.050 | 0.1 | 0.1010 |
| -0.06 | 0.02 | 6.592 \times 10^{-4} | 0.750 | -0.04 | -0.040 | 0.1015 | 0.1024 |
| -0.06 | 0.03 | 1.703 \times 10^{-3} | 0.651 | -0.031 | -0.0316 | 0.103 | 0.1041 |
| -0.06 | 0.04 | 3.714 \times 10^{-3} | 0.542 | -0.022 | -0.021 | 0.104 | 0.1059 |
| -0.06 | 0.05 | 6.798 \times 10^{-3} | 0.443 | -0.013 | -0.011 | 0.105 | 0.1078 |
| -0.14 | 0 | 1.813 \times 10^{-3} | 0.965 | -0.14 | -0.14 | 0.1 | 0.1 |
| -0.14 | 0.02 | 2.195 \times 10^{-3} | 0.955 | -0.12 | -0.1207 | 0.1013 | 0.1013 |
| -0.14 | 0.05 | 6.452 \times 10^{-4} | 0.928 | -0.092 | -0.0934 | 0.105 | 0.1039 |
| -0.14 | 0.1 | 6.416 \times 10^{-4} | 0.763 | -0.048 | -0.0500 | 0.11 | 0.1126 |
| -0.14 | 0.15 | 1.005 \times 10^{-3} | 0.402 | -0.01 | 0.0008 | 0.116 | 0.1250 |
| -0.14 | 0.2 | 2.882 \times 10^{-2} | 0.220 | 0.027 | 0.0535 | 0.12 | 0.1316 |
| -0.25 | 0 | 1.115 \times 10^{-3} | 0.865 | -0.07 | -0.0947 | 0.111 | 0.1219 |
| -0.25 | 0.23 | 6.430 \times 10^{-4} | 0.771 | -0.048 | -0.0706 | 0.11 | 0.1311 |
| -0.25 | 0.3 | 9.369 \times 10^{-3} | 0.443 | -0.013 | 0.008 | 0.12 | 0.1528 |

**FIG. 1:** Effective Curie constant \( k_BT\chi(T)/(g\mu_B)^2 \) and specific heat \( C(T)/k_B \) for \( E_f = -0.14, V = 0.1 \). Solid line corresponds to finite \( G \), and the dotted line to the case \( G=0 \) with parameters \( E_f^{(G=0)} \) and \( V^{(G=0)} \) (see their values in Table I). Below \( T_K \) we have the universal Wilson curve.

**FIG. 2:** The dependences of \( n_f(\bullet) \) and \( T_K(\circ) \) on \( G \). \( (E_f = -0.14, V = 0.1) \).
One can see that the temperature dependence of the magnetic susceptibility is always similar to that in the Anderson model without $d-f$ Coulomb interaction. At the same time, the specific heat behavior can be considerably different, especially for sufficiently large $G$.

Similar to Ref. 12, the Kondo temperature $T_K$ was determined from the condition $k_B T \chi(T)/\langle g\mu_B \rangle^2 = 0.0701$ at $T = T_K$. The dependence of the ground-state occupation number of $f$-level $n_f$ and the Kondo temperature on $G$ are illustrated by Fig. 2. A more detailed information is presented in the Table I.

There is an important question whether the effects of the $d-f$ Coulomb interaction can be described just by the renormalization of the parameters usual Anderson Hamiltonian (without the Falicov interaction) or they can result in qualitatively new effects. To investigate this problem we defined the effective hybridization parameter $V(G=0)$ and the effective position of the $f$-level, $E_f^{(G=0)}$, as the parameters of the standard Anderson model (with $G = 0$) that gives the same values of $n_f$ (at zero temperature) and the Kondo temperature, as our Hamiltonian (1). A comparison of our computational results with those for the model with $G = 0$ and with the effective parameters introduced above shows (Fig. 3 and 4) that for the susceptibility the effects of $G$ in the temperature dependence can be completely eliminated by the parameter renormalization. At the same time, for the specific heat this is, generally speaking, possible for low enough temperatures, of order of $T_K$ or below. This means that the Wilson ratio is not influenced by the $d-f$ interaction at $T \leq T_K$, but its “temperature dependence” at higher temperatures is different for the cases $G = 0$ and $G \neq 0$. Of course, it is not surprising that the $d-f$ Coulomb (but not exchange) interaction is less important for the magnetic susceptibility (which is connected only with spin degrees of freedom) than for the specific heat.

FIG. 3: The same data as in Fig. 1 for $E_f = -0.25, V = 0.1$.

FIG. 4: Effective Curie constant $k_B T \chi(T)/(g\mu_B)^2$ and specific heat $C(T)/k_B$ for $E_f = -0.3, V = 0.1, G = 0.3$ (solid) and $E_f^{(G=0)} = -0.0475, V^{(G=0)} = 0.109, G = 0$ (dotted). For these parameter sets we have $n_f = 0.77$. Insert shows the dependence $V^{HF}(T)$ according to Eq. 4.

FIG. 5: Effective Curie constant $k_B T \chi(T)/(g\mu_B)^2$ and specific heat $C(T)/k_B$ for $E_f = -0.5, V = 0.1, G = 0.4$ (solid) and $E_f^{(G=0)} = -0.14, V^{(G=0)} = 0.1, G = 0$ (dotted). For these parameter sets we have $n_f = 0.96$ at $T = 0$. Insert shows the dependence $V^{HF}(T)$.
(which characterizes both spin and charge fluctuations).

It is interesting to compare our renormalized model parameters with their values from the unrestricted Hartree-Fock approximation \[ \text{(2)}. \]

\[
E_{HF}^f = E_f + G \sum_{\sigma} \langle c_\sigma^\dagger c_\sigma \rangle, \quad V_{HF}^f = V - G \langle c_\sigma^\dagger f_\sigma \rangle.
\]

A comparison of the parameters of the effective Anderson model and of the Hartree-Fock values (2), which are presented in the Table I, shows that this approximation works well enough, at least for not too large \(d-f\) interaction \((G < 0.25)\). Thus corresponding Coulomb correlation effects are not important. This justifies the implementation of the Hartree-Fock approximation into the first-principle electronic structure calculations in Ref. 10.

The dependences \(V_{HF}^f(T)\) according to Eq. (2) are shown in inserts in Figs. 4, 5. One can see that in the Kondo regime a maximum occurs which is qualitatively similar to the result of the poor-man scaling consideration \[ \text{18}. \]

To conclude, we have obtained an accurate NRG solution of the one-impurity Anderson model with inclusion of the Falicov-Kimball interaction (excitonic effects). Some new features in comparison with the standard Anderson model (in particular, in the temperature dependence of specific heat) occur. A generalization of the results to a lattice case would be of interest for the theory of the Kondo lattices and IV compounds.

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[1] Valence Instabilities and Related Narrow-Band Phenomena, edited by R. D. Parks (Plenum Press, New York, 1977).

[2] Proceedings of the International Conference on Valence Fluctuations, ed. by E. Müller-Hartmann, B. Roden, and D. Wohlleben [J. Magn. Magn. Mater. 47&48, p. 1-620 (1985)].

[3] J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. 44, 1 (1981).

[4] P. S. Riseborough, Adv. Phys. 49, 257 (2000).

[5] G. R. Stewart, Rev. Mod. Phys. 56, 755 (1984); ibid. 73, 797 (2001).

[6] A. C. Hewson, The Kondo Problem to Heavy Fermions (Cambridge University Press, Cambridge, 1993).

[7] R. Ramirez, L. M. Falicov, and J. C. Kimball, Phys. Rev. B 2, 3383 (1970); C. E. T. Goncalves da Silva and L. M. Falicov, J. Phys. C 5, 906 (1972).

[8] K. W. H. Stevens, J. Phys. C 9, 1417 (1976); J. Phys. C 11, 985 (1978).

[9] V. Yu. Irkhin and M. I. Katsnelson, J. Phys. C 17, L699 (1984); Solid State Commun. 58, 881 (1986); Sov. Phys. JETP 63, 631 (1986).

[10] M. Colarieti-Tosti, M. I. Katsnelson, M. Mattesini, S. I. Simak, R. Ahuja, B. Johansson, O. Eriksson, and C. Daller, Phys. Rev. Lett. 93, 096403 (2004).

[11] K. G. Wilson, Rev. Mod. Phys. 47, 773 (1975).

[12] H. R. Krishna-murthy, J. W. Wilkins, and K. G. Wilson, Phys. Rev. B 21, 1003 (1980); ibid. 21, 1044 (1980).

[13] A. M. Tsvelick and P. B. Wiegmann, Adv. Phys. 32, 453 (1983).

[14] N. Andrei, K. Furuya and K.H. Lowenstein, Rev. Mod. Phys. 55, 331 (1983).

[15] P. B. Wiegmann and A. M. Finkelstein, Sov. Phys. JETP 48, 102 (1978).

[16] P. Schlottmann, Phys. Rev. B 22, 613, 622 (1980).

[17] D. L. Cox and A. Zawadowski, Adv. Phys. 47, 599 (1998).

[18] V. Yu. Irkhin and M. I. Katsnelson, JETP Lett. 80, 312 (2004).

[19] P. W. Anderson, J. Phys. C 3, 2346 (1970).

[20] F. D. M. Haldane, Phys. Rev. Lett. 40, 416 (1978).

[21] A. Okiji and N. Kawakami, Phys. Rev. Lett. 50, 1157 (1983).

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