

## Electronic specific heat and spin-susceptibility of heavy fermion systems: Role of $s$ - $f$ interactions

Meenakshi Sharma & Ishwar Singh

Department of Physics, University of Roorkee, Roorkee 247 667

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Representing the heavy fermion systems by the periodic Anderson model, we use variational method to study the behaviour of electronic specific heat  $C_v(T)$  and magnetic susceptibility  $\chi_s(T)$  of these systems. We have studied the effect of intra-site  $s$ - $f$  interactions on the properties. We find that as  $s$ - $f$  interactions increase, the low temperature peak in  $C_v$  lowers in magnitude whereas the peak in  $\chi_s$  lowers, broadens and shifts a bit towards high temperature region.

### 1 Introduction

Some of the lanthanide and actinide intermetallic compounds, known as heavy fermion (HF) systems, show a variety of anomalous electronic and magnetic properties. The experimental results of electronic specific heat  $C_v(T)$  and magnetic susceptibility  $\chi(T)$  of many heavy fermion systems, e.g. Ce compounds  $\text{CePd}_3$ ,  $\text{CeAl}_3$  etc. at low temperature

show unusual behaviour in that  $\frac{C_v(T)}{T} = \gamma + AT^2$ ,

where  $A$  is positive. While most of the HF systems show Curie-Weiss behaviour of magnetic susceptibility  $\chi(T)$  at higher temperatures, some of these like  $\text{CeAl}_3$ ,  $\text{CeCu}_6$ ,  $\text{UAl}_2$  do not order (magnetically) down to the lowest temperatures, some like  $\text{CeAl}_2$ ,  $\text{CeB}_6$ ,  $\text{UCd}_{11}$  order magnetically<sup>1-4</sup>.

The HF compounds have got a broad conduction band (formed of overlapping  $s$ -orbitals and  $p$ -orbitals; but generally called as  $s$ -band) and atomic-like  $f$ -orbitals on Rare Earth (RE) or actinide ions. The  $f$ -states hybridize with conduction states thus giving rise to the itinerant character to  $f$ -electrons.

Recently these systems have been studied in detail<sup>5-10</sup> using the periodic Anderson model (PAM) which includes strong intra-site interactions between  $f$ -electrons and considers the coherent hybridization between  $f$ -states and  $s$ -band states on all sites of the lattice. It has been suggested by the work of Nunez-Regueiro and Avignon<sup>11</sup>, and Liu and Ho<sup>12</sup> that the

localized (i.e. intra-site) interactions between  $f$ -electrons and conduction electrons (the  $s$ - $f$  interaction) play a crucial role in Ce compounds along with the intra-site  $f$ - $f$  interactions. In fact, it has been very well established that  $s$ - $f$  interaction (considered in the Falicov-Kimball model<sup>13,14</sup>) plays a dominant role in deciding/governing the temperature- and pressure- induced metal-semiconductor transitions in the mixed-valence (MV) systems<sup>15-18</sup>.

In this work we study the electronic specific heat and magnetic susceptibility of HF systems representing these by the PAM including  $s$ - $f$  interactions along with the  $f$ - $f$  interactions.

### 2 Basic Formulations

The orbitally non-degenerate Periodic Anderson Model including intra-site  $s$ - $f$  interactions is described by the Hamiltonian

$$\begin{aligned}
 H = & \sum_k \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + E_f \sum_{j\sigma} b_{j\sigma}^\dagger b_{j\sigma} + \frac{U}{2} \sum_{j\sigma} n_{j\sigma}^\dagger n_{j\sigma} + \\
 & \sum_{jk\sigma} V_{kj} (c_{k\sigma}^\dagger b_{j\sigma} + b_{j\sigma}^\dagger c_{k\sigma}) \\
 & + \frac{G}{2N} \sum_{jkk'\sigma} b_{j\sigma}^\dagger b_{j\sigma} c_{k-\sigma}^\dagger c_{k'-\sigma} e^{i(k-k')R_j} \\
 & + \frac{(G-J)}{2N} \sum_{jkk'\sigma} b_{j\sigma}^\dagger b_{j\sigma} c_{k\sigma}^\dagger c_{k'\sigma} e^{i(k-k')R_j} \quad \dots(1)
 \end{aligned}$$

The first term describes the uncorrelated conduction band resulting from  $5p$  and  $6s$  states of RE or actinide ions. Here  $c_{k\sigma}^+$  ( $c_{k\sigma}$ ) creates (annihilates) a conduction electron with wave vector  $k$  and spin  $\sigma$ .  $\varepsilon_k$  is the conduction band energy of  $f$ -electrons. Here  $b_{j\sigma}^+$  ( $b_{j\sigma}$ ) creates (annihilates) a  $f$ -electron of spin  $\sigma$  at site  $j$ . In the third term,  $U$  is the Coulomb repulsion between two  $f$ -electrons (of opposite spin) simultaneously occupying same site, ( $n_{j\sigma}^f = b_{j\sigma}^+ b_{j\sigma}$  is the number operator). The orbital degeneracy of true  $f$ -state is neglected here for simplicity. Fourth term describes the mixing (hybridization) between conduction- and  $f$ -states. Here  $V_{kj}$  is the hybridization matrix element. The strength of  $s$ - $f$  hybridization in Bloch representation takes the form

$$V_k = \frac{1}{\sqrt{N}} \sum_j e^{ikR_j} V_{kj} \quad \dots(2)$$

where  $N$  is the number of sites. In our calculations, we shall take  $V_k$  to be  $k$ -independent. The fifth term represents the Coulomb repulsion between a  $f$ -electron and a conduction electron of opposite spins simultaneously occupying site  $j$ . Here  $G$  is the strength of this Coulomb repulsion. The sixth term represents similar interaction between  $f$ - and conduction electrons of same spin. Thus  $J$  represents the (intra-site) exchange interaction between  $f$ - and conduction electrons

In the Bloch representation Hamiltonian Eq. (1) may be written as

It =

$$\begin{aligned} & \sum_{k\sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma} + E_f \sum_{k\sigma} b_{k\sigma}^+ b_{k\sigma} + \frac{U}{2} \sum_{j\sigma} n_{j\sigma}^f n_{j-\sigma}^f - \\ & \sum_{k\sigma} (V_k c_{k\sigma}^+ b_{k\sigma} + V_k^* b_{k\sigma}^+ c_{k\sigma}) \\ & + \frac{G}{2N} \sum_{jkk'\sigma} n_{j\sigma}^f c_{k-\sigma}^+ c_{k-\sigma} e^{i(k-k')R_j} + \\ & \frac{(G-J)}{2N} \sum_{jkk'\sigma} n_{j\sigma}^f c_{k\sigma}^+ c_{k'\sigma} e^{i(k-k')R_j} \quad \dots(3) \end{aligned}$$

In this work we have used variational technique<sup>19,23</sup> to study electronic specific heat and

magnetic susceptibility. The interaction terms shall be treated within mean-field approximation.

For example

$$U \sum_{j\sigma} n_{j\sigma}^f n_{j-\sigma}^f = U \sum_{j\sigma} [n_{j\sigma}^f n_{j-\sigma}^f + n_{j\sigma}^f n_{j-\sigma}^f] \dots(4a)$$

$$\frac{G}{2N} \sum_{jkk'\sigma} n_{j\sigma}^f c_{k-\sigma}^+ c_{k-\sigma} e^{i(k-k')R_j} = \frac{G}{2} \sum_{j\sigma} [n_{j\sigma}^f n_{j-\sigma}^f + n_{j\sigma}^f n_{j-\sigma}^f] \dots(4b)$$

$$\frac{(G-J)}{2N} \sum_{jkk'\sigma} n_{j\sigma}^f c_{k\sigma}^+ c_{k'\sigma} e^{i(k-k')R_j} = \frac{(G-J)}{2} \sum_{j\sigma} [n_{j\sigma}^f n_{j\sigma}^f + n_{j\sigma}^f n_{j\sigma}^f] \dots(4c)$$

$$\text{where } n_{j\sigma}^c = \frac{1}{N} \sum_{kk'} c_{k\sigma}^+ c_{k'\sigma} e^{i(k-k')R_j} \quad \dots(5)$$

where  $n_{j\sigma}^f$  and  $n_{j\sigma}^c$  are respectively the average number of  $f$ -electrons and conduction-electrons per site of spin  $\sigma$ .

When interaction term  $U$  is not too large all the three configurations  $f^0$ ,  $f^1$  and  $f^2$  on each site are energetically possible and we may use the following variational wave function for the Anderson Lattice<sup>21</sup>.

$$|\phi_0\rangle = \prod_{j\sigma} \left[ I + \sum_k a_{jk\sigma} b_{j\sigma}^+ c_{k\sigma} \right] |F\rangle \quad \dots(6)$$

where  $|F\rangle = \prod_{k < k_F, \sigma} c_{k\sigma}^+ |0\rangle$  is the Fermi sea of conduction electrons in which all conduction states with  $k < k_F$  are filled. The  $a_{jk\sigma}$  are the variational parameters. For the homogeneous case where the system realizes complete site equivalence, the variational parameters may be represented as

$$a_{jk\sigma} = \frac{1}{\sqrt{N}} A_{k\sigma} e^{ikR_j} \quad \dots(7)$$

Then the wave function  $|\phi_0\rangle$  becomes

$$|\phi_0\rangle = \prod_{k\sigma} \left[ I + A_{k\sigma} b_{k\sigma}^+ c_{k\sigma} \right] |F\rangle \quad \dots(8)$$

The energy expectation value from Hamiltonian Eq. (3) using approximations [ Eq. (4) ] may easily be obtained as:

$$E = \frac{\langle \phi_0 | H | \phi_0 \rangle}{\langle \phi_0 | \phi_0 \rangle} = \sum_{k\sigma} \frac{\left[ \varepsilon_k + E_f A_{k\sigma}^2 + (1/n_{-\sigma}^f A_{k\sigma}^2 - 2V_k A_{k\sigma} + (i/n_{-\sigma}^f + n_{-\sigma}^c A_{k\sigma}^2) + (i-J)(n_{-\sigma}^f + n_{-\sigma}^c A_{k\sigma}^2) \right]}{[1 + A_{k\sigma}^2]} \quad \dots(9)$$

Using the minimization condition,  $\frac{\partial E}{\partial A_{k\sigma}} = 0$ , we find the variational parameters

$$A_{k\sigma}^{\pm} = \frac{1}{2V_k} \left[ \left\{ \varepsilon_k - E_f - U n_{-\sigma}^f + (2G - J)(n_{-\sigma}^f - n_{-\sigma}^c) \right\} \mp \sqrt{\left\{ \varepsilon_k - E_f - U n_{-\sigma}^f + (2G - J)(n_{-\sigma}^f - n_{-\sigma}^c) \right\}^2 + 4V_k^2} \right] \quad \dots(10)$$

One gets the resultant states in the form of two quasi-particle bands. The lower (-) and upper (+) branches of the spectra may be obtained by putting values of  $A_{k\sigma}^{\pm}$  from Eq. (10) in Eq. (9). It takes the form

$$E_{k\sigma}^{\pm} = \frac{1}{2} \left[ \left\{ \varepsilon_k + E_f + U n_{-\sigma}^f - (2G - J)(n_{-\sigma}^f - n_{-\sigma}^c) \right\} \pm \left[ \left\{ \varepsilon_k - E_f - U n_{-\sigma}^f + (2G - J)(n_{-\sigma}^f - n_{-\sigma}^c) \right\}^2 + 4V_k^2 \right]^{1/2} \right] \quad \dots(11)$$

At finite temperature, the number of conduction and  $f$ -electrons are given by

$$n_{\sigma}^c = \frac{1}{N} \sum_k n_{k\sigma}^c = \frac{1}{N} \sum_k \left\{ \frac{f_{k\sigma}}{1 + (A_{k\sigma}^-)^2} + \frac{f_{k\sigma}^*}{1 + (A_{k\sigma}^+)^2} \right\} \quad \dots(12)$$

$$n_{\sigma}^f = \frac{1}{N} \sum_k n_{k\sigma}^f = \frac{1}{N} \sum_k \left\{ \frac{(A_{k\sigma}^-)^2 f_{k\sigma}}{1 + (A_{k\sigma}^-)^2} + \frac{(A_{k\sigma}^+)^2 f_{k\sigma}^*}{1 + (A_{k\sigma}^+)^2} \right\} \quad \dots(13)$$

where

$$f_{k\sigma}^{\pm} = f_{k\sigma}^{\pm}(E_{k\sigma}^{\pm} - \mu) = \frac{1}{\exp[\beta(E_{k\sigma}^{\pm} - \mu)] + 1}, \quad \beta = \frac{1}{k_B T}$$

is the Fermi function for the lower branch ( $E_{k\sigma}^-$ ) and upper branch ( $E_{k\sigma}^+$ ) of the quasi particle spectrum.

**Density of states** - Let  $\rho_{\sigma}^c(\varepsilon_k)$  denote the density of states (dos) of the unperturbed conduction band with spin  $\sigma$ ,  $\rho_{\sigma}^f(E_{k\sigma}^{\pm})$  the total dos for lower and upper quasi-particle bands. Then  $\rho_{\sigma}^c(E_{k\sigma}^{\pm})$  and  $\rho_{\sigma}^f(E_{k\sigma}^{\pm})$  respectively the density of perturbed conduction states and the density of perturbed  $f$ -states of lower (-) and upper (+) bands is given by

$$\rho_{\sigma}^c(E_{k\sigma}^{\pm}) = \frac{\rho_{\sigma}^c(\varepsilon_k)}{\left( \frac{dE_{k\sigma}^{\pm}}{d\varepsilon_k} \right)} \frac{1}{1 + (A_{k\sigma}^{\pm})^2} \quad \dots(14)$$

$$\rho_{\sigma}^f(E_{k\sigma}^{\pm}) = \frac{\rho_{\sigma}^c(\varepsilon_k)}{\left( \frac{dE_{k\sigma}^{\pm}}{d\varepsilon_k} \right)} \frac{(A_{k\sigma}^{\pm})^2}{1 + (A_{k\sigma}^{\pm})^2} \quad \dots(15)$$

**Electronic specific heat** — The electronic specific heat  $C_v$  is obtained by the numerical differentiation of the total energy  $\langle E \rangle$  at finite temperature  $T$  with respect to  $T$ . The total specific heat gets the contribution from both the lower as well as the upper quasi-particle bands. One gets

$$C_v(T) = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial}{\partial T} \left\{ \sum_{k\sigma} \left[ (E_{k\sigma}^- - \mu) f_{k\sigma} + (E_{k\sigma}^+ - \mu) f_{k\sigma}^* \right] \right\} \quad \dots(16)$$

Noting that the temperature-dependence of quasi-particle bands is very weak,  $C_v$  takes the form

$$C_v(T) = \sum_{k\sigma} \left\{ (E_{k\sigma}^- - \mu) \frac{\partial f_{k\sigma}}{\partial T} + (E_{k\sigma}^+ - \mu) \frac{\partial f_{k\sigma}^*}{\partial T} \right\} \quad \dots(17)$$

**Spin susceptibility** — The static magnetic susceptibility is obtained by differentiating the induced magnetic moment with respect to the magnetic field  $B$ :

$$\chi_s(T) = g\mu_B\sigma \frac{\partial}{\partial B} \left[ n_{\sigma}^f - n_{-\sigma}^f \right] \Big|_{B \rightarrow 0} \quad \dots(18)$$

Using the expressions of  $n_{\sigma}^f$ 's from Eq. (13) we get an expression of susceptibility, in units of  $(g\mu_B)^2$  as

$$\chi_s(U, G, J) = \frac{\chi_0}{1 - \frac{U}{2} \chi_0 + (2G - J)(\chi_2 - \chi_1)} \quad \dots(19)$$

where

$$\chi_0 = \chi_1 + \chi_2 \quad \dots(20)$$

$$\chi_1 = 2 \sum_k \frac{A_{k\sigma}^2}{1 + A_{k\sigma}^2} \frac{\left[ \beta \exp[\beta(E_{k\sigma} - \mu)] (f_{k\sigma})^2 \right] \left[ \varepsilon_k + (2G - J)n_{-\sigma}^f - E_{k\sigma} \right]}{\left[ \varepsilon_k - E_f - U n_{-\sigma}^f + (2G - J)(n_{-\sigma}^f - n_{-\sigma}^c) \right]^2 + 4V_k^2} \quad \dots(21)$$

$$\chi_2 = 4 \sum_k \frac{A_{k\sigma}^2}{1 + A_{k\sigma}^2}$$

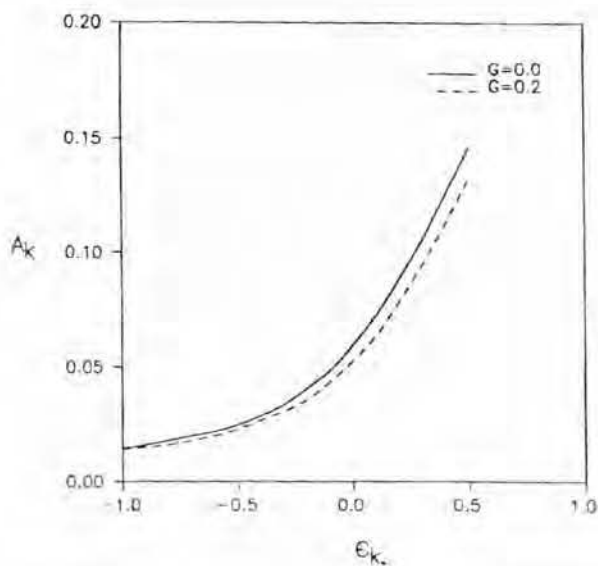


Fig. 1 — Variational parameter  $A_k$  as a function of  $\varepsilon_k$ . Here  $U = 0.85$ ,  $V = 0.25$ ,  $E_f = -0.2$

$$\frac{f_{k\sigma}^-}{\left[ \varepsilon_k - E_f - U n_{-\sigma}^f + (2G - J)(n_{-\sigma}^f - n_{-\sigma}^c) \right]^2 + 4V_k^2} \quad \dots(22)$$

$$\chi_2 = 2 \sum_k \frac{A_{k\sigma}^2}{1 + A_{k\sigma}^2} \frac{\left[ \beta \exp[\beta(E_{k\sigma} - \mu)] (f_{k\sigma})^2 \right] \left[ E_f + U n_{-\sigma}^f (2G - J) n_{-\sigma}^f - E_{k\sigma} \right]}{\left[ \varepsilon_k - E_f - U n_{-\sigma}^f + (2G - J)(n_{-\sigma}^f - n_{-\sigma}^c) \right]^2 + 4V_k^2} \quad \dots(23)$$

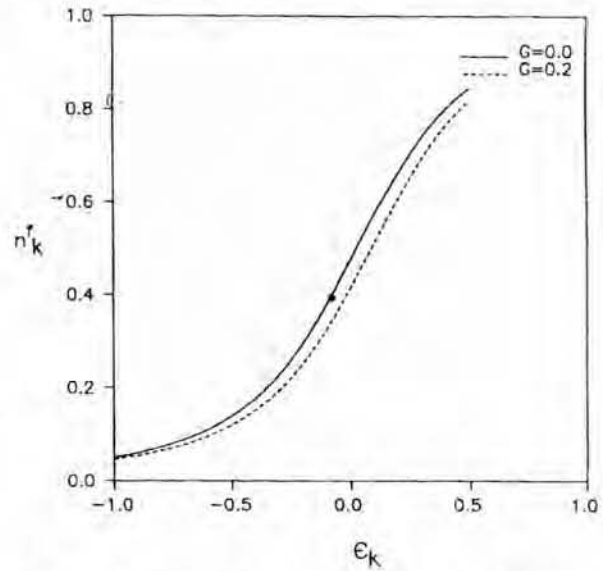


Fig. 2 — Momentum distribution function  $n_k^f$  as a function of  $\varepsilon_k$ :  $U = 0.85$ ,  $V = 0.25$ ,  $E_f = -0.2$

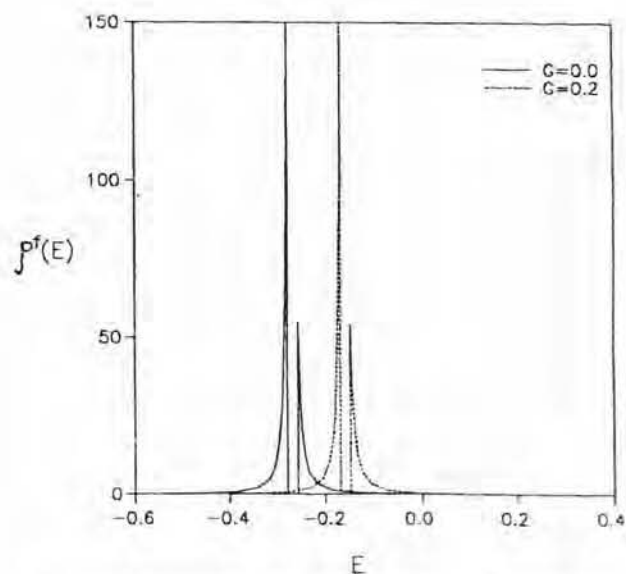


Fig. 3 — Variation of  $f$ -state density of states  $\rho^f(E)$  with quasiparticle energy  $E$ :  $U = 0.85$ ,  $V = 0.1$ ,  $E_f = -0.6$

Here

$$\left. \begin{aligned} A_{k\sigma} &= A_{k-\sigma} = A_k \\ E_{k\sigma}^\mp &= E_{k-\sigma}^\mp = E_k^\mp \\ n_\sigma^f &= n_{-\sigma}^f = n^f/2 \\ n_\sigma^c &= n_{-\sigma}^c = n^c/2 \\ f_{k\sigma}^\mp &= f_{k-\sigma}^\mp = f_k^\mp \end{aligned} \right\}$$

...(24)

### 3 Results and Discussions

In these calculations we have taken the form of conduction band to be linear with the dispersion

$$\text{relation } \varepsilon_k = \frac{2}{\pi} \left[ |k| + D_- \left( \frac{\pi}{2} \right) \right]. \quad \text{Here } D_-$$

represents the band bottom. We take conduction bandwidth  $W = 2$  eV with  $-1 < \varepsilon_k < 1$ . The total number of electrons per site,  $(n^c + n^f)$ , has been taken as 1.5.

In the process of evaluation of electronic specific

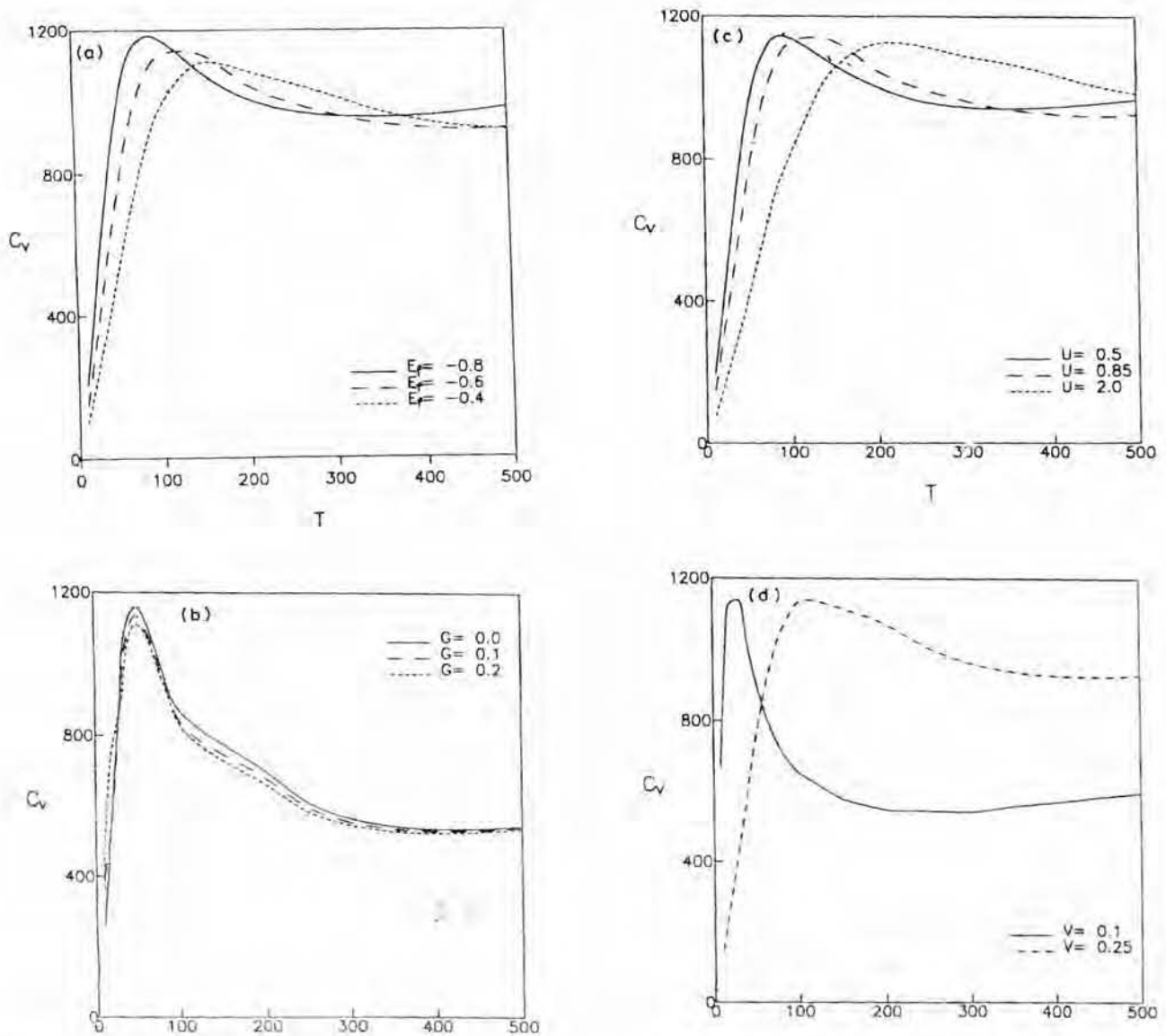


Fig. 4 — Specific heat  $C_v$  as a function of temperature  $T$  (a)  $U = 0.85, V = 0.25, G = 0.2$ ; (b)  $U = 2.0, V = 0.1, E_f = -0.6$ ; (c)  $V = 0.25, G = 0.2, E_f = -0.6$ ; (d)  $U = 0.85, G = 0.1, E_f = -0.6$ .

heat  $C_v$  and magnetic susceptibility  $\chi_s$  we had to calculate the variational parameter  $A_k$ , momentum distribution function  $n_k^f$  and density of  $f$ -states  $\rho^f(E)$  for different set of parameters  $U, G, J, V, E_f$  etc. In Figs. 1-3 we show variation of  $A_k$  (Fig. 1) and  $n_k^f$  (Fig. 2) as a function of  $\epsilon_k$  for same set of parameters (indicated in the figure caption) and variation of  $\rho^f(E)$  as a function of  $E$  (Fig. 3). We observe that both  $A_k$  and  $n_k^f$  increase with  $\epsilon_k$  and  $n_k^f$  decrease (in the whole energy range) with the increase of the  $s$ - $f$  interactions ( $G$  and  $J$ ). The density of  $f$ -states curves show two sharp peaks separated by a narrow gap around the position of  $f$ -level  $E_f$ . It is clear from the Fig. 3 that the  $f$  spectral density is concentrated around Fermi energy  $E = E_f$ .

Figs. 4(a) - 4(d) show the variation of specific heat  $C_v$  with temperature for different set of parameter values. In Fig. 5 we show variation of  $\gamma (= \frac{C_v}{T})$  as a function of  $T$  for different  $f$ -level position  $E_f$ . Fig. 4(a) shows the peak in  $C_v$  becomes sharper and shifts towards lower temperature as the  $f$ -level  $E_f$  shifts downwards away from the Fermi

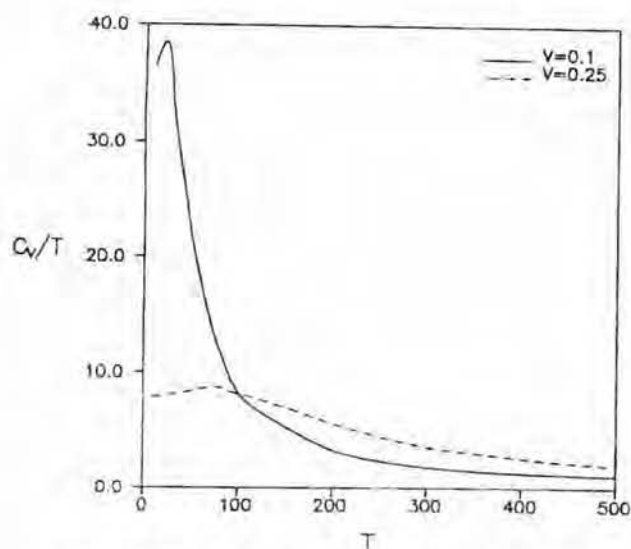


Fig. 5 — Linear coefficient of specific heat  $\gamma (= C_v/T)$  as a function of temperature :  $U = 2.0, G = 0.2, E_f = -0.6$

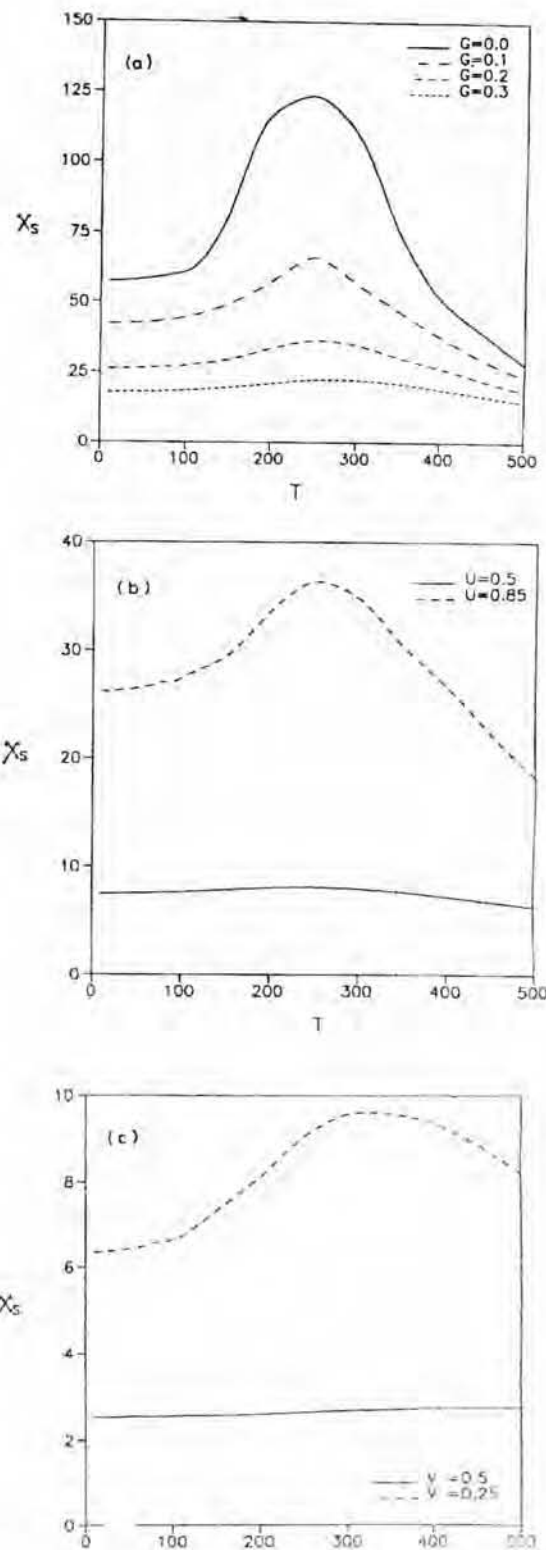


Fig. 6 — Magnetic susceptibility  $\chi_s$  [in units of  $(g \mu_B)^2$ ] as a function of temperature : (a)  $U = 0.85, V = 0.5, E_f = -0.2$ ; (b)  $G = 0.2, V = 0.5, E_f = -0.2$ ; (c)  $U = 0.85, G = 0.2, E_f = 0.1$

energy  $E_f$ . Fig. 4(b) shows that as  $G$  (and  $J$ ) increases,  $C_v$  decreases in whole temperature range except at very low temperatures. Fig. 4(c) shows the effect of  $U$ . In high temperature region  $C_v$  increases as  $U$  is increased whereas in the low temperature region  $C_v$  decreases when  $U$  increases. The peak in  $C_v$  broadens and shifts towards high temperature region as the hybridization  $V$  increases [Fig. 4(d)]. In

Fig. 5 one finds that  $\gamma \left( = \frac{C_v}{T} \right)$  increases slowly in

low temperature region, shows a maxima and decreases in high temperature region. In our variational approach along with the coherent hybridization scheme used,  $f$ -level contributes a sharp peak in the electronic density of states in the vicinity of Fermi energy. This explains the high value of  $C_v$  and  $\gamma$ . As temperature increases from  $T = 0$ , the quasi-particles are excited to higher energy states available within the lower band. When temperature is further increased the quasi-particles are excited to upper (quasi-particle) band which is separated from the lower band by a relatively narrow

gap  $\Delta \cong \frac{V^2}{W}$ . This results in the peak of  $C_v$  at low temperature. Here it may be mentioned that as hybridization  $V$  decreases, the peaks in the density of states become more sharp and the band gap (between the lower and upper quasi-particle bands) decreases. That is why the peak in  $C_v$  becomes narrower and shifts towards low temperature when  $V$  is decreased (Fig. 5). As the  $f$ -level  $E_f$  goes down the band gap decreases and one has more sharp peak at low temperature [Fig. 4(a)]. This behaviour of specific heat curves has been the main characteristic of many heavy fermion materials like  $\text{NpSn}_3$ <sup>25</sup>. In particular, it is observed from Figs. 4(b) and 4(d) that the behaviour of  $C_v$  (for the value of hybridization  $V = 0.1$ ) matches very well with the experimental results of Pott et al.<sup>26</sup> on the specific heat of  $\text{YbCuAl}$ .

Figs 6(a)-(c) show the variation of magnetic susceptibility  $\chi_s$  as a function of temperature for different set of parameters. At low temperatures  $\chi_s(T)$  rises to a maximum. This low- $T$  peak in susceptibility gets sharpened as the  $f$ -level  $E_f$  goes deep into the conduction band. Also at a fixed value

of  $E_f$  the peak sharpens as value of intra-site  $f$ -interaction  $U$  increases [Fig. 6(b)]. In fact the peak becomes extremely large (and  $\chi$  diverges in this range of temperature) even for a moderately increased value of  $U$ . This susceptibility behaviour is characteristic of many heavy fermion systems like  $\text{CeAl}_3$  and  $\text{UPt}_3$ <sup>6,27,28</sup>. The behaviour of magnetic susceptibility in compounds  $\text{UPd}_{2-x}\text{Au}_x\text{Sn}$ <sup>29</sup> and  $\text{YbPd}_2\text{Si}_{2-x}\text{Ge}_x$ <sup>30</sup> (for various values of  $x$ ) as a function of temperature is similar as shown in Fig. 6(a). However, both the  $s$ - $f$  hybridization as well as the  $s$ - $f$  interactions ( $G$  and  $J$ ) reduce the magnitude of magnetic susceptibility [Figs 6(a) and (c)].

The role of  $s$ - $f$  interactions may be summarized as follows : As  $s$ - $f$  interactions increase, the low temperature peak in  $C_v$  lowers in magnitude whereas the peak in  $\chi_s$  lowers, broadens and shifts a bit towards high temperature region.

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