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The magnetic susceptibility of an ion fluctuating between two magnetic valence states

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Abstract. Using a variational technique, we consider the magnetic susceptibility, χ , of a magnetic impurity with lowest ionic configurations f^1 and f^2 (for minimal orbital degeneracy and j - j coupling) embedded in a free-electron continuum.

For the simplest variational wavefunctions (no electron-hole excitations) we find that the susceptibility in the f^1 limit is anomalously large compared to the f^2 limit and is enhanced throughout the mixed valence regime. $1/\chi$ is strongly correlated to the binding energy of the singlet relative to the magnetic states.

The inclusion of the first excited state of the Fermi sea gives rise to a large effect and the susceptibility is enhanced considerably in the f^2 limit. The results in the two Kondo limits can be expressed in a renormalised form and are seen to correspond to exact results for Ce. Examination of higher-order terms makes us believe that these do not alter the results in any qualitative way. The charge susceptibility can be calculated and is seen to be small throughout the mixed valent regime. We consider also the dynamical susceptibility, $\chi(\omega)$, and compare this with experimental results. The extension of the above results to actinide impurities, which fluctuate between f^2 and f^3 , and the relevance to uranium heavy fermion compounds is discussed.

1. Introduction

The theory of mixed valence systems, and in particular their relevance to heavy fermion materials, continues to present many theoretical problems. Materials exhibiting mixed valence fall into two distinct categories. The rare earths (RE) Ce and Yb are examples of the first category where we have an ion fluctuating between a non-magnetic state, f^0 , and a magnetic state, f^1 . For a single impurity, this problem has been solved exactly, at least for thermodynamic properties (Schlottman 1983a, b, Ogievetski *et al* 1983). The ground state is seen to be a singlet, characterised by a small binding energy which defines an energy scale, T_K . Approximate solutions may also be found by taking an expansion in $1/N$, where N , the degeneracy of the f^1 state, is large ($N = 6$ or 8) (Gunnarsson and Schönhammer 1983a, b, Rasul and Hewson 1983, 1984, Read 1985). Accurate results may be obtained by keeping only the first two terms in such an expansion (Rasul and Hewson 1984). We note in particular that good results are obtained even for N as low as 2. The $1/N$ technique may be extended to a lattice of RE ions (Rasul and Degrange 1986, Millis and Lee 1987).

The second category, in which both valence states have magnetic moments, presents a much more difficult problem. Examples of materials in this category are Tm (RE ion

with valence states f^1 and f^2), and U (actinide ion with valence states f^2 and f^3). There is no exact solution. Using a variational technique Yafet *et al* (1985, which we shall denote by I) and Nunes *et al* (1985), have shown that for a single ion the ground state is again a singlet which now has a small energy scale for all values of f occupation, n_f . We can also extend the arguments of Cragg and Lloyd (1979) to show that the electron gas has sufficient channels to compensate the magnetic moment. The small energy scale implies an enhanced susceptibility and specific heat even in a mixed valent regime. This would provide an explanation for the experimental results that certain U systems show the existence of heavy fermion behaviour even with $n_f \approx 2.5$ (Frick *et al* 1984, 1985) and TmSe which has $n_f \approx 1.5$ becomes magnetic at $T = 3$ K (Batlogg *et al* 1979). It has, however, been suggested (Yafet and Varma 1984) that the existence of a small matrix element between the variational singlet and triplet states tends to offset the effect of the small energy denominator leading to a susceptibility which is not appreciably enhanced. It is no longer clear how useful approximation techniques will be, as the expansion parameter is now $1/R$ where R , the ratio of the degeneracies of the f^n and f^{n+1} states, is less than 2 (though in analogy with Ce this may not matter too much). We note that results differ according to the method of solution used. The zeroth-order results from a functional integral calculation (Rasul and Harrington 1987, Read 1986) give an energy scale which is linear with n_f in both Kondo limits. Analogous results from a variational technique (Read *et al* 1986), however, establish rather different energy scales near the f^1 and f^2 limits. In the f^2 limit the energy scale is again linear in n_f but the f^1 limit contains an exponential in $1/(1 - n_f)$. This marked asymmetry in the two Kondo limits is difficult to understand. It would suggest that if we consider $n_f = m + \eta$ where m is an integer and $\eta \rightarrow 0$ the form of the result depends on the sign of η . In I a calculation involving all higher-order terms is performed, however they consider only one point in the middle of the valence regime which leads to the mistaken conclusion that the effect of the higher-order states is to enhance the energy separation between the singlet ground state and higher-energy magnetic states.

In this paper we use an extension of the methods used in I to calculate the magnetic susceptibility of a Tm ion as a function of f occupation. We consider first of all the simplest variational wavefunctions, i.e., those with no electron-hole excitations of the Fermi sea (this is just the zeroth-order term in a $1/R$ expansion). We consider an f level with only two orbitals ($m_l = 0, 1$), since this has the advantage of avoiding the complication of angular momentum recoupling. j - j coupling in the limit of zero j - j coupling is also considered for this reason.

The calculation of the susceptibility shows that it is closely correlated to $1/(\omega_S - \omega_D)$ and thus reflects the asymmetry found by Read *et al* (1986). We have also calculated a Van Vleck-type term arising from the mixing of the lowest-energy singlet and triplet states. This term is seen to vanish in the f^1 Kondo limit indicating that it cannot be the major contribution to χ .

In § 3 we consider the effect of including the first electron-hole excitation (this gives terms $\sim 1/R$). This leads to a large enhancement in the f^2 limit removing the asymmetry. χ is also enhanced by approximately 30% in the middle of the valence regime. The effect of higher-order terms is discussed.

So far our equations have depended on the band cut-off D . Following Read *et al* (1986) we use scaling theory to renormalise our equations to remove D . Our results may then be compared with exact results for f^0, f^1 and are seen to correspond.

The charge susceptibility can be calculated. It is seen to be small for all n_f . The result can be used to evaluate the Wilson ratio.

We consider also the real and imaginary parts of the dynamical susceptibility, $\chi(\omega)$, and show that this has a two peak structure in contrast to that for Ce, which has one peak only. This feature is a direct consequence of the fact that both valence states are magnetic. We compare our results with experiment. Finally, we discuss the extension of the above results to uranium systems.

The details of our model are as follows. The Hamiltonian we use is

$$H_0 = H_{\text{band}} + H_f + H_{\text{mix}} \quad (1.1)$$

where for minimal degeneracy the f^1, f^2 configurations hybridise with the conduction electrons in one of two partial wave states via an interaction term

$$H_{\text{mix}} = \sum_{km_l\sigma} V(c_{km_l\sigma}^\dagger f_{m_l\sigma} + \text{HC}) \quad (1.2)$$

where $c_{km_l\sigma}$ destroys band electrons in the m_l th channel with spin σ . $f_{m_l\sigma}$ denotes localised electrons. The bare energies of the f^1, f^2 states are E_1 and E_2 , respectively. We assume that V and the density of states ρ_0 are constant. Using the variational procedure followed in I, wavefunctions are written down for states of different symmetry with the minimum possible number of electron-hole pairs. Let $|\psi_0\rangle$ be the ground state of the Fermi sea. The doublet state has wave-function

$$|\psi_{\text{D}}\rangle_{\uparrow} = \alpha_{\text{D}} f_{0\uparrow}^\dagger |\psi_0\rangle + \sum_k \frac{1}{\sqrt{6}} \beta_{\text{D}}(k) [(f_{1\uparrow}^\dagger f_{0\downarrow}^\dagger + f_{1\downarrow}^\dagger f_{0\uparrow}^\dagger) c_{k1\downarrow} + 2f_{1\uparrow}^\dagger f_{0\uparrow}^\dagger c_{k1\uparrow}] |\psi_0\rangle. \quad (1.3)$$

We consider the variational equations

$$\delta_{\text{V}}[\langle\psi_{\text{D}}|H_0|\psi_{\text{D}}\rangle - (E_{\text{FS}} + E_1 - \omega_{\text{D}})\langle\psi_{\text{D}}|\psi_{\text{D}}\rangle] = 0 \quad (1.4)$$

where E_{FS} is the energy of the full Fermi sea. The binding energy of the impurity to the Fermi sea is ω_{D} if $\delta \geq 0$ and $\omega_{\text{D}} + \delta$ if $\delta < 0$. ω_{D} is given by

$$\omega_{\text{D}} = \bar{\Gamma} \ln \left(\frac{D + \omega_{\text{D}} + \delta}{\omega_{\text{D}} + \delta} \right) \quad (1.5)$$

where $\delta = E_2 - E_1$, and $\bar{\Gamma} = (3/2)\Gamma = (3/2\pi)V^2\rho_0$.

The wavefunction for the singlet state is

$$\begin{aligned} |\psi_{\text{S}}\rangle = & \frac{1}{\sqrt{2}} \sum_k \alpha_{\text{S}}(k) (f_{1\uparrow}^\dagger c_{k1\uparrow} + f_{1\downarrow}^\dagger c_{k1\downarrow}) |\psi_0\rangle + (\text{terms for } m_l = 0) \\ & + \frac{1}{\sqrt{3}} \sum_{k,k'} \beta_{\text{S}}(k, k') [f_{1\uparrow}^\dagger f_{0\uparrow}^\dagger c_{k'0\uparrow} c_{k1\uparrow} + f_{1\downarrow}^\dagger f_{0\downarrow}^\dagger c_{k'0\downarrow} c_{k1\downarrow} \\ & + \frac{1}{2} (f_{1\uparrow}^\dagger f_{0\downarrow}^\dagger + f_{1\downarrow}^\dagger f_{0\uparrow}^\dagger) (c_{k'0\uparrow} c_{k1\downarrow} + c_{k'0\downarrow} c_{k1\uparrow})] |\psi_0\rangle. \end{aligned} \quad (1.6)$$

Defining ω_{S} analogously to ω_{D} , we find ω_{S} from the integral equation

$$\alpha_{\text{S}}(k) (\omega_{\text{S}} + \varepsilon_k) = \bar{\Gamma} \int_0^D \frac{\alpha_{\text{S}}(k) + \alpha_{\text{S}}(k')}{\omega_{\text{S}} + \delta + \varepsilon_k + \varepsilon_{k'}} d\varepsilon_{k'}. \quad (1.7)$$

A state of triplet symmetry may also be formed. The wavefunction is

$$\begin{aligned}
|\psi_T\rangle = & \frac{1}{\sqrt{2}} \sum_k \alpha_T(k) (f_{1\uparrow}^\dagger c_{k1\uparrow} - f_{1\downarrow}^\dagger c_{k1\downarrow}) |\psi_0\rangle + (\text{terms for } m_l = 0) \\
& + \sum_{k,k'} \left[\frac{1}{2} \beta_T(k, k') (f_{1\uparrow}^\dagger f_{0\downarrow}^\dagger + f_{1\downarrow}^\dagger f_{0\uparrow}^\dagger) (c_{k'0\uparrow} c_{k1\downarrow} - c_{k'0\downarrow} c_{k1\uparrow}) \right. \\
& \left. - \frac{1}{\sqrt{2}} \gamma_T(k, k') (f_{1\uparrow}^\dagger f_{0\uparrow}^\dagger c_{k'0\uparrow} c_{k1\uparrow} - f_{1\downarrow}^\dagger f_{0\downarrow}^\dagger c_{k'0\downarrow} c_{k1\downarrow}) \right] |\omega_0\rangle \quad (1.8)
\end{aligned}$$

with ω_T given by

$$\alpha_T(k) (\omega_T + \varepsilon_k) = \bar{\Gamma} \int_0^D \frac{\alpha_T(k) + \frac{1}{3} \alpha_T(k')}{\omega_T + \delta + \varepsilon_k + \varepsilon_{k'}} d\varepsilon_{k'}. \quad (1.9)$$

Equations (1.7) and (1.9) do not have analytic solutions except in the two Kondo limits. They may however be solved numerically throughout the mixed valence regime. As shown in I, the singlet state has the lowest energy. The energy separation between the singlet and the magnetic states is small (at most 10% of $\bar{\Gamma}$).

2. Lowest-order calculation of the magnetic susceptibility

The susceptibility can be calculated by allowing the coefficients, α_S and β_S to be spin-dependent and adding a perturbation $H_1 = h\mu_z$ to (1.1), where h is the applied magnetic field and μ_z is given by

$$\mu_z = \mu_{Bgf} \sum_{\sigma m_l} \sigma f_{m_l\sigma}^\dagger f_{m_l\sigma} + \mu_{Bgc} \sum_{k m_l\sigma} \sigma c_{k m_l\sigma}^\dagger c_{k m_l\sigma}. \quad (2.1)$$

We have assumed that the field couples only to the spin of the f and c electrons.

The resulting eigenvalue equations are

$$\begin{aligned}
\alpha_\uparrow(k) (\varepsilon_k + \omega_S + \tilde{h}) \\
= \frac{3}{2} \bar{\Gamma} \int_0^D \left\{ \frac{\alpha_\uparrow(k) + \alpha_\uparrow(k')}{\delta + \omega_S + \varepsilon_k + \varepsilon_{k'} + 2\tilde{h}} + \frac{1}{2} \frac{\alpha_\uparrow(k) + \alpha_\downarrow(k')}{\delta + \omega_S + \varepsilon_k + \varepsilon_{k'}} \right\} d\varepsilon_{k'} \quad (2.2)
\end{aligned}$$

$$\begin{aligned}
\alpha_\downarrow(k) (\varepsilon_k + \omega_S - \tilde{h}) \\
= \frac{3}{2} \bar{\Gamma} \int_0^D \left\{ \frac{\alpha_\downarrow(k) + \alpha_\downarrow(k')}{\delta + \omega_S + \varepsilon_k + \varepsilon_{k'} - 2\tilde{h}} + \frac{1}{2} \frac{\alpha_\downarrow(k) + \alpha_\uparrow(k')}{\delta + \omega_S + \varepsilon_k + \varepsilon_{k'}} \right\} d\varepsilon_{k'} \quad (2.3)
\end{aligned}$$

and $\beta_{\sigma\sigma'}$ is given by

$$\beta_{\sigma\sigma'}(k, k') [\delta + \omega_S + \varepsilon_k + \varepsilon_{k'} + 2\tilde{h}(\sigma + \sigma')] = -\sqrt{\frac{3}{2}} V [\alpha_\sigma(k) + \alpha_{\sigma'}(k')] \quad (2.4)$$

where $\tilde{h} = \frac{1}{2} h g \mu_B$, $g = g_f - g_c$. As they stand these coupled equations are relatively difficult to solve. A simpler way to calculate the susceptibility is as follows. We rewrite the field-dependent wavefunction explicitly as a perturbation series in h :

$$|\psi_S(h)\rangle = |\psi_S(0)\rangle + \tilde{h} |\delta\psi_T\rangle + \tilde{h}^2 |\delta\psi_S\rangle \quad (2.5)$$

where $|\delta\omega_T\rangle$ is a state of triplet symmetry of the same form as (1.8) with $\alpha_T(k)$, $\beta_T(k, k')$ and $\gamma_T(k, k')$ replaced by $A^-(k)$, $B^-(k, k')$ and $C^-(k, k')$ respectively, where

$$A^-(k) = (\alpha_\uparrow - \alpha_\downarrow)/2\hbar \quad B^-(k, k') = [\beta_{\uparrow\uparrow}(k, k') - \beta_{\downarrow\downarrow}(k, k')]2\hbar$$

$$C^-(k, k') = [\beta_{\uparrow\downarrow}(k, k') - \beta_{\downarrow\uparrow}(k, k')]/2\hbar \tag{2.6}$$

$|\delta\psi_S\rangle$ is a singlet state of the form (1.6) with $\alpha_S(k)$ replaced by

$$A^+(k) = [\alpha_\uparrow(k) + \alpha_\downarrow(k) - 2\alpha_S(k)]/2\hbar^2$$

and $\beta_S(k, k')$ replaced by two coefficients

$$B^+(k, k') = [\beta_{\uparrow\uparrow}(k, k') + \beta_{\downarrow\downarrow}(k, k') - 2\beta_S(k, k')]/2\hbar^2$$

multiplying $[(f_{1\uparrow}^\dagger f_{0\uparrow}^\dagger c_{k'0\uparrow} c_{k1\uparrow} + f_{1\downarrow}^\dagger f_{0\downarrow}^\dagger c_{k'0\downarrow} c_{k1\downarrow})|\psi_0\rangle]$, and

$$C^+(k, k') = [\beta_{\uparrow\downarrow}(k, k') + \beta_{\downarrow\uparrow}(k, k') - 2\beta_S(k, k')]/2\hbar^2 \tag{2.7}$$

multiplying $[\frac{1}{2}(f_{1\uparrow}^\dagger f_{0\downarrow}^\dagger + f_{1\downarrow}^\dagger f_{0\uparrow}^\dagger)(c_{k'0\uparrow} c_{k1\downarrow} + c_{k'0\downarrow} c_{k1\uparrow})|\psi_0\rangle]$.

We now consider taking the overlap $\langle\psi_S(0)|H_0 + H_1|\psi_S(h)\rangle = E\langle\psi_S(0)|\psi_S(h)\rangle$ where E may be expanded in h , $E = E_0 + \hbar^2 E_2$, with $E_0 = E_{FS} + E_1 - \omega_S$. This leads to the equation

$$E_2 = \frac{2\sum_k A^-(k)\alpha_S(k) + \frac{1}{3}\sum_{kk'} B^-(k, k')\beta_S(k, k')}{\langle\psi_S(0)|\psi_S(0)\rangle} \tag{2.8}$$

$A^-(k)$ and $B^-(k, k')$ may be found either from equations (2.2)–(2.4) or by considering the overlaps $\langle(f_{1\uparrow}^\dagger c_{k'0\uparrow} + f_{1\downarrow}^\dagger c_{k'0\downarrow})|H_0 + H_1|\psi_S(h)\rangle$ and $\langle(f_{1\uparrow}^\dagger f_{0\uparrow}^\dagger c_{k'0\uparrow} c_{k1\uparrow} + f_{1\downarrow}^\dagger f_{0\downarrow}^\dagger c_{k'0\downarrow} c_{k1\downarrow})|H_0 + H_1|\psi_S(h)\rangle$.

Both methods give the same equation for $A^-(k)$. Noting that to lowest order in \hbar we may replace $A^+(k)$ by $\alpha_S(k)$ and $\omega_S(k)$ by its zero-field value we have

$$A^-(k)(\omega_S + \epsilon_k) - \tilde{\Gamma} \int_0^D \frac{A^-(k) + \frac{1}{3}A^-(k')}{\delta + \omega_S + \epsilon_k + \epsilon_{k'}} d\epsilon_{k'} = -\alpha_S(k)$$

$$- \frac{1}{3}\tilde{\Gamma} \int_0^D \frac{\alpha_S(k) + \alpha_S(k')}{(\delta + \omega_S + \epsilon_k + \epsilon_{k'})^2} d\epsilon_{k'} \tag{2.9}$$

$$B^-(\omega_S + \delta + \epsilon_k + \epsilon_{k'}) = -2\beta_S(k, k') - \sqrt{\frac{3}{2}}V[A^-(k) + A^-(k')] \tag{2.10}$$

This is an integral equation for $A^-(k)$ which depends only on $\alpha_S(k)$ and $\omega_S(0)$, which we already know how to calculate. An extension of the numerical method which solves (1.7) may be used to find $A^-(k)$ and hence E_2 . E_2 may be calculated throughout the valence regime and is seen to give an enhanced susceptibility χ ($\chi = -2g^2\mu_B^2 E_2$). We can also find χ exactly in the two Kondo limits. As $n_f \rightarrow 1$,

$$\omega_S - \omega_D = D \exp(-\delta/\tilde{\Gamma}) \tag{2.11}$$

and

$$\chi = (g^2\mu_B^2/4)(\omega_S - \omega_D)^{-1} = (g^2\mu_B^2/4D) \exp(\delta/\tilde{\Gamma}) \tag{2.12}$$

and as $n_f \rightarrow 2$,

$$\omega_S - \omega_D = 2D \exp(-|\delta|/\tilde{\Gamma}) \tag{2.13}$$

and

$$\chi = (4g^2\mu_B^2/3)(\omega_S - \omega_D)^{-1} = (2g^2\mu_B^2/3D) \exp(|\delta|/\tilde{\Gamma}) \tag{2.14}$$

n_f can be calculated as a function of δ by using the Hellman–Feynman expression

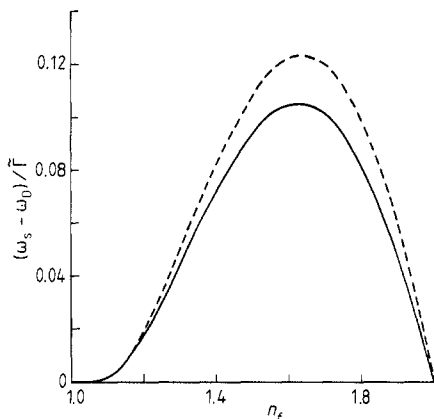


Figure 1. A plot of the energy scale (full curve) and $1/\chi$ (broken curve) against n_f to zeroth order.

$$n_f = 1 - (\partial \omega_S / \partial \delta). \quad (2.15)$$

The results for the two local moment regimes differ sharply. For $n_f \rightarrow 1$,

$$n_f - 1 = \tilde{\Gamma} D / \delta^2 \quad (2.16)$$

while for $n_f \rightarrow 2$,

$$2 - n_f = (2D/\tilde{\Gamma}) \exp(-|\delta|/\tilde{\Gamma}). \quad (2.17)$$

The behaviour of χ is thus seen to be quite different in the two limits.

$$\chi = (g^2 \mu_B^2 / 4D) \exp[D/\tilde{\Gamma}(n_f - 1)]^{1/2} \quad (2.18)$$

in the f^1 limit and

$$\chi = (2g^2 \mu_B^2 / 3\tilde{\Gamma})(2 - n_f)^{-1} \quad (2.19)$$

in the f^2 limit. To compare χ with $1/(\omega_S - \omega_D)$ we need to consider a form of χ in which we have removed the effective magnetic moment. We look at $\chi = n_f \mu_{\text{eff}}^2 \tilde{\chi}$, where $\mu_{\text{eff}}^2 = \frac{1}{3} g^2 \mu_B^2 S(S+1)$ and we take $S = n_f/2$. Clearly this has the required form in the two Kondo limits. In figure 1 we plot $\omega_S - \omega_D$ and $1/\tilde{\chi}$ as a function of n_f . There is a close correlation between the two. The result shows the marked asymmetry commented on earlier.

We can also try to calculate the susceptibility approximately by considering a Van Vleck-type term of the form

$$2 \frac{|\langle \tilde{\psi}_S | \mu_z | \tilde{\psi}_T \rangle|^2}{\omega_S - \omega_T} \quad (2.20)$$

where $|\tilde{\psi}_S\rangle$ and $|\tilde{\psi}_T\rangle$ are the normalised wavefunctions (1.6) and (1.8).

Equation (2.20) may be evaluated exactly in the two local moment regimes and numerically in the intermediate region. For $-\delta \gg D \gg \Gamma$, i.e., $n_f \rightarrow 2$, we find that the susceptibility diverges as $\exp(|\delta|/\tilde{\Gamma})$. This is the expected form. In the middle of the valence regime ($n_f = 1.5$) the matrix element $\langle \tilde{\psi}_S | \mu_z | \tilde{\psi}_T \rangle$ is approximately $0.3g\mu_B$ leading to a susceptibility, $\chi \approx 2g^2 \mu_B^2 / \tilde{\Gamma}$, which does not reflect the smallness of $\omega_S - \omega_D$. In the opposite Kondo limit $\delta \gg D \gg \Gamma$ ($n_f \rightarrow 1$), χ is vanishingly small, $\chi \sim \exp - \delta/\Gamma$, which

seems unlikely as is confirmed by the above calculation. It thus appears that the major contribution to χ does not arise from a term of the form (2.20) and that the triplet state determined by a variational calculation has little significance as far as the susceptibility is concerned.

3. Inclusion of electron-hole excitations

So far our calculations have not included any electron-hole excitations. Since the energy of these excitations is arbitrarily small such an approximation cannot be justified. As shown in I, including excited states introduces terms that are of higher order in $1/R$ so a perturbation series is obtained. However, for the case of minimal orbital degeneracy $1/R = \frac{4}{3}$ so we do not get a genuine expansion. In this section we look in some detail at what happens when we include the first electron-hole pair. We consider again the doublet, singlet and triplet states.

(i) *Doublet.* The f^2 term in equation (1.3), $f_{1\sigma}^\dagger f_{0\sigma'}^\dagger c_{k1\sigma'}$, is connected by H_{mix} to excited states $f_{1\sigma}^\dagger c_{q'0\sigma'}^\dagger c_{k1\sigma'}$ and $c_{q1\sigma}^\dagger f_{0\sigma'}^\dagger c_{k1\sigma'}$, where $q1\sigma$ and $q'0\sigma'$ are unoccupied electron states. These terms differ from the f^1 terms in equation (1.3) in having an electron-hole pair. They can be included by simply adding terms to the wavefunction in which $f_{1\sigma}^\dagger$ is replaced by $c_{q1\sigma}^\dagger$ etc. This gives

$$|\psi_D\rangle_\uparrow = |\psi_D\rangle_\uparrow^0 + \sum_{qk} \frac{1}{\sqrt{6}} \eta_D(k) [(c_{q1\uparrow}^\dagger f_{0\downarrow}^\dagger + c_{q1\downarrow}^\dagger f_{0\uparrow}^\dagger) c_{k1\downarrow} + 2c_{q1\uparrow}^\dagger f_{0\uparrow}^\dagger c_{k1\uparrow}] |\psi_0\rangle \quad (3.1)$$

where $|\psi_D\rangle_\uparrow^0$ is the zero-order state of equation (1.3). This leads to the equation for ω_D

$$\omega_D = \bar{\Gamma} \int_0^{D'} \frac{d\varepsilon_k}{\omega_D + \delta + \varepsilon_k + \delta_{\text{se}}(\varepsilon_k)} \quad (3.2)$$

where $\delta_{\text{se}}(\varepsilon_k)$ is a self-energy term given by

$$\delta_{\text{se}}(\varepsilon_k) = -\frac{4}{3} \bar{\Gamma} \ln \left(\frac{D' + \omega_D + \varepsilon_k}{\omega_D + \varepsilon_k} \right) \quad (3.3)$$

D' is the width of the unoccupied part of the band which we shall take as equal to D from now on.

(ii) *Singlet and triplet.* To calculate their binding energies in the same approximation, terms similar to those of (3.1) are added to the variational functions (1.6) and (1.8). We replace, for example, $f_{1\uparrow}^\dagger f_{0\uparrow}^\dagger$ by $c_{q1\uparrow}^\dagger f_{0\uparrow}^\dagger$ and $f_{1\uparrow}^\dagger c_{q'0\uparrow}^\dagger$ with coefficients $\eta_S(q, k, k')$ and $\eta_S(q', k, k')$ and sum over q, q', k, k' . The following eigenvalue equation is obtained for the singlet

$$\alpha_S(k) (\omega_S + \varepsilon_k) = \bar{\Gamma} \int_0^D \frac{\alpha_S(k) + \alpha_S(k')}{\omega_S + \delta + \varepsilon_k + \varepsilon_{k'} + \delta_{\text{se}}(\varepsilon_k, \varepsilon_{k'})} d\varepsilon_{k'} \quad (3.4)$$

where the self-energy term is

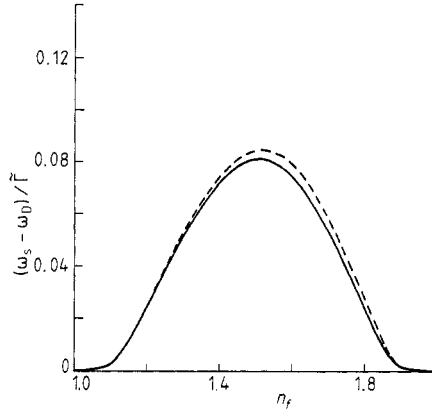


Figure 2. A plot of the energy scale (full curve) and $1/\bar{\chi}$ (broken curve) against n_f including the first self-energy term.

$$\delta_{\text{se}}(\varepsilon_k, \varepsilon_{k'}) = -\frac{4}{3}\bar{\Gamma} \ln \left(\frac{D + \omega_S + \varepsilon_k + \varepsilon_{k'}}{\omega_S + \varepsilon_k + \varepsilon_{k'}} \right). \quad (3.5)$$

The eigenvalue equation for the triplet is the same, except that just as in equation (1.9) the term in $\alpha_T(k')$ acquires a coefficient $\frac{1}{3}$.

The magnetic susceptibility is calculated as before by allowing the coefficients $\eta(q, k, k')$ to be spin-dependent leading to the following equation for E_2

$$E_2 = \frac{2 \sum_k A^-(k) \alpha_S(k) + \frac{4}{3} \sum_{kk'} B^-(k, k') \beta_S(k, k') + \frac{4}{3} \sum_{q,k,k'} D^-(q, k, k') \eta_S(q, k, k')}{\langle \bar{\psi}_S(0) | \bar{\psi}_S(0) \rangle} \quad (3.6)$$

where

$$D^-(q, k, k') = \frac{\eta_{\uparrow\uparrow}(q, k, k') - \eta_{\downarrow\downarrow}(q, k, k')}{2\hbar}. \quad (3.7)$$

The equations for $A^-(k)$, $B^-(k, k')$, $D^-(q, k, k')$ are

$$\begin{aligned} A^-(k)(\omega_S + \varepsilon_k) - \bar{\Gamma} \int_0^D \frac{A^-(k) + \frac{1}{3}A^-(k')}{\delta + \omega_S + \varepsilon_k + \varepsilon_{k'} + \delta_{\text{se}}(\varepsilon_k, \varepsilon_{k'})} d\varepsilon_{k'} = -\alpha_S(k) \\ - \frac{4}{3}\bar{\Gamma} \int_0^D \frac{\alpha_S(k) + \alpha_S(k')}{[\delta + \omega_S + \varepsilon_k + \varepsilon_{k'} + \delta_{\text{se}}(\varepsilon_k, \varepsilon_{k'})]^2} \\ + \left(1 + \frac{2}{3} \frac{D}{(\omega_S + \varepsilon_k + \varepsilon_{k'} + D)(\varepsilon_k + \varepsilon_{k'} + D)} \right) d\varepsilon_{k'} \end{aligned} \quad (3.8)$$

$$\begin{aligned} B^-(k, k')(\omega_S + \delta + \varepsilon_k + \varepsilon_{k'} + \delta_{\text{se}}(\varepsilon_k, \varepsilon_{k'})) = -\sqrt{\frac{3}{2}}V[A^-(k) + A^-(k')] \\ - 2\beta_S(k, k') \left[1 + \frac{2}{3} \frac{D}{(\omega_S + \varepsilon_k + \varepsilon_{k'} + D)(\varepsilon_k + \varepsilon_{k'} + D)} \right] \end{aligned} \quad (3.9)$$

$$D^-(q, k, k')(\omega_S + \varepsilon_q + \varepsilon_k + \varepsilon_{k'}) = -VB^-(k, k'). \quad (3.10)$$

This produces a large effect as can be seen from figure 2, where we have again plotted

$\omega_S - \omega_D$ and $1/\chi$ as a function of n_f . The energy scale is greatly reduced in the f^2 limit, removing the asymmetry. It is also substantially lowered in the middle of the valence regime. The difference between $\omega_S - \omega_D$ and $1/\chi$ is also lessened. In the f^1 Kondo limit we again get the result (2.18), while for the f^2 limit we now obtain

$$\chi = (2g^2 \mu_B^2 / 3D) \exp[D/R\tilde{\Gamma}(2 - n_f)]^{1/2}. \quad (3.11)$$

The change in the behaviour of χ in the f^2 limit is analogous to the change in χ in the f^1 limit for Ce-type impurities when the first excited state is included (Rasul and Hewson 1984).

We note that in I a calculation was performed for one set of parameter values, with $\delta = 0$ only. They show that introducing excited states *increases* the energy separation, which appears to contradict the results found above for the following reason. For the zeroth-order result, $\delta = 0$ corresponds to a point in figure 1 which is well to the left of the maximum. When we include the first excited state, however, $\delta = 0$ is very close to the maximum value. Therefore the energy scale at this particular value of δ increases while the energy scale as a whole decreases.

If we try to include the next excited state exactly we encounter difficulties. The coefficients of the higher-order terms cannot be eliminated algebraically to give a simple eigenvalue equation for α_S . We therefore follow the procedure used in I and by Inagaki (1979) and retain only the dominant logarithmic contributions to the self-energies (this is equivalent to keeping only 'non-crossing' diagrams). This leads to the following eigenvalue equation for ω_S

$$\alpha_S(k)(\omega_S + \varepsilon_k) = \tilde{\Gamma} \int_0^D \frac{\alpha_S(k) + \alpha_S(k')}{\omega_S + \delta + \varepsilon_k + \varepsilon_{k'} - G(\omega_S + \varepsilon_k + \varepsilon_{k'})} d\varepsilon_{k'} \quad (3.12)$$

where

$$G(\omega_S) = \frac{\tilde{\Gamma}}{R} \int_0^D \frac{d\varepsilon_k}{\omega_S + \varepsilon_k - F(\omega_S + \varepsilon_k)} \quad (3.13)$$

$$F(\omega_S) = \tilde{\Gamma} \int_0^D \frac{d\varepsilon_k}{\omega_S + \delta + \varepsilon_k - G(\omega_S + \varepsilon_k)}. \quad (3.14)$$

If the two Kondo limits are taken results identical to those found above for $\omega_S - \omega_D$ are obtained. We have not attempted to solve the integral equations in the mixed valence region. Instead we have looked at the effect of adding only one extra term in this approximate way. The result is to further decrease the energy scale by a small amount.

The coupling scheme we have used so far is not realistic although its simplicity allows the physics to be clearly demonstrated. In § 4 we show that using a different coupling scheme produces only a small change in our results.

4. Other coupling schemes

We consider now the changes to our results when we look at other coupling schemes. In particular we look in some detail at a general j - j coupling model in the limit of zero j - j coupling. The band and local electrons are labelled by their magnetic quantum number $-j \leq m \leq +j$ and mix via a term

$$H_{\text{mix}} = \sum_{k'mm'} V(|2mm'\rangle\langle 1m|c_{k'm'} + c_{k'm'}^\dagger|1m\rangle\langle 2mm'|). \quad (4.1)$$

The singlet state has wavefunction

$$|\psi_S\rangle = \sum_{km} a_m(k) f_m^\dagger c_{km} |\psi_0\rangle + \sum_{kk'm < m'} \beta_{mm'}(k, k') f_m^\dagger f_{m'}^\dagger c_{k'm'} c_{km} |\psi_0\rangle. \quad (4.2)$$

This has the same eigenvalue equation as before except that we now have $\tilde{\Gamma} = (N - 1)\Gamma$. Introducing a magnetic field gives a perturbation term $H_1 = h\mu_z$, where $\mu_z = \mu_B g_f \sum_m m f_m^\dagger f_m + \mu_B g_c \sum_{km} m c_{km}^\dagger c_{km}$. We obtain a series similar to (2.5). The f^1 component of $|\delta\psi_T\rangle$ is a sum of $N/2$ terms. One of these terms is the antisymmetric combination

$$\sum_m m f_m^\dagger c_{km} \quad (4.3)$$

with coefficient

$$A^-(k) = \left(\sum_m m \alpha_m(k) \right) / \left(\hbar \sum_m m^2 \right) \quad (4.4)$$

and all the other terms, $|\delta\psi_T'\rangle$, may be chosen to give $\langle \psi_S(\hbar = 0) | H_1 | \delta\psi_T' \rangle = 0$ so the only terms that contribute to χ are of the form $\sum_k A^-(k) \alpha_S(k)$. Similarly the only relevant term for the f^2 component is

$$\sum_{mm'} (m + m') f_m^\dagger f_{m'}^\dagger c_{k'm'} c_{km} \quad (4.5)$$

with coefficient

$$B^-(k, k') = \left(\sum_{m < m'} (m + m') \beta_{mm'}(k, k') \right) / \left(\hbar \sum_{m < m'} (m + m')^2 \right). \quad (4.6)$$

This gives a contribution to χ of the form $\sum_{kk'} B^-(k, k') \beta(k, k')$, leading to the following equation for E_2

$$E_2 = \sum_m m^2 \frac{\sum_k A^-(k) \alpha_S(k) + (N - 2) \sum_{kk'} B^-(k, k') \beta_S(k, k')}{\langle \psi_S(0) | \psi_S(0) \rangle}. \quad (4.7)$$

This is identical to (2.8) apart from the coefficients of the two terms which take into account the different spin dependence. The equations for $A^-(k)$ and $B^-(k, k')$ are also similar.

$$\begin{aligned} A^-(k)(\omega_S + \varepsilon_k) - \tilde{\Gamma} \int_0^D \frac{A^-(k) - (N - 1)^{-1} A^-(k')}{\delta + \omega_S + \varepsilon_k + \varepsilon_{k'}} d\varepsilon_{k'} \\ = -\alpha_S(k) - \frac{N - 2}{N - 1} \tilde{\Gamma} \int_0^D \frac{\alpha_S(k) + \alpha_S(k')}{(\delta + \omega_S + \varepsilon_k + \varepsilon_{k'})^2} d\varepsilon_{k'} \end{aligned} \quad (4.8)$$

$$B^-(\omega_S + \delta + \varepsilon_k + \varepsilon_{k'}) = -\beta - V[A^-(k) + A^-(k')]. \quad (4.9)$$

Solving these in the Kondo limits as before gives equations analogous to (2.12) and (2.14) but with different spin dependent factors. As $n_f \rightarrow 1$

$$\mu_{\text{eff}}^2 = (1/3N) \sum_m m^2 = (1/12)(N-1)(N+1) \quad (4.10)$$

and as $n_f \rightarrow 2$

$$\mu_{\text{eff}}^2 = [2/3N(N-1)] \sum_{m < m'} (m+m')^2 = (1/6)(N+1)(N-2). \quad (4.11)$$

As before we define a function of n_f which extrapolates between these limits to give $\bar{\chi} \cdot \bar{\chi}$ is less closely correlated with $(\omega_S - \omega_D)^{-1}$ than previously, differing by up to 30%.

Next we consider adding a term containing one electron-hole pair to (4.2). The term we add is

$$\sum_{qkk'mm'} \eta_{mm'}(q, k, k') c_{qm}^\dagger f_m^\dagger c_{k'm'} c_{km}. \quad (4.12)$$

The changes introduced are equivalent to before. The susceptibility in the two local moment regimes is given by (2.18) and (3.11) with μ_{eff} as above and $R = 7/2$. The change in the energy scale is less marked (it is reduced by only 7%). The result is no longer so symmetrical, the maximum lying closer to $n_f = 2$ as would be expected due to the higher degeneracy of the f^2 state. The discrepancy between $\omega_S - \omega_D$ and $1/\bar{\chi}$ remains. The inclusion of one extra term further reduces the energy scale by a similar amount.

For Tm the spin-orbit coupling is large and we should really use intermediate coupling. However, $j-j$ coupling gives a reasonable description. This has $R = (4j-1)/(2j+1) = 13/8$ which lies between the two values of R we have considered so far.

It is interesting to compare the two equations we have obtained for A^- , which differ in two respects.

(i) The coefficient of $\tilde{\Gamma} \int_0^D [\alpha_S(k) + \alpha_S(k')] / (\delta + \omega_S + \varepsilon_k + \varepsilon_{k'})^2 d\varepsilon_{k'}$. This is given by $\mu_{\text{eff}2}^2 / 2\mu_{\text{eff}1}^2$ in both cases where $\mu_{\text{eff}1}$ and $\mu_{\text{eff}2}$ are the relevant spin factors for the f^1 and f^2 limits, respectively. This implies a coefficient $J(J+1)/2j(j+1) = 4/3$ (where $J = 2j-1$) for $j-j$ coupling.

(ii) The coefficient of $A^-(k')$. This is just the factor which occurs in the eigenvalue equation for the variational triplet states. For $j-j$ coupling this is $(j-2)/(j+1) = \frac{1}{3}$ (see I).

It would appear that the equations for $j-j$ coupling are close to those for minimal degeneracy apart from the factor R . We have calculated the energy scale including terms to $O(1/R)$ for $R = 13/8$ and find that the self-energy terms reduce the value of the maximum by approximately 25%.

For rare earths LS coupling is appropriate. This gives a slightly smaller factor multiplying $\alpha_S(k')$ compared to that multiplying $\alpha_S(k)$ in the eigenvalue equations (1.7) and (3.4) which reduces the energy scale.

We have still not rigorously justified neglecting higher-order terms in the middle of the valence regime. As a check that this is reasonable we have performed a calculation using the parameters which were used in I to calculate $\omega_S - \omega_D$ to all orders, i.e., $R = 2$, $D = 200$, for both $j-j$ and spin-orbit coupling. Our results are approximately 20% too high in both cases so the approximation does appear to be reasonable.

5. The dependence on D

So far our equations have depended on the band cut-off D . To zeroth order in $1/R$ this dependence is logarithmic, suggesting that we may use scaling theory (Haldane

1978a, b) to renormalise (1.7) enabling all physical quantities to be expressed in terms of scaling invariants. This procedure has been considered by Read *et al* (1986) in the limits of zero and large j - j coupling. Doing this enables us to compare our results with exact results for Ce from the Bethe ansatz (Rasul and Hewson 1984).

We need to look at the effect on the low-energy processes produced by states within dD of the band edge. We calculate the self energies for E_1 and E_2 due to hopping into the other configuration and emitting an electron or hole between D and $D - dD$. So we reduce D but compensate for this by altering δ . The energy of the f^1 state is reduced by

$$2R\Gamma dD/D = \tilde{\Gamma} dD/D \quad (5.1)$$

and the energy of the f^2 state is reduced by

$$2\Gamma dD/D = (1/R)\tilde{\Gamma} dD/D \quad (5.2)$$

where the factor in (5.1) comes from the matrix element connecting f^1 to f^2 and the factor of 2 in (5.2) comes from the two ways in which a transition to f^1 can be made. The change in δ is just the difference between the two. The expressions obtained can be integrated to give

$$E_1^*(D) = E_1(D_0) - \tilde{\Gamma} \ln(D_0/D) \quad (5.3)$$

$$E_2^*(D) = E_2(D_0) - R^{-1}\tilde{\Gamma} \ln(D_0/D) \quad (5.4)$$

$$\delta(D) = \delta(D_0) + (1 - R^{-1})\tilde{\Gamma} \ln(D_0/D). \quad (5.5)$$

Scaling breaks down when D is roughly equal to either $|\delta(D)|$ or to Γ . Assuming that as D is reduced the first such crossover is when $\delta(D) = D \gg \Gamma$, i.e., when $D = T^*$, leads to

$$T^* = \delta(D_0) + (1 - R^{-1})\tilde{\Gamma} \ln(D_0/T^*) \quad (5.6)$$

with equivalent expressions for E_1^* and E_2^* . We note that this expression is quite general and holds for all coupling schemes provided we define $\tilde{\Gamma}$ and R appropriately. We now rewrite (1.7) in terms of T^* . First we redefine $\omega_s \rightarrow \omega_s + E_1$. Performing the first integration on the right-hand side gives a term containing $\ln D$ which, when taken over to the left-hand side, may then be absorbed into E_1 . Strictly speaking, we need to take a large R limit in order to renormalise the right-hand side. We note however that the dependence on D of the simplest self-energy term is $(1/R) \ln D$, which is precisely what we need to take $E_2 \rightarrow E_2^*$, so our procedure may be more accurate than it first appears. Defining $\tilde{\omega} = \omega_s + E_1^*$ gives

$$\alpha(k) \left[\tilde{\omega} + \varepsilon_k - \tilde{\Gamma} \ln \left(\frac{T^*}{\tilde{\omega} + T^* + \varepsilon_k} \right) \right] = \tilde{\Gamma} \int_0^\infty \frac{\alpha(k')}{\tilde{\omega} + T^* + \varepsilon_k + \varepsilon_{k'}} d\varepsilon_{k'}. \quad (5.7)$$

This is precisely the equation obtained by Read *et al* (1986) although it is now more general.

We now compare the results obtained using (5.7) with those obtained from (1.7) with $D = 20\tilde{\Gamma}$. There is *no discernible difference* for the vast majority of the valence range. A slight discrepancy is observed in the f^1 limit. The reason for this is as follows. Both ω_s and ω_D contain the same logarithmic dependence on D so when we take their difference this drops out. There is still some dependence on D since this is the upper limit on the integral over $\alpha_s(k')/(\omega_s + \delta + \varepsilon_k + \varepsilon_{k'})$, but since $\alpha_s(k)$ falls off very

rapidly with k this upper limit is not important. The discrepancy in the f^1 limit arises because for $D = 20\tilde{\Gamma}$ we only approach $n_f \approx 1$ for $\delta \approx 10\tilde{\Gamma}$ so we do not have the condition $\delta \ll D$ needed for the scaling limit. For a larger initial value of D this discrepancy would not arise until we are very much closer to the local moment regions. We note that this result again contradicts that in I where it is claimed that increasing D decreases the energy scale. As before the error lies in only considering one value for δ .

The inclusion of the first excited state leads to a dependence on D which is more complicated than logarithmic and simple scaling theory does not help us. To obtain some idea as to whether this dependence is important we re-do our calculations with $D = 100\tilde{\Gamma}$. The curves we get are very similar, suggesting that the cancellation is going through as before. This indicates that the value of the band width has little effect of the properties of the system.

In the two scaling limits, $D \gg |\delta| \gg \tilde{\Gamma}$, we can rescale our equations leading to the following equations for $\tilde{\omega}$ and χ

$$\tilde{\omega} = \omega_s + E_1^* = T^* \exp(-T^*/\tilde{\Gamma}) \tag{5.8}$$

where

$$T^* = \tilde{\Gamma}/(n_f - 1) \tag{5.9}$$

$$\chi = \mu_{\text{eff1}}^2/\tilde{\omega} = (\mu_{\text{eff1}}^2/T^*) \exp(T^*/\tilde{\Gamma}) = [\mu_{\text{eff1}}^2 (n_f - 1)/\tilde{\Gamma}] \exp[1/(n_f - 1)] \tag{5.10}$$

in the f^1 limit, and

$$\tilde{\omega} + T^* = \omega_s + E_2^* = 2T^* \exp(-T^*/\tilde{\Gamma}) \tag{5.11}$$

where

$$T^* = \tilde{\Gamma}/R(2 - n_f) \tag{5.12}$$

$$\begin{aligned} \chi &= 2\mu_{\text{eff2}}^2/(\tilde{\omega} + T^*) = (\mu_{\text{eff2}}^2/T^*) \exp(T^*/\tilde{\Gamma}) \\ &= [\mu_{\text{eff2}}^2(2 - n_f)/\tilde{\Gamma}] \exp[1/R(2 - n_f)] \end{aligned} \tag{5.13}$$

in the f^2 limit. So we find an essential singularity rather than just a simple pole in the susceptibility which is just what was found for the exact result for Ce in the f^1 limit (Rasul and Hewson 1984).

6. The charge susceptibility

It is straightforward to extend our method to calculate the charge susceptibility. This can be done by adding an extra term $\epsilon \sum_{m_1\sigma} f_{m_1\sigma}^\dagger f_{m_1\sigma}$ into the Hamiltonian and calculating the dependence of ω_s on ϵ . We then have $\chi_c = d^2\omega_s/d\epsilon^2$. This can be seen to be equivalent to $\chi_c = -dn_f/d\delta$.

Working to zeroth order and using the rescaled equations we find for the results in the two Kondo limits

$$\chi_c = (n_f - 1)^2/\tilde{\Gamma} \tag{6.1}$$

as $n_f \rightarrow 1$ and

$$\chi_c = (2 - n_f)/\bar{\Gamma} \quad (6.2)$$

as $n_f \rightarrow 2$. These can be compared with the zeroth-order result for Ce

$$\chi_c = n_f^2(1 - n_f)/\bar{\Gamma}. \quad (6.3)$$

We see that the behaviour in the f^2 limit is analogous to that for Ce while that in the f^1 limit is different.

If we now include the first excited state we find that (6.1) remains unchanged while (6.2) is modified to become

$$\chi_c = R(2 - n_f)^2/\bar{\Gamma}. \quad (6.4)$$

The equivalent expression for Ce in the f^1 limit is

$$\chi_c = (1 - n_f)^2/\bar{\Gamma}. \quad (6.5)$$

We have also calculated χ_c in the middle of the valence regime. For $\delta = -2$ we found $\chi_c = 0.06\bar{\Gamma}$ so χ_c is very small and is $\ll \chi$ for all n_f between 1 and 2. This is in contrast to the case for Ce where as we go into the mixed valence regime the spin and charge susceptibilities are of the same order of magnitude. It appears that in the case of Tm spin fluctuations are dominating the behaviour even for intermediate valence.

There exists an exact relation between χ , χ_c and the linear coefficient of specific heat, γ , due to Yoshimori (1976)

$$\bar{\gamma} = R^{-1}[\chi_c + (R - 1)\bar{\chi}] \quad (6.6)$$

where $\gamma = (\pi^2 k_B^2/3)\bar{\gamma}$. Using this formula we can calculate the Wilson ratio $\bar{\chi}/\bar{\gamma}$. This is given by

$$\bar{\chi}/\bar{\gamma} = R/(R - 1 + \chi_c/\bar{\chi}). \quad (6.7)$$

In the two Kondo limits the ratio $\chi_c/\bar{\chi}$ is vanishingly small. In the middle of the valence regime the ratio is also very small ~ 0.006 for $\delta = -2$. It appears that the Wilson ratio is to a good approximation given by its Kondo limit value of $1/(1 - R^{-1})$ throughout the mixed valent regime in contrast to Ce where there is a significant dependence on n_f .

7. The frequency-dependent susceptibility

The variational method used so far can also be extended to calculate the frequency dependent susceptibility, $\chi(\omega)$. This is related to the inelastic neutron scattering and gives important information about the low-energy excitations of the system. For the case of Ce this has been calculated by Gunnarsson and Schönhammer (1985) and, using a different technique, Kuramoto and Kojima (1984).

The method we use is as follows. We add into our Hamiltonian (1.1) a *time-dependent* perturbation $H_1 = \mu_z h \cos \omega t$. We can then use standard perturbation theory, i.e., we substitute (2.5) into

$$i\hbar \frac{\partial |\psi_S(h)\rangle}{\partial t} = H |\psi_S(h)\rangle \quad (7.1)$$

where the coefficients $\alpha_S(k)$, $A^-(k)$ etc. are now time-dependent. Having obtained expressions for these coefficients we can define a time-dependent magnetic moment

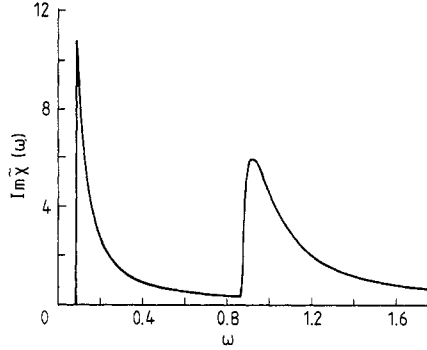


Figure 3. A plot of the imaginary part of the susceptibility against ω for $\delta = -2.5$.

$$M(t) = \langle \tilde{\psi}_S(h) | H_1 | \tilde{\psi}_S(h) \rangle \quad (7.2)$$

$\chi(\omega)$ is then given by $\partial M / \partial (h \cos \omega t)$.

This method is somewhat different to that used by Gunnarsson and Schönhammer (1985), but we note that it gives identical results for Ce.

For the present problem it yields the following equations

$$\chi(\omega) = \frac{1}{2}[F(\omega) + F(-\omega)] \quad (7.3)$$

where

$$F(\omega) = \frac{\mu_{\text{eff1}}^2 \sum_k A^-(k, \omega) \alpha_S(k) + \mu_{\text{eff2}}^2 \sum_{kk'} B^-(k, k', \omega) \beta_S(k, k')}{\langle \psi_S(0) | \psi_S(0) \rangle} \quad (7.4)$$

$A^-(k, \omega)$ is defined by an integral equation similar to (2.9)

$$\begin{aligned} A^-(k, \omega)(\omega_S + \varepsilon_k - \omega) - \tilde{\Gamma} \int_0^D \frac{A^-(k, \omega) + bA^-(k', \omega)}{\delta + \omega_S + \varepsilon_k + \varepsilon_{k'} - \omega} d\varepsilon_{k'} \\ = -\alpha_S(k) - a\tilde{\Gamma} \int_0^D \frac{\alpha_S(k) + \alpha_S(k')}{(\delta + \omega_S + \varepsilon_k + \varepsilon_{k'}) (\delta + \omega_S + \varepsilon_k + \varepsilon_{k'} - \omega)} d\varepsilon_{k'} \end{aligned} \quad (7.5)$$

$$\begin{aligned} B^-(k, k', \omega)(\omega_S + \delta + \varepsilon_k + \varepsilon_{k'} - \omega) \\ = -\beta(k, k') - \tilde{V}[A^-(k, \omega) + A^-(k', \omega)] \end{aligned} \quad (7.6)$$

where a and b depend on the coupling scheme used. The susceptibility clearly diverges for certain values of ω . The integral equation becomes more difficult to solve in view of this and for simplicity we have chosen to use zero j - j coupling as $N \rightarrow \infty$ for which $b = 0$.

We wish to look at both the real and imaginary parts of $\chi(\omega)$. Letting $\omega \rightarrow \omega + i\nu$ where $\nu \rightarrow 0$ we can find the imaginary part which is shown in figure 3. The real part can also be calculated (see figure 4). We can see by inspection that $A^-(k, \omega)$ has poles at $\omega = \varepsilon_k + \omega_S - \omega_D$ and $\omega = \varepsilon_k + \omega_S + \delta$. There is no pole for $\omega < \omega_S - \omega_D$ so the imaginary part of χ is zero below $\omega_S - \omega_D$. The real part of the susceptibility diverges at $\omega = \omega_S + \omega_D$ and at $\omega = \omega_S + \delta$.

This can be compared with the equivalent results for Ce where the real part of the susceptibility diverges only once at $\omega = \omega_S$ and the imaginary part is given by

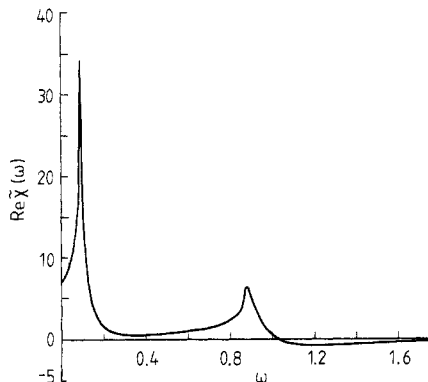


Figure 4. A plot of the real part of the susceptibility against ω for $\delta = -2.5$.

$$\text{Im } \tilde{\chi}(\omega) = [\pi\theta(\omega - \omega_s)\omega_s]/\omega^2. \quad (7.7)$$

If we now include all excited states then the poles in $A^-(k, \omega)$ occur at

$$\varepsilon_k + \omega_s - \omega - F(\varepsilon_k + \omega_s - \omega) = 0 \quad \Rightarrow \omega = \varepsilon_k + \omega_s - \omega_D \quad (7.8)$$

and

$$\varepsilon_k + \omega_s + \delta - \omega - G(\varepsilon_k + \omega_s - \omega) = 0. \quad (7.9)$$

The first pole corresponds to excitations across the gap between the singlet ground state and the higher-energy magnetic states. To understand (7.9) it is useful to consider the following wavefunction

$$|\psi'_T\rangle = \alpha'_T f_{m'}^\dagger f_m^\dagger |\psi_0\rangle + \sum_{qmm'} \beta'_T(q) f_m^\dagger c_{qm'}^\dagger |\psi_0\rangle + \text{excited states} \quad (7.10)$$

which has an eigenvalue equation

$$\omega'_T + \delta = G(\omega'_T) \quad (7.11)$$

and we see that (7.9) can be rewritten $\omega = \varepsilon_k + \omega_s - \omega'_T$.

The situation is as follows. For Ce we can define two wavefunctions, one consisting of the f^0 state plus all terms connected to this via H_{mix} (this is the singlet) and the second consisting of the f^1 state plus all terms connected by H_{mix} (the doublet state). The dynamic susceptibility has a threshold at the energy difference of these two states. For Tm we can define two states by considering the f^1 state plus all terms connected by H_{mix} and the f^2 state plus all terms connected by H_{mix} (equations (1.3) and (7.10), respectively). Both these states are magnetic but we can also define a singlet state which lies below both of them. The two threshold energies we see in the dynamical susceptibility correspond to excitations from the singlet to these two magnetic states. The presence of the second peak is then a direct consequence of the fact that both valence states have a non-zero magnetic moment.

The Korrunga relation causes there to be an exact relationship between $\chi(0)$ and $\lim_{\omega \rightarrow 0} \text{Im } \tilde{\chi}(\omega)/\omega$ (Shiba 1975).

$$\lim_{\omega \rightarrow 0} \text{Im } \tilde{\chi}(\omega)/\omega = \pi \tilde{\chi}(0)^2. \quad (7.12)$$

The right-hand side is $O(1/N)$ so we would expect to get zero when we work to zeroth

order. Gunnarsson and Schönhammer (1985) have shown that including excited states closes the gap and (7.12) can be shown to hold in the $N \rightarrow \infty$ limit. The extra terms are of order $1/N$ so an approximate threshold still remains. This can be seen in the following way. In calculating the susceptibility we will always obtain a term of the form $\sum_k \alpha_s(k) A(k, \omega)$, where $A(k, \omega) = \alpha / [\omega_s + \varepsilon_k - \omega - G(\omega_s + \varepsilon_k - \omega)]$. This clearly has a pole at $\omega = \varepsilon_k + \omega_s - \omega_D$, where ω_D is given by the solution of $\omega_D = G(\omega_D)$. $G(\omega_s + \varepsilon_k - \omega)$ is defined by the integral equation (3.13) and ω_s is found from $\omega_s = F(\omega_s)$. We see that the integrand has a pole at $\omega = \varepsilon_k$ so has a pole even as $\omega \rightarrow 0$. It is this fact that gives rise to the Fermi liquid relation.

The situation is different for Tm. The functions $F(\omega_s)$ and $G(\omega_s)$ which again occur in the equations for $\chi(\omega)$ do not contain poles and the imaginary part of the susceptibility is zero below $\omega_s - \omega_D$ or $\omega_s - \omega'_T$, whichever is smaller. Including excited states will smooth the curve for $\text{Im } \chi(\omega)$ at the first threshold but will not remove the gap. It is hard to imagine that this is an intrinsic property of the model and we suspect that it arises due to the approximations we have made. Kuramoto and Kojima (1984) have already suggested that while giving accurate values for the binding energies the 'non-crossing' approximation does not describe the low-energy excitations very well.

Experimentally, the neutron spectrum for Ce is qualitatively different from that for Tm. The former has a quasi-elastic peak with a weakly temperature-dependent width. For Tm, however, the neutron scattering consists of two peaks, one quasi-elastic and one inelastic. The latter, of appreciable intensity, is broad and cannot be explained as arising from crystal field splitting. The width of the quasi-elastic peak tends to zero as T approaches 0 K. These features are seen both in the concentrated system TmSe and in the dilute systems $\text{Tm}_{0.05}\text{Y}_{0.95}\text{Se}$ and $\text{Tm}_{0.05}\text{La}_{0.95}\text{Se}$, indicating that they are due to a local property of the ion (Holland-Moritz and Prager 1983, Holland-Moritz 1983). The experimental neutron scattering curve can be compared with our theoretical curve for $\text{Im } \chi(\omega)/\omega$ ($\text{Im } \chi(\omega)$ is shown in figure 3). We note in particular the fact that a second peak is found. The parameters used for the diagram give $n_f \approx 1.5$ which is about right for $\text{Tm}_{0.05}\text{Y}_{0.95}\text{Se}$. The position of the first peak is at $0.08 \bar{\Gamma}$ and the halfwidth of the line is $\sim 0.02 \bar{\Gamma}$. Our value for the second threshold, Δ , is $\omega_s - \omega'_T \approx 0.85 \bar{\Gamma}$ and the line has a halfwidth of $0.1 \bar{\Gamma}$. Better estimates for the thresholds can be obtained by including terms to $O(1/R)$, with $R = 13/8$. This gives $\omega_s - \omega_D = 0.09 \bar{\Gamma}$ and $\Delta = 0.6 \bar{\Gamma}$. The frequency-dependent susceptibility is more difficult to calculate but we do not expect the linewidths to change greatly. To make a quantitative comparison with our theory we need an estimate for $\bar{\Gamma}$. Read *et al* (1985) take $\bar{\Gamma} = 40$ meV, having assumed that Γ has the same value as for Ce. Here we use the experimental value for Δ to give an estimate for $\bar{\Gamma}$ and use this to determine the other quantities. For $\text{Tm}_{0.05}\text{Y}_{0.95}\text{Se}$ $\Delta = 11$ meV. This gives $\bar{\Gamma} \approx 18$ meV. The halfwidth of the second peak is ~ 3.6 meV, which is in agreement with the experimental value 3 meV. The first peak is at 1.6 meV with half-width 0.4 meV. The agreement between this and the experimental data which shows a quasi-elastic width of 0.2 meV is not good. We note that the Kondo temperature, T_K , defined as being equal to the energy gap $\omega_s - \omega_D$ is ~ 19 K. The condition for Fermi-liquid-like behaviour, i.e., $T \ll T_K$, is not therefore being met by experiments carried out at 15 K. What appears to be happening is that the doublet state is appreciably occupied and as this state is degenerate the low-energy behaviour is dominated by zero-energy excitations.

Data are also presented on $\text{Tm}_{0.05}\text{La}_{0.95}\text{Se}$ which have $n_f \approx 1.6$. The position of the inelastic peak for this compound is ~ 3 meV, i.e., the excitation energy is much reduced

compared to the previous case. Theoretically we find $\Delta \approx 0.4\tilde{\Gamma}$, giving $\tilde{\Gamma} \approx 7.5$ meV, which is significantly smaller than that found before. $\omega_S - \omega_D$ is reduced to $0.08\tilde{\Gamma} = 0.6$ meV which is of the same order of magnitude as the experimental width of 0.75 meV. However, it is not clear that a direct comparison is meaningful.

We note that a previous attempt has been made to explain the inelastic peak using a variational method (Mazzafarro *et al* 1981). However, they considered a *magnetic* variational wavefunction (equivalent to $|\psi_D\rangle$) rather than the singlet ground state, so their results are not really valid.

8. Extension of results to uranium compounds

The properties of uranium ions are of particular interest in view of the wide variety of behaviours exhibited by different compounds at low temperatures. While certain compounds appear to have localised 5f electrons, others show itinerant 'heavy fermion' behaviour. Much attention has been given to uranium compounds showing heavy fermion superconductivity since these have unusual properties that are not thought to be consistent with simple BCS theory. It seems clear that the explanation for the different possible ground states must lie in the details of the particular lattice and the interactions between ions. In concentrated salts the hopping of electrons between ions (double exchange) and the RKKY interaction provide two mechanisms for the occurrence of ordered magnetism (Varma 1979). One kind of classification has been provided in the form of Hill plots (Hill 1970) where it is seen that compounds with local magnetic moments usually have small U-U internuclear distances compared to those exhibiting itinerant behaviour.

It is interesting then to ask what properties a single uranium ion will possess. Physically it would seem reasonable that the properties would resemble those of a Tm ion in that again we have an ion fluctuating between two magnetic valence states, the states being in this case f^2 and f^3 . This is also the conclusion reached by the theories we have discussed. The results of a mean-field functional integral calculation are trivially extended to all cases of ions fluctuating between f^n and f^{n+1} ($n \neq 0$) leading to the same conclusions as for Tm, i.e., that we have a singlet ground state with small energy scale. Extending the variational method that we have considered here is considerably harder because the singlet state involves an increasing number of holes. To zeroth order, variational wavefunctions have been found and the corresponding eigenvalues calculated by solving a two-dimensional integral equation (Nunes *et al* 1985). Again there is a close correspondence with the results for Tm. It is entirely possible to extend all our results to the case of uranium, although in view of the added complexity of the wavefunctions we have in fact only considered the analytical results for the two Kondo limits. It is readily seen that the results are entirely equivalent. With no self-energy terms the energy scale shows the asymmetry found earlier with the energy scale being anomalously large in the f^3 limit as compared to the f^2 limit. Including the first self-energy term corrects this leading to the following results (after renormalisation)

$$\omega_S - \omega_T = 2T^* \exp(T^*/\tilde{\Gamma}) \quad (8.1)$$

$$\chi = 2\mu_{\text{eff}}^2/(\omega_S - \omega_T) = (\mu_{\text{eff}}^2/T^*) \exp(T^*/\tilde{\Gamma}) \quad (8.2)$$

where $T^* = \tilde{\Gamma}/(n_f - 2)$, in the f^2 limit and

$$\omega_s - \omega_T = 3T^* \exp(T^*/\bar{\Gamma}) \quad (8.3)$$

$$\chi = 3\mu_{\text{eff}3}^2/(\omega_s - \omega_T) = (\mu_{\text{eff}3}^2/T^*) \exp(T^*/\bar{\Gamma}) \quad (8.4)$$

with $T^* = \bar{\Gamma}/[R(3 - n_f)]$ in the f^3 limit. The extra factors of 2 and 3 in (8.1) and (8.3) come from the fact that the binding energy is proportional to the number of electrons. ω_T is the binding energy of the no-hole triplet and has an eigenvalue equation identical to that for the doublet in the case of Tm. Although we have not solved the integral equations throughout the mixed valence region it is difficult to imagine that our conclusions would differ.

9. Conclusions

In this paper we have considered an extension of the method used in I to include a calculation of the magnetic susceptibility and of the energy scale to $O(1/R)$ throughout the mixed valence regime. Our results are best illustrated by figures 1 and 2, where it is seen that (i) χ is closely correlated to the energy scale; (ii) to zeroth order there is a marked asymmetry in the energy scale in the two local moment regimes; and (3) the inclusion of the first electron-hole excitation removes the asymmetry and significantly reduces the energy scale. Analytical results in the two Kondo limits are equivalent to the exact results for Ce. We have also considered the dependence of our equations on the band cut-off D and shown that this is very weak. The charge susceptibility has been shown to be small even in the middle of the valence regimes and the spin fluctuations dominate the behaviour for all n_f .

Calculating the dynamical susceptibility $\chi(\omega)$ shows that this has extra structure compared with that for Ce found experimentally. At low energies our expression does not satisfy the Shiba-Fermi liquid relation due to the approximations used. Our results easily extend in the Kondo limits to give equivalent results for uranium ions. We note that the susceptibility is proportional to $(g_f - g_c)^2$, in contrast with the result from the functional integral method where the contribution to the susceptibility from the c electrons is $O(m/m^*)$ compared to that from the f electrons.

Although the energy scale we find is small it does not appear to be small enough to account for the results from neutron scattering. This fact was commented on by Read *et al* (1986). Including excited states reduces the energy slightly below that found by Read *et al* (1986) and treating $\bar{\Gamma}$ as a parameter determined by the position of the second peak in the frequency dependent susceptibility reduces the energy scale further. However the agreement with experiment is still not good. Crystal field splittings have been ignored and it may be that these are playing an important role. A similar problem arises in the case of uranium compounds. The calculated energy scale is about a factor 10 too big to account for the observed magnetic ordering in UN at 50 K. Estimates of the mass enhancements in the heavy fermion systems also tend to be too low. The inclusion of the self-energy terms improves the agreement, but not by nearly enough. The situation remains that comparison between theory and experiment is not very satisfactory though we note that our theory is for zero temperature and it is not clear that a direct comparison is meaningful.

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