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Localised description of valence fluctuations

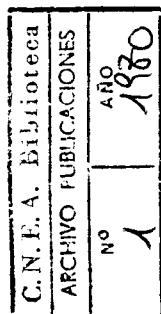
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Abstract. We set up a model for an intermediate valence equivalent to the 'atomic' limit of the Anderson Hamiltonian. Detailed analysis of this model shows that most of the essential characteristics of valence fluctuators are already present in this crudely simplified Hamiltonian. We study the spin-spin and the 4f charge-charge correlation functions and show that it is possible to define a spin fluctuation frequency ω_{sf} and a charge fluctuation frequency ω_{cf} . ω_{sf} and ω_{cf} can differ considerably for some values of the parameters of the model. We calculate the magnetic susceptibility and the specific heat as functions of temperature and show how the results simulate the behaviour found in valence fluctuators.

1. Introduction

Recently there has been a considerable amount of theoretical effort devoted to the understanding of valence fluctuations. Most of the theoretical models considered in the literature contain two more or less realistic correlated ionic configurations hybridised to a set of uncorrelated conduction-like states (Hist 1979, Alascio 1977). The complexity of the problem has forced researchers in this area to make simplifying assumptions in order to keep the mathematics of the models tractable.

In order to gain insight into this problem we have reduced it to that of an aggregate of independent sites, where intra-atomic correlations and hybridisation can be treated exactly. This limitation prevents us from calculating any transport properties. However, it can be used to calculate different thermodynamic properties related to the 4f shell. These properties are similar to those found in valence fluctuating systems and provide a framework within which one can reach a conceptual understanding of most of the essential characteristics of those compounds where valence fluctuations take place.

In § 2 we set up the model Hamiltonian and analyse its eigenfunctions and eigenvalues in § 3. In § 4 we calculate different thermodynamical quantities and discuss their physical implications with respect to experiment.

Section 5 contains a discussion and conclusion of the results.

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2. The model

Our aim here is to set up the simplest model that still retains the essential features of intermediate valence systems.

We adopt the point of view that, besides the coincidence of the energies needed to add one electron to the 4f shell or to the Fermi sea of conduction electrons, it is the interplay of two energies that gives rise to the properties of valence fluctuators: the Coulomb repulsion U between 4f electrons and the mixing energy V that hybridises these states with those of the conduction band. The Coulomb repulsion not only excludes the possibility of more than two successive 4f shell configurations, but also introduces a correlation in the mixing of states. It is this feature that extremely complicates the mathematics of the problem.

Our model system consists of:

- (i) A set of uncorrelated states representing the conduction band of energies ϵ_k and with creation and annihilation operators $c_{k\sigma}^+$, $c_{k\sigma}$, where σ indicates the spin.
- (ii) A set of localised states with a strong Coulomb repulsion between electrons of opposite spin. These states have single-particle energy E_σ , creation and annihilation operators $f_{i\sigma}^+$, $f_{i\sigma}$. They represent the more complex highly correlated 4f states.
- (iii) A mixing term which hybridises localised and band states by exchanging electrons between these states.

With these considerations we are led to an Anderson lattice Hamiltonian (in similitude to the Kondo lattice (Jullien *et al* 1979))

$$H = \sum_{i\sigma} E f_{i\sigma}^+ f_{i\sigma} + U n_{fi\uparrow} n_{fi\downarrow} + \sum_{ki\sigma} [V(k) f_{i\sigma}^+ c_{k\sigma} + V^*(k) c_{k\sigma}^+ f_{i\sigma}] + \sum_{k\sigma} \epsilon_{k\sigma} C_{k\sigma}^+ C_{k\sigma}$$

where

$$n_{f\sigma} = f_{i\sigma}^+ f_{i\sigma}.$$

As was mentioned earlier, the highly simplified model Hamiltonian (1) presents unsurmountable difficulties if one attempts to obtain its eigenfunctions and eigenvalues.

Different approximations and techniques have been used and they have had some success in providing a qualitative understanding for some range of the values of the parameters involved.

However, many questions remain open. Conceptual points are not always clear, and extensions of Hamiltonian (1) to include the effects of phase transitions, coupling to lattice vibrations, magnetic ordering, etc must rely on approximations that destroy some of the essential features of intermediate valence.

We want to present here a further simplification of (1) that allows us to find quite easily its eigenfunctions and eigenvalues and that still retains a good deal of the physics of intermediate valence systems.

The following arguments apply to metallic systems, but they can be adapted to apply to semiconductors also.

We know that valence fluctuations occur when the one-particle energies of the 4f states (E or $E + U$ in this model) lie at a distance comparable to V from the Fermi energy. It is the mixing of these highly correlated states with the band states that produces the phenomena found in intermediate valence systems. In order to include this fact, together with the effect of large U , correctly in our model, we shall take the following steps:

(i) We shall push together a set of $2N$ states $|k\sigma\rangle$ from the band near the Fermi energy (N being the total number of sites) and place them just at the Fermi energy. This allows us to define new creation and annihilation operators through

$$c_{j\sigma} = N^{-1/2} \sum_k \exp(ikR_j) c_{k\sigma} \quad (2)$$

j runs from 1 to N and

$$[c_{j\sigma}^\dagger, c_{j'\sigma'}] = \delta_{jj'} \delta_{\sigma\sigma'}$$

is satisfied.

(ii) Since the new operators create or annihilate electrons from more or less localised sites, we shall assume that the mixing Hamiltonian can now be written as:

$$H_{\text{Mix}} = \sum_{j\sigma} (V f_{j\sigma}^\dagger c_{j\sigma} + V^* c_{j\sigma}^\dagger f_{j\sigma}). \quad (3)$$

This on-site mixing is usually forbidden by symmetry considerations. However, since this point is not essential for our conclusions we will take form (3) for simplicity.

With these assumptions, Hamiltonian (1) separates into a sum of disconnected Hamiltonians of the form

$$H = \sum_{\sigma} E f_{\sigma}^\dagger f_{\sigma} + U n_{\uparrow} n_{\downarrow} + \epsilon_F \sum_{\sigma} c_{\sigma}^\dagger c_{\sigma} + \sum V (f_{\sigma}^\dagger c_{\sigma} + c_{\sigma}^\dagger f_{\sigma}) \quad (4)$$

where we have dropped the now irrelevant subscript j and taken V real.[†] Note that if there were more than $2N$ states in the bands, pulling more than $2N$ states together would have no effect since they become degenerate at ϵ_F ; we can then form a new set of $2N$ band states that will mix with the f states, while the others remain unaffected.

Hamiltonian (4) is our model Hamiltonian. In what follows we shall find its eigenfunctions and eigenvalues. In §3 we shall study its predictions for different physical quantities and show that they contain most of the physics of intermediate valence systems.

To this purpose, we must make a choice of parameters. First, we must choose either E or $E + U$ to lie close to the Fermi energy. In the following we take E to be near ϵ_F . In this case the results are applicable to Ce compounds. The case $E + U$ near ϵ_F is more appropriate to describe Sm or Yb compounds (Alascio *et al* 1979a). To describe the case where the two configurations are magnetic it is necessary to generalise the Hamiltonian. This will be the subject of a future publication. Furthermore, we shall take $U \rightarrow \infty$, i.e. much larger than any of the energies involved in our calculations. We shall go back to this point when we discuss xps experiments.

Table 1 shows the eigenstates and eigenvalues of our model Hamiltonian. They are listed according to the total number of electrons (third column). The total spin is shown in the fourth column.

Three parameters enter into the definition of the eigenfunctions and eigenvalues of table 1, ϵ_F , E and V .

For further discussions, it will be convenient to choose $\Delta = E - \epsilon_F$, ϵ_F and V as independent parameters.

Figure 1(a) shows the energy levels as functions of E/V for $\epsilon_F = 0$. The numbers near each curve indicate the corresponding states in table 1. When ϵ_F is varied, the

[†] Based on similar considerations, Foglio and Falicov (1979), Balseiro *et al* (1979) have approached intermediate valence through Hamiltonian (4), extending it (for some of the values of the parameters) to include the kinetic energy of the conduction electrons. Alascio *et al* (1979a) have also used a Hamiltonian similar to (4) to discuss phase transitions in intermediate valence compounds.

Table 1.

Eigenstates	Energies	N	S
$ 1\rangle = 0\rangle$	0	0	0
$ 2\rangle = \cos \phi f_{\downarrow}^+ 0\rangle - \sin \phi c_{\downarrow}^+ 0\rangle$	$\frac{1}{2}(\epsilon_F + E) - [(\frac{1}{2}(\epsilon_F - E))^2 + V^2]^{1/2}$	1	$\frac{1}{2}$
$ 3\rangle = \cos \phi f_{\uparrow}^+ 0\rangle - \sin \phi c_{\uparrow}^+ 0\rangle$	$\frac{1}{2}(\epsilon_F + E) - [(\frac{1}{2}(\epsilon_F - E))^2 + V^2]^{1/2}$	1	$\frac{1}{2}$
$ 4\rangle = \sin \phi f_{\downarrow}^+ 0\rangle + \cos \phi c_{\downarrow}^+ 0\rangle$	$\frac{1}{2}(\epsilon_F + E) + [(\frac{1}{2}(\epsilon_F - E))^2 + V^2]^{1/2}$	1	$\frac{1}{2}$
$ 5\rangle = \sin \phi f_{\uparrow}^+ 0\rangle + \cos \phi c_{\uparrow}^+ 0\rangle$	$\frac{1}{2}(\epsilon_F + E) + [(\frac{1}{2}(\epsilon_F - E))^2 + V^2]^{1/2}$	1	$\frac{1}{2}$
$ 6\rangle = c_{\downarrow}^+ f_{\downarrow}^+ 0\rangle$	$\epsilon_F + E$	2	1
$ 7\rangle = (1/\sqrt{2})(c_{\downarrow}^+ f_{\uparrow}^+ + c_{\uparrow}^+ f_{\downarrow}^+) 0\rangle$	$\epsilon_F + E$	2	1
$ 8\rangle = c_{\uparrow}^+ f_{\uparrow}^+ 0\rangle$	$\epsilon_F + E$	2	1
$ 9\rangle = (\cos \lambda/\sqrt{2})(c_{\downarrow}^+ f_{\uparrow}^+ - c_{\uparrow}^+ f_{\downarrow}^+) - \sin \lambda c_{\downarrow}^+ c_{\uparrow}^+ 0\rangle$	$\frac{1}{2}(E + 3\epsilon_F) - [(\frac{1}{2}(\epsilon_F - E))^2 + 2V^2]^{1/2}$	2	0
$ 10\rangle = (\sin \lambda/\sqrt{2})(c_{\downarrow}^+ f_{\uparrow}^+ - c_{\uparrow}^+ f_{\downarrow}^+) + \cos \lambda c_{\downarrow}^+ c_{\uparrow}^+ 0\rangle$	$\frac{1}{2}(E + 3\epsilon_F) + [(\frac{1}{2}(\epsilon_F - E))^2 + 2V^2]^{1/2}$	2	0
$ 11\rangle = c_{\downarrow}^+ c_{\uparrow}^+ f_{\downarrow}^+ 0\rangle$	$E + 2\epsilon_F$	3	$\frac{1}{2}$
$ 12\rangle = c_{\downarrow}^+ c_{\uparrow}^+ f_{\uparrow}^+ 0\rangle$	$E + 2\epsilon_F$	3	$\frac{1}{2}$

With

$$\tan \phi = V / \{ \frac{1}{2}(\epsilon_F - E) + [(\frac{1}{2}(\epsilon_F - E))^2 + V^2]^{1/2} \} = V / \{ -\frac{1}{2}\Delta + [(\frac{1}{2}\Delta)^2 + V^2]^{1/2} \}$$

$$\tan \lambda = \sqrt{2}V / \{ \frac{1}{2}(\epsilon_F - E) + [(\frac{1}{2}(\epsilon_F - E))^2 + 2V^2]^{1/2} \} = \sqrt{2}V / \{ -\frac{1}{2}\Delta + [(\frac{1}{2}\Delta)^2 + 2V^2]^{1/2} \}.$$

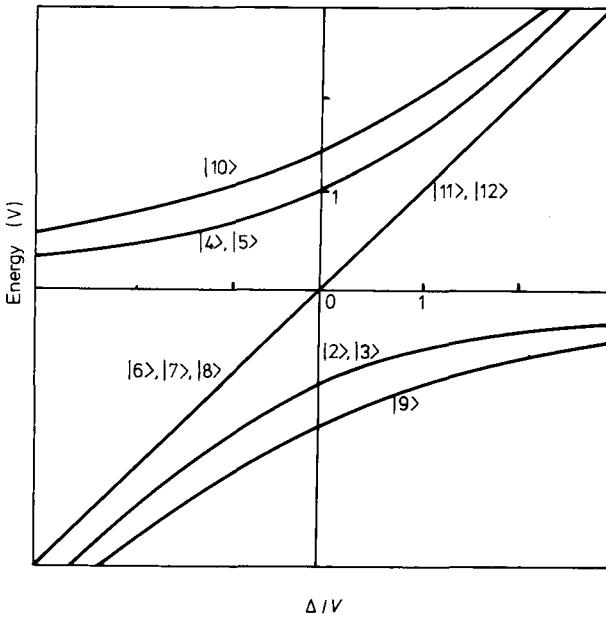


Figure 1. Energy levels of H_L as functions of Δ/V . Numbers indicate the corresponding eigenstates in table 1.

energies corresponding to a different number of particles shift. For example, as ϵ_F increases the n particle states shift upwards by $n\epsilon_F$, thus favouring the vacuum state.

At zero temperature the number of particles is given by the lowest energy state. In figure 2 the regions of values of ϵ_F/V and E/V that make the zero-, one-, two- or three-particle states lowest are depicted. When the kinetic energy of the band electrons is included, states with a different number of particles mix thus making the zone boundaries in figure 2 less defined.

Going back to table 1, we can see that the trivial eigenstates corresponding to zero and three particles are irrelevant to valence fluctuations. The same applies to the one-particle states where U plays no role. The most interesting states in relation to valence fluctuations are the five two-particle states $|6\rangle |7\rangle |8\rangle |9\rangle$ and $|10\rangle$.

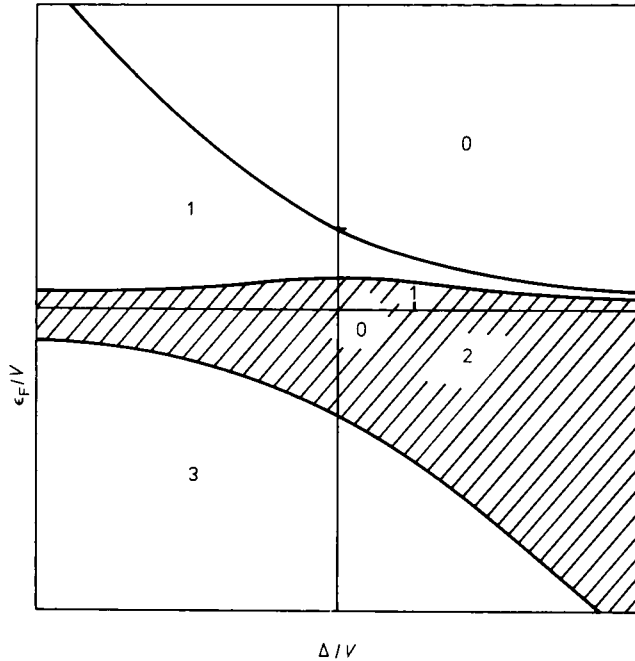


Figure 2. Regions of values of ϵ_F/V and Δ/V , where the ground state corresponds to zero, one two or three particles.

For this reason we shall restrict our study to region 2 in figure 2 where $|9\rangle$ is the ground state. This does not imply that we will not include all twelve states whenever it is necessary to do so.

3. Physical properties

3.1. Zero temperature properties

Here we shall discuss the quantities that can be calculated starting from the ground state (state $|9\rangle$).

3.1.1. *f-level occupation.* According to the model, the occupation of the f-level at $T = 0$ is given by

$$\langle n_f \rangle = \langle 9 | f_{\uparrow}^{\dagger} f_{\uparrow} + f_{\downarrow}^{\dagger} f_{\downarrow} | 9 \rangle = \cos^2 \lambda.$$

λ is defined in terms of Δ and V in table 1. Figure 3(a) shows the behaviour of $\langle n_f \rangle$ as a function of Δ/V . Clearly $\langle n_f \rangle$ takes values intermediate between 0 and 1 and decreases as the f-level energy increases crossing the Fermi level.

3.1.2. *Zero temperature susceptibility.* In order to evaluate the magnetic susceptibility we add to Hamiltonian (4) a term of the form

$$\mu S_z B = \frac{1}{2} \mu B (f_{\uparrow}^{\dagger} f_{\uparrow} - f_{\downarrow}^{\dagger} f_{\downarrow}).$$

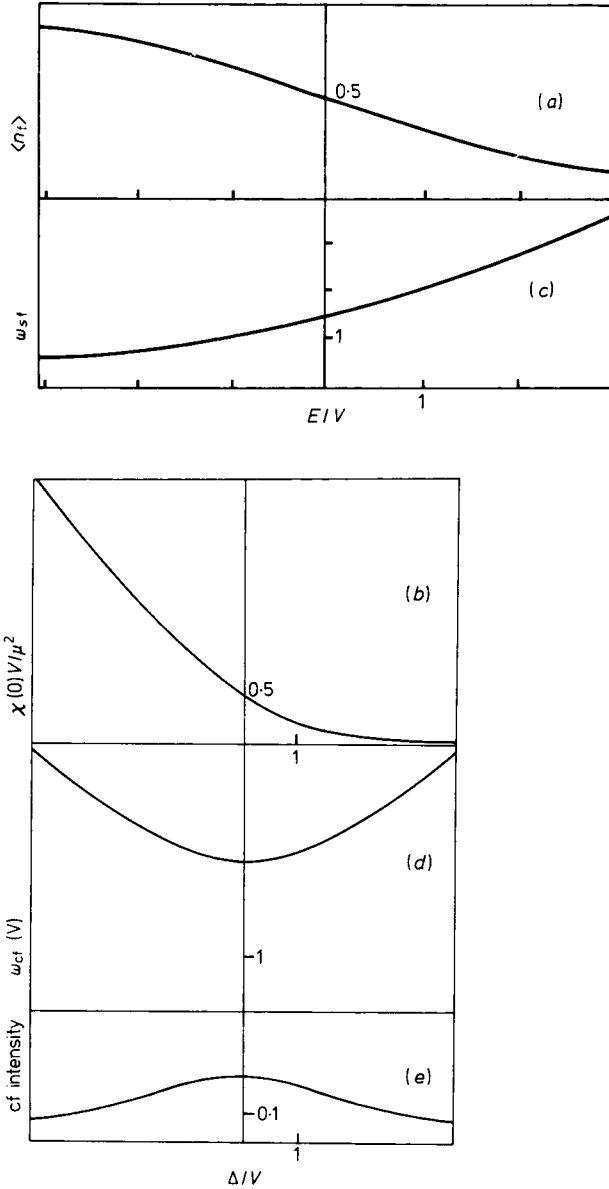


Figure 3. Different properties of the system at zero temperature as functions of Δ/V :

- (a) f-level occupation;
- (b) magnetic susceptibility;
- (c) spin fluctuation frequency;
- (d) charge fluctuation frequency;
- (e) intensity of charge fluctuations.

This term couples state $|9\rangle$ to state $|7\rangle$ thus inducing a Van Vleck susceptibility given by

$$\chi(0) = \frac{1}{2}\mu^2 \frac{|\langle 7|S_z|9\rangle|^2}{E_7 - E_9} = \frac{1}{2}\mu^2 \frac{n_f}{\frac{1}{2}\Delta + \sqrt{[(\frac{1}{2}\Delta)^2 + 2V^2]}}. \quad (5)$$

Here E_n is the energy of the n th state in table 1. In figure 3(b) we plot $\chi(0) V/\mu^2$ as a function of Δ/V . It is seen that as E crosses the Fermi level the zero temperature susceptibility decreases, corresponding to a lowering of the 4f level occupation and to an increase of the energy separation between the two states involved.

3.1.3. Spin correlation function. The magnetic neutron scattering cross section is directly related to the spin correlation function

$$\langle S^+(0)S^-(t) + S^-(0)S^+(t) \rangle \quad (6)$$

where

$$S^+ = f_{\uparrow}^{\dagger}f_{\downarrow}.$$

Its Fourier transform $F(\omega)$ measures the capacity of the system to absorb energy ω by flipping its spin. (In the following we take $\hbar = 1$.) It can easily be shown that at zero temperature

$$F(\omega) = \cos^2 \lambda \delta(\omega - E_8 + E_9) = \langle n_f \rangle \delta(\omega - E_8 + E_9). \quad (7)$$

There are two contributions to $F(\omega)$, one coming from the promotion from $|9\rangle$ to $|8\rangle$ and another from $|9\rangle$ to $|6\rangle$. They appear together in (7) because $E_6 = E_8$.

Since $F(\omega)$ consists of a single peak, it can be characterised by two quantities: intensity and position. The first is shown in figure 3(a) as a function of Δ/V , and the position of the peak is shown in figure 3(c). This implies that the correlation function oscillates harmonically with a frequency equal to $E_8 - E_9$. We identify this frequency with the spin fluctuation frequency.

It can be seen that, as Δ increases from negative values, the position of the absorption peak shifts towards higher values while its intensity decreases†.

3.1.4. f level occupation correlation function. If the rare-earth atom response to a certain external perturbation is characterised by a certain frequency ω_0 when the 4f shell is empty and by another frequency ω_1 when it is singly occupied, we can ask ourselves what the response would be in an intermediate valence situation. The answer to this question is intimately related to the f-level occupation correlation function

$$\langle [n_f(t) - \langle n_f \rangle] [n_f(0) - \langle n_f \rangle] \rangle. \quad (8)$$

Here again we shall calculate the Fourier transform of (8): $G(\omega)$. At zero temperature it can easily be calculated from the model Hamiltonian (4) and is given by

$$G(\omega) = \sin^2 \lambda \cos^2 \lambda \delta(\omega - E_{10} + E_9) = \langle n_f \rangle (1 - \langle n_f \rangle) \delta(\omega - E_{10} + E_9). \quad (9)$$

The position and intensity of the peaks of $G(\omega)$ are plotted as functions of Δ/V in figures 3(d) and (e).

† While the intensity of the peak is a realistic feature of the model, the position of the peak should be interpreted only as an indication of the width of the quasi-elastic peak found in real systems. This interpretation stems from the fact that in real systems the large spread of band energies makes the effect of hybridisation much less effective for states far from the Fermi level.

Here we see that as Δ increases from negative values, the 'charge fluctuation frequency' $\omega_{cf} = E_{10} - E_0$ starts from a high value, decreases to a minimum at $\Delta = 0 (E = \epsilon_F)$ and then increases again, while its intensity is low for large $|\Delta/V|$ and has a maximum at $\Delta = 0$.

Again, for the same reasons pointed out with respect to $F(\omega)$, there should be a large width associated with the charge fluctuation peak.

3.2. Thermodynamic properties

While it is not difficult to calculate spin or charge dynamics at finite temperatures, most of the physics contained in them is already present in the zero temperature results we have already worked out. For this reason we shall restrict ourselves to the calculation of the most 'popular' thermodynamic quantities: magnetic susceptibility and specific heat. (We take $k_B = 1$).

3.2.1. The magnetic susceptibility It is again a very simple exercise in statistical mechanics to calculate the magnetic susceptibility from the model Hamiltonian. It can be calculated from the two-particle states or from all states adjusting the Fermi energy in such a way that the mean total number of particles is always two. There is little numerical difference between these alternative approaches. The conditions of adjusting the Fermi energy clearly applies only for intermediate valence compounds. In the case of diluted impurities, the Fermi energy is fixed by the matrix and consequently it is temperature independent for our purposes. The two-particles inverse magnetic susceptibility is shown in figure 4 as a function of temperature for $\Delta = -0.95$ and different values of V . The full curve corre-

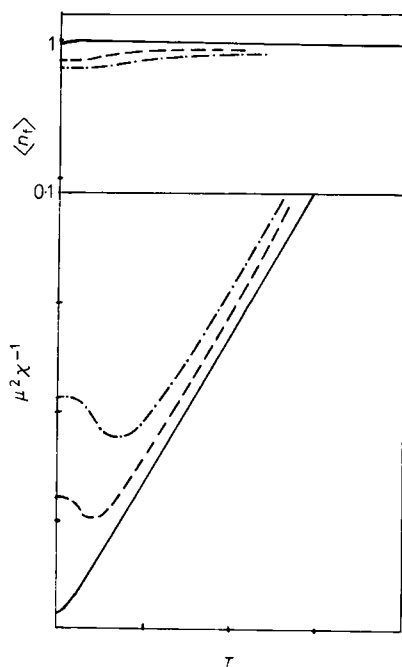


Figure 4. Inverse magnetic susceptibility as a function of temperature for $\Delta = 0.95$. Full curve $V = 0.1$, broken curve $V = 0.3$, chain curve $V = 0.4$. Upper part contains a plot of $\langle n_i \rangle$ (units of temperature).

sponds to $V = 0.1$. The magnetic susceptibility deviates appreciably from the Curie law (straight line through zero) only at low temperatures $T \sim \omega_{\text{sf}}$. The broken curve corresponds to $V = 0.3$ and the chain curve to $V = 0.4$. In the high-temperature region of these curves the apparent Curie–Weiss behaviour is found. They show a minimum at temperatures corresponding approximately to their respective spin fluctuation frequencies.

3.2.2. The specific heat. The model specific heat can also be calculated in a straightforward way. Figure 5 shows the model specific heat as a function of temperature for $\Delta = -0.5$

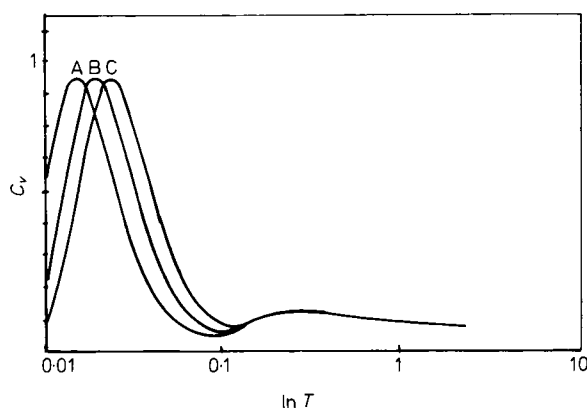


Figure 5. Model specific heat as a function of temperature for $\Delta = -0.5$. Curve: A $V = 0.11$, B $V = 0.13$ C $V = 0.15$. Note the logarithmic scale of temperature.

and $V = 0.11, 0.13$ and 0.15 . For higher values of V the two Schottky-like peaks merge into one. Analysing the energy levels one can recognise the origin of the two peaks: the first peak stems from excitations of energy ω_{sf} , while the second corresponds to excitations of energy ω_{cf} .

Here again, according to our interpretation of the spin–spin correlation function, the first peak in the specific heat is an indication of the magnitude of the γ term in real systems: a superposition of Schottky anomalies corresponding to a distribution of excitation energies leads to a linear term in the specific heat.

3.3. The linear response

In order to answer the question posed in § 3.1.4 regarding the f-level occupation correlation function, we follow Goncalves da Silva and Falicov (1976): assume that there is a certain new degree of freedom, described by Fermi operators a^+ and a , which has excitation energies ω_0 or ω_1 , when the f-level is empty or singly occupied, respectively. Then we add to the Hamiltonian a term

$$H_{\text{exc}} = \omega_0(1 - n_f)a^+a + \omega_1n_fa^+a. \quad (10)$$

At zero temperature, the correlation function $\langle a(t)a^+(0) \rangle$ describes the response of the system at intermediate valence. The total Hamiltonian $H_{\text{total}} = H_{\text{model}} + H_{\text{excitation}}$, can again be solved exactly, its eigenstates and eigenfunctions being characterised by the eigenvalues of the operator a^+a (0 or 1) and by the electronic eigenstates n or n' . Thus we label the complete eigenfunctions and eigenvalues $|0, n\rangle$ or $|1, n'\rangle$.

The $|0, n\rangle$ eigenfunctions are the same as shown in table 1, the vacuum now means electron and excitation vacuum. The $|1, n'\rangle$ eigenfunctions are also obtained from table 1 by replacing the zero of energies by ω_0 , Δ by $\Delta + \omega_1 - \omega_0$ and the vacuum by $a^+|0\rangle$. We call the corresponding angles ϕ' and λ' .

Evaluation of $M(\omega)$, the Fourier transform of $\langle a(t)a^+(0) \rangle$, in terms of the complete Hamiltonian eigenfunctions gives

$$M(\omega) = \cos^2(\lambda' - \lambda)\delta(\omega - E_{g'} - E_g) + \sin^2(\lambda' - \lambda)\delta(\omega - E_{10'} - E_{10}). \quad (11)$$

Two extreme regimes can be analysed:

(i) $|\omega_0 - \omega_1| \gg \omega_{\text{cf}}$ then $M(\omega)$ reduces to

$$M(\omega) = (1 - \langle n_f \rangle)\delta(\omega - \omega_0) + \langle n_f \rangle\delta(\omega - \omega_1). \quad (12)$$

(ii) $|\omega_0 - \omega_1| \ll \omega_{\text{cf}}$, in this case

$$M(\omega) = \delta(\omega - [(1 - \langle n_f \rangle)\omega_0 + \langle n_f \rangle\omega_1]). \quad (13)$$

These results being identical to those obtained by Goncalves da Silva and Falicov (1976). The point here is that the characterisation of the two regimes is given by ω_{cf} , thus giving ω_{cf} a physical meaning. We should point out that while Mössbauer experiments can be cast in this picture, as well as some optical experiments, this is not the case with the response function corresponding to xps experiments, because an analysis of the coupling between x-rays and 4f electrons reveals that it is given directly by the one-electron correlation function $\langle f_\sigma(t)f_\sigma^+(0) \rangle$. However, from a conceptual point of view, the former calculation can also be applied satisfactorily to xps experiments.

4. Discussion and conclusions

We have shown that many of the most characteristic features of intermediate valence systems are already present in the very simplified model described by Hamiltonian (4). The approach leading to Hamiltonian (4), which amounts to neglecting the role of the conduction electrons' kinetic energy in valence fluctuations, clearly overestimates the effect of the mixing energy V .

In order to scale the results obtained from the model to those expected from Hamiltonian (1) the mixing energy V could be replaced by the mixing strength $\rho V^2 \sim V^2/W$ (where ρ is the density of band states and W is the bandwidth). This seems to be a reasonable assumption for $\Delta/V \lesssim 1$.

For Δ/V large and negative, it is shown in figure 1 that the energy levels separate into two groups: those corresponding to states $|2\rangle, |3\rangle, |6\rangle, |7\rangle, |8\rangle, |11\rangle$ and $|12\rangle$ lie near the ground state $|9\rangle$, while the others lie at a large distance from it, of the order of ω_{cf} . The energy structure of the lower states can be approximately simulated by a narrow band version of the Kondo Hamiltonian by choosing $J \sim V^2/E$. Their energy spread corresponds approximately to the Kondo temperature $\sim J$. On the other hand, we know that the Kondo temperature shows an exponential behaviour on J for the impurity problem with wide bands. Thus if the scaling $V \rightarrow V^2/W$ were used in the 'Kondo regime' (Δ/V negative and large) we would have an energy spread $\sim V^4/W^2\Delta$, which does not seem quite convincing.

In § 3 we have calculated different properties, mainly low-temperature properties, as

functions of the distance between the 4f level and the Fermi energy. Experimentally this parameter can be varied with pressure or with chemical composition and it is found that E increases with pressure (Jayaraman and Maines 1979). The trends predicted by the model Hamiltonian are indeed found in all Ce systems: decrease of f-shell occupancy and of magnetic susceptibility due to pressure are common phenomena in these materials. Increase of the f-level energy with respect to the Fermi level can also take place in some of the compounds where a transition similar to the χ - γ transition in pure Ce is found. Unfortunately, in pure Ce the transition is too abrupt at reasonable temperatures to be indicative. The case of $\text{Ce}_{1-x}\text{Th}_x$ (Shapiro *et al* 1977) alloys seems to be more suited. Here again, we find that the trend predicted by the model for inelastic neutron scattering is found: as the f-level crosses the Fermi level, the total intensity of the quasi-elastic peak decreases, while its width increases in energy.

In view of the above facts we can conclude the following.

(i) Correlation and mixing are essential to describe valence fluctuations, while the detailed character of the band states is not of primary importance to valence fluctuations.

(ii) Kondo behaviour is to be expected for Ce systems when the f-level lies well below the Fermi level.

(iii) Charge and spin fluctuations correspond to different physical processes. The difference being more important in the above mentioned 'Kondo regime', where $\omega_{\text{sf}} \ll \omega_{\text{cf}}$.

Even if the model presented here cannot be used for a quantitative comparison with experiment (a feature shared with all other models based on non-degenerate 4f orbitals) it provides a conceptual framework within which many questions concerning valence fluctuations can be answered in a simple way.

The model can be extended to more realistic 4f-shell configurations and one can think of many possible schemes to include the conduction electrons' kinetic energy effects. The perturbative approach valid for very narrow bands (Alascio *et al* 1979a) is already illuminating.

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