

The Method of Thermodynamic Perturbation in the Intermediate Valence Problem*

M. E. FOGLIO

Instituto de Física "Gleb Wataghin", Universidade Estadual de Campinas, 13100 – Campinas, SP, Brasil

Recebido em 14 de Dezembro de 1981

We study the effect of hybridization on the free energy and the magnetic susceptibility χ of intermediate valence compounds, employing the method of thermodynamic perturbation in second order. We apply this method to a lattice with a variable concentration c of impurities that are described by the Anderson model.

A non-divergent logarithmic correction appears when the chemical potential μ_e is not in the middle of the rectangular conduction band, and it is shown by a different method that this correction is also present in the exactly soluble case of independent electrons with hybridization.

When $c=1$ the logarithmic term is cancelled by a term proportional to $(\partial^2 \mu_e / \partial H^2)$. By thermodynamic arguments we show that this concentration dependent contribution coincides with a different expression that was recently obtained by another approach.

We discuss the contribution of the third state of charge to χ ; this state is usually neglected in intermediate valence models.

Estuda-se o efeito da hibridização sobre a energia livre e a susceptibilidade magnética χ de compostos de valência intermediária, empregando o método da perturbação termodinâmica em segunda ordem. Aplica

* Work supported in part by a grant from CNPq (Brasil) - NSF (USA) under the Cooperative Science Program in Latin America

-se esse método a uma rede com uma concentração variável c de impurezas que são descritas pelo modelo de Anderson.

Uma correção logarítmica não divergente aparece quando o potencial químico μ_e não está no meio da banda retangular de condução, e é mostrado por um método diferente que esta correção esta presente também no caso. exatamente solúvel, de elétrons independentes com hibridização.

Quando $c=1$ o termo logarítmico é cancelado por um termo proporcional a $(\partial^2 u / \partial H^2)$. Por argumentos termodinâmicos mostra-se que essa contribuição dependente da concentração coincide com uma expressão diferente que foi obtida recentemente por outra abordagem.

Discute-se a contribuição do terceiro estado de carga para χ ; este estado é usualmente desprezado em modelos de valência intermediária.

1. INTRODUCTION

Intermediate valence compounds have been the subject of many recent studies (see references (1-4) for reviews on this problem). They have rare earth elements in their composition that seem to be in two different ionic states of charge (e.g. Ce^{3+} and Ce^{4+} in $CePd_3$, Sm^{2+} and Sm^{3+} in SmS , Tm^{2+} and Tm^{3+} in $TmSe$), as evidenced by: lattice parameters that are intermediate between those expected for the two ionic radii, spectra that show the presence of the two ionic species (e.g. electron photo-emission), and several other static and dynamic properties. They have rather unusual specific heats and magnetic susceptibilities, and in this paper we shall concentrate on the second of these two properties.

The high temperature susceptibility follows a typical Curie-Weiss behaviour and can be well described by a simple theory, as shown by Jefferson and Stevens⁵. The low temperature behaviour is puzzling, because most of the intermediate valence compounds do not show ordered states ($TmSe$ being one exception) but the susceptibility tends to a high but constant value.

The intermediate valence compounds are usually described by a lattice of ions with two states of charge plus a band of conduction electrons that interact with the ions through an hybridization term. One

electron of the more negative state of charge can thus be transferred from the intermediate valence ion to the conduction band and viceversa. A model for intermediate valence compounds that has a narrow conduction band⁶ has been successfully employed⁷ to study magnetic properties at $T=OK$; in this model the hybridization term is reduced to diagonal form, and the "hopping term", that gives a width to the conduction bands, has been treated as a perturbation. When a broad band is considered, the hybridization term is usually treated as a perturbation and the method of thermodynamic perturbation^{8,9} has been employed to calculate the susceptibility from the high temperature side^{5,10-12}. The same property has also been calculated by perturbation methods using Green's functions¹³. In this paper, we focus our attention into the method of thermodynamic perturbation; the expansion parameter is Δ/kT , where Δ is the "strength" of the hybridization term as defined in section 3. We shall employ the Anderson model of a magnetic impurity¹⁴ to describe the rare earth ions; the thermodynamic perturbation of the single Anderson impurity has been recently re-examined by Haldane¹⁵ as a complement of the scaling theory he has briefly reported¹⁶. Two excitation energies, named E_d and U' in this paper, characterize the Anderson impurity, and the method should be valid when Δ/kT is small even for large values of $|E_d/kT|$ and $|U'/kT|$. When Δ is not too large, this range of temperature would be sufficiently low to be interesting. By a simple modification we have extended to this parameter region the validity of the method employed in previous work¹¹⁻¹² (these two references will be respectively named I and II in what follows) and we have thus been able to discuss contributions to the magnetic susceptibility that do not appear in similar treatments of the problem.

In the Anderson model of a magnetic impurity, a single ion with three states of charge is considered together with the conduction band. In the present paper, we shall study a lattice with a variable concentration c of Anderson magnetic impurities: the single magnetic impurity is then obtained in the limit $c \rightarrow 0$, and the pure compound when $c=1$. An extra contribution to the magnetic susceptibility appears when the concentration changes from $c=0$ to $c=1$, because the electronic chemical potential μ_e varies with the magnetic field H when c is appreciably different from zero. Employing Green's functions, Hewson¹³ has obtained different values

of χ for the two extreme cases $c=0$ and $c=1$: this difference in χ is proportional to the derivative of V_e with respect to A . The concentration dependence we have obtained is instead proportional to the second derivative of μ_e with respect to H : by employing thermodynamic techniques we have been able to prove that these two apparently different concentration dependent contributions are the same, and this result is presented in Appendix III.

The three states of charge in the Anderson model can be described, in the absence of hybridization and magnetic field, by a ionic core plus: i) zero electrons (state $|\rho\rangle$, energy E_ρ^0), ii) one s electron with spin up or down (states $|\nu\sigma\rangle$ with $\sigma=\pm 1$ and energy E_ν^0), and iii) two s electrons (state $|\tau\rangle$ and energy E_τ^0), and there are four available ionic states per impurity.

In each of the examples of intermediate valence ions considered above (Ce, Sm, Tm), the multiplicity of one of the two states of charge is larger than two, because the ionic electron shared with the band is an f electron. Our calculations are easily extended in higher multiplicities at the cost of some extra algebra particularly if one wants a hybridization term with the right symmetry properties¹⁷. The important aspect of the Anderson impurity is the presence of the inter-electronic Coulomb repulsion U in the state with two electrons. The energy necessary to add a Fermi level electron to the impurity with zero electrons is $E_d^0 = E_\nu^0 - E_\rho^0 - \mu_e$ in this model, while to add a second Fermi-level electron it is needed an extra energy $U = E_d^1 - U = E_\tau^0 - E_\nu^0 - \mu_e$.

With our model of intermediate valence with three states of charge, we have found the conditions that must be satisfied to neglect the extra state of charge: it is not enough to forbid the thermal excitation of conduction band electrons into the $|\tau\rangle$ state, i.e. $U \gg kT$, but more stringent conditions are necessary. The effect of $|\tau\rangle$ is negligible when $U \gg W_t + W_b$, where W_t and $-W_b$ are the energies of the top and bottom of the conduction band respectively, but when $U < W_t - \mu_e$ (state τ "inside" the band) the extra state gives a contribution to the susceptibility that is proportional to $\ln(U/kT)$ when $U \gg kT$, and is therefore important at sufficiently low T ; it produces also a cancellation of a term with $\ln[\beta(W_b + \mu_e)]$ that appears when τ is neglected or when $U > W_t - \mu_e$. When τ

is inside the band, it is therefore U and not W that provides an effective high-energy cut-off, as has been pointed out by Haldane¹⁵.

In the intermediate valence compounds $E_V^0 - E_C^0$ is well within the conduction band, but U can be large enough to take $E_\tau^0 - E_V^0$ well outside the conduction band (i.e. $U + \mu_e \gg W_t$ and the state τ is "outside the band"). In this case a term proportional to $\ln(x_u)$ with $r_u = (U - W_t + \mu_e) / (U + W_b + \mu_e)$ gives the remnant effects of state τ on the magnetic susceptibility.

Both when τ is inside or outside the band, all the logarithmic contributions that are present in the impurity case ($c=0$) are cancelled out in the pure compound ($c=1$) as pointed out by Hewson¹³ for SmS, and only a partial contribution appears for intermediate values of c .

The symmetric problem with negative U' would also correspond to a possible physical situation, but will not be considered in this work.

Haldane¹⁵ has employed a diagrammatic technique up to fourth order perturbation to calculate the susceptibility of Anderson's impurity, and his calculation relies on the infinite bandwidth model^{18,19}. In our models we have calculated only up to second order perturbation but we have considered arbitrary values of the energies W_t and $-W_b$.

To compare our results with those derived within the infinite bandwidth model the excitation energies $E_V^0 - E_C^0$ and $E_\tau^0 - E_V^0$ must be well within the conduction band ($-W_b, W_t$).

In the spectral ranges of temperature considered by Haldane¹⁵ we reproduce his results (up to second order) for $r = (W_t - \mu_e) / (W_b + \mu_e) = 1$, but when the chemical potential μ_e is not symmetrically placed in the band, a contribution proportional to $\ln(x)$ appears. The fact, pointed out by Haldane¹⁵, that electrons or holes that have energies much larger than U can be considered as effectively free, is not relevant to the existence of the term proportional to $\ln(x)$ when $U \neq 0$: in Appendix 3 we employ a different method to prove that this term is already present in the exactly soluble model of free electrons ($U=0$) with hybridization. Note that $\ln(x)$ is not a divergent contribution: its value remains constant when both W_b and $W_t \rightarrow \infty$ keeping $r = (W_t - \mu_e) / (W_b + \mu_e)$ a constant. Terms of the type $\ln(W/kt)$ appear in the second order correction

to χ , but only when there are impurity states outside the band: this situation is clearly incompatible with W_b and $W_c \rightarrow \infty$ unless the energy of the impurity also diverges. From our expression for the susceptibility, follows that i) the asymmetric position of μ_e (i.e. when $r \neq 1$), ii) the variation of μ_e with H (i.e. when $(\partial^2 \mu_e / \partial H^2) \neq 0$) and iii) the presence of the third state of charge, give important correction only in the intermediate valence region (i.e. $|E_d|/kT \gtrsim 5$), namely when both the $|\nu\sigma\rangle$ and $|\rho\rangle$ states are simultaneously occupied in the absence of hybridization.

In section 2 of this paper we briefly discuss the model employed, and give the change Δ in the Helmholtz free energy when the hybridization term is added to the unperturbed Hamiltonian. In section 3 we obtain the magnetic susceptibility using the free energy discussed in the previous section, and a discussion of the formula (3.1) employed to calculate the magnetization is given in Appendix 1. The general expression of ΔF is particularized for the model discussed in this introduction, and the results are expressed in terms of three functions $Y_0(x)$, $Y_1(x)$ and $Y_2(x)$ that are studied in appendix 2. In section 4 we give approximate analytical expressions of χ for special limits of E_d/kT and U'/kT , and they are shown to agree, for the appropriate values of concentration c and U' , with those obtained by Haldane¹⁶. The concentration dependence of $\Delta\chi$ is also discussed in this section and results of the numerical calculation of the second order correction are plotted.

Summary and conclusions are presented in section 5, where the method used in this paper is compared with those employed by Hewson¹³ and by Haldane¹⁵ to treat the same type of problem.

2. HYBRIDIZATION CORRECTION TO THE FREE ENERGY IN SECOND ORDER

The techniques we employ in this paper are essentially the same used in I and II, where a more detailed discussion was given. The unperturbed Hamiltonian is

$$H_0 = \sum_n \left[\sum_j E_j^+ B_{nj}^+ B_{nj} + E_0 B_{n1} B_{n1}^+ \right] + \sum_n E_x b_x^+ b_x - \sum_{njx} \frac{G_j}{N} B_{nj}^+ B_{nj} b_x^+ b_x. \quad (2.1)$$

where B_{nj}^+ acts like a creation operator: when there is a reference $+$ ion in its ground state of energy E , at site n , it is transformed by B_{nj} in an impurity in quantum state $|j\rangle$ of energy E_j^i ; the inverse process is accomplished by B_{nj}^+ .

The following rules of product follow from simple physical arguments for a fixed site n (cf. I. §2).

$$\begin{aligned}
 B_{nk} B_{nj} &= B_{nk}^+ B_{nj}^+ = \theta \quad (\theta \text{ is the null operator}) \\
 B_{nk} B_{nj}^+ &= \delta_{kj} B_{nk} B_{nk}^+ \\
 B_{nj}^+ B_{nk} B_{nk}^+ &= B_{nj}^+ \\
 B_{nk} B_{nk}^+ B_{nj} &= B_{nj}
 \end{aligned} \tag{2.2}$$

and the product $B_{nj}^+ B_{nk}$ is equivalent to the standard basis operator $|nj\rangle\langle nk|$ employed by Haldane¹⁵ and Hewson¹³ (cf. I §§2,3), where j and k are quantum states that differ by one or zero electronic charges.

The B_{nj} and B_{mk} for different sites n and m commute (anticommute) when the states $|j\rangle$ and $|k\rangle$ differ by an even (odd) number of fermions, and the same rule applies for B_{nj}^+ , B_{mk}^+ and $B_{nj}^+ B_{mk}^+$ (for the particular problem considered in this paper, one could assume that all the B and B^+ at different sites commute, but it is more consistent to use the definition employed here, cf. I §2). The terms $B_{n1} B_{n1}^+$ in (2.1) count those crystal sites in which a reference ion (rather than an impurity) is present in its ground state, and we neglect excited states of the reference ions. The $B_{n1} B_{n1}^+$ terms can be eliminated from (2.1), and the E_3^i are then replaced by $E_j^i = E_3^i - E_0$, which is the energy necessary to substitute a reference ion by an impurity in state $|j\rangle$. The operators b_x and b_x^+ are the usual Fermion operators, and the subindex x identifies the conduction state $|x\rangle = |k\sigma\rangle$. They commute (anticommute) with B_{nj} and B_{nj}^+ , when the number of electrons in state $|j\rangle$ is even (odd). The last term in (2.1) describes the Coulomb interaction between the magnetic ions and the conduction electrons that was employed by Ramirez and Falicov²⁰ to study the metal-insulator transition. We shall carry the G in the general expressions of the free energy and susceptibility, but we shall

put $G_{jx}=0$ in the model discussed in the present paper. The hybridization term, which will be employed as a perturbation in our calculation, is

$$H_{hyb} = N^{-1/2} \sum_{njlx} [V_{nljx} B_{nl}^+ b_x + V_{nljx}^* b_x^+ B_{nl}] , \quad (2.3)$$

and charge conservation implies that $V_{nljx}=0$ unless the state $|l\rangle$ has one more electronic charge than the state $|j\rangle$. Under translational invariance $V_{nljx} = V_{l,jx} \exp(-ik.Rn)$ and then $|V_{nljx}| = |V_{l,jx}|$.

As was discussed in I (§5) the use of B operators makes it possible to consider an ensemble closely related to the grand canonical for the impurity ions. The chemical potential of the impurities in state $|j\rangle$ is then obtained from the assumed value of the ensemble average $\langle N_j \rangle$ of the number of impurities in that state, and by the same procedure we obtain the electronic μ_e as a function of the ensemble average of the total number N_e of conduction electrons. The V_j and μ_e are not arbitrary, but they must satisfy three type of relations discussed below.

a) All states $|j\rangle$ belong to the same chemical element (or to a reduced number of elements in more complex problems not discussed in this paper), so that in thermodynamic equilibrium it is

$$\mu_j = \mu_0 + v_j \mu_e \quad (2.4)$$

where we have generically denoted with $|\rho\rangle$ all the states that correspond to the most positive state of charge that will be considered for the impurity, and by v_j the extra number of electrons that the state $|j\rangle$ has. The $\mu_j = \mu_j^! - \mu_0$ is the chemical potential of state $|j\rangle$ minus that of the reference ions (μ_0).

In our model the total number of sites is not subject to the grand canonical fluctuations but has a fixed value N , and the number N_0 of reference ions is determined by the relationship

$$N = N_0 + \sum_j N_j \quad (2.5)$$

As a consequence, the chemical potential μ_0 is not an arbitrary variable but can be expressed as a function of the pressure P of the system (cf. §§4,5).

b) The total number of impurities is $N_{\underline{c}} = N \cdot c$ so that

$$\sum_j \langle n_j \rangle = c \quad (2.6)$$

where

$$n_j = N_j / N$$

c) Let $N_c = N \cdot n_c$ be the total number of conduction electrons that would be present if all the impurities were in states of type ρ ; one should then satisfy the equation

$$\langle n_e \rangle + \sum_j v_j \langle n_j \rangle = n_c \quad (2.7)$$

where $n_e = N_e / N$. With (2.4), (2.5) and (2.6) one should be able to find μ_e and the μ_j and express μ_0 as a function of the total pressure P . With $\mu_j = \mu_j^0 - \mu_0$ one then writes the Gibbs free energy per site of the system as

$$\frac{1}{N} G = \mu_e \langle n_e \rangle + \mu_0 + \sum_j \langle n_j \rangle \mu_j \quad (2.8)$$

We have obtained ΔG at constant V , T , N , $N_{\underline{c}}$ and N_c as the difference between the G calculated from (2.8) with and without H_{hyb} respectively. In the calculation we have only kept terms quadratic in the $|V_{\ell j}|$ and neglected in the final result quadratic and higher order terms in the variations ΔR of any quantities R that appear in ΔG , as well as terms of the type $|V_{\ell i x}|^2 (\Delta \langle n_j \rangle)$. The expression obtained is

$$\Delta G - V \Delta P = N \sum \langle n_j \rangle_0 f_j \quad (2.9)$$

where

$$N f_j = -\beta \sum_{\ell x} \{ |V_{\ell j x}|^2 \langle n_x \rangle_0 g_c(\gamma_{\ell j x}) + |V_{j \ell x}|^2 (1 - \langle n_x \rangle_0) g_c(-\gamma_{j \ell x}) \} \quad (2.10)$$

and

$$g_c(x) = \theta(x) |1 - \exp(-x)|/x \quad (2.11)$$

where $\theta(x)$ is the step function. The general expression of $\gamma_{j\ell x}$ is given in II (4.5) and when all $G_{jx} = 0$

$$\gamma_{j\ell x} = \theta(E_3 - E_x) \quad (2.12)$$

where $\beta = 1/kT$. Both $\langle n_{j0} \rangle$ and $\langle n_{x0} \rangle$ correspond to the problem without hybridization, because we have neglected corrections of the form $|V_{j\ell x}|^2 (\Delta \langle n_x \rangle)$ and $|V_{j\ell x}|^2 (\Delta \langle n_j \rangle)$, so that from (2.4) and (2.6) follows

$$\langle n_{j0} \rangle = c \{ \exp[-\beta(E_j - v_j \mu_e)] \} / \{ \sum_k \exp[-\beta(E_k - v_k \mu_e)] \} \quad (2.13)$$

and

$$\langle n_{x0} \rangle = \{ 1 + \exp[\beta(E_x - \mu_e)] \}^{-1} \quad (2.14)$$

where the E_3 correspond to zero hybridization but to an arbitrary magnetic field. These are several important points to notice about (2.9).

- i) The improvement of the present treatment over the previous one in II, is that $\Delta \hat{G}$ in (2.9) can be small even for large values of $|\gamma_{j\ell x}|$ when the $\beta |V_{j\ell x}|^2$ are moderately small. In II (4.1) the definition of f_j^c is just like (2.10) but with $g_c(x)$ replaced by

$$g(x) = \{ 1 + [\exp(-x) - 1]/x \} / x \quad (2.15)$$

This $g(x)$ is very large when $x \ll -1$, and the physical explanation of this contribution is that a highly excited state can have a probability much larger than be expected from its Boltzmann factor because of quantum mixing with states of a much lower energy, and therefore a much larger probability. The large exponential in $g(x)$ is then compensated in the partition function by the very small Boltzmann factor, and the overall effect is reasonably bounded. We did not take advantage of this fact in the previous derivation of AG, and the result in II is

only valid when all the arguments of $g(x)$ are sufficiently small: in our intermediate valence model this requirement means that $|E_d| \ll kT$ and $|U'| \ll kT$, and the range of allowed values of T is then severely restricted to rather high values. The expression in (2.10) was obtained by simple rearrangements of the terms in the partition function, that were suggested by the physical arguments given above. In (2.10) both $|E_d|$ and $|U'|$ can be much larger than kT and the hybridization strength A , and the only restriction is that Δ/kT be sufficiently small.

ii) The meaning of the quantum numbers that in the unperturbed system give the occupation number of state $|j\rangle$ at site n and of electron in state $|x\rangle$, is somewhat altered by the rearrangement of terms employed to derive (2.10), and the values of $\langle n_{3j} \rangle$ and $\langle n_x \rangle$ are different in the two treatments. Nevertheless as a consequence of charge conservation and (2.4), (2.6) and (2.7) the μ_i , μ_e and G remain unchanged in the range of validity of the two methods.

iii) The AG obtained from (2.9) and (2.10) is correct to second order in the perturbation parameters V_{jlx} , and it is the final result of a calculation in which higher order terms have been neglected from the final expression. When the hybridization is added to the system, one should not add extra correction to the unperturbed G_0 , (e.g. like the (23) in ref. 13) because these have been already consistently considered.

iv) As we have calculated AG at constant V and T , the left hand side of (2.9) gives the change in the Helmholtz free energy, and this would be the thermodynamic function we shall use to calculate the magnetic susceptibility. This function is more convenient than the Gibbs free energy at constant pressure, because one would then have to consider how all the parameters in the Hamiltonian (2.1) and (2.3) change with the volume (cf. the discussion of this problem in II§5).

3. MAGNETIC SUSCEPTIBILITY IN SECOND ORDER

From the Helmholtz free energy $F=G - PV$ one can calculate the magnetization M

$$M = - \left(\frac{\partial F}{\partial H} \right) \quad (3.1)$$

In this expression and in all the other partial derivatives that appear in the text, it is the variable V , T , N , N_t , N_c that remain constant, unless explicitly stated otherwise.

At zero magnetic field it must be $M=0$ if the system is paramagnetic. The susceptibility is

$$\chi = \left(\frac{\partial M}{\partial H} \right)$$

and we can use (2.9) to calculate the second order corrections. We assume that the state $|j\rangle$ has an unperturbed energy

$$E_j = E_j^0 + \alpha_j H + \frac{1}{2} b_j H^2 \quad (3.2)$$

where $b_j H$ gives the magnetic moment induced in the state $|j\rangle$ by the magnetic field H . We then obtain

$$\Delta\chi = -\sum_j \left\{ \left(\frac{\partial^2 \langle n_j \rangle_0}{\partial H^2} \right) \cdot f_j + 2 \left(\frac{\partial \langle n_j \rangle_0}{\partial H} \right) \cdot \left(\frac{\partial f_j}{\partial H} \right) + \langle n_j \rangle_0 \cdot \left(\frac{\partial^2 f_j}{\partial H^2} \right) \right\} \quad (3.3)$$

where $\Delta\chi$ is given per site, i.e. is the total $\Delta\chi$ divided by N . Both $\langle n_j \rangle_0$ and f_j depend on μ_e , and this can be a function of H . If we assume that at $H=0$ and for each state of charge of the impurity is

$$\sum_j \langle n_j \rangle_0 \alpha_j = 0 \quad (3.4)$$

where the summation is over all the j of that state of charge, we find from (2.7) that $(\partial \mu_e / \partial H)_{V,T} = 0$ at $H=0$, and that

$$\left(\frac{\partial^2 \mu_e}{\partial H^2} \right) = - \frac{\sum_{j\ell} \langle n_j \rangle_0 \langle n_\ell \rangle_0 (v_j - v_\ell) [\beta (\alpha_j^2 - \alpha_\ell^2) - b_j + b_\ell]}{4 \alpha R(T) \frac{\rho(\mu_e)}{N} + \sum_{j\ell} \langle n_j \rangle_0 \langle n_\ell \rangle_0 (v_j - v_\ell)^2} \quad (3.5)$$

In this formula

$$R(T) = kT \left[1 + \frac{\pi^2}{6} (kT)^2 \frac{\rho''(\mu_e)}{\rho(\mu_e)} + \dots \right] \quad (3.6)$$

where $\rho(\mu_e)$ and $\rho''(\mu_e)$ are the density of conduction electrons and its second derivative at the energy μ_e . For a rectangular density of states it is $R(T) \rho / N^2 kT / (W_c + W_b)$, which for a typical conduction band is a very small quantity even at room temperature. It then follows from (2.13) that (3.5) goes to zero when $c \rightarrow 0$ but that at very small values of c it is already very close to the value it takes at $c=1$ and then $(\partial^2 \mu_e / \partial H^2)$ contributes to $\Delta\chi$ through both $(\partial^2 \langle n_j \rangle_0 / \partial H^2)$ and $(\partial^2 f_j / \partial H^2)$. In Appendix 3 we show that this contribution has the same origin as the tying of the effective f levels to the Fermi level in the intermediate valence compound and the lack of such strong constraint for the impurity^{13,21}. Using thermodynamic techniques we also show that the corresponding concentration dependent contribution to χ is equal to that obtained by Hewson¹³ by employing a rather different approach.

From (3.3) we obtain essentially the same expression given in II (but note the $1/c$ factors and the contribution of $(\partial^2 \mu / \partial H^2)$ that were inadvertently left out in II (4.17))

$$\begin{aligned} \Delta\chi = & -\beta^2 \sum_j \langle n_j \rangle_0 \left(a_j^2 - \frac{1}{c} \sum_k \langle n_k \rangle_0 a_k^2 \right) f_j + \\ & + 2\beta \sum_j \langle n_j \rangle_0 a_j \left(\frac{\partial f_j}{\partial H} \right) - \sum_j \langle n_j \rangle_0 \left(\frac{\partial^2 f_j}{\partial H^2} \right) + \\ & + \beta \sum_j \langle n_j \rangle_0 \left(b_j^! - \frac{1}{c} \sum_k \langle n_k \rangle_0 b_k^! \right) \cdot f_j \end{aligned} \quad (3.7)$$

where

$$b_j^! = b_j - v_j \left(\frac{\partial^2 \mu_e}{\partial H^2} \right) \quad (3.8)$$

but notice that f_j in (2.10) is defined with $g_c(x)$ rather than with the $g(x)$ employed in II.

The expression (3.7) is very general, and could be employed for any system within the specifications discussed in § 2; in what follows we apply (3.7) to the model discussed in this paper, namely, a lattice

of Anderson impurities. We shall neglect polarization effects in (3.2), and take $E_{\rho} = E_{\rho}^0$, $E_{\nu\sigma} = E_{\nu}^0 + \alpha\sigma H$ and $E_{\tau} = E_{\tau}^0$ so that only the $|\nu\sigma\rangle$ states are magnetic in the unperturbed state; notice also that (3.4) is satisfied. We assume $E_{k\sigma} = E_k + \sigma H$ for the conduction electrons, and that the only non-zero coefficients V_{ijx} are $V_{(\nu\sigma)\rho}(k\sigma)$ and $V_{\tau(\nu\sigma)}(k\bar{\sigma})$ where $\bar{\sigma}$ is the spin component opposite to σ along the magnetic field. This restriction means that H_{hyb} conserves the spin component along the field. We also assume that all these coefficients have the same dependence with the wave vector \vec{k} of the conduction electrons, given by a single function $V(k)$. Many cancellations of terms of the type $\ln(W/kT)$ that occur in our model would not be complete if this assumption were relaxed. As the one-electron wave functions of the impurity (say the $4f$ orbitals in the rare-earth problem) probably change their extension with the ionic state of charge, the hybridization will be different and we should then expect partial cancellations only.

In the calculation of f_{ρ} , $f_{\nu\sigma}$ and f_{τ} we replace the sums over \vec{k} by integrations over the Brillouin zone, and only the average of $|V(\vec{k})|^2$ over surfaces of constant electronic energies are required:

$$N \cdot \Delta(x) = \Pi (V/8\pi^3) \int_{\sigma(x)} |V(\vec{k})|^2 \cdot [\text{grad}_{\vec{k}} E(\vec{k})]^{-1} d\sigma \quad (3.9)$$

so that $\Delta(x) = 0$ when x is outside the conduction band $(-W_b, W_t)$. Following Haldane¹⁵ we assume that $\Delta(x) = \Delta$ is a constant inside the band but we depart from his "infinite bandwidth" model by letting U_e be anywhere in the band, i.e. we do not set $W_t - \mu_e = \hbar^2 k_b^2 + \mu_e = W$. To write a convenient expression for the f_j we introduce

$$X(x, W) = \theta(W) \int_0^W \frac{1 - \exp(-t)}{t} [\exp(x-t) + 1]^{-1} dt \quad (3.10)$$

and

$$Y_0(x, W) = \theta(W) \int_0^W \frac{1 - \exp(-t)}{t} [\exp(t-x) + 1]^{-1} dt \quad (3.11)$$

that will be studied in appendix 2, and for $W \gg 1$ the difference between $Y_0(x, W)$ and $Y_0(x) = Y_0(x, \infty)$ is very small. If we assume that $-\mu_b \ll \mu_b + \mu_e \ll \beta W_t$ we find

$$\begin{aligned}
f_{\rho} &= -\frac{\Delta}{\pi} \sum_{\sigma} X [\beta(E_d + \sigma\alpha H) , \beta(W_b + \mu_e + E_d + \sigma(\alpha-1)H)] \\
f_{\nu\sigma} &= -\frac{\Delta}{\pi} \{X[\beta(U' - \sigma\alpha H) , \beta(W_b + \mu_e + U' - \sigma(\alpha-1)H)] - \\
&\quad - X[\beta(U' - \sigma\alpha H) , -\beta(W_t - \mu_e - U' + \sigma(\alpha-1)H)] + \\
&\quad X[-\beta(E_d + \sigma\alpha H) , \beta(W_t - \mu_e - E_d - \sigma(\alpha-1)H)]\} \\
f_{\tau} &= -\frac{\Delta}{\pi} \sum_{\sigma} [-\beta(U' - \sigma\alpha H) , \beta(W_t - \mu_e - U' + \sigma(\alpha-1)H)] \quad (3.12)
\end{aligned}$$

As discussed in the introduction there are several qualitatively different regions of values of U' : we shall consider

$$i) -\beta W_b \ll \beta(U' + \mu_e) \ll \beta W_t \quad \text{and} \quad ii) \beta(U' + \mu_e) \gg \beta W_t > -\beta W_b.$$

We shall say that " τ is inside (outside) the band" in case i (case ii). When τ is inside the band the second term in $f_{\nu\sigma}$ vanishes because $X(x, W) = 0$ for negative W , and when τ is outside the band $f_{\tau} = 0$ and the two first terms in $f_{\nu\sigma}$ nearly cancel each other; the state τ gives therefore rather different contributions to $\Delta\chi$ in the two cases.

3.1. State $|\tau\rangle$ inside the band

In the expression below, we have neglected contributions proportional to (kT/W) and its square, as well as E_d/W and U'/W , where $W = W_b + \mu_e$ or $W = W_t - \mu_e$. We have kept terms with a $\langle n_{\tau} \rangle_0$ factor to include the case of small values of the Coulomb repulsion U , and we have used (2.6) to obtain a more compact formula

$$\begin{aligned}
\Delta\chi &= \frac{\beta^2 \Delta (2\alpha)^2}{\pi e} \cdot \\
&\quad \left\{ \frac{1}{2} \langle n_{\rho} \rangle_0 \langle n_{\nu} \rangle_0 \{ \ln(x) + 2Y_0(\beta E_d) - Y_0(-\beta E_d) - Y_0(+\beta U') \} \right. \\
&\quad + \frac{1}{2} \langle n_{\nu} \rangle_0 \langle n_{\tau} \rangle_0 \{ -\ln(x) + 2Y_0(-\beta U') - Y_0(\beta U') - Y_0(-\beta E_d) \} \\
&\quad \left. - \sigma \langle n_{\nu} \rangle_0 \{ Y_1(\beta U') + Y_1(-\beta E_d) \} \right. \quad (3.13)
\end{aligned}$$

$$\begin{aligned}
& - \frac{1}{2} e \{ \langle n_p \rangle_0 Y_2(\beta E_d) + \langle n_v \rangle_0 [Y_2(\beta U') + Y_2(-\beta E_d)] + \\
& + \langle n_\tau \rangle_0 Y_2(-\beta U') \} + M_\mu \Big]
\end{aligned}$$

where $Y_1(x)$ and $Y_2(x)$ are the first and second derivatives of $Y_0(x)$ respectively, $x = (\bar{W}_t - \mu_e) / (\bar{W}_b + \mu_e)$ and M_μ is the contribution proportional to $(\partial^2 \mu_e / \partial H^2)$.

In cases of interest it is usually $\beta U' \gg 1$, so that $\langle n_\tau \rangle_0 \sim 0$ and the second term in (3.13) can be neglected. The first term is proportional to $\langle n_p \rangle_0 \langle n_v \rangle_0$, and contributes only when the corresponding states of charge are both appreciably populated; i.e. in the intermediate valence regime, which corresponds approximately to $|E_d| \lesssim 5kT$. In this regime there is near degeneracy of unperturbed states associated to different states of charge, and their relative probability would be a sensitive function of their energy difference, which in our problem is affected by changes in the magnetic field. We therefore expect in the intermediate valence regime some large contributions to χ and other differential properties that would vanish when $\langle n_v \rangle_0 \langle n_p \rangle_0$ goes to zero, i.e., in the single valence regime. The thermodynamic perturbation method shows in this problem its superiority over the ordinary perturbation theory, because the use of the trace in the calculation of the partition function automatically corrects the difficulties associated with degeneracy.

Two important effects appear in the intermediate valence region. The first is related to the term $\ln(x)$, that vanishes in the "infinite bandwidth" calculation of Haldane¹⁵. It seems then clear that his method corresponds to taking a principal value around infinity and that there is a non-zero but finite contribution when both \bar{W}_b and \bar{W}_t tend to infinity but keeping constant the ratio. Earlier in this section we discussed that terms of the type $\ln(\bar{W}/kT)$ would also be present if the hybridization constant between different states of charge were not the same: their cancellation seems therefore more an artifact of the model than an essential property of the system.

This second effect is produced by the state through τ the $Y_0(\beta U')$ present in the first term of (3.13). When $\beta U' \gg 1$ its contribu-

tion is proportional to $\ln(\beta U')$, and the $Y_1(\beta U')$ and $Y_2(\beta U')$ appearing in the remaining terms of (3.13) can be neglected.

It is therefore clear that excited states that are inside the conduction band should not be forgotten even when they are not thermally excited, and we remark that the two effects discussed above vanish in the single valence region.

In the contribution proportional to $(\partial^2 \mu_e / \partial H^2)$ we assume again that $\beta U' \gg 1$, because then $\langle n_{\tau} \rangle_0 \sim 0$ and the expression of M_{μ} is simplified:

$$M_{\mu} = c_{\mu} \left[\frac{1}{2} \langle n_{\rho} \rangle_0 \langle n_{\nu} \rangle_0 \{ \ln(x) + 2Y_0(\beta E_d) - Y_0(-\beta E_d) - Y_0(\beta U') \right. \\ \left. + \frac{c}{2} \{ \langle n_{\rho} \rangle_0 Y_1(\beta E_d) + \langle n_{\nu} \rangle_0 [Y_1(\beta U') - Y_1(-\beta E_d)] \} \right] \quad (3.14)$$

here δ_{μ} is equal to (3.5) divided into $\beta \alpha^2$, and varies from $c_{\mu}=0$ at $c=0$ to $c_{\mu}=-1$ at $c=1$. It is then clear, that M_{μ} would produce significant cancellations in (3.13) in the intermediate valence compound (cf. discussion after (3.6)): in particular, all the logarithmic contributions vanish for $c=1$.

3.2. State $|\tau\rangle$ outside the band

We assume here that τ is well outside the band i.e. that $\beta(U' + \mu_e - W_{\tau}) \gg 1$, and we have neglected $|E_d|/W$. We have kept small terms in kT/W , because they correspond to those of the type kT/U' that are present when τ is inside the band and kT/U' is very small:

$$\Delta\chi = \frac{\beta^2 \Delta(2\alpha^2)}{c\pi} \cdot \\ \cdot \left[\frac{1}{2} \langle n_{\rho} \rangle_0 \langle n_{\nu} \rangle_0 \left\{ \ln \frac{kT}{W} + 2Y_0(\beta E_d) - Y_0(0) - Y_0(-\beta E_d) \right\} \right. \\ \left. - c \langle n_{\nu} \rangle_0 Y_1(-\beta E_d) - \frac{1}{2} c \left\{ \langle n_{\rho} \rangle_0 Y_2(\beta E_d) + \langle n_{\nu} \rangle_0 Y_2(-\beta E_d) \right\} \right. \\ \left. + c \frac{\alpha-1}{\alpha} \langle n_{\nu} \rangle_0 \frac{kT}{W_{\tau} - \mu_e} - \frac{1}{2} c \left(\frac{\alpha-1}{\alpha} \right)^2 \left\{ \langle n_{\rho} \rangle_0 \left(\frac{kT}{W_{\tau} + \mu_e} \right)^2 + \langle n_{\nu} \rangle_0 \left(\frac{kT}{W_{\tau} - \mu_e} \right)^2 \right\} + M_{\mu} \right]$$

where

$$W_2 = (W_b + \mu_e) \frac{r_u}{r} \exp[\gamma - Y_0(0)] \quad (3.16)$$

$\gamma = 0.57721\dots$ is Euler's constant and

$$r_u = (U' + \mu_e - W_t) / (U' + \mu_e + W_b) .$$

it is then clear that when $U' \gg (W_t + W_b)$ it is $r_u = 1$ and the state τ can be left completely out of the calculation. Even if $r_u \neq 1$, the contribution of $\ln(r_u)$ would not be too large when $U' \gg W_t - \mu_e$. The contribution $\ln[kT/(W_b + \mu_e)]$ is present both when τ is outside the band or when this state is neglected. Jefferson and Stevens⁹ obtained this term with a coefficient 5/6, because they considered the ground state of Sm^{3+} , which is sixfold degenerate. In our case the coefficient is 1/2 because we only considered two magnetic states $|\uparrow\sigma\rangle$.

Only 1/2 of the contribution proportional to $\ln(r)$ remains when τ is outside the band, and the contribution proportional to $(\partial^2 \mu_e / \partial H^2)$ is

$$M_\mu = c_\mu \left[\frac{1}{2} \langle n_p \rangle_0 \langle n_v \rangle_0 \{ \ln(kT/W_2) + 2Y_0(\beta E_d) - Y_0(0) - Y_0(-\beta E_d) \} + \right. \\ \left. + \frac{1}{2} c \{ \langle n_p \rangle_0 Y_1(\beta E_d) - \langle n_v \rangle_0 Y_1(-\beta E_d) \} \right] \quad (3.17)$$

When $c=1$ the first term cancels exactly the first term in (3.15), this effect was already noted by Hewson¹³ in the case of SmS .

3.3. Unperturbed susceptibility

In our model the unperturbed susceptibility is $\chi = \chi_{op} + \chi_{op}'$, where χ_{op} is the Pauli susceptibility per site of the unperturbed conduction electrons, and

$$(3.18)$$

is the Curie susceptibility of the unperturbed magnetic ions. In our theory all charges produced by H_{hyb} are already included in (3.3) and therefore in (3.13) and (3.15).

4. THE SUSCEPTIBILITY IN VARIOUS LIMITS AND NUMERICAL RESULTS

It is now easy to derive analytical approximations to (3.13) and (3.15) in various interesting limits by use of the results presented in Appendix 1. We shall consider in each limit the two cases of τ inside or outside the band, and compare in the first case with the results obtained by Haldane¹⁵ for the Anderson impurity.

4.1. High-temperature limit: $|E_d|, |U'| \ll kT$

We expand all the functions in (3.13) as a series in βE_d and $\beta U'$ about the value zero, and we find

$$\chi = .c(2\alpha)^2 \left\{ \frac{1}{8kT} + \frac{1}{8(kT)^2} \left[\frac{U}{4} - 4 \frac{\Delta}{\pi} (Y_1(0) + Y_2(0)) \right] - \frac{1}{8(kT)} \left[\left(\frac{U+2E_d}{4} \right)^2 + \frac{\Delta}{\pi} (2(Y_1(0) + Y_2(0))v - \frac{U+2E_d}{4} \ln(x)) \right] \right\} + \chi_{op} \quad (4.1)$$

This expression corresponds to the state τ inside the band, and when $r=1$ coincides to first order in A with the expansion of formula (23) of Haldane, provided that $2(Y_1(0) + Y_2(0))$ be equal to the constant $A=0.85255$ that appears in that expressions: our numerical calculation gives the value 0.8525568; and in what follows we shall write $2(Y_1(0) + Y_2(0)) = A$. We have assumed that T is sufficiently small so that the Pauli susceptibility χ_{op} still describes the conduction electrons.

When the state τ is outside the band it is $U' > W_t - \mu_e$ which is not compatible with $\beta U' \ll 1$ and $\beta(W_t - \mu_e) \gg 1$, so we shall not give an analytical expression in this case.

4.2. Intermediate Temperature Asymmetric limit, $U \gg kT \gg |E_d|$

This is the most interesting case for the intermediate valence problem. We neglected E_d/U against 1, and for the state τ inside the band we find

$$\begin{aligned} \chi = & (2\alpha)^2 e \left[\frac{\Delta}{6\pi U^2} \left\{ 1 + \frac{\pi^2}{18} + o\left|\frac{kT}{U}\right| + o\left|\frac{E_d}{kT}\right| \right\} + \right. \\ & + \frac{1}{6kT} \left\{ 1 - \frac{2\Delta}{\pi U} + o\left|\frac{E_d}{kT}\right| \right\} - \\ & - \frac{1}{18(kT)^2} \left\{ E_d - \frac{\Delta}{\pi} \left[\ln\left(\frac{kT}{W_1}\right) - 3A \right] \right\} \\ & \left. - \frac{1}{108(kT)^3} \left\{ E_d - \frac{\Delta}{\pi} E_d \left[2\ln\left(\frac{kT}{W_1}\right) + 15A \right] + \dots \right\} \right] \quad (4.2) \end{aligned}$$

where

$$W_1 = (U/r) \exp(\gamma - Y_0(0)) . \quad (4.3)$$

When $r=1$, the definition (4.3) of W_1 coincides with Haldane's, provided that $\exp(Y_0(0)) = \pi/2$. With the $Y_0(0)$ obtained by numerical integration we have found 1.570796334 rather than $\pi/2 = 1.570796327$, which serves to verify the accuracy of our numerical method. The only differences with Haldane to first order in A are the $\pi^2/18$ in the first term, that comes from the $1/x^2$ term in (1.6) and a minus sign rather than a plus in the term with $30 E_d$. Because of the agreement with the rest of the formula, we believe that this is only a typographical error in Haldane's paper.

When the state τ is outside the band we find

$$\begin{aligned} \chi = & (2\alpha)^2 e \left[-\frac{\Delta}{6\pi} \left(\frac{\alpha-1}{\alpha}\right)^2 \left\{ \left(\frac{1}{W_t - \mu_e}\right)^2 + \left(\frac{1}{W_b + \mu_e}\right)^2 \right\} \left(1 + o\left|\frac{E_d}{kT}\right| \right) \right. \\ & + \frac{1}{6kT} \left\{ 1 + 2\frac{\Delta}{\pi} \left(\frac{\alpha-1}{\alpha}\right) \frac{1}{W_t - \mu_e} \left(1 + o\left|\frac{E_d}{kT}\right| \right) \right\} \\ & \left. - \frac{1}{18(kT)^2} \left\{ E_d - \frac{\Delta}{\pi} \left[\ln\left(\frac{kT}{W_2}\right) - 3A \right] \right\} \right] \end{aligned}$$

$$- \frac{1}{108(kT)^3} \left\{ E_d^2 - \frac{\Delta}{\pi} E_d \left[2 \ln \left(\frac{kT}{W_2} \right) + 15A \right] + \dots \right\} \quad (4.4)$$

(W_2 was defined in (3.16)).

Comparing (4.3) with (4.4) we see that when state τ goes from inside to outside the band, U' is replaced by $W_t - \mu_e$ or $W_b + \mu_e$ as was pointed out by Haldane¹⁶.

4.3. Low-Temperature Kondo Limit – $E', U' \gg kT$

In this limit $\langle n_v \rangle_0 = c/2$ and $\langle n_p \rangle_0 = \langle n_\tau \rangle_0 = 0$. When τ is inside the band

$$\chi = (2\alpha)^2 c \left\{ \frac{1}{4kT} \left[1 + 2 \frac{\Delta}{\pi} \left(\frac{1}{E_d} - \frac{1}{U'} \right) \right] + \frac{\Delta}{4\pi} \left[\left(\frac{1}{U'} \right)^2 + \left(\frac{1}{E_d} \right)^2 \right] + \dots \right\} \quad (4.5)$$

and this χ coincides up to linear terms with Haldane's result when we neglect $(U')^{-2}$ against $(E_d)^{-2}$. The expression for τ in (4.5) and the state τ could have been left out from the calculation because these terms can be neglected.

4.4. Low Temperature Asymmetric Singled Limit $U' \gg E, \gg kT$

It is now $\langle n_p \rangle_0 = c$ and $\langle n_v \rangle_0 = \langle n_\tau \rangle_0 = 0$, and when τ is outside the band we find

$$\chi = (2\alpha)^2 c \frac{\Delta}{2\pi} \left[\frac{1}{2} - \left(\frac{\alpha-1}{\alpha} \right)^2 \left(\frac{1}{+\mu} + \right)^2 \right] \quad (4.6)$$

When τ is inside the band, the second term inside the bracket disappears and we obtain Haldane's result up to first order in Δ . As in the previous case the state τ can be neglected in this regime.

4.5. The Intermediate Valence Compound

As we discussed in section 3 fairly large cancellations in χ are produced by a term proportional to $(\partial^2 \mu_e / \partial H^2)$ at rather small values of c when c increases from $c=0$ to $c=1$. When $H=0$ it is $(\partial \mu_e / \partial H)=0$, but

the second derivative is given by (3.5) and is of the order $\beta\alpha^2$ when at least two states of charge are appreciably occupied in the unperturbed system.

In the high temperature limit $\langle n_p \rangle_0 = \langle n_v \rangle_0 = \langle n_\tau \rangle_0 = 1/4$, and only the case of τ inside the band is interesting. When $x \neq 1$ there is a contribution proportional to $T^{-3} \ln(x)$ and the largest correction is proportional to T^{-4} when $x=1$; the effect is therefore not important in this temperature range. The case $\beta U' \gg 1$ is more interesting: it is $\langle n_\tau \rangle_0 = 0$ and from (3.5) we find

$$c_\mu = (\beta\alpha^2)^{-1} \left(\frac{\partial^2 \mu_e}{\partial H^2} \right) = - \frac{\langle n_v \rangle_0 \langle n_p \rangle_0}{(eR(T) \rho(\mu_e)/N) + \langle n_v \rangle_0 \langle n_p \rangle_0} \quad (4.7)$$

so that c_μ can be close to -1 only when $\langle n_v \rangle_0 \langle n_p \rangle_0$ is much larger than $eR(T) \rho(\mu_e)/N$, which is fairly small (cf. discussion after (3.6)). This contribution to χ is therefore important only in the intermediate valence region. For temperatures in the region $|E_d| \ll kT \ll U$ the correction to χ when τ is inside the band is

$$\begin{aligned} & - (2\alpha)^2 e \frac{\Delta}{\pi} \left\{ \frac{1}{6U^2} \frac{\pi^2}{18} + \frac{1}{18 (kT)^2} \ln \left(\frac{kT}{W_1} \right) + \right. \\ & \left. + \frac{1}{108 (kT)^3} E_d \left[2 \ln \left(\frac{kT}{W_1} \right) + \frac{1}{2} 4 \right] \right\} \quad (4.8) \end{aligned}$$

and when τ is outside the band it is equal to

$$- (2\alpha)^2 e \frac{\Delta}{\pi} \left\{ \frac{1}{18 (kT)^2} \ln \left(\frac{kT}{W_2} \right) + \frac{1}{108 (kT)^3} E_d \left[2 \ln \left(\frac{kT}{W_2} \right) + 18A \right] \right\} \quad (4.9)$$

The expressions (4.8) and (4.9) should be added to (4.2) and (4.4) respectively which then have some of their terms, and in particular all the logarithmic ones, cancelled out. In the low temperature regions discussed in sections 4.3 and 4.4 only one state of charge is appreciably populated, so that $c_{\mu} = 0$ and the corresponding correction to χ vanishes.

4.6. Numerical calculations

With the numerical values of Y_0 , Y_1 and Y_2 discussed in Appendix 1 we can calculate the $\Delta\chi$ given in (3.13) and (3.16) for arbitrary values of E_d , U and T . We shall only give the values for the single impurity case when τ is inside the band. The curves should retain their qualitative features when τ is outside the band, but with $W_b + \mu_e$ and $W_t - \mu_e$ taking the place of U ; this relationship is clearly seen when (4.4) is compared with (4.2). As discussed in section 4.5, there are important cancellations in the intermediate valence compound, but again the qualitative features of the curves should be maintained in the transition from $c=0$ to $c=1$.

In figure 1 we plot $T\Delta\chi$ (in units of $c(2\alpha)^2 \Delta / (\pi k |E_d|)$) as a function of E_d/kT for several values of the constant ratio (U/E_d) ; this procedure corresponds to give $T\Delta\chi$ as a function of $1/T$ when U and E_d are kept constant.

The values $E_d/kT \ll -1$ correspond to the low-temperature Kondo limit, and the ordinate in fig. 1 is close to $-1/2$ when $|U/E_d| \gg 1$, in agreement with (4.5). In the low temperature singlet limit ($E_d/kT \gg 1$) the value $T\Delta\chi$ tends to zero as the inverse of the abscissa E_d/kT . The values $|E_d/kT| < 5$ correspond to the intermediate valence region, and the dependence of $T\Delta\chi$ with $|U/E_d|$ is clearly shown. The contribution of $\ln(x)$, that was set equal to zero in figure 1, would also affect the susceptibility but only in this region.

The neighbourhood of the origin in figure 1 is described by the terms proportional to Δ in (4.2) when $U/kT = (U/E_d) \cdot (E_d/kT) \gg 1$ and to those in (4.1) when $U/kT \ll 1$. As this region corresponds to very large T , both for positive and negative values of E_d , the behaviour of $T\Delta\chi$ near the origin is not surprising.

The rather special case $U=0$ has been calculated both with (3.13) and with the expression (3.8) that is obtained in Appendix 3 by a different method. There is perfect agreement between the two numerical results, and the curve is symmetrical in E_d/kT as it is shown in the graph.

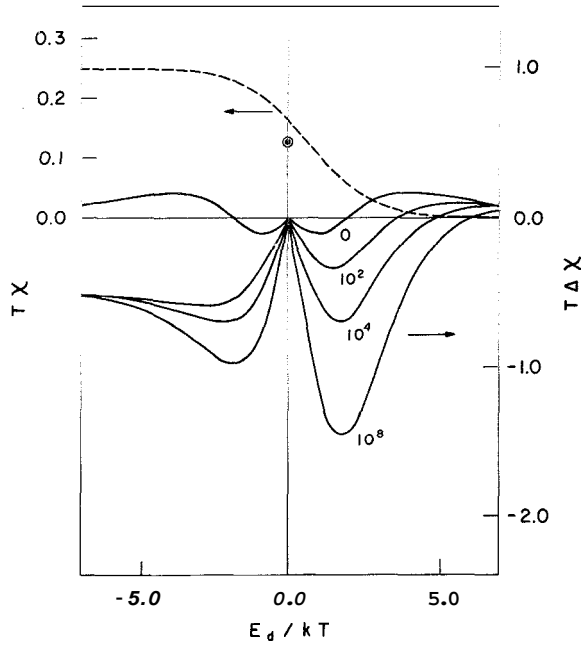


Fig. 1 - Full lines represent $T\Delta\chi$ (where $\Delta\chi$ is the second order correction to the susceptibility) as a function of E_d/kT for constant values $10^8, 10^4, 10^2$ and 0 of the ratio $U/|E_d|$. The dashed line represents the unperturbed ionic susceptibility $T\chi_{0c}$ at constant $U/|E_d|$. This curve takes the value 0.125 at the origin and the plot has a dip in that neighbourhood that is not represented in the figure and depends on the value of $U/|E_d|$. The units are $c(2\alpha)^2 \Delta/(mk|E_d|)$ for $T\Delta\chi$ and $c(2\alpha)^2/k$ for $T\chi_{0c}$; note the different scales employed in the figure. The curves at constant $U/|E_d|$ correspond to plots of $T\chi_{0c}$ and $T\Delta\chi$ at constant U and E_d as a function $1/T$.

In fig. 1 we have also plotted $T\chi_{0c}$ in units of $C(2\alpha)^2/k$ as given in (3.18) but note the different scale. The plot is a function of $1/T$ at constant E_d and U , and takes the value 0.125 at the origin (i.e. for $T=\infty$). In this neighbourhood there is a dip that is more pronounced when $|UE_{ex}|$ is larger and can not be distinguished clearly in the scale used to draw fig. 1.

In all cases, the perturbed values of χ are a reasonable approximation only for sufficiently small values of BA .

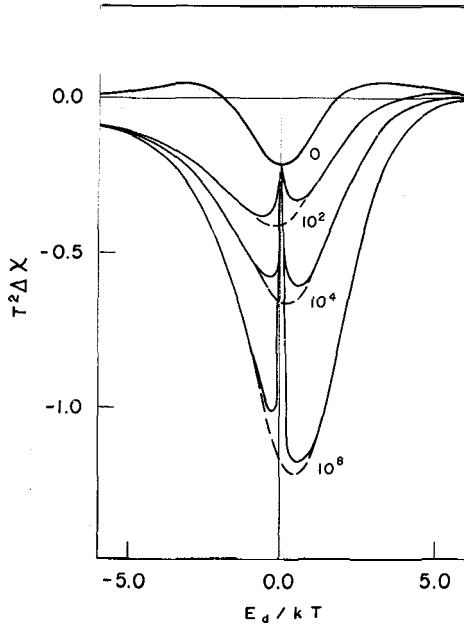


Fig. 2 - Full lines represent $T^2\Delta\chi$ as a function of E_d/kT for constant values 10^8 , 10^4 , 10^2 and 0 of the ratio $U/|E_d|$: they correspond to the plot of $T^2\Delta\chi$ as a function of $1/T$ with E_d and U kept constant, and all take the value -0.21314 at the origin.

The dashed lines represent $T^2\Delta\chi$ but for constant values 10^8 , 10^4 , 10^2 of U/kT : they correspond to a plot of $T^2\Delta\chi$ as a function of E_d with U and T kept constant. When $U=0$ the curve at constant U/kT coincides with that at constant $U/|E_d|$.

The two types of curves are indistinguishable far from the origin. The units employed here are $\sigma(2\alpha)^2\Delta/\pi k^2$.

In figure 2 we plot $T^2\Delta\chi$ as a function of E_d/T in adequate units; the full lines correspond again to constant values of U/E_d , i.e., to variable $1/T$ and constant U and E_d . The value at the origin is $-A/4 \approx -0.21314$ in the units employed, and the same type of slope discontinuity observed in fig. 1 is present here.

In the region $|E_d/kT| > 5$, the plots of $T^2\Delta\chi$ at constant U/kT are practically coincident with those at constant $U/|E_{ex}|$, but close to the origin they are rather different, and have been drawn as dashed lines. The curves have continuous slope at the origin, and they represent $T^2\Delta\chi$ as a function of E_d at constant T and U . The neighbourhood of the origin

then corresponds to an arbitrary value of T but for sufficiently small E_d . The values $|E_d/kT| < 5$ correspond therefore to very different physical parameters in the two cases (constant U/kT . vs. constant $U/|E_d|$), but it is in this region of E_d/kT that the values of U and $\ln(x)$ affect $\Delta\chi$ when τ is inside the band

The case $U=0$ is also plotted in fig. 2 and the same graphs are obtained at constant $U/|E_d|$ and constant U/kT .

5. SUMMARY AND CONCLUSIONS

We have employed the method of thermodynamic perturbation up to second order to calculate the change of the Helmholtz free energy and the magnetic susceptibility when the hybridization term is considered as a perturbation and V , T , N , N_C and N_t are kept constant.

We have employed a sort of grand canonical ensemble introduced previously^{11,12}, but we have rearranged the summation in the grand canonical partition function to extend the validity of our expressions to large values of $|E_d|/kT$.

It is interesting to compare our technique to those employed by Hewson¹³ and Haldane¹⁵ in the study of similar problems. Both Hewson and Haldane use the standard basis operators $X_{n,pq} = |np\rangle\langle nq|$ of Hubbard²² to write the model Hamiltonian; we employ instead creation and destruction operators for impurities^{11,12} defined through (2.2) and related to the $X_{n,pq}$ by $X_{n,pq} = B_{np}^+ B_{nq}$. Our extension has the advantage that arbitrary concentrations of impurities are treated naturally with the B operators, which are well suited to an ensemble with variable number of electrons and impurities.

The three techniques are rather different: Hewson uses Green's functions to treat the $c=1$ case of SmS, with only two states of charge (Sm^{3+} and Sm^{2+}). Haldane considers the impurity Anderson's model ($c \rightarrow 0$) with all the three possible states of charge and uses a diagrammatic technique assuming an "infinite bandwidth". Our expressions (3.3) was obtained by a rather straightforward calculation with the thermodynamic

perturbation method, and is applicable to any of the two other models; we have employed (3.3) to study the Anderson's model for arbitrary concentration c and for a rectangular band. Our method agrees perfectly well with the other two in the proper limits. In the impurity case ($c \rightarrow 0$) we obtain a perfect agreement when we employ Haldane's symmetric "infinite bandwidth" model. In the $c=1$ case we obtain an extra contribution to χ that coincides numerically with the correction predicted by Hewson's technique for our model: the analytic expressions seem rather different, but we have been able to prove using thermodynamic arguments that the two are equal.

All these results give confidence in our method, and it is interesting to consider departures from the conditions set by the other two methods. A new contribution proportional to $\ln(x)$ with $r = (W_t - \mu_e) / (W_b + \mu_e)$ appears in our calculation, but it vanishes when the electronic chemical potential μ is just in the middle of the conduction band $(-W_b, W_t)$ as should be the case with the "infinite-bandwidth" model employed by Haldane¹⁵. The two calculations then give the same results up to second order and it seems therefore clear that the method of Haldane forces the system to a symmetry, which in general is not present in physical situations. It has been argued that states that are near the top or the bottom of the conduction band have such a large energy difference with the Fermi energy that are effectively free with regard to the Coulomb repulsion U , and that therefore a term like $\ln(x)$ should not be present. This argument is invalidated by the presence of the $\ln(x)$ even in the free electron case ($U=0$) with hybridization.

In intermediate valence problem only two states of charge are usually considered, on the grounds that it is necessary a very large energy to create those that are neglected. As we have studied a lattice of Anderson impurities that have three states of charge, we have been able to analyse the approximation of considering only two of them in the calculation. The energy difference between the neglected state (τ) and those with one electron less ($\nu\sigma$) is $U' + \mu_e = E_\tau^0 - E_\nu^0$ and we assume $\beta U' \gg 1$: this guarantees that there is a negligible thermal occupation of the state τ in the unperturbed problem. Two physical situations are possible

- 1) $U' + \mu_e > W_t$, i.e. there are states of the band with energy equal to $E_\tau^0 - E_\nu^0$
- 2) $U' + \mu_e < W_t$, i.e. there are no such states

It is enough to consider $\beta |U' + \mu_e - W_t| \gg 1$. In case 1) we have found that the third state of charge has two effects on the susceptibility: 1a) it gives a contribution proportional to $\ln(\beta U')$, 1b) produces a cancellation of a term with $\ln[\beta(W_b + \mu_e)]$ leaving only a contribution to the $\ln(x)$ discussed above.

In case 2) the extra states has very little effect on the susceptibility: it contributes a term with $\ln(x_u)$, but because of the absence of 1a) and 1b), there is a term proportional to $\ln \beta(W_b + \mu_e)$ instead of the $\ln(\beta U')$. It is then clear that extra states of charge can be neglected in case 2) but not in case 1). We should remark that all these terms with $\ln(x)$, $\ln(x_u)$, $\ln(\beta U')$ and $\ln[\beta(W_b + \mu_e)]$ are proportional to $\langle n_\rho \rangle_0 \langle n_\nu \rangle_0$ and therefore contribute only in the intermediate valence regime. We have also concluded that the cancellation 1b) would be only a partial one if the hybridization coefficients between different pairs of states of charge were not the same.

It has been pointed out by Hewson¹³, that some of the $\ln(W/kT)$ terms that appear in the impurity case are cancelled out in the pure compound. In our case all the logarithmic terms are cancelled out at $c=1$ and they give a partial contribution that is not linear in c at intermediate values of concentration.

I would like to express my gratitude to Prof. Leo Falicov for many enlightening comments and for critically reading the manuscript.

APPENDIX I

The Helmholtz free energy and susceptibility in the grand canonical ensemble.

Sometimes it is found in the literature that the Helmholtz free energy F is equal to $-kT \ln z$, where z is the grand partition function; the correct expression for a system with a single component is rather

$$F = N\mu - kT \ln z(\mu, T, V) \quad (1.1)$$

where we write N to indicate $\langle N \rangle$ (in this Appendix only $\langle N \rangle$ should appear) and use V for the total volume of the system. Nevertheless, the use of a formula that would be wrong for F gives the correct expression for the magnetization when $kT \ln z$ is employed:

$$M = kT \left(\frac{\partial \ln z}{\partial H} \right)_{\mu, V, T} \quad (1.2)$$

To express M in terms of F , we take the partial derivative of (1.1) at constant N, V, T

$$\left(\frac{\partial F}{\partial H} \right)_{NVT} = N \left(\frac{\partial \mu}{\partial H} \right)_{NVT} - kT \left(\frac{\partial \ln z}{\partial H} \right)_{NVT} \quad (1.3)$$

We assume that the equation

$$N = \langle N \rangle = \left(\frac{\partial \ln z}{\partial \mu} \right)_{VTH} \quad (1.4)$$

can be solved in μ , to give

$$\mu = \mu(N, V, T, H) \quad (1.5)$$

and we apply the chain rule of partial derivatives to the last term in (1.3)

$$\left(\frac{\partial \ln z}{\partial H} \right)_{NVT} = \left(\frac{\partial \ln z}{\partial H} \right)_{\mu VT} + \left(\frac{\partial \ln z}{\partial \mu} \right)_{VTH} \left(\frac{\partial \mu}{\partial H} \right)_{NVT} \quad (1.6)$$

so that together with (1.2) and (1.4) we obtain

$$kT \left(\frac{\partial \ln z}{\partial H} \right)_{NVT} = M + N \left(\frac{\partial \mu}{\partial H} \right)_{NVT} \quad (1.7)$$

and replacing (1.7) into (1.3)

$$\left(\frac{\partial F}{\partial H}\right)_{NVT} = -M \quad (1.8)$$

This is a very well known relationship, and is given here only to indicate the idea behind a similar but more involved derivation of equation (3.1) for a system with one type of impurity ions in several states of charge j . The concentrations corresponding to the different states of charge is not arbitrary, but the relations (2.4) must be satisfied. There are left only two independent concentrations and we chose $N_t = N_c$ (cf. (2.6)) and $N_c = N_c$ (cf. (2.7)) to describe the state of system.

From the general expression (cf. (5.9) in reference 11)

$$M = kT \left(\frac{\partial \ln z}{\partial H}\right)_{\mu_j, \mu_e, \mu_0} VT \quad (1.9)$$

and

$$F = N\mu_0 + N_t\mu_p + N_c\mu_e - kT \ln z \quad (1.10)$$

one derives the equation that corresponds to (1.8) namely

$$M = - \left(\frac{\partial F}{\partial H}\right)_{N_t, N_c} NVT \quad (1.11)$$

which is just (3.1). It is then clear that (3.1) is equivalent to (1.9), and not incompatible to that expression of M.

APPENDIX II

The properties of $X(x, W)$ and $Y_0(x, W)$ defined in (3.10) and (3.11) are studied here. They are both related by

$$X(x, W) = \theta(W) [\gamma + \ln W + E_1(W)] - Y_0(x, W) \quad (11.1)$$

where $\gamma = 0.57721\dots$ is Euler's constant, and

$$E_1(W) = \int_W^\infty \exp(-t) \cdot d \ln t \quad (11.2)$$

When $W \gg 1$, one can use the asymptotic expansion given by Abramowitz and Stegun²³

$$E_1(W) = \exp(-W) \cdot \left[\frac{1}{W} - \frac{1}{W^2} + \frac{2}{W^3} - \dots \right] \quad (11.3)$$

The $E_1(W)$ appears also in the relationship between $Y_0(x, W)$ and $Y_0(x, \infty)$:

$$Y_0(x, W) = Y_0(x, \infty) - \exp(x) \cdot E_1(W) + [1 + \exp(-x)] \cdot [E_1(2W) \cdot \exp(2x) - E_1(3x) \cdot \exp(3x) + \dots] \quad (11.4)$$

and we can then replace $Y_0(x, W)$ by $Y_0(x)$ in all the $X(x, W)$ of (3.12) when $\beta(\bar{W}_t - \mu_e) \gg 1$.

For negative $x \ll -1$ we have

$$Y_0(x) = (\ln 2) \cdot \exp(x) - (\ln \frac{3}{2}) \cdot \exp(2x) + (\ln \frac{4}{3}) \cdot \exp(3x) - \dots \quad (11.5)$$

and for positive $x \gg +1$

$$Y_0(x) = \gamma + \ln(x) + E_1(x) - \frac{\pi^2}{6} \frac{1}{x^2} [1 - (1+x) \cdot \exp(-x)] - \frac{7\pi^4}{60} \frac{1}{x^4} [1 - (1+x + \frac{1}{2}x^2 + \frac{1}{6}x^3) \cdot \exp(-x)] - \dots \quad (11.6)$$

The functions $Y_1(x, W)$ and $Y_2(x, W)$, defined respectively as the first and second derivatives of $Y(x, W)$ with respect to x , are also expressed as integrals, and similar relationships to $Y_1(x)$ and $Y_2(x)$ and approximate analytical expressions for large $|x|$ can be easily found.

We have also calculated $Y_0(x)$, $Y_1(x)$ and $Y_2(x)$ by numerical integration up to a large W and subsequent use of (A.4) for $Y_0(x)$ and the

equivalent relationships for $Y_1(x)$ and $Y_2(x)$. The values are presented in Figure 3, where $Y_0(x)$ has been plotted in a different scale than $Y_1(x)$ and $Y_2(x)$.

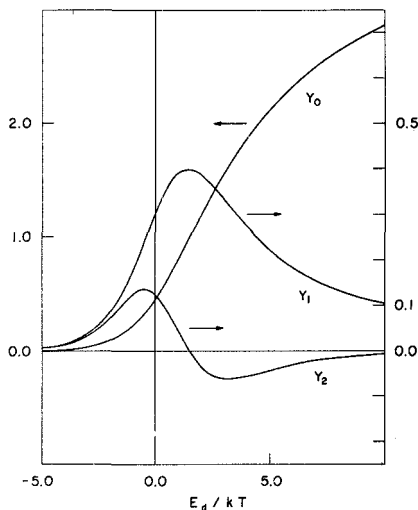


Fig. 3 - The function $Y_0(x)$ and its two derivatives $Y_1(x)$ and $Y_2(x)$ are plotted in this graph. Note the different scale used for $Y_0(x)$.

APPENDIX III

The case of a single impurity with no correlation ($U=0$) can be solved exactly (see e.g. ²⁴) and one can express the susceptibility in a closed form. This expression can be expanded in a power series of the parameter A employed in the text and compared with the results obtained by thermodynamic perturbation in the case $U=0$.

Following Haldane²⁴, we obtained the exact Green's functions of Zubarev that are relevant to the problem, and employed the Hellmann-Feynman theorem to express the logarithm of the grand partition function $z(\mu, \Delta)$ as an integral over the hybridization constant \bar{V} . We shall use $\Delta = \pi \rho (\bar{V})^2$ as parameter, where ρ is the density of states in the rectangular band assumed in the present derivation, and \bar{V} is an average hybridization constant. We find

$$\ln z(\mu, \Delta) - \ln z(\mu, 0) = \frac{\beta}{2\pi i} \oint_{\Gamma} d\omega f(\beta\omega) \sum_{\sigma} \ln \left(\frac{\omega - \epsilon_{\sigma} - \bar{V}^2 g_{\sigma}(\omega)}{\omega - \epsilon_{\sigma}} \right) \quad (III.1)$$

where

$$g_{\sigma}(\omega) = \sum_{\vec{k}} 1/(\omega - \epsilon_{\vec{k}\sigma}) \quad (111.2)$$

$$\epsilon_{\sigma} = E + \alpha\sigma H - \mu_e \quad (111.3)$$

$$\epsilon_{\vec{k}\sigma} = E_{\vec{k}} + \sigma H - \mu_e \quad (111.4)$$

$$f(x) = 1/(1 + \exp(x)) \quad (111.5)$$

and Γ is the contour $(-A-i\eta) \rightarrow (+A-i\eta) \rightarrow (+A+i\eta) \rightarrow (-A+i\eta) \rightarrow (-A-i\eta)$. Both A and η are real positive numbers, η is smaller than π (so that there are no singularities of f inside Γ) and we presently take $A \rightarrow \infty$. In zero field the energy of an electron in the band state \vec{k} or in the impurity are $E_{\vec{k}}$ and E respectively, and $E_d = E - \mu_e$. For sufficiently small A we can expand the logarithm in (111.1) as a series of powers in Δ when ω is on Γ ; in lowest order we obtain

$$\begin{aligned} \ln z(\mu, \Delta) - \ln z(\mu, 0) = \\ = -\frac{\beta\Delta}{\pi} \sum_{\sigma} \left\{ f(\beta\epsilon_{\sigma}) \ln \left| \frac{\epsilon_{\sigma} + W_{t\sigma} + \mu_e}{\epsilon_{\sigma} - W_{b\sigma} + \mu_e} \right| + \int_{-W_{b\sigma} - \mu_e}^{W_{t\sigma} - \mu_e} \frac{f(\beta\omega)}{\omega - \epsilon_{\sigma}} d\omega \right\} \end{aligned} \quad (111.6)$$

where \int is the principal value of the integral and

$$\begin{aligned} W_{t\sigma} &= W_t + \sigma H \\ W_{b\sigma} &= W_b - \sigma H \end{aligned} \quad (111.7)$$

An important point noticed by Hewson¹³ is that when the hybridization constant changes from zero to its final value \bar{V} , the chemical potential μ_e must change from μ_0 to $\mu = \mu_0 + \Delta\mu_0$ if the total number of electrons is to be kept constant, and that $\Delta\mu_0$ is of order A . The $\Delta\mu_0$ and the corresponding change in the susceptibility $\Delta\chi_0 = \chi(\mu, 0) - \chi(\mu_0, 0)$ depend on the impurity concentration c and they are negligible when c tends to zero, as it is the case of a single impurity and a large number N of sites. Nevertheless, we shall give $\Delta\chi_0$ for two purposes: 1) to compare with

the result derived in the text and 2) to see how small c should be to neglect $\Delta\chi_0$. It should be emphasized that the corresponding correction to AG has been included in the derivation of (2.9) as implied in the comment iii near the end of section 2.

With the use of (1.2) we calculated the total change of χ per site:

$$\Delta\chi = \chi(\mu, \Delta) - \chi(\mu_0, 0) = \frac{\Delta}{2\pi} \beta^2 (2\alpha)^2 \frac{1}{N} \cdot \left\{ \ln \left| \frac{W_t - E_d - \mu_e}{W_b + E_d + \mu_e} \right| \cdot f''(\beta E_d) \cdot [1 - C_1] - \left[\int \frac{f''(t)}{t - \beta E_d} dt + (1 - 2f) \cdot C_1 \cdot \int \frac{f'(t)}{t - \beta E_d} dt \right] \right\} \quad (111.8)$$

where the terms proportional to

$$C_1 = \frac{f(1-f)}{kT\rho + f(1-f)} \quad (111.9)$$

appear when we consider the $\Delta\mu_0$ discussed above, and we have used $f=f(\beta E_d)$ to shorten the formulas. When terms of the order $E_d/(W_t - \mu_e)$ and $E_d/(W_b + \mu_e)$ are neglected, the logarithm in (111.8) is equal to the $\ln(x)$ that appears in (3.13), and it is indeed present in $\Delta\chi$ when C_1 is negligible.

To compare (111.8) with (3.13) we notice that when $U=H=0$ it is

$$\begin{aligned} \langle n_\rho \rangle &= c(1-f)^2 \\ \langle n_{\nu\sigma} \rangle &= cf(1-f) \\ \langle n_\tau \rangle &= cf^2 \end{aligned} \quad (111.10)$$

where as before $f=f(\beta E_d)$.

In the equation (3.14) for M_μ we have neglected $\langle n_\tau \rangle$, and in the present calculation we have to use (3.5) and (3.7) instead. The expression for $\Delta\chi$ is then obtained:

$$\Delta\chi = \frac{\Delta}{2\pi} \beta^2 (2\alpha)^2 c.$$

$$\begin{aligned} & \cdot \left\{ f'(\beta E_d) \cdot [\ln(x) + Y_0(\beta E_d) - Y_0(-\beta E_d)] (1-C_2) + \right. \\ & + 2f'(\beta E_d) \cdot [Y_1(\beta E_d) + Y_1(-\beta E_d)] - [(1-f)Y_2(\beta E_d) + fY_2(-\beta E_d)] \\ & \left. + (1-2f) \cdot C_2 \cdot [(1-f) \cdot Y_1(\beta E_d) - f Y_1(-\beta E_d)] \right\} \end{aligned} \quad (111.11)$$

where

$$C_2 = \frac{cNf(1-f)}{kT\rho + cNf(1-f)} \quad (111.12)$$

In the single impurity case it is $c=1/N$ and then $C_1=C_2$. From (111.11) we see that C_2 is appreciably different from zero when

$$c \cdot N \cdot \left| \frac{df(\beta E_d)}{dE_d} \right| \gg \rho$$

i.e. when the change in the occupation number of the $N_t = N \cdot c$ impurities per unit variation of the impurity energy is much larger than the density of band states. In this case, a change in the energy E of the impurity requires an approximately equal change in μ so that the total number of electrons be a constant ($E-\mu$ then remains practically the same). For the usual densities ρ , the opposite situation is true when $N_t \ll 1$, and the change of the impurity population because of the variation of E is easily absorbed by the band states. In this case μ remains approximately constant to keep unchanged the total number of electrons.

We have compared formulas (111.8) and (111.10) analytically in the two extreme limits $|\beta E_d| \ll 1$ and $|\beta E_d| \gg 1$, and numerically for intermediate values of βE_d : the results coincide for all βE_d .

Although the mechanism by which this concentration dependence appears in $\Delta\chi$ varies with the mode of calculation, the final contribution should be the same, as it is indeed the case. In (111.8) the energy of the impurity is altered by the hybridization with the band states, and a $\Delta\mu_0$ (negligible for usual values of ρ in the single impurity case) is necessary to keep the total number of electrons constant; when M is

calculated with (1.2), only $(\partial\mu/\partial H)_{N=0}$ appears in χ and $(\partial^2\mu/\partial H^2)_N$ does not contribute. In the derivation of (111.10) we employ (1.8) to obtain M , and $(\partial^2\mu/\partial H^2)_N$ contributes to $\Delta\chi$: in this case it is the variation with H of the energy level of the impurity that causes the concentration dependence (the changes in μ produced by changes in A have already been included in ΔF , which is given at a constant number of electrons).

The fact that depending on the mode of derivation the concentration dependence is given by two different expressions, seems to indicate that there should be some relationship between $(\partial^2\mu/\partial H^2)_{\Delta,N}$ and $(\partial\mu/\partial\Delta)_{N,H}$. We have indeed obtained this relationship by calculating $(\partial\chi/\partial\Delta)_{NH}$ in two different ways, and we have found

$$\left(\frac{\partial\chi}{\partial\Delta}\right)_{NH} = -\left(\frac{\partial F_{\Delta}}{\partial\mu}\right)_{\Delta H} \left(\frac{\partial^2\mu}{\partial H^2}\right)_{\Delta N} - \left(\frac{\partial^2 F_{\Delta}}{\partial H^2}\right)_{\mu\Delta} \quad (111.13)$$

and

$$\left(\frac{\partial\chi}{\partial\Delta}\right)_{NH} = \left(\frac{\partial\mu}{\partial\Delta}\right)_{NH} \left(\frac{\partial\chi}{\partial\mu}\right)_{\Delta H} - \left(\frac{\partial^2 F_{\Delta}}{\partial H^2}\right)_{\mu\Delta} \quad (111.14)$$

where

$$F_{\Delta} = \left(\frac{\partial F}{\partial\Delta}\right)_{NH} \quad (111.15)$$

The two relations (111.12-13) were obtained by the usual techniques employed in thermodynamics, and are valid at $B=0$ in the paramagnetic case (we have used $(\partial\mu/\partial H)_N = 0$ in the derivation of (111.12-13)). The derivation is somewhat involved and shall not be given here. The meaning of these formulas is apparent when we note that in the linear approximation, A times $(\partial\chi/\partial\Delta)_{NH}$ calculated at $A = 0$ gives the change in χ at constant N produced by the hybridization and that ΔF_{Δ} gives the ΔF that corresponds to (2.9). Equating (111.12) to (111.13) we find

$$-\left(\frac{\partial F_{\Delta}}{\partial\mu}\right)_{\Delta H} \left(\frac{\partial^2\mu}{\partial H^2}\right)_{\Delta N} = \left(\frac{\partial\chi}{\partial\mu}\right)_{\Delta H} \left(\frac{\partial\mu}{\partial\Delta}\right)_{NH} \quad (111.16)$$

which provides the relation that would be expected to hold between the two derivatives of μ at constant N . The left hand side (times A) is the

contribution M_{μ} to (3.13) and the right hand side (times A) is the correction (22) employed by Hewson¹³ in his derivation.

We have also extended the proof of (III.15) to the model employed in the text, in which there is a variable number of impurities in different states of charge: the total number of impurities is $N_t = N_c$ and the total number of electrons is $N_e = N_c n_c$. We have been able to prove the equality

$$-\left(\frac{\partial F_{\Delta}}{\partial \mu_e}\right)_{N_t, N_{\Delta}, H} \left(\frac{\partial^2 \mu_e}{\partial H^2}\right)_{N_t, N_c, N_{\Delta}} = \left(\frac{\partial \chi}{\partial \mu_e}\right)_{N_t, N_{\Delta}, H} \left(\frac{\partial \mu_e}{\partial \Delta}\right)_{N_t, N_c, N_H} \quad (III.17)$$

where

$$F_{\Delta} = \left(\frac{\partial F}{\partial \Delta}\right)_{N_t, N_c, N_H} \quad (III.18)$$

The (III.16) is the natural extension of (III.15), and again it is $(\partial \mu_e / \partial H)_{N_t, N_c, N} = 0$ for $H = 0$ in the paramagnetic phase.

From this appendix, little doubt can remain that the term with $\ln(x)$ is present in the impurity case, as well as to the existence of the concentration dependent term. This last term appears even in this "single ion" approximation in which the interaction between impurities is neglected. Depending on the mode of calculation the expressions obtained seem different, but (III.16) shows that the contribution is indeed the same in the two cases.

REFERENCES

1. J.M. Robison, Physics Reports 51, 1 (1979).
2. J.M. Jefferson and K.W.H. Stevens, J. Phys. C 21, 4171 (1978).
3. A.C. Hewson, J. Magnetism Mag. Mat. 12, 83 (1979).
4. C.M. Varma, Rev. Mod. Phys. 48, 219 (1976).
5. J.H. Jefferson and K.W.H. Stevens, J. Phys. C., 9, 2151 (1976).
6. M.E. Foglio and L.M. Falicov, Phys. Rev. 820, 4554 (1979).
7. M.E. Foglio, C.A. Balseiro, L.M. Falicov, Phys. Rev. 820, 4560 (1979).
8. T. Matsubara, Progr. Theor. Phys. (Kyoto) 14, 351 (1955).

9. L.D.Landau and E.M.Lifshitz, *Statistical Physics* (Pergamon, Press, Lorida, 1959) p. 93.
10. T.Huber and B.R.Alascio, *Statistical Mechanics of Intermediate valence*, Preprint, C.A.B., Argentina (1976).
11. M.E.Foglio, *Phys.Stat.Sol. (b)* 86, 459 (1978).
12. M.E.Foglio, *Phys.Stat.Sol. (b)* 87, 87 (1978).
13. A.C.Hewson, *J.Phys. C.* 10, 4973 (1977).
14. P.W.Anderson, *Phys. Rev.* 124, 41 (1961).
15. F.D.M.Haldane, *J.Phys. C.*, 11, 5015 (1978).
16. F.D.M.Haldane, *Phys. Rev. Letters*, 40, 416 (1978).
17. L.L.Hirst, *Advances in Physics* 27, 231 (1978).
18. K.Yamada, *Progr. Theor. Phys.* 53, 970 (1975).
19. H.R. Krishna-murthy, K.C.Wilson and J.W.Wilkins, *Phys.Rev.Letters* 35, 1101 (1975).
20. R.Ramirez and L.M.Falicov, *Phys. Rev. B* 3, 2425 (1971).
21. N.F.Mott. *Phil. Mag.* 30, 403 (1974).
22. J.Hubbard, *Proc. R. Soc. A* 277, 237 (1964).
23. M.Abramovitz and I.Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965) p. 231.
24. F.D.M.Haldane, *Phys. Rev. B* 15, 281 (1977).