LA-UR -80-1005

TITLE: MODEL VALENCE-FLUCTUATION SYSTEMS: VARIATIONAL GROUND STATES AND MAGNETIC RESPONSES

AUTHOR(S): Baird H. Brandow, Group T-11
Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545

SUBMITTED TO: "Proceedings of the International Symposium on the Physics of Actinides and Related 4f Materials" (Zürich, Switzerland, April 9-11, 1980), to appear in a special issue of Physica B.

Model Valence-Fluctuation Systems: Variational Ground States and Magnetic Responses

B. H. Brandow
Theoretical Division
Los Alamos Scientific Laboratory
University of California
Los Alamos, New Mexico 87545, U.S.A.

Abstract

Variational ground-state wavefunctions are presented and optimized for two model valence-fluctuation systems, based on Anderson lattice Hamiltonians in the $U \to \infty$ limit. Although these wavefunctions are approximate, they are treated in an essentially exact manner. The $\{f^0, f^1; n = 1\}$ system has an intuitively reasonable ground-state susceptibility, while the $\{f^1, f^2, n = 2\}$ system is found to exhibit an insulating gap. Due to their different crystal symmetries, this gap should be realized in SmB_6 but not in SmS.

1. Introduction

An obstacle for the understanding of valence-fluctuation materials has been the absence of a suitable model to illustrate the essential nature of the valence-fluctuation ground state We have recently developed two closely related models which should serve to fill this role [1, 2]. The basic program is to construct variational ground states, and then to study how they respond to applied magnetic fields. Physical features will be emphasized in this report, at the expense of mathematical detail.

For reasons discussed elsewhere [1, 2], we describe the electrons by means of the Anderson lattice Hamiltonian,

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma}^{\dagger} n_{k\sigma} + \epsilon_f \sum_{j\sigma} n_{j\sigma}^{f} n_{j\sigma}^{f} + \sum_{kj\sigma} (V_{kj} n_{k\sigma}^{\dagger} n_{j\sigma}^{f} + h.c.) + H_U \quad , \qquad (1)$$

in common with a number of previous investigations [3]. Here the 5d conduction electrons are represented by "5c" Bloch orbitals, with a total bandwidth W. The 4f electrons are replaced by "4c" Wannier orbitals with site index j and energy ϵ_f. Thus, orbital degeneracy and any intrinsic 4f bandwidth are neglected.

We consider two different models, as follows: The $\{f^0, f^1\}$ model has one electron per site, and its one-site Coulomb interaction term is

$$H_U^{(0)} = U \sum_j n_{j\uparrow} n_{j\downarrow} \quad , \qquad (2)$$

where $n_{j\sigma} = n_{j\sigma}^{f} n_{j\sigma}^{f}$. The $\{f^1, f^2\}$ model has two electrons per site, and

$$H_U^{(2)} = U \sum_j (1 - n_{j\uparrow} - n_{j\downarrow} + n_{j\uparrow} n_{j\downarrow}) \quad . \qquad (3)$$

Although these models appear quite similar, their magnetic responses turn out to be strikingly different. Reasonable values for the parameters are $U = 5 - 8eV$, $W = 2eV$, and $V_k = N^{-\frac{1}{2}} \sum_j v_{kj} \exp(-ik \cdot R_j)$ $\sim 0.07eV$, where N is the number of lattice sites. In practice we take $U \to \infty$, so that the configurations f^2(for $\{f^0, f^1\}$) or f^0(for $\{f^1, f^2\}$) can be simply ignored. We also set the f-electron level ϵ_f equal to zero, thereby defining the origin for the energy scale.

2. Variational Ground States

For the $\{f^1, f^2\}$ model we assume a ground state trial wavefunction of the form

$$\Psi_{12} = \prod_j (\eta_{j\uparrow}^\dagger \eta_{j\downarrow}^\dagger + \sum_k a_{kj} (\eta_{k\uparrow}^\dagger c_{j\uparrow}^\dagger + \eta_{k\downarrow}^\dagger \eta_{j\uparrow}^\dagger \eta_{j\downarrow}^\dagger)) |\text{vacuum}\rangle \quad . \tag{4}$$

Note that each site involves a coherent superposition of f^1 and f^2 configurations (zero-point fluctuation feature), and all sites are physically equivalent. These features are consistent with X-ray and Mössbauer isomer shift spectra, with the lattice-constant systematics, and with the absence of low-temperature lattice distortions. Each site also displays a spin-singlet character, implying a low-temperature quenching of the local moments.

This wavefunction is formally equivalent to one studied previously by Stevens [4], but his use of a Wannier rather than Bloch representation for the conduction electrons led to unfortunate mathematical complications. We have found that the expectation value $\langle \Psi | H | \Psi \rangle$ can be obtained quite easily, by means of an elementary physical argument [1]. Given the present Ψ and H, the only possible interaction between the various sites j is

via the exclusion prinicple, namely, the fact that two sites cannot simultaneously make use of the same kσ Bloch orbital. That is, if site j has made the (virtual) transition jσ → kσ, then the corresponding transition j'σ → kσ is momentarily forbidden for all of the other sites j' ≠ j. It follows that the kσ orbital occupation number can be evaluated as a sum of quasi-independent one-site contributions,

$$n_{k\sigma} = \langle \hat{n}_{k\sigma} \rangle = \sum_j (|a_{kj}|^2/D)[1 - (N-1)n_{k\sigma}/N] \quad , \tag{5}$$

where $[1 - (N-1)n_{k\sigma}/N]$ represents the probability that kσ is not already occupied by an electron from some other site j' ≠ j. For large N this simplifies to

$$n_{k\sigma} = (\Lambda_k^2/D)(1 - n_{k\sigma}) = \Lambda_k^2/(D + \Lambda_k^2) \quad , \tag{6}$$

where $\Lambda_k = N^{-\frac{1}{2}} \sum_j a_{kj} \exp(-ik\cdot R_j)$. Similarly, the normalization denominator becomes

$$D = 1 + N^{-1} \sum_{k\sigma} \Lambda_k^2 (1 - n_{k\sigma}) = 1 + (D/N) \sum_{k\sigma} \Lambda_k^2/(D + \Lambda_k^2). \tag{7}$$

The energy expectation value is then found to have the very simple form

$$\cdot H \cdot = \sum_{k\sigma} (\epsilon_k \Lambda_k^2 + 2V_k \Lambda_k)(1 - n_{k\sigma})/D = \sum_{k\sigma} (\epsilon_k \Lambda_k^2 + 2V_k \Lambda_k)/(D + \Lambda_k^2). \tag{8}$$

Although first obtained by the above intuitive arguments, this result has been confirmed by means of diagrammatic perturbation theory. That analysis showed that, given the (admittedly approximate) trial function (4), the $\cdot H \cdot$ expression (8) is exact to terms of order N^{-1}. An important consequence of (5) (8) is that there can be no Kondo like divergences. These are eliminated by the destructive interference resulting from the exclusion principle, as manifested in (5)

Minimization of < H > leads to a quadratic expression for A_k. Inserting the solution in (6), the conduction band occupation numbers are found to resemble a finite-temperature Fermi distribution, with half-width "k_BT" of order V, where V is a mean value for the d-f hybridization matrix elements V_k. The midpoint "ε_F" for this distribution is found to fall below the f-electron level ε_f by an amount which varies as $-\ln(1-\xi)$, where ξ is the fractional f^1 character of the system. Throughout the valence-fluctuation regime (i.e., for ε_f between the bottom and the midpoint of the conduction band) this shift is quite small, of the order of the "resonance width" $\Gamma \approx \pi V^2/W$. This shift becomes large, however, when ε_f lies above the middle of the conduction band. This feature ensures that $0 < \xi < 1$ regardless of the position of ε_f, which is an obvious physical requirement here.

Numerical results are shown in Fig. 1(a), based on the parameters $W = 2eV$, $V_k = V = 0.1eV$, and $U = \infty$, together with a constant density of states ($\rho_0 = W^{-1}$) for the conduction band. The parameter D represents the energy difference between ε_f and the bottom of the conduction band, and $|C|$ is the above-mentioned shift, $\varepsilon_f - "\varepsilon_f"$. Note that for ε_f above the band midpoint ($D = 1eV$), the quantity $(1-\xi)$ falls exponentially at a very rapid rate, the e-folding distance being of the order of the resonance width $\Gamma \approx 10^{-2}eV$. For ε_f below the conduction band ($D < 0$), however, ξ falls off far more slowly; perturbation theory shows that here $\xi \sim [D\,(W-D)]^{-1}$.

Our trial wavefunction for the $\{f^0, f^1\}$ model is

$$\Psi_{01} = \prod_j \left\{ \sum_\sigma \alpha_\sigma (\eta^\dagger_{j\sigma} + \sum_k a_{kj\sigma} \eta^\dagger_{k\sigma}) \right\} |\text{vacuum}\rangle \quad , \tag{9}$$

where, in the absence of a magnetic field, $\alpha_\sigma = \alpha$ and $a_{kj\uparrow} = a_{kj\downarrow}$. The expectation value $\langle H \rangle$ is again found to have the form (8), although the D expression now differs from (7). Still using ξ to denote the fractional f^1 character, the main difference in the ground state results is simply that the roles of ξ and $(1 - \xi)$ are interchanged. This is illustrated in Fig. 1(b), based on the same parameters as Fig. 1(a).

3. Magnetic Susceptibility and Insulating Gap

The response of the $\{f^0, f^1\}$ ground state to a magnetic field can be studied by relaxing the above-mentioned symmetry restrictions in Ψ_{01}. The resulting magnetic susceptibility χ_{01} is plotted in Fig. 1(b), in units of $\mu^2 W/V^2$ (per site). Note that χ_{01} is closely proportional to ξ throughout most of the valence fluctuation regime. This is intuitively reasonable, because ξ (= fractional f^1 character) can equally well be described as the "fractional magnetic character" of the rare earth ions. In fact, for $D \gg 2|V|$ it can be shown analytically that

$$\chi_{01} \approx \frac{2\xi^2}{W} \left[1 + \xi \frac{W}{V^2} \right] . \tag{10}$$

On the other hand, χ_{01} should increase rapidly as ε_f falls below the bottom of the conduction band, since the system then approaches that of a collection of free f^1 ions. Even then, however, χ_{01} must remain

finite, because there must still be some weak coupling to the conduction band; perturbation theory shows that asymptotically $\chi_{01} \sim |D_-|^3$.

A difficulty is encountered when we attempt to apply this approach to the $\{f^1, f^2\}$ model, because there is no corresponding minor generalization of Ψ_{12} to describe the response to a magnetic field. A more drastic alteration is required, and the reliability of the results may well be sensitive to the choice adopted. We use the form

$$\Psi_{12} = \prod_j \left(\eta^\dagger_{j\uparrow}\eta^\dagger_{j\downarrow} + \sum_k \left(a_{kj\uparrow}\eta^\dagger_{k\downarrow}\eta^\dagger_{j\downarrow} + a_{kj\downarrow}\eta^\dagger_{j\uparrow}\eta^\dagger_{k\downarrow} \right) + d\eta^\dagger_{j\uparrow} \right) \times \prod_{k'} (1 + B_{k'}\eta^\dagger_{k'\uparrow}) |\text{vacuum}\rangle , \tag{11}$$

which is suggested by the approximate theory of quasiparticle excitations described in [1].

The d here is fixed by electron conservation, leaving $A_{k\uparrow}$, $A_{k\downarrow}$, and B_k as the free parameters. Optimizing the $A_{k\alpha}$'s as before, we now find that $\delta \langle H \rangle / \delta(B_k^2)$ cannot vanish for small applied magnetic fields. This implies an insulating gap, as well as the vanishing of χ_{12} at $T = 0$. The resulting gap is the minimum value possible for $|V_k/A_{k\uparrow}|$, which occurs here for k's at the bottom of the conduction band. This gap, Δ, is shown in Fig. 1(a). The gap approaches $|D_-|$ for ϵ_f far below the conduction band, as one would expect. For $D_- \sim |V|$, however, $\Delta \sim (1 - \frac{1}{2})$, and it therefore vanishes very rapidly for $D_- > \frac{1}{2} W$. This, too, meets physical expectations.

4. Discussion

The present $\{f^1, f^2\}$ model is more relevant for SmS and SmB_6 than one might initially surmise, thanks to the fact that the lowest branch of the 5d band manifold is nondegenerate for both of these cubic materials. On

the other hand, of course, V_k cannot be constant throughout the Brillouin zone; in fact, there must be symmetry points where V_k vanishes. It is therefore quite possible for SmS and SmB_6 to have qualitatively different electronic properties, since these materials have NaCl and CsCl-like crystal structures, respectively. In view of the effect of these crystal symmetries upon V_k[5], we conclude that the above insulating gap Δ should be present in SmB_6, but not in SmS. Recent specific heat data [6] for SmB_6 now provides strong evidence for an insulating gap of order 70K (our estimate). This does not imply a vanishing χ at $T = 0$, however, because the $Sm^{2+}(4f^6, J = 0)$ ion has a large Van Vleck susceptibility; the available data show impurity tails which seem to be obscuring a moderate dip below 40K. The strong low-temperature increase in resistivity is certainly consistent with an insulating gap, but this should also be assisted by the very small group velocities of carriers near the gap [1]. It is therefore not surprising that SmS (which has a very high low-temperature electronic specific heat) has a qualitatively similar (although quantitatively much weaker) low-temperature increase in resistivity.

References

[1] B. H. Brandow, Int. J. Quantum Chem., Symposium Vol. 13 (1979) 423.

[2] B. H. Brandow, in "Crystalline Electric Field Effects in f-Electron Systems," J. E. Crow, R. P. Guertin, and T. Mihailisin, eds. (Plenum, N.Y., 1980).

[3] See, for example, C. M. Varma and Y. Yafet, Phys. Rev. B13 (1976) 2950; J. H. Jefferson and K. W. H. Stevens, J. Phys. C. 11 (1978) 3919.

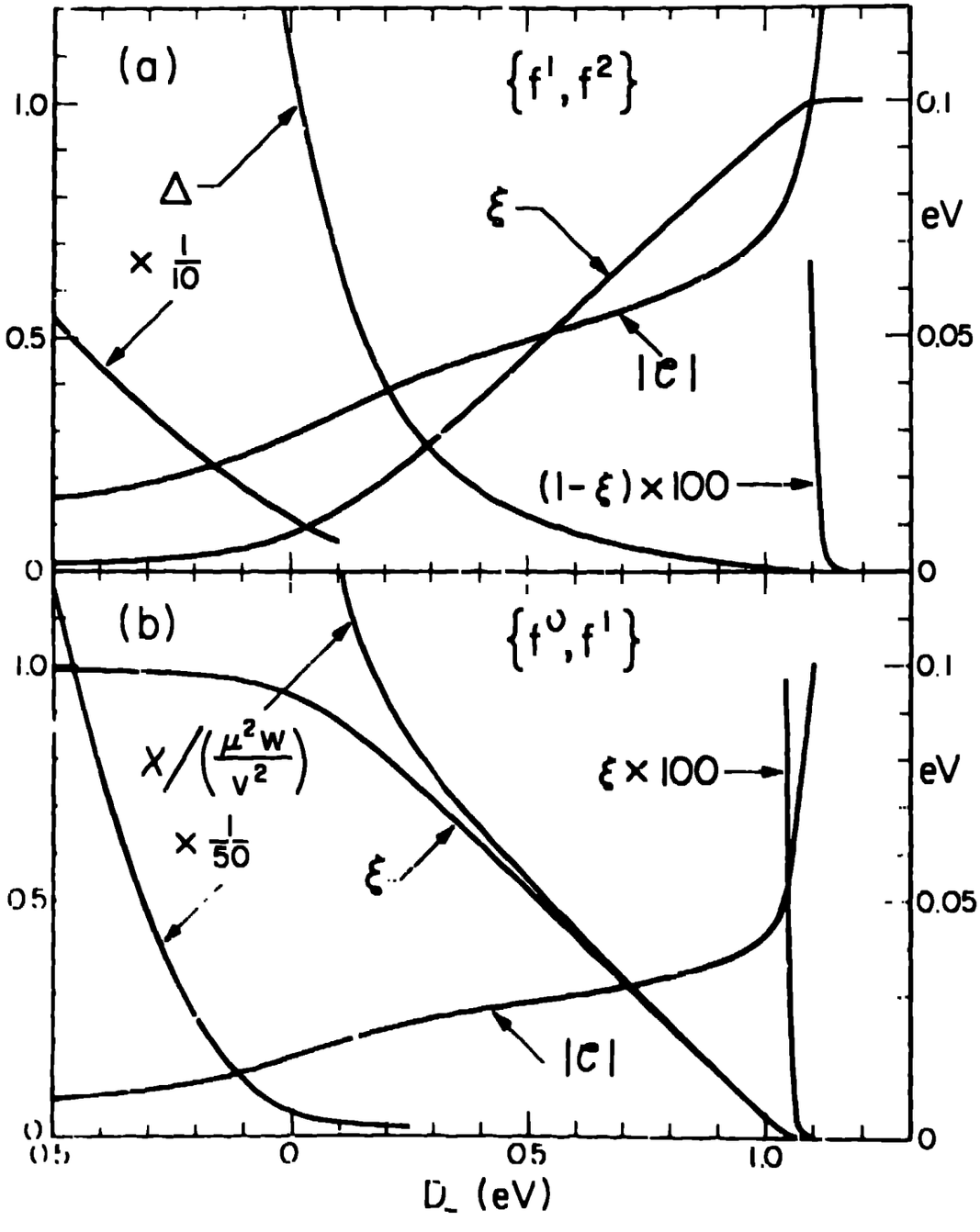
[4] K W. H. Stevens, J. Phys. C11 (1978) 985.

[5] R. M. Martin and J. W. Allen, J. Appl. Phys. (in press).

[6] T. Kasuya, K. Takegahara, T. Fujita, T. Tanaka, and E. Bannai, J. de Physique 40 (1979) C5-308.

Figure Caption

Fig. 1. (a) $\{f^1, f^2\}$ model: ξ on left-hand scale, $|\mathcal{C}|$ and Δ on right-hand scale; (b) $\{f^0, f^1\}$ model: ξ and $\chi/(\mu^2 W/V^2)$ on left-hand scale, $|\mathcal{C}|$ on right-hand scale.


(a)
$\{f^1, f^2\}$
1.0
0.5
0
0.1
0.05
eV
Δ
× 1/10
ξ
|c|
(1-ξ)×100
(b)
$\{f^0, f^1\}$
$X/\left(\frac{\mu^2 W}{v^2}\right)$
× 1/50
ξ
ξ × 100
|c|
-0.5
0
0.5
1.0
D_ (eV)