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

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ABSTRACT SHEET

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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.

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INTRODUCTION

One of the main obstacles for the understanding of valence-fluctuation materials has been the absence of a clear model to illustrate the essential nature of the valence-fluctuation ground state. Our goal here is to present such a model, or rather, two closely related models, and to demonstrate that they have a number of intuitively reasonable features.

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

$$H = \sum_{k\sigma} \varepsilon_k \eta^\dagger_{k\sigma}\eta_{k\sigma} + \varepsilon_f \sum_{j\sigma} \eta^\dagger_{j\sigma}\eta_{j\sigma} + \sum_{kj\sigma} (v_{kj}\eta^\dagger_{k\sigma}\eta_{j\sigma} + \text{h.c.}) + H_U, \qquad (1)$$

in common with many previous investigators.* The 5d conduction electrons are represented here by "5s" Bloch orbitals, with a total bandwidth W. The 4f electrons are represented by "4s" Wannier orbitals, where j is a site index. Thus, orbital degen-

*The Kondo analogy suggests that one might replace the Anderson lattice Hamiltonian by a Kondo lattice Hamiltonian. We reject this suggestion, because the valence-fluctuation regime lies outside the region of validity for the Schrieffer-Wolff transformation. We note also that phonon effects can be transformed away, as far as the electronic properties are concerned, at the cost of introducing renormalized (and somewhat temperature-dependent) electronic parameters[2].

eracy and any intrinsic 4f bandwidth are being neglected. The f-electron level ε_f is set equal to zero, to define the origin for the energy scale.

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

$$H_U^{01} = U\sum_j \hat{n}_{j\uparrow}\hat{n}_{j\downarrow} \ , \tag{2}$$

where $\hat{n} = \eta^\dagger\eta$. The $\{f^1,f^2\}$ model has two electrons per site, and

$$H_U^{12} = U\sum_j (1 - \hat{n}_{j\uparrow} - \hat{n}_{j\downarrow} + \hat{n}_{j\uparrow}\hat{n}_{j\downarrow}) \ . \tag{3}$$

Although these models appear quite similar, we shall see that their magnetic responses are strikingly different. Reasonable values for the parameters are U = 5-8eV, W = 2eV, and $V_k = N^{-\frac{1}{2}}\sum_j v_{kj} \exp(-ik\cdot R_j) \sim 0.07$eV, where N is the number of sites. In practice we take $U^j \to \infty$, so that the configurations f^2 (for $\{f^0,f^1\}$) or f^0 (for $\{f^1,f^2\}$) can be simply ignored.

VARIATIONAL GROUND STATES

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

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

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 photoelectron 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 previously proposed by Stevens[3], but his use of a Wannier rather than Bloch representation for the conduction electrons led to unfortunate complications. We have found that the expectation value <H> can be obtained quite easily, by means of an elementary physical argument[1]: Given the present H and Ψ, the only possible interaction between the various sites j is via the exclusion principle, namely, the fact that two sites cannot simultaneously make use of the same $k\sigma$ Bloch orbital. That is, if site j has made the (virtual) transition $j\uparrow \to k\uparrow$, then the corresponding transition $j'\uparrow \to k\uparrow$ is momentarily forbidden for all other sites j'. It is therefore rather obvious that the $k\sigma$ occupation number can be evaluated

as a sum of quasi-independent one-site contributions,

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

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

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

where $A_k = N^{-\frac{1}{2}} \Sigma_j a_{kj} \exp(-ik \cdot R_j)$, and the normalization denominator is now

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

Continuing with this quasi-independent-site philosophy, the energy expectation value is found to have the very simple form

$$\begin{aligned} \langle H \rangle &= \sum_{k\sigma} (\varepsilon_k A_k^2 + 2V_k A_k)(1 - n_{k\sigma})/D \\ &= \sum_{k\sigma} (\varepsilon_k A_k^2 + 2V_k A_k)/(D + A_k^2). \end{aligned} \tag{8}$$

Minimization of this $\langle H \rangle$ leads to the condition

$$A_k^2 - A_k D(\varepsilon_k - C)/V_k - D = 0. \tag{9}$$

Inserting the resulting A_k in (6), one finds that the momentum distribution $n_{k\sigma}$ is very similar to a finite-temperature Fermi distribution, and thus differs only slightly from an ordinary Fermi sea. More specifically, $n_{k\sigma} = \frac{1}{2}$ for $\varepsilon_k = C$, $n_{k\sigma} \approx |V_k|^2/D(\varepsilon_k - C)^2$ for large positive ε_k, and $n_{k\sigma} \approx 1 - |V_k|^2/D(\varepsilon_k - C)^2$ for large negative ε_k. The "half-width" (analogous to $k_B T$) is of order $V_k(2/D)^{\frac{1}{2}}$. One easily finds that $D = (1 - \xi)^{-1}$, where ξ is the fractional f^1 character of the system ($0 < \xi < 1$), and is determined by

$$\xi = N^{-1} \sum_{k\sigma} n_{k\sigma} . \tag{10}$$

The "pseudo Fermi level" is shifted downwards from the f-electron level $\varepsilon_f (\equiv 0)$ by the amount

$$C = (D/N) \sum_{k\sigma} V_k A_k/(D + A_k^2). \tag{11}$$

This C arises formally from the $(\partial\langle H\rangle/\partial D)(\partial D/\partial A_k)$ term encountered in the minimization of $\langle H\rangle$.

Assuming a constant density of states ($\simeq W^{-1}$), and a constant V_k ($= V$), the above sums for ξ and C become elementary integrals, giving two coupled equations which determine ξ and C. Numerical results are plotted in Fig. 1(a) as a function of D_-, the distance from the bottom of the band to the f-electron level ε_f. (The parameters used here are $W = 2.0$eV, $V = 0.1$eV, and $U \to \infty$.) As expected, ξ varies linearly with ε_f (i.e., with D_-) when ε_f lies between the bottom and the midpoint of the conduction band, and C remains small (a few times $\Gamma = \pi V^2/W$, the resonance width).

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

For $D_- > \frac{1}{2}W$, however, where there might be a danger of ξ exceeding unity, one finds that $|C|$ increases as $-\ell n(1-\xi)$. This has the effect of keeping the pseudo Fermi level below the middle of the band (i.e., $D_- + C < \frac{1}{2}W$), thereby ensuring that $\xi < 1$. For $D_- > \frac{1}{2}W$ $(1-\xi)$ vanishes very rapidly in an exponential manner. In the opposite regime where $D_- \to -\infty$, perturbation theory shows that ξ must vary as $[-D_-(W-D_-)]^{-1}$.

For the $\{f^0, f^1\}$ model we use as trial wavefunction

$$\Psi_{01} = \prod_j \{\sum_\sigma \alpha_\sigma (\eta^\dagger_{j\sigma} + \sum_k a_{kj\sigma}\eta^\dagger_{k\sigma})\}|\text{vacuum}\rangle \ , \qquad (12)$$

where, in the absence of a magnetic field, $\alpha_\sigma = 1$ and $a_{kj\uparrow} = a_{kj\downarrow}$. The formal development is nearly identical to the preceding case, the main difference being simply to replace ξ everywhere by $1 - \xi$, where ξ still represents the fractional f^1 character. The normalization denominator is also somewhat different,

$$D = \alpha^2_\uparrow + \alpha^2_\downarrow + (D/N)\sum_{k\sigma} A^2_{k\sigma}/(D + A^2_{k\sigma}) = 2/\xi \ . \qquad (13)$$

Results for ξ and C are shown in Fig. 1(b).

To study the reliability of these results, we have used diagrammatic analysis based on a many-body perturbation theory developed for open-shell systems[4]. (This formalism has previously been shown to be well-suited for studies of large-U magnetic ions in solids[5].) We find that: (1) Given the above trial wavefunctions, the $\langle H \rangle$ of (8) is exact to terms of order N^{-1}. (2) The trial Ψ's are inexact, since there are perturbative contributions to many-electron amplitudes (such as for $j\sigma j'\sigma \to k\sigma k'\sigma$) which do not simply factorize into a product of one-electron amplitudes a_{kj}. Physical consequences of this non-factorizability remain to be investigated.

It is now clear that there can be no Kondo-like divergences -- these are eliminated by the destructive interference which results from the exclusion principle, as manifested in (5). On the other hand, studies of a low-density system ($Tm_xY_{1-x}Se$) have revealed a distinctive Kondo feature (resistivity $\sim \log T$ for T below a resistivity minimum) for $x \lesssim 0.25$[6]. Although we would expect automatic cutoffs of divergences for <u>all</u> nonvanishing densities of magnetic ions, it does seem quite reasonable that Kondo phenomenological features should emerge in a continuous manner as the concentration of valence-fluctuating ions is decreased. The nonfactorizable amplitudes just mentioned appear to represent dense-system precursers of such Kondo features.

MAGNETIC SUSCEPTIBILITY AND INSULATING GAP

The response of the $\{f^0,f^1\}$ ground state to a magnetic field may be studied by relaxing the previous symmetry restrictions ($\alpha_\uparrow = \alpha_\downarrow$, $a_{ki\uparrow} = a_{kj\downarrow}$) in the above Ψ_{01}. The magnetic susceptibility is found to be

$$\chi_{01} = (\mu^2/R)[(2R^2/V^2\xi) + (\xi + S)^2], \tag{14}$$

where

$$R = -\frac{2}{N}\sum_{k\sigma}\frac{V_k A_{k\sigma}}{D+A_{k\sigma}^2}\, n_{k\sigma}(1 - n_{k\sigma}), \tag{15}$$

$$S = \frac{1}{N}\sum_{k\sigma} n_{k\sigma}(1 - n_{k\sigma})(1 - 2n_{k\sigma}) . \tag{16}$$

The resulting χ_{01} is presented in Fig. 1(a).

For a qualitative understanding of this result, we note that S can be neglected ($S/\xi < 0.035$ for all ξ), and that $R \approx V^2\xi/W$ when $D_- \gtrsim 2|V|$, whereby

$$\chi_{01} \approx \mu^2\left[\frac{2}{W} + \xi\,\frac{W}{V^2}\right] \tag{17}$$

The calculated χ_{01} is seen to follow this estimate quite closely for $D_- > 2|V|$. On the other hand, one would expect that $\chi_{01} \to \infty$ for ε_f far below the bottom of the conduction band, since the vanishing of the hybridization energy should leave the moments free to align with the external field. The calculated χ_{01} does indeed increase very rapidly for $D_- < 0$, and asymptotically it grows as $|D_-|^3$.

A difficulty is encountered when we attempt to follow the same approach for the $\{f^1,f^2\}$ model, since there is no corresponding minor generalization of Ψ_{12} by means of which this system can respond to an external field. A more drastic alteration is required, and the reliability of the results may be sensitive to the choice adopted. We use the form

$$\Psi_{12} = \prod_j\{\eta_{j\uparrow}^\dagger\eta_{j\downarrow}^\dagger + \sum_k(a_{kj\uparrow}\eta_{k\uparrow}^\dagger\eta_{j\downarrow}^\dagger + a_{kj\downarrow}\eta_{j\uparrow}^\dagger\eta_{k\downarrow}^\dagger) + d\eta_{j\uparrow}^\dagger\}$$

$$\times \prod_k(1 + B_k\eta_{k\uparrow}^\dagger)|\text{vacuum}\rangle , \tag{18}$$

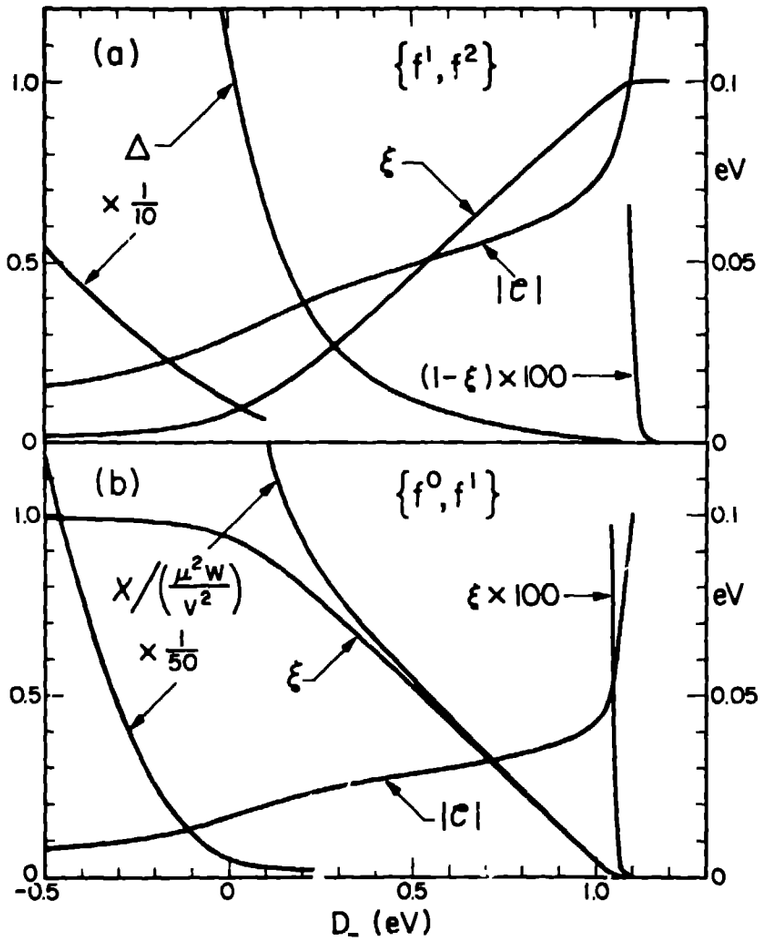
which is suggested by the approximate theory of quasi-particle excitations presented in Ref. 1. The d here is fixed by electron conservation, leaving $A_{k\uparrow}$, $A_{k\downarrow}$, and B_k as the free parameters. Optimizing the $A_{k\sigma}$'s as before, we find that $\delta\langle H\rangle/\delta(B_k^2)$ 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 $|V_k^2/A_{k\uparrow}|$, which occurs for k's at the bottom of the conduction band. This gap, Δ, is shown in Fig. 1(b). The gap approaches $|D_-|$ for ε_f far below the bottom of the band ($D << -|V|$), as expected. For $D_- >> |V|$, the gap becomes $V^2(1 - \xi)/(D + C)$, and it therefore vanishes rapidly for $D_- > \frac{1}{2}W$.

The $\{f^1,f^2\}$ model should be relevant for SmB_6 and SmS. Although the present finding of an insulating gap contradicts our previous study[1], recent specific heat data[7] for SmB_6 now provides strong evidence for an insulating gap of order 70°K[6] (our estimate). This does not imply a vanishing of the χ's at T = 0, however, because the $S_m^{++}(4f^6,J = 0)$[8] ion has a large Van Vleck susceptibility. The available data[8] shows evidence of impurity tails which may well be obscuring moderate dips in the χ's below 40°K. To establish contact with the large number of intermetallic valence-fluctuation compounds, this study must be extended to lower densities, i.e., to systems having "intrinsic" conduction electrons.

REFERENCES

1. B. H. Brandow, Ground State and Elementary Excitations of a Model Valence-Fluctuation System, Int. J. Quantum Chem., Symposium Vol. 13 (1979)(in press).
2. M. Avignon, F. Brouers, and K. H. Bennemann, Effects of Phonons in Mixed Valence Systems, J. de Physique 40:C5-377 (1979).
3. K. W. H. Stevens, Non-Orthogonal Orbitals in Intermediate Valency, J. Phys. C11:985 (1978).
4. B. H. Brandow, Linked-Cluster Expansions for the Nuclear Many-Body Problem, Rev. Mod. Phys. 39:771 (1967).
5. B. H. Brandow, Electronic Structure of Mott Insulators, Adv. Phys. 26:651 (1977).
6. F. Holtzberg, T. Penny, and R. Tournier, Valence Instabilities of Tm in its Compounds and Solid Solutions, J. de Physique 40:C5-314 (1979); A. Berger, P. Haen, F. Holtzberg, F. Lapierre, J. M. Mignot, T. Penny, O. Peña, and R. Tournier, One Impurity Effect of Tm in YSe -- Kondo Effect and Van Vleck Behavior, J. de Physique 40:C5-364 (1979).
7. T. Kasuya, K. Takegahara, T. Fujita, T. Tanaka, and E. Bannai, Valence Fluctuating State in SmB_6, J. de Physique 40:C5-308 (1979).
8. J C. Nickerson, R. M. White, K. N. Lee, R. Bachmann, T. H. Geballe, and G. W. Hull, Jr., Physical Properties of SmB_6, Phys. Rev. B3:2030 (1971); T. Kasuya, K. Kojima, and M. Kasaya, Theory and Experiment on SmB_6, in "Valence Instabilities and Related Narrow-Band Phenomena", R. D. Parks, ed., Plenum Press, New York (1977); M. B. Maple and D. Wohlleben, Nonmagnetic 4f Shell in the High-Pressure Phase of SmS, Phys. Rev. Lett. 27:511 (1971).


(a)
{f¹, f²}
Δ
× 1/10
ξ
|c|
(1-ξ)×100
eV
(b)
{f⁰, f¹}
X/(μ²W/v²)
× 1/50
ξ
ξ×100
|c|
eV
1.0
0.5
0
0.1
0.05
-0.5
0.5
1.0
D_ (eV)