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VARIATIONAL GROUND STATES, MAGNETIC RESPONSES, AND DILUTION BEHAVIOR OF MODEL VALENCE-FLUCTUATION SYSTEMS*

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Variational ground-state wavefunctions are presented and optimized for two model valence-fluctuation systems. One system exhibits an intuitively reasonable ground-state magnetic susceptibility, while the other is found to have an insulating gap. In view of their different crystal structures, this gap should be realized in SmB$_6$ but not in SmS, in agreement with experiment. One of these model systems is analyzed[6] for diluted cases, where only a fraction of the sites contain valence-fluctuation cations, and connections are made with several Kondo theoretic results.

1. INTRODUCTION

A major obstacle for the understanding of valence-fluctuation (VF) materials has been the absence of a suitable model to illustrate the essential nature of the VF ground state. We have developed two closely related models which should serve to fill this role.[1,2] The basic program is to construct variational ground states, and to study how they respond to applied magnetic fields. Our choices of model Hamiltonians and trial wavefunctions are fairly straightforward; the main new ingredient here is a simple and accurate many-body technique to calculate the required expectation values.[1] We are thus able to demonstrate that these assumptions do in fact lead to intuitively reasonable results, consistent with the zero-temperature properties of many VF materials.[2] In addition, we have now extended one of these models to diluted systems, where only a fraction of the sites are occupied by VF cations. This establishes several connections with the theory of Kondo systems, as discussed below.

Our models are based on the Anderson lattice Hamiltonian,

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

which has been used previously by a number of investigators[3]. Here the conduction Bloch orbitals have energies ε_k and total bandwidth W, while the localized Wannier orbitals have 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 $\{f^1,f^2\}$ model has two electrons per site, and its Coulomb interaction term is

$$H_U^{12} = U\sum_j (1 - \hat{n}_{j\uparrow})(1 - \hat{n}_{j\downarrow}) \quad , \qquad (3)$$

where $\hat{n} = \eta^\dagger\eta$. The $\{f^0,f^1\}$ model has one electron per site, and $H_U^{01} = U\Sigma_j \hat{n}_{j\uparrow}\hat{n}_{j\downarrow}$. 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 choose $\varepsilon_f = 0$, 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

$$\Psi_{12} = \prod_j \left\{ \eta^\dagger_{j\uparrow}\eta^\dagger_{j\downarrow} + \sum_k a_{kj} (\eta^\dagger_{k\uparrow}\eta^\dagger_{j\downarrow} + \eta^\dagger_{j\uparrow}\eta^\dagger_{k\downarrow}) \right\} \times \mid \text{vacuum} >. \qquad (3)$$

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, consistent with the observed low-temperature quenching of the local moments. This occurs here because the f^1 and f^2 terms at each site can hybridize only if they have the same spin symmetry, and f^2 (actually s^2) is necessarily a singlet. This wavefunction is formally equivalent to one considered previously by Stevens.[4]

Given the present Ψ and H, we find that the <u>only</u> possibility for 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 blocked (momentarily forbidden) for all of the other sites $j' \neq j$. It follows that the $k\sigma$ orbital occupation number can be evaluated as a sum of quasi-independent one-site contributions,

$$n_{k\sigma} = \sum_j (|a_{kj}|^2/\mathcal{D}) [1 - n_{k\sigma}(N - 1)/N], \qquad (4)$$

where $[1 - n_{k\sigma}(N - 1)/N]$ represents the probability that $k\sigma$ is not already occupied by an electron from some other site $j' \neq j$, and $\mathcal{D}$ is a single-site normalization denominator. (N = number of lattice sites.) For large N this simplifies

to

$$n_{k\sigma} = (A_k^2/\mathcal{D})\,(1 - n_{k\sigma}) = A_k^2/(\mathcal{D} + A_k^2), \qquad (5)$$

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

$$\mathcal{D} = 1 + \sum_{k\sigma} |a_{kj}|^2 (1 - n_{k\sigma}) =$$

$$= 1 + N^{-1} \sum_{k\sigma} A_k^2 \mathcal{D}/(\mathcal{D} + A_k^2) \quad , \qquad (6)$$

and the energy expectation value is found to have the simple form

$$< H > \; = \sum_{k\sigma} (\varepsilon_k A_k^2 + 2V_k A_k)/(\mathcal{D} + A_k^2). \qquad (7)$$

Although first obtained by the above intuitive argument[1], this result has been confirmed by diagrammatic analysis based on a form of many-body perturbation theory for magnetic ions in solids[5]. This analysis shows that the errors in (7) are only of order N^{-1}, as suggested already by (4).

Minimization of $< H >$ leads to the quadratic expression

$$A_k^2/\mathcal{D} = 1 + (\varepsilon_k - \tilde{\varepsilon})\, A_k/V_k. \qquad (8)$$

Inserting the resulting A_k's in (5), the conduction band occupation numbers are found to resemble a finite-temperature Fermi distribution,[1,4] with half-width "k_BT" of order V, where V is a mean value for the hybridization elements V_k. The midpoint "ε_F" for this distribution is found to fall below the f-electron level ε_f by the amount $|\tilde{\varepsilon}|$, which varies as $-\ln(1 - \xi)$, where ξ is the fractional f^1 character of the system. Throughout the valence-fluctuation regime this shift is quite small, of the order of the resonance width Γ. This shift becomes large, however, when ε_f lies above the middle of the conduction band, thereby keeping "ε_F" below the middle of the conduction band regardless of the position of ε_f. This feature ensures that $0 < \xi < 1$, which is an obvious physical requirement.

Numerical results are shown in Fig. 1(a), based on the parameters W = 2 eV, $V_k = V = -0.1$ eV, and $U = \infty$, together with a constant density of states for the conduction band. The parameter D_- represents the energy difference between ε_f and the bottom of the conduction band, and $|\tilde{\varepsilon}|$ is the above-mentioned shift, "ε_f-ε_F." Although the calculated parameters are all smooth functions of D_-, their qualitative behaviors differ in the following three regimes: (1) perturbative or weak-coupling regime--ε_f below bottom of conduction band, (2) valence-fluctuation regime--ε_f between bottom and middle of band; (3) Kondo regime--ε_f above middle of band. In the VF regime ($0 < D_- < 1$eV) ξ varies linearly with D_-, as one would expect. In the Kondo regime ($D_- > 1$eV) the quantity $(1-\xi)$ falls exponentially at a very rapid rate, the e-folding distance being of order

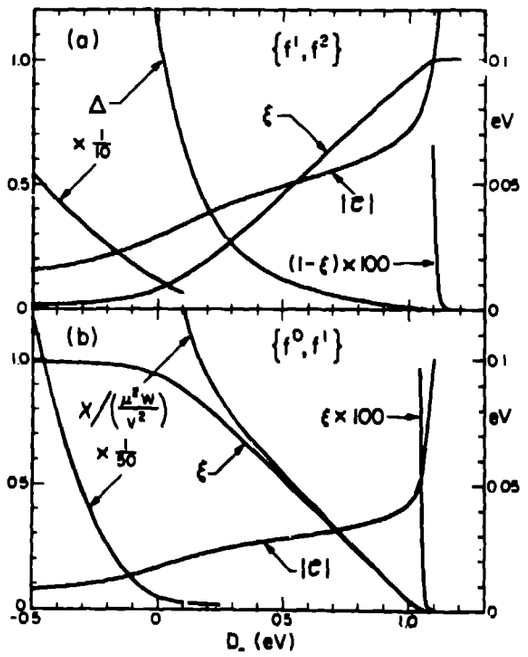

Figure 1: (a) $\{f^1,f^2\}$ model: ξ on left-hand scale, $|\tilde{\varepsilon}|$ and Δ on right-hand scale; (b) $\{f^0,f^1\}$ model: ξ and $\chi/(\mu^2W/V^2)$ on left-hand scale, $|\tilde{\varepsilon}|$ on right-hand scale.

$\Gamma = \pi V^2/W \sim 10^{-2}$ eV. In contrast, when ε_f is below the conduction band ($D_- < 0$) ξ falls off rather slowly; perturbation theory applies here and shows that $\xi \approx 2V^2/[|D_-|\,(W + |D_-|)]$.

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

$$\Psi_{01} = \prod_j \Big\{ \alpha_\uparrow (\eta_{j\uparrow}^\dagger + \sum_k a_{kj\uparrow} \eta_{k\uparrow}^\dagger) + e^{i\phi_j} \alpha_\downarrow (\eta_{j\downarrow}^\dagger + \sum_k a_{kj\downarrow} \eta_{k\downarrow}^\dagger) \Big\} | \text{ vacuum} >, \qquad (9)$$

where, in the absence of a magnetic field, $\alpha_\downarrow = 1$ and $a_{kj\uparrow} = a_{kj\downarrow}$. The phases ϕ_j are largely arbitrary, but must be distributed so as to satisfy $\Sigma_j \exp(i\phi_j) = 0$; otherwise there will be a net transverse spin, $S_\perp = (S_x^2 + S_y^2)^{\frac{1}{2}} \neq 0$. We find that $\partial < H > /\partial(S_\perp^2) > 0$ for all $S_\perp^2 \geq 0$, consistent with the expected singlet character of the ground state. This feature now originates entirely from the singlet character of the non-interacting Fermi sea. Still using ξ to denote the f^1 fraction, the main difference in the ground state results (for $S_\perp = 0$) is simply that the roles of ξ and $(1 - \xi)$ are interchanged. This is illustrated in Fig. 1(b), based on the same parameter values.

3. MAGNETIC RESPONSES

Applying a magnetic field to the $\{f^0,f^1\}$ model, we find a well-behaved susceptibility χ_{01}.

This is plotted in Fig. 1(b) in units of μ^2W/V^2 (per site). Note that χ_{01} is closely proportional to ξ throughout most of the valence-fluctuation regime; for $D_- \gtrsim 2|V|$ we find analytically that $\chi_{01} \approx \mu^2[(2/W) + \xi(W/V^2)]$. This is reasonable because ξ represents the "fractional magnetic character" of the f-electron configurations. 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 the f's are still weakly coupled to the conduction band; we find 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. We use the form

$$\Psi_{12} = \prod_j \left\{ \eta^\dagger_{j\uparrow}\eta^\dagger_{j\downarrow} + \sum_k \left(a_{kj\uparrow}\eta^\dagger_{k\uparrow}\eta^\dagger_{j\downarrow} + a_{kj\downarrow}\eta^\dagger_{j\uparrow}\eta^\dagger_{k\downarrow}\right) + b\eta^\dagger_{j\uparrow} e^{-ik''\cdot R_j} \right\} X(\cos\theta_{k'} + \eta^\dagger_{k'\uparrow}\sin\theta_{k'})|\text{vacuum}\rangle, \tag{10}$$

which is suggested by a simple theory[1] of the quasiparticle excitations; k' and k" represent quasiparticle and quasihole momenta. The b here is fixed by electron conservation, leaving $A_{k\uparrow}$, $A_{k\downarrow}$, and $\theta_{k'}$ as the nontrivial parameters. Optimizing the $A_{k\sigma}$'s as before, we now find that $\delta\langle H\rangle/\delta(\sin^2\theta_{k'})$ 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 attained by $|V_{k'}/A_{k'\uparrow}|$, which occurs here for k' at the bottom of the conduction band. This insulating gap, Δ, is shown in Fig. 1(a). This gap approaches $|D_-|$ for ε_f below the conduction band ($D_- \lesssim -2|V|$), as one would expect. For $D_- \gtrsim 2|V|$, however, $\Delta \approx (1-\xi)V^2/D_-$, and it therefore vanishes very rapidly for $D_- \gtrsim \frac{1}{4}W$. This, too, meets physical expectations. These reasonable limiting behaviors suggest that the choice (10) for Ψ_{12} is adequate here.

4. RELEVANCE FOR SmS AND SmB_6

The present $\{f^1,f^2\}$ model should be relevant for SmS and SmB_6, because (a) the f^2 (actually s^2) configuration mimics nonmagnetic Sm^{2+} ($4f^6$, J=0), and (b) 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, and there must also be some symmetry points where V_k vanishes.

Noting that SmS and SmB_6 have NaCl and CsCl-like crystal structures, respectively, it has been shown[6] that V_k must vanish at the bottom of the 5d band (X point) in SmS, in contrast to the case for SmB_6. We therefore conclude that SmS (at high pressure) and SmB_6 should have metallic and insulating ground states, respectively, in agreement with the quasiparticle theory of Ref. 6. (The insulation of SmS at atmospheric pressure is also consistent with our model, assuming negative D_- for this case.) Recent data on specific heat[7], electrical conductivity,[8] and Hall effect[8] now provide strong evidence for an insulating gap of around 70K in SmB_6. This does not imply a vanishing χ at T = 0, however, because the Sm^{2+} ion has a large Van Vleck susceptibility; the available data[9] show impurity tails which seem to be obscuring a moderate dip below 40K. On the other hand, the strong low-temperature increase in resistivity may be partially due to very small group velocities for the carriers near the Fermi level[1]. It is therefore not surprising that high-pressure SmS (which has a very large low-T electronic specific heat[10]) has a qualitatively similar but quantitatively much weaker low-T increase in resistivity.

5. DILUTED SYSTEMS

The $\{f^1,f^2\}$ model has now been extended to diluted systems, in the following manner. Of the N cation sites, let N_{VF} be "magnetic" as in (1), the remaining $(N-N_{VF})$ sites being inert. Having in mind compounds as $Sm_xY_{1-x}S$ and $Tm_xY_{1-x}S$, we assume that each inert site contributes one electron to the conduction band, so that when $N_{VF} \to 0$ we obtain a precisely half-filled nondegenerate band. In the course of analyzing (10) above, we found the "added" electron (k'↑) did not hybridize at all with the f's - it remained effectively inert and preferred to fully occupy the lowest Bloch orbital. This implies that the conduction electrons from the inert sites will simply delete the lowest $\frac{1}{2}(N-N_{VF})$ k-states from the "active space" for VF correlations. Except for this truncation of the various k-summations, and some factors of N_{VF}/N, the preceeding formalism remains intact. This clean division of the conduction band into inert and active Bloch states is, of course, an artifact due to the simplicity of our trial wavefunction. In improved treatments, the f^1 configurations should produce particle-hole excitations from all of the occupied band states, as in the ground state of the Kondo model.[11]

The Kondo regime is now particularly interesting. In the low-density limit ($N_{VF}/N \to 0$) we find for the interaction energy (energy due to V≠0)

$$\langle H\rangle_I/N_{VF} = -\tfrac{1}{4}W\exp(-1/\rho J), \tag{11}$$

where $\rho = W^{-1}$ and $J = 2V^2/|\mathcal{E}|$. This is just the expected answer, for the following reasons. In this limit the "blocking coefficient" $(1-n_{k\sigma})$ is essentially unity (no blocking) for all of the active states, hence Ψ reduces (for $N_{VF} = 1$) to the simplest trial function of Yosida.[11] His corresponding result, however, has the J of (11) replaced by $\frac{1}{2}J$. This discrepancy is accounted for by noting that the Schrieffer-Wolff transformation also leads, in the present case, to a spin-independent effective interaction term $K = \frac{1}{4}J$, whereby the total effective interaction becomes $\frac{1}{2}J + K = J$.

The previous insulating gap survives even in the low-density limit ($N_{VF} = 1$), where it becomes equal and opposite to (11). This gap must now be an unphysical artifact of our Ψ, however, since exact susceptibility and specific heat results[12,13] demonstrate that the Kondo system has no such gap. Evidently, the gap must disappear somewhere between the VF regime of the concentrated ($N_{VF} = N$) system and the Kondo regime for dilute systems. It is significant that studies of the (concentrated) Kondo lattice model[14] have found a gap appearing for sufficiently large J/W; indeed, the onset value corresponds to the boundary region between the present VF and Kondo regimes. For the present type of diluted systems, on the other hand, intuition suggests that there should never be an insulating gap.

A surprising outcome of this study is that the interaction energy result (11) is essentially independent of the concentration N_{VF}/N, within the Kondo regime. This agrees with a recent analytic solution of a one-dimensional metal with an arbitrary density of Kondo sites.[13] It should be noted, however, that our Ψ is too simple to produce the expected intersite RKKY coupling.

In the VF regime, we find that $\langle H \rangle_I / N_{VF}$ varies only logarithmically with the quantity $(N_{VF}/N)(1-\xi)$. For fixed ξ, therefore, an N_{VF}/N as low as 1% (a typical experimental lower limit) should not strongly alter the characteristic energy, nor (presumably) the characteristic temperature. This is consistent with the insensitivity to density that has been observed in a number of diluted systems.[15] On the other hand, the energy width of the VF regime is only of order $\frac{1}{4}W(N_{VF}/N)$, hence for small N_{VF}/N it is *a priori* unlikely for ε_f to fall within this regime unless some additional mechanism conspires to keep it there. We conclude that the remarkable insensitivity of the average valence to dilution, observed in several systems,[15] must be due to the local lattice stiffness, acting via the strong coupling between average valence and the effective ionic radius.

6. CONCLUSIONS

Several features of these results should be noted: (1) Although our models display some deviations from known or expected VF physics (absence of a Fermi surface, absence of RKKY coupling and/or a metal-insulator transition for the concentrated $\{f^1, f^2\}$ system in the Kondo regime), these defects are probably due to the simplicity of our trial Ψ's. The overall results provide strong support for the view[3] that the Anderson lattice Hamiltonian contains the essence of the VF phenomena. (2) Within the VF regime we find a strong interaction among the VF sites, due to the exclusion principle. This is a *destructive interference*, which explains why the temperature dependence of properties such as the susceptibility is smooth and noncooperative, with no sign of a phase transition. Moreover, this interference remains strong even in fairly dilute systems. These observations serve to resolve the paradox that the VF sites *appear* to be noninteracting even in concentrated systems. (3) This interaction is intrinsically a finite-density (finite N_{VF}/N) effect, thus it may well escape notice in studies of systems with only two VF sites.

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