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The magnetic phase diagram of the p–d model

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Abstract. In this paper we attempt to calculate the magnetic phase diagram for the p–d model using the Gutzwiller approximation (GA). This is equivalent to the mean-field approximation in the Kotliar–Ruckenstein slave-boson formulation. We find that we do not obtain the expected behaviour in the region where the number of carriers, n, is < 1 and the ratio of the hybridization, V, to the p–d energy difference, ϵ, goes to zero. In this limit the p–d model maps onto the Hubbard model and we would expect to find the same results as when we perform the GA on this Hamiltonian. This is not the case and we discuss the reason for this. The region $n > 1$ is also investigated and similar problems arise. Ways of improving the solution are proposed for a modified Hamiltonian.

1. Introduction

The Cu–O planes in the high-temperature superconductors are thought to be described by a model close to the periodic Anderson model [1–6]. In the appropriate parameter regime this model is referred to either as the 'p–d model', which is how we shall refer to it here, or as the 'extended Hubbard model'. For a certain region of parameters this maps onto the Hubbard model [7, 8]. Much interest has, therefore, been generated in the phase diagrams of both the Hubbard and p–d models.

The Hubbard model can be reformulated using the slave-boson (SB) approach introduced by Kotliar and Ruckenstein (KR) [9, 10] which in the mean-field (MF) limit is equivalent to the Gutzwiller approximation (GA) [11]. This gives us a means of calculating an approximate magnetic phase diagram. A small ferromagnetic region is found for n, the number of carriers, close to one and U/t, the ratio of the on-site Coulomb repulsion to the band width, large. This region is in reasonable agreement with the essentially exact results of Von der Linden and Edwards [12] for a 2D square lattice. The paramagnetic–antiferromagnetic boundary can also be calculated [9, 10]. The method, however, only includes magnetic interactions arising from spin-dependent band renormalization and does not include the intersite antiferromagnetic exchange terms. These need to be included to give a full description. An insulating phase is found for $n = 1$ and U/t greater than some critical value.

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In this paper we are interested in applying the KR formulation to the p–d model. The Coulomb repulsion, U, on the d sites is large and it is convenient to consider the strong-coupling limit with $U \rightarrow \infty$. This limit has previously been considered by several groups using a different variety of SBs [3–6] originally introduced by Coleman and used extensively in the theory of heavy-fermion systems [13]. In both SB theories the auxiliary bosons prevent double occupancy and the MF solutions describe a band-narrowing effect due to the strong interaction. The KR method has the advantage of incorporating magnetic interactions at the MF level and we use this method to calculate the magnetic phase diagram. Again the antiferromagnetic superexchange terms are not included at this level. For the p–d model there is an insulating phase for $n = 1$ and V/ε below a critical value. This is analogous to the insulating transition found in the Hubbard model,

We start by considering the region where the number of holes, n, is less than one, which corresponds to the electron-doped systems. It is known that for $V/\varepsilon \rightarrow 0$ the model maps onto the Hubbard model [7]. We therefore expect that the critical value of n below which the ferromagnetism disappears will be the same for the p–d model with $V/\varepsilon \rightarrow 0$ as for the Hubbard model. This is found not to be the case. We see that performing the Gutzwiller approximation for the p–d model, then expanding in V/ε, does not produce the same results as expanding in V/ε, then using the GA. The problem can be seen to arise in the former approach through renormalizing those terms $O(V^2/\varepsilon)$ that shift the on-site energy by the same factor as those that produce the intersite term. It appears that the GA gives spurious results when used for the p–d model and has to be modified.

In section 2.2 we propose a simple modification to the quasiparticle bands which gives the correct limiting behaviour as $V/\varepsilon \rightarrow 0$. We recalculate the magnetic phase diagram and far smaller magnetic regions are found. The superexchange terms are discussed and included in a simple way.

In section 3 we consider what happens for $n > 1$. We note that in this region the original SB solution [3–6] is non-perturbative in V/ε in the sense that taking the limit $V/\varepsilon \rightarrow 0$ does not reproduce the bare p and d energy levels. The physical picture is then necessarily different to the perturbation expansion described by Zhang and Rice [8]. For the SB MF solution we have $n_d < 1$, where n_d is the average d valence, and the only dispersion is via unoccupied d sites. The band-narrowing factor is given by $1 - n_d$ and tends to 0 for $V/\varepsilon \rightarrow 0$. In the Zhang–Rice picture, on the other hand, $n_d = 1$ but propagation can still take place via the formation and destruction of singlets. Here the band-narrowing factor is given by $n - 1$. It is, therefore, no longer surprising that the GA in the limit $V/\varepsilon \rightarrow 0$ does not reproduce the results of the GA to the Hubbard model.

We would like to find a solution that explicitly reduces to the perturbation limit as in section 2.2. There appears to be no simple modification to the quasiparticle bands that does this. We can, however, proceed by considering a slightly different model where we include both on-site and intersite hybridization terms, V_0 and V_1 respectively. For certain parameters this is equivalent to our original model with the p states expanded in Wannier functions [8]. We then take proper account of the on-site terms and expand in V_1 [14]. The limit $V_1/\varepsilon \rightarrow 0$ gives us an effective Hubbard model for both $n < 1$ and $n > 1$. We now include excitations to the first excited state and calculate the magnetic phase diagram. This is found to be approximately symmetric about $n = 1$.

2. The Gutzwiller approximation for the p–d model with $n < 1$

2.1. First approximation

The p–d model is written as

$$H = \sum_{i\sigma} \varepsilon_{d0} d^{\dagger}_{i\sigma} d_{i\sigma} + \sum_{j\sigma} \varepsilon_p p^{\dagger}_{j\sigma} p_{j\sigma} + \sum_{\{ij\}\sigma} V_{ij}(d^{\dagger}_{i\sigma} p_{j\sigma} + \text{HC}) + U \sum_i n^d_{i\uparrow} n^d_{i\downarrow} \quad (2.1)$$

where $d_{i\sigma}$ and $p_{j\sigma}$ are the annihilation operators for d and p hole states respectively and $n^d_{i\sigma} = d^{\dagger}_{i\sigma} d_{i\sigma}$. $V_{ij} = (-1)^{M_{ij}} V$ with $M_{ij} = 2$ if $j = i - \frac{1}{2}\hat{x}$ or $j = i - \frac{1}{2}\hat{y}$ and $M_{ij} = 1$ otherwise. The lattice structure in the planes is shown in [8]. We have taken the lattice constant to be 1. In the limit $U \to \infty$ we can write an effective Hamiltonian using the MF approximation to the KR SB formulation [9, 10] or, equivalently, the Gutzwiller approximation [15] giving

$$H_{\text{eff}} = \sum_{i\sigma} \varepsilon_{d\sigma} d^{\dagger}_{i\sigma} d_{i\sigma} + \sum_{j\sigma} \varepsilon_p p^{\dagger}_{j\sigma} p_{j\sigma} + \sum_{\{ij\}\sigma} \tilde{V}_{ij\sigma}(d^{\dagger}_{i\sigma} p_{j\sigma} + \text{HC}) - \mu n_d + sm + \text{constant} \quad (2.2)$$

where $\varepsilon_{d\sigma} = \varepsilon_d - \sigma s$ and ε_d is now an effective d level energy, $\varepsilon_d = \varepsilon_{d0} + \mu$. $\tilde{V}_\sigma = q_\sigma V$ where q_σ is the ratio of the hopping probability for $U \to \infty$ to that at $U = 0$ given by $q_\sigma = [(1 - n_d)/(1 - n_{d\sigma})]^{1/2}$ with $n_{d\sigma}$ = average number of d holes with spin σ per site and $n_d = \sum_\sigma n_{d\sigma}$. m is the average magnetization and s acts somewhat like an internal magnetic field. In the SB theory, s and μ are connected with enforcing constraints on the d-site occupations. The constant term contains boson terms. We can calculate the free energy for the ferromagnetic or paramagnetic state,

$$F = -\beta^{-1} \sum_{\alpha=\pm,\sigma} \sum_k \ln[1 + \exp(-\beta E_{\alpha\sigma}(k))] - \mu n_d + sm + \text{constant} \quad (2.3)$$

where

$$E_{\pm\sigma} = 0.5\left[\varepsilon_p + \varepsilon_{d\sigma} \pm \sqrt{(\varepsilon_p - \varepsilon_{d\sigma})^2 + 16\tilde{V}^2(1 - x)}\right] \quad (2.4)$$

with $x = 0.5[\cos(k_x) + \cos(k_y)]$. There are also local levels at $\varepsilon_{d\sigma}$ but we shall ignore these from now on. Four self-consistent equations are then found by minimizing F with respect to n_d, μ, s and m. We see that the factor q_σ describes a band-narrowing effect which is different for different spin directions when there is a finite magnetization. In the Coleman SB approach [3–6, 13] the band narrowing is the same for both spin directions whatever the magnetization and a ferromagnetic state is not naturally described. The parameter s gives the splitting between the down- and up-spin bands in the ferromagnetic case. The susceptibility can be calculated by coupling an external magnetic field to the d sites then calculating dm/dh taking into account the implicit dependence of the MF variables on h. Ferromagnetic instabilities are signalled by the vanishing of the inverse susceptibility. The results are shown in figure 1 where we have used an elliptical density of states, as in [9] and [10]. We find a large ferromagnetic region with the critical value of V/ε only falling to 0

for n close to 0. We know, however, that as $V/\varepsilon \to 0$ the p–d model maps onto the Hubbard model [7]. In the Hubbard model with $U \to \infty$ there exists a critical value of $n \approx 0.7$ below which the model is not ferromagnetic [12]. This behaviour is reproduced by the GA to the Hubbard model giving $n_c \sim 0.6$ [9, 10]. The numerical values cannot, however, be compared directly, firstly because the results in [12] are calculated using tight-binding bands for a 2D square lattice while an elliptical density of states is used in [9] and [10], and secondly because in [12] it is the instability from a saturated magnetic state that is calculated while the GA calculates instabilities to a weak ferromagnetic state. We see that the GA for the p–d model in the limit V/ε goes to zero does not reproduce the results of expanding in V/ε and then using the GA on the resulting Hamiltonian. If we examine our expressions as $V/\varepsilon \to 0$ we see that the discrepancy arises due to the fact that when we expand our Hamiltonian exactly in V/ε then to $O(V^2/\varepsilon)$ there are two terms: the bare d-level energy is shifted by an amount $\sim V^2/\varepsilon$ and there are intersite terms again $\sim V^2/\varepsilon$. When we now perform the GA the intersite terms are renormalized but the on-site terms are not. Applying the GA directly to the p–d model, both these terms are renormalized. Since the renormalization factor depends on σ, the effective on-site energy term acquires a dependence on m and it is this that leads to the discrepancy between the two approaches. Physically it is clear that these on-site terms should not be renormalized.

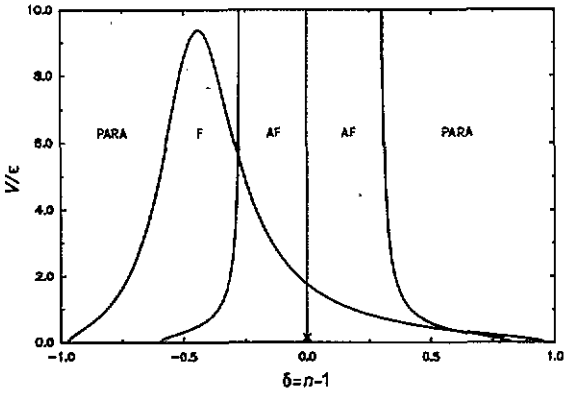

Figure 1. Magnetic phase diagram showing the boundaries of stability of the paramagnetic phase (PARA) for the approximation described in section 2.1 with respect to ferromagnetism (F) and antiferromagnetism (AF).

We can similarly consider the condition for antiferromagnetism by dividing the system into two sublattices, A and B, and applying a staggered magnetic field $+h$ on sites in the sublattice A and $-h$ on sites in the sublattice B. We assume that

$$n^{\mathrm{A}}_{\mathrm{d}\sigma} = n^{\mathrm{B}}_{\mathrm{d}-\sigma} = n_{\mathrm{d}}/2 + \sigma m/2 \qquad \varepsilon^{\mathrm{A}}_{\mathrm{d}\sigma} = \varepsilon^{\mathrm{B}}_{\mathrm{d}-\sigma} = \varepsilon_{\mathrm{d}} - \sigma(h+s) \tag{2.5}$$

The results are shown in figure 1 where we have assumed an alternated structure and have again used an elliptical density of states. There is a large antiferromagnetic region and the antiferromagnetism only goes away as $V/\varepsilon \to 0$ for $n \approx 0.5$. This can be compared to calculations using the Hubbard model where the critical value of n below which there is no antiferromagnetic state for $U \to \infty$ is given by $n \approx 0.9$ [9, 10].

There is a localization transition at $n = 1$ at a critical value of $V/\varepsilon \approx 0.15$ shown by the cross on figure 1. This is analogous to the Brinkman–Rice insulator

transition in the Hubbard model. We note that below the transition not only is there no propagation but virtual fluctuations onto the p sites are also forbidden.

2.2. Modified approximation

The problems arising in the previous subsection come about through the failure to distinguish between virtual fluctuations that shift the on-site energy, and processes that contribute to the kinetic energy. A somewhat analogous situation arises in the Hubbard model where for large U and $n \leqslant 1$ there are two processes involving doubly occupied states: virtual processes that cause Heisenberg spin–spin coupling and the propagation of holes. If we use the Gutzwiller approximation only the second term is included. A better way of proceeding in this case is to use a transformation that produces an effective Hamiltonian in which the two physical processes are separated [16]. This effective Hamiltonian is known as the t–J model. In the present case such a transformation cannot be realised. This is because the on-site energy shift is of the same order of magnitude as the kinetic energy term. We can, however, imagine in some qualitative sense that we can absorb the effect of intrasite terms into a shift in the on-site energy and then calculate the quasiparticle bands taking into account intersite terms only. We propose the following approximate form for the quasiparticle bands:

$$E_{\pm\sigma} = 0.5\left[\tilde{\varepsilon}_{d\sigma} + \varepsilon_p \pm \sqrt{(\varepsilon_p - \tilde{\varepsilon}_{d\sigma})^2 - 16V^2 x q_\sigma}\right] \tag{2.6}$$

where $\tilde{\varepsilon}_{d\sigma}$ is the renormalized value of $\varepsilon_{d\sigma}$. For $V/\varepsilon \to 0$ we have $\tilde{\varepsilon}_{d\sigma} \to \varepsilon_{d\sigma} - 4V^2/\varepsilon$ and (2.6) reduces to the expression expected. We assume that any shift in $\varepsilon_{d\sigma}$ is small and take $\tilde{\varepsilon}_{d\sigma} \approx \varepsilon_{d\sigma}$. We can now recalculate the paramagnetic–ferromagnetic phase boundary. This is shown in figure 2. The ferromagnetic region is seen to be much smaller.

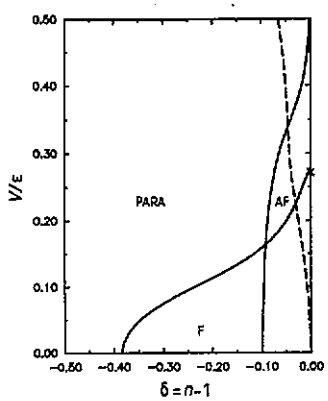

Figure 2. Magnetic phase diagram for the approximation described in section 2.2. The broken line shows the antiferromagnetic boundary when the superexchange terms are included explicitly.

Considering now the antiferromagnetism, we again modify our theory to give the correct behaviour in the limit $V/\varepsilon \to 0$. We obtain an expression for the free energy of the form (2.3) but where the quasiparticle bands, ω, are given by solutions of

$$\left[\omega - \varepsilon_d + \frac{4V^2\tilde{q}x}{\omega - \varepsilon_p}\right]\left[\omega - \varepsilon_d - \frac{4V^2\tilde{q}x}{\omega - \varepsilon_p}\right] - (s+h)^2 = 0 \tag{2.7}$$

We can again minimize with repect to our four MF variables to obtain self-consistent equations. $\bar{q}$ represents the renormalization of the kinetic energy terms and is given by

$$\bar{q} = (q_\uparrow q_\downarrow)^{1/2} = (1 - n_d)/[(1 - n_d/2)^2 - m^2/4]^{1/2} \tag{2.8}$$

This reflects the fact that a hole moving from one sublattice to another then back to the original experiences one 'difficult' hop, where the strong correlation forbids double occupancy, and one 'easy' hop, where the only restriction is from the Pauli principle. s gives the spin-density-wave gap. We note that a similar interpretation is not consistent with the original approximation of section 2.1. We can now calculate the antiferromagnetic–paramagnetic phase boundary shown in figure 2. We have not calculated the ferromagnetic–antiferromagnetic boundary. According to Lavagna [10] this is asymptotic to the line $n = 1$ in the limit $U \to \infty$.

The calculation does not so far include the superexchange terms that arise in the expansion of the p–d model to order V^4/ε^3. We see this by considering $n = 1$ and V/ε small. Here n_d is very close to one and the only movement allowed is the lowering of the zero-point energy by fluctuations onto the p sites. These fluctuations are the same, independently of the spins of nearest-neighbour sites. To $O(V^4/\varepsilon^3)$, however, we expect two neighbouring sites that are antiferromagnetically aligned to lower their zero-point energy by a process in which both holes hop onto the intervening p site and then 'exchange' their positions [7]. This cannot happen for ferromagnetically aligned holes. This process is not included in the SB approximation where all terms involving a hop from one site to another have a band-narrowing factor q. In analogy with the Hubbard model, we can write down a two-band t–J model that explicitly includes the superexchange terms:

$$H \to H + J \sum_{\{ii'\}} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} \tag{2.9}$$

and use this as our starting point. The expansion is only valid for $V/\varepsilon \ll 1$. J is given approximately as $J \sim (2V^4/\varepsilon^3)$. Alternatively we can consider the fluctuations in the boson fields. For the Coleman SBs, magnetic fluctuations arise to second order in the boson propagators. A ladder summation can be performed to give [17]

$$\chi^{AF} = \chi_0^{AF}/(1 - J\chi_0^{AF}) \tag{2.10}$$

where χ_0^{AF} is the antiferromagnetic susceptibility in the absence of interactions. J here describes both superexchange and RKKY interactions the former being dominant close to $n = 1$. This is equivalent to decoupling the spin term in (2.9) in k-space. We take $J \sim (2V^4/\varepsilon^3)n_d^2$, with the factor of n_d^2 reflecting the fact that neighbouring sites must be occupied for the interaction to occur, and use (2.10) to calculate the antiferromagnetic boundary. The results are shown by the broken line in figure 2. We see that superexchange and the GA produce AFM in somewhat different regions of the phase diagram. Superexchange terms would also occur in the expansion of the KR SBs around their MF limit.

A different decoupling has been considered by Grilli *et al* [6] where the spin interaction term is written

$$J \sum_{\{ii'\}} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} \approx J \left\langle \sum_\sigma d_{i\sigma}^\dagger d_{i+1\sigma} \right\rangle \sum_{i\sigma} d_{i\sigma}^\dagger d_{i+1\sigma} \tag{2.11}$$

This introduces an effective d–d hopping term where the magnitude of the hopping has to be determined self-consistently. This decoupling does not by itself give antiferromagnetic long-range order, although if it were included along with the GA the phase diagram of figure 2 would be modified.

We note finally that for $n = 1$, n_d becomes $= 1$ at a critical value of V/ε shown in figure 2 by a cross. The critical value of V/ε is ≈ 0.27 and is close to that found in section 2.1.

3. Extension of results to $n > 1$

The region where $n > 1$ has been more widely studied, as this is the more common case physically. The original approximation set out in section 2.1 is easily generalized and gives the results shown in figure 1. Here the SB MF solution is non-perturbative in V, as in the heavy-fermion case, and taking the limit $V/\varepsilon \to 0$ does not recover the original local p and d levels. This means that we cannot directly compare with a perturbation expansion of the Hamiltonian in V/ε such as that performed by Zhang and Rice [8]. The non-perturbative solution derived by the SB method may lead us to question the validity of such an expansion. There appears, however, to be an intrinsic problem with the SB picture. In the MF approximation, holes can only propagate via unoccupied d sites. For $n > 1$, however, we in fact expect the dominant kinetic energy terms to be of the form $V p^\dagger_{j\sigma} n^d_{i\sigma} p_{j'\sigma}$ and $V p^\dagger_{j\sigma} d^\dagger_{i-\sigma} d_{i\sigma} p_{j'-\sigma}$ in which n^d_i remains equal to one and the p holes move by 'pushing' the d holes along, with or without a spin flip. There does not seem to be an obvious way of taking these processes into account within the SB theory for the present form of the Hamiltonian.

We would like to construct a solution to the p–d model that does in fact reduce to the Hubbard model in the perturbation limit. It is, however, no longer straightforward to write down quasiparticle bands that explicitly have the correct limiting behaviour as we did in section 2.2. We note also that the Zhang–Rice transformation, while being based on a perturbation in V/ε, also relies on the condition that $8V/\varepsilon \gg 1$, and so in fact breaks down as $V/\varepsilon \to 0$ and is not rigorously correct in any limit. The transformation can, however, be thought to be valid for values of V/ε that are small but not too small. It turns out to be more convenient to consider a modified form of the Hamiltonian described in the next section.

4. The Gutzwiller approximation for a modified Hamiltonian

4.1. $n < 1$

In order to investigate these difficulties more fully, we now consider a somewhat different Hamiltonian where we have two hybridization terms: on-site terms with matrix element $2V_0$ and intersite terms with matrix element $-V_1$:

$$H = \sum_{i\sigma} \varepsilon_{d0} d^\dagger_{i\sigma} d_{i\sigma} + \sum_{i\sigma} \varepsilon_p p^\dagger_{i\sigma} p_{i\sigma} + \sum_{i\sigma} 2V_0 (d^\dagger_{i\sigma} p_{i\sigma} + \text{HC}) + U \sum_i n^d_{i\uparrow} n^d_{i\downarrow} - \sum_{\{ij\}\sigma} V_1 (d^\dagger_{i\sigma} p_{j\sigma} + \text{HC}) \tag{4.1}$$

If we take our original p–d model (2.1) and expand the p states in Wannier functions [8] we do indeed get a Hamiltonian of this form, with V_0 and V_1 both approximately equal to V. $p_{i\sigma}$ is approximately the symmetric linear combination of p holes around a d site; $p_{i\sigma} \approx 0.5 \sum_{\{ij\}} (-1)^{M_{ij}} p_{j\sigma}$ and the intersite term represents the fact that neighbouring d sites share a common p site. In what follows we shall, however, consider V_0 and V_1 as independent variables. As we shall see in section 4.2 this has the advantage that for $n > 1$ we can keep V_0 finite and the limit $V_1 \to 0$ then produces an exact mapping of this model onto the Hubbard model.

Using the GA directly involves similar problems to those described in section 2.1. No distinction is made between kinetic energy and fluctuation terms and, for example, if we expand in both V_0 and V_1, terms $O(V_0^2)$ which simply shift the on-site enery are renormalized by the same factor as terms $O(V_0 V_1)$ which take us from one site to another.

We consider instead an alternative approach by performing an expansion in V_1 on the original Hamiltonian [14]. We start by considering the eigen-states and eigen-energies of the atomic Hamiltonian with $V_1 = 0$. The lowest-energy single-hole state with spin σ can be written

$$|iA_\sigma\rangle = a_{i\sigma}^\dagger |i0\rangle = (\sin\theta p_{i\sigma}^\dagger - \cos\theta d_{i\sigma}^\dagger)|i0\rangle \tag{4.2}$$

with corresponding energy $E_A = -0.5\left[\varepsilon + \sqrt{\varepsilon^2 + 16V_0^2}\right]$. $|i0\rangle$ is the state with no hole on site i and $\sin^2\theta = 0.5[1 - \varepsilon/\sqrt{\varepsilon^2 + 16V_0^2}]$.

For $0 \leqslant n \leqslant 1$ the unperturbed ground state consists of a proportion n of sites occupied by one hole in the state $|iA_\sigma\rangle$, the other sites being unoccupied. We can define a subspace Ω generated by the set of all possible configurations.

To first order in V_1 the perturbation moves a state A_σ onto a neighbouring empty site with matrix element $t = \langle i0, jA_\sigma | H | iA_\sigma, j0\rangle = 2V_1 \sin\theta\cos\theta$ where i and j are nearest-neighbour sites. The first-order effective Hamiltonian will then contain a hopping term, but it must also forbid double occupancy in order to stay in the subspace Ω. This is realized by including an infinite on-site repulsion:

$$\tilde{H} = t \sum_{\{i,j\}\sigma} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i n_{i\uparrow}^a n_{i\downarrow}^a \tag{4.3}$$

with $U = \infty$.

We see that we have explicitly derived a Hubbard model in this limit. Using now the GA we find a quasiparticle band with dispersion relation

$$E_\sigma(x) = -0.5\left[\varepsilon + \sqrt{\varepsilon^2 + 16V_0^2}\right] + 4V_1 V_0 q_\sigma x / \sqrt{\varepsilon^2 + 16V_0^2}. \tag{4.4}$$

We now attempt to generalize the approach leading to (4.3) and allow for the fact that the perturbation V_1 also produces transitions between the lowest-energy states (4.2) and higher-lying states.

The lowest-energy two-hole state is a singlet given by

$$|iS_1\rangle = [\sin\phi p_{i\uparrow}^\dagger p_{i\downarrow}^\dagger + 2^{-1/2}\cos\phi(d_{i\downarrow}^\dagger p_{i\uparrow}^\dagger - d_{i\uparrow}^\dagger p_{i\downarrow}^\dagger)]|i0\rangle \tag{4.5}$$

where $\sin^2\phi = 0.5[1 - \varepsilon/\sqrt{\varepsilon^2 + 32V_0^2}]$. This has energy

$$E_S = -0.5\left[\varepsilon + \sqrt{\varepsilon^2 + 32V_0^2}\right] \tag{4.6}$$

The lowest excitation energy is $E_m = E_S - 2E_A$.

We note that the second excited state is a two-particle triplet with energy $-\varepsilon$. There are also other higher-lying one-, two- and three-particle states. To a first approximation we neglect all of these and consider the subspace, Λ, in which a site can be in one of four states: it can be empty, can be occupied by a quasiparticle (with spin up or down) or can be occupied by the singlet S_1. This is reminiscent of some effective Hubbard model with finite on-site energy E_m.

To the first order in V_1 we have to consider the following matrix elements:

$$\langle iS_1, j0|H|iS_1, j0\rangle - \langle iA_\sigma, jA_{-\sigma}|H|iA_\sigma, jA_{-\sigma}\rangle = E_S - 2E_A \tag{4.7}$$

$$\langle iA_\sigma, j0|H|i0, jA_\sigma\rangle = 2V_1 \sin\theta\cos\theta \tag{4.8}$$

$$\langle iS_1, j0|H|iA_{-\sigma}, jA_\sigma\rangle = -(\sigma V_1/\sqrt{2})(\cos\phi + \sqrt{2}\cos\theta\sin\theta\sin\phi) \tag{4.9}$$

$$\langle iS_1, jA_{-\sigma}|H|iA_{-\sigma}, jS_1\rangle = -V_1(\sin\theta\cos\theta\cos^2\phi + \sqrt{2}\sin^2\theta\cos\phi\sin\phi). \tag{4.10}$$

We note that for a simple Hubbard model equations (4.8)–(4.10) would all have the same value.

To write the effective Hamiltonian that reproduces the matrix elements (4.7)–(4.10) we need to consider the isomorphism from the subspace Λ to a modified subspace Λ' defined by the replacement of the doubly occupied state iS_1 by the state $|iS'\rangle = a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger|i0\rangle$. Following Bastide and Lacroix [14] we can now define the appropriate effective Hamiltonian. We choose to represent this Hamiltonian using auxiliary boson fields and introduce boson operators e_i, $c_{i\sigma}$ and s_i representing empty, singly occupied and singlet states respectively. In the restricted subspace we can write a Hamiltonian

$$H_{\text{eff}} = -\sum_{\{ij\}\sigma} V_1(z_{j\sigma}^{\text{p}\dagger} z_{i\sigma}^{\text{d}} a_{i\sigma}^\dagger a_{j\sigma} + \text{HC}) + \sum_i (E_S - 2E_A) s_i^\dagger s_i \tag{4.11}$$

with the constraints

$$e_i^\dagger e_i + \sum_\sigma c_{i\sigma}^\dagger c_{i\sigma} + s_i^\dagger s_i = 1 \tag{4.12}$$

$$a_{i\sigma}^\dagger a_{i\sigma} - c_{i\sigma}^\dagger c_{i\sigma} - s_i^\dagger s_i = 0 \tag{4.13}$$

and where

$$z_{i\sigma}^{\text{d}} = (1 - c_{i\sigma}^\dagger c_{i\sigma} - s_i^\dagger s_i)^{-1/2}(\cos\theta\ c_{i\sigma}^\dagger e_i + 2^{-1/2}\sin\theta\cos\phi\ s_i^\dagger c_{i-\sigma}) \times (1 - e_i^\dagger e_i - c_{i-\sigma}^\dagger c_{i-\sigma})^{-1/2} \tag{4.14}$$

$$z_{j\sigma}^{p} = (1 - c_{j\sigma}^\dagger c_{j\sigma} - s_j^\dagger s_j)^{-1/2}[\sin\theta\ c_{j\sigma}^\dagger e_j + (2^{-1/2}\cos\theta\cos\phi + \sin\theta\sin\phi) s_j^\dagger c_{j-\sigma}](1 - e_j^\dagger e_j - c_{j-\sigma}^\dagger c_{j-\sigma})^{-1/2}. \tag{4.15}$$

We note that this differs from the representation of the pure Hubbard model with finite U in that the factors z contain factors of $\cos\theta$, $\sin\theta$, $\cos\phi$ and $\sin\phi$. These differences arise as follows. The original Hamiltonian has a term

$$-V_1 \sum_{\{ij\}\sigma} (d_{i\sigma}^\dagger p_{i\sigma} + \text{HC}).$$

We can represent the creation of a d hole in our new set of states either by the creation of a quasiparticle and destruction of an empty site or by the creation of a singlet and the destruction of an opposite-spin quasiparticle. Since the d and p weights in a quasiparticle are $\cos\theta$ and $\sin\theta$ respectively, and the weight of the relevant part of the singlet is $\cos\phi/\sqrt{2}$, we need to include a factor $\cos\theta$ with the first process and a factor $\sin\theta\cos\phi/\sqrt{2}$ with the second. We can consider the destruction of a p hole in a similar way. We can check that our effective Hamiltonian is correct by calculating the following matrix elements: $\langle iS', j0|H_{\text{eff}}|iS', j0\rangle - \langle iA_\sigma, jA_{-\sigma}|H_{\text{eff}}|iA_\sigma, jA_{-\sigma}\rangle$, $\langle iA_\sigma, j0|H_{\text{eff}}|i0, jA_\sigma\rangle$, $\langle iS', j0|H_{\text{eff}}|iA_{-\sigma}, jA_\sigma\rangle$ and $\langle iS', jA_{-\sigma}|H_{\text{eff}}|iA_{-\sigma}, jS'\rangle$. It is easily verified that these have the same values as (4.7)–(4.10) respectively.

We can now go ahead and calculate the phase diagram in the MF limit in the standard way. While (4.1) is most closely related to the original p–d model for $2V_0 = -V_1 = V$, inconsistencies arise if V is then taken to be very small. Firstly, as $V \to 0$, the singlet–triplet energy gap goes to zero and we would therefore need also to include triplet states as well as other higher-lying states and secondly we have kept terms $O(V_0V_1)$ whilst neglecting terms $O(V_1^2)$. We therefore keep V_0 finite and let only V_1 vary. The phase diagram is shown in figure 3. We see that the ferromagnetic region is suppressed whilst the antiferromagnetic region is larger with respect to figure 2. This is probably related to the fact that in our subspace, Λ', ferromagnetically aligned holes cannot propagate via doubly occupied states whilst antiferromagnetically aligned holes can. We may expect a larger ferromagnetic region if the triplet states are included.

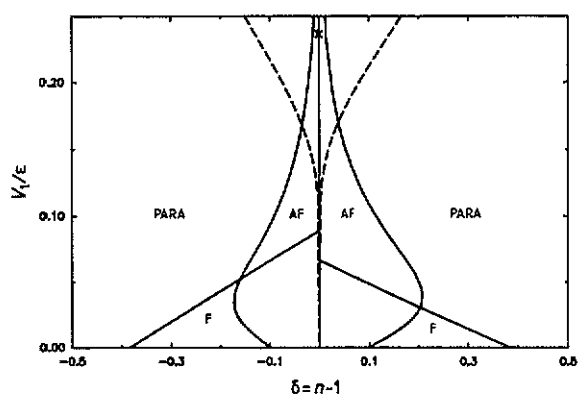

Figure 3. Magnetic phase diagram for the model described in section 4 with $V_0/\varepsilon = 1$. The broken line shows the antiferromagnetic boundary when superexchange is included.

An antiferromagnetic superexchange term can be calculated by including terms $O(V_1^2)$ [14]. In the general case we need to consider transitions to all excited states which gives a very complicated expression. Here we pick out the term that reduces to $J = 2V^4/\varepsilon^3$ in the limit $2V_0 = -V_1 = V \to 0$. This gives

$$J = \sqrt{2}\cos\theta\sin\theta\cos\phi\sin\phi V_1^2/(E_S - 2E_A). \tag{4.16}$$

We can decouple as before and the antiferromagnetic region is shown by the broken line in figure 3.

There is a localization transition at $n = 1$. The critical value of V_1/ε at $n = 1$ for $V_0/\varepsilon = 1$ is given by $V_1/\varepsilon = 0.24$ which is comparable to the value found in section 2.2.

4.2. $n > 1$

We can now generalize this to $n > 1$. Starting from (4.1) we see that for $n > 1$ and $V_1 = 0$ the ground state consists of a mixture of singly occupied sites in the state A_σ and doubly occupied sites in the singlet state S_1. Switching on V_1 allows the singlets to move around and we obtain an effective Hubbard model. This is just the Zhang–Rice picture. V_1 also produces excitations to higher-energy states and we can consider excitations out of the singlet-spin subspace. For $V_0/\varepsilon \to 0$ the lowest excitation energy is given by the singlet–triplet energy difference, $E_T - E_S = 8V_0^2/\varepsilon^2$. We see that for $V_0 = V_1 = V$, the singlet and triplet states become degenerate in the perturbation limit. This is the problem with the Zhang–Rice theory refered to earlier. For values of $(V_0/\varepsilon)^2 > 0.4$, however, the lowest-energy excitation is given by a process in which two singly occupied nearest-neighbour sites are replaced by a singlet and an empty site. Including the triplet states, T, would be relatively complicated and we consider instead the situation where we have some unoccupied states mixed in. The four possible states are then just those available for $n < 1$. We note that this is further justified by considering the matrix elements for the two types of excitation. We have

$$\langle iS_1, jA_\sigma | H_{\text{eff}} | iA_{-\sigma}, jT \rangle = (V_1/\sqrt{2}) \sin\theta \cos\theta \cos\phi. \tag{4.17}$$

We see from (4.9) that the matrix element for excitations involving unoccupied states is much larger than (4.17) if V_0/ε is small and is a factor ~ 3 larger for $V_0/\varepsilon = 1$.

The results are shown in figure 3 for $V_0/\varepsilon = 1$. While the results on the line $V_1 = 0$ are symmetric for $n < 1$ and $n > 1$ a slight asymmetry is present $V_1 > 0$. In both regions the phase diagram is very similar to that found for the Hubbard model.

5. Conclusion

We have shown that care is needed in applying the GA to the p–d model. This also has consequences for other SB techniques. We note that the GA was originally devised for the Hubbard model while the Coleman SB approach was developed to treat the periodic Anderson model in the heavy-fermion regime. It does not necessarily follow that methods that have had some success in a certain regime will correctly describe a regime with very different parameters. We have illustrated the problems with two slightly different models, the first the usual p–d model and the second a modified p–d model containing both on-site and inter-site hybridization terms. The original approximation fails for $n < 1$ through failing to distinguish between fluctuation and kinetic energy terms and for $n > 1$ by excluding processes in which n_d remains $= 1$. We have indicated a possible way forward using the second of these Hamiltonians where we can treat on-site terms correctly and then expand in the kinetic energy terms. At the simplest level of approximation this modified p–d model maps onto the Hubbard model for both $n < 1$ and $n > 1$. The extra degree of freedom of the p–d model compared with the Hubbard model can be approximately included by considering excitations out of the lowest-energy subspace. We have included only the lowest-energy excitation but it may be possible to extend our treatment to include more states making the model more realistic. One effect of including, for example, the higher-lying triplet states will be to increase the ferromagnetic region.

While we may hope that the GA gives us approximately the correct result for the ferromagnetism, we need a better approximation to describe the antiferromagnetism. It is necessary to include the superexchange terms explicitly. We have only included these terms in a very simple way here and a fuller investigation is needed.

We note finally that to provide a realistic description we need to include also direct p–p hopping and a p–d Coulomb repulsion term. The Gutzwiller approximation also neglects the nearest-neighbour p–d antiferromagnetic exchange which will be particularly important for $n > 1$. In principle all these terms could be included.

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