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A single oxygen hole in the copper–oxide planes

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Abstract. The strong-coupling behaviour of a single oxygen hole in the copper–oxide planes of the high-T_c superconductors is determined by exact diagonalisation on a finite cluster. The only energy scales are those determined by the hybridisation of the hole via Cu^+ or Cu^{3+} excitations. As is already known for hole motion via virtual Cu^{3+} excitations the relevant two-band model ('d–p' model) may be mapped onto an effective one-band model, and the constant phase Nagaoka 'ferromagnetism' ($S = (N-1)/2$, where N is the number of lattice sites) is the ground state. However, hole motion via virtual Cu^+ excitations is more interesting and it is shown that the one-band model is not a useful approximation: the magnetic phase coherence preferred by the propagating hole is a total spin singlet. The stability of the total spin singlet state with respect to the 'ferromagnetic' state is discussed as the oxygen energy level is raised from the lower Hubbard copper band to the upper Hubbard band. Finally, the consequences of this calculation if super-exchange between the copper spins were included are considered.

1. Introduction

The understanding of the behaviour of a single oxygen hole in the indigenous copper–oxide planes of high-T_c superconductors is an important step to the complete understanding of superconductivity in these materials. Many authors have chosen as their starting point the simplified 't–J' model assuming that a one-band model includes the basic physics (Anderson 1987, Zhang and Rice 1988). In this paper no such assumption is made but rather the behaviour of a single hole is analysed in the full two-band model in which the oxygen states are explicitly taken into account (the 'd–p' or 'Emery' model Emery 1987). It will be shown that, in general, the ground state and low-lying excitations of the two-band model *do not* resemble those of a one-band model except in the specific case where oxygen hole motion arises predominantely via Cu^{3+} excitations. In the limit for which hole motion via Cu^+ excitations is forbidden the mapping is indeed exact (Long and Barford 1990a, Zhang 1989).

The strong-coupling limit is assumed so that the occupation of copper sites is restricted to one, and super-exchange is suppressed since the magnetic coherence of the copper spins induced by the propagating hole will be of particular interest here. The problem is solved by exact diagonalisation of the relevant Hamiltonian for a non-trivial cluster. The

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evolution of the ground state will be calculated as the oxygen energy level is lowered from the Cu^{3+} limit to the Cu^{+} limit.

In the Cu^{3+} limit the added oxygen hole is bound in a singlet to a copper spin and this quasiparticle propagates through the lattice like a vacancy in a one-band model. In the strong-coupling limit the ground state consists of the remaining copper spins being driven ferromagnetic with a total $S = (N-1)/2$ (Nagaoka 1966)—and this is derived in the cluster calculation. As the Cu^{+} limit is approached, however, there is an amplitude for the oxygen hole to be bound in a triplet with a copper spin and this seriously complicates the issue. The mapping to a one-band model is now not exact but it is approximate provided Cu^{3+} excitations dominate. When Cu^{+} excitations dominate, however, the mapping is not even approximate: the magnetic coherence of the copper spins is a total spin singlet with the ferromagnetic solution considerably higher in energy. Furthermore this paramagnetic state is stable over a wide range of energies. The exotic ground state found when Cu^{+} excitations predominate is not surprising as the CuO_2 lattice is frustrated and the hopping matrix element is positive in this limit.

The plan of this paper is as follows: in the rest of this section the nomenclature will be introduced by writing down the two-band tight-binding Hamiltonian and its unitary transformation to second order in the hopping amplitude. In section 2 it is shown that the Hamiltonian can be considerably simplified as the anti-symmetric oxygen states are decoupled from the symmetric states. In the third section the exact diagonalisation is performed and the results discussed. Section 4 concludes.

The natural tight-binding Hamiltonian is

$$H = \varepsilon_{\mathrm{d}} \sum_{i\sigma} d^{\dagger}_{i\sigma} d_{i\sigma} + \varepsilon_{\mathrm{p}} \sum_{j\sigma} p^{\dagger}_{j\sigma} p_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + U_{\mathrm{p}} \sum_{j} n_{j\uparrow} n_{j\downarrow} + V \sum_{\langle ij\rangle\sigma\sigma'} n_{i\sigma} n_{j\sigma'} + t \sum_{\langle ij\rangle\sigma} (d^{\dagger}_{i\sigma} p_{j\sigma} + p^{\dagger}_{j\sigma} d_{i\sigma}) \tag{1.1}$$

where $d^{\dagger}_{i\sigma}$ and $p^{\dagger}_{j\sigma}$ create holes with spin σ in a copper $d_{x^2-y^2}$ orbital (site i) and oxygen p_σ orbital (site j) respectively.

The copper Hubbard U is large ($\simeq$10 eV) so it will be assumed to be limiting large and therefore doubly occupied copper sites are forbidden. The oxygen Hubbard U (denoted U_{p}) is also not small ($\simeq$5 eV) and the nearest-neighbour Coulomb repulsion, V, probably plays an important role in pairing mechanisms (Long and Barford 1990a, b). Nevertheless it is convenient to set both of them to zero which considerably simplifies matters as will be explained later. Finally, the hopping amplitude, t, is assumed to be much smaller than U and Δ ($\equiv \varepsilon_{\mathrm{p}} - \varepsilon_{\mathrm{d}}$), and hence is treated as a perturbation parameter. (See Hass (1989) for a review of the spectroscopic data.) As in Long and Barford (1990a), a unitary transformation on (1.1) is performed so that the leading order term is $O(t^2)$. The effective Hamiltonian that describes the motion of the hole is then

$$H = -2t_2 \sum_{\langle ji\rangle} \sum_{\langle ij'\rangle} S^{\dagger}_{ij} S_{ij'} + t_1 \sum_{\langle ji\rangle} \sum_{\langle ij'\rangle\sigma\sigma'} p^{\dagger}_{j\sigma} d^{\dagger}_{i\sigma'} d_{i\sigma} p_{j'\sigma'} - t_1 \sum_{\langle ij\rangle} \tag{1.2}$$

where

$$S^{\dagger}_{ij} = \frac{1}{\sqrt{2}} \sum_{\sigma} \mathrm{sgn}(\sigma) p^{\dagger}_{j\sigma} d^{\dagger}_{i\bar{\sigma}} \tag{1.3}$$

is the singlet operator and $\langle ij\rangle$ represents nearest-neighbour copper and oxygen sites. (Henceforward the constant energy term in (1.2) will be ignored.)

The first term arises from motion of the oxygen hole via Cu^{3+} excitations with the amplitude $-2t_2 = -2[t^2/(U - \Delta)]$. The sum includes $j = j'$. The second term represents hole motion via Cu^{+} excitations with the amplitude $t_1 = t^2/\Delta$ which is *positive* and therefore topological frustration will play a role in this limit. The sum includes $j = j'$ *only* if $U_p = 0$. In the next section this Hamiltonian will be simplified by decoupling the anti-symmetric oxygen orbitals.

2. Decoupling of the anti-symmetric oxygen states

There is an important simplification of the Hamiltonian, valid only for $U_p = 0$, that is worth emphasising (see also Zhang and Rice 1989). Consider the part of the Hamiltonian arising from Cu^{+} excitations. It may be written in the form

$$H = t_1 \sum_i H_i \tag{2.1}$$

the sum being over the copper sites and where

$$H_i = \sum_{\{j,j' \in i\}\sigma\sigma'} p^\dagger_{j\sigma} d^\dagger_{i\sigma'} d_{i\sigma} p_{j'\sigma'} \tag{2.2}$$

(j and j' both being neighbours of i).

H_i can now be diagonalised for the ith plaquette (namely one copper atom and four surrounding oxygen atoms) for a copper and an oxygen hole. Consequently

$$H_i = \sum_{\alpha=1}^{16} \varepsilon_\alpha X^\dagger_\alpha X_\alpha \tag{2.3}$$

where ε_α is the eigenvalue corresponding to the eigenfuction $|X_\alpha\rangle = X^\dagger_\alpha|0\rangle$. Since H_i commutes with S^2, the eigenfunctions will be eigenstates of S^2 with $S = 0$ or 1.

There are four non-zero eigenvalues: one at $-4t_1$ corresponding to the constant phase singlet solution:

$$|S_i\rangle = \frac{1}{2}\sum_{j\in i} |S_{ij}\rangle \tag{2.4}$$

and three at $+4t_1$ corresponding to the constant phase triplet solutions, with $S_z = -1, 0$ and 1, denoted by $|\boldsymbol{T}_i\rangle$ and defined in (3.2). All the anti-symmetric solutions are non-bonding orbitals at $\varepsilon = 0$ and so may be discarded. Thus, upon reconstituting the lattice, the Cu^{+} Hamiltonian is

$$H = -4t_1 \sum_i S^\dagger_i S_i + 4t_1 \sum_i \boldsymbol{T}^\dagger_i \cdot \boldsymbol{T}_i \tag{2.5}$$

where the four bonding states have been decoupled from the remaining four anti-symmetric states (since there are eight spin degrees of freedom per unit cell). It should be emphasised that this simplification only works if $U_p = 0$, since otherwise the anti-symmetric solutions have non-zero eigenvalues.

The Cu^{3+} Hamiltonian can likewise be diagonalised in the $S = 0$ sub-space obtaining for the full Hamiltonian:

$$H = -4(t_1 + 2t_2)\sum_i S^\dagger_i S_i + 4t_1 \sum_i \boldsymbol{T}^\dagger_i \cdot \boldsymbol{T}_i. \tag{2.6}$$

This Hamiltonian does represent hole motion through the lattice because a singlet

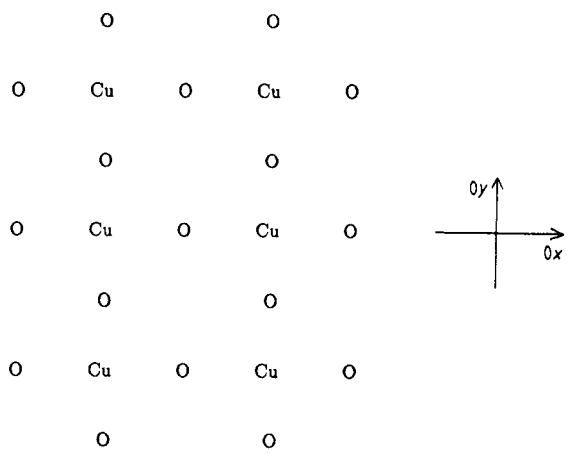

Figure 1. The cluster used in the exact diagonalisation.

or triplet state on the ith site is in general not orthogonal to a singlet or triplet state on the neighbours of i; the overlaps are shown in the appendix. (The overlaps show that a singlet quasiparticle on the ith site can be scattered into a triplet ($S_z = 0$) quasiparticle on the neighbours of i with a matrix element $\frac{1}{2}t_1$, for example.) Furthermore the Hamiltonian represents the motion of singlet and triplet quasiparticles on the *square lattice* topology. This Hamiltonian will now be solved for a finite cluster; the primary utility of this section being to halve the necessary number of basis states needed in the diagonalisation which follows.

3. Exact diagonalisation and discussion

To understand the behaviour of the Hamiltonian (2.6) for the motion of a single oxygen hole, (2.6) is exactly diagonalised for the cluster as shown in figure 1 which consists of six copper–oxygen plaquettes. Free boundary conditions are used and full use is made of the point group symmetries. A calculation on a cluster of this size will provide valid qualitative insight to the lattice problem.

The form of the Hamiltonian (2.6) suggests a natural representation for the basis states which is convenient to employ. For the full lattice (of N copper sites) the Hilbert space of (2.6) is spanned by the $4N2^{N-1}$ (symmetric) basis states

$$S_i^\dagger d_{i\sigma_i} \prod_{j=1}^{N} d_{j\sigma_j}^\dagger |0\rangle \tag{3.1a}$$

$$T_{-,i}^\dagger d_{i\sigma_i} \prod_{j=1}^{N} d_{j\sigma_j}^\dagger |0\rangle \tag{3.1b}$$

$$T_{0,i}^\dagger d_{i\sigma_i} \prod_{j=1}^{N} d_{j\sigma_j}^\dagger |0\rangle \tag{3.1c}$$

$$T_{+,i}^\dagger d_{i\sigma_i} \prod_{j=1}^{N} d_{j\sigma_j}^\dagger |0\rangle \tag{3.1d}$$

where

$$T^{\dagger}_{-,i} = \frac{1}{2}\sum_{j\in i} p^{\dagger}_{j\downarrow}\, d^{\dagger}_{i\downarrow} \tag{3.2a}$$

$$T^{\dagger}_{0,i} = \frac{1}{2}\sum_{j\in i} \frac{1}{\sqrt{2}} \sum_{\sigma} p^{\dagger}_{j\sigma} d^{\dagger}_{i\bar{\sigma}} \tag{3.2b}$$

$$T^{\dagger}_{+,i} = \frac{1}{2}\sum_{j\in i} p^{\dagger}_{j\uparrow}\, d^{\dagger}_{i\uparrow} \tag{3.2c}$$

are the constant phase triplet operators ($S_z = -1$, 0 and 1 respectively). These basis states form a complete but not orthogonal set (as shown in the appendix). Thus it is impossible to diagonalise each of the components of the Hamiltonian (2.6) in one of the sub-spaces represented by (3.1*a*, *b*, *c*, *d*) as one might naively hope (unless $t_1 = 0$).

There are seven spins in the cluster of figure 1 and hence 35 eigenstates of S^2. The Hamiltonian is diagonalised in the sub-space of total $S_z = \frac{1}{2}$ (which include $S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$) and of $S_z = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$ using basis states of the form of (3.1). The energies and total spin of the lowest lying eigenfunctions for $t_1 = 0$ (Cu^{3+} limit) and $t_2 = 0$ (Cu^{+} limit) will now be calculated.

In the Cu^{3+} limit an exact mapping exists onto a one-band model *with only nearest-neighbour hopping*. The Hamiltonian is completely diagonalised in the singlet sub-space (3.1*a*) (Zhang 1989) and may be written as

$$H = -8t_2 \sum_{i} S^{\dagger}_{i} S_i - t_2 \sum_{\langle ii'\rangle\sigma} S^{\dagger}_{i} d^{\dagger}_{i'\sigma} d_{i\sigma} S_{i'} \tag{3.3}$$

if the $S^{\dagger}_{i}$ are assumed to be orthogonal.

In the strong coupling limit the singlet drives the remaining $(N-1)$ copper spins ferromagnetic with the spectrum given by

$$\varepsilon_k = -8t_2 - 2t_2(\cos(k_x a) + \cos(k_y a)) \tag{3.4}$$

for the lattice. The ground state is therefore the constant phase ($\boldsymbol{k} = \boldsymbol{0}$) solution

$$|\psi\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} S^{\dagger}_{i} d_{i\uparrow} \prod_{j=1}^{N} d^{\dagger}_{j\uparrow} |0\rangle \tag{3.5}$$

with energy $-12t_2$ and total $S = (N-1)/2$.

By exactly diagonalising this Hamiltonian on the cluster this result is reproduced along with the excited states. The energy, total spin and point group symmetry of the lowest lying states are shown in table 1. Since free boundary conditions are used there is no translational invariance and hence no Bloch momenta. However, $\boldsymbol{k} = \boldsymbol{0}$ and $\boldsymbol{k} = (\pi/a)(1, 0)$ are included in the fully symmetric point group and $\boldsymbol{k} = (\pi/a)\ (0, 1)$ is included in the class which is symmetric for a reflection along the $0x$ axis and anti-symmetric for a reflection along the $0y$ axis.

As expected the ground state is at $-(9 + \sqrt{2})t_2$ with five of the copper spins polarised; the oxygen hole being bound in a singlet with the remaining copper spin, which is delocalised with constant phase.

Table 1. The $t_1 = 0$ case, Cu^{3+} excitations.

State	Energy (t_2)	Total spin	y-symmetry	x-symmetry
$\|\alpha\rangle$	−10.414	5/2	+	+
	−10.363	3/2	+	−
$\|\beta\rangle$	−10.310	1/2	+	+
	−10.259	3/2	−	+
	−10.243	3/2	−	−
	−10.192	1/2	+	−

Table 2. The $t_2 = 0$ case, Cu^{+} excitations.

State	energy (t_1)	Total spin	y-symmetry	x-symmetry
$\|\beta\rangle$	−4.932	1/2	+	+
	−4.919	1/2	+	−
	−4.912	3/2	−	−
	−4.900	3/2	+	−
	−4.891	1/2	−	+
$\|\alpha\rangle$	−4.878	5/2	+	+

Turning to the more interesting limit in which hole motion via Cu^{3+} excitations are excluded by setting $t_2 = 0$ in (2.6) and diagonalising the Hamiltonian the ground state and low-lying excitations are found to be as shown in table 2.

Clearly, the ground state and low-lying excitations are significantly different from those of table 1. The ground state is not the 'Zhang and Rice' state (denoted by $|\alpha\rangle$) but a total spin singlet (denoted by $|\beta\rangle$) with $|\alpha\rangle$ considerably higher in energy. The $|\alpha(t_2 = 0)\rangle$ state differs from the $|\alpha(t_1 = 0)\rangle$ state as in the former there is a probability of approximately 0.04 for the oxygen hole to be bound with a copper spin in a triplet quasiparticle.

The cluster calculation suggests that the ground state in the Cu^{+} limit is a total spin singlet; however, this is not a proof. Nevertheless, the following observations are suggestive and together with the calculation make the proposition that the ground state is a total spin singlet very plausible:

(i) Eigenstates of the Cu^{+} Hamiltonian (2.5) contain *total* ferromagnetism, i.e. $S = S_{\max} = (N+1)/2$ and if $t_1 \rightarrow -t_1$ this is the ground state. The $S = (N+1)/2$ branch of the excitation spectrum would then be described by the Hamiltonian

$$H = -4t_1 \sum_i T^{\dagger}_{+i} T_{+i} - t_1 \sum_{\langle ii' \rangle} T^{\dagger}_{+i} d^{\dagger}_{i'\uparrow} d_{i\uparrow} T_{+i'} \tag{3.6}$$

if the $T^{\dagger}_{+i}$ are assumed to be orthogonal (cf (3.3) and the appendix). The spectrum is then

$$\varepsilon_k = -4t_1 - 2t_1(\cos(k_x a) + \cos(k_y a)) \tag{3.7}$$

with a ground state with energy $-8t_1$ at $\boldsymbol{k} = \boldsymbol{0}$, and a maximum energy of $0t_1$ at $\boldsymbol{k} = \boldsymbol{Q}_{\mathrm{AF}}$.

(ii) If there was no amplitude for the scattering of a singlet quasiparticle into a triplet quasiparticle, then the ground state and low-lying excitations would be exactly described by (3.3) with $t_2 \rightarrow \frac{1}{2}t_1$. Thus, the ground state would be 'Zhang and Rice' ferromagnetism (total $S = (N-1)/2$) at an energy $-6t_1$. However, since there *is* an amplitude for the hole to be in a triplet quasiparticle, hybridisation energy is lost as, firstly these hop with a positive hopping matrix and secondly they have a positive 'on site' energy. $-6t_1$ is therefore a lower bound on the 'Zhang and Rice' state. The cluster calculation confirms this: $|\alpha(t_2 = 0)\rangle = -4.878t_1 > -(9+\sqrt{2})\frac{1}{2}t_1$.

(iii) It is useful to define a 'frustration gap': the loss of hybridisation energy of the 'Zhang and Rice' state because of frustration. For the cluster this is $(9+\sqrt{2})\frac{1}{2}t_1 - 4.878t_1$, which is positive.

(iv) The corollary of (i) and (ii) is that the ground state energy of the Cu^+ Hamiltonian is asymmetric for $t_1 \rightarrow -t_1$, with $t_1 < 0$ yielding the lower ground state energy. Thus, the Hamiltonian resembles the motion of one hole at half filling in the strong-coupling Hubbard Hamiltonian on a fustrated lattice where the ground state energy is also asymmetric if the sign of the hopping matrix is changed. It is known, in that case, that for $t > 0$ (for hole motion) the ground state is not total spin maximum (Nagaoka 1966). The Cu^+ Hamiltonian is also in the frustrated limit ($t_1 > 0$) and therefore the ground state is certainly not total $S = (N+1)/2$.

(v) Finally, (iii) suggests that the hole motion in the $S = (N-1)/2$ state is also frustrated and therefore the best candidate for the ground state is paramagnetism.

(It is worth remarking here that the ground state energy of the Cu^{3+} Hamiltonian is also asymmetric for a change of sign in t_2. For a negative hopping amplitude (in this case $t_2 > 0$) the ground state energy is $-12t_2$ whereas for a positive hopping amplitude the ground state is the degenerate non-bonding orbitals at $0t_2$. Since the Cu^{3+} Hamiltonian is in the unfrustrated limit, however, the ground state is ferromagnetic consistent with the Pauli exclusion principle, i.e. total $S = (N-1)/2$.)

It has been shown that the ground state of the Cu^+ limit is a total spin singlet for this cluster. The question therefore arises: How stable is this state with respect to the 'Zhang and Rice' state ($|\alpha\rangle$) as the oxygen energy level is raised from the Cu^+ limit ($\Delta = 0$) to the Cu^{3+} limit ($\Delta = U$) for this particular cluster? (Finite size effects will be considered shortly.) With this aim in mind the evolution of the energy of the states $|\alpha\rangle$ and $|\beta\rangle$ are calculated as a function of Δ for $0 \leqslant \Delta \leqslant U$. Figure 2 shows the relative energy difference $(\varepsilon(|\alpha\rangle) - \varepsilon(|\beta\rangle))/((\varepsilon(|\alpha\rangle) + \varepsilon(|\beta\rangle))$ as a function of Δ/U.

For $0 \leqslant \Delta \leqslant 0.37U$ the total spin singlet is the ground state whereas for $0.37U \leqslant \Delta \leqslant U$ 'Zhang and Rice' is the ground state. (At $\Delta = 0.37U$ these states are degenerate and for this cluster there are no other ground states.) Thus the total spin singlet is stable over a wide energy range, and certainly stable over the energy range which corresponds to the experimental limit (Hass 1989).

4. Conclusions

In this paper the motion of an oxygen hole in the CuO_2 lattice has been considered by exact diagonalisation of the strong-coupling Hamiltonian on a finite cluster. In the limit where virtual Cu^{1+} are excluded it was confirmed that the oxygen hole is bound in a singlet quasiparticle to a copper spin and that there is a direct mapping onto a one-band model *with only nearest-neighbour hopping*. The singlet

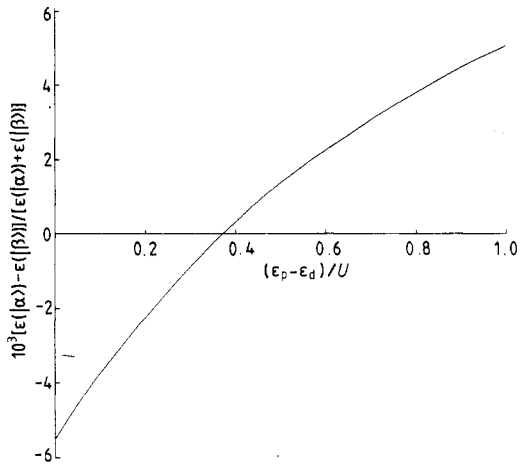

Figure 2. Plot of the relative energy difference between the 'Zhang and Rice' state ($|\alpha\rangle$) and the total spin singlet state ($|\beta\rangle$) as a function of $(\varepsilon_p - \varepsilon_d)/U$. The total spin singlet is the ground state for $0 \leqslant (\varepsilon_p - \varepsilon_d)/U < 0.37$.

polarises the remaining copper spins. However, in the more likely experimental scenario (Hass 1989)—namely when virtual Cu^{1+} excitations *dominate*—a one-band model (with only nearest-neighbour hopping) is not a useful approximation. For, in this case, the motion of the oxygen hole is frustrated and it drives the remaining copper spins into a total spin singlet: a result which would not have been predicted from a strong-coupling Hubbard Hamiltonian on a square lattice. Moreover, the paramagnetic state is stable with respect to the 'Zhang and Rice' ferromagnetic state for a wide energy range: $0 \leqslant \Delta \leqslant 0.37U$. It is worth while mentioning, however, that a one-band model with frustration, such as a strong-coupling Hubbard model with next-nearest-neighbour hopping of positive amplitude, would also give a low-spin ground state (Takano and Sano 1989). Thus it is important to distinguish between the deficiency of using a single-band model which includes only nearest-neighbour hopping and the *possible* deficiency of using a reduced Hilbert space.

It is not posible to find the Bloch momentum of the hole in the ground state in this calculation because of the use of free boundary conditions. In an earlier paper (Long and Barford 1990a), however, an attempt was made to find the ground state for the Cu^{1+} limit using a 2×2 plaquette (i.e. five spins) with free and periodic boundary conditions. There are two noteworthy features from the calculation. Firstly, for the free boundary condition calculation, the $S = \frac{1}{2}$ (paramagnet) and $S = \frac{3}{2}$ ('Zhang and Rice') states had remarkably similar energies of $-4.738t_1$ and $-4.753t_1$ respectively. The $S = \frac{3}{2}$ state is just the ground state. This result is not equivocal however as the boundary effects favour high spin. In particular there is a loss of on-site energy arising from the copper atoms cut off from the exterior oxygen atoms. There would be a gain of t_1 for a hole occupying one of these oxygen atoms in a singlet with the (cut-off) copper spin and a loss of t_1 if they were in a triplet.

Secondly, for the periodic boundary condition calculation, which although introduces additional bonds does not suffer boundary effects and has translational invariance, $S = \frac{1}{2}$ is the ground state with an energy of $-5.293t_1$ and a Bloch momentum $\boldsymbol{k} = (\pi/a)(\frac{1}{2}, \frac{1}{2})$ compared to $-4.900t_1$ and $\boldsymbol{k} = \boldsymbol{0}$ for the $S = \frac{3}{2}$ state.

The cluster in the present calculation is significantly larger than the 2×2 cluster. Not only are there the loops associated with a particular plaquette and the perimeter loop but the square is two-dimensionally connected and, of course, boundary effects are

reduced. The total spin singlet ground state is substantially lower in energy than the 'Zhang and Rice' solution and in view of the considerations above this is the expected ground state for the lattice. Moreover the cluster calculation that the spin singlet state is stable with respect to the 'Zhang and Rice' state for $\Delta > 0.37U$ is probably a lower bound on Δ. Finally, the Bloch momentum of the hole is expected to be at the non-interacting Fermi surface in the low-spin case.

What has this calculation to say about the real cuprate superconductors? Experimentally it is observed that the undoped materials have a long-range staggered magnetisation which is very well explained by a spin-$\frac{1}{2}$ Heisenberg Hamiltonian with an antiferromagnetic exchange coupling constant $J \simeq 300$ K (Chakravarty *et al* 1989). Thus a model describing holes doped into the copper oxide planes should have an antiferromagnetic Heisenberg term. As holes are doped into the planes, the antiferromagnetic correlations are scrambled so that for sufficient concentration (~ 0.1) the Néel ordering is destroyed, although it is not yet known which spin correlations replace the Néel ones.

In the t–J model one may qualitatively picture this as arising from polaronic distortions of the Néel ordering due to the propagating holes. There is a competition between minimising the kinetic energy of the holes (which means delocalising the hole in a region determined by Nagaoka phase coherence) and maximising the energy gained from Néel ordering. Since the kinetic energy of the holes prefer high spin, and antiferromagnetic interactions prefer low spin, these processes are at variance with one another.

In contrast to this the kinetic energy of the hole in the two-band model with virtual Cu^{1+} excitations and the t–t'–J model (namely both frustrated) prefer low spin and therefore there is less competition with the super-exchange. Thus, while all three models may well predict low-spin polaronic distortions of the Néel order (provided J/t is not vanishingly small in the t–J model) the internal structure of these polarons may be quite different in the frustrated models and unfrustrated model.

Acknowledgment

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Appendix. The non-orthogonality of the basis states

In this appendix the overlap of the basis states (3.1) are shown. The relevant part of the basis states are represented in the following by $|ij\rangle$ where i and j represent nearest-neighbour lattice positions. Thus, $\langle S+|+S\rangle = \frac{1}{8}$ shows that a state with a singlet quasiparticle on the ith site and an up spin on the jth site has an overlap of one eighth with

a state with a singlet and an up spin on the jth and ith sites respectively provided that the spins on the remaining lattice sites are the same. The non-zero overlaps are therefore:

$$\langle S+|+S\rangle = 1/8 \qquad \langle T_0+|+T_0\rangle = 1/8$$
$$\langle S+|+T_0\rangle = -1/8 \qquad \langle T_0+|-T_+\rangle = -1/4\sqrt{2}$$
$$\langle S+|-T_+\rangle = 1/4\sqrt{2} \qquad \langle T_0-|-T_0\rangle = 1/8$$
$$\langle S-|-S\rangle = 1/8 \qquad \langle T_0-|+T_-\rangle = 1/4\sqrt{2}$$
$$\langle S-|-T_0\rangle = 1/8 \qquad \langle T_+ +|+T_+\rangle = 1/4$$
$$\langle S-|+T_-\rangle = -1/4\sqrt{2} \qquad \langle T_- -|-T_-\rangle = 1/4$$

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