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Low spin correlations between copper spins in oxygen hole superconductors

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Abstract. We compare three basic physical mechanisms which induce correlations between the copper spins of a single strong-coupling plane of copper oxide in the perovskite superconductors. Motion of holes by virtual Cu^{3+} excitations induces ferromagnetic correlations, hole motion by Cu^{+} excitations induces paramagnetism, and Heisenberg interactions induce antiferromagnetism. We study the smallest clusters which exhibit the phenomena and examine the competition between these effects by exact diagonalisation. The paramagnetism and antiferromagnetism are quite similar and readily coexist locally. The ferromagnetic correlations are rapidly destroyed by increasing the Heisenberg interactions which stabilise the paramagnetic state locally. The mechanism which leads to paramagnetism via hole motion by virtual Cu^{+} excitations is investigated by solving a one-dimensional chain topology using short-range valence bonds. The paramagnetic correlations seem the only phenomenon which is likely to be relevant in the experimental systems. The inclusion of the Heisenberg interactions may be considered a minor perturbation to the paramagnetic correlations induced by the hole motion, and so may be neglected to a first approximation for this limit.

1. Introduction

The main interest in the perovskite superconductors is the superconductivity. Before this phenomenon, which is a low-energy many-particle effect, can be investigated however, an understanding of the single-particle effects must be achieved. Some of the necessary physics is contained in the strong-coupling limit of the square lattice Hubbard model or 't–J model' but is this model sufficient?

The majority of published work is firmly in favour of a t–J model description [1], let us review this decision. The experimental evidence is in favour of the charge carriers being on oxygen atoms and *not* copper atoms as the square lattice model might suggest. This fact led to the 'd–p model' which puts the oxygen p orbitals on an equal footing with the copper d orbitals [2]. Evidence was then produced suggesting that the strong-coupling limit of the d–p model is similar to that of the t–J model [3], culminating in a limit where the mapping is exact [4]. We have been trying to redress the balance by pointing out that there is a second limit which exhibits quite different phenomena [5]. Indeed, as well as observing the low spin correlations which are absent in the t–J model and of interest here, a novel attraction between charge carriers mediated by the repulsion between the two types of electrons was also found [5]. In this article we investigate the competition between the effects found in these two limits and introduce Heisenberg interactions in order to determine whether these

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spin interactions are complementary or contradictory to the correlations induced by the hole motion. The phenomena we describe are separated on very small energy scales and so we cannot afford to employ uncontrolled approximations. We exactly solve small clusters involving only boundary effects as approximations. The basic ideas are illustrated by our calculations although the square lattice topology is still beyond our present level of technical expertise.

The only relevant experimental evidence is the relationship between doping and magnetism. In the absence of doping, antiferromagnetism is stable. Holes doped into the system soon destroy the the long-range Néel coherence but there is neutron scattering evidence that short-range Néel fluctuations remain [6]. The superconducting phase exhibits the short-range antiferromagnetic correlations, but there is no evidence of any other magnetic phase coherence, other than 'rare earth' magnetism in layers well removed from the copper oxide planes. This is the basic physical picture which requires a single-particle explanation.

With the advent of electron-doped 'high T_c' superconductors, a comparison between positively and negatively doped systems could be achieved. Although the corresponding superconducting properties appear very similar, the antiferromagnetism is quite asymmetrical. Holes appear to destroy antiferromagnetism with tiny concentrations, whereas electrons seem to kill the Néel order only when they start to conduct at an order of magnitude higher concentration. Early attempts at an understanding of this fact have attributed it to a comparison between 'dilution', for the case of electrons, and 'frustration' for the case of the holes. The 'frustration' argument relies on the fact that a static hole prefers its two copper hole neighbours to be parallel, and this local inclusion of ferromagnetic bonds in some way frustrates the antiferromagnetism. We believe that this effect is minor and qualitatively incorrect. We present a *dynamical* argument for the effect based upon the different correlations that particle motion induces when comparing electrons and holes.

A certain quantity of experimental spectral evidence is building up as to the density of states and energy scale of the excitation spectrum in these superconductors. Unfortunately, although our modelling predicts excitation spectra, the number and variety of possibilities are too large to be useful.

In section 2 we compare the correlations on our finite clusters and in section 3 we look at the paramagnetic correlations found in the solution to the linear chain of copper oxide.

2. Comparison of copper spin correlations

We employ the strong-coupling limit of the d–p model [2]. This model has been derived and used in various forms by various authors [7]. The initial Hamiltonian is

$$H = T\sum_{i\sigma} d_{i\sigma}^{\dagger} d_{i\sigma} + U\sum_{i} d_{i\sigma}^{\dagger} d_{i\bar{\sigma}}^{\dagger} d_{i\bar{\sigma}} d_{i\sigma} + E\sum_{j\sigma} p_{j\sigma}^{\dagger} p_{j\sigma} + t\sum_{\langle ij\rangle\sigma} (d_{i\sigma}^{\dagger} p_{j\sigma} + p_{j\sigma}^{\dagger} d_{i\sigma}) \tag{2.1}$$

where $d_{i\sigma}^{\dagger}$ creates a *hole* of spin σ (complementary spin $\bar{\sigma}$) on a copper atom (denoted by i) and $p_{j\sigma}^{\dagger}$ creates a *hole* of spin σ on an oxygen atom (denoted by j). There are three relevant energy scales; $\Delta = E - T$, the relative stability of a single hole on a copper atom versus an oxygen atom; U, the Coulombic penalty against adding a second hole

to a copper atom and, t, the hybridisation energy between orbitals on neighbouring atoms (denoted by $\langle ij \rangle$).

The superconducting compounds are modelled with one hole per copper atom corresponding to the parent compounds and then doping of extra oxygen holes leading to the superconductivity. The parent compounds are insulating and antiferromagnetic, which suggests a parameterisation with $U > \Delta > |t|$.

We study the strong-coupling limit of this model where the hybridisation is assumed small and is used as an expansion parameter. We will use the representation [8]

$$H = -X(1+\alpha)\sum_i B_i^\dagger B_i + X(1-\alpha)\sum_i \boldsymbol{T}_i^\dagger \cdot \boldsymbol{T}_i + \frac{J}{2}\sum_{\langle ii' \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} \tag{2.2}$$

in terms of the symmetrically averaged singlet and triplet pair creation operators

$$B_i^\dagger = \frac{1}{\sqrt{2}}\sum_{\langle ij \rangle \sigma} \sigma p_{j\sigma}^\dagger d_{i\bar{\sigma}}^\dagger \tag{2.3a}$$

$$\boldsymbol{T}_i^\dagger = \frac{1}{\sqrt{2}}\sum_{\langle ij \rangle \sigma\sigma'} p_{j\sigma}^\dagger \hat{\sigma}_{\sigma\sigma'} d_{i\bar{\sigma}'}^\dagger \tag{2.3b}$$

where $\hat{\sigma}$ are Pauli matrices, and the copper spin operators

$$\boldsymbol{S}_i = \frac{1}{2}\sum_{\sigma\sigma'} d_{i\sigma}^\dagger \hat{\sigma}_{\sigma\sigma'} d_{i\sigma'} \tag{2.3c}$$

In the same way that the t–J model [3] corresponds to the strong-coupling limit of the Hubbard model [9], the above Hamiltonian corresponds to the strong-coupling limit of the d–p model. Although the Heisenberg interactions are identical, the hopping contribution, the X term, is rather different from the t term of the t–J model.

The reparametrisation of the system in this limit is achieved with, firstly

$$\alpha = \Delta/U \tag{2.4a}$$

the measure of whether the oxygen level is close to the Cu^+/Cu^{2+} level ($\alpha \mapsto 0$) or to the Cu^{2+}/Cu^{3+} level ($\alpha \mapsto 1$); secondly

$$X = \frac{t^2 U}{\Delta(U-\Delta)} \tag{2.4b}$$

the hopping energy scale, which corresponds to t in the t–J model, and limits to $t_1 = t^2/\Delta$ and $t_2 = t^2/(U-\Delta)$ in the Cu^+ limit ($\alpha \mapsto 0$) and the Cu^{3+} limit ($\alpha \mapsto 1$) respectively; and thirdly

$$J = \frac{4X^2}{\Delta}(1-\alpha)^2(1+\alpha) \tag{2.4c}$$

which is the strength of the superexchange interaction between neighbouring copper spins (denoted by $\langle ii' \rangle$) in the absence of added oxygen holes. It is important to realise that the superexchange *vanishes* in the absence of Cu^+ excitations and the

experimental antiferromagnetism on a 250 K energy scale, together with the lack of Cu^{3+} in spectroscopic experiments, strongly suggest that the experimental limit has a small value of α.

There are *three* quite natural limits, each with quite particular copper spin correlations; $\alpha = 1$ and $J = 0$ corresponds to hole motion by virtual Cu^{3+} excitations and finds a mapping of the model onto the strong-coupling Hubbard model [9] for which hole motion yields Nagaoka ferromagnetism; $\alpha = 0$ and $J = 0$ corresponds to hole motion by virtual Cu^{+} excitations and yields a form of paramagnetism [10]; $X = 0$ corresponds to the absence of holes and yields the square lattice Heisenberg model and probably long-range antiferromagnetism [11]. The correlations which are the least well understood are the paramagnetic correlations of the Cu^{+} limit. This is the situation where motion on a *frustrated* topology leads to *low* spin Nagaoka coherence and we give evidence for a low spin ground state in this section together with some interpretation of the mechanism in the next section.

Our main motivation in this article is the *competition* between these three phenomena. We study the exact solutions of the two clusters depicted in figure 1. The first cluster is the smallest relevant topological loop. The second cluster has been chosen for its high symmetry, which facilitates calculations, and because it has an *even* number of relevant fermions, which allows total spin-zero solutions.

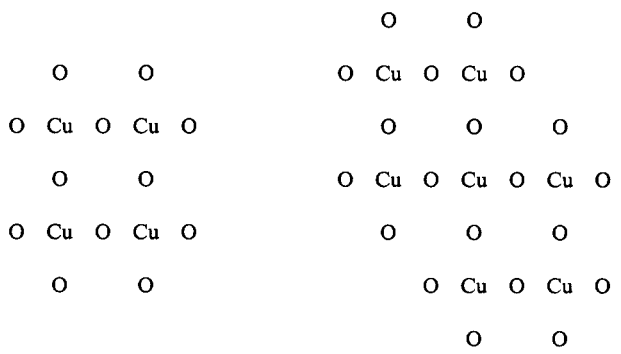

Figure 1. The two clusters that we have analysed using exact diagonalisation.

There are two types of state competing for the role of ground state. Firstly there is the state proposed by Zhang and Rice [12], which is the ferromagnetic ground state to the Hubbard model limit ($\alpha \mapsto 1$). This state finds the oxygen hole in a relative singlet with one of its two neighbouring copper holes and all the other copper holes aligned ferromagnetically. The hole has uniform phase which optimises coherence around all the closed loops. Secondly there is a low spin state with the minimum allowable total spin and a wavevector corresponding to the non-interacting Fermi surface.

The comparison between the high spin and low spin states is complicated by the boundary conditions. There is an on-site *diagonal* contribution to the hopping energy. The oxygen hole either gains $X(1 + \alpha)$, if it is a relative singlet with the neighbouring copper hole, or loses $X(1 - \alpha)$, if it is in a relative triplet. The omission of the neighbouring copper atoms to the boundary oxygen atoms corrupts the relationship between the cluster and the lattice, since this on-site contribution is missing. A careful consideration of this contribution indicates that the omission favours the ferromagnetic state, since there is a higher probability of finding triplets with ferromagnetism. This

was the motivation for studying larger clusters, which, having a smaller fraction of boundary atoms, should better model the lattice. As the above argument suggests, the low spin state is much more stable for the larger cluster, being stable for all α in the absence of J, whereas for the small cluster it is never stable in the absence of J.

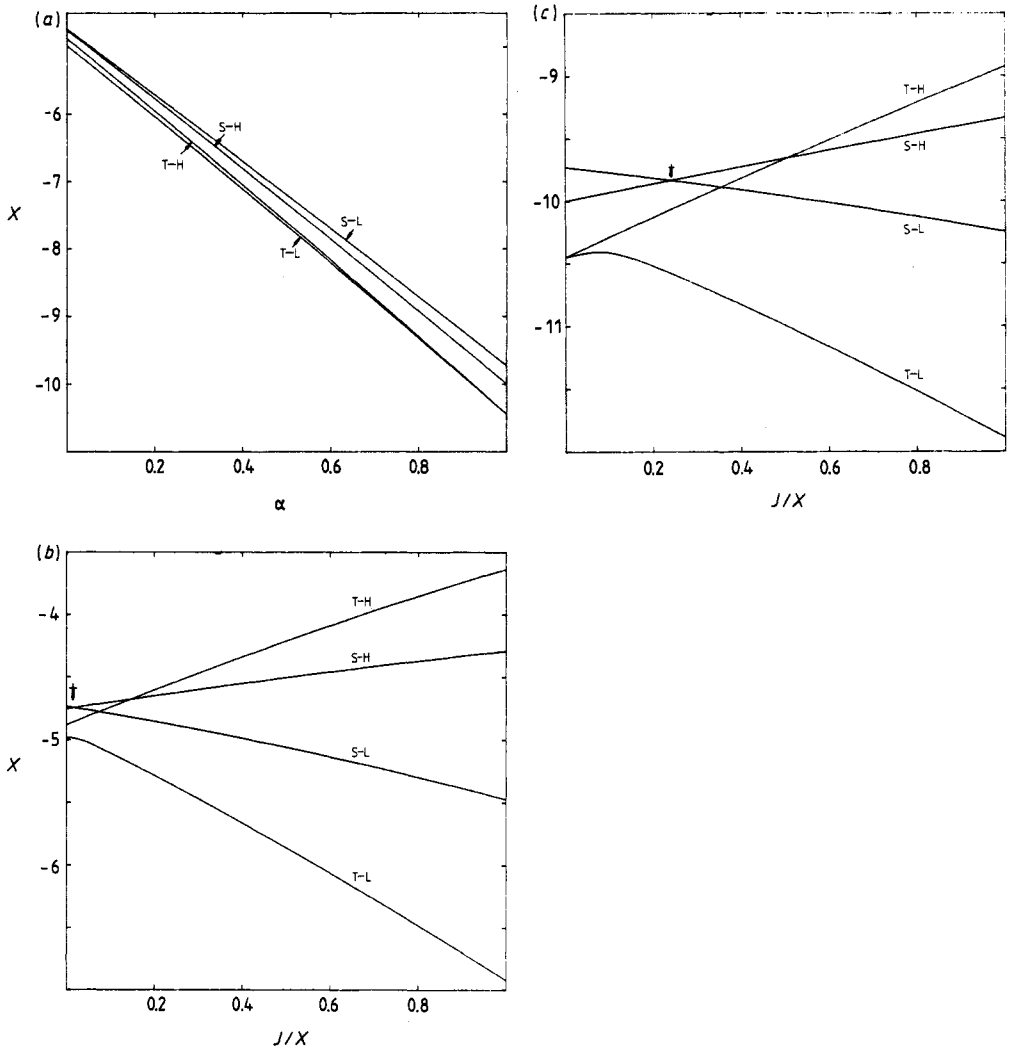

Figure 2. A comparison between the total energies of the ferromagnetic bound magnon state and the low spin ground state. Both clusters are presented and marked S (square) and T (two squares) for the small and large clusters, respectively. (*a*) Comparing the two types of hopping in the absence of Heisenberg interactions (namely $J = 0$). Virtual Cu^{+} hopping and virtual Cu^{3+} hopping correspond to $\alpha = 0$ and $\alpha = 1$ respectively. (*b*) The comparison between virtual Cu^{+} hopping and increasing Heisenberg interactions. The symbol † marks the value above which the low spin state becomes the ground state of the square. For $J = X$, the gap between the two states is approximately J and $3J$, scaling like a simple bond counting argument. (*c*) The comparison between virtual Cu^{3+} hopping and increasing Heisenberg interactions. The symbol † marks the value above which the low spin state becomes the ground state of the square. For $J = X$, the gap between the two states is very similar to that in figure 2(*b*).

We picture the ground state energies of the low spin and high spin bound magnon [12] states as the parameters are varied in figure 2. The basic physics is clear, the low spin state is vigorously favoured by both hole motion via virtual Cu^+ excitations *and* by the Heisenberg interactions, whereas the high spin state is only favoured by hole motion by Cu^{3+} excitations.

The calculations involving the Heisenberg interactions yield rather different behaviour for the two clusters. The reason is simply that the Heisenberg energy scales with the cluster size, whereas the hopping contribution is fixed by the number of charge carriers. One should consider the calculations to be studying the stability of polarons of different sizes.

For the larger cluster, the ground state to the Cu^{3+} problem is degenerate, with both high *and* low spin states. The consistency with Nagaoka's theorem [9] is subtle and deserves explanation. Nagaoka's result implies that the best hopping phase coherence requires ferromagnetism around all closed loops, but *not* global ferromagnetism. Only if all the loops are *interconnecting* is global ferromagnetism required. For the present case, ferromagnetism can be maintained around both loops using *independent* spin directions for the moments on each loop. Averaging the antiparallel orientations over all directions then leads to the paramagnetic ground state. Both Heisenberg and Cu^+ fluctuations then break the degeneracy and stabilise the low spin state. The relative stability of Nagaoka ferromagnetism is therefore smaller than might be expected.

Although the total energy calculations of figure 2 give a comparison which is of use in determining the phase diagram, they do not lead to insight into the types of correlations inherent in the competing low-energy states. The remainder of the article will try to address the possible ways of comparing and interpreting these correlations.

It is easy to understand the difference between the high spin and low spin states, but is there a big difference between the low spin correlations induced by hopping via Cu^+ excitations and those induced by the Heisenberg interactions?

We may only address this problem locally on such small clusters, but for our square the question is quite easy to answer. We calculate the probability that the *diagonal* bond is triplet in figure 3. Antiferromagnetism and the Heisenberg ground state would make the diagonal bond a triplet. For the square there are only two spin-zero states, one with triplet diagonals and one with singlet diagonals. The hopping via Cu^+ excitations does not enjoy as large a sublattice magnetisation as the Heisenberg cluster, but it prefers the Heisenberg ground state to the other state. We have included the corresponding results for the high spin state for comparison, although the interpretation is different since the overall spin is not small and so the moments on the two sublattices do not *require* to be antiparallel. The comparison is more involved for the larger cluster because the Heisenberg interactions involve a reduced Néel moment due to quantum mechanical fluctuations. We have elected to calculate the *square of the total spin* on each of the two sublattices as a measure of the Néel order. In the absence of hopping, the small sublattice of three sites achieves 87.5% of the maximum possible value (3.75), whereas the large sublattice of four sites achieves 89.3% of the maximum value (6). The values of these unit normalised sublattice moments are plotted in figure 3, for the cases where the hole neighbours the central copper atom (denoted by a) and where the hole is on a square but not neighbouring the central copper atom (denoted by b). Ignoring the initial behaviour, which corresponds to the irrelevant crossing of two eigenstates, it is clear that the hopping is not inconsistent with a large local *unoriented* antiferromagnetic moment.

A second method of comparing the two correlations is to evaluate the overlap of

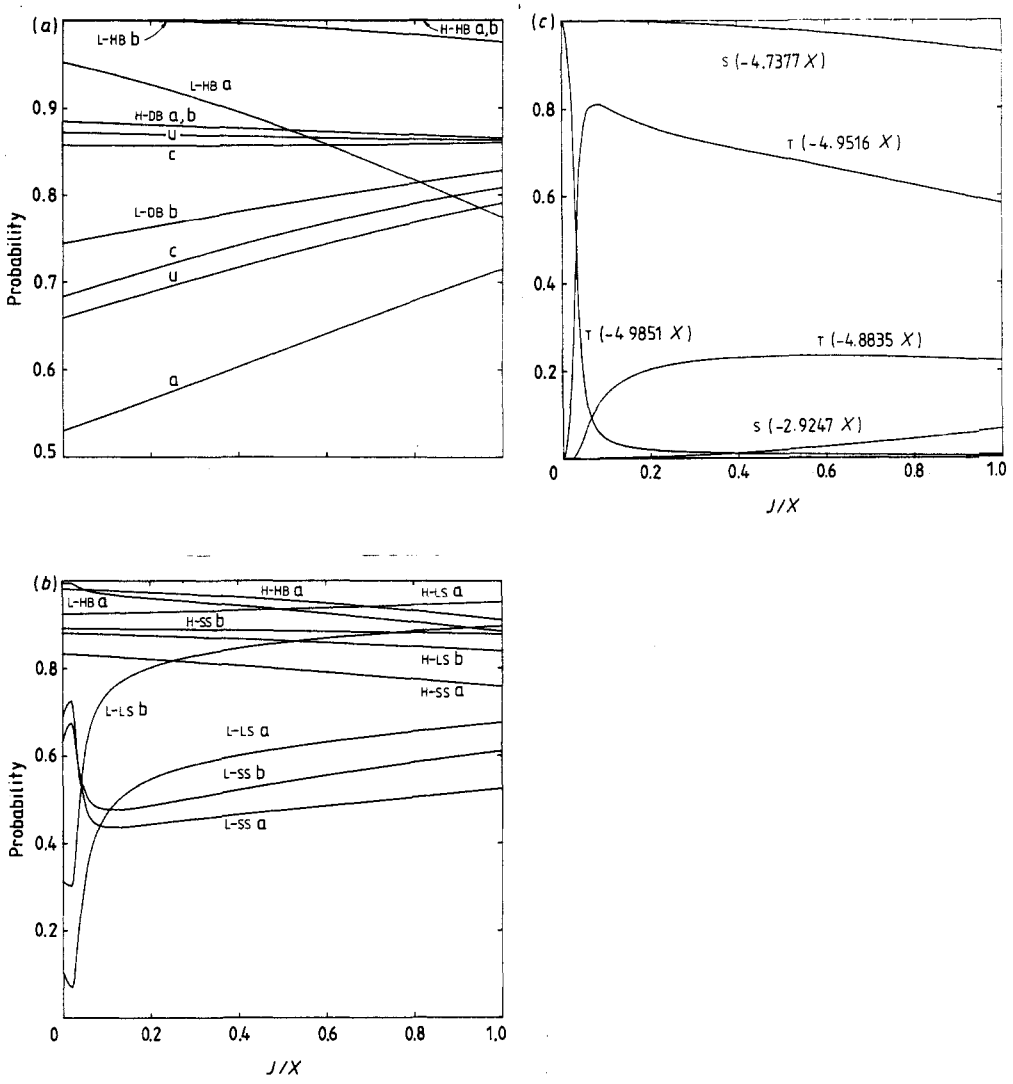

Figure 3. (*a*) Calculations of spin–spin correlation functions for the low (L) and high (H) spin ground states of the square. The curves marked u are unconditional probabilities, whereas the curves marked a–c are conditional on the position of the hole. If the hole is on a boundary oxygen the curve is marked c and if the hole is on a central oxygen the curve is marked a or b. The low spin state breaks rotational invariance and the curves a and b denote the two types of sites. We plot the probability that the two copper spins neighbouring the hole are in a triplet, denoted by HB (hole bond), and the probability that the diagonal bond is in a triplet, denoted by DB (diagonal bond). All the correlation functions are linear combinations of $\langle(\boldsymbol{S}_i + \boldsymbol{S}_{i'})^2 \sum_\sigma p^\dagger_{j\sigma} p_{j\sigma}\rangle$. All the bonds have strong triplet components suggesting the existence of both local *unoriented* Néel correlations and the ferromagnetic bond of Aharony *et al* [13] (and independently Emery *et al* [14]). (*b*) Calculations of spin–spin correlation functions which correspond directly to the calculations depicted in (*a*). The curves marked a and b are conditional on the hole residing on a neighbour to the central copper site and on one of the other oxygen atoms with two copper neighbours, respectively. There are three types of calculations: the probability that the two copper neighbours to the oxygen hole are spin triplet, denoted by HB (hole bond); the square of the total spin of the three spins along the diagonal of the cluster, normalised to unity and

Figure 3. (Continued) denoted by SS (small sublattice); the square of the total spin of the four spins which are nearest neighbours of the central copper site, normalised to unity and denoted by LS (large sublattice). After the initial 'transition', all the bonds have strong triplet character suggesting both local *unoriented* Néel correlations and the ferromagnetic bond neighbouring the hole for the low spin ground state. (*c*) The 'overlap probabilities' for the low spin states of our two clusters, denoted S (square) and T (two squares), respectively. The curves denote the breakdown of the ground state in the presence of the Heisenberg interactions, in terms of the low-energy low spin states for virtual Cu^+ hopping in the absence of the Heisenberg interactions. The energies of the states are included in parentheses, and it is clear that the second lowest state for the larger cluster has both *intrinsic* unoriented Néel fluctuations and is nearly degenerate with the hopping ground state. The virtual Cu^+ hopping and Heisenberg correlations are *not* locally in conflict.

the Cu^+ wavefunction with the ground state wavefunction of the problem with the Heisenberg correlations included. We depict the 'overlap probabilities' (namely, the squares of the overlap amplitudes) for our clusters in figure 3(*c*). For the square, even when the Heisenberg exchange parameter is *equal* to the hopping parameter, the ground state has a larger than 90% probability of being the ground state in the absence of the Heisenberg interactions. Since the exchange parameter in the experimental systems is probably much smaller than the hopping parameter, we conclude that the relevant hopping coherence in this limit will extend over at least a local square. For the larger cluster, we also plot the 'overlap probabilities', but for this case we consider the *two* lowest energy total spin singlet states, which are nearly degenerate for the Cu^+ limit (a difference of $0.033X$). It is clear that the second lowest energy state has a very low Heisenberg energy, and quite naturally describes *both* effects which are locally in sympathy. We will argue in the conclusion, that this is the basic reason for the dramatic destruction of Néel order in the simplest perovskite superconductor for only minor doping concentrations.

A second correlation which is of some interest is the spin coherence of the pair of copper spins which neighbour the hole. The exchange arguments of Aharony [13] and the hybridisation arguments of Emery [14] both suggest a local ferromagnetic correlation. The probability that the relevant pair of spins is in a triplet is a straightforward calculation and the result is plotted in figure 3. The local ferromagnetic correlations are clearly observed for both clusters.

The reduction in the triplet character of this bond, as J is increased, is somewhat spurious. We have included this bond in our Heisenberg term, although we know that the presence of the hole prohibits it. Some of the loss in Heisenberg energy can also be attributed to this unphysical inclusion, but the dominant behaviour is well represented by the model.

The relevance of these local high spin correlations is also doubtful. For the Cu^+ limit, the hole can be considered to play the role of an additional spin, and so the local spin structure may be considered 'locally compressed' with three copper spins being reduced to two copper spins and one oxygen spin. The main consequence of this idea, is that once the hole has moved on, the triplet correlations around the hole are left between *next* nearest neighbours, as the compression is released, and so correspond to local *antiferromagnetic* correlations in complete contradiction to the static picture, but in agreement with our calculations. This dynamic idea of considering the correlations once the hole has passed by, is much more relevant when the localisation length of the hole is larger than a lattice spacing, since the hole is only on one bond but the hole disturbs many bonds.

Finally in this section we analyse the correlations in our square cluster calculation

of the low spin states preferred by the hopping via Cu^+ excitations. We present a symmetrically chosen basis set in figure 4. The final basis states for each figure have a '+' hole whereas the first sets have a '−' hole. The ground state for each symmetry finds *all* the states which are connected between these two classes to be *anti-phase*. This is the dominant physical process which makes all such states have relative *singlet* spin correlations between the hole and its neighbouring spins. This is the input into the Zhang and Rice calculation [12]. The more subtle question relates to the spin correlations amongst the surrounding copper spins. The energies of the states in each of the four classes are $-4.7531t$, $-4.7377t$, $-4.1425t$ and $-4.4244t$, respectively.

The next most important contribution comes from the local triplet configurations. The best *ferromagnetic* state has antiferromagnetic phase coherence or is *non-bonding*.

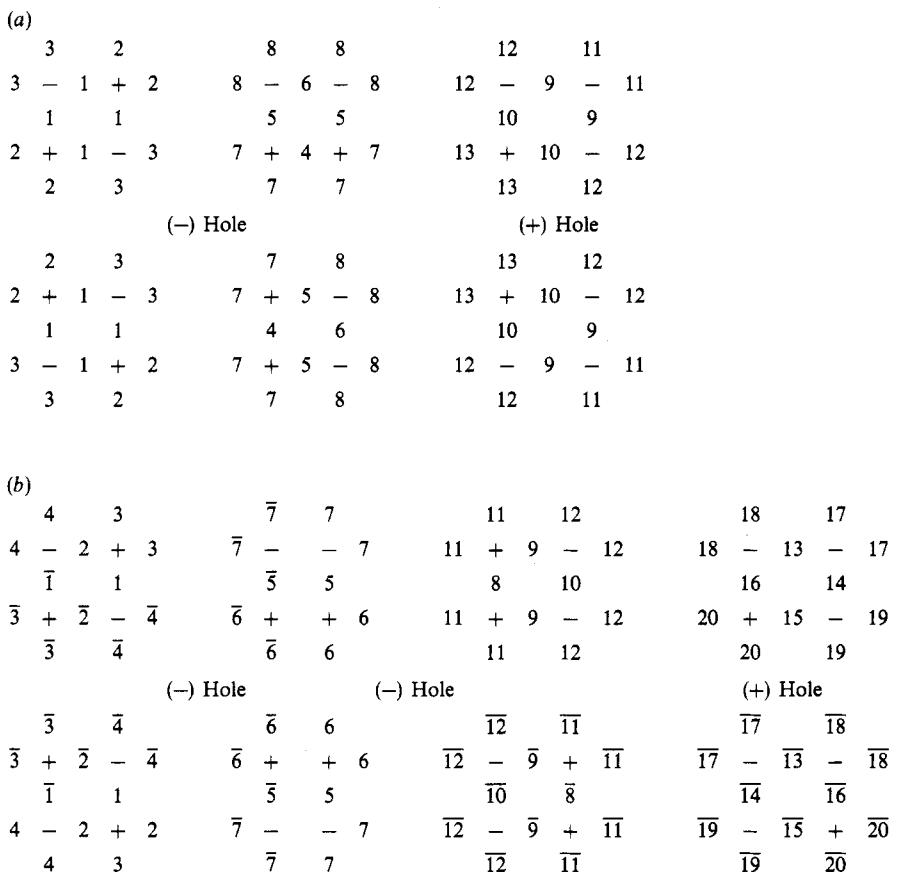

Figure 4. A pictorial representation of the states which make up the basis for our square cluster calculations. The copper spins are up or down, denoted by (+) and (−) respectively. The numbers denote the oxygen atoms on which the hole sits. 'Barred' numbers denote contributions with opposite phase. The 'blank' sites denote configurations which cannot be reached with the assumed phase coherence. (*a*) Uniform phase. (*b*) Phase corresponding to the non-interacting Fermi surface.

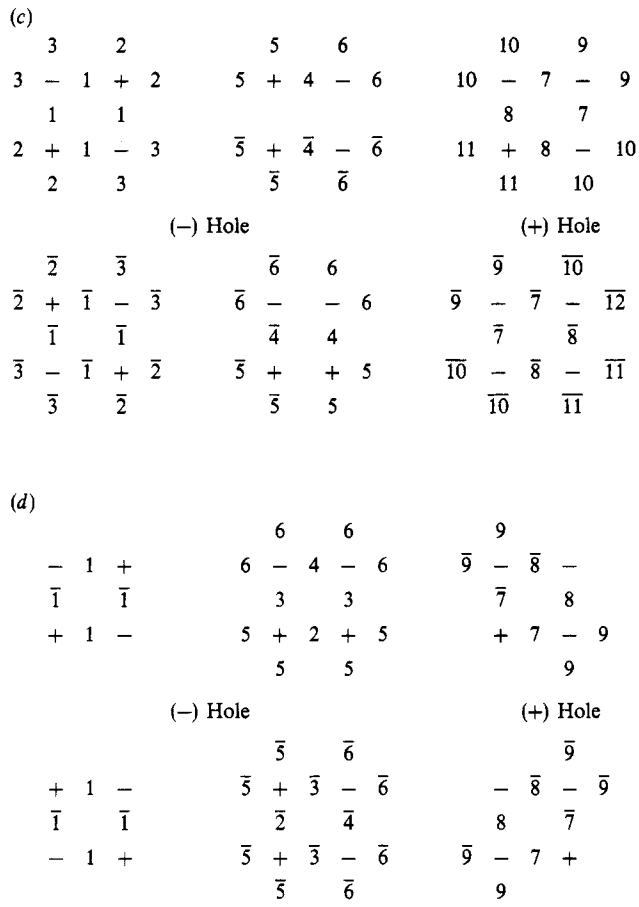

Figure 4. (Continued) (*c*) Néel ordering phase with the 'spinon' dominantly carrying the momentum. (*d*) Néel ordering phase with the 'holon' dominantly carrying the momentum.

Each copper atom has the holes with opposite phase on pairs of neighbouring oxygen atoms and so hopping across each copper site cancels. The states in figure 4(*b*) obviously optimise this contribution, while those in figure 4(*a*) ignore this contribution. Why then does figure 4(*a*) produce the ground state? Although the introduction of 'phase slips' enhances the non-bonding contributions, it also introduces *phase cancelling*. The configurations in figure 4(*a*) are symmetric whereas those in figure 4(*b*) have reduced symmetry because of the 'phase slips'. In the ground state the probability of finding the configuration 15 is negligible because the contributions from the left and right around the square destructively interfere! The corresponding states in figure 4(*a*) have higher energy but constructively interfere.

There is therefore a competition between introducing phases to optimise the hybridisation energy of the local hopping, and eliminating phases in order to fully delocalise the hole.

3. Paramagnetic correlations

In this section we are primarily interested in the low spin correlations induced by virtual Cu^+ excitations. The simplest analogous problem, which has so far been tackled in the literature, is the Nagaoka problem for the Hubbard model [9]. The basic result that Nagaoka deduced was that for most simple topologies the motion of a single charge carrier in an otherwise singly occupied lattice induces ferromagnetic correlations amongst the surrounding spins. He also showed that there is one special case where ferromagnetism is not to be expected, although he did not derive the coherence that would be expected. This special case is hole motion on a topologically frustrated lattice where the hopping matrix element is positive. An example of such a case is motion on the two-dimensional triangular lattice. Although the true ground state has never been found for this example, we believe that the ground state exhibits a form of the paramagnetism to be expected in our own Cu^+ limit.

One fruitful avenue in the study of the Nagaoka problem, was to study *loops* of atoms of different sizes. This study led, quite naturally, to an explanation for the topological problem and further gave an indication that the expected phase coherence for a lattice problem is likely to be similar to the coherence found in the smallest non-trivial loop. We will now proceed to an analysis of the corresponding loop problem for the present case in order to test the extent of the analogy.

We solve the loops depicted in figure 5. These problems are small enough to be exactly soluble and we have detailed the ground state energies of the two states introduced in the last section in table 1.

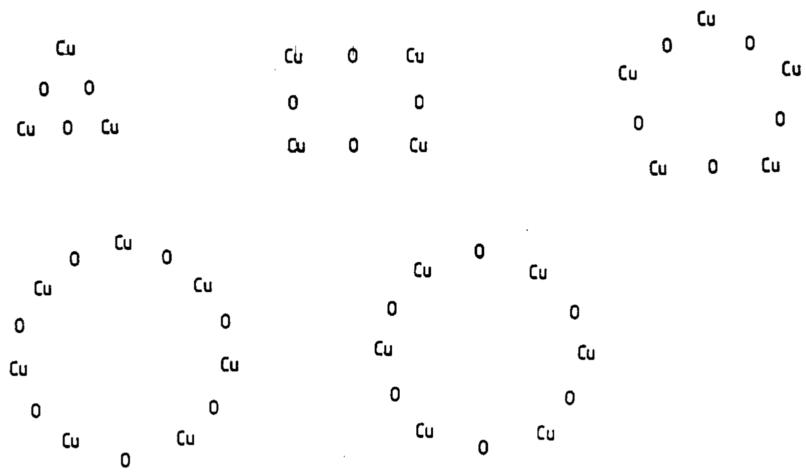

Figure 5. The loops which have been solved using exact diagonalisation.

For the bound magnon, there is an alternation in the energy, with the odd loops being more stable. The convergence to the infinite loop limit is fast, being effectively realised at the 'pentagon' level. When we compare this result to the Hubbard model, *we find completely opposite behaviour*. For the Hubbard model, the *even* membered loops are unfrustrated and are relatively stable. This is quite a surprising result, if we recall that in the Cu^{3+} limit, the strong-coupling d–p model with a single mobile hole maps onto the Hubbard model. Our result suggests that the effective topology is quite different in the two limits.

Table 1. The total energies of a single oxygen hole hopping around the loops of figure 5 by virtual Cu^+ excitations. The finite loops are solved by exact diagonalisation and the chain is solved variationally, as suggested by figure 7.

	High spin	Low spin
Triangle	−2.5616	−2.0000
Square	−2.4495	−2.6458
Pentagon	−2.4774	−2.9254
Hexagon	−2.4709	−2.8095
Heptagon	−2.4724	−2.8478
Chain	−2.4721	−2.8688

A careful analysis of the bound magnon in the Cu^+ limit, shows that the minimum number of intermediate states in a non-trivial path around a loop, is one more than the number of relevant sites in the loop. Although a hole can arrive at the original *site* by hopping across each atom in turn, the magnon must be moved from its original position in the process, and a further hop is required in order to replace the magnon. The minimum *effective* connectivity for the bound magnon problem is therefore one link larger than the ring size, with odd loops becoming effectively even, and the role of the topology being reversed from the Hubbard model. In the Cu^+ limit the role of the square loops is to *frustrate* the ferromagnetism that naive appeals to the Hubbard model would suggest.

This 'even into odd' idea is also related to the topological invariants of Thouless [15] and permeates low spin descriptions.

The low spin calculations on our loops show even more intriguing behaviour. At a first pass, the even and odd loops show quite different characteristics. This may be traced to the fact that even loops cannot achieve total spin-zero and therefore involve a 'spinon' as well as the hole. The even loops seem to tend monotonically towards the infinite loop limit.

The odd loops show oscillatory behaviour tending relatively slowly towards the infinite chain limit. The simplest understanding of this behaviour is in terms of resonating valence bonds [16], and in particular the resonating character. For odd loops, we may construct total spin singlet states, and in particular, states with all the copper holes paired up into nearest neighbour singlets with the final copper hole in a singlet with the oxygen hole which neighbours it. These states make up an excellent representation for the ground state. The oxygen hole has four hops open to it. Three of these hops can be chosen, with an appropriate choice of relative phases, to be negative hops onto other nearest neighbour valence bond states. The final hop is the problem.

At first sight it might be thought that, with a careful choice of spin configuration, even this final hop might be chosen to have negative phase, but this is in fact not possible. Two of the hops involve rearranging the spin configuration without moving the hole. Relative singlet configurations for neighbouring copper–oxygen pairs involve savings in energy while relative triplet configurations lead to a loss in energy. *A spin may not be simultaneously in a singlet with two other spins.* Indeed, the best simultaneous probability for the spin to be found in a singlet with each of the two other spins is three-quarters of the time each. Counting up the energies indicates that three hops is an absolute bound on the permissible ground state. A linear superposition of the valence bond states very nearly achieves this bound. Three of the hops are in phase and the final hop is fifty per cent relative singlet and fifty per cent relative triplet. If the relative

singlet hop were into another nearest neighbour singlet state *with a negative phase*, then we would achieve the bound, but once again this is not possible. At this point the resonating character of the superposition becomes important. An oxygen hole may be paired either to the left or to the right, and the relative phase of these two contributions in the superposition is crucial. For loops of length five, nine etc, the final hop takes the hole into a state which has a *negative* overlap with the resonating contribution, whereas for loops of length seven, eleven etc, there is a positive overlap. As the loop size diverges the overlap becomes exponentially small and so the alternating resonant contribution decreases with size, being maximal for the loop of five copper sites.

Although these arguments successfully explain the basic topological properties of the model, the experimental systems, with square connectivity, are members of the class which does not close at the one loop level, and so at this level are probably best represented by the infinite chain problem, where the resonating character of loops is avoided. Indeed, if we restrict attention to states where all bar the copper atom paired to the oxygen atom are paired up in nearest neighbour singlets, the smallest non-trivial topological loop involves *nine* copper sites and *twenty* hops to close.

The linear chain is depicted in figure 6. The state corresponding to Zhang and Rice [12] exists in a simplified form and we can easily solve the problem of a single short-range singlet moving around in a ferromagnetic background. We find that the singlet is basically one or two lattice spacings wide and the corresponding energy is $-2.4721X$ (satisfying $E^3 - 8XE^2 + 64X^3 = 0$).

The variational calculation which we believe leads to the low spin ground state, is also depicted in figure 6. The states are all orthogonal and the relevant Hamiltonian matrix for this basis is

$$H|\psi\rangle = \begin{bmatrix} -\frac{5}{2} & -\sqrt{\frac{3}{2}} & 0 & 0 & 0 & 0 & 0 & 0 \\ -\sqrt{\frac{3}{2}} & -\frac{1}{2} & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & \frac{3}{2} & -1 & 0 & -\frac{1}{2} & 0 & -\frac{1}{\sqrt{2}} \\ 0 & 0 & -1 & -\frac{1}{2} & -1 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & -1 & -\frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & 0 & -\frac{3}{2} & 1 & -\frac{1}{\sqrt{2}} \\ 0 & 0 & 0 & \frac{1}{2} & 0 & 1 & \frac{3}{2} & 0 \\ 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} |1\rangle \\ |2\rangle \\ |3\rangle \\ |4\rangle \\ |5\rangle \\ |6\rangle \\ |7\rangle \\ |8\rangle \end{bmatrix} \tag{3.1}$$

The background spin configuration is a *symmetry broken spin Peierls state*. The ground state is approximately three-quarters $|1\rangle$ and a quarter $|2\rangle$, with less than five per cent probability of being found in the other states. The ground state energy is approximately $-2.87X$ and is very stable when compared to the ferromagnetic state. Even the state $|1\rangle$ has a lower energy than the ferromagnetic state and with energy $-2.5X$, it contains the dominant low spin mechanism. Indeed for the case $U_p \mapsto \infty$ (a limit not previously considered in this article) this state becomes a ground state. The same basic ideas used for the loop problem apply to the present case, although for this case there is no resonating contribution and the 'extra hop' simply connects the state to a less useful spin configuration with a corresponding minor gain in hybridisation energy.

The state $|1\rangle$ is *three* times connected to itself in a relative singlet, then half connected to itself in a relative triplet, and half connected to $|2\rangle$. The corresponding ferromagnetic state is only connected to itself *twice* directly and the third connection for the state $|1\rangle$ is traced to a *valence bond* spin configuration in the copper spin

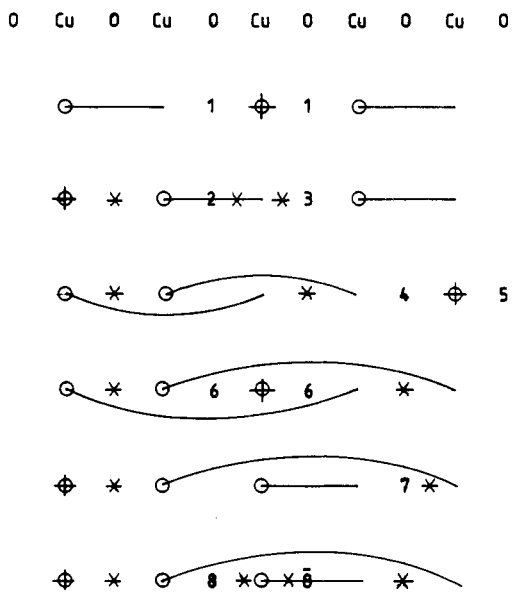

Figure 6. The linear chain geometry with maximal oxygen coordination, and a pictorial representation of our variational basis. The numbers denote the oxygen atoms on which the hole sits. 'Barred' numbers denote states with opposite phase. Pairs of sites connected by a line with an encircled end, correspond to local singlet configurations. All copper sites not depicted are paired up into nearest neighbour singlets. 'Starred' bonds, denoted by (*), denote linear combinations where the spins at the ends of the bond are averaged with respect to their interchange. This averaging ensures that the bond is locally triplet. The symbol + denotes the other end of a local singlet which includes the hole. The states as pictured are not normalised but are orthogonal.

background. The hole can move from a singlet based around one copper atom to a singlet based around another copper atom separated by *two* from the original. The background singlet configuration was originally between the final copper atom and the copper atom 'passed over'. This is the basic mechanism stabilising the low spin frustrated ground state and clearly it can only act on nearest neighbour *valence bonds*. The hybridisation into the state $|2\rangle$ simply enhances the probability that the hole is in a relative singlet with the other copper atom and is a minor contribution since all the states bar $|1\rangle$ connected to $|2\rangle$ have strong local triplet correlations.

We consider Heisenberg correlations on this topology, only in the present limit, because the spin configurations on the chain all remain degenerate under the action of the strong-coupling Hubbard model and so the Cu^{3+} limit is dull. The Heisenberg Hamiltonian on a one-dimensional chain has been solved [17] and does *not* yield the spin Peierls symmetry breaking. The spin correlations in the Heisenberg ground state are low spin but long range and so once again we might expect a modification in local correlations around the hole, but not a dramatic effect since both states are total spin-zero with a high probability of nearest neighbour bonds.

In figure 7 we picture a linear chain with maximum copper atom connectivity in order to estimate the linear chain contribution to the lattice problem. We must bear in mind that leaving out neighbouring *copper* atoms drops a self energy contribution and

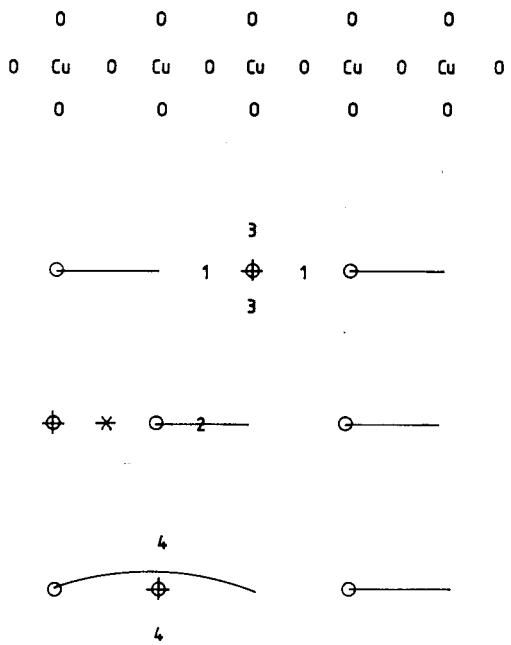

Figure 7. The linear chain geometry with maximal copper coordination, and a pictorial representation of *part* of our variational basis. The symbols have identical meaning to those in figure 6.

so the comparison is not direct.

The ferromagnetic state of Zhang and Rice [12] yields $-4.755X$ whereas the low spin state yields $-4.919X$. Once again the low spin ground state is well represented by only a few states and for this case the four states in figure 7 make up 99% of the ground state.

Although the relative stability is much reduced, the lattice ferromagnet state yields only $-5.324X$ and so the simple picture of a dominant direction of motion with parallel valence bonds and sophisticated 'phase slips' orthogonal to that direction is likely to be a fair representation for the low spin state on the lattice.

4. Conclusions

Our first, and perhaps most important, conclusion is that the Cu^+ limit of the strong-coupling d–p model is quite different in behaviour to the t–J model.

The largest energy scale in the strong-coupling limit is the hopping matrix element, although at low doping it does not lead to the largest energetic contribution, which comes from the Heisenberg interactions. For the Cu^{3+} limit of the d–p model, which has the same physics at the one particle level as the t–J model, this leads to a conflict of interests. Locally, the hole wants to see ferromagnetism around closed loop trajectories, while the dominant energy is the Heisenberg interaction which forces low spin Néel fluctuations further from the hole. *There is no similar conflict for the Cu^+ strong-coupling limit of the d–p model!*

The motion of the oxygen holes in this limit is topologically frustrated, and this induces low spin fluctuations amongst the background spins. The induced low spin

correlations are *not* in serious conflict with the Heisenberg interactions and, in the locality of the hole, readily coexist. From a practical point of view, the low spin correlations may be studied in isolation by analysing the hopping contribution alone. This obviates some of the more unpleasant problems inherent in studying the t–J model.

There is an important *experimental* consequence to the lack of local competition between the hopping and Heisenberg contributions. The long-range Néel order would be expected to be destroyed for very small concentrations of holes. Although at a local level the two low spin correlations coexist, the low spin motional coherence would not be expected to contain long-range Néel order. Since the motional state achieves most of the Heisenberg energy, the minor contribution associated with long-range Néel order can be lost for only a minor doping concentration. Another way to think about this effect is to use the idea of polarons. For one doped hole, the long-range Néel order will remain far from the hole. In the vicinity of the hole the local correlations will be more suitable for the motional contribution. Since the expected loss in Heisenberg energy is small, the region around the hole without the Néel order would be expected to be correspondingly large. Only a small concentration of such holes would then be required for the regions without Néel order to percolate, and the long-range Néel order would be lost. The corresponding argument for the Hubbard Hamiltonian finds the holes trying to instigate ferromagnetic coherence at a huge loss in Heisenberg energy. The polarons would be expected to be small, and the doping required to destroy the Néel order would be expected to be large.

For the simplest perovskite superconductors, *precisely* this behaviour is observed. When holes are doped into the La_2CuO_4 compound, the Néel order is destroyed remarkably quickly, whereas when electrons are doped into the Nd_2CuO_4 system, yielding a Hubbard model description, the Néel order is relatively stable, awaiting the metal–insulator transition before becoming lost.

A recent neutron scattering experiment seems to find a gap at low energies in the spin excitation spectrum [18]. The short-range singlet correlations induced by the hole motion in the Cu^+ limit of this article *require* such a gap. Although the spin-wave excitations for an antiferromagnet are expected to be gapless, the spin excitations for short-range resonating valence bond states have a gap.

Our final conclusion is that the topological effects in the strong-coupling limit of the d–p model are surprisingly subtle and worthy of further study.

Acknowledgments

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