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A theory of one and two holes in antiferromagnetic CuO_2

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Abstract. We consider a low density of positive charge carriers (holes on oxygen ions) interacting with magnetic degrees of freedom (spins on copper ions) in a single CuO_2 plane, assumed to be antiferromagnetic and electrically insulating. Analysing the interaction of a single hole with the spins, we find it to be a strongly coupled non-topological soliton carrying spin $\frac{1}{2}$. Various energies, spin correlations and overlap parameters are calculated and tabulated. Pairs of solitons are determined to be weakly coupled; hence we conclude *bi*-solitons to be an improbable species.

1. Introduction

There is by now conclusive evidence that the insulators La_2CuO_4‖ and $Y_1Ba_2Cu_3O_6$¶ contain two-dimensional spin-$\frac{1}{2}$ Heisenberg antiferromagnets. This is quite plausible, considering the existence of isolated layers of $Cu^{2+}(O^{2-})_2$ in these materials. Spins of individual electrons localised on Cu^{2+} interact antiferromagnetically via the (filled) oxygen orbitals, by the same mechanism ('superexchange') as in classic antiferromagnets such as MnF_2 [5]††. The insertion of a number of holes (charge carriers) in concentrations ρ ranging from less than 0.15 hole per CuO_2 unit in $La_{1.85}Sr_{0.15}CuO_4$ to as many as about 0.5 or 1 hole per CuO_2 unit in $Y_1Ba_2Cu_3O_7$ (depending on the valency assignments that one favours in these materials) eliminates this antiferromagnetism in favour of the spectacular, newly discovered [9, 10] high-T_c superconducting (HTS) phase. We wish to examine semi-quantitatively some of these features theoretically. This is facilitated by the observation that the very same physical parameters (the position of atomic levels ε, the strength of on-site Coulomb interactions U and the hopping matrix element (t) required in linear combination of atomic orbitals (LCAO) type band-structure calculation

‖ The *insulating* character of La_2CuO_4-based materials (hopping-type conductivity, etc) was noted in [1]. *Antiferromagnetism*, especially as relating to oxygen vacancies but also to strontium alloying, was noted in [2].

¶ The insulating antiferromagnetic phase of $Y_1Ba_2Cu_3O_{6-x}$ near $x \simeq 0$ was studied in [3]. The exchange parameter ($J \simeq 0.137$ eV) has been determined in [4].

†† See review on the topic of superexchange in [6]. Specific application to CuO_2 has been given in [7] and also in [8]. (Note that [7] contains some misprints, which are corrected in the present text.)

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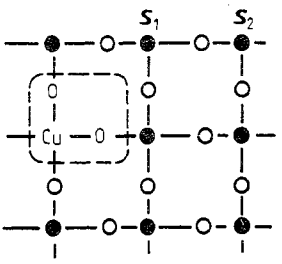

Figure 1. A portion of the CuO_2 plane, indicating the basic CuO_2 unit cell. In the *insulating antiferromagnetic* phase, oxygen ions (○) have a nominal valence of 2− (spin zero), and copper ions (●) a valency of 2+ (spin $\frac{1}{2}$). Neighbouring copper spins S_1 and S_2 are antiferromagnetically coupled (by 'superexchange' via the intervening oxygen), as in $H_{12} = JS_1 \cdot S_2$.

are also used in the calculation of the superexchange couplings. In the absence of a theory of superconductivity, we can at least attempt to examine the insulating phase quantitatively.

We indeed find solitons. Each hole effectively 'swallows up' one of the copper ion spins and affects a number of additional neighbouring links of the antiferromagnetic lattice. The spin correlations are computed and displayed in table 1 below. We also examine the ground state of 16 copper ion spins in the presence of two holes, by diagonalising a matrix of dimension 2^{18} (262,144). A spin- and space-dependent potential between holes is barely sufficient to cause them to bind; therefore, soliton pairs appear to have a marginal existence. Examining two-hole ground-state correlation functions, we find them to be oscillatory and spin dependent (see table 2).

Starting with Anderson's [11] RVB picture, a number of proposals have linked the suppression of antiferromagnetism to the HTS phenomena†. These include the formation of solitons, magnetic polarons or bipolarons, variously fermions or bosons, as precursor phenomena in the low-density limit. The present paper addresses numerically this issue directly. In the case of a single particle, semi-quantitative results *can* be obtained. Indeed, the magnetic polaron in a *ferro*magnetic semiconductor has long ago been solved exactly and in closed form [17], although vacuum fluctuations in the antiferromagnet render the problem considerably more complex.

We simplify the analysis by expressing all energies in the same units: $D \equiv U/4$ (U is the Coulomb energy parameter on copper ions). The remaining parameters are uncertain. We therefore allow for a range of values to achieve a reasonably complete theory. As a start, let us examine a single stoichiometric antiferromagnetic $Cu^{2+}(O^{2-})_2$ plane (illustrated in figure 1) into which the holes are subsequently to be injected.

2. The antiferromagnetic insulator

In the band-structure calculation for non-magnetic $Y_1Ba_2Cu_3O_7$ in [18], it was noted that a single 'hopping' matrix element $t = -1.85$ eV characterises the relevant O–Cu

† A review of early work linking suppression of antiferromagnetism to superconductivity has been given in [12]. The most recent arguments favouring this general approach ('. . . Evidence for the close connection between magnetism and high-temperature superconductivity is steadily mounting . . .') are briefly sumarised in [13]. However, the copper-free Ba–K–BiO_3 superconductors [14] provide counter-arguments favouring bipolaronic conductivity, according to [15] (see theory in [16]). Regardless of the merits of this explanation, it should alert one to the possible diversity of unusual mechanisms producing a high T_c.

overlap, while the respective (Hartree–Fock) orbital energies are equal at $\varepsilon_p = \varepsilon_d = -3.2$ eV relative to the Fermi level μ. Identical numbers have been used in the band-structure calculation [19] of La_2CuO_4; we need to extract the one-particle orbital energies from these data. Now, it is generally accepted that a substantial two-electron on-site Coulomb repulsion parameter U operates on the d electrons in copper ions, albeit, enormously reduced from $U \simeq 17$ eV for the same ion in vacuum [20], while the analogous Coulomb repulsion U_0 on the oxygen ions is generally considered to be negligible. Although we include both the following considerations, we shall observe that a large value of U_0 is incompatible with the established magnitudes of antiferromagnetic exchange.

In the absence of hopping, we extract the *one*-electron orbital energies (denoted e_d and e_p) from the restricted Hartree–Fock relations $\varepsilon_d = e_d + \frac{1}{2}U\langle n_d\rangle$ and $\varepsilon_p = e_p + \frac{1}{2}U_0\langle n_p\rangle$, using $\langle n_d\rangle \simeq 1$ and $\langle n_p\rangle \simeq 2$ (equivalent to a typical copper valency of about 2+ and assuming a typical oxygen valency of 2− to be operative in the LCAO calculations in [18] and [19].) With $\mu = 0$ and $\varepsilon = -3.2$, the one-electron orbitals lie at

$$\begin{aligned} e_p &= \varepsilon - U_0 \qquad (\text{oxygen } O^-) \\ e_d &= \varepsilon - U/2 \qquad (\text{copper } Cu^{2+}) \end{aligned} \tag{1a}$$

while the total energies of two electrons on each ion are

$$\begin{aligned} 2e_p + U_0 &= 2\varepsilon - U_0 \qquad (\text{oxygen } O^{2-}) \\ 2e_d + U &= 2\varepsilon \qquad (\text{copper } Cu^{+}). \end{aligned} \tag{1b}$$

If the CuO_2 unit cell were to contain six relevant electrons, then according to (1*b*) its energy would be $6\varepsilon - 2U_0$. However, it is generally believed to contain only five electrons. Removal of a single electron from one of the oxygen ions lowers the total energy by an amount ε. However, removal of a single electron from the copper ion also lowers the total energy, and by a greater amount $\varepsilon + U/2$. Thus, when there is a total of five electrons per cell, the energetically preferred valences are the familiar ones of elementary chemistry: 2+ for copper, and 2− for oxygen.

The antiferromagnetic exchange parameter J depends strongly on t and U and also depends somewhat on U_0. We shall consider the extreme instances, $U_0 = 0$ and $U_0 = \infty$. J is the coupling constant in the effective Heisenberg antiferromagnet

$$H_{AF} = J \sum_{i,j} \boldsymbol{S}_i \cdot \boldsymbol{S}_j \tag{2}$$

which describes the spin correlations between the copper ions. It can be calculated by considering a single pair of Cu^{2+} ions and the intervening O^{2-} ions, and comparing singlet and triplet energies up to $O(t^6)$. To leading order, $J \propto U(t/U)^4$; the next-higher-order contribution, $O(t^6/U^5)$, is given below. Although experiment [1–4, 21] favours J to be of the order of 0.1 eV $\simeq$ 1000 K for the insulating antiferromagnet, neither this parameter nor any other (t, the U-values or the ε-values) has ever been unambiguously determined, and presumably all vary from one oxide compound to the next. Such uncertainty requires us to examine a *range* of resonable values. Towards this end, we have found it convenient to define $g \equiv U^2/8t^2$, using $D = U/4$ to set the scale of energy and $1/g$ as the expansion parameter. Expressing the exchange constant in this notation, after some algebra [5–8] we find that in the two limiting cases,

$$J = D(3/g^2)(1 - 2/g) \qquad (\text{for } g \geqslant 2,\ U_0 = 0) \tag{3a}$$

and

$$J = D(1/g^2)(1 - 3/g) \qquad (\text{for } g \geqslant 3,\ U_0 = \infty) \tag{3b}$$

including all the $O(t^6)$ corrections. According to this, J vanishes for $g \leqslant 2$ ($U_0 = 0$) or $g \leqslant 3$ ($U_0 = \infty$), and also at $g = \infty$. Depending on U_0, it reaches its maximum J_{max} at an intermediate value of g:

$$J_{max} = 0.1111D \qquad \text{at } g = 3 \qquad (U_0 = 0) \tag{4a}$$

or

$$J_{max} = 0.0165D \qquad \text{at } g = 4.5 \qquad (U_0 = \infty) \tag{4b}$$

ultimately decreasing as g^{-2} at large g. We use equation (4*b*) to rule out $U_0 = \infty$ (or indeed *any* large value), simply because it causes the corresponding J_{max} to be too low. (For J to assume the value of 0.1, equation (4*b*) requires that $D > 6$ and hence $U > 24$, which is half an order of magnitude too high!) It follows that $U_0 \ll U$ is a better approximation than $U_0 \gg U$.

The mapping onto the Heisenberg model and the accuracy of equation (3), are only ensured for $g > 3$. In the weak-coupling region $g < 2$, it is reasonable to expect some sort of Landau Fermi liquid theory to be appropriate while, in the intermediate-coupling range, *no* systematic expansion is expected to be valid in general. The present paper is predicated on the validity of the Heisenberg mapping and hence on strong coupling; both are suggested by experiment [1–4, 21].

The two-dimensional Heisenberg $s = \frac{1}{2}$ antiferromagnet of equation (2), with J given in equation (3), has a ground state, denoted $|\mathrm{AF}\rangle$ and ground-state energy $E_{AF} = -NJe_{AF}$ (where N is the number of CuO_2 cells and $e_{AF} = 0.672$ [22]). This state is non-degenerate, has total spin zero, is translationally invariant and has the point group symmetry of the square lattice on which the copper ions are disposed. From this antiferromagnet with $5N$ electrons, we shall now abstract a *single* electron, i.e. create *one* hole.

3. One hole: plane-wave states

The reader can easily verify that in creating a hole, the energetics of equations (1) *always* favour removal of the electron from the O^{2-} bonds of the antiferromagnetic insulator rather than from the Cu^{2+} itself. (This was first suggested in [23] and subsequently confirmed by a number of data [24] showing Cu^{3+} to be a *rara avis* compared with O^-.) Because the lattice and the antiferromagnetic state are both translationally invariant, the resultant hole can be present on *any* bond, e.g. the reference bond indicated in figure 2. If we label by i_1 and i_2 the two copper spins bridged by the bond at $\boldsymbol{R}_i$, and use the Kronecker δ-notation ($\delta(\boldsymbol{R} - \boldsymbol{R}_i) = 1$ if the hole coordinate $\boldsymbol{R}$ is at $\boldsymbol{R}_i$, and $\delta(\boldsymbol{R} - \boldsymbol{R}_i) = 0$ otherwise) the total Hamiltonian governing hole plus spins is

$$H = H_{AF} + H_{hop} - J\sum_i \boldsymbol{S}_{i_1} \cdot \boldsymbol{S}_{i_2}\delta(\boldsymbol{R} - \boldsymbol{R}_i) + J'\sum_i (\boldsymbol{S}_{i_1} + \boldsymbol{S}_{i_2}) \cdot \boldsymbol{\sigma}\delta(\boldsymbol{R} - \boldsymbol{R}_i) \tag{5}$$

in which σ is the hole's Pauli spin operator. This Hamiltonian contains two principal perturbations, proportional to J and J', respectively. J' can be estimated by comparing the singlet and triplet energies of a single $[Cu^{2+}O^-]$ pair. The singlet is *always* preferred, and hence $J' > 0$. To leading orders in $1/g$, we find after some algebra [5–8] that

$$J' = D(2/g)(1 - 1/g) \qquad (U_0 = 0) \tag{6a}$$

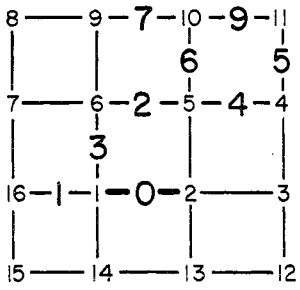

Figure 2. Singling out one (oxygen) bond at $\boldsymbol{R}_0$ (——) and numbering the other bonds **1**, **2**, **3**, . . . and the sites 1, 2, 3, . . . for future reference.

and

$$J' = D(1/g)(1 - 1/2g) \qquad (U_0 = \infty). \tag{6b}$$

J' exceeds J by a factor $8g/3$ (if $U_0 = 0$) and by an even greater factor if $U_0 > 0$; thus, it is always an order of magnitude larger than J. In a plane-wave state, the hole has an equal probability of $1/2N$ to be on each bond. Taking the expectation value in any plane-wave state for the hole, we obtain an effective spin Hamiltonian $\mathcal{H}$ in first-order perturbation theory:

$$\mathcal{H}_{\mathrm{AF}} = E_{\mathrm{hop}} + (1 - 1/2N)H_{\mathrm{AF}} + (J'/N)\boldsymbol{\sigma} \cdot \mathbf{S}_{\mathrm{T}}. \tag{7}$$

The last term $\boldsymbol{S}_{\mathrm{T}} \equiv \Sigma_i \boldsymbol{S}_i$ is the total spin operator, all components of which are identically zero in the ground state of H_{AF}. Thus the energy of $\sigma_z = \uparrow$ is the same as for $\downarrow$, as might be expected in view of the singlet ground state. The $1/2N$ multiplicative correction to H_{AF} amounts to an energy cost of breaking one antiferromagnetic bond, precisely $Je_{\mathrm{AF}}/2$. It must be included in the hole's total energy $e(\boldsymbol{k})$. Adding all the contributions up to second order in the perturbation theory, and measuring the hole's energy from $-\varepsilon$, we find that

$$e(\boldsymbol{k}) = -W(4\kappa^2\varphi_k^2) + Je_{\mathrm{AF}}/2 - \delta E_k(J'^2/W). \tag{8}$$

W is the eigenvalue of the hopping Hamiltonian:

$$W(4\kappa^2\varphi_k^2) = [(U/4)^2 + 4\kappa^2 t^2 \varphi_k^2]^{1/2} - U/4 = D[(1 + 8\kappa^2\varphi_k^2/g)^{1/2} - 1] \tag{9}$$

where $\varphi_k^2 \equiv \cos^2(k_x/2) + \cos^2(k_y/2)$. As hole diffusion takes place via the copper ions, the factor κ^2 takes into account the parallelism (or lack thereof) of the spin on the copper ion to that of the hole. In the absence of any correlation between the spin of the hole (here *specified* as $\sigma_z = \uparrow$ or $\downarrow$) and the spins on the copper ions, in the antiferromagnetic state the probability that a given copper ion has the appropriate spin orientation is $\frac{1}{2}$; hence $\kappa^2 = \frac{1}{2}$ precisely.

The term indicated as $\delta E_k(J'^2/W)$ is the second-order contribution of virtual magnon emission–absorption, obtainable from (5) To estimate this self-energy contribution to the $\boldsymbol{k} = \mathbf{0}$ state, one ignores the magnon energies in the energy denominator $\mathrm{d}(\boldsymbol{q})$ (the electronic excitations are $\mathrm{O}(1/g)$ whereas the magnon excitations are $\mathrm{O}(1/g^2)$) and uses completeness to reduce the spin matrix elements to a ground-state expectation value:

$$\delta E_0\left(\frac{J'^2}{W}\right) = -J'^2(\tfrac{3}{2})\sum_q \frac{n^2(\boldsymbol{q})}{d(\boldsymbol{q})}\langle \mathrm{AF}|\frac{1}{N}\left|\sum_i \exp(i\boldsymbol{q}\cdot\boldsymbol{R}_i)S_i^z\right|^2|\mathrm{AF}\rangle \tag{10}$$

with $n^2(\boldsymbol{q}) = [\cos(q_x/2) + \cos(q_y/2)]^2$ and $d(\boldsymbol{Q}) = W(2\varphi_0^2) - W(2\varphi_q^2) \simeq (2D/g)(2 - \varphi_q^2)$, after setting $\kappa^2 = \frac{1}{2}$. Further approximating $n^2(\boldsymbol{q})$ by its average over the Brillouin zone, $\langle n^2(\boldsymbol{q})\rangle = 1$, and similarly for $\langle d(\boldsymbol{q})\rangle = 2D/g$, we can evaluate

$$N^{-2} \sum_q \langle \mathrm{AF}| \left| \sum_i \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}_i) S_i^z \right|^2 |\mathrm{AF}\rangle = \tfrac{1}{4}.$$

With substitution of J' (equation (6*a*)), the final result to leading orders in $1/g$ is approximately

$$\delta E_0(J'^2/W) \simeq -D(3/4g)(1 - 2/g). \tag{11}$$

(Had equation (6*b*) been used instead of (6*a*), this contribution would have been reduced by a factor $\frac{1}{4}$. Had we retained ground-state spin correlations $\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j\rangle$, which are negative for (i, j) nearest neighbours, it would have been further reduced.) However small it appears here, the magnon emission–absorption interaction *is* nevertheless of potential interest in the HTS phenomenon (in so far as *two* travelling waves can conceivably exchange a magnon, possibly binding into a Cooper pair), but further elaboration is beyond the scope of the present investigation. In summary, the energetically most favoured state of a free hole lies at $\boldsymbol{k} = \boldsymbol{0}$ (at the bottom of the plane-wave continuum of energies) and has an energy that we have estimated to be

$$\begin{aligned} e(\boldsymbol{0}) &= -D[(1 + 8/g)^{1/2} - 1 - 3e_{\mathrm{AF}}/2g^2 + 3/4g - 3/2g^2] \\ &= -D[(4 + \tfrac{3}{4})/g + \mathrm{O}(1/g^2)] \end{aligned} \tag{12}$$

(as measured from $-\varepsilon$). The leading terms are the motional energy $4/g$ and the virtual magnon emission contribution $3/4g$ to the self-energy. Corrections to the latter and to the energy of the broken antiferromagnetic bond each contribute in the next order $\mathrm{O}(1/g^2)$ of the $1/g$ expansion.

4. One hole: soliton states

We now compare the energies of free-particle states with those of better-localised, i.e. strong-coupling states. There are several consequences of localisation, notably the antiferromagnetic bond on which the hole principally resides disappears, becoming essentially ferromagnetic, the ground state of the now-frustrated spin system is altered from the original antiferromagnetic ground state $|\mathrm{AF}\rangle$ owing to the presence of this anomalous bond, and the hopping parameter t is reduced to $t\lambda^{1/2}$, where $\lambda < 1$ is an overlap parameter. By way of compensation, however, κ^2 is simultaneously *increased*, rising from its original value of $\frac{1}{2}$ to $\frac{3}{4}$ ultimately at large g, owing to enhanced correlation between the spin of the hole and that of its neighbouring copper ions. As a second consequence of this enhanced correlation at large g, the hole loses its individual spin (but not its charge), as does one of the two neighbouring copper ions; however, the complex as a whole retains spin $s = \frac{1}{2}$.

Additionally, the effective geometry for antiferromagnetism is now locally frustrated as this composite lies at the apex of two triangles as shown in figure 3. The soliton ultimately consists of this entity, hopping from bond to bond, in a wavepacket state.

We examine each consequence of strong coupling in turn. Figure 2 singles out a bond and labels its nearest neighbours for future reference. If, at first, the hole is localised on the bond at $\boldsymbol{R}_0$ without being permitted to hop, its interaction with two neighbouring

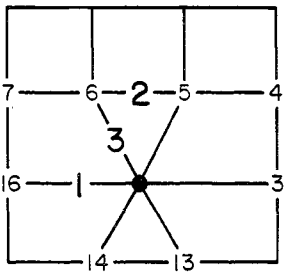

Figure 3. At large g', the bond occupied by a hole effectively disappears. The unpaired electron on the oxygen bond ($\boldsymbol{R}_0$) and those on the two neighbouring copper bonds (sites 1 and 2 in figure 2) combine into a new effective spin $\frac{1}{2}$, shown as a full circle in this figure. Like all other vertices, it represents a spin $\frac{1}{2}$ interacting antiferromagnetically with neighbouring spins connected by a line (e.g. bonds **1** and **3**) all with exchange parameter J. For $g' \equiv J'/J > 4$, this localised holes has energy $\Delta E(J, g') = J(1.82 - g')$ relative to the perfect antiferromagnet illustrated in figure 2. Note that two squares are effectively transformed into triangles and thereby 'frustrated'.

copper ions involves just two terms from equation (5). We write the relevant Hamiltonian as $H = H_{AF} + H_{int}$, with

$$H_{int}(\boldsymbol{R}_0) = -JS_1 \cdot S_2 + J'(S_1 + S_2) \cdot \boldsymbol{\sigma}. \tag{13}$$

Although not identical, the two perturbations (in J and in J') are similar, in that both tend to force S_1 and S_2 into parallelism.

The new ground-state energy is given by $E_{AF} + \Delta E(J, J')$, with ΔE remaining to be calculated. Before doing so, we obtain upper and lower bounds to ΔE. For the upper bound, start by 'cutting' the six bonds which connect S_1 and S_2 to S_3, S_5, S_6, S_{13}, S_{14} and S_{16} (see figure 2) and thus to the rest of the lattice, at a cost not exceeding $3e_{AF}$; then add $Je_{AF}/2 - J'$, the ground-state energy of $H_{int}(\boldsymbol{R}_0)$. For a lower bound, we simply add the ground-state energies of H_{AF} and of $H_{int}(\boldsymbol{R}_0)$. Consequently,

$$7Je_{AF}/2 - J' > \Delta E(J, J') > Je_{AF}/2 - J'. \tag{14}$$

Over the range $J' > 4J$, our *calculated results* are found to lie on a straight line and to be adequately represented (to % accuracy) by a simple formula

$$\Delta E(J, g') = J(1.82 - g') \tag{15}$$

with $g' \equiv J'/J$, where 1.82 can be written $5.4e_{AF}/2$, showing (15) to lie rather closer to the upper bound (in which the soliton is magnetically decoupled from the rest of the lattice) than to the lower. However, is J' in the stated range greater than $4J$? Comparison of (6*a*) and (3*a*) shows that $g' \equiv J'/J = 8g/3 + 8/3 + O(1/g) \geqslant 10$ for all $g > 3$. Even at the opposite extreme, had we chosen (6*b*) and (3*b*) instead, the ratio $g' = g + 5/2 + O(1/g) \geqslant 7$ for all $g > 4.5$. Thus, for *any* admissible scenario, the simple formula (15) is sufficiently accurate.

With the defective bond located at $\boldsymbol{R}_0$, the magnetic ground state of $H_{AF} + H_{int}(\boldsymbol{R}_0)$, hereafter denoted $|g', \boldsymbol{R}_0\rangle$, has lost the translational invariance of the former ground state $|AF\rangle$. In calculating the hopping of the hole from $\boldsymbol{R}_0$ to a neighbouring bond located at $\boldsymbol{R}_i$, it is necessary to take this feature into consideration. Towards this end, we calculated overlaps $\lambda(\boldsymbol{R}_i, \boldsymbol{R}_0) \equiv \langle g', \boldsymbol{R}_i | g', \boldsymbol{R}_0\rangle$, as plotted in figure 4 where $\boldsymbol{R}_i$ is one of

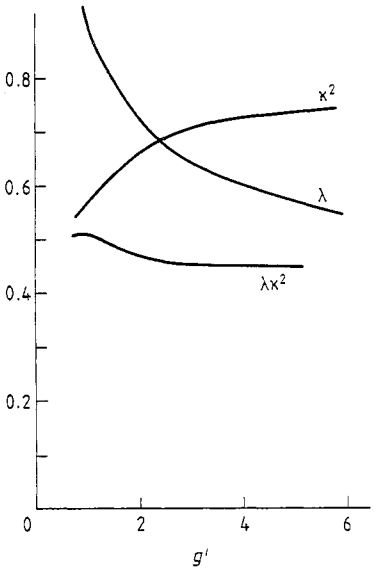

Figure 4. Overlap parameters λ, κ^2 and $\lambda\kappa^2$ as functions of $g' = J'/J$.

two ostensibly inequivalent neighbour sites of $\boldsymbol{R}_0$ (labelled $i = 1, 3$ in figure 2.) In so far as λ is not zero, allowing the particle to hop lowers its energy.

In the course of its motion, this composite transports a positive charge, a spin $\frac{1}{2}$ and a distortion in the surrounding spins along with it; we use the generic title 'soliton', in the non-topological sense for the composite moving particle. Owing to a subtle underlying symmetry, we *always* obtain $\lambda_1 \equiv \lambda_3$; therefore the soliton's band structure is $W(4\kappa^2\lambda\varphi_k^2)$, identical *in form* with that of the free hole studied earlier. At arbitrary $\boldsymbol{k}$, when measured from $-\varepsilon$, the soliton's energy is

$$e_{\mathrm{sol}}(\boldsymbol{k}) = -W(4\kappa^2\lambda\varphi_k^2) + \Delta E(J, g') \tag{16}$$

with W the function previously defined in equation (9) and the calculated ΔE given in (15).

The effects on W of the interactions are characterised by λ (which we find to drop from a maximum of about unity at small g' to an asymptotic value of about 0.4775 at large g') and by κ^2 (which, as we shall see, increases with g' from a starting value of about 0.5 to a theoretical maximum of 0.75). Because the spin orientation of the hole cannot be specified, owing to its interactions with both its copper neighbours, the correct expression for κ^2 differs from that of the free hole (with its specified $\uparrow$ or $\downarrow$ spin orientation) treated previously. In the present instance, it is given by

$$\kappa^2 = \tfrac{1}{4} - \langle g', \boldsymbol{R}_0 | \boldsymbol{\sigma} \cdot \boldsymbol{S}_1 | g', \boldsymbol{R}_0 \rangle \tag{17}$$

where S_1 refers to the spin of either of the copper ions neighbouring the hole at $\boldsymbol{R}_0$. The computed quantities λ, κ^2 and $\lambda\kappa^2$ are displayed in figure 4 as functions of g'. In strong coupling, the hole correlates strongly with *both* its neighbours, with $\langle \boldsymbol{\sigma} \cdot \boldsymbol{S}_1 \rangle$ reaching its theoretical limit of $-\frac{1}{2}$ (in the ground state of equation (13)) at large g'.

The very existence of the soliton hinges on whether the enhanced magnetic interaction energy overcomes a possible loss in motional energy compared with the free hole

Table 1. Ground-state *hole–spin* correlations $\langle g', \boldsymbol{R}_0|\boldsymbol{\sigma}_0 \cdot \boldsymbol{S}_i|g', \boldsymbol{R}_0\rangle$ in both weak- and strong-coupling limits for the hole at $\boldsymbol{R}_0$ and copper ion spins at i (vertices shown in figure 2).

	$\langle g', \boldsymbol{R}_0|\boldsymbol{\sigma}_0 \cdot \boldsymbol{S}_i|g', \boldsymbol{R}_0\rangle$	
i	$g' \equiv J'/J = 1$	$g' = 5$
1, 2	−0.3220	−0.4830
3, 5, 6, 13, 14, 16	+0.0023	+0.0218
4, 7, 9, 10, 12, 15	−0.0540	−0.0257
8, 11	−0.0217	−0.0004

discussed earlier. The optimal soliton energy, at $\boldsymbol{k} = \boldsymbol{0}$, is

$$e_{\text{sol}}(\boldsymbol{0}) = -D[(1 + 16\lambda\kappa^2/g)^{1/2} - 1 - 1.82 \times 3/g^2 + (2/g)(1 - 1/g)]$$
$$= -D[(8\lambda\kappa^2 + 2)/g + O(1/g^2)]. \tag{18}$$

Comparison of the leading-order terms here with the equivalent in (12) indicates the soliton to be stable relative to the free hole provided that $8\lambda\kappa^2 + 2 > 4.75$, i.e.

$$\lambda\kappa^2 > 0.344. \tag{19}$$

Using the data in figure 4, we obtain $\lambda\kappa^2 = 0.5116$ at $g' = 1$, amply satisfying (19). Although $\lambda\kappa^2$ decreases with the increasing g', even at $g' = 20$ (with κ^2 and λ at their asymptotic limits of 0.75 and 0.4775, and $\lambda\kappa^2 = 0.3581$), it still satisfies the criterion (19) by a margin of some 4%. Our conclusion is that the single *soliton always has a lower total energy than the free-hole state*.

In an attempt to throw some additional light on the nature of the solitonic state, we also computed the correlations between the hole (at $\boldsymbol{R}_0$) and its neighbouring copper ion spins (light-faced numerals in figure 2). Table 1 lists the results in both weak- and strong-coupling limits; as might be expected, the correlations are small but long ranged at $g' = 1$ and are close to asymptotic (i.e. $-\frac{1}{2}$ for $i = 1, 3$ and about 0 for all other spins) already at $g' = 5$.

5. Bi-soliton: bound or unbound?

In two dimensions, all purely attractive potentials bind in principle. However, we now find that the *optimal* attraction between two solitons to be $O(J)$ rather than $O(J')$ or $O(D)$. The heretofore neglected hole–hole repulsion U_0 might then be sufficient to prevent a bound bi-solitonic state from being realised. Table 2 includes the calculated interaction energy $V(\boldsymbol{R}_0 - \boldsymbol{R})$ of two localised holes. Although attractive, its magnitude never exceeds about $1.2\,J \simeq 3.6\,D/g^2$ over the entire range of g. In comparison with the energy W of translation and the hole–hole repulsion U_0 such an interaction is too small for us to come to any favourable conclusion concerning its possible bound states.

In performing these calculations, we localised one hole at $\boldsymbol{R}_0$ and the other at $\boldsymbol{R}_i$ (bold numerals in figure 2). While the total ground state (spin plus holes) is *always* found to be a singlet for an even number of sites, the two holes may have their spins parallel or anti-parallel on average, depending on their separation. If separated by an odd number of copper ion sites we find them to be parallel; if separated by an even number of copper

Table 2. *Two-hole* ground-state interaction energies $V(\boldsymbol{R}_0, \boldsymbol{R})$ and spin correlations $\langle \boldsymbol{\sigma}_0 \cdot \boldsymbol{\sigma}_R \rangle$ in both weak- and strong-coupling limits. One hole is at $\boldsymbol{R}_0$ and the second at $\boldsymbol{R}$ (as shown in bold numerals in figure 2).

	$g' \equiv J'/J = 1$		$g' = 5$	
$\boldsymbol{R}$	$\langle \boldsymbol{\sigma}_0 \cdot \boldsymbol{\sigma}_R \rangle$	$V(\boldsymbol{R} - \boldsymbol{R}_0)$	$\langle \boldsymbol{\sigma}_0 \cdot \boldsymbol{\sigma}_R \rangle$	$V(\boldsymbol{R} - \boldsymbol{R}_0)$
1, 3	+0.2331	$-0.93092J$	+0.1743	$-1.14844J$
2	−0.4361	$-0.87835J$	−0.1030	$-1.09968J$
4	−0.3357	$-0.83513J$	−0.0732	$-0.95193J$
6	−0.4846	$-0.69023J$	−0.0474	$-0.72413J$
7	+0.2261	$-0.56771J$	+0.0754	$-0.43100J$
5, 9	+0.2289	$-0.49276J$	+0.0693	$-0.36962J$

sites, they are anti-parallel. (The sign of the ground-state correlation function appears to be exactly the same as in the corresponding Néel state, the ground state of the Ising antiferromagnet, although the magnitudes are quite different. In fact, the Ising model† provides a helpful guide to some of the results reported here.)

Because the ground state of N copper spins plus two holes is a global singlet, the *individual* spins of the two holes *cannot* be specified. If, nevertheless, it were desirable to eliminate the background of copper ion spins in favour of an effective two-body potential connecting the two holes, this potential would have to take an unusual spin-dependent form. For, if the spins of the two solitons were *maintained* parallel, their interaction would be attractive for nearest neighbours but repulsive at next-nearest-neighbour positions. Conversely, if the spins were artificially maintained anti-parallel, in a relative singlet the interaction of the two solitons would be repulsive at the nearest-neighbour sites and attractive at next-nearest-neighbour positions. Thus the simplest possible effective interaction between two solitonic holes takes the form

$$V(1, 2) = v_0(R_{12}) + \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 v_1(R_{12}) \tag{20}$$

with both v_0 and v_1 oscillatory, decreasing functions of distance, which do not exceed $O(J)$ at their maximum magnitude.

6. Summary

In summary, in this paper it has been demonstrated that carriers introduced into the insulating phase of CuO_2 planes are positively charged, strongly coupled entities, living on the oxygen ligands and carrying spin $\frac{1}{2}$. The self-energy and band structure of these soliton entities have been determined in equation (16).

Because of the relatively extended spin cloud surrounding each carrier (see table 1), the mean-free path (owing to scattering by magnetic defects, thermal fluctuations in the underlying antiferromagnet and other inhomogeneities) is expected to be relatively short. This is in accord with the hopping-type conductivity characteristic of, and observed in [1–4], the insulating phase. We have also determined that *pairing* of such solitons in the low-density phase is not particularly favoured, but neither is it definitely ruled out.

† The critical density ρ_0 can be estimated by assuming that seven bonds are affected by each hole (cf figures 2 and 3); thus all bonds are affected when $\rho \approx \frac{2}{7} \approx 29\%$. The exact solution of the appropriate two-dimensional Ising model yields 28.3%, in close agreement with this estimate [25].

At a higher carrier density a non-magnetic metallic phase is known to replace the antiferromagnetic phase. The conditions for this to occur are amenable to analysis [25]. However, examination of this metallic phase, and of its possible superconducting properties, lies outside the purview of the present calculations.

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