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LETTER TO THE EDITOR

Low-energy magnetic excitations in $La_2Cu_{0.5}Li_{0.5}O_4$

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Abstract. Recent experiments have revealed a magnetic excitation with an unexpectedly low energy of ∼130 meV in $La_2Cu_{0.5}Li_{0.5}O_4$. Having noticed that the effective oxygen–oxygen hopping t_{pp} is driven to be *positive* by the surrounding Li ions with s orbitals, we employ a three-band Peierls–Hubbard model with inhomogeneous Hartree–Fock and random-phase approximations and show that this low-energy magnetic excitation can be due to the local triplet–singlet transition in a novel 'spin–Peierls' phase where one half of the CuO_4 clusters carry spin, while in the other half spin is quenched. Exact diagonalization of an isolated CuO_4 cluster with a positive t_{pp} further supports this assignment.

A comprehensive understanding of the doped-hole state in the cuprates is of fundamental importance for further studying the normal state behaviour of the layered cuprate oxides, the melting of strong broken-symmetry ground states and the mechanism leading to superconductivity [1, 2]. In the cuprates, doped holes are believed to reside primarily on oxygen $2p_\sigma$ orbitals rather than on the Cu $d_{x^2-y^2}$ orbitals. Zhang and Rice proposed in particular that the doped hole forms a local singlet state which involves a phase coherent combination of the $2p_\sigma$ orbitals of the four nearest-neighbour oxygens [2]. Although the concept of the Zhang–Rice singlet has been widely adopted in doped cuprates, the direct experimental evidence for the existence of this singlet, and the measurement of its excitation in high-T_c superconducting oxides, are still a major challenge because of the difficulty of identifying the magnetic behaviour of such a singlet in a background of antiferromagnetically correlated copper moments. Substitution of Li for Cu in $La_2Cu_{1-x}Li_xO_4$ appears to provide a good opportunity to experimentally study the doped-hole state [3–6]. In particular, at $x = 0.5$, crystallography indicates that the Li and Cu ions form an ordered superlattice in which all Cu ions are surrounded by four in-plane Li ions. Thus each individual CuO_4 plaquette is essentially isolated, carrying an extra hole doped from adjacent Li ions [3, 4]. Recently, Yoshinari *et al* reported a Cu nuclear quadrupole resonance (NQR) measurement for the hole state in $La_2Cu_{0.5}Li_{0.5}O_4$ [7]. They observed a magnetic excitation of the doped-hole state with an energy of $\sim$ 130 meV above 170 K. This is very unusual since, according to the theory of Zhang and Rice, the energy gap between the ground state singlet and the lowest-lying triplet state is estimated to be several eV [7, 8]. Suggestions that this low-energy magnetic excitation may come from an anti-Jahn–Teller triplet polaron have been made [7, 9].

To resolve the contradiction between the NQR measurement and the Zhang–Rice theory, we propose here to explicitly consider only $d_{x^2-y^2}$ orbitals for Cu ions as in Zhang and Rice [2]. We note that $La_2Cu_{0.5}Li_{0.5}O_4$ is distinct from many other doped cuprates because the orbital symmetry of Li ions is not $d_{x^2-y^2}$ but s, leading to a competition between Cu d and Li s orbitals, and a positive t_{pp} since Li is a strong hole donor. In fact, recent

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local-density-approximation (LDA) calculations indicate that in $La_2Cu_{0.5}Li_{0.5}O_4$, Cu d_{3z^2-1} orbitals are dramatically pushed toward Cu $d_{x^2-y^2}$ and O p_σ ones by surrounding Li ions [9]. This implies that the nearest-neighbour O–O hopping through d_{3z^2-1}, $\sim +t'^2/\delta\epsilon$ (t' is the hybridization between d_{3z^2-1} and O p_σ orbitals, and $\delta\epsilon$ the energy difference between d_{3z^2-1} and p_σ) [10], can dominate over the direct O–O hopping (negative) in pure CuO_2 layers, resulting in a *positive* effective t_{pp}.

In $La_2Cu_{0.5}Li_{0.5}O_4$, the CuO_4 plaquettes are well separated from each other, and, from the experiments, the low-energy excitation arises from transitions between localized states [11]. Thus, to capture the essential physics, first we solve an isolated CuO_4 cluster with a positive t_{pp} in fixed geometry, using exact diagonalization. The Hamiltonian for this cluster reads

$$H = \sum_{i\neq j,\sigma} t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \sum_{i\sigma} e_i c^\dagger_{i\sigma} c_{i\sigma} + \sum_i U_i c^\dagger_{i\uparrow} c^\dagger_{i\downarrow} c_{i\downarrow} c_{i\uparrow} + \sum_{i\neq j,\sigma,\sigma'} U_{ij} c^\dagger_{i\sigma} c^\dagger_{j\sigma'} c_{j\sigma'} c_{i\sigma}. \tag{1}$$

In equation (1), the vacuum is defined as filled Cu d^{10} and O p^6 states. $c^\dagger_{i\sigma}$ ($c_{i\sigma}$) creates (destroys) a hole of spin σ at site i in the Cu $d_{x^2-y^2}$ or the O $p_{x,y}$ orbital. The hopping $t_{ij} = t_{pp}$ is between adjacent oxygen sites, and t_{pd} between nearest-neighbour Cu and O sites. The site energy $e_i = \epsilon_p$ is for O sites, and ϵ_d for Cu sites. We include Hubbard repulsion on both Cu (U_d) and O sites (U_p), and the nearest-neighbour Cu–O repulsion (U_{pd}). Since in $La_2Cu_{0.5}Li_{0.5}O_4$, every CuO_4 cluster obtains an extra hole from the adjacent Li ions, we place two holes in the cluster. In this system, total spin is a good quantum number and the states can be classified into singlet and triplet.

In the original calculation of Zhang and Rice, t_{pp} has not been taken into account. In usual cuprates, a simple symmetry argument shows that *negative* t_{pp} makes the Zhang–Rice singlet more stable and, therefore, the Zhang–Rice theory is valid. We vary t_{pp} to explore the effect of positive t_{pp} on the lowest singlet and triplet states. Other parameters are taken representatively from constrained LDA calculations for La_2CuO_4 since equivalent parameters are not available for $La_2Cu_{0.5}Li_{0.5}O_4$: $t_{pd} = 1$, $U_d = 10$, $U_p = 3$, $U_{pd} = 1$ and $\Delta \equiv \epsilon_p - \epsilon_d = 4$ [12, 15]. Here we use t_{pd} as the energy unit; $t_{pd} = 1.3$ eV is a good estimate for the cuprates [15]. From figure 1, we can see that as t_{pp} increases, the energy of the lowest singlet increases, while the energy of the lowest triplet decreases. Around $t_{pp} = 0.4$, a crossover occurs, beyond which the triplet state becomes more stable than the singlet. As we further increase t_{pp}, the energies of both the singlet and the triplet states decrease, and the gap between them does not change much. This calculation shows that t_{pp} is crucial to the singlet–triplet splitting, since the triplet can gain energy from the O–O hybridization t_{pp}. For the plausible value $t_{pp} = 0.5$, the energy difference between the triplet and singlet is ~ 0.2 eV, close to the energy scale of the observed low-lying magnetic excitation in $La_2Cu_{0.5}Li_{0.5}O_4$ [7].

Although individual CuO_4 clusters are well separated from each other in $La_2Cu_{0.5}Li_{0.5}O_4$, weak communication between them is still possible via direct oxygen–oxygen hopping between the adjacent CuO_4 clusters, via electron–lattice couplings, or through Li ions. To gain a better understanding of the real material $La_2Cu_{0.5}Li_{0.5}O_4$, we substitute Li for half the Cu ions in a CuO_2 plane so that all Cu ions are surrounded by four Li ions, and consider the two-dimensional three-band Peierls–Hubbard model:

$$H = \sum_{i\neq j,\sigma} t_{ij}(\{u_k\}) c^\dagger_{i\sigma} c_{j\sigma} + \sum_{i,\sigma} e_i(\{u_k\}) c^\dagger_{i\sigma} c_{i\sigma} + \sum_i U_i c^\dagger_{i\uparrow} c^\dagger_{i\downarrow} c_{i\downarrow} c_{i\uparrow} + \sum_{\langle i\neq j\rangle,\sigma,\sigma'} U_{ij} c^\dagger_{i\sigma} c^\dagger_{j\sigma'} c_{j\sigma'} c_{i\sigma} + \sum_l \frac{1}{2M_l} p_l^2 + \sum_{k,l} \frac{1}{2} K_{kl} u_k u_l. \tag{2}$$

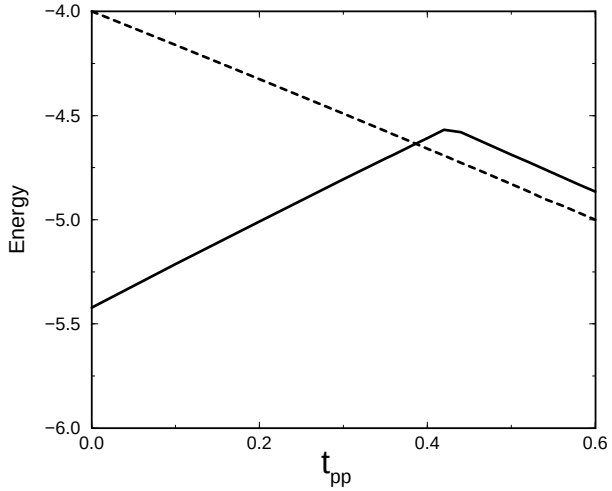

Figure 1. Energies of the lowest singlet and triplet states of a CuO_4 cluster as a function of direct oxygen–oxygen hopping t_{pp}. The solid and dashed lines correspond to the singlet and the triplet, respectively. The parameters are $t_{pd} = 1$, $\Delta = 4$, $U_d = 10$, $U_p = 3$ and $U_{pd} = 1$.

This Hamiltonian contains much richer physics than the conventional one-band Hubbard or t–J model, and has been employed to study polaron states, stripes and other effects involving the freedom of the lattice in copper oxides [15, 16]. In this Hamiltonian, both electron–electron and electron–phonon (e–ph) interactions are explicitly considered. For the e–ph coupling, it is assumed that the nearest-neighbour Cu–O (Li–O) hopping is modified by the O-ion displacement u_k as $t_{ij} = t_{pd}\,(t_{ps}) \pm \alpha u_k$, where the $+$ $(-)$ applies if the bond shrinks (stretches) with positive u_k, where t_{ps} is the nearest-neighbour Li–O hopping strength. The Cu (Li) site energy is assumed to be modulated by the O-ion displacement u_k linearly as $e_i = \epsilon_d\,(\epsilon_s) + \beta \sum_k (\pm u_k)$, where the sum extends over the four surrounding O ions and ϵ_s is the site energy of Li. To imitate the Li ions donating holes to the system, we assume simply that the Li ion has a very large site energy $\epsilon_s = \epsilon_p + 2\Delta$ and small on-site Hubbard repulsion $U_{Li} = U_d/3$, and $t_{ps} = t_{pd}$. For the lattice part, we study only the motion of O ions along the Cu–O (Li–O) bonds and assume, for simplicity, that only diagonal components of the spring-constant matrix are finite, $K_{kl} = \delta_{kl} K$.

Using Hamiltonian (2), we first obtain the (possibly inhomogeneous) spin–charge–lattice configuration of the ground state in an unrestricted Hartree–Fock (HF) approximation; then we study the excitations from the ground state by numerical random-phase-approximation (RPA) calculations. Mean-field states were obtained by solving the unrestricted HF Hamiltonian with self-consistency conditions for on-site and nearest-neighbour charge and spin densities [15]. The self-consistent equations are obtained by minimizing the total energy with respect to these quantities. From these calculations, we find *three* mean-field local energy-minima states by tuning the e-ph strength (these three phases persist over large parameter regimes in model (2) with positive t_{pp}). The phase diagram is shown in figure 2. The first phase, which is the most stable state when α is small, is basically a magnetic state ('spin phase') where every Cu carries a 1/2-spin forming an antiferromagnetic ground state, and the spins on the adjacent oxygen ions are negligibly small. Another phase, which is the most stable when α is large, is a charge state ('charge phase') where all spins on Cu and O ions are quenched, and all CuO_4 clusters are equivalent, forming a charge-density-wave

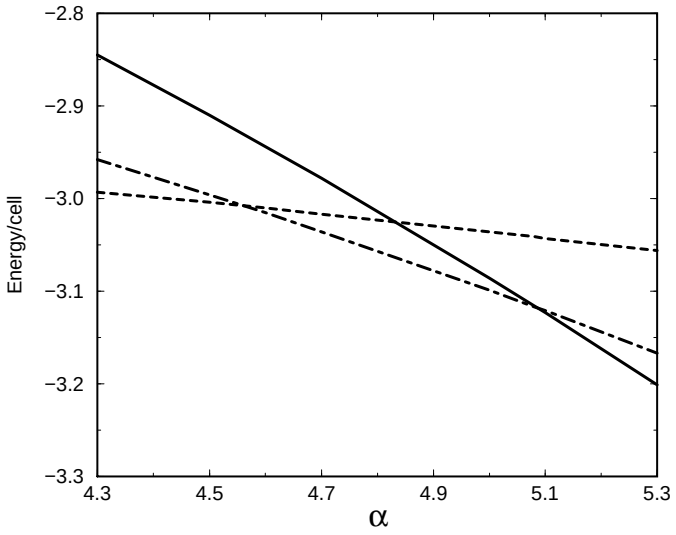

Figure 2. Phase diagram for $La_2Cu_{0.5}Li_{0.5}O_4$ as a function of the e-ph coupling strength α (in unit t_{pd} Å^{-1}). The solid, dashed and dot–dashed lines describe the energies of the charge, spin and spin–Peierls phases, respectively. Here we set $\beta = 1$ (t_{pd} Å^{-1}), $K = 32\,t_{pd}$ Å^{-2} and $t_{pp} = 0.5$, and other parameters are as in figure 1.

state. Most interestingly, a mixed phase has the lowest energy when α has a range of intermediate values. Here, in one half of the CuO_4 clusters the spin is quenched, and in the other half of the clusters both copper and oxygen ions carry spin, locally forming a triplet ('spin–Peierls phase'). Globally, this state is an antiferromagnetic phase and the total spin is zero. The spin and charge configurations of these three phases are illustrated in figure 3. It is seen that the doped hole primarily occupies the O sites in all three phases. In the spin and the charge phases, all CuO_4 clusters are equivalent. The spin–Peierls phase, however, contains two kinds of CuO_4 cluster, and the lattice distortion in the spin-carrying cluster is a little smaller than that in the spin-quenched one. Therefore in the spin–Peierls phase, there should exist two Cu–O and two Li–O bond lengths.

We have carried out a numerical RPA analysis for these three phases. The kinetic part of the lattice is incorporated with particle–hole excitations into the RPA calculations [15]. To examine the magnetic excitations in the system, we focus on the spectral weight for magnetic excitation, which is the imaginary part of the spin-spin correlation,

$$f(\boldsymbol{k},\omega) \propto \frac{\pi}{N_{cell}} \sum_{n\neq 0} |\langle 0|S^{\perp}_{Cu}(\boldsymbol{k})|n\rangle|^2 \delta(\omega - (E_n - E_0)) \tag{3}$$

where

$$\boldsymbol{S}_{Cu}(\boldsymbol{k}) = \sum_{m\in Cu} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{m}} \frac{1}{2} \sum_{\tau,\tau'} c^{\dagger}_{m\tau} \sigma_{\tau,\tau'} c_{m\tau'}$$

with $\sigma_{\tau,\tau'}$ standing for Pauli matrices, the superscript $\perp$ for the transverse components, and N_{cell} for the number of unit cells. In figure 4, we depict the spectral weight $f(\boldsymbol{k},\omega)$ for different $\boldsymbol{k}$. We find that, uniquely in the spin–Peierls phase, there exists a low-energy excitation around $0.1\ t_{pd}$. Neither the spin nor the charge phases have similar low-energy excitations. In the spin phase, there is a zero-energy spin-wave excitation from the antiferromagnetic ground state. Because the magnetic coupling between copper ions is

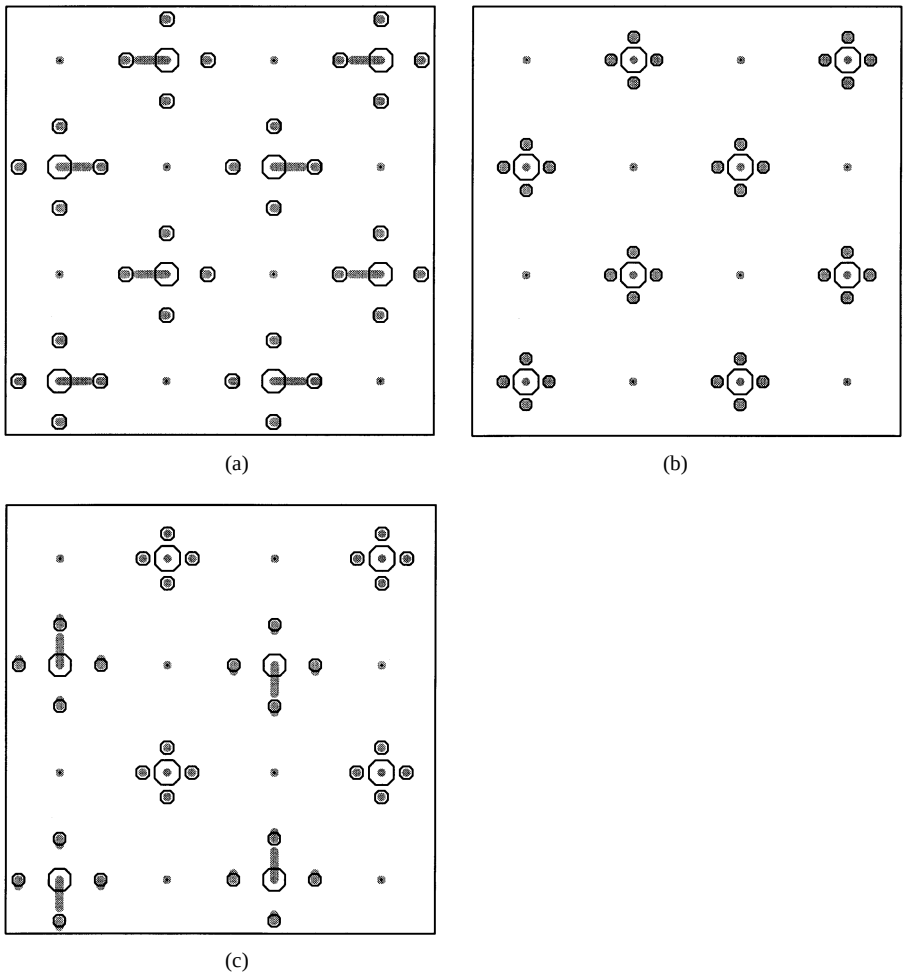

Figure 3. Charge (radii of the circles) and spin (arrows) densities in the spin phase (a), the charge phase (b) and the spin–Peierls phase (c) of our $La_2Cu_{0.5}Li_{0.5}O_4$ model (2). Cu sites have the most charge (largest circles) and Li sites have the least charge (smallest circles).

very small due to the isolation by Li ions, the ground state will easily become disordered by the fluctuations and this spin-wave excitation will disappear.

Within the spin–Peierls phase, this low-energy magnetic excitation is only weakly dependent on the parameters. Table 1 reports the lattice distortion in the spin-carrying and spin-quenched clusters and the corresponding energy of the low-lying magnetic excitation as a function of e-ph coupling α. For different α, the low-lying magnetic excitation remains on the same energy scale $\sim 0.1\ t_{pd}$, and the change of the lattice distortion is also small. We have examined the wave function from the RPA calculation to understand the origin of this low-energy excitation. It arises from local spin-flips of four oxygen ions in the spin-carrying CuO_4 cluster, while the spin on the copper remains the same, leading to a triplet–singlet transition. In the charge and spin phases, however, the spins on oxygen sites are negligibly small and the local spin-flip in a CuO_4 cluster cannot give rise to an excitation with finite energy. If the ground state of $La_2Cu_{0.5}Li_{0.5}O_4$ in the experiments of Yoshinari *et al* is the

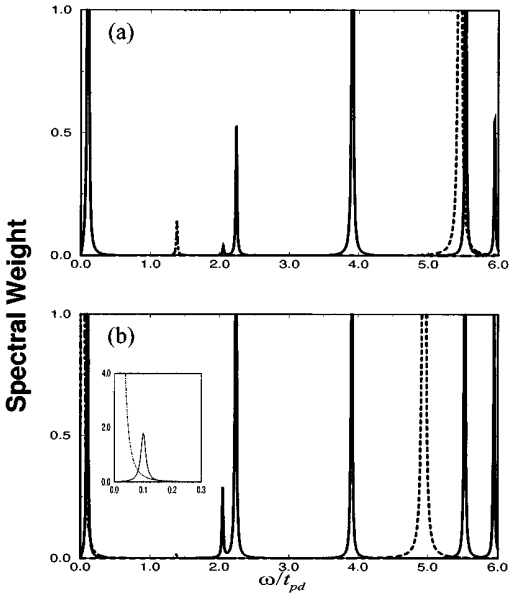

Figure 4. Spectral weight of the magnetic excitation in our model of $La_2Cu_{0.5}Li_{0.5}O_4$ for different momenta $\boldsymbol{k}$. Panels (a) and (b) are for $\boldsymbol{k} = (0, 0)$, $(\pi/2a,\pi/2a)$, respectively, where a is unit cell size for the undoped CuO_2 lattice. The solid, dashed and dot–dashed lines correspond to the spin–Peierls ($\alpha = 4.7$), charge ($\alpha = 5.1$) and spin ($\alpha = 4.5$) phases, respectively. The inset of (b) is the amplified low-frequency part of the spectrum.

Table 1. Lattice distortions and energy of the low-lying magnetic excitation in the spin–Peierls phase for different e-ph coupling strengths α. The experimental average Cu–O and Li–O bond lengths are 1.79 Å and 1.93 Å, respectively [4].

α (t_{pd} Å^{-1})	Lattice distortion (Å)		Excitation energy (t_{pd})
4.6	0.077	0.174	0.093
4.7	0.078	0.178	0.099
4.8	0.079	0.182	0.105
4.9	0.080	0.186	0.108
5.0	0.081	0.189	0.114

above spin–Peierls phase, we should have two Cu–O and two Li–O bond lengths. From the crystal structure data of $La_2Cu_{0.5}Li_{0.5}O_4$, the peaks of the neutron diffraction profile are indeed split [4], possibly supporting this prediction.

In summary, to understand the nature of the doped-hole state in $La_2Cu_{0.5}Li_{0.5}O_4$, we have: (i) Observed that the sign of the effective t_{pp} is driven to be opposite to that in pure CuO_2 layers by the surrounding Li ions with s orbitals and solved a CuO_4 cluster with positive t_{pp} using exact diagonalization, showing that the direct oxygen–oxygen hopping t_{pp} is critically important to determine the singlet–triplet splitting. When t_{pp} is larger than a critical value, the triplet state become the ground state. (ii) Studied a two-dimensional Peierls–Hubbard model for $La_2Cu_{0.5}Li_{0.5}O_4$. Within an unrestricted HF approximation, we find three mean-field local energy-minima states by tuning the e-ph coupling α. When α is small the ground state is a spin phase; when α is large, a charge phase is the most stable; when α is of intermediate strength, the ground state is a spin–Peierls phase in which the

spin and charge are separated, resulting in two kinds of CuO_4 cluster. Applying an RPA analysis for these three phases, we find that in the spin–Peierls phase, there exists a magnetic excitation with an energy ~ 0.12–0.15 eV. This novel excitation is attributed to the spin-flip of the four oxygens in the spin-carrying CuO_4 clusters, leading to a transition from the triplet to the singlet state. Our results provide an explanation for the recently observed low-energy magnetic excitation in $La_2Cu_{0.5}Li_{0.5}O_4$. According to this explanation, there are two Cu–O and two Li–O bond lengths in $La_2Cu_{0.5}Li_{0.5}O_4$. Alternatively, considering the isolated cluster results of figure 1, it is possible that the singlet ground state in the charge phase may also have a low-energy magnetic excitation if t_{pp} is close to the singlet–triplet crossover value. Careful crystallography to distinguish the number of different bond lengths should clarify which scenario holds in $La_2Cu_{0.5}Li_{0.5}O_4$. However, for both scenarios, sensitivity to pressure (and magnetic field) is likely and should be tested experimentally. The different symmetries of Cu $d_{x^2-y^2}$ and Li s orbitals and the resulting sign change of t_{pp} may be responsible for the non-90° bonding of O(I)–Cu–O(I) in $La_2Cu_{0.5}Li_{0.5}O_4$ [4], and could also lead to frustrated ground states if the Li level can be tuned by using other s-orbital ions (Li is an extremely strong hole donor and dominates the competition with the Cu d symmetry). In this respect $La_2Cu_{0.5}Li_{0.5}O_4$ may be less representative of hole-doped CuO_2 layers than it is interesting in its own right. Further considerations from our approach will include the effects of thermal and quantum fluctuations, which can allow tunnelling between discrete degenerate configurations, and topological excitations. The very weak coupling between CuO_4 clusters suggests that a disordered phase is likely which may be consistent with the experimentally suggested diamagnetic behaviour of $La_2Cu_{0.5}Li_{0.5}O_4$ [3, 7].

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