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LETTER TO THE EDITOR

Charge and spin fluctuations in planar and non-planar orbitals of cuprate superconductors

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Abstract. Considering in-plane (Cu $3d_{x^2-y^2}$ and O $2p_\sigma$) and out-of-plane (Cu $3d_{2z^2-r^2}$ and apical O $2p_z$) orbitals, a new lowest-energy spin-bag is found for doped cuprates in the strong-coupling regime. While Zhang–Rice correlations are enhanced, a broad structure appears in the Fermi-level region with mainly non-planar character at E_F. Both features may be relevant in the high-T_c superconductivity scenario. This description stems from a mean-field calculation in terms of a general, two-centre, six-band Hamiltonian for $2n \times 2n$ (up to 8×8) cuprate clusters. Other previously known solutions are also found and discussed. Different apical O $2p_z$ levels are considered in order to study their possible effects.

Copper oxide superconductors exhibit strong-correlation effects, their physical properties being difficult to study theoretically. It is widely accepted that the CuO_2 planes are the most relevant structures of these high-T_c superconductors [1–4], which at half-filling are charge-transfer insulators with antiferromagnetic (AF) order, their spins lying mainly on copper sites while their mobile holes occupy oxygen sites [5–7]. One- and three-band Hubbard Hamiltonians [8–11] have been adopted, obtaining, with different calculational techniques, many useful results [8–11]. Recently, many authors claim the importance of out-of-plane orbitals such as Cu $3d_{3z^2-r^2}$ (d_z) and apical oxygen O $2p_z$ (O_a) whose occupancies, although low, are non-negligible [12–15]. The difficulty found in explaining the broad variation of T_c over different cuprates on the basis of models restricted to the CuO_2 planes [14] has led us to consider those out-of-plane orbitals in many calculations [17–22]. Some controversy is going on at present about the role that these orbitals can play in superconductivity (SC). On the one side, there are theories explaining SC by d–d excitations [23], triplet-hole models [24] and anharmonicity of O vibrations [14, 21]. On the other, some authors [19, 20] predict a negative influence of non-planar orbitals in SC as they could destabilize the Zhang–Rice (ZR) singlet [8], considered the most important ingredient in SC. It seems reasonable that, whatever the answer, off-plane orbitals will play a role in SC, as it is now accepted in recent experimental and theoretical work [22].

In order to further investigate this role, the following six-band two-centre Hamiltonian has been adopted here, where in-plane Cu $3d_{x^2-y^2}$ (d_x) and O $2p_\sigma$ (O_p) as well as out-of-plane Cu d_z and O_a orbitals are considered on the same footing:

$$H = \sum_{is} E_i n_{is} + \sum_{\langle ij\rangle s} t_{ij} c_{is}^+ c_{js} + \sum_i U_{ii} n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{i=js} \left[(U_{ij} - J_{ij}) n_{is} n_{js} + U_{ij} n_{is} n_{j-s} \right] + \frac{1}{2} \sum_{i=js} J_{ij} c_{i-s}^+ c_{j-s} c_{js}^+ c_{is} + \sum_{i=j} J_{ij} c_{i\uparrow}^+ c_{i\downarrow}^+ c_{j\downarrow} c_{j\uparrow}. \quad (1)$$

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Indices i and j are composite indices running over both lattice sites and the corresponding symmetry orbitals on each site (e.g. on copper sites two orbitals are considered, d_x and d_z), whereas s denotes the spin. The symbol $\langle ij \rangle$ denotes sum over nearest-neighbour sites only. The $c_{is}(c_{is}^{+})$ are annihilation (creation) operators for holes with bare atomic levels E_i, while the t_{ij} represent the hopping integrals, U_{ij} the Coulomb interactions and J_{ij} the exchange couplings. The first line of (1) is just the Hubbard Hamiltonian, whereas the second line specifies the interatomic Coulomb interactions and the (Pauli principle) diagonal exchange of the standard Hartree–Fock (HF). In the third line, finally, the first term describes non-diagonal exchange incorporating the vector character of the spin (product of two opposite-spin hoppings), while the last term transfers antiparallel-spin pairs from one site to another previously vacant. Upon linearization by standard mean-field techniques, the corresponding single-particle Hamiltonian describes several processes: (i) normal scattering in terms of the average local charges and bond orders; (ii) spin-flip scattering in terms of the average local-spin and spin-transfer operators. It is just the presence of these spin-flip terms which breaks the spin-symmetry of the original Hamiltonian by mixing opposite-spin states and thus allowing a great deal of correlation between antiparallel spins. This Heitler–London type of exchange is entirely absent in a standard HF approximation.

The presence of the above average quantities defines a self-consistency problem that must be solved by some iterative algorithm. After diagonalizing the Hamiltonian matrix, charge and spin averages are easily found and fed back into the eigenvalue problem until self-consistency is achieved. Finally, one-hole spectral functions, as well as charge *and* spin correlations, are straightforwardly calculated and constitute the basis of our subsequent analysis. Clusters of even $2n \times 2n$ unit cells are considered here in order to avoid spin-frustration problems. The unit cell has five sites and six orbitals (each copper atom is at the centre of an elongated octahedron formed by six oxygen atoms). Periodic boundary conditions (PBC) are imposed along the planar axes, the convenience of this choice instead of the open BC having been discussed elsewhere [25] for the 1BH and 3BH models. It applies equally well to the present six-band case. Parameter values calculated by the constrained-occupation local-density method, consistent with photoemission spectroscopy, are adopted [19, 22, 26] in this work. We vary the O_a-level energy (E_a) with respect to the O_p-level energy (E_p) in order to study the possible effect of these orbitals on the final states, upon doping. We have also made calculations for clusters of increasing size, from 2×2 up to 8×8, to study size effects. The ground-state energy per cell, the staggered spin and the mean-square AF order parameter stabilize at their 4×4 cluster values and the main features of the one-particle density of states (DOS) are already present in the 4×4 cluster spectral densities.

At half-filling ($x = 0$) a charge-transfer insulator with AF order is of course obtained, the gap being in agreement with experiment for all the E_a values tried. It is wider the higher the O_a level is (for $\Delta O = E_a - E_p = -1.5$ eV the gapwidth is 1.8 eV while for $\Delta O = 0.3$ eV the gapwidth is 2.4 eV). The intrinsic holes are of dominant in-plane character (67% d_x, 31% O_p), the hole populations of d_z and O_a being negligible (0.3%) for any E_a, in agreement with experimental results [16, 27, 28].

Upon doping the following types of solutions are found.

(i) Homogeneous solution. Doped holes are uniformly distributed over all the cells. These states retain the AF order of the insulating parent material although the AF correlations among Cu orbitals decrease with doping. The doped holes go mainly to O_p orbitals, in good agreement with experiment. While the d_x–O_p spin–spin correlations (SSC) are negative, suggesting formation of ZR singlets, the d_x–d_z and d_x–O_a SSC are positive. Non-planar orbital occupancies are very small up to a doping of about $x \simeq 0.25$ (at $x = 0.15$, one has

1.65%(2.44%) of d_z and 9.13%(3.4%) of O_a for $\Delta O = -1.5(0.3)$ eV respectively). The effect of the apical level increases with doping, in agreement with other works [20]. Thus at $x = 0.25$, the non-planar occupancies rise to 14% (2.8%) of O_a and 2.4% (1.9%) of d_z again for $\Delta O = -1.5(0.3)$ eV. The SSC are as well enhanced at this doping rate for both planar and non-planar symmetries. Likewise, the single-particle DOS shows upon doping the expected behaviour (steady rise of the chemical potential, reduction of the gap by transfer of spectral weight, etc). This homogeneous solution could correspond to the 'doped Néel' configuration found by Grant and McMahan [22] in an eight-band calculation, the O_a admixture clearly dominating over the d_z one.

(ii) Spin-flip solution. In the trial state, we reverse one of the d_x spins with respect to the AF background and distribute the added holes uniformly over the whole cluster. After convergence, the final state shows a singular cell, the spin-flipped one, surrounded by an almost undistorted AF background with small deviations in hole population never exceeding 0.1. The spin-flipped cell shows a hole population higher than, and with a hole distribution different from, the rest. Its d_x occupancy is slightly higher than the background one, at the expense of its O_p and O_a occupancies. Its SSC are likewise different from those of the other cells, with ZR SSC. Thus, d_x has positive SSC with its nearest-neighbour (NN) d_x (ferromagnetic polaron) [21], negative with its two in-cell O_a, and again positive with its surrounding O_p. In recent HF solutions of a 2B Hamiltonian reported by Vergés *et al* [29], the so-called magnetic polaron shows ferromagnetic coupling between the central Cu and its four NN coppers as well as some ferromagnetic Cu–O bonds; these solutions introduce localized states into the AF gap, as in our case.

The corresponding DOSs show some d_x spectral-weight transfer upwards into the gap, an effect especially clear when a d_x spin is reversed at half-filling ($x = 0$). This transferred d_x spectral weight forms a peak just at the Fermi level (E_F) for $\Delta O = -1.5$ eV and below E_F for higher ΔO. It is mainly a local effect taking place at the spin-flipped cell. At higher doping ($x = 0.15, 0.25$) a larger spectral weight is transferred upwards and, at $\Delta O = 0.3$ eV, two peaks of overwhelming in-plane character appear. Let us now compare the energies of these spin-flip solutions and the corresponding homogeneous solutions (same x and ΔO). Below $x = 0.2$, the homogeneous solution is always lower in energy. Above $x = 0.2$, the same situation is found for $\Delta O = -1.5$ eV and doping rates as high as 0.5. For $\Delta O = 0.3$ eV, however, the spin-flip solution energy comes below as soon as $x > 0.2$.

(iii) Inhomogeneous solution. Although this solution appears for different doping rates, we describe only, for the sake of clarity, the $(N + 1)$-hole state, since it already contains the essential features. In this solution the doped hole is localized in a cell which in addition captures the intrinsic hole population of a NN d_x. The system thus presents an almost empty cell (only the in-plane O_p orbitals remain hole-populated), and an overpopulated cell ($\simeq 3$ holes). The rest of the cluster keeps the AF order and hole admixtures of the insulating parent.

This overpopulated cell maintains its total s_z component, now lying at the d_z orbital, with about the background value. Since the doped hole and its associated backflow from the opposite-spin NN d_x go to the d_x minority-spin component and to the empty d_z and O_a levels of the overpopulated cell, d_x loses its s_z component while d_z acquires a hole density and s_z very close to the d_x values at half-filling. Although such a strong hole localization on the same Cu atom might be at first surprising due to the high U_d values, it should be borne in mind that two Cu orbitals, coupled by an exchange (Hund's rule) interaction, are included. In fact other authors [21, 30] also find solutions with large hole concentration on a Cu atom.

The orbital proportions of the overpopulated cell are 48% (49%) of d_x, 27% (30%) of

d_z, 18% (18%) of O_p, and 8% (3%) of O_a when $\Delta O = -1.5(0.3)$ eV. The corresponding SSC are all negative, the in-plane ones (d_x–O_p) being -6.98×10^{-2} (-7.79×10^{-2}), stronger than those of the corresponding homogeneous state, namely -1.7×10^{-2} (-1.8×10^{-2}), once again for $\Delta O = -1.5$ (0.3) eV. The main effect of the apical level is, therefore, to modify its hole occupancy as well as that of d_z. This leads, as also found in recent work [19, 20], to an enhancement of the ZR correlations for increasing ΔO. The local ZR singlet is maintained even when ΔO is as low as -1.5 eV despite the high population of non-planar orbitals. This is because the d_z and O_a occupations are not drawn, as in other solutions [20], from their in-cell d_x but rather from a NN cell d_x (as well as from doped holes). As for non-planar SSC, note that d_z has non-negligible SSC with O_a: -1.4×10^{-2} (-4.15×10^{-3}) for $\Delta O = -1.5(0.3)$ eV. Although the d_z–d_x SSC are weak ($<10^{-3}$), a more sizeable interaction among planar and non-planar orbitals is found with the O_p orbitals giving d_z–O_p SSC of -1.4×10^{-2} (-1.6×10^{-2}).

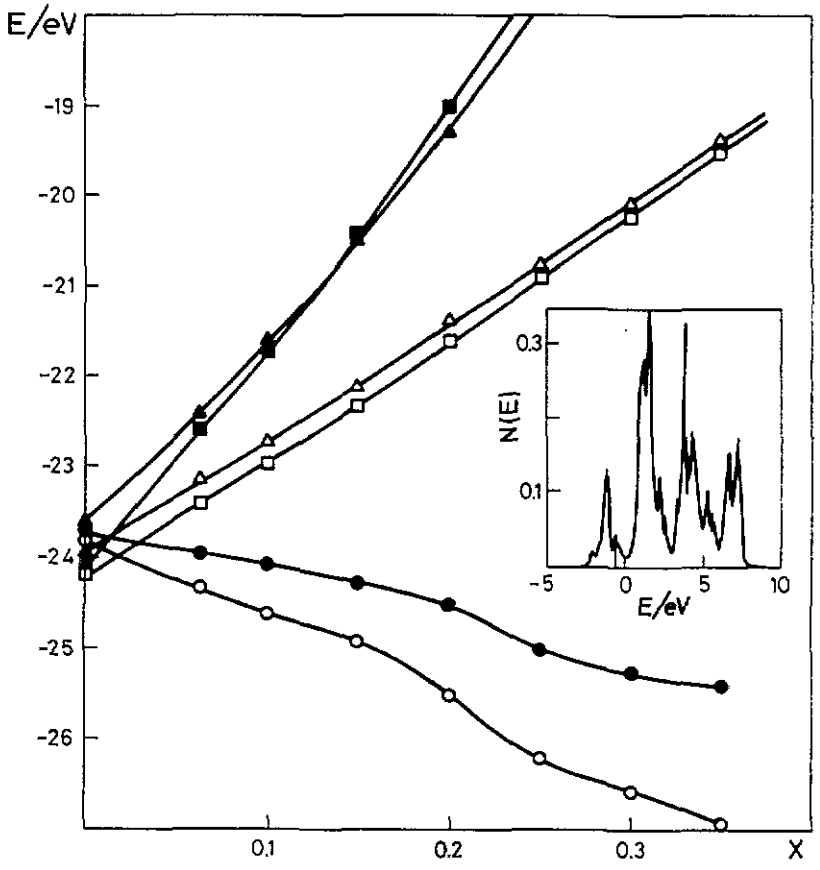

Figure 1. Total energy versus doping rate for a 4 × 4 cluster. Triangles denote the spin-flip solution; squares denote the homogeneous solution and circles denote the inhomogeneous solution. Open(closed) symbols correspond to $\Delta O = -1.5(0.3)$ eV. The inset shows the DOS for the 17-hole inhomogeneous solution of the 4 × 4 cluster.

Finally the one-particle DOS shows a small peak just at E_F (inset on figure 1). This peak is a local effect, since its main contribution is due to the partial DOS of the overdoped

cell. Indeed, the d_z-projected DOS of this particular cell has a maximum at this eigenvalue E_F. This small peak, however, is part of a broader structure having a maximum whose main contributions come from the rest of the cells as well as from the in-plane projected DOS of the overpopulated cell. The composition of the E_F peak is mainly 65% (85%) of d_z and 20% (8%) of O_a for $\Delta O = -1.5(0.3)$ eV. This composition is modulated, in the total DOS, by the rest of the cells, with very low d_z admixture: 32%(35%) of d_x, 18%(26%) of d_z, 19%(24%) of O_p, and 30%(15%) of O_a. The composition at the maximum below E_F is, however, quite different: 57%(60%) of d_x, 2.9%(3.6%) of d_z, 33%(32%) O_p, and 6%(4.4%) of O_a for $\Delta O = -1.5(0.3)$ eV. In the maximum, the p_z to p_0 ratio is 18%(14%) in agreement with polarized spectroscopy experiments results 14% [15] and 8% [16], the d_z to d_x ratio 5% (6%) is of the same order as the experimentally obtained 1.5% [15] and 3% [16] values.

Insofar as in-plane properties are concerned this state may be somehow related to the charge-bag obtained by Yonemitsu and Bishop [30] in a HF–RPA calculation with a two-dimensional Hubbard model, as well as to the spin-bag found by Anisimov *et al* [21] in a 2×2 cluster with an additional hole. The d_x magnetic moment of their overpopulated cell ($0.55\ \mu_B$) coincides with that found here. Upon reduction of the Cu–O_a bond-length, they found [21] an 'anti-Jahn–Teller polaron' with an additional hole localized, with about equal weights, in the d_z and O_a orbitals, but the in-plane electronic structure is similar to the insulator and has an energy slightly higher than the spin-bag state [21]. By means of the Green's function method in the p–d mixing model, Matsumoto *et al* [31] have found that, upon hole doping, a narrow band develops at E_F with states split from the main p band exhibiting similar properties to Kondo-like states.

The new type of solutions reported here appear in a broad range of doping (up to 0.6), for all cluster sizes, and always have lower energies than the spin-flip and homogeneous solutions for the same doping rate (figure 1). At higher doping rates, which allow for more localized cells, the lowest-energy solution always corresponds to the largest number of overpopulated and empty-cell pairs, the associated energy-lowering increasing almost linearly with the number of these pairs, perhaps suggesting that they behave as nearly independent entities. Irrespective of the number of localized cells, the characteristic features are always the same, in particular the E_F level peak mainly due to d_z and O_a orbitals. This inhomogeneous solution does not appear for $U/t < 4$, a value close to the $U/t \simeq 5.8$ which separates the itinerant from the localized electron picture [32]. Although the d_z hole population significantly increases in overpopulated cells, such a big increase cannot be detected on the average. Since only a few cells undergo localization, the dominant planar d_x and O_p character is maintained in these solutions, showing an overall agreement with experimental data [15, 16]. Furthermore, as to the nature of the states near E_F, there is experimental evidence of both Fermi liquid and localized Cu 3d states [7, 33], in qualitative agreement with the electronic structure suggested by these solutions.

To conclude, we think it important to stress that these new lowest-energy solutions appear in the strong correlation region, show enhanced ZR spin correlations in the overpopulated cells, and produce a peak at the Fermi level mainly due to the non-planar symmetry orbitals d_z and O_a of those cells. Both features, an E_F peak and the enhancement of ZR SSC, may be relevant to possible high-T_c mechanisms for cuprates [32, 34]. Indeed, both features tend to increase T_c. In addition, the states lying at E_F are susceptible to pairing interactions. Polarization of the Fermi liquid as well as lattice anharmonicities, induced by charge and spin fluctuations between planar and non-planar orbitals, are reasonable candidates to pairing mechanisms [14]. Finally, it is intriguing whether the E_F peak reported

here may constructively interfere with the van Hove logarithmic singularity characteristic of two-dimensional metallic DOS. This would contribute to enhance T_c [34].

Recent measurements [35] suggesting inter-bilayer charge transport in $YBa_2Cu_3O_{6+x}$ emphasize the convenience of including non-planar orbitals to study the copper oxide properties.

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