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LETTER TO THE EDITOR

The validity of the Hartree–Fock approximation for studying the Fermi surfaces of doped cuprates

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Abstract. It is shown here that the band structure and Fermi surface of $Bi_2Sr_2CaCu_2O_{8+\delta}$, recently measured by angle-resolved photoemission spectroscopy, can be obtained via an extended three-band Hubbard model, within the unrestricted Hartree–Fock approximation, provided oxygen–oxygen hopping is included and the oxygen–copper hopping is reduced below a critical value. This applies to other copper oxides provided that the appropriate parameters are considered for each compound. The results agree remarkably well with earlier local density calculations and spectroscopic measurements.

One of the most frequently addressed topics since the discovery of the high-T_c superconductors has been the study of their near-Fermi-energy (E_F) band structure. Their ground state is still controversial, since the strong correlations of their parent CuO_2 compounds might lead to the breakdown of the Fermi liquid picture [1] in the doped systems. Recent angle-resolved photoemission experiments (ARPES) [2, 3, 4, 5] have shown the existence of a Fermi surface (FS) in the normal state obeying Luttinger's theorem and apparently supporting the conventional Fermi liquid regime. The measured FS is in good agreement with local density approximation (LDA) calculations [6, 7].

$Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) is among the most commonly experimentally studied cuprates because its easy cleavage between the two Bi–O layers gives a high-quality surface representative of the bulk [2]. The FS of Bi2212 has been mapped out with ARPES following two different procedures. Dessau *et al* [2] have measured the energy distribution curves (EDCs) at different $k_\parallel$ of the Brillouin zone (BZ), detecting the locations where the bands cross the Fermi energy. Aebi *et al* [3] have mapped the FS at nearly 6000 points in k-space by using sequential angle scanning data acquisition within a narrow energy window at E_F. The two resulting FSs have many common points but the interpretations differ greatly. Aebi *et al* [3] explain their results by claiming short-range AF spin correlations as an alternative to the highly nested nature invoked by Dessau *et al* [2]. In this work the main features of the FS and near-E_F electronic structure of Bi2212 are correctly reproduced by straightforward one-electron theory work carried out to the mean-field stage, provided large enough oxygen–oxygen transfer integrals are included. The antiferromagnetic (AF) spin correlations between copper atoms, however, cannot be neglected since they play an important role in determining the right periodicity of the lattice. They are essential for the copper band, which lies below E_F.

To be precise, we have calculated the electronic structure of doped CuO_2 planes with an extended two-dimensional (2D) three-band (3B) Hubbard model within the framework of the unrestricted Hartree–Fock (UHF) approach. The model and calculation method

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are well known and have been described extensively elsewhere [8], so only the main features are outlined here. The 3B Hubbard Hamiltonian has been adopted, in the hole representation ($3d_{x^2-y^2}$ and $2p_\sigma$ orbitals for Cu and O are considered), with interatomic Coulomb interactions. Upon linearization by standard techniques, the corresponding single-particle Hamiltonian describes normal scattering in terms of the average local spin and spin-transfer operators. After diagonalizing the Hamiltonian matrix, charge and spin averages are easily found and fed back into the eigenvalue problem until self-consistency is achieved. On the basis of the 2D character of the near-E_F band structure [2, 3, 9], the CuO_2 planes are simulated by square clusters of even $2N \times 2N$ unit cells (up to 10×10) with periodic boundary conditions.

We have obtained a FS which agrees remarkably well not only with earlier LDA [6, 7] calculations, but also with experiment [2, 3]. In order to obtain this result, it is essential to consider strong enough (see below) next-nearest-neighbour interactions (oxygen–oxygen hopping). The need for considering O–O hopping (t_{pp}) has already been pointed out by other authors [4, 10, 11, 12]. Although many interesting results have been reported with models where these next-nearest-neighbour interactions are neglected, the correct description of the near-E_F electronic structure of the CuO_2 planes is not obtained, within the UHF approximation, until the O–O overlap is taken into account. Otherwise this approximation gives incorrect results for the 3B Hubbard model. This is not surprising since, away from half-filling, doped holes lie in a band of mainly p-type symmetry and, therefore, O–O overlaps greatly affect the band dispersion near E_F. One should then be very cautious when comparing the results of more elaborate calculations, e.g., quantum Monte Carlo and Lanczos, with mean-field results not taking t_{pp} into consideration, as this comparison could be misleading. The inclusion of t_{pp}, however, is not sufficient by itself. Once t_{pp} is taken into account, its ratio to the Cu–O hopping (t_{pd}) turns out to be crucial in determining the correct FS shape, which varies for different Cu–O families. This is readily understood. A doped hole may go into the oxygen band, gaining thereby the band energy or, else, it may prefer the copper sites where it gains the magnetic energy associated with the exchange interaction. The ratio t_{pp}/t_{pd} regulates which mechanism dominates—and this depends on the family of compounds that we are considering. Although a large covalent interaction between nearest-neighbour Cu and O atoms has been generally accepted, such covalency is limited by correlation effects. The degree of covalency, on the other hand, is related to the Cu valence in the metallic state, which in turn is strongly affected by oxygen stoichiometry. Due to conflicting experimental interpretations, there is uncertainty about the Cu valence state in different cuprates. Large Cu–O transfer integrals (1–1.6 eV) [14, 15] were obtained mainly for $LaCuO_4$ material via a tight-binding fitting of band structures [10, 13], giving a small t_{pp}/t_{pd} ratio of $\approx$0.5. These values, although widely and successfully used for some compounds, need not to be universal since different electronic environments (rare earth, Tl, Bi, ...) usually give rise to diverse bonding character and transport behaviour in the Cu–O layers [7]. To obtain the right FS for Bi2212, we use a parameter set with $t_{pp}/t_{pd} \approx 1.2$. This implies a highly ionic character for the Cu–O hybridization (small t_{pd}) with the corresponding weakening of the Zhang–Rice (ZR) singlets [11]. Simply, in this compound the holes gain more energy going to the O band than remaining in the ZR singlets. Consequently, the doped holes predominantly go into the oxygen sites while Cu spins remain AF ordered. This is quite in line with estimations of hopping amplitudes of $\approx$0.2–0.4 eV not infrequently quoted in the literature [11, 16, 17] as well as with the possible ionicity of the Cu–O bond [7, 11, 13]. This also has important implications for the doping level of the CuO_2 layers, which would be higher if this ionic model was assumed. Indeed, there are claims in recent literature that Bi2212 samples may be in a doping regime (further

away from half-filling than the single-plane compounds $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$) where some aspects of the Fermi liquid description are recovered [19].

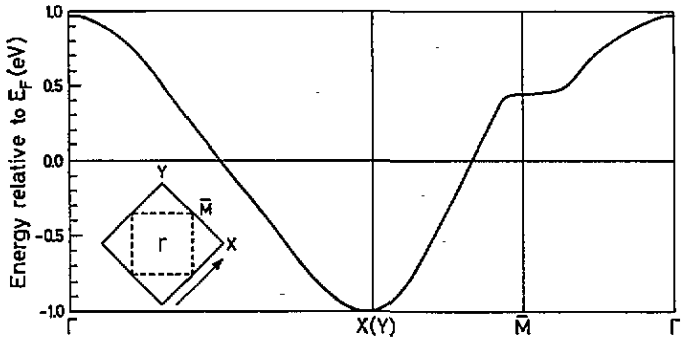

Figure 1. The energy dispersion curve along the high-symmetry directions of the two-dimensional Brillouin zone shown as an inset. The folded zone (dashed lines) corresponds to a doubled unit cell due to AF spin correlations between Cu atoms. The arrow indicates the Cu–O bond direction.

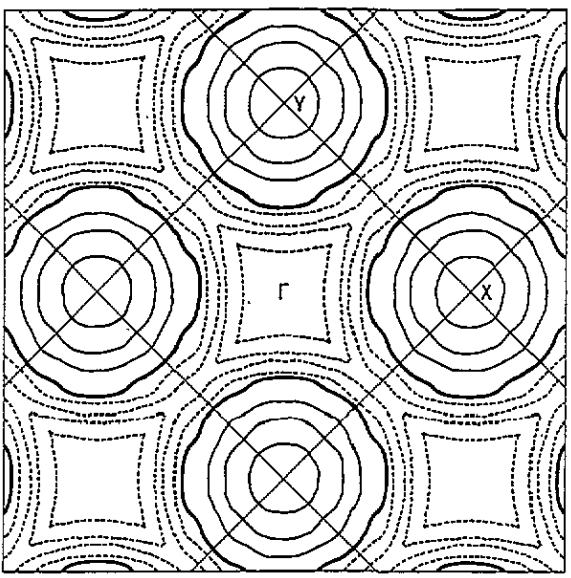

Figure 2. Constant-energy contours for $Bi_2Sr_2CaCuO_{8+\delta}$, in an extended zone scheme. The thick contours represent the Fermi surface, the weak solid lines denote the under-E_F contours and the dashed lines stand for the above-E_F contours.

Although there has been considerable discussion about the permanence of AF spin correlations in doped cuprates, it has lately seemed more than probable that short-range AF spin correlations exist even in superconducting samples [3, 17, 18]. Accordingly, we have taken an AF unit cell containing six sites, two Cu $3d_{x^2-y^2}$ with antiparallel spins and four O $2p_\sigma$, to generate clusters of up to 10×10 cells (600 sites) which seem large enough given that site effects in energy per cell, spin–spin correlations, charge distribution, etc, are negligible for sizes above 4×4 cells. For definiteness we have used the parameter set:

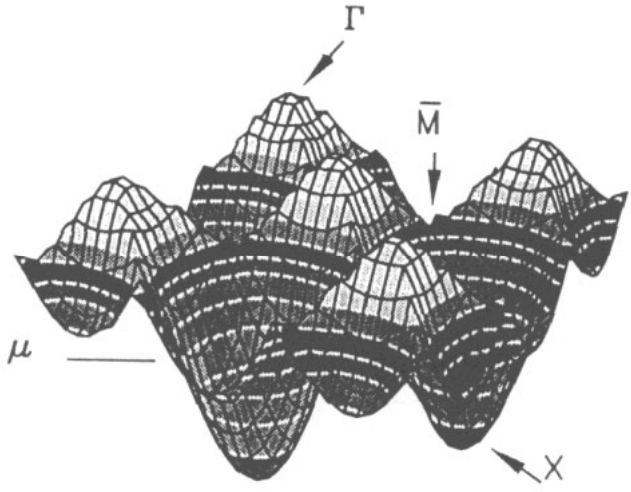

Figure 3. The energy surface dispersion, within the two-dimensional Brillouin zone in the extended zone scheme. The Fermi level μ and the high-symmetry points Γ, X, and M̄ are shown.

$\Delta = \varepsilon_p - \varepsilon_d = 3$ eV, $U_d = 8$ eV, $U_p = 3$ eV, $U_{pd} = 0.75$ eV, $t_{pp} = \pm 0.3$ eV, and $t_{pd} = \pm 0.25$ eV (the sign depending on the orbital phase factors), which gives a consistent description of several features of the cuprates within the considerations explained above. However, we have checked that the discussion which follows is valid for a broad range of parameters ($4 \leqslant U_d \leqslant 8$, $1.5 \leqslant U_p \leqslant 3$,and $0.2 \leqslant U_{pd} \leqslant 0.75$ for the quoted values of t_{pd} and t_{pp}). The lower band, fully occupied, is mainly of Cu character. The next band of hybridized Cu–O states, with predominant O p_σ symmetry, crosses E_F. Its energy dispersion is plotted in figure 1 along the high-symmetry directions of the two-dimensional BZ (shown as an inset for clarity). This dispersion closely resembles [20] both that experimentally observed by Dessau *et al* [2] and that obtained in LDA calculations [6, 7] for the band which crosses E_F, i.e., the Cu–O band of strong dp_σ character. In agreement with the Aebi *et al* experiment [3] we did not find any band crossing the Fermi level at the M̄ point. We certainly find a flat band around M̄, as reported by Dessau *et al* [2], but rather above E_F. This is indeed remarkable since the Bi–O layers were not considered in our calculation and it is just the interaction of these Bi–O layers with the Cu–O planes that explains the absence of the E_F crossing around M̄ in the LDA calculations [6]. Figure 2 shows, in an extended zone scheme, the constant-energy contour map within the 2D BZ. The FS is shown in thick lines, while the weak lines denote the occupied, and the dashed lines the unoccupied energy contours. As can be seen, the FS consists of several hole surfaces centred at the zone corners X and Y. This FS, calculated via a mean-field approximation and considering only one CuO_2 plane, is in excellent agreement with both the LDA-calculated [6, 7] and the ARPES-measured FS [2, 3]. It is important to stress here that a calculation without O–O hopping generates instead a rounded square FS centred at Γ. The energy surfaces corresponding to the contours of figure 2 are shown for perspective in the three-dimensional plot of figure 3. This clearly shows that M̄ is a saddle point. The dispersion of these energy surfaces below E_F coincides [20] with that measured by Aebi *et al* [3] (a strong set of lines of their mapping) along the high-symmetry lines (see figure 3 in [3]). The weak set of lines of this mapping must correspond just to the shadow bands resulting

from a folding of the zone due to AF order as discussed by Kampf and Schrieffer [21] and clearly explained in their figure 6. Recent ARPES measurements on the insulating cuprate $Sr_2CuO_2Cl_2$ report a spectral weight variation of the bands, analogous to that expected for a weak-coupling spin-density-wave model [22]. If, as is suggested in [22], these conclusions apply to the FS of doped Bi2212, our assumption that the doped holes in Bi2212 are in the intermediate- to weak-coupling regime would be confirmed.

Since the above FS was calculated considering a single CuO_2 plane, we have also considered the case of two coupled CuO_2 planes with a coupling energy of 0.03 eV. This gives two almost degenerate sets of bands with a dispersion similar to that obtained with a single plane.

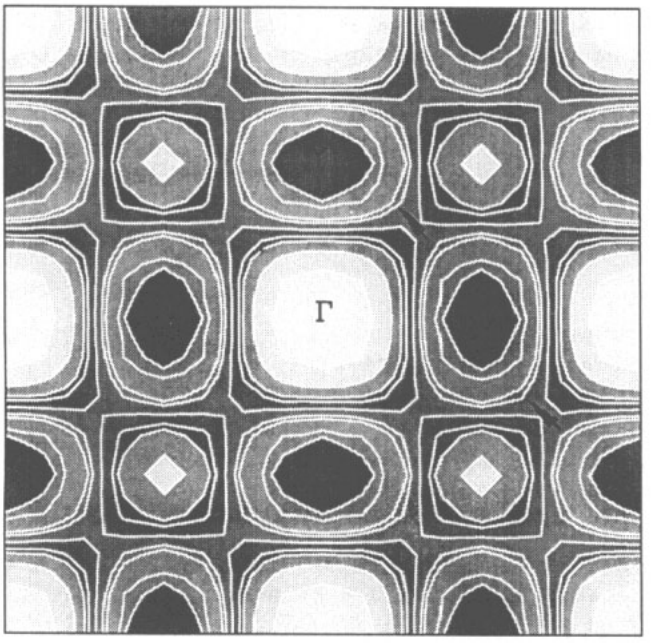

Figure 4. Constant-energy contours, in the repeated zone scheme of the folded BZ, obtained with $t_{pd} = 1$ eV and $t_{pp} = 0.5$ eV. The arrows indicate the FS contours.

Let us finally note that calculations made with the traditional parameter values $t_{pd} = 1$ eV and $t_{pp} = 0.5$ eV for the same square cluster describing a single CuO_2 plane give the constant-energy contours shown in figure 4 (repeated zone scheme). The FS is now around the X and Y high-symmetry points corresponding to the folded BZ (standard notation). The similarity of this picture with the FS of the $(HgBa_2Ca_2Cu_3O_8)_2O$ supercell obtained by Singh and Pickett [23] within the LDA is remarkable. In our case, the square energy contour around Γ lies above E_F whereas, in [21], it lies just at E_F and is primarily Hg–O(4) derived. This parameter set gives a fairly covalent picture of the CuO_2 planes which are thereby placed in a different doping regime. The doping level is now considerably lower than in the Bi2212 case.

All the above suggests that the UHF approximation gives very good results for the description of the FS and near-E_F band structure of the hole-doped cuprates provided that the appropriate parameter set is adopted for each family of compounds. This parameter set must be taken as describing an effective copper oxide layer conveying all the information

about the specific electronic environment of each compound. This would provide an apparently simple explanation of the optimum doping level needed in different cuprates. The results presented here seem to agree with the Fermi liquid description of holes in an AF background [19]. Notice that, while the $d_{x^2-y^2}$ orbitals are strongly correlated, forming local moments, the doped holes, predominantly in the $2p_\sigma$ orbitals in the Fermi level region, seem weakly correlated. As has been known for some time, the copper–oxygen hybridization strongly reduces the effective value of U_d, for states near the FS, by providing a screening mechanism through the (weakly correlated) oxygen band, as remarked by Luo and Bickers [24]. Therefore it is not surprising that there was no need for vertex corrections in this calculation. This gives some substance to the success of the UHF approximation in the description of the near-E_F electronic structure of the doped cuprates. Recent work within the 2D (one-band) Hubbard model [25] seems to suggest that vertex corrections are not large (less than 20%) as far as the quasiparticle band structure is concerned. Correlation effects, however, are known to have a large effect near the critical points of phase transitions, e.g., the magnetic transition [25, 26], in 2D systems.

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