Quasiparticle bands in cuprates by quantum chemical methods: towards an *ab initio* description of strong electron correlations

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Realistic electronic-structure calculations for correlated Mott insulators are notoriously hard. Here we present an *ab initio* multiconfiguration scheme that adequately describes strong correlation effects involving Cu 3d and O 2p electrons in layered cuprates. In particular, the O 2p states giving rise to the Zhang-Rice band are explicitly considered. Renormalization effects due to nonlocal spin interactions are also treated consistently. We show that the dispersion of the lowest band observed in photoemission is reproduced with quantitative accuracy. Additionally, the evolution of the Fermi surface with doping follows directly from our *ab initio* data. Our results thus open a new avenue for the first-principles investigation of the electronic structure of correlated Mott insulators.

Angle-resolved photoemission spectroscopy (ARPES) has proved to be an invaluable tool for probing the correlated electronic structure and the one-particle spectral function, \( A(k, \omega) \), of interacting many-body systems such as the 3d transition-metal (TM) oxides. In addition to the ubiquitous strong d-d Hubbard correlations, for late TM oxide compounds like the cuprates and nickelates, the electron-removal spectra are strongly affected by O 2p–TM 3d charge transfer and rehybridization effects. Detailed analysis of the photoemission data, see Ref. [1], led to the conclusion that the valence-band states at low binding energies actually have predominant O 2p character in nickelates and cuprates. Of particular interest is the nature of the first electron-removal states in the high-\( T_c \) superconductors. For the (Mott) insulating parent compounds, the formal valence states of copper and oxygen are Cu\(^{2+}\) 3d\(^6\) and O\(^{2-}\) 2p\(^6\), respectively, with one 3d hole at each Cu site. In a seminal work, Zhang and Rice (ZR) [2] argued that extra holes doped into the CuO\(_2\) layers mainly populate the ligand 2p levels and give rise to impurity-like states involving singlet coupling with Cu 3d holes. This was indeed confirmed by both quantum chemical wave-function based calculations on finite clusters [3,4] and periodic density-functional calculations within the LDA+U approximation [5]. Matrix elements associated with the hopping of the 2p hole to neighboring plaquettes were also computed in Ref. [6]. However, the moderate size of the clusters (up to four CuO\(_4\) plaquettes [4]) precluded a study of the effect of the antiferromagnetic (AF) spin background on the effective hoppings.

Calculations based on t–J model Hamiltonians predict that the dispersion of the quasiparticle bands is strongly renormalized by the underlying AF interactions to \( O(J) \ll t \) [6]. A relatively small width for the bands close to the Fermi level was indeed observed by ARPES investigations. ARPES thus plays a central role in studying the dressing of charge carriers by interactions with the spin (and lattice) degrees of freedom [3,8]. In addition, these measurements provide detailed information on the doping dependence of the Fermi surface (FS). In particular, the “nodal-antinodal” dichotomy in underdoped cuprates [8] was also emphasized by very recent Raman scattering data [10]: the intensity along the nodal direction scales with \( T_c \), while the antinodal signal actually anti-correlates with \( T_c(x) \). The details of the FS are important for the proper interpretation of other experiments as well, such as the inelastic neutron scattering [11], and put strong constraints on theoretical models for cuprates.

To date, the above issues have been systematically addressed by cluster dynamical mean-field investigations on *effective* one-band Hubbard models [12, 13, 14]. A first-principles correlated electronic-structure calculation, however, is still quite a distant goal, especially for late TM oxides. Here, we present an *ab initio* quantum chemical study, describing how the detailed quasiparticle dispersion can be obtained with quantitative accuracy. To this end, multiconfiguration (MC) calculations were performed on clusters that are large enough to account for spin interactions in the neighborhood of the ZR hole. Renormalization effects on the nearest-neighbor (NN) effective hopping were previously investigated at the *ab initio* level in Ref. [15]. In this Letter, we show that accurate estimates for the longer-range hoppings are crucial for explaining both, the dispersion observed by ARPES measurements, as well as the Fermi surface, in detail.

The *ab initio* calculations are performed on finite fragments cut from the periodic system. In constructing the MC wave-function, the orbitals of each finite cluster are partitioned into three different sets: the inactive levels, doubly occupied in all configurations, the virtual orbitals, empty in all configurations, and the active orbital set, where no occupation restrictions are imposed. This type of MC wave-function is also referred to as a complete-active-space (CAS) wave-function [10]. In the case of an undoped cluster, for example, with formal Cu 3d\(^6\) and O 2p\(^6\) occupations of the valence levels, the most natural choice for the active space is to include all copper 3d\(_{x^2−y^2}\) orbitals, akin to the wave-function in the one-band Hubbard model at half filling. Still, all integrals, including the on-site and longer range Coulomb interactions, are here computed *ab initio*. Although electrons in lower
those plaquettes involved in the hopping process. We call

$$H_{ij} = H_{ij} - H_{ii}$$

matrix elements between the individually

lowest electron-removal state, for example, the orbital

of its own, separately optimized set of orbitals. For the

orbitals, it is important to express each state in terms

single doped hole requires one orbital to be transferred

from the inactive to the active space. Since different elec-

tronic states have in many cases very differently shaped

orbitals, it is important to express each state in terms

of its own, separately optimized set of orbitals. For the

lowest electron-removal state, for example, the orbital

added to the active space turns into a ZR p-d composite

in the variational calculation, localized on a given

CuO₄ plaquette. The character of the active orbitals may

change substantially, however, when separate CAS self-

consistent-field (CASSCF) optimizations are performed

for higher-lying hole states, see below.

The effective hoppings (and quasiparticle bands) are

computed by using the overlap, $S_{ij}$, and Hamiltonian,

$H_{ij}$, matrix elements between ($N-1$) wave-functions hav-
ing the extra hole located on different plaquettes ($i,j,...$)
of a given cluster. Each of these ($N-1$) wave-functions,

$|\Psi_i^{N-1}\rangle$, is obtained by separate CASSCF optimiz-

ations. A similar approach was previously applied to sim-

pler, noncontroversial systems such as MgO (see, e.g., [17]

and references therein). For degenerate ($H_{ii} = H_{jj}$) hole

states: $t = 1/2(\epsilon_j - \epsilon_i) = (H_{ij} - S_{ij}H_{ii})/(1 - S_{ij}^2)$, where $\epsilon$ and $\epsilon_j$ are the eigenvalues of the 2x2 secu-
lar problem. For non-degenerate ($H_{ii} \neq H_{jj}$) hole states,

$t = 1/2[(\epsilon_j - \epsilon_i)^2 - (H_{jj} - H_{ii})^2]^{1/2}$. The overlap and Hamiltonian matrix elements between the individually

optimized, nonorthogonal CASSCF wave-functions are

obtained by State-Interaction (SI) [18] calculations.

The short-range magnetic correlations are described by

including in our finite clusters extra CuO₄ units around

those plaquettes involved in the hopping process. We call

those latter plaquettes “active”. All-electron basis sets of

TABLE I: Occupation numbers (ON’s) of the Cu $d_{z^2}$, in-plane $\sigma$-type O $p_z$, and apical (ap.) O $p_z$ atomic orbitals for the ZR and the $d_{3z^2-r^2}$ hole states. For undoped plaquettes, the ON’s of the $\sigma$ $2p_z$ orbitals are $\approx 1.85$.

| ON’s     | $d_{z^2}$ | $d_{3z^2-r^2}$ | $\sigma$ $p_z$/ap. $p_z$ |
|----------|-----------|----------------|-------------------------|
| ZR hole  | 1.05      | 2.00           | 1.60                    |
| $d_{3z^2-r^2}$ hole | 1.40      | 1.15           | 1.70                    |

The “missing” charge is in the Cu 4s and 4p orbitals.

TABLE I: Occupation numbers (ON’s) of the Cu $d_{z^2}$, in-plane $\sigma$-type O $p_z$, and apical (ap.) O $p_z$ atomic orbitals for the ZR and the $d_{3z^2-r^2}$ hole states. For undoped plaquettes, the ON’s of the $\sigma$ $2p_z$ orbitals are $\approx 1.85$.

The core electrons of the re-

maining ions in each cluster are modeled by effective core potentials (ECP’s) [20]. That this approximation works

very well was shown for the NN hoppings in Ref. [15]. To
decribe the finite charge distribution at the sites in the immediate neighborhood of the cluster, we model those

ions by effective ionic potentials, see [21]. Beyond these

neighbors, we use large arrays of point charges that repro-
duce the Madelung field within the cluster region. The

various clusters employed in our calculations are sketched in Fig. 1. Apical ligands are explicitly included in our
calculations only for the active plaquettes. Other apex oxy-

gens are represented by formal point charges. All cal-

culations were performed with the MOLCAS package [22].
The structural data reported for the La₁₈₅Sr₀₁₅CuO₄
compound [23] were used, with an in-plane lattice con-
tant $a = 3.78$ Å.

The dispersion of $d$-like states on a square lattice is
given by the following relation: $\epsilon(k) = -2t_0 \cos k_x a +

\cos k_y a - 4t' \cos k_x a \cos k_y a - 2t'' \cos 2k_x a + \cos 2k_y a$,... where $t, t', t''$ are the hopping integrals between NN,

second-NN, and third-NN sites and each effective site is

a whole CuO₄ plaquette. As discussed in Ref. [15], a hole in an O $2p$ $\sigma$-type orbital induces ferromagnetic (FM) correla-
tions among the NN Cu 3d spins. These spin polari-

zation “tails” around each 2p hole might actually play a role in pairing. When moving through the AF back-
ground, the hole must drag along this spin polarization cloud at nearby Cu sites, which gives rise to a substan-
tial reduction of the effective hopping parameters. The

spin polarization and relaxation effects at nearby sites

are treated consistently in our approach because a sepa-

rate optimization is performed for each particular $|\Psi_i^{N-1}\rangle$ configuration. A renormalization by a factor of four was

found for the NN effective hopping, from $t_0 = 0.5 - 0.6$ eV to $t = 0.135$ eV [15]. The renormalized values for $t'$ and $t''$, obtained by CASSCF and SI calculations on clusters

like those shown in Fig. 1, are $-0.015$ and $0.073$ eV, re-

spectively. Surprisingly, $t''$ turns out to be about half of

the renormalized NN hopping $t$. The effect of such a large third-NN hopping is illustrated in the upper panel of

Fig. 2. It leads to a weakly dispersing band at the $(\pi/2,\pi/2)$ point.
For comparison, we also plotted in Fig. 2 the dispersion along the nodal direction for $t'' = 0$ (the dotted curve).

An important issue that must be clarified is whether there is significant mixing between the lowest-energy hole state, the ZR-like state, and hole states at higher binding energies. LDA+$U$ calculations [3] indicate that the separation between the ZR configuration and the next electron-removal state is of the order of $0.1 \text{ eV}$. This second state is related to the creation of a $3d_{3z^2-r^2}$ hole. Using model Hamiltonian calculations, Eskes and Sawatzky [20] predicted a separation of about $1.5 \text{ eV}$. They also pointed out that the largest mixing should occur along the antinodal $(0,0)-(\pi,0)$ direction.

Quantum chemical calculations [3] were previously used for the interpretation of the optical absorption [27]. The shoulder at $1.5-2.0 \text{ eV}$ was assigned to transitions between the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ levels [27]. Regarding the electron-removal spectrum, our CASSCF calculations indicate a separation $\Delta \epsilon = 0.60 \text{ eV}$ between the ZR and the $d_{3z^2-r^2}$ $(N-1)$ states. Occupation numbers of the relevant atomic orbitals ( Mulliken charges, see [16]) are listed in Table I. For the $d_{3z^2-r^2}$ hole state, the two holes on a given plaquette are high-spin coupled. Due to the mutual Coulomb repulsion and strong $p-d$ hybridization, the $(x^2-y^2)$ hole has large weight at the ligand sites. Highly accurate results for the on-site energies of the ZR and $d_{3z^2-r^2}$ hole states require calculations beyond the CASSCF level. It is known, however, that the corrections brought by more sophisticated techniques such as the multi-reference configuration-interaction method [16] to the on-site CASSCF relative energies are usually not larger than 20% in TM oxides. Illustrative in this respect are the results of Martin and Hay [3] for the $d-d$ excitations in undoped clusters. For the inter-site matrix elements, the corrections to the CASSCF results are much smaller, see, e.g., the discussion in Refs. [15, 17].

We found that the mixing between ZR and $z^2$ hole states on the same plaquette is negligible. However, the inter-site matrix elements are large. The SI calculations indicate a NN effective hopping of $0.15 \text{ eV}$ between the ZR and $z^2$ $(N-1)$ states. We denote this quantity as $t_m$. The $k$-dependent term describing the mixing between the two bands, ZR and $z^2$, now reads $t_m (\cos k_1 a - \cos k_2 a)$. The NN hopping between degenerate $z^2$ hole states is much smaller, $t_z = 0.01 \text{ eV}$. It is now trivial to diagonalize the $k$-dependent $2 \times 2$ matrix to yield the renormalized quasiparticle bands. The resulting dispersion of the “$(x^2-y^2)$” band is compared to the ARPES data in Fig. 2. It is known that as the $\Gamma$ point is approached, spectral weight is transferred from the lowest binding-energy peak to a higher-energy, rapidly dispersing feature whose origin is a matter of active debate. This higher-energy feature, not visible in the lower panel of Fig. 2 but clearly observed in Ref. [28] and other studies, and the spectral-weight transfer at the $\Gamma$ point are not addressed in this work. Remarkably, in all other respects, our $ab$-initio data agree very well with the dispersion of the lowest ARPES band. In particular, the flat dispersion around $(\pi,0)$, the maximum near $(\pi/2, \pi/2)$, the asymmetry along the nodal direction with respect to the $(\pi/2, \pi/2)$ point [24, 25], and a renormalized bandwidth of nearly $1 \text{ eV}$ are all faithfully reproduced in the theoretical results. Further, in the lightly doped ($x \ll 1$) cuprates, the added holes would immediately populate states near $k_n = \frac{\pi}{a} (\pi/2, \pi/2)$: this would give rise to nodal quasiparticles whose weight grows linearly with $x$. In a rigid-band picture, the quasiparticle dispersion plotted in Fig. 3 suggests the formation of small hole pockets in the deeply underdoped regime (see the dotted contour), as inferred from recent magnetoresistance oscillation mea-

FIG. 2: (upper panel:) The lowest electron-removal band, without including the interaction with the $d_{3z^2-r^2}$ hole state (dashed line) and after including this interaction (solid line). There is no mixing along the nodal direction. Close to the $\Gamma$ point, the two bands cross. For simplicity, only the lowest electron-removal band is shown. The reference is the value of the on-site Hamiltonian matrix element of the ZR state, see text. The dotted line along the nodal direction corresponds to $t'' = 0$. (lower panel:) ARPES data obtained for La$_2$CuO$_4$ by Ino et al. [24]. Units of eV are used in both plots.

FIG. 3: Three-dimensional plot of the ZR-like quasiparticule dispersion, including the effect of the ZR–$z^2$ interaction. Constant-energy contours are also drawn in the figure. The dashed line resembles the “FS” measured in doped La$_2$CuO$_4$ [25] and other cuprates [7], see the sketch in the inset.
measurements, the appearance of a holelike cylindrical "Fermi surface" at intermediate dopings, and a change to an electronlike FS in the overdoped samples (the full lines in Fig. 3). Interestingly, a nearly rigid shift of the chemical potential was clearly observed with doping in several cuprates. The renormalized FS which would result at intermediate dopings (the dashed curve in Fig. 3) shows all the characteristics of that measured experimentally: correlations induce pronounced flattening of the dispersion near the antinodal points, while electronic states in the nodal region remain dispersive. That the ZR–$z^2$ mixing is important is shown by the fact that it drastically reduces the dispersive character close to $k_{\text{an}} = (\pi/a, 0)$, bringing the computed ZR dispersion as well as the FS in much closer agreement with the experiment. The band at higher binding energy, associated with the charge transfer from the $d_{3z^2-r^2}$ level to the in-plane $p$-$d$ orbitals, was not resolved experimentally. More conclusive elaboration of this aspect requires one to explicitly treat the dynamical spectral-weight transfer between the ZR and higher excited states: whether this can lead to an understanding of "waterfalls" in the dispersion at higher binding energy is out of scope of the present work.

Our theoretical findings have other important implications. Very recent electronic Raman scattering measurements clearly show the "nodal-antinodal" dichotomy in cuprates. For small $x$, the nodal lineshape exhibits a low-energy increase, roughly $\sim x$, while the antinodal lineshape is almost independent of $x$, fully in agreement with our results above. Further, the shape of the derived FS implies existence of the "nesting" vectors, $Q$, joining the flat-band parts of the renormalized dispersion, see the inset in Fig. 3: these are important when a description of the inelastic neutron scattering (INS) measurements is attempted. ARPES, Raman, and INS results can thus be reconciled with our calculated FS.

To conclude, quantum chemical MC calculations were employed to study the lowest electron-removal states in an undoped layered cuprate. The method is sufficiently general and readily adaptable for studying the correlated band structure of other 3$d$-oxides of intense current interest. The ZR physics and farther spin interactions around a ZR hole are treated on equal footing in our approach, which allows an accurate description of the renormalization effects on the dispersion of the ZR-like quasiparticle band. FM correlations involving spins at nearest Cu sites and AF couplings beyond these nearest neighbors are both treated consistently. The mixing with "triplet" $d_{3z^2-r^2}$ hole states at higher binding energy is also investigated. We show that all these effects are important for describing the dispersion of the lowest ($N-1$) band. In contrast, the FM $d$-$d$ correlations induced by the ZR 2$p$ hole and the ZR–$z^2$ mixing are missing in standard $t$-$J$ or single-band Hubbard models. The agreement between our theoretical results and the available ARPES data is remarkable. We are able to reproduce all the important details of the experimental spectrum. Extension of our ab initio approach to tackle dynamical responses is an outstanding open problem, which we leave for future consideration.

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